

Combination of Micro-Fluidics and Sol-Gel Templating for Nanostructuring of Titania Thin Films for Photovoltaic Application

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Introduction

Nanostructured titania is of great interest because of its huge application potential in sensors, biotechnology, photocatalysis and inorganic-organic hybrid photovoltaics. The so-called dye-sensitized solar cell (DSSC) is one promising candidate to tackle tomorrow's energy problems. The DSSC requires a titania film with a large surface-to-volume ratio.[1] Sol-gel chemistry templated with a structure-directing micro-phase separation of an amphiphilic diblock copolymer solution results in a control of the structure on the nanoscale. Mostly this structure is not very well ordered because of the fast reaction kinetics. Micro-fluidic cells, where small quantities of fluids can be controlled precisely, are widely used to control reaction kinetics.[2] Thus the combination of the two concepts, polymer templated sol-gel chemistry and micro-fluidics is very promising to get better ordered titania nanostructures.[3]

Sample preparation

The amphiphilic diblock copolymer poly(dimethyl siloxane) *-block-* methyl methacrylate poly(ethylene oxide) [PDSM-*b*-MA(PEO)] has been previously used to create hierarchically structured porous titania films.[4] This polymer is dissolved in tetrahydrofuran and 2-propanol, which are good solvents for both polymer blocks. Hydrochloric acid and titanium isopropoxide are added in a well-defined way controlled by a micro-fluidic cell with adjustable flow rate.

The structure from the sol-gel is transferred to pre-cleaned silicon substrates via spin-coating. The nanocomposite films are calcined to combust the structure-directing polymer and transfer the amorphous titania to the semiconducting anatase polymorph.

Results and Discussion

Real space investigations with scanning electron microscopy (SEM) reveal a pore structure with mesopores with a diameter of several tens of nanometers and macropores with a diameter of several hundreds of nanometers, see figure 1.

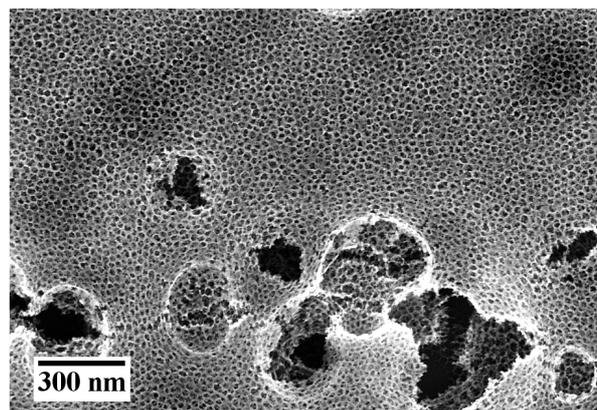


Fig. 1: SEM graph of the titania sponge structure with mesopores and macropores that extend through the volume of the film. The structure was derived from a sol-gel mixed in the micro-fluidic cell with 1 ml/min.

Reciprocal space investigations with grazing incidence small angle x-ray scattering (GISAXS) have been performed to gain quantitative information on the structure in

the volume of the film, averaged over a large sample area. Figure 2 shows the two-dimensional GISAXS scattering pattern of a titania structure, which shows many distinct features. To quantify these features, cuts along the q_y - and along the q_z -direction are performed.

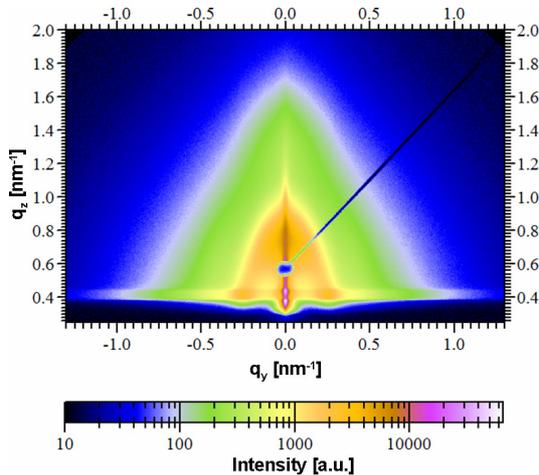


Fig. 2: 2d-scattering pattern of a titania film as measured with GISAXS at the beamline BW4, HASYLAB, DESY (Hamburg). The titania film was derived from a sol-gel mixed in the micro-fluidic cell with 1 ml/min.

From the detector cuts (figure 3a) information on structures perpendicular to the sample surface can be gained. From the position of the Yoneda peak, the first prominent maximum in the detector cut, the material specific scattering length density can be obtained. This allows for the determination of the porosity of around 0.75, which is a promising value for solar-cell applications. The out-of-plane cuts (figure 3b) show two distinct structure sizes of 36 nm and 21 nm without higher orders for the titania film templated by the usual sol-gel without the usage of the micro-fluidic cell. In the case of the titania film derived from the sol-gel mixed in the micro-fluidic cell peaks with several higher orders corresponding to a disordered hexagonal arrangement of the mesopores are observed. The structure size is determined to 25 nm. The structure sizes are promising, as they provide on the one hand the high surface-to-volume ratio necessary for effective charge separation, and on the other hand are large enough to allow the infiltration of the hole-conductor.

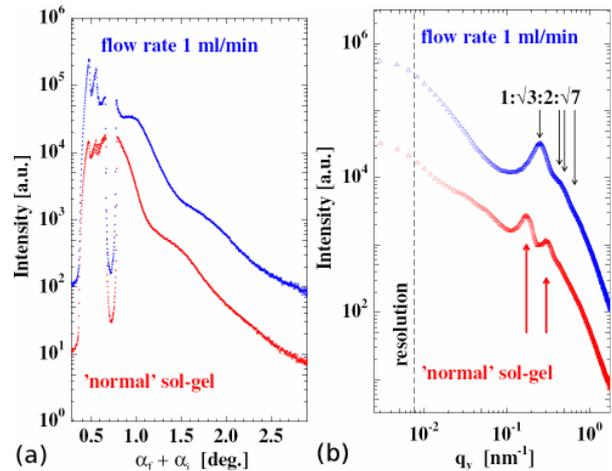


Fig. 3: Detector cuts along $q_y=0$ (a) and out-of-plane cuts with $q_z=q_c(\text{TiO}_2)$ (b) for the film derived from the usual sol-gel as well as a film prepared with the sol-gel mixed in the micro-fluidic cell with a flow rate of 1 ml/min. The cuts are shifted along the intensity axes for illustrative purposes.

Optical investigations with UV/Vis spectroscopy complement the structure investigations. An increase in the light scattering can be observed when templating the titania structure with the sol-gel mixed in the micro-fluidic cell, which render the structures interesting for applications in photovoltaics, as an increased light path results in higher absorption.

Conclusion

A new approach to structure titania by the combination of sol-gel templating with a diblock copolymer and micro-fluidics gives the possibility to obtain morphologies with a higher structural order and a high porosity. Together with an increased light scattering the obtained titania structures are highly interesting for applications in inorganic-organic hybrid photovoltaics.

References

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