Comparison of synthetic routes for large-scale synthesis of spherical BiVO$_4$ with photocatalytic and superhydrophobic properties

Wen Meng, Linrong Bai, Taohai Li and Wei Cao

The spherical BiVO$_4$ in tetragonal and monoclinic scheelite phases have been prepared through five general methods by using K$_6$V$_{10}$O$_{28}$$\cdot$9H$_2$O as self-sacrifice templates. Morphology of these BiVO$_4$ is kept spherical because of K$_6$V$_{10}$O$_{28}$$\cdot$9H$_2$O as self-sacrifice templates. The microwave-assisted synthesis of tetragonal BiVO$_4$ is convenient and ultrasonic synthesis is the best choice for the synthesis of monoclinic BiVO$_4$.

New strategies of BiVO$_4$ fabrications have been developed for a long time following advancements of science and technology. The emphasis on the BiVO$_4$ not only arise from their ionic conductivity, photoelectrochemical, ferroelasticity and photochromism but also due to its nature of nontoxic yellow pigment for high-performance lead-free paints. BiVO$_4$ can be synthesized by different methods, such as metal-organic decomposition, classical solid state reaction, sonochemistry, solvothermal or hydrothermal methods, and supracrystals and co-precipitation. A unified approach to the synthesis of a large variety of materials with different physical and chemical properties had been reported diversely in inorganic compounds. However, several methods to the synthesis of a product with nearly uniform morphology starting from the same raw materials have been rarely reported. Herein, we report two different crystalline phases of spherical BiVO$_4$ prepared with five general methods. The phases are tetragonal and monoclinic scheelites.

The tetragonal BiVO$_4$ products were prepared by microwave-assisted synthesis and chemical bath deposition synthesis. This microwave-assisted synthesis is to heat the suspension in a domestic microwave oven for ten minutes. A main step for chemical bath deposition synthesis is immersing the suspension in a water jacket for 30 min. Compared with microwave-assisted synthesis, chemical bath deposition synthesis was more complicated and time consuming. Hence, it is obvious that microwave-assisted synthesis is more convenient to the fabrication of tetragonal BiVO$_4$. Monoclinic BiVO$_4$ samples were fabricated through mechanochemical synthesis, ultrasonic synthesis, and hydrothermal method. The mechanochemical synthesis is approved as an efficient and facile method. Using a conventional agate mortar the time of milling and annealing are 20 min and 30 min, respectively. However, the key step of ultrasonic synthesis was to sonicate the precursors for 20 min at room temperature. Finally, the hydrothermal synthesis was carried out in a teflon-lined stainless steel autoclave at 180℃ for 24 h. It was found that the ultrasonic synthesis is the best choice for the synthesis of monoclinic BiVO$_4$ considering the reaction time and operations.

As a kind of polyoxometalates (POMs), the K$_6$V$_{10}$O$_{28}$$\cdot$9H$_2$O is not only a reactant but also a template in this work. Such functions are different from other synthesis where the POMs always acted as templates of organic compounds due to the structure of inorganic metal oxide cluster. Meanwhile, POMs have been employed as inorganic templates due to their special structures and abundant chemical combinations. Furthermore, K$_6$V$_{10}$O$_{28}$$\cdot$9H$_2$O can be dissolved into deionized water, enabling decavanadate cores of (V$_{10}$O$_{28}$)$^{6-}$ in solutions. However, V$_{10}$O$_{28}$$^{7-}$ can combine with H$^+$ easily, forming several protonation states including H$_2$V$_{10}$O$_{28}$$^-$, H$_2$V$_{10}$O$_{28}$$^-$ and H$_2$V$_{10}$O$_{28}$$^{3-}$ at different acidic pH. The pKa values of H$_3$V$_{10}$O$_{28}$$^-$, H$_2$V$_{10}$O$_{28}$$^-$ and H$_3$V$_{10}$O$_{28}$$^{3-}$ are around 1.2, 3.6, and 6.1, respectively. Therefore there is a tendency to form protonated decavanadates in the solution with the decreases of pH. It is evidentially that the structure of decavanadate core is stable at the acidic solutions (pH<6). Noteworthy, all pH values of reaction environment were under 7 in this work. Thus, the decavanadate core was stable at the first stage of reactions. It could be served as an inorganic template to construct the BiVO$_4$ spherical particles. In addition, decavanadate core was consisted of ten edge-shared VO$_6$ octahedra. When reactions happened, Bi$^{3+}$ can easily combine with one of ten edge-shared VO$_6$ octahedra to form BiVO$_4$. We suggest that using K$_6$V$_{10}$O$_{28}$$\cdot$9H$_2$O as reactants can greatly improve the possibility of reactions. A similar result through the hydrothermal synthesis of BiVO$_4$ starting from K$_6$V$_{10}$O$_{28}$$\cdot$9H$_2$O was also reported in our latest article.

The powders were detected by X-ray powder diffractometer (MiniFlex II) with Cu Kα radiation (λ=0.15406 nm). The scanning electron microscopy (SEM) images were recorded on JEOL JSM-6700F electron microscope. The UV-Vis diffuse reflectance spectra were obtained with a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). UV-spectrophotometer (Lambda 25 spectrometer) was used to detect the concentration of MB solution. Water contact angle (CA) measurements were carried out by Ra-me-hart Model p/n 250-F1. Bi(NO$_3$)$_3$$\cdot$5H$_2$O, K$_6$V$_{10}$O$_{28}$$\cdot$9H$_2$O were analytical grade that were used without any purification. Anhydrous ethanol, 1H, 1H, 2H - perfluorodecytriethoxysilane (PFOTS) were purchased from commercial suppliers and used without further purification. The glass, copper and aluminium substrates were obtained locally, which was cut into smaller 1.0 cm $\times$ 1.0 cm squares before usage. Then the substrates...
were further purified by ultrasonic washing with acetone, anhydrous ethanol, deionized water for 15 min, respectively, and dried in a clean oven at 60 °C for 1 h.

Microwave-assisted synthesis of BiVO₄. Using 1.0 g K₆V₁₀O₂₈·9H₂O and 9.7 g Bi(NO₃)₃·5H₂O as the initial materials, BiVO₄ powder could be obtained by a microwave-assisted reaction. The start materials were mixed together after dissolved by 10 mL distilled water respectively, and stillled for 30 min. Then, the pH value of the suspension was adjusted to 1 by HNO₃ (2M) under stirring. The mixture were transferred into a 10 mL teflon-lined after standing for sometimes and sucking the supernatant totally, which was carried out in a domestic microwave oven where working at one minute once for ten times. After cooling down to room temperature naturally, the resulting product were washed alternately by distilled water and absolute ethanol, and then dried in vacuum at 60 °C for 10 h. Finally, the precipitate was milled to powders by an agate mortar.

Chemical bath deposition synthesis of BiVO₄. The precursors were immersed in a water jacket to ensure constant temperature (60 °C) for 30 min. Lastly, the precipitate was washed with deionized water and ethanol three times, then dried in vacuum at 60 °C for 9 h.

Mechanochemical synthesis of BiVO₄. In the simple experiment, 0.677 g K₆V₁₀O₂₈·9H₂O, 2.425g Bi(NO₃)₃·5H₂O were putted into an agate mortar, and the mixture was ground for 20 min. The precursor was washed alternately with deionized water and ethanol three times. Further it was dried at 60 °C in air for 8 h. The final step was an annealing process. The product was completed by annealing at 500 °C for 30 min in a muffle furnace.

Ultrasound synthesis of BiVO₄. 0.322 g Bi(NO₃)₃·5H₂O and 1.21 g K₆V₁₀O₂₈·9H₂O were dissolved into 10 mL deionized water with stirring. Respectively, the two solutions were mixed together, and the mixture was sonicated for 20 min at room temperature. The precipitate was washed alternately by deionized water and ethanol three times, dried in vacuum at 60 °C for 9 h.

Hydrothermal synthesis of BiVO₄. In a typical synthetic process, 2.578 g K₆V₁₀O₂₈·9H₂O and 9.7 g Bi(NO₃)₃·5H₂O were dissolved into 30 mL NaOH solution (2M) and 30 mL HNO₃ solution (2M) under stirring, respectively. After Bi(NO₃)₃·5H₂O and K₆V₁₀O₂₈·9H₂O both dissolved, K₆V₁₀O₂₈·9H₂O solution was added into former, and stirred for 30 min. The pH value of the final suspension was adjusted to 2 by 2M HNO₃. The resulting suspension was transferred into 100 mL teflon-lined stainless steel autoclaves, which was accomplished at 180 °C for 24 h under sealing and heating. After cooling down to room temperature naturally, the precipitates were washed alternately by distilled water and absolute ethanol for several times, and then dried in vacuum at 60 °C for 10 h.

The BiVO₄ of tetragonal phase obtained by microwave-assisted method and the BiVO₄ of monoclinic structure acquired by ultrasonic method were detected with the X-ray diffraction (XRD). BiVO₄ showed well crystallized tetragonal zircon type (JCPDS file no. 14-0133). No other impurities could be found. The XRD peaks are narrow, indicating the well-crystallized BiVO₄ product. The XRD patterns of the BiVO₄ samples prepared by five synthesis methods. The BiVO₄ of microwave-assisted synthesis (Fig. 1a, donated as BiVO₄(ma)) and chemical bath deposition synthesis (Fig. 1b, donated as BiVO₄(c)) were pure tetragonal zircon type (JCPDS file no. 14-0133). The XRD patterns of the BiVO₄ samples prepared by following the same procedure.

The phase purity and chemical composition of the obtained product were affirmed by XRD. Fig. 1 shows the XRD patterns of the BiVO₄ samples prepared by five synthesis methods. The BiVO₄ of monoclinic scheelite (Fig. 1c, labelled as BiVO₄(m)) and chemical bath deposition synthesis (Fig. 1b, donated as BiVO₄(c)) were pure tetragonal zircon type (JCPDS file no. 14-0133). Other two different superhydrophobic surfaces were also prepared following the same procedure.

Superhydrophobic surfaces were prepared via a facile drop-casting method. Typically, the as-prepared BiVO₄ samples were ultrasonically dispersed in ethanol to form a uniform suspension, then several drops of the suspension were dropped on the glass substrate. Finally, in order to reduce the surface energy of the fabricated structures, the film on glass substrate was modified by PFOTS. The treatment with PFOTS was conducted by adding a methanol solution of 2% (v:v) PFOTS. Then, the BiVO₄-coated glasses were dried for 24 h in the atmosphere at ambient temperature. Finally, the superhydrophobic BiVO₄ coatings were fabricated on the glass surface by the single-step procedure. Other two different superhydrophobic surfaces were also prepared following the same procedure.

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The tetragonal phase is preferable kinetically. Microwave-provided during the reaction. The formation of \( \text{BiVO}_4 \) of transformation can occur when incident higher energy is reaction temperature. It has been proved that phase phase formations by each method is proposed. The \( \text{BiVO}_4 \) are shown in Table S1. The particle size of \( \text{BiVO}_4 \) products have good dispersion. Thus, all of the five methods samples have good dispersion. While it can be found in Fig. 2(c) and (d) that the \( \text{BiVO}_4(c) \) was smaller and rugged without particles compared to the \( \text{BiVO}_4(ma) \). The spherical \( \text{BiVO}_4(u) \) was combined with irregular cubic granules displayed in the Fig. 2(e) and (f). Interestingly, the spherical \( \text{BiVO}_4(m) \) was composed of small pieces shown in the Fig. 2(g) and (h). Similarly, the \( \text{BiVO}_4(h) \) is also spherical particle constituted by smaller granules in the Fig. 2(i) and (j). All of the \( \text{BiVO}_4 \) samples have good dispersion. Thus, all of the five methods can prepare spherical \( \text{BiVO}_4 \) due to the \( k_{\text{V}_3\text{O}_62\text{H}_2\text{O}} \) as self-sacrifice templates. The particle size of \( \text{BiVO}_4 \) products are shown in Table S1.

**Figure 1.** XRD patterns of samples obtained through different method: (a) Microwave-assisted synthesis; (b) Chemical bath deposition synthesis; (c) Mechanochemical synthesis; (d) Ultrasonic synthesis; (e) Hydrothermal synthesis.

The morphology of \( \text{BiVO}_4 \) products was revealed through scanning electron microscopy (SEM). The SEM images of the obtained \( \text{BiVO}_4 \) samples are shown in Fig. 2. It can be observed in Fig. 2(a) and (b) that the \( \text{BiVO}_4(ma) \) prepared through microwave-assisted method is composed of smooth microspheres with some little particles on the surface. The size of the spheres is around 10-20 \( \mu \text{m} \) with good dispersion. While it can be found in Fig. 2(c) and (d) that the \( \text{BiVO}_4(c) \) was smaller and rugged without particles compared to the \( \text{BiVO}_4(ma) \). The spherical \( \text{BiVO}_4(u) \) was combined with irregular cubic granules displayed in the Fig. 2(e) and (f). Interestingly, the spherical \( \text{BiVO}_4(m) \) was composed of small pieces shown in the Fig. 2(g) and (h). Similarly, the \( \text{BiVO}_4(h) \) is also spherical particle constituted by smaller granules in the Fig. 2(i) and (j). All of the \( \text{BiVO}_4 \) samples have good dispersion. Thus, all of the five methods can prepare spherical \( \text{BiVO}_4 \) due to the \( k_{\text{V}_3\text{O}_62\text{H}_2\text{O}} \) as self-sacrifice templates. The particle size of \( \text{BiVO}_4 \) products are shown in Table S1.

**Figure 2.** SEM images of the \( \text{BiVO}_4 \) samples prepared with different method (a, b) Microwave-assisted synthesis; (c, d) Chemical bath deposition synthesis; (e, f) Mechanochemical synthesis; (g, h) Ultrasonic synthesis; (i, j) Hydrothermal synthesis.

A possible principle for tetragonal and monoclinic phase formations by each method is proposed. The \( \text{BiVO}_4 \) of tetragonal and monoclinic phases were able to be selectively synthesized by increasing the preparation time or reaction temperature. It has been proved that phase transformation can occur when incident higher energy is provided during the reaction. The formation of \( \text{BiVO}_4 \) of tetragonal phase is preferable kinetically. Microwave-assisted synthesis and chemical bath deposition synthesis undergo relatively milder conditions compared to the other three methods. The tetragonal phase of \( \text{BiVO}_4 \) is formed at the beginning stage of the preparations. It typically has large particle sizes as observed in SEM images. However, the monoclinic-phased \( \text{BiVO}_4 \) is thermodynamically more stable than the product of the tetragonal phase at room temperature. Therefore, when the total energy of the reaction was increased, the particles became smaller during the preparation, and then dissolved and recrystallized. \( \text{BiVO}_4 \) of monoclinic phase is finally formed at the recrystallization and/or in the small particles in which the stress can easily be released. The proposed reaction mechanism is consistent with the SEM and XRD results.

The band gap energy is one of key factors in determining the photocatalytic activity. To get the precise values, the optical properties are investigated via the UV-Vis diffuse reflectance spectroscopy for two as-prepared \( \text{BiVO}_4 \) compounds. They were prepared through ultrasonic synthesis and microwave-assisted synthesis, and differed in phases. The absorption spectra are depicted in Fig. S1. A general survey shows that all absorption edges are within ultraviolet to visible-light region. The primary edges are determined to 640 nm and 560 nm, respectively, for the samples prepared by ultrasonic synthesis (\( \text{BiVO}_4(u) \)) and microwave-assisted (\( \text{BiVO}_4(ma) \)) synthesis. Compared to the microwave-assisted method, the ultrasonic synthesis of \( \text{BiVO}_4 \) increases photoabsorption at ultraviolet light region and extend it to visible light region by shifting the edges to longer wavelengths. Therefore, the \( \text{BiVO}_4 \) via ultrasonic synthesis is expected to possess higher photocactivity compared to the microwave-assisted counterpart.

To test the photocatalytic performances of the products, two \( \text{BiVO}_4 \) with different phases were employed in the catalytic experiments in this communication. The photocatalytic abilities of \( \text{BiVO}_4 \) were evaluated by comparing degradation rates of MB under UV light. The results were shown in Fig. S2. It can be seen that the final discoloration rate of \( \text{BiVO}_4(ma) \) was 34.3%. On the contrary the photocatalytic degradation rate of \( \text{BiVO}_4(u) \) was nearly 100%. As shown in Fig. 3(B), the photocatalytic degradation of MB with reaction time follows first order kinetics that could be confirmed by the linear transforms of \( \ln(\text{C}_0/\text{C}_t) \approx \text{t} \). In addition, the reaction rate constant (k) of \( \text{BiVO}_4 \) made by ultrasonic synthesis was calculated to 0.03449 min\(^{-1}\), much higher than 0.00217 min\(^{-1}\) of the \( \text{BiVO}_4 \) made by microwave-assisted synthesis from Fig. S2(B). Note that the photocatalytic activity of \( \text{BiVO}_4 \) prepared through ultrasonic synthesis was higher than \( \text{BiVO}_4 \) prepared with microwave-assisted synthesis. This is consistent with the fact that the monoclinic \( \text{BiVO}_4 \) had a higher photocatalytic activity than tetragonal \( \text{BiVO}_4 \).

Vis diffuse reflectance spectroscopy for two as-prepared \( \text{BiVO}_4 \) compounds. They were prepared through ultrasonic synthesis and microwave-assisted synthesis, and differed in phases. The absorption spectra are depicted in Fig. S1. A general survey shows that all absorption edges are within ultraviolet to visible-light region. The primary edges are determined to 640 nm and 560 nm, respectively, for the samples prepared by ultrasonic synthesis (\( \text{BiVO}_4(u) \)) and microwave-assisted (\( \text{BiVO}_4(ma) \)) synthesis. Compared to the microwave-assisted method, the ultrasonic synthesis of \( \text{BiVO}_4 \) increases photoabsorption at ultraviolet light region and extend it to visible light region by shifting the edges to longer wavelengths. Therefore, the \( \text{BiVO}_4 \) via ultrasonic synthesis is expected to possess higher photocactivity compared to the microwave-assisted counterpart.

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Fig. S2 represents the water contact angle for the \( \text{BiVO}_4(h) \). The \( \text{BiVO}_4(h) \) thin films were prepared via a facile and dip-coating method. All of the \( \text{BiVO}_4(h) \) thin films was modified by 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFOTS). We also changed the substrates to glass, copper and aluminium. It can be found that the highest water contact angle (165°) was using...
glass as substrate in the Fig. S2(a). It can be seen from Fig. S2(b) and Fig. S2(c), using copper and aluminium as substrates have water contact angles of 158° and 152°, respectively.

Figure 3(A). The photocatalytic degradation efficiency of MB by BiVO₄ made by microwave-assisted synthesis (a); and ultrasonic synthesis (b).

Figure 3(B). Kinetics of the MB degradation catalyzed by the BiVO₄ prepared by different methods: (a) microwave-assisted synthesis and (b) ultrasonic synthesis.

In conclusion, the BiVO₄ products have been successfully synthesized by using K₂V₁₀O₃₂·9H₂O and Bi(NO₃)₃·5H₂O as reactant materials through five methods. The BiVO₄ powders prepared with microwave-assisted synthesis and chemical bath deposition synthesis were tetragonal phase. The microwave-assisted synthesis of tetragonal BiVO₄ is more convenient than chemical bath deposition synthesis. In contrast, the BiVO₄ samples of monoclinic scheelite were fabricated by other three ways. Among them, ultrasonic synthesis is the best choice for the synthesis of monoclinic BiVO₄ considering the reaction time and operation. Using decavanadate as template, structures of BiVO₄ can be designed to spherical through the five general methods. The photocatalytic activity of BiVO₄(u) was higher than BiVO₄(tm) that is associated with crystalline phase. We also found that the BiVO₄(h) thin films exhibited excellent superhydrophobicity. Furthermore, other functionalities of BiVO₄ are very important in practical industrial application, so research on other performances of these BiVO₄ crystals prepared herein is in progress.

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References and Notes

6  A. T’ucks and H. P. Beck, Dyes Pigments. 2007, 72, 163.
BiVO₄ has been prepared by five general methods using decavanadate (K₆V₁₀O₂₈·9H₂O) as vanadium source. And the morphology of these BiVO₄ is spherical.

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**Graphical Information**

![Graphical representation of BiVO₄ synthesis methods](image)

- Microwave-assisted synthesis
- Chemical bath deposition synthesis
- Mechanochemical synthesis
- Ultrasonic synthesis
- Hydrothermal synthesis