



Annual Report 2023

Chair for Functional Materials with the Soft Matter Physics Group

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Cover page picture:

The artwork on the front cover - the E13 flagship - illustrates the key research activities of the chair, that is, the investigation of functional films for energy materials utilizing grazing-incidence scattering methods to analyze the films' structure-function-relationship on the nanoscale. "E13" is the department internal description of the Chair for Functional Materials.

Editor: Dr. Julian Eliah Heger

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Preface

It is a great pleasure to present the annual report for the year 2023 in the name of the staff of the Chair for Functional Materials and the Soft Matter Physics Group. It provides an overview of our teaching, research, and development activities. Our research activities are focused on functional materials and cover a broad range from soft matter physics to developments of methods and instrumentation. We examine the fundamental physics of material properties using mainly scattering methods (neutron, x-ray, and light scattering). The general goal of our research is to explain the functional characteristics of soft condensed matter from the knowledge of molecular dynamics and nanostructure as well as their kinetics.

In 2023, the research activities covered the specific areas of polymer solutions and gels, responsive thin films, functional thin films, photovoltaics, polymer-hybrid systems, materials for energy storage, real-time characterizations, and the development of instrumentation and software. In 2023, we had, in particular, many guests visiting us in Garching and presenting their research work. We also traveled to many international conferences and workshops to interact with international scientists and present our results.

The activities in the fields of polymer films for application in photovoltaics and polymer-hybrid systems were successfully continued. With *"TUM.solar"*, the Keylab in the network of the Bavarian Collaborative Research Project *"Solar Technologies go Hybrid"* (SolTec) headed by Prof. Müller-Buschbaum was running in its 12th year of funding. Research activities covered a broad area of next-generation solar cells, including organic solar cells, dye-sensitized solar cells, hybrid solar cells, perovskite solar cells, and quantum dot solar cells. Moreover, thermoelectric materials and energy storage materials with a focus on lithium-ion battery technology were investigated. In addition, we investigated novel self-assembling responsive polymers, also under high pressure, orthogonally switchable polymers, polymeric hydrogels, and bio-nanoparticles for medical applications such as 3D bioprinting and drug delivery, as well as conjugated polymers for colorimetric sensors.

The in-house experiments available in the laboratories of the chair were supplemented by many activities at large-scale facilities, comprising synchrotron radiation and neutron scattering experiments. In particular, the in-house x-ray scattering experiments for SAXS/WAXS/GISAXS/GIWAXS as well as XRR/XRD were heavily booked. Importantly, a new XRD instrument with the possibility of covering a large temperature range was newly installed.

In 2023, the Chair for Functional Materials and the Soft Matter Physics Group comprised 5 fellows, 62 PhD students, 33 master students, 17 bachelor students, 1 student assistant, and 5 administrative and technical staff members. 8 PhD theses were accomplished; moreover, 17 master theses as well as 17 bachelor theses were finished. We were happy to have hosted 14 guests.

Importantly, we held our internal summer school again. It took place in the beautiful place Nassfeld in Tirol, Austria, near the border to Italy and was dedicated to research topics of interest for the group. Another highlight was the 8th European Conference on Neutron Scattering (ECNS) being organized by the MLZ in Garching. 538 participants from all around the world joined a very lively atmosphere.

Regarding teaching activities of the chair, we offered the lectures "Materials science" (Papadakis). Special lectures comprised "Polymer physics" (Müller-Buschbaum), "Nanostructured soft materials" (Papadakis and Müller-Buschbaum) and "Measurement and sensor technology" (Müller-Buschbaum). Prof. Papadakis acted again as a deputy women's representative of the Physics Department, and Prof. Müller-Buschbaum started as supervising Professor of the "Electronic Lab" of the TUM School of Natural Sciences. Moreover, Prof. Müller-Buschbaum headed the activities in the "Network Renewable Energies (NRG)" in the MEP.

As a service to the community, Prof. Papadakis acted as one of the Editors-in-Chief of "Colloid and Polymer Science", and Prof. Müller-Buschbaum served as Executive Editor at "ACS Applied Materials & Interfaces".

This annual report comprises a selection of the different research topics and projects carried out in the individual groups of the chair. It highlights the dedicated and successful research activities and collaborations with other groups and large-scale facilities. We wish all chair members a fruitful continuation and a very successful year 2024.

Peter Müller-Buschbaum and Christine M. Papadakis

April 2024

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1 Polymer solution and gels



1.1 Effect of pressure on the micellar structure and aggregation behavior of PMMA-*b*-PNIPAM in a water/methanol mixture

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Stimuli-responsive materials exhibit strong physical and chemical changes when exposed to different stimuli, as changes in temperature, pressure, or solvent composition. Thermoresponsive polymers, for example, have been of great interest because they exhibit a drastic change in solvation with temperature, which can be used in applications like drug delivery systems, tissue engineering, and sensors. In aqueous solution, amphiphilic diblock copolymers consisting of a permanently hydrophobic poly(methyl methacrylate) (PMMA) block and a thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) block self-assemble into core-shell micelles [1]. At atmospheric pressure, the micellar shell and the inter-micellar regions strongly dehydrate when heated above the cloud point T_{cp} of PNIPAM. Besides temperature, adding a water-miscible co-solvent also influences the self-assembly behavior of PMMA-b-PNIPAM. In particular, below T_{cp} , adding 10 % v/v of methanol leads to the softening of the PMMA core and a slight shrinkage of the PNIPAM shell [1]. When pressure is applied, PNIPAM homopolymers remain hydrated, even above T_{cp} . Moreover, pressure increases their solubility in a water/methanol mixture due to the weakening of the preferential adsorption of methanol in PNIPAM [2]. However, the effect of pressure on the micellar structure of PMMA-b-PNIPAM in a water/methanol mixture is still unknown.

In the present study, we investigate the effect of pressure on the micellar structure and the aggregation behavior of PMMA₂₁-*b*-PNIPAM₂₈₃ in a 90:10 v/v water/methanol mixture by synchrotron small-angle X-ray scattering (SAXS). Among others, a pressure scan with steps of 25 MPa was carried out at 31 °C, i.e. the coexistence line is crossed two times as indicated in Fig. 1.1a. The scattering intensity as a function of the momentum transfer q, which depends on the scattering angle and the wavelength of the incident beam, is shown in Fig.1.1b for different pressures.



Figure 1.1:

a) Phase diagram of PMMA-*b*-PNIPAM in a 90:10 v/v water/methanol mixture. The pressure scan is indicated with a green arrow. b) Representative SAXS data with model fits (solid black lines). Curves in the one- and two-phase regions are bluish and reddish, respectively.

At 10 MPa, i.e., in the low-pressure regime of the two-phase region, the curve shows a weak

shoulder at $q \simeq 0.1$ nm⁻¹ and a smooth decay at higher q-values, indicating the formation of large agglomerates in which the single micelles cannot be distinguished. We attribute this to the low degree of solvation of the micellar shell and the inter-micellar regions, which leads to the loss of the scattering contrast between the core and the shell of the micelles. In the onephase region, i.e., at pressures between 25 and 200 MPa, the curves feature a weak maximum at $q \simeq 0.2$ nm⁻¹ and a shoulder at $q \simeq 0.6$ nm⁻¹, which we attribute to the scattering of single micelles. At 250 MPa, a strong correlation peak is present at $q \simeq 0.3$ nm⁻¹, indicating that the spatial correlation between the micelles strongly increases upon crossing the coexistence line. Detailed structural information is obtained by fitting the SAXS data using suitable models. For instance, the pressure dependence of the core radius R_c , the micellar radius R_m , the halfdistance between the correlated micelles R_{HS} , and the volume fraction of correlated micelles f_s were deduced (Fig. 1.2a). At 10 MPa, the densely packed agglomerates have an overall radius of ca. 105 nm. In the one-phase region, R_c decreases with pressure while R_m increases up to 75 MPa and slightly decreases as pressure is increased further. There is no correlation between the micelles ($f_s = 0$) between 50 and 175 MPa. However, f_s increases strongly at 200 MPa, indicating that ordered clusters of micelles form as the coexistence line is approached. In the high-pressure regime of the two-phase region, i.e., at pressures higher than 200 MPa, R_m decreases with pressure, which we attribute to the lower degree of solvation of the micellar shell. Moreover, $R_{HS} > R_m$; thus, the correlated micelles do not interpenetrate in this regime.



Figure 1.2:

a) Structural parameters for the pressure scan at 31 °C. Upper graph: Core radius R_c (red circles), micellar radius R_m (blue squares), and hard-sphere radius R_{HS} (green hexagons). Lower graphs: Volume fraction of correlated micelles, f_s . The dashed vertical lines indicate the coexistence line deduced from SAXS. b) Schematic representation of the effect of pressure at 31 °C on the micellar structure of PMMA-*b*-PNIPAM in a D₂O/CD₃OD mixture.

Our main findings are depicted in the scheme shown in Fig. 1.2b. In the low-pressure regime of the two-phase region, the micelles form agglomerates with a low solvent content. After crossing the coexistence line by increasing the pressure, these agglomerates dissociate into single micelles, which are not spatially correlated. Aggregation of micelles begins in the one-phase region near the coexistence line. After crossing the coexistence line for a second time, i.e., in the high-pressure regime of the two-phase region, the clusters of micelles further grow with pressure, which leads to the formation of large agglomerates of non-interpenetrating micelles.

- C.-H. Ko, C. Henschel, G. P. Meledam, M. A. Schroer, R. Guo, L. Gaetani, P. Müller-Buschbaum, A. Laschewsky, C. M. Papadakis, *Macromolecules* 54, 5825-5837 (2021)
- [2] S. Bharadwaj, B.-J. Niebuur, K. Nothdurft, W. Richtering, N. A. van der Vegt, C. M. Papadakis, Soft Matter 18, 2884-2909 (2022)

1.2 Micellar solutions of PMMA-b-PNIPAM in water/methanol mixtures

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For thermoresponsive polymers of lower critical solution (LCST) type, their cloud point temperature, $T_{\rm CP}$, may be reduced upon addition of a cosolvent, that itself is a good solvent for the polymer (Fig. 1.3a). This co-nonsolvency effect has been employed in a wide range of applications such as the sensing of volatile organic compounds, and it has predominantly been studied using poly(*N*-isopropylacrylamide) (PNIPAM) homopolymers in aqueous solution in the presence of methanol. Here, we address the question which effect the cosolvent methanol has on the micellar structures of diblock copolymers of PNIPAM with a hydrophobic poly(methyl methacrylate) (PMMA) block in aqueous solution.



Figure 1.3:

(a) Schematic representation of the phase diagram of PMMA₂₁-*b*-PNIPAM₂₈₃ in water/methanol mixtures in dependence on the methanol volume fraction. The green line indicates $T_{\rm CP}$, i.e. the coexistence line. The micellar structures on both sides of the coexistence line are depicted. (b) Representative SAXS data of the PMMA₂₁-*b*-PNIPAM₂₈₃ solution in an 80:20 v/v water/methanol mixtures (symbols). The full lines are fits of structural models. The curves are shifted vertically. (c) Resulting structural parameters. $R_{\rm core}$: radius of the micellar core, $R_{\rm micelle}$: radius of the entire micelle, $R_{\rm cluster}$: radius of fractal clusters formed by the micelles. The grey dashed lines indicate $T_{\rm CP}$. In (b) and (c), the colors indicate different regimes.

In our previous work, we found that, in aqueous solution, $PMMA_{21}$ -*b*-PNIPAM₂₈₃ forms spherical core-shell micelles [1]. Upon heating through T_{CP} , the shell dehydrates and contracts, and the micelles form large, compact aggregates. When methanol is added, the structure of the micelles as well as their interactions change strongly, when the phase boundary is approached at room temperature [2]. These findings were attributed to (i) the softening of the PMMA micellar core by methanol and (ii) the cononsolvency effect of methanol for the PNIPAM blocks. Here, we present a synchrotron small-angle X-ray scattering (SAXS) study of the temperature-dependent structures and interactions of micellar solutions of PMMA₂₁-*b*-PNIPAM₂₈₃ in an 80:20 v/v water/methanol mixture.

At this, a 10 g/L solution of PMMA₂₁-*b*-PNIPAM₂₈₃ was prepared in a water/methanol mixture having a mixing ratio of 80:20, respectively. Measurements were performed at the BioSAXS beamline of the EMBL in Hamburg with an X-ray wavelength of 0.124 nm and a sample-detector distance of 3.0 m. The samples were flowed through an in-vacuum quartz capillary using an automatic sample changer. Heating scans were carried out around the respective $T_{\rm CP}$.

Representative SAXS data are shown in Figure 1.3b. Changes in the curve shapes are observed throughout the entire temperature range, especially at low momentum transfers q, where the intensity grows significantly upon heating. The data are analyzed by using a structural model including, among others, the form factor of spherical core-shell micelles, a structure factor as well as a form factor describing clusters of micelles.

In the PMMA₂₁-*b*-PNIPAM₂₈₃ solution in the 80:20 mixture, spherical core-shell micelles are formed, however, they are smaller than the ones in neat water [1]. Already below $T_{\rm CP}$, the micelles form loosely packed clusters, which is due to the enhanced attractive micellar interaction in the water/methanol mixture compared to the one in neat water. This points to a weakening of the hydrophobic effect between the PNIPAM shell blocks. As $T_{\rm CP}$ is crossed, both, the micellar core and the shell shrink strongly, i.e. the aggregation number decreases and the PNIPAM shell block contracts. Moreover, the clusters become more compact and grow into large, compact and smooth aggregates far above $T_{\rm CP}$.

By comparing these data with the ones from solutions in neat water and in a 90:10 v/v water/methanol mixture [3], it is seen that the presence of methanol and the distance to the coexistence line have a significant influence on the temperature-induced morphological transition of the micelles and their aggregation behavior. The higher the methanol content, the smaller are the micelles, both due to their smaller core and their thinner shell. These reflect the interplay of the change of the solubility of the PMMA block and the cononsolvency effect of the PNI-PAM block. This comparatively simple system consisting of self-assembled micelles may help in tuning switchable delivery systems by a cosolvent.

- C.-H. Ko, C. Henschel, G. P. Meledam, M. A. Schroer, P. Müller-Buschbaum, A. Laschewsky, C. M. Papadakis, *Macromolecules* 54, 384-397 (2021)
- [2] C.-H. Ko, C. Henschel, G. P. Meledam, M. A. Schroer, R. Guo, L. Gaetani, P. Müller-Buschbaum, A. Laschewsky, C. M. Papadakis, *Macromolecules* 54, 5825-5837 (2021)
- [3] C.-H. Ko, C. Henschel, G. P. Meledam, M. A. Schroer, R. Guo, P. Müller-Buschbaum, A. Laschewsky, C. M. Papadakis, *Macromolecules* 56, 8980-8992 (2023)

1.3 Biocompaticle nanocarriers from trypsin and chondroitin sulfate

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Nanoparticles (NPs) based on proteins are stimuli-responsive biomaterials that find applications, among others, in pharmaceutical and food systems. A promising way to control the aggregation of proteins into nanoparticles with a narrow size distribution is their complexation with polysaccharides, i.e. non-toxic biological macromolecules, and their stabilization by thermal treatment. Previously, we succesfully prepared rather monodisperse NPs from the globular protein trypsin (TRY) and the negatively charged polysaccharide chondroitin sulfate (CS) and thus, exploiting the positive charge state of TRY at pH 4 [1]. In the present study, we extended this work to a higher TRY concentration, which is of interest for applications as nanocarriers [2]. We used a mixing ratio that corresponds to a 1:1 stoichiometry in the charge neutralization and assessed the stability of the thermally treated NPs in a wide range of pH-values. Experiments using modulated 3D cross-correlation dynamic light scattering (3D-DLS) revealed significant changes at pH 9. Here, we report on the underlying changes of the inner structure of the NPs as determined using synchrotron small-angle X-ray scattering (SAXS).

For our study, we used TRY from the bovine pancreas and the sodium salt of CS having a molar mass of 23 000 g/mol. Aqueous stock solutions of TRY with citric acid and of CS were diluted and mixed, and after equilibration, their pH-value was found at 4.3. Thermal stabilization was achieved by keeping the dispersions for 20 min at 60 °C. Afterwards, the pH-value was altered by adding small amounts of 1 M NaOH. SAXS measurements were performed at 20 °C at the BioSAXS beamline of EMBL at DESY. X-rays with a wavelength of 0.155 nm were used together with a 2D Pilatus 6M detector placed at a distance of 3.0 m. The 2D intensities were azimuthally averaged, brought to absolute scale and averaged, and the background was subtracted.



Figure 1.4:

Results from SAXS on dispersions of CS/TRY NPs [2]. (a) Representative SAXS data of the untreated sample and the thermally treated ones at the pH-values given in the graphs. The arrows indicate the shoulders. (b) Length scales from model fitting in dependence on pH. Open and closed symbols indicate the untreated and the thermally treated dispersions. R_s denotes the radius of the spherical substructure, R_{g1} and R_{g2} the radii of gyration of the smaller substructures.

3D-DLS revealed that the untreated NPs and the thermally treated ones up to pH 8 have a hydrodynamic radius in the range of 204 ± 13 nm and a narrow size distribution, i.e. they are stable against disintegration in this pH-range. In contrast, at pH 10.1-11.2, the distributions of hydrodynamic radii are very broad, which may be assigned to an interplay of the ionic interactions of the negatively charged TRY and the hydrophobic interactions.

The SAXS data from the identical dispersions feature strong forward scattering at low momentum transfers q, i.e. below 0.1 nm⁻¹ (Figure 1.4a). We attribute this contribution to the form factor scattering from the entire NPs, whose overall size cannot be resolved with the SAXS setup used. For the untreated dispersion, several shoulders are observed, pointing to a hierarchical inner structure. The curves are similar for the thermally treated dispersions up to pH 8.0. In contrast, at pH-values of 10.1-11.2, the data look qualitatively different: The forward scattering is significantly weaker, and the shoulders are at different locations. To quantify these differences, the curves are fitted by structural models, namely the sum of form factors of structures on different length scales.

Figure (Figure 1.4b) shows the resulting length scales. The untreated dispersion features compact NPs with inner structures that are spherical with an average radius $R_s = 28$ nm along with a smaller structure having a radius of gyration of 10 nm. We attribute the spheres to complexes from positively charged TRY and negatively charged CS, which form due to the ionic interactions, and the smaller structures to the inner structure of the complexes, namely extended CS chains, that are decorated by TRY molecules. Upon thermal treatment and at pH 4.3-8.0, the spherical substructures have average radii R_s of 40-46 nm, i.e. they have grown significantly during thermal treatment. Since thermal treatment is known to result in partial unfolding of TRY, the hydrophobic interactions between the proteins become more important and may be at the origin of the growth of these complexes. As pH is increased to 8.0, the radius of gyration of the smaller substructures decreases slightly from 11.9 to 8.7 nm. When the pH is increased from 8.0 to 10.1, drastic changes are observed: (i) The large, spherical substructure has vanished. We hypothesize that the charge and the hydrophobic protein-protein interactions are no longer sufficient to stabilize the TRY-CS clusters, because TRY becomes less positively charged and the electrostatic attraction with CS weakens. (ii) While the small substructure at 8 nm persists, an additional, even smaller substructure appears, having a radius of gyration of 1.1-1.4 nm. We attribute these two smaller structures partially to the inner structure of the NPs and partially to fragments that have been released from the NPs and that may consist of small TRY-CS clusters and single TRY and/or CS molecules.

To summarize, NPs from TRY and CS have proven to be stable after thermal treatment up to pH 8.0 with an unaltered size and with an inner structure that is mainly a result of the ionic interaction between TRY and CS. At pH-values of 10.1-11.2, the size distribution is very broad, and their inner structure is increasingly due to hydrophobic interactions. Apart from being an interesting, biocompatible system for drug or nutrient delivery, the TRY-CS system is a model system to determine the effects of the electric charge of the protein, of unfolding and exposing hydrophobic residues upon thermal treatment and pH-increase in the presence of the negatively charged polysaccharide.

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1.4 Gelation mechanism of alginate-g-PNIPAM-based thermoresponsive copolymer in aqueous solution

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Alginate is a naturally occurring, edible polysaccharide found in brown algae which is wellknown for its biocompatibility, degradability, and nontoxicity. These properties have made alginate-based polymers a suitable biomaterial for various medical applications including drug delivery and tissue regeneration [1]. In addition, the pendant group on the monomer unit of the alginate macromolecule allows functionalizing them with thermoresponsive polymers.

In the current study, we investigate sodium alginates that are grafted with random copolymers of *N*-isopropylacrylamide (NIPAM) and *N-tert*-butyl-acrylamide (NtBAM) (NaALG-*g*-P(NIPAM₉₄-*co*-NtBAM₆), see Fig. 1.5 (a)). The side chains are thermoresponsive and become water-insoluble at 25 °C. Above, the side chains collapse, resulting in gel formation. Besides, the presence of divalent Ca²⁺ ions will bind two negatively charged alginate chains, which also induces gel formation. Due to the two co-existing gelation mechanisms, the system is a dual cross-linked hydrogel (see Fig. 1.5 (b) and (c)) [2]. The roles of the two gelators (Ca²⁺ and thermoresponsive PNIPAM) and the molecular building blocks of the gels are studied in aqueous solutions. The collapse of PNIPAM is induced by preparing the sample solution above its collapse temperature.



Figure 1.5:

Structure of the (a) grafted alginate copolymer, (b) Ca²⁺-induced cross-linked alginate copolymers in 'egg-box' conformation, (c) thermally induced cross-linked alginate copolymer.

Dynamic light scattering (DLS) was applied to characterize the diffusion of the alginate copolymers, i.e., their hydrodynamic radius R_h and scattering intensity. The modified alginate was dissolved in a PBS buffer (polymer concentration 0.1 wt.%) under three different conditions: the first solution was unmodified (solution 1), the second solution was mixed with a calcium chloride solution ($C_{Ca} = 0.14$ mM) at room temperature (solution 2), and the third solution was preheated to 45 °C (above the cloud point of PNIPAM block) before the addition of calcium chloride ($C_{Ca} = 0.14$ mM) (solution 3). DLS temperature scans were carried out from 20 °C to 50 °C at a scattering angle of 90° using an LS spectrometer (LS Instruments) equipped with a 660 nm laser.





DLS results: (a) Hydrodynamic radii in dependence of temperature; (b) Scattered intensity in dependence of temperature. (c) Anticipated structural changes of alginate copolymers.

Fig. 1.6(a) shows the temperature dependence of R_h . At 20 °C, the copolymer in solution 2 has a larger R_h (900 nm) than in solution 1 (600 nm), which is attributed to the cross-linking effect of the Ca²⁺ ions. Solution 3 shows the smallest R_h (400 nm). The significant shrinkage in particle size is assigned to the collapse of the side chain during sample preparation. The effect of Ca²⁺ on the particle size of the specific sample therefore became insignificant. When the solutions are heated, their R_h -value decreases with increasing temperature between 30 °C and 35 °C. At 50 °C, the R_h from solution 2 has decreased from 900 nm (at room temperature) to 400 nm, while that of solution 3 is only slightly affected. We conclude that the different solution preparation approaches have led to the formation of two different microstructures. The wide transition range also indicates that the collapse of the side chain is a gradual process. Fig. 1.6(b) shows the scattered intensity of the sample solution at various temperatures at scattering angle 90°, which reflects the scattering contrast of the alginate with respect to the buffer. Solution 3 shows a significantly higher scattering intensity, i.e., the packing of the alginate induced by the collapsed side chains is different from the one induced by Ca²⁺ (Fig. 1.6(c)).

Our study has revealed the differences between the two cross-linking mechanisms present in the PNIPAM grafted alginate solution. The preparation method plays an important role in the solution properties, especially the size of the dissolved molecules, which may be of importance for the microstructure of the hydrogels prepared under the same conditions.

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1.5 Phase behavior of thermo- and photoresponsive diblock copolymers in aqueous solution

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Stimuli-responsive diblock copolymers (DBCPs) have gathered considerable interest for drug delivery due to their ability to alter the properties upon exposure to external stimuli, such as temperature and light. Notably, thermoresponsive polymers such as poly(N-isopropyl acryl amide) (PNIPAM) and Poly(*N*-dimethyl acrylamide) (PNDMAM) feature lower critical solution temperature (LCST) behavior with a coil-to-globule transition at the cloud point (CP). By employing PNIPAM as one of the blocks and incorporating a photo-active group into PNDMAM as the other block, a dual-responsive DBCP with two distinct CPs is expected (Fig. 1.7a). Here, azopyrazole (AzPy) was used as the photo-sensitive moiety due to its long half-time and well distinguishable *E* and *Z* isomers. This way, the CP of the PNIPAM block remains unchanged, while the CP of the PNDMAM block can be altered by exposure to UV light. This enables the formation of unimers at low temperatures, micelles at intermediate and inverse micelles at high temperatures, thereby achieving a dual switching of the structures (Fig. 1.7b), which is of interest for uptake, transport and release purposes.



Figure 1.7:

a) Structural formula of the DBCP under investigation. The inset shows the isomerization of AzPy. b) Schematics of thermoresponsive switching behavior of the DBCP in the *E*- (left) and *Z*-state of AzPy (right).

We investigated the phase behavior of PNIPAM₈₃-*b*-P(NDMAM₅₁-*co*-AzPyNDMAM₆) in aqueous solution at a concentration of 5 mg/ml. It was irradiated by a 365 nm UV light (200 mW/cm²) for 15 min to achieve a complete conversion from the *E*-state into the *Z*-state. The solution structure, i.e. the polymer size and solvent quality as well as micelle and aggregate formation, were investigated using synchrotron small-angle X-ray scattering (SAXS). The wavelength used here was 0.124 nm, and the sample-detector distance (SDD) was 3.0 m.

For analysis of the SAXS data, the excluded-volume model was utilized. The scattering curves of the *E*- and *Z*-state of the DBCP exhibit first individual chain scattering at lower temperatures. For the *E*-state, additional forward scattering was observed at 35 °C and above, while for *Z*-state, forward scattering occurred starting from 30 °C (Fig. 1.8b). This suggests a CP at 30 - 35 °C for the *E*-state and 25 - 30 °C for the *Z*-state.



Figure 1.8: SAXS data of the diblock copolymer solution in the E-state (a) and Z-state (b).

Below the CP, the radius of gyration of the chains, R_g , is in the range of 4-6 nm for both polymers. It is slightly larger in the Z-state than in the E-state (Fig. 1.9a). This can be attributed to the more bent structure of the Z-state, which is sterically more demanding. Above the CP, the single chains collapse, resulting in lower R_g values, implying the collapse of the chains (Fig. 1.9a). Regarding the lower excluded volume parameter D_m of the the Z-state compared to that of the E-state, it can be inferred that the Z-state is more water-soluble (Fig. 1.9b). This is consistent with the increased dipole moment resulting from the more symmetric configuration of the Z-state. Regardless of the isomeric state, both of the samples exhibit decreased solubility with increased temperature, which implies the collapse of the chains (Fig. 1.9b).



Figure 1.9: Resulting structural parameters: radius of gyration R_g (a) and excluded volume parameter D_m (b) of the diblock copolymer.

In conclusion, the thermo- and photoresponsive PNIPAM₈₃-*b*-P(NDMAM₅₁-*co*-AzPyNDMAM₆) lead to comparable CPs before and after irradiation with UV light, i.e. regardless of the conformation of the AzPy group, each forming dissolved chains below the CP and aggregates above the CP. In contrast to expectation, no micelles have been observed yet, thus, further tuning of the block properties is needed.

1.6 Injectable hydrogels from thermoresponsive tri- and tetrablock terpolymers investigated using small-angle neutron scattering

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Lower critical solution temperature (LCST) polymers have attracted great interest for 3D bioprinting or drug delivery, as they can form a runny solution at room temperature, but a hydrogel at body temperature [1]. Here, the effect of polymer architecture of fully biocompatible poly(ethylene glycol) (PEG) based thermoresponsive terpolymers featuring three different blocks is addressed. These consist of the permanently hydrophilic oligo(ethylene glycol) methyl ether methacrylate (OEGMA300, A), hydrophobic *n*-butyl methacrylate (BuMA,B), and thermoresponsive di(ethylene glycol) methyl ether methacrylate (DEGMA300, A), hydrophobic *n*-butyl methacrylate (DEGMA, C). A POEGMA300₁₇-*b*-PBuMA₁₇-*b*-PDEGMA₁₃ (ABC) triblock terpolymer and a PBuMA₁₀-*b*-POEGMA300₁₁-*b*-PBuMA₁₀-*b*-PDEGMA₁₁ (BABC) tetrablock terpolymer were synthesized via group transfer polymerization (GTP) and have an overall molar mass of 8300 g mol⁻¹.

It was previously shown that, in aqueous solutions, both polymers show LCST behaviours and form gels at sufficiently high polymer concentrations and temperatures. Interestingly, BABC forms a gel at lower temperatures than ABC, but only at higher concentrations, namely 15 wt% and above [2]. Here, we investigate the gel mechanism and the mesoscopic solution and gel structures of both polymers at 15 wt% solution in dependence on temperature.



Figure 1.10:

SANS curves from 15 wt% solutions of a) ABC triblock and b) BABC tetrablock terpolymers in D_2O at the temperatures given in the plots. The grey, blue and green colours indicate regime I (solution), regime II (gel), and regime III (phase separated), respectively. The black full lines fits of structural models. The curves are shifted vertically for better visibility.

ABC and BABC terpolymers were dissolved in D₂O at a concentration of 15 wt%. Small-angle neutron scattering (SANS) measurements of both polymer solutions were performed at SANS-I at Paul Scherrer Institut (PSI), to characterize the changes of the inner structures on temperature. The neutron wavelength λ was 0.8 nm with a spread of 10%. The sample-detector distances of 1.8 and 8.0 m were used to cover a *q* range of 0.03-3 nm⁻¹.

The SANS curves are shown in Figure 1.10, indicating the presence of three distinct regimes for both polymer solutions. For both polymers, the SANS curves exhibit shoulders at $q \sim 0.4 \text{ nm}^{-1}$ at low temperatures in the solution regime, which can be attributed to the presence of weakly correlated micelles. The curves from BABC show a more pronounced increase in forward scattering at intermediate temperatures compared to ABC. Within the

phase-separated state, the curves from ABC feature narrower peaks in the high q region in comparison to BABC, which suggests ABC forms more ordered structures upon further heating.

From the fitting results shown in Figure 1.11(a-b), it is observed that there are three regimes in dependence on temperature. In regime I, ABC forms spherical micelles with a constant micellar radius of ~5.9 nm, comprising the hydrophobic PBuMA core and the mixed shell from hydrophilic POEGMA and thermoresponsive PDEGMA. In the gel regime (II), the correlation between micelles becomes weaker, and the hydrophobicity of the thermodynamic PDEGMA block increases, resulting in a sphere-to-cylinder shape change. In regime III, large aggregates with high internal order are formed. BABC self-assembles into spherical core-shell micelles in regime I, as depicted in the sketch of the structure shown in Figure 1.11(c). The thermore-sponsive PDEGMA block collapses upon heating, leading to the formation of micelles with a dumbbell-shaped structure in the gel region. Regime III is characterised by an increased correlation of micelles, with a change in their interactions from attracting to repulsive. This results in the formation of a micellar network consisting of two types of compartments. The hydrophilic POEGMA bridge that connects the hydrophobic cores enhances the overall flexibility of the network.





Temperature dependence of the structural parameters from SANS curves in Figure 1.10. (a) ABC and (b) BABC in D_2O at the concentration of 15 wt%. The three regimes are indicatd by Roman letters at the top. (c) Sketch of the structure of micelles of both architectures with increasing temperature.

In summary, the SANS measurements on solutions of both types of terpolymers elucidate the effect of architecture on the process of gel formation and the resulting gel structure. The triblock terpolymer ABC self-assembles into spherical core-shell micelles at room temperature, that transform into cylinders to form gels at high temperatures. In contrast, the tetrablock terpolymer BABC forms spherical core-shell micelles that aggregate at higher temperatures without a shape change. Upon further heating, BABC transforms into a two-compartment elastic micellar network.

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2 Responsive thin films



2.1 Photoswitchable molecules: impact on swelling in thermoresponsive polymer films under UV irradiation

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Photoswitchable dyes, like azobenzene and azopyrazole, have proven effective in manipulating material properties. These azo-dyes undergo double-bond isomerization upon specific wavelength irradiation, offering a non-invasive and high-temporal-resolution external stimulus [1]. Incorporating photoswitchable molecules into thermoresponsive polymers presents a strategy for harnessing photoswitching to modify macroscopic bulk properties. Light-induced water uptake, expansion, and morphology changes hold promise for applications in light-sensing devices, photo-actuators, and light-induced drug delivery systems.

In this study, we combined azobenzene-acrylamide (AzAm) with the lower critical solution temperature (LCST) type polymer poly(dimethylacrylamide) (pDMAm) to create statistical copolymers. While aqueous solutions of these polymers have been shown to exhibit shifts in their LCST when irradiated, their behavior has not been studied in thin films. We investigated the swelling characteristics of p(AzAm-co-DMAm) thin films in both isomer states of the photoswitchable molecule azobenzene (Az). The influence of UV irradiation on the swelling behavior in water vapor was explored, aiming to control its thickness and water content.

With kinetic Fourier-transform infrared (FTIR) spectroscopy, we probed the vibrations of the photoactive moiety while irradiated with UV-light. Fig. 2.1a shows the far infrared section of the kinetic measurement. It can be seen that there is a shift in several peaks, which respond to different C-H out-of-plane bending modes. Fig. 2.1b shows the peak position of the low-wavenumber peak. A shift from ~692 cm⁻¹ to ~700 cm⁻¹ is evident, showing the successful photoisomerization of the azobenzene moiety in the polymer film.



Figure 2.1:

a) Kinetic FTIR data of a dry p(AzAm-co-DMAm) film during irradiation with a UV lamp. The peaks are marked as *trans* (before irradiation) and *cis* (after irradiation). b) Position of the maximum of the \sim 700 cm⁻¹ peak.

Utilizing in-situ time-of-flight neutron reflectometry (ToF-NR) measurements with high temporal resolution at the D17 instrument at ILL, we obtained depth-resolved data about the water distribution during swelling, drying, and irradiation with UV-light. A custom-made sample environment, which allows for the control of temperature, humidity and irradiation was used for the measurements [2]. The film was swollen in D₂O-vapor and then irradiated with UV-light for one hour. Fig. 2.2a-b shows the static measurements taken in each of these states and the scattering length density (SLD) profiles of the fit models. It can be seen that there is an increase in film thickness and SLD when the film is swollen. When the film is irradiated, its thickness and SLD decrease, indicating a loss of D_2O . When the lamp is switched off, they increase towards their previous values, with the exception of a water-rich layer between substrate and polymer. This demonstrates a measurable, albeit small effect of UV light on the swelling of the polymer film. Fig. 2.2c-d shows the time-resolved ToF-NR results of the initial swelling of the film in *trans* state. The fit results show an increase in thickness from 53 to 64 nm, due to uptake of D_2O by the polymer film. The fit results show that the dry polymer with a thickness of 53 nm experiences an increase of thicknes when D_2O is introduced to the sample environment, reaching a final thickness of 64 nm when saturated with D_2O molecules.





a) Static ToF-NR curves (symbols) and fits (lines). b) SLD profiles of the models used for fitting the data. c) Kinetic ToF-NR curves at different points in time (bottom to top), showing data (symbols) and fits (lines). d) Thickness of the polymer film versus time (left axis, red) and D_2O volume fraction versus time (right axis, green).

In summary, the kinetic FTIR shows a successful isomerization of the azobenzene moiety in the thin polymer film. Static ToF-NR results show a change in the film's water content after irradiation with UV-light and the time-resolved measurements shed light on the kinetics into water uptake of the film. Our results reveal insights into how photoswitchable moieties affect the microscopic properties of thin polymer films.

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2.2 Influence of salts on the solubility properties of PNIPMAM thin films

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Poly(N-isopropylacrylamide) (PNIPMAM) is a thermoresponsive polymer that exhibits unique properties, making it an intriguing subject of study in polymer science. One of its particular features is its responsiveness to temperature changes around its lower critical solution temperature (LCST). When PNIPMAM is dissolved in water, it undergoes a phase transition at its LCST, resulting in a reversible change in its solubility. Below the LCST, the polymer is hydrophilic and water-soluble, while above the LCST, it becomes hydrophobic and precipitates out of solution. Additionally, it displays a cononsolvency effect in mixed solvents, particularly in water-acetone systems.[1,2] Unlike most polymers, which typically become more soluble with the addition of a cosolvent, PNIPMAM exhibits a counter intuitive behavior by decreasing in solubility when acetone is added to the in water dissolved polymer. The polymer's versatility is enhanced by the cononsolvency effect, which provides opportunities to adjust its solubility characteristics in different solvent environments. The solubility transition of PNIPMAM in response to temperature and solvent composition allows for the design of smart materials with specific functionalities. Furthermore, these properties can be influenced by the addition of salts to provide the possibility to tune the response behavior of PNIPMAM towards different kinds of stimuli. It is known that certain ions can influence the solubility of a polymer system due to electrostatic interactions between polymer chains, solvent molecules, and ions.[3] The specific ion effect is particularly noticeable when ions selectively interact with specific functional groups on the polymer chain, leading to changes in the interactions between the polymer and the solvent.

Inspired by the unique properties of PNIPMAM and the interplay between the mentioned phenomena PNIPMAM thin films containing different kinds of salt and coated on silicon substrates are fabricated and studied. To study the effect of salts on the cononsolvency effect, the saltcontaining PNIPMAM thin films are firstly swollen in a water-rich atmosphere before they are exposed to a water-acetone vapor mixture atmosphere in a certain ratio to induce the collapse transition of the polymer thin films. The experiment is conducted at a constant temperature to exclude effects originating from the thermoresponsive behavior of PNIPMAM. Two different perchlorate salts are chosen to be added to the polymer films, namely sodium and magnesium perchlorate.

These systems were investigated with time-of-flight neutron reflectometry (ToF-NR) to obtain the thickness evolution over time and to elucidate the solvent distribution inside the films upon the introduction of the different kind of solvent atmospheres. In Fig. 2.3 the fitted reflectivity patterns obtained during the dynamic measurements, i.e., the swelling and collapse process upon the introduction of the different solvent vapors and the thickness evolution over time of the salt-containing PNIPMAM thin films are shown. By inspection of the obtained reflectivity curves it can be seen that the modulations of the Kiessig fringes are changing during the individual processes. When the spacing of the fringes decreases, a thickness increase is observed and *vice versa*. Additionally, the position of the critical edge gives information about the overall scattering length density (SLD) of the system which is comprised by the individual SLDs of the different components inside the film. If the edge is moving towards higher q_z values a component with a higher SLD is incorporated into the films and *vice versa*. As D₂O has a rather high SLD compared to acetone and the polymer system, it is expected that the critical edge moves towards higher q_z values when D₂O is incorporated into the film. Contrarily, when acetone is introduced, a shift towards lower q_z values is expected.



Figure 2.3:

a,b) Reflectivity patterns and the corresponding fits obtained during the swelling and collapse processes for both investigated systems. c) Thickness evolution over time for the PNIP-MAM thin films containing either NaClO₄ (green) or Mg(ClO₄)₂ (orange).

By comparing the thickness evolution over time of both systems it can be seen that in pure D_2O vapor atmosphere (100% D_2O gas flow) both systems show an increase in film thickness, where the NaClO₄ containing PNIPMAM thin film shows the strongest increase. After an equilibrated swollen state of the films is reached, a water-acetone vapor mixture with the ratio of 90:10 was introduced into the surrounding of the films. Both investigated films show a film thickness decrease which is attributed to a volume contraction of the films. Again, the NaClO₄ containing PNIPMAM thin film shows the strongest response with a film thickness decrease of over 50%. This investigation shows that the addition of salt can influence the response towards solvent vapor atmospheres of PNIPMAM thin films. The pronounced difference in the solvent uptake behavior is remarkable since both salts consist of the same anion (perchlorate) and only differ in the type of the cation. It is believed that this effect is not only due to the different solubilities of the salts in water, i.e., higher solubility of sodium perchlorate in water, but also due to the influence of the salts on the electrostatic interactions between the individual components in the system leading to a change in the solubility of the polymer in the different solvents. However, these observations demonstrate the potential of salts to influence solubility properties of polymer thin films and thereby salt can act as a tuning parameter to either increase or decrease the responsiveness of such systems. In summary, this highlights the possibility to fine tune specific properties of an already known polymer system and to be able to adapt these to the desired requirements for a given application instead of the *de novo* design of materials.

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2.3 Salt series modulated solvation behavior of poly(sulfobetaine)-based diblock copolymer thin films in mixed water/methanol atmosphere

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Over the past decades, many experimental works illustrated that the presence of salts plays a widespread specific ion effect (SIE) on the phase transition behavior of thermoresponsive polymers, following a well-known Hofmeister series: $CO_3^{2-} > SO_4^{2-} > PO_4H^{2-} > F^- > CH_3COO^- > CI^- > Br^- > I^- > NO_3^- > CIO_4^- > SCN^-.[1-4]$ In our previous studies, the added cosolvent (methanol or acetone) disrupts the water structure, resulting in a collapse of poly(sulfobetaine)-based diblock copolymer (DBC) thin films.[5,6] This phenomenon is known as "cononsolvency behavior". Thus, the presence of salts (water structure makers or breakers) is expected to have a dramatic effect on the cononsolvency behavior of DBC films. To study the salt effect on the conosolvency behavior, the PSBP-*b*-PNIPMAM thin films, loaded with five different potassium salts (anions are CH_3COO^- , CI^- , Br^- , I^- , NO_3^-) respectively, are prepared to examine the solvation behavior upon water and subsequent mixed water/menthol atmosphere via *in situ* spectral reflectance (SR) and Fourier-transform infrared (FT-IR) spectroscopy.



Figure 2.4:

Evolution of the swelling ratio d/d_{ini} obtained from SR measurements as a function of time for PSBP-*b*-PNIPMAM thin films upon a) vapor switching process and b) pure methanol swelling process. The black arrows indicate the positions where the swelling ratios changes.

Obviously, the synchronously developed thicknesses of DBC thin films obey an independent salt series: $CH_3COO^- > CI^- > Br^- > NO_3^- > I^-$, as shown in Fig. 2.4 a. Importantly, except for the maximum swelling ratio upon H₂O swelling process (stage *II* in Fig. 2.4 a), both the times to end the middle near-linear or subsequent slow contraction (black arrows, stage *III* in Fig. 2.4 a), also obey the established salt series. Besides, the salt effect on the swelling ratio of DBC films realizes a continuous and uniform layer distribution without changing the variation trend. Compared to salt-free samples, a higher swelling ratio for salt-loaded samples illustrates a significant salting-in effect even in a mixed water/methanol atmosphere. Upon pure methanol swelling process (stage *IV* in Fig. 2.4 b), all DBC films swell instantaneously to a high ratio and then contract immediately to the equilibrium in a short time. This implies that all films experienced a process of instantaneous absorption and subsequently brief release of methanol molecules. We clarified this phoneme as "methanol self-relaxation". The relaxation time (black arrow, stage *IV* in Fig. 2.4 b) depend on the anion species loaded but is difficult to

distinguish due to partial overlapping or interspersing.

Upon D₂O hydration (Fig. 2.5 a), the height and area of the hydroxyl band of D₂O (*vas*(O-D₂) $\approx 2540 \text{ cm}^{-1}$) increases while decreasing for H₂O (*vas*(O-H₂) $\approx 3400 \text{ cm}^{-1}$), since the absorbed D₂O molecules replace the residual H₂O. Analogously, the reversed variations in both hydroxyl bands upon mixed vapor switching, illustrate the coexistence of water release and methanol-d₃ absorption. As expected, the salt effect on absorbed D₂O contents upon D₂O hydration (solid lines, stage *II* in Fig. 2.5 b) obeys the salt series founded with SR, that CH₃COO⁻ > Cl⁻ > Br⁻ > NO₃⁻ > I⁻ for DBC films. Differently, upon vapor switching, the salt series above are inherited clearly by the equilibrated methanol-d₃ contents (dashed lines, stage *III* in Fig. 2.5 b) instead of D₂O contents. This implies that the determined salt series mainly maintained by the absorbed methanol-d₃ content in the presence of nearly equal amounts of D₂O content. In addition, the phenomena of methanol self-relaxation, leading to a short reswelling process in the first 10 min, is observed clearly in methanol-d₃ content.



Figure 2.5:

a) FT-IR spectra and b) temporal evolution of normalized peak areas of O-D and O-H stretching vibrations of salt-loaded DBC films. The black arrows in panel a) highlight the growth or decay of characterized signals. The peak areas of O-H stretching vibrations in panel b) are plotted as dotted lines corresponding to the right y-axis, to distinguish them from O-D stretching vibrations.

In short, the salt effect of potassium salts (KCH₃COO, KCl, KBr, KI and KNO₃) on the solvation behavior of DBC thin films is systematically studied via SR and FT-IR in water and subsequent mixed water/methanol atmosphere. Compared to the reference studied salt-free samples we observe a salting-in effect.

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3 Functional thin films



3.1 Synthesis and self-assembly of gold nanoparticles for optoelectronic devices

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Plasmonic nanostructures such as gold nanoparticles (AuNPs) have gained significant attention for their unique plasmonic properties, which make them useful for a range of applications, including chemical and biological sensing, solar energy harvesting, and plasmon-enhanced spectroscopies [1]. The tailoring of plasmonic arrangement size and inter-particle distance allows for precise control of optical and electrical properties. This can enhance the light-matter interaction resulting from localized surface plasmon resonances (LSPRs). Due to their LSPRs, AuNPs exhibit size- and shape-dependent light absorption and scattering, as well as near-field amplification. Integrated nanocomposites that combine photoactive materials with plasmonic metals are of particular interest due to their ability to enhance the overall properties of the hybrid film. The hybrid nanostructures offer several advantages, including high processability, spectral tunability, and compatibility achieved by tuning the morphology and arrangement of plasmonic nanoparticles [2]. To fully explore the benefits of plasmonic-enhanced optoelectronic devices, it is crucial to optimize plasmonic nanostructures based on AuNPs to achieve high-efficiency optoelectronic devices. Therefore, it is necessary to produce AuNPs with high monodispersity and shape control across a wide range of sizes. Additionally, it is important to prevent NP aggregation as it can significantly impact film morphology and charge carrier efficiency. The self-assembly of AuNPs is a frequently used strategy for fabricating large-area plasmonic structures and preventing NP aggregation [3].





Starting with the synthesis, small AuNPs were prepared using a seed-mediated growth procedure. Large AuNPs were produced by overgrowing the small AuNPs with mild oxidation [1]. The method's basic principle involves reducing the precursor using a strong reducing agent to form seed particles and then add them to a metal salt. The final size of the NPs was controlled by the amount of AuNPs seeds added for growth, assuming that the amount of metal salt remains constant. Due to their LSPRs, AuNPs exhibit size-dependent light absorption. As the diameter of the NP increases, the wavelength of maximum absorbance shifts towards longer wavelengths (Fig. 3.1a). The change in color of the NP solution with increasing size can also be observed visually, as demonstrated in the Fig. 3.1b.

After synthesizing AuNPs of different sizes, hybrid nanostructures were developed that contain self-assembled AuNPs embedded in a solid matrix of PbS colloidal quantum dots (CQDs) for use in optoelectronic devices. As shown in Fig. 3.2b-c the AuNPs array was successfully dispersed on Si substrates using the self-assembly monolayer (SAM) method. These nanostructures could effectively prevent the aggregation problem of plasmonic metallic NPs. Therefore, they could be applied in optoelectronic devices based on CQDs to enhance their performance. From the SEM images (Fig. 3.2a-c) it is evident that the AuNPs have a significant impact on the formation of the PbS film, thereby affecting the morphology of the hybrid film. Grazing-incidence small-angle X-ray scattering (GISAXS) has also been used to investigate the hybrid film (Fig. 3.2d-f) , as it has been proven to probe quantum dimension and inner film morphology [4]. Fitting the GISAXS data is expected to provide a better understanding of the hybrid film morphology. To gain insight into the device's performance improvement, electrical measurements are necessary. Further investigation of the morphology and optoelectronic properties of the hybrid nanostructure could provide guidance for its application in optoelectronic devices in the near future.



Figure 3.2:

SEM and GISAXS measurements of the hybrid film a,d) bare Si/PbS film, b,e) Si/PbS with 10nm AuNPs, c,f) Si/PbS with 20nm AuNPs

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3.2 Sputter deposition of Ag on self-assembled Au nanoarrays

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The intensified interactions between light and matter, driven by Localized Surface Plasmon Resonance (LSPR), arise from the electromagnetic fields generated at the junctions between metallic nanostructures.[1] Structural strategies design can alter the plasmonic characteristics, as arranging metallic nanostructures enables the control of plasmonic coupling interactions, thus influencing their overall optical features. These distinctive properties make metallic nanostructures suitable for analytical purposes, such as surface-enhanced Raman scattering (SERS). For improved sensitivity in SERS, it's crucial to have precisely defined plasmonic structures that can effectively create and enhance these "hotspots".[2] The characteristics of LSPR are greatly influenced by the type of metal used and the distance or nanogaps between particles in the metallic nanostructure. In the field of SERS applications, gold (Au) and silver (Ag) are particularly favored due to their plasmonic properties. Additionally, one method to further enhance plasmonic properties is creating a bimetallic or polymetallic plasmonic structure. These bimetallic systems, as opposed to single-metal systems, can merge the unique benefits of each metal, leading to an overall enhancement of their properties. To optimize the functionality and application possibilities of such metal structures, a careful monitoring of their formation process is essential. Therefore, there is an urgent need for an in situ technique with high-resolution capabilities to observe and track their developmental process.



Figure 3.3:

SEM images of both 10 nm and 20 nm Au NPs array on the Si substrate and schematic diagram of GIXS measurement.

Grazing-incidence X-ray scattering (GIXS) stands out as an effective method for analyzing nanostructures at the nanoscale level.[3] Its popularity in in situ experiments stems from its ability to capture high-temporal-resolution data and its strong penetration detection capabilities. Furthermore, GIXS is useful for examining the size, spatial distribution, and crystalline
properties of metallic.[4] Herein, we propose creating a bimetallic nanostructure by sputterdepositing Ag onto self-assembled Au nanoarray with in situ monitoring using GIS/WAXS (grazing-incidence/small and wide-angle X-ray scattering). In particular, we constructed arrays of both 10 nm and 20 nm Au NPs on a Si substrate and then applied high-power impulse sputtering of Ag with a deposition rate of approximately 3.06 Å/s on top, to form an Au/Ag bimetallic nanostructure (Fig.3.3). Fig. 3.4a depicts the time-dependent changes in the GIWAXS data for 10 nm and 20 nm samples. Comparable to the GIWAXS outcomes for the uncoated Au nanoparticles, two prominent peaks are observed, which align with the (111) and (200) crystallographic planes of the Au/Ag structure. As the Ag deposition time extends, there is a noticeable and steady increase in the intensity of these peaks. Fig. 3.4b displays contour plots that evolve corresponding to the horizontal line cuts at the Yoneda peak position in the Au/Ag samples. The detailed examination of these binary structures will further analyze and study their potential application as SERS substrates. We anticipate that the developed binary nanostructure will offer valuable guidance for analytical applications in the near future.



Figure 3.4:

a) Mapping of vertical line cuts from 2D GIWAXS data and b) horizontal line cuts from 2D GISAXS data measured during the sputter deposition of Ag on both 10 nm and 20 nm nanoarrays.

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3.3 Polymer hydrogel films for green hydrogen production

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Hydrogen (H₂) is an increasingly in-demand resource across various sectors. The majority of this demand surge arises from conventional applications, notably in refining and industrial processes. Moreover, the energy sector is actively exploring hydrogen-based alternatives to address the substantial increase in energy consumption. Hydrogen production methods are categorized along a color spectrum. *Grey* denotes processes utilizing natural gas or methane, relying on non-renewable resources. Conversely, hydrogen is labeled *green* when produced exclusively using energy from renewable sources. Presently, *grey* hydrogen dominates the overall production landscape. The production of *green* hydrogen is on the rise, with water electrolysis emerging as the predominant technology in the *green* hydrogen sector.

This project aims to create a device for producing green hydrogen using a less-explored technology: water photocatalysis derived from the water splitting reaction. The core concept involves utilizing hydrogel polymers in a thin film configuration as a water storage material to accommodate an appropriate photocatalyst. This innovative system is positioned to serve as an efficient and environmentally friendly method for producing green hydrogen.

The initial phase of this project focuses on identifying a suitable polymer. For this purpose, poly(*N*-isopropylacrylamide) (PNIPAM) and its structural isomer, poly(*N*-isobutyramide) (PNVIBAM), have been selected for comparison. PNIPAM is recognized for its favorable water swelling capacity below its transition temperature (approximately 32 °C in water).[2] However, PNVIBAM is a promising candidate due to its heightened thermal stability (transition temperature approximately 39 °C in water).[3] This study aims to provide a comparison of the water swelling behaviors of PNIPAM and PNVIBAM, employing neutron reflectivity. PNIPAM and PNVIBAM thin films were placed in a custom-made chamber connected to a gas-flow set-up. The films were exposed to deuterated water (D₂O) vapors to enhance a better contrast under neutron characterization. Knowing the scattering length density (SLD) of the polymers, the volume fraction of the absorbed D₂O of the films has been determined. It was observed, as depicted in Fig. 3.5, that the PNIPAM film exhibits a superior swelling capacity compared to PNVIBAM. Specifically, PNIPAM achieves a volume fraction of D₂O 6% higher than PNVIBAM. Consequently, PNIPAM has been selected as the polymer water storage for the hydrogen evolution system.

The subsequent phase of this project focused on loading the PNIPAM film with a suitable catalyst for the photocatalytic water-splitting reaction. As a candidate, platinum-loaded carbon nitride (Pt-CN) was chosen due to its favorable bandgap of 2.7 eV and environmentally friendly characteristics. Additionally, carbon nitride presents a straightforward and cost-effective synthesis route, enabling large-scale production.[4] A new home-built setup was designed to facilitate the production and detection of hydrogen from thin films. This setup incorporates a solar simulator light source (class ABA) with a light intensity of 100 $mW.cm^{-2}$. The hydrogen detection is performed using an online gas chromatograph. For the photocatalytic experiment, a Pt-CN-loaded PNIPAM solution was drop cast onto a glass substrate. The swelling of the polymer film was induced by the presence of water channels within the sample environment. The schematic representation of the experimental setup is illustrated in Fig. 3.6. This setup not



Figure 3.5: Time evolution of the D₂O content of PNIPAM and PNVIBAM films.



Figure 3.6:

Schematic view of the experimental design of the hydrogen production via photocatalytic water splitting reaction.

only allows controlled production of hydrogen from thin films but also enables accurate detection, providing valuable insights into the efficiency of the Pt-CN-loaded PNIPAM system in the photocatalytic water splitting reaction.

Following a swelling duration of 20 hours, the film underwent light irradiation to initiate the water-splitting process. The exposure to light was maintained for a period of 3 hours, after which a fraction of the head volume from the sample environment was introduced into the gas chromatograph. Subsequently, the hydrogen evolution rate was determined, revealing a note-worthy value of $2777 \,\mu mol \cdot g^{-1} \cdot h^{-1}$. This observed rate highlights the efficiency of the system in producing hydrogen through the photocatalytic water-splitting reaction, offering promising implications for its practical application and sustainability in the field of green hydrogen production.

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3.4 Tunable mesoporous films with ZnTi-mixed metal oxides via diblock copolymer templating

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Zinc titanium oxides (ZnTiO₃, Zn₂TiO₄, and Zn₂Ti₃O₈), serves as an efficient heterogeneous catalyst, notably enhancing reaction rates by improving the charge separation efficiency of photogenerated electron-hole pairs within the intra-heterojunction.[1] It is a promising and environmentally friendly material with various applications, for example, dehydrogenation reactions,[2] photostable perovskite solar cells,[3] photocatalyst.[4] The synthesis strategies contain the sol-gel process, hydrothermal method, solid-state reaction, precipitation method, and electrochemical method. [5] The sol-gel process is commonly used in the production of mesoporous structure films for organic-inorganic hybrid films due to its ability to precisely control their shape and size. In this work, we used the sol-gel process to prepare the hybrid films of diblock copolymers polystyrene-block-polyethylene oxide and the precursors of titanium dioxide and zinc oxide. Then, the hybrid films were calcined to obtain zinc titanium oxide mesoporous films. The differences in the film morphologies before and after calcination demonstrate the function of the polymer template and calcined temperature in the mesoporous films. The impact of these variables on the hybrid film structures and crystal films is examined by scanning electron microscope based on the surface morphologies. This study explores the impact of temperature and precursor ratios on the morphologies of mesoporous zinc titanium oxide films, providing insights for optimizing their properties for potential applications.



Figure 3.7:

SEM images of the mesoporous zinc titanium oxide films when the ratio of two precursors is 1:1 by changing calcination temperature (a) room temperature, (b) 300° C, (c) 400° C, (d) 600° C.

Two precursors of titanium oxide and zinc oxide with two mass ratios of 1:1 and 3:7, respectively, were used in sol-gel solutions containing the diblock copolymers. The prepared hybrid films consisting of the copolymers and the precursors will be calcined at 300°C, 400°C, and 600°C. The surface morphologies of the fabricated films were characterized using scanning electron microscopy (SEM). Fig. 3.7 shows the surface morphologies of the films when the ratio of two precursors is 1:1. Comparing the hybrid film before calcination (a) and after calcination (b-d), the images illustrate the morphology evolution from small holes and unclear worm-like structures to clear worm-like structures, with an increase in the width of the worm-like structures. The small hole of the hybrid film may be attributed to solvent evaporation during the drying process. The worm-like structures were observed in the hybrid film before and after calcination. The increased width of the worm-like structures with increasing calcination temperature implies that they were formed by the diblock copolymer templates.



Figure 3.8:

SEM images of the mesoporous zinc titanate films when the ratio of two precursors is 3:7 by changing calcination temperature (a) room temperature, (b) 300° C, (c) 400° C, (d) 600° C.

The self-assembly structure of amphiphilic diblock polymers can be affected by the additives due to differences in interfacial energy. Thus, here we assume that the ratio of the two precursors may also impact the final morphologies. In order to investigate the effects of the precursors, we prepared a hybrid film with a titania-to-zinc ratio of 3:7. The resulting hybrid films were calcined at 300°C, 400°C, and 600°C, as shown in Fig. 3.8. Fig. 3.8 illustrates the film morphologies of the films with and without a polymer template. When comparing the morphology of Fig. 3.7 (a) to that of Fig. 3.8 (a), it is evident that the increasing content of zinc precursor causes the polymer templates to change from worm-like to spherical surface morphologies. This change may be due to the altered interfacial energy in the film. As the calcination temperature is increased from 300 to 600°C, the surface morphologies exhibit not only ordered spherical structures but also ellipsoid particles. The porous structures are a result of the polymer template, with pore sizes slightly increasing as the temperature rises. The formation of aggregates after calcination is assumed to be related to the different temperatures required for different crystalline formations.

Due to the possibility of having different morphologies of a film on the surface and inside, grazing incidence small-angle X-ray scattering (GISAXS) measurements will be used to gain the size and shape of nanostructures into the inner structures. The crystal structures formed in the calcined films, as shown in Fig. 3.7 and Fig. 3.8, are different which probably caused due to different crystal type. The crystal types of the calcined films will be proved using X-ray diffraction, which has high potential in photoelectric applications.

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3.5 Humidity influence on ionic liquid post-treated PEDOT:PSS films

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Organic electronics have gained increasing significance in various applications, such as lightemitting diodes, bioelectronics, displays, transistors, solar cells, and sensors. Notably, organic electronics, including the widely used polymer blend poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), exhibit unique advantages over their inorganic counterparts. These advantages include low toxicity, lightweight, transparency, mechanical flexibility, and cost-efficient large-scale fabrication processes. The following study focuses on the effects of environmental factors[1], specifically ambient humidity[2], on the performance and stability of PEDOT:PSS thin films post-treated with the ionic liquid 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA). The intricate nanoscale domain structure of PEDOT:PSS, altered by the post-treatment, plays a crucial role in the material's properties.[3]



Figure 3.9:

a) Film thickness evolution, b) water uptake, c) electronic conductivity, and d) ionic conductivity of PEDOT:PSS thin films post-treated with different concentrations of EMIM DCA. Adapted with permission from reference [2]. Copyright (2023) American Chemical Society.

In situ spectral reflectance (SR) and time-of-flight neutron reflectometry (ToF-NR) were employed to investigate the swelling behavior of PEDOT:PSS films during exposure to defined humidity protocols. The study focuses on two concentrations of EMIM DCA (0.05 M and 0.35 M), with a 0 M reference sample. The results reveal that post-treatment with EMIM DCA influences the film's swelling behavior and water uptake, presented in Figure 3.9 a) and b). The films exhibit significant swelling, with the maximum relative swelling ratio being higher for a higher EMIM DCA concentration. In-depth analysis through static ToF-NR measurements confirms

the changes in film thickness and provides insights into the water incorporation and polymer layer evolution.

In situ electrochemical impedance spectroscopy (EIS) was conducted to assess the humiditydependent conductivity behavior of the PEDOT:PSS films. The results are shown in Figure 3.9 c) and d). The 0 M reference sample exhibits only electronic conductivity, while the 0.05 M and 0.35 M samples display both electronic and ionic conductivity contributions. The electronic conductivity decreases with increasing humidity, whereas ionic conductivity increases, reaching maxima at 80% RH. The influence of post-treatment on the conductivity behavior is attributed to changes in the PEDOT:PSS domain morphology and the incorporation of ionic liquid ions.[3]



Figure 3.10:

Schematic sketch of the charge carrier transport properties at different humidites of PEDOT:PSS thin films post-treated a) without or b) with EMIM:DCA. All figures are adapted with permission from reference [2]. Copyright (2023) American Chemical Society.

A comprehensive model is proposed to illustrate the influence of humidity on the morphology and charge carrier transport in PEDOT:PSS films, both with and without EMIM DCA posttreatment, as presented in Figure 3.10 a) and b). The untreated film experiences decreased electronic conductivity with rising humidity due to water uptake in the hygroscopic PSS matrix and increasingly hindered intra-domain charge transport. In contrast, EMIM DCA post-treated films exhibit an additional ionic conductivity, which is enhanced at higher humidity levels. These films also undergo swelling and water uptake into the PSS matrix, which positively affects the ionic charge transport of ionic liquid ions incorporated inside the thin film and subsequently increases the ionic conductivity.

This research provides valuable insights into the humidity-dependent conductivity behavior of PEDOT:PSS thin films post-treated with EMIM DCA. The study emphasizes the intricate interplay between film morphology, water uptake, and charge carrier transport, shedding light on the potential of ionic liquid post-treatment to influence the performance of organic electronic devices. Understanding these effects is crucial for optimizing the utilization of PEDOT:PSS in various applications exposed to diverse environmental conditions.

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3.6 Time-dependent morphology evolution of templated mesoporous titanium films

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Mesoporous materials have gained significant attention across diverse applications such as catalysis, adsorption, energy conversion and storage, sensing, filtration, and separation[1]. Due to its precise control over porosity and texture, the soft-templating method has been employed in designing mesoporous silica-based, carbon-based, and metal-based materials. In this method, precursors and soft templates collaboratively form mesostructured composites through non-covalent bonds[2]. General precursors, typically metal alkoxides, undergo hydrolysis and condensation, yielding various products at different reaction stages in an aqueous solution and leading to diverse final morphologies. Several titanium alkoxides have been selected as examples to illustrate the general time-dependent morphology evolution.



Figure 3.11:

Structural evolution of titanium films prepared with EGMT under different reaction time. SEM images (a-e) and corresponding 2D GISAXS data (f-j) of structural evolution of titania thin films. The upper right insets in SEM images refer to the corresponding fast Fourier transform (FFT) patterns. Horizontal line profiles extracted from 2D GISAXS data (k). Sketch of the morphology evolution(l).

Fig. 3.11 shows the structural evolution of titanium films prepared with ethylene glycolmodified titanate (EGMT) under different reaction times. According to the SEM images, a short reaction time leads to disordered foam-like structures. With increasing reaction time, the ratio of cylinders decreases, and finally, the film evolves into ordered mesopores after 12 h reaction. The horizontal line profiles extracted from 2D GISAXS data confirm the structure evolution over time. The interaction between metallic species and polymer template is too strong at short reaction time and drives block copolymer forming cylindrical micelles. With increasing reaction time, precursor is transformed into small and uniform nanoparticles. The interaction between nanoparticles and PEO is appropriate for co-assembly, thus delivering ordered mesostructures. A sketch of this morphology evolution was given in Fig. 3.11.



Figure 3.12:

General structural evolution over time from different precursors, TTIP (a-d), TB (e-h), and TIPA (i-l). The first column is the structures of different precursors. The corresponding structural evolution (2D GISAXS data) is presented in the same row as the precursor structure. A very similar structural evolution was observed over time for all these precursors.

While EGMT is solid due to a higher coordination number of Ti and bridging oxygen atoms, commercial metal oxides, such as titanium isopropoxide (TTIP), titanium diisopropoxide bis(acetylacetonate) (TIPA), titanium butoxide (TB), are liquid and sensitive to moisture[4]. These liquid precursors have a much faster hydrolysis rate in aqueous solution due to their structures shown in Fig. 3.12a, e, and i. According to the 2D GISAXS data, a similar structural evolution was observed with TTIP, TIPA, and TB despite their distinct structures and hydrolysis rates. The morphology of thin films undergoes disordered foam, cylinder-sphere hybrid, spheres with short-range order, and crystalline structures. The similar morphology evolution demonstrates the general time-dependent tunability of the block copolymer templated sol-gel method.

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3.7 Diblock copolymer directed co-assembly for mesoporous ZnO films

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Nanostructured ZnO architectures, distinguished by their morphological richness and intrinsic multifunctionality, have emerged as a flexible and effective platform that can be integrated into interdisciplinary nanotechnologies, ranging from photoelectric conversion, environmental monitoring, and biomedical diagnoses.[1] In particular, introducing mesoporous frameworks into ZnO structures would further broaden the dimension of their practical applications by creating higher surface area, more reaction active sites, and favorable electron/ion/mass transport pathways.[2] Over the past decades, extensive research efforts have been devoted to the fabrication and device assembly of mesoporous ZnO, witnessing the critical role of morphology on final performance. In the present work, we fabricate different mesoporous ZnO thin films by exploiting block copolymers as structure-directing agents and investigate the template effects on both the surface and inner morphologies of ZnO films.

As for the structure-directing agents, amphiphilic polystyrene-block-polyethene oxide (PSb-PEO) and polystyrene-block-poly(4-vinyl pyridine) (PS-b-P4VP) with different molecular weights are selected here due to the strong repulsive interaction between the hydrophobic PS and hydrophilic PEO (or P4VP) segments. Scanning electron microscopy (SEM) images are first taken to reveal the surface morphologies of as-obtained mesoporous ZnO films after eliminating the sacrificial polymer templates via high-temperature calcination (Fig. 3.13). The completely different ZnO scaffolds are readily distinguished from the viewpoint of shapes, dimensions, and accessibility of pores. Irrespective of the polymer chosen as the building block, three representative samples exhibit pronounced structuring on the nanometer length scale, which predominantly benefits from the intrinsic self-assembly features of DBCs. The formation of a wormlike structured film is guided by the lower-molecular-weight $PS_{20.5k}$ -b- $PEO_{8.0k}$ polymer, with the subscripts representing the number-average molar mass of the corresponding blocks. This porous film demonstrates randomly distributed yet highly interconnected ZnO nanostructures across the entire film volume (Fig. 3.13a). As opposed to this, the sponge-like film templated by the higher-molecular-weight $PS_{60.0k}$ -b- $PEO_{36.0k}$ polymer possesses relatively well-defined spherical pore arrays with more densely packed inorganic ZnO walls (Fig. 3.13b). In stark contrast, the grid-like film derived from the $PS_{11.8k}$ -b- $P4VP_{10.8k}$ polymer exhibits more ordered structures, which highly resemble the nanowires stacked in an orthogonal way (Fig. 3.13c).

Such a discrepancy in structural ordering can also be reflected by the 2D Fast Fourier Transformation patterns shown in the insets in Fig. 3.13a-c. Different from the fuzzy sphere characteristic of the former two films, the square-like 2D FFT pattern observed in the grid-like film further verifies that the ZnO nanostructures are more regular in spatial arrangements. Correspondingly, the extracted power spectral density functions are shown in Fig. 3.13d. Compared to the others, a more well-defined peak shape in the grid-like ZnO film suggests its relatively higher level of nanostructural ordering, that is, such periodic arrangements are maintained over a larger macroscopic area. Combining the peak values in the curves and Bragg's equation $d = 2\pi/k$, the structural ordering on the film surface can be quantified by the interdomain distance d. Accordingly, the d value can be calculated to be 35.3 nm, 58.9 nm and 32.7 nm for worm-like, sponge-like and grid-like ZnO films, respectively. Compared to a well-defined peak in grid-like ZnO film, the larger peak width in worm-like and sponge-like ZnO film is indicative of the poorer structural order. Meanwhile, the smallest inter-domain distance implies that the ZnO nanostructures in this film are more closely packed.



Figure 3.13:

Surface and inner morphologies. Top-view SEM images of a) $PS_{20.5k}$ -b- $PEO_{8.0k}$ templated worm-like, b) $PS_{60.0k}$ -b- $PEO_{36.0k}$ templated sponge-like and c) $PS_{11.8k}$ -b- $P4VP_{10.8k}$ templated grid-like ZnO thin films. All samples share the same scale bar (200 nm). d) Power spectral density (PSD) functions extracted from azimuthal integration of the intensity distribution in the corresponding 2D FFT patterns calculated from the SEM images for mesoporous ZnO thin films. All PSD profiles are shifted along y-axis for clarity.

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3.8 Freestanding polymeric films via one-step ionic salt post-treatment

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The organic conducting polymer poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) has garnered enormous attention in the field of organic electronic devices due to low-cost solution processability, highly tunable conductivity, superior mechanical flexibility, good biocompatibility together with excellent atmospheric stability. However, the low electrical properties and instability in water of the pristine PEDOT:PSS film limit its wide range of applications.[1,2] In this work, we present a facile but effective one-step ionic salt post-treatment strategy to boost the electrical properties and water stability of PEDOT:PSS via an ionic exchange reaction. We investigate the effect of cationic species of ionic salts on the electrical properties of dropcasted PEDOT:PSS films by introducing three ionic salts with three cations (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM)/lithium (Li)/zinc (Zn)) but the same bis(trifluoromethylsulfonyl)imide (TFSI⁻) anion. It was elucidated that simultaneous enhancement in the Seebeck coefficient and conductivity is achieved for all post-treated PEDOT:PSS films, but the Zn(TFSI)₂-post-treated one shows the optimized enhancement of thermoelectric properties.

Fig. 3.14a-c compares the in-plane thermoelectric properties of all the salt-post-treated PE-DOT:PSS films varying with the salt concentration. The electrical conductivity (σ) of the pure film is measured to be ca. 0.9 S cm^{-1} , comparable to previously literature-reported values. Such a low conductivity primarily stems from the poor charge carrier transport caused by the presence of excess insulating PSS species within the film. By implementing the salt post-treatment, the σ of the PEDOT:PSS film can be dramatically improved by 2-3 orders of magnitude. The σ of the PEDOT:PSS films is gradually enhanced with the increasing concentration of the salts in an aqueous solution as shown in Fig. 3.14a. The maximum σ for each salt post-treated PEDOT:PSS series is achieved at a high concentration of salt in the range of 0.3-0.5 mM. For Zn(TFSI)²-post-treated PEDOT:PSS films, the σ increases up to 892.4 S cm⁻¹ when the concentration of $Zn(TFSI)_2$ solution is 0.4 mM. The maximum σ is in the order of EMIMTFSI-post-treated PEDOT:PSS film (228.8 S cm⁻¹) < LiTFSI-post-treated PEDOT:PSS film $(548.3 \text{ S cm}^{-1}) < \text{Zn}(\text{TFSI})_2$ -post-treated PEDOT:PSS film (892.4 S cm⁻¹) under the optimal salt concentration. As shown in Fig. 3.14b, the obtained positive Seebeck coefficients (S) of the pure film is 17.3 μ V/K, which is in agreement with the values observed in previous reports.[3,4] The S of all post-treated PEDOT:PSS films instantaneously follows the salt concentration rise and slightly varies at a narrow range value of ca. 24-27 μ V K⁻¹. The strong drop of S for EMIMTFSI-post-treated films at the salt concentration >0.5mM is attributed to the residual salts within the film. Thus, the salt post-treatment gives rise to the simultaneous enhancement of S and σ . Considering the anti-correlation between S and σ (typically σ increases whereas S changes inversely) in terms of the charge-carrier concentration and charge-carrier-mobilityindependent S, such a simultaneous increase in S and σ implies the effective improvement of the charge-carrier mobility, suggesting that the enhancement in mobility caused by a high proportion of quinoid structure outcompetes the reduction in charge carrier concentration upon dedoping. An optimized power factor of 16.8 μ W mK⁻², 39.9 μ W mK⁻², and 63.1 μ W mK^{-2} (Fig. 3.14c) is obtained for the PEDOT:PSS film post-treated with EMIMTFSI, LiTFSI, and $Zn(TFSI)_2$, respectively.

In addition, the as-prepared $Zn(TFSI)_2$ -post-treated PEDOT:PSS film exhibits enhanced ductility and flexibility. The strip of this freestanding film can wrap around a rod with a radius of 2.5 mm in an intact way and be easily folded (Fig. 3.15a). Its resistance change (R/R_0) was examined



Figure 3.14:

a) Electrical conductivity, b) Seebeck coefficient and c) power factor of PEDOT:PSS films after post-treatment with different concentrations of salt solution at room temperature.

as a function of the radius of curvature to evaluate the flexibility. In contrast to the pure film, the Zn(TFSI)₂-post-treated PEDOT:PSS film shows extremely high mechanical endurance, as evidenced by almost negligible fluctuation in resistance during bending tests (Fig. 3.15b). The enhanced mechanical properties of Zn(TFSI)₂-post-treated PEDOT:PSS film can be attributed to salt-induced favorable morphological rearrangements. Because of the strong Coulomb attraction between PEDOT and PSS and disorder, the pure film favors a coil-like structure within the film, making the slippage of the polymer chains difficult under stress.[5] The salt post-treatment weakens the Coulomb attraction between PEDOT and PSS as a result of the ion exchange, leading to the formation of the continuous network structure of polymer chains in an expanded coil-like conformation. This unique structure arrangement endows the slippage of the polymer chains under stress and releases more stress.



Figure 3.15:

a) Digital photographs of $Zn(TFSI)_2$ post-treated PEDOT:PSS film in its original state, wrapping around a rod and simple folding. b) The normalized resistance of PEDOT:PSS film w or w/o of $Zn(TFSI)_2$ post-treatment as a function of curvature radii.

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3.9 Nanoscale morphological transformation of PEDOT: PSS during ultrasonic spray deposition

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Organic solar cells (OSCs) have recently attracted much attention due to their various advantages and rapidly evolving performance. For solution-treated cells, most OSC layers are fabricated by spin-coating methods, which, however, are not suitable for roll-to-roll fabrication and have high material loss with limited substrate size [1]. With its potential advantages of not being limited by substrate size and low polymer utilization, the spray coating technique is expected to be a promising alternative to overcome the drawbacks of the conventional spin-coating process. With these merits, spray coating methods have been developed for OSC fabrication with many advantages, such as large-area coating, uniform coating, roll-to-roll compatibility, and a low-cost process[2]. In addition, the spray-coating method can be used for a wide range of fluids with various rheological properties, thus providing the opportunity to adapt the system to deposit virtually any type of solution and obtain a film with the desired properties[3]. Poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS) is to date the most commonly used hole transport layer for organic solar cells. This is due to its good transparency, hole affinity, and suitable work function (around 5.2 eV). It is generally fabricated from a green, nontoxic water solution. Nevertheless, for many applications in solution-processed electronic devices, control over optical and electronic properties is critical in order to optimize device performance and efficiency.

In this work, ultrasonic spray deposition (USD) as an automated and large-area compatible deposition method provides a way to scale up OSC production. It is desirable to develop improved processing routes to optimize the properties of PEDOT: PSS for device applications and maintain a wide processing window. Therefore, a fine-tuned, low-waste, scalable spray coating method is used to obtain uniform, high-quality, large-area films with the intention of increasing scalability for device application upgrades. Here, the hierarchical structure of spray-deposited thin PEDOT: PSS films and structural information such as object geometry, size distribution, and spatial correlation at the nanoscale were quantitatively and systematically investigated using grazing-incidence small-angle X-ray scattering (GISAXS).



Figure 3.16:

(a) Horizontal line cuts and data modelling of 2D GISAXS data; (b) Average domain size distribution; data for ultrasonic spray-coating PEDOT: PSS thin films prepared at different sprayed conditions; The colors of the domain size from small to large are light to dark (S: small domains, M: medium domains, L: large domains).

Figure 3.16(a) shows the horizontal line cuts obtained from the GISAXS data at the critical angle of PEDOT for different spray-coating parameters (different flow rates) of PEDOT: PSS

thin films during USD. As these horizontal line cuts are performed at the Yoneda region of PEDOT, the model fits, shown as lines, provide information about the PEDOT nanostructure, namely, the PEDOT domain radii, domain distances, and domain size distributions, which are presented in Figure 3.16(a). Assuming a spherical object and specifying three shape factors to model the curves, the domain size distributions of PEDOT: PSS films fabricated under different spraying parameter conditions are shown in Figure 3.16(b). As the solution flow rate increases during the spray deposition process, more medium-sized and small-sized regions are formed in the film. More large-size domains are also added before the flow rate increases to a flow rate threshold of 3.5 ml/min. When this threshold is exceeded, the flow rate leads to a smaller size distribution and reduces the number of large aggregates. We also observe an increase in medium-sized domains. These results suggest a structural rearrangement of PEDOT: PSS due to the ink flow rate during the coating process.



Figure 3.17:

X-ray reflectometry (XRR) data and model fit (red line) for PEDOT: PSS thin film spray deposited (a) S1 at 1.5ml/min, (b) S2 at 3.5ml/min, (c) S3 at 5.5ml/min. (d) Scattering length density (SLD) profile of S1, S2, S3.

The morphology and composition depth profile of the sprayed deposited PEDOT: PSS thin films are characterized using XRR for the different flow rates during spray deposition (1.5ml/min, 3.5ml/min, 5.5ml/min, respectively) are shown in Figure 3.17(a-c). The XRR curve was fitted using the software Motofit [4]. The different scattering length density (SLD) profiles for the different spraying conditions are shown in Figure 3.17(d). The film thickness first increases and then decreases with the increase in flow rate (S1: 47.5nm, S2: 53nm, S3: 49nm).

In this work, homogeneous PEDOT: PSS thin films as the hole transport layer of OSC are fabricated using a large-area scalable technique, namely an ultrasonic spray process. After the optimization process, high-quality films fabricated at different spray parameters are studied by finding suitable parameters for spraying.

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4 Photovoltaics



4.1 Investigation of radiation exposure on organic solar cells for potential space application

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As space technologies and space missions develop rapidly, the demand for solar cells dedicated to space applications is increasing. Space solar cells face more critical challenges than before. Higher conversion efficiency and better radiation resistance are the primary keys. This project aims to investigate the degradation of organic solar cells in the space environment. Based on previous work regarding the deployment of organic solar cells (OSC) and perovskite solar cells (PSC) in space on a suborbital rocket [1], we are working on long-term experiments to study the degradation mechanisms in space. For that, we do space environmental simulations on the ground to prepare for long-term experiments in orbit. The main objective is to emulate every significant parameter that can cause damage to solar cells.

Organic solar cells used in space exploration devices are mainly exposed to energetic electrons and protons [2], which causes damage to the morphological and chemical structure of the organic bulk heterojunction through ionization. Therefore, it is interesting to study the impact of ionizing radiation to evaluate the possibilities and prospects for optimizing the performance of solar cells in space. Gamma-ray radiation test is conducted at FRM II, MLZ to investigate the morphology and performance changes at different total ionizing doses. This test will give us a clear idea of how space radiation will affect the structure of our OSCs.



Figure 4.1: Gamma irradiation facility in a spent fuel element at FRM II, MLZ

An irradiation test performed at FRM II, MLZ was using spent fuel elements as a gamma-ray source [3]. Right after the test, a solar simulator was used to characterize the solar cells and compare the performance before and after the irradiation, a UV-Vis spectrometry for samples to investigate the absorbance change, and finally, GISAXS experiments were performed at DESY in Hamburg to investigate in details the structural change of the bulk heterojunction (BHJ).

OSC are a type of photovoltaic cell that use organic materials, to convert sunlight into electricity. High performance OSC materials such as PTQ-2F: BTP-4F as an active layer, with PTQ-2F as polymer donor and BTP-4F as small molecule acceptor, can be spin coated or even printed to form a thin film BHJ. One important aspect of organic solar cell technology is encapsulation, which involves protecting the cells from environmental factors that can degrade their performance. Encapsulation can be achieved through specialized coatings or by enclosing the cells in a protective material, such as a transparent polymer film. The choice of encapsulation method will depend on the specific requirements of the application and the desired level of protection [4]-[5]. Proper encapsulation is essential for organic solar cells' long-term stability and efficiency, as it helps maintain their performance over time. One promising encapsulation. Its features are low thermal conductivity, optical transparency, weather resistance, and high-temperature resistance, and it has good adhesive properties on glass and plastic [6].

Finally, this project will give us a unique chance to investigate the long-term impact of the space environment on solar cells. By analyzing the data from the previous mission and comparing them to lab simulation, we can upgrade and build new solar cells especially to space.

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4.2 Mixed halide perovskite quantum dot layers

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Since the worldwide energy demand has been increasing over the last few years and this trend will continue in the future, producing energy from photons coming from the sun will be more important in the future. Therefore, perovskite nanocrystals are chosen as active material in perovskite solar cells (PSCs) due to its bandgap tunability based on the quantum confinement, its low costs, multi-exciton generation and its compatibility with several different deposition techniques (spin coating, slot-die coating). This results in an increased power conversion efficiency of the devices, and the current record solar cell using perovskite nanocrystals as active material has a power conversion efficiency of 17.4%, which is in the range of the commonly used solar cells.[1] Based on [2] slot-die coated perovskite nanocrystal solar cells have already been produced at the chair of functional materials but still face a few problems during their fabrication, as they have a thickness of only 120 nm compared to thicker bulk perovskite as active material. By just increasing the number of deposited layers on top of each other a further interface was introduced, which is limiting the device's performance. Therefore, in this work, the deposition of the self-synthesized perovskite nanocrystals was investigated, including the washing steps.

The used nanocrystals are synthesized following the protocol described in [3]. The deposition of the perovskite nanocrystal layers consists of several steps. After depositing one perovskite nanocrystal sublayer two washing steps are introduced to remove the ligands on top of the nanocrystals. After having finished the deposition of the final perovskite nanocrystal sublayer a final washing step is done, as can be seen in Figure 4.2, and a perovskite nanocrystal layer results.



Figure 4.2: Concept of the washing and deposition steps[4].

The influence of the washing step was investigated by comparing the photoluminescence (PL) spectra of different films (different amounts of deposited nanocrystal sublayers) and changing the number of washing steps in between, which means that the "layer washing" (compare fig 4.2) was repeated once before a second nanocrystal sublayer was deposited. This is done to ensure that all ligands are removed by the washing, and the remaining ones might not cause

the interface after several deposited sublayers. In addition to the PL spectra, scanning electron microscopy (SEM) pictures were taken to investigate the surface of the created films. The results are shown in figure 4.3.



Figure 4.3:

PL spectra (a)) and SEM pictures (b)-g)) of perovskite layer produced with different amounts of washing steps, b) one layer and final washing step, c) two perovskite layers & layer and final washing, d) two perovskite layers & twice layer and once final washing, e) eight perovskite layers & layer and final washing, f) three perovskite layers & layer and final washing, three perovskite layers & twice layer and once final washing.

The PL spectra show that the number of deposited nanocrystal sublayers does have an impact on the peak position, which gives information about the optical properties of the investigated film. There is a redshift of the PL peak with increasing deposition steps.

The SEM pictures show that the sample is covered homogeneously with nanocrystals. The nanocrystals have an equal size, as can be seen in Figure 4.3b) for just one deposited sublayer. Adding further sublayers does not change the size distribution, as long as only one layer washing step is done. As soon as a second layer washing step is induced, the crystals are larger. The larger colloids might refer to not only removing the ligands at the surface but also some of the ligands between the nanocrystals might be removed. This would result in a merging of several nanocrystals into one larger colloid. This results in a rougher surface, as can be seen in the SEM pictures as well (figure 4.3 d) & g)).

Further investigations of the influence will be done in the future by using grazing-incidence small/wide angle x-ray scattering (GISAXS/GIWAXS) to obtain further information about crystal orientation within the film and during deposition by using slot-die coating.

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4.3 Tuning the crystal-orientation of perovskite thin films via nanocrystal seeds for large-scale applications

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Organic-inorganic halide perovskites have gained a huge interest in the scientific community owing to their favorable optoelectronic properties combined with their ease of production and abundance of raw materials [1]. The combination of the aforementioned factors deems the class of hybrid halide perovskites attractive for low-cost manufacturing of optoelectronic devices such as lasers, photodetectors and solar cells [1]. Most fabrication methods for producing perovskite thin films are based on laboratory scale techniques such as spin coating or drop casting. For real-life applications outside of research however, low-cost, large scale coating methods are required [2]. Amongst the various large-scale fabrication methods, the slot-die coating technique is a promising contender as it offers a stable coating and easily controllable thin film thickness via adapting the respective printing parameters. However, key parameters for the performance of a perovskite based device is also thin film's crystallinity and microstructure. In particular, it has been found that the crystal grain orientation in these thin films plays a significant role for the device as differently oriented grains exhibit local fluctuations in the thin film's optoelectronic properties [3]. Therefore, tuning the grain orientation in perovskite thin films is of particular interest for more reliable devices. Here, we show a novel approach of tuning said orientation in FAPbI₃ thin films by utilizing perovskite nanocrystals that act as seeds for an epitaxial induced crystal growth during the slot-die coating procedure.

The synthesized perovskite nanocrystals are cubic in shape as shown in the SEM measurement (Fig. 4.4 a). X-ray diffraction (XRD) measurements on such nanocrystal thin films also reveal an inherent alignment of the nanocrystals such that the {100} faces are parallel to the substrate as only the {100} peak and its respective higher ordered peak was observed in the diffractogram (Fig. 4.4 b). The average crystal size of the nanocrystals was determined via the Scherrer equation to 26 nm.



Figure 4.4:

a) SEM image of the perovskite nanocrystal thin film. b) Fitted XRD diffractogram of the perovskite nanocrystal thin film

Grazing incidence wide angle X-ray scattering (GIWAXS) measurements with varying incidence angles were carried out for thin film characterization in order to obtain structural information about the printed thin film at different penetration depths. They reveal highly oriented thin films where the FAPbI₃ 100 peak is in the "face-on" orientation. The degree of orientation is also increasing with increased thin film depth (Fig. 4.5). Furthermore, material quantity analysis on the FAPbI₃ 100 peak reveal the "face-on" material quantity relative to the isotropically oriented

grains. In comparison to an unseeded FAPbI₃ thin film where the "face-on" and isotropically oriented grain quantities are almost equal throughout the respective probe depths, the seeded thin films exhibit an improvement of the "face-on" orientation of roughly 50 % (Fig. 4.6).



Figure 4.5:

GIWAXS images of the FAPbI₃ thin film at penetration depths of a) 3 nm and b) 328 nm. It is to be noted that the detected scattering signal stems from the thin film's cumulative depth profile for each measurement respectively.

Since the nanocrystal seeds are cubic in shape with the respective faces corresponding to the 100 faces, their 100 plane tends to naturally align in the "face-on" configuration in order to minimize their surface energy. Therefore, we come to the conclusion that the orientation of the nanocrystal seeds predominates the resulting thin film's orientation. Further studies on the thin film's crystallization kinetics are ongoing.



Figure 4.6:

Material quantity analysis of an unseeded- (control) and the seeded $FAPbI_3$ thin film at various probe depths based on GIWAXS azimuthal cuts of the 100 peak.

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4.4 Printing n-type PbS quantum dot inks for use in solar cells

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Colloidal Quantum dots (CQDs) such as PbS have garnered significant interest for advancing next-generation photovoltaic devices. The quantum confinement effect and size tunability of QDs have enabled customization of their electronic properties in addition to multi-electron generation, leading to prospective increase in photo-conversion efficiency.

However, the long, insulating ligands of the as synthesized QDs prevent dot-to-dot charge carrier transport. This necessitates a ligand exchange (LE) to replace these by shorter ligands enhancing charge carrier mobility and ensuring complete surface passivation to prevent trap states that may lead to increased charge recombination and reduced photovoltaic efficiency. The conventional solid state ligand exchange process is multi-step process and faces the limitations of inefficient exchange of ligands leading to surface defects along with considerable time required for the process [1]. One way to overcome these is the liquid state ligand exchange (LSLE), a single-step deposition which achieves LE by phase transfer and subsequent dispersal of the QD powder to obtain QD ink. This process is known for its efficiency and reduced fabrication time.

We used this method of LSLE to investigate the effect of different ligands. It involved the exchange of the long oleic acid (OA) ligands with shorter halide ligands. Research in the past years indicates the better passivation properties of I⁻ ligands compared to other halides. This can be attributed to the increased stability of the Pb²⁺ and I⁻. bond due to the Hard Soft Acid Base principle (HSAB). Following existing literature, we used ammonium iodide (AI) [2] for this purpose and compared it with the more commonly used (methylammonium lead iodide) MAPbI₃ ligands [3]. Verification of the success of the ligand exchanges was achieved through FTIR spectra measurements (Fig. 4.7). The significantly reduced peaks of (COO-) at (1400-1600) cm⁻¹ and (2800-3000) cm⁻¹ (CH) peaks, indicate that AI can remove OA ligands more effectively.



Figure 4.7: FTIR measurements of AI and MAPI ligands compared to the original OA ligands

Following LE, the next step is dispersion of the QD powder in a suitable solvent and fabrication of the QD film. While spin-coating is a prevalent method, it suffers from scalability issues

due to material wastage. To address this, we focused our efforts on a more scalable technique of slot-die coating which allows reduced material consumption along with superior control over film properties. Currently, very few studies on slot-die coated CQD solar cells have been reported. Consequentially, challenges arise in finding a suitable solvent for slot-die coating. Butylamine (BTA) is the most commonly used solvent for spin coating [2]. It is considered a good solvent due to the fact that its strong affinity to the CQD surface enables concentrated colloidal dispersions. However, it is not compatible with scalable deposition techniques due to low boiling point which makes film morphology difficult to control. Additionally, it is neither polar enough nor does it provide enough steric hindrance for a stable ink, causing QD precipitation within hours.

Therefore, for the purpose of our work, we explored alternate polar solvents such as propylene carbonate (PC) and formamide (FA) and a mixture of N-methylpyrrolidone (NMP) with 1 wt% BTA to redisperse QDs powder to obtain stable PbS inks. Absorption spectra measurements (Fig 4.8) revealed shifts of the exciton peak towards higher wavelengths, with PC solvent exhibiting the most prominent shift. Additionally, the peaks show greatly diminished intensity after LE of CQDs.

Our future work involves enhancing quantum confinement for improved absorption properties and studying the impact of parameters such as printing speed and temperature on the slot-diecoated films. Characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS), will be used for a comprehensive analysis.



Figure 4.8: Absorption measurements of PbS inks with different solvents and the original PbS-OA solution

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4.5 Enhanced air stability of tin-based perovskite solar cells with quercetin

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Perovskite solar cells (PSCs) are believed as one of the most promising photovoltaic technologies because of the fast development of their power conversion efficiency (PCE) from 3.8% to 26.1% in the last decade [1]. Despite the excellent advancements achieved in the Pb-based PSCs, the inherent toxicity of Pb caused some worries because of their potential environmental and health problems. In scenarios where Pb-based perovskites encounter environmental exposures, such as device encapsulation failures and landfills as they reach the end of their life cycles, there exists the possibility of Pb²⁺ leakage into the environment.[2]

In order to solve this problem, researchers are developing some low-toxic materials or lead-free photovoltaic materials. In the pursuit of finding a suitable substitute for Pb in PSCs, Sn-based perovskites have emerged as a primary and highly promising candidate which is primarily caused by Sn's significantly lower toxicity levels observed across various testing conditions and the same valence electron layer structure as Pb and the most similar ionic radius (118 vs 119 pm) with Pb. In addition, Sn-based perovskite exhibits similar or in some cases superior electronic and optical properties compared with lead-based perovskite, such as low exciton binding energy (<100 meV), higher charge carrier mobility ($10^2 - 10^3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$), and high absorption coefficient (> 10^{-4} cm^{-1}), conductivity, longer charge carrier diffusion length ($10^2 - 10^5 \text{ nm}$) and hot charge carrier lifetime. Moreover, Sn-based perovskites have narrow bandgaps that can absorb a broader light spectrum, that is, infrared (NIR) region.[3] Therefore, Sn-based perovskite has great potential in developing high-efficiency solar cells.



Figure 4.9: Schematic diagram of the PSCs, perovskite (a) and quercetin (b) structure

However, the device efficiency and stability of Sn-based PSCs significantly lag behind the Pbbased ones. This disparity is caused by the instability of Sn^{2+} species within the perovskite structure. The intrinsic structure of Sn^{2+} renders them easy to convert into Sn^{4+} products at various stages throughout the lifespan of the material. Sn-containing perovskite materials show high p-type doping characteristics because of Sn^{2+} oxidation, which leads to a shortened carrier lifetime and damages the overall device performance. Moreover, the degradation products like SnI_4 and I_2 , can actively participate in and catalyze the degradation process and consequently impact the stability of Sn-containing PSCs. Secondly, there is the problem of Sn-based perovskite's rapid crystallization. This means it could be difficult to control the film morphology during solvent processing. The poor film quality will lead to short circuits of devices, low charge transfer/collection efficiency and carrier recombination. Meanwhile, due to the energy levels of tin-perovskite mismatch with the electron transport layer (ETL) or the hole transporting layer (HTL) in the device structure, resulting in large open circuit voltage (V_{oc}) loss (V_{loss}) in PSCs, their best record PCE has reached 14.81%, which is still lagging behind the Pb-based PSCs.[4]



Figure 4.10: XRD (a) and PL spectra (b) for $FASnI_3$ perovskite films without and with Q.

In this work, we focus on the anti-oxidation problem of the Sn perovskite film, so we introduced antioxidant quercetin (Q) as the secondary additive to assist the fabrication of FASnI₃ perovskite films containing excess SnF_2 and fabricated the PSCs with a device structure ITO/perovskite/PCBM/BCP/Ag as shown in Fig. 4.9a). The quercetin, with the phenolic derivatives containing the hydroxyl groups (Fig. 4.9b)), can react with oxygen free radicals and have strong reducing properties. It also contains the conjugated Lewis base molecules with high electron density and large steric hindrance that can slow down the crystallization speed of perovskite, which could become the promising perovskite additive.

To better understand the influence of the Q addition on the perovskite crystallization process, X-ray diffraction (XRD) was performed to probe the crystalline phases formed (Fig. 4.10a)). The characteristic XRD peaks of FASnI₃ films with 1% Q all match the orthorhombic lattice structure of FASnI₃, implying that Q do not affect the crystal phase of FASnI₃ perovskite. Furthermore, the XRD intensity of FASnI₃ films with 1% Q is higher than it of FASnI₃ films without Q, which means that the introduction of Q can enhance the degree of crystallization of FASnI₃ films. Notably, the intensity of steady-state photoluminescence (PL) characterizations were performed on FASnI₃ films without and with 1% Q additive to gain insight into the performance enhancement introduced by Q additive as shown in Fig. 4.10b). Both films were processed on ITO substrates, and the laser was irradiated from the ITO side with a wavelength of 500 nm. The plain FASnI₃ film with Q additive shows stronger PL intensity compared to the film without Q, indicating the decreased density of trap states in the perovskite film induced by Q which is consistent with the XRD results.

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4.6 Organic solar cells for space application: investigation of the nanostructure and degradation effects due to mechanical stress

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Organic Solar Cells (OSCs) stand out as promising candidates for space applications due to their exceptional gravimetric power density and flexibility. This promising feature set not only reduces payload mass but also enables more compact storage during rocket flights. However, realizing their full potential in space demands the resolution of significant challenges, particularly in addressing degradation issues occurring during the harsh conditions of space travel. The examined OSCs consist of a BTP-4F and PTQ-2F bulk heterojunction (BHJ), a zinc oxide hole-blocking layer, a molybdenum oxide electron-blocking layer, a silver anode and an indium tin oxide cathode. They were fabricated on glass and flexible PET substrates in six and eight-cell geometries (Fig. 4.11).



Figure 4.11: OSCs on a) glass and b) flexible PET substrates in a) eight and b) six cell geometries.

This study aims to investigate the degradation of OSCs in simulated space conditions, focusing primarily on the cell's properties under intense mechanical stress. Building upon prior research that included deploying OSCs in a suborbital rocket flight [1], this investigation seeks to replicate and understand the impact of intense accelerations and vibrations experienced during launch and re-entry through a shaker stress test.

Custom interfaces between the cell holder and the shaker were developed for the shaker test to enable vibrations in all three axes. The setup can be seen in Fig. 4.12. In the mechanical stress test, the OSCs were exposed to a similar vibration profile that NASA uses to verify their rocket parts. It consists of a sine and a random test in all three axes. [2] OSC modules on glass and PET were exposed to the vibrations on the shaker. Additionally, control groups were produced so that other degradation effects due to air exposure, transportation and light exposure could be separated from the effects due to the mechanical stress.

Preliminary results from solar simulator measurements, grazing-incidence wide- and smallangle X-ray scattering, and optical microscopy images indicate promising stability against strong vibrations for OSCs on both glass and PET substrates.





Another topic of this research aims to better understand the impact of the annealing processes on BTP-4F and PTQ-2F components within the OSCs. This exploration allows for the fine-tuning of band gap and absorption spectrum characteristics, offering more profound insights into the crucial structural modifications to reach optimal performance. For the measurements, BTP-4F and PTQ-2F films were spin-coated on glass or silicon and OSCs were built on glass and PET substrate. All samples were annealed at 100 °C for different times between 0 - 20 min on a heating plate after the spin coating of the active layer.



Figure 4.13:

Results of the annealing experiments. a) Performance of the annealed cells measured in a solar simulator. b) Normalized values of the PL peak intensity of the BHJ. UV-Vis spectroscopy results of the BHJ in terms of c) peak position and d) absorption coefficient.

UV-Vis spectroscopy analysis demonstrates a decrease in the absorption coefficient with longer annealing times, potentially attributed to alterations in surface reflection or structural changes. Additionally, an energy shift in the peak positions indicates a tuning of the band gap. (Fig. 4.13 c), d)) Photoluminescence spectroscopy (PL), on the other hand, reveals a significant drop in the intensity of the BTP-4F peak after only 3 minutes of annealing, indicating internal molecular restructuring that leads to less recombination and enhances charge transport within the bulk heterojunction. (Fig. 4.13 b))

Functional cells exhibit rising efficiency levels concerning longer annealing times, suggesting that the improved charge transport is dominating the effect of reduced absorption coefficients (Fig. 4.13 a)). This theory is supported by the fact that the rising short circuit current over time is the main factor leading to improved efficiency.

Continued research into material properties and degradation mechanisms holds the potential for OSCs to become a vital energy source for future space exploration missions.

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4.7 Effect of additives on Dion-Jacobson two-dimensional perovskite thin films

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Over the past years, researchers have shown tremendous interest in perovskite solar cells because of perovskite's high optical absorption, high tolerance to defects, high charge carrier mobility, low binding energy, and long diffusion length of charge carriers [1]. While threedimensional (3D) perovskite solar cells have power conversion efficiencies (PCEs) approaching the Shockley–Queisser limit, two-dimensional (2D) perovskite films are receiving more attention in solar cell fabrications recently as they have higher stability against moisture due to the existence of a bulky organic spacer [2]. However, the PCEs of 2D perovskite solar cells are still not high enough to allow the commercialization of these solar cells. Efforts have been made to boost the PCEs of these solar cells, and additive engineering is one of the methods to improve perovskite film quality by reducing the density of traps and defects, thus improving the PCEs of the solar cells [3]. In particular, chloride additives are often used, and they are found to affect the equilibrium of the complex ions and may affect the nucleation [3] and improve the crystallinity and orient the 2D perovskite layers into the preferred vertical orientation for efficient charge transport [4]. In this work, 2D perovskite films (PDMA)(MA)₃Pb₄I₁₃ (PDMA represents 1,4-phenylenedimethanammonium) are fabricated, and the effects of different amounts of the additive methylammonium chloride (MACl) on the films will be investigated.

The investigation is carried out by preparing two perovskite precursor solutions, while one of them is added with a small amount of MACl. Then, the solutions are spin-coated on glass substrates and annealed. After that, the spin-coated films are examined and characterized by photoluminescence (PL) spectroscopy and ultraviolet-visible (UV-vis) spectroscopy.



Figure 4.14: The normalized PL intensity of perovskite films with and without MACl additive.

Fig. 4.14 shows the normalized PL intensity of the perovskite films. The dominant emission peak for the film without additive is at 766 nm, while that for the film with additive shows

a blue shift and is at 758 nm. The excitation peaks for low-*n* phases at 530, 570 and 615 nm are also sharper in the film with additives compared to the film without additives, implying a higher concentration of the low-*n* phases.





Fig. 4.15 shows the normalized UV-vis absorption spectrum of the perovskite films. The absorbance of the film with additives is generally higher than the film without additives. As the absorbance at the wavelengths corresponding to the low-n phases is higher for the film with additive, which may be caused by the higher concentrations of the low-n phases, the result agrees with that of the PL spectrum.

The investigation above shows the effect of the MACl additive on the optical properties of perovskite films. Our future work will examine the internal structure of the perovskite films using static grazing-incidence small-angle X-ray scattering (GISAXS) or grazing-incidence wide-angle X-ray scattering (GIWAXS) to analyze the crystal orientations in the perovskite films. We will fabricate solar cells with these films and determine how the additive affects the PCEs of the solar cells. Additionally, we can explore the use of other additives such as PbCl₂ and mixtures of different additives.

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4.8 The effect of sputter-deposited TiO_x interfacial modification layer on the stability of perovskite solar cells

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Despite perovskite solar cells (PSCs) based on the SnO₂ hole-blocking layer (HBL) are achieving excellent performance, the non-perfect buried interface between SnO₂ HBL and the perovskite layer is still an obstacle to achieving further improvement in power conversion efficiency (PCE) and stability [1]. The non-radiative recombination induced by defects is an important factor affecting the charge carrier extraction and transport, resulting in low device performance. The poor morphology with numerous defects and the energy level mismatch at the buried interface would constrain the open circuit voltage (V_{OC}) and cause instability. As we know from the literature, the defect density at the interface is much higher than that in the bulk of perovskite crystal [2,3]. Herein, a sputter-deposited TiO_x thin film is used as a buried interface modification layer to address the aforementioned issues.

An n-i-p device structure of $ITO/SnO_2/TiO_x/perovskite/spiro-OMeTAD/Au$ is used in this work. The TiO_x modification layer is deposited atop the SnO_2 surface via sputter deposition. To reveal the effect of the sputter-deposited TiO_x interface modification layer, we monitor the perovskite structure change by grazing-incidence wide-angle X-ray scattering (GIWAXS) and track the performance evolution of solar cells simultaneously. The experimental setup (Fig. 4.16a) used at DESY synchrotron consists of a solar simulator, integrated with a water-cooling system, a gas-flow setup, a pocket solar, and a Keithley source meter. As shown in Fig. 4.16b, a reflective mirror is used to enable the light to illuminate the samples.



Figure 4.16:

(a) The experimental setup installed in the DESY beamline. (b) The magnified view of the experimental setup with a mirror.

We track the performance evolution of PSCs under a nitrogen atmosphere and one-sun solar illumination (ISOS-L-1I) for 120 min. The normalized photovoltaic parameters are shown in Fig. 4.17a and b. As expected, the SnO₂-based device exhibits lower stability compared with the SnO₂-TiO_x-based device. The V_{OC} and J_{SC} of the SnO₂-TiO_x-based devices remain at 98% of their initial value, while the FF shows a decrease of 23%, resulting in a PCE decrease of 25%, which is much lesser than the 45% of the SnO₂-based device.



Figure 4.17:

The evolution of photovoltaic parameters of (a) SnO_2 and (b) SnO_2 -TiO_x. The selected pseudo XRD of (c) SnO_2 and (d) SnO_2 -TiO_x. The evolution of full width at half maximum (FWHM) of (001) peak and integral area of lead iodide peak extracted from pseudo XRD.

To reveal the perovskite structure evolution, the *operando* GIWAXS method was used during the device operation process. The pseudo-XRD is commonly used to track the crystal structure evolution. To better understand the perovskite crystal structure change under operando measurement, the pseudo-XRD information is extracted from the radial GIWAXS profile by integrating over all azimuth angles. The magnified pseudo-XRD at the q region of 0.6-1.3 $Å^{-1}$ is shown in Fig. 4.17c and d. There is no peak position shift or splitting in (001) Bragg peaks (q = ~ 1.0 Å⁻¹) for all samples, indicating there is no detectable phase segregation in perovskite. However, for both samples, the full width at half maximum (FWHM) of (001) Brag peak broad continuously during operation, meaning the decreased crystallinity during operation. Interestingly, the FWHM of the SnO₂-based device increases dramatically during the operando measurement, compared with the SnO_2 -TiO_x-based devices. In addition, we integral the peak area of lead iodide (at $q = \sim 0.9 \text{ Å}^{-1}$) to monitor the evolution of lead iodide, as shown in Fig. 4.17e and f. Despite the integral area increasing continuously for both devices, the SnO₂-based device shows a lager increase rate during the whole operando measurement process. The higher integral area means more PbI₂ in the perovskite layer, indicating more perovskite decomposition [4]. In conclusion, the sputter-deposited TiO_x as a buried interface modification layer can improve the operation stability of PSCs.

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4.9 Tuning the band gap of double perovskite by anion exchange

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Double perovskites, a relatively new kind of lead-free perovskite materials, have emerged with compelling characteristics, including low toxicity, extended charge carrier lifetime, and a small effective charge carrier mass. These unique attributes make them promising material for photovoltaic applications and draw considerable research interest. The difference of crystal structure between double perovskite and common perovskite is showed in Fig. 4.18. Among bismuth-based double perovskites, Cs₂AgBiX₆ (where X can be Cl, Br, or I) has stood out for its potential in photovoltaic applications, primarily attributed to its suitable band gap. This specific composition has attracted significant attention in recent years due to its promising features, making it a prime candidate for further exploration in solar cell technologies. Some researchers have delved into the optoelectronic and thermoelectric properties of a specific double halide perovskite, Cs₂AgBiI₆ [1]. Their investigations have demonstrated that its excellence as a thermoelectric and optoelectronic candidate, further expanding the potential applications of double perovskites. Wu et al. [2] investigated that Cs₂AgBiI₆ nanocrystals possess narrower band gap than other halide Cs₂AgBiX₆ can effectively narrow the band gap.



Figure 4.18: Crystal structure of single perovskite $AM^{2+}X_3$ and double perovskite $A_2M^+M^{3+}X_6$.

Building on this foundation, the current work focuses on optimizing $Cs_2AgBiBr_6$, a member of the Cs_2AgBiX_6 family, by introducing iodide ions with trimethysilyl iodide (TMSI). Kyle et al. [3] prepared $Cs_2AgBiBr_6$ polycrystalline thin films (100-200 nm grain sizes) by thermal evaporation and attempted to convert these to Cs_2AgBiI_6 by anion exchange. TMSX reagents possess (i) inertness toward undesired side reactions, (ii) favorable thermodynamics, which allow nearly stoichiometric incorporation of heavier halides into proposed nanocrystals, and (iii) volatility, which enables nanocrystal purification with no workup other than drying at room temperature. Therefore, $Cs_2AgBi(Br_xI_{1-x})_6$ perovskite solar cells will be fabricated by solution method in this work. The balanced chemical reaction describing $Cs_2AgBi(Br_{1-x}I_x)_6$ is given by: $2CsBr + BiBr_3 + AgBr \rightarrow Cs_2AgBiF_6$, $Cs_2AgBiBr_6 + 6xTMSI \rightarrow Cs_2AgBi(Br_{1-x}I_x)_6 + 6xTMSBr$.

During the film fabrication process, it was discovered that the annealing temperature of $Cs_2AgBiBr_6$ thin films after spin-coating has influence on the crystallization of $Cs_2AgBiBr_6$. The structures of the $Cs_2AgBiBr_6$ films annealed at 200 °C, 250 °C and 300 °C were assessed by X-ray diffraction (XRD) showed in Fig. 4.19 a). The diffraction peaks observed in the X-ray diffraction (XRD) analysis were successfully assigned to specific crystalline planes, namely



Figure 4.19: Characterizations of Cs₂AgBiBr₆ films annealed at different temperature: a) XRD patterns; b) UV–Vis absorption spectra; c) Tauc plot.

(111), (002), (022), (113), (222), (004), (024), (224), (044), and (244) of Cs₂AgBiBr₆, indicating a cubic perovskite structure with the Fm3m space group [4]. In accordance with the extinction law, the ordering degree of Cs₂AgBiBr₆ can be quantitatively assessed by the intensity ratio (I_{111}/I_{022}), where a higher ratio corresponds to improved ordering and fewer defects in the double perovskite structure [5]. This study reveals that the Cs₂AgBiBr₆ ratio, annealed at 300 °C (0.365), surpasses that of films annealed at 200 °C (0.164) and 250 °C (0.213). This suggests enhanced ordering when the annealing temperature is relatively higher. Notably, the (002) and (004) peaks of Cs₂AgBiBr₆ films annealed at 300 °C and 250 °C. The underlying mechanism behind this phenomenon will be a subject of further investigation.

Examining the ultraviolet–visible (UV–Vis) absorption spectra of $Cs_2AgBiBr_6$ annealed at different temperatures, consistent features are observed in Fig. 4.19 b). A pronounced absorption peak around 445 nm is attributed to the s–p transition of bismuth within the $[BiBr_6]^{3-}$ octahedra of $Cs_2AgBiBr_6$ [6]. The bandgap energies (E_g) derived from Tauc plots using an indirect bandgap model indicate values of 2.15 eV for $Cs_2AgBiBr_6$ annealed at 300 °C and 2.23 eV or 2.25 eV for $Cs_2AgBiBr_6$ annealed at lower temperatures as shown in Fig. 4.19 c). This underscores the conclusion that the annealing temperature plays a crucial role in relatively narrowing the band gap of $Cs_2AgBiBr_6$ thin films. The upcoming investigation will maintain its focus on characterizing the films annealed at different temperature and anion exchange approach.

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4.10 Impact of temperature on the active layer of non-fullerene organic solar cells

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In the past few years, thanks to the development of non-fullerene materials and fabrication processes, the power conversion efficiency (PCE) of single organic solar cell (OSC) devices has approached 20%. Additionally, compared to traditional silicon-based photovoltaics, the advantages of OSCs, such as flexibility and solution processability, are also prominent. Despite this, poor device stability remains the main drawback hindering the widespread application of OSCs. The reasons for device degradation are numerous. Some can be classified as chemical processes, such as reactions with water and oxygen. Others can be categorized as physical processes, such as changes in surface morphology due to the working temperature [1]. Solar cells need to be exposed to light to work, which inevitably generates heat. Therefore, understanding the impact of working temperature on the degradation of OSCs is a topic that aligns with practical needs.

The most common structure of OSC nowadays includes electrodes, hole/electron blocking layers, and an active layer. The active layer, which is primarily composed of donor and acceptor materials, determines the device's performance. The active layer absorbs photons to form excitons. When excitons migrate to the donor-acceptor interface, electron-hole pairs separate. The electrons move to the negative electrode through the acceptor material, while holes move to the positive electrode through the donor material. This creates a potential difference between the two electrodes, resulting in an electric current in the external circuit. Currently, the exciton diffusion length in organic photovoltaic materials is about several tens of nanometers. Therefore, researchers have designed active layers with a bulk heterojunction (BHJ) structure, mixing donor and acceptor materials to increase the probability of excitons reaching the interface [2].



Figure 4.20: Chemical structure of the used acceptor molecule BTP-4F and donor polymer D18.

In this study, the non-fullerene acceptor material BTP-4F, donor polymer D18 (Fig. 4.20), and their blend were separately spin-coated onto glass substrates. Three samples were prepared for each film. The ultraviolet-visible spectrum (UV-Vis) of each sample was measured before light exposure. Then, the samples were promptly placed in a chamber that had reached the target temperature. After turning on the vacuum pump and waiting for the vacuum to stabilize (approximately $5 \times 10^{-2} kPa$), the solar simulator was switched on. The vacuum environment is created to reduce the impact of water and oxygen on sample degradation, thereby ensuring that the working temperature is the only variable. Three hours later, we took out the sample and the second UV-Vis was measured.


Figure 4.21:

UV-vis absorption spectra of a) blend film, b) acceptor film, and c) donor film before and after illumination at various temperatures for 3 hours. The dashed lines mark the positions of the peaks.

As we can see in Fig. 4.21 c), at three different temperatures, the spectral shape for the donor film before and after illumination is almost the same. Fig. 4.21 a) and b) exhibit clear differences that can be observed for blend and acceptor films, respectively. At $55 \ ^{\circ}C$, the peak positions of both the acceptor film and the blend film shows a redshift of 6 *nm*. At room temperature, the magnitude of the redshift is $3 \ nm$. As for $15 \ ^{\circ}C$, there was no significant change before and after illumination.

In summary, the redshift observed in the blend films appears to be solely contributed by the acceptor material BTP-4F, while temperature does not seem to significantly affect the donor polymer D18. The magnitude of the peak shift is related to temperature; the higher the temperature, the greater the redshift, and the lower the temperature, the less the redshift.

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4.11 Printing of Perovskite and Organic Solar Cells

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The popularity along with awareness of perovskite and organic solar cells (PSCs, OSCs) has grown significantly in recent years. The reasons for this are their low weight, potential upscaling due to a solution-based fabrication process, and high power conversion efficiency (PCE) values. PSCs already achieved efficiencies up to 25% [1], while OSCs reached 19% [2]. Both solar cell (SC) types are very promising also for the industry due to their low cost and upscalability with fabrication methods like slot-die coating. However, the actual upscaling process and the degradation of the solar cells still need to be improved and better understood. Therefore, in this work, we optimize the slot-die printing technique of these SCs under ambient conditions. The cells are compared using measuring techniques such as spectroscopy and real-space imaging in combination with X-ray scattering.

In the first part of this work, the slot-die printing process of the active layer was optimized for PSCs and OSCs. The perovskite precursor solution consisted of methylammonium lead triiodide (MAPI) solved in a 2-methoxyethanol and dimethyl sulfoxide mixture. For optimization, the hole blocking layer underneath the active layer was treated with potassium just before the active layer deposition to improve the interface and therefore the efficiency of the solar cell. For further improvement, the influence of the humidity in ambient atmosphere needed to be reduced. To minimize this influence of water, all samples were placed into a nitrogen environment in between layer deposition to cool down before the next fabrication step. The I-V-curve of the champion MAPI solar cell can be seen in figure 4.22 a).



Figure 4.22: Comparison of the I-V curves of a) a slot-die coated perovskite solar cell with an MAPI active layer from and b) a slot-die coated organic solar cell with a D18:BTP-4F active layer.

For the organic active layer a precursor solution out of the donor D18, the non-fullerene small molecule acceptor BTP-4F solved in the non-toxic solvent ortho-xylene was used. When printing this solution, another challenge occurred, the print-head and stage needed to be heated, so that the polymers stayed in solution during printing. Analogous to the production of perovskite solar cells, the organic films were also stored in a nitrogen atmosphere to cool down between the production steps. The I-V-curve of the champion OSC can be seen in figure 4.22 b).





Stability tests of a slot-die coated organic solar cell with a D18:BTP-4F active layer are shown. In a), the sinusoidal thermal cycling with increasing amplitude from 20°C to 120°C (0°C in between) is shown. In b) long term test at stable 20°C and 100°C for 120 min under illumination with an AM1.5 spectrum is performed.

In the second part of this work, long-term stability measurement tests were performed with the OSCs. Firstly, the influence of thermal cycling on the performance was tested. For this reason, the OSC was continuously illuminated with an AM1.5 spectrum for 120 minutes, while the temperature was increased with a sinusoidal profile from 20 to 120°C. The measured relative PCE can be seen in figure 4.23 a). It turns out that with increasing temperature, the power conversion efficiency also rises, due to an increased charge carrier mobility. Also, the first pixels started to fail at 120°C. To further test the stability during constantly high temperatures, the solar cells were tested at 20°C and 100°C for 120 min under illumination. The result can be seen in figure 4.23 b). The findings indicate that at 20°C, the solar cell shows greater stability compared to the cell measured at 100°C. After 120 min, the 20°C solar cell retains 86% of its original PCE, while the 100°C solar cell only reaches 64%. This finding suggests a significant degradation in performance at higher temperatures. While the open circuit voltage remains relatively constant across both temperatures, the short circuit current experiences a faster reduction at 100°C. This observation implies that the decrease in overall performance is primarily attributed to the degradation of the short circuit current.

In summary, this study focused on optimizing the slot-die printing process for both perovskite and organic solar cells. We showed that it is possible to print both these types of solar cells in an ambient atmosphere. Furthermore, this study provides valuable insights into the temperature-dependent stability of OSCs. Understanding the temperature sensitivity of solar cells is crucial for developing strategies to mitigate degradation and enhance overall performance, ultimately contributing to the advancement of sustainable energy technologies.

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4.12 Improved surface passivation of AgBiS₂ quantum dots for photovoltaic applications

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Colloidal quantum dots (CQDs), as inorganic semiconductor nanocrystals, have shown great promise for next-generation optoelectronic devices due to a size tunable bandgap and solution processability. AgBiS₂ CQDs, featuring high absorption coefficient, good water stability and photon harvesting in the near-infrared range, have emerged and serve as eco-friendly, non-toxic and abundant alternatives to PbS CQDs in optoelectronic applications.

Up to now, there is much less research about AgBiS₂ CQDs based devices than PbS CQDs primarily due to less mature and reproducible synthesis of the former material. The insulating and long-chain organic ligands of synthesized CQDs, a commonly shared issue in CQDs towards device applications, impede charge carriers transport within CQDs film. Additionally, cation disordering around Ag-Ag sites impairs CQDs' optoelectronic properties due to interactions of surface ligands.

There has been much research into surface passivation of AgBiS₂ QDs. The idea is to minimize the interparticle spacing, which promotes carrier transport and lowers defect density, in turn reducing recombination losses. Ligand exchange with organic ligands has shown improvement, but their bulkiness and vulnerability to oxidation have motivated an inorganic ligand strategy [1]. Namely, metal chalcogenide complexes lead to increased carrier mobility; they offer a negative charge to the QDs and provide a strong electrostatic repulsion, which in turn leads to stable dispersion. Monovalent inorganic ligands bound to cations would offer highly effective passivation and could even form charge-neutral films at room temperature, while keeping band gap retained. Research has shown that treatment of PbS QDs with TMAI, which reduces in-gap states by preventing oxidization, improved open circuit voltage but suffers from low mobility and poor charge transport. However, treatment with an inorganic halide such as zinc iodide (ZnI₂), improved charge transport and increased short circuit current. In addition to ZnI₂, tetrabutylammonium iodide (TBAI) is used in ligand exchange because it provides better QD stability. Additionally, previous work [2] reported that ligand exchange with bromide halide instead of iodide could lead to better passivation of AgBiS₂ CQDs, which is something that could be further explored by using $ZnBr_2$ ligands and TBABr.



Figure 4.24: Chemical structure of TBAI (left), TBABr (centre) and ZnI₂ (right)

Inspired by the strategies of PbS CQDs, TBAI, tetrabutylammonium bromide (TBABr) and zinc iodide (ZnI₂), shown in Fig. 4.24, are used to explore the anions' role of surface ligands in AgBiS₂ CQDs. Chosen ligands introduce I^- and Br^- ions to the QD surface, resulting in passivation of trap states. However, research has shown that different counterions which deliver iodine and bromine have different effects on the QDs. Depending on the counterion,

QD surface morphology and charge carrier mobility change, along with trap density, e.g. TMAI treated QDs showed less trap states and higher carrier mobility than TBAI treated QDs [4]. Solid-state ligand exchange was performed on AgBiS₂ QDs by applying the ligand solution to each QD layer upon deposition in a layer-by-layer fashion. First, ligand solutions of TBAI, TBABr and ZnI₂ have been created according to literature [1][2][4]. After spin coating the QD solution at 2500 rpm for 10 seconds, five drops of ligand solution are applied, left on the sample for 30 seconds, and spun to dry for 10 seconds. This process was repeated, after which the sample was washed twice with methanol and once with toluene and again spun to dry for 10 seconds. After waiting 60 seconds, the process is repeated for the next QD layer. A reference sample was then created by depositing layers of AgBiS₂ QDs without the ligand exchange. For FTIR measurement, the sample was prepared by simple drop casting followed by solid state ligand exchange.





Figure 4.25: UV-vis absorption spectra of a QD film with different surface ligands on glass substrate

Figure 4.26: FTIR spectra of a QD film with different surface ligands on glass substrate

As shown in Fig. 4.25, we can see absorption peaks of the reference sample at 900 nm, TBAI treated sample at 910 nm and TBABr treated sample at 913 nm. From this data, we can notice that there is a red shift in wavelength after the solid state ligand exchange, as well as broadening of the peak. No noticeable peak is observed for the sample treated with ZnI_2 . There is also a second peak in the 600 nm wavelength region, which indicates that our sample might contain QDs of different sizes.

FTIR spectra on Fig. 4.26 shows that the surface ligands were successfully removed, with a certain degree of success for each ligand solution. We can see that TBAI did not completely remove OA ligands, but did decrease their concentration, whereas TBABr and ZnI_2 completely removed them.

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4.13 Investigating the additive impact on slot-die coated quasi-2D Ruddlesden-Popper perovskite thin films for potential photovoltaic applications

N. L. W. Pyae , K. Sun, P. Müller-Buschbaum

In the domain of third-generation photovoltaic technologies, perovskite solar cells have achieved a breakthrough, demonstrating a substantial improvement in power conversion efficiency (PCE). Over the past two decades, single-layer perovskite solar cells have evolved from a modest 3.8% to an impressive PCE of 26.1% [1] as of 2023. Currently, the spin-coating deposition technique dominates the small-scale production of perovskite solar cell films. However, this method, while effective, operates slowly and generates significant waste. To transition from laboratory-scale to industrial-scale production, roll-to-roll (R2R) manufacturing processes, such as the R2R-compatible slot-die coating technique, demonstrate useful for achieving cost-effective production rates. One such method, the R2R compatible slot-die coating technique, enables solution-based processing and minimizes material wastage.

In recent times, quasi-2D perovskites in solar cells (PSCs) have garnered substantial interest due to their enhanced stability compared to their 3D counterparts. Notably, recent achievements have demonstrated a remarkable power conversion efficiency (PCE) of 21.07% [2] in quasi-2D-based PSCs. Despite their great potential, a significant challenge persists: the comparatively lower efficiency compared to 3D-based counterparts. Overcoming this obstacle requires addressing issues such as controlling crystal orientation and fine-tuning multiple phase distributions. This study addresses these challenges by utilizing methylammonium chloride (MACl) as an additive to control crystal orientation and phase distribution within quasi-2D perovskite thin films. Additionally, a novel solvent system, a blend of 2-methoxyethanol (2ME) and acetonitrile (ACN), is employed for preparing the perovskite precursor solution, aiming for faster deposition of perovskite films at room temperature. This study explores the impact of the novel solvent system and MACl additive on slot-die coated film quality, the film formation process, optoelectronic properties, and crystal orientation.



Figure 4.27:

Normalized photoluminescence (PL) spectra of $BA_2MA_3Pb_4I_{13}$ perovskite films illuminated from a) front side, b) back side, and c) X-ray diffraction (XRD) spectra of all printed perovskite films, showing XRD spectra of 0 wt% and 5 wt% sample in the inset.

In order to enhance the understanding of the composition of layered perovskite films, steadystate photoluminescence (PL) spectra of all slot-die coated quasi-2D perovskite thin films was conducted from both sides of the film. In Fig. 4.27 a), the normalized PL spectra from the front side (air-film interface) reveal multiple low-n phases in all films, characterized by relatively low-intensity peaks at shorter wavelengths and a dominant long-wavelength PL peak. Notably, the suppression of low-n phases is evident in samples with added MACl. In contrast, PL spectra obtained from the film-glass interface (Fig. 4.27 b) predominantly feature the long-wavelength peak from the 3D-like perovskite phase. This PL data leads to the conclusion that layered perovskite phases with smaller n tend to reside closer to the film surface, while 3D-like perovskite phases prefer the bottom layers.

The X-ray diffraction (XRD) patterns of all the printed quasi-2D perovskite thin films in Fig 4.27 c) exhibited preferential growth along the (111) and (202) reflections[3], indicative of vertical growth of perovskite compound. Increasing the amount of MACl resulted in sharper diffraction peaks and narrower FWHM (full width at half maximum), suggesting improved crystallinity and well-oriented crystal growth. This observation was further corroborated by grazing-incidence wide-angle X-ray scattering (GIWAXS) analysis, which examines the phase distribution and orientation profiles of quasi-2D perovskite layers. In Fig. 4.28 a) and b), Debye-Scherrer rings were recorded for the 0 wt% and 5 wt% MACl-added films, indicating less well-oriented crystallization, while films with 15 wt% and 30 wt% MACl addition exhibited more well-oriented crystalline nature, as depicted in Fig. 4.28 c) and d). These results acquired suggest that the incorporation of MACl serves to suppress low-n phases while improving both the crystallinity and crystal orientation of quasi-2D perovskite films coated via the slot-die method.



Figure 4.28:

2D GIWAXS data of slot-die coated $BA_2MA_3Pb_4I_{13}$ perovskite films with a) 0 wt%, b) 5 wt%, c) 15 wt%, and d) 30 wt% MACl.

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4.14 Comprehensive Analysis of PTQ-2F:BTP-4F-Based Organic Solar Cells Fabricated with Various Solvents

L. V. Spanier, P. Müller-Buschbaum

Organic solar cells present a promising avenue for renewable energy due to their lightweight, flexible nature and the potential for low-cost manufacturing. Understanding the influence of fabrication parameters, such as the choice of solvent, on the performance and stability of these solar cells is crucial for their practical implementation [1]. This project presents a comprehensive analysis of organic solar cells based on the PTQ-2F:BTP-4F blend, fabricated using various solvents, including halogenated (chloroform (CF), chlorobenzene (CB)) and non-halogenated (ortho-xylene (oXY), trimethylbenzene (TMB)) options. The investigation primarily focused on understanding the influence of solvent-induced morphology changes on the performance of the solar cells. Operando grazing-incidence small-angle X-ray scattering (GISAXS) was used to monitor morphological alterations during operation, revealing significant differences in degradation behavior based on the nature of the solvent.



Figure 4.29:

Operando analysis of PTQ-2F:BTP-4F OSCs produced from CF, CB, oXY, TMB solutions. The OSCs were operated under 1 SC of illumination with an AM 1.5G solar simulator. a) Horizontal GISAXS linecuts through the Yoneda-region of the active layer. b) Domain size distribution as obtained from GISAXS utilizing cylindrical form factors. c) Time evolution of respective domain sizes. d) Time evolution of normalized OSC performance parameters.

The organic solar cells were fabricated using the PTQ-2F:BTP-4F blend with different solvents, and their morphologies were characterized using in-operando GISAXS. This technique allowed for real-time observation of morphological changes during the operation of the solar cells. Additional characterizations were performed using ultraviolet-visible spectroscopy (UV-Vis), photo-

luminescence spectroscopy (PL), grazing-incidence wide-angle X-ray scattering (GIWAXS), and solar simulation experiments. These analyses aimed to provide insights into the performance and morphology of static solar cells.

The investigation into PTQ-2F:BTP-4F-based organic solar cells, fabricated with various solvents, yielded insightful findings through a multi-faceted approach. The study revealed significant differences in degradation behavior contingent on solvent type. Halogenated solvents, namely chloroform and chlorobenzene, exhibited distinct morphological alterations compared to non-halogenated solvents like ortho-xylene and trimethylbenzene. UV-Vis spectroscopy and photoluminescence spectroscopy analyses provided further understanding of the solar cells' optical properties. Shifts in absorption and emission spectra were observed, aligning with the morphological changes identified by GISAXS. Analysis of PL, UV-Vis, and GIWAXS data revealed notable differences in molecular aggregation, specifically into H- and J-aggregates of the small molecule acceptor, depending on the solvent used during fabrication. Solar simulation experiments evaluated the overall performance of the organic solar cells. Notably, the best-performing solar cell achieved an efficiency of 13.4%, underlining the potential of PTQ-2F:BTP-4F-based organic solar cells.



Figure 4.30:

Optical analysis of PTQ-2F:BTP-4F bulk heterojunctions produced from CF, CB, oXY, TMB solutions. a) UV-Vis spectroscopy on glass substrates with highlighted relative absorbance normalized to the BTP-4F absorbance maximum. b) PL spectroscopy on silicon substrates.

Collectively, these results underscore the intricate relationship between solvent selection, morphological evolution, and device performance. The observed disparities in degradation behavior emphasize the critical role of solvent choice in optimizing the fabrication processes of organic solar cells. These findings contribute significantly to advancing the understanding of structure-performance relationships in organic photovoltaics, with implications for enhancing device design and efficiency. This study highlights the impact of solvent selection on the morphological evolution and degradation behavior of PTQ-2F:BTP-4F-based organic solar cells. The results provide valuable insights into the relationship between solvent choice, morphology, and performance. The observed differences in degradation behavior emphasize the importance of considering solvent effects in the optimization of organic solar cell fabrication processes. The findings contribute to advancing the understanding of structure-performance relationships in organic photovoltaics, paving the way for enhanced device design and efficiency.

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4.15 Degradation mechanisms of layered perovskites under light and heat conditions

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Layered two-dimensional perovskites have received tremendous interest due to their unique features, e.g., tunable electronic and optoelectronic properties and versatile structures by choosing different organic bulky cation. The typical Ruddesden-Popper (RP) perovskites have the general formula of $A'_2A_{n-1}B_nX_{3n+1}$, where A', A, B, X, and n represent monovalent bulky organic cations, monovalent cations, divalent metal cations, halide, and inorganic slabs, respectively. Quasi-2D perovskite solar cells (PSCs) have surpassed 21 % power conversion efficiency (PCE), approaching the PCE of their 3D counterparts [1]. In addition, the organic bulky cation can prevent oxygen and moisture invasion, impeding ion migration and leading to the overall enhanced stability. Notwithstanding the big success in PCE, the operational stability of PSCs limits real-world application. In particular, mixed perovskites undergo element and phase segregation which undermines device efficiencies and lifetime under heat condition [2]. Moreover, it was found that voids closed to the buried interface of PSCs can be formed during device operation, which leads to the increased defect densities and is detrimental to device stability [3]. In this perspective, understanding degradation mechanism of layered perovskites under external stimuli is the perquisite of enhancing the operational stability of PSCs and further promoting their commercialization.

In the present work, we investigated the structural changes of butylammonium (BA⁺)–based layered perovskites ($BA_2A_{n-1}B_nX_{3n+1}$) under constant AM 1.5 illumination and heat conditions at 80 °C with grazing-incidence X-ray small-angle scattering (GISAXS) at the Austrian SAXS beamline, ELETTRA. Moreover, we also compared the degradation behavior of layered perovskites under different external stimuli, *i.e.*, under light illumination, heat, and combined light and heat conditions. The crystal structure of these layered perovskites with different thickness is shown in Figure 4.31.



Figure 4.31:

The crystal structure of RP perovskites with different n values, showing the dimensionality from 2D (n=1) to quasi-2D ($1 < n < \infty$) and 3D-like phase.

Figure 4.32 shows 2D GISAXS detector images of the BA-based layered perovskite samples before and after degradation. The reflex at around 2.55 nm^{-1} contains the desired information about morphology of the layered perovskite. For the subsequent analysis, the 2D GISAXS data is reduced to a 1D intensity profile by azimuthal integration. The degradation of the layered perovskite film under combined exposure to heat and light is most prominent in the broadening of the reflex peak (Figure 4.32E). In addition, we observe a slight peak shift with respect to the dashed line, manifesting a microscopic structure change of the perovskite. These alterations in peak characteristics offer insights into the degradation mechanism of layered perovskites under heat and light conditions. To qualitatively analyze the morphological change, horizontal linecuts at respective Yoneda peak are performed (Figure 4.32F). These notable shifts towards both smaller and larger q-values showcase significant morphological change under different degradation conditions over time, as indicated by black arrows. Notably, we observe the most drastic changes in lateral morphology of layered perovskite under the condition of combined heat and light illumination. Interestingly, when layered perovskites are solely exposed to light illumination, the observed shifts are less pronounced compared to layered perovskites subjected to both light and heat. Notably, during degradation due exclusively to heat exposure, a distinct shift towards smaller q-values is evident. In summary, layered perovskites are relatively stable under light illumination, while structural changes become apparent when exposed to heat conditions and combined heat and light conditions.



Figure 4.32:

Selected 2D GISAXS detector images of BA-based perovskite samples (a) before degradation, (b) after heating at $80^{\circ}C$, (c) after light-illumination, and (d) after light and heat $(80^{\circ}C)$ degradation. (e) Azimuthally integrated cuts of samples under different degradation conditions, indicating q-position shifts and prominent perovskite peak at q $2.55 nm^{-1}$, (f) horizontal line cuts of samples under different degradation conditions, showing the varying intensity in the low-and high-q ranges.

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4.16 P-type PbS CQD ink for slot-die coating of solar cells

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Colloidal quantum dots (CQDs) exhibit remarkable efficiency as nanomaterials, featuring adjustable opto-electronic properties, versatile surface chemistry, and easy deposition through solution-based methods. Lead chalcogenide CQDs, in particular, are widely used in photo-voltaic devices due to their tunable band gap, broad light absorption spectrum, high dielectric constant, and through multiple exciton generation has the potential to overcome the Shockley-Queisser limit [1]. Among lead chalcogenide CQDs, PbS CQDs have demonstrated high efficiency, with record power conversion efficiency (PCE) of about 16.4% in solar cells [2]. Fig. 4.33(A) shows the wavelength range that CQD PbS can harvest.

Optimizing charge collection in solar cells is crucial for enhancing efficiency. Implementing appropriate electron and hole-blocking layers improves both open-circuit voltage and photocurrent. Research has extensively explored modifications to the n-type metal oxide hole-blocking layer (HBL). However, investigation of the electron-blocking layer (EBL) is rarely seen. The overall performance of colloidal quantum dot (CQD) solar cells can be enhanced by striking a balance between hole extraction and photo-voltage. Additionally, the EBL plays a pivotal role in ensuring the long-term stability of the solar cell device in ambient conditions [4].

Our work aims to design P-type ink of PbS CQDs for CQDs solar cell to improve the PCE. This study explores the optimal EBL based on PbS, investigating suitable QD surface ligands to minimize the recombination of charge carriers at the EBL/active layer interface and capture a significant portion of the infrared rays. CQD ink is prepared to fabricate the solar cell's EBL using the slot-die deposition technique. For p-type CQD for the EBL, we aim to use the solution-processed ligand exchange technique to replace the original organic oleic acid ligands (long chain and insulating) from the PbS QD surface with 3-mercaptopropionic acid(3-MPA). Solution-processed ligands exchange has the advantages over solid-state ligands exchange as the former ensures a homogeneous ligands coverage over the QD surface, makes highly concentrated CQD ink with highly efficient ligands exchange, and prevents material waste and defects formation and oxidation.



Figure 4.33: A) PbS solar energy harvesting spectrum [5] B) Slot die coating process [6]



Figure 4.34:

Comparison of the films made with the solid state and solution-processed ligands exchange. Films produced with the former technique deteriorate and have cracks [7]

Fig. 4.34 shows the comparison between the two methods. We chose 3-MPA ligands for the PbS CQD because of better colloidal stability and high oxidation stability over extended periods of air exposure during storage [8]. For the CQD ink preparation, we plan to use butylamine solvent, according to the literature, to dissolve the 3-MPA capped PbS CQD as it further enhances the colloidal stability of the ink for months, suppresses the trap states, ensures film smoothness, and shows a PCE of approx 11%. The valance band of EBL made from this ink is shallower than the valance band of the active layer, making it a good choice for hole extraction at the respective electrode [9].

The next step will be to make solar cells with the CQD ink for EBL film using the slot-die coating technique and do the necessary characterization to understand the relationship between underlying material characteristics and device performance. Fig. 4.33(B) shows how the coating process works. The advantages of slot-die coating in solar cell fabrication include high precision, excellent material utilization, and compatibility with potential large-scale, high-throughput industrialization.

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4.17 Setup for rapid thermal cycling of perovskite solar cells

S. A. Wegener, P. Müller-Buschbaum

Perovskite solar cells are a new class of solar cells that has gained more and more attention within the last decade. Perovskite solar cells get their name from the perovskite crystal structure of their active layer. The great interest in this technology is due to its ability to be manufactured in a solution-based process while maintaining similar performance compared to conventional silicon-based solar cells. Further, their thickness lies at less than 1 μ m way below those of conventional solar cell technologies. This drastically reduced the needed material per covered area. For this reason, they are characterized as thin-film solar cells. The perovskite structure allows for a broad stoichiometric selection enabling band gap tunability that depends on the chosen precursor's chemical make up. A commonly used composition is methylammonium lead triiodide. Depending on the optical bandgap the perovskite can be used for different applications. So the bandgap can be chosen close to the Shockley-Queisser limit, which determines the optimal bandgap for solar cell application. This tunability also enables the use of perovskites for sensor applications [1].

However, the intensive research in this field is not only justified by the great potential of perovskites but also by the challenges that come along with their real-world application. One of the most focused goals is here to increase the stability of the material against moisture, which is still one of the keys to allowing the economic use of perovskites.

One major field of application for solar cells is space. Here, gallium arsenide (GaAs) multijunction solar cells are state-of-the-art. These high-end cells provide efficiencies way above those of conventional silicon-based devices. Nevertheless, perovskites outperform GaAs in terms of power-to-weight ratio [2] and this is one of the main factors in space due to launch costs. Besides these, the main weakness of perovskites, humidity, is not important for space applications. As a result, the great potential of perovskites for space applications is out of the question. The challenges are now to back up this potential, locate other weak points, understand those, and find adequate solutions.



Figure 4.35:

Temperature and normalized PCE of a perovskite solar during thermal cycling between 0 and 120 $^\circ\text{C}.$

To investigate the interplay of rapid temperature change that are prominent in most orbits around the earth [3], vacuum, solar cell performance, and material structure of the perovskite

solar cells, we upgraded an already proven experimental setup at our chair. The so-called "pocket-solar" solar simulator has been a for years successfully used sample environment for thin-film samples. The setup was designed to do gracing incidence X-ray scattering experiments, while the sample is irradiated with artificial sunlight and electrically characterized. The setup is built into a vacuum chamber to allow measurements under no atmosphere or different atmospheric conditions. As the name suggests, the setup is relatively small and fits into a normal suitcase. This allows easy travel to large-scale X-ray facilities.





Exemplary 2D GIWAXS data for a single temperature point during thermal cycling of a perovskite solar cell under operation.

The recent upgrade includes a thermal cycling stage that is integrated into the setup. The aim was to allow fast and precise temperature changes between 0 and 120 °C. This is technically implemented by the usage of Peltier elements and a water coolant circuit. The setup allows heating rates of over 100 °C/min. These fast changes are needed for two reasons. First, the low thermal mass of perovskite solar would lead to a fast-rising temperature under sun illumination in space. Second, the opportunity to perform a high number of thermal cycles allows us to investigate induced sample degradation in operando on reasonable timescales. This is especially important because beam time on large-scale X-ray sources is limited and expensive. The first in situ thermal cycling experiments were performed at Elettra synchrotron in Trieste and at the Petra III beamline at DESY in Hamburg in October 2023.

Various types of perovskite solar cells and also organic solar cells were thermally cycled with different temperature profiles. Figure 4.35 exemplary shows the temperature and power conversion efficiency (PCE) of a perovskite solar cell. Besides the short-term temperature dependence of the PCE also a long time change over several cycles is visible. In parallel to the thermal cycling grazing incidence small angle and wide angle scattering (GIWAXS / GISAXS) was performed. The GIWAXS measurements allow the determination of lattice strain in the thin-film and also report changes in the crystal phase. In contrast, GISAXS gives information about larger domains in the solar cell. Figure 4.36 shows the example of 2D GIWAXS data from a perovskite solar cell.

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4.18 Hybrid energy harvester based on the combination of triboelectric nanogenerator and solar cell

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Developing clean energy lies in the heart of human society.[1] Triboelectric nanogenerator (TENG) originating from Maxwell's displacement current is a new type of energy harvester for harnessing ambient mechanical energy. Based on the coupling effect of triboelectrification and electrostatic induction, TENG can directly convert ambient mechanical energy into electricity.[2] Compared with other counterparts, such as electromagnetic generator, owing to the advantages of lightweight, low cost, and easy fabrication, TENG becomes one of the most promising candidates to replace fossil fuels and attracts worldwide attention in the past decade. Since TENG has been first proposed in 2012, many kinds of TENGs have been fabricated for converting different types of mechanical energies into electricity.[3] However, to further increase the energy harvesting efficiency and broaden application fields, integrating the TENGs with other kinds of energy harvesters in one device is a possible way to meet these needs.

In the present work, in order to suit for potential applications in robotics and smart home systems, we design a TENG based hybrid energy harvester and fabricate it on the flexible polyethylene terephthalate (PET) substrate. This hybrid device consists of a single-electrode mode TENG component and a PbS quantum dot (QD) based solar cell component, which can harness both mechanical and solar energy from ambient environment to directly generate electricity through two different working mechanisms. The structure of as-fabricated hybrid energy harvester is schematically shown in Fig. 4.37a, which is with the common configuration of ITO-PET/ZnO/PbS QDs/Au as the solar cell under the bottom and further covered by the polydimethylsiloxane/Triton X-100 (PDMS/TX100) mixture thin film on the top as the dielectric material for forming a TENG component. Here, Au serves as both the bottom electrode for TENG and the anode for solar cell. Fig. 4.37b presents a photograph of the hybrid device at bending state, showing its good flexibility.



Figure 4.37:

a) Schematic illustration of as-fabricated hybrid energy harvester. b) Photograph of the realized hybrid device at bending state.

For the output performance of the hybrid device, we begin the measurement with the solar cell component. It can be observed from Fig. 4.38a that the power conversion efficiency (PCE) of the solar cell component from the champion sample achieves 4.92% with a short-circuit current of



Figure 4.38:

a) Output performance of the solar cell component. b) The setup of the GISAXS measurement. c) PCE of the solar cell component from the champion sample at different states.

22.8 mA/cm², an open-circuit voltage of 0.56 V and a fill factor of 41%. Moreover, in order to investigate the bending stability of the whole device, grazing incidence small-angle X-ray scattering (GISAXS) is used to characterize the morphology changes of the mesoscale structure.[4] Fig. 4.38c shows the setup of the GISAXS measurement used in this work. From Fig. 4.38c, we can see that there is only a 4.1% decrease on the output performance of the solar cell component after 1000 times bending, demonstrating the high bending stability on the outputs of the whole hybrid device. Finally, the charging capability of the fabricated device has also been characterized in this work to further demonstrate potential applications in future robotics and smart home systems.

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4.19 Stacking kinetics of PbS quantum dots orientated by the perovskite matrix during printing

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PbS colloidal quantum dots (CQDs), which are synthesized and processed in solution, are greatly attractive in solution-processed optoelectronic devices owing to their tunable photophysical properties. Up to now, the commonly used CQDs ink for the absorption active layer, which has achieved the best performances of PbS CQD PVs [1], is through lead iodide and bromide passivation, where the Pb X_2 (X = I or Br) capped CQDs powder obtained from the ligand exchange in liquid phase is re-dispersed in a polar solvent to form a concentrated ink for the next film deposition. Towards the commercialization of PbS CQDs solar cells, there is no doubt that a stable CQDs ink with high concentration and the fabrication of a good-quality PV film with homogeneous energetic configuration and excellent surface passivation are the keys. In terms of the energetic landscape, the excessive PbI₂ matrix in CQDs film, which remains an amorphous and inhomogeneous configuration, causes the energetic disorder of CQDs film and impedes the effective electron coupling. To solve this issue, one of the effective strategies to flatten the energy landscape in CQDs solids has been demonstrated to improve diffusion length and open circuit voltage (Voc) deficit by confining excessive PbX₂ matrix with amorphous state into 2D structure via hybrid amine solvents [2]. Inspired by this strategy, we investigated the interaction of each amine solvent with the excess lead halides, revealing its impact on chemical passivation and structure configuration of CQDs solids, providing significant insight for solvent engineering in CQDs ink.



Figure 4.39:

a) Schematic of CQDs ink preparation. b) FTIR spectra of CQDs film prepared with different amine solvents.

In this work, the ligand exchange was performed and the resultant CQDs powder was redispersed with butylamine (BTA), pentylamine (PTA), hexylamine (HXA), and mixed amine solvents (BTA: PTA: HXA=10:3:2), which is denoted as solvent engineering in Fig. 4.39. The red-shift peaks at N-H stretching mode and N-H scissoring mode presented in Fourier transform infrared (FTIR) spectroscopy indicates the emergence of PbI₂-amine coordination complexes, compared to pure amines [3]. O 1s spectra deconvoluted into Pb-OH, COO-/CO₂, and OH species is presented in X-ray photoelectron spectroscopy (XPS), as is seen in Fig.



Figure 4.40:

XPS spectra of the CQDs for a) I 3d and b) O 1s. c) 2D GISAXS data of CQDs film prepared with BTA(black), PTA(red), HXA(blue) and mixed solvent (green). d) Azimuthallyintegrated intensities of Bragg peak in the 2D GISAXS data.

4.40. Low sub-bandgap states and reduced OA ligands in CQDs mix-based amine can reduce the charge carrier recombination, yet substantial signal at -OH suggests that ambient H2O adsorption which may impede the effective passivation of iodide moieties in mix-amine treated QDs film, as is presented in I 3d spectra in Fig. 4.40.

To determine the average center-to-center spacing of nanoparticles as well as their packing uniformity, Grazing-incidence small-angle X-ray scattering (GISAXS) was used. As is seen in 2D GISAXS data, all the samples show distinct Bragg peaks, suggesting CQDs configuration is well-ordered. To quantitatively analyze the inner structure, the azimuthal cut at the Bragg peak is conducted in each sample to extract inter-dot distance and its distribution. All CQD films share close inter-dot spacing with 3.7 nm, yet PTA-based CQDs film has slightly smaller distance distribution than the others. The CQDs size is 3.2 nm, thus the interstitial thin matrix layer around neighboring CQDs is 0.5 nm. The PTA-based CQDs film with ordered structure is favorable to the diffusion length of minority charge carriers. The device performance of PbS CQDs can be further investigated to connect its relations to the chemical passivation and inner structure.

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5 Polymer-hybrid systems



5.1 Comparison of direct current magnetron sputtering (dcMS) and high power impulse magnetron sputtering (HiPIMS) of Ag on structured PS-*b*-P4VP

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Structured surfaces are of vital interest for applications in organic electronics [1]. Over the time different approaches were investigated and were improved to fabricate structures on the nano scale for example with nanoimprint lithography, scanning beam lithography and self-assembly. Especially, the polymer class of diblock copolymer is excellently suited to produce nanostructured templates via self-assembly. Furthermore, different shapes like spheres, lamellae, squares, relief and cylinders can be fabricated due to the various types of diblock copolymers, their block ratio and their treatment respectively. Thus, patterning the nano size regime based on soft materials are desired for lithographic applications due to their low cost. Especially, the combination of soft matter with metals forming metal-polymer composites are of vital interest for sophisticated devices. Especially silver (Ag) as a metal can be used in a versatile fashion. In particular the optoelectronic properties of Ag can be used in the nanoscale regime as photonic crystals, sensors, catalysts and flexible electrodes. The aim is to quantitatively evaluate the differences between direct current magnetron sputtering (dcMS) and high power impulse magnetron sputtering (HiPIMS) of Ag on these polystyrene-b-poly-4-vinylpyridine pattern [3].



Figure 5.1: Displayed is the inner part of the sputter chamber of CAU Kiel.

For the substrate preparation we used acid pre-cleaned si substrates. These si substrates undergo a spin-coating procedure with a PS-b-P4VP solution to obtain a structured micellar pattern consisting of PS-b-P4VP. The in-situ GISAXS/GIWAXS investigations were performed with

a custom-made mobile deposition chamber developed by the group of CAU Kiel [2]. This deposition chamber was mounted at the beamline P03, PETRA III, DESY, Hamburg. For the in-situ experiments, a PILATUS 2M detector (Dectris, Switzerland) with a pixel size of 172x172 μ m² was used as GISAXS detector and a custom-shaped LAMBDA 9M detector (Xspectrum, Germany) with a pixel size of 55 μ m in simultaneous GIWAXS geometry. The experiments were performed using an incident angle of $\alpha_i = 0.4^\circ$ and an X-ray wavelength of 1.05 Å. The sampleto-detector distance (SDD) was set to SDD = 3415 mm. For quantitative analysis, horizontal line cuts were done at the Yoneda peak of PS-b-P4VP to obtain the average distance of the Ag clusters on the structured polymer surface[3].

GISAXS experiments were performed to analyze the patterned surface. The GISAXS pattern of the sample show a pseudo hexagonal arrangement of the PS-b-P4VP micellar film. Additionally, it shows that the structural arrangement is homogeneous throughout the sample. In the beginning dcMS and HiPIMS show during the growth of Ag on the PS-b-P4VP micellar film the same average correlated distance in the regime $\delta_{Ag} = 0$ nm until $\delta_{Ag,dcMS} = 2.6$ nm for dcMS conditions and $\delta_{Ag,HiPIMS} = 2.8$ nm for HiPIMS conditions. Afterwards, reaching these amount of deposited material, the structural peak of PS-b-P4VP is in superposition with the structural peak of the Ag cluster. Thus, for a quantitative comparison of dcMS and HiPIMS $\delta_{Ag} = 2$ nm was chosen as under both conditions the same correlated distance is observed. Particularly, in the atomic force microscopy and field emission scanning electron microscopy images the size of the Ag clusters growing on the PS-b-P4VP micelles are on the average larger than the Ag clusters grown on the silicon substrate between the micelles [3].

Additionally, aqueous tests were performed to test a potential application of these structure under aqueous conditions. In particular, a test was performed upon drying of a water droplet. In case of PS-b-P4VP a partial structural degradation of can be observed upon drying of a water droplet. Particularly, after drying of a water droplet, Ag_{dcMS} :PS-b-P4VP shows that the structural integrity of the micellar pattern is preserved. Interestingly, the silver cluster grown on top of the silicon wafer is being partially removed and agglomerates as larger silver particles occur. In case of Ag_{HiPIMS} :PS-b-P4VP upon drying of a water droplet the sample was preserved [3]. This shows the advantage of using HiPIMS for facile lithography patterning.

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5.2 Investigation of film morphology in hybrid ternary thin diblockcopoymer/magnetic nanoparticle films by in situ GISAXS

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Diblock copolymers (DBCs) are polymers composed of two blocks, each with distinct properties. Amphiphilic block copolymers can undergo microphase separation when deposited out of solution as thin films. By tuning the volume ratio of the two blocks in relation to one another and the segregation strength of the copolymer, which is dependent on the block-block interaction parameter (χ) and the number of repeating units (N), it is possible to manipulate and control the morphology of the resulting thin films. For diblock copolymers, spherical, cylindrical, and lamellar nanostructures can be obtained [1]. Furthermore, the size of the domains can be modulated by varying the molecular weight of the polymer block, with higher molecular weights leading to an increase in domain size. This makes DBC thin films interesting as scaffolds and templates for inorganic materials, such as nanoparticles (NPs) [2].

Binary DBC/NP thin films have gained much attention with research focused on controlling the localization of the NPs into a specific polymer domain. This is typically accomplished by decorating the NPs with ligands that are chemically similar to one block, thus driving the localization of the nanoparticles into that block [3]. In this work, we focus on the synthesis of ternary DBC/NP thin films containing two different types of NPs (DBC/NP1/NP2). Polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA), nickel oxide NPs (NiO) coated with short PMMA-like ligands, and cobalt ferrite NPs (CoFe₂O₄) coated in oleic acid ligands were chosen for the investigated system. Both types of NPs are ferrimagnetic. Thin films with varying NP concentrations were printed from solution in a one-step slot-die coating process. The morphology evolution of the hybrid magnetic thin films was monitored with grazing-incidence small-angle X-ray scattering (GISAXS) during the drying process.



Figure 5.2: a) GISAXS images of as-printed, dry films. b) Fitted line cuts taken from the Yoneda region of the thin films.

Figure 5.2a shows the GISAXS images from the investigated hybrid films: no NPs, 2 wt% CoFe₂O₄, and 2 wt% NiO with 2 wt% CoFe₂O₄. From the 2D GISAXS data, it is seen that the pure DBC with no NPs shows a high correlated roughness with the substrate. In addition, the typical polymer domain peak, correlating to the structure and form factor of the polymer nanostructure, is observed. As CoFe₂O₄ is added, scattering at higher q_y values becomes more pronounced and can be described as a 'wing'. This 'wing' is even more evident in the ternary hybrid film, corresponding to the increase in NPs and the scattering from NP agglomerates, while the polymer nanostructure is maintained. Fitted line cuts taken from the Yoneda region of the DBC thin films are shown in Figure 5.2b, confirming the incorporation of the NPs into the DBC. The extracted structural information does not show significant changes, suggesting either the successful incorporation of the NPs into the polymer domains or, due to the large size of the NPs (> 20 nm), the localization of the NPs to the surface of the thin film while the DBC nanostructure underneath remains undisturbed.

Using a superconducting quantum interference device (SQUID) magnetometer, the functionality and magnetic characteristics of the binary and ternary hybrid films are investigated. Figure 5.3a and Figure 5.3b show the temperature-dependent magnetization curves for the binary and the ternary composite. As expected, the saturation magnetization and remanence increase for the ternary film when compared to the binary film. Interestingly, the magnetic hysteresis curves of the ternary film show a unique 'pinched' shape at temperatures below 200 K. This behavior, not observed in films containing only NiO NPs, indicates an interaction between the two types of magnetic particles, leading to trapping of the magnetic domains and thus the unique hysteresis behavior. While localization of two types of NPs is challenging to control in a one-step deposition technique, the magnetic properties of the ternary film highlight the potential for such films to be used in magnetic sensing or magnetic storage applications.



Figure 5.3: Temperature-dependent magnetization curves of the a) binary composite containing $CoFe_2O_4$ and the b) ternary composite containing both NiO and $CoFe_2O_4$. The ternary composite hysteresis curve shows a unique 'pinched' shape at temperatures below 200 K.

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5.3 Biopolymer-templated deposition of hierarchical 3D-structured graphene oxide/gold nanoparticle hybrids for surface-enhanced raman scattering

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Surface-enhanced Raman scattering (SERS) is a detection technology for non-destructive, rapid detection of DNA, RNA, or single molecules[1]. Thus far, there are two main origins of SERS: electromagnetic mechanism (EM) and chemical mechanism (CM). EM is derived from the amplified electromagnetic field induced by localized surface plasmon resonance (LSPR) around noble metal nanoparticles (NPs) triggered by incident light, thereby increasing the Raman scattering cross section of nearby molecules. CM is closely related to charge transfer (CT) between the substrate and molecules. It is believed that EM is the main contribution to SERS [2]. Strong near-field coupling, i.e., hot spots, can occur between two metal NPs. By adjusting the size, shape of the NPs or the distance between the NPs, the distribution of "hot spots" can be tailored [3]. Also, the signal intensity of SERS can be improved by increasing the density of "hot spots". In our work, cellulose nanofibers (CNF) are used as a 3-dimensional (3D) template. When combined with NPs, they form a 3D "hot spots" network, thus increasing the density of "hot spots" [4].

In addition, CM-based two-dimensional (2D) materials for SERS offer some decisive advantages over EM-based noble metals, such as low cost, high specificity, and superior biocompatibility. Meanwhile, when a molecule is directly in contact with metal NPs, electrons are easily transferred between the NPs and molecule, but it is complex to extract the molecular Raman signal due to the chemisorption between the molecule and metal NPs [3]. Hence, the introduction of 2D graphene oxide (GO) with unique single sheet of carbon atoms in a 2D honeycomb crystal structure of constituting a large delocalized π bond is a good candidate for making good charge transfer between the detected molecule and SERS substrate [5]. Compared to conventional SERS substrates, the hybrid 3D structures comprising GO/AuNPs would significantly enhance the SERS sensitivity due to their synergistic effect of CM and EM.



Figure 5.4: SEM images of CNF based substrates: (a) CNF/Au, (b) CNF/Au/GO,(c) CNF/GO/Au, and (d) CNF+Au+GO mixture.

Herein, we present a straightforward approach utilizing the layer-by-layer (LBL) spray coating method to fabricate CNF films loaded with gold nanoparticles (Au NPs) and GO to serve as SERS substrates. As shown in Fig. 5.4, SEM images of spray-deposited CNF based SERS substrates were performed. In Fig 5.4 (a) Au NPs are directly sprayed on CNF substrate. Fig 5.4 (b) shows GO sprayed on the template of Fig. 5.4 (a), while in Fig. 5.4 (c) first CNF, then GO, then Au NPs were sprayed. In Fig. 5.4 (d), the mixture of CNF, Au NPs and GO was directly sprayed and resulted in the uniform loading of Au NPs. The high specific surface area of GO provides many binding sites with Au NPs, which is beneficial to obtain a uniform and dense distribution of "hot spots" over the entire substrate.



Figure 5.5:

Electromagnetic field distributions simulated by finite difference time-domain (FDTD): (a1) X/Z plane (a2) X/Y plane of CNF/Au/GO, (b1) X/Z plane (b2) X/Y plane of CNF/GO/Au, and (c1) X/Z plane (c2) X/Y plane of CNF+Au+GO mixture.

The distribution and intensity of electromagnetic "hot spots" on the surface of the CNF film by FDTD near-field simulations were calculated. We simulated the electromagnetic field distribution with the size value of Au NPs around 35 nm and the gap value of particles is 2 nm. It can be seen from Fig. 5.5 that the intensities of the "hot spots" at the gaps of the Au NPs are considerably stronger. The GO layers which distributed in the top (Fig. 5.5 (a1)) and middle (Fig. 5.5 (c1)) of Au NPs don't provide obvious enhancement to the electromagnetic field due to the weak interaction between single/few-layer GO and Au NPs, but they can prevent distortion of Raman signals caused by direct metal-molecule interactions.

In future, we plan to use grazing incidence small-angle X-ray scattering (GISAXS) to reveal the 3D template structure in full detail. The intrinsic relationship between 3D CNF network, 3D hybrid Au NPs/GO and SERS property will be established to provide a solid theoretical and experimental basis for the preparation of high-performance SERS for diagnostics and health applications.

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5.4 Correlating nanostructures and optical properties of cellulose-colloid films

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Tailoring the optoelectronic characteristics of thin films holds significant importance for various industrial applications, such as interference colors [1] or anti-counterfeiting [2]. In our approach, we enhance the optical properties of thin cellulose films through the application of core-shell polymer colloidal inks. Using a scalable layer-by-layer slot die coating method, we fabricate thin films consisting of cellulose nanofibrils (CNF) and core-shell polymer colloids yielding ultimately hybrid materials. The outcomes of this procedure offer potential applications in functional coatings and the printing of porous materials, enabling the tailoring of their optical properties. This technique is particularly valuable in the development of structural inks that replicate hierarchical nanostructures found in nature [1].



Figure 5.6:

Two-dimensional (2D) GISAXS data of a spray coated a) and pristine slot-die coated CNF layer b,c) with printing directing perpendicular (b)) and parallel (c)) to the print direction.[3]

The grazing incidence small-angle X-ray scattering (GISAXS) data Figure 5.6 b)& c) prove that the pristine CNF films coated with slot-die coating are very homogeneous and smooth. The strong resonant diffuse scattering which is very visible as fringes in q_z direction at $q_y = 0 nm^{-1}$, in contrast to the reference spray-coated CNF film Figure 5.6 a). The 2D GISAXS data in Figure 5.6c) shows a slightly larger extension of the Yoneda wing compared to Figure 5.6b), indicating a slightly higher orientation of the CNF in the printing direction.

The CNF layer establishes a 3D porous nanostructure capable of accommodating the infiltration and imbibition of small colloids [4-5], as illustrated in Figure 5.7. In this study, we broaden our exploration to nanoporous substrates, employing CNF with surface charges of $-1000 \frac{\mu \text{mol}}{\text{g}}$ for slot-die coating and spray coating, resulting in a layer thickness of 140 nm (Figure 5.6). The colloids [6], dispersed in aqueous solution with different glass transition temperature T_g's of ~74 °C and ~126 °C, and sizes of ~40 nm and ~80 nm diameter, infiltrate into the CNF void network after water evaporation, where the CNF cavities are predominantly filled with small colloids of





The spectroscopic ellipsometry model for slot-die coated films: a) pristine CNF films, b) deposited colloids on the CNF layer with a smaller size than CNF void structure, and c) deposited colloids on the CNF layer with a larger size than CNF void structure. The smaller colloids have the ability to penetrate the CNF layer, while the larger colloids do not show imbibition.[3]

 \sim 40 nm. Subsequently, we annealed the multicomponent colloid-CNF hybrid layer, investigating its structural dynamics during annealing using GISAXS. The incorporation of colloids into the CNF template is observed by GISAXS, atomic force microscopy (AFM), spectroscopic ellipsometry, and scanning electron microscope (SEM).

Spectroscopic ellipsometry reveals that the small colloids are capable of penetrating the CNF layer, inducing a change in the refractive index of the pure CNF layer. The depth of penetration of small colloids correlates with a gradient in the refractive index within the CNF layer of the small colloidal system (Figure 5.7b). On the other hand, large colloids only form an upper layer on top of the CNF without creating a gradient layer (Figure 5.7c). Throughout the annealing process, shape changes in the colloids are observed. The depth-dependent refractive index of colloids with a high T_g remains unchanged during annealing. Conversely, for colloids with a small T_g , the layer thickness of the colloidal layer in the CNF-colloidal system is reduced, and the refractive index correlates with the agglomeration and integration of colloids into the CNF layer. These findings offer insights for the improved and stable coating of nanoparticles on porous materials.

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6 Materials for energy storage



6.1 Operando scanning nanobeam studies of lithium metal batteries with polymer electrolyte

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Lithium metal is regarded as the ideal battery anode owing to its high theoretical specific capacity of 3860 mAh g^{-1}) which is approximately ten times higher compared to graphite (372 mAh g^{-1}). Furthermore, its high negative potential of -3.040 V vs. SHE enables high-voltage batteries. However, in combination with conventional liquid electrolyte, the practical use is still limited due to the formation of lithium dendrites. A decrease of coulombic efficiency and short circuits as well as thermal runaways are possible consequences. To bypass these issues, polymer electrolytes are regarded as a safe alternative to liquid electrolytes. Especially single-ion conducting polymers, in which the anions are covalently bonded to the polymer matrix and only the lithium cations are moving, are believed to suppress lithium dendrites.[1]

Most of the time, the cells for operando X-ray experiments are designed in a way, that all layers of the components are penetrated by the beam.[2] For instance, in modified coin cells with kapton window or pouch cells, the beam travels through the cathode, electrolyte and anode and thus every layer contributes to the final scattering data. In this work, we present two methods to investigate only the polymer electrolyte in lithium metal batteries during operation. In the first project, a free-standing single-ion conducting gel-type polymer electrolyte film composed of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and poly((trifluoromethane) sulfonimide lithium styrene) (PSTFSILi) swollen in a solution of ethylene carbonate (EC) and propylene carbonate (PC) (1:1 v/v) is prepared and used in a special setup designed for grazing incidence X-ray scattering (GIWAXS) experiments. The electrochemical cell consists of the polymer, which is sandwiched between a copper and lithium electrode. A cyclic voltammogram is recorded while simultaneously GIWAXS measurements are performed (Fig. 6.1a)). The corresponding GIWAXS detector image is shown in Fig. 6.1a). A broad halo at $q \approx 1.5$ Å⁻¹, which originates from the PVDF-HFP polymer, is clearly visible. On top of that, the crystallites exhibit a slight orientation with respect to the copper substrate.

Moehl et al. showed the feasibility of X-ray operando studies on the polymer electrolyte in a capillary cell in transmission geometry with an in-house X-ray source.[3] Furthermore, Nian et al. have utilized scanning nanofocus WAXS to study structure heterogeneities and moisture degradation in perovskite films.[4] In this project, the ideas of the aforementioned projects are merged and therefore, a custom built operando cell for X-ray transmission experiments, which imitates the principle of a coin cell, is designed and successfully operated at the P03 nanofocus end-station at DESY. Here, the gel-type polymer electrolyte, which performs in a conventional symmetric coin cell for around 330 hours, is placed between two lithium metal electrodes and scanned by the nanosized X-ray beam in a mesh grid pattern during lithium plating and stripping (Fig 6.1b)). Each row, defined as parallel to the stack, consisted of five measurement points and each column was probed with sixteen points. With this setup, possible lithium crystallization inside the polymer can be traced. In Fig 6.2a) the radial integrations of the scanning nanobeam WAXS data of five different horizontal positions of the first half cycle show the broad halo of PVDF-HFP. In the second half cycle (Fig 6.2b)), the same positions are measured again and a sharp peak arises at $q \approx 1.55$ Å⁻¹ for x = 2, which is attributed to lithium and indicates the formation of crystallites in the polymer. Also, for x = 0 and x = 1 small peaks appeared, which are not visible in the first half cycle. In addition to the peaks at $q \approx 1.55$ Å⁻¹, a small sharp peak on top of the polymer halo arises for every position at $q \approx 1.45 \text{ Å}^{-1}$.

For the upcoming analysis, 2D color maps of the scanned area, in which the color corresponds to the intensity of the arising peaks, will be created. This map will provide a spatial and temporal



Figure 6.1:

a) Grazing incidence wide angle X-ray scattering and b) nanofocus wide angle X-ray scattering on gel-type single-ion conducting polymer electrolytes. Only the polymer is investigated with these measurement setups.



Figure 6.2:

Selected nanobeam WAXS radial integrations of the first (a) and second (b) half cycle of the symmetric lithium cell. Sharp peaks at $q \approx 1.55$ Å⁻¹ arise during lithium plating and stripping for different horizontal positions.

understanding of the growth of lithium crystallites inside the polymer electrolyte and thus, irreversible (dead) and reversible (active) plated lithium can be distinguished. The presented measurement setups show the feasibility and importance of X-ray scattering in lithium-based battery research.

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6.2 3D electrodeposition porous Cu for long-cycling lithium-metal batteries

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Lithium (Li) metal is the ultimate anode for rechargeable batteries. Its high specific capacity (3860 mAh g⁻¹) and low voltage (-3.04 V vs standard hydrogen electrode) warrant optimal cell energy density. However, these anodes rely on repeated plating and stripping of Li, which leads to consumption of Li inventory and the growth of dendrites that can lead to self-discharge and safety issues. To address these issues and problems related to the volume change of these anodes, a number of different porous conductive scaffolds have been reported to create high surface area electrodes on which Li can be plated reliably. While impressive results have been reported in literature, current processes typically rely on either expensive or poorly scalable techniques. Herein, we report a scalable fabrication method to create porous Cu anodes using a one-step electrodeposition process. The areal loading, pore structure, and electrode thickness can be tuned by changing the electrodeposition parameters, and we test the in-situ WAXS images with lithium growth which can help explain the mechanism of dendrites. We also provide a feasible method to fabricate the porous Cu cathodes with different electrodeposition solution concentrations.[1-3]

The progress of "anode-free" lithium-metal batteries, known for their high energy densities, is currently impeded primarily by the insufficient control of lithium nucleation directly on the copper current collector, especially within conventional carbonate electrolytes. However, for the consistent use of anode-free lithium batteries, challenges related to the formation of dead lithium, porous lithium, and lithium dendrites during lithium electrodeposition on copper current collectors must be addressed. Although the electrodeposition of lithium on a copper current collector differs from that on a lithium-metal electrode, the aforementioned problems are essentially the same in both cases. These issues arise from the inability to effectively control the lithium nucleation process, preventing the achievement of 2D homogeneous lithium electrodeposition.Numerous strategies have been proposed to enhance lithium electrodeposition in anode-free cells. Among them, the central chemistry-related approach involves the development of new electrolyte formulations that impact the solvation structure of lithium ions and/or the compositions and morphologies of the solid electrolyte interphase (SEI) layer. Other material-related approaches include i) modifying copper current collectors by synthesizing 3D structures to reduce local current densities and encapsulate electrodeposited lithium, ii) designing artificial SEI layers that are more stable during lithium electrodeposition, and/or iii) coating "lithiophilic" materials on the copper surface to facilitate lithium nucleation. Improving our understanding of the lithium nucleation process and its intricate interactions with the copper substrate is crucial. The diffusion process described above presents a challenge in achieving a large number of evenly distributed lithium nuclei on the copper surface, resulting in non-uniform electrodeposition. However, it has been demonstrated that the nucleation of lithium on copper significantly improves with an initial chemical prelithiation of the copper surface. This prelithiation saturates the copper surface with lithium, reducing the impact of lithium diffusion through grain boundaries. Consequently, lithium nucleation becomes more homogeneous see in Fig. 6.3, particularly when employing a specific type of electrolyte. Herein we use the copper chloride. After using direct pulse electrodeposition 5mv for 10 minutes the surface is uniquely covered with copper and the boundaries are clearly illustrated in Fig. 6.3 (a) and (b).

The coin cells were assembled to evaluate the battery's performance using electrolytes of 4M LiFSI in DME solvent. In order to explore the stability of the designed 3D electrodeposition porous Cu with Lithium anode, the Li-Cu and anode-free Cu-LFP full cells are both tested.



Figure 6.3: SEM images of 3D electrodeposition porous Cu at different scales.

Fig. 6.4 (a) shows the Li-Cu half cell with over 200 cycles stability. And the charge-discharge curves at the 1st, 5th, 50th, 100th, 150th, 200th, there is no gradual increase of the electrochemical polarization from the 1th to the 200th implies very few slow SEI film growth on the Cu collector due to the unavoidable decomposition of electrolytes, which also reflects the protection of our 3D structure can stabilize the formation of lithium deposition and furthermore prevent the decomposition of electrolytes. To further explore the structural advantages of the full cells' performance, We also tested the anode-free Cu-LFP full cells in Fig. 6.4 (b) . After the first cycle of lithium deposition, we can see clearly the uniform deposition of lithium in the copper surface from the SEM images. Thus, the cycling performance 30 cycles is better than commercial copper film, which is around 15 cycles. We believe the 3D electrodeposition porous Cu structure is of significant influence in this cycling test because it can help to improve the lithium nucleation process and its interactions with the copper substrate.



Figure 6.4:

The electrochemical performance of Li-metal cells. (a) Charge-discharge curves of Li-Cu half-cells over 200 cycles. (b) Cycling performance of anode-free Cu-LFP full cells with stable 30 cycles.

In summary, the 3D electrodeposition porous Cu can help stabilize and help uniform the lithium deposition by the results of SEM and electrochemical performances. More tests are needed in future experiments such as XPS to understand the decomposition of electrolytes, in-situ WAXS data for inside structures analysis, TEM for copper and lithium nanoscale observation and XRD for copper structural tests. Also, different types of electrodeposition solutions, the conditions such as time, current of electrodeposition can be explored in the future.

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6.3 **PEO/PVP** based flexible and biocompatible batteries

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Polymer electrolytes based on the biocompatible and biodegradable polymers poly(ethylene oxide) (PEO) and poly(vinyl pyrrolidone) (PVP) have emerged as promising materials for flexible and thin film batteries, drawing considerable interest for diverse applications. PEO, known for its heightened safety, stability, and ionic conductivity, is particularly well-suited for applications in biomedical devices. PVP facilitates efficient ion transport owing to its film-forming properties. The use of methanol as a solvent enables the dissolution of both PEO and PVP and facilitates the fabrication of polymer electrolyte films [1]. Additionally, the incorporation of the lithium salt LiTFSI as a dopant has been employed to augment the critical ionic conductivity of the PEO/PVP-based electrolyte system [2].

In this study, we used a solution casting approach to prepare PEO/PVP blend polymer electrolyte films with varying concentrations of LiTFSI dopant salt. Figure 6.5 illustrates the solution casting technique utilized for synthesizing these films, illustrating the fabrication process.



Figure 6.5: PEO/PVP with LiTFSI salt synthesized by solution casting technique.

The prepared electrolyte was then converted to a full battery cell with stainless-steel electrodes to conduct photoelectrochemical impedance spectroscopy (PEIS) measurements at different temperature ranges, to determine the optimum battery operating temperature, and the relation between ionic conductivity and temperature. It was found that the device is functional between $20 - 70^{\circ}$ C temperature range, as can be seen from figure 6.6, after which the battery electrolyte degrades at around 75° C. Additionally, the ionic conductivity and inverse temperature are plotted in figure 6.7, showing increase in ionic conductivity with temperature, with optimum operating temperature as 60° C.

Subsequent structural and optical characterization of the solid polymer electrolyte (SPE) films shall be conducted using a comprehensive array of analytical techniques, including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and field emission scanning electron microscopy (FE-SEM).

The crystal structure of the polymer electrolyte film is evaluated using X-ray diffraction (XRD) analysis. XRD is a powerful technique that allows for the determination of the arrangement and periodicity of the crystal lattice within the polymer electrolyte film.


Figure 6.6:

Temperature-dependent Nyquist analysis of PEO/PVP blend polymer electrolyte films with fixed LiTFSI dopant concentration

Figure 6.7:

Ionic conductivity v/s inverse temperature plot for PEO/PVP blend polymer electrolyte films with fixed LiTFSI dopant concentration

FTIR spectroscopy is used to investigate the chemical composition and interactions within the polymer electrolyte system. By analyzing the infrared absorption spectra, FTIR spectroscopy provides valuable insights into the functional groups present in the polymer electrolyte and any molecular interactions occurring within the system.

Field emission scanning electron microscopy (FE-SEM) is utilized to examine the surface morphology of the polymer electrolyte film. FE-SEM enables high-resolution imaging to assess the integrity, uniformity, and topography of the electrolyte film. By evaluating the surface characteristics, FE-SEM analysis ensures the absence of defects, cracks, or irregularities that could compromise the performance and reliability of the film.

In summary, this research presents a comprehensive exploration of PEO/PVP blend polymer electrolyte films, emphasizing their enhanced ionic conductivity through the addition of LiTFSI dopant salt. The fabrication process with solution casting technique enables rapid optimization and production of the SPE film. The Nyquist plot measured at different temperatures helps to find the operating temperature range of the device between $20 - 70^{\circ}$ C. Within this temperature range, the ionic conductivity increases with temperature. Further characterization and electrochemical analysis is required to further understand and optimize the SPE film and full battery cell.

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6.4 Operando study of poly(ethylene oxide) composite electrolytes in all-solid-state lithium batteries

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Lithium batteries (LBs) have become highly promising for a variety of applications, owing to their impressive specific energies, volumetric energy densities, and power densities. Lithiumion batteries have become pivotal in various applications, emphasizing the need for enhanced performance, safety, and energy density. The development of all-solid-state lithium batteries (ASSLBs) with composite electrolytes presents a promising results [1].

The main is on the operando study of poly(ethylene oxide) (PEO) composite electrolytes in all-solid-state lithium batteries with lithium lanthanum zirconate (LLZTO). LLZTO is a cubic-phase garnet ceramic material used as a solid electrolyte in all-solid-state lithium batteries. It is preferred for its better electrochemical stability compared to other solid electrolyte materials, making it a promising choice for enhancing the performance and safety of LBs as shown in Fig. 6.8, describing the different types of electrolytes that can be used for LBs with its advantage. Coin cells were assembled using stainless steel (SS) electrodes and lithium foils, forming SS-SS, Li-Li, and Li-SS cells. The study combines in-operando grazing incidence wide-angle X-ray scattering (GIWAXS) and electrochemical performance evaluations. [2]



Figure 6.8:



Composite electrolytes combine the advantages of polymers and ceramics, aiming to improve ion conductivity and mechanical strength. PEO, a flexible polymer, is combined with LLZTO, a ceramic known for its high ionic conductivity. The weight percentages 10%, 20%, and 50 % of LLZTO in the composite electrolyte were varied to observe their impact on the overall performance [3]. The 10 wt% LLZTO is termed "ceramic in polymer" composite electrolyte (CIP), leveraging the ceramic additive within a polymer matrix. With 20 wt% LLZTO, an Intermediate composite electrolyte (IM) is achieved, balancing the ceramic and polymer components. The 50 wt% LLZTO variant is denoted as "polymer in ceramic" composite electrolyte (PIC), emphasizing a higher proportion of the polymer phase within the composite. These tailored composite electrolytes, namely CIP, IM, and PIC, offer versatile options for optimizing lithium battery performance.

The electrolyte preparation involved dissolving 72 mg/ml of polyethylene oxide (PEO) in acetonitrile. A lithium to ethylene oxide (Li:EO) ratio of 1:14 was maintained in the solution. The



Figure 6.9: Illustration of the pathways followed by various electrolytes within lithium-ion batteries (LIBs).

mixture was stirred at 55°C overnight to ensure proper blending. Subsequently, the solution underwent a vacuum evaporation process for a duration of 72 hours as shown in Fig. 6.9



Figure 6.10: Electrochemical performance of electrolytes of CIP, IM and PIC.

The transference number, denoted as t_i , is the fraction of the total electric current carried in an electrolyte by a specific ionic species *i*. For instance, the transference number for lithium-ion (t_{Li^+}) is the proportion of the Li+ current to the total electric current contributed by Li+ and the anion of the salt. It is defined as the ratio of the electric current derived from the cation to the total electric current.

For transfer number, $t^+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \Delta V$ refers to the voltage change (10 mV). I_s and I_o are recorded current and R_o and R_s are resistance from two impendence measurement. From Fig. 6.10The transference numbers for different composite electrolytes are as follows CIP : $t_{Li^+} = 0.45$; IM : $t_{Li^+} = 0.47$; PIC: $t_{Li^+} = 0.34$ From an electrochemical performance perspective, the composite electrolyte "IM" with 20 wt% LLZTO demonstrates favorable characteristics, including good conductivity and a smooth, flexible surface. This is evidenced by its high transference number (t^+) of 0.47, indicating that a significant fraction of the total electric current is carried by the lithium-ion within this electrolyte composition.

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6.5 Insights into low-temperature lithiated graphite behavior: structural analyses and electrolyte dynamics in lithium-ion batteries

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Regarding sustainable energy alternatives, the focus has shifted from traditional combustion engines to electric drivetrains, primarily powered by lithium-ion batteries (LIBs), known for their relatively high energy and power densities, long lifetimes, and cost-effectiveness. The current industry standard comprises LIBs with liquid electrolytes, featuring high-performance graphite-based electrodes used as the anode in the LiB [1]. Recent developments in graphite anodes, particularly with the usage of nanostructural-silicon, have optimized volumetric capacity, elevating specific capacity and performance while reducing costs [2]. However, the temperature-resolved phase stability of lithiated graphite anodes at low temperatures remains a complex topic in the literature, marked by structural anomalies and capacity retention in LIBs [3]. Furthermore, the liquid electrolyte's composition and properties have a significant impact on the ion mobility, charge transfer kinetics, and overall battery efficiency [4]. In the following contribution a temperature-resolved structural in situ neutron powder diffraction study was carried out on real LIBs of 18650 type (ICR1865026F), measured at the instrument SPODI (FRM II, Garching) using a wavelength of $\lambda = 2.536$ Å. The cells were previously charged to specific state of charge between 0% and 100%. A top loading closed cycle refrigerator was used for the cooling of the LIBs to 300K, 270K, 250K, 240K, 235K, 230K and 200K. In Fig. 6.11 the first order 00l reflections of the lithiated graphite electrode are shown for selected charge states revealing their structural behavior during the cooling process. While the cell is being cooled, the 001 reflections are shifted towards higher diffraction angles, which is associated with thermal contraction. Moreover, the 00l reflections at state of charge 10% and 30% show a perceptible overlap, indicating the presence of various lithiated phases. An additional diffraction signal is occurring at diffraction angles around 44.5° at temperatures < 240K for samples with state of charge > 10%, as shown in Fig. 6.11. Such reflections are associated with the frozen electrolyte present in the commercial LIB. Furthermore, a series of weak reflections are appearing at lower diffraction angles ($2\theta \sim 25^{\circ}$). Simultaneously to the 00l reflections, the reflections dedicated to the frozen electrolyte are experiencing thermal contraction upon cooling. However, at lower charging states, such electrolyte reflections are not visible, as they overlap with the pure/low lithiated graphite reflections [5].



Figure 6.11:

High resolution neutron powder diffraction data for selected LIBs with defined state of charge (0%, 50%, 100%), showing first order 00l reflections for different lithiated phases (pure/low lithated graphite, LiC_{12} and LiC_{6}) and additional electrolyte reflections observed below 240K.



Figure 6.12:

Temperature dependent XRD measurements of a) lithiated graphite corresponding to a state of charge 100% (ESRF) and b) nearly lithium free graphite (DESY) extracted from previously charged 18650-type cells

Furthermore ex situ X-Ray powder diffraction was carried out on lithiated graphite electrode material extracted from 18650 type cells (NCR186550B and NCR18650GA) measured at the Swiss-Norwegian beamline (SNBL/ESRF, Grenoble) using a wavelength of $\lambda = 0.668$ Å and at the powder diffraction and total scattering beamline P02.1 (DESY, Hamburg) using a wavelength of $\lambda = 0.207$ Å. Low temperatures were supplied by an Oxford Cryostream in both cases and showed similar to the neutron data small changes in the position of lithiated graphite reflections dedicated to thermal expansion, as seen in Fig. 6.12. Besides this, additional long range order reflections appeared below 330K in both measurements, attributed to the liquid electrolyte. However, as the material was extracted from the commercial LIBs, the liquid electrolyte is partially evaporating. Thus, the observed reflections belong to a mixture of the frozen electrolyte and the remaining dried out residues of the liquid electrolyte, e.g. lithium salt $(LiPF_6)$ and ethylene carbonate. The diffraction data indicates a better stability of the reflections up to much higher temperatures, when compared to reflections related to the liquid electrode in the neutron data vanishing at a much lower temperature. Consequently, in the context of low temperatures, the lithiated graphite showed a remarkable stability in the XRD measurements. However some fluctuations in the lithiated graphite intensities were observed with neutron measurements, possibly due to their improved sensitivity to lithium. In addition, reflections associated with the liquid electrolyte and its dried-out residues were observed during the cooling process, paving the way for structural analysis of the liquid electrolytes and their composition in commercial LIBs [5].

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6.6 Polymers as protective coating layers on the electrodes for applications in lithium-ion batteries

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Lithium-ion batteries play an essential role in today's energy supply in industrial sectors. Due to the increasing demand for environmentally friendly power supply options, such as batteries, the improvement of their performance is of great importance. One parameter that contributes to the overall efficiency of the battery is the anode material. Particularly, lithium as an anode material has drawn much attention due to its high theoretical specific capacity of 3860 mAh/g. However, problems such as the formation of an unstable solid-electrolyte interface (SEI) formed between the Li-electrode and the electrolyte interface, as well as subsequent dendrite growth and low coulombic efficiency, create serious safety issues and shorter cycling lifetimes for the battery. In order to avoid those degradation mechanisms, a large variety of strategies have been developed, such as solid polymer electrolytes (SPE). Another approach that has drawn extensive attention, is the polymer-coating process of the electrodes of the battery. The coating of the Li-electrode with polymeric thin films can prevent lithium-ion accumulation on the anode electrode and subsequent degradation mechanisms [2], [3]. So far, a large variety of different materials have been tested as coatings for lithium-ion batteries, such as PDMS, PVDF-HFP with LiF, and more [1].

In this work, we focus on the synthesis of a thin polymer film, which is a blend of poly-ethyleneoxide (PEO) and poly(trifluoromethane)sulfonimide-lithium-methacrylate (PMTFSILi), for the coating of the Li-electrode. The goal of this study is to enhance and, at the same time, regulate the lithium-ion transport on the Li-electrolyte interface. PEO is a well-known solid polymer, which has been tested in previous studies as a polymer coating layer for the Li-electrode [4]. The main disadvantage of the PEO polymer is that it has relatively poor ionic conductivity due to its high crystallinity. Therefore, we mix PEO with a second polymer, namely PMTFSILi, which has an amorphous structure, in order to decrease the crystallinity of PEO, and subsequently to improve the lithium-ion conductivity of the polymer film. Both polymers are compatible with water, thus we choose to mix them in deionized (DI) water.



Figure 6.13:

a) Preparation of PEO-PMTFSILi solution in DI water, and b) static spin-coating process of the solution on copper foils or stainless steel chips.

The initial stages of this study involve the coating of copper foils in order to determine the applicability of the solution on coin-cell batteries. As a first step, PEO and PMTFSILi were dissolved in DI water and the solution was stirred for 48 hours, as shown in Fig.2. The concentration of the solvent is 20 mg/mL. Then, the solution is spin-coated on pre-cleaned copper foils and stainless steel chips. The solution appears to be rather viscous, thereby we performed spin-coating for a large number of different spin-coating velocities, ranging from 2000 rpm to 4000 rpm. The, as prepared, samples are shown in Fig.2. The thin film created on the samples can become visible by its blueish (stainless steel chip) or pinkish (copper foil) color. Furthermore, the thickness of the thin polymer film is determined by profilometry. Finally, the value of 4000 rpm was chosen to use in subsequent steps, since the thickness of the thin polymer film with the literature [4].



Figure 6.14: Samples of spin-coated stainless steel chips (left) and copper foils (right) at 4000 rpm.

To ensure that the polymer film is completely dry, the spin-coated copper-foils are heated at $T = 60^{\circ}C$ for 24 hours, in order for the DI water to evaporate. As a next step, our study will focus on the electrochemical performance of Li—Cu cells. Subsequently, Li—Cu cells will be fabricated and their electrochemical performance will be investigated. Also, the performance between coated and uncoated Li—Cu cells will be compared.we intend to spin-coat lithium -foils with the PEO-PMTFSILi solution and investigate the electrochemical performance of Li—Li coin cells. However, the composition of the solvent for application on Li—Li cells needs to change since water solution cannot be put into the glovebox for spin-coating on lithium foils. Furthermore, lithium is known to react violently with water, creating lithium hydroxide (LiOH) and hydrogen gas.

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6.7 Optimization of electrode structures for oxide Li-metal solid state batteries

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Solid-state batteries (SSBs) based on solid electrolytes are considered inherently safer and provide a higher theoretical energy density than conventional Li-ion batteries with liquid electrolytes, when used with a Li-metal anode. Oxide based Li-Garnet electrolytes, such as $Li_7Zr_2O_{12}$ (LLZO) have displayed conductivities greater than 1mS/cm and can be processed as ceramic pellets, tapes and films. LLZO also offers a wide electrochemical stability window and compatibility with a high-capacity Li-metal electrode. [1]

The aim of this research is to manufacture a 3D porous scaffold structure of LLZO as a host for Li-metal, as an anode. We were successful in the multi-step route to synthesize high quality LLZO powders for fabricating the 3D scaffold. It is crucial to manufacture powders with low size and mono-modal particle size distribution, so as to ensure homogeneity and prevent agglomeration during fabrication of LLZO tapes.[2] LLZO is synthesized by ball milling the precursors with Ethanol and Triton/Oleic acid as dispersants, which is followed by drying, pelletizing and calcination followed by a second ball-milling step to reduce the particle size below 1 μ m. The powders are then annealed again, sieved and then sintered as pellets at 1050°C for 5h in oxygen atmosphere. We were able to bring down the particle size by using smaller size of beads (0.5mm beads) for ball milling, successfully producing a mono-modal particle size distribution and the size of particles \approx 330nm. This resulted in decreased agglomeration, reduced number of pores, and more uniformity in a pellet fabrication. These factors double the conductivity as seen in Figure 6.15.



Figure 6.15: Reduction in particle size and achieving mono-modal distribution, and its effect on conductivity.

To build a porous 3D structure, tapes were casted using corn-starch (CS) and polystyrene (PS) as pore forming polymers. Porous layers were fabricated by slurry casting of LLZO and pore formers in a 80:20 (LLZO : pore formers) ratio by weight. 3D porous bilayers and tri-layers (porous-dense or porous-dense-porous) were formed by laminating dense and porous LLZO layers. The solvent for the slurry comprised of Toluene and Ethanol, with PVB-79 and DOP as binder and plasticizer, and Fish oil as dispersant. Tapes formed with CS showed uniform pore distribution compared to tapes formed with PS as pore formers as seen in figure 6.16. The tapes are then sintered at 1050°C for 2h in oxygen atmosphere.



Figure 6.16: 3D Porous-Dense Bilayer tapes SEM cross section.

However, the densification of the LLZO layers observed could be improved, as we can still see a grain-like texture. The tapes after sintering were also bent in shape, and we conducted a few experiments to make them flat, to be able to test them in a cell setup. To further densify the LLZO layers, we sintered the LLZO tapes at a higher temperature (1050°C to 1100°C) and for a longer time (2h to 5h) in oxygen atmosphere. We obtained much better quality of tapes as seen in figure 6.17, where we can see the uniformity of the layer throughout without any presence of a grain like texture. We observed that increasing temperature and time also had a positive impact on the tape's shape, making them flatter than before. The final tapes produced were flat, and translucent in nature as seen in figure 6.17.



Figure 6.17: Increased densification reduction of flatness in tapes caused due to increasing temperature and time of sintering.

The future work shall comprise of reduction in particle size of the powders, followed by building bilayers out of this newly obtained dense LLZO tape and testing it in an electrochemical setup.

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6.8 Lithium distribution in the graphite anode of cylindrical 21700 Li-ion cells during degradation

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Despite the overall success of lithium-ion batteries since their commercialization in 1991, a number of open questions remained, e.g. safety challenges due to flammable liquid electrolytes, finite lifetime, limited availability of transition metals like cobalt and nickel, etc. Among the listed concerns the capacity and power fade as a result of cyclic and calendar aging directly affects cell performance. Reduction of active (movable) lithium is the main driving force of capacity degradation, where the active lithium gets built into passive products of side reactions, like the solid-electrolyte-interphase (SEI).

Increased passivation layers, in turn, are contributing to the internal cell resistance and causing its increase, thereby, leading to a power fade. Increased cell resistances lead to increase of the temperature during operation due to Joule heating, thus accelerating decomposition of the electrolyte, consequently promoting capacity fading at the end of the batteries lifetime.

In this contribution a combination of diffraction and imaging-based experimental methods along with electrochemical and thermal characterization were used for investigation of structural and spatial aspects of the degradation of cylindrical 21700-type lithium-ion batteries.



Figure 6.18:

Extracted graphite anode sheets (SOC=100%) in a) fresh and c) aged state. Mean (thickness averaged) lithium concentration in the lithiated graphite anode calculated from the XRD measurements in b) fresh and d) aged state represented in false colors.

As the graphite anode changes its color continuously from dark blue (LiC_{18}) through red (LiC_{12}) to a golden color (LiC_6) upon lithiation, the color can be used as an indicator for the lithiation

grade. The extracted lithiated graphite anode sheets are shown in 6.18a) for the fresh cell and in 6.18c) for the aged cell. The lithiated graphite anode in the fresh state (6.18a)) is dominated by a golden color corresponding to the fully lithiated state of LiC₆. Black-colored regions at the beginning, end and at about 1/3 length of the electrode stripe area are attributed to sections lacking of counter electrode material. Additionally, at middle height of the electrode, a narrow region with a systematically darker shade was observed, possibly indicating an average lithium content of $Li_{x<0.5}C_6$ on the electrode surface. The visual inspection of the anode extracted from the aged cell (125 cycles using 2C/1C dis-/charge current rates; remaining capacity of ca. 60% of initial capacity) showed a series of pronounced changes compared to the "initial" state (6.18c)). Due to the generally lower degree of lithiation of the anode, the electrode stripe displays significantly darker colors with red and dark-red shades. At the electrode center an area with a different color distribution from that at the outer electrode width can be clearly identified. The uniformity of the lithium distribution was additionally quantified *ex situ* using X-ray diffraction radiography (XRDR) characterization in order to add depth information over the electrode thickness. The experimental setup was adapted from Ref. [1]. Analysis of the diffraction signal from lithiated graphite phases leads to an area map of the lithium content x in Li_xC_{6} , which are shown in false colors in 6.18b) for the fresh cell and in 6.18d) for the aged one. Except minor systematic differences between the individual frames, an initially homogeneous lithium distribution can be concluded for the fresh negative electrode. The black regions revealed by the visual inspection can be clearly associated to the regions with systematically lower lithium content in the false color plots. Comparing the cell layout structure to the lithium distribution yields that the narrow areas of lower lithiation correlate to the positions of the current tabs and areas with no counter electrode. No lithium gradient can be seen in the lithium distribution across the electrode height, apart from a very sharp drop at the very bottom and top of the cell, which again can be related to the absence of the counter electrode material in this region. In the aged cell the average lithium content in the graphite anode is reduced to $Li_{0.541}C_6$ com-

In the aged cell the average influtin content in the graphite anode is reduced to $L_{10.541}C_6$ compared to a value of $L_{10.723}C_6$ in the fresh cell. The relative loss of active lithium can, therefore, be calculated as approx. 25% of the value of the pristine electrode. Additionally to the general reduction of lithium content, the remaining lithium in the aged cell is distributed more heterogeneous, which is reflected in sprinkle like areas of higher lithiation, especially close to the center pin. Besides, two concentration maxima of $L_{10.569}C_6$ and $L_{10.565}C_6$ can be identified over the aged anode height at around 14.7 mm (24.5% tot. height) and 44.1 mm (73.5% tot. height), respectively. These features are also seen in the photo of the electrode (6.18c)). Here again one has to distinguish between the "thickness" averaged character of XRDR and the sensitivity of the visual inspection to the electrode surface. A grey-red film on top of the aged anode is usually attributed to the formation of covering/passivation layers on top of the electrode resulting from reactions of plated lithium and electrolyte.

The *ex situ* XRDR observations of the aged anode have been confirmed using non-destructive *in situ* X-Ray diffraction computed tomography (XRD-CT) adopting [2] (results not shown here). XRDR and XRD-CT have shown both quantitatively and qualitatively a similar character of the lithium distribution pointing to the systematic nature of the observed features of the electrode aging. Such inhomogeneous cell aging can be attributed to a variety of factors potentially involved, such as current distribution, gas release, electrolyte wetting, losses of active lithium, etc. and have a crucial effect on the cycling performance of the cell.

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6.9 Lithium plating and SEI formation studies on Si/graphite electrodes via neutron depth profiling and GD-OES

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Given the increasing demand for lithium-ion batteries with high energy density, substantial efforts have been invested in recent decades towards their innovation. Silicon-based materials have emerged as promising candidates for improving the capacity and performance of battery anodes due to their high theoretical capacity, cost-effectiveness, and abundant natural resources [1]. Among these materials, Si/graphite composite anodes have gained considerable attention due to their ability to combine the high capacity of silicon with the mechanical stability of graphite. Commercial cell anodes presently incorporate up to 4 wt.% Si. However, the (de-)lithiation processes causes morphological transformations in silicon particles, leading to a continuous decomposition of the electrolyte at the solid electrolyte interface (SEI). To gain a good understanding of both reversible and irreversible degradation mechanisms in Si/graphite electrodes, it is necessary to employ depth-resolved analytical methods, which provide insights into the decomposition products of the lithium-containing electrolyte across the thickness of the electrode.

Neutron depth profiling (NDP) is a non-destructive nuclear analytical method, and because of its high sensitivity for ⁶Li, NDP has become a well-established technique for the quantification of Li depth concentration profiles in battery electrodes [2]. In contrast, glow discharge optical emission spectroscopy (GD-OES) is a spectroscopic method where a designed area on the sample is ablated in a controlled manner and excited in the GD plasma to emit visible light. GD-OES can be used for both qualitative and quantitative elemental analysis of almost all elements in solid samples as a function of depth. GD-OES has also been successfully applied to measure battery electrodes as well [3].





In this study, we compared these two methods to determine Li concentration profiles in

Si/graphite anodes [4]. Both fresh and aged anodes were measured to look into GD-OES calibration accuracy issues beyond the calibration range. It has been revealed how the properties of the non-destructive (NDP) and destructive (GD-OES) methods affect the experimental results. The Li concentration profile of aged anode A, which underwent the aging with induced Li plating is shown in Figure 6.19. An obvious peak, which shows that Li has a very inhomogeneous distribution inside the anode. The Li concentration is rapidly decreasing towards the bulk.

Moreover, a new adapted method for calculating Li depth profiles for GD-OES, based on different ablation speeds of Li and graphite during measurement, was developed. The adapted GD-OES Li profile was confirmed by NDP measurements, and vice versa. Furthermore, Figure 6.20 displays cross-sectional images of aged anodes. In Figure 6.20a, the thickness of the Li-rich surface layer is likely 6–10 μ m. This observation aligns with the NDP and GD-OES depth profile of anode A, where Li content decreases rapidly after 6 μ m, reaching bulk Li concentration around 10 μ m.

Figure 6.20b shows no distinct Li surface layer for the anode with SEI layers. The SEI is most visible around Si particles. In Figure 6.19b, Li concentration depth profiles of fresh anode B and aged anodes C and D with SEI layers are presented. Anode B is from a pristine/fresh cell (100% SOH), while anodes C and D were aged at 45 °C until 90% and 76% SOH, respectively. All NDP and GD-OES depth profiles exhibit a Li peak on the anode surface, and Li content in the bulk continues to increase with aging. The Li peak on the anode surface is more pronounced in GD-OES depth profiles than in NDP, likely due to preferential sputtering, a phenomenon further described in our publication.



Figure 6.20:

Cross-section of (a) anode with Li plating on the surface and (b) SEI formation recorded with SEM/EDX elemental mapping. Li deposition is indicated by the O signal because deposited Li was oxidized by contact with air.[4]

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6.10 In situ interface film forming on the high-voltage LiCoO₂ cathode by a tiny amount of nanoporous polymer additives

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LiCoO₂ (LCO) has been foreseen for extensive commercial applications owing to its high specific capacity and stability. Therefore, there has been considerable interest in further enhancing its specific capacity by increasing the charging voltage. However, single-crystal LCO suffers from a significant capacity degradation when charged to 4.5 V due to the irreversible phase transition and unstable structure. Herein, an ultra-small amount of multi-functional PIM-1 (a polymer with intrinsic microporosity) additive is utilized to prepare a kind of binder-free electrode. PIM-1 modulate the solvation structure of LiPF₆ due to its unique structure, which helps to form a stable, robust and inorganic-rich CEI film like an umbrella on the surface of LCO at a high voltage of 4.5 V as shown in Fig. 6.21. This reduces the irreversible phase transition of LCO, thereby enhancing the cyclic stability and improving the rate performance, providing new perspectives for the electrodes fabrication and improving LCO-based high-energy-density cathodes.



To show the function of the 'umbrella', the structure evolution of single-crystalline LCO cathodes before and after the cycling process is characterized by X-ray diffraction (XRD) as the cycling stability of LiCoO₂ is closely related with maintain the crystalline structure. Fig. 6.22a and b present the XRD comparison of the LCO structure before and after 100 cycles at 4.5 V. The width and position changes of the (003) peak, located at 18.7°-19.0°, reveal the crystallinity evolution in the LCO/PVDF and LCO/PIM-1 electrodes. After 100 cycles, the peak in the case of LCO/PVDF broadens, shifts from 18.8° to 18.9°, and its intensity decreases by 90%. These changes indicate that the crystallinity of LCO has been significantly disrupted. In comparison, the peak position in the case of LCO/PIM-1 almost remains unchanged after cycling with only a 50% decrease in intensity, demonstrating that the crystallinity of LCO was protected by the CEI. [1-3] The microstructure and crystal lattice pattern of LCO before and after cycling are analyzed by high-resolution transmission electron microscopy (HRTEM) as shown in 6.22c-e. 6.22c illustrates the structure of single-crystal LCO before cycling, with an interplanar spacing of 4.65 Å. The structures of LCO in the LCO/PVDF and LCO/PIM-1 electrodes after 100 cycles are seen in 6.22d and e. The related interplanar spacing is 4.78 Å and 4.69 Å, respectively. 6.22d indicates that a significant phase transition occurs in the LCO/PVDF electrode after 100 cycles due to the repeated lithiation/ delithiation process. It leads to a considerable increase in the interplanar spacing by more than 0.01 nanometers, and a surface lattice damage can be clearly observed in the TEM pattern. In contrast, in 6.22e, the lattice stripes of LCO in the LCO/PIM-1 electrode maintain a layered and orderly structure, with almost no significant change in the interplanar spacing after 100 cycles. This finding demonstrates that with the assistance of an extra-tiny amount of PIM-1, a uniform and stable CEI layer is formed on the LCO surface, which significantly reduces surface erosion and structural changes of LCO during the cycling process. [4]



Figure 6.22:

(a) XRD patterns of LCO/PIM-1 and LCO/PVDF electrodes before and after cycling and (b) zoom-in to the region of the (003) peak; high-resolution TEM images of single-crystalline LiCoO2 (c), of the surface on the LCO/PVDF electrode (d) and LCO/PIM-1 electrode (e).

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6.11 Improving carbonate battery electrolytes with single-ion conducting polymers

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To increase battery capacity compared to traditional anodes, the cells investigated consist of a lithium metal anode. So far this makes cycling stability more difficult.[1] By adding single-ion conducting polymers like fluorinated polysulfonimide lithium methacrylate to varying more conventional electrolyte solutions, we aim to improve cycle stability and longevity of lithium-metal batteries.

We first used nickel manganese cobalt 8:1:1 (NMC811) cathodes because of their higher specific capacity of around 170 mAh/g, but they are also more chemically reactive and often decline in capacity already after 100 cycles due to their higher voltage compared with lithium iron phosphate cathodes. These show an almost constant voltage from 20% to 80% charge, with a capacity at about 150mAh/g of active LiFePO₄. The cathodes prepared contain a mixture of lithium iron phosphate (LFP), PVDF as binder and nano-carbon particles that have been shown to improve performance.[2] The cells tested are assembled in CR2032-type coin cells.

Aside from these considerations, the electrolyte is at the center of our attention. As reference we start with a standard liquid electrolyte consisting of ethylene carbonate (EC) and dimethyl carbonate (DMC, 1:1) and LiTFSI or LiPF₆. Because LiTFSI has often not been able to reach higher voltages than 4.0 V, which we also confirmed with linear sweep voltammetry, we now mostly relied on LiPF₆ as basis for the electrolytes. But because it is strongly hygroscopic, even trace amounts of water can accumulate over time, which likely showed up in some of the lower efficiencies in figure 6.23. A new batch of LiPF₆ showed clearly better results, showing the importance of preventing water from entering.





Now we want to include the fluorinated single-ion conducting polymers in the electrolyte. My attention has been centered on PMTFSILi, which consists of a polymethacrylate backbone with a lithium salt whose anion is bound to the polymer. Because the anion is bound in the polymer, only the lithium can move freely, which results in a higher transference number closer to one.

This has been theorized to reduce the formation of lithium dendrites that form due to the polarity of anion and cations moving in opposite directions in the cell.[3] The formation of lithium dendrites lowers the lifespan of cells, can damage the separator and even be a safety hazard with metallic lithium. Therefore their formation should be avoided.

Because PMTFSILi (PM) turned out the be soluble in the EC/DMC mixture we use a 0.1 molar concentration (with a monomer weight of 345.2 g/mol as reference) together with 1M LiPF₆ as starting point. Higher concentrations of 0.2 M and 0.5 M do work even without additional salts, but they become more and more viscous, which also raises the resistance to the ion movement.



Figure 6.24: Impedance spectroscopy showing resistances of different electrolyte compositions.

So far, the measurements in figure 6.23 show the reference cell rapidly losing capacity after around 200 cycles, while the addition of 0.1M increases this somewhat by 50 cycles. Higher concentrations might go further, but the resistance of the viscous 0.5M electrolyte already reduces the measured capacity. PMTFSILi might therefore be applicable only at lower concentrations. In figure 6.23, efficiencies are shown, with high nineties percentages being needed to prevent side reactions that degrade the electrolyte. A new batch of LiPF_6 showed drastically better values than before. Also, on the very left, the first few cycles show the formation of the solid electrolyte interface.

All cells are measured using electrochemical impedance spectroscopy and show a resistance lower than 100Ω , except for the increased resistance at 0.5 M as seen in figure 6.24. The cells are cycled at a 0.5 C rate. Although promising at 2 C, their stability at higher rates still needs to be investigated.

Further methods that give a more inside view are needed. We plan to use Fourier transform infrared spectroscopy as well as SAXS to get insights into the structure of the dissolved polymer.[4] Microscopic methods like scanning electron microscopy might show changes in dendrite formation on the anode surface.

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6.12 Temperature dependent crystal structure of ethylene carbonate

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For more than three decades, lithium-ion batteries (LIBs) have been widely used as power sources for portable electronics but are also of interest for electric vehicles and network applications (electricity storage from renewable energies to balance generation and usage). While there have been significant changes from the initial design of the LIBs, the main solvents making up the liquid electrolyte, responsible for the charge transfer between the electrodes, remained almost unchanged [1]. Typical components used to form the electrolytes of commercially available LIBs are a mixture of cyclic and linear carbonates together with a lithium salt and additives [1, 2]. Mixing two or more organic liquids leads to the high ionic conductivity, high dielectric constant, low viscosity and large liquid temperature range necessary for them to be used in LIBs [1, 2]. The cyclic carbonate ethylene carbonate (EC) is the only solvent able to provide the protective solid electrolyte interface (SEI) layer and, therefore, present in almost all commercial batteries, mixed with other solvents [3], making it a vital part of the modern battery. Additionally, with it being the only solvent that is solid at room temperature, it is well suited for diffraction measurements at ambient conditions.

In the past, EC has been investigated by single crystal diffraction, using x-rays and neutrons at room temperature and 15 K respectively [4, 5] finding that the organic molecules order in the monoclinic space group C2/c, with four molecules in one unit cell. Their arrangement can be seen in Fig. 6.25.



Figure 6.25:

Unit cell of ethylene carbonate at room temperature, showing the layer of molecules with alternating orientation. Carbon atoms are shown in brown, oxygen in red and hydrogen in white.

In this contribution the temperature dependent evolution of the unit cell from 3 K up to its melting point at about 310 K is presented, by means of neutron and synchrotron powder diffraction. The neutron data was collected at the high resolution powder diffractometers SPODI, FRM II (Munich, Germany) at room temperature and temperature dependent from 3 K up to 300 K at Echidna, ANSTO (Sydney, Australia), data acquisition done while heating of the sample. Additionally, synchrotron measurements from 100 K to 310 K, data again acquired while heating, were performed at the powder diffraction beamline P02.1, DESY (Hamburg, Germany). The full-profile Rietveld method was applied to refine the unit cell dimensions displayed in Fig. 6.26, fractional coordinates, displacement and profile shape parameters.

The presented cell parameters a, b and c, the monoclinic angle β and the resulting unit cell volume V show a positive thermal expansion over the temperature range from 3 K to 310 K, with no indication of phase transitions. The combined neutron and synchrotron values for the



Figure 6.26:

Powder diffraction patterns at 300 K and Rietveld refined models applying the same unit cell model for measurements at a) P02.1 (DESY), b) Echidna (ANSTO) and c) SPODI (FRM II). d) Plot containing the cell parameters (left axis), monoclinic angle and resulting unit cell volume (both axes on the right) obtained by Rietveld refinement of temperature dependent powder diffraction data collected using neutrons (filled symbols) and synchrotron radiation (empty symbols).

unit cell volume can be described using the Mie-Grüneisen equation of state with the use of Debye approximation for the internal energy of a crystal, assuming the Grüneisen parameter and bulk modulus to be temperature independent [6]. This approximation is extended by a quadratic term to account for the anharmonicity of atomic vibrations near the melting point of the sample:

$$V(T) = V_0 + \frac{\gamma}{K} \left[9Nk_{\rm B}T \left(\frac{T}{\theta_{\rm D}}\right)^3 \int_0^{\frac{\theta_{\rm D}}{T}} \frac{x^3 \mathrm{d}x}{\mathrm{e}^x - 1} \right] + const \cdot T^2$$

with V_0 the volume at 0 K, Grüneisen parameter γ , bulk modulus K, number of atoms per unit cell N and Debye temperature θ_D . The fit to the data is also shown in Fig. 6.26, obtaining the parameters $V_0 = 361.9 \text{ Å}^3$, $\gamma/K = 1.14 \times 10^{-12} \text{ Pa}^{-1}$ and $\theta_D = 90 \text{ K}$.

In summary the crystal structure of ethylene carbonate has been investigated using neutron and x-ray powder diffraction as complementary techniques, together covering the whole temperature range from 3 K up to its melting point, continuing single phase structural behavior in studied region.

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6.13 Surface coating of NCM523 cathode by the difunctional block copolymer PDMS-*b*-PAA and LiTFSI

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Lithium-ion batteries have been widely used in portable electronic devices, electric vehicles, and energy storage grids. Layered $\text{LiNi}_x \text{Co}_y \text{Mn}_z \text{O}_2$ (x+y+z=1) (NCM) is one of the major cathode materials used in state-of-the-art lithium-ion battery technology. The interface between the NCM cathode and electrolyte plays a key role in the fundamental electrochemical process. The cathode electrolyte interface (CEI) layer is formed via electrolyte's decomposition, induced by Ni⁴⁺ at high voltage during the charging/discharging process. Subsequently, Ni⁴⁺ ions are spontaneously reduced to stable Ni²⁺ and oxygen-containing compounds, such as NiO, and O₂ release. The stress generated by the different crystals in the bulk and on the surface causes the CEI layer to crack so that more Ni⁴⁺ is exposed, which will catalyze the electrolyte to form a new CEI layer and further continue to form NiO. This chain side reaction not only continuously consumes the electrolyte, but also reduces the ionic and electronic conductivity between electrolytes and electrodes, leading to capacity fading and gas production. In addition, the residual lithium-lithium hydroxide (LiOH) on the surface can react with LiPF_6 to generate water (H₂O), which can further react with LiPF₆ to produce hydrofluoric acid (HF). Once HF is generated, it can dissolve the transition metal and produce water again. However, these chain side reactions also will bring about electrode failure. To make matters worse, LiOH can defluorinate polyvinylidene fluoride (PVDF) as well, causing binder failure.



Figure 6.27: a,b) SEM images of P0; c,d) SEM images of P1.

Using an amphiphilic block copolymer -poly (dimethyl siloxane)-*block*-poly (acrylic acid) (PDMS-*b*-PAA) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to modify the cathode surface is an alternative approach,. Polysiloxanes possesses a highly flexible backbone (Si-O), enabling them to adapt to volume changes of active materials during the charging and discharging process. Furthermore, hydrophilic functional groups on the polymer facilitate the diffusion of the electrolyte and bind trace amounts of H₂O remaining in the electrolyte as well as HF generated during cycling. PAA possesses carboxyl groups (-COOH), which can interact with transition metal ions, allowing PAA to be well adsorbed on the surface of metal oxide particles, and enhancing the adhesion with the conductive agent current collector. In the meantime, -COOH can react with LiOH to reduce the occurrence of side reactions between LiOH and LiPF₆. The generated Li₂CO₃ can promote inorganic LiF and Li_xPF_yO_z with high ion conductivity, which then stabilizes the electrode. Concerning the LiTFSI, it can be easily oxidized and produce some inorganic materials, such as LiF. As a result, an elastic and robust cathode/electrolyte interface

is constructed and the cathode electrode is stabilized by modifying the cathode surface with PDMS-*b*-PAA/LiTFSI.

The morphologies of the P0 (pristine electrodes) and P1 (electrodes modified with PDMS-*b*-PAA and LiTFSI) before cycling were characterized by SEM (Fig. 6.27). For P0, before cycling, the particles on the surface of NCM523 particles were smooth, as evidenced by the large micrometer-sized particles shown in the SEM images. However, after spin coating with PDMS-*b*-PAA/LiTFSI, (Fig. 6.27d), a layer, indicated by the red circles, was observed on the surface of NCM523 particles. This result confirms that PDMS-*b*-PAA/LiTFSI had been successfully coated on the electrodes.



Figure 6.28:

a,b) CV curves of the initial three cycles for the P0 and P1 electrodes, performed at a scanning rate of 0.1 mV/s; c) Long term cycling performance of the P0 and P1 electrodes at 1.0 C between 2.8 V and 4.3 V (1 C = 170 mA g⁻¹); d) Rate performance test at different current densities.

Cyclic voltammetry (CV) was used to study the fundamental electrochemical process of the P0 and P1 electrodes (Fig.6.28a, b). Both the P0 and P1 samples exhibited typical redox patterns in the first three cycles of the CV profile. Although the oxidation peak of P1 moved to a higher potential in the first cycle, in subsequent cycles, the oxidation peak of P1 was consistent with that of P0, which indicates that the PDMS-b-PAA/LiTFSI layer does not change the fundamental delithiation/lithiation process of the NCM523 cathode during the subsequent charging and discharging process. The cyclic performance of the P0 and P1 samples are shown in Fig. 6.28c with five activation cycles at 0.2 C, followed by the continuation of the cycling test at 1.0 C for the rest of the measurement. An activation process was observed for the P1 sample, which did not appear in the P0 sample. This implies that the coating of PDMS-b-PAA/LiTFSI layer influences the electrochemical kinetics in the first few cycles at 0.2 C. After the activation process, similar capacities were displayed in both the P0 and P1 samples. In detail, the capacities of the P0 sample were comparable to the P1 sample. Along with extended cycles, the P0 sample showed a gradual capacity decay, which was accelerated after around 130 cycles, and dropped to 86.4 mAh g^{-1} after 190 cycles. Compared to the P0 sample, the P1 sample exhibited an improved cyclic stability, where its capacity dropped to 108.7 mAh g^{-1} after 200 cycles. The rate performance shown in Fig. 6.28d suggests that the spin-coating treatment did not modify the capacities at different current densities significantly, as the capacity difference was within 5 mAh g^{-1} between the two samples. Thus, the PDMS-*b*-PAA coating improved the cycle stability of the Li-ion battery and had no negative effects on the performance.

6.14 Multipoint anionic bridge: asymmetric solvation structure improves the stability of lithium ion batteries

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In electrolytes, various interactions coexist, including cation-solvent, cation-anion, anionsolvent, and solvent-solvent interactions. The solubility of lithium salts and the cation transfer number is directly influenced by the relative strength of cation-solvent interactions compared to cation-anion complexes. Notably, the solvation structures of Li+ (solvent-separated ion pairs, SSIPs; contact ion pairs, CIPs; or ion aggregates, AGGs) are determined by the relative strength of these two complexes.[1-2]

Due to the impact of solvation structure on various aspects of battery operation, such as lithium-ion transport, electrochemical stability, and formation of solid electrolyte interface (SEI) layer, the design of the solvation shell is crucial and has emerged as a prominent research area. Therefore, there were various alternative and novel electrolytes reported, including high-concentration electrolytes (HCE), polymer electrolytes (PE), weakly solvating electrolytes (WSE), among others. However, limited attention has been devoted to investigating the role of various solvation structures of AGGs in the electrolyte. Cheng reported on n-AGGs, which are significantly larger and contain tens and hundreds of ions. Furthermore, the presence of anion-dominated AGGs has been observed, where the anion is selected as the central component in the solvation structure. However, there remains a lack of investigation into the overall evolution of solvation structures when the anion possesses weak and strong coordinate points as shown in Fig. 6.29, where distinct functional groups of an anion facilitate the connection between two lithium ions, resulting in the formation of two dissimilar solvated shells, asymmetric solvation structure (ASS). Herein, we chose lithium difluoro(oxalate)borate (LiODFB) as the main salt based on the hypothesis of the multipoint anionic bridge (MAB) mentioned above to connect different solvation shells. LiODFB, a hybrid salt of lithium bis(oxalate)borate (Li-BOB) and lithium tetrafluoroborate (LiBF4), contains two functional groups, C-F and C=O, and exhibits advantageous characteristics inherited from both parent anions, such as relatively high ionic conductivity, solubility, low viscosity, and high performance. Additionally, commercially prevalent and cost-effective EC and propylene carbonate (PC) are employed as co-solvents due to their high dielectric constants, which facilitate the dissolution of LiODFB. Moreover, these solvents possess comparable structures and exhibit good thermal stability at elevated temperatures.

The coin cells were assembled to evaluate the battery's performance using electrolytes of varying concentrations under rigid high-temperature conditions. At 100 ŰC, which is the extremely high temperature, all the batteries exhibited a distinct downward trend in Fig. 6.30a The initial battery capacity gradually increased with the electrolyte concentration, which may be attributed to the enhanced conductivity of high-concentration electrolytes at elevated temperatures. Furthermore, the half-cell exhibited a discernible increase in capacity during the initial cycles, which can be attributed to the widening of graphite layers upon cycling, resulting in reduced impedance. This phenomenon is expected to be more pronounced under elevated temperatures. 37 The first discharge curve of the battery in varying electrolytes is depicted in Fig. 6.30b an initial plateau emerges at approximately 1.6 V, which is attributed to the decomposition of ODFB-. This reaction promotes the formation of a robust SEI layer, effectively preventing direct contact between the solvent and electrode surface, which inhibits the over-decomposition of the solvent. The disappearance of EC/PC decomposition platforms located at about 0.8 V at high concentrations further supports this finding. 38 Moreover, the impedance of the battery



Figure 6.29: Explanation of the different solvation structure

also exhibits a correlation with its capacity. After 100 cycles, the higher impedance observed at low concentrations can be attributed to the occurrence of a pronounced side reaction resulting from direct contact between solvent molecules and the electrode surface at high temperature. This leads to an increase in organic byproducts, consequently elevating the impedance. Conversely, the significantly lower impedance observed for 3.0 M concentration suggests that HCE facilitates the formation of a highly conductive and stable SEI layer, thereby enhancing cell performance under harsh high-temperature conditions in Fig. 6.30d. The CV curve also exhibits reduction peaks at approximately 1.6 V, along with symmetrical oxidation/reduction peaks below 0.5 V, which provide evidence for the formation of the solid electrolyte interphase (SEI) layer during the first cycle. Moreover, an increase in LiODFB concentration leads to a more pronounced decomposition peak of ODFB that shifts towards higher potentials, consistent with observations from the initial discharge cycle curve.



Figure 6.30:

Electrochemical performance of Li/MCMB (a) Long cycling performance under 1.0 C at 100 ŰC. (b) First discharge curves of Li/MCMB cells in different concentration electrolytes. (c) CV curves of Li/MCMB cells in different concentration electrolytes under 0.1 mVÅ·s-1 at 100 ŰC. (d) Impedance results of Li/MCMB cells after 100 cycles at 100 ŰC.

In summary, the high concentrated LiODFB electrolyte may significantly increase the stability of lithium metal batteries at high temperatures, which is due to the huge amount of LiODFB dissolved in the solvent, which prevents solvent molecule disintegration and promotes the formation of a denser, more inorganic SEI film.

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6.15 Inorganic fillers in PEO-based solid polymer electrolytes for all-solid-state lithium batteries

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All-solid-state lithium-ion batteries (ASSLIBs) have received extensive attention as one of the most promising candidates for next-generation energy storage systems [1]. However, the practical application of ASSLIBs has been hindered by the inferior ionic conductivity and poor interfacial stability. Solid electrolytes play a crucial role in determining the overall electrochemical properties, specifically for PEO-based composite electrolytes, because of their superior interfacial compatibility, high ionic conductivity, and outstanding solubility against lithium salts [2]. In particular, incorporating inorganic fillers into the polymer matrix to obtain organic-inorganic composite polymer electrolytes (CPEs) is one of the most effective strategies to enhance polymer electrolytes. This approach has been extensively explored for developing perfect solid-state batteries. Moreover, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were used to observe the crystal structure changes of the CPEs.



Figure 6.31:

a) Linear sweep voltammetry curves of Li/PSPEs/Stainless steel cell. b) The Nyquist plot of SS/CPEs/SS cell. c) The voltage-time profile on galvanostatic cycling with different CPEs at different current densities.

In the present work, the layered double hydroxide (LDH) was used as functional filler to produce high-performance CPEs for ASSLIBs. The electrochemical stability window is a crucial parameter to evaluate the electrochemical performance of CPEs. Linear sweep voltammetry

test was conducted to determine the electrochemical stability voltage of the prepared CPEs (Fig. 6.31a). It demonstrated that LDH-incorporated CPEs were more resistant to high pressure and oxidation than those without LDH. Electrochemical impedance spectroscopy was carried out to determine the ionic conductivity. According to the Nyquist plot (Fig. 6.31b), the LDH-incorporated CPEs have a higher ionic conductivity than those without LDH, which reach 1.32 × 10^{-4} S cm⁻¹. The Li symmetric cells were assembled and tested to testify the reliability and endurance of CPEs in ASSLIBs. Fig. 6.31c shows the polarized voltage versus measured time of Li symmetric cell with different CPEs at different current densities. The LDH-incorporating CPEs have a higher critical current density than those without LDH, which can effectively suppress the growth of lithium dendrite.



Figure 6.32:

a) Operando setup for GIWAXS measurements at the DESY beamline P03. b) Operando GIWAXS data during voltage evolution on PEO composite electrolyte of Li/Cu cell.

To determine the stability of the electrolyte structure under working conditions, the operando GIWAXS measurements were performed. The operando setup (Fig. 6.32a) used at the P03 beamline consists of a thermostatic system integrated with a gas-flow setup and electrochemical workstation. According to the 2D GIWAXS data (Fig. 6.32b), we found that there is a strong face on orientation at $q_z = 0.75 \text{ Å}^{-1}$, which was attributed to the crystalline peak of LDH. During the discharge process, the crystallinity and intensity of the peak did not exhibit significant changes, indicating that LDH as filler has a relatively stable structure in ASSLIBs.

In summary, LDH, as a functional filler, can fully interact with the polymer matrix due to its large specific surface area, effectively increasing the ionic conduction path and ionic conductivity, and its relatively stable structure is more conducive to developing ASSLIBs.

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7 Real-time characterizations



7.1 Printing protein templated inorganic-organic hybrid nanostructures

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Globally most electricity is still produced by burning fossil fuels like gas, coal or oil.[1] Typical efficiencies for state of the art fossil fuel heat engines in power generation are between 30 % and 50 %. Therefore, more than 60 % of the global energy for electricity generation is lost to waste heat.[2] Thus, there is a tremendous potential for energy recovery.

The Seebeck effect enables the conversion of low-grade waste heat into electrical power. Our research is focused on replacing state-of-the-art, scarce, and hazardous thermoelectric materials such as lead and tellurium with abundant and environmentally friendly alternatives. Modi-fying the nanostructure of thermoelectric materials has the potential to significantly enhance the thermoelectric figure of merit (ZT).[3,4] Nanostructured titania is achieved through protein templating. We employ a meniscus-guided slot-die coater to print the organic-inorganic layer, allowing for cost-effective and large-scale solution-based production. Betalactoglobulin serves as the chosen template due to its structural responsiveness to pH values, facilitating the creation of different morphologies. It is also a well understood foaming agent in the food industry, enabling a porous structure.



Figure 7.1:

2D in situ GISAXS data of the structure formation of printed betalactoglobulin titania thin films (pH=2) on glass substrates. 0 seconds represents pure glass before printing.

To understand the structure formation during printing, the time evolution of the average domain sizes and the average domain distances can be analyzed. This can be done with high statistical relevance by performing in situ GISAXS and in situ GIWAXS measurements.[5] Grazingincidence X-ray scattering is a powerful non-destructive technique that enables morphological investigation at the nanoscale. These experiments were performed at the P03 beamline at the DESY synchrotron in Hamburg. From the 2D detector images (figure 7.1), horizontal line cuts near the Yoneda region are made and then fitted in GISAXSfit. The fitting results can be seen in 7.2. Several differences can be seen in the structure formation. Acidic templates lead to a stronger reduction of large and medium sized structures. The medium sized structures are almost unchanged for neutral thin films. At higher template concentrations the same general trend can be observed, however it is less pronounced and has a slower onset. This might be caused by higher steric hindrance and therefore a less pronounced templating effect. Overall protein assisted sol gel synthesis represents a novel route to achieve nanostructured titania thin films and can be used to tailor the domain size and porosity. In addition, static GISAXS and GIWAXS measurements were made to understand the titania morphology after calcination. SEM was measured to investigate the surface morphology and UV-Vis and PL was analyzed to understand differences in the optical properties.



Figure 7.2: Modelling results for in situ printing structure formation with different solution parameters a) 10 $\frac{mg}{ml}$ protein,pH 7 b) 10 $\frac{mg}{ml}$ protein,pH 2 c) 20 $\frac{mg}{ml}$ protein,pH 7 d) 20 $\frac{mg}{ml}$ protein,pH 2

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7.2 Operando GIWAXS observation of the degradation process in air of greensolvent based PBDB-TF-T1: BTP-4F-12 organic solar cells with solid additive

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Solid additives have received high attention in organic solar cells due to their various advantages, such as morphology-directing abilities, post treatment, enhanced device performance and stability [1]. An effective solid additive EH-P was explored here in green-solvent based organic solar cells (PBDB-TF-T1: BTP-4F-12). Fig. 7.3 a) showed the molecular structures of the materials mentioned and the energy level diagram as well as the UV-vis spectra were shown in Fig. 7.3 b) and c), respectively. The device performance of EH-P as additive are summarized in Fig. 7.3 d), where the V_{OC} remains basically the same with increasing concentration while the J_{SC} and FF increase gradually, resulting in obvious increased device performance via doping EH-P with a concentration range of 0.5 % to 3.0 %.



Figure 7.3:

a) Molecular structures and device structure, b) energy levels and c) UV-vis spectra of the materials mentioned, d) device performance

These three cells were aged in air under illumination, the J-V curves as well as the in situ GIWAXS data were recorded accompanying. Fig. 7.4 a) to c) showed the J-V curves evolution, where the V_{OC} got significantly stable with the addition of EH-P even if the concentration is only 0.5 % in weight. The J_{SC} and FF were further stabilized with more EH-P doping (0.5 %). The signal of q at around 1.7 in out-of-plane is $\pi - \pi$ stacking (010) of the conjugated materials, which plays a key role in device performance, thus the line-cut in out-of-plane was made and summarized from Fig. 7.4 d) to f). The coherent length (L_C) and stacking distance was calculated with the peak position (q value) and FWHM, where the evolution trends were listed in Fig. 7.4 g) to h). The peak of $\pi - \pi$ stacking (010) changed a lot during aging, in stacking distance, intensity and L_C. For the ref. cell, the degradation could be divided into two stages: first rapid process with a short recovery for L_C following and the second stable stage. Interestingly, EH-P would decrease the crystallinity of fresh T1:Y12 films, which would be recovered under illumination so it wouldn't matter lot for the device performance. EH-P was found to be able to suppress the rapid L_C evolution at the first stage and further stable the films crystallinity.

Fig. 7.4 analyzes the difference of crystallinity during aging. Charge mobility and UV-Vis spectra were then carried out to see if the films aging is related somehow to light induced oxidation. Charge mobility was got from SCLC measurements and the values were listed in Fig. 7.5 a) to d), where the doped devices shown similar trend after aging compared with the reference





Evolution of J-V curves during aging process of a) reference cells, b) 0.5 % doped cells, c) 1.0 % doped cells. Evolution of line cut at out-of-plane direction of GIWAXS patterns during aging process of d) reference cells, e) 0.5 % doped cells, f) 1.0 % doped cells. The evolution of g) coherent length and stacking distance of $\pi - \pi$ stacking ((010) at out-of-plane).

one. UV-Vis spectra were listed in Fig. 7.5 e) and f) and almost no difference was found here. These results suggest that the enhanced stability with EH-P doping is mainly caused by the crystallinity rather than any chemical factor.

In summary, already a tiny amount of EH-P could serve as additive in green solvent (THF) based organic solar cells, offering improved efficiency, and the degradation in air under light was suppressed as well with stabilized film crystallinity





a) to d) J-V curves of SCLC measurement for the calculation of election or hole mobility of the reference cells and 1.0 % doped cells. Evolution of UV-vis spectra for e) reference film and f 1.0 % doped film.

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7.3 In situ studies revealing the effect of Au surfactant on the formation of ultrathin Ag layers

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Silver (Ag) is a very promising electrode candidate for various electronic devices due to its high conductivity, high optical transparency in the visible region among metals, and relatively low costs. In recent years, various studies reported their efforts to prepare ultra-thin silver layers (UTSLs) assisted with metallic surfactants or seed layers, such as gold (Au), aluminum (Al), copper (Cu), germanium (Ge), and so on.[1-2] However, only few studies focused on the underlying mechanisms of how metallic surfactants affect the growth of UTSLs. Therefore, we apply *in situ* grazing incidence small/wide-angle X-ray scattering (GISAXS/GIWAXS), to probe the effects of Au surfactants on the formation of UTSLs in real time.

We prepare bare zinc oxide (ZnO) support by spin-coating ZnO sol on silicon wafer and Au-decorated ZnO support by evaporating Au nanoparticles (as surfactant) on the bare ZnO support as the substrates for the further Ag sputtering deposition. Their morphologies are shown as Figure 7.6(a-i) and Figure 7.6(b-i). Then, the UTSLs are deposited on ZnO supports without and with Au surfactant via magnetron sputtering up to the effective Ag thickness (δ_{Ag}) of 9.4 nm.At first glance, the growth processes of the UTSLs are revealed by scanning electron microscopy (SEM) at different effective Ag thicknesses, as presented in Figure 7.6(a) and Figure 7.6(b). At δ_{Ag} = 3.1 nm, the deposited Ag layer remains in discrete clusters on the bare ZnO support (Figure 7.6(a-iii)), whereas a mainly continuous Ag layer has already formed on the ZnO support with Au surfactant (Figure 7.6(b-iii)). When increasing the effective Ag thickness to 9.4 nm, the deposited Ag layer still does not form a completely continuous morphology, as shown in Figure 7.6(a-v).



Figure 7.6:

SEM images of sputter-deposited UTSLs on (a) the bare ZnO support and (b) the ZnO support with Au surfactant at different thicknesses of the UTSL δ_{Ag} = 0, 1.6, 3.1, 6.4, and 9.4 nm, respectively.

We firstly investigate the crystalline structure evolution of sputter-deposited Ag layers on both ZnO supports, without and with Au surfactant based on the *in situ* GIWAXS data. As shown in Figure 7.7(a) and (b), we separately plot several azimuthal integration lines of 2D GIWAXS data for the Ag sputter processes on both supports at selected Ag effective thicknesses. By comparing the peak positions of Ag(111) and Ag(200), it is suggested that the pre-posited Au

surfactant has no obvious effect on the crystal phase of later deposited UTSLs. However, the existence of the Au nanoparticles can enhance the contrast in the GIWAXS signal and also increase the crystallinity of the later formed Ag clusters.



Figure 7.7:

Selected azimuthal integrations of the GIWAXS data for the Ag sputter processes on (a) the bare ZnO support and (b) the ZnO support with Au surfactant at different δ_{Ag} . Evolution of morphological parameters as a function of δ_{Ag} extracted from GISAXS data: Ag cluster diameter to distance ratio 2R/D, Ag layer surface coverage ϑ , and Ag layer porosity Φ , for Ag sputtering on (c) the bare ZnO support and (d) the ZnO support with Au surfactant.

Then, we focus on decoding the morphology evolution during the formation processes of sputter-deposited UTSLs on both, the bare ZnO support and the ZnO support with Au surfactant based on the analysis of the *in situ* GISAXS data. Figure 7.7(c) and (d) presented the evolution of morphological parameters as a function of δ_{Ag} extracted from the analysis of the obtained *in situ* GISAXS data on the bare ZnO support and the ZnO support with Au surfactant, respectively. Among them, here we only focus on the Ag cluster diameter to distance ratio 2R/D. The point when 2R/D = 1 is regarded as an important indicator when most of the deposited Au clusters interconnect with each other and form compact regions at local areas, which is the so-called percolation threshold. We observe that the percolation threshold of the UTSL formed by Ag sputter deposition on the ZnO support with Au surfactant is reached at a lower thickness of $\delta_{Ag} = 2.9$ nm compared to the case without Au surfactant ($\delta_{Ag} = 3.3$ nm).

On the basis of the comprehensive analysis of *in situ* GIWAXS/GISAXS data, we propose an assumption mechanism to elucidate the effect of the Au surfactant on the formation of the UTSL on the ZnO support that suggests that the pre-deposited Au nanoparticles act as nuclei or growth cores for the faster formation of fixed Ag clusters.

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7.4 Operando study of poly(ethylene oxide) composite electrolyte in all-solid-state lithium batteries

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Lithium batteries (LBs) with wide applications have emerged as the most promising candidate for electrochemical energy storage. Replacing the flammable and toxic liquid electrolyte with a lightweight and highly conductive solid electrolyte with a broad electrochemical window allows all-solid-state LBs to commercialize and also improve the safety of LBs.[1] Polyethylene oxide (PEO)-based composite electrolytes (PCEs) present high safety, easy fabrication and good electrochemical stability. However, the material suffers from low conductivity and high crystallinity, which inhibits its commercialization. Therefore, it is crucial to understand the electrochemical process and Li+ transfer pathway within PEO-based batteries.

choose In the present work, we PEO as the polymer matrix, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as the lithium salt, and a certain amount of Al_2O_3 nanoparticle was added to modify the mechanical strength of the electrolyte. Apart from this basic composition, Succinonitrile (SN) was added to the solution as plasticizer to increase the conductivity.[2] After the fabrication of composite electrolyte, types of coin cells were assembled to measure the electrochemical performance. In addition, we pursue using the Grazing-Incident Wide angle X-ray scattering measurement(GIWAXS) to observe the crystallization change of the electrolyte.



Figure 7.8: Battery performance of PEO composite electrolyte: a) Ionic conductivity, b) Li||Li cell cycling profile.

To evaluate the ion transition character of the electrolyte, the impedance spectroscopy was applied to Li blocking cell, as shown in Fig. 7.8a. The electrolyte with SN additive exhibits a good Ionic conductivity of 2.18×10^{-4} S cm⁻¹, which is higher than that of PEO composite electrolyte without SN (1.34×10^{-4} S cm⁻¹). Li symmetrical cells with two electrolyte are assembled to estimate the stability of the electrolyte displays an excellent long-term stability over 550 h at 0.1 mA cm⁻², coupling with a steady overpotential of 79 mV, which is ascribed to the good ionic conductivity. In contrast, the cell without SN additive only cycled in 450 h with a large overpotential of 96 mV. Therefore, we can conclude that the electrolyte with SN exhibit a higher conductivity and a better compatibility with Li metal.

For the operando X-ray scattering measurements on PEO composite electrolyte, a homemade

operando chamber with temperature and gas control was assembled at beamline P03 DESY, as shown in the Fig. 7.9, in which Li||Cu cell was used. The copper foil was used as substrate and the electrolyte was covered on it to realize a flat surface. In order to detect the electrolyte change, a half lithium chip was used. The cell was connected to a potentiostat to apply a reversible voltage from 2.5 to 0 V with a scan rate of 1 mV/s to record the cyclic voltammetry.



Figure 7.9: Image of the homemade operando measurement setup.

The information about the crystal structure of the electrolyte is determined with GIWAXS measurements, as seen in the reshaped 2D GIWAXS data in Fig. 7.10. A broadened halo region can be observed in Fig. 7.10 b), meaning that adding SN can help to decrease the crystallinity of EO segment to promote the Li+ diffusion. Besides, the sample with SN present a more stable amorphous status during the whole sweep compare to the reference sample.



Figure 7.10:

2D GIWAXS data measured during voltage oscillation on PEO composite electrolyte: a) without SN additive and b) with SN additive.

In summary, PEO-SN composite electrolyte presents a good ionic conductivity and a compatibility to Li metal in comparison to PEO electrolyte. GIWAXS successfully detected the crystal structure evolution of the two electrolytes.

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7.5 Operando neutron diffraction to study the ageing of multilayer pouch cells

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One of the main focus points in battery research is to improve the electrode materials and, thus, increase the capacity of the cells. For example, higher capacities in electric vehicles (EVs) enable longer driving ranges. While small cell formats such as coin or single-layer pouch cells are often employed in the lab, large battery formats are used for various commercial applications as they can store significantly more energy. The most commonly used battery formats for EVs are cylindrical, prismatic and pouch cells, as they offer high specific and gravimetric energy. [1] Here, 5 Ah multilayer pouch cells with NCA electrodes are studied with operando neutron diffraction to retrieve the structural information during cycling. An uncycled cell was studied with an aged cell with a remaining capacity of 65% that has been cycled for around 320 cycles. LiNi_{0.8}Co_{0.15}Al_{0.5}O₂ (NCA) was used as cathode and silicon as anode material for these cells.

The neutron diffraction experiment was performed with the Wombat instrument at the Australian Nuclear Science and Technology Organisation in Lucas Heights, Australia. For the operando measurement, a cell holder of aluminum plates was fabricated to maintain a contact pressure of 2 bar. This is necessary to ensure electric contact during the measurement. Primarily since silicon is known for its substantial volume expansion upon lithiation.

Figure 7.11 shows the diffraction patterns during one cycle with a charge rate of C/10 and one cycle with C/4, as well as the corresponding potential curve for the uncycled cell. In the diffraction patterns, multiple reflections stay constant, which can be assigned to Al and Cu. The Al reflections originate from the cell holder, while the Cu stems from the current collector of the anode. Since these phases are not electrochemically active during the cycling process, we do not expect any changes. The remaining peaks are moving during the cycling and belong to NCA. Furthermore, no silicon could be detected in the diffraction patterns. Silicon is known to become amorphous once it is lithiated. Since all the studied cells were already charged during the formation procedure, the amount of the remaining crystalline silicon is too little to detect them.



Figure 7.11:

Neutron diffraction pattern of the uncycled cell as well as the corresponding potential evolution during the measurement. Al and Cu peaks are indexed. The remaining peaks belong to the NCA. Crystalline Si was not visible.
NCA is fully lithiated in the discharged state. Li will be extracted upon charging, leading to a change in the crystal structure. This can be followed by the movement of the peaks of NCA. Generally, NCA has a layered structure with the space group $R\overline{3}m$ crystal structure with the Li and transition metals sitting in the octahedral sites of the oxygen structure (Fig. 7.12 (a)). [2] The evolution of the peak position is illustrated in Figure 7.12 (b) and (c) for the uncycled and aged cell. Tracking the movement of the 003 peak gives further information about the *c*-axis. While the position of the 113 peak can describe the elongation of the *a*-axis.





NCA structure with $R\overline{3}m$ space group (a). Evolution of the 113 and 003 peaks for both the C/10 and C/4 cycle for the uncycled cell (b) and the aged cell (c).

The 113 peaks of the uncycled cell move within a higher 2θ window than the aged cell. Similarly, the 003 peak position of the uncycled cell starts at $2\theta = 22.55^{\circ}$, whereas the aged one starts around 24° . This means that the aged cell cannot achieve its initial state before cycling. This indicates that the Li inventory decreases during ageing, and therefore, the expansion of the NCA structure is limited. It is also visible that the hysteresis of the aged cell is higher than for the uncycled cell. The hysteresis can be explained by higher overpotentials inside the aged cells, leading to more sluggish kinetic processes. [3] This effect is aggravated when the C-rate is increased to C/4 as the higher rates lead to a stronger polarization.

Generally, it is possible to study multilayer pouch cells with neutron diffraction due to the high penetration depth of neutrons. The effect of cyclic ageing can be traced by studying the peak positions of the NCA. Rietveld refinement, as well as post-mortem measurements, are being conducted to gain more insight into the details of the mechanism.

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- [3] A. Van der Ven, K. A. See, L. Pilon, Battery Energy 1, 1-16 (2022)

7.6 Revealing the formation kinetics in slot-die coated active layers for organic solar cells

J. Zhang, P. Müller-Buschbaum

Organic solar cells have received tremendous attention due to superior flexibility and being lightweight.[1] However, most research focuses on spin coating, which can achieve excellent photovoltaic conversion efficiency but is primarily confined to laboratory-scale applications. Therefore, the slot-die coating technique, as an advanced large-scale fabrication technology, has significant potential. Nowadays, the power conversion efficiency achieved through slot-die coating still falls behind that achieved through spin coating, mainly due to poor morphology. Hence, it is urgent to understand the formation kinetics of slot-die coated active layers to optimize the phase separation and crystallinity. In situ grazing-incidence wide-angle X-ray scattering (GIWAXS) and in situ UV-vis absorption spectra are highly effective methods for monitoring the drying process to analyze the kinetics. Here, we choose PBDB-T-2F as the donor, BTP-C3-4F as the acceptor, and chloroform as the solvent for a precursor that has achieved a remarkably high power conversion efficiency. In situ GIWAXS and in situ UV-vis absorption are assembled with slot die coating (Fig. 7.13). We use Kapton foils to seal the frame to avoid the leakage of chloroform. Regarding in situ GIWAXS, an exposure time of 0.1 seconds is applied to capture a more detailed drying process. The incident angle and sample-to-detector distance are 0.12° and 204.8 mm respectively. As for in situ UV-vis absorption, we also employ an integration time of 0.1 seconds to ensure consistency with in situ GIWAXS. However, the initial 3.7 seconds of the signal cannot be gathered because of the fixed detector on the printing head. Besides, the transmittance results need to be converted to absorption data using the formula A = -lg(T). With respect to in situ GIWAXS results, we perform radial cake cuts in the out-of-plane direc-



Figure 7.13: The sketch of slot- die coating installed with in situ GIWAXS and in situ UV-vis absorption.

tion (Fig. 7.14a) and then use Gaussian peaks to fit (010) Bragg peak to extract the II-II stacking distance, crystal size and intensity of PBDB-T-2F (Fig. 7.14b) and BTP-C3-4F (Fig. 7.14c) respectively. The crystallization of both PBDB-T-2F and BTP-C3-4F is regarded as an isothermal process. Hence, the intensity, referred to as crystallinity, can be analyzed using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model [2]. Five evident stages are distinguished during the drying process for the blend film [3]. Stage I is attributed to the solvated state with solvent evap-

oration. During Stage II, nucleation takes place while the molecular packing is self-optimized. In Stage III, crystallites experience rapid growth, leading to a significant increase in both crystal size and intensity. Stage IV is dominated by secondary crystallization, characterized by a gradual increase in intensity. Stage V is the final drying state. As for in situ UV-vis absorption spectra (Fig. 7.14d), we use the simplified Franck-Condon deconvolution approach to extract the (0-0) transition energy, intensity, full width at half maximum (FWHM) of PBDB-T-2F (Fig. 7.14e) and BTP-C3-4F (Fig. 7.14f). Referring to the in situ GIWAXS results, the aggregation process can also be divided into 5 stages. During drying process, PBDB-T-2F has become a fully aggregated state in Stage III and Stage IV. However, BTP-C3-4F goes through the transformation from a solvated stage to an aggregated state in Stage III, but also a fully aggregated state in Stage IV. These indicate that crystallization still occurs in aggregated molecules.



Figure 7.14:

a) Radial cake cuts of in situ GIWAXS data in the out-of-plane direction. Corresponding fit results of b) PBDB-T-2F and c) BTP-C3-4F. d) Temporal evolution of UV-vis absorption spectra. Fitting results of e) PBDB-T-2F and f) BTP-C3-4F using the simplified Franck-Condon deconvolution approach.

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8 Development of instrumentation and software



8.1 Strategy to simulate and fit 2D GISAXS patterns of nanostructured thin films

F. A. Jung, C. M. Papadakis

Grazing-incidence small-angle X-ray scattering (GISAXS) is a widely used tool for the structural characterization of the surface and the inner structures of nanostructured thin films, also in real time, in situ and in operando. However, the potential of GISAXS is not always fully exploited, because it may be difficult to extract quantitative information from the 2D patterns. Fitting of realistic structural models is often hampered, because the reflection of the X-ray beam at the film-substrate interface and its refraction at the film surface must be taken into account. This introduces several complications: Analysis of the two-dimensional (2D) patterns is computationally heavy, background scattering cannot be subtracted, and absolute intensity calibration is not possible. Furthermore, the scattering due to surface roughness of the film or the substrate may overlap with scattering from the nanostructure. Numerous methods to perform the analysis of GISAXS data with justifiable effort have emerged, such as the analysis of the position and width of Bragg reflections, if the structures are sufficiently ordered. Moreover, simulations of 2D GISAXS patterns of the assumed real-space structure are routinely carried out using available software packages. However, when the number of structural parameters is large, simulating full 2D GISAXS patterns is time-consuming and not yet possible in quasi real time, e.g. during real-time, in situ measurements during beamtimes at large-scale facilities.

In view of these challenges, we have developed a strategy to stepwise simulate and fit 2D GISAXS patterns [1]. Each step targets a specific contribution to the scattering pattern, and only the corresponding parameters are adjusted. To reduce the computation time, not the entire measured 2D GISAXS pattern is considered, but the adjustment or fitting of parameters is performed by choosing suitable linecuts. We demonstrate this strategy at the example of 2D GISAXS pattern from a nanostructured block copolymer thin film on a Si substrate, similar to the ones described in detail in [2]. At the surface, it features relatively ordered cylindrical protrusions, as evident from the real-space surface topography measured by atomic force microscopy (AFM, Figure 8.1a). Inside, it is assumed that the block copolymer microphase into randomly distributed short, vertically oriented cylinders in a matrix (Figure 8.1b). The measured 2D GISAXS pattern is shown in Figure 8.2a.



Figure 8.1:

(a) AFM surface topgraphy from a nanostructured block copolymer film. (b) Schematics of the structural model used to describe the 2D GISAXS pattern. From Ref. [1].

By stepwise simulations of the 2D GISAXS pattern of the bare Si substrate, the homogeneous thin film on top of this substrate, the protrusions at the film surface and the nanostructure inside the film, it emerged that the contributions appear in different regions of the 2D pattern: The substrate gives rise to a narrow vertical streak in the center, captured by linecut IV (see the dashed lines in Figure 8.2a). The homogeneous film leads to a broadening of this streak because of its surface roughness (captured by linecut III). Protrusions at the film surface give a strong out-of-plane scattering signal because their scattering contrast with vacuum is significantly higher than the one between the nanodomains in the film and its matrix (captured by linecuts I, III and V). Finally, the inner film structure gives a diffuse signal in the central part (captured by linecuts I and II). Hence, structural features can be separately addressed by fitting the corresponding line

cuts by adjusting the corresponding parameters individually. This protocol leads to a significant reduction of fit parameters in the particular fitting step; and in the subsequent steps, the already determined parameters can be kept fixed. This way, the linecuts I-V could be fitted nearly quantitatively (Figure 8.2b-f). Among others, the radius and the distance of the cylinders inside the film as well as the size and distance of the protrusions at the film surface could be determined, in accordance with the results from AFM (Figure 8.1a).



Figure 8.2:

(a) Measured 2D GISAXS pattern (shown on the side $q_y > 0$) and simulated one (shown on the side $q_y < 0$). The black stripes are detector gaps. White dashed lines indicate the linecuts shown in (b-f). Black symbols: experimental data, red lines: fitted intensities. Green areas indicate the range included in the fit. $\alpha_{c,film}$ and $\alpha_{c,sub}$ denote the critical angles of the film and the substrate, indicative of their electron densities. From Ref. [1].

This example demonstrated that the strategy outlined in this work captures all relevant features of the 2D GISAXS patterns. At this, it turned out to be beneficial to measure the scattering from a blank Si substrate separately. Moreover, the AFM image of the film surface allowed to identify the contributions of the protrusions at the film surface in the 2D GISAXS patterns and enabled a quantitative fit of the inner structure parameters. We note that these quantitative GISAXS simulations allow obtaining the detailed information from weakly scattering and weakly ordered polymer thin films that feature structures on multiple length scales. Our approach is not restricted to a certain available simulation software, but is rather a guideline, that can be followed using all available simulation software packages. However, some challenges remain which hinder a broader application. For instance, choosing a suitable real-space model based on a 2D GISAXS pattern requires a certain understanding of reciprocal space maps and the typical distortion effects by the thin film geometry. The upcoming possibilities of machine learning aided pattern recognition by means of convolutional neural networks will likely simplify this choice.

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8.2 Time-resolved GISAXS data as training sets for machine learning

J. E. Heger, P. Müller-Buschbaum

Grazing-incidence small-angle X-ray scattering (GISAXS) is an indispensable tool in material science to reveal the structure on the nanoscale in thin films and coatings. Emerging technologies and an increasing focus in research on functional films based on, e.g., semiconductors yield to an increased use of these scattering methods. At synchrotron sources, a high temporal and spatial resolution allows for advanced experiments, revealing fast kinetics during film formation, deformation or degradation. From the in-situ and operando experiments crucial and unique information on the investigated system is obtained, which yields necessary knowledge for a fundamental understanding and for optimization of working devices in applications. Meanwhile, a single experiment creates on comparably short timescales such as minutes large quantities of data in the order of several gigabytes, which need to be handled and processed. Furthermore, the data treatment and analysis is non-trivial in nature, as it is a matter of transferring the probed reciprocal space into the real space. While GISAXS probe the Fourier transform of the spatial arrangement of a change in refractive index, a direct access to the inverse via Fourier transformation is not possible, as the complex phase information on the system is lost upon measurement. This inverse problem leads to an ambiguous set of possible film morphologies, which could give raise to the measured data. For the successful analysis and interpretation of the data, it usually needs experts with special focus and knowledge on this particular matter. However, as GISAXS are of broad use and interest in research, not every experimenter at the synchrotron has the time and the capacity to analyze the obtained data in a self-dependent manner. To overcome this barrier and create a user-friendly interface between the instrument at the synchrotron and the experimenter to deal with the large quantity of complex data, deep learning of invertible neural networks (INN) offer promising solutions. [1,2]



Figure 8.3: Illustration of the fundamental algorithm: 1. training, 2. sample retrieval, 3. prediction

A trained INN has the potential to infer the full information from the reciprocal space and solve the inverse problem. For this, the INN needs to be trained on large sets of characteristic GISAXS data under the guidance of experts from the field. In this process of supervised machine learning, an important step is the correct and efficient labeling and annotation of data, so that the the INN can make reliable prediction on a given set of unknown data. Fig. 8.3 illustrates the algorithm in a simplified schematic. Synthetic data which is generated by simulation with software such as BornAgain [3] is an important resource for training sets, however, experimental data includes characteristic features from real experiments which are essential to be covered in the training process. Here, the creation of a data base with data sets being already analyzed by experts is important, to achieve a well-founded source for training. The known reciprocal 2D data will be put into the INN for training so that it will be able to correctly classify unknown data obtained from an experiment and provide numerical output on, e.g., the length scales of the probed structure.



Figure 8.4:

Vertical and lateral film formation with exemplary labels of typical GISAXS features, comprising the time-resolved information in a single image.

For example, the structure investigation with GISAXS of porous metal oxides for the application in energy materials is intensively performed. A possible approach to test the reliability of the INN is to feed the network with an analyzed and published data set A and let it interpret an unknown data set B, which was acquired under very same instrumental and experimental conditions with a single parameter changed. For example, the kinetics of film formation during spray deposition of porous titania films, which are understood, is used as data set A. [4] The sole difference to the unknown data set B is the variation of a single parameter in solution synthesis. A strategy to reduce computing time and enable faster evaluation of formation kinetics is to reduce the 2D data of a single detector images into two distinct 1D intensity profiles via line integration, giving information about the vertical film profile and its material density, as well as on the formation of laterally arranged structures. For time resolved experiments this strategy could yield the interpretation of a single image for vertical and lateral film formation, respectively, by stacking the respective line cuts as a function of time to a 2D contour plot (Fig. 8.4). The changes in intensity as function of time can then be directly classified and numerical information on the film formation in real space inferred from the reciprocal data.

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8.3 Using INSIGHT for in situ GIXS data analysis of slot-die coated quantum dots

M. A. Reus, D. P. Kosbahn, L. K. Reb, T. Baier, C. Lindenmeir, A. Buyan-Arivjikh, M. Schwartzkopf¹, S. V. Roth^{1,2}, P. Müller-Buschbaum

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- ² KTH, Stockholm, Sweden

Perovskite quantum dots have emerged as promising materials for applications in optoelectronic devices, owing to their exceptional electronic and optical properties. The controlled deposition of perovskite quantum dots onto substrates is crucial for achieving uniform and highperformance films. Among various deposition techniques, slot-die coating has gained prominence due to its scalability and versatility. In this context, we present a novel approach to slotdie coating perovskite quantum dots, coupled with an advanced batch processing software, INSIGHT, designed for analysis of time-resolved grazing-incidence wide- and small-angle scattering (GIXS) data.

The simplicity and scalability of slot-die coating make it an attractive choice for large-scale production of perovskite quantum dot films. However, achieving uniformity and reproducibility in the film properties remains a challenge, especially when coupled with advanced scattering techniques as GIXS.[1] Therefore, a newly conceptualized slot-die coater was commissioned, building on previous works in this group.[2] The custom-built slot-die coater enables accurate and controlled deposition during GIXS experiments. The printer is compatible with a multitude of different material classes that are usable with the liquid ink slot-die coating approach. The concept of the printer is introduced in Fig. 8.5a, showing the open design, unhindered scattering openings towards the GISAXS and GIWAXS detectors, the temperature controlled stage and static sample to fix alignment during the grazing-incidence scattering experiments. A detailed CAD drawing is shown in Fig. 8.5b. To address the need for analyzing time-resolved GIXS data recorded during slot-die coating, we have developed INSIGHT, a new Python-based batch processing software.[3] Using INSIGHT to analyze time-resolved GIXS data facilitates the monitoring of structural evolution, crystallographic orientations, and grain sizes during the slot-die coating of, e.g., perovskite quantum dots as shown in Fig. 8.6.[4] This comprehensive approach allows researchers to gain valuable insights into the dynamics of film formation, aiding in the optimization of deposition parameters and enhancing the reproducibility of printed films for diverse optoelectronic applications. Exemplary this is shown by the kinetic analysis of the solvent removal (Fig. 8.6a) and Bragg spot indexing (Fig. 8.6b). A vertical cut in the 2D GISAXS data (Fig. 8.6c, red outline) provides in-depth insights into the superlattice formation. Line cuts plotted versus time (Fig. 8.6d) hint towards a superlattice contraction and a thinning of the solvent layer during the gradual solvent removal from the liquid film.[5]

The lightweight and modular design of the printer, and the comprehensive data analysis provided by INSIGHT offer valuable insights into the deposition dynamics of slot-die coated thin films, paving the way for enhanced optoelectronic devices.

- M. A. Reus, L. K. Reb, A. F. Weinzierl, C. L. Weindl, R. Guo, T. Xiao, M. Schwartzkopf, A. Chumakov, S. V. Roth, P. Müller-Buschbaum, *Adv. Optical Mater.* 10, 2102722 (2022)
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Figure 8.5:

a) Conceptual design of the newly developed slot-die coater for in situ grazing-incidence wide- and small-angle scattering experiments. b) Detailed CAD drawing of the slot-die coater, showing the two motors that move the slot die, the sample stage with heating, the alignment goniometer, and the housing that allows for quick disassembly for transport.



Figure 8.6:

a) Radial cake cuts from in situ 2D GIWAXS data of printing perovskite quantum dots versus time after deposition. The solvent evaporation is clearly visible, forcing the quantum dots into a superlattice. b) The strong ordering of the quantum dots is visible by Bragg spots in the 2D GIWAXS image. Indexing was done with INSIGHT, revealing a superposition of (001) and (122) orientation with respect to the substrate. c) Exemplary 2D GISAXS image. The red outline shows the cut area for vertical line cuts that are shown in d). d) Vertical GISAXS linecuts plotted versus time. A thinning of the solvent layer is suspected coupled with a vertical superlattice contraction, which might be caused by the gradual removal of solvent after the printing.

9 Teaching and outreach

9.1 Lectures, seminars and lab courses

Spring Term 2023

- Prof. Dr. Peter Müller-Buschbaum Angewandte Physik: Polymerphysik 2
- Prof. Christine M. Papadakis, PhD *Materialwissenschaften*
- Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christian Große Mess- und Sensortechnologie
- Prof. Dr. Peter Müller-Buschbaum, Nanostructured Soft Materials 2
- Prof. Dr. Winfried Petry *Physik mit Neutronen 2*
- Prof. Dr. Winfried Petry Workshop: Quantenphysik in der Anwendung
- Prof. Dr. Peter Müller-Buschbaum, Prof. Christine M. Papadakis, PhD Bachelor-Seminar: Funktionelle weiche Materialien
- Prof. Dr. Peter Müller-Buschbaum Seminar: Current problems in organic photovoltaics
- Prof. Dr. Bastian Märkisch, Prof. Dr. Peter Müller-Buschbaum, Dr. Christoph Morkel, Prof. C. Pfleiderer *Seminar: Neutronen in Forschung und Industrie*
- Prof. Dr. Peter Müller-Buschbaum, Prof. Christine M. Papadakis, PhD *Seminar: Polymers*
- Prof. Dr. Peter Müller-Buschbaum, Prof. Christine M. Papadakis, PhD *ProSeminar: Structure und dynamics of condensed matter*
- Prof. Dr. Peter Müller-Buschbaum Führung durch die Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) für Studierende der Physik

Autumn Term 2023/24

- Prof. Christine M. Papadakis, PhD Angewandte Physik: Polymerphysik 1
- Prof. Christine M. Papadakis, PhD Nanostructured Soft Materials 1
- Prof. Dr. Winfried Petry *Physics with neutrons* 1

- Prof. Dr. Winfried Petry Workshop: Quantenphysik in der Anwendung
- Prof. Dr. Peter Müller-Buschbaum Seminar: Current problems in organic photovoltaics
- Prof. Dr. Bastian Märkisch, Dr. Theresia Heiden-Hecht, Dr. Jitae Park, Dr. Christoph Morkel, Prof. Dr. Peter Müller-Buschbaum *Seminar: Neutronen in Forschung und Industrie*
- Prof. Dr. Peter Müller-Buschbaum, Prof. Christine M. Papadakis, PhD *Seminar: Polymers*
- Dr. Peter Müller-Buschbaum, Prof. Christine M. Papadakis, PhD *ProSeminar: Structure und dynamics of condensed matter*
- Prof. Dr. Peter Müller-Buschbaum Führung durch die Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) für Studierende der Physik

Lab Courses 2023 (Fortgeschrittenenpraktika)

- Atomic Force Microscopy
- Neutron scattering at FRM II
- Characterization of Polymers with Differential Scanning Calorimetry

9.2 Conferences and public outreach

Heinz Maier-Leibnitz Zentrum (MLZ) European Conference on Neutron Scattering 2023 Garching, MLZ/FRM II, 20 – 23 March 2023

From March 20 to 23, the eighth European Conference on Neutron Scattering (ECNS) took place in Garching. After St. Petersburg (2019) and Zaragoza (2015), the Heinz Maier-Leibnitz Zentrum was this year's host. MLZ welcomed 538 conferees from Europe but also from the rest of the world. The researchers listened to 165 presentations in 39 sessions. Topics ranged from work on fundamental physics to structure determination and new methods of neutron application. In addition, there were a total of 277 posters, which participants discussed at length during two afternoon rounds. On Wednesday, everyone was also invited to the conference dinner at the world-famous Hofbräuhaus in downtown Munich. The next conference of the field will be the International Conference on Neutron Scattering ICNS 2025 in Copenhagen.



Heinz Maier-Leibnitz Zentrum (MLZ) MORIS User Workshop Garching, MLZ/FRM II, 26 – 27 April 2023

"Science is moving", said Prof. Dr. Peter Müller-Buschbaum at the start of a workshop where 85 participants discussed the planned MORIS modernization program at the Heinz Maier-Leibnitz Zentrum. In 50 presentations, the scientific use of neutrons from the user side and the currently discussed project ideas for the upgrade of the MLZ instrument portfolio were presented. MORIS stands for MLZ-Organized Refurbishment of the Instrument Suite. The workshop in Garching was the first detailed presentation of project ideas for a refurbishment and upgrade program to the user community.



P. Müller-Buschbaum Lehrerfortbildung "Quantenphysik in der Anwendung" 44. Edgar-Lüscher-Seminar Zwiesel, 22 - 24 April 2023

45. Edgar-Lüscher-Seminar am Gymnasium Zwiesel Thema: Quantenphysik in der Anwendung

Freitag, 21. April bis Sonntag, 23. April 2023

Schirmherr: Prof. Dr. Thomas Hofmann, Präsident der TU München

Veranstalter: Der Ministerialbeauftragte für die Gymnasien in Niederbayern, Ltd. OStD Peter Brendel

Wissenschaftliche Leitung: Prof. Dr. Peter Müller-Buschbaum und Prof. Dr. Winfried Petry, TU München

Org. am Gymnasium Zwiesel: OStD Dr. Wolfgang Holzer, StR Stephan Loibl und OStR Claus Starke

Freitag, 21. April 2023

10:00-12:00 Experimente zur Quantenphysik für und mit Schüler – Dr. Kratzer, TUM School of Education, Leiter TUM Science Lab

14.45-15.15 Begrüßung

15.15-16.30 "*Einführung in die Quantenphysik und das Rechnen mit Qubits*" Prof. Klaus Mainzer, Präsident der European Academy of Sciences and Arts, TUM Emeriti of Excellence, TUM Senior Excellence Faculty

16.30-17.15 Diskussion und Kaffeepause

17.15-18.30 "*Quanten Computing mit supraleitenden Qubits*", Dr. Franz Haslbeck, Walther Meißner Institut, Bayerische Akademie der Wissenschaften & TUM

18.30-18.45 Diskussion

Samstag, 22. April 2023

09.00-10.15 "Quantenkryptographie und andere photonische Quantentechnologien". Dr. Lukas Knips, Max Planck Institute for Quantum Optics & Faculty for Physics LMU

10.15-11.00 Diskussion und Kaffeepause

Heinz Maier-Leibnitz Zentrum (MLZ) *MLZ Conference 2023: Neutrons for Biomaterials* Fürstenried, MLZ, 22 – 25 May 2023

For the MLZ Conference 2023 more than 50 conference participants met at Schloss Fürstenried from May 22 to 25. A total of 44 speakers discussed the application of neutrons in biomaterials research. Exciting lectures were given about the SARS-CoV-2 fusion process and new possibilities for cancer therapy. On the second day of the conference, Dr. Hermis Iatrou, from the University of Athens, opened the round of lectures. He studied a hydrogel consisting of amino acids using neutrons. The protein components are the basis for the gel's action and neutrons have elucidated the exact structure. Hermis Iatrou said, "Studies have already confirmed its therapeutic effect in treating cancer." Dr. Regine Willumeit-Römer of the Helmholtz Center Hereon spoke about another medical topic: 'Degradable metallic implants: Details of the Magnesium-Bone Interface.' In the future, this could be used to surgically stabilize bone fractures, for example, without having to remove the material afterwards. A significant factor in the aggressiveness of SARS-CoV-2 is the fusion of the pathogen's spike protein with the human ACE2 receptor. But how fast is this fusion? This question was addressed by the research team led by Dr. Sebastian Jaksch from the European Spallation Source.



Heinz Maier-Leibnitz Zentrum (MLZ) MLZ Biennial Internal MLZ Meeting Grainau, 19 – 22 June

MLZ internal workshop in Grainau 2023

From 19.6-22.6.23 the MLZ biennial internal workshop took place again in the picturesque environment of Grainau close to Garmisch-Partenkirchen. 130 participants from the Heinz Maier-Leibnitz Zentrum (MLZ), the universities TU München (Physik E13), Aachen, Köln and LMU, as well as the colleagues from the Max-Plank institutes and the KIT, Karlsruhe met for discussing about the science and instrumentation on the MLZ.

The program consisted of discussions in plenary and parallel sessions managed by the science groups of MLZ as well as in plenary scientific talks about particle physics with neutrons, magnetic interactions and neutrons for food. A conference dinner after a hike to the hotel at the Riessersee and an excursion to the research station in the Schneefernerhaus on the Zugspitze offered ample time for discussion with the colleagues. A very exiting evening talk by Dr. Sandra Kortner from Max-Planck Institute of Physics "revealed nature's secrets with the Higgs boson".



P. Müller-Buschbaum, C. M. Papadakis

Summer School of the Chair of Functional Materials and Soft Matter Group Hotel Berghof, Sonnenalpe Nassfeld, Kärnten, Austria, 18 – 21 July 2023

	Jugendsporthotel Leitner, Nassfeld/Tröpolach July 18 - 21, 2023				
	Tuesday, 18.07.2023	Wednesday, 19.07.2023	Thursday, 20.07.2023	Friday, 21.07.2023	
09:00		Polyelectrolytes	Introduction	Metal nanoparticles	
09:45		Perovskites		Presentation Discussion groups	
10:30-11:00	Journey from Garching start 7:30	Cottee break		Coffee break	
11:00		Battery electrodes		Presentation Discussion groups	
11:45		Crystallization in polymers			
13:00	Lunch	Lunch		Lunch	
14:00	Polymer blends	3 discussion groups:	Excursion		
14:45	Block copolymers in the bulk	polyelectrolytes, perovskites, battery electr.		Journey to Garching	
15:30-16:00	Coffee break	Coffee break			
16:00	Conjugated polymers	Amphiphilic block copolymers in solution			
16:45	Oxide nanoparticles	Thermoresponsive polymers			
17:30					
17:30-20:00	Dinner	Dinner	Dinner		
20:00	4 discussion groups:	3 discussion groups:	Poster Session	1	
20:45	blends, BCPs bulk, conj. pol., oxide NPs	cryst. pol., amphiphil. BCPs, thermoresp. pol.		1	
21:30				1	

E13 Summer School

<image>

Heinz Maier-Leibnitz Zentrum (MLZ) Sino-German Forum STRESS-SPEC Garching, MLZ/FRM II, 24 – 28 July 2023

Prof. Tianjiao Liang and scientists from the China Spallation Neutron Source (CSNS) have visited the Heinz Maier-Leibnitz Zentrum (MLZ) for a joint workshop titled "Complementary Neutron Methods in Engineering Science". They engaged in in-depth discussions and exchanges with scientists from the MLZ, on aspects of modern neutron instrumentation and current topics in materials science. The visit was intended as a kick-off to pave the way for further collaboration between MLZ and CSNS. The workshop was funded through the National Science Foundation of China (NSFC) and the Deutsche Forschungsgemeinschaft (DFG) and marks a new phase in the collaboration between China and Germany in the fields of neutron sources and neutron instruments.



P. Müller-Buschbaum, Akademie für Lehrerfortbildung Dillingen Lehrerfortbildung "Erneuerbare Energien" Edgar-Lüscher Lectures Dillingen, 20 - 22 September 2023

> EDGAR-LÜSCHER-LECTURES DILLINGEN/DONAU 2023 Thema: Erneuerbare Energien Datum: Mittwoch, 20. September bis Freitag, 22. September 2023 Tagungsort: Akademie für Lehrerfortbildung Dillingen Veranstalter: Akademie für Lehrerfortbildung Dillingen und TU München wissenschaftliche Leitung: Prof. Dr. Peter Müller-Buschbaum, Technische Universität München.

Programm

Mittwoch, 20. 09. 2023 15:00 – 15:30 Begrüßung OStR Beate Landherr / Prof. Dr. Peter Müller-Buschbaum (TUM, Physik)

15:30 – 17:00 Energetische Biomassenutzung Bernhard Huber (TUM Campus Straubing)

18:30 – 20:00 Windenergie Prof. Dr.-Ing. Simon Schramm (Hochschule München)

Donnerstag, 21. 09. 2023 8:30 – 10:00 Organische Solarzellen Prof. Dr. Simon Kahmann (Physik, TU Chemnitz)

10:00 - 10.30 Kaffeepause

10:30 – 12:00 Neue Solarzellen basierend auf Perowskiten Manuel E. Reus (Physik, TU München)

15:30 – 17:00 Thermoelektrische Energiekonversion Prof. Dr. Helmut Karl (Physik, Universität Augsburg)

18:30 – 20:00 Neutronenstreuung zur Untersuchung von Batterien Dr. habil. Ralph Gilles (FRM II, TU München)

Freitag, 22. 09. 2023

8:30 – 10:00 Geothermie Prof. Dr. Michael Drews (Geothermal Technologies, TU München)

10:00 - 10.30 Kaffeepause

10:30 – 12:00 Wasserkraft Prof. Dr. Stefan Riedelbauch (Institut für Strömungsmechanik und Hydraulische Strömungsmaschinen, Universität Stuttgart)

Ab 12:00 Lehrgangsabschluss Prof. Dr. Peter Müller-Buschbaum / OStR Beate Landherr P. Müller-Buschbaum, Stephan V. Roth *TUM/DESY VIPR WP5/WP6 Kick-off Workshop* Garching 25 September 2023

Sustainable e	nergy harvesting and machine learning (VIPR WP5/WP6 kick off)						
25.09.2023							
06:15	06:15 Departure Hamburg via flight						
09:00	09:00 Arrival at TUM						
09:00	09:30 Registration						
09:30	09:45 Welcome	Peter Müller-Buschbaum & Stephan V. Roth					
Session 1 Machine learning and scattering techniques							
09:45	10:05 Analysis of GISAXS data via model-based machine learning	Stephan V. Roth	20min				
10:05	10:25 Neutron techniques	Apostolos Vagias	20min				
Session 2 Photovoltaics							
10:25	10:40 Enhanced operational stability of polymer solar cells through	additiv Zerui Li	15min				
10:40	10:55 Sunny Cellulose I - Challenges for operando studies	Xinyu Jiang	15min				
10:55	11:10 Printing of Perovskite Solar Cells	Manuel Reus	15min				
11:10	11:25 Sunny Cellulose II - Material concepts	Yingjian Guo	15min				
Lunch break							
12:30	13:30						
Session 3 Sustainable Materials							
12:30	12:45 Sustainable printed organic solar cells	Jinsheng Zhang	15min				
12:45	13:00 Sustainable thermoelectrics, GISAXS, and machine-learning	Anuradha Bhogra	15min				
13:00	13:15 Tailoring Mesoporous Titania Zinc Oxide Film Morphologies	Yanan Li	15min				
13:15	13:30 Interaction of polymer colloidal inks with paper	Constantin Harder	15min				
Session 4	Challenges of HiPIMS						
13:30	13:45 HiPIMS for battery applications	Zhuijun Xu	15min				
13:45	14:00 HiPIMS for use in lithography	Yusuf Bulut	15min				
Coffee break							
14:00	15:00						
Session 5	and-on training for Organic Photovoltaics (OPV)						
15:00	17:30 Hands on training OPV part 1						
Dinner							
18:00	22:00						



Heinz Maier-Leibnitz Zentrum (MLZ) SPLENDID Workshop, Fürstenried Fürstenried, MLZ/FRM II, 26 – 27 September 2023

The SPLENDID workshop gathered 18 experts from the fields of neutron detection, scintillator development, simulation and software development to discuss the implementation of a proposal to be submitted in the framework of the Horizon Europe call HORIZON-INFRA-2024-TECH-01. In the two day workshop, the participants drafted an outline of the work package structure for the future proposal, distributed responsibilities and tasks among the members of the consortium and defined the way forward towards submission of a proposal by 12 March, 2024.



Heinz Maier-Leibnitz Zentrum (MLZ) JCNS Workshop 2023 - Trends and Perspectives in Neutron Scattering: Future Instruments at Pulsed Sources Tutzing, 9 - 12 October 2023

The JCNS Workshop 2023 was dedicated to future instruments at pulsed sources and had the aim of discussing the last and new developments in instrumentation for such sources together with the new opportunities offered by complementary techniques and by industrial applications. The neutron landscape has undergone some changes in recent years after the closure of several research reactors in Europe. Therefore, making available stateof-the-art new high-performance neutron sources with an optimized range of instruments is one of the issues that is occupying the modern neutron scatterer community.



Heinz Maier-Leibnitz Zentrum (MLZ) JANA Workshop 2023 Garching, MLZ/FRM II, 18 – 20 October 2023

After a series of very successful Jana2006 workshops in 2014 and 2017 and Jana2020 in 2022, MLZ was happy to welcome Václav Petříček and colleagues back in Garching. The Jana2020 Workshop 2023 was organized by the MLZ Science Group "Structure Research" and the Data Evaluation Group. The workshop's main topic was recent developments and new functionalities of Jana2020 – a crystallographic program dedicated to the solution, refinement, and interpretation of complex and modulated structures. The program dealt with various types of diffraction data, including single crystal and powder diffraction, as well as X-rays and neutrons as sources, which can be analyzed either separately, in combination or in complex sequences.



Heinz Maier-Leibnitz Zentrum (MLZ) SR2A 2023 – 10th International Conference on Synchrotron Radiation and Neutrons in Art and Archaeology Garching, MLZ/FRM II, 21 – 24 November 2023

From November 21 to 24, more than 80 internationally renowned scientists met at the Pinakothek der Moderne to discuss the benefits of synchrotron radiation and neutrons for art and archaeology. The MLZ organized the event with the Doerner Institut of the Bayerische Staatsgemäldesammlungen (Bavarian State Painting Collections). The SR2A conference ("Synchrotron Radiation and Neutrons in Art and Archaeology") celebrated an anniversary this year: for the tenth time since 2005, the conference was dedicated to the question of how X-ray and neutron radiation can be used to research archaeological finds and works of art. With seven top-class keynote speakers from Australia, China, and the USA, over 30 talks, and numerous poster contributions, a wide range of topics were covered – from the conservation of important works of art, provenance and object research to production techniques.



Heinz Maier-Leibnitz Zentrum (MLZ) Sample Environment Meeting Garching, MLZ/FRM II, 27 November 2023

The JCNS and TUM sample environment groups together with the Neutron Methods group have organized an MLZ internal meeting on sample environment on 27 November as a full day event. In this meeting, the following three main topics were addressed: 1) News from the sample environment groups (recently developed/purchased equipment, high pressure activities at JCNS, etc.), 2) Development of a science-based roadmap for MLZ sample environment, 3) Organizational aspects of future sample environment developments. In order to involve as many MLZ scientists as possible in a structured way, the science group coordinators had previously collected and presented input regarding the development of a science-based SE roadmap.



Heinz Maier-Leibnitz-Zentrum (MLZ) *MLZ User Meeting* Munich Marriott Hotel/MLZ, 4/5 December 2023

Neither snow nor ice could keep 208 users and MLZ employees away on December 4 and 5: They came to Munich for the 9th MLZ User Meeting. The ca. 40 registered participants who could not make it due to canceled public transport or freezing rain at Munich Airport could join in via video conference. In total, there were 63 presentations and 116 posters, a new record number of contributions in the history of the MLZ User Meetings. The two invited talks were particular highlights. Prof. Dr. Michael Gradzielski from TU Berlin gave his presentation on polyelectrolytes online after his flight was canceled due to freezing rain. Prof. Dr. Piero Baglioni had made it from Florence and reported on the cleaning of works of art, such as church frescoes or Picasso paintings. He had investigated the environmentally friendly organogels developed by his team using small-angle neutron scattering at the MLZ. The Chairman of the Committee Research with Neutrons, Prof. Dr. Frank Schreiber from the University of Tübingen, used his presentation to introduce the representation of the approximately 1,400 neutron researchers in Germany.



9.3 Service to the community

Prof. Dr. Peter Müller-Buschbaum:

- Since 11/2023 Supervising Professor "Elektronic Lab" of TUM School of Natural Sciences
- Since 05/2023 Member of TUM Sustainability Board
- From 01/2023 to 12/2023 Excecutive Editor of the journal "ACS Applied Materials and Interfaces" of American Chemical Society (ACS)
- Since 10/2021 Core Member of Integrated Research Institute (IRI), Munich Institute of Integrated Materials, Energy and Process Engineering (MEP) at TUM
- Since 1/2019 council member of excellence cluster "ORIGINS"
- From 04/2018 until 12/2023 Scientific Director of Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) and Heinz Maier-Leibnitz Zentrum (MLZ)
- Since 04/2018 Full Professor (W3), Head of Chair for Functional Materials at TUM School of Natural Sciences
- Since 3/2015 member of "Advanced Light Source (ALS) Review Panel"
- Since 6/2014 member of Stanford Synchrotron Radiation Lightsource (SSRL) Review Panel
- Since 3/2012 head of KeyLab "TUM.Solar" of the Bavarian research project "Solar Technologies Go Hybrid" (SolTech) at TUM
- Since 2011 member of European Spallation Source (ESS) Scientific Advisory Panel (Reflectivity)
- Since 2011 German representative at the European Polymer Federation (EPF) for polymer physics
- Since 02/2010 Spokesman of the energy section of TUM Physics Department
- Since 02/2010 Member of TUM.Energy
- Since 2010 German representative at the European Synchrotron User Organization (ESUO)
- Since 2008 chairman of "DESY Photon Science User Committee" at the synchrotron radiation laboratory DESY in Hamburg

Prof. Christine M. Papadakis, PhD:

- Since 4/2015 Editor-in-Chief for Colloid & Polymer Science, Springer-Verlag
- Vice women's representative of the Physics Department at TU München
- Member of the Beamtime Allocation Panel C08 at the European Synchrotron Radiation Facility, Grenoble, France

Prof. Dr. Winfried Petry:

- Since 2018 TUM Emeritus of Excellence
- Since 2016 member of the Evaluation Panel for Neutron Research of the Swedish Research Council
- Since 2015 member of the Neutron Scientific Advisory Committee of the National Research Center Kurchatov Institute "Petersburg Nuclear Physics Institute" (PNPI, Gatchina)
- Since 2012 member of the Scientific Advisory Board of NaWi Graz
- Since 2007 member of the Steering Comittee of the Laue Langevin Institute and chairman of the instrumentation review panel of the CEA Leon Brillouin Laboratory
- Since 1999 liaison professor of Bayerische Eliteakademie (Bavarian Leadership Academy) and since May 2011 member of the Board of Trustees

10 Publications, talks, posters, and funding

10.1 Publications

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 Energy Storage Mater. 59, 102782 (2023)
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10.2 Talks

• F. A. C. Apfelbeck, J. E. Heger, T. Guan, M. Schwartzkopf, S.V. Roth, P. Müller-Buschbaum *Grazing incidence X-ray scattering on lithium iron phosphate electrodes with polymer blend binders*

DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023

- Y. Bulut, B. Sochor, K. Reck, J. Drewes, S. Liang, T. Guan, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth *The influence of increased kinetic energy of gold deposition onto polymers* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- Y. Bulut, B. Sochor, K. Reck, J. Drewes, S. Liang, T. Guan, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth *In-situ GISAXS/GIWAXS investigation of dcMS and HiPIMS deposited gold onto polymers* ACS Fall 2023, San Francisco, 13 – 17 August 2023
- Y. Bulut, B. Sochor, K. Reck, J. Drewes, S. Liang, T. Guan, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth *In-situ GISAXS/GIWAXS investigation of dcMS and HiPIMS deposited gold onto polymers* Nanoworkshop 2023, Schloss Plön, 12 – 15 September 2023
- Y. Bulut, B. Sochor, C. Harder, K. Reck, A. Meinhardt J. Drewes, Z. Xu, X. Jiang, A. Jeromin, M. Kohantorabi, H. Noei, T.F. Keller, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth *HiPIMS for use in lithography*

Sustainable Energy Harvesting and Machine Learning (VIPR WP5/WP6 kick-off), Garching, 25 – 26 September 2023

- A. Buyan-Arivjikh, M. Schwartzkopf, S. Vayalil, S. V. Roth & P. Müller-Buschbaum *Effect Of Perovskite Nanocrystal Nucleation Seeds on Microstructure and Crystallization Path ways in Organic-Inorganic Halide Perovskite Thin Films* 12th SolTech Conference, Munich, 03 – 05 October 2023
- C. R. Everett, G. Pan, M. A. Reus, D. P. Kosbahn, F. Hartmann, M. Bitsch, M. Opel, M. Gallei, M. Schwartzkopf, P. Müller-Buschbaum Morphology evolution and nanoparticle localization in printed hybrid nanoparticle-diblock copolymer thin films investigated by in situ GISAXS
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- Y. Guo, J. Zhou, C. Harder, G. Pan, S. Tu, T. Tian, Y. Bulut, D. Söderberg, P. Müller-Buschbaum and S. V. Roth Biopolymer-Templated Deposition of Hierarchical 3D-Structured Graphene/Gold Nanoparticle Hybrids for Surface-Enhanced Raman Scattering (SERS)
 Sustainable Energy Harvesting and Machine Learning (VIPR WP5/WP6 kick-off), Garching, 25 – 26 September 2023

- C. Harder, M. Betker, A. E. Alexakis, M. Gensch, Q. Chen, E. Erbes, B. Sochor, A. Chumakov, A. Vagias, C. J. Brett, J. Rubeck, M. Schwartzkopf, D. Söderberg, E. Malmström, P. Müller-Buschbaum and S. V. Roth
 Light properties and water resistance of combined sobrerol methacrylate cellulose thin films DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 31 March
 2023
- C. Harder, M. Betker, A. E. Alexakis, M. Gensch, Q. Chen, E. Erbes, B. Sochor, A. Chumakov, A. Vagias, C. J. Brett, J. Rubeck, M. Schwartzkopf, D. Söderberg, E. Malmström, P. Müller-Buschbaum and S. V. Roth *Slot-die coating of hybrid cellulose colloid inks* 18th Coatings Science International 2023, Noordwijk, Netherlands, 26 29 June 2023
- C. Harder, L. Plunkte, S. Chen, I. Ribca, M. Betker, B. Sochor, D. Söderberg, E. Malmström, P. Müller-Buschbaum and S. V. Roth *Functionalising wearables and nanopaper by wood-derived nanoparticles* Sustainable Energy Harvesting and Machine Learning (VIPR WP5/WP6 kick-off), Garching, 25 – 26 September 2023
- J. E. Heger, W. Chen, S. Yin, N. Li, V. Körstgens, C. J. Brett, W. Ohm, S. V. Roth, P. Müller-Buschbaum Low-temperature and water-based biotemplating of nanostructured foam-like titania films using β-lactoglobulin
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- J. E. Heger, W. Chen, S. Yin, N. Li, V. Körstgens, C. J. Brett, W. Ohm, S. V. Roth, P. Müller-Buschbaum
 X-ray and neutron scattering data for machine learning of invertible neural networks
 ErUM-Data-Workshop on Inverse Problems, Garching, 05 – 06 December 2023
- T. Hölderle, M. Monchak, V. Baran, O. Dolotko, S. Bette, D. Mikhailova, A. Voss, M. Avdeev, H. Ehrenberg, P. Müller-Buschbaum, A. Senyshyn *Structural response in NCA-type battery cathodes* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- T. Hölderle, M. Monchak, V. Baran, A. Kriele, M. J. Mühlbauer, V. Dyadkin, A. Schökel, H. Ehrenberg, P. Müller-Buschbaum, A. Senyshyn *Thermal and structural behavior of graphite battery anodes* 5th internal biannual science meeting of the MLZ, Grainau, 19 – 22 June 2023
- T. Hölderle
 PhD project of Tobias Hölderle "Structural analysis of real Li-ion battery electrodes"
 5th internal biannual science meeting of the MLZ, Grainau, 19 22 June 2023
- T. Hölderle, M. Monchak, V. Baran, A. Kriele, M. J. Mühlbauer, V. Dyadkin, A. Schökel, H. Ehrenberg, P. Müller-Buschbaum, A. Senyshyn Thermal and structural stability of lithiated graphite battery anodes MLZ User Meeting 2023, Munich, 04 – 05 December 2023

- L. F. Huber, P. Müller-Buschbaum Inorganic-organic hybrid nanostructures based on biopolymer templating for thermoelectric application Nanoworkshop 2023, Schloss Plön, 12 – 15 September 2023
- M. P. Le Dû, P. Ching, P. Wang *Thermo-responsive polymers* E13 Summer School, Nassfeld, Austria, 18 – 21 July 2023
- S. Liang, T. Guan, S. Yin, E. Krois, W. Chen, C. R. Everett, J. Drewes, T. Strunskus, M. Gensch, J. Rubeck, C. Haisch, M. Schwartzkopf, F. Faupel, S. V. Roth, Y.-J. Cheng, P. Müller-Buschbaum
 *Template-Induced Growth of Sputter-Deposited Gold Nanoparticles on Ordered Porous TiO*₂ *Thin Films for Surface-Enhanced Raman Scattering Sensors* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 31 March 2023
- S. Liang, T. Zheng, T. Guan Metal Nanoparticles
 E13 Summer School, Nassfeld, Austria, 18 – 21 July 2023
- C. G. Lindenmeir, L. K. Reb, M. A. Reus, P. Müller-Buschbaum *Printing of Perovskite and Organic Solar Cells* ATUMS: Annual Meeting, 12 -- 17 November 2023
- Y. Li, N. Li, S. Yin, C. Harder, Y. Bulut, A. Vagias, S. V. Roth, P. Müller-Buschbaum Shape-controlled mesoporous hybrid films with binary metal oxide obtained via sol-gel route for photovoltaic application
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- Y. Li, S. Yin, N. Li, C. Harder, Y. Bulut, A. Vagias, S. V. Roth, P. Müller-Buschbaum Mesoporous hybrid films of mixed metal oxides fabricated via sol-gel method
 5th internal biannual science meeting of the MLZ, Grainau, 19 – 22 June 2023
- P. Müller-Buschbaum
 Functional materials
 TUM-National Tsing Hua University (NTHU) Workshop, 13 January 2023
- P. Müller-Buschbaum Report of the Users Committee (DPS-UC) - report 2022 DESY Users' Meeting, Hamburg, 25 – 27 January 2023
- P. Müller-Buschbaum Advanced in-situ GISAXS/GIWAXS studies during printing of thin organic films 22nd SAXS/WAXS/GISAXS Satellite Workshop of DESY Users Meeting, Hamburg, 25 – 27 January 2023
- P. Müller-Buschbaum Welcome to ECNS 2023
 European Conference on Neutron Scattering ECNS 2023, Garching, 20 – 23 March 2023

- P. Müller-Buschbaum The research neutron source Heinz Maier-Leibnitz (FRM II) European Conference on Neutron Scattering ECNS 2023, Garching, 20 – 23 March 2023
- P. Müller-Buschbaum
 Progress in organic solar cells based on advanced neutron scattering methods
 European Conference on Neutron Scattering ECNS 2023, Garching, 20 23 March 2023
- P. Müller-Buschbaum TOF-GISANS - challenges and opportunities SAGA Satellite Workshop 2023, Garching, 24 March 2023
- P. Müller-Buschbaum Structure control during in-situ printing of donor-acceptor blend films ACS Spring Meeting 2023, Indianapolis, USA, 26 – 30 March 2023
- P. Müller-Buschbaum
 Perovskite and organic solar cells for space applications
 2023 MRS Spring Meeting and Exhibit, San Francisco, USA, 10 14 April 2023
- P. Müller-Buschbaum
 In Situ and Operando Scattering Studies on Perovskite Solar Cell
 2023 MRS Spring Meeting and Exhibit, San Francisco, USA, 10 14 April 2023
- P. Müller-Buschbaum Use of machine learning, artificial intelligence and robotics at the Heinz Maier-Leibnitz Zentrum (MLZ)
 Machine Learning in X-Ray and Neutron Scattering, Berkeley (USA), 16 – 17 April 2023
- P. Müller-Buschbaum Welcome, motivation and tasks
 MORIS MLZ Workshop 2023, Garching, 26 – 27 April 2023
- P. Müller-Buschbaum MLZ-LLB workshop introduction MLZ-LLB Workshop 2023, Gif-sur-Yvette, France, 9 – 11 May 2023
- P. Müller-Buschbaum Neutronen für Forschung und Innovation FRM II Besuch der Ständigen Vertretung der Bundesrepublik Deutschland bei dem Büro der Vereinten Nationen und bei anderen internationalen Organisationen, Garching, 19 May 2023
- P. Müller-Buschbaum Scientific Missions of the FRM II FRM II Besuch McMaster Delegation, Garching, 22 May 2023
- P. Müller-Buschbaum MLZ Conference Neutrons for Biomaterials - welcome MLZ Konferenz 2023, Fürstenried, 22 – 25 May 2023
- P. Müller-Buschbaum
 Grainau setting the scene
 5th internal biannual science meeting of the MLZ, Grainau, 19 22 June 2023

- P. Müller-Buschbaum Next Generation Solar Cells Studied With Advanced Neutron Techniques Gordon Research Conference "Neutron Scattering for a Sustainable Society", Ventura, USA, 24 June – 1 July 2023
- P. Müller-Buschbaum
 Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II)
 FRM II Besuch: Klinik für Nuklearmedizin der TUM, Garching, 4 July 2023
- P. Müller-Buschbaum
 Progress in perovskite and organic solar cells for space applications
 PV Space Konferenz, Rome, Italy, 5 7 July 2023
- P. Müller-Buschbaum Neutronen für Forschung und Innovation
 FRM II Besuch der Bundesministerin für Bildung und Forschung Bettina Stark-Watzinger am FRM II, 3 August 2023
- P. Müller-Buschbaum
 Perovskite and organic solar cells for space applications
 ACS Fall Meeting 2023, San Francisco, USA, 11 18 August 2023
- P. Müller-Buschbaum Structure control during in situ printing of functional nanocomposite films for solar cell applications Nanoworkshop 2023, Schloss Plön, 12 – 15 September 2023
- P. Müller-Buschbaum Neutronen für Forschung und Innovation
 FRM II Besuch des Stadtrats von Ahaus am FRM II, 26 September 2023
- P. Müller-Buschbaum
 Perovskite and organic solar cells measured in space 12th SolTech Conference, Würzburg, 1 5 October 2023
- P. Müller-Buschbaum Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II)
 1st Faculty Retreat of the TUM School of Natural Sciences (NAT), Garching, 11 – 12 October 2023
- P. Müller-Buschbaum Scientific Missions of FRM II and MLZ 2023
 10th SR2A International Conference on Synchrotron Radiation and Neutrons in Art and Archeology 21 – 22 November 2023
- P. Müller-Buschbaum MLZ and FRM II – Directors' Report 2023 MLZ User Meeting 2023, München, 04 – 05 December 2023
- A. L. Oechsle, J. E. Heger, N. Li, S. Yin, S. Bernstorff, P. Müller-Buschbaum In situ investigation of the domain morphology and doping level of thermoelectric PEDOT:PSS thin films under different ambient conditions ACS Spring Meeting 2023, Indianapolis, USA, 26 – 30 March 2023

- G. Pan Morphology Control of Titanium Thin Films in a Low-Temperature Process
 5th internal biannual science meeting of the MLZ, Grainau, Germany, 19 – 22 June 2023
- C. M. Papadakis *Thermoresponsive polymers under pressure* National Cheng Kung University, Tainan, Taiwan, 03 March 2023
- C. M. Papadakis Micellar hydrogels from responsive triblock copolymers National Taiwan University, Taipei, Taiwan, 10 March 2023
- C. M. Papadakis, B.-J. Niebuur, L. Chiappisi, A. Schulte *Kinetics of mesoglobule formation and disintegration in solutions of thermoresponsive polymers after fast pressure jumps* European Conference on Neutron Scattering, Garching, 20 – 23 March 2023
- C. M. Papadakis Block copolymers with differently responsive blocks – from hydrogels to tunable thin films Treffen der Forschergruppe FOR2811, Darmstadt, 22 – 24 March 2023
- B.-J. Niebuur, B. Yazdanshenas, F. Zheng, W. Lohstroh, M. Wolf, M.-S. Appavou, M. Zamponi, A. Schulte, C. M. Papadakis Hydration Water Dynamics in a Thermoresponsive Polymer Solution Under Pressure DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- C. M. Papadakis, F. Zheng, W. Xu, E. Melampianaki, P. Alvarez Herrera, J. Kohlbrecher, A. P. Constantinou, T. K. Georgiou *Highly tunable nanostructures in a doubly pH-responsive pentablock terpolymer in solution and in thin films* MLZ Conference 2023: Neutrons for Biomaterials, Munich, 22 – 25 May 2023
- C. M. Papadakis, F. A. Jung, C. Tsitsilianis Highly Tunable Nanostructures in a Doubly pH-Responsive Pentablock Terpolymer in Thin Film Geometry Ostwald-Colloquium: Interface mediated processes in soft matter, Darmstadt, 13 – 15 September 2023
- C.-H. Ko, C. Henschel, P. Müller-Buschbaum, A. Laschewsky, C. M. Papadakis Self-assembly of thermoresponsive block copolymers
 Chulalangkorn University, Bangkok, Thailand, 28 September 2023
- D. Petz P. Müller-Buschbaum, A. Senyshyn *Aging-driven compositional changes in Li-ion batteries* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- D. Petz, P. Müller-Buschbaum, A. Senyshyn Non-destructive characterization of lithium distribution in cylinder-type Li-ion batteries Virtual Battery Day 2023, online, 15 November 2023

- I. Pivarníková, S. Seidlmayer, M. Finsterbusch, G. Dück, N. Jalarvo, P. Müller-Buschbaum, R. Gilles *Investigation of sodium-ion diffusion in NASICON solid-state electrolyte materials* European Conference on Neutron Scattering 2023, Garching, 20 – 23 March 2023
- I. Pivarníková, S. Seidlmayer, M. Finsterbusch, G. Dück, N. Jalarvo, P. Müller-Buschbaum, R. Gilles Sodium diffusion mechanism in NASICON solid electrolyte materials studied via quasi-elastic

neutron scattering

DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023

- I. Pivarníková, M. Flügel, N. Paul, A. Cannavo, G. Ceccio, J. Vacík, P. Müller-Buschbaum, M. Wohlfahrt-Mehrens, T. Waldmann, R. Gilles *Neutron depth profiling and GD-OES as tools for characterization of Li plating in Si/graphite anodes from Li-ion battery cells* MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- J. Reitenbach, C. Geiger, P. Wang, A. Vagias, R. Cubitt, D. Schanzenbach, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum *Tuning the sensitivity of PNIPMAM-based nanosensors by the addition of salts* ACS Spring 2023, Indianapolis, USA, 26 – 30 March 2023
- J. Reitenbach, C. Geiger, P. Wang, T. Widmann, L. P. Kreuzer, R. Cubitt, D. Schanzenbach, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum *Investigation of the Solvent Uptake in Salt Containing PNIPMAM Thin Films* MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- M. A. Reus, L. K. Reb, A. Krifa, D. P. Kosbahn, Q. A. Akkerman, A. Biewald, M. Schwartzkopf, A. Chumakov, J. Feldmann, A. Hartschuh, S. V. Roth, P. Müller-Buschbaum *Processing in situ GIWAXS data of slot-die coated perovskite thin-film materials* DESY User Meeting 2023, Hamburg, 25 – 27 January 2023
- M. A. Reus, L. K. Reb, A. Krifa, D. P. Kosbahn, Q. A. Akkerman, A. Biewald, M. Schwartzkopf, A. Chumakov, J. Feldmann, A. Hartschuh, S. V. Roth, P. Müller-Buschbaum *Slot-die coating of nanocrystal and bulk perovskite thin films for photovoltaics* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- M. A. Reus, L. K. Reb, D. P. Kosbahn, A. Krifa, M. Stoian, A. Sytchev, S. V. Roth, P. Müller-Buschbaum *Processing of QD deposition GIXS data with INSGIGHT* 5th internal biennial science meeting of the MLZ, Grainau, 19 – 22 June 2023
- M. A. Reus Neue Solarzellen basierend auf Perowskiten Lüscher Lectures, Dillingen, 20 – 22 September 2023

- M. A. Reus, L. K. Reb, Q. A. Akkerman, A. Biewald, M. Schwartzkopf, A. Chumakov, J. Feldmann, A. Hartschuh, S. V. Roth, P. Müller-Buschbaum *Printing of Perovskite Solar Cells* Sustainable energy harvesting and machine learning (VIPR WP5/WP6 kick-off), Garching, 25 26 September 2023
- D. M. Schwaiger
 Quasielastic neutron scattering in polymer-fullerene blends 5th MLZ internal biannual science meeting, Grainau, 19 22 June 2023
- D. M. Schwaiger, G. Pan, Z. Li Conjugated Polymers
 E13 Summer School, Nassfeld, Austria, 18 – 21 July 2023
- P. Wang, C. M. Papadakis, P. Müller-Buschbaum KCl modulated D₂O Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- P. Wang, C. M. Papadakis, P. Müller-Buschbaum KCl modulated Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films
 5th internal biannual science meeting of the MLZ, Grainau, 19 – 22 Jun 2023
- P. Wang, P. Zhang, L. D. Morgan *Thermoresponsive polymers* E13 summer school, Nassfeld, Austria, 18 – 21 July 2023
- S. A. Wegener, A. Buyan-Arivjikh1, G. Pan, K. Sun, Z. Li, X. Jiang, M. Schwarzkopf, P. Müller-Buschbaum Rapid Thermal Cycling of Perovskite Solar Cells MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- Z. Xu, Y. Xia, Y. Cheng, P. Müller-Buschbaum Facile Scalable Single Step Multi-Level Structure Engineering Makes TNO₄/Carbon Nanohybrids a New Promising Lithium-Ion Battery Anode Nanoworkshop 2023, Schloss Plön, 12 – 15 September 2023
- Z. Xu, X. Jiang, Y. Bulut, B. Sochor, K. Reck, T. Strunskus, F. Faupel, S. V. Roth, P. Müller-Buschbaum *HIPIMS Technology for Lithium Metal Battery* Sustainable energy harvesting and machine learning (VIPR WP5/WP6 kick-off), Munich, 25 – 26 September 2023
- J. Zhang, P. Müller-Buschbaum
 Effect of solvent additive selectivity on crystallization kinetics in organic solar cells
 5th internal biannual science meeting of the MLZ, Grainau, 19 22 June 2023
- J. Zhang, P. Müller-Buschbaum Sustainable printed organic solar cells
 Sustainable energy harvesting and machine learning (VIPR WP5/WP6 kick-off), Munich, 25 – 26 September 2023

• F. Zheng, P. A. Álvarez Herrera, J. Kohlbrecher, A. Constantinou, T. K. Georgiou,

C. M. Papadakis Injectable hydrogels from thermoresponsive tri- and tetrablock terpolymers investigated using neutron scattering method DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023

- F. Zheng, P. A. Álvarez Herrera, J. Kohlbrecher, S. Da Vela, W.Xu, E. Melampianaki, A. Constantinou, T. K. Georgiou, C. M. Papadakis *Thermoresponsive hydrogels of increasing architecture complexity from PEG-based terpolymers* 5th Internal Biannual Science Meeting of the MLZ, Grainau, 19 – 22 June 2023
- F. Zheng, P. A. Álvarez Herrera, J. Kohlbrecher, A. Constantinou, T. K. Georgiou,

C. M. Papadakis Effect of architecture in thermoresponsive hydrogels from PEG-based terpolymers MLZ User Meeting 2023, Munich, 04 – 05 December 2023

H. Zhong, W. Chen, M. A. Scheel, L. Spanier, C. R. Everett, X. Jiang, S. Yin, M. S. Hörtel, J. Zhang, B. B. O. Seibertz, M. Schwartzkopf, S. V. Roth, P. Müller-Buschbaum *In-situ GISAXS investigation of sputtering IZO thin film for optoelectronic applications* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023

10.3 Posters

• P. A. Alvarez Herrera, G. P. Meledam, C. Henschel, A. Laschewsky, L. Chiappisi, C. M. Papadakis

Effect of pressure on the micellar structure of PMMA-b-PNIPAM in aqueous solution DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023

- P. A. Alvarez Herrera, G. P. Meledam, C. Henschel, A. Laschewsky, L. Chiappisi, C. M. Papadakis
 Effect of pressure on the micellar structure of PMMA-b-PNIPAM in aqueous solution European Conference on Neutron Scattering 2023, Garching, 20 23 March 2023
- P. A. Alvarez Herrera, G. P. Meledam, C. Henschel, A. Laschewsky, L. Chiappisi, C. M. Papadakis
 Effect of pressure on the micellar structure of PMMA-b-PNIPAM in aqueous solution 18th Zsigmondy Colloquium, Berlin, 04 06 April 2023
- P. A. Alvarez Herrera, F. Zheng, P. Zhang, J. Reitenbach, H. Amenitsch, P. Müller-Buschbaum, C. Henschel, A. Laschewsky, C. M. Papadakis *Effect of pressure on the micellar structure of PMMA-b-PNIPAM in a water/methanol mixture* MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- F. A. C. Apfelbeck, J. E. Heger, T. Guan, M. Schwartzkopf, S.V. Roth, P. Müller-Buschbaum Grazing incidence X-ray scattering on lithium iron phosphate electrodes with polymer blend binders
 GRC Neutron Scattering for a Sustainable Society 2023, Ventura, USA, 25 – 30 June 2023
- T. Baier, Y. Li, P. Müller-Buschbaum Fabrication and Characterisation of Cesium-Formamidinium Lead Iodide Perovskite Quantum Dot Layers
 3rd e-conversion conference 2023, Tutzing, 15 – 18 October 2023
- T. Baier, Y. Li, P. Müller-Buschbaum Fabrication and Characterisation of Cesium-Formamidinium Lead Iodide Perovskite Quantum Dot Layers
 MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- Y. Bulut, B. Sochor, J. Drewes, K. Reck, S. Liang, T. Guan, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth *In-situ investigation during gold HiPIMS deposition onto polymers* DESY Users' Meeting, Hamburg, 25 – 27 January 2023
- Y. Bulut, B. Sochor, J. Drewes, K. Reck, S. Liang, T. Guan, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth *In-situ investigation during gold HiPIMS deposition onto polymers* NanoMat Science Day 2023, Hamburg, 24 May 2023
- Y. Bulut, B. Sochor, K. Reck, J. Drewes, S. Liang, T. Guan, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth *In-situ GISAXS/GIWAXS investigation of dcMS and HiPIMS deposited gold onto polymers* RÅC International Summer School, Lüneburg, 20 – 27 August 2023

- Y. Bulut, B. Sochor, K. Reck, J. Drewes, S. Liang, T. Guan, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth *In-situ GISAXS/GIWAXS investigation of dcMS and HiPIMS deposited gold onto polymers* From Matter to Materials and Life, Jena, 27 – 29 September 2023
- Y. Bulut, B. Sochor, K. Reck, A. Meinhardt, J. Drewes, S. Liang, T. Guan, A. Jeromin, T. F. Keller, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth Comparison of dcMS and HiPIMS Gold Deposition on Polystyrene, Poly-4-vinylpyridine and Polystyrenesulfonicacid
 MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- A. Buyan-Arivjikh, P. Müller-Buschbaum Exploring the Impact of Nucleation Seeds on the Formation of Printed Hybrid Perovskite Films DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- A. Buyan-Arivjikh, G. Pan, J. Zhang, Z. Xu, T. Baier, Y. Li, C.R. Everett, M. Schwartzkopf, S.K. Vayalil, S.V. Roth & P. Müller-Buschbaum
 Effect of perovskite nanocrystal nucleation seeds on microstructure and crystallization pathways in organic-inorganic halide perovskite thin films MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- X. Ci, K. Sun, X. Jiang, G. Pan, Z. Xun, P. Müller-Buschbaum Enhanced air stability of Tin-Based Perovskite Solar Cells with Quercetin MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- J. Darsow, L. V. Spanier, C. Gscheidle, P. Müller-Buschbaum Investigation of the Structure of Organic Solar Cells for Space Application and Degradation Due to Mechanical Stress
 MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- Jasper G. Ebel, Huaying Zhong, P. Müller-Buschbaum *PbS Quantum Dot Solar Cells for Space Applications* DPG Spring Meeting of the Condensed Matter Section 2023, 26 – 31 March 2023
- C. R. Everett, G. Pan, M. A. Reus, D. P. Kosbahn, A. Lak, M. Opel, M. Plank, M. Bitsch, M. Gallei, M. Schwartzkopf, P. Müller-Buschbaum *Incorporatzion and localization of magnetic nanoparticles in printed hybrid thin nanoparticlediblock copolymer films investigated by GISAXS* MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- K. N. Gavriilidou, T. Guan, P. Müller-Buschbaum Hybridizing plasmonic nanostructures with Quantum Dots MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- T. Guan, S. Liang, Y. Bulut, K. Reck, M. Schwartzkopf, J. Drewes, T. Strunskus, F. Faupel, S. V. Roth, P. Müller-Buschbaum *Influence of thermal effects on a combinatorial plasmonic nanostructure for bio-detection* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023

- Y. Guo, C. Harder, J. Zhou, S. Chen, Y. Bulut, G. J. Pan, P. Müller-Buschbaum, S. V. Roth Biopolymer-Templated Deposition of Hierarchical 3D-Structured Graphene/Gold Nanoparticle Hybrids for Ultrasensitive Surface-Enhanced Raman Scattering RÅC International Summer School 2023, Lüneburg, 20 – 27 August 2023
- Y. Guo, C. Harder, J. Zhou, S. Chen, Y. Bulut, G. J. Pan, P. Müller-Buschbaum, S. V. Roth Biopolymer-Templated Deposition of Hierarchical 3D-Structured Graphene/Gold Nanoparticle Hybrids for Ultrasensitive Surface-Enhanced Raman Scattering Nanoworkshop 2023, Schloss Plön, 12 – 15 September 2023
- Y. Guo, J. Zhou, C. Harder, G. Pan, S. Tu, Y. Bulut, B. Sochor, S. Vayalil, D. Söderberg, P. Muller-Buschbaum, S. V. Roth, Biopolymer-Templated Deposition of Hierarchical 3D-Structured Graphene/Gold Nanoparticle Hybrids for Surface-Enhanced Raman Scattering MLZ User Meeting 2023, Munich, 4 – 5 December 2023
- C. Harder, M. Betker, A. Alexakis, Y. Bulut, S. Xiong, E. Erbes, B. Sochor, K. Goordeyeva, M. Gensch G. Pan, H. Zhong, M. Reus, Q. Chen, A. Chumakov, J. Rubeck, V. Körstgens, M. Schwartzkopf, A. Jeromin, T. Keller, D. Söderberg, E. Malmström, P. Müller-Buschbaum and S. Roth Slot-die conted cellulose colloid layer

Slot-die coated cellulose colloid layer MLZ User Meeting 2023, Munich, 04 – 05 December 2023

• C. Harder, M. Betker, A. Alexakis, Y. Bulut, S. Xiong, E. Erbes, B. Sochor, K. Goordeyeva, M. Gensch G. Pan, H. Zhong, M. Reus, Q. Chen, A. Chumakov, J. Rubeck, V. Körstgens, M. Schwartzkopf, A. Jeromin, T. Keller, D. Söderberg, E. Malmström, P. Müller-Buschbaum and S. Roth Influence of the imbibition of colloids through the optical and wetting properties of porous CNF layer

DESY Users' Meeting, Hamburg, 25 – 27 January 2023

J. E. Heger, J. Reitenbach, C. Geiger, T. Widmann, L. P. Kreuzer, C. L. Weindl, A. Koutsioumpas, C. Harder, B. Sochor, M. Schwartzkopf, S. V. Roth, P. Müller-Buschbaum *Tuning the morphology of biohybrid β-lg:titania films with pH for water-based and nanostructured titania*

MLZ User Meeting 2023, Munich, 04 - 05 December 2023

- T. Hölderle, M. Monchak, V. Baran, O. Dolotko, S. Bette, D. Mikhailova, A. Voss, M. Avdeev, H. Ehrenberg, P. Müller-Buschbaum, A. Senyshyn Li/Ni disorder of electrochemically cycled NCA-type battery cathodes European Conference on Neutron Scattering 2023, Garching, 20 – 23 March 2023
- T. Hölderle, M. Monchak, V. Baran, A. Kriele, M. J. Mühlbauer, V. Dyadkin, A. Schökel, H. Ehrenberg, P. Müller-Buschbaum, A. Senyshyn Thermal and structural stability of lithiated graphite battery anodes MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- L. F. Huber, P. Müller-Buschbaum Inorganic-organic hybrid nanostructures based on biopolymer templating DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023

- L. F. Huber, P. Müller-Buschbaum In situ GISAXS printing of biotemplated titania nanostructures MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- Z. Jin, X. Jiang, P. Müller-Buschbaum *Tuning the band gap of double perovskite by anion exchange* MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- D. P. Kosbahn, M. A. Reus, C. R. Everett, G. Pan, M. Schwartzkopf, S. V. Roth, P. Müller-Buschbaum
 In situ study of superlattice self-assembly during slot-die coating of perovskite quantum dot films
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- D. P. Kosbahn, M. P. Le Dû, J. Reitenbach, L. V. Spanier, R. Steinbrecher, A. Laschewsky, R. Cubitt, T. Saerbeck, C. M. Papadakis, P. Müller-Buschbaum Influence of Photoswitchable Molecules on the Swelling Behavior of Thermoresponsive Poly(Dimethylacrylamide) Films in Water Vapor under UV-Irradiation MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- M. P. Le Dû, J. Reitenbach, M. A. Reus, K. Sun, Z. Li, S. Bernstorff, C. Henschel, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum *Hybrid hrydrogel films for salable hydrogen production* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 31 March 2023
- M. P. Le Dû, J. Reitenbach, H. Ubele, N. Chaulagain, C. Henschel, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum Catalyst-enhanced polymer films for green H2 production 12th SolTech Conference, Würzburg, 3 – 5 October 2023
- M. P. Le Dû, J. Reitenbach, D. P. Kosbahn, L. V. Spanier, C. Henschel, A. Laschewsky, R. Cubitt, C. M. Papadakis, P. Müller-Buschbaum *Exploring hydration mechanisms in PNVIBAM and its isomer PNIPAM* MLZ User Meeting 2023, Munich, 04 05 December 2023
- S. Liang, T. Guan, S. Yin, E. Krois, W. Chen, C. R. Everett, J. Drewes, T. Strunskus, M. Gensch, J. Rubeck, C. Haisch, M. Schwartzkopf, F. Faupel, S. V. Roth, Y.-J. Cheng, P. Müller-Buschbaum Template-Induced Growth of Sputter-Deposited Gold Nanoparticles on Ordered Porous TiO₂ Thin Films for Surface-Enhanced Raman Scattering Sensors MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- Y. Liang, T. Zheng, K. Sun, Z. Xu, T. Guan, F. A. C. Apfelbeck, P. Ding, I. D. Sharp, Y. Cheng, M. Schwartzkopf, S. V. Roth, P. Müller-Buschbaum *Real-Time Monitoring the Li⁺ Plating/Stripping Process in All-Solid-State Lithium Battery by Simutanepous Grazing-Incident Small-Angle/Wide-Angle X-ray Scattering* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 31 March 2023

- C. G. Lindenmeir, M. A. Reus, J. E. Heger, S. Wegener, C. R. Everett, S. Bernstroff, P. Müller-Buschbaum
 Optimization of Slot-Die Printed Organic Solar Cells
 MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- Y. Li, N. Li, S. Yin, C. Harder, Y. Bulut, A. Vagias, S. V. Roth, P. Müller-Buschbaum *Tunable mesoporous zinc titanate films via diblock copolymer-directed cooperative self-assembly and a sol-gel technique* DESY User meeting 2023, Hamburg, 25 – 27 January 2023
- Y. Li, N. Li, S. Yin, C. Harder, Y. Bulut, A. Vagias, S. V. Roth, P. Müller-Buschbaum Mesoporous hybrid films obtained via sol-gel route for photovoltaic application MLZ User Meeting, Munich, 04 – 05 December 2023
- Z. Li, C. Q. Ma, Peter Müller-Buschbaum Simultaneously Enhanced Performance and Stability of NFA Solar Cells with PETMP Interfacial Process
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 - 31 March 2023
- Z. Li, S. Vagin, K. Sun, X. Jiang, R. Guo, J. Zhang, M. Schwartzkopf, S. V. Roth, B. Rieger, P. Müller-Buschbaum
 Operando GIWAXS Observation of Green-solvent Based PBDB-TF-T1: BTP-4F-12 Organic Solar Cells with EH-P as Solid Additive
 MLZ User Meeting 2023, Munich, 04 05 December 2023
- P. Lovric, H. Zhong, P. Müller-Buschbaum Improved surface passivation of AgBiS2 quantum dots for photovoltaic applications DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- P. Lovric, H. Zhong, P. Müller-Buschbaum Improved surface passivation of AgBiS2 quantum dots for photovoltaic applications MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- G. Pan, S. Yin, S. Liang, L.F. Huber, T. Tian, Z. Li, L. Spanier, H. Zhong, C. Ehgartner, N. Hüsing, M. Schwartzkopf, S.V. Roth, P. Müller-Buschbaum *Morphology Control of Titanium Thin Films in a Low Temperature Process* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- G. Pan, T. Zheng, S. Liang, A. Buyan-Arivjikh, Z. Li, C. Ehgartner, N. Hüsing, M. Schwartzkopf, S.V. Roth, P. Müller-Buschbaum *Time-dependent morphology evolution of templated mesoporous titanium films* MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- D. Petz, P. Müller-Buschbaum, A. Senyshyn Lithium Distribution in 18650-type Li-ion batteries over its lifetime European Conference on Neutron Scattering ECNS 2023, Garching, 20 – 23 March 2023

- D. Petz, V. Baran, C. Peschel, M. Winter, S. Nowak, M. Hofmann, R. Kostecki, R. Niewa, M. Bauer, P. Müller-Buschbaum, A. Senyshyn *Fatigue induced composition and distribution changes of electrolyte and lithiated graphite in 18650-type lithium-ion batteries* Lithium Battery Discussions (LIBD) 2023, Arcachon, 18 23 June 2023
- D. Petz, V. Baran, C. Peschel, M. Winter, S. Nowak, M. Hofmann, R. Kostecki, R. Niewa, M. Bauer, P. Müller-Buschbaum, A. Senyshyn Aging-related changes in the Lithium Distribution of 18650-type Li-ion batteries MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- T. A. Pham, L. Wells, S. Seidlmayer, G. Ceccio, A. Cannavo, V. Jiri, P. Müller-Buschbaum, E. Figgemeier, R. Gilles *Neutron Depth Profiling Measurements to Study Lithiation Mechanism of LiAl Electrodes* European Conference on Neutron Scattering ECNS 2023, Garching, 20 – 23 March 2023
- T. A. Pham, R. Gilles, P. Müller-Buschbaum Influence of Al2O3 concentration in poly(propylene carbonate) based solid polymer electrolyte DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- T. A. Pham, L. Wells, S. Seidlmayer, G. Ceccio, A. Cannavo, V. Jiri, P. Müller-Buschbaum, E. Figgemeier, R. Gilles
 Investigation of Lithiation Mechanism of Al Electrodes with Neutron Depth Profiling and Complementary Methods
 Gordon Research Conference Neutron Scattering for a Sustainable Society, 25 30 June 2023
- T. A. Pham, S. Seidlmayer, I. Pivarnikova, S. Friedrich, A. Sommer, C. Didier, B. Maroti, L. Szentmiklosi, A. Jossen, R. Daub, V. Peterson, P. Müller-Buschbaum, R. Gilles *Operando neutron diffraction experiments in order to investigate the lithiation and ageing mechanism of industrial scale multi-layer 5 Ah pouch cells with LiNi0.8Co0.15Al0.05O2 cathodes and silicon anodes*

MLZ User Meeting 2023, 04 - 05 December 2023

• I. Pivarníková, S. Seidlmayer, M. Finsterbusch, G. Dück, N. Jalarvo, P. Müller-Buschbaum, R. Gilles

Sodium diffusion mechanism in NASICON solid electrolyte materials studied via quasi-elastic neutron scattering

Gordon Research Conference - Neutron Scattering for a Sustainable Society, 25 – 30 June 2023

- R. Qi, P Müller-Buschbaum, Y-J Cheng Less is more: tiny amounts of insoluble multi-functional microporous additive plays a big role in lithium secondary batteries MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- R. Qi, P Müller-Buschbaum, Y-J Cheng Less is more: tiny amounts of insoluble multi-functional microporous additive plays a big role in lithium secondary batteries
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023

- J. Reitenbach, C. Geiger, P. Wang, A. Vagias, R. Cubitt, D. Schanzenbach, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum *Fine-Tuning the Swelling Behavior of PNIPMAM Thin Films* — *The Case of Salt Addition* European Conference on Neutron Scattering ECNS, Garching, 20 – 23 March 2023
- L. V. Spanier, L. K. Reb, M. Böhmer, C. Dreissigacker, Z. Li, E. Anwander, A. Krifa, C. L. Weindl, G. I. Ivandekic, P. Müller-Buschbaum *Validating Novel Solar Cells in Space* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 31 March 2023
- L. V. Spanier, H. Balakrishnan, A. Hartschuh, P. Müller-Buschbaum Solvent Dependent Changes in Morphology and Degradation of PTQ-2F:BTP-4F Organic Solar Cells
 12th SolTech Conference 2023, Würzburg, 03 – 05 October 2023
- L. V. Spanier, H. Balakrishnan, J. E. Heger, M. Schwartzkopf, R. Houssaini, R. Guo, A. Hartschuh, S. V. Roth, P. Müller-Buschbaum *Green Solvents in Organic Solar Cells and their Influence on Performance and Stability* MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- K. Sun, R. Guo, L. F. Huber, M. A. Reus, J. Zhou, M. Schwarzkopf, P. Müller-Buschbaum *In-situ observation of growth mechanisms during printing of 2D perovskite film* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March
- T. Tian, S. Yin, S. Tu, A. Vagias, A. L. Oechsle, T. Xiao, S. Bernstorff, P. Müller-Buschbaum Insights into the morphology-structure-property relationship of mesoporous ZnO films during humidity sensing
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- S. Tu, T. Tian, T. Xiao, S. Yin, J. Heger, G. Pan, S. Hou, A. S. Bandarenka, M. Schwartzkopf, S. V. Roth, P. Müller-Buschbaum *Humidity Stable Thermoelectric Hybrid Materials for A Self-Powered Sensing System* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- P. Wang, C. Geiger, J. Reitenbach, A. Vagias, L. P. Kreuzer, S. Liang, R. Cubitt, V. Hildebrand, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum KCl modulated D₂O Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films
 European Conference on Neutron Scattering ECNS 2023, Garching, 20 – 23 March 2023
- P. Wang, C. Geiger, J. Reitenbach, A. Vagias, L. P. Kreuzer, S. Liang, R. Cubitt, V. Hildebrand, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum KCl modulated D₂O Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- S. A. Wegener, A. Buyan-Arivjikh, G. Pan, C. R. Everett, P. Müller-Buschbaum Rapid thermal cycling of perovskite solar cells
 PVSPACE-23 Conference, Munich, 05 – 07 July 2023

- L. Westphal, V. Baran, F. Porcher, P. Müller-Buschbaum, A. Senyshyn Long and short range order of Ethylene Carbonate
 MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- T. Xiao, S. Tu, T. Tian, W. Chen, W. Cao, S. V. Roth, P. Müller-Buschbaum Hybrid Energy Harvester based on Triboelectric Nanogenerator and Solar Cell
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- S. Xiong, C. Harder, B. Sochor, P. Müller-Buschbaum, S. V. Roth *Cellulose-based recyclable efficient solar cells by ultrasonic spray process* DESY Users' Meeting, Hamburg, 25 27 January 2023
- S. Xiong, M. Betker, B. Sochor, C. Harder, Y. Bulut, L. D. Söderberg, P. Müller-Buschbaum, S. V. Roth *Recyclable-refabricated efficient solar cells with cellulose-based materials* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- S. Xiong, B. Sochor, C. Harder, M. Betker, Y. Bulut, L. D. Söderberg, P. Müller-Buschbaum, S. V. Roth *Recyclable all-layer fully sprayed solar cell with cellulose-based material* MML Materials Workshop 2023, Jülich, 20 – 21 April 2023
- S. Xiong, B. Sochor, C. Harder, Y. Bulut, M. Betker, L. D. Söderberg, P. Müller-Buschbaum, S. V. Roth *Recyclable cellulose-based solar cells using fully sprayed all-layer materials* 18th Coatings Science International 2023, Noordwijk, Netherlands, 26 – 29 June 2023
- Z. Xu, G. Pan, Y. Xia, Y. Cheng, P. Müller-Buschbaum Design, Fabrication and Nano-Scale Characterization of Novel SEI Layers DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023.
- Z. Xu, G. Pan, Y. Xia, Y. Cheng, P. Müller-Buschbaum Design, Fabrication and Nano-Scale Characterization of Novel SEI Layers MLZ User Meeting 2023, Munich, 04 – 05 December 2023.
- W. Xu, L. Fietzke, R. A. Gumerov, F. Zheng, P. Zhang, M. Román-Quintero, D. Soloviov, I. Potemkin, R. Jordan, C. M. Papadakis
 Conformation of Star-like Molecular Brushes with Amphiphilic Diblock Copolymer Side Arms MLZ User Meeting 2023, Munich, 04 05 December 2023
- Y. Yan, P. Müller-Buschbaum Design, fabrication and application of PEO-based solid polymer electrolyte for all-solid-state lithium batteries
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- Y. Yan, Y. Liang, F. A. C. Apfelbeck, P. Müller-Buschbaum Operando study on structure-activity relationship between electrolyte components and electrochemical performance for all-solid-state lithium-ion batteries MLZ User Meeting 2023, Munich, 04 – 05 December 2023

- B. Yazdanshenas, F.A. Jung, S. Ariaee, D. Posselt, H. Amenitsch, C. Tsitsilianis, C.M. Papadakis *Tunable Morphologies in Charged Multiblock Terpolymers in Thin Film Geometry: effect of solvent vapor annealing* DPG Spring Meeting of the Condensed Matter Section 2023, 26 – 31 March 2023
- J. Zhang, P. Müller-Buschbaum Exploring the kinetics of pseudo-bilayer architectureCformation during sequential deposition via slot die coating
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- J. Zhang, P. Müller-Buschbaum Revealing the effect of solvent additive selectivity on formation kinetics in slot-die coated organic solar cells at ambient conditions MLZ User Meeting 2023, Munich, 4 – 5 December 2023
- P. Zhang, R. Steinbrecher, A. Laschewsky, P. Müller-Buschbaum, C. M. Papadakis *Azobenzene-containing thermo- and photoresponsive polymers* DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- P. Zhang, R. Steinbrecher, A. Laschewsky, P. Müller-Buschbaum, C. M. Papadakis *Azobenzene-containing thermo- and photoresponsive polymers* MLZ User Meeting 2023, Munich, 04 – 05 December 2023
- F. Zheng, P. A. Álvarez Herrera, J. Kohlbrecher, S. Da Vela, W.Xu, E. Melampianaki, A. Constantinou, T. K. Georgiou, C. M. Papadakis
 Injectable hydrogels from thermoresponsive tri- and tetrablock terpolymers European Conference on Neutron Scattering ECNS 2023, Garching, 20 23 Mar 2023
- F. Zheng, P. A. Álvarez Herrera, J. Kohlbrecher, S. Da Vela, W.Xu, E. Melampianaki, A. Constantinou, T. K. Georgiou, C. M. Papadakis *Thermoresponsive hydrogels from PEG-based terpolymers with increasing architecture complexity investigaed using scattering methods* 37th conference of European Colloid & Interface Society (ECIS) 2023, Naples, 03 – 08 Sep 2023
- T. Zheng, Y. Cheng, P. Müller-Buschbaum High-concentration Lithium-ion Electrolyte Overcomes the Challenges of High-temperature Lithium Batteries
 DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- H. Zhong, J. G. Ebel, W. Chen, K. Sun, S. V. Roth, P. Müller-Buschbaum Solvent Engineering of PbS Colloidal Quantum Dot Inks for Infrared Solar Cells e-conversion conference, 15– 18 October 2023
- H. Zhong, W. Chen, M. A. Scheel, L. Spanier, C. R. Everett, X. Jiang, S. Yin, M. S. Hörtel, J. Zhang, B. B. O. Seibertz, M. Schwartzkopf, S. V. Roth, P. Müller-Buschbaum *In-situ study of IZO growth for the application of PbS Quantum Dot Solar Cells* MLZ User Meeting 2023, Munich, 04 05 December 2023

10.4 Invited Talks at the Institute of Functional Materials and Soft Matter Physics Group

- Prof. Dr. Alessio Gagliardi, TUM Electrical and Computer Engineering, Munich Data Science Institute *Machine learning to investigate material properties* 18 January 2023
- Antonia Hager, LMU München, EPFL Lausanne What I learned from sailing boats and embryos on silicon wafers 8 February 2023
- Matthias Heck, Karlsruhe Institute of Technology Anionic Polymerization - a technique to obtain polymeric model systems 26 February 2023
- Dr. Pascal Kaienburgm University of Oxford, UK All-Small-Molecule Organic Solar Cells – electronic and microstructure properties
 6 March 2023
- Víctor Marrugat Arnal Causes of photoinduced halide segregation in wide-bandgap perovskite solar cell
 7 March 2023
- Prof. Chang-Qi Ma, Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO), Chinese Academy of Sciences (CAS)
 Printable Thin Film Organic/Perovskite Solar Cells: From Materials to Device Stability
 8 September 2023
- Prof. Guiseppe Portale, University of Groningen, The Netherlands Synthesis and structure-property of polymer electrolytes for fuel cell and battery applications
 5 June 2023
- Prof. Dr. Venkataraman Thangadurai, University of Calgary, Canada Li-stuffed Garnets for All-Solid-State Lithium Metal Batteries
 6 June 2023
- Prof. Vladimir Tsukruk, Georgia Institute of Technology, Atlanta, USA Bio-enabled Functional Nanomaterials: from Actuating Flexible Magnets to Photonically-Assisted Logic
 18 September 2023
- Prof. Robert J. Hickey, Pennsylvania State University, USA Polymer Actuators from Hierarchically Ordered Hydrogels 30 October 2023
- Prof. Chris McNeil, Monash University, Clayton, Australia Resonant Tender X-ray Scattering of Conjugated Polymer in Colloquium of Solid State Physics 9 November 2023

10.5 Funding

Deutsche Forschungsgemeinschaft:

- *Oberflächenmodifikation von Lithium-Batterie-Anoden mit multifunktionalen Block-Copolymeren* Grant Number: MU 1487/38-1 Project Leader: Prof. Dr. Peter Müller-Buschbaum
- In-Situ Untersuchungen von Keimbildungs- und Wachstumsprozessen Grant Number: MU 1487/39-1 Project Leader: Prof. Dr. Peter Müller-Buschbaum
- Amphiphile Selbstorganisation komplett nicht-invasiv orthogonal schaltbarer Blockcopolymere Grant Number: MU 1487/42-1, Project Leader: Prof. Dr. Peter Müller-Buschbaum Grant Number: PA 771/31-1, Project Leader: Prof. Christine M. Papadakis, PhD
- Einstellbare Morphologien in dünnen Filmen aus geladenen Multiblockpolymeren Grant Number: PA 771/30-1 Project Leader: Prof. Christine M. Papadakis, PhD
- Molekulare Bürsten mit amphiphilen thermoresponsiven Seitenketten von der Synthese über Lösungen zu selbtassemblierten Gelen
 Grant Number: PA 771/27-1, Project Leader: Prof. Christine M. Papadakis, PhD
- Teilprojekt Inorganic-organic hybrid photovoltaic solar cells using novel hybrid materials im GRK 2022: University of Alberta / Technische Universität München Internationale Graduiertenschule für Funktionelle Hybridmaterialien (ATUMS) der DFG IRTG-2022
 Project Leader: Prof. Dr. Peter Müller-Buschbaum

Bundesministerium für Bildung und Forschung:

• VIPR: Vielseitiges Software Framework zur Lösung inverser Probleme Teilprojekt: 5 Project Leader: Prof. Dr. Peter Müller-Buschbaum

Bundesministerium für Wirtschaft und Klimaschutz/ DLR:

• *Erprobung und Untersuchung neuartiger Solarzelltechnologien im Weltraum:* Project Leader: Prof. Dr. Peter Müller-Buschbaum

Bayerisches Staatsministerium für Wissenschaft und Kunst:

 Im Rahmen des Munich Institute of Integrated Materials, Energy and Process Engineering (MEP):
 Solar Tacknologiae Co. Hubrid (SolTack) – Foreshumoenstranerk TLUM color

Solar Technologies Go Hybrid (SolTech) - Forschungsnetzwerk TUM.solar Project Leader: Prof. Dr. Peter Müller-Buschbaum

 Im Rahmen des Munich Institute of Integrated Materials, Energy and Process Engineering (MEP)/ Netzwerk Regenerative Enegien: Aufbau eines interdisziplinären Netzwerks aus Lehrstühlen der Technischen Universität München und anderen Forschungseinrichtungen zur Förderung der Forschungsaktivitäten im Bereich der regenerativen Energien Project Leader: Prof. Dr. Peter Müller-Buschbaum

Others:

• Im Rahmen des Exzellenzclusters e-conversion:

e-conversion Principal Investigator: Prof. Dr. Peter Müller-Buschbaum

Impact of morphology on the polaron dynamics in polymer: nonfullerene blends for photovoltaic applications Principal Investigators: Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Reinhard Kienberger

Defect and energy level tuning of printed hybrid perovskite films for photovoltaic applications Principal Investigators: Prof. Dr. Peter Müller-Buschbaum, Dr. Johanna Eichhorn

11 The Chair

11.1 Staff



Chair:

Prof. Dr. Peter Müller-Buschbaum

Professor:

Prof. Christine M. Papadakis, PhD

Emerited Professor:

Prof. Dr. Winfried Petry

Fellows:

Dr. Michael Leitner Dr. Wiebke Lohstroh Dr. Jürgen Neuhaus Dr. Neelima Paul Dr. Apostolos Vagias Dr. Anatoliy Senyshyn

PhD Students:

Pablo Andres Alvarez Herrera Fabian Alexander Christian Apfelbeck Thomas Baier **Daniel Bonete-Wiese** Kevin Buducan Yusuf Bulut Altantulga Buyan-Arivjikh Lyuyang Cheng Christopher Reck Everett Marc Gensch Tianfu Guan Yingjian Guo Constantin Harder Julian Eliah Heger Tobias Hölderle Linus Huber Xinyu Jiang Xiongzhuo Jiang Zhaonan Jin David Kosbahn Morgan Le Dû Lixing Li Yanan Li Zerui Li Suzhe Liang Yuxin Liang Christoph Gernot Lindenmeir Anna Oberbauer Anna Lena Oechsle Guangjiu Pan Dominik Petz

Thien An Pham Ivana Pivarnikova Ruoxuan Oi Lennart Klaus Reb Julija Reitenbach Manuel Andree Reus Ronja Schoenecker Dominik Schwaiger Christian Schwarz Ali Semerci Kaltrina Shehu Lukas Viktor Spanier Kun Sun **Ting Tian** Suo Tu Peixi Wang Simon Wegener Christian Ludwig Weindl Lea Westphal Tianxiao Xiao Shuxian Xiong Wenqi Xu Zhuijun Xu Yingying Yan Bahar Yazdanshenas Jinsheng Zhang Peiran Zhang Feifei Zheng **Tianle Zheng** Huaying Zhong Yuqin Zou

Master Students:

Abdel Rahman Yousef Al-Falou **Emanuel Anwander** Tarek Azzouni Thomas Baier Mrinalini Chatterjee Sebastian Coen Jan Darsow Nikan Dehghan-Manschadi Jasper Guido Ebel Lorenz Fischer Kin Long Fong Mayank Garg Tannu Garg Kyriaki Nektaria Gavriilidou David Kosbahn Christoph Gernot Lindenmeir Petar Lovric

Lorenzo Nastasi Paraskevi Papadaki Antariksh Parichha **Timo Piecuch** Antonio Prior Fernández Amat Ni Lar Win Pyae Montserrat Roman-Quintero **Tobias Schöner** Martin Seiter Cagla Sipahi Mario Strahberger Hagen Tockhorn Faryal Talib Manuel Trigueros Galdòn Paul Aaron Weimer Daniel Wenczel

Bachelor Students:

Tim Bohnen Adrian Börngen Thomas Bullinger Eric Fuchs Julius Karliczek Yi Lyu Adrian Margieh Elisabeth Obermeier Lorenz Pech Josef Pflanz Matthias Quintern Kotone Tomioka Florian Troll Valentin Walbrunn Maximilian Wimbauer Ruodong Yang Leart Zuka

Student Assistants:

Jascha Fricker

Technical/Administrative Staff:

Reinhold Funer Andreas Huber Josef Kaplonski Carola Kappauf Marion Waletzki

11.2 Guests

- Watsapon Yimkaev, Chulalongkorn University, Bangkok, Thailand 05 August 2022 31 May 2023
- Prof. Dr. Alessio Gagliardi, TUM Electrical and Computer Engineering, Munich Data Science Institute *18 January 2023*
- Prof. Dr. Stephan V. Roth, DESY Hamburg, KTH Royal Institute of Technology, Stockholm, Sweden
 6/7 February, 4/5 July, 25/26 September 2023
- Dr. Matthias Heck, Karlsruhe Institute of Technology 26 27 *February* 2023
- Dr. Pascal Kaienburg, University of Oxford, UK 6 March 2023
- Víctor Marrugat Arnal 7 March 2023
- Prof. Alfons Schulte, University of Central Florida, USA 16 May – 26 May 2023
- Prof. Guiseppe Portale, University of Groningen, The Netherlands *5 June 2023*
- Prof. Dr. Venkataraman Thangadurai, University of Calgary, Canada 6 June 2023
- Prof. Chang-Qi Ma, Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO), Chinese Academy of Sciences (CAS) 8 September 2023
- Prof. Vladimir Tsukruk, Georgia Institute of Technology, Atlanta, USA 18 September 2023
- Prof. Robert J. Hickey, Pennsylvania State University, USA 30 October 2023
- Prof. Chris McNeil, Monash University, Clayton, Australia 9 November 2023
- Prof. Dr. André Laschewsky and René Steinbrecher, Universität Potsdam 14 December 2023

11.3 Graduations

• Accomplished PhD Theses

Kevin Buducan

Development of European manufacturing process for bare uranium-molybdenum monolithic foils

Marc Gensch

Investigation of the evolution from nanostructured metal clusters to thin metal films on diblock copolymer templates

Xinyu Jiang Active layer morphology in non-fullerene organic solar cells

Lennart Klaus Reb Perovskite and organic solar cells studied in space

Dominik Mathias Schwaiger

Internal dynamics and stability of bulk heterojunction films for application in organic photovoltaics

Christian Schwarz

Towards FRM II LEU conversion: viable barriers to prevent excessive radiation - induced interdiffusion in monolithic U-Mo fuel plates

Kaltrina Shehu

Coupled thermohydraulic and mechanic calculations for FRM II

Yuqin Zou *Functional ligands for optimization of device performance and stability of perovskite solar cells*

Accomplished Master Theses

Abdel Rahman Yousef Al-Falou

Optimization of the small angle neutron scattering instrument SANS-1 for advanced materials research: McStas simulations and construction of a compact high-T furnace

Emanuel Anwander Lightweight organic solar cells on flexible substrates for space applications

Thomas Baier *Two-step slot-die coated perovskite thin films from a y-Butyrolacto-based solvent system*

Sebastian Elias Leopold Coen

3-((2-(methacryloyloxy)ethyl)dimethylammonio)propane-1-sulfonate as hole blocking layer in organic solar cells

Nikan Dehghan-Manschadi

Degradation of organic solar cells in air in comparison to an inert nitrogen environment".

Jasper Guido Ebel

Solvent engineering of PbS colloidal quantum dot inks for infrared solar cells towards space application

Lorenz Fischer

Application of Modelica/TRANSFORM to system modeling of the molten salt reactor experiment

David Kosbahn

In situ study of perovskite quantum dot self-assembly in thin films during deposition by slot-die coating

Christoph Lindenmeir

Optimization of morphology and efficiency of slot-die printed perovskite solar cells

Timo Piecuch

Interfacial engineering via modifications of the electron blocking layer in PbS quantum dot solar cells

Montserrat Roman Quintero

Hydrogels from thermoresponsive triblock terpolymers for 3D bioprinting

Tobias Schöner

Investigation of the charge transport in ionic liquid post-treated poly(3,4-*ethylene dioxythio-phene*):*poly*(*styrene sulfonate*) *thin films with electrochemical impedance spectroscopy*

Cagla Sipahi

Performance and stability of high-efficiency organic solar cells

Mario Johannes Strahberger

Physical analysis of degradation effects on fast-charge capability of Lithium-Ion battery cells

Manuel Trigueros Galdòn

Characterization of neutron response of Ionization Chambers

Erik Walz

Diffraction based microstructural investigation of fcc alloys used in additive manufacturing

Paul Aaron Weimer AI applications in reactor physics

• Accomplished Bachelor Theses

Tim Bohnen Thin films for triblock copolymers with charged blocks

Adrian Börngen

Environmentally friendly perovskite solar cells

Thomas Bullinger Composite polymer electrolytes with LGPS for high voltage Lithium metal batteries

Philipp Hummelsberger Comparison of Different Cleaning Procedures of U-Mo Fuel Elements for IDB coating Preparatio

Julius Karliczek Data analysis of X-ray/neutron scattering images using Jupyter Notebook

Adrian Margieh Mechanosynthetical Lithiation of Graphite by Ball Milling

Elisabeth Obermeier

Umweltfreundliche Perowskitsolarzellen: Der einfluss der Vor- und Nachheiztemperatur auf heißschleuderbeschichtete Cs2AgBiBr3I3-Dünnfilme

Lorenz Pech

In situ photoluminenscence of 2D perovskite solar cells printed using the slot-die coater

Josef Pflanz

Air degradation process of green-solvent based organic solar cells

Matthias Quintern

Triboelectric nanogenerator-based material classification with machine learning assistance

Florian Rauscher

Diffusion behavior of U-Mo-Nb with AI cladding

Kotone Tomioka Synthesis and optical properties of multi-sized gold nanoparticles

Florian Troll W Coatings as Diffusion Barrier in the U-Mo/Al fuel system

Ruodong Yang Composite polymer electrolytes with LLZTO for high voltage Lithium metal batteries

Valentin Walbrunn Printed 2D perovskite solar cells

Maximilian Wimbauer Anisotropic breathing of Li-ion batteries studied by optical microscop

Leart Zuka Analysis of X-ray/neutron scattering data using Bornagain