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In situ anion exchange synthesis of β-Ag_2MoO_4/AgBr heterojunctions with enhanced photocatalytic activity and stability

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ABSTRACT

β-Ag_2MoO_4/AgBr heterojunctions were successfully prepared by a facile ultrasonic-assisted *in-situ* anion-exchange method, anchoring sphere-like AgBr particles on the surface of octahedral β-Ag_2MoO_4. Photocatalytic performances of the obtained samples were studied by the degradation of Rhodamine B (RhB), tetracycline hydrochloride (TC) and 4-Chlorophenol (4-CP) under visible-light irradiation. Results proved that the introduction of β-Ag_2MoO_4 had improved the photocatalytic activity of AgBr, and 5% β-Ag_2MoO_4/AgBr composites exhibited the highest degradation efficiency with degrading 98.4% RhB during 5 min, which was about 1.05 times and 13 times higher than that of pure AgBr and Ag_2MoO_4, respectively. Meanwhile, cycling test of as-prepared samples had indicated the excellent cycling stability of as-prepared samples. The obviously enhanced photocatalytic activity and stability could be attributed to the well-matched binding energies and heterostructure between AgBr and β-Ag_2MoO_4, where the utilization efficiency of solar light was improved, and charge separation at the heterojunction interfaces was accelerated. Besides, trapping experiments implied that holes and $\cdot O^{2-}$ were the predominant active species during the degradation process of RhB. Meanwhile, a possible mechanism for the degradation of organic pollutants by β-Ag_2MoO_4/AgBr photocatalysts was proposed.

1. Introduction

As an efficient and environmentally benign process in mitigating pollution and harnessing solar energy, semiconductor photocatalysis has attracted considerable attention [1–3]. However, traditional semiconductors like TiO_2 have inherent defects such as wide band gap, which resulted from its low efficiency in utilizing solar energy and limited practical application [4,5]. Thus, it's of utmost significance to develop visible-light-responsive photocatalysts, which can utilize 43% of total solar light.

Lately, silver halide (AgBr) has been one of the research focuses in the field of photocatalyst owing to its narrow band gap and high sensitivity to visible-light [6–8]. Nevertheless, it should be noticed that the same as other silver-based photocatalysis, AgBr is liable to photocorrosion to generate Ag^0 when exposed to solar light, which will drastically reduce the photocatalytic activity and stability of AgBr, thus hampering its practical application [9–12]. And it was widely accepted that photocatalytic activity and stability of silver-containing photocatalysts can be improved by fabricating heterostructures *via* coupling silver-based photocatalysts with each other or other semiconductors [13–16]. Accordingly, several AgBr-containing heterojunctions, such as AgBr/Ag_3PO_4 [17], AgBr/g-C_3N_4 [18], $AgIO_3$/AgBr [12], AgBr/Ag_2MoO_4 [19] have also been reported to display excellent photocatalytic activity and stability for the degradation of organic pollutants, indicating that AgBr-based heterostructure is an promising system to develop visible light responsive photocatalysts with excellent redox ability. Therefore, it's still significant to find a cost-effective and more suitable semiconductor to construct heterojunction with excellent photocatalytic activity and stability.

According to literatures, Ag_2MoO_4 can exhibit two kinds of different phases, including α-Ag_2MoO_4 having tetragonal structure and β- with cubic structure [20]. Besides, Ag_2MoO_4 has controllable morphology, which includes nanoparticle [21], as well as linear [22], flower like [23] and cubic [24]. However, because of its wide band gap and low visible-light absorption rate, β-Ag_2MoO_4 has very few applications in photocatalysis [25]. To amend these drawbacks and widen its practical application, β-Ag_2MoO_4 had been coupled with other semiconductors to form heterojunctions with enhanced photocatalytic performances, such as flower-like Ag_2MoO_4/Bi_2MoO_6 [26], AgI/β-Ag_2MoO_4 [27], AgBr/Ag_2MoO_4 [19], β-Ag_2MoO_4/g-C_3N_4 [28]. On the base of analysis, coupling of AgBr and β-Ag_2MoO_4 is expected to be a very promising

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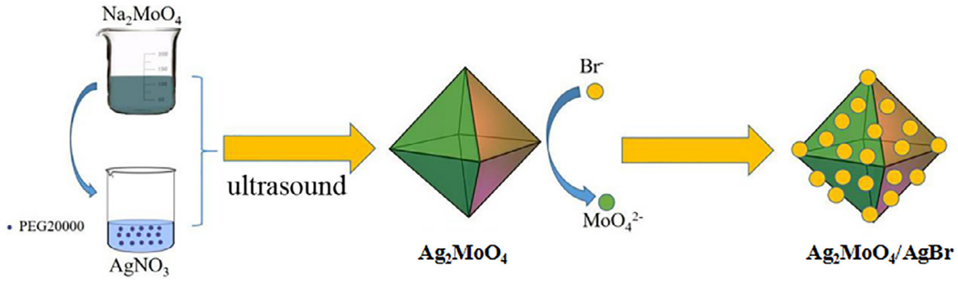

Scheme 1. Schemetic diagram for the formation of β-Ag_2MoO_4/AgBr.

system, by which not only the practical application of β-Ag_2MoO_4 in photocatalysis can be extended, but also the photocorrosion of AgBr can be prevented. To the best of our knowledge, there are only a few reports on the photocatalysis over AgBr/β-Ag_2MoO_4 heterojunctions [19]. For example, Zhang et al. [19] had prepared AgBr/Ag_2MoO_4composite with outstanding photocatalytic efficiency through a facile in- situ method, however, the preparation of Ag_2MoO_4 precursor involves hydrothermal method, which is very time-consuming and requires sophisticated autoclave process

In our work, sphere-like AgBr particles were assembled on the surface of octahedral β-Ag_2MoO_4 by ultrasound-assisted *in-situ* anion-exchange method to form β-Ag_2MoO_4/AgBr heterojunctions. And octahedralβ-Ag_2MoO_4 was obtained by a very facile green ultrasonic method. Resultant samples showed improved photocatalytic properties for the degradation of RhB, TC and 4-CP under visible-light irradiation. At the same time, influence of β-Ag_2MoO_4 content on the photocatalytic activity of β-Ag_2MoO_4/AgBr heterojunctions was discussed. And possible photocatalytic mechanism was proposed according to band gap structures and experimental results.

2. Experimental

2.1. Materials

All reagents were of analytical grade and purchased from Tianjin Yong Sheng Chemical Factory of China and used without further purification. Distilled water was employed throughout the experiment.

2.2. Synthesis of β-Ag_2MoO_4/AgBr heterojunctions

β-Ag_2MoO_4/AgBr heterojunctions were prepared by ultrasonic-assisted *in-situ* anion exchange method. Briefly, a certain amount of octahedral β-Ag_2MoO_4 was dissolved in 100 mL water, and dispersed by ultrasound for 30 min, then a certain amount of KBr solution was added drop by drop under stirring for 1 h, thus, β-Ag_2MoO_4/AgBr precipitation with β-Ag_2MoO_4 content of 2.5%, 5%, 10% and 30% (wt%) were obtained. Subsequently, the resultant precipitations were washed by absolute alcohol and distilled water for 5 times in turn, and dried for 12 h at 60 °C. For comparison, pure β-Ag_2MoO_4 and AgBr were prepared in the similar procedure.

In a typical synthesis of octahedral β-Ag_2MoO_4 (Scheme 1), 0.68 g $AgNO_3$ and 0.484 g Na_2MoO_4 were dissolved in 60 mL and 10 mL distilled water, respectively. 0.2 g PEG 2000 was added to the $AgNO_3$ solution under magnetically stirring for 10 min, then, Na_2MoO_4 solution was added into the mixture under the ultrasound irradiation (ultrasound frequency: 20 kHz, ultrasonic power: 200 W, ultrasonic mode: 1 s off 9 s/ on), and reacted for 15 min to get white precipitate. Obtained samples were centrifuged and washed by absolute ethanol and distilled water for 5 times, then dried at 60 °C.

In the process of AgBr synthesis, 0.34 g $AgNO_3$ and 0.238 g KBr were dissolved in 50 mL and 20 mL distilled water, respectively. Then, the KBr solution was mixed dropwise into the $AgNO_3$ solution under slow agitation for 30 min, after getting a yellow precipitate, obtained sample was separated by centrifugation and washed by absolute alcohol and distilled water for 5 times, then dried at 60 °C.

2.3. Characterization of the catalyst

The crystal phase of the samples were collected on X-ray diffractometer (Shimadzu XRD-6000) equipped with a Cu-Kα radiation at a scanning rate of 5°/min in the 2θ range of 10–80°. The overall morphology, structure and particle size of the samples were analyzed by field emission scanning electron microscopy (SEM, SU-8010, Hitachi, Japan), and the composition and content of elements were tested by its matched X-ray energy scattering spectroscopy (EDS). Transmission electron microscopy (TEM) images were conducted by using a JEM-2100 microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed by using a Kratos Axis Ultra system (Kratos Analytical Ltd, Manchester, UK) with monochromatic Al Kα X-rays (1486.6 eV) operated at 10 mA and 15 kV, and with a background pressure of approximately5.0×10^{-9} Torr. UV–vis diffuse reflectance spectra (UVDRS) were obtained on UV–vis spectrophotometer (U-3010, Hitachi, Japan) by using $BaSO_4$ as the matrix. Photoluminescence spectra were measured by aF-4500 FL spectrophotometer. The photoelectrochemical characterization was carried on CHI 660E (China) with a three electrodes electrochemical system.

2.4. Photocatalytic experiments

In this experiment, organic dye Rhodamine B (RhB), TC and 4-CP were selected as the analogue pollutants, and the photocatalytic activities of the photocatalysts were investigated by visible light photocatalytic degradation experiments. Briefly, 0.1 g sample was suspended in 100 mL 10 mg/L (10 ppm) RhB, TC or4-CP in a beaker. The mixture was stirred for 30 min under dark condition to reach adsorption–desorption equilibrium on the surface of the photocatalyst powder. Then, a filter ($\lambda \geq 420$ nm) was placed on the beaker, and the mixture was irradiated under the 300 W Xeon light source (CEL-S500, China). During the process, mixture was sampled in certain time intervals and centrifuged, and the supernatant was monitored (RhB: 653 nm, TC: 357 nm, 4-CP: 279 nm) by UV–vis spectrophotometer (U-3010, Hitachi, Japan).

3. Results and discussion

3.1. Preparation and characterization

The crystalline phase structure and purity of the samples were tested by the XRD patterns. As shown in Fig. 1, diffraction peaks at 2θ values of 16.46°, 27.06°, 31.84°, 33.29°, 38.62°, 42.21°, 47.83°,