Materials Letters 217 (2018) 239–242

Contents lists available at ScienceDirect

Materials Letters

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

Facile fabrication of magnetically separable $Ag_3PO_4/CoFe_2O_4/GO$ composites with enhanced visible light photocatalytic performance

Daiyong Chao [a], Yingbo Liu [b], Zhongli Zhu [a,*]

[a] Chemistry and Environmental Engineering College, Changchun University of Science and Technology, Changchun 130022, China
[b] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

ARTICLE INFO

Article history:
Received 1 November 2017
Received in revised form 1 January 2018
Accepted 15 January 2018

Keywords:
Semiconductors
Magnetic materials
Photocatalysts
Ag_3PO_4

ABSTRACT

Novel magnetically separable $Ag_3PO_4/CoFe_2O_4$/graphene oxide (GO) composites with different mass ratios were prepared through a facile precipitation process. Photocatalytic activity of the as-prepared composites was evaluated by degrading methyl orange (MO) under visible light irradiation. The results indicated that $Ag_3PO_4/CoFe_2O_4/GO$ exhibited higher degradation efficiency for MO compared with pure Ag_3PO_4. The enhanced photocatalytic performance of $Ag_3PO_4/CoFe_2O_4/GO$ can be attributed to the effective separation of photoinduced electron-hole pairs. Radical-trapping experiments showed that holes and superoxide radicals were dominant radicals in the degradation process. According to the experimental results, a possible photocatalytic mechanism was also proposed. Furthermore, the $Ag_3PO_4/CoFe_2O_4/GO$ composites can be easily separated from the reaction solution by an external magnet due to the existence of $CoFe_2O_4$.

1. Introduction

As a rising star in the world of visible-light-active photocatalysts, silver orthophosphate (Ag_3PO_4) has drawn much attention in recent years for the oxidation of water and photodecomposition of organic contaminants [1]. Unfortunately, Ag_3PO_4 suffers from the structural stability issues because Ag^+ is easy to get photoinduced electrons to be reduced to Ag^0 in the absence of sacrificial reagent [2]. However, coupling Ag_3PO_4 with other semiconductors or carbon-based materials has been demonstrated a good strategy [3]. To date, some Ag_3PO_4-based hybrid photocatalysts, such as $Ag_3PO_4/TiO_2/GO$ [4], $Ag_3PO_4/g\text{-}C_3N_4/ZnIn_2S_4$ [5] and Ag_3PO_4/carbon quantum dots [6] have been successfully prepared with enhanced photocatalytic activity. But these composites are generally used in powdery form, it is difficult to separate and recycle, seriously limiting their further practical application. Magnetic photocatalysts are alternatives for addressing this problem.

Cobalt ferrite ($CoFe_2O_4$), a visible light responsive semiconductor with a narrower band gap of approximately 1.2 eV and high electron transfer capability, has been widely applied in photocatalysis [7]. It is also noteworthy that $CoFe_2O_4$-based composites can be magnetically separable in the suspension because of the satisfactory magnetic property of $CoFe_2O_4$ [8]. Recently, graphene oxide (GO) with large specific surface area, exceptional electrical conductivity and good solution-dispersibility, has been demonstrated to be an attractive support material in the field of photocatalysis [9,10]. Considering the excellent properties of $CoFe_2O_4$ and GO, we attempted to synthesize $Ag_3PO_4/CoFe_2O_4/GO$ composites for degrading MO. To the best of our knowledge, any report about the synthesis of ternary $Ag_3PO_4/CoFe_2O_4/GO$ composites has not been found.

In this study, ternary $Ag_3PO_4/CoFe_2O_4/GO$ photocatalysts were first synthesized through a simple chemistry precipitation approach. Photocatalytic performance and stability of the magnetic materials were evaluated over MO degradation under visible light irradiation. Finally, the capture experiments of reactive species and possible photodegradation mechanism were also studied.

2. Experimental

Preparation of $CoFe_2O_4$:$CoFe_2O_4$ was prepared by a hydrothermal method. 0.5948 g $CoCl_2{\cdot}6H_2O$ and 1.3515 g $FeCl_3{\cdot}6H_2O$ were dissolved in 30 mL deionized water. Further, the pH of the mixture was adjusted to 11 using 6 M NaOH solution. The reaction mixture was then transferred to a 50 mL Teflon-lined stainless steel autoclave for 12 h at 180 °C. The black precipitate was collected by a magnet, filtered and washed with deionized water and absolute ethanol, and then dried at 60 °C.

* Corresponding author.
E-mail address: zhuzhongli321@163.com (Z. Zhu).

https://doi.org/10.1016/j.matlet.2018.01.084
0167-577X/

Preparation of $Ag_3PO_4/CoFe_2O_4$/GO: GO was prepared according to a modified Hummers method [11]. For a typical preparation process, 13 mg GO was added to 50 mL deionized water and treated with ultrasound for 1 h, then 10 mL of $AgNO_3$ (311 mg) solution was added and sonicated for another 2 h. $CoFe_2O_4$ and Na_2HPO_4 mixture was obtained through a similar procedure. Subsequently, the Na_2HPO_4 solution containing $CoFe_2O_4$ was added dropwise to the $AgNO_3$ solution containing GO and stirred for 3 h. The obtained product was washed and dried. By adjusting the weight of $CoFe_2O_4$/GO (MG), a series of Ag_3PO_4/MG composites with different MG content were obtained. The weight ratio of MG to Ag_3PO_4 was 3%, 15%, 30% and 45%, which named as Ag_3PO_4/MG-3%, Ag_3PO_4/MG-15%, Ag_3PO_4/MG-30% and Ag_3PO_4/MG-45%, respectively. The weight ratio of $CoFe_2O_4$ to GO was 2:1.

3. Result and discussion

XRD patterns of as-prepared samples are shown in Fig. 1a. For the pattern of GO, there is a dominated diffraction peak at around 12° corresponding to the (002) reflection of GO [12]. From the spectra of $CoFe_2O_4$ and Ag_3PO_4, the indexed diffraction peaks can be assigned to $CoFe_2O_4$ (JCPDS no. 22-1086) and body-centered cubic structure of Ag_3PO_4 (JCPDS no. 06-0505), respectively. All of the diffraction peaks in Ag_3PO_4/MG-15 can be assigned to $CoFe_2O_4$ and Ag_3PO_4. The peak relative to GO was not observed because the regular layer-stacking of GO sheets was destroyed [13]. Similar intensity ratio (I_D/I_G) of GO (0.8547) and Ag_3PO_4/MG-15% (0.8536) can be observed, implying that the GO was not reduced during the composite synthesis process (Fig. S1a). This wide peak existed in ~24° should be the background of the glass (Fig. S1b).

Fig. 1b shows FTIR spectra of GO, $CoFe_2O_4$, Ag_3PO_4 and Ag_3PO_4/MG-15. In the GO spectrum, several characteristic peaks of GO can be seen [14]. For $CoFe_2O_4$ sample, the strong absorption peak at 579 cm^{-1} is attributed to Fe(Co)–O bonds in $CoFe_2O_4$ [15]. In the case of Ag_3PO_4, two characteristic absorption peaks at 1010 cm^{-1} and 561 cm^{-1} are corresponding to the asymmetric stretching and bending vibration of PO_4^{3-} groups, respectively [14]. In the spectrum of Ag_3PO_4/MG-15%, the absorption peaks of Fe(Co)–O bonds and the P–O stretching vibrations of PO_4^{3-} are also observed.

The UV–vis diffuse reflectance spectra of Ag_3PO_4 and Ag_3PO_4/MG composites are shown in Fig. 1c. Pure Ag_3PO_4 shows an obvious absorption edge at about 530 nm, which conforms to the previously reported results [16]. Clearly, all the Ag_3PO_4/MG composites present enhanced absorption over the whole visible-light region compared with Ag_3PO_4. The band gaps of Ag_3PO_4, Ag_3PO_4/MG-3%, Ag_3PO_4/MG-15%, Ag_3PO_4/MG-30% and Ag_3PO_4/MG-45% were estimated to be 2.38 eV, 2.28 eV, 2.22 eV, 1.85 eV and 1.55 eV, respectively (Fig. 1d).

The SEM images of the as-prepared products are shown in Fig. 2. Pure Ag_3PO_4 possesses smooth surface with diameters of about 400 nm (Fig. 2a). It is noticeable that the Ag_3PO_4 are enwrapped by GO sheets and tiny $CoFe_2O_4$ are decorated on the surface of Ag_3PO_4 (Figs. 2b-–d and S2). Furthermore, Ag_3PO_4/MG could be easily separated from aqueous dispersion by a magnet (Fig. 2c inset).

Fig. 3a shows the photocatalytic activity of different photocatalysts for MO under visible light irradiation. The degradation rate can be neglected in the absence of photocatalysts. All the Ag_3PO_4/MG photocatalysts showed higher photocatalytic activity than pure Ag_3PO_4. Among the ternary composites, Ag_3PO_4/MG-15% exhibited the highest photocatalytic activity.

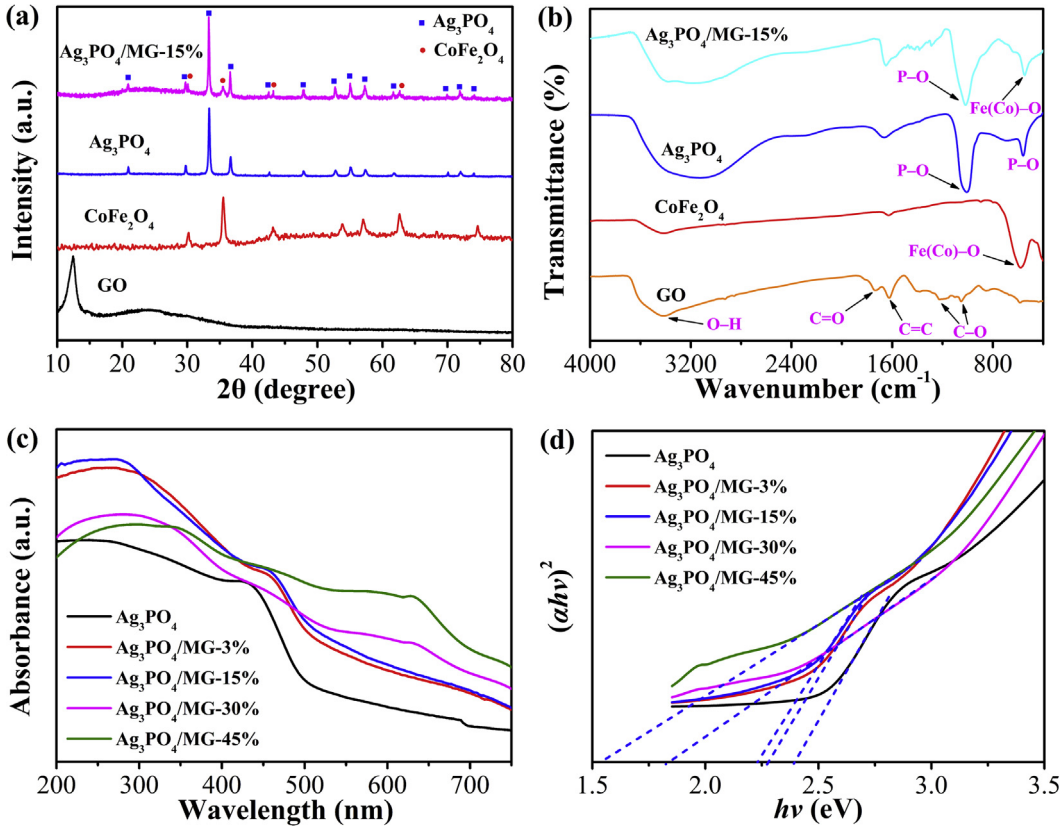

Fig. 1. (a) XRD patterns, (b) FTIR spectra of the as-prepared samples, (c) UV–vis diffuse reflectance spectra of different samples, (d) Plots of $(ahv)^2$ versus energy (hv) for different samples.