Photocatalytic Degradation of Organic Contaminants by BiVO₄/Graphene Oxide Nanocomposite

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Received: 1 November 2017, Revised: 24 January 2018, Accepted: 7 March 2018

Abstract

In the present work, a nanocomposite of bismuth vanadate (BiVO₄) and Graphene oxide (GO) was synthesized successfully by using hydrothermal process. The properties of BiVO₄/GO nanocomposite were examined by various techniques including X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD data indicated that pure BiVO₄ nanoparticles had a monoclinic structure. Similarly, BiVO₄/GO nanocomposite had the same structure without the peak of GO due to the transmission from GO to reduced GO during hydrothermal process. TEM images revealed that BiVO₄ particles were integrated effectively with the GO sheets. The photocatalysis performance was evaluated by the degradation of methylene blue (MB) in an aqueous under the irradiation of visible light. The result showed that BiVO₄/GO nanocomposites had higher photocatalytic activity than pure BiVO₄ nanoparticles. The explanation was that GO sheets enhanced the separation of electron–hole pairs and the adsorbent capacity leading to improved photocatalytic activity.

Keywords: BiVO₄, Graphene oxide, photocatalysis, nanocomposite, visible light

Introduction

In recent years, photocatalytic technology using nanomaterials has attracted much attention of scientists due to its variety of applications such as solar cells, water splitting and environmental remediation [1,2]. At the present, among the different photocatalysts, titanium dioxide (TiO₂) is considered as the benchmark catalysts and used widely in many photocatalytic reactions because it is nontoxic, chemically stabilized and photostable [3-5]. However, the main drawback of TiO₂ is its band gap (3.2 eV) which needs to be activated by ultraviolet (UV) irradiation. This is a big problem because most of the solar spectrum is visible light, while only 4% of the whole solar spectrum is occupied by UV [6,7]. To resolve this, researchers have been recently developing photocatalysts which are able to be excited under the irradiation of visible light. Among the researches, bismuth vanadate (BiVO₄) with a band gap of 2.4 eV has shown that it is an ideal photocatalyst with outstanding features such as...
inexpensiveness, environmental friendliness, and high stability [8-10]. However, the extensive application of BiVO₄ is limited by its poor adsorptive ability and the difficult migration of photogenerated charge pairs [7, 11, 12]. To improve the photocatalytic activity of BiVO₄, many researches have proposed doping routes on BiVO₄ with other materials such as Ag/BiVO₄ [13], Cu/BiVO₄ [14], Fe/BiVO₄ [14], AgO/BiVO₄ [15], WO₃/BiVO₄ [16], Bi₂O₃/BiVO₄ [17].

Graphene processes are known as new two-dimensional materials which have excellent properties such as high specific surface area, high electrical conductivity and high carrier mobility [18, 19]. Graphene oxide (GO) is a derivative of graphene with structure and properties which are similar to graphene. With reactive oxygen groups on the surface, GO is considered as a perfect support for several graphene-based composites that reported in the recent researches: TiO₂/Graphene [20], CdS/Graphene [21], C₃N₄/Graphene [22], due to the enhanced transfer and separation of photogenerated electron-hole pairs [23].

Therefore, with the goal of enhancing photocatalytic efficiency under the irradiation of visible light, the synthesis and characterization of BiVO₄-Graphene oxide nanocomposites were investigated in this work. In addition, photocatalytic activity of this nanomaterial was also evaluated in detail by the degradation of organic dye.

Materials and methods

Material

In this work, pure chemicals were used including bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O), sodium hydroxide (NaOH), nitric acid (HNO₃), sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), methylene blue (MB) from Ajax Finechem Pty Limited; ammonium metavanadate (NH₄VO₃) from Loba Chemie Pvt Ltd; sulfuric acid (H₂SO₄) and hydrochloric acid (HCl) from Rci Labscan Limited; hydrogen peroxide (H₂O₂) and graphite flake from Merck KGaA, Germany.

Synthesis of BiVO₄/GO nanocomposite

The GO was prepared from the oxidation of graphite flake by Hummer’s method with a modification [24, 25] as follows: graphite and NaNO₃ with the ratio of 2:1 were mixed in 100 mL of the concentrated H₂SO₄ under stirring in an ice bath. Then 8 g of KMnO₄ was slowly added to the above mixture, the temperature was kept lower than 20 °C. Afterward, the ice bath was removed, and the mixture was stirred at 35 °C for 10 h. Then, the mixture was diluted with 200 mL of DI water, this process made the color of solution became to dark brown. Subsequently, 15 mL of H₂O₂ was added to the above solution to stop reaction. Finally, the solution was centrifuged at 4000 rpm for 30 min, and then the obtained sample was washed with 10 % HCl and DI water until the pH was neutral.

In this work, the hydrothermal method was used to synthesize BiVO₄/GO nanocomposites by the following steps: 2.5 mmol of Bi(NO₃)₃·5H₂O and 2.5 mmol of NH₄VO₃ were stirred separately in 10 mL of HNO₃ 4M and 10 mL of NaOH 2M for 30 min. Next, a calculated amount of GO solution (0.5 mg/mL) was added to the Bi(NO₃)₃·5H₂O solution and stirred for 1 h. Afterwards, all these solutions were mixed together to form a homogenous solution, follow by heating at 180 °C in a Teflon-lined stainless-steel autoclave for 12 h. The obtained sample was washed with DI water for three times and dried at 60 °C to achieve the final product as BiVO₄/GO nanocomposites.

Characterization

The phase composition of the sample powder was determined by X-ray diffraction (XRD) analysis. The morphology was observed by transmission electron microscope (TEM).

Photocatalytic experiment

The photocatalytic performance of BiVO₄/GO nanocomposites was evaluated via the photodegradation of methylene blue (MB) under the irradiation of visible light at ambient condition. The experiment was carried out as follows: 1 g/L of BiVO₄/GO nanocomposites was added to 50 mL of the MB solution with 10⁻⁵ M in a beaker. Initially, the solution was stirred magnetically for 30 min in dark
condition to get the adsorption-desorption equilibrium. Subsequently, the solution was irradiated by visible light under constant magnetic stirring. The sample was collected every 30 min and measured by UV-Vis absorption spectra (UV-6100 Double beam spectrophotometer) at 664 nm of MB [26]. In comparison, the photocatalytic performance of pure BiVO₄ was also conducted in the same condition.

Results and discussion

Characterizations

Figure 1 shows the XRD patterns of pure BiVO₄, graphene oxide and BiVO₄/GO nanocomposites. For BiVO₄ particles, generally, the XRD patterns are similar to the diffraction data in ICDD Powder Diffraction File with card No.14-0688 [27] which is known as the monoclinic structure of BiVO₄ with the highest photocatalytic activity, that characterized by the peaks 18.5, 35 and 46° at 2θ [28,29]. The XRD patterns of GO are mainly observed at 11° of 2θ along with the disappearance of graphite peak at around 26° of 2θ. Meanwhile, the peaks of BiVO₄/GO exhibit similarly as BiVO₄. Additionally, there are no peaks of GO that observed in the XRD patterns of BiVO₄/GO due to the higher content of BiVO₄ in the BiVO₄/GO system and the transformation of GO to reduced GO during the hydrothermal condition [6].

![Figure 1 XRD patterns of pure BiVO₄, GO and BiVO₄/GO.](image1)

Figure 1 shows the morphology of BiVO₄, GO and BiVO₄/GO nanocomposites which were examined by the TEM analysis.

![Figure 2 TEM images of (a) BiVO₄, (b) GO and (c) BiVO₄/GO.](image2)
It can be seen that the pure BiVO$_4$ particles were rod-like crystals with an average size of 50 nm. Meanwhile, the obtained GO were nanosheets with size of 500 nm as shown in Figure 2b. The image of BiVO$_4$/GO nanocomposites suggested that BiVO$_4$ particles were effectively deposited on GO nanosheet.

**Photocatalytic activity**

The photocatalytic performances of pure BiVO$_4$ and BiVO$_4$/GO were evaluated by the photodegradation of MB as shown in Figure 3. Generally, the results showed clearly that the photocatalytic activity was enhanced significantly when graphene oxide was integrated with BiVO$_4$ particles.

![Photocatalytic degradation of methylene blue.](image)

The photocatalytic degradation of MB under 2 h of visible light irradiation reached about 70 % for pure BiVO$_4$ particles. Whereas it is noticed that adsorption ability is improved significantly in the case of BiVO$_4$/GO nanocomposites leading to 80 % of MB removed from the solution under the same conditions. The reason is that GO has promoted the transport of photogenerated electrons resulting in the effective separation of photogenerated electron-hole pairs [30]. As a result, the photocatalytic activity was enhanced efficiently for BiVO$_4$/GO nanocomposites.

**Conclusions**

In summary, BiVO$_4$/GO nanocomposite has been synthesized effectively by the hydrothermal method in this work. The morphology and structure of the BiVO$_4$/GO system were characterized by XRD and TEM analysis. This nanocomposite demonstrated its excellent ability in the adsorption and the photocatalysis compared to pure BiVO$_4$ nanoparticle. The enhanced efficiency of photocatalytic process could be attributed to GO which promotes the separation and transfer of photogenerated carriers.

**Acknowledgments**

This work was supported by grant from the Office of the Higher Education Commission and the Thailand Research Fund (TRF, Grant No. MRG6080097).
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