Preparation of Monoclinic Scheelite $BiVO_4$ Photocatalyst by an Ultrasound-assisted Solvent Substitution Method

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An ultrasound-assisted solvent substitution method was first developed to synthesize monoclinic scheelite (s-m) $BiVO_4$. The $BiVO_4$ (s-m) crystals exhibited flower-like and hierarchical dendrite morphologies and a far higher photocatalytic activity than that made by solid-state reaction for degradation of rhodamine B under visible light. This novel ultrasound-assisted solvent substitution method should be extendable to other materials.

Bismuth vanadate ($BiVO_4$), which has good performance in ferroelasticity, ion conductivity, and lithium batteries,[1,2] exhibits good photocatalytic activity not only in O_2 evolution from aqueous $AgNO_3$ solution[3] but also in the degradation of organic pollutants.[4,5] $BiVO_4$ has three crystalline phases: zircon structure with a tetragonal system (z-t), scheelite structure with monoclinic (s-m), and tetragonal (s-t) systems.[6] It has been proven that $BiVO_4$ (s-m) has higher photocatalytic activity than the other two.[7,8] By now, $BiVO_4$ (s-m) crystals have been prepared by methods such as solid-state reaction,[9] hydrothermal methods,[10] aqueous synthesis,[11] and sonochemical methods.[12] It is still significant to develop new methods for the synthesis of $BiVO_4$ (s-m).

Solvent substitution is a facile preparation route.[13] In this method, a solution of the reactants is first prepared. Then another solvent, which is miscible with the first one, is added into the solution to alter the solubility of the reactants in the first solvent, and hence crystals or noncrystalline precursors are obtained. On the other hand, ultrasonication is a general and efficient method for the preparation of nanomaterials.[14,15] Recently, it has been exploited for the preparation of photocatalysts because it can facilitate crystallization and improve photocatalytic activity.[16,17]

Herein, an ultrasound-assisted solvent substitution method, which combines the advantages of solvent substitution and ultrasonication, was first employed to synthesize $BiVO_4$ (s-m) (US-$BiVO_4$) with uniform crystal size. The US-$BiVO_4$ crystals showed flower-like and hierarchically dendrite morphologies and possess a wide absorption band from 470 to 850 nm. The degradation of Rhodamine B (RhB) was carried out under visible light irradiation, which reveals a much higher photocatalytic activity of the US-$BiVO_4$ than that synthesized by solid-state reaction.

In a typical preparation, 1 mmol of NH_4VO_3 was dissolved into 10 mL of ethylene glycol (EG) at 60 °C. Then 1 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was added and the EG solution was stirred at room temperature until the formation of a clear orange solution. Afterward, the EG solution was added dropwise into 100 mL of deionized water at 60 °C under ultrasonication, and sequent bright yellow precipitate was obtained. The precipitate was centrifuged, washed with deionized water and absolute ethanol several times, and dried in air. $BiVO_4$ (s-m) was also synthesized by the traditional solid-state reaction (SSR-$BiVO_4$) according to ref 9.

The XRD patterns of the US-$BiVO_4$ and SSR-$BiVO_4$ are shown in Figure 1a and Figure S1a,[20] respectively. It can be seen that all the diffraction peaks both in Figure 1a and Figure S1a[20] can be indexed to $BiVO_4$ (s-m) (JCPDS No. 14-0688, space group: $I2/a$, unit cell parameters: $a = 5.195$ Å, $b = 5.092$ Å, $c = 11.701$ Å). The characteristic splitting of the peaks at 18.5, 35, and 46° of 2θ for $BiVO_4$ (s-m) phase is observed, which confirms a single $BiVO_4$ (s-m) phase in both products. The average crystal size of the US-$BiVO_4$ was estimated to be 43 nm by using the Scherrer equation, which is much smaller than that (186 nm) of the SSR-$BiVO_4$. In addition, the diffraction peaks of the two types of $BiVO_4$ both possess high intensity and sharp shape, indicating the high crystallinity of them.

The panoramic SEM image in Figure 1b shows that the US-$BiVO_4$ crystals are cube-like and uniform in size. The side of each cube is ca. 1.5 μm. Magnified images demonstrate the cube-like product is actually composed of dendrite (Figure 1c)

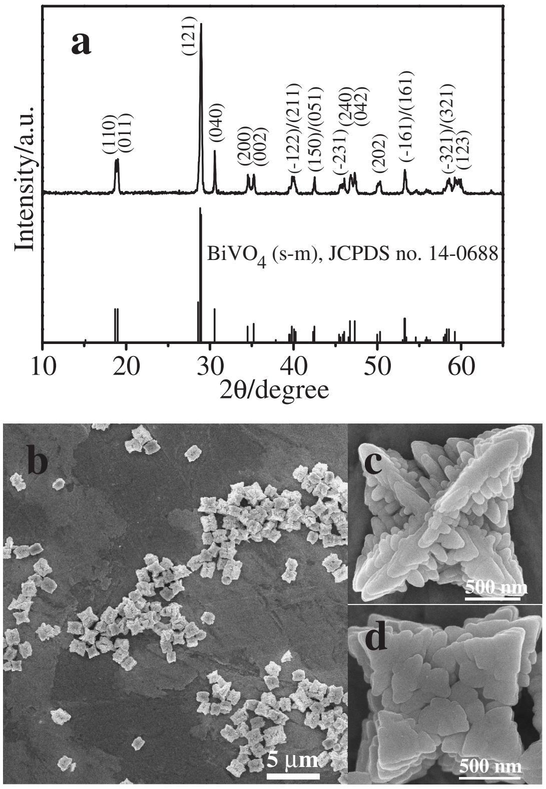

Figure 1. XRD pattern (a) and SEM images (b, c, and d) of the US-$BiVO_4$ crystals.

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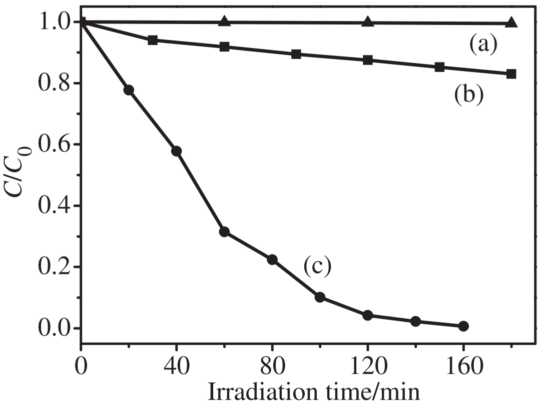

Figure 2. Variation of RhB concentrations (C/C_0) with the irradiation time without photocatalyst (a), over the SSR-$BiVO_4$ (b), and over the US-$BiVO_4$ (c).

and flower-like (Figure 1d) morphologies. The dendrite crystals possess unique hierarchical structures which are composed of long central trunks and secondary branches distributed on the opposite sides of each trunk. The trunks are 0.5–1.0 µm in length and about 200 nm across the section. The branches are ca. 100 nm across the section but differ significantly in length. Moreover, all the trunks grow along the four directions of a cross and have a laminate structure along the direction perpendicular to the cross plane. The flower-like crystals consist of four petals and exhibit the same laminate structure as the dendrite structures. Each petal is composed of plate-like particles with sharp tips. Careful observations reveal that some plate-like particles show a trace of branches mentioned above, suggesting that the flower-like crystals probably evolve from the dendrites. The SSR-$BiVO_4$ crystals show irregular shapes with the sizes ranging from 2 to 7 µm (Figure S1b).[20] The Brunauer–Emmett–Teller (BET) surface area of the US-$BiVO_4$ was about 12.6 $m^2\,g^{-1}$, which is much larger than that (0.26 $m^2\,g^{-1}$) of the SSR-$BiVO_4$ (Table S1).[20]

Figure S2 shows the diffuse reflectance spectra of the US-$BiVO_4$ and SSR-$BiVO_4$.[20] It can be seen that the US-$BiVO_4$ crystals possess a wide absorption band from 470 to 850 nm. The steep shape of the absorption edge between 470 and 520 nm indicates a band-gap transition rather than a transition from the impurity level.[18] The prolonged absorption tail, which lies between 520 and 850 nm, is probably due to surface defects arising from ultrasonication.[7] The SSR-$BiVO_4$ shows an absorption edge between 470 and 550 nm (Figure S2).[20] According to the formula in ref 19, the band gaps of the US-$BiVO_4$ and SSR-$BiVO_4$ were calculated from their absorption edge to be 2.23 and 2.20 eV, respectively (inset of Figure S2).[20]

The photocatalytic activity of the US-$BiVO_4$ (0.1 g) and SSR-$BiVO_4$ (0.1 g) were evaluated by the degradation of RhB (100 mL, 10^{-5} M) under visible light irradiation ($\lambda > 420$ nm). Before illumination, the RhB suspensions were stirred in the dark for 12 h to reach an adsorption/desorption equilibrium. Figure 2 represents the variation of RhB concentrations (C/C_0) with the irradiation time over the two types of $BiVO_4$ (s-m) crystals. Here C is the absorption of RhB at the wavelength of 553 nm, and C_0 is the absorption of RhB after the adsorption equilibrium. Direct photolysis of RhB was also performed under the same conditions (Figure 2a), which reveals that the photolysis of RhB under visible light irradiation is neglectable. The SSR-$BiVO_4$ shows a very low photocatalytic activity under visible light irradiation (Figure 2b). Only 17% of RhB was degraded even after 180 min of irradiation. The concentration of RhB, however, decreases remarkably over the US-$BiVO_4$ crystals with the irradiation time prolonged (Figure 2c). Concretely, the RhB can be completely degraded in about 160 min. This demonstrates a much higher photocatalytic activity of the US-$BiVO_4$ than that of the SSR-$BiVO_4$ due to the larger surface area and the expansion of the absorption band resulting from the ultrasonication treatment.

In summary, single-phase $BiVO_4$ (s-m) crystals have been successfully prepared by an ultrasound-assisted solvent substitution method for the first time. The $BiVO_4$ (s-m) crystals, with a size of ca. 1.5 µm, showed flower-like and hierarchical dendrite morphologies and possessed a wide absorption band from 470 to 850 nm and a large surface area of 12.6 $m^2\,g^{-1}$. The band gap of the $BiVO_4$ (s-m) crystals was about 2.23 eV. Compared with the conventional SSR-$BiVO_4$, the synthesized $BiVO_4$ (s-m) exhibited much higher photocatalytic activity in the degradation of RhB under visible light.

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