The formation of visible light-driven Ag/Ag₂O photocatalyst with excellent property of photocatalytic activity and photocorrosion inhibition

Hui Xu, Jing Xie, Wei Jia, Guangming Wu, Yali Cao

Key Laboratory of Energy Materials Chemistry, Ministry of Education, Key Laboratory of Advanced Functional Materials, Autonomous Region, Institute of Applied Chemistry, Xinjiang University, Urumqi, Xinjiang 830046, China

GRAPHICAL ABSTRACT

A visible light-driven plasmonic photocatalyst Ag/Ag₂O with excellent property of photocatalytic activity and photocorrosion inhibition was synthesized through a simple solid-state technology.

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ABSTRACT

Ag/Ag₂O composites were prepared via an extremely simple solvent-free chemical technique. The obtained Ag/Ag₂O samples exhibited superior visible-light degradation efficiency for methyl orange removal. The degradation rate constant of as-obtained composite is almost 2 times as that of commercial Ag₂O, and has only little change after five cycles of utilization. The excellent photocatalytic properties of Ag/Ag₂O materials could be ascribed to desirable absorption property and surface plasmon resonance of metal silver on the surface of semiconductor Ag₂O. Meanwhile, the unstable and photo-sensitive disadvantages of commercial Ag₂O due to the photocorrosion could be largely suppressed in the presence of metallic Ag for Ag/Ag₂O composites, which plays an important role as an electron sink to receive the photo-generated electrons from Ag₂O, accordingly restraining the reduction of Ag⁺ in Ag₂O and improving the recyclability of Ag₂O. With the assistance of scavengers and ESR technique, the h⁺ and \(^{1}O_2\) were proved to be crucial reactive species in the pathways of photocatalytic degradation reaction.

1. Introduction

Semiconductor photocatalysis, as one of the most prospective technology for solar energy conversion and environmental remediation, has attracted tremendous attention since semiconductor
TiO$_2$ were applied to the decomposition of organic contaminants and the evolution of H$_2$ via a photocatalytic process [1–3]. As the most studied photocatalysts, TiO$_2$ only utilize 4% UV light because of low adsorption capacity in the solar irradiation, greatly limiting their practical applications. Consequently, it is necessary to discover new-type photocatalysts that can effectively respond to the visible light. At present, some Ag-based semiconductors, such as Ag$_2$PO$_4$ [4], AgVO$_3$ [5], Ag$_2$CO$_3$ [6,7], have aroused more and more attention due to the characteristics of easy visible-light excitation and low mammalian toxicity. Among these Ag-based semiconductor photocatalytic materials, silver oxide (Ag$_2$O) is a p-type semiconductor with a narrow band gap of 1.3 eV [1], which can be considered as one of the most prospective alternatives to the conventional photocatalysts due to its prominent visible-light absorption performance and extremely high photo-oxidative properties for organic pollutants. Nevertheless, the photo-sensitive and unstable properties of Ag$_2$O materials make it exhibit poor stability and rapid recombination of photo-induced electron-hole pairs. Faced with practical applications, it still has a lot of problems to solve for researchers.

In order to settle unstability of Ag$_2$O photocatalyst, the formation strategy of noble metal/semiconductor (M/S) hybrid material has been devoted to an effective method to improve the catalytic activity and stability in the purification of water contamination [8]. For Ag/semiconductor material, metallic silver demonstrates strong visible-light absorbance due to the strong surface plasmon resonance (SPR) effect [9,10]. Moreover, the photo-generated electrons prone to move to the surface of noble Ag. At this moment, metal Ag can work as an electron pool in virtue of low Fermi energy level of Ag, bringing about effective segregation capability of photo-excited electron-hole pairs [11], and also suppressing photo-reduction of Ag-based semiconductor. Recently, Lin et al. reported a plasmonic photocatalyst Ag/AgCl, which has proved to be stable, and it demonstrates superior visible-light photocatalytic property due to the plasmon resonance of metal Ag on the surface of AgCl particles [12]. Plasmonic Ag on Ag$_2$PO$_4$, Ag$_2$CO$_3$ could promote the photocatalytic degradation and enhance the durability of the Ag-based photocatalysts for Yu’s group [13,14]. The Hu’s research reveals that Ag particles optimize the photocatalytic performance and reusability of the Ag-based semiconductor, such as AgX@Ag, Ag$_2$CrO$_4$@Ag and Ag$_3$PO$_4$@Ag [15]. Meanwhile, Ag$_2$O nanoparticles as active photocatalysts can exhibit great self-stability once the Ag$_2$O structure is formed during the process of photodegradation, which has been reported by Yu’s group [16]. Thus the formation of Ag/Ag$_2$O hybrid structures is effective measures to improve the photocatalytic property of Ag/semiconductor material. Generally, composite material are prepared through the hydrothermal reaction, chemical precipitation and ion-exchange process, plasmonic metallic silver is simultaneously introduced by the photoreduction methods and chemical reduction in solution environment, which greatly rely on solvent and equipment condition, leading to a complicated, time-consuming, energy-consuming and hazardous operation process. Hence, the research of a facile solvent-free chemical method is necessary to be proposed to prepare the Ag/Ag$_2$O composite photocatalyst.

Herein, Ag/Ag$_2$O composites were fabricated by an extremely facile solvent-free chemical synthesis route. The composites were easily obtained only through simple two-step solid-state synthetic steps under the condition of no organic solvent in the whole process. The synthesis approach has several advantages, including mild reaction conditions, environmental-friendly, low cost and easy handling [17–19]. The photocatalytic activities of as-synthesized composites were investigated by degradation of methyl orange (MO), methyl blue (MB), Rhodamine B (RhB), Bisphenol A, Phenol and 2,4-dichlorophenol under the visible-light illumination. Ag/Ag$_2$O composites exhibits high catalytic activity and excellent stability, which could be attributed to good absorption property and surface plasmon resonance of metal silver on the surface of semiconductor Ag$_2$O. Ag/Ag$_2$O composites possess the practical potential for toxic and dangerous water contamination treatment under the visible light irradiation.

2. Experimental

2.1. Materials

Silver nitrate (AgNO$_3$, 99.8% A.R.) and sodium hydroxide (NaOH, 96.0% A.R.) are analytically pure and purchased from Tianjin Chemical Reagent Co., Ltd.

2.2. Synthesis of Ag/Ag$_2$O photocatalyst

For the synthesis of Ag/Ag$_2$O heterostructures, 10 mmol (1.6987 g) of solid AgNO$_3$ was accurately weighed and grounded into powder in an agate mortar, then 40 mmol (1.6 g) of solid NaOH with chemical reduction was added into an agate mortar and mixed by grinding to guarantee the occurrence of solid-phase chemical reaction. After the mixtures were ground for 40 min at room temperature, the obtained sticky brown products were washed with de-ionized water for several times to remove the byproducts, and then dried under natural conditions. Subsequently, the acquired dry powder was respectively annealed at 180 °C, 220 °C, 260 °C and 300 °C for 2 h to improve crystallization in a muffle furnace of air atmosphere. As the calcining temperature rises, the color of as-prepared samples deepens gradually. The final products (Ag/Ag$_2$O-180 °C, Ag/Ag$_2$O-220 °C, Ag/Ag$_2$O-260 °C and Ag/Ag$_2$O-300 °C) were collected, and marked as A1, A2, A3 and A4 for further characterization and testing.

2.3. Characterization of photocatalysts

The crystallographic characters of as-synthesized samples were measured by powder X-ray powder diffraction (XRD) spectrums (a Bruker D8 X-ray diffractometer) equipped with Cu-K$_\alpha$ radiation (\(\lambda = 1.54056 \, \text{Å}\)) at a scanning speed of 2° min$^{-1}$, in the 20 ranging from 10° to 80°. The morphology and size of as-prepared samples were obtained by a field emission scanning electron microscopy (FESEM, Hitachi S-4800 at accelerating voltage of 5 kV). The component element and content of the products were measured by energy disperse X-ray spectroscopy (EDS) on EDAXTLS attachment with an operating voltage of 30 kV. High resolution transmission electron microscope (HRTEM) images of the obtained products were collected to understand the lattice fringe with an accelerating voltage of 200 kV on a JEOL JEM-2100F. The X-ray photoelectron spectroscopy (XPS) signals was performed to characterize the surface components and structure of as-obtained samples in a Thermo ESCALAB 250 system employing a monochromated Al X-ray source. UV–vis diffuse reflectance spectroscopy (DRS) was characterized on a UV–vis spectrophotometer U-3900 using BaSO$_4$ as a reflectance standard. The UV–vis absorption spectra of the samples were recorded by a Hitachi U-3010 UV–vis spectrophotometer during 200–800 nm using distilled water as a reference sample. The photoluminescence (PL) spectra of photocatalytic materials were detected using fluorescence spectrophotometer (Hitachi F-4500). The surface photovoltage spectroscopy (SPS) tests of products were performed with a home-built apparatus, and the powder sample was sandwiched between ITO glass electrodes by employing outer electric field. The electron spin resonance spectra (ESR) techniques with spin-trapped reagents 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-Tetramethylpiperidinooxy (TEMPO) were performed to confirm radical generation in the photocatalytic system.
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