



Ultrasonic-assisted synthesis of plasmonic Z-scheme Ag/AgCl/WO₃-nanoflakes photocatalyst in geothermal water with enhanced visible-light photocatalytic performance

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ABSTRACT

In this study, the Ag/AgCl/WO₃ plasmonic Z-scheme photocatalysts with different contents of Ag/AgCl nanoparticles (NPs) were prepared through a facile ultrasonic precipitation method in geothermal water, wherein the geothermal water served as the chlorine source. Then the photocatalytic activity was investigated by degradation of 4-Aminobenzoic acid (4-ABA) under visible-light irradiation. It was found that the as-prepared 50 wt% Ag/AgCl/WO₃ photocatalyst showed the highest photocatalytic efficiency with 25.12 and 3.53 times higher than those of pure WO₃ and Ag/AgCl, respectively. The active species trapping experiments indicated that h⁺ and ·O₂⁻ were key factors in 4-ABA photodegradation process. The possible plasmonic Z-scheme photocatalytic mechanism of photocatalytic reaction for 4-ABA degradation was proposed based on systematical characterizations. We hope this paper could give new ideas for further exploiting geothermal energy to design and fabricate highly efficient visible-light-driven photocatalysts for environmental remediation.

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1. Introduction

As an n-type semiconductor, tungsten trioxide (WO₃) has gained increasing research interest for its utilization in a series of different fields, such as photocatalysts [1,2], photoelectrocatalysts [3,4], gas sensing [5,6] and lithium battery [7,8]. Tungsten trioxide is able to absorb approximately 12% of solar light reached to the earth surface due to suitable band gap about 2.4–2.8 eV. Additionally, tungsten trioxide is also endowed with some features, including a moderate hole diffusion length (~150 nm), a high oxidation potential of valence band (VB) holes (+3.1–3.2 eV versus SHE), and a good stability in acidic solution (below ca. pH 4) [4,9–11]. These advantages mentioned-above make WO₃ stick out from the nanostructured metal oxides semiconductors to be a research hot. Nevertheless, pure WO₃ shows low photocatalytic quantum efficiency because of its low conduction band (CB) edge that has not enough ability to reduce oxygen to generate superoxide radical. Besides, the fast recombination of electron-hole and sluggish kinetics of holes are also of deadliness factors, limiting the improvement of photocatalytic activity [12]. Fortunately, substantial great efforts have been devoted to overcoming these drawbacks to improve the photocatalytic activity of WO₃, including material

phase/morphology control, surface sensitization, selective doping, and construction of hybrid structures [13–16]. In particular, loading different noble or non-noble metal nanoparticles (i.e., Au, Ag, Pt, Cu, etc.) has been considered as a promising means to enhance the visible-light absorption of photocatalysts, which effectively avoid the serious problem of self-degradation encountered with organic sensitizers during photocatalytic process because of their surface plasmon resonances (SPR) and subsequently serving as an alternative type of sensitizers [17–19]. Besides serving as role of sensitization, another effective strategy to achieve excellent photocatalytic performance of catalysts is preparation of composite photocatalysts based on the Z-scheme principle [20]. In the Z-scheme system, the composite photocatalysts possess strong reduction and oxidation potentials as well as high charge-separation efficiency simultaneously, thus overcoming the obstacle of traditional heterojunction photocatalysts [21–23]. Although some Z-scheme photocatalysts based on WO₃ or Ag/AgX (X = Br, Cl) have been investigated such as CdS/WO₃ [24], NaNbO₃/WO₃ [25], Ag@AgBr/g-C₃N₄ [26] and Ag@AgCl/BiVO₄ [27], the researches about highly efficient Z-scheme visible-light-driven photocatalysts are still insufficient. Therefore, it is necessary for materials scientists to explore and design highly efficient Z-scheme photocatalysts system for practical application.

Natural geothermal water, as the critical carrier of geothermal energy, has been widely exploited for physical therapy and power generation because it is extensively distributed and practically lim-

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itless as well as renewable [28]. The exploitation of geothermal water utilized for energy purposes is increasingly regarded as a valid method of dealing with the energy crisis and alleviating the pollution of environmental [29,30]. Geothermal water is produced from groundwater going through the natural heating process by geothermal energy and hot magma [31]. It is commonly known that some ions such as Cl^- , SO_4^{2-} , HCO_3^- , Na^+ , Ca^{2+} and trace silica are found in geothermal water [32]. Herein, we selected the representative geothermal water (Tengchong County, Yunnan Province, China) as the source of Cl^- to form AgCl.

In this work, the Ag/AgCl/ WO_3 plasmonic Z-scheme visible-light composite photocatalyst was successfully constructed in the natural geothermal water for the first time, in which Ag/AgCl nanoparticles were uniformly deposited on the surface of WO_3 nanoflakes under the ultrasonic stirring. Furthermore, the obtained Ag/AgCl/ WO_3 photocatalyst was characterized in detail and the photocatalytic performance was investigated by photodegradation of 4-Aminobenzoic acid (4-ABA). The possible Z-scheme photocatalytic mechanism of the charge transport process in Ag/AgCl/ WO_3 composites was proposed and discussed in detail on the basis of band structure analysis and trapping experiments. This study may give new ideas for further exploitation of geothermal water resources and design of novel Z-scheme photocatalysts.

2. Experimental

2.1. Materials

Silver nitrate (AgNO_3), sodium tungsten oxide ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), nitric acid (HNO_3) and ethanol ($\text{C}_2\text{H}_6\text{O}$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 4-Aminobenzoic acid (4-ABA) was bought from Aladdin Industrial Corporation, Shanghai. Sodium bisulfate ($\text{NaHSO}_4 \cdot \text{H}_2\text{O}$) was supported by Shanghai Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were of analytic grade without further purification, and deionized water and geothermal water were used throughout this work.

2.2. Synthesis of WO_3 nanoflakes

In a typical experimental, HNO_3 (65%, 5 mL) was added dropwise to deionized water solution (25 mL) under rapid magnetic stirring lasting around 15 min at room temperature. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.4950 g) and $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.5954 g) were dissolved in deionized water (10 mL) and stirred for 5 min to form suspension. Then the above suspension was added into the above HNO_3 solution to form the precursor solution, and stirred for another 30 min. Meanwhile, the color of mixed solution gradually turned from white to creamy yellow. After that, the above mixed solution was transferred into a Teflon-lined stainless steel autoclave (50 mL). The autoclave was sealed and held at 180 °C under autogenous pressure for 9 h in an electric oven and then cooled down to room temperature naturally. The resulting yellowish precipitates were collected by centrifugation and rinsed several times by deionized water and ethanol, and subsequently dried in air at 60 °C for 12 h.

2.3. Synthesis of hierarchical Ag/AgCl/ WO_3 photocatalysts

The Ag/AgCl/ WO_3 photocatalysts were prepared through an ultrasonic precipitation method in geothermal water. The representative geothermal water used here came from Tengchong County, Yunnan Province, China and the Cl^- concentration had been detected to be 1131.1 mg/L from ion chromatography analysis according to our previous work [33]. Briefly, the suspension was obtained by mixing 70 mg of WO_3 and 25 mL of geothermal water

into 100 mL of deionized water and was then ultrasonicated for 2 h to perfectly disperse the WO_3 nanoflakes, followed by slowly dribbling AgNO_3 solution (20 mL, 0.025 M) under continuous ultrasonic stirring. This prepared suspension was then stirred for another 1 h under ultrasonic condition. Meantime, the color of the suspension changed from light yellow to grayish white to reddish-brown resulting from the formation of AgCl and Ag NPs produced by the partial degradation of AgCl under solar light irradiation. The resulting product was washed with distilled water several times and dried at 60 °C. Similarly, Ag/AgCl/ WO_3 photocatalysts with different contents of Ag/AgCl were prepared by controlling the amount of WO_3 and were marked as x Ag/AgCl/ WO_3 ($x = 10, 20, 30, 40, 50, 60$ wt%). For comparison, Ag/AgCl photocatalyst was synthesized using similar process without adding WO_3 , and the mechanical mixture was acquired by grinding same weight of Ag/AgCl and WO_3 .

2.4. Characterization

The crystalline structures of the samples were measured by powder X-ray diffraction (XRD) on a Bruker Advanced D8 diffractometer (Germany) using monochromatized $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation at 40 kV and 40 mA. The morphologies were analyzed by transition electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) on a JEOL JEM-2100 instrument (Japan) under an acceleration voltage of 200 kV and equipped with an X-ray energy dispersive spectrometer (EDS). The bonding state of photocatalysts was recorded by a Renishaw inVia (England) Raman spectrometer with a laser excitation of 514.5 nm and a power of 20 mW. The optical property of the products was observed using UV-vis spectrophotometer (Shimadzu UV-2500) with BaSO_4 as a standard reference. The surface compositions and electronic binding energy were studied by X-ray photoelectron spectroscopy (XPS) on a Perkin-Elmer PHI 5300 with an $\text{AlK}\alpha$ ($h\nu = 1486.7 \text{ eV}$) X-ray as the exciting source. Photoluminescence (PL) spectra were provided using a FL3-TCSPEC fluorescence spectrophotometer (HORIBA Jobin Yvon, France) with excitation wavelength of 323 nm.

2.5. Photoelectrochemical (PEC) measurements

The PEC performance was determined with the electrochemical impedance spectra (EIS) and transient photocurrent responses of the samples using an electrochemical workstation (CHI 760E Chenhua Instrument Company) in a standard three-electrode system. The EIS measurement was carried out in the presence of a 2.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) mixture, and transient photocurrent response was performed in Na_2SO_4 (0.5 M, pH 7.0) aqueous solution. A Pt wire, a saturated calomel electrode (SCE) and the samples loaded onto the bottom middle of FTO slice were utilized as the counter electrodes, reference electrode, and working electrodes, respectively.

2.6. Photoactivity test

In this section, 20 mg of catalyst was dispersed in 30 mL of 4-ABA solution (10 mg/L) and then the suspension stirred for 30 min in dark to achieve adsorption-desorption equilibrium. After that, photocatalytic experiments were performed by utilizing a 300 W Xenon lamp (XL-300, Yirda) equipped with a 420 nm cut-off filter as light source. During photocatalytic reaction, the above suspension was collected at every 10-min time interval and centrifuged to separate the photocatalysts. Subsequently, the absorbance of 4-ABA was measured by on a Shimadzu UV-1201 spectrophotometer at its characteristic wavelength of 280 nm. After the reaction, the used catalysts were collected for cycling experiments.

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