Influence of pH Value on Photocatalytic Activity of Bi₄Ti₃O₁₂ Crystals Obtained by Hydrothermal Method

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Bi₄Ti₃O₁₂ (BIT) crystals were controllably synthesized via a facile hydrothermal process without adding any surfactant or template. The morphologies of BIT with nanosphere, nanoplate, nanobelt, and nanosheet can be selectively obtained by adjusting the pH value of the reactant. The formation mechanisms of these distinctive morphologies were then discussed based on the structural analysis of samples obtained at different pH values. BIT sample prepared at pH=1 showed the highest photocatalytic activity under visible light irradiation. The photocatalytic activities difference for the BIT samples synthesized at different pH values was studied based on their shape, size, and the variation of local structure.

Key words: Photocatalysis, Bi₄Ti₃O₁₂, pH value, Local structure

I. INTRODUCTION

Environmental problems, such as organic pollutants and toxic water pollutants, provide the impetus for the fundamental and applied research in the environmental area. Photocatalysis using solar energy is favorably expected to be an ideal “green” technology for sustainable development of human beings where an active photocatalytic material offers the potential for the elimination of toxic chemical through its efficiency and broad applicability [1]. As a most promising photocatalyst, TiO₂ possesses many advantages such as chemical stability, low cost, nontoxicity, and high photocatalytic activity [2–7]. However, the band gap energy (3.2 eV) and the low quantum efficiency limit the practical application of TiO₂ photocatalyst. In order to improve the efficiency of the sunlight utilization, many efforts have been made to develop photocatalysts with high activity under a wide range of visible light [8–12].

In the past decades, bismuth titanate attracted much interest because it has many applications in the field of microelectronics, electro-optics and dielectrics [13–16]. Several phases in Bi-Ti-O system are known, including Bi₄Ti₃O₁₂ [17], Bi₄Ti₂O₇ [18], Bi₁₂TiO₂₀ [19], Bi₂₀TiO₃₂ [20], and so on. In recent years, for Bi-doped TiO₂ catalysts, the formation of Bi₄Ti₃O₁₂ (BIT) phase in Bi-doped TiO₂ inhibits the recombination of electrons-holes pairs and increases the photocatalytic activity of TiO₂ [6]. It is, therefore, of great interest to examine the photocatalytic properties of pure BIT crystals. In BIT-based layered-perovskites, pseudo-perovskite blocks are interleaved with (Bi₂O₃)²⁺ layers along the c-axis and an intraelastic field can be formed between them [17]. The bond angle of Ti–O–Ti is about 180°. This special structure is beneficial to reduce the recombination of the charge carriers and is helpful for photocatalytic oxidation of organic pollutants, since it might stimulate the separation of electron-hole pairs and facilitate the mobility of photogenerated carriers to the surface of the crystals. Photocatalytic properties of BIT have been examined. Kudo et al. has reported the preparation of BIT by the solid-state method and examined the photocatalytic activity of BIT for water splitting [13]. Yao et al. reported the preparation of BIT by the chemical solution decomposition (CSD) method and examined the photocatalytic activity of BIT [17]. In our previous work, we presented the hydrothermal synthesis of BIT micro/nano-structures and tested the photocatalytic properties of BIT [21, 22]. However, further research on the improvement of the BIT photocatalytic activity is still indispensable because of its poor quantum yield. In addition, there were few reports on the influence of morphology and variation in local structure upon the photocatalytic activity of BIT crystals obtained at different pH values.

Herein, we report a facile hydrothermal route without the use of any surfactant or template to synthesize BIT photocatalysts. The influence of reaction parameter (pH value) on the BIT morphology, structure, and the relationship between the morphology and photo-
catalytic activities was investigated. We develop a method for the fabrication of different-dimensional BIT nanomaterials enriching the available methods for preparation of multicomponent metal oxide, and adjust the properties by modulating the morphology and size of the materials, thus facilitating their applications.

II. EXPERIMENTS

A. Preparation of BIT photocatalysts

All the chemicals were analytically graded (purchased from Shanghai Chemical Industrial Company) and used without further purification. Bismuth nitrate (Bi(NO$_3$)$_3$·5H$_2$O) and titanium tetrachloride (TiCl$_4$) were chosen as starting materials. The BIT synthesis was as follows: 10 mL of TiCl$_4$ was dissolved in 50 mL cold H$_2$O under vigorous stirring, then mixed with Bi(NO$_3$)$_3$·5H$_2$O. KOH aqueous solution was also added slowly to adjust the pH value and the transparent solution changed to a white suspension. This suspension was stirred for 30 min and then transferred into a 20 mL stainless steel autoclave up to about 70% of its capacity. The autoclave was kept at 180°C for 24 h, and cooled to room temperature after the reaction. The precipitates were washed with deionized water and ethanol three times, respectively, and then dried at 100°C for 2 h to obtain the final products.

B. Characterization of BIT photocatalysts

The crystal structures of the samples were characterized by X-ray diffraction (XRD, D/max 2500) with Cu Kα radiation. Transmission electron microscopy (TEM) was conducted using a JEM-2100F instrument. The specific surface areas of BIT samples were measured through nitrogen adsorption BET method (3H-2000PSI BET/BJH Surface Area). Raman spectra of BIT samples were obtained by a micro laser Raman spectrometer (LabRam inva). Raman spectra were excited with the 514 nm line of an Ar$^+$ laser at an incident power of 20 mW. The UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded for the dry-pressed disk sample using a scan UV-Vis spectrophotometer (UV-Vis, UV-2550) equipped with an integrating sphere assembly. BaSO$_4$ was used as the reflectance standard material.

C. Photocatalytic activities

The photocatalytic activities of BIT series catalysts were evaluated by using rhodamine B (Rh B) dye as a model compound. In experiments, the Rh B dye solution (0.01 mmol/L, 100 mL) containing 100 mg of BIT photocatalyst were mixed in a pyrex reaction glass. A 500 W Xe lamp was used to provide visible light irradiation. A glass sheet was inserted between the lamp and the sample to filter out UV light ($\lambda<400$ nm). Prior to illumination, the suspension was strongly magnetically stirred for 30 min in the dark for adsorption/desorption equilibrium. Then the solution was exposed to visible light irradiation under magnetic stirring. At given time intervals, about 4 mL of the suspension was periodically withdrawn and analyzed after centrifugation. The Rh B concentration was analyzed by a UV-2550 spectrometer to record intensity of the maximum band at 552 nm in the UV-Vis absorption spectra.

III. RESULTS AND DISCUSSION

XRD patterns of BIT powders synthesized by hydrothermal method are shown in Fig.1. All diffraction peaks can be indexed to orthorhombic Bi$_4$Ti$_3$O$_{12}$ (JCPDS card No.36-1486), which are consistent with Ref.[23–25]. No peaks of impurities were detected from these patterns. The strong and sharp peaks indicate high crystallinity of the as-prepared BIT samples. TEM was used to observe the morphologies of BIT products. Figure 2 shows the TEM images of the as-prepared BIT samples obtained at different pH values of 1, 3, 5, 7, 9, 11, 12, and 14, respectively. Figure 2 (a) and (b) give the TEM images of a typical example of nanospheres, with average size around 5 and 10 nm, respectively. However, when the pH value increased to 5, a large number of nanoplates of BIT were formed, accompanied by the disappearance of nanospheres, as illustrated in Fig.2(c). With the increase of pH value (pH=7, pH=9), the sizes of BIT nanoplates increased, as shown in Fig.2 (d) and (e). Figure 2 (f) and (g) show BIT samples obtained at pH values of 11 and 12, respec-
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It can be observed that there are BIT nanobelts with widths of approximately 50 nm and lengths up to several micrometers. When the OH$^-$ concentration is further increased (pH=14), as shown in Fig. 2(h), BIT nanosheets are obtained. It should be noted that all the hydrothermally synthesized BIT crystals with different shapes and morphologies were formed simply by changing the pH of the synthesis.

Figure 3 schematically outlines the possible mechanism involved in the hydrothermal synthesis. Although the crystal growth habit is mainly determined by the intrinsic structure, it is also affected by the external conditions, such as pH of the solution, saturation, temperature, and so on [26, 27]. As we all know, pH value in the precursor solution has been found to be very important for the formation of the nanostructures. In this work, the condition of the alkaline medium as a factor is considered to play a key role in the formation of BIT nanospheres, nanoplates, nanobelts and nanosheets. At lower pH value (pH<3), BIT nuclei produced in solution can aggregate to form nanospheres. These nanospheres may serve as crystal seeds to grow the nanoplates and nanobelts structure. With the increase of alkalinity (pH=11), a large amount of BIT nuclei produced in the solution, lead to form the very high supersaturation solution, which favors the formation of nanobelts structure [5]. Besides, when the OH$^-$ concentration is further increased (pH=14), BIT nanosheets are obtained. Thus, the pH value plays an important role in controlling the formation of seeds and the growth rates to shape the BIT particles.

The UV-Vis diffuse reflectance spectroscopy (DRS) of the as-prepared BIT samples are shown in Fig. 4. As a comparison, the spectrum of commercial P25 is also measured. The absorption onset wavelength $\lambda_g$ of BIT samples prepared at pH values of 1, 3, 5, 7, 9, 11, 12, and 14 are around 402, 404, 406, 415, 416, 420, 434, and 442 nm, respectively. The band gap energy $E_g$ of

FIG. 2 TEM images of the as-prepared BIT samples prepared at different pH values of (a) 1, (b) 3, (c) 5, (d) 7, (e) 9, (f) 11, (g) 12, (h) 14.

FIG. 3 Schematic syntheses illustration of different morphologies of BIT crystals.

FIG. 4 UV-Vis DRS of P25 (a) and BIT samples prepared at different pH values of (b) 1, (c) 3, (d) 5, (e) 7, (f) 9, (g) 11, (h) 12, (i) 14.
BIT samples obtained at pH values of 1, 3, 5, 7, 9, 11, 12, and 14 are calculated to be about 3.08, 3.07, 3.05, 2.99, 2.95, 2.86, 2.80, and 2.78 eV, respectively, which show marked red shift in the absorbance compared to P25, due to the contribution of 6s electrons from Bi$^{3+}$ [14]. It indicates that BIT photocatalysts have a suitable band gap for photocatalytic decomposition of organic contaminants under visible light irradiation. In this system, slight blue shift of the absorption band edge of BIT samples (from 2.78 eV to 3.08 eV) can be observed with the pH value increasing from 1 to 14. It is well known that the band gap energy of semiconductor nanoparticles increases with the decrease of grain size [28]. Herein, BIT with 1D microstructure (pH=11, 12, 14) had a blue shift in the band-gap transition compared with spherical and plate-like BIT (pH=1−9), attributed to the smaller grain sizes of BIT nanospheres and nanoplates than that of the 1D nanobelts and nanosheets.

Photodegradation experiments of Rh B were carried out under visible light irradiation in order to test the photocatalytic performance of BIT photocatalysts. For comparison, the photodegradation of Rh B by P25 and that without any catalyst was also carried out. Temporal course of the photodegradation of Rh B in different catalyst aqueous dispersions is shown in Fig.5(a). The temporal evolutions of the spectral changes during the photodegradation of Rh B over BIT sample obtained at pH=1 under visible light illumination are displayed in Fig.5(b). Visible light irradiation of an aqueous Rh B/BIT (pH=1) product suspension led to an apparent decrease in absorption. It can be seen that Rh B solution is stable under visible light irradiation in the absence of any catalyst. It can also be observed that P25 exhibits inefficient photocatalytic degradation with Rh B decomposition rate of 50.0% within 360 min irradiation. In contrast, BIT samples reveal high photocatalytic activities with the Rh B degradation efficiencies of 72.0%, 74.0%, 79.0%, 81.0%, 84.0%, 87.0%, 90.0%, and 93.0%, respectively. Obviously, BIT sample obtained at pH=1 exhibited the highest photocatalytic degradation efficiency among those samples, which may be associated with the bigger BET surface area and smaller size, as shown in Table I.

The photocatalytic property of BIT is also related to...
the distortion of the M-O polyhedron in crystal structure. Laser Raman spectra of BIT samples are shown in Fig. 6. It can be observed that the as-prepared BIT samples exhibited only modes corresponding to BIT orthorhombic structure, in agreement with that reported in the Ref. [25]. The band located at 270 cm\(^{-1}\) is ascribed to the Ti-O bending vibration modes into the TiO\(_6\) octahedral, while the modes situated at 564 and 852 cm\(^{-1}\) correspond to the O-Ti-O stretching modes. However, an obvious change of the Raman band intensity occurred in this range varying with the increasing of pH values in reaction system. The dependence of the relative intensities of bending vibration of the TiO\(_6\) octahedral on the synthesis conditions is observed, demonstrating that different space symmetries are formed and the variation or rearrangement of the crystal structure exist under the influence of reaction conditions (pH value). A similar change of Raman-band intensity of the Mo-O stretching vibration was also observed in the Raman spectrum of Bi\(_2\)MoO\(_6\) [28]. It indicated slight changes in the structure, even though all the powders exhibited the orthorhombic structure. Based on the above results and analysis, it can be concluded that the change of pH value in reaction system may influence the crystal structure and corresponding photocatalytic performance.

IV. CONCLUSION

BIT photocatalysts with different morphologies have been synthesized through a facile, pH-controlled, surfactant-free hydrothermal route. XRD results confirmed that the composition of the as-fabricated samples is of orthorhombic structure. The energy band gaps of BIT samples are found to be about 2.78–3.08 eV. Due to the structure property relationships, BIT photocatalysts show enhanced visible photocatalytic activity over P25 in the decomposition of Rh B in water. It is suggested that the photocatalytic performance of BIT is greatly dependent on the local structure and the morphology. The hydrothermal technique presented here seems an economical and easy way for the morphology and local structure control of such material.

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