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Enhanced visible light-photocatalysis by hydrothermally synthesized thallium-doped bismuth vanadate nanoparticles

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ABSTRACT

Thallium-doped (1.5, 2.3 and 19.3 at%) bismuth vanadate ($BiVO_4$) and pristine $BiVO_4$ nanoparticles were hydrothermally synthesized. They were characterized by powder X-ray and selected area electron diffractometries, high resolution scanning electron and transmission electron microscopies, and energy dispersive X-ray, Raman, UV–visible diffuse reflectance and photoluminescence spectroscopies. Tl-doping reduces the band gap energy and recombination of charge carriers. The visible light photocatalytic activity of 19.3% Tl-doped $BiVO_4$ nanoparticles is larger than those of the other Tl-doped $BiVO_4$ and pristine $BiVO_4$ nanoparticles. The synthesized Tl-doped $BiVO_4$ nanoparticles displaying enhanced photodegradation of dye could find potential applications as visible light photocatalyst for the abatement of various organic pollutants.

1. Introduction

Bismuth vanadate, a typical ternary semiconductor oxide with a layered structure, attracted considerable attention recently [1,2]. This is because of its unique properties like ferroelasticity, ionic conductivity, photocatalysis, color, etc., resulting in its potential applications in electronic devices, pigment industry and photocatalytic mineralization of organic pollutants [3]. Unlike the widely used wide band gap semiconductors like TiO_2 and ZnO (band gap 3.2 eV) $BiVO_4$ is an ideal photocatalytic material (band gap 2.5 eV) for mineralization of organic pollutants under visible light irradiation [1,2]. In addition to the high stability against photocorrosion, low cost and non-toxicity, the fascination of $BiVO_4$ also comes from the peculiar crystal structure affording photocatalysis. However, $BiVO_4$ photocatalysis faces several significant limitations because of its low photoquantum efficiency, resulting from a low interfacial charge transfer rate and high recombination of photoproduced electron–hole pairs [4]. Many efforts have been made to improve the photocatalytic activity of $BiVO_4$. Doping with metal ion of variable oxidation state or loading metal or metal oxide may enhance the photocatalytic activity by improved separation of the photogenerated electrons and holes. Enhanced photocatalysis by noble metal deposited $BiVO_4$ nanoparticles (*e.g.*, Ag/$BiVO_4$ [5]) and nonmetal loaded nanoparticulate $BiVO_4$ such as carbon quantum dot/$BiVO_4$ [6] is known. Recently, Ag_3PO_4/$BiVO_4$ [7], BiOCl/$BiVO_4$ [8], core–shell $BiVO_4$@γ-Bi_2O_3 [9], $ZnFe_2O_4$/$BiVO_4$, [10], $BiPO_4$/$BiVO_4$ [11], Bi_2WO_6/$BiVO_4$ [12] and WO_3/$BiVO_4$ [13] coupled semiconductors have been prepared for enhanced visible light photocatalysis. Although $BiVO_4$ is reported to be photostable, the photocorrosion of the other semiconductor constituting the heterojunction is a serious problem for application of the synthesized nanocomposite by industries for mineralization of pollutants. However, such contingency does not occur with the doped $BiVO_4$ and synthesis of doped $BiVO_4$ nanoparticles like Mo- or W-doped $BiVO_4$ [14], Er-doped $BiVO_4$ [15] and C-doped $BiVO_4$ with hierarchical structure [16] have been reported recently; the synthesized doped $BiVO_4$

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nanomaterials exhibit larger visible light photocatalytic activity than that of the undoped $BiVO_4$. Here we report hydrothermal synthesis of nanoparticulate thallium-doped $BiVO_4$ for enhanced visible light-photocatalytic activity.

2. Materials and methods

2.1. Materials

Bismuth nitrate pentahydrate (Sigma Aldrich), ammonium metavanadate (Sigma Aldrich), thallium nitrate (Sigma Aldrich), nitric acid (Merck), sodium hydroxide (SD Fine) and methylene blue (SD Fine) of LR grade were used as received. Deionized distilled water was used throughout the investigation.

2.2. Synthesis

Bismuth nitrate pentahydrate (1 mmol, 0.485 gm) was dissolved in 20 mL of 1 M nitric acid at room temperature. Alkaline ammonium vanadate solution was obtained by dissolving 0.117 gm (1 mmol) of ammonium vanadate in 20 mL of 0.5 M sodium hydroxide at room temperature. Thallium nitrate (0.013 or 0.065 g) was dissolved in a few drops of 70% HNO_3 and added drop wise to bismuth nitrate solution with stirring for 0.5 h. To the solution containing thallium nitrate and bismuth nitrate, the ammonium nitrate solution was added drop wise with stirring to get a transparent homogeneous solution. Then the pH of the solution was adjusted to 2 or 5 (in the case of 0.013 g addition of thallium nitrate) and 7 for the other with 2 M NaOH to obtain the precursor. It was transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed and heated at 120 °C for 12 h under autogeneous pressure and allowed to cool to room temperature. The obtained sample was filtered, washed with deionized distilled water followed by absolute ethanol. Finally, the obtained solid sample was dried at 50 °C for 12 h in a hot air oven. Similar procedure was followed without the addition of thallium nitrate to prepare pristine $BiVO_4$ nanoparticles.

2.3. Characterization techniques

The high resolution scanning electron micrographs (HR-SEM) and the energy dispersive X-ray (EDX) spectra of the synthesized nanomaterials were obtained with a FEI Quanta FEG 200 HR-SEM in high vacuum mode. The transmission electron microscopic (TEM) images and the selected area electron diffraction (SAED) patterns of the synthesized nanoparticles were obtained with a Philips CM200 TEM. The nanomaterials were dispersed in acetone and spread on the grids for imaging. A FEI Tecnai G2 F30 S-Twin TEM was employed to obtain the TEM images at high resolution and also the SAED patterns. The nanoparticles were dispersed in acetone and spread on carbon grids for imaging. A PANalytical X'Pert PRO diffractometer was used to record the powder X-ray diffraction (XRD) patterns of the synthesized materials in a 2θ range of 10–80° employing Cu Kα rays at 1.5406 Å with a tube current of 30 mA at 40 kV. A Princeton Action SP2500 Raman spectrometer was employed to obtain the Raman spectra of the synthesized samples. The samples were excited at 514.5 nm. The UV–visible diffuse reflectance spectra (DRS) were recorded with a Shimadzu UV-2600 spectrophotometer with ISR-2600 integrating sphere attachment. A PerkinElmer LS 55 fluorescence spectrometer was employed to obtain the photoluminescence (PL) spectra at room temperature. The nanoparticles were dispersed in carbon tetrachloride under sonication and excited using light of wavelength 435 nm.

2.4. Photocatalytic test

The photocatalytic activity of the nanomaterials under visible light was evaluated with a 150 W tungsten halogen lamp fitted into a double walled borosilicate vessel with an inlet and outlet for circulation of water. Sodium nitrite solution was employed to filter the UV light. Circulation of 2 M $NaNO_2$ solution in place of water curtails 99% of UV light of wavelength between 320 and 400 nm. The light intensity was measured (415 W m^{-2}) using a Daystar solar meter (USA). The photocatalytic degradation was carried out in a wide cylindrical borosilicate glass vessel of uniform diameter (7.0 cm). The visible light source was placed above the reaction vessel (13 cm). A freshly prepared methylene blue solution (100 mL) with a known amount of the photocatalyst (0.100 g) was taken in the reaction vessel and was saturated with air using a micro air pump. The solution was stirred continuously using a magnetic stirrer. The photocatalytic degradation of the dye was followed by determining the concentration of methylene blue spectrophotometrically at 662 nm. A calibration curve was constructed by measuring the absorbance of methylene blue at different ppm.

3. Results and discussion

3.1. Morphology

The high resolution scanning electron microscopic (HR-SEM) images of hydrothermally synthesized Tl-doped $BiVO_4$ and pristine $BiVO_4$ are displayed in Fig. 1. The images reveal the particulate nature of the doped and pristine $BiVO_4$. The particles are in nanoscale and are devoid of any regular shape or structure. In addition, they agglomerate. The transmission electron microscopic (TEM) images of hydrothermally synthesized Tl-doped $BiVO_4$ and pristine $BiVO_4$ are presented in Fig. 2. The TEM images confirm the synthesized materials as nanoparticles. Also they show agglomeration of the nanoparticles.

3.2. Crystalline structure

Fig. 3 presents the energy dispersive X-ray (EDX) spectra of the synthesized doped and undoped $BiVO_4$ nanoparticles. The EDX spectrum of pristine $BiVO_4$ shows the presence of bismuth, vanadium and oxygen. The absence of any other element reveals the purity of the prepared sample. The EDX spectra of the doped $BiVO_4$ confirm doping $BiVO_4$ with thallium. Furthermore, the absence of any element other than bismuth, vanadium, thallium and oxygen shows the purity of the synthesized doped nanoparticles. The atomic