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Synthesis and photocatalytic performance of the efficient visible light photocatalyst Ag–AgCl/$BiVO_4$

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ABSTRACT

A visible-light responsive photocatalyst consisting of Ag–AgCl composite dispersed over $BiVO_4$ (Ag–AgCl/$BiVO_4$) was synthesized via a photolysis and calcination method. The effects of synthetic conditions such as Ag contents, molar ratios of chlorine to silver and calcination temperatures have been discussed. The coupling Ag–AgCl composite structure, which is necessary for the high photoactivity, comes into being by partially converting Ag nanoclusters into AgCl during heat treatment. The discoloration efficiency of methyl orange over the as-prepared Ag–AgCl/$BiVO_4$ was more than 90% after 120 min under visible light irradiation. In the Ag–AgCl/$BiVO_4$ system, the coupled processes of excitation from valence band of AgCl to the sensitizer Ag nanoparticles and the surface plasmonic resonance of Ag nanoparticles mainly contributed to its high activity. In addition, the presence of $BiVO_4$ changed the hole transfer process, and $O_2^{-\bullet}$ became to be the solely main active specie in the degradation reaction. The photocatalytic activity can be further improved by the addition of hole scavengers.

1. Introduction

Heterogeneous photocatalysis has been regarded not only as a cost-effective technology for the reduction and elimination of persistent toxic organic pollutants, but also as a promising alternative for solar energy utilization [1–3]. However, in practical applications it has been limited for the low utilization of solar energy in both optical absorption and energy conversion. Therefore, the development of efficient photocatalysts responsive in a wide range of solar spectrum has played an important role in this field. Two approaches have been developed to exploit desirable photocatalysts: the first one involves doping or modifying UV active semiconductor oxides (such as TiO_2) to turn them into visible light responsive photocatalysts [4–6]; the second is to design novel complex compounds or fabricate composites [7,8], such as $PbBi_2Nb_{1.9}W_{0.1}O_9/CaFe_2O_4$ [9], graphene oxide enwrapped Ag/AgX (X = Br, Cl) [10], and so on. At present, solar energy photocatalytic conversion for environment and energy applications still requires more efficient visible light driven photocatalysts.

The surface plasmonic resonance (SPR) nanostructures, which are originated from the coupling collective oscillations of surface electrons with the incident photons [11,12], have already gained considerable attention in many fields, including nanoscale optical devices [13], enhanced spectroscopy [14], solar cells [15], and so on [16]. Recently, further applications have been explored in the field of photocatalysis for organic decomposition [12,17,18], CO oxidation [19] and water splitting [16] under visible light irradiation. It is well known that noble metal nanoparticles (NPs) show strong UV–vis absorption due to their SPR nanostructures. Moreover, AgCl, AgBr and AgI [20,21], known as widely applied photosensitive materials, were firstly reported as photocatalysts for water splitting in 1999. Inspired by the photosensitive properties and the SPR effect of Ag NPs, high efficient plasmonic photocatalysts Ag/AgX have been developed and aroused broad interesting and concerning [1,17,22–26]. Wang et al. synthesized AgCl particles with silver NPs deposited on their surface (Ag@AgCl), by first treating Ag_2MoO_4 with HCl in an ion-exchange reaction to form AgCl powder and then irradiating AgCl to reduce some Ag^+ ions [17]. Hu et al. prepared Ag–AgI/Al_2O_3 via a photocatalytic reduction method [1]. Yu et al. obtained visible-light-driven plasmonic photocatalyst Ag/AgCl/TiO_2 nanotube arrays by first depositing AgCl nanoparticles (NPs) into the self-organized TiO_2 NTs, and then reducing partial Ag^+ ions to Ag^0 species upon irradiation [26]. Although there are a few approaches to fabricate highly activity Ag/AgX structures, effects of synthetic conditions on the formation and the components of the active Ag/AgX are still not clear. According to the results of photocurrent measurements, radical analysis and photocatalytic activity tests, the $O_2^{-\bullet}$ and holes have been regarded as the main active species. However, it is unknown which substance, plasmon-excited Ag-NPs [1] or photosensitized AgX [17], generates these active species. In fact, exclusive Ag or AgX shows very low photocatalytic activity.

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$BiVO_4$ is a kind of visible light driven photocatalysts with a band gap of 2.4 eV for the monoclinic scheelite structure. The $BiVO_4$ microparticles can be facilely obtained via a homogeneous precipitation method [27], and applied in water purification due to its good precipitation performance [9]. However, its activity is restricted by large particles and serious recombination of charge carriers. Herein, $BiVO_4$ was employed as a support for the highly active Ag–AgCl structure, and a new Ag–AgCl/$BiVO_4$ composite photocatalyst was prepared via a facile photolysis and calcination method. The prepared samples showed high visible light photocatalytic activity for the photocatalytic degradation of methyl orange (MO) aqueous solution. Furthermore, the effect of source materials and the synthetic conditions have been studied, and a charge transfer mechanism has been discussed.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$), ammonia chloride (NH_4Cl), bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$), ammonium metavanadate (NH_4VO_3) and methyl orange (MO) were procured from Sinopharm Chemical Reagent Co., Ltd. Ammonia was obtained from Pinghu Chemical Reagent Factory. All chemicals are of analytical-grade and used without further purification.

2.2. Sample preparation

$BiVO_4$ was synthesized in aqueous media via a homogenous precipitation method with $Bi(NO_3)_3$ and NH_4VO_3 [27]. $AgNO_3$ was employed as the source of silver and dissolved in the aqueous ammonia to obtain a $[Ag(NH_3)_2]^+$ solution with a concentration of 0.373 mol/L. NH_4Cl was selected as the source of chlorine. In a typical synthesis procedure, 1 g $BiVO_4$ powder was dispersed in 8 ml deionized water, and then 2 ml NH_4Cl solution (0.373 mol/L) and 1 ml of $[Ag(NH_3)]^+$ solution were added in turn. After being stirred at room temperature for 6 h, the mixture solution, accompanying with continuous stirring, was irradiated with 1000 W xenon lamp for 1 hour. Finally the resulting powder was dried completely at 60 °C overnight (the dried sample designated as S-D). The sample S-D was calcined at 500 °C for 3 h to obtain a light yellow powder, referred as Ag–AgCl/$BiVO_4$ for convenience. A control sample S-W was prepared by washing S-D with a large amount of water, drying and calcining at 500 °C for 3 h. The influence of temperatures (T), amounts of silver (Ag%) and molar ratios of chlorine and silver (Cl/Ag) has been investigated.

2.3. Photocatalytic activity measurements

The optical system for photocatalytic reaction consists of a 1000 W xenon lamp operating at an output power of 700 W and a cutoff filter with larger than 90% transmission ($\lambda > 400$ nm). The batch reactor is a 100 ml glass container with circulating cooling water outside in a homemade dark box, and the light illuminated from the upside with a distance of 1.2 m away from the reactor surface. In a typical photocatalytic activity test, 0.05 g prepared catalyst was added into a 50 ml methyl orange (MO) solution (10 mg L^{-1}), then the dispersion was kept in dark for 10 min to obtain the equilibrium adsorption state. During the irradiation, the temperature of the solution was maintained by cooling water. Under continuous stirring, samples were taken at half-hourly intervals, filtered and then analyzed by a UNICO UV-2102 spectrometer at 464 nm. The leached metal ions were measured by an inductive coupled plasma (ICP) spectrometer (Thermo, iCAP 6000 Radial).

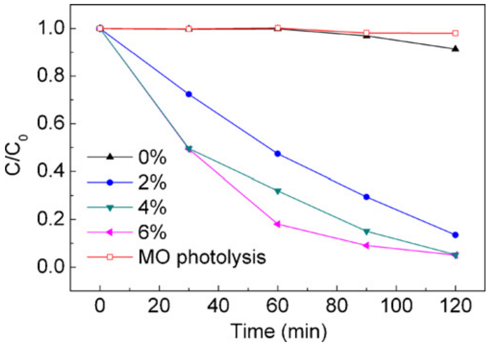

Fig. 1. The decrease of MO as a function of irradiation time over photocatalysts with various Ag content (Cl/Ag = 2; T = 500 °C, catalyst load = 1 g L^{-1}) or without photocatalyst (initial concentration of MO = 10 mg L^{-1}).

2.4. Material characterization

The crystal phase of samples were characterized by powder X-ray diffraction (XRD, D/max-2200/PC, Rigaku Corporation, Japan), operating at 40 kV and 30 mA, where $\lambda = 0.15418$ nm for the Cu K_α line. Diffuse reflectance spectra (DRS) were obtained on a UV–Vis spectrophotometer (TU-1901, China) equipped with a diffuse reflectance accessory, and the reflectance was converted to $F(R_\infty)$ values according to the Kubelka–Munk method. The chemical states of elements were measured by a RBD upgraded PHI-5000C ESCA system (Perkin Elmer, USA), and the shift of the binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard. Differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) were carried out to track the changes during the heat treatment by a simultaneous thermal analyzer (NETZSCH STA 449 F3 Jupiter). The nanometric structure and the morphology of the catalysts were observed by transmission electron microscope (TEM, JEM-100CX, JEOL, Japan) and a field emission scanning electron microscope (FE-SEM, FEI SIRION 200).

3. Results and discussion

3.1. Effect of Ag content

As shown in Fig. 1, the photolysis of MO under visible light is negligible. Without modification, the activity of pure $BiVO_4$ is weak, resulting in less than 10% of MO reduction after 120 min irradiation. It can be attributed to large particle sizes of the synthesized $BiVO_4$ and the poor migration of photogenrated carriers over $BiVO_4$ [9]. However, by importing silver compounds over the surface of $BiVO_4$ particles with only a very small amount, the photocatalytic activity has been enhanced dramatically. It indicates that the presence of plasmonic Ag–AgCl components great contributes to the MO reduction and is crucial for the high photocatalytic activity. Although the sample with Ag content of 6% showed a little higher activity, the sample of 4% Ag content was employed for the following investigations due to the consideration of its lower cost.

3.2. Effect of the ratio of NH_4Cl to Ag

NH_4Cl is selected as the source of chloride for the consideration of not importing foreign cations after calcinations. In Fig. 2, only in the presence of $[Ag(NH_3)]^+$ without NH_4Cl, the as-prepared catalyst shows an even lower activity than that of pure $BiVO_4$, with nearly no reduction of MO observed. According to the reports by Kohtani et al. [28,29], Ag-loaded $BiVO_4$ exhibits enhanced photocatalytic activity due to the synergetic effects of the specific adsorption by silver oxides and an increase in the reaction rates by metallic Ag