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Synthesis of Highly Stable and Crystalline Mesoporous Anatase by Using a Simple Surfactant Sulfuric Acid Carbonization Method

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Titania-based materials, especially TiO_2, have been extensively studied because of their unique electronic and optical properties as well as potential applications in photocatalysis, solar cells, sensing, energy conversion, and water purification.[1–7] Several efforts have been made to synthesize ordered mesoporous TiO_2 with high surface area and uniform pore size.[8–17] It is known that the evaporation-induced self-assembly (EISA) process is the most efficient method to prepare ordered mesoporous TiO_2. Yang et al. reported a synthesis of mesoporous TiO_2 based on an ethanolic EISA process by using titanic chloride ($TiCl_4$) as a precursor and triblock copolymer Pluronic P123 as a template.[8,9] Tian et al. demonstrated an "acid–base pair" route to obtain ordered mesoporous TiO_2 materials.[11] On the other hand, high-crystalline titania is always in demand for many applications.[2] For example, in photocatalysis, the amorphous domains are known to be trap sites for the recombination of photoexcited electrons and holes, decreasing the efficiency of the device.[18]

Therefore, it remains a great challenge to obtain ordered mesoporous TiO_2 with highly crystalline frameworks. In most cases, mesoporous TiO_2 structures collapse after being heated at temperatures higher than 450 °C because of the intrinsic crystallization of anatase phase. Many attempts have been made to improve their thermal stabilities.[14–16,19–21] More recently, a combined assembly by soft and hard chemistry (CASH) method had been reported by Wiesner and co-workers.[22] However, only block copolymer with sp^2-hybridized carbon-containing hydrophobic block (e.g., PI-*b*-PEO) could be used as a structure-directing agent and a wormlike TiO_2 mesostructure with a relatively low surface area ($89\,m^2g^{-1}$) was obtained. An alternative route to resolve the problem of thermal stability is to add the amorphous components such as P_2O_5, SiO_2, or carbon into the mesostructured TiO_2 frameworks,[23,24] while the amorphous domains decrease the efficiency in many applications.

In this paper, we demonstrate a simple surfactant sulfuric acid carbonization method to synthesize ultra-stable ordered mesoporous titania with highly anatase crystalline frameworks. The synthesis is firstly based on an ethanolic EISA process using titanium isopropoxide (TIPO) as a precursor and commercial amphiphilic triblock copolymers (Pluronic P123, F127 or F108) as a template and a mixture of HCl and H_2SO_4 as the acidic catalyst. The copolymer surfactant template was first carbonized by H_2SO_4 to form amorphous carbon inside the prime mesochannels, which could support the TiO_2 framework during the high temperature crystallization (550, 650 °C). The mesoporous TiO_2 samples obtained after the carbon is burned out at 450 °C in air atmosphere has both high crystallinity of anatase and thermal stability (>650 °C). The BET surface area is as high as $193\,m^2g^{-1}$. The ordered mesoporous anatase materials exhibit excellent photocatalytic activities for the degradation of rhodamine B (RhB) than the commercial P25.

Powder X-ray diffraction (XRD) patterns (Figure 1) of the mesoporous titania samples show well-resolved diffractions, suggesting an ordered mesostructure. The as-made sample shows two diffraction peaks, after being calcined at 350 °C in nitrogen, three well-resolved peaks which can be indexed as the 100, 110 and 200 reflections are observed, indicating a highly ordered 2D hexagonal structure (space group *P6mm*). The XRD pattern of the mesoporous TiO_2 sample reveals one broad diffraction peak after being calcined at 450 °C in air to burn out the carbon support, suggesting that the mesostructural regularity is retained. The removal of the carbon was confirmed by TG analysis (Figure S1 in Supporting Information). With the increase of the calcination temperature, the diffraction intensity decreases and the width of the peaks increases, suggesting a degradation of the mesostructure, which may be related to the increase size of the nanocrystals. The mesoporous TiO_2 sample can also show one broad diffraction peak after being

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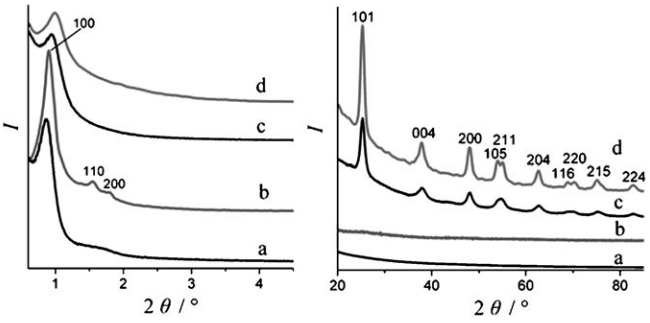

Figure 1. Small-angle (left) and wide-angle (right) X-ray diffraction (XRD) patterns of the ordered mesoporous TiO_2 samples prepared by the surfactant sulfuric acid carbonization method: a), as-made sample; b), calcined at 350 °C in N_2; c), calcined at 550 °C in N_2 and then 450 °C in air to burn out the carbon support; d), calcined at 650 °C in N_2 and then 450 °C in air to burn out the carbon.

calcined at 650 °C, suggesting that the mesostructure becomes more degraded. These results clearly reveal that the ordered mesoporous TiO_2 samples prepared by the surfactant sulfuric acid carbonization method have excellent thermal stability up to 650 °C.

The wide-angle X-ray diffraction pattern (Figure 1) of the ordered mesoporous TiO_2 sample after being calcined at 350 °C in N_2 shows no resolved diffraction peak, indicating an amorphous nature. After being calcined at 550 °C, the wide-angle XRD pattern reveals eight well-resolved diffraction peaks, all of which can be well indexed to the anatase phase reflections according to the JCPDS Card Number 21-1272. The average crystal size is estimated from the Scherrer equation to be ~6.7 nm. With the increase of the calcination temperature (to 650 °C), the diffraction intensity greatly enhances. Ten well-resolved diffraction peaks from anatase phase can be observed, suggesting that the crystallinity increases and the average crystal size estimated from the Scherrer equation is about 8.1 nm. No other diffraction is observed, suggesting a pure anatase phase.

Transmission electron microscope (TEM) images (Figure 2) of the mesoporous TiO_2 samples prepared by the simple surfactant sulfuric acid carbonization method show typical morphologies of ordered 2D hexagonal mesostructure with *p6mm* symmetry. TEM images of the mesoporous TiO_2 sample reveal a high degree of periodicity of 2-D hexagonal arrangements over large domains after being calcined at 350 °C in N_2, viewed from [100][001] directions (Figure 2 a and b). The selected area electron diffraction (SAED) image shows very weak diffraction rings, suggesting an amorphous framework. After being calcined at high temperature (550, 650 °C), the mesostructure shows signs of degradation, which is consistent with the XRD results. HRTEM images (Figure 2 d, f) clearly show that the mesopore walls consisted by well-crystalline small anatase nanoparticles with random orientation. The high crystallinity can also be confirmed by the SAED image (Figure 2 e, inset) of the sample after being calcined at 650 °C in air, which reveals at least six well-resolved diffraction rings and many diffraction spots.

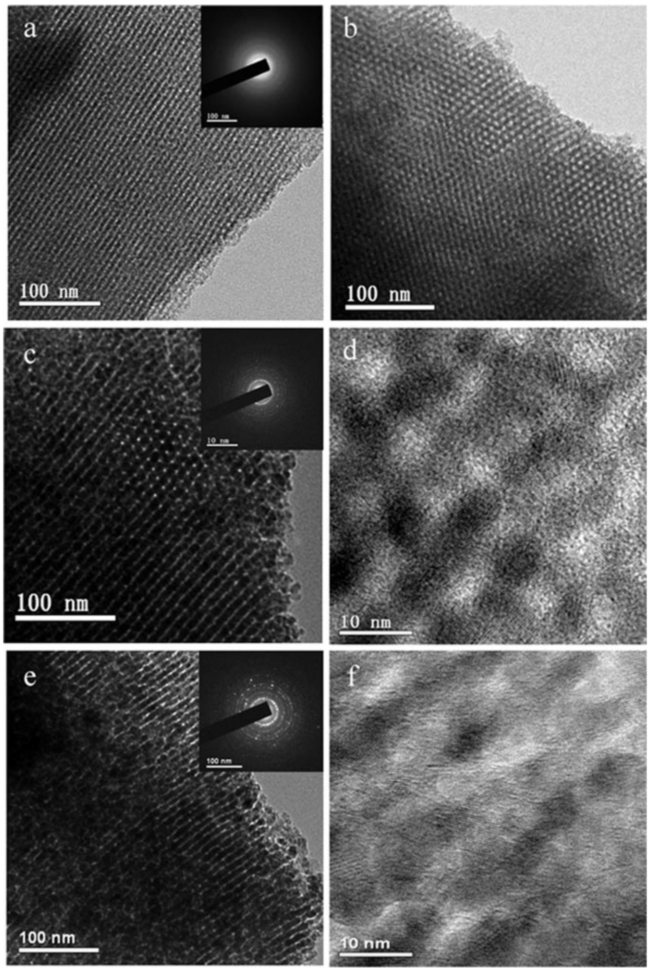

Figure 2. TEM images of the mesoporous TiO_2 samples prepared by the surfactant sulfuric acid carbonization method after being calcined at different temperatures: a), b), 350 °C in N_2, c), d), 550 °C in N_2 and then 450 °C in air to burn out the carbon, e), f), 650 °C in N_2 and then 450 °C in air to burn out the carbon.

Nitrogen sorption isotherms (Figure 3) of all ordered mesoporous TiO_2 samples prepared by the surfactant sulfuric acid carbonization method show representative type-IV curves, which are characteristic of mesoporous materials with uniform pore structure. The isotherms of the ordered mesoporous TiO_2 sample after being calcined at 350 °C in N_2 shows a sharp capillary condensation step at a relative pressure (P/P_0) of 0.6–0.7, suggesting a narrow pore size distribution. The hysteresis loop is a typical H1 type, implying a uniform cylindrical pore geometry. The pore size is calculated from the adsorption data using the Barrett–Joyner–Halenda (BJH) method to be as large as ~6.5 nm. The specific BET surface area is as high as 202 $m^2 g^{-1}$. After being calcined at a high temperature, the mesoporous TiO_2 samples show sharp capillary condensation steps at a little lower relative pressure of 0.5–0.6, suggesting a smaller pore size. This can be explained as the framework shrinks during the calci-

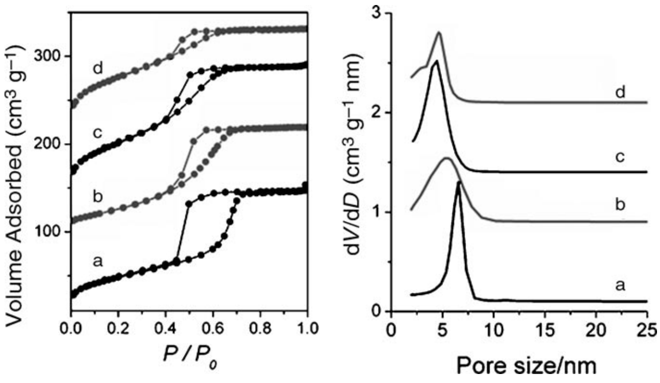

Figure 3. N_2 sorption isotherms (right) and the pore size distributions (left) of the ordered mesoporous TiO_2 sample prepared by the surfactant sulfuric acid carbonization method after being calcined at different temperatures: a) 350 °C in N_2; b) 550 °C in N_2 and then 450 °C in air to burn out the carbon; c) 650 °C in N_2; d) 650 °C in N_2 and then 450 °C in air to burn out the carbon. For clarification, the adsorption isotherms for b), c), and d) are shifted by 80, 120, and 200 cm^3 g^{-1} (STP), respectively.

nation process. The ordered mesoporous TiO_2 sample after being calcined at 550 °C in N_2 and then at 450 °C in air to burn out the carbon presents a specific surface area of 193 m^2 g^{-1} and a pore size of 5.1 nm, while the sample calcined at 650 °C in air has a specific surface area of 180 m^2 g^{-1} and a large pore size of 4.6 nm. Considering the large density of crystalline titania (4.2 g cm^{-3}), this value is very high for mesoporous TiO_2 with highly crystalline frameworks. All mesoporous TiO_2 samples prepared by the surfactant sulfuric acid carbonization method have much higher surface areas than the commercial nanocrystal TiO_2 (P25) (~45 m^2 g^{-1}). The mesoporous TiO_2 samples also have high pore volume (~0.23 cm^3 g^{-1}, Table S1). Interestingly, it is found that the pore size (4.6 nm) of the mesoporous TiO_2 samples calcined at 650 °C after the carbon removal is a little larger than that of the sample calcined at 650 °C before the carbon removal (4.5 nm), implying that the carbon formed by the surfactant sulfuric acid carbonization is located around the TiO_2 framework to form a tubular-like layer.

Our results show that the use of H_2SO_4 as a catalyst during the self-assembly and carbonization processes plays an important role to the formation of well-organized, highly crystalline mesoporous anatase. For comparison, a mesoporous TiO_2 sample was synthesized without H_2SO_4 keeping all other conditions the same. After being calcined under N_2 atmosphere at 650 °C, the small-angle XRD pattern shows no diffraction peaks as expected, implying that the mesostructure completely collapses (Figure S2). The wide-angle XRD pattern (Figure S3) shows very sharp diffraction peaks, indicating that the crystallite size of anatase phase is very large. The average crystal size is estimated from the Scherrer equation to be ~22 nm, which much larger than the mesopore wall thickness. This also implies that the mesostructure completely collapses after being calcined at 650 °C, even in N_2 atmosphere. On the other hand, no ordered mesostructure is obtained for the TiO_2 sample prepared with large amount of the H_2SO_4 (Figure S4).

We speculate that the formation of highly thermally stable mesoporous anatase materials undergoes a surfactant carbonization catalyzed by sulfuric acid and carbon-supporting crystalline process (Figure 4). The titania oligomers hydrolyzed from TIPO precursor can assemble with Pluronic P123 to form ordered mesostructure via the EISA process. During the evaporation, the volatile HCl catalyst is removed while H_2SO_4 is not volatile and can be remained. The assembly of the Ti species and triblock copolymer templates undergoes an $S^0H^+X^-I^+$ process ($X=SO_4^{2-}$ or HSO_4^-). In the case, most of the H_2SO_4 molecules are found near the hydrophilic segments (PEO blocks) of Pluronic P123 because of hydrogen-bonding interactions. After the sample is heated to 350 °C under N_2 atmosphere, the triblock copolymer P123 templates are first carbonized by H_2SO_4 to form rigid carbonaceous layers on the surface of the mesoporous TiO_2 primary channels since the H_2SO_4 molecules are located around the PEO blocks on the surface inside of the channels of the as-made sample. Therefore, an in situ carbonization catalyzed by H_2SO_4 can be assumed. The tubular-like carbon formed on the surface can act as a rigid support to stabilize the TiO_2 frameworks during a further calcination and crystalline process at 550–650 °C. The ordered mesostructure can be stable and well-retained with the carbon protection during the heating process and the TiO_2 frameworks are fully crystallized to form anatase. The anatase nanocrystals formed by high temperature (up to 650 °C) are connected to each other to form a continuous and ultrastable architecture with the carbon support confinement, which is confirmed by the HR-TEM images. Once the fully crystalline anatase frameworks are formed at high temperatures, the ordered mesostructure is thermally stable and can be well retained when the sample is calcined at 450 °C in air to burn out the carbon support.

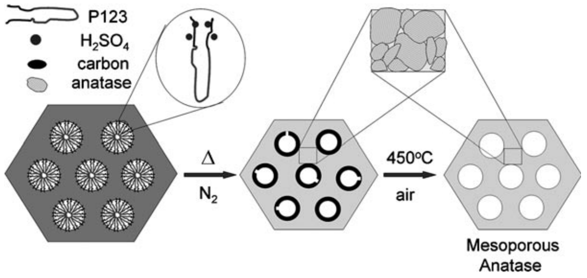

Figure 4. Scheme of the synthesis process of the ordered mesoporous anatase.

This surfactant sulfuric acid carbonization method is very simple and facile, just by adding HCl to H_2SO_4 during the ethanolic solution synthesis. This method is also useful for a general application and can be extended to use other surfactants as templates and synthesize ordered mesoporous metal oxides with different compositions. For examples, Pluronic F127 and F108 can also be used as a template to synthesize highly stable mesoporous anatases (Figure S5). TEM images

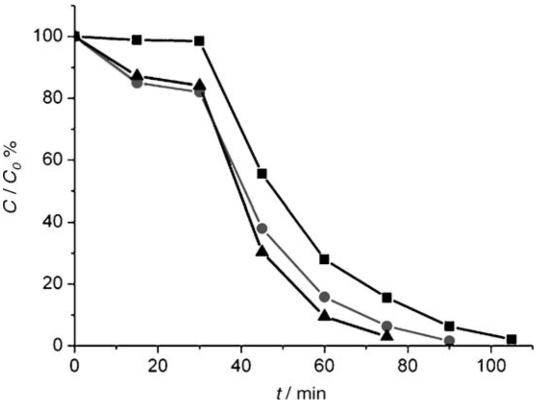

Figure 5. Photocatalytic degradation of RhB monitored as the normalized concentration change versus irradiation time in the presence of commercial P25 (■), the ordered mesoporous anatase samples after being calcined at 550 °C in N_2 and then 450 °C in air (●), and at 650 °C in N_2 and then 450 °C in air (▲) to burn out the carbon.

of the mesoporous TiO_2 templated by Pluronic F108 from this surfactant sulfuric acid carbonization method show a cubic geometry structure (Figure S6). On the other hand, thermally stable and high crystalline ordered mesoporous ZrO_2 materials with 2D hexagonal structure can also be synthesized by using the surfactant sulfuric acid carbonization method (Figure S7 and S8). The mesoporous ZrO_2 obtained has a high surface area of 98 $m^2 g^{-1}$ and large pore size of 5.1 nm.

Photocatalytic activities for the resultant ordered mesoporous anatase samples were evaluated by degradation of a RhB solution under UV light irradiation. As shown in Figure 5, before the irradiation, an adsorption process of RhB on the mesoporous TiO_2 channels occurs. The adsorption amount on the ordered mesoporous TiO_2 samples prepared by the simple surfactant sulfuric acid carbonization method after being calcined at 550, 650 °C is measured to be 1.8 and 1.6 $\mu mol\, g^{-1}$, respectively, which is much higher than that on P25 (0.11 $\mu mol\, g^{-1}$). The high adsorption amount is ascribed to the high surface area of the ordered mesoporous TiO_2 samples. Upon irradiation, the concentration of RhB rapidly decreases with time. The ordered mesoporous TiO_2 sample obtained from our surfactant sulfuric acid carbonization method after being calcined at 550 °C shows a significantly higher decomposition rate (Figure S9) and catalytic activities ($k = 0.0569\ min^{-1}$) compared with the commercially available P25 photocatalyst ($k = 0.0414\ min^{-1}$). This can be attributed to the higher surface area of the ordered mesoporous TiO_2 samples. On the other side, the crystal structure may also play an important role.[25] The mesoporous anatase sample after being calcined at 650 °C shows an even higher decomposition rate and catalytic activities ($k = 0.0744\ min^{-1}$), probably due to the higher crystallinity of the mesostructural frameworks. Our results clearly suggest that the photocatalytic activity is mainly dependent on the crystallinity and the surface area of catalysts. The higher crystallinity and larger surface can provide more catalytic sites to degrade RhB molecules, while the mesopore channels can also enrich the RhB molecules. This unique feature makes the mesoporous anatase materials exhibit excellent photodegradation activity.

In summary, we demonstrate a new simple surfactant sulfuric acid carbonization method for the synthesis of highly stable mesoporous anatases with full crystalline frameworks by using commercial amphiphilic triblock copolymer as a template. The synthesis is facile, based on an enthanolic EISA process by using a mixture of HCl and H_2SO_4 as the acidic catalyst. The surfactant templates (triblock copolymers) are first carbonized by the residual H_2SO_4 inside the samples via heating to 350 °C in N_2 to obtain rigid carbon on the surface of mesochannels. The tubular carbon formed could support and stabilize the TiO_2 frameworks of the mesostructure during the high-temperature crystallization. The mesoporous TiO_2 materials after being calcined at a high temperature (550 and 650 °C) in N_2 and then at 450 °C in air to burn out the carbon show highly ordered 2D hexagonal mesostructure and their frameworks are fully crystalline, which are formed by the connection of anatase nanocrystals. The ordered mesoporous TiO_2 materials obtained have a high surface area (~193 $cm^2 g^{-1}$), uniform pore size (4.6–5.1 nm), large pore volume (~0.23 $cm^3 g^{-1}$) and high thermal stability (~650 °C). The samples show high performance in the photocatalysis using the RhB dye as an example. This synthesis approach is facile and generally applicable and can be used to prepare other thermally stable and ordered mesoporous metal oxides with high crystalline frameworks, such as ZrO_2.

Experimental Section

Chemicals: Titanium isopropoxide [$Ti(OCH(CH_3)_2)_4$, TIPO] was purchased from Acros. Triblock copolymers, Pluronic P123, F127 and F108 were received from Aldrich. Ethanol (absolute), concentrated HCl (36.5 wt %), concentrated H_2SO_4 (98 wt %), tetraethyl orthosilicate [$Si(OC_2H_5)_4$, TEOS] and rhodamine B (RhB) were purchased from China Medicines Corp. Titania nanoparticle P25 was supplied by Degussa Corp. All chemicals were used as received without further purification.

Synthesis: As-made mesoporous titania samples were prepared via the ethanolic EISA method by using titanium isopropoxide (TIPO) as a precursor and commercial amphiphilic triblock copolymers (Pluronic P123, F127 and F108) as a surfactant template and a mixture of HCl and H_2SO_4 as the acidic catalyst. For a typical synthesis, Pluronic P123 (1.0 g) was dissolved in ethanol (30 g) with vigorous stirring, concentrated HCl (1.4 g) and 44 wt % H_2SO_4 (0.46 g) were added to the solution. After being heated at 40 °C for 3 h, TIPO (3.0 g) was added with vigorous stirring for 20 h at 40 °C. The solution was poured into the dishes and evaporated at 40 °C in air under 50–60 % relative humidity for about 2 d, and the resultant membranes were dried at 100 °C for 2 d. The surfactant sulfuric acid carbonization method was adopted to form mesoporous titania with crystalline anatase frameworks and then the templates were removed by burn out at 450 °C in air. The as-made products were firstly carbonized by the residual H_2SO_4 catalyst at different temperature (350, 550, 650 °C) under N_2 atmosphere for 3 h, and subsequently heated at 450 °C in air atmosphere for 6 h to burn out the carbon. Finally white powder samples were obtained.

Characterizations: XRD patterns were recorded with a Bruker D4 powder X-ray diffractometer using $Cu_{K\alpha}$ radiation (40 kV, 40 mA). Nitrogen sorption isotherms were measured with a Micromeritics Tristar 3000 analyzer at 77 K. Before the measurements, the sample was degassed in vacuum at 180 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the surface areas. The pore size distributions were calculated by the BJH method. TEM images were recorded on a JEOL 2011 microscope operated at 200 kV. Thermogravimetric (TG) analyses were carried out using a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 25 to 700 °C under air atmosphere with a heating rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$. The UV-visible spectra of the RhB supernates were recorded on a JASCO UV-550 (Japan).

Photocatalysis: The photocatalytic activities were evaluated by the decomposition reaction of RhB molecules under UV light irradiation from a 20 W Hg lamp ($\lambda = 254$ nm) according to the literature.[23] The radiant flux was measured with a photometer (International Light model IL1400 A). 50 mL of aqueous suspensions containing RhB ($1\times 10^{-5}\,\mathrm{mol\,L^{-1}}$) and 50 mg of the mesoporous anatase samples were placed in a quartz vessel. Before irradiation, the suspensions were stirred in the dark for 30 min to establish the adsorption-desorption equilibrium between RhB and the sample. At given time intervals, the supernate was analyzed by recording variations of the absorption band maximum (554 nm).

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Keywords: mesoporous materials · photocatalysis · synthesis design · titanium

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