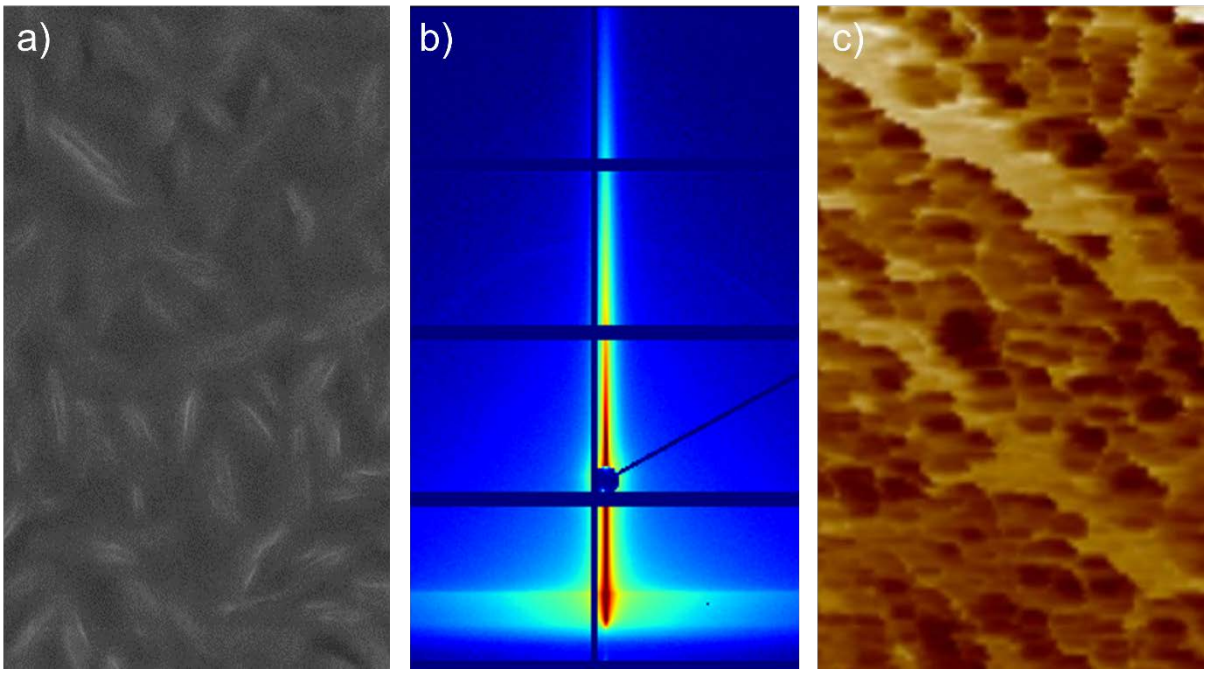
Biopolymer and biohybrid nanostructures

Apart from synthetic polymers, natural abundant biopolymers are in our scope of research. Analogical to their synthetic siblings, they show compatibility with common solution-processed thin film deposition techniques, e.g. spin-coating, solution-casting or spray-coating. Moreover, due to a higher potential in environmental-friendly processing based on aqueous solutions and tunable morphological and functional characteristics, biopolymeric systems play an interesting role in modern applications even beyond the scope of food industry. In combination with other material classes, biohybrid systems with combined properties can be achieved. These biohybrid systems improve and stabilize medical functions [1] and are promising agents in nanotechnologies, e.g. hybrid solar cells, nanopapers and supercapacitors. In general, functionality and application of bio-based systems are of crucial dependence on morphology, processing and wetting characteristics. To understand these criteria, real-space microscopy techniques, light scattering and reflectometry are crucial tools for probing the systems either in solutions or in film geometries. Especially the use of advanced X-ray or neutron scattering techniques reveals their inner constitution in a powerful manner. [2] Our main focus is to study the bio-based systems with respect to the mentioned criteria and the use of advanced measurement techniques, accessible at large-scale facilities like synchrotrons and neutron sources.



Biohybrid materials made of whey proteins and TiO_2. Structure investigation with a) electron microscopy b) grazing incidence small-angle X-ray scattering, and c) atomic force microscopy.

In previous studies we were focusing on casein systems. Müller-Buschbaum et al. demonstrated the facility to install homogenous and isotropic thin casein films out of aqueous solution by spin-coating [3]. Dynamic light scattering (DLS) was used to probe the polydisperse hydrodynamic diameter in solution. With increasing pH value, an increase in diameter was observed due to lower electrostatic repulsion. Atomic force microscopy (AFM) and grazing incidence small-angle X-ray scattering (GISAXS) confirmed this trend for the thin film geometry. This suggested a film of closely and dense packed casein micelles, not being disintegrated during spin-coating. The influence of film thickness was probed in terms of casein concentrations used for preparation. At higher concentrations, DLS and GISAXS again showed

good agreement in measured length scales, whereas at lower concentrations the micelle size decreased. This can be attributed to a rearrangement into a more compact non-equilibrium structure of low aggregation that is accessible and trapped in the dry film by spin-coating. In another work of Müller-Buschbaum et al., the structural dependence on calcium concentrations was examined [4]. For this, calcium was added to the aqueous solution in different concentrations below the critical value causing precipitation. Calcium ions change the interaction between two micelles, destabilizing the hydrophilic κ-casein shell of the micelles, and the attraction between individual micelles becomes feasible. This leads to an increase in radius upon aggregations in solution. GISAXS reveals that these aggregates correspond to closely packed micelles with smaller sizes and correlation distances in thin film geometry. Gebhardt et al. extended this work by investigating casein films with a superposed calcium gradient, as well as a superposed rennin gradient with GISAXS [5,6]. Both gradients showed a decrease in casein micelle diameters and a constant size of calcium particles upon higher concentrations of calcium and rennin, respectively. In addition, Gebhardt et al. showed that microfiltration of casein on silicon nitride micro-sieves caused fractionized micelles [7]. Larger micelles formed a hexagonal lattice with voids. These voids were consecutively filled by smaller micelles. Metwalli et al. probed the hydration of lactose-casein films at different D_2O vapor temperatures with grazing incidence small-angle neutron scattering (GISANS) [8]. The basic structural nature of casein micelles is not affected by the present lactose and micelles grown upon hydration and aggregation. Furthermore, a higher water uptake with elevating temperatures claims for a steady rearrangement of the film morphology due to continuous accessible new equilibrium states. Metwalli et al. additionally investigated the temporal evolution of the saturation profile after water ingress into casein films with neutron radiography [9]. They explained water ingress with two mechanisms: First, infiltrating of water into the voids between the micelles as the dominant driving force and second, a consecutive diffusion between the bulk water, the already infiltrated water and water initially stored in the casein micelles.

In addition to casein films, we investigated cellulose films in close collaboration with the Söderberg and Roth groups. Roth et al. prepared cellulose films by Langmuir-Blodgett (LB) transfer and observed lateral structural changes in the arrangement of cellulose parallel to the dipping direction of the LB coated samples, appearing within 100 µm. [10] Ultrathin regenerated cellulose films were prepared on silicon substrates by LB deposition and tested under various humidity conditions with AFM and GISAXS by Rossetti et al. [11] The regeneration of trimethylsilylcellulose in hydrochloric vapor caused bundles of rod-like regenerated cellulose with a dominant length scale of 50 nm. Surface and bulk sensitive GISAXS measurements below and above the critical angle of total reflection proved this length scale to be present in the whole film rather than restricted to the surface. Compared to LB transfer, spin-coating showed similar surface roughness and characteristic length scales. Ohm et al. focused on the investigation of spray-deposited enzymatic cellulose films with AFM and GISAXS [12]. They demonstrated the necessity for pulsed deposition to establish a linear layer growth with the number of spray pulses. Without intermediate drying steps, the film thickness saturated. Moreover, a hierarchically dependence of the total film morphology on the smallest cellulose building blocks claimed for a high impact by modifying the cellulose nanofibers (CNF). Spray-deposited ultrathin films of CNF with different surface charge densities were probed by contact angle measurements by Brett et al [13]. Results showed a linear tunability of surface free energy with increasing surface charge. In addition, surface-sensitive GISANS showed a reversable structural rearrangement from spherical to cylindrical domains, introduced by

swelling and drying in controlled humidity. This yields fundamental insights for further processing with polar solvents as used for instance in the field of organic photovoltaic.

Furthermore, the CNF films acted as a stabilizer for organic electrodes based on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) that are exposed to humidity [14]. Time-of-fight neutron reflectometry (TOF-NR) and GISANS revealed the water uptake and the morphology rearrangement with changing humidity in cycles from 5% to 95%, which are relevant conditions for device fabrication. The results show reversible changes on the nanoscale along with a reversible gain and loss in simultaneously measured conductivity at high and low humidity, respectively. In another work, Brett et al. demonstrated the thermal-induced growth of silver nanoparticles (AgNP) on CNF, forming a biohybrid film with a tunable optical bandgap promising for photovoltaic applications [15]. By comparing the deposition of AgNP on SiO_2 substrates, on CNF films, and mixed with CNF before deposition, Chen et al. showed that the functionalization of the AgNP benefit from a more uniform distribution in the CNF:AgNP biohybrid film than the pure AgNP deposited on glass substrates [16]. Besides biohybrid CNF:AgNP films, also TiO_2 nanomaterials benefit from CNF biotemplating. Chen et al. produced highly ordered 3D TiO_2 networks by combining oblique incidence spray deposition of CNF networks and subsequent atomic layer deposition of TiO_2 [17]. After thermal treatment, the tailored and crystalline TiO_2 morphologies showed improved sensitivity as a substrate for 4-mercaptobenzoic acid molecules in surface-enhanced Raman scattering.

Besides CNF a broad range of proteins rich in ß-sheets form silk and amyloid-like fibrils when denatured. After the unfolding of the protein, the exposed ß-sheets stack on each other, leading to fibril formation with a high aspect ratio and long-range order. Hierarchical assembly of the fibrils can lead to materials of improved mechanical strength and functionality. In close collaboration with the Lendel group, we found that in these materials, the fibril length distribution and solvent evaporation are mainly controlling the microstructure built up by fibrils obtained from whey proteins [18]. Together with the Yang group, Han et al. investigated the ß-sheet stacking mechanism on a molecular level at the air-water interface [19]. In contrast to conventional fibril growth, ß-sheets crystallize from an amorphous state to a polymorph core-shell nanostructure by chain relaxation when the surface tension at the air-water interface is lowered. Based on the major whey protein ß-lactoglobulin, Heger et al. investigated biopolymer templating in a low-temperature and water-based synthesis of foam-like TiO_2 film via spray deposition [20]. The results showed TiO_2 agglomerates in the porous fibrillar biomatrix, which sterically directs the crystal growth and film formation during drying. After biopolymer extraction, foam-like TiO_2 films with pearl-necklace nanostructure and a mixed brookite-anatase crystal phase were achieved.

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