Materials Research Bulletin 56 (2014) 25–33

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Synthesis and photocatalytic performance of an efficient Ag@AgBr/$K_2Ti_4O_9$ composite photocatalyst under visible light

Yinghua Liang, Shuanglong Lin, Li Liu, Jinshan Hu, Wenquan Cui *

College of Chemical Engineering, Hebei United University, Tangshan 063009, PR China

ARTICLE INFO

Article history:
Received 7 January 2014
Received in revised form 20 April 2014
Accepted 22 April 2014
Available online 24 April 2014

Keywords:
A. Layered compounds
B. Chemical synthesis
C. X-ray diffraction
D. Catalytic properties

ABSTRACT

Ag@AgBr nanoparticle-sensitized $K_2Ti_4O_9$ composite photocatalysts (Ag@AgBr/$K_2Ti_4O_9$) were prepared by a facile precipitation–photoreduction method. The photocatalytic activities of the Ag@AgBr/$K_2Ti_4O_9$ nanocomposites were evaluated for photocatalytic degradation of (RhB) under visible light irradiation. The composites exhibited excellent visible light absorption, which was attributable to the surface plasmon effect of Ag nanoparticles. The Ag@AgBr was uniformly scattered on the surface of $K_2Ti_4O_9$ and possessed sizes in the range of 20–50 nm. The loading amount of Ag@AgBr was also studied, and was found to influence the absorption spectra of the resulting composites. Approximately 95.9% of RhB was degraded by Ag@AgBr (20 wt.%)/$K_2Ti_4O_9$ after irradiation for 1 h. The stability of the material was also investigated by performing consecutive runs. Additionally, studies performed using radical scavengers indicated that $^{\bullet}O_2^-$ and Br^0 acted as the main reactive species. Based on the experimental results, a photocatalytic mechanism for organics degradation over Ag@AgBr/$K_2Ti_4O_9$ photocatalysts was proposed.

1. Introduction

Industrial pollution and problems caused by organic pollutants have become a severe threat to human health and the environment. An interesting phenomenon which has been used for the preparation of efficient visible-light photocatalysts for photocatalytic degradation of environmental pollutants is the localized surface plasmon resonance (SPR) exhibited by nanoparticles (NPs) of noble metals. Silver NPs exhibiting SPR can be formed on the surface of silver halides (AgX, X = Cl, Br), and such silver@silver halide (Ag@AgX, X = Cl, Br) structures act as plasmonic photocatalysts with enhanced visible light absorption, where the AgNPs and AgX act together to polarize the photo-induced charges, inhibiting electron-hole recombination [1]. The AgX can also generate reactive species, such as $^{\bullet}Cl$ or $^{\bullet}Br$. Recently, Ag@AgCl and Ag@AgBr were synthesized by ion exchange and photoreduction method by Wang et al. [2,3], and the prepared materials showed efficient photocatalytic degradation activity.

However, these catalysts are associated to certain limitations such as the need for post-treatment separation in a slurry system after reaction, and impractical cost. These drawbacks can be overcome through the use of silver/silver halide composite materials. Such composites can be prepared to possess higher visible light response and increased rates of electron-hole separation during the photocatalytic process. For example, AgI/TiO_2 was prepared by Hu et al. [4] via the deposition–precipitation method, and was found to exhibit high efficiency for the degradation of non-biodegradable azodyes under visible light irradiation. Rodrigues et al. [5] have prepared AgBr/Al–MCM-41, which exhibited excellent photocatalytic activity for the photooxidation of acetaldehyde in the gas phase under UV and visible light. Ag–AgI/Al_2O_3 was also prepared by Hu et al. [6], and the photocatalytic reaction mechanism was suggested. These materials were promising for the photocatalytic degradation of organic pollutants.

$K_2Ti_4O_9$ can also be used in photocatalyst composites, and is a two-dimensional layered compound [7] with high specific surface area, which is formed by the connection of oxygen bridging atoms and octahedral units of TiO_6. Under visible light irradiation, it exhibits negligible photocatalytic activity, owing to its large band gap of ca. 3.2–3.4 eV. Therefore, the improvement of the photocatalytic activity of $K_2Ti_4O_9$ is of interest [8]. Herein, we prepared Ag@AgBr/$K_2Ti_4O_9$ by depositing Ag@AgBr particles on $K_2Ti_4O_9$ via a precipitation–photoreduction method and discussed its photocatalytic activity for organic compounds degradation under visible light irradiation. To the best of our knowledge, there are no existing reports on such an Ag@AgBr/$K_2Ti_4O_9$ system.

---

* Corresponding author. Tel.: +86 13292508307; fax: +86 315 2592169.
E-mail address: wkcui@163.com (W. Cui).

http://dx.doi.org/10.1016/j.materresbull.2014.04.043
0025-5408/© 2014 Elsevier Ltd. All rights reserved.

2. Experimental

2.1. Photocatalyst synthesis

A solid-phase reaction [9] was used to synthesize the $K_2Ti_4O_9$ powders. The detailed synthesis procedure is as follows: Anhydrous K_2CO_3 and TiO_2 was ground sufficiently in agate mortar with absolute ethyl alcohol at a molar ratio of 1.1:4. Then the ground compound was then calcinated in a chamber electric furnace at 1000 °C for 12 h.

The Ag@AgBr/$K_2Ti_4O_9$ sample was prepared via a precipitation–photoreduction method. Briefly, $K_2Ti_4O_9$ powder, NaOH, and $AgNO_3$ were dissolved into ethylene glycol and a given mass of NaBr–ethylene glycol solution was added to the mixture under stirring. The solution was then stirred for 30 min at room temperature. After the reaction, the mixed suspension was filtered, and washed with distilled water and absolute ethyl alcohol. The obtained AgBr/$K_2Ti_4O_9$ powder was dispersed into 50 mL distilled water, which was then photoreduced with a metal halogen lamp (250 W/$K_2Ti_4O_9$) was washed with deionized water and anhydrous ethanol to remove surfactant. The final products were dried at 80 °C for 8 h in the dark.

Pure Ag@AgBr was synthesized by a direct precipitation method with $AgNO_3$, NaBr, and ethylene glycol.

2.2. Photocatalyst characterization

X-ray diffractometry (XRD) were carried out at room temperature. Scanning electron microscope (SEM) (Hitachi, s-4800) and energy dispersive X-ray spectroscopy (EDX) were employed to observe the morphology of as-prepared catalysts. Additionally, selected area electron diffraction (SAED) patterns were collected via TEM. UV–vis diffuse reflectance spectroscopy (DRS) measurements were recorded on a UV–vis spectrometer (Puxi, UV1901). XSAM800 X-ray photoelectron spectroscopy (XPS) was employed to analyze the chemical states of the photocatalysts. The luminescence of the powdered samples was measured on a fluorescence spectrophotometer (Hitachi, f7000).

2.3. Photocatalytic activity

The photocatalytic activities of Ag@AgBr/$K_2Ti_4O_9$ composites were evaluated by the degradation of RhB under irradiation of visible light. There are two parts in the experimental apparatus. First part: A 250 W halide lamp (Philips) with a 420 nm cutoff filters to ensure the needed visible light at a distance of 10 cm from the unsealed beaker. Second part: A glass reactor with circulating water flowing outside to control the temperature to 25 ± 2 °C. During each test, 0.25 g catalyst powder was added into 250 mL RhB solution. Prior to irradiation, the test solution was stirred in the dark for 30 min. During irradiation, a 3 mL sample suspension was withdrawn every 15 min, and was centrifuged at 10,000 rpm for 6 min to remove the particles. The collect supernatant solutions were analyzed by the UV–vis spectrophotometer.

The degradation efficiency (%) as follows:

$$\text{Degration}(\%) = \frac{C_0 - C}{C_0} \times 100\%$$

where C_0 is the initial concentration of RhB, and C is the RhB concentration at time t.

Photocatalytic activities for RhB in the dark in the presence of the photocatalyst and under visible-light irradiation in the absence of the photocatalyst were also evaluated.

3. Result and discussion

3.1. Catalyst characterization

Typical XRD patterns for Ag@AgBr, $K_2Ti_4O_9$ and 10–20 wt.% -loaded Ag@AgBr/$K_2Ti_4O_9$ composites prepared via the precipitation synthesis are shown in Fig. 1, respectively. The Ag@AgBr was found to be mainly composed of AgBr, and all of the peaks matched with the JCPDS standard data of AgBr (JCPDS file: 06-0438). The diffraction peaks obtained were intense and sharp, indicating that the obtained Ag@AgBr photocatalysts were well crystallized. As shown in Fig. 1, the diffraction peaks (2θ) at 26.7° (1 1 1), 55.0° (2 2 2) and 64.5° (4 0 0) were ascribed to the diffractions of cubic phase of AgBr, while the peaks at 38.2° and 44.4° were ascribed to the metallic Ag. The diffraction peaks for $K_2Ti_4O_9$ and Ag@AgBr/$K_2Ti_4O_9$ appearing at 2θ of 10.1° (2 0 0), 14.3° (2 0 1), 31.0° (0 0 4) and 41.3° (5 1 2) were ascribed to monoclinic $K_2Ti_4O_9$ (JCPDS 32-0861). This suggested that the structure of $K_2Ti_4O_9$ did not transform after deposition of Ag@AgBr [10]. When the loading amount of Ag@AgBr was 10 wt.% in the Ag@AgBr/$K_2Ti_4O_9$ composite, because of the low content of Ag@AgBr, the diffraction peaks related to AgBr were not easily observed. However, the AgBr

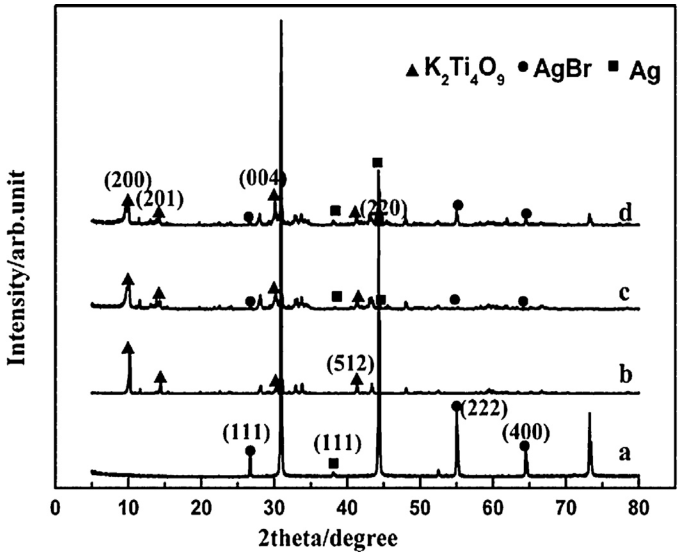

Fig. 1. XRD patterns of (a) Ag@AgBr, (b) $K_2Ti_4O_9$, (c) 10 wt.% Ag@AgBr/$K_2Ti_4O_9$ and (d) 20 wt.% Ag@AgBr/$K_2Ti_4O_9$.