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Original article

Synthesis and study of $Bi_2Ti_2O_7/TiO_2$ composites as efficient visible-light-active photocatalysts in the reduction of aqueous Cr(VI)

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ABSTRACT

In this work, $Bi_2Ti_2O_7/TiO_2$ composites were synthesized and studied as potential visible-light-activated photocatalysts in the reduction of aqueous Cr(VI). $Bi_2Ti_2O_7/TiO_2$ composites with tunable compositions were synthesized *via* a solvothermal-calcination two-step method, simply by changing the molar ratios of $Bi(NO_3)_3{\cdot}5H_2O$ to tetrabutyl titanate in the reactants. The compositions, structures and optical properties of the as-synthesized $Bi_2Ti_2O_7/TiO_2$ composites were characterized by X-ray diffraction, field emission scanning electron microscopy and UV–vis diffuse reflectance spectra. The photocatalytic activity of the as-synthesized $Bi_2Ti_2O_7/TiO_2$ composites was tested in the reduction of aqueous Cr(VI) under visible-light ($\lambda > 420$ nm) irradiation, and compared with that of TiO_2 nanoparticles. It was observed that the as-synthesized $Bi_2Ti_2O_7/TiO_2$ composites exhibited much higher photocatalytic activity than TiO_2 nanoparticles, and the most efficient composite (300 mg) can achieve the complete reduction of Cr(VI) in 300 mL of 50 mg/L $K_2Cr_2O_7$ aqueous solution under visible-light ($\lambda > 420$ nm) irradiation in 90 min.

1. Introduction

Hexavalent chromium (Cr(VI)) is highly toxic and highly soluble in water, and has been classified as a priority pollutant by many countries in the world [1–3]. Photocatalytic reduction has now been widely considered as a simple, effective, low cost and environmentally-friendly method for the treatment of aqueous Cr(VI) [4–8]. However, at present, the lack of efficient visible-light-activated photocatalysts has hindered the industrial application of photocatalysis technology in treating large-scale Cr(VI) wastewater. For instance, TiO_2, the most studied photocatalyst hitherto, can absorb only the UV light (only ~5% of solar energy) and exhibits little photocatalytic activity in the reduction of aqueous Cr(VI) under visible-light irradiation, due to its large bandgap (E_g = 3.2 eV) [8–10].

The modification of TiO_2 by smaller bandgap semiconductors has been proved to be a simple and effective way to achieve the visible-light photocatalysis [9–11]. Furthermore, composite photocatalysts can exhibit higher photocatalytic efficiency than their individual components, because of the synergistic effect of their components, such as the enhanced separation of photogenerated electrons and holes [9–12]. $Bi_2Ti_2O_7$ has a bandgap of 2.58–2.74 eV [13,14], and has been studied as a visible-light-active photocatalyst in the degradation of organics [14,15] and production of hydrogen by splitting water [16]. However, the reports on the use of $Bi_2Ti_2O_7/TiO_2$ composites as photocatalysts were scarce so far. Herein, we report the synthesis of $Bi_2Ti_2O_7/TiO_2$ composites by modifying the method proposed to synthesize $Bi_2Ti_2O_7$ [17], and the initial study of $Bi_2Ti_2O_7/TiO_2$ composites in the photocatalytic reduction of aqueous Cr(VI).

2. Experimental

Preparation: 18 mL of absolute ethanol and 7 mL of glycerin were added to a 50 mL Teflon jar, and the mixture was stirred until a homogeneous solution was obtained. A certain amount (0–1.76 mmol) of $Bi(NO_3)_3{\cdot}5H_2O$ was added to the absolute ethanol–glycerin solution and the mixture was stirred until the dissolution of $Bi(NO_3)_3{\cdot}5H_2O$. 1.5 mL (4.4 mmol) of tetrabutyl titanate was added dropwise to the above solution under magnetic stirring, and after the addition of tetrabutyl titanate, the resulting mixture was further magnetically stirred for 20 min. Diethyl ether (5 mL) was added to the above mixture and the mixture was stirred for 5 min.

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Table 1
Abbreviations and compositions of the products prepared using different Bi/Ti molar ratios in the reactants.

Bi/Ti molar ratios (%)	Abbreviations of products	Compositions (mass%)
0	BT-0	TiO_2 (100%)
10	BT-10	TiO_2 (90.8%) and $Bi_2Ti_2O_7$ (9.2%)
20	BT-20	TiO_2 (59.9%) and $Bi_2Ti_2O_7$ (40.1%)
30	BT-30	TiO_2 (13.4%) and $Bi_2Ti_2O_7$ (86.6%)
40	BT-40	TiO_2 (7.6%), $Bi_2Ti_2O_7$ (64.0%) and $Bi_4Ti_3O_{12}$ (28.4%)

The Teflon jar containing the reactants was placed into a stainless steel autoclave, sealed and heated at 110 °C for 12 h, then cooled to ambient temperature naturally. The resultant amorphous precipitate was centrifuged, washed with absolute ethanol and deionized water, dried in air at 100 °C for 10 h, and finally calcined at 500 °C for 3 h.

For the convenience of description, the products prepared using the Bi/Ti molar ratios of 0, 10%, 20%, 30% and 40% were abbreviated as BT-0, BT-10, BT-20, BT-30 and BT-40 (Table 1), respectively.

Characterization: The compositions, structures and optical properties of the products were characterized by X-ray diffraction (XRD, German Bruker AXS D8 ADVANCE X-ray diffractometer), field emission scanning electron microscopy (FESEM, Japan Hitachi S-4800 field emission scanning electron microscopy) and UV–vis diffuse reflectance spectra (American Varian Cary 5000 UV–vis–NIR spectrophotometer). Photocatalytic properties of the products (whose dosage was 300 mg) were tested in the reduction of Cr^{6+} in 300 mL of 50 mg/L $K_2Cr_2O_7$ aqueous solution under visible-light ($\lambda > 420$ nm) irradiation, with the addition of 1.0 mL of 100 mg/mL citric acid aqueous solution as the sacrificing reagent [18]. The photocatalytic reaction process was monitored by measuring the Cr(VI) concentration using the standard diphenylcarbazide colorimetric method [19].

3. Results and discussion

Fig. 1 shows the XRD patterns of BT-0, BT-10, BT-20, BT-30 and BT-40. All the XRD peaks of BT-0 can be indexed to pure anatase TiO_2 (Joint Committee on Powder Diffraction Standards (JCPDS) card number 89-4921). The XRD peaks of BT-10, BT-20 and BT-30 revealed the preparation of the composites of anatase TiO_2 and cubic phase $Bi_2Ti_2O_7$ (JCPDS card number 32-0118), whereas those

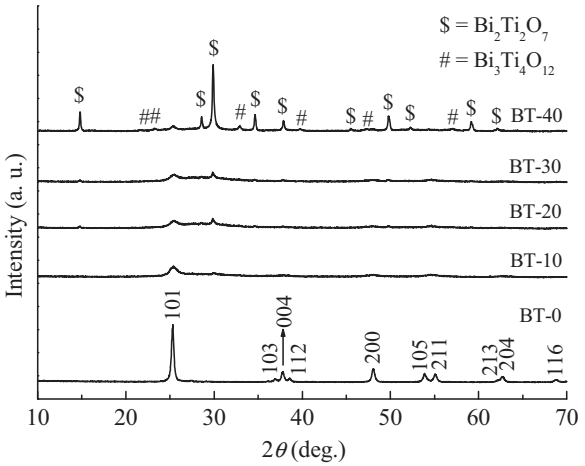

Fig. 1. XRD patterns of BT-0, BT-10, BT-20, BT-30 and BT-40.

of BT-40 suggested the formation of a mixture of anatase TiO_2, cubic phase $Bi_2Ti_2O_7$ and orthorhombic phase $Bi_4Ti_3O_{12}$ (JCPDS card No. 35-0795). The phase compositions of BT-10, BT-20, BT-30 and BT-40 were estimated by the method of XRD quantitative analysis, and the obtained results are shown in Table 1. The results revealed that the molar ratio of Bi/Ti played a crucial role in the phase compositions of the resultant products. This was also consistent with the previous report [20]. The formation mechanisms of different products may be described as the following equations:

$$Ti(OC_4H_9)_4 + 6ROH \rightarrow Ti(OH)_6^{2-} + 2R^+ + 4ROC_4H_9 \quad (1)$$

$$Bi^{3+} + 6ROH \rightarrow Bi(OH)_6^{3-} + 6R^+ \quad (2)$$

$$Ti(OH)_6^{2-} \rightarrow TiO_2{\cdot}nH_2O + (3 - n)H_2O \quad (3)$$

$$2Bi(OH)_6^{3-} \rightarrow Bi_2O_3{\cdot}mH_2O + (3 - m)H_2O + 6OH^- \quad (4)$$

$$Bi_2O_3{\cdot}mH_2O + 2TiO_2{\cdot}nH_2O \rightarrow Bi_2Ti_2O_7 + (m + 2n)H_2O \quad (5)$$

$$2Bi_2O_3{\cdot}mH_2O + 3TiO_2{\cdot}nH_2O \rightarrow Bi_4Ti_3O_{12} + (2m + 3n)H_2O \quad (6)$$

The microstructures of BT-0, BT-10, BT-20, BT-30 and BT-40 were characterized by FESEM (Fig. 2). The FESEM image of BT-0

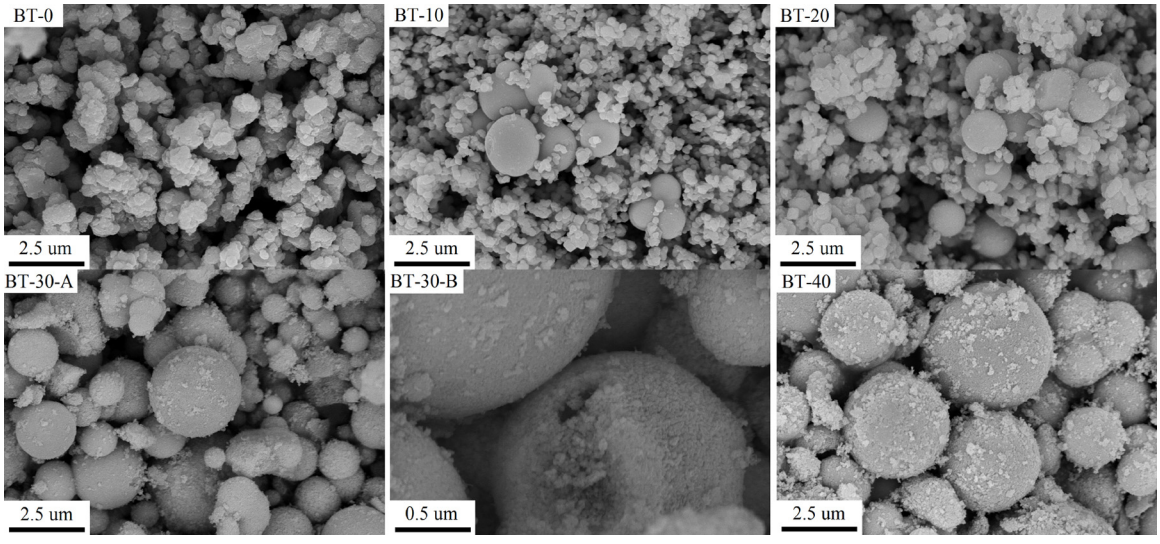

Fig. 2. FESEM images of BT-0, BT-10, BT-20, BT-30 and BT-40.