Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–7

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

AgI/β-Ag_2MoO_4 heterojunctions with enhanced visible-light-driven catalytic activity

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ARTICLE INFO

Article history:
Received 7 June 2017
Revised 30 September 2017
Accepted 18 October 2017
Available online xxx

Keywords:
AgI/β-Ag_2MoO_4
Heterojunctions
Photocatalysis
Dyes
Tetracycline hydrochloride

ABSTRACT

Visible-light-driven photocatalysis for removing industrial dyes and antibiotics in waste water has attracted much interest. New catalysts with enhanced photocatalytic performance have been actively sought. Herein, via a simple sequential precipitation method, AgI nanoparticles were anchored onto micron-sized β-Ag_2MoO_4 particles to form AgI/β-Ag_2MoO_4 p–n heterojunctions. These heterojunctions exhibited remarkably upgraded activities in the visible-light-driven photocatalytic degradation of rhodamine B, methyl orange, and tetracycline hydrochloride compared with pristine AgI and β-Ag_2MoO_4. The enhanced photocatalytic activity can be mainly attributed to the tight heterojunction structure and well matched energy band that may facilitate the separation and transfer of photogenerated electron–hole pairs. Photogenerated holes (h^+) and superoxide radical anions ($\bullet O_2^-$) were found to be the main active species. A possible photocatalytic mechanism was proposed.

1. Introduction

Environmental pollution caused by toxic and harmful organic pollutants is exacerbating the danger to humans and other living species. Photocatalysis, an environment-benign technology, can be used to eliminate organic contaminants [1]. A key research topic of photocatalysis is the development of highly efficient photocatalysts.

Semiconductors based on silver halides (AgX, X = Cl, Br, or I) have attracted increasing interest [2–4]. Compared to AgCl and AgBr, AgI exhibits high potential in the development of visible-light-driven photocatalysts because of the relatively high photo-stability and suitable band gap (E_g = ~2.8 eV) [4,5]. AgX (X = Cl, Br, or I) can be modified by plasmonic silver to obtain stable photocatalysts [6,7]. For instance, Ghosh et al. reported that Ag–AgI composite exhibited higher photocatalytic antibacterial activity than AgI [8]. Wang et al. found that Ag/AgI heterojunction prepared by one-step hydrothermal synthesis exhibited stable and efficient photocatalytic activity [9]. Other AgI-based/containing composites, such as Ag–AgI/Al_2O_3 [10], Ag–AgI/Fe_3O_4@SiO_2 [11], $K_4Nb_6O_{17}$/Ag@AgI [12], Ag/AgI/BiOI [13], Ag/AgI@TNTs [14], g-C_3N_4/Fe_3O_4/AgI [15], AgI/$ZnSn(OH)_6$ [16], AgI/BiOIO$_3$ [17], RGO/BiOI/AgI [18], Ag@AgI/ZnS [19], ZnO/AgI/Fe_3O_4 [20], AgI/TiO_2/rGO [21], AgI/BiOI–Bi_2O_3 [22], AgI/WO_3 [23], AgI/$AgVO_3$ [24], $Bi_7O_9I_3$/AgI/$AgIO_3$ [25], Ag_2ZnI_4/AgI [26], and AgI/$Bi_2O_2CO_3$ [5], have been developed. It is still interesting to develop AgI-based new photocatalysts for fundamental research and practical applications.

Ag_2MoO_4 has been used in the preparation of high-temperature lubricants [27], ion-conducting glasses [28], photoluminescent materials [29], and photoswitch devices [30], owing to its good thermal stability, conductivity, and photosensitivity. However, reports on the photocatalytic application of β-Ag_2MoO_4 are rare [31], due to the wide band-gap (~3.3 eV) of β-Ag_2MoO_4 [32]. To develop better photocatalysts, β-Ag_2MoO_4 has been coupled with other substances to form heterojunctions such as Ag@Ag_2MoO_4–AgBr [33], Ag_2MoO_4/Ag_3PO_4 [34], Ag_2MoO_4/Ag/AgBr/GO [35], β-Ag_2MoO_4/Bi_2MoO_6 [36], and β-Ag_2MoO_4/g-C_3N_4 [37]. However, to the best of our knowledge, AgI/β-Ag_2MoO_4 heterojunctions have not been reported.

Considering that the band edges between AgI (E_{CB}: −0.40 eV; E_{VB}: 2.40 eV [24]) and β-Ag_2MoO_4 (E_{CB}: −0.18 eV; E_{VB}: 3.02 eV [37]) are well matched, in this work we developed AgI/β-Ag_2MoO_4 composites by a sequential precipitation method. These catalysts were tested in the visible-light-driven photocatalytic degradation of rhodamine B (RhB), methyl orange (MO), and tetracycline hydrochloride (TC). Relevant samples were characterized, and possible reasons for the enhanced photocatalytic activity were investigated.

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https://doi.org/10.1016/j.jtice.2017.10.018
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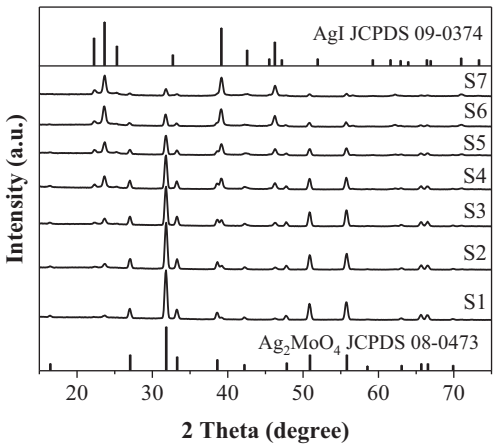

Fig. 1. XRD patterns of AgI/β-Ag_2MoO_4 composites and standard XRD patterns of β-Ag_2MoO_4 (JCPDS 08-0473) and AgI (JCPDS 09-0374).

2. Experimental

2.1. Materials

$AgNO_3$, $Na_2MoO_4{\cdot}2H_2O$, KI, rhodamine B (RhB), and methyl orange (MO) of analytical grade were purchased from Sinopharm Chemical Reagent. Tetracycline hydrochloride (TC) was purchased from Aladdin. All reagents were used as received.

2.2. Synthesis of AgI/β-Ag_2MoO_4

AgI/β-Ag_2MoO_4 composites were prepared by a sequential precipitation method at room temperature. In a typical synthesis, 4 mmol $AgNO_3$ was dissolved in a 100 mL breaker containing 30 mL deionized water to form solution A, and 2 mmol $Na_2MoO_4{\cdot}2H_2O$ was dissolved in another 100 mL breaker containing 30 mL deionized water to form solution B. Solution B was then added dropwise into solution A, under vigorous stirring (1200 r/min), to obtain β-Ag_2MoO_4. Then, a certain amount of $AgNO_3$ (0.25, 0.5, 1, 2, 4, 8, or 16 mmol) was added into the above system, and the mixture was magnetically stirred for 30 min to obtain Ag^+-β-Ag_2MoO_4. Subsequently, a solution containing 0.25, 0.5, 1, 2, 4, 8, or 16 mmol KI was added dropwise into the above mixture, and the mixture was continuously stirred for 4 h. The solid collected by filtration was washed with deionized water for three times, and dried at 60 °C for 24 h. These AgI/β-Ag_2MoO_4 composites were named as S1, S2, S3, S4, S5, S6, and S7, respectively. The theoretical AgI/β-Ag_2MoO_4 molar ratios of these composites (S1–S7 samples) are 1/8, 1/4, 1/2, 1/1, 2/1, 4/1, and 8/1, respectively.

For comparison, the same procedure was adopted to prepare pristine AgI (or β-Ag_2MoO_4) using 2 mmol $AgNO_3$ and 2 mmol KI (or 1 mmol $Na_2MoO_4{\cdot}2H_2O$) as the starting materials.

2.3. Characterization

X-ray diffraction (XRD) experiments were carried out on a MSAL XD2 X-ray diffractometer using CuKα radiation at 40 kV and 30 mA with a scanning speed of 8°/min. X-ray photoelectron spectroscopic (XPS) data were collected via a multifunctional photoelectron spectroscopy instrument (Axis Ultra Dld, Kratos). Scanning electron microscopy (SEM) experiments were conducted on a Shimadzu SUPERSCAN SSX-550 field emission scanning electron microscope. Optical diffuse reflectance spectra were recorded on a UV–Vis–NIR scanning spectrophotometer (Lambda 35, Perkin-Elmer) with an integrating sphere accessory. Photoluminescence (PL) spectra were collected using a LabRAM HR Evolution in-

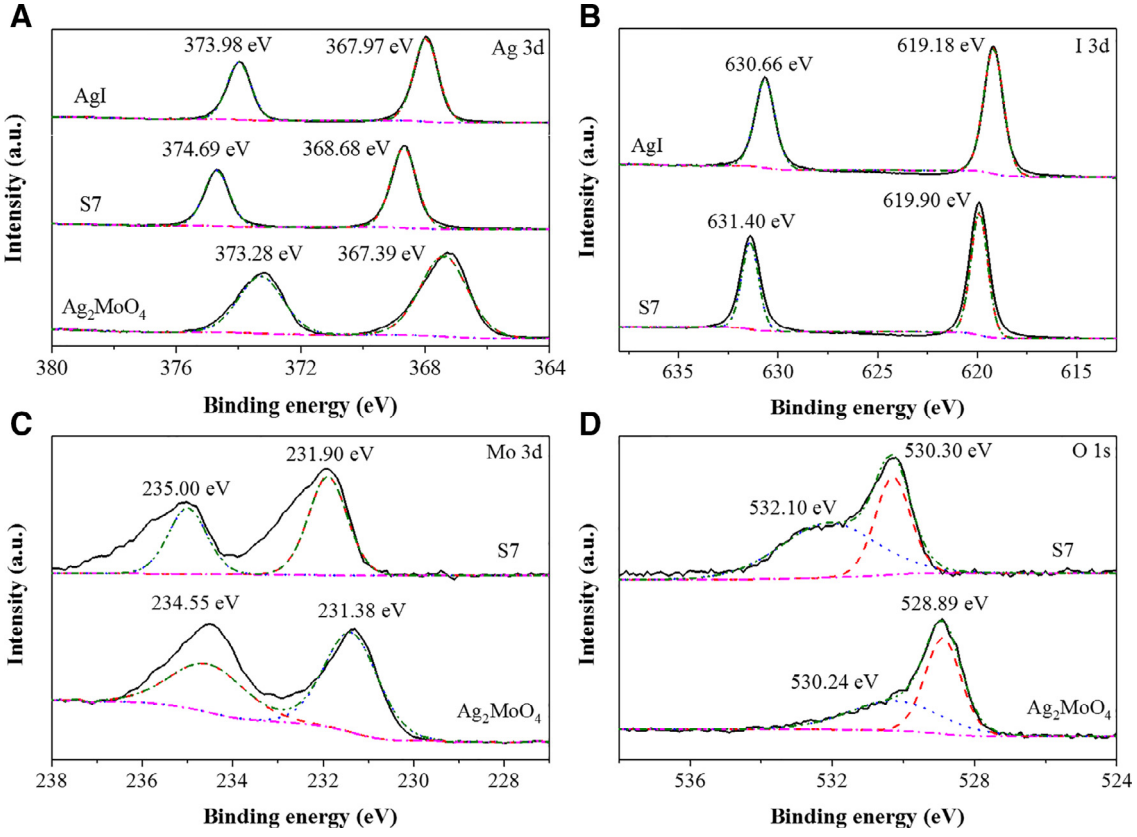

Fig. 2. XPS spectra of (A) Ag 3d, (B) I 3d, (C) Mo 3d and (D) O 1s peaks related to the samples.

Please cite this article as: J. Zhang, Z. Ma, AgI/β-Ag_2MoO_4 heterojunctions with enhanced visible-light-driven catalytic activity, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.10.018