Solid State Sciences 56 (2016) 10–15

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

$BiPO_4$ photocatalyst employing synergistic action of Ag/Ag_3PO_4 nanostructure and graphene nanosheets

N. Mohaghegh [a, *], E. Rahimi [b]

[a] Department of Chemistry, Sharif University of Technology, Azadi Avenue, Tehran, Iran
[b] Department of Mining Engineering, Islamic Azad University-South Tehran Branch, Tehran, Iran

ARTICLE INFO

Article history:
Received 11 January 2016
Received in revised form
31 March 2016
Accepted 1 April 2016
Available online 2 April 2016

Keywords:
$BiPO_4$ nanocomposite
Ag/Ag_3PO_4
Graphene
Photocatalysis

ABSTRACT

Graphene-supported $BiPO_4/Ag/Ag_3PO_4$ photocatalyst has been fabricated by simple hydrothermal and impregnation reaction. In $BiPO_4/Ag/Ag_3PO_4$ based on Reduced Graphene Oxide (RGO), this network renders numerous pathways for rapid mass transport, strong adsorption and multireflection of incident light; meanwhile, the interface between $BiPO_4/Ag/Ag_3PO_4$ and RGO increases the active sites and electron transfer rate. $BiPO_4/Ag/Ag_3PO_4$ based on RGO noticeably exhibited high photocatalytic activity than that of $BiPO_4/Ag/Ag_3PO_4$ and P25 under visible light irradiation for cationic dye (Rhodamine B), anionic dye (methyl orange) and 4-chlorophenol (4-CP) as a neutral pollutant, which are usually difficult to be degraded over the other catalysts. This enhanced photocatalytic activity of Graphene-supported $BiPO_4/Ag/Ag_3PO_4$ for all pollutants could be mainly ascribed to the reinforced charge transfer from $BiPO_4/Ag/Ag_3PO_4$ to RGO, which suppresses the recombination of electron/hole pairs. Besides that, this photocatalyst can be used repetitively with a high photocatalytic activity and no apparent loss of activity occurs. The results reveal that the RGO nanosheets work as a photocatalyst promoter during the photocatalytic reaction, leading to an improved photocatalytic activity.

1. Introduction

At present, the environmental pollution caused by textile dyes has emerged as the global concerns and is associated with the industrialization. So, the decolorization and mineralization of textile dyes from wastewater is a pertinent issue [1]. Currently, there is no simple and economical treatment that can efficiently remove dyes. Therefore, selective and sensitive detection of dye pollution as well as effective methods for the treatment are the main steps for diminishing the environmental pollutant effects. Visible-light photocatalysis has attracted tremendous interest due to their potential utilization for solar energy in the wastewater treatment for environmental remediation [2–4]. Therefore, search for the alternate effective and more potential visible-light responsive photocatalytic materials that are efficient is urgently required. In this context, variety of semiconductor photocatalysts mostly focused on the novel type inorganic nonmetal salts of oxy-acid and their derivatives have been examined in order to overcome the drawbacks of TiO_2 as a benchmark material [5–11].

Bismuth phosphate ($BiPO_4$), an oxy-acid salt photocatalyst, with a wide band gap (E_g = 3.85 eV) has been an emerging family of promising photocatalysts paid special interest since 2010 [12]. $BiPO_4$ has shown superior potential performances in the photocatalysis field. However, it should be noted that $BiPO_4$ only presents UV light photocatalytic activity and poor solar efficiency hinders the applicability of it [12–15]. In this regard, the development of efficient visible-light responsive photocatalysts is crucial for overcoming the drawbacks of $BiPO_4$. Recently, silver orthophosphate (Ag_3PO_4) as a visible light driven photocatalyst was found to demonstrate high performance in the photodegradation of hazardous contaminants in wastewater [16–18]. Obviously, hybridizing of $BiPO_4$ with narrow band-gap Ag_3PO_4 semiconductor has shown advantages in the prior studies [16–18].

Here, it is demonstrated that the addition of inorganic nonmetal salts of oxy-acid and their derivatives in combination with wide delocalization of negative charges on RGO nanosheets can promote the photocatalytic efficiencies. Individually, the application of these kinds of photocatalysts and RGO has shown advantages in prior studies [16,19–21]. In this paper, concerted and synergistic role of these two materials is studied. Through application of various characterization techniques, it was tried to shed a detailed light on

* Corresponding author.
E-mail address: mohaghegh@ch.sharif.edu (N. Mohaghegh).

http://dx.doi.org/10.1016/j.solidstatesciences.2016.04.001
1293-2558/

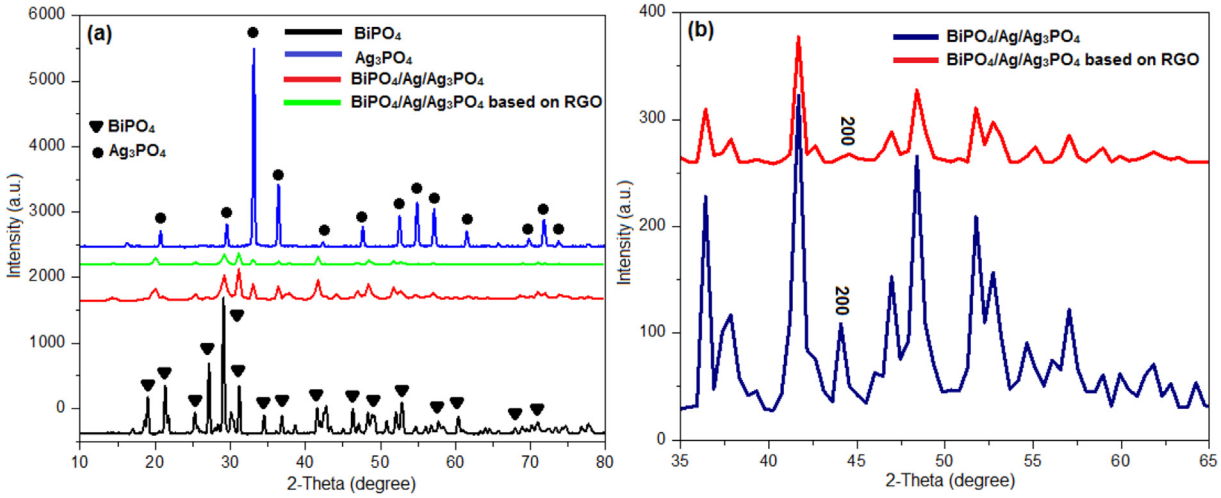

Fig. 1. XRD patterns of the prepared samples.

the underlying fundamental processes. In addition, the activity of the prepared samples was examined by investigating the degradation of cationic dye (Rhodamine B), anionic dye (methyl orange) and 4-chlorophenol (4-CP) as a neutral pollutant under visible light irradiation.

2. Experimental

2.1. Reagents and apparatus

All chemicals used were of an analytical grade and of the highest purity available. Rhodamine B (RhB), Methyl Orange (MO) and 4-chlorophenol (4-CP) were purchased from Sigma Aldrich and selected as the probe molecules to examine the photocatalytic activity of the prepared photocatalysts in this study. Milli-Q water was used in all of the experiments.

The crystal structures of the product powders were evaluated by X-ray powder diffraction (XRD) analysis using Philips X'pert instrument operating with Cu Kα (λ = 0.15406 nm) irradiation at 40 kV and 40 mA. The morphology of the fabricated samples was characterized using a field-emission scanning electron microscopy (model XL30, Philips). The Fourier transformed infrared (FT-IR) spectra were analyzed in the transmission mode on ABB BOMER MB series spectrophotometer. Impedance analyses were performed by Voltalab10 electrochemical system.

2.2. Catalyst preparation

The $BiPO_4/Ag/Ag_3PO_4$ was synthesized with a simple co-impregnation hydrothermal method in a two-step process. At first, $Bi(NO_3)_3 \cdot 5H_2O$ (0.012 mol) was dissolved in a highly dispersed solution (4 mL of concentrated HNO_3 and 32 mL of Milli-Q water sonicated for 15 min). Then, an aqueous solution of $Na_2HPO_4 \cdot 2H_2O$ (0.024 mol, 24 mL) was added dropwise to the above-mentioned mixture while it was stirring vigorously. The white precipitate was treated with a hydrothermal (HT) method at 180 °C for 24 h. A white $BiPO_4$ powder was collected by centrifugation, washed five times with Milli-Q water and ethanol, and then dried. Then, $AgNO_3$ was dissolved in 3 mL of Milli-Q water, and the obtained $BiPO_4$ powder (0.5 g) was dispersed in the $AgNO_3$ solution and sonicated for 1 h to yield a homogenous precursor. For the evaporation of water, this precursor was kept at 80 °C for 10 h. At last, the obtained product was calcined at 500 °C for 6 h to form $BiPO_4/Ag/Ag_3PO_4$.

The $BiPO_4/Ag/Ag_3PO_4$ based on RGO was prepared by the HT treatment. At first, 0.1 mL of GO aqueous solution (5000 ppm) was dispersed in a highly dispersed solution of Milli-Q water (20 mL) and ethanol (10 mL) under sonication for 1 h. 0.2 g of $BiPO_4/Ag/Ag_3PO_4$ was then added to the above prepared GO solution and stirred for another 2 h to get a homogeneous suspension. The prepared suspension was treated with a HT method at 120 °C for 3 h to simultaneously achieve the reduction of GO to RGO and the deposition of $BiPO_4/Ag/Ag_3PO_4$ on the RGO. At last, the product was collected by filtration, washed with Milli-Q water for five times and finally dried. By the way, the change of the solution colour containing $BiPO_4/Ag/Ag_3PO_4$ and GO to black which confirms the reduction of GO to RGO by HT treatment.

2.3. Photocatalytic experiments

Photoirradiation experiments were conducted on the photochemical Pyrex reactor. The visible light source was provided by inserting the UV cut-off filter after the Xe lamp 150 W for absorbing the UV irradiation and this visible source covered the wavelengths of λ > 420 nm. This reactor set-up was surrounded by the circulating water jacket to keep constant temperature at 23 °C. Experiments were conducted as follows: 10 mg of the photocatalyst was dispersed within a 100 mL of RhB aqueous solution (20 ppm). Prior to the irradiation, the suspension was continuously stirred for 1 h in the dark condition to reach the adsorption-desorption equilibrium between the catalyst surface and RhB to exclude the effect of dye adsorption in the photodegradation process. At a given time interval (20 min), 5 mL of suspension was withdrawn and centrifuged to remove the remnant catalyst particles. The supernatant was then recorded in the UV-vis spectrophotometer for determination of RhB concentration.

3. Results and discussion

3.1. Structural and morphological characteristics of prepared samples

Crystallinity of the prepared samples is reported via XRD patterns which are illustrated in Fig. 1. As displayed in Fig. 1a, no diffraction peaks are seen in the XRD patterns of $BiPO_4/Ag/Ag_3PO_4$ nanocomposite based on RGO due to the RGO. The characteristic peak of RGO at 24.5° might be shielded by the main peak of $BiPO_4/$