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Significantly enhanced visible light photocatalytic activity and surface plasmon resonance mechanism of $Ag/AgCl/ZnWO_4$ composite

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ABSTRACT

An efficient visible-light-driven $Ag/AgCl/ZnWO_4$ photocatalyst was synthesized by a facile ultrasonic-assisted precipitation-photoreduction method. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) and UV–vis diffuse reflectance spectroscopy (DRS) were employed to characterize the composition, morphology, structure, and optical property of the obtained catalysts. The results indicated that the as-prepared photocatalyst, formed by Ag/AgCl nanoparticles dispersed on the surface of $ZnWO_4$ nanorods, demonstrated remarkable absorbance in the visible light region. The $Ag/AgCl/ZnWO_4$ composite displays much superior visible light photocatalytic activity for methyl orange (MO) and methylene blue (MB) degradation compared with pure $ZnWO_4$ and Ag/AgCl nanocrystals, as well as the conventional visible-light photocatalyst N-doped TiO_2. On the basis of the active species trapping experimental results and band structure analysis, a photocatalytic mechanism is proposed. The predominantly enhanced performance can be ascribed to the surface plasmon resonance of Ag nanoparticles and the high separation efficiency of photogenerated electron–hole pairs. In addition, the sample of $Ag/AgCl/ZnWO_4$ also exhibits good stability and durability due to it depicts high photocatalytic activity even after five cycles.

1. Introduction

Since the discovery of mental tungstate's photocatalytic activity under solar illumination, those semiconductor photocatalysts have been considered as promising candidates for their potential application in utilization of solar energy to eliminate the contaminants in water [1–5]. As an important kind of tungstate, zinc tungstate ($ZnWO_4$) with a prototype wolframite structure has been wildly investigated due to its high chemical stability, low light radiation damage, relatively high catalytic activity and inexpensive commercial availability [6–8]. However, as a single component semiconductor with a wide band gap, $ZnWO_4$ cannot reveal superior photocatalytic activity attributing to poor visible-light absorption, low separation efficiency and fast recombination of photoelectron–hole pairs. Over the past several years, many efforts devoted to improve the photocatalytic properties of $ZnWO_4$ proved to be resultful, such as, tuning morphologies [9], controlling crystallinity [10], coupling with other semiconductors [11] and ion doping [12]. For example, Chen et al. investigated that F-doped $ZnWO_4$ showed higher photocatalytic efficiency than that of single $ZnWO_4$ nanocrystals owing to the extension of its photoresponse region and improvement of the photocurrent density [13]. Su et al. fabricated $ZnWO_4$ with controlled size via Sn^{2+} doping through a microwave-assisted hydrothermal method. Their results indicated that the valance band of Sn^{2+}-doped $ZnWO_4$ nanocrystals shifted toward deeper energy, which make it exhibits much higher photocatalytic activity [14]. More recently, for accelerating the separation of charge carriers and for reducing the recombination of electron–hole pairs, $ZnWO_4$ was alloyed with other semiconductors ($BiWO_4$ [11], Graphene [15], C_3N_4 [16], etc.) to fabricate various heterostructures. Modified $ZnWO_4$ has achieved an efficient photocatalytic activity to some extent, but in order to make the best use of the visible light, it is necessary to develop new highly-efficiency visible-light-driven (VLD) photocatalysts.

Currently, a new strategy to develop VLD photocatalysts has been applied via the surface plasmon resonance (SPR), which is the collect oscillation of free electrons on the surface of noble-metal nanoparticles (such as Au, Ag and Pt). The resonance condition is tenable when the frequency of light photons couples with the natural frequency of surface electrons against the restoring force

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of positive nuclei [17], so SPR can remarkably utilize the visible light which accounts for about 43% of the entire sunlight. Among various plasmonic photocatalytic systems, the silver/silver halides (denoted as Ag/AgX, X = Cl, Br, I) have attracted particular attention as a consequence of their outstanding photocatalytic performances for pollutant degradation, water inactivation, carbon dioxide reduction [18–20]. In addition, Ag/AgX is used as a dopant to decorate photocatalytic materials, to amplify the photo-response range and to accelerate the charge separation in the catalysts simultaneously. Recently, a series of nanocomposite photocatalysts made of Ag/AgX loaded carbon nanotubes (CNTs) (Ag/AgX–CNTs) were acquired by a deposition–precipitation method, the fabricated composite photocatalysts show a great activity to destruction of 2,4,6-tribromophenol (TBP) [21]. Other Ag/AgX-based plamonic photocatalytic materials were also successfully synthesized, including Ag/AgBr/TiO_2 [22], Ag/AgCl/ZnO [23], Ag/AgCl/$BiVO_4$ [24], etc. These plasmonic photocatalysts were verified to be excellent VLD photocatalysts. It can be inferred that there appears a synergetic effect between Ag/AgX and the materials, and Ag/AgX acts not only as an active photocatalyst, but also as a potential co-catalyst. Based on the above consideration, the combination of $ZnWO_4$ with Ag/AgCl nanoparticles to rationally design a catalyst, which has not been previous reported, could obtain highly efficient use of the visible region of the solar spectrum.

In this paper, we have successfully decorated the $ZnWO_4$ nanocrystals with dispersed Ag/AgCl NPs by a facile ultrasonic-assisted precipitation-photoreduction method for the first time. The photoactivity of the catalyst was evaluated by decomposition of organic dyes under visible light irradiation. Compared with AgCl/Ag and pure $ZnWO_4$ crystals, the as-prepared Ag/AgCl/$ZnWO_4$ was proved much higher photoactivity. Furthermore, a mechanism for the improved photocatalytic efficiency of Ag/AgCl/$ZnWO_4$ photocatalyst was proposed through a systematic investigation and analysis.

2. Experimental

2.1. Materials

Sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), sodium hydroxide (NaOH), silver nitrate ($AgNO_3$) and sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical reagent grade and used without further purification. Deionized water was used as the solvent throughout this experiment.

2.2. Synthesis of $ZnWO_4$

$ZnWO_4$ was prepared by a simple hydrothermal procedure, $Na_2WO_4{\cdot}2H_2O$ (3 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (3 mmol) were each dissolved in 15 mL of deionized water. The two above aqueous solutions were mixed together under magnetically stirring at room temperature. The pH value of the mixed solution was adjusted to nine using diluted NaOH. The mixture was loaded into a 50 mL Teflon-lined stainless steal autoclave and then heated at 160 °C for 24 h. After the hydrothermal reaction, the white precipitate was isolated by filtration and washed with ethanol and deionized water several times, and dried at 80 °C for 8 h.

2.3. Synthesis of Ag/AgCl/$ZnWO_4$ composite

The preparation of Ag/AgCl/$ZnWO_4$ composite was achieved by an ultrasonic assistant precipitation-photoreduction reaction. A suspension of $ZnWO_4$ (1 mmol) in 40 mL deionized water was ultrasonicated for 20 min. After that, 2 mL of 0.1 M $AgNO_3$ was dripped slowly to the above solution in a dark condition. The mixture was stirred for a few minutes and then was ultrasonicated for another 20 min. Subsequently an excessive amount of 0.1 M NaCl was added drop by drop to the mixture. After being continuously stirring for 1 h, the resulting solution was irradiated under a 40 W ultraviolet lamp for 30 min to reduce particle silver ions (Ag^+ ions) on the surface of AgCl/$ZnWO_4$ to silver nanoparticles (Ag^0 species). The color of the sample changed from white to grayish. Finally, the grayish powder was collected by centrifugation, thorough washing with deionized water. Finally, the sample was transferred to a vacuum oven to dry at 80 °C for 8 h.

For comparison, Ag/AgCl photocatalyst was synthesized by a similar way as follows: 20 mL of 0.1 M $AgNO_3$ was injected into 20 mL of 0.1 M NaCl aqueous solution under continuously stirring to obtain AgCl particles. Then the suspension was placed under irradiation by a 40 W ultraviolet lamp for 30 min to obtain Ag/AgCl photocatalyst. The reference N-doped TiO_2 was prepared by nitridation of the commercial TiO_2 (P25) at 500 °C for 10 h under NH_3 flow [25].

2.4. Characterization methods

The crystal structures of the samples were characterized by X-ray diffraction (XRD) analysis using a Bruker D8-advance X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) at a setting of 40 kV and 40 mA. The morphology of the samples was examined with a field emission scanning electron microscope (FESEM, Hitachi S-4800) with 5.0 kV scanning voltages. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were performed with a transmission electron microscope (TEM, FEI Tecnai G20) at an accelerating voltage of 200 kV. The elementary composition was conducted by Energy dispersive X-ray (EDX) analysis attached to the Tecnai G20. UV–vis diffuse reflectance spectra (DRS) were recorded on a UV–vis spectrophotometer (Hitachi U-4100) with $BaSO_4$ as the reflectance standard material.

2.5. Photocatalytic experimental

The application of the Ag/AgCl/$ZnWO_4$ composite to the degradation of organic dyes MO and MB was evaluated under visible light irradiation using a 300 W Xe lamp (CEL-HXF300, Beijing) with a cutoff filter ($\lambda > 420$ nm). Briefly, 0.100 g of photocatalyst was inspersed into 100 mL of MO (or MB) aqueous solution (10 mg/L). Prior to illumination, the suspension was magnetically stirred in dark for 30 min to reach desorption–adsorption equilibrium between the photocatalyst and dyes. Afterward the suspension was exposed to visible light irradiation while the temperature of the solution was kept unchanged by cooling water. The analytical samples (about 4 mL) were taken at an interval of 10 min and centrifugated at a rate of 8000 rpm for 5 min to remove the remaining particles. The degradation efficiency was monitored by recording the absorbance of supernatants at maximum absorption wavelength (664 nm for MB, 463 nm for MO) using an UV–vis spectrophotometer (Shimadzu 2550, Japan). As a comparison, the photocatalytic experiments of $ZnWO_4$, Ag/AgCl, N-doped TiO_2 and blank experiments without catalyst were also performed under the same condition. Additionally, the cycling experiments for testing the stability and reusability of the photocatalyst were carried out according to the above procedure. After each cycle, catalyst was collected by filtration and washed with deionized water and ethanol, and then dried at 80 °C before reuse.