

## Comparison of synthetic routes for large-scale synthesis of spherical BiVO<sub>4</sub> with photocatalytic and superhydrophobic properties

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1 The spherical BiVO<sub>4</sub> in tetragonal and monoclinic  
2 scheelite phases have been prepared through five general  
3 methods by using K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O as self-sacrifice templates.  
4 Morphology of these BiVO<sub>4</sub> is kept spherical because of  
5 K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O as self-sacrifice templates. The microwave-  
6 assisted synthesis of tetragonal BiVO<sub>4</sub> is convenient and  
7 ultrasonic synthesis is the best choice for the synthesis of  
8 monoclinic BiVO<sub>4</sub>.

9 New strategies of BiVO<sub>4</sub> fabrications have been  
10 developed for a long time following advancements of  
11 science and technology. The emphases on the BiVO<sub>4</sub> not  
12 only arise from their ionic conductivity,<sup>1</sup>  
13 photoelectrochemical,<sup>2,4</sup> ferroelasticity,<sup>5</sup> and  
14 photochromism<sup>6</sup> but also due to its nature of nontoxic  
15 yellow pigment for high-performance lead-free paints.<sup>7</sup> The  
16 BiVO<sub>4</sub> can be synthesized by different methods, such as  
17 metal-organic decomposition,<sup>8</sup> classical solid state  
18 reaction,<sup>9,10</sup> sonochemistry,<sup>11,12</sup> solvothermal or  
19 hydrothermal methods,<sup>13-17</sup> sol-gel,<sup>18</sup> and co-  
20 precipitation.<sup>19,20</sup> A unified approach to the synthesis of a  
21 large variety of materials with different physical and  
22 chemical properties had been reported diversely in inorganic  
23 compounds.<sup>21</sup> However, several methods to the synthesis of  
24 a product with nearly uniform morphology starting from  
25 same raw materials have been rarely reported. Herein, we  
26 report two different crystalline phases of spherical BiVO<sub>4</sub>  
27 prepared with five general methods. The phases are  
28 tetragonal and monoclinic scheelites.

29 The tetragonal BiVO<sub>4</sub> products were prepared by  
30 microwave-assisted synthesis and chemical bath deposition  
31 synthesis. This microwave-assisted synthesis is to heat the  
32 suspension in a domestic microwave oven for ten minutes.  
33 A main step for chemical bath deposition synthesis is  
34 immersing the suspension in a water jacket for 30 min.  
35 Compared with microwave-assisted synthesis, chemical  
36 bath deposition synthesis was more complicated and time  
37 consuming. Hence, it is obvious that microwave-assisted  
38 synthesis is more convenient to the fabrication of tetragonal  
39 BiVO<sub>4</sub>. Monoclinic BiVO<sub>4</sub> samples were fabricated through  
40 mechanochemical synthesis, ultrasonic synthesis, and  
41 hydrothermal method. The mechanochemical synthesis is  
42 approved as an efficient and facile method. Using a  
43 conventional agate mortar the time of milling and annealing  
44 are 20 min and 30 min, respectively. However, the key step  
45 of ultrasonic synthesis was to sonicate the precursors for 20  
46 min at room temperature. Finally, the hydrothermal  
47 synthesis was carried out in a teflon-lined stainless steel  
48 autoclave at 180 °C for 24 h. It was found that the ultrasonic

49 synthesis is the best choice for the synthesis of monoclinic  
50 BiVO<sub>4</sub> considering the reaction time and operations.

51 As a kind of polyoxometalates (POMs), the  
52 K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O is not only a reactant but also a template in  
53 this work. Such functions are different from other synthesis  
54 where the POMs always acted as templates of organic  
55 compounds due to the structure of inorganic metal oxide  
56 cluster.<sup>22</sup> Meanwhile, POMs have been employed as  
57 inorganic templates due to their special structures and  
58 abundant chemical combinations.<sup>23</sup> Furthermore,  
59 K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O can be dissolved into deionized water,  
60 enabling decavanadate cores of (V<sub>10</sub>O<sub>28</sub>)<sup>6-</sup> in solutions.  
61 However, V<sub>10</sub>O<sub>28</sub><sup>6-</sup> can combine with H<sup>+</sup> easily, forming  
62 several protonation states including HV<sub>10</sub>O<sub>28</sub><sup>5-</sup>, H<sub>2</sub>V<sub>10</sub>O<sub>28</sub><sup>4-</sup>  
63 and H<sub>3</sub>V<sub>10</sub>O<sub>28</sub><sup>3-</sup> at different acidic pH. The pKa values of  
64 H<sub>3</sub>V<sub>10</sub>O<sub>28</sub><sup>3-</sup>, H<sub>3</sub>V<sub>10</sub>O<sub>28</sub><sup>3-</sup> and H<sub>3</sub>V<sub>10</sub>O<sub>28</sub><sup>3-</sup> are around 1.2, 3.6,  
65 and 6.1, respectively.<sup>24</sup> Therefore there is a tendency to form  
66 protonated decavanadates in the solution with the decreases  
67 of pH. It is evidentially that the structure of decavanadate  
68 core is stable at the acidic solutions (pH<6).<sup>25</sup> Noteworthy,  
69 all pH values of reaction environment were under 7 in this  
70 work. Thus, the decavanadate core was stable at the first  
71 stage of reactions. It could be served as an inorganic  
72 template to construct the BiVO<sub>4</sub> spherical particles. In  
73 addition, decavanadate core was consisted of ten edge-  
74 shared VO<sub>6</sub> octahedra. When reactions happened, Bi<sup>3+</sup> can  
75 easily combine with one of ten edge-shared VO<sub>6</sub> octahedra  
76 to form BiVO<sub>4</sub>. We suggest that using K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O as  
77 reactants can greatly improve the possibility of reactions. A  
78 similar result through the hydrothermal synthesis of BiVO<sub>4</sub>  
79 starting from K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O was also reported in our latest  
80 article.<sup>26</sup>

81 The powders were detected by X-ray powder  
82 diffractometer (MiniFlex II) with Cu K $\alpha$  radiation  
83 ( $\lambda=0.15406$  nm). The scanning electronic microscopy (SEM)  
84 images were recorded on JEOL JSM-6700F electron  
85 microscope. The UV-Vis diffuse reflectance spectra were  
86 obtained with a UV-visible spectrophotometer (UV-2550,  
87 Shimadzu, Japan). UV-spectrophotometer (Lambda 25  
88 spectrometer) was used to detect the concentration of MB  
89 solution. Water contact angle (CA) measurements were  
90 carried out by Rame-hart Model p/n 250-F1.  
91 Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O were analytical grade that  
92 were used without any purification. Anhydrous ethanol, 1H,  
93 1H, 2H, 2H - perfluorodecyltriethoxysilane (PFOTS) were  
94 purchased from commercial suppliers and used without  
95 further purification. The glass, copper and aluminium  
96 substrates were obtained locally, which was cut into smaller  
97 1.0 cm  $\times$  1.0 cm squares before usage. Then the substrates

1 were further purified by ultrasonic washing with acetone,  
2 anhydrous ethanol, deionized water for 15 min, respectively,  
3 and dried in a clean oven at 60 °C for 1 h.

4 Microwave-assisted synthesis of BiVO<sub>4</sub>. Using 1.0 g  
5 K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O and 9.7 g Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O as the initial  
6 materials, BiVO<sub>4</sub> powder could be obtained by a  
7 microwave-assisted reaction. The start materials were mixed  
8 together after dissolved by 10 mL distilled water  
9 respectively, and stirred for 30 min. Then, the pH value of  
10 the suspension was adjusted to 1 by HNO<sub>3</sub> (2M) under  
11 stirring. The mixture were transferred into a 10 mL teflon-  
12 lined after standing for sometimes and sucking the  
13 supernatant totally, which was carried out in a domestic  
14 microwave oven where working at one minute once for ten  
15 times. After cooling down to room temperature naturally,  
16 the resulting product were washed alternately by distilled  
17 water and absolute ethanol, and then dried in vacuum at  
18 60 °C for 10 h. Finally, the precipitate was milled to powers  
19 by an agate mortar.

20 Chemical bath deposition synthesis of BiVO<sub>4</sub>. The  
21 materials of reaction was 1.0 g Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 1.21 g  
22 K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O, BiVO<sub>4</sub> powder could be achieved by  
23 chemical bath deposition method. The two materials were  
24 grinded by an agate mortar respectively for 2 min to make  
25 them smaller and dissolve easily. The powders were  
26 dissolved by 10 mL deionized water with stirring. Then,  
27 putted K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O solution into another solution under  
28 stirring and adjusted the pH to 1 by HNO<sub>3</sub> (2M). The  
29 precursor immersed in a water jacket to ensure constant  
30 temperature (60 °C) for 30 min. Lastly, the precipitate was  
31 washed with deionized water and ethanol three times, then  
32 dried in vacuum at 60 °C for 9 h.

33 Mechanochemical synthesis of BiVO<sub>4</sub>. In the simple  
34 experiment, 0.677g K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O, 2.425g Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O  
35 were putted into an agate mortar, and the mixture was  
36 ground for 20 min. The precursor was washed alternately  
37 with deionized water and ethanol three times. Further it was  
38 dried at 60 °C in air for 8 h. The final step was an annealing  
39 process. The product was completed by annealing at 500 °C  
40 for 30 min in a muffle furnace.

41 Ultrasonic synthesis of BiVO<sub>4</sub>. 0.322 g Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O  
42 and 1.21 g K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O were dissolved into 10 mL  
43 deionized water with stirring, respectively. Then, the two  
44 solutions were mixed together, and the mixture was  
45 sonicated for 20 min at room temperature. The precipitate  
46 was washed alternately by deionized water and ethanol three  
47 times, dried in vacuum at 60 °C for 9 h.

48 Hydrothermal synthesis of BiVO<sub>4</sub>. In a typical  
49 synthetic process, 2.578 g K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O and 9.7 g  
50 Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O were dissolved into 30 mL NaOH solution  
51 (2M) and 30 mL HNO<sub>3</sub> solution (2M) under stirring,  
52 respectively. After Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O both  
53 dissolved, K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O solution was added into former,  
54 and stirred for 30 min. The pH value of the final suspension  
55 was adjusted to 2 by 2M HNO<sub>3</sub>. The resulting suspension  
56 was transferred into 100 mL teflon-lined stainless steel  
57 autoclaves, which was accomplished at 180 °C for 24 h  
58 under sealing and heating. After cooling down to room  
59 temperature naturally, the precipitates were washed

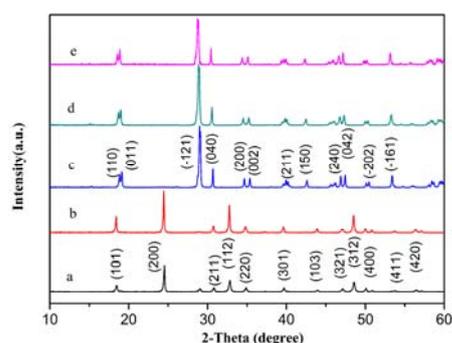
60 alternately by distilled water and absolute ethanol for  
61 several times, and then dried in vacuum at 60 °C for 10 h.

62 The BiVO<sub>4</sub> of tetragonal phase obtained by  
63 Microwave-assisted method and the BiVO<sub>4</sub> of monoclinic  
64 structure acquired by ultrasonic method were detected with  
65 methylene blue (MB) in an aqueous solution under UV-light  
66 irradiation. The aqueous system containing 100 mL 0.01 g/L  
67 MB and 0.1 g BiVO<sub>4</sub> powers was magnetically stirred for 30  
68 min in the dark to reach the adsorption equilibrium of MB  
69 with the photocatalyst, and then exposed under UV light.  
70 The mixture was actively stirred with the photoreactor  
71 during the process and temperature of suspension was kept  
72 at 22 to 28 °C by circulation of water. At 30 min intervals,  
73 around 5 mL of the suspensions were collected and  
74 centrifugalized to remove the photocatalyst particles. The  
75 remained MB solution was analyzed by a UV-visible  
76 Spectrophotometer (Lambda 25 spectrometer) with a  
77 maximum absorbance at 665 nm.

78 Superhydrophobic surfaces were prepared via a facile  
79 drop-casting method. Typically, the as-prepared BiVO<sub>4</sub>  
80 samples were ultrasonically dispersed in ethanol to form a  
81 uniform suspension, then several drops of the suspension we  
82 re dropped on the glass substrate. Finally, in order to reduce  
83 the surface energy of the fabricated structures, the film on  
84 glass substrate was modified by PFOTS. The treatment with  
85 PFOTS was conducted by adding a methanol solution of 2%  
86 (v:v) PFOTS. Then, the BiVO<sub>4</sub>-coated glasses were dried  
87 for 24 h in the atmosphere at ambient temperature. Finally,  
88 the superhydrophobic BiVO<sub>4</sub> coatings were fabricated on  
89 the glass surface by the single-step procedure. Other two  
90 different superhydrophobic surfaces were also prepared  
91 following the same procedure.

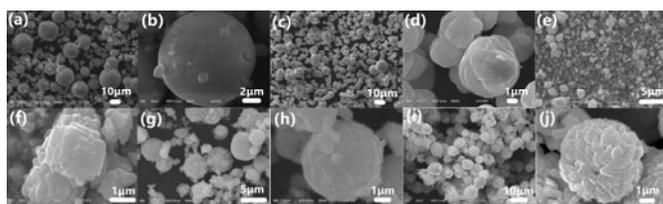
92 The phase purity and chemical composition of the  
93 obtained product were affirmed by XRD. Fig. 1 shows the  
94 XRD patterns of the BiVO<sub>4</sub> samples prepared by five  
95 synthesis methods. The BiVO<sub>4</sub> of microwave-assisted  
96 synthesis (Fig. 1a, donated as BiVO<sub>4</sub>(ma)) and chemical  
97 bath deposition synthesis (Fig. 1b, donated as BiVO<sub>4</sub>(c))  
98 were pure tetragonal zircon type (JCPDS file no. 14-0133).  
99 No other impurities could be found. The XRD peaks are  
100 narrow, indicating the well-crystallized BiVO<sub>4</sub> product. The  
101 XRD patterns of the BiVO<sub>4</sub> samples prepared by  
102 mechanochemical synthesis (Fig. 1c, labelled as BiVO<sub>4</sub>(m)),  
103 ultrasonic synthesis (Fig. 1d, BiVO<sub>4</sub>(u)) and hydrothermal  
104 method (Fig. 1e, BiVO<sub>4</sub>(h)) were single monoclinic  
105 scheelite type (JCPDS file no. 14-0688) with good  
106 crystallinity. It reveals that the pure monoclinic scheelite  
107 type of BiVO<sub>4</sub> could be prepared by the three methods under  
108 certain conditions. Clearly, the BiVO<sub>4</sub> prepared with five  
109 general methods had two phases, including tetragonal phase  
110 and monoclinic scheelite. Result suggest that, by changing  
111 the preparation methods, BiVO<sub>4</sub> powder with different  
112 crystalline phase be synthesized with the raw material of  
113 K<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·9H<sub>2</sub>O.

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**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  $\text{BiVO}_4(\text{ma})$  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  $\text{BiVO}_4(\text{c})$  was smaller and rugged without particles compared to the  $\text{BiVO}_4(\text{ma})$ . The spherical  $\text{BiVO}_4(\text{u})$  was combined with irregular cubic granules displayed in the Fig. 2(e) and (f). Interestingly, the spherical  $\text{BiVO}_4(\text{m})$  was composed of small pieces shown in the Fig.2(g) and (h). Similarly, the  $\text{BiVO}_4(\text{h})$  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  $\text{K}_6\text{V}_{10}\text{O}_{28}\cdot 9\text{H}_2\text{O}$  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.<sup>27</sup> Microwave-

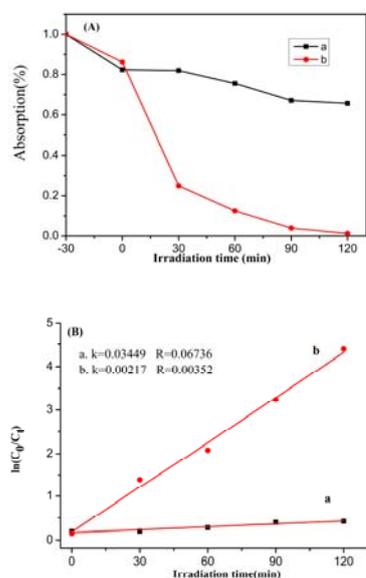
assisted synthesis and chemical bath deposition synthesis undergo relatively milder conditions compared to the other three methods. The tetragonal phase of  $\text{BiVO}_4$  is formed at the beginning stage of the preparations. It typically has large particle sizes as observed in SEM images. However, 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 ( $\text{BiVO}_4(\text{u})$ ) and microwave-assisted ( $\text{BiVO}_4(\text{ma})$ ) 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 photoactivity 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. 3(A). It can be seen that the final discoloration rate of  $\text{BiVO}_4(\text{ma})$  was 34.3%. On the contrary the photocatalytic degradation rate of  $\text{BiVO}_4(\text{u})$  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  $\ln(C_0/C_t) \sim t$ . In addition, the reaction rate constant ( $k$ ) of  $\text{BiVO}_4$  made by ultrasonic synthesis was calculated to  $0.03449 \text{ min}^{-1}$ , much higher than  $0.00217 \text{ min}^{-1}$  of the  $\text{BiVO}_4$  made by microwave-assisted synthesis from Fig. 3(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  $\text{BiVO}_4$ .

Fig. S2 represents the water contact angle for the  $\text{BiVO}_4(\text{h})$ . The  $\text{BiVO}_4(\text{h})$  thin films were prepared via a facile and dip-coating method. All of the  $\text{BiVO}_4(\text{h})$  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 ( $165^\circ$ ) was using

1 glass as substrate in the Fig. S2(a). It can be seen from Fig.  
 2 S2(b) and Fig. S2(c), using copper and aluminium as  
 3 substrates have water contact angles of  $158^\circ$  and  $152^\circ$ ,  
 4 respectively.



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6  
7 **Figure 3(A).** The photocatalytic degradation efficiency of MB by  
 8  $\text{BiVO}_4$  made by microwave-assisted synthesis (a); and ultrasonic  
 9 synthesis (b).

10 **Figure 3(B).** Kinetics of the MB degradation catalyzed by the  
 11  $\text{BiVO}_4$  prepared by different methods: (a) microwave-assisted  
 12 synthesis and (b) ultrasonic synthesis.

13 **In conclusion, the  $\text{BiVO}_4$  products have been**  
 14 **successfully synthesized by using  $\text{K}_6\text{V}_{10}\text{O}_{28}\cdot 9\text{H}_2\text{O}$  and**  
 15  **$\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$  as reactant materials through five methods.**  
 16 **The  $\text{BiVO}_4$  powders prepared with microwave-assisted**  
 17 **synthesis and chemical bath deposition synthesis were**  
 18 **tetragonal phase. The microwave-assisted synthesis of**  
 19 **tetragonal  $\text{BiVO}_4$  is more convenient than chemical bath**  
 20 **deposition synthesis. In contrast, the  $\text{BiVO}_4$  samples of**  
 21 **monoclinic scheelite were fabricated by other three ways.**  
 22 **Among them, ultrasonic synthesis is the best choice for the**  
 23 **synthesis of monoclinic  $\text{BiVO}_4$  considering the reaction**  
 24 **time and operation. Using decavanadate as template,**  
 25 **structures of  $\text{BiVO}_4$  can be designed to spherical through the**  
 26 **five general methods. The photocatalytic activity of**  
 27  **$\text{BiVO}_4(\text{u})$  was higher than  $\text{BiVO}_4(\text{ma})$  that is associated**  
 28 **with crystalline phase. We also found that the  $\text{BiVO}_4(\text{h})$  thin**  
 29 **films exhibited excellent superhydrophobicity. Furthermore,**  
 30 **other functionalities of  $\text{BiVO}_4$  are very important in**  
 31 **practical industrial application, so research on other**  
 32 **performances of these  $\text{BiVO}_4$  crystals prepared herein is in**  
 33 **progress.**

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