Synthesis and effects on visible light photocatalytic activity of Bi$_2$Ti$_2$O$_7$ photocatalyst

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Abstract. Bi$_2$Ti$_2$O$_7$ photocatalysts were successfully synthesized via the co-precipitation method and the solvothermal method and further characterized by XRD, SEM, BET, XPS and UV-vis DRS. Under visible light irradiation, the photocatalytic performance of Bi$_2$Ti$_2$O$_7$ photocatalysts were evaluated by the degradation of RhB solution. The results indicated that the as-synthesized Bi$_2$Ti$_2$O$_7$ photocatalyst via co-precipitation method has better photocatalytic activity than the photocatalyst prepared by the solvothermal method. The larger surface area and special morphology of the Bi$_2$Ti$_2$O$_7$ synthesized by co-precipitation method were responsible to enhanced photocatalytic performance.

1. Introduction
The energy crisis and environmental pollution problem, such as toxic water pollutants and organic pollutants, have become increasingly severe, and the quest to develop and utilize the energy resources of novel and renewable features without harmful effect has been considered as an important test. Photocatalysis employing solar power is friendly looking forward to be a desired “green” technique over the environmental sustainability where the effective photocatalytic materials provide a potential to the treatment of noxious chemicals via its performance and practical applicability [1-2]. TiO$_2$ is one of the most extensive and in-depth photocatalysts in the application of many photocatalysts while there are still many defects in the application progress such as the limits in the ultraviolet light ($\lambda<$400 nm) and photo-quantum efficiency [3-5]. In order to use visible light more effectively, developing the effective visible light-respond photocatalyst had been attracting increasing interest. Lately, abundant oxides (SrTiO$_3$, NaTaO$_3$, BiVO$_4$ and Bi$_2$WO$_6$) [6-7], due to its high performance, have been
Bi-Ti-O system includes several kinds of phases such as Bi$_2$Ti$_2$O$_7$, Bi$_2$Ti$_4$O$_{11}$, and Bi$_{20}$TiO$_{32}$ [8-12], which is formed by the different synthesis condition [13]. Bi$_2$Ti$_2$O$_7$, for example, as one of the A$_2$B$_2$O$_7$ compounds family, crystallizes with pyrochlore structure. It has plentiful crystalline morphologies, including nanowires, nanoparticles and nanotube, which have been obtained by using the high-temperature quenching method, facile hydrothermal method and wet chemical approach [14]. In previous study, with the visible-light irradiation the structure of pyrochlore (Bi$_2$Ti$_2$O$_7$), sillenite (Bi$_{12}$TiO$_{20}$) and Aurivillius-type (Bi$_4$Ti$_3$O$_{12}$) exhibited high performance for decomposing methyl orange [15], but there were few reports on preparing Bi$_2$Ti$_2$O$_7$ photocatalyst. The current work reported the synthesis method of Bi$_2$Ti$_2$O$_7$ photocatalyst using a chemical solution deposition method and a facile solvothermal method. The influence of the preparation method on the degradation of RhB solution is also investigated and discussed under the visible light irradiation.

2. Experimental

2.1 Synthesis

In this work, all the chemicals reagents were obtained commercially without further purification. The powders of Bi$_2$Ti$_2$O$_7$ photocatalyst were synthesized by coprecipitation and solvothermal methods.

Co-precipitation method: First, 0.005 mol Bi(NO$_3$)$_3$·5H$_2$O was added into 30 mL CH$_3$COOH to form solution with 40 minutes continuous stirring at room temperature. Second, 1.7 mL Ti(OC$_4$H$_9$)$_4$ was added slowly into above settled solution to form a suspension with white precipitate with 30 minutes constant stirring. Then, 60 mL NH$_3$·H$_2$O was added drop by drop in above solution to form a mass of white precipitate. Next, the white precipitate was filtrated and washed three times with distilled water and ethanol until no impurity was left, dried at 60 °C for 12 h. At last calcinated at 500 °C for 180 minutes, after grinding, the yellow Bi$_2$Ti$_2$O$_7$ was obtained and remarked BT1.

Solvothermal method: First, 50 mL C$_2$H$_5$OH and 5 mL C$_3$H$_8$O$_3$ were mixed in the 100 mL beaker with magnetic stirring about 1 h. Second, 0.003 mol Bi(NO$_3$)$_3$·5H$_2$O was added into this solution with constant stirring about 1.5 h at room temperature until a settled solution was obtained. Third, 2.55 mL Ti(OC$_4$H$_9$)$_4$ was added slowly into above settled solution to form a suspension with white precipitate. Before transferred into a 100 mL Teflon-lined autoclave, the obtained mixture in an oven after 15 minutes ultrasonic treatment, then maintained at 120 °C for 12 h. Finally, the Bi$_2$Ti$_2$O$_7$ precursor was filtered, dried at 60 °C for 3 h. At last calcinated at 500 °C for 180 minutes, and grind into yellow solid and remarked BT2.

2.2 Characterization

The as-synthesized BT1 and BT2 photocatalysts were characterized by the X-ray power diffraction (Cu Ka radiation, Bruker D8-2-Advanced, Germany), the scanning electron microscopy (Quanta FEG 250, USA), the physical adsorption of N$_2$ in ASAP2020, UV-vis spectrometer (Puxi TU-1901, China), and X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, UK).

2.3 Photocatalytic degradation

To explored the photocatalytic activity of the Bi$_2$Ti$_2$O$_7$, BT1 and BT2 samples were studied by the degradation of RhB under visible-light irradiation using 300 W xenon lamp with the light of λ > 420 nm. In the typical photocatalytic degradation activity experiment, 0.1 g BT1 and BT2 photocatalysts
were added into 100 mL RhB solution (10 mg/L), respectively. The solution was stirred in the dark for 30 min at room temperature in order to achieve the adsorption-desorption equilibrium. Every 60 minutes, 5 mL of solution was taken out and removed the power by a centrifuge. At last the solution was analyzed by UV-ultraviolet spectrophotometry.

3. Results and discussion

3.1 Crystal structure and morphology

The crystal structure of the Bi$_2$Ti$_2$O$_7$ synthesized via two different methods was characterized by XRD, and illustrated in Figure 1. It can be observed that there are two diffraction peaks of XRD patterns, which was consistent with pyrochlore Bi$_2$Ti$_2$O$_7$ (JCPDS No.89-4723) perfectly. Additionally, no any secondary phase was detected in the XRD patterns and the sharp diffraction peaks indicated the as-obtained samples were well-crystallized. The main X-ray diffraction peaks of the BT1 and BT2 samples located at $2\theta = 14.8^\circ$, 24.2°, 28.5°, 29.8°, 34.6°, 37.8°, 45.4°, 49.7°, 52.2°, 59.1° and 62.0° corresponded to the facets of (111), (220), (311), (222), (400), (331), (511), (440), (531), (622) and (444), respectively. The grain size was calculated as follows:

$$L = \frac{0.89\lambda}{\beta \cos \theta}$$

where $\lambda$ is the incident light wavelength, $\theta$ is the X-ray diffraction angle of incidence, and $\beta$ is the full width at half-maximum (FWHM) of the diffraction peak. According to calculation, the calculated average crystallite size of BT1 is around 97 nm, being over two times larger than that of BT2 sample (46 nm).

![Figure 1. XRD patterns of BT1 and BT2 photocatalysts.](image)

SEM analysis was conducted to observe the morphology of photocatalysts under different preparation conditions. Figure 2 is the SEM images of the BT1 and BT2 samples. It is clearly observed that the morphology is obvious different between the BT1 and BT2 samples. The BT2 photocatalysts have a ball-like morphology with smooth surface (Figure 2(a-c)). The SEM image with higher magnification (Figure 2(d)) indicates that the BT2 sample with diameters about 2-4 $\mu$m. The SEM image of BT1 in Figure 2(e) and (f) show that the BT1 is composed of particles with irregular shapes. Besides, the size of particles is chiefly distributed in the range of 1-2 $\mu$m.
Figure 2. SEM images of pure B$_2$T$_2$O$_7$ photocatalytic: (a-d) BT2 sample, and (e-f) BT1 sample

3.2 BET analysis
Figure 3 shows Barret-Joyner-Halenda pore size distributions and nitrogen adsorption-desorption isotherms of the BT1 and BT2 samples. In Figure 3(a), the adsorption-desorption curves of BT2 sample belong to the type V isotherm with hysteresis loops typical of mesoporous materials. The BT1 sample, however, belongs to the type III adsorption-desorption isotherm. From Figure 3(b) and (c), we calculated the average diameters of pore size distribution for the BT2 and BT1 samples were 10.47 nm and 42.15 nm. The BET surface areas of BT2 and BT1 samples were 13.35 and 16.38 cm$^2$/g, respectively. The BET surface area of BT1 was superior to the BT2 sample. As the previous reports, the increase of average crystallite size could increase the surface areas [16]. This also can be confirmed by the previous results of XRD and SEM analysis.

Figure 3. Nitrogen sorption isotherm of (a) BT2, BT1 sample and pore volume distribution curve of (b) BT2 sample, (c) BT1 sample

3.3 UV-visible adsorption spectra
The optical absorption properties of the semiconductor materials play a major role in the photocatalytic activity. Figure 4 displayed the typical UV-vis absorption spectra of all the as-synthesized samples at the wavelength in the range of 250-850 nm. The band gap absorption edge
of BT1 and BT2 samples are determined to be 430 nm and 431 nm, respectively, which shows quite good visible light absorption performance. The band gap can be further calculated from the equation:

\[ E_g = \frac{hc}{\lambda} \]  

(2)

Where \( E_g \) is the optical band gap, \( h \) is Planck’s constant, \( \lambda \) is the wavelength corresponding to the onset of absorbance, and \( c \) is the velocity of light [17]. Thus, the calculated \( E_g \) values of BT1 and BT2 samples are 2.88 and 2.87 eV, respectively. These results indicated that the Bi\(_2\)Ti\(_2\)O\(_7\) has potential photocatalytic ability.

**Figure 4.** UV-visible diffuse absorption spectra (DRS) of the BT1 and BT2 samples

### 3.4 XPS analysis

In order to further obtain the insight of the valence state and surface chemical composition of photocatalysts, the survey spectra of BT2 and BT1 are displayed at Figure 5(a), respectively. The high-resolution XPS spectra of the Bi 4f, Ti 2p and O1s for these two photocatalysts were also studied and displayed in Figure 5(b-d). The peak located at 284.68 eV belongs to C 1s peak, which is a standard of the peak positions of this element. The XPS spectrum of Bi 4f in Fig. 5(b) shows that the higher banding energy peak at 164.58 is Bi 4f\(_{5/2}\) and the lower banding energy peak at 159.18 eV is characteristic to Bi 4f\(_{7/2}\). In the Figure 5(c), two peaks are observed around binding energies at 464.88 eV and 458.08 eV, which are ascribed to the Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) binding energies, respectively. As displayed in Figure 5(d), the high resolution O 1s spectrum of BT2 and BT1 shows that two peaks located at 529.58 eV and 531.88 eV. The one of peaks at 529.58 eV attributes to the Bi-O bond at the lower binding energy [18], the other attributes to Ti-O bond at the higher binding energy peaks at 531.88 eV.

### 3.5 Photocatalytic activity

All the as-synthesized photocatalysts were measured by degradation of RhB (10 mg/L, 100 mL) under visible light irradiation (\( \lambda > 420 \) nm). According to the formula of \((C_0–C)/C_0 \times 100\%\) (\( C \) is the time-dependent concentration of mixture solution, and the \( C_0 \) is the initial concentration of mixture solution) and analytical concentration of RhB aqueous solution during the process of photocatalytic experiments, the removal rates of RhB are calculated and summarized in Figure 6. The results revealed that RhB solution can’t degrade itself without photocatalyst. This can also demonstrate that under
visible-light irradiation RhB organic dyestuff is fairly stable. Whereas, the photocatalytic degradation of RhB happened when the BT1 and BT2 photocatalysts were added into solution. The Figure 6(a) revealed that the photo-degradation efficiency of RhB solution for the pure BT1 sample is about 92.8% after 240 minutes under the visible-light irradiation, while that of BT2 sample is only about 74.6%. From the above results, the photocatalytic performance of BT1 was more excellent than BT2, which can be ascribed to the larger specific surface area of BT1. The larger surface area of photocatalyst could provide abundant bonding sites to degradation of organic [19], so that the photocatalytic performance of the photocatalyst has been efficaciously improved.

Figure 5. XPS spectra of BT1 and BT2 samples (a) survey spectrum, (b) Bi 4f, (c) Ti 2p, (d) O 1s
4. Conclusions

Bi₂Ti₂O₇ photocatalysts were successfully synthesized via the co-precipitation method and a solvothermal method in this paper. The photocatalytic activity of BT1 synthesized by co-precipitation method was obviously superior to the BT2 synthesized by solvothermal method in degradation of RhB under visible-light irradiation. The degradation efficiency of RhB solution for the BT1 and BT2 samples were about 92.8% and 74% after 240 minutes photocatalytic reactions. The larger surface area and special morphology of the BT1 photocatalyst were responsible to enhanced photocatalytic activity.

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Figure 6. Photodegradation of RhB in the presence of BT1 and BT2 samples (a) the UV-vis absorption of RhB-BT1 (b), the UV-vis absorption of RhB-BT2 (c).
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