Structuring of titania thin films on different length scales via combining block copolymer assisted sol-gel templating with wet-imprinting

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Electronic Supplementary Information

Experimental

Titania Thin Film Preparation

Silicon wafers or soda-lime glass slides were used as substrates which were cleaned in an acid bath before use [1]. The sol-gel was prepared using the commercial diblock copolymer poly(styrene-block-ethylene oxide) (P(S-b-EO)) as obtained from the manufacturer (Polymer Source Inc., polydispersity 1.04, $M(PS) = 16000$ g mol^{-1}, $M(PEO) = 5000$ g mol^{-1}). To obtain the foam-like nanostructure a weight ratio of 1,4-dioxane, hydrochloric acid (HCl) and titanium tetraisopropoxide (TTIP) of 92:1:6.5 was chosen. This ratio is expected to yield a foam-like nanostructure with effective surface areas of roughly 100 cm²/g as determined with BET measurements. First, the diblock copolymer was dissolved in 1,4-dioxane, which acts as a good solvent for both blocks. Next, HCl, which acts as a selective solvent, and TTIP were added drop wise under constant stirring. After a stirring time of one hour, the sol-gel solution is deposited on the PDMS stamp with a pipette. To remove the polymer matrix and to convert the titania into its anatase phase, the sample was put into a tube furnace after the imprinting step (400 °C, 4 hours, heating ramp 6.25 °C min^{-1}).

Fabrication of the master structure

The master structure used for this work was made on a silicon wafer with optical lithography. For this, the silicon substrate is first cleaned with an acidic bath, and subsequently coated with a photoresist (S1805, Microposit, 2000 rpm, 30 s). Using a mask aligner (MJB 3, Karl Suss) with a chromium mask, the resist is illuminated and afterwards developed (Microposit 351 Developer) [1]. The chromium mask was custom made having a parallel line structure of 4 μm periodicity and a line width of 2 μm. After the developing step, the structured resist is rinsed with deionized water and then dried with nitrogen. In the end, the resist is hard baked in an oven for 2 hours at 120 °C.

Fabrication of the PDMS stamp

As mentioned in the main article, the master structure is not directly used for imprinting. Instead, a negative replica from PDMS is made. For the fabrication of the PDMS stamps the commercially available product Sylgard 184 (Dow Corning) is used. First, the two components, polymer and curing agent, are mixed together with a ratio of 10:1. The mixture is treated repeatedly in an ultrasonic bath and in a vacuum chamber to remove any air bubbles. Then, the clear, viscous liquid is poured into aluminum forms which are placed on top of the master structure. The whole system of master structure/aluminum form/PDMS solution is placed in a vacuum furnace. After a vacuum is applied at room temperature for a short time (to remove any trapped air between the master structure and the PDMS solution), the temperature is increased to 100 °C for 1 hour to cure the PDMS. Afterwards, the stamp is cooled down to room temperature and then it is pressed out of the aluminum form and peeled off from the master structure. Prior to imprinting with the PDMS stamp, it is cleaned in an ultrasonic bath in deionized water for 10 minutes and subsequently dried with nitrogen.

Characterization

Topography: Micrographs were taken with an optical microscope (Zeiss Axiolab A) with a resolution of 610 nm. The images were analyzed with the software ImageJ v1.43u. The topography measurements were performed with an Autoprobe CP Research AFM instrument. The employed tip had a conical shape with a tip radius of 10 nm, which was small compared to the investigated structures. The obtained data was analyzed with the Gwyddion AFM software v2.20. To obtain height profiles, line cuts were taken perpendicular to the channel structure and averaged over 50 pixels. The nanomorphology was probed with a Zeiss Gemini NVision 40 field emission scanning electron microscope (2.0 kV, working distance 2.5 mm, aperture 10 μm). The images were analyzed with the software ImageJ v1.43u.

Crystallinity: The crystallinity was investigated with x-ray diffraction, using a Bruker D8 equipped with a Cu cathode operated at 40 kV and 40 mA. The XRD pattern was directly obtained from the thin film on a silicon substrate. The reference peaks for anatase titania were taken from The International Centre of Diffration Data (ICDD).

Spectroscopic characterization: The photoluminescence was studied with a LS 55 fluorescence spectrometer (Perkin Elmer) equipped with a xenon discharge lamp. The excitation wavelength was 300 nm and thus chosen well below the band gap energy of anatase TiO_2 [2]. Additionally, a 350 nm cutoff filter was used to block the excitation source. For measuring the absorbance of the titania films, a Lambda35 UV/Vis spectrometer (Perkin Elmer) was used.

Crystallinity Investigation

The crystallinity of titania films is an important aspect with regard to applications. After the drying process of the wet-imprinting routine, the titania, which is still embedded in the polymer matrix, is in its amorphous phase. Therefore, the calcination step is necessary to convert the titania into its crystalline phase on the one hand and to remove the polymer template on the other hand. The crystallinity was investigated with x-ray diffraction (XRD). **Figure S1** shows the XRD curve of

a titania film after calcination. As indicated by the red vertical lines, which represent the theoretical values along with the respective peak height, all of the observed Bragg peaks correspond to anatase crystal phase of titania. Quantitative
5 information about the crystallite size is obtained by fitting and evaluating the peaks with the Scherrer equation. This way, an average crystal size of 11 nm is found for the investigated titania film.
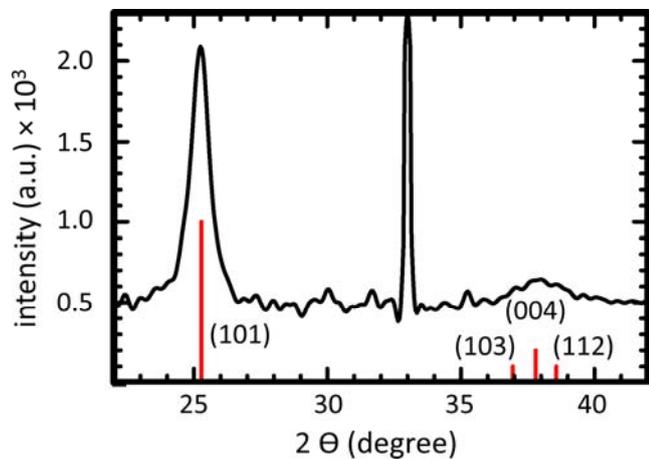
10 **Fig. S1** (XRD data of a titania film after calcination. The red vertical lines indicate the theoretical peak positions of anatase titania along with the respective relative intensities and the corresponding crystal orientations. The strong, sharp peak at 33° originates from the silicon substrate.

Notes and references

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