Mesoporous bismuth titanate with visible-light photocatalytic activity

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Visible-light-driven mesoporous bismuth titanate photocatalyst, which possesses wormlike channels, mixed phase mesostructured frameworks, large pore diameter ($\sim$6.1 nm), and low band gap energy (2.5 eV), has been successfully prepared *via* a modified evaporation-induced self-assembly technique (EISA).

Mesoporous materials prepared through an assembly between organic surfactant molecules and inorganic species have seen a tremendous development since their discovery in the early 1990s.[1] Their tunable mesoporous structures, tailored framework composition, narrow pore size distribution, large surface area and large pore volume have stimulated active research works in different fields of application.[2] Among this material family, photoactive mesoporous titania has been studied extensively. However, a fatal disadvantage for the mesoporous titania photocatalyst, same as titania, is its large band gap, which makes mesoporous titania absorb only UV light. Therefore, in view of better utilization of solar energy, development of efficient mesoporous photocatalysts that can be used for the degradation of harmful organic compounds under visible-light irradiation is becoming more and more attractive. Great efforts have been made to improve the visible-light photocatalytic activity of mesoporous titania by impurity doping.[3] However, such methods are not very effective. To date, great challenges do exist in finding a new mesoporous material system that can effectively utilize the visible-light irradiation. Although some multiple-metal oxide semiconductors display very interesting and promising functionality for visible-light photocatalytic applications in the treatment of pollutants,[4] extension of the surfactant templating process to the formation of mesoporous multiple-metal oxide semiconductors has been less studied because their synthesis are more difficult than that of conventional silicon-based mesoporous materials,[5] and few photoactive mesoporous multiple-metal oxide semiconductors have been reported.[5c]

On the other hand, bismuth titanate is of interest because it has many applications in the field of microelectronics, electro-optics and dielectrics.[6] Several phases in the Bi–Ti–O system are known, including $Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7$, $Bi_2Ti_4O_{11}$, $Bi_{12}TiO_{20}$, $Bi_{20}TiO_{32}$ and so on. Some of them possess high visible-light-response abilities and are of increasing interest for their photocatalytic applications.[7] Applying synthetic strategies of mesoporous structures to bismuth titanate compounds will be a very interesting topic and may bring some new exciting discoveries.

In this study, mesoporous bismuth titanate with visible photocatalytic activity was prepared *via* a modified synthesis procedure based on the so-called evaporation-induced self-assembly technique (EISA).[8] Its photocatalytic activity for degradation of 2,4-dichlorophenol (2,4-DCP) in aqueous solution under visible-light irradiation has been evaluated. To the best of our knowledge, this is the first report on the synthesis of visible-light photocatalytic active mesoporous bismuth titanate.

The modified EISA method was carried out by using acetic acid rather than ethanol as solvent. In a typical synthesis, 1.0 g of Pluronic P-123 was dissolved in 8.0 g of glacial acetic acid, followed by the addition of 1.0 g of acetylacetone and stirred homogeneously (solution A). 6.4676 g of $Bi(NO_3)_3\cdot5H_2O$ was dissolved in 6.8 g of acetic anhydride by stirring to give a clear solution (solution B). Solution B was then added dropwise to solution A. After stirring the mixture at 38 °C for 4 h, 3.4036 g of tetrabutyl titanate was added dropwise to the above mixed solution. Then further stirring for 2–4 h. The resulting mixture was transferred into an open Petri dish, evaporated at 40 °C in air with relative humidity of 60–100% for 3–8 days, aged at 100 °C for 24 h and then at 180 °C for another 12 h. The as-made sample was calcined at 380 °C for 5 h to remove the block copolymer species.

The visible-light photocatalytic activity of the calcined sample was evaluated by the degradation of 2,4-DCP in aqueous solution. The photocatalytic reaction procedure was as follows; aqueous suspension (70 mL) of 2,4-DCP (1×10^{-4} mol L^{-1}) and 0.07 g of calcined sample was put in a reaction cell made of quartz. Light coming from a 500 W Xe arc lamp passed through a 10 cm IR water filter and a cutoff filter ($\lambda > 420$ nm), and then focused onto the reaction cell. The average light intensity measured with a photometer (International Light model IL 1400 A) was 78.2 mW cm^{-2}. Compressed air was purged into the solution by bubbling from the bottom to maintain an aerobic condition, and a magnetic stirrer was also used to keep the solution chemically uniform. Prior to irradiation, the suspension was stirred in the dark for 40 min to establish an adsorption–desorption equilibrium between the catalyst and 2,4-DCP. Afterward, the solution was irradiated with the visible-light. 3 mL of samples were taken at given time intervals and separated through centrifugation. The supernatants were analyzed by recording variations of the absorption band maximum (285 nm) in the UV-Vis spectra of 2,4-DCP by using a ThermoSpectronic UV

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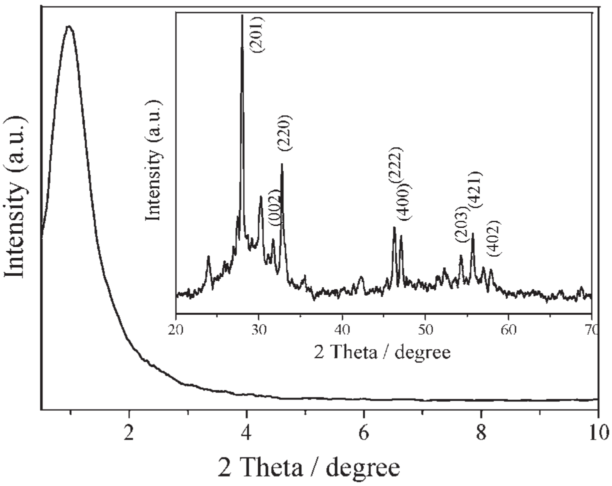

Fig. 1 XRD patterns of calcined sample. (Inset) High-angle peak.

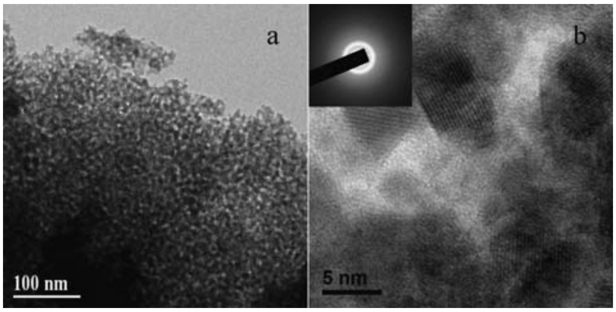

Fig. 2 TEM images and ED pattern (inset) of calcined mesoporous bismuth titanate.

500 UV-Visible spectrometer. According to the standard curve of concentration and absorption, the value of C/C_0 was calculated and indicated the degradation efficiency.

The powder X-ray diffraction (XRD) patterns of calcined sample are shown in Fig. 1. An intense and relatively broad reflection in the low-angle region is observed, and no other small angle peaks are discernible, suggesting that the product is MSU mesoporous material with wormlike framework structure. This result is further confirmed by the transmission electron microscopy (TEM) observations (Fig. 2a). The above result reveals that mesoporous bismuth titanate has been successfully synthesized through the modified EISA method under the controlled atmospheric humidity using acetic acid as solvent and P-123 as the template.

The calcined sample also presents some diffraction peaks in the wide angle X-ray diffraction region, as shown in Fig. 1, suggesting that the mesoporous pore walls possess crystalline nature to a certain extent. But no Bi_2O_3, anatase and rutile crystalline phases are formed. Besides the amorphous phase and some small unidentified crystalline phase peaks, most of the characteristic peaks emerged can be indexed according to the bismuth titanium oxide ($Bi_{20}TiO_{32}$) crystalline phase (JCPDS, Card No. 42-202), indicating that the mesoporous wall is consisted of mixed phases and the major phase is $Bi_{20}TiO_{32}$. The TEM images and electron diffraction (ED) pattern further confirm the above XRD results (Fig. 2). The ED pattern indicates the calcined mesoporous bismuth titanate possesses low crystallinity. Fig. 2b shows some crystal domains with size ~12 nm, which is consistent with that calculated from the (201) diffraction peak of $Bi_{20}TiO_{32}$ using the Sherrer formula (*ca.* 15.5 nm). This result indicates further that the crystals shown in the TEM image are $Bi_{20}TiO_{32}$ crystalline phase. However, it is difficult to obtain pure $Bi_{20}TiO_{32}$ phase because the $Bi_{20}TiO_{32}$ is a metastable phase and can transform gradually into the $Bi_2Ti_2O_7$ phase with an increase in temperature.[9] Meanwhile, the mesopore will gradually collapse at high temperatures because calcination always leads to the transition from amorphous to crystalline state and crystal growth, which is fatal to the mesoporous structure when the nano-sized crystallites grow beyond the wall thickness.[5c] In addition, it is worth noting that the aged process at 180 °C is important for the formation of mesoporous structures because this heat treatment process will make the pores pre-filled with carbon which is produced from the decomposition of surfactant, and prevents the pore structure from collapsing during calcination.

Fig. 3 shows N_2 sorption isotherms that are representative of mesoporous bismuth titanate. Barrett–Joyner–Halenda (BJH) analyses show that the calcined mesoporous samples exhibit a mean pore size of 6.1 nm (Fig. 3 inset) with a BET surface area of 50.1 $m^2 g^{-1}$. The large hysteresis is believed to be related to the capillary condensation associated with large pore channels. The low surface area may be due to the large density of bismuth titanate compounds.

The UV-Vis diffuse reflectance spectra of the calcined mesoporous bismuth titanate and Degussa P-25 are shown in Fig. 4. Compared to the P-25 powder, the synthesized mesoporous bismuth titanate demonstrates an obvious photoabsorption in the visible-light region, and its absorption edge shifts to the visible-light region, which is consistent with the yellowish color of the sample. The band gap absorption edge of the prepared mesoporous sample is determined to be 495 nm, corresponding to the band gap energy of 2.5 eV, which is different from those of the pure Bi_2O_3 (2.8 eV), anatase (3.2 eV) and rutile (3.0 eV). This result verifies further

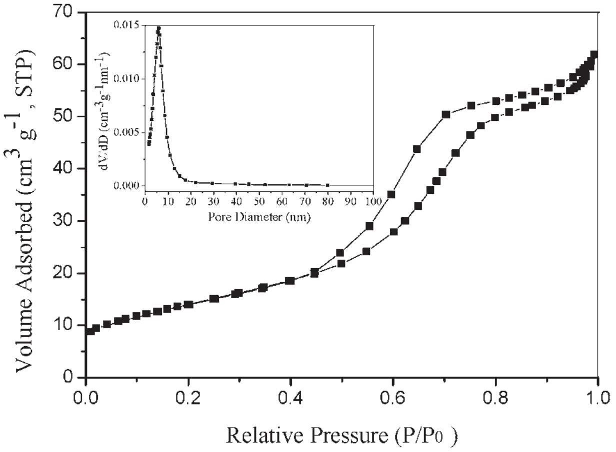

Fig. 3 N_2 adsorption–desorption isotherms and BJH pore diameter distribution determined from the adsorption branch of the isotherm (inset) for the calcined sample.

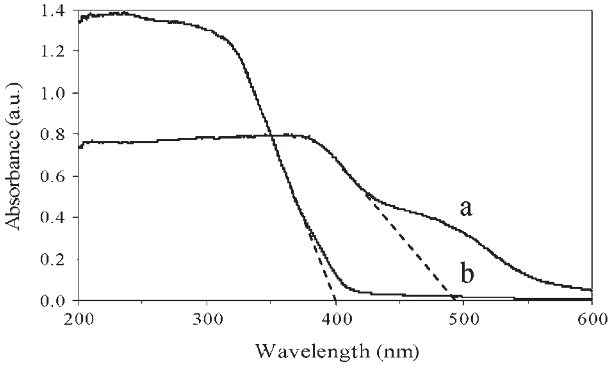

Fig. 4 UV-Vis diffuse reflectance spectra of mesoporous sample calcined at 380 °C for 5 h (a) and P-25 titania (b).

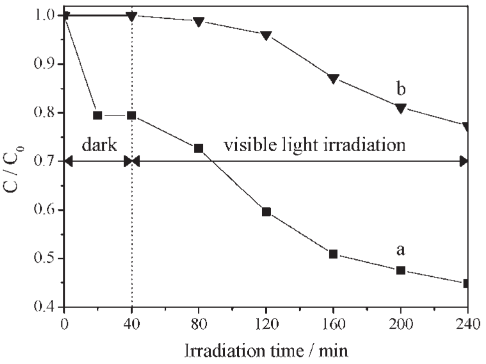

Fig. 5 Photodegradation of DCP (DCP: 1.0×10^{-4} M; 70 mL) under visible-light irradiation with 0.07 g of catalyst (a) and without catalyst (b).

that Bi_2O_3, anatase and rutile crystalline phases are not formed and the obtained sample is mesoporous bismuth titanate with mixed phase frameworks. Meanwhile, the above result also means that the obtained sample has the ability to respond to visible-light, and will exhibit visible-light photocatalytic activity.

2,4-DCP, a member of chlorinated phenols, is a good target for the evaluation of the obtained photocatalytical material because it has no absorption in the visible region. Fig. 5 shows the time profiles of C/C_0 under visible-light irradiation for the degradation of 2,4-DCP, where C is the concentration of 2,4-DCP at the irradiation time t and C_0 is the initial concentration. As shown in Fig. 5a, the adsorption–desorption equilibrium is quickly established within about 20 min for the calcined mesoporous sample, which may be attributed to the relatively high surface area and particularly to the much stronger adsorption ability of the sample. Considering that the decrease in the absorbance band at 285 nm reflects the disappearance of 2,4-DCP as it gets oxidized at the active sites on the catalyst and the concentration of 2,4-DCP decreases slightly over the time span of the experiments in the absence of a photocatalyst, the experimental results indicate that 2,4-DCP undergoes more extensive degradation in the presence of a catalyst, which suggests that the mesoporous material thus prepared has visible-light photocatalytic activity.

In summary, mesoporous wormhole-like bismuth titanate has been successfully synthesized *via* a modified synthesis procedure based on the EISA method. The calcined sample exhibited visible-light photocatalytic reactivity valued by the degradation of 2,4-DCP in aqueous media. The methodology may be extended to the synthesis of other mesoporous visible-light photocatalysts. This work provides a new pathway to design and fabricate novel mesoporous materials. With further improvement of the pore structures, pore ordering and framework composition, such materials will offer more opportunities for practical application in catalysis and environmental cleaning.

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