CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 45, Issue 3, March 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Chin J Anal Chem, 2017, 45(3), 357–362.

RESEARCH PAPER

Facile Solvothermal Synthesis of Reduced Graphene Oxide-$BiPO_4$ Nanocomposite with Enhanced Photocatalytic Activity

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Abstract: In this study, reduced graphene oxide-$BiPO_4$ (RGO-$BiPO_4$) nanocomposite was synthesized successfully via a one-pot solvothermal method using graphene oxide and bismuth nitrate as precursors and glycerin as solvent at 200 °C for 1 h. The morphology and structure of as-prepared nanocomposite was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), surface enhanced Raman spectroscopy (SERS) and UV-visible spectrum. The photocatalytic activity of the nanocomposite was evaluated by the photodegradation of Rhodamine B (RhB) dye under UV irradiation. The experimental results showed that RGO-$BiPO_4$ nanocomposite possessed higher photocatalytic activity than that of pure $BiPO_4$. RhB could be decomposed about 87.5% within 2 h. Under the same conditions, only 45.7% of RhB dye could be decomposed by $BiPO_4$. The enhancement of photocatalytic activity could be attributed to the effective charge separation due to the electron-accepting and transporting properties of RGO.

Key Words: Reduced graphene oxide; $BiPO_4$; Nanocomposite; Photocatalytic activity; Rhodamine B

1 Introduction

Semiconductor-based photocatalytic degradation process has gained increasing attention owing to its highly efficient, eco-friendly removal of organic contaminations present in the environment[1,2]. Among various semiconductor materials, TiO_2 is the mostly investigated material for photocatalytic decomposition because of its good photocatalytic activity, chemical stability, non-toxicity, and low cost[1,3–5]. However, the fast recombination rate of photogenerated electron-hole pairs of TiO_2, which reduces its photocatalytic activity[2,6], inhibits its promising applications in the environmental analyses. Therefore, other new types of photocatalysts have been designed and explored in order to overcome this shortcoming. Recently, some studies have demonstrated that Bi-based photocatalysts possessed superior photocatalytic activity compared to the commercial TiO_2 (P25)[7–16]. For instance, Pan and coworkers[8,9] introduced a new type of $BiPO_4$ oxy-acid salt photocatalyst, in which they found that the photocatalytic activity of $BiPO_4$ was twice that of P25 due to the high position of the valence band, high separation efficiency of electron-hole pairs, and inductive effect of PO_4^{3-}. Meanwhile, there had some reports on the photocatalytic activity of Bi_2WO_6, which exhibited high photoacatalytic activity in the visible light region[17–20]. These results provided a solid foundation for the design and synthesis of novel bismuth salt based photocatalysts in place of P25 in the field of environmental science.

Graphene, a monolayer of carbon atoms packed into a dense honeycomb crystal structure, has gained increasing

Received 29 September 2016; accepted 23 December 2016
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This work was supported by the Scientific and Technological Project of Henan Province, China (No. 162102310262), the Key Project of Colleges in Henan, China (No. 16A150015), and the Open Project Program of Key Laboratory for Photonic and Electric Bandgap Materials, Ministry of Education, Harbin Normal University, China (No. PEBM201510).

DOI: 10.1016/S1872-2040(17)61000-4

attention due to its unique physical, chemical properties, and potential applications. For example, it possesses high thermal conductivity, excellent mobility of charge carriers, large specific surface area, and good mechanical stability[21–24]. It is well known that photocatalytic activity is closely associated to the adsorption, conductivity, and controllability of the photocatalyst. In this sense, the properties of graphene may be expected to be beneficial for enhancing photocatalytic activity of photocatalyst. Thus, it is reasonable to assume that the effective incorporation of graphene into photocatalyst may enhance the photocatalytic activity. Recently, several groups reported their works on graphene-based nanocomposite materials for various applications[23–33]. Nevertheless, considerable efforts were taken to synthesize graphene-based nanocomposites by other means. Ng *et al*[26] reported the preparation of RGO-$BiVO_4$ nanocomposite using a visible light photocatalyst $BiVO_4$ to reduce GO photocatalytically to RGO, which exhibited remarkable enhancement effect compared to pure $BiVO_4$ in photoelectrochemical water splitting reaction. RGO-Bi_2WO_6 nanocomposite was also synthesized by in-situ hydrothermal reaction to form GO-Bi_2WO_6 nanocomposite and followed by reducing GO to RGO using ethylene glycol as reductant[30]. The obtained photocatalyst showed enhanced photocatalytic activity for the degradation of RhB. To the best of our knowledge, however, no research concerned on the synthesis and application of RGO-$BiPO_4$ nanocomposite has been reported. In this work, a facile route to prepare chemically reduced graphene oxide-$BiPO_4$ (RGO-$BiPO_4$) nanocomposite via a one-pot solvothermal method was demonstrated. In this approach, GO could be reduced solvothermally to RGO in glycerol at 200 °C. The photocatalytic activity of the as-synthesized product was examined by the photodegradation of RhB dye. As expected, the as-synthesized RGO-$BiPO_4$ nanocomposite exhibited remarkably enhanced photocatalytic activity compared to pure $BiPO_4$. The mechanism of enhanced photocatalytic activity was also discussed.

2 Experimental

2.1 Chemicals

Graphite was purchased from Alfa Aesar. $Bi(NO_3)_3·5H_2O$, $NaH_2PO_4·2H_2O$, and glycerol were bought from Beijing Chemical Factory (Beijing, China). Unless otherwise stated, all reagents were of analytical grade and were used as received without further purification. All aqueous solutions were prepared with distilled water.

2.2 Preparation of GO

The graphite oxide was synthesized from natural graphite powder based on Hummers method with slight modification[34]. Then, the exfoliation of graphite oxide to GO was obtained by ultrasonication of its dispersion for 2 h (100 W, 20% amplitude). Finally, a homogeneous GO aqueous dispersion (1 mg mL^{-1}) was obtained.

2.3 Preparation of reduced graphene oxide-$BiPO_4$ (RGO-$BiPO_4$) nanocomposite

RGO-$BiPO_4$ nanocomposite was prepared via a facile solvothermal method. In a typical procedure, 1 mmol of $Bi(NO_3)_3·5H_2O$ was added to 45 mL of glycerol/GO aqueous dispersion (volume ratio is 2:1) containing 3.2 mg GO under magnetic stirring. After the solution was stirred vigorously for 1 h, 1 mmol of $NaH_2PO_4·2H_2O$ was added to the mixture and stirred for 1 h. Finally, the mixture was transferred into a Teflon-lined autoclave, sealed, and maintained at 200 °C for 1 h. The final product was collected by centrifugation, washed with distilled water and absolute alcohol, and then dried at 60 °C. Pure $BiPO_4$ was also prepared under the same condition without the addition of GO for comparison purpose.

2.4 Characterization

TEM images were obtained with a TECNAI G20 high-resolution transmission electron microscope (FEI, USA) operating at 200 kV. SEM images were taken with a XL30 ESEM-FEG field-emission scanning electron microscope (FEI, USA) at an accelerating voltage of 15 kV. X-ray diffraction (XRD) patterns were collected by a D8 ADVANCE (Bruker, Germany) with Cu Kα radiation (λ = 1.54056 Å) in the range of 10°–80° (2θ). X-ray photoelectron spectroscopy (XPS) analysis was carried on an ESCALAB MK II X-ray photoelectron spectrometer (Microlab, The Great Britain). Raman spectra were obtained on a J-Y T64000 Raman spectrometer (JY, France) with 514.5 nm wavelength incident laser light. UV-vis absorption spectra were obtained with a Cary 100 UV-vis spectrophotometer (Varian, USA.).

2.5 Evaluation of photocatalytic activity

Photocatalytic degradation of RhB was carried out with 0.04 g of the powdered photocatalyst suspended in 40 mL of RhB solution (10^{-5} M) in a homemade photochemical reactor at room temperature under air. Before light irradiation, the mixture was first sonicated for 5 min and then kept in the dark for 30 min with stirring to reach an adsorption-desorption equilibrium. The optical system for detecting the catalytic reaction included a 3-W UV lamp. At the given time intervals, analytical samples were taken from the suspension and immediately centrifuged at 6000 rpm for 5 min. The concentration of RhB was determined by UV-vis spectroscopy method.

2.6 Measurements of electrochemical performances