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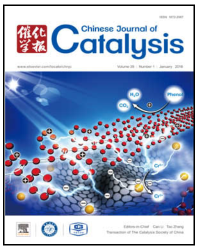

Article

Ag nanoparticles deposited on oxygen-vacancy-containing $BiVO_4$ for enhanced near-infrared photocatalytic activity

Chunjing Shi, Xiaoli Dong *, Xiuying Wang, Hongchao Ma, Xiufang Zhang

School of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, Liaoning, China

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ABSTRACT

This study investigates the photodegradation of the organic dye rhodamine B by Ag-nanoparticle-containing $BiVO_4$ catalysts under different irradiation conditions. The catalysts consist of Ag nanoparticles deposited on oxygen-vacancy-containing $BiVO_4$. The morphology of the $BiVO_4$ is olive shaped, and it has a uniform size distribution. The $BiVO_4$ possesses a high oxygen vacancy density, and the resulting Ag nanoparticle-$BiVO_4$ catalyst exhibits higher photocatalytic activity than $BiVO_4$. The RhB degradation by the Ag nanoparticle-$BiVO_4$ catalyst is 99% after 100 min of simulated solar irradiation. $BiVO_4$ containing oxygen vacancies as a rationally designed support extends the catalyst response into the near-infrared region, and facilitates the trapping and transfer of plasmonic hot electrons. The enhanced photocatalytic efficiency is attributed to charge transfer from the $BiVO_4$ to Ag nanoparticles, and surface plasmon resonance of the Ag nanoparticles. These insights into electron-hole separation and charge transfer may arouse interest in solar-driven wastewater treatment and water splitting.

1. Introduction

Continuously increasing energy demands and environmental problems have drawn widespread global attention [1–8]. These problems have arisen from rapid population growth and developments in manufacturing and industry. This has led to a recent surge in sustainable and environmentally friendly energy technologies. Among these technologies, metal oxide semiconductors are efficient catalysts for photocatalytic pollutant degradation and water splitting. However, solar wavelengths are not efficiently utilized by most photocatalysts for solar-electricity conversion, which only efficiently absorb ultraviolet-visible (UV-Vis) wavelengths [9–16]. An example is $BiVO_4$ which is an environmentally friendly, low-cost, and high-performance photocatalyst [17–21], but has no response to near-infrared (NIR) wavelengths. Another challenge is the weak interaction of O_2 with the photocatalyst surface, especially with defect-free surfaces, which leads to inefficient photooxidation of pollutants. The participation of O_2, either directly as a reactant or indirectly as an electron acceptor, should be accompanied by interfacial electron transfer.

To overcome this challenge, $BiVO_4$ containing oxygen vacancies (OVs) has been prepared. It exhibits a photocatalytic response under NIR wavelengths, which leads to an increase in adsorbed O_2. The formation of OVs narrows the band gap of $BiVO_4$ [22]. OVs on the $BiVO_4$ surface also facilitate the trapping and transfer of photogenerated electrons. While NIR wavelengths can be harvested by the photocatalyst, its photocatalytic activity is suppressed by other factors. The application of $BiVO_4$ as an efficient photocatalyst is hindered by poor electron transmission and insufficient charge separation [23–25]. Obtaining reliable materials that exhibit efficient performance for

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* Corresponding author. E-mail: dongxl@dlpu.edu.cn

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solar-driven wastewater treatment and water splitting remains a challenge.

The last few years have seen a significant increase in the preparation of hybrid nanomaterials. Despite this, the tailored syntheses of photocatalytic heterostructures have been limited by structural incompatibility within hybrid materials. Facile and reliable strategies for synthesizing practical heterostructured semiconductors are therefore required. Au and Ag have been shown to be efficient agents for harvesting solar energy in chemical processes involving localized surface plasmon resonance (SPR) [26,27]. SPR refers to the collective oscillation of conduction band (CB) electrons that are in resonance with the oscillating electric field of incident light. The decay of SPR can generate hot electrons and holes, which in turn can initiate chemical reactions [27–29]. Of interest is the oxidizing ability of hot holes within Ag, which is thought to be much milder than that of holes in the valence band (VB) of most photocatalytic semiconductors. This offers the possibility for application in oxidative organic transformations [30–32]. Hot carriers also rapidly decay, so inorganic supports are often integrated with Ag to promote the separation of hot electrons and holes [33–35]. The surface properties of the support are therefore very important, because they determine the dynamics of plasmonic hot carriers and the interaction of the support surface with reactants.

In the current study, we have prepared and investigated a plasmonic catalyst consisting of Ag nanoparticles deposited on $BiVO_4$ containing OVs (hereafter referred to as $BiVO_4$-OV). The introduction of OVs enables synergistic action of the plasmonic hot electrons and holes, and provides a new reaction pathway. Charge transfer from $BiVO_4$-OV to the attached Ag nanoparticles, as well as the SPR absorption of the Ag nanoparticles, further enhances the photocatalytic efficiency [36].

2. Experimental

2.1. Syntheses of materials

Commercial chemicals were of analytical grade and used as received without further purification.

$BiVO_4$-OV was prepared by a hydrothermal method. In a typical procedure, 0.4 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ power was dissolved in 16 mL of glycerol under vigorous stirring for 1 h. 0.4 mmol of $NaVO_3{\cdot}2H_2O$ was dissolved in 16 mL of deionized water under vigorous stirring for 0.5 h, until it became homogeneous and transparent under room temperature conditions. Then, the $NaVO_3{\cdot}2H_2O$ solution was added dropwise to the $Bi(NO_3)_3{\cdot}5H_2O$ solution under vigorous stirring for 0.5 h, to form a yellowish suspension. The resulting suspension was heated in a 50-mL polytetrafluoroethylene-lined stainless steel autoclave at 180 °C for 8 h. After cooling to room temperature, the precipitate was collected by centrifugation, thoroughly washed with distilled water and then absolute ethanol, and then dried in air at 60 °C for 4 h to yield $BiVO_4$-OV. The OVs would be expected to vanish through redox reaction, so the obtained $BiVO_4$-OV powder was calcined in a muffle furnace at 300 °C for 5 h in air. The power was then removed from the furnace, and stored at 20 °C in a hermetic bag. The sample is hereafter referred to as $BiVO_4$.

$BiVO_4$-OV (0.1 g) was dispersed in 50 mL of deionized water. A given amount of $AgNO_3$ was dissolved in 10 mL of deionized water, to provide Ag/$BiVO_4$-OV mass rates of 1.0, 2.0, 2.5, and 3.0Wt%. The $AgNO_3$ solution was then added to the $BiVO_4$-OV dispersion under stirring. The resulting dispersion was subjected to UV treatment as described above, at room temperature under stirring. After 5 min of irradiation, the light grey product was collected by centrifugation, washed with water, and then dried in a vacuum oven. The product was then subjected to various characterizations and catalysis experiments. Samples are referred to as $BiVO_4$, Ag-$BiVO_4$ (Ag2.5%-$BiVO_4$), $BiVO_4$-OV, Ag1.0%-$BiVO_4$-OV, Ag2.0%-$BiVO_4$-OV, Ag2.5%-$BiVO_4$-OV (Ag-$BiVO_4$-OV), and Ag3.0%-$BiVO_4$-OV. The Ag loading content could be easily tuned by varying the $AgNO_3$ solution concentration.

2.2. Photocatalytic activity

The light source for the photocatalytic reactions was a 300-W Xe lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd., China). The photocatalytic activities of the samples were determined by measuring the degradation rate of rhodamine B (RhB) dye under different irradiation conditions. NIR irradiation was obtained from simulated solar irradiation by using a cut-off filter with that omitted wavelengths of <800 nm. 20 mg of sample was dispersed in 50 mL of RhB solution (10 mg/L), by sonication for 10 min. For comparison, the degradation of phenol solution (10 mg/L) was also measured with 20 mg of Ag-$BiVO_4$-OV under the same conditions. Then, the solution was stirred for 30 min in the dark to establish adsorption-desorption equilibrium. The reaction solution was then irradiated with different sources for the degradation of RhB. At 20 min intervals, 4 mL aliquots of suspension were removed, and the catalyst was separated by centrifugation. The degradation of RhB was monitored by measuring the absorbance of the aliquot supernatant at a wavelength of 554 nm, using a UV-Vis spectrophotometer. The RhB concentration after irradiation for a certain duration is indicated by C, while C_0 is the RhB concentration at adsorption-desorption equilibrium prior to irradiation [37].

2.3. Characterization

The crystallinities and purities of samples were characterized by powder X-ray diffraction (XRD) using a Shimadzu XRD-6100 diffractometer, operated at 40 kV and 40 mA with Cu K_α radiation. Scanning electron microscopy (SEM) images were collected using a field-emission scanning electron microscope (JSM-7800F, JEOL). Transmission electron microscopy (TEM) images were collected using a JEOL JEM-2100F transmission electron microscope. The absorption properties were evaluated using a UV-Vis diffuse reflectance (UV-Vis DRS) spectrometer (CARY 100&300, VARIAN), with $BaSO_4$ as a reflectance standard. Raman spectra were recorded using a LabRam-1B Raman spectroscope, with He-Ne laser excitation