

High thermal stability PS-*b*-PEO templated mesoporous titania film

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Abstract For many advanced applications, high thermal stability above 400 °C remains as a challenge for the ordered mesoporous titania films. In this work, we attempt to increase the thermal stability of mesoporous structure in titania film crystallization via PS-*b*-PEO block copolymer templating route. This paper reports the highly crystallized mesoporous titania film on silicon substrate thermally stable at 600 °C. The photocatalytic activity of the titania mesoporous film was also shown to be twice of that templated by F127 for degradation of methylene blue (MB). The present results also indicate that at low crystallinity, photocatalytic activity is controlled primarily by crystal perfection rather than surface area.

Introduction

Research has been directed towards mesostructured materials since the self-assembling theory was applied to achieve highly ordered mesoporous and microporous silica in the 1990s [1]. Among these mesostructured materials, amorphous or partial crystalline mesostructured titania films were a great success in this methodology, which produce an ordered mesoporous structure with a distinct

space group through PEO-PPO-PEO tri-block copolymers templating [2–4]. Mesostructured titania attracted extensive research interests due to its wide applications in solar cells [5], water purifications [6] and various functional coatings [7] for photocatalytic reaction. However, its use is limited practically because the regularity of mesostructure is difficult to control in macro-scale, especially at high temperature. This, in turn, limits its crystallinity and performance as a photocatalyst. Nevertheless, it is reported that versatile micelle structures of polystyrene-block-polyethylene oxide (PS-*b*-PEO) diblock copolymer in EISA could be applied to geometrically patterned titania nanoparticles on silicon substrate [8–12]. Recently, Russeau et al. found that the cylindrical microdomains of asymmetric PS-*b*-PEO diblock copolymer could facilitate the formation of ordered mesoporous structure perpendicular to substrate surface [13, 14]. Nonetheless, study on the thermal stability and structure of mesostructured titania templated by PS-*b*-PEO is still seldom found in reports [15].

This paper reports a new approach for the enhancing of the crystallinity and thermal stability of mesoporous structured titania using PS-*b*-PEO template. Early efforts using ionic surfactants have led to poor thermal stability and low crystallinity of the mesoporous framework due to relative thin walls (~1 nm) [16]. A promising alternative solution by PEO-based block polymers templating yields thicker titania walls that are robust towards crystallization (>10 nm). However, the grain growth of sintering titania may still change the mesoporous symmetry and decrease the range of order when annealing. For example, Sanchez et al. reported that a titania mesoporous film with p6 mm plane symmetry transformed to c2 mm at 350 °C due to unidirectional contraction [17]. Although attempts recently to increase titania crystallinity including incremental heat

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treatments, delayed rapid crystallization (DRC) and substrate-assisted crystallization achieved progress in crystallinity, the destruction of mesoporous structure in these methods still resulted in a decrease of porosity and surface area [18–20]. Not only for mesoporous titania but also for most of the non-silica mesoporous materials, the low thermal stability becomes a serious limitation to their performance. When faced with this problem, we attempted to use a new polymer template with higher decomposition temperature blocks such as PS block. Large scale homogeneous mesoporous titania film templated by PS-*b*-PEO was formed after annealing at 600 °C. The PS blocks can serve as a scaffold for the mesostructure in titania crystallization before they decompose at ~450 °C, which is much higher than the traditional PEO-based block copolymer such as F127 and P123 templates that decompose at ~250 °C. In addition, the parameters in the solution or PS volume fraction were also studied.

Experimental

Two kinds of PS-*b*-PEO block copolymer with PEO volume fraction of 0.25 (P25) and 0.35 (P35) having molecular weights of 25,400 and 90,000, respectively, were dissolved in 1,4-dioxane, which is a good solvent for PS and PEO blocks. Titanium isopropoxide $Ti[(CH_3)_2CHO]_4$ (TIP, 99.9%, Aldrich) and hydrochloric acid (HCl, 37%, Honeywell) was slowly added in the prepared solution with 2 molar ratios: 1,4-dioxane:TIP:HCl:H₂O:P35 = 45.4:3:1:3.7:0.44 and 1,4-dioxane: TIP:HCl:H₂O:P25 = 45.4:1:1:3.7:1.58, from which films were spin-coated at 2,000 rpm for 1 min on silicon substrate. The samples were named as TP35 and TP25, respectively. Then the film was aged in evaporation-induced self-assembling process at 80 °C for 48 h, followed by 400 °C for 4 h, and finally the template was removed at 600 °C for 2 h.

The surface morphology of the mesostructured titania film was observed using a field emission scanning electron microscope (SEM, JEOL JSM 6300F, Japan). XRD pattern was obtained from wide-angle powder X-ray diffraction (XRD, Shimadzu) using CuK α radiation (50 kV, 40 mA) with a scan speed of 0.5°/min in θ -2 θ mode. The divergence, anti-scatter and receiving slits were fixed at 1°. The temperatures at which PEO and PS decompose were studied by TGA-DSC analysis (Thermogravimetric analyser, PerkinElmer; TA instrument SDT 2960).

The photocatalytic activity of the mesoporous film was evaluated by the degradation of methylene blue (MB). 7.5 cm² of film on silicon substrate was placed in a glass container containing 15 mL of 3.7×10^{-5} M MB solution. The set-up was placed in a UV reaction chamber (RPR-100) where the light intensity at 365 nm at the centre of the

glass container was 213 μ W/cm². The concentration of MB remaining after each experiment was determined with a UV-VIS-NIR scanning spectrophotometer (Shimadzu UV-3101PC) at the wavelength of 664 nm. The adsorption intensity at 664 nm is linearly related to MB concentration ($C = 1.33 \times 10^{-5}I$, C, MB concentration; I, adsorption intensity at 664 nm).

Results and discussion

Thermal analysis of mesophase hybrid titania and PS-*b*-PEO shows that PEO block was decomposed at around 260 °C indicated by exothermic peak corresponding to the weight lost of PEO block combustion in Fig. 1b. On the other hand, PS block was found to decompose around 450 °C after titania crystallization (crystallization at ~350 °C) in air shown as Fig. 1c. Hence, PS blocks could serve as a scaffold to titania crystallization in the mesophase.

In PS-*b*-PEO templated mesoporous materials, large scale (>1 mm²) mesoporous titania with homogeneous pore diameter ($\sim 30 \pm 3$ nm) was formed after annealing TP35 film at 600 °C for 2 h (Fig. 2a). These nearly hexagonal packed mesopores were normal to substrate surface. The pore size is commonly determined by the size of block copolymer inside the micelles. Pore diameter of titania film templated by PEO-based block polymer was controlled in the range of 8–20 nm as reported [8–12, 21–25]. However, in the TP35 film, because of the larger molecular volume fraction of PS block inside the micelle, larger pore size was formed. The orientation of these hexagonal PEO domains could be explained by the micelle formation mechanism in PS-*b*-PEO films with the absence of titania by EISA method [14]. Through careful control of the parameters in

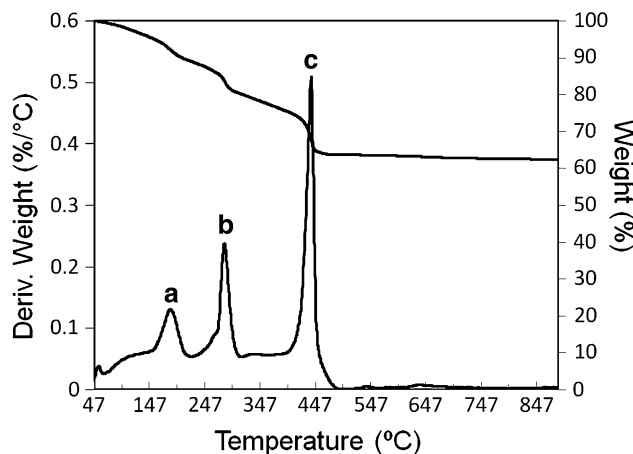
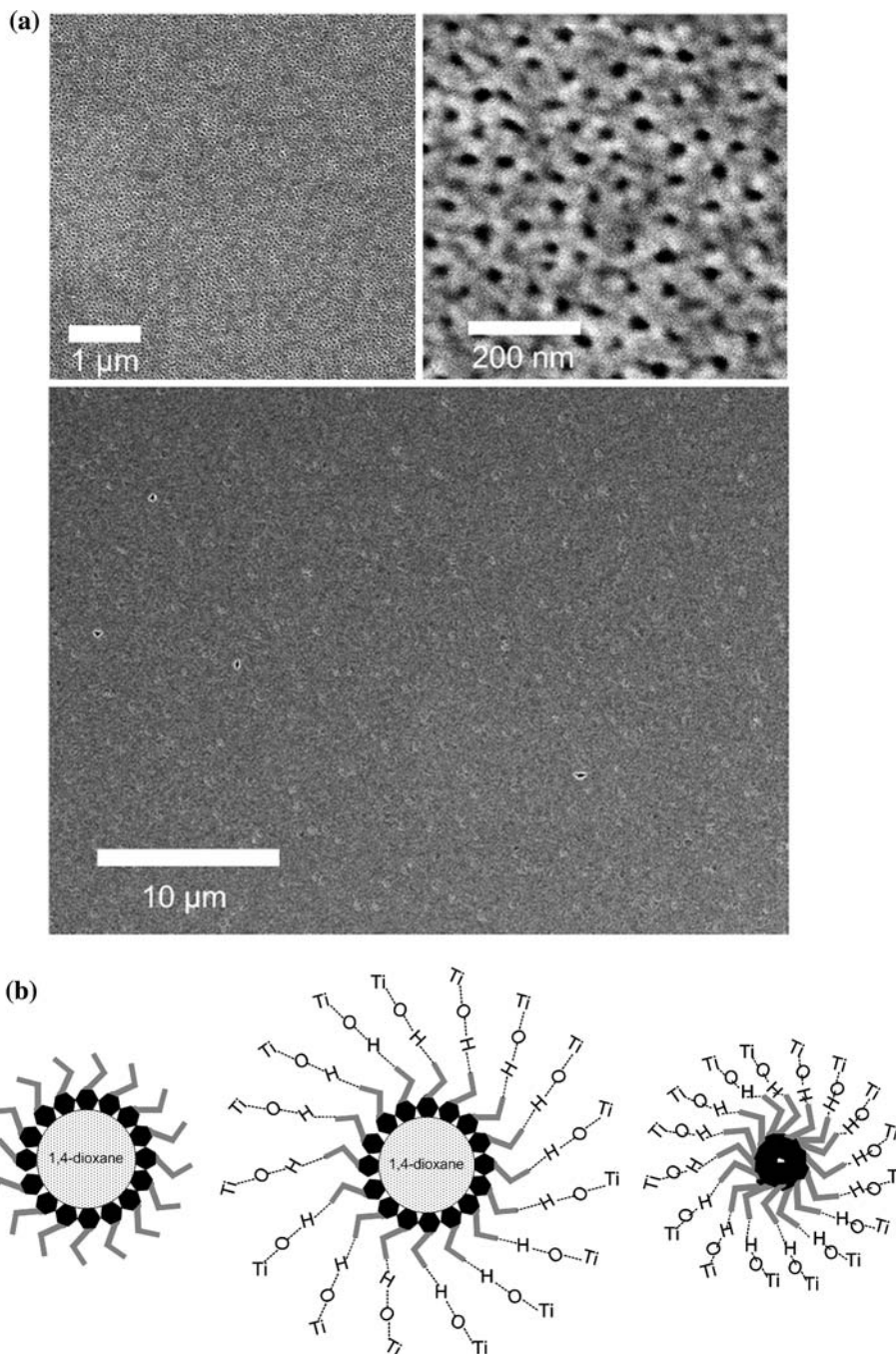


Fig. 1 TGA-DSC curve obtained for TP35 mesostructured titania film. (a) decomposition of 1,4 dioxane solvent, (b) decomposition of PEO blocks, (c) decomposition of PS blocks

Fig. 2 (a) FESEM images of TP35 mesoporous titania film after annealing at 600 °C for 2 h, (b) the formation mechanism of PS-*b*-PEO templated TP35 mesostructured titania



the solution, titania in hydrophilic PEO domain can be subsequently formed with the same mesostructure.

Firstly, hexagonal micelle formation in the solution is induced by addition of HCl in the PS-*b*-PEO solution, in which water is a poor solvent for PS block. Through hydrogen bonding provided by HCl, titania was formed by TTIP hydrolysis and condensation, attaching the hydrophilic PEO block. Finally, the mesostructured titania hybrid film was formed by EISA (Fig. 2b).

It is interesting to note that various mesostructured titania films can be obtained by adjusting TIP, HCl content

and PS block volume fraction. In this section, several structures will be discussed. Firstly, titania islands can be aligned on the substrate surface (Fig. 3). TP25 film consisting of hexagonal packed titania islands was observed. The diameters of titania islands were 440 ± 10 nm at 80 °C and decreased to 330 ± 10 nm due to shrinkage from annealing at 600 °C. The micelle of block copolymer can form a variety of ordered structures via the repulsion of the immiscible blocks such as polystyrene (PS) and polypropylene oxide (PPO). As Segalman studied [25], this micelle inverse process can proceed by increasing the

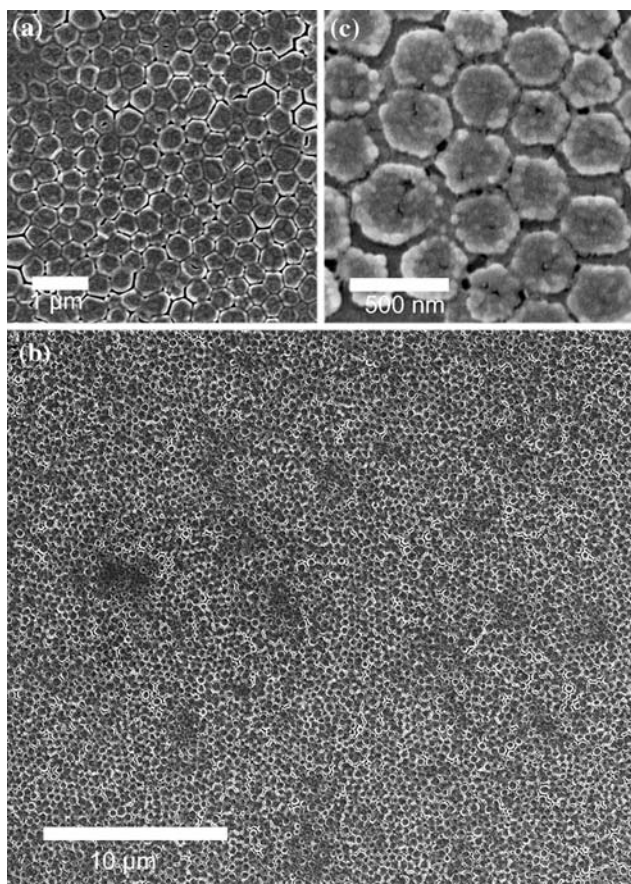


Fig. 3 FESEM images of TP25 mesoporous titania film after aging at 80 °C (a, b) and annealing at 600 °C for 2 h (c)

volume fraction of immiscible blocks (PS block). Then, titania was formed inside the micelle with PEO domains. Hence, the TP25 film is a result of inversed micelle structure in TP35 film because of the increase of PS volume fraction in P25. Moreover, the size of the titania island in TP25 film can be controlled by adjusting the TIP content in the solution. Increasing TIP content in the solution of TP25 results in an increase of the titania islands' size in TP25. On the other hand, decreasing the TIP content in the solution will decrease the titania islands' size. Large distribution size of titania nanoparticles on the substrate surface could be achieved by control of the TIP content in the solution, but the arrangement of this particles is related to water/HCl content as reported [9–12]. For TP35 film, decreasing TIP content in the solution changes the mesostructure to nanowires. This may be attributed to the incomplete formation of a mesoporous structure, which resulted from the lack in titania source. With the increase of titania source, the mesoporous structure was observed in TP35 film (shown in supplementary figure). Therefore, the thickness of the titania wall in TP35 could be further increased by increasing the TIP content.

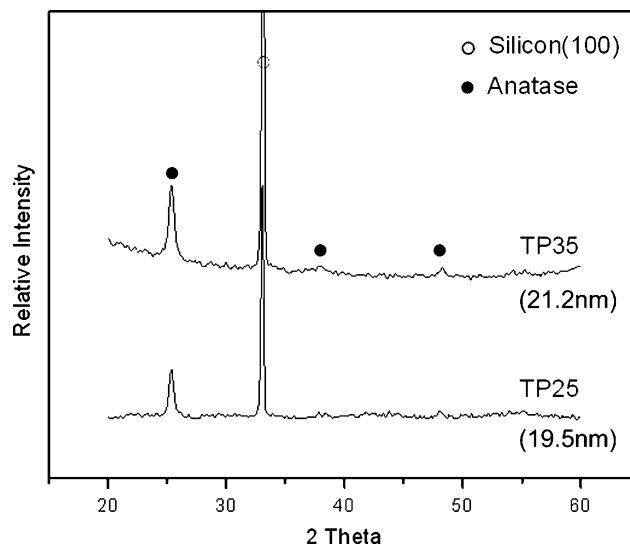


Fig. 4 XRD patterns of mesostructured titania film TP25 and TP35 after annealing at 600 °C for 2 h

XRD patterns of the TP35 and TP25 films have shown the titania crystallinity and crystalline size (~ 20 nm) are both high (Fig. 4). This could be attributed to the thicker wall in the mesoporous TP35 film and titania crystallizations at 600 °C. However, after annealing at 700 °C for 2 h, the rutile phase started to appear in TP35 film and shrinkage has caused the cracking of mesoporous structure. The crystallite size is also found to be consistent with that observed from TEM images. Properties of mesoporous titania are commonly limited by its low crystallinity. The present work would like to introduce the novelty of mesostructured titania synthesized by PS-*b*-PEO block polymer, and remains thermally stable up to 600 °C with the help of PS block. The undecomposed PS block served as scaffold to support the titania crystallization.

The photocatalytic activity of the mesoporous titania film TP35 was evaluated by degradation of MB in aqueous solution. The reference test was carried out on silicon substrate in the absence of titania film. Adsorption and desorption equilibrium was established in the dark. Through the comparison of the adsorption ability between mesoporous films and blank silicon substrate, it is noted that the MB molecules were trapped in the titania walls (Fig. 5a). It is clearly shown that MB in the solution has decomposed at a faster rate by TP35 titania mesoporous film than by blank silicon substrate. The photocatalytic efficiency reaches 45.5%/5 h. Since the MB degradation by titania obeys pseudo-first-order kinetics in the initial period, the apparent rate constant can be determined by the slope of a straight line plotting $\ln(C_0/C)$ against irradiation time (Fig. 5b). This apparent rate constant of TP35 film (thickness = 130 nm) is 2.5 times higher than that of the reference. Moreover, the normalized rate

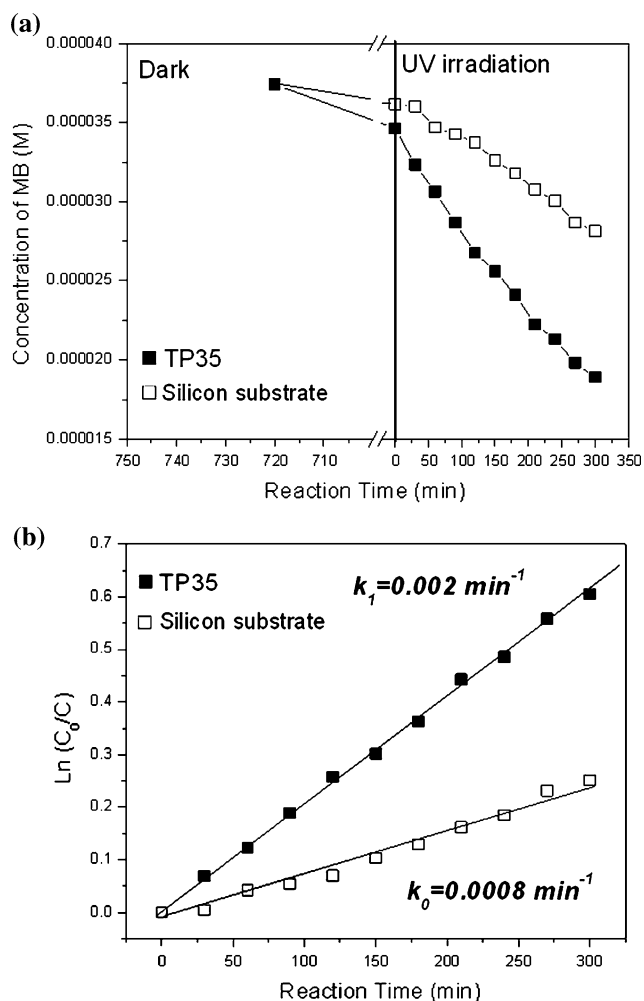


Fig. 5 (a) Adsorption and degradation of MB by TP35 mesoporous titania film and reference pure silicon substrate as function of time, (b) first-order linear relation and the determination of the apparent first-order degradation rate constant, k

constant (0.011 min^{-1}) of TP35 mesoporous film on silicon substrate is twice higher than that of the F127 templated mesoporous titania films laminated from silicon substrate; the crystallinity of the F127 templated mesoporous titania had been improved by substrate effect (0.0094 min^{-1}) [20]. It can be concluded that the method in this paper are more effective to achieve high photocatalytic activity of titania.

Conclusion

Large scale homogeneous mesoporous anatase film was formed by PS-*b*-PEO block copolymer templating. Through adjusting the TIP and HCl concentration in the solution, homogeneous and nearly hexagonal $\sim 30 \text{ nm}$ pore diameter mesoporous titania film perpendicular to

substrate surface was fabricated by spin-coating on silicon wafer. However, with the volume fraction of PEO block decreasing, inversed hexagonal packed titania islands were formed. The effects of TIP and HCl content on the mesostructured titania film were also discussed through micelle formation mechanism of PS-*b*-PEO block copolymer. The fabricated high crystallinity mesostructure anatase film was thermally stable at 600°C , with the assistance of the PS block of PS-*b*-PEO during synthesis. Although the surface area of the mesoporous titania is lower than that of the film templated by PEO-PPO-PEO block copolymer due to its larger diameter of mesopores, it still exhibits higher photocatalytic activity with decomposing MB in aqueous solution. So, for titania with low crystallinity, the photocatalytic activity is governed primarily by the perfection of the crystal, if one takes into account the fact that photocatalytic activity of amorphous titania is nil.

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