Titania-based hybrid solar cells and solid-state dye-sensitized solar cells

Hybrid solar cells (HSCs) and solid-state dye-sensitized solar cells (ssDSSCs) have attracted high attention for solar energy conversion since they hold the promise to combine the advantages of both organic and inorganic materials. Among those are benefits such as low-cost synthesis, ease of production and nano-scale morphology with controllable structures through the inorganic scaffold. Especially, extensive studies investigated titania as an electron transport material in such HSCs and ssDSSCs. Until now, ssDSSCs based on interpenetrating titania networks showed high efficiencies above 10%. A simple schematic of titania-based HSC and ssDSSC device configuration is shown in Figure 1. For HSCs merely consisting of n-type inorganic materials and p-type conjugated polymers, solar light is harvested by p-type semiconducting polymers. In contrast, for ssDSSCs, the dye molecules are absorbing the photons.

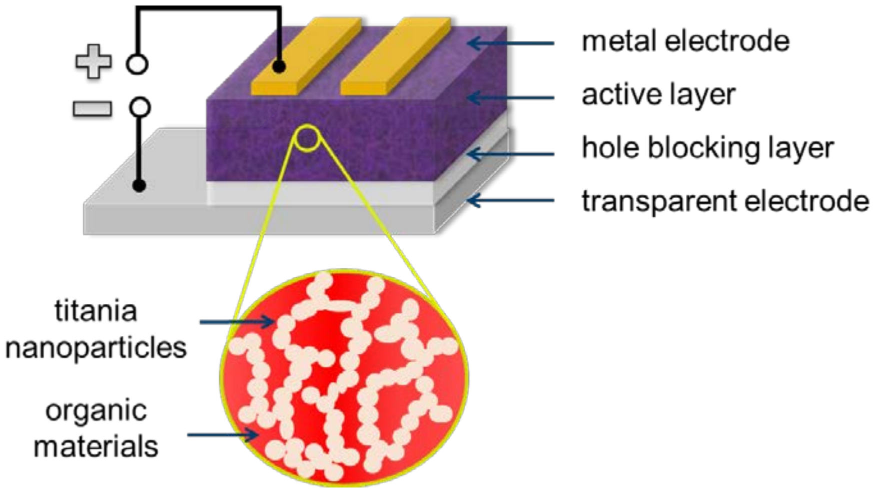

Figure 1. Schematic of titania-based HSC resembling the ssDSSC device configuration without having a dye at the interface between titania and the organic semiconductor

Moreover, the performance of these hybrid devices significantly depends on the morphology of the nanostructured titania films, since the morphology determines the volume-to-surface ratio, and thus the effective interface for reactions. In addition, the morphology tailors the charge-carrier transport routes, and thus influences electron-hole recombination probabilities. It was proven that the combination of sol-gel chemistry with an amphiphilic block copolymer as a structure-directing template is a promising route for fabricating mesoporous titania films. The obtained sol-gel solution can be directly deposited by various approaches, such as spin coating, doctor blading, spray coating or slot-die printing. There are numerous works reported by our group which focused on tailoring the titania morphology based on sol-gel chemistry and different deposition methods. For example, Song et al. used two types of the amphiphilic diblock copolymer PS-b-PEO with varied molecular weights to fabricate two kinds of mesoporous titania films, consisting of large-pores and small-pores respectively, and investigated the degradation of P3HT-titania-based solid-state dye-sensitized solar cells influenced by the different titania pore sizes [1]. Niedermeier et al. fabricated nanoporous titania films with additional superstructure in the micrometer range on large surface areas via combining block copolymer assisted sol-gel templating with wet-imprinting [2]. Recently Yin et al. investigated the influence of solvents and catalysts on the polymer template and the final titania film morphology [3]. Besides different concepts of polymer directed templating, different deposition methods were adopted, such as wet spray coating used by Song et al [4] and dry spray coating Su et al. [5], blade coating by Hohn et al. [6], and slot-die printing by Li et al [7]. For the latter we use a favorable route, slot-die printing, as an example to fabricate the nanostructured TiO_2 films on a large scale (Figure 2). In this approach, the diblock copolymer PS-b-PEO is firstly dissolved in 1,4-dioxane as a good solvent for both blocks, then followed by addition of a titania precursor (titanium tetraisopropoxide, TTIP) and a bad solvent (hydrochloric acid, HCl). Due to this so-called good-bad solvent pair, the amphiphilic diblock copolymer goes through microphase separation and self-assembly to form different morphologies, e.g. spherical micelles, cylindrical micelles, bicontinuous structures, lamellae, or vesicles. Moreover, the titania precursors prefer to coordinate into hydrophilic domains of the block copolymer via hydrogen bonds and therewith undergo hydrolysis and condensation reactions to form Ti-O bonds. Next, the sol-gel solution is deposited by the slot-die printing. Finally, after calcination, the polymer template is combusted and titania crystallizes. In our group, we successfully fabricated mesoporous titania films for an up-scaled solar cell fabrication.

Note that it is also of crucial importance to understand the kinetics of the structure evolution of deposited films since morphology formation is closely related with the conditions of film preparation. In order to have deep insights, we employed advanced synchrotron radiation based scattering methods to reveal the structure length-scale change in real-time and in situ. Song et al. performed an in-situ study of spray deposited titania photoanodes for scalable fabrication of ssDSSCs [8]. Hohn et al. studied the impacts of catalytic additive on spray deposited and nanoprous titania thin films via in situ grazing incidence small angle X-ray scattering (GISAXS) measurements [9]. These findings provide an essential piece to optimize the behaviors of HSCs and ssDSSCs.

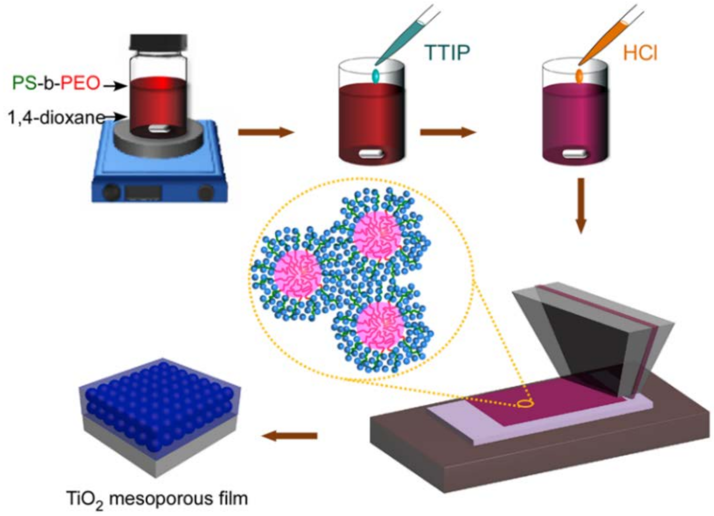

Figure 2. Schematic of a sol-gel chemistry combined with the slot-die printing to achieve nanostructured titania films

Another important part of the studies performed in our group is the investigation of the porosity of titania nanostructures and the filling degree of the solid hole-conductors into the mesoporous titania films via time-of-flight grazing incidence small-angle neutron scattering (TOF-GISANS). For example, Rawolle et al. used TOF-GISANS to investigate the filling degree of the hole-conducting polymer poly(3-hexylthiophene) (P3HT) into titania films and further compared different infiltration ways [10]. Märkl et al. reported the backfilling of mesoporous titania thin films with hole conductors of different sizes [11]. Besides, Song et al. investigated the titania morphology change under D_2O vapor by GISANS [12].

Interestingly, our group also focused on environmentally friendly hybrid solar cell fabrication routes to meet the advocacy of green technology. Körstgens et al. used the laser ablation process to deliver titania nanoparticles in water and built water-soluble titania-P3P6T hybrid solar cells [13]. Following this concept, one special interest but rarely reported branch of our current work is to investigate more environmentally friendly bio-based templating for titania nanostructures. Heger et al. used ß-lactoglobulin as a bio-template for low-temperature and water-based titania [14].

In future work, we address another main challenge, which is to increase the device efficiencies. Via incorporating nanoparticles like germanium nanocrystals into the titania films, we will further improve the properties or morphologies of titania films, thereby optimizing device performance. In addition, different dye sensitizers (dye molecules, quantum dots) or donor polymers which demonstrate a high efficiency in organic solar cells will be introduced in the device architecture to target a high efficiency. However, there are still many process parameters for fabricating solar cells which need to be optimized.

Featured publications:

(1) L. Song; W. Wang; S. Pröller; D. Moseguí González; J. Schlipf; C. J. Schaffer; K. Peters; E. M. Herzig; S. Bernstorff; T. Bein; et al: *In Situ Study of Degradation in P3HT-Titania-Based Solid-State Dye-Sensitized Solar Cells*; ACS Energy Lett. **2**, 991–997 (2017).

(2) M. A. Niedermeier; I. Groß; P. Müller-Buschbaum: *Structuring of Titania Thin Films on Different Length Scales via Combining Block Copolymer Assisted Sol–gel Templating with Wet-Imprinting*; J. Mater. Chem. A **1**, 13399–13403 (2013).

(3) S. Yin; L. Song; S. Xia; Y. Cheng; N. Hohn; W. Chen; K. Wang; W. Cao; S. Hou; P. Müller-Buschbaum: *Key Factors for Template-Oriented Porous Titania Synthesis: Solvents and Catalysts*; Small Methods **4**, 1900689–1900689 (2020).

(4) L. Song; W. Wang; V. Körstgens; D. Moseguí González; Y. Yao; N. K. Minar; J. M. Feckl; K. Peters; T. Bein; D. Fattakhova-Rohlfing; et al: *Spray Deposition of Titania Films with Incorporated Crystalline Nanoparticles for All-Solid-State Dye-Sensitized Solar Cells Using P3HT*; Adv. Funct. Mater. **26**, 1498–1506 (2016).

(5) B. Su; V. Körstgens; Y. Yao; D. Magerl; L. Song; E. Metwalli; S. Bernstorff; P. Müller-Buschbaum: *Pore Size Control of Block Copolymer-Templated Sol-Gel-Synthesized Titania Films Deposited via Spray Coating*; J. Sol-Gel Sci. Technol. **81**, 346–354 (2017).

(6) N. Hohn; S. J. Schlosser; L. Bießmann; S. Grott; S. Xia; K. Wang; M. Schwartzkopf; S. V. Roth; P. Müller-Buschbaum: *Readily Available Titania Nanostructuring Routines Based on Mobility and Polarity Controlled Phase Separation of an Amphiphilic Diblock Copolymer*; Nanoscale, **10**, 5325–5334 (2018).

(7) N. Li; L. Song; L. Bießmann; S. Xia; W. Ohm; C. J. Brett; E. Hadjixenophontos; G. Schmitz; S. V. Roth; P. Müller-buschbaum, *Morphology Phase Diagram of Slot-Die Printed TiO2 Films Based on Sol – Gel Synthesis*. Adv. Mater. interface **1900558**, 1–9 (2019).

(8) L. Song; W. Wang; V. Körstgens; D. Moseguí González; F. C. Löhrer; C. J. Schaffer; J. Schlipf; K. Peters; T. Bein; D. Fattakhova-Rohlfing; et al: *In Situ Study of Spray Deposited Titania Photoanodes for Scalable Fabrication of Solid-State Dye-Sensitized Solar Cells*. Nano Energy **40**, 317–326 (2017).

(9) N. Hohn; S. J. Schlosser; L. Bießmann; L. Song; S. Grott; S. Xia; K. Wang; M. Schwartzkopf; S. V. Roth; P. Müller-Buschbaum: *Impact of Catalytic Additive on Spray Deposited and Nanoporous Titania Thin Films Observed via in Situ X-Ray Scattering: Implications for Enhanced Photovoltaics*; ACS Appl. Nano Mater. **1**, 4227–4235 (2018).

(10) M. Rawolle; K. Sarkar; M. A. Niedermeier; M. Schindler; P. Lellig; J. S. Gutmann; J. F. Moulin; M. Haese-Seiller; A. S. Wochnik; C. Scheu; et al: *Infiltration of Polymer Hole-Conductor into Mesoporous Titania Structures for Solid-State Dye-Sensitized Solar Cells*; ACS Appl. Mater. Interfaces **5**, 719–729 (2013).

(11) R. S. Markl; N. Hohn; E. Hupf; L. Bießmann; V. Korstgens; L. P. Kreuzer; G.

Mangiapia; M. Pomm; A. Kriele; E. Rivard; et al: *Comparing the Backfilling of Mesoporous Titania Thin Films with Hole Conductors of Different Sizes Sharing the Same Mass Density*; IUCrJ **7**, 268–275 (2020).

(12) L. Song; M. Rawolle; N. Hohn; J. S. Gutmann; H. Frielinghaus; P. Müller-Buschbaum: *Deformation of Mesoporous Titania Nanostructures in Contact with D2O Vapor*; Small **14**, 1–7 (2018).

(13) V. Körstgens; S. Pröller; T. Buchmann; D. Moseguí González; L. Song; Y. Yao; W. Wang; J. Werhahn; G. Santoro; S. V. Roth; et al: *Laser-Ablated Titania Nanoparticles for Aqueous Processed Hybrid Solar Cells*; Nanoscale **7**, 2900–2904 (2015).

(14) Heger, J. E., Chen, W., Yin, S., Li, N., Körstgens, V., Brett, C. J., Ohm, W., Roth, S. V., Müller-Buschbaum, P., *Low-Temperature and Water-Based Biotemplating of Nanostructured Foam-Like Titania Films Using ß-Lactoglobulin*. Adv. Funct. Mater. 2113080 (2022).