Materials Letters 214 (2018) 257–260

Contents lists available at ScienceDirect

Materials Letters

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

Construction of magnetic AgBr/Cu/$CuFe_2O_4$ Z-scheme photocatalyst with improved photocatalytic performance

Zhenlu Li, Jianchang Lyu, Kelei Sun, Ming Ge *

College of Chemical Engineering, North China University of Science and Technology, Tangshan 063210, Hebei, China

ARTICLE INFO

Article history:
Received 26 September 2017
Received in revised form 25 November 2017
Accepted 8 December 2017
Available online 9 December 2017

Keywords:
Magnetic materials
AgBr/Cu/$CuFe_2O_4$
Oxidation
Z-scheme mechanism
Reusability

ABSTRACT

A novel magnetic AgBr/Cu/$CuFe_2O_4$ composite was prepared by a two-step synthesis method, and this ternary composite exhibited an excellent photocatalytic performance for rhodamine B (RhB) and tetracycline (TC) degradation under visible light. The photocatalytic activity improvement of AgBr/Cu/$CuFe_2O_4$ composite could be attributed to the efficient space separation of photogenerated charge carriers through a Z-scheme configuration. As-synthesized AgBr/Cu/$CuFe_2O_4$ could be easily recovered by a magnetic field along with good reusability.

1. Introduction

Heterogeneous photocatalysis has a great potential to solve energy and environmental problems [1]. Mimicking the natural photosynthesis process, the Z-scheme photocatalytic system with the excellent photocatalytic performance has been developed in recent years [2].

AgBr photocatalyst has attracted attention due to its high visible-light photocatalytic activity [3], however, the consumption of noble metal silver strongly limits its practical application. To settle this problem, AgBr-based composites have been developed to reduce the use of AgBr [4,5]. $CuFe_2O_4$ with a narrow band gap of 1.4 eV is a magnetic visible-light-driven photocatalyst [6], and it could be easily recovered by a magnet after the photocatalytic reactions. Furthermore, $CuFe_2O_4$ has suitable band edges (E_{CB} ~−1.22 eV, E_{VB} ~+0.22 eV) [7], which can match well with AgBr (E_{CB} ~+0.08 eV, E_{VB} ~+2.54 eV) [8] to probably construct a Z-scheme photocatalytic system [2]. To date, there is no report combining AgBr and $CuFe_2O_4$ as a Z-scheme photocatalyst.

Herein, a magnetic Z-scheme AgBr/Cu/$CuFe_2O_4$ photocatalyst was firstly synthesized by coupling a solvothermal method with a precipitation route, and its photocatalytic activity was evaluated for RhB and TC degradation under visible light. The charge transfer mechanism for the enhancement in the photocatalytic performance of the AgBr/Cu/$CuFe_2O_4$ composite was also proposed.

2. Experimental

The synthesis of Cu/$CuFe_2O_4$ is shown in the Supplementary data. The AgBr/Cu/$CuFe_2O_4$ composite was synthesized by a precipitation method. The Cu/$CuFe_2O_4$ (0.034 g) was added into a solution consisting of 20 mL of distilled water and 20 mL of ethanol and sonicated for 20 min. 0.002 mol $AgNO_3$ and 0.6 mL aqueous ammonia were added into 30 mL of distilled water to form the silver ammonia solution, which was poured into the Cu/$CuFe_2O_4$ suspension and stirred for 20 min using a mechanical agitation. Then, the NaBr solution was added dropwise into the above suspension. After stirring for 3 h, the precipitate was gathered by a magnet, washed with distilled water and ethanol, and then dried at 80 °C. Pure AgBr was obtained when Cu/$CuFe_2O_4$ was absent. Details about the characterization of the samples can be found in the Supporting Information.

The photodegradation experiments were carried out in a simple photocatalytic reactor [9]. A 10 W LED lamp was used as visible light source. The catalyst (0.10 g) was added into RhB or TC solution (100 mL), which was stirred in the dark for 30 min. During each photocatalytic experiment, 3 mL of the suspension was taken at given time intervals and separated by centrifugation. The concentration of RhB and TC was calculated from the absorbance at 554 and 359 nm, respectively.

* Corresponding author.
E-mail address: geminggena@163.com (M. Ge).

https://doi.org/10.1016/j.matlet.2017.12.034
0167-577X/

3. Results and discussion

XRD patterns of AgBr, $Cu/CuFe_2O_4$ and $AgBr/Cu/CuFe_2O_4$ are displayed in Fig. 1a. All of the diffraction peaks of AgBr sample match well with cubic AgBr (JCPDS no. 06-0438). The $Cu/CuFe_2O_4$ sample exhibits the coexistence of Cu (JCPDS No. 85-1326) and $CuFe_2O_4$ (JCPDS No. 77-0010) structure [10], and $AgBr/Cu/CuFe_2O_4$ composite contains AgBr, Cu and $CuFe_2O_4$ phases (Fig. 1a). The survey XPS spectrum indicates that $AgBr/Cu/CuFe_2O_4$ composite mainly consists of Ag, Br, Cu, Fe and O elements (Fig. S1a). As shown in Fig. S1b and c and , the peaks of Ag 3 d at 373.7 and 367.6 eV are attributed to Ag^+ in AgBr, and the peaks of Br 3 d at 69.8 and 68.8 eV are ascribed to Br^- in AgBr [11]. The Cu 2p peaks is divided into Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks (Fig. S1d). The 934.5 and 954.4 eV peaks originate from Cu^{2+} in $CuFe_2O_4$ and those 932.5 and 952.4 eV are attributed to Cu [10]. Two peaks at 711.4 and 724.6 eV are separately ascribed to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ of Fe^{3+} (Fig. S1e).

Fig. 1b shows the SEM image of $Cu/CuFe_2O_4$ nanoparticles with an average diameter of 80 nm, and AgBr is composed of irregular particles (Fig. 1c). Obviously, $Cu/CuFe_2O_4$ nanoparticles are loaded on the AgBr to form $AgBr/Cu/CuFe_2O_4$ composite (Figs. 1d and S2a). The HRTEM result indicates Cu closely contacts with AgBr and $CuFe_2O_4$ (Fig. S2b). The EDS result illustrates that the elements of Ag, Br, Cu, Fe and O are from $AgBr/Cu/CuFe_2O_4$ (Fig. S3). The UV–vis DRS show that all the three catalysts exhibit absorption in the visible range (Fig. S4a). The band gap (E_g) of a photocatalyst can be calculated by the following equation:

$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

where α, h, ν, and A are absorption coefficient, Planck constant, light frequency, and proportionality constant, respectively. The value of n is determined from the type of optical transition of a semiconductor (n = 1 for direct transition and n = 4 for indirect transition). For both $CuFe_2O_4$ and AgBr, the value of n is 4 [7,8]. The E_g estimated by extrapolation of the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ are 1.50 and 2.54 eV for $Cu/CuFe_2O_4$ and AgBr, respectively (Fig. S4b). The values of E_{CB} and E_{VB} for AgBr and $CuFe_2O_4$ are described in the Supporting Information.

As shown in Fig. 2a, only 5.8% of RhB was decomposed by $Cu/CuFe_2O_4$ after 60 min, and about 94.6%, and 95.2% of RhB was degraded over AgBr, and $AgBr/Cu/CuFe_2O_4$ composite, respectively. The variation of the UV–vis adsorption spectrum of RhB degraded by the ternary composite shows that the intensity of the peak at 554 nm decreased significantly over time (the inset of Fig. 2a). Clearly, $AgBr/Cu/CuFe_2O_4$ composite has a superior photocatalytic performance compared with AgBr (Fig. 2a), indicating that a synergetic effect of AgBr and $Cu/CuFe_2O_4$ was present to improve the photocatalytic activity. Besides RhB, TC was also chosen to test the photocatalytic activity of the $AgBr/Cu/CuFe_2O_4$ composite. Nearly 71.0% of TC was photodegraded after 60 min, and the intensity of the absorption peak at 359 nm decreased drastically over time (Fig. 2b).

The photoluminescence (PL) spectra were detected to understand the higher photocatalytic performance of $AgBr/Cu/CuFe_2O_4$ composite relative to AgBr. As is illustrated in Fig. S5, the higher PL intensity of the composite than that of pure AgBr could be ascribed to the higher recombination rate between photoinduced electrons in the conduction band (CB) of AgBr and photogenerated

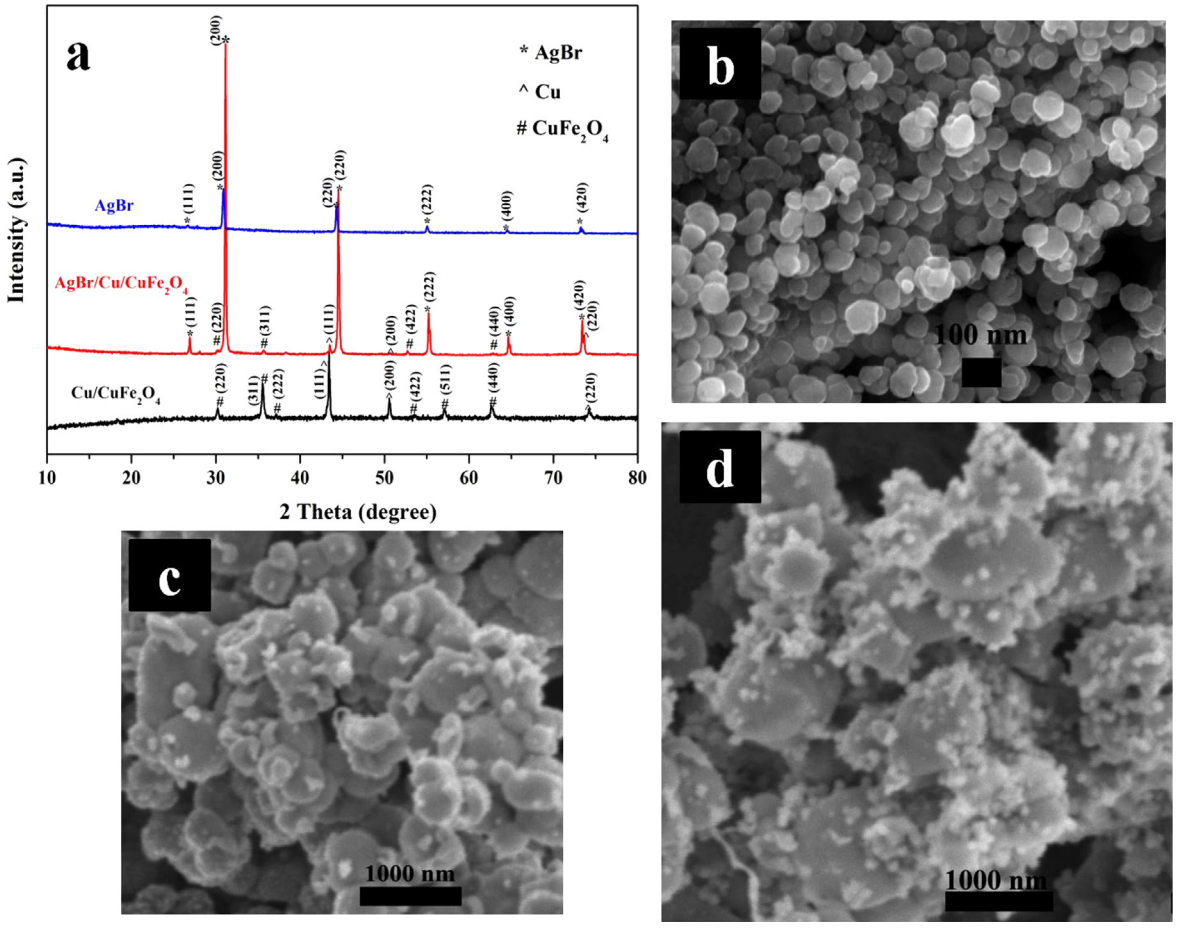

Fig. 1. XRD patterns of the samples (a); SEM images of $Cu/CuFe_2O_4$ (b); AgBr (c); $AgBr/Cu/CuFe_2O_4$ (d).