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Hydrothermal synthesis and photoelectric properties of $BiVO_4$ with different morphologies: An efficient visible-light photocatalyst

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ABSTRACT

Different morphologies of monoclinic $BiVO_4$ with smaller size were hydrothermal synthesized by simply adjusting the amount of surfactant (polyvinyl pyrrolidone PVP K30) added. The detailed field emission scanning electron microscope (FESEM) analysis revealed that the amount of PVP added could significantly affect the morphology and size of $BiVO_4$. Their photocatalytic activities were evaluated by the decolorization of methylene blue (MB) aqueous solution under visible-light irradiation ($\lambda > 400$ nm), and the as-prepared sample with well-assembled flower-like morphology showed a much higher photocatalytic activity due to larger specific surface area and higher separation efficiency of photo-induced carriers. The relationship between the behavior of photo-induced carriers and photocatalytic activity was studied using the surface photovoltage spectroscopy (SPS) and corresponding phase spectra.

1. Introduction

Semiconductor photocatalysis, an ideal "green" technology, is attracting considerable attention for the environmental cleaning and H-energy production, where the active photocatalytic material is definitely an important key. In most cases, photocatalytic degradation is conducted over the TiO_2 owing to its peculiarities of chemical inertness, no-photocorrosion, low cost, and nontoxicity [1–3]. However, its wide band gap (~3.2 eV) greatly hinder their practical application. In view of the efficient utilization of visible light, the largest proportion of the solar spectrum and artificial light sources, the development of visible-light driven photocatalyst with high activity is indispensable.

A feasible approach to realize visible-light photocatalysis is to develop a new photocatalytic material independent of TiO_2. Recently, monoclinic bismuth vanadate ($BiVO_4$) has gained much attention due to its narrow band gap (2.4 eV) and excellent photocatalytic performance under visible light illumination [4–13]. It is well known that $BiVO_4$ mainly exists in three crystalline phases: monoclinic scheelite (s-m) structure, tetragonal zircon (z-t) structure, and tetragonal scheelite (s-t) structure [14]. Peng et al. synthesized microspheric and lamellar $BiVO_4$ powders through a hydrothermal process using cetyltrimethyl ammonium bromide (CTAB) as a template-directing reagent. Experimental results indicate that microspheric $BiVO_4$ with particle sizes in the range of 7-12 μm with a mixed crystal consisting of tetragonal and monoclinic phases can be derived from a relatively low hydrothermal temperature (<160 °C), whereas lamellar $BiVO_4$ with a pure monoclinic phase can be obtained at a higher hydrothermal temperature (200 °C) and $BiVO_4$ (s-m) possesses higher photocatalytic activity than $BiVO_4$ (z-t) under visible light [15]. Shao et al. reported the synthesis of an active monoclinic bismuth vanadate visible photocatalyst with nanoribbons structure. The as-prepared $BiVO_4$ nanoribbons were up to hundreds of micrometers in length, 60–80 nm in width, 15–20 nm in thickness, and grew along the (0 1 0) direction [16]. Zhao and co-workers prepared hyperbranched monoclinic $BiVO_4$ on a large scale and with good uniformity by a surfactant-free hydrothermal route. As-synthesized monoclinic $BiVO_4$ exhibits excellent photocatalytic ability in the photodegradation reaction of an aqueous solution of RB under visible light [17]. Although many works have been reported on the synthesis of highly efficient $BiVO_4$ catalyst, most of them have a larger size (about 5 μm), thus, the specific surface areas are relatively lower. Until now, only a few works have concentrated on the exact effect of charge transfer properties on the photocatalytic properties of $BiVO_4$ catalysts. The photocatalytic activity is mainly affected by three factors including absorbance efficiency of photons, specific surface area and the photo-carrier transport properties [18]. Therefore, the synthesis of $BiVO_4$ catalyst with larger specific surface areas and studying the behavior of photo-generated charge carriers are necessary. And a better understanding of this information will provide greater insight into the intrinsic reasons of the enhancement in photocatalytic activity.

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In this paper, we report the preparation of monoclinic $BiVO_4$ with different morphologies via a facile surfactant-assisted hydrothermal method. The advantage of the surfactant added lies in the fact that it can change the micro-environment of reaction and adjust the growth habit of particles, thus, leading to the formation of products with a final desirable morphology and relatively larger surface area. Further as a well-established contactless and non-destructive technique, surface photovoltage technique studies were carried out to investigate the correlation between the photo-induced charge transfer properties and photocatalytic activity of the samples. It relies on analyzing illumination-induced changes in the surface voltage, especially when combined with the electric field-modified technique, which can provide a rapid and direct investigation of the band-gap transition [19].

2. Experimental

2.1. Preparation of the $BiVO_4$ samples

All reagents were of AR grades and used without further purification. In a typical synthesis, 0.24 g $Bi(NO_3)_3{\cdot}5H_2O$ and a certain amount of PVP (PVP K30) were dissolved into 90 mL H_2O under vigorous stirring to form a transparent solution. Then 0.4 g $Na_3VO_4{\cdot}12H_2O$ was added. After stirring for 30 min, the pH of the resulting solution was adjusted to 1 with HNO_3 (65–68 wt%) solution. After stirring for another 30 min, the suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed, followed by a heat treatment at 200 °C for 6 h. The yellow precipitate was centrifuged, rinsed with distilled water and ethanol repeatedly, and finally dried at 60 °C under air, then calcined at 500 °C for 2 h in order to eliminate the remaining PVP [20]. The resulted samples were marked as S5, S10, S20, and S30, corresponding to the samples with PVP/VO_4^{3-} molar ratio of 5:1, 10:1, 20:1, 30:1, respectively.

2.2. Photo-catalytic activity test

Photo-catalytic activities of samples were determined by the decolorization of methylene blue (MB) aqueous solution under visible light irradiation ($\lambda > 400$ nm) in a home-made quartz photochemical reactor. A 500 W Xenon lamp (CHFXQ500 W) was used as a light source with a UV filter that can cut off the UV light ($\lambda < 400$ nm). Experiments were performed at ambient temperature as follows: 0.020 g photo-catalyst was added to 20 mL MB (20 mg/L) aqueous solution, before irradiation, the mixture was first sonicated 5 min and then kept in the dark for 1 h to reach adsorption–desorption equilibrium under magnetically stirring. At the same irradiation time intervals, 1 mL mixture was removed from the suspension and immediately centrifuged at 10,000 rpm for 5 min, the concentration analysis of MB was determined by using an UV–vis spectrometer.

2.3. Characterization

The crystalline phases were identified by X-ray diffraction (XRD) using a Rigaku D/Max-2550 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) at 50 kV and 200 mA in the range of 10–55° (2θ) at a scanning rate of 10° min^{-1}. The morphologies of the samples were investigated by field emission scanning electron microscope (FESEM, FEI company). The UV–vis diffuse reflectance spectra were recorded with a Shimadzu 3600 UV–vis–NIR spectrophotometer equipped with an integrating sphere diffuse reflectance accessory, while $BaSO_4$ was used as a reference. Specific surface areas were performed using N_2-BET method (Quantachrome Corporation NOVA-1000). The value of COD was based on the standard method of potassium dichromate (GB-11914-89), measured with COD analyzer.

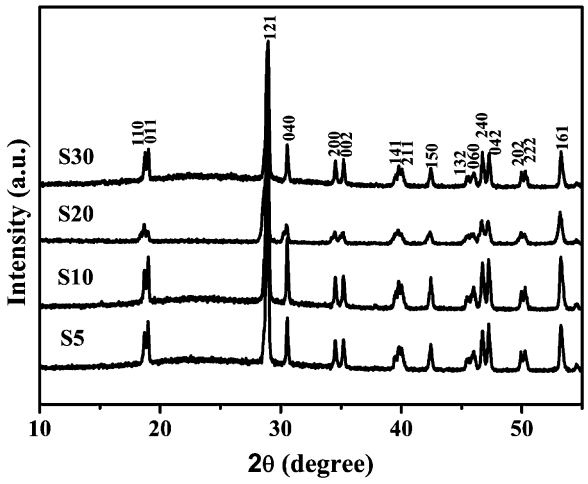

Fig. 1. The XRD patterns of $BiVO_4$ made with the different molar ratios of PVP/VO_4^{3-} calcined at 500 °C for 2 h.

The SPS system included: a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a photovoltaic cell, and a computer. A 500 W xenon lamp (CHFXQ500 W, Global Xenon Lamp Power) and a double-prism monochromator (Hilger and Watts, D 300) provided monochromatic light as source light. The samples were studied without further treatment during the SPV measurements, and the contact between samples and the indium tin oxide (ITO) electrode was not ohmic when we carried out the measurement of surface photovoltage. The construction of the photovoltaic cell is a sandwich-like structure of ITO–sample–ITO. The ITO electrodes were connected to the voltage getting a field induced surface photovoltage (FISPS). And we defined the applied voltage was positive when the ITO electrode of light connected to the positive of power supply.

3. Results and discussion

Fig. 1 shows the XRD patterns of $BiVO_4$ with different molar ratios of PVP/VO_4^{3-} calcined at 500 °C for 2 h. All $BiVO_4$ samples exhibited a similar XRD pattern that can be indexed to monoclinic $BiVO_4$ (JCPDS card No. 14-0688). There are no peaks of any other phases or impurities. And the peak intensity of S20 is much weaker than the other three samples indicating its poor crystallinity. The relative diffraction intensity ratio about the (0 4 0)/(1 2 1) planes of S10 is much higher than the corresponding standard value indicating that the S10 might have anisotropic growth along the (0 1 0) plane [21].

The morphology of as-synthesized $BiVO_4$ products is characterized by FESEM. As shown in Fig. 2, the amount of PVP added in the reaction system significantly affects the morphology of as-synthesized $BiVO_4$. When the PVP/VO_4^{3-} molar ratio is 5:1 (S5), the near-monodispersed spheres with the diameter of about 2.5 μm are obtained (Fig. 2a). Interestingly, the morphology of S10 changes from sphere to star with the size of 2.5 μm by increasing the molar ratio to 10:1, obviously, it is composed of smaller microscopic particles approximately 200 nm (Fig. 2b). Further increasing the amount of PVP to 20:1, the S20 are more complex which includes sphere, star-like, cubic (Fig. 2c), and the crystalline size is much smaller but the macro-size has no changes. The S30 is flower-like which is composed of numerous $BiVO_4$ sub-nanoparticles (400–500 nm) as shown in Fig. 3d. All the as-prepared samples possess smaller size about 2.5 μm and relatively larger specific surface areas (Table 1), which facilitate the enhancement of photocatalytic activity.

The above FESEM results confirm that the introduction of PVP could significantly affect the morphology and size of $BiVO_4$. When a