Synthesis of highly ordered macro-mesoporous anatase TiO₂ film with high photocatalytic activity

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Abstract
Highly ordered macro-mesoporous anatase TiO₂ film was synthesized by sol–gel method in an acidic medium, using polystyrene (PS) colloidal crystal and triblock copolymer P123 (EO₂₀PO₇₀EO₂₀) as dual templating. The resulting film was characterized by Raman spectroscopy, X-ray diffraction (XRD), N₂ adsorption–desorption analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The photocatalytic activity of the porous TiO₂ film was evaluated by characterizing its photocatalytic effect on the photodegradation process of Rhodamine B (RhB). The results reveal that the bimodal porous material is in anatase phase, and the three-dimensionally ordered macroporous walls are composed of highly ordered mesopores. The average size of the mesopores and the BET surface area are 6.70 nm and 143.37 m² g⁻¹, respectively. The obtained TiO₂ film shows a higher photocatalytic activity than commercial photocatalyst Degussa P25.

Keywords:
Macro-mesoporous structures; Dual templating; Photocatalytic activity; Raman spectroscopy

1. Introduction
Over the past decades, porous materials have attracted increasing interest owing to their potential applications in the fields of catalysis, ion exchange, adsorption and separation [1–4]. Since the successful preparation of ordered mesoporous silicas [5], a great deal of progress has been made in the synthesis of ordered microporous (pore size below 2 nm), mesoporous (2–50 nm) and macroporous (beyond 50 nm) materials [6–9]. The ordered mesoporous materials have been obtained by using surfactants or amphiphilic block copolymers as structure-directing agents [10–14], and latex spheres can be used as templates to form ordered macroporous materials [15–18].

Recently, bimodal macro-mesoporous materials have been investigated intensively due to the improved textural properties and potential applications [19]. Compared with single-sized pore materials, the bimodal porous materials combine the advantages of both mesoporous and macroporous structures. The textural mesopores with high surface area and intrinsic interconnected pore systems of the macrostructures can improve the reaction/diffusion properties efficiently for catalysis and separation processes. Typically, the bimodal macro-mesoporous materials are usually prepared by using supramolecular assemblies of amphiphilic polymers and surfactants as the structure-directing agents of mesostructures; and colloidal crystals, emulsion droplets, vesicles or polymer foams are employed as templates to control the interconnected macropores [20–27]. This strategy is mainly focused on the preparation of bimodally ordered macro-mesoporous silicas and is extended to the synthesis of metal oxides including TiO₂ and Al₂O₃ [22–27]. Bimodal macro-mesoporous metal oxide materials such as ZrO₂, Al₂O₃ and TiO₂ are also prepared via the self-assembly of a single surfactant template under hydrothermal conditions [28,29], or even through a template-free synthesis route [30,31].

TiO₂ is a very useful semiconducting metal oxide material and exhibits extensive potential applications in catalysis, photocatalysis, sensors and dye-sensitized solar cells [32]. The photocatalytic activity of TiO₂ is one of its most distinctive features, which is mainly determined by properties involving the crystalline phase, specific surface area and porous structures. In photocatalytic applications, bimodally ordered macro-mesoporous TiO₂ materials in anatase crystalline phase are desirable to improve the photocatalytic activity. The textural mesopores possess high specific surface area and the active sites are usually located in the mesopores.
Meanwhile, the interconnected macropores can optimize the transportation of matter and reduce transport limitations [29]. In addition, the anatase phase of TiO$_2$ has been proved to have the highest photocatalytic activity compared with amorphous, rutile and brookite TiO$_2$ [33,34]. Therefore, many efforts have been performed to fabricate the bimodally ordered macro-mesoporous anatase TiO$_2$ materials. Several research groups have reported the preparation of crystalline anatase TiO$_2$ materials with bimodal macro-mesoporous structures. However, all the mesoporous structures of these TiO$_2$ materials are disordered. Up to now the crystalline anatase TiO$_2$ materials with highly ordered macro-mesoporous structures have not been obtained, mainly because the hydrolysis and condensation rates of titanium precursors (generally chlorides or alkoxides) are hard to control. Heat treatment at elevated temperature which can give high crystallinity is also responsible for the collapse of the ordered macro-mesoporous structures (the loss of the mesopores).

In this paper, we reported a strategy for preparing highly ordered macro-mesoporous anatase TiO$_2$ film by utilization of dual templating of polystyrene (PS) colloidal crystal and triblock copolymer P123. The former was employed to produce controllable three-dimensionally ordered macropores and the latter to produce highly ordered mesopores. Through controlling the heating conditions, highly crystalline anatase TiO$_2$ film with perfect and intact macro-mesoporous structures was obtained. The walls of the three-dimensionally ordered macropores were composed of highly ordered mesopores. The possible formation mechanism of such a highly ordered macro-mesoporous structures of TiO$_2$ was proposed. Moreover, the resulting sample exhibited a higher photocatalytic activity than commercial photocatalyst Degussa P25.

2. Experimental section

2.1. Materials

Triblock copolymer Pluronic P123 (molecular weight, Mw = 5800 g mol$^{-1}$, EO$_{20}$PO$_{70}$EO$_{20}$) was purchased from Aldrich. Noncross-linked, monodisperse PS microspheres (mean diameter 1.0 μm) that were originally dispersed in ethanol at 5 wt.% were purchased from Tianjing Baseline ChromTech Research Centre (Tianjing, China). P25 was obtained from Guangzhou Hualisen Trade Co., Ltd. (Guangzhou, China). Tetrabutyl titanate (Ti(OC$_4$H$_9$)$_4$), acetylacetone (CH$_2$(COCH$_3$)$_2$), hydrochloric acid, ethanol and Rhodamine B (Rhb) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were of analytical grade and were used as received without further purification. Ultrapure water (18.2 MΩ) was obtained from a Milli-Q water system.

2.2. Fabrication of PS colloidal crystal template

The PS colloidal crystal template was assembled onto a silicon substrate by vertical deposition that relies on capillary forces [35]. The original PS suspension was diluted with ultrapure water to a concentration of 0.1 wt.% A piece of cleaned silicon substrate (~2 cm × 4 cm) was vertically placed into a 2.0-cm-internal-diameter cylindrical Teflon vial filled with the diluted PS suspension. The vial was kept in an incubator under controlled temperature at 60 °C. After the suspension was completely dried, the PS colloidal crystal template was formed on the side of the silicon substrate, and then was thermostat at 90 °C for 2 h to enhance the bonding among PS microspheres.

2.3. Synthesis of highly ordered macro-mesoporous anatase TiO$_2$ film

In a typical synthesis, P123 was dissolved in an ethanolic HCl solution, which contained a small quantity of water, under vigorous stirring for 1 h. Then, acetylacetone was added into this transparent solution, followed by stirring for an additional 20 min. Tetrabutyl titanate was added in the solution and the mixture was further stirred at room temperature in a sealed bottle for 24 h at a slow speed. The final molar ratio was Ti(OC$_4$H$_9$)$_4$:P123:HCl:EtOH:H$_2$O:CH$_2$COCH$_3$$_2$ = 1:0.01:0.79:12.86:4.89:0.10. The TiO$_2$ film was prepared by the dip-coating method with a drawing rate of 30 mm min$^{-1}$. The silicon substrate with PS colloidal crystal template was immersed vertically into the resulting sol solution and was held for 30 s to let the TiO$_2$ precursor fill into the close-packed PS colloidal crystal. The dip-coated sample was dried at room temperature for 4 days. In the drying process, the optimal relative humidity (RH) was 70–75%. After drying, the sample was submitted to thermal treatment at 90 °C for 24 h to consolidate the inorganic network, and was then calcined in air at 350, 400 and 550 °C for 3 h at a heating rate of 1 °C min$^{-1}$ to remove the dual templating. With the above procedure, the TiO$_2$ film was obtained.

2.4. Characterization

Raman spectroscopy was employed to determine the crystal phases of TiO$_2$ film. A Raman spectrum was obtained using a Raman microspectrometer (LabRam HR800, Jobin Yvon, France) with the 632.8 nm line of a He–Ne laser as excitation source. The collection time of TiO$_2$ spectrum was 3 s over a spectral range from 100 to 800 cm$^{-1}$. X-ray diffraction (XRD) pattern was recorded on an X-ray diffractometer (D/max-A, Rigaku, Japan) with CuK$_{α}$ radiation ($λ = 1.5406$ Å) operated at 40 kV and 50 mA. The data were collected in a step of 0.05° s$^{-1}$ with the scattering angles (2θ) ranging from 10° to 90°. N$_2$ adsorption–desorption isotherm was determined on a Micromeritics Tristar 3000 system (USA) at 77 K. The sample was degassed in a vacuum at 180 °C prior to the measurements. The surface area was obtained by the Brunauer–Emmett–Teller (BET) method, and the pore-size distribution was estimated from the nitrogen desorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) model. Morphological investigations were carried out by using an environmental scanning electron microscope (Quanta200, FEI, Netherlands) and two transmission electron microscopes (Tecnai G2, FEI, Netherlands and 2010FF, JOEL, Japan). The samples for characterization were obtained by gently scraping the films off the silicon substrates.

2.5. Photocatalytic activity test

The photocatalytic activity experiment on the obtained TiO$_2$ film was performed by photodegradation of Rhb under UV-light irradiation at ambient temperature and pressure. The UV source was a 250 W Hg lamp with a maximum emission at approximately 365 nm. The lamp was placed above the Rhb solution with a distance of about 30 cm and was kept cool by a recirculating water jacket (Pyrex). The TiO$_2$ film in the photocatalytic activity experiment was obtained by gently scraping the film off the silicon substrates. In a typical protocol, the TiO$_2$ sample (0.01 g) was dispersed in Rhb dye solution (80 ml, C$_{Rhb}$ = 1 × 10$^{-5}$ M, pH 6.0) in ultrasonication. The suspension was then magnetically stirred in dark for 30 min to establish an adsorption–desorption equilibrium between the catalyst surface and the dye, and then the reaction mixture was exposed to the UV light with continuous magnetic stirring. The suspension (5 ml) was centrifuged to remove the catalysts every 20 min and the residual Rhb solution was analyzed by a UV–Vis scanning spectrophotometer (UV-2550, Shimazu, Japan) at $λ_{max}$ = 554 nm. For comparison, the photocatalytic activity of commercial photocatalyst Degussa P25 was also characterized under the identical experimental conditions.
3. Results and discussion

3.1. The microstructure of TiO2 film

Fig. 1 shows the Raman spectrum of the TiO2 film calcined at 400 °C for 3 h. The four bands located at 148, 400, 520 and 642 cm\(^{-1}\) in Fig. 1 can be assigned to the characteristic pattern of pure anatase, without any trace of rutile or brookite phase [36].

XRD was used to investigate the crystal phase and crystallite size of the TiO2 film. As shown in Fig. 2, eight diffraction peaks, indexed as (1 0 1), (0 0 4), (2 0 0), (2 1 1), (2 0 4), (2 2 0), (2 1 5) and (224) reflections of anatase phase (JCPDS, No. 21-1272), indicating a formation of TiO2 nanocrystals after calcination at 400 °C. The average crystallite size calculated by the Scherrer formula using the (1 0 1) peak of anatase is 9.8 nm for the TiO2 sample. The temperature is an important factor of the crystal phase and the calcined temperature of 400 °C favors the formation of anatase phase. Meanwhile, this small size of the crystal grains can be helpful to the stabilization of anatase phase. According to the literature, the thermodynamic phase stability is generally dependent on particle size, and the anatase phase is more thermodynamically stable than the rutile phase at the particle size smaller than 14 nm [37].

The XRD date reveals that the frameworks of the macro-mesoporous TiO2 film upon calcination at 400 °C are composed of anatase crystallite, which is consistent with the result of the Raman spectrum.

The physicochemical sorption properties and pore parameters of the sample were detected by N\(_2\) adsorption–desorption measurements. Fig. 3 shows the N\(_2\) adsorption–desorption isotherm and the corresponding pore-size distribution curve of the TiO2 film calcined at 400 °C for 3 h. The isotherm (Fig. 3, inset) is of classic type IV, which can be recognized as the characteristic curve of mesoporous materials, according to the IUPAC classification. A hysteresis loop with a sloping adsorption branch and a relatively sharp steep desorption branch is observed at a relative pressure (P/P\(_0\)) range of 0.6–0.9, which belongs to the type H2 hysteresis loop, suggesting the presence of pores with narrow necks and wider bodies (ink-bottle pores) [38]. This type of pores may be related to the blockage of the mesochannels by large TiO2 nanocrystals. The hysteresis loop occurred at high relative pressure (\(\sim 0.7\) P/P\(_0\)) indicates that the relatively large pores are dominant. The narrow pore size (2–50 nm) distribution curve (Fig. 3) demonstrates a high degree of order on the mesoporous length scale. Based on the BJH method, the estimated corresponding pore size is 6.70 nm. In addition, the total pore volume and the BET surface area of the TiO2 film are 0.3390 cm\(^3\) g\(^{-1}\) and 143.37 m\(^2\) g\(^{-1}\), respectively.

Scanning electron microscopy (SEM) was used to characterize the morphologies of the PS colloidal crystal template and the TiO2 sample. Fig. 4a shows that the PS colloidal crystal template is in a typically ordered hexagonal pattern, corresponding to the (1 1 1) plane of fcc close packing. The diameter of the PS microspheres measured from the SEM image is about 1.0 \(\mu\)m. Fig. 4b shows the SEM image of the PS colloidal crystal template coated with TiO2 precursor gel after thermal treatment at 90 °C for 24 h. As can be seen, the ordered structure of PS colloidal crystal template is well preserved and the interstitial voids of closely-packed microspheres are fully filled with TiO2 precursor gel. The diameter of microspheres decreases to approximately 900 nm because of thermal treatment. After calcination at 400 °C for 3 h, the interconnected three-dimensional ordered macrostructures can be clearly observed (Fig. 4c). The macropore size calculated from the SEM image with greater magnification (Fig. 4c, inset) reduces to about 700 nm, which is 30% smaller than the size of the initial PS spheres used as template. It can be understood easily that the decrease of pore size is due to the removal of PS microspheres by calcination. The macropore size mainly depends upon the initial size of the microspheres, so the dimension of the pores can be fully controlled by varying the size of the microspheres used to assemble the template.
Transmission electron microscopy (TEM) images of the TiO$_2$ film calcined at 400°C for 3 h with different magnifications are shown in Fig. 5a and b. The ordered fcc macropores are uniform and the pore size is around 700 nm, which is consistent with the result from the SEM image. Moreover, it also clearly shows that the walls of these uniform macropores are made of highly ordered mesopores with hole and layer structures. The high-resolution TEM (HRTEM) image of the TiO$_2$ sample (Fig. 5c) clearly shows the uniform, well-ordered hexagonal arrays in large area, which confirms the highly ordered mesostructures. It also reveals that the mesoporous walls are composed of TiO$_2$ anatase nanoparticles. The crystallite size of the anatase nanoparticles measured from HRTEM image is in accordance with the average crystallite size (~9.8 nm) calculated from the XRD pattern (Fig. 2). Further observation finds that some of the large TiO$_2$ nanoparticles even thrust into the channels and block the mesopores, indicating the formation of ink-bottle pores, which should be responsible for the presence of the type H2 hysteresis loop in the N$_2$ adsorption–desorption isotherm (Fig. 3, inset). As can be seen from Fig. 5c, the mesopore size and the wall thickness of the sample are estimated to be around 6.70 and 3.30 nm, respectively. This mesopore size corresponds well to the result from the N$_2$ adsorption–desorption analysis. Meanwhile, the thick mesoporous walls are helpful to keep the mesoporous structures from collapsing during calcination. The magnified HRTEM image (Fig. 5c, inset) shows clear lattice fringes, and the fringes of around 3.52 and 2.42 Å match well with the crystallographic spacings of the (1 0 1) and (0 0 4) planes of anatase phase, respectively. This finding confirms that the TiO$_2$ nanoparticles are highly crystallized and the crystalline form is anatase phase as suggested by the Raman spectrum and XRD pattern. From the selected-area electron diffraction (SAED) pattern recorded on TiO$_2$ sample (Fig. 5d), a sequence of diffraction rings can be clearly observed, which is consistent with the polycrystalline anatase structure (JCPDS, No. 21-1272). It further confirms that the mesoporous walls are indeed made up of highly crystalline TiO$_2$ anatase nanoparticles. The changes in pore structure and crystallinity of TiO$_2$ films prepared at different temperatures were also characterized by TEM. As shown in Fig. 5e, after calcination at 350°C for 3 h, the TiO$_2$ film shows ordered macro-mesoporous structures, and the corresponding SAED pattern shows diffused diffraction rings (inset Fig. 5e). However, upon calcination at 550°C for 3 h, the ordered macroporous structures of the TiO$_2$ film are well preserved but the mesoporous structures collapse (Fig. 5f). Meanwhile, distinct diffraction rings are observed in SAED pattern (inset Fig. 5f). These results demonstrate that both the well-ordered macro-mesoporous structures and good crystallinity can only be obtained for TiO$_2$ film when calcined at 400°C for 3 h; and with the temperature increases from 350 to 550°C, crystallinity improves while the mesoporous structures collapse. The phenomenon is consistent with the results reported by Agarwala and Ho [13].

3.2. Proposed formation mechanism

Based on the existing models [20,39,40] and the new data reported in the present work, a proposed mechanism for the formation of such a highly ordered macro-mesoporous structures of TiO$_2$ is illustrated in Fig. 6. Firstly, the PS colloidal crystal assembled by vertical deposition served as a template to produce macropores, as shown in Fig. 6a. Then, the interstices of close-packed PS colloidal crystal were filled with the TiO$_2$ precursor sol by a dip-coating method. During the subsequent drying process, this dip-coated composite material was kept at moisture. With the evaporation of volatile species and the introduction of water molecules from air moisture, the formation of Ti-oxo clusters took place through the hydrolysis-condensation reaction of titanium alkoxides in the solution. In this process, diffusion of moisture was expected to be an important water source. The addition of hydrochloric acid and acetylacetone chelator was helpful to control the fast hydrolysis/condensation rates of titanium alkoxide and avoid precipitation. Meanwhile, in the presence of ethanol and water, the surfactant P123 in the sol formed a micelle where hydrophobic PPO chains stayed in the core of the micelle and the hydrophilic PEO chains...
stayed around the core. These surfactant micelles and Ti-oxo clusters can self-assemble cooperatively to form the initial mesostructured hybrid phase (Fig. 6b, right panel). The driving force for the self-assembly process should be ascribed to the hydrogen-bonding interactions between the hydrophilic clusters and the PEO moieties of the polymers. Subsequently, the co-condensation of the hydrophilic clusters around well-defined micelles allowed the formation of the inorganic network. However, this stage was partially

Fig. 5. (a–d) Correspond the TiO$_2$ film after calcination at 400°C for 3 h: (a) and (b) are TEM images at different magnifications; (c) is the HRTEM image and (d) is the SAED pattern after calcination at 400°C for 3 h. (e) and (f) are TEM images after calcination at 350 and 550°C for 3 h, respectively. The inset in (c) is HRTEM image at higher magnification; the inset in (e) and (f) shows the corresponding SAED pattern.
The photocatalytic activity of the calcined TiO$_2$ film was detected by the photodegradation of RhB aqueous solution under UV irradiation, and was compared with that of the commercial photocatalyst P25 (Fig. 7a). For comparison, a blank experiment (self-photosensitized process) was also measured under UV illumination in the absence of any catalyst. As shown in Fig. 7a, it can be seen that the RhB concentration is decreased upon prolonging the irradiation time. Under irradiation for 120 min, a small RhB concentration decrease (17.7%) takes place without any catalyst, while in the presence of the obtained macro-mesoporous TiO$_2$ film and Degussa P25, large concentration decrease of 92.1% and 89.6% occur, respectively. Meanwhile, the photodegradation of RhB can be assumed to follow a pseudo-first-order reaction, and its kinetics may be expressed as follows: $\ln(C_0/C) = kt$ [30], where $k$ is the apparent reaction rate constant (min$^{-1}$) and $C_0$ and $C$ are the initial concentration and the reaction concentration of RhB, respectively. From the plots of $\ln(C_0/C)$ versus the irradiation time (Fig. 7b), the UV photodegradation rate constants obtained from the slopes of the simulated straight lines are $2.057 \times 10^{-2}$ and $1.874 \times 10^{-2}$ min$^{-1}$ for the obtained TiO$_2$ film and P25, respectively. These results indicate that both photocatalysts have a high photocatalytic activity, however, the obtained TiO$_2$ film exhibits better photocatalytic performance than P25. The superior photocatalytic activity of the TiO$_2$ film can be explained by the bimodally ordered macro-mesoporous structures and the high crystallinity of anatase phase. First, the macroporous structures can enhance the effective light-activated surface area significantly and allow rapid diffusion of reactants and products, which can improve the photoabsorption efficiency and the transport of matter. Meanwhile, the stable ordered mesostructures with high specific surface area can offer more active adsorption sites and photocatalytic reaction centers, since the active sites are usually located in the mesopores and a high specific surface area means a high adsorptive capacity. Therefore, such highly ordered macro-mesoporous structures are beneficial to improve the photocatalytic activity [29]. Then, the TiO$_2$ film with highly crystalline anatase phase can also enhance the photocatalytic performance, because the anatase phase of TiO$_2$ shows a
holes by decreasing the number of defects.[31] It may reduce the recombination of photo-excited electrons and contribute activity in the photodegradation of RhB in aqueous suspensions, using Degussa P25, the TiO₂ film exhibited better photocatalytic activity at 400°C, and higher degree of crystallization of the brookite phase.[33,34] and higher degree of crystallization may be attributed to the bimodally ordered macro-mesoporous structures and highly crystalline anatase phase. Furthermore, such obtained TiO₂ film with above excellent properties should find extensive applications in catalysis, separation, sensors and dye-sensitized solar cells. We anticipate that with this strategy, the syntheses of other highly ordered macro-mesoporous crystalline metal oxide films should also be possible.

4. Conclusions

In summary, a highly ordered macro-mesoporous anatase TiO₂ film was successfully prepared by using PS colloidal crystal as macrotemplate and triblock copolymer P123 as a mesostructure-directing agent in a sol–gel reaction. Hydrochloric acid, nonaqueous media (ethanol) and acetylacetone chelator were employed as directing agent in a sol–gel reaction. Hydrochloric acid, nonaqueous media (ethanol) and acetylacetone chelator were used to control the fast hydrolysis and condensation rates of titanium alkoxides. The highly crystalline anatase phase and bimodally well-ordered macro-mesoporous structures were preserved after calcination at 400 °C. In comparison with commercial photocatalyst Degussa P25, the TiO₂ film exhibited better photocatalytic activity in the photodegradation of RhB in aqueous suspensions, which could be attributed to the bimodally ordered macro-mesoporous structures and highly crystalline anatase phase. Furthermore, such obtained TiO₂ film with above excellent properties should find extensive applications in catalysis, separation, sensors and dye-sensitized solar cells. We anticipate that with this strategy, the syntheses of other highly ordered macro-mesoporous crystalline metal oxide films should also be possible.

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