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Photocatalytic water splitting for O_2 production under visible-light irradiation on $BiVO_4$ nanoparticles in different sacrificial reagent solutions

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ABSTRACT

Monoclinic $BiVO_4$ nanoparticles were prepared through a homogeneous co-precipitation process. The products calcined at different temperatures were characterized by X-ray diffraction, transmission electron microscopy and UV–vis diffused reflectance spectroscopy. The photocatalytic O_2 evolution efficiencies over the $BiVO_4$ nanoparticles under visible-light ($\lambda > 420$ nm) irradiation were also investigated comparatively by using $AgNO_3$ and $Fe(NO_3)_3$ as sacrificial reagents. Experimental results indicate that $AgNO_3$ is a more effective sacrificial reagent for the photocatalytic O_2 evolution over $BiVO_4$ than $Fe(NO_3)_3$ due to the efficient separation of the photogenerated electron–hole pairs at the Ag/$BiVO_4$ interfaces, but the $BiVO_4$/$Fe(NO_3)_3$ system is more promising in the aspect of practical applications due to its more steady photoactivity and more convenient reactivation of the photocatalyst.

1. Introduction

Since photoelelctrochemical splitting of water into H_2 and O_2 on titanium dioxide (TiO_2) electrode was first reported in 1971 [1], water photosplitting for H_2 and/or O_2 production over semiconductors has been attracting extensive attention [2,3]. There are numerous researches focused on the modification of TiO_2 in order to enhance the conversion efficiency of the incident light to clean H_2 energy [4,5]. However, most of semiconductors such as TiO_2 mainly absorb the ultraviolet light due to their wide band gap (*ca.* 3.2 eV for TiO_2), which only contains *ca.* 4% energy of the sunlight. Therefore, to develop novel photocatalysts with visible-light response is indispensable for the water photosplitting techniques [6–8].

Recently, $BiVO_4$ has inspired some research interest because of its excellent photoactivity under visible-light irradiation [9–15]. Bismuth vanadate ($BiVO_4$) is generally used as a yellow pigment to replace cadmium-based material due to its low environmental toxicity [16]. According to previous reports, $BiVO_4$ has three main crystal phases: zircon structure with tetragonal (z–t) system, scheelite structure with monoclinic (s–m) and tetragonal (s–t) system [17]. Among those, $BiVO_4$ (s–m) is usually obtained from solid-state and melting reaction and $BiVO_4$ (z–t) is prepared via precipitation process from $Bi(NO_3)_3$ and NH_4VO_3 solutions at room temperature [18]. The phase transition between $BiVO_4$ (s–m) and $BiVO_4$ (s–t) is reversible at about 255 °C [18], and $BiVO_4$ (z–t) can be transformed into $BiVO_4$ (s–m) after heat treatment at 400–600 °C [17]. Among the three crystal phases, $BiVO_4$ (s–m) is the best one as photocatalyst for the photocatalytic degradation of organic pollutants and O_2 production from water splitting due to its narrow band gap (*ca.* 2.4 eV) [9–12]. For example, Kohtani et al. have found that $BiVO_4$ (s–m) was able to degrade alkylphenols in wastewater under solar light irradiation [9]. It has also been used as a visible-light response photocatalyst simultaneously for the photooxidation of phenol and photoreduction of Cr (VI) [11]. Furthermore, $BiVO_4$ (s–m) shows the highest photocatalytic activity for O_2 evolution under visible-light irradiation [13–15].

The photogenerated holes in the valence band (E_{VB} = 2.4 V vs. NHE) of $BiVO_4$ (s–m) are energetically favorable to oxidize water into O_2 [11], but the photoexcited electrons in the conduction band (E_{CB} = 0 V vs. NHE) cannot be easily captured by H^+. Therefore, it is necessary to find a suitable electron scavenger in order to accelerate the water photosplitting for O_2 production. Considering that the redox potential (0.799 V vs. NHE) of Ag^+/Ag is higher than the conduction band potential of $BiVO_4$, it is thermodynamically possible that Ag^+ will capture the photoexcited electrons. Hence, Ag^+ is broadly used as an electron scavenger for the photocatalytic O_2 evolution over $BiVO_4$ [9–15]. On the other hand, the redox potential (0.771 V vs. NHE) of Fe^{3+}/Fe^{2+} is similar to Ag^+/Ag, so Fe (III) is also a potential electron scavenger for the photocatalytic O_2

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evolution over $BiVO_4$. To the best of our knowledge, there is no research focused on the effect of different sacrificial reagents on the photocatalytic O_2 evolution over $BiVO_4$. Herein, monoclinic $BiVO_4$ nanoparticles were synthesized through a homogeneous co-precipitation process [15]. The effect of calcination temperature on the crystal phase, microstructure and optical absorption property of $BiVO_4$ was discussed, and the photocatalytic O_2 evolution efficiencies under visible-light ($\lambda > 420$ nm) irradiation on $BiVO_4$ in $AgNO_3$ or $Fe(NO_3)_3$ solution were comparatively investigated in detail.

2. Experimental

2.1. Preparation of $BiVO_4$ nanoparticles

All chemicals were obtained and used from commercial sources as analytical pure reagents without further purification. $BiVO_4$ was prepared through a homogeneous co-precipitation process (HCP) [15]. A typical synthesis process is as follows: 2.9100 g of $Bi(NO_3)_3{\cdot}5H_2O$ (Sinopharm Chemical Reagent Co., Ltd., 99%) and 0.7204 g of NH_4VO_3 (Sinopharm Chemical Reagent Co., Ltd., 99%) were added into 30 mL of 1.0 M HNO_3 under magnetic stirring for 1 h. 3 g of $CO(NH_2)_2$ (Sinopharm Chemical Reagent Co., Ltd., 99%) was added into the above mixed solution, and then the resulting solution was maintained at 80 °C for 24 h under continuous stirring. The color of the solution was changed from reddish-brown to colorless, and then to vivid yellow precipitation. This precipitation was recovered by centrifugation, washed with water and dried at 65 °C and then calcined at different temperatures to obtain a $BiVO_4$-HCP series of products. $BiVO_4$ film electrodes were prepared by spreading viscous slurries of the as-synthesized $BiVO_4$-HCP paste containing actylacetone and tritonX-100 on conducting glass (FTO). The films were then dried at room temperature and calcined at 400 °C for 1 h in sequence.

For comparison, $BiVO_4$ was also prepared through a conventional solid-state reaction (SSR) according to the previous report [19]. The mixtures of Bi_2O_3 (Sinopharm Chemical Reagent Co., Ltd., 99%) and NH_4VO_3 (Sinopharm Chemical Reagent Co., Ltd., 99%) was mixed thoroughly and calcined at 700 °C for 5 h in an alumina crucible to obtain $BiVO_4$-SSR.

2.2. Characterization of $BiVO_4$ nanoparticles

X-ray diffraction (XRD) patterns were obtained on an XRD-6000 diffractometer using Cu Kα as radiation (λ = 0.15418 nm). Transmission electron microscope observations were carried out on a LaB6 JEM-2010 (HT)-FEF electron microscope (HRTEM). UV–vis diffuse reflectance spectra (DRS) were performed with a Cary 5000 UV–vis–NIR spectrophotometer equipped with an integrating sphere.

A three-electrode system was applied in the photoelectrochemical measurement under visible-light irradiation ($\lambda >$ 420 nm). A $BiVO_4$-HCP electrode, a large area platinum electrode and a KCl-saturated Ag/AgCl electrode were used as working electrode, counter electrode and reference electrode, respectively. A 0.5 M Na_2SO_4 solution was used as supporting electrolyte [20]. The data of photocurrent response were collected at a bias potential of −0.1 V.

2.3. Photocatalytic activity test

The photocatalytic O_2 evolutions over photocatalysts from $AgNO_3$ or $Fe(NO_3)_3$ solution were carried out in a closed gas-circulation system. Photocatalyst powders (0.100 g) was dispersed by a magnetic stirrer in $AgNO_3$ or $Fe(NO_3)_3$ solution (100 mL) in a reaction cell (Pyrex glass). A 300 W Xe-illuminator (CHF-XM-300 W, Beijing Trusttech Co.) was used as light source. A cutoff filter (Kenko, L-42; $\lambda > 420$ nm) was employed for visible-light irradiation. The amount of evolved O_2 was determined by gas chromatography (GC, SP-6800A, thermal conductivity detector, 5 Å molecular sieve columns and Ar carrier).

3. Results and discussion

3.1. The crystal phase analyses of $BiVO_4$

Fig. 1 shows the XRD patterns of the $BiVO_4$-SSR, as-synthesized $BiVO_4$-HCP and its series of products after calcination at different temperatures. Although the XRD pattern of $BiVO_4$ (s–m) is similar to that of $BiVO_4$ (s–t) due to their scheelite structures, $BiVO_4$ (s–m) and $BiVO_4$ (s–t) can be differentiated by observing whether the splitting peaks at 2θ = 18.5°, 35° and 46° appear or not [18]. As can be seen from Fig. 1, all diffraction patterns for the $BiVO_4$-HCP series of products can be clearly ascribed to the $BiVO_4$ (s–m) crystal phase (JCPDS No. 14-688), which is consistent with the $BiVO_4$ (s–m) derived from a solid-state reaction [12,19]. It is reasonable that the $BiVO_4$-HCP series of products calcined at different temperatures are monoclinic phases, considering that the phase transition between $BiVO_4$ (s–m) and $BiVO_4$ (s–t) is reversible at about 255 °C as described above and that their XRD patterns were obtained at room temperature [18]. Generally, a precipitation procedure at room temperature just gives $BiVO_4$ (z–t), which shows a low photocatalytic activity [13], whereas $BiVO_4$ (s–m) was attained through the present homogeneous co-precipitation process. This success can be ascribed to the gradual formation of BiO^+ during the progressive hydrolysis of $CO(NH_2)_2$ at 80 °C; this gradual formation of BiO^+ is beneficial for the preparation of $BiVO_4$ (s–m) with higher crystallinity [13]. Moreover, the elevated reaction temperature (80 °C) may also promote the formation of $BiVO_4$ (s–m) according to Zhang's viewpoint [12].

The intensities of the diffraction peaks for $BiVO_4$ (s–m) are slightly enhanced upon increasing the calcination temperature to 400 °C, indicating the improvement in the crystallnity of $BiVO_4$-HCP, while their intensities are considerably reduced once the calcination temperature is higher than 400 °C. Such a dependence can be attributed to the formation of crystal defects due to the oxygen evolution and the volatilization of vanadium and bismuth oxides from $BiVO_4$ at an elevated temperature, which results in the decrease in crystallinity of $BiVO_4$ [13,21]. Moreover, the diffraction peaks of the $BiVO_4$-HCP series of products are much more intense

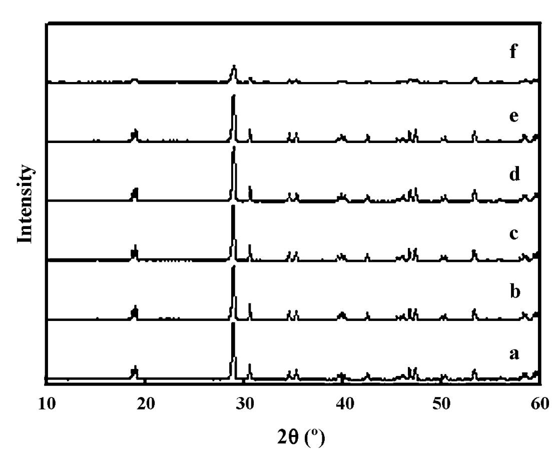

Fig. 1. XRD patterns of the $BiVO_4$-HCP series of products and $BiVO_4$-SSR. The as-synthesized $BiVO_4$-HCP (a) and its products after calcination at 200 °C (b), 400 °C (c), 600 °C (d), 800 °C (e), and $BiVO_4$-SSR (f).