

Crystalline titania network structures prepared in a low temperature-route

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Titania nanostructures are highly interesting for many applications because of their photoelectric and photochemical properties. In its crystalline polymorphs anatase or rutile, titania constitutes a semiconductor with a band gap of 3.0 and 3.2 eV, respectively. Tailoring of the nanostructures is of high importance, because for many applications, for example in photocatalysis or photovoltaics, a high surface-to-volume ratio is needed. As a consequence many different experimental routes towards titania nanostructures were reported. One frequently used approach is based on the combination of sol-gel chemistry with a structure directing template, which consists of a micro-phase separated block copolymer. Based on such approach we have shown recently, that the quality of the titania nanostructure can be significantly improved further by a combination with microfluidics [1]. However, typically high temperatures have to be applied in this approach, which is limiting it to solid supports. To make use of flexible supports, which cannot stand high temperatures, a low temperature route is desired.

A novel titania precursor, an ethylene glycol modified titanate (EGMT), allows for the tailoring of crystalline titania nanostructures at low temperatures [2]. This precursor is used in combination with an amphiphilic diblock copolymer, poly(styrene-*block*-ethylene oxide) [P(S-*b*-EO)] to tailor the nanostructures of the resulting titania thin films below 100 °C. After dissolving the polymer in a good solvent for both polymer blocks, a micro-phase separation is initiated by the addition of HCl. Furthermore, the precursor is added, and the HCl starts the sol-gel reaction as well, where the resulting titania coordinates to the PEO block of the block copolymer. Finally, the polymer template is removed by means of a solvent treatment after structure direction.

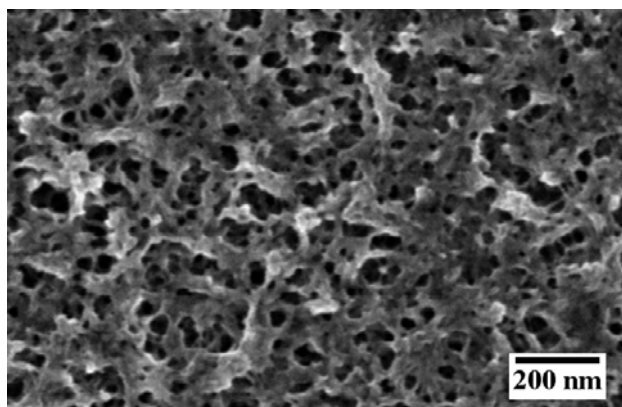


Figure 1: SEM image of the nanostructured surface of the titania film after polymer extraction. A porous network structure with pore sizes in the range of 25 to 30 nm is observed.

Structural investigation of the resulting titania nanostructures was performed with grazing incidence small angle x-ray scattering (GISAXS) at the beamline P03 at the storage ring PETRA III. The synchrotron radiation with a wavelength of 0.0941 nm and a beam size of 20×40 μm² (vertical × horizontal direction) was impinging on the sample under an angle of 0.39 °, illuminating the sample with a footprint of 2.95 mm×40 μm. The scattered radiation was detected on a Pilatus 300k detector with 487×619 pixels of a pixel size of 172×172 μm² and an active area of 83.8×106.5 mm² with no read-out noise at a sample-to-detector distance of 2.18 m. The related

crystalline structure was investigated with grazing incidence wide angle x-ray scattering (GIWAXS) at the beamline BW4 at the storage ring DORIS III [3]. An incident angle of 0.21° was used to illuminate the sample with the synchrotron radiation of a wavelength of 0.138 nm and with a beam size of $23 \times 36 \mu\text{m}^2$ (vertical \times horizontal direction). The footprint of the synchrotron beam on the sample was $6.22 \text{ mm} \times 36 \mu\text{m}$. The scattered signal was detected on a MarCCD detector with 2048×2048 pixels of a pixel size of $79.1 \times 79.1 \mu\text{m}^2$ at a sample-to-detector distance of 107 mm.

Figure 1 shows scanning electron microscopy (SEM) image of the titania nanostructure under investigation (after polymer extraction), revealing the nanoporous titania network structure with pore sizes of 25 to 30 nm at the surface. The GISAXS data of the corresponding sample are shown in figure 2 (a). The strong scattering at the position of the Yoneda peak, which reveals the material composition, shows the presence of titania nanostructures in the whole volume of the film and not just at the film surface.

As can be seen in figure 2 (b), the GIWAXS measurements reveal the crystallinity of both the titania film and the PEO block of the templating block copolymer [2]. Both the crystallites of PEO and titania in the rutile phase are smaller than 5 nm, as can be calculated from the fitted peak widths. The small remaining PEO crystallites indicate that still some polymer is left inside the titania nanostructures after polymer extraction by a solvent, but the crystallites are small enough so that they are not disadvantageous for applications. The small crystallite size of the titania is due to the confinement within the pore walls of the network structure. As the crystallites are not growing too large, the network structure remains intact and is not distorted by the crystallites.

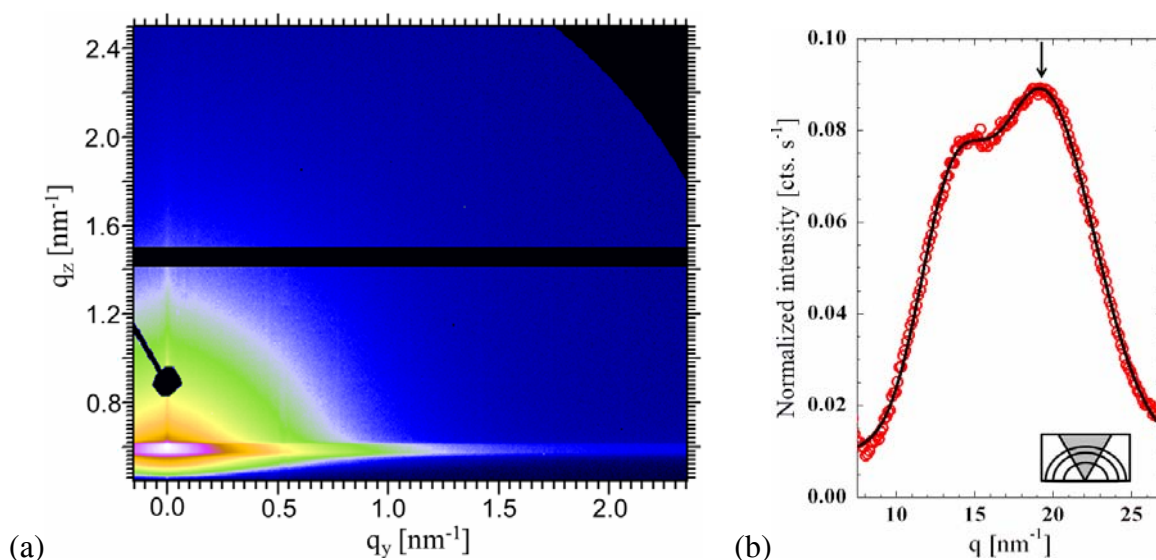


Figure 2: GISAXS data as measured at the beamline P03 (a) and GIWAXS data as measured at the beamline BW4 with the corresponding fit to the data (b) of the titania sample prepared at temperatures below 100°C . The GIWAXS signal was integrated around the sample horizon from 60° to 120° , as indicated in the inset in (b), the rutile peak of the titania is marked with an arrow.

In conclusion, a novel route to titania network structures at low temperatures is presented. The resulting titania structures show a defined crystallinity, as probed with GIWAXS. The nanostructures are investigated with SEM on the surface and with GISAXS in the bulk of the thin film.

References

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