Sponge-like structures for application in photovoltaics

BY JAN PERLICH1, GUNAR KAUNE1, MINA MEMESA2, JOCHEN S. GUTMANN2,3 AND PETER MÜLLER-BUSCHBAUM1,*

1Physik-Department LS E13, Technische Universität München, James-Franck-Strasse 1, 85747 Garching, Germany
2Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany
3Institut für Physikalische Chemie, Universität Mainz, 55099 Mainz, Germany

Large surface areas at an interface between two different materials are desired in many research fields where the interaction between these materials significantly affects the performance of the physical system. This behaviour is illustrated on sponge-like structures, which assign for such a high surface area, and demonstrate the development from bulk material to thin films and a variety of applications. The focus is on sponge-like nanostructures consisting of a network of aggregated titania nanoparticles applied in hybrid structures for photovoltaics. Examples based on a sol–gel process for the preparation of titania nanostructures in thin films, mimicking the sponge morphology, are shown. In general, titania films are widely used in photovoltaics, contributing to a large surface area available for interfacial reactions, e.g. charge carrier transfer routes. Interpenetrating networks with dimensions matching exciton diffusion lengths in the polymer component of a hybrid organic–inorganic photovoltaic structure are highly desirable. To characterize the fabricated morphology, atomic force microscopy and field-emission scanning electron microscopy are employed in real space. The advanced scattering technique of grazing-incidence small-angle X-ray scattering complements the characterization in reciprocal space. From the obtained results, the sponge-like morphology is verified, a physical description of the morphology with statistical relevance is constructed and the successful complete filling of the network is shown. According to this description, the presented sponge-like titania nanostructures are well suited for use in hybrid organic–inorganic solar cells.

Keywords: sponge-like structures; titania; sol–gel; organic photovoltaics; X-ray scattering

1. Introduction

Morphology in nature is a subject that has long fascinated. As with the morphology of a sponge, researchers try to replicate these natural morphologies in order to make use of its partially unique properties. In common use, the term sponge is applied to a rubber-like, flexible and bulky material with dimensions of several

* Author for correspondence (muellerb@ph.tum.de).

One contribution of 9 to a Theme Issue ‘Biomimetics II: fabrication and applications’.
centimetres interspersed with pores ranging from millimetres down to micrometres in size. The material has a high absorptivity and thus the ability to retain large amounts of a liquid. In this sense, natural sponge is actually the skeleton of a sea animal, consisting of a flexible network of spongin (type of collagen protein) filaments. In addition, the network of the spongin filaments forms a system of channels for the inflow of nutritive substances. In order to obtain a common natural sponge, the tissue of the sea animal is removed by a maceration process (physical decomposition by solvents) and washing, leaving just the spongin scaffold. These natural sponges are obtained from various species and available in different grades from soft to coarse.

Besides the function of giving a distinct shape to the sea animal, the flow functionality of the network is of major importance for its existence. Naturally, the system was designed by evolution to provide a rapid absorption of nutrients from the flowing substances into the surrounding tissue. This is realized most efficiently by the large surface area of the filament network.

However, the natural material has inspired industry to replicate synthetically the biomaterial with rubber-, plastic- and cellulose-based sponges, adapting to new material systems. The replicated sponges resemble nicely the size of the natural counterpart and the primary function is the enormous absorption capability of liquid substances provided by the porous structure, the so-called sponge-like morphology. Ultimately, for many applications, the reason for replicating this kind of morphology originates most probably not because of its function in a ‘real’ sponge, but because of its primary property of having a large surface area. Nevertheless, the authors’ intention is not to discuss the linguistic roots of the terms used, but rather focus on such a morphology being similar to a sponge.

Materials with a sponge-like morphology are found in a variety of shapes and sizes in many fields (Reeja-Jayan et al. 2008). Therefore, the replicating of the sponge-like morphology is inevitably accompanied by a change of the typical structure sizes by several orders of magnitude to adjust to a model system (Jinnai et al. 2002). For example, in medicine, polymeric sponge-like scaffolds are employed for tissue regeneration by cell transplantation acting as biodegradable porous substrate material with pore sizes ranging from 10 to 110 μm, providing adequate space for cell seeding (Lazzeri et al. 2007). The so-called microsponges with diameters up to 100 μm, pore sizes of 70–260 nm, total pore areas ranging from 24 to 125 m² g⁻¹ and porosities from 61 to 72 per cent are employed as drug delivery systems, e.g. providing a delay in drug absorption when a local delivery is required (Orlu et al. 2006). Furthermore, several applications use different metallic sponges with porosities ranging from approximately 50 to 70 per cent, e.g. from gold, silver, aluminium, etc., for catalysis, but also for filtering purposes (Banhart 2000; Jürgens et al. 2007). Other applications rely on micrometre-thick membranes with a sponge-like morphology and pore diameters of 2–7 nm (Albrecht et al. 2007). Conventional membranes mostly consist of polymeric materials, with the main purpose to separate substances in combination with a selective permeability. Various functionalities are realized by so-called hybrid material systems. In such a hybrid membrane system, the polymer or organic component contributes to the desired mechanical, thermal and chemical stability and the functionality is achieved by the incorporation of an inorganic component, e.g. titania (Yang & Wang 2006). Hence, the combination makes such a system highly desirable to meet some specific industrial requirements.
Besides these applications, there are various others which rely on sponge-like morphologies but in the form of a thin film on top of a solid support (Han et al. 2007). Hence, sponge-like layers of various materials can be confined in one dimension, namely thickness, down to a few nanometres depending on the application. Nevertheless, such layers can extend to areas of several square centimetres. One of the simplest ways to produce sponge-like surface structures is by using the microphase separation mechanism of block copolymers resulting in mesoporous polymer networks resembling a sponge-like morphology (Joo et al. 2006). However, sponge-like thin films of other materials are more attractive than purely polymeric films for applications such as catalysis, separations, environmental absorbents, sensors, electrodes and electrochromic or photovoltaic devices. The group of Wiesner has contributed significantly to the research on templating mesoporous material with the help of block copolymers (Finnefrock et al. 1999; Renker et al. 2004; Jain et al. 2005; Warren et al. 2007; Lee et al. 2008). For instance, they employ block copolymers as templating agents that form gyroid or bicontinuous morphology, respectively, hence resulting in bicontinuous or sponge-like morphology of the inorganic material.

Since there has been an increasing interest in light-harvesting systems, the focus here will be on sponge-like structures in photovoltaics. In this regard, after a brief introduction to the variety of applications in photovoltaics, the sol–gel process for the preparation of sponge-like titania nanostructures is presented followed by the results of structural characterization with different experimental techniques. The paper concludes with a summary of recent results.

2. Sponge-like structures in photovoltaics

So far, in photovoltaics, sponge-like morphologies solely appear in the form of thin films. The application of sponge-like purely polymeric structures as antireflective coatings is rather old and novel ideas are meanwhile rarely found (Joo et al. 2006). However, thin films with a sponge-like morphology are commonly employed as an electrode or a barrier layer for a specified type of charge carrier in a light-harvesting system. For this reason, the aim of preparing such layers is to achieve a morphology with a high surface area. As in most of the above applications, the performance significantly depends on the morphology of the structures because the morphology determines the surface-to-volume ratio and thus the surface available for interfacial reactions (Mohanta et al. 2007). Especially in photovoltaics, the morphology influences charge carrier transfer routes and therewith electron–hole recombination probabilities (Wang et al. 2004). Compared with the macroscopic characteristic length scales (e.g. pore size) of the natural sponge, for a photovoltaic system, the length scales have to be decreased by approximately five orders of magnitude, thus reaching nano-sized structures.

In conventional, purely inorganic solar cells, e.g. silicon solar cells, a nanostructuring is commonly used for reasons of light trapping and antireflective coatings consisting, for example, of nanostructured multilayers. The nanostructures are mainly simple ordered comprising lines and spaces or a saw-tooth pattern, which are fabricated by etching methods. Nevertheless, there are other approaches that are aimed at improving efficiency by introducing
additional layers, for example, porous silicon, where the improvement is assigned to antireflective and surface passivating effects. Although there are porous silicon layers, the present morphologies are not sponge-like.

In organic and hybrid solar cells, nanostructured layers are essential for the light-harvesting mechanisms. They are commonly applied in the dye-sensitized solar cell (DSSC), also known as the Grätzel cell (O'Regan & Grätzel 1991; Grätzel 1999). The DSSC consists of dye-sensitized nanostructured titania on a compact thin transparent semiconducting oxide (titania) and a multi-component redox electrolyte filled in between the polarized electrodes. The semiconducting titania (wide band gap of 3.18 eV (anatase)) is used solely for the charge carrier transport, whereas the photoelectrons are provided by the photosensitive dye (Paek et al. 2006). The actual charge separation occurs at the interface of the titania/dye/electrolyte. However, other semiconducting materials such as ZnO, SnO₂, CeO₂, SrTiO₃ and Nb₂O₅ could also do the task. For solar cell operation, the dye molecules have to capture a reasonable amount of the incoming light. Owing to their small size, the layer of dye molecules needs to be thick. In this respect, the distinct titania morphology also provides a large surface area serving as a scaffold to hold a large number of dye molecules. This results in an increase in the number of molecules for any given surface area. For the sponge-like morphology of the titania nanostructures, the surface area can be larger by a factor of 1000 compared with the area of a planar titania layer on top of the solid support, namely the FTO electrode.

A slight modification of the DSSC represents the so-called hybrid solar cell, where the electrolyte is replaced by a p-type conducting polymer acting as a hole-conducting and electron-blocking layer of the device (Lancelle-Beltran et al. 2006). The influence of the available surface area for a hybrid material system with a porous titania layer based on experimental data was reported by Feng et al. (2004). They found that the enlargement of the effective interface between conducting polymer and titania resulted in a significant improvement of the conversion efficiency. This matches nicely with the expectations resulting from the conclusions drawn from the working mechanism. Also Wang et al. (2004) observed a significant influence of the titania morphology on the energy conversion efficiency of DSSCs.

3. Sol–gel-templated sponge-like structures

(a) Sol–gel process of titania nanostructures

The common methods to prepare thin titania films are sputtering techniques (e.g. reactive DC magnetron sputtering), spray pyrolysis, chemical vapour deposition and spin coating or solution casting of commercially available titania nanoparticle solutions. Although these methods are combined with other processes to achieve a desired morphology, a variety of structures of the thin films is rather restricted. A further method is the preparation by a sol–gel synthesis in solution, which is then spin coated on the substrate (Kim et al. 2005). The applied procedure yields a variety of morphologies and hence can be adapted according to the required function.

In the literature, there are numerous publications about the fabrication of nanoscale titania materials with varied morphologies ranging from simple nanoparticles, nanorods and tubes, nanowires or lamellae to complex network
structures, as the sponge-like structures. Most of the applied preparation recipes use titanium inorganic salts or alkoxides as the titanium source. They are hydrolysed and condensed to form Ti–O networks in the presence of small-molecule surfactants or block copolymers as structure-directing agents. However, block copolymers have been widely used for templating non-titania systems (Finnefrock et al. 1999; Renker et al. 2004; Jain et al. 2005; Warren et al. 2007). Fewer results are reported for templating titania nanostructures with block copolymers (Smarsly et al. 2004; Sun & Gutmann 2004; Lee et al. 2008). Wang et al. (2005) used the diblock copolymer polystyrene-block-polyethyleneoxide (P(S-b-EO); $M_n=25.3$ kg mol$^{-1}$, weight ratio 75 : 25 (PS : PEO)) as a templating agent and obtained foam-like bicontinuous titania nanostructures. We also worked with P(S-b-EO) combined with sol–gel chemistry and obtained ordered titania nanocomposite films.

Recently, Cheng & Gutmann (2006) developed a simple recipe for the preparation of titania thin films with variable morphologies in a reproducible way. As the structure-directing agent, an amphiphilic diblock copolymer of P(S-b-EO) is used and a so-called ‘good–poor solvent pair’ induced phase separation in combination with sol–gel chemistry. The PEO is the minor constituent part of the P(S-b-EO) diblock copolymer. For the preparation, the diblock copolymer is first dissolved in 1,4-dioxane, which is a non-selective solvent, hence a good solvent for both blocks: the hydrophobic (PS) and hydrophilic (PEO) blocks. This is followed by the successive addition of concentrated HCl and titanium tetraisopropoxide (TTIP), which is the titanium source. The ingredients of the sol–gel chemistry are concentrated HCl, which is a poor solvent for the PS block, but a good solvent for PEO, hence a so-called selective solvent. As a result, the interfacial energy between the PS block and the solvents increases, leading to the formation of micelles in the solution. Their shape and size is mainly determined by the interfacial interactions between the PS domain and the solvents surrounding the PS domain, the interaction between the PEO domains as well as the degree of stretching of the PS domains. Therefore, the HCl and TTIP as components of the solution will influence the morphology of the micelles. In particular, TTIP can be incorporated into the hydrophilic PEO domains through coordination bonds. Moreover, the hydrolysis and condensation of TTIP turn the PEO domains chemically reactive and the titania species on the surface of the PEO domains are able to form covalent bonds with other titania species on the surface of neighbouring PEO domains. Since the dynamic behaviour forces the micelles to constantly fuse together and break apart, permanent covalent bonds of titania can be formed between neighbouring PEO domains. As a consequence of this complex force balance, various morphologies can be obtained by adjusting the weight fractions of 1,4-dioxane, HCl and TTIP. Via spin-coating (Schubert 1997) polymer nanocomposite thin films are obtained consisting of the organic diblock copolymer template with incorporated amorphous Ti–O functional parts. During the spin-coating process, a solvent evaporation-induced arrangement of the nanostructures inside the film takes place, which might result in an ordering of the nanostructures. Finally, the desired thin films of titania nanostructures are obtained via calcination, which burns away the polymer matrix and nanostructured crystalline titania thin films remain on top of the substrate (Sun et al. 2006). The results were summarized by a phase diagram of the titania morphologies representing the rich possibilities of the preparation of tailor-made morphologies (Cheng & Gutmann 2006; Perlich et al. 2007).
Preparation of samples

According to the specified recipe (Cheng & Gutmann 2006; Kaune et al. 2008), the asymmetric diblock copolymer P(S-b-EO) was used in the recent experiment and was purchased from Polymer Source Inc. (Montreal, Canada). The number average molecular weight is $M_n(PS)=19$ kg mol$^{-1}$ for PS and $M_n(PEO)=6.4$ kg mol$^{-1}$ for PEO with a polydispersity of the copolymer of $M_w/M_n=1.05$. The volume fraction or block ratio of PEO is $f_{PEO}=N_{PEO}/N=0.25$, resulting in an unperturbed microstructure of hexagonally ordered cylinders of PEO embedded in a PS matrix. The non-selective solvent for the preparation is 1,4-dioxane, and the ingredients for the sol–gel process are TTIP and concentrated HCl (37%).

The reported titania thin films were prepared on FTO-coated glass substrates (Solaronix, Switzerland) with a FTO layer thickness of approximately 490 nm. Before the preparation of the thin films, the substrates were rinsed with a detergent, then consecutively rinsed with deionized water, acetone, ethanol and isopropanol, and afterwards cleaned for 15 min in an ultrasonic bath with isopropanol. Finally, the substrates were plasma etched for 10 min in oxygen atmosphere ($p=1.5$ mbar) at 300 W.

The solution was prepared according to the following procedure: an amount of 0.0535 g of P(S-b-EO) was dissolved in 2.19 g of 1,4-dioxane. For the sol–gel process, 0.0115 g HCl and 0.1039 g TTIP were added slowly under constant stirring. After the complete addition, the stirring of the solution was continued for approximately 1 hour. The films were prepared on the pre-cleaned substrates by spin coating the solution for 30 s at 2000 g rotational speed under ambient conditions (temperature 27.3°C, relative humidity 25%; Schubert 1997). The obtained polymer nanocomposite thin films were calcined for 4 hours at a temperature of 400°C in air with a heating rate of 6.25°C min$^{-1}$. After calcination, the samples were left inside the furnace to cool down. By this final step, the amorphous titania nanostructures were converted to anatase phase, which was determined by X-ray diffraction experiments (Cheng & Gutmann 2006).

Ultimately, the selected amounts of the sol–gel components TTIP and HCl and hence the selected perturbation of the ideal cylindrical morphology yield the formation of sponge-like titania structures.

4. Morphological characterization of surface structures

(a) Real-space analysis

The most natural way to investigate surface structures of thin films is by scanning electron microscopy (SEM) as well as atomic force microscopy (AFM). Since the investigations are in real space, both techniques provide a direct image of the surface, hence making an interpretation much easier than any characterization method in reciprocal space, such as scattering experiments. Furthermore, AFM and SEM are performed in a laboratory and do not require large-scale facilities for the experiments. Field-emission SEM (FESEM) produces high-resolution images of the surface structures as a rapid imaging technique. The characteristic three-dimensional appearance of the recorded images provides an evaluation of the morphology and, in the employed top-down mode, lateral
structure sizes are extracted. AFM produces topographic images comprising structure heights and widths, as well as related statistical information. Both techniques are available in a variety of modes in order to adapt to the needs of a certain structural characterization and provide resolution on a nanometre scale. However, because only a very small area of the surface is probed by both methods, the extracted quantities have a very limited statistical relevance.

(i) *Field-emission scanning electron microscopy*

SEM images were obtained with a field-emission SEM (Zeiss LEO 1530 Gemini) operated at an accelerating voltage from 1 to 3 kV and at low working distances from 1 to 3 mm. FESEM is employed for a rapid characterization for a simple qualitative judgement of the surface structures. However, from the obtained high-resolution images, lateral structure sizes as well as correlation lengths can be extracted with statistical relevance by FFT pattern analysis.

The FESEM image presented in figure 1 shows nicely the sponge-like morphology of the titania nanostructures. The structure is formed by single nano-sized titania particles linked together, resulting in a random arrangement of holes and cavities. The holes have a roundish shape and most are merged together forming bigger holes with an irregular shape. The in-plane diameter of the holes ranges from 20 to 60 nm and some irregularly shaped holes reach lateral sizes up to 100 nm. The average diameter is approximately 35 nm. The application of the sponge-like titania thin film as a functional layer in a solar cell has to fulfil the precondition of a complete filling of the holes and cavities with the conductive polymer in order to create a large interface between them. As illustrated recently by the studies of Kaune et al. (2008) of titania:PVK
(poly(\(N\)-vinylcarbazole)) nanocomposite thin films, the size of the holes in the sponge-like nanostructure matches nicely with the extension of the PVK chains used having a radius of gyration \(R_g\) of approximately 20.6 nm. Hence, the PVK chains can easily penetrate the sponge-like titania network when appropriate wetting conditions are installed. From the image brightness also the larger size structure can be deduced by superimposing the sponge-like thin film as a whole. Hills are indicated by the brighter spots and the hilly surface originates from the replicated prominent surface structure of the FTO substrate. The FFT pattern analysis yields a structural length of approximately 70 nm derived from the radius of the central spot and is attributed to the mean distance of the larger sized holes of the sponge-like structure.

(ii) Atomic force microscopy

The local surface structure is investigated using AFM in non-contact mode using an Autoprobe CP research instrument at room temperature in ambient air (Binning et al. 1986). The non-contact mode minimizes tip-induced structure as well as damage of the soft polymer surface; tapping mode is employed to obtain phase contrast from different materials. The cantilevers used are gold-coated silicon cantilevers (Ultragold cantilevers) with a resonance frequency from 60 to 80 kHz. The tip has a high aspect ratio and an asymptotic conical shape with a radius of curvature of approximately 10 nm. In the non-contact mode, the lateral resolution of the tip is approximately 1–5 nm.

The recorded micrographs consist of 256 lines scanned at rates from 0.2 up to 1.0 Hz. For a detailed characterization, scans with different ranges from 0.5 \(\mu\)m \(	imes\) 0.5 \(\mu\)m to 8 \(\mu\)m \(	imes\) 8 \(\mu\)m are typically recorded. For a further analysis of the micrographs, image processing software (IP v. 1.3) was used to calculate the root-mean-squared (r.m.s.) roughness of the sample surface. The r.m.s. roughness represents the deviation of the individual local heights from the mean height of the scanned surface, hence statistically describes the structures perpendicular to the surface (Russ 1994).

The scanned micrographs of the sample surface are shown in figure 2, with scan sizes ranging from 0.5 \(\mu\)m \(	imes\) 0.5 \(\mu\)m to 2 \(\mu\)m \(	imes\) 2 \(\mu\)m. The topographical AFM images clearly show the porous structure of the sponge-like titania thin film.
Especially in the $2 \mu m \times 2 \mu m$ micrograph, the hilly surface similarly found in the FESEM image is clearly recognizable. Again, the bright spots are the hills and dark areas the valleys replicating the prominent FTO surface structure and resulting in the large-scale structure of the titania thin film.

For the statistical structure information perpendicular to the sample surface, the r.m.s. roughness was obtained from the micrographs. The r.m.s. roughness increases from $38.9 \AA$ for the $0.5 \mu m \times 0.5 \mu m$ scan to $45.1 \AA$ for the $2 \mu m \times 2 \mu m$ scan. The increase simply results from the fact that the large-scale structure comes into play considerably.

(b) Reciprocal space analysis: grazing-incidence small-angle X-ray scattering

(i) A short introduction to GISAXS

Grazing-incidence small-angle X-ray scattering (GISAXS) complements the structural characterization in reciprocal space by assessing the morphology of the titania nanostructures (Müller-Buschbaum 2003; Müller-Buschbaum et al. 2003, 2007; Lee et al. 2005; Müller-Buschbaum & Stamm 2008). In addition to high surface sensitivity, X-rays as a probe enable one to simply look inside and obtain information of structures hidden inside the thin film, which are mostly invisible to AFM and FESEM, but of high interest for application in photovoltaics. The increasing use of the GISAXS technique is also because of the fact that it is a non-destructive, non-contact structural probe where no special sample preparation is required. Therefore, GISAXS is suitable for in situ experiments, e.g. kinetic investigations devoted to structural development as a function of time. Further arguments for its employment are the material selectivity and excellent sampling statistics, because it averages over macroscopic regions to provide information on a nanometre scale, in contrast to AFM and FESEM. However, the real-space techniques are still considered as important complementary techniques providing the order of magnitude of the correlation length of the surface structure as well as necessary input for the modelling of GISAXS data.

The basic experimental set-up of the scattering geometry is shown schematically in figure 3. The two-dimensional detector records only the intensity reflected above the sample surface. For measurements, the coordinate system is chosen in such a way that the $x-y$-plane is defined by the sample surface, with the $x$-axis oriented along the direction of the X-ray beam. Consequently, the $z$-axis is perpendicular to the surface. For this case,

\begin{align*}
q_x &= 2\pi(\cos \psi \cos \alpha_f - \cos \alpha_i)/\lambda, \\
q_y &= 2\pi(\sin \psi \cos \alpha_f)/\lambda, \\
q_z &= 2\pi(\sin \alpha_i + \sin \alpha_f)/\lambda
\end{align*}

\[ (4.1) \]

\[ (4.2) \]

\[ (4.3) \]

denote the components of the wavevector $\mathbf{q}$.

In the case of specular scattering, with $\alpha_i = \alpha_f$ and $\psi = 0$, for the components of the wavevector $q_x = q_y = 0$ and $q_z \neq 0$ hold, hence sampling depth sensitive information only. For the off-specular scattering, the lateral component is $q_{||} = (q_x, q_y) \neq 0$, probing the lateral structure of the sample surface (e.g. geometry,
size distribution and spatial correlation). For a rapid analysis, two distinct cuts are performed instead of handling the complete two-dimensional scattering pattern: vertical slices at constant $q_y$ (detector cuts) and horizontal slices at constant $q_z$ (out-of-plane cuts or GISAXS cuts) with the naming referring to the sample surface (Müller-Buschbaum 2003; Müller-Buschbaum et al. 2007). To improve statistics, the intensity is integrated over a few detector lines. To model the out-of-plane cut, in the framework of the ‘effective surface’ approximation, the differential cross section according to the distorted-wave Born approximation can be written as

$$
\frac{d\sigma}{d\Omega} = \frac{C\pi^2}{\lambda^4} (1 - n^2)^2 \left| T_i \right|^2 \left| T_f \right|^2 F(q) \propto F(q),
$$

(4.4)

where $C$ is the illuminated surface area; $\lambda$ is the wavelength; $n$ is the refractive index; $T_{i,f}$ represents the Fresnel transmission function; and $F(q)$ is the diffuse scattering factor (Salditt et al. 1995). Since the incidence and exit angle are fixed, the diffuse scattering factor is directly probed, and in the case of $N$ identical and centrosymmetric objects with a random orientation, the approximation

$$
F(q) \propto NP(q)S(q)
$$

(4.5)
holds (Naudon et al. 2000), where \( P(q) \) is the form factor of the individual objects and \( S(q) \) is the structure factor giving the correlation of these objects with each other.

(ii) GISAXS on sponge-like titania nanostructures

The recent measurements were performed at the synchrotron beamline BW4 of the DORIS III storage ring at DESY HASYLAB (Hamburg, Germany; Roth et al. 2006). Synchrotron radiation with a wavelength of 0.138 nm and a typical sample-to-detector distance of approximately 2 m were used. The beam divergence in and out of the plane of reflection was set by two entrance cross slits and a moderate microbeam was achieved by the use of beryllium compound refractive lenses yielding a beam size of approximately \( 80 \times 40 \mu \text{m}^2 \) (horizontal \( \times \) vertical). In addition, a mostly evacuated beam pathway was used. For the measurement, the sample was placed horizontally on the goniometer. The incidence angle was fixed to \( \alpha_i = 0.487^\circ \), which further results in a footprint of the beam on the sample surface of approximately 4.7 mm in length. The incidence angle is well above the critical angle \( \alpha_c \) of the investigated titania nanoparticles (0.250\(^\circ\)). For this reason, the Yoneda peak and the specular peak are very well separated on the detector, which is a two-dimensional detector (MarCCD 165 by Mar Research, 2048 \( \times \) 2048 pixels). In order to block the high intensity from the direct beam, a diode beam stop was used in front of the detector. In addition, two further beam stops were employed: a movable point-like beam stop to block the specularly reflected beam and a rod beam stop blocking the intensity in the scattering plane on the detector.

Figure 4 shows the recorded two-dimensional scattering image of the sponge-like titania nanostructures for photovoltaic applications. Qualitatively, the broad scattered intensity resembles a nearly semicircular shape. For further quantitative analysis of the two-dimensional scattering images, cuts were taken along the \( q_z \) direction at \( q_y = 2.85 \times 10^{-5} \text{ Å}^{-1} \) (vertical cut) and along

\[ q_y \]

\[ \psi \]
the \( q_y \) direction at \( q_z = q_c(\text{TiO}_2) \) (horizontal cut). Since the rod beam stop employed shields the high Yoneda intensity along the scattering plane, the vertical cut had to be taken slightly off the centre of the two-dimensional scattering pattern, whereas the given \( q_y \) value corresponds to \( \psi = 0.0004^\circ \). The vertical or the so-called detector cut is presented in figure 5. It has to be noted that the rod beam stop is used in order to realize longer counting times, which enables one to resolve features appearing at large \( q_y \) values resulting from small lateral structures that are typical for sponge-like morphologies. The strong decay of the intensity from the Yoneda peak towards higher \( q_z \) can be attributed to the FTO layer roughness (Müller-Buschbaum et al. 2007). Furthermore, the inset of figure 5 reveals a prominent splitting of the Yoneda peak, where the positions of the critical angle of titania and FTO are marked by the arrows. The visible intensity modulation corresponds to conformal roughness of the titania layer on top of the FTO substrate.

Figure 5. Detector cut of the two-dimensional scattering pattern at a horizontal angle \( \psi = 0.0004^\circ \) with respect to the scattering plane. The scattering intensity is plotted versus the \( q_z \) component of the scattering vector. The inset shows a zoom-in of the Yoneda peak, where the positions of the critical angle of titania and FTO are marked by the arrows. The visible intensity modulation corresponds to conformal roughness of the titania layer on top of the FTO substrate.
between adjacent minima is \((167 \pm 5)\) nm for the titania thin film. Therefore, the correlated thickness can be attributed to the titania layer, and it can be concluded in accordance with the AFM and FESEM images that the thin titania film follows the FTO topography partially and replicates the FTO surface structure. From the device point of view, the findings verify the absence of gaps, which provides an efficient direct contact of the electrode and the semiconducting layer for charge carrier transport.

The lateral structure information of the sponge-like morphology is extracted from the out-of-plane cut in figure 6. The cut shows a single characteristic peak marked by the arrow. To extract the corresponding characteristic length in real space, the cut is modelled assuming a Lorentzian-type distribution function to account for statistical deviations and the resolution function. The assumption relates to a single structure peak corresponding to the nearest-neighbour distance \(d\). A characteristic length \(d\) of 70 nm was obtained, which is related to the mean distance of the holes in the sponge-like titania nanostructure. The result agrees very well with the AFM and FESEM images, where an equal length was found in the FFT analysis. The extraction of a single length scale for such a complex structure is simply caused by the fact that only this length scale repeats itself over the probed area and therefore always gives a contribution to the same scattering feature, denoted as the most prominent length scale. All other dimensions of the porous structure, such as hole or pore sizes, exhibit a very large size distribution resulting in the broad intensity distribution in the two-dimensional scattering pattern. Ultimately, the sponge-like titania nanostructures exhibit a minor ordering or regularity. However, it has to be taken into consideration that GISAXS probes the entire depth of the titania layer, whereas AFM and FESEM provide only surface structure information.

Figure 6. Double-logarithmic plot of the titania out-of-plane cut (symbols) of the two-dimensional intensity as a function of the \(q_y\) component of the scattering vector. The solid line is the mathematical fit for determining the most prominent in-plane length scale of the sponge-like structure. The feature representing the characteristic hole structure is marked by the arrow. The dashed line indicates the resolution limit of the GISAXS experiment.
Finally, by combining the local structure information of AFM and FESEM with the insight gained by GISAXS, it can be concluded that the observation of a sponge-like morphology is not only limited to the investigated spots, but also extends over square millimetres, hence providing a continuous sponge-like titania structure. As stated in §1, this is one important prerequisite for the application in photovoltaics, because it provides the porous scaffold that interpenetrates with the conducting polymer, giving rise to large interfacial areas, and thus efficient transport of charge carriers.

5. Summary

The aim of this paper was to present a brief overview of the recent research on the preparation and applications of materials possessing sponge-like morphologies. The strong interest in this field of research was illustrated by an original contribution from our group and collaborators focusing on sponge-like titania nanostructures for hybrid organic–inorganic photovoltaics. Successful preparation has been accomplished by the combination of a diblock copolymer, acting as a structure-directing agent, with sol–gel chemistry, which provides the titanium source and enables the selective incorporation into the block copolymer. By calcination, the final titania thin film having a sponge-like morphology and an anatase crystalline phase is obtained. The distinct morphology was characterized using AFM and FESEM as common methods on hand in most research laboratories. Nevertheless, these techniques are very local spatial probes and only a few exemplar spots can be probed, and hence results are of less statistical significance. The advanced scattering technique of GISAXS has been introduced as a complementary method to enable the non-destructive exploration of the interior of the thin film and thus providing access to buried structures. In contrast to AFM and FESEM, scattering yields an increase in statistical significance due to the significantly larger probed surface.

From the obtained results, it has been concluded that the prepared sponge-like titania thin films are very well suited for application in hybrid organic–inorganic photovoltaics. The obtained pore sizes match the chain lengths of potential conducting polymers, enabling the complete filling of the pores and the thin film follows nicely the surface roughness of the electrode material providing a gap-free contact.

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG) in the priority programme SPP1181 ‘NanoMat’ (MU 1487/5 and GU 771/2).

References


Phil. Trans. R. Soc. A (2009)


