Ultra thin Anatase TiO₂ Films with Stable Vesicle Morphology Templated by PMMA-b-PEO**

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Synthesis of nanostructured anatase TiO₂ thin films has attracted considerable interests in the past decade due to their intriguing physical properties and potential applications in photocatalysis,

photovoltaics, gas sensing, and Li ion battery materials.^[1] It is of crucial importance to control the morphology of the TiO₂ nanostructures because it determines the active-site surface density available for interfacial reactions and charge carrier transfer rate.^[2] In terms of structural diversity of TiO₂ nanostructures various morphologies including nanoparticles, nanorods, nanotubes, lamellae, and mesoporous structures have been reported.^[3] Compared to the conventional morphologies mentioned above, titania nanovesicle structures have been relatively rarely reported due to difficulties in their preparation;^[4] Nevertheless the nanovesicle morphology is intrinsically very important because it has several attractive advantages: first, it is a core-shell like multi-compartment system and possesses different environments between inside and outside the vesicle, which allows a selective incorporation of chemical species into the vesicles. Second, for porous Titania, the multi-compartment nature increases the surface area available in interfacial processes, compared to solid nanoparticles.

Recently we reported a convenient method to prepare Titania films with morphologies determined by the lyotropic phase behavior of amphiphilic block copolymer. An asymmetric diblock copolymer of poly (styrene)-*block*-poly (ethylene oxide) (PS-*b*-PEO) was used as a templating agent, coupling a so-called good-poor solvent pair induced phase separation process with sol-gel chemistry.^[5, 6] By variation of relative weight ratios among 1, 4-dioxane, HCl, and TTIP, various morphologies including nanovesicles were obtained and a ternary morphology phase diagram was mapped.^[5]

Based on the results from PS-*b*-PEO we want to prove in this communication that templating via lyotropic phases available for PS-*b*-PEO can be generally extended to other amphiphilic block copolymers. To this end an amphiphilic block copolymer of poly (methyl methacrylate)-*block*-poly (ethylene oxide), PMMA-*b*-PEO, was synthesized and used as a templating agent to prepare TiO₂ ultrathin films with nanovesicle morphology (**Scheme 1** in supporting information).^[7] We further show that at large wall thickness to diameter ratios the nanovesicle morphology is stable enough to survive calcination at 400°C, at which the amorphous structure is converted to anatase crystalline

phase. Compared to the PS-b-PEO block the use of PMMA as the hydrophobic block is advantageous for functional particles. PMMA is readily removed by either chemical etching or UV radiation, enabling an easy access to the functional Titania surface.

To structurally characterize the thin films we used AFM in tapping mode to record both height and phase images and SEM. Through the combination of these three imaging methods, we are able to separate the surface topology (AFM height mode) from the sub-surface morphology of the film. We do so via their mechanical response in AFM phase mode and integrated electron density in the SEM imaging.^[8] Because AFM and SEM imaging methods are intrinsically local imaging characterization techniques, we have applied grazing incidence small angle x-ray scattering (GISAXS) to obtain averaged structure information over a large length scale of the films. With GISAXS the lateral structures parallel to the substrate surface was studied.^[9, 10] As a further complementary method, x-ray reflectivity experiments were also used to study the electron density gradient normal to the substrate.^[11]

In the AFM height image of the titania-block copolymer composite film before calcination (**Figure 1a**), a seemingly mesoporous structure is visible on the free film surface. However, instead of “holes” the structure is composed of vesicles, which is confirmed by a closer inspection of the phase image (**Figure 1b**). In the phase image, the bright dots have comparable hardness to the background, which is the soft continuous PMMA phase. Around the bright dots are dark regions, which are assumed to be a harder Ti-O-PEO phase. It can therefore be deduced that the structures are vesicles composed of hard Ti-O-PEO walls and soft PMMA interior pocket regions, as sketched in **Figure 1c**. In the height image, the average overall size of the vesicles is about 50nm and the average center-to-center distance indicated by the power spectral density (PSD) peak is 76nm, which is in agreement with the value (76nm) obtained from the phase image (bottom right insets in **Figure 1a** and **1b** respectively). However, there are multiple peaks present in the PSD profile of the phase image. The presence of an additional peak with an index value of 38nm is ascribed to the nature of vesicle structures. The vesicle structure is confirmed by the SEM top view image (**Figure**

1d). The inner ring of the SEMs FFT pattern corresponds to the center-to-center distance of the nanovesicles (81nm). The second ring corresponds to a structural size of 41nm. Since no other structural features of this length scale are visible in the SEM and AFM images, we interpret the second ring as a higher order of the 81nm signal, indicating a higher degree of lateral order between the nanovesicles. The SEM side view image (**Figure 1e**) shows that the vesicle structure is a monolayer film on the Si substrate.

After calcination the as-prepared amorphous TiO_2 nanovesicles are converted to anatase phase (determined by XRD, see supporting information **Figure S-1**). In **Figure 2a** the height difference between the vesicle wall and interior region is visible and in **Figure 2b** there is a clear mechanical property contrast between the interior and wall region. The TiO_2 wall has a similar hardness to the substrate and in contrast, the interior region is much soft. The average overall size of the vesicles is 47nm, which is slightly smaller than the size before calcination. Both height and phase images have double-ring FFT patterns. The double PSD peaks in **Figure 2a** correspond to 72nm and 36nm and in **Figure 2b** 70 and 35nm respectively. It's noteworthy that the bearing, correlation and depth profiles are all bimodal, which further proves the existence of a vesicle structures (See supporting information **Figure S-2**). The SEM top view image (**Figure 2d**) shows the vesicle structure in agreement with the AFM image. Again as in the case of the unannealed films the double-ring FFT pattern corresponds to the center-to center distance (75 nm), and second higher order (30nm). The SEM side view image (**Figure 2e**) further confirms a monolayer of TiO_2 vesicles on top of a thin Titania layer, in agreement with the AFM phase image. Further proof of the thin layer is obtained from the x-ray reflectivity experiments.

The x-ray reflectivity measurement enables it possible to study the structure gradient throughout the film in the direction normal to the substrate surface.^[9] **Figure 3** shows the x-ray reflectivity profile of the film before (**Figure 3a**) and after (**Figure 3b**) calcination. **Figure 3a** indicates a multiple layer structure with a total thickness of *ca.* 26nm. The topmost layer (15.5nm thickness) has a low scattering length density and it is supposed to be composed of air, PMMA corona, and

part TiO₂-PEO core (as indicated in the sketch **Figure 1c**). Compared to the first layer, the second layer indicated in figure 1c consists of PMMA corona, more PEO-Titania components and the vesicle pocket region composed of PMMA (thickness: 10.8nm), leading to a higher scattering length density. The bottom thin layer (0.6nm) is composed of Titania with a scattering length density even higher than that of the bulk Silicon substrate. Furthermore, the assignment of the Titania thin layer in the model is also in agreement with the AFM and SEM results. The formation of the thin titania layer is likely due to a preferential wetting of the silicon oxide surface by the sol-gel solution and a subsequent reaction between the titania precursor and water molecules attached to the SiO_x surface.

The x-ray reflectivity profile of the film after calcination does not show similar oscillation patterns compared to the profile before calcination because the roughness of the surface is high (1.9nm σ_{RMS} from AFM analysis and 1.6nm σ_{RMS} from the model of x-ray reflectivity).

As a complementary method to x-ray reflectivity, GISAXS is conducted to study the lateral structure of the TiO₂ film parallel to the substrate.^[9-11] **Figure 4** shows the 2D scattering images and corresponding out-of-plane (OOP) cuts along the Yoneda peak position of TiO₂ (parallel to q_y). Since a GISAXS scattering image is recorded at very small incident angle, the scattering image is heavily influenced by refraction effects along the q_z -axis (the z-axis is defined by the surface normal). However since OOP cuts are perpendicular to the q_z -axis they are not influenced by refraction effects and therefore selectively probe lateral structures at a fixed penetration depth of the x-rays. Consequently the information obtained from the OOP cuts is the surface scattering analog to a classical SAXS experiment. The peaks in the OOP profile therefore refer to the characteristic lateral dimensions of the TiO₂ nanovesicles obtained from an average over a large surface area (mm² magnitude). The first-order maximum of the as-prepared sample is located at 73nm, which is in agreement with the inter particle distance obtained from the imaging analysis. The second peak indicating a structure of 18nm size is attributed to the diameter of the depressed region of the nanovesicles and the third peak indicating 4nm structures 4nm is probably due to domains of PEO

inside the titania wall. The profile of the calcined film is very similar. It shows a first-order maximum at 72nm consistent with the imaging analysis results, indicating that the nanovesicles remained fixed on the surface during calcination. The second peak indicating 25nm structures again corresponds to the depressed region of the calcined nanovesicles. Compared to the uncalcined vesicles, the size of the depression was enlarged, since the PMMA corona was burned away. The 4nm structural peak present in the uncalcined sample however has vanished during calcination, indication a fusion of the nanopores inside the Titania wall upon thermal treatment.

The formation of the vesicles can be understood as following: The block copolymer is fully dissolved in pure 1, 4-dioxane at the used concentration of 1 wt. % since 1, 4-dioxane is a good solvent for both PMMA and PEO blocks. The addition of concentrated HCl solution increases the surface energy between the PMMA block and the solvent because it is a poor solvent for PMMA. In order to minimize the surface energy, the block copolymer self-assembles into a vesicle structure with a core of PEO and a corona of PMMA.^[12, 13] HCl solution and TTIP are incorporated into the hydrophilic PEO cores, where TTIP is hydrolyzed and condensed into Ti-O- nanostructures. With the composition ratio applied in this paper (weight ratios: $W_{1, 4\text{-dioxane}}$: 0.963; W_{HCl} : 0.022; W_{TTIP} : 0.015), the resulting morphology is a vesicle structure. The structure is similar to that templated by PS-b-PEO.^[5] Especially, the vesicle morphology can be further tuned by changing the relative ratios among 1, 4-dioxane, Con. HCl, and TTIP (see **Figure S-3** in supporting information). During spin coating, there is a solvent evaporation induced particle rearrangement process and as a result the vesicles in the solution are transformed into an ordered pattern on the substrate.

In summary we have obtained Titania block copolymer composite films with a nano vesicle structure stable enough to survive calcination. AFM and SEM imaging techniques, x-ray reflectivity, and GISAXS characterizations have been combined to study the detailed structure information in the film and the results from different characterization techniques are in good agreement with each other. In addition we have shown that our recipe using a good/bad solvent pair is generally applicable to amphiphilic block copolymers.

Experimental Section

Typically, PMMA-b-PEO block copolymer (0.0406g) (M_n for PMMA: 57.7k; M_n for PEO: 17.88k) was added into a mixture of 1, 4-dioxane (4.0091g), 37% HCl solution (0.0910g) and TTIP (0.0612g). The solution was stirred for about one hour and spin coated onto Si (100) substrates. The prepared film was calcined at 400°C for 4 hours in air to burn off the organic polymer template and crystallize TiO₂ simultaneously (Experimental details given in the supporting information).

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Figure 1: AFM and SEM images of the titania-block copolymer composite film before calcination.

a: AFM height image, height scale: 20nm; b: AFM phase image, phase scale: 20°; c: side-view sketch of the nanovesicle structure; d: SEM image top view; e: SEM image side view. The upper right inset is a FFT pattern of each image (AFM image: FFT over the whole image; SEM image: 512×512 pixels, 1838nm×1838nm); the lower right inset is a power spectral density profile of each AFM image over 2μm×2μm. The double-ring FFT pattern of the SEM image corresponds to 81 (inner ring) and 41nm (outer ring) respectively.

Figure 2: AFM and SEM images of the film after calcination. a: AFM height image, height scale: 20nm; b: AFM phase image, phase scale: 20°; c: side view sketch of the nanovesicles; d: SEM image top view; e: SEM image side view. The upper right inset is a FFT pattern of each image (AFM image: FFT over the whole image; SEM image: 512×512 pixels, 1838nm×1838nm); the lower right inset is a power spectral density profile of each AFM image over 2μm×2μm.

Figure 3. X-ray reflectivity profiles and corresponding fitting curves of the films before (a) and after (b) calcination. Modelling was conducted using the Parratt32 software of available from the HMI, Germany.

Figure 4. GISAXS 2D images and corresponding out of plane (OOP) scan profiles of the films before (a) and after calcination (b).

Table of Content

Titania ultrathin films of anatase phase with stable nanovesicle morphology were achieved using amphiphilic block copolymer of PMMA-*b*-PEO as a templating agent, coupling a good-poor solvent pair induced phase separation process and sol-gel chemistry. X-ray reflectivity experiment revealed the multiplayer nature of the block-copolymer-titania composite film and GISAXS studies indicated ordered structures over large length scale parallel to the substrate before and after calcination.

Key Words

Titanium, block copolymers, X-ray scattering, thin film, sol-gel processes

Supporting information for Ultra Thin Anatase TiO₂ Films with Stable Vesicle Morphology Templated by PMMA-b-PEO **

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Experimental

An asymmetric diblock copolymer of poly (methyl methacrylate) and poly (ethylene oxide) (PMMA-b-PEO) was synthesized in the Max-Planck Institute for Polymer Research via the combination of anionic polymerization (PEO block) and ATRP (PMMA block). (**Scheme 1.**) The number average molecular weight is 57.7k for PMMA and 17.88k for PEO respectively with a polydispersity of 1.22.

Titanium tetra-isopropoxide (TTIP, 97%) was purchased from Aldrich. 1, 4-dioxane of analytical reagent grade was obtained from Fisher Scientific and concentrated HCl (Puriss, p.a.) (min. 37%) was purchased from Riedel-de Haën.

Sample solutions were prepared according to the following procedure. PMMA-b-PEO (0.0406g) and 1, 4-dioxane (4.0091g) were mixed together, followed by the addition of 37% concentrated HCl solution (0.0910g) and TTIP (0.0612g) within 4 minutes. After complete addition the common solution was stirred for one hour.

Films were prepared on Si (100) substrate by spin coating for 30.0s using a Süß MicroTec Delta 80 spin coater at a rotation speed of 2000rpm, and acceleration speed of 2000rpm/s.

Calcination of the films was carried out at 400°C for 4 hours in air with a heating rate of 6°C/min from room temperature. After calcination, the samples were cooled in the furnace to room temperature.

Samples for XRD measurement were prepared by adding a few drops of the solution onto 2.5cm×2.5cm Si (100) substrate, allowing the solution to dry under ambient conditions.

AFM images were recorded using a Digital Instruments Dimension™ 3100 scanning force microscope in the tapping mode equipped with Olympus cantilevers (spring constant ranging

between 33.2 – 65.7 N/m and resonant frequency of 277.3 – 346.3 kHz). The images were analyzed using software Nanoscope 5.12r5.

Scanning electron microscopy (FESEM) images were obtained on field emission SEM (LEO 1530 “Gemini”) under 1kV accelerating voltage. FFT pattern was obtained using the software Image J (Version: 1.33U). Areas of 512×512 pixels of the SEM images are randomly selected and studied.

θ - θ measurements were conducted on Siemens D8 diffractometer equipped with a Cu anode operated at a current of 30mA and a voltage of 30KV. Scans were taken in a 2θ range from 20° to 80° with a step size of 0.05° and integration time of 30.0s.

X-ray reflectivity experiment was conducted using a surface XRD-TT3003 diffractometer equipped with Göbel mirror. The modelling of the experimental profiles was conducted, using the Parratt 32 software, version 1.5 provided by the Berlin Neutron Scattering Center at the Hahn-Meitner-Institute.

GISAXS measurements were performed at the A2 beamline of the DORIS III storage ring at HASYLAB/DESY. Using a completely evacuated sample-detector pathway of 1.08m and a wavelength of $\lambda = 1.54\text{\AA}$. An in-plane resolution of $6.02 \times 10^{-4} \text{ \AA}^{-1}$ was achieved. The scattering image was analyzed in terms of out-of-plane (OOP) scans along the q_y -axis of the scattering image at a q_z values corresponding to the critical angle of TiO_2 . For such cuts the transmission function of the incident and scattered waves only enter as constant scaling factors and do not depend on the precise functional shape of the transmission functions. In this way, the OOP scans are selective to the scattering information of a particular material, i.e. a given scattering length density, as they take advantage of the intensity increase of the transmission function at the critical angle.

PMDTA = Pentamethyldiethylenetriamine
 2-EiBBr = Ethyl-isobromobutyrate = Ethyl-2-Bromo-2-methylpropionate

Scheme 1. The synthesis scheme of the block copolymer PMMA-b-PEO.

Figure S-1. XRD result of the TiO₂ films on Si (100) substrate.

Figure S-2. Particle analysis profiles of the AFM height image after calcination.

Figure S-3. SEM image of the film with nanovesicles modified by relative ratios among 1, 4-dioxane, concentrated HCl, and TTIP. Before calcination: a; after calcinations: b. relative weight ratios: $W_{1,4\text{-dioxane}}$: 0.873, W_{HCl} : 0.022, W_{TTIP} : 0.105.