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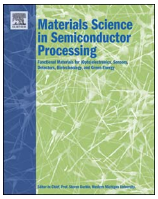

Fabrication of walnut-like $BiVO_4@Bi_2S_3$ heterojunction for efficient visible photocatalytic reduction of Cr(VI)

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ABSTRACT

As a typical visible-light-responsive photocatalyst, the photoreactivity of $BiVO_4$ is not high enough for practical application due to its limited visible light harvesting ability and quick recombination rate of photo-generated electron-hole pairs. In the present study, surface modification of $BiVO_4$ with Bi_2S_3, forming walnut-like core-shell structured $BiVO_4@Bi_2S_3$, was achieved by a simple ion-exchange reaction between Na_2S and $BiVO_4$. The photoreactivity of the photocatalyst was evaluated by photoreduction of Cr(VI) in solution under visible light irradiation ($\lambda \geq 420$ nm). The effect of weight ratio of $Na_2S{\cdot}9H_2O$ to $BiVO_4$ on the structure and photocatalytic performance of $BiVO_4@$ Bi_2S_3 hybridized photocatalyst was systematically studied. It was found that a layer of Bi_2S_3 was successfully covered on the surface of walnut-like $BiVO_4$ microspheres after introduction of Na_2S. The formed Bi_2S_3 shell not only widely extends the visible-light-responsive range, but also sharply retards the recombination of photo-generated electrons and holes of $BiVO_4$ photocatalyst. With increase in the weight ratio of $Na_2S{\cdot}9H_2O$ to $BiVO_4$, the photoreactivity of $BiVO_4$ increases first and then decreases with an optimal wight ratio of 3.0 (S3 sample). The photocatalytic activity of S3 sample ($BiVO_4@Bi_2S_3$) increases 57.2 times when compared with that of pristine $BiVO_4$ sample after irradiation for 40 min. The enhanced photocatalytic activity of walnut-like $BiVO_4@Bi_2S_3$ microsphere was attributed to the synergistic effect of enhanced visible light harvesting ability due to the sensitization of Bi_2S_3 and retarded recombination of carriers because of the formation of heterojunction between two semiconductors of $BiVO_4$ and Bi_2S_3.

1. Introduction

Chromium is one of the most widely used metals in industries such as wood preservation, leather tanning, metal finishing, and pigments. Although Cr(III) has low toxicity and can easily be removed from water via precipitation, the strong oxidant Cr(VI) is toxic, mutagenic, teratogenic and carcinogenic [1,2]. Up to now, many strategies have been used to remove pollutants including Cr(VI) from wastewater such as adsorption [3–6], precipitation [2], biodegradation [7,8], photochemical reduction [9], electrochemical reduction [10] and/or the combination of these methods. However, these methods mentioned above are complex, either time-consuming or costly. Semiconductor photocatalysis has also been used to oxidize organic pollutants and reduce metal ions [11,12]. For example, Zhu et al. reported the photocatalytic reduction of Cr(VI) on TiO_2 which was in situ modified with small molecular weight organic acids under visible light irradiation. However, the reduction rate is slow, possibly due to the limited visible light harvesting ability of the modified TiO_2 photocatalyst [13].

Recently, monoclinic bismuth vanadate ($BiVO_4$) with a medium bandgap of about 2.4 eV [14–18] has received much attention due to its visible-light-responsive property, chemical stability, nontoxicity as well as relatively high photocatalytic activity for water splitting and degradation of organic compounds [19,20]. However, from the viewpoint of practical applications, the photocatalytic activity of $BiVO_4$ is not high enough due to the quick recombination rate of photo-generated carriers and limited visible-light-responsive property. To improve the photocatalytic activity of pure $BiVO_4$, a number of $BiVO_4$-based heterojunction photocatalysts such as $CaFe_2O_4/BiVO_4$ [21], $BiVO_4/Bi_4V_2O_{11}$ [22] and $Ag_3PO_4/BiVO_4$ [23] were prepared. Very recently, Zhao et al. reported the fabrication of a heterojunction photocatalyst $BiVO_4@$ MoS_2 with core–shell structure by a precipitation-deposition method, which showed enhanced visible-light photocatalytic activity towards Cr(VI) reduction [24].

Inspired by the methods about the synthesis of functional inorganic

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oxide nanostructures such as coupling or surface modification [25–32], we studied the fabrication of walnut-like core-shell structured $BiVO_4$@Bi_2S_3 microsphere by simple in-situ ion exchange between $BiVO_4$ and Na_2S. Both the aims of extending the visible-light-responsive range and improving the separation efficiency of photo-generated electrons and holes were achieved by using this method. The effects of Na_2S amount on the structure and visible photocatalytic reduction of Cr(VI) over $BiVO_4$@Bi_2S_3 microsphere were systematically studied.

2. Experimental

2.1. Synthesis of $BiVO_4$ decahedron

All chemicals used are from Shanghai Pharmacy Co. China. $BiVO_4$ decahedron was prepared according to literature [19]. Typically, 0.776 g (1.6 mmol) of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 64 ml glycerin aqueous solution (50 v/v%). Then 0.640 g (1.6 mmol) of $Na_3VO_4 \cdot 12H_2O$ was dissolved in 64 ml DI water. After that, the Na_3VO_4 solution was slowly dropped into the $Bi(NO_3)_3$ solution under vigorous stirring. After finishing the addition for 30 min, the pH value of the solution was adjusted to 3.0 by HNO_3, which was further stirring for another 30 min. The mixed solution was transferred into a 200 ml Teflon-lined stainless steel autoclave and heated at 180 °C for 8 h. After cooling to room temperature, the resulted precipitates were filtered and washed by DI water and ethanol for three times, which is followed by drying at 80 °C for 12 h.

2.2. Fabrication of walnut-like $BiVO_4$@Bi_2S_3 microsphere

1.0 g of the as-prepared $BiVO_4$ and 2.0 g of PVP (K-30) were added into a beaker containing 80 ml of DI water. After ultra-sonicating for 20 min, 80 ml of Na_2S solution containing 3.0 g of $Na_2S \cdot 9H_2O$ was dropwise added into the $BiVO_4$ solution under vigorous stirring. The mixed solution was transferred into a 200 ml Teflon-lined stainless steel autoclave and kept at 150 °C for 8 h. The precipitates were collected, filtered and washed with DI water and ethanol repeatedly for three times, and finally dried at 80 °C for 4 h. The as-prepared sample is denoted as S3 sample, where 3 represents the mass of $Na_2S \cdot 9H_2O$ used (3.0 g).

Similarly, S2, S2.5, S4 and S5 samples were also prepared for comparison. Please note that $BiVO_4$ precursor was simply denoted as S0 sample.

2.3. Characterization

The crystal phase of the photocatalyst was determined by powder X-ray diffraction (XRD) patterns, which were obtained on an X-ray diffractometer (Rigaku, Japan), were recorded with Cu-Kα radiation operated in a 2 theta range of 10–80° with a step width of 0.02°. The surface morphology of the sample was characterized by scanning electron microscopy (SEM) images, which were performed on an S-4800 Field Emission SEM (FESEM, Hitachi, Japan) at an accelerating voltage of 4 kV. X-ray photoelectron spectra (XPS) were performed on Multilab 2000 XPS system with a monochromatic Mg Kα source. The Brunauer-Emmett-Teller surface area (S_{BET}) of the samples was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). UV–Vis diffused reflectance spectra (DRS) of the sample was measured on a UV–Vis spectrophotometer (UV2550, Shimadzu, Japan) using $BaSO_4$ as the reflectance standard. Photoluminescence (PL) spectrum was measured on a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan).

2.4. Photoelectrochemical measurement

Transient photocurrent response and Mott-schottky plots were carried out on an electrochemical analyzer (CHI760e Instruments) in a standard three-electrode system using Pt wire as the counter electrode and Ag/AgCl electrode as the reference electrode. The working electrode was prepared on an ITO conductive glass using Nafion as adhesive. The visible-light source was a 420 nm LED (3W, Shenzhen LAMPLIC, China).

2.5. Photocatalytic reduction of Cr(VI)

The photocatalytic activity of the as-prepared photocatalyst was evaluated by photocatalytic reduction of Cr(VI). The visible-light source was a 350 W Xenon arc lamp with a UV-cutoff filter ($\lambda \geq 420$ nm). In a typical process, 50 mg of the photocatalyst was added into 50 ml of Cr (VI) solution (5 mg L^{-1} based on Cr in a dilute $K_2Cr_2O_7$ aqueous). Then the photocatalyst was dispersed in the solution with an ultrasonic bath for 5 min, and followed by stirring for 1 h in the dark to reach adsorption-desorption equilibrium before being irradiated under the irradiation of Xenon arc lamp. After the photocatalyst was removed by centrifugation and filtering, the concentration of Cr(VI) was determined at 365 nm using a UV–vis spectroscopy.

2.6. Detection of the formation of hydroxyl radicals

The method of hydroxyl radicals detection was similar to that of evaluating the photocatalytic activity of the photocatalyst [33,34]. The photoluminescence spectra (PL) of photocatalysts were carried out by a fluorescence spectrophotometer (FS-2500, Japan) equipped with an Xe lamp with an optical filter as excitation source. In detail, 50 mg of the photocatalyst was added into 50 ml terephthalic acid (TA) solution (5×10^{-4} M). Then the photocatalyst was dispersed in the solution with an ultrasonic bath for 5 min, and followed by being irradiated under the irradiation of Xenon arc lamp (350 W). After the photocatalyst was removed by centrifugation and filtering, the concentration of hydroxyl radicals was determined using the PL with excitation wavelength of 315 nm.

3. Results and discussions

3.1. Morphology

Fig. 1 compares the SEM images of $BiVO_4$ sample before (S0 sample, Fig. 1a-c) and after treatment with Na_2S (S3 sample, Fig. 1d-f). From Fig. 1a and b, it can be seen the monodispersed walnut-like $BiVO_4$ precursor, which is predominant 2 µm in length (along long-axis) and 1 µm in diameter (along short-axis). Carefully view shows that the walnut-like $BiVO_4$ precursor is the condense aggregation of small nanoparticles (Fig. 1c).

According to the low magnified SEM image shown in Fig. 1d, the morphology of the obtained sample almost keeps unchanged even treated by Na_2S. However, some needle-like particles were found to be formed, possibly due to the separation of the formed Bi_2S_3 layer from the core-shell structured $BiVO_4$@Bi_2S_3, which was further confirmed by the SEM image of a broken walnut-like microsphere (Fig. 1f).

Further experiment results showed that, core-shell structured $BiVO_4$@Bi_2S_3 can not be obtained if keep the same reaction time (8 h) but the temperature is lower than 150 °C (Fig. 2a), or keep the same temperature (150 °C) but the reaction time is shorter than 8 h (Fig. 2c). Improvement the reaction temperature to 200 °C (Fig. 2b) or extension the reaction time to 16 h (Fig. 2d), only hollow Bi_2S_3 spheres can be obtained.

Fig. 3 shows the TEM images of S0 and S3 samples. Their dark images reflect the large particle sizes of $BiVO_4$ and $BiVO_4$@Bi_2S_3 photocatalysts. High resolution TEM images show the lattice fringes of 0.308 nm (Fig. 3b) and 0.374 nm (Fig. 3d), which correspond to the (121) lattice plane of $BiVO_4$ and (101) lattice plane of Bi_2S_3, respectively.