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Low-temperature synthesis of $BiVO_4$ crystallites in molten salt medium and their UV–vis absorption

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Abstract

$BiVO_4$ crystallites were successfully synthesized by a low-temperature molten salt method. XRD analysis and SEM observation showed that the incorporation of salt medium in the preparing process would greatly lower the formation temperature of $BiVO_4$ phase, and promote their crystallization. UV–vis spectra evidenced their better optical absorption and visible light response than that of TiO_2-P25.

Keywords: Photocatalyst; Bismuth vanadate; UV–vis; Low-temperature molten salt

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1. Introduction

In recent years, environmental remediation using photocatalysts is currently of interest for their low price and absence of toxicity and much attention has been focused on titanium dioxide (TiO_2), mainly due to its possible applicability to detoxification of environmental pollutants [1–5]. However, TiO_2 photocatalyst only responds to UV light which occupies ca. 4% of the whole solar energy because of its large band gap energy of 3.2 eV. This limits its further application in the visible-light region ($\lambda > 400$ nm). The development of visible-light-driven photocatalysts, therefore, has become one of the most challenging topics recently.

Bismuth vanadate ($BiVO_4$) as an important functional material has various technological properties which depend strongly on crystalline form and microstructure. There are three crystalline phases reported: monoclinic scheelite-type, tetragonal sheelite-type and tetragonal zircon-type [6,7]. The monoclinic-phase $BiVO_4$ has been reported to show higher photocatalytic activity for O_2 evolution compared to the other two phases [8,9], and would transform to the tetragonal form near 255 °C. Therefore, much effort has been also devoted to the mechanism of $BiVO_4$ phase transformation because of the obvious difference in optical, electrical and magnetic properties of these polymorphs [10–13]. $BiVO_4$ has found a wide application: e.g. it can be used as the substitute for the yellow pigments in the painting industry due to its high performance and being free of ecotoxicological problems [14], and as a birefringent material since it presents a large refractive index variation with the temperature [15]. Especially, the photocatalytic property of $BiVO_4$ in water splitting and oxidative dehydrogenation has drawn extensive attention recently because of its strong absorption and good response to visible light [8,16]. Several methods have been developed to prepare $BiVO_4$ crystallites: conventional solid-state reaction [17], solution coprecipitation [13,18,19], hydrothermal and sonochemical reactions [20–22], metalorganic decomposition [15,23,24], the sol–gel process [25], chemical bath deposition [26], and the hybrid organic–inorganic precursor route [27].

However, these methods still have such limitations as high calcining temperature, complicated manipulation, and large consumption of organic agents and/or specific requirement of

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equipment. The molten salt method has been considered as a good technological process for preparing inorganic material [28–33], where the synthetic temperature can be greatly lowered, and the diffusion speeds of reacting constituents be obviously accelerated due to the incorporation of salt medium; so products generally possess a good crystallinity and crystalline morphology.

In this paper, we report on a low-temperature preparing method of $BiVO_4$ crystallites, where a pure tetragonal-phase of $BiVO_4$ crystallites with homogeneous particle sizes can be synthesized at 200 °C. And the monoclinic and tetragonal-phases can be easily prepared by only adjusting the calcining temperature in the range of 200–410 °C. All the as-prepared samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and UV–vis spectra technique (UV–vis), respectively. To the best of our knowledge, no such studies have ever been reported.

2. Experimental procedure

2.1. Preparation

Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) and ammonium metavanadate (NH_4VO_3) were used as starting materials, and both of them are analytic grade without further purification. A typical preparing procedure is described as follows: $Bi(NO_3)_3 \cdot 5H_2O$ and NH_4VO_3 were respectively dissolved in distilled water to form aqueous solutions with 0.2 M, and then, both solutions were mixed together in a 1:1 molar ratio by constant stirring at room temperature for 1 h, a precipitate was formed. The precipitate was filtered and thoroughly washed with distilled water, and dried in an oven at 70 °C for 6 h to obtain $BiVO_4$ precursor (Precursor). By ball milling in absolute ethanol for 1 h, the precursor was well mixed with a complex-salt $LiNO_3$–$NaNO_3$ (the weight ratio of $LiNO_3/NaNO_3 = 27/23$, melting point (m.p.): 193 °C) and $LiNO_3$ salt (m.p.: 253 °C) [34], respectively. A series of the weight ratios (1:0, 1:4, 1:8, 1:16 and 1:24) of the precursor to the salt were chosen. The obtained mixture was put into an alumina crucible and calcined at a certain temperature ranging from 200 to 410 °C for a given time (1, 4 and 8 h). Finally, the product was dissolved in hot distilled water, and then filtered and thoroughly washed with distilled water for several times, and dried at 70 °C for 6 h for characterization.

2.2. Characterization

To determine the crystal phase composition of the prepared powders, X-ray diffraction (XRD) measurement was carried out at room temperature by using an X-ray diffractometer (Rigaku D/max, Japan) with Cu K_α radiation. A scanning electron microscope (JSM-840, Japan) was employed to observe the particle size and morphology of the as-prepared crystallites. Their UV–Vis absorption spectra were recorded on a spectrophotometer (U-3101, Japan) in the wavelength range of 200–800 nm.

3. Results and discussion

3.1. Phase composition, particle size and morphology of the samples

XRD patterns of the samples, prepared by the molten salt process at different calcining temperatures for 8 h in a 1:8 weight ratio of the precursor to the salt, are shown in Fig. 1(a)–(d). Obviously, all the samples are well-crystallized. At 200 °C, a pure tetragonal-phase of $BiVO_4$ can be obtained by using $LiNO_3$–$NaNO_3$ complex salt, and well matched with the reported data (JCPDS No. 14-0133). Nevertheless, with the increase of the calcining temperature ($LiNO_3$ was used as salt medium), the tetragonal-phase gradually transforms to the

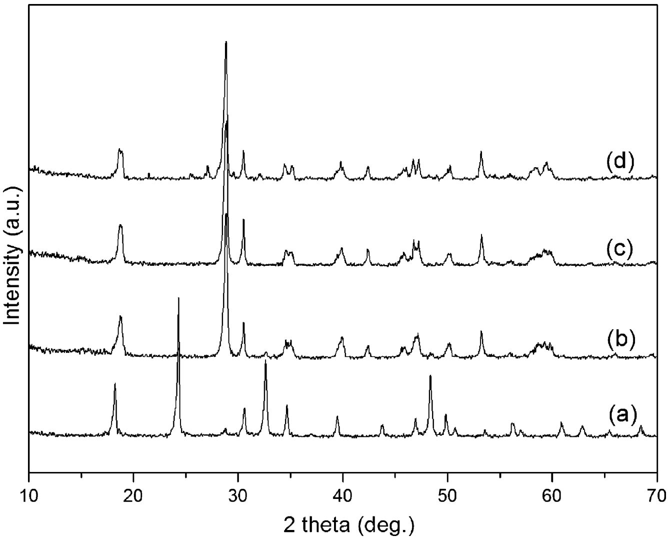

Fig. 1. XRD patterns of the samples obtained at different calcining temperatures for 8 h: (a) 200 °C; (b) 270 °C; (c) 340 °C; and (d) 410 °C (the weight ratio of the precursor to the salt: 1:8).

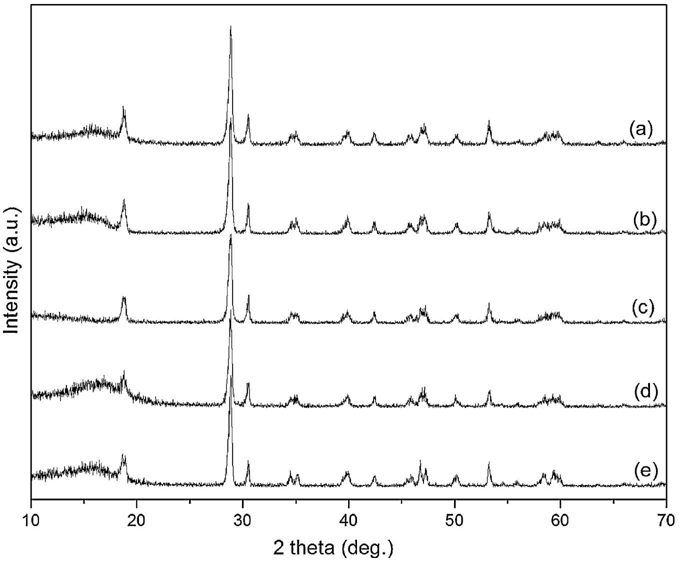

Fig. 2. XRD patterns of the samples prepared by calcining at 340 °C for 8 h in various weight ratios of the precursor to the salt: (a) 1:0; (b) 1:4; (c) 1:8; (d) 1:16; and (e) 1:24.

monoclinic form (JCPDS No. 14-0688). At 340 °C, the irreversible phase transformation is finished completely. Therefore, the tetragonal and monoclinic $BiVO_4$ crystallites can be selectively synthesized in our molten salt process simply by adjusting the calcining temperature.

The effect of the weight ratio of the precursor to the salt on the formation of $BiVO_4$ phase was also investigated. Fig. 2 presents XRD patterns of the samples prepared by calcining at 340 °C for 8 h in various weight ratios.

Obviously, at 340 °C, the incorporation of the salt or not does not bring about any significant changes in their XRD patterns, which all can be indexed to the monoclinic-phase of $BiVO_4$.

SEM images of the precursor and $BiVO_4$ crystallites prepared under different experimental conditions are shown in Fig. 3. The precursor appears in the morphology of irregular-shaped particles with ca. 2–5 μm in diameter (Fig. 3(a)). Once adding the salt, uniform and spherical tetragonal-phase $BiVO_4$

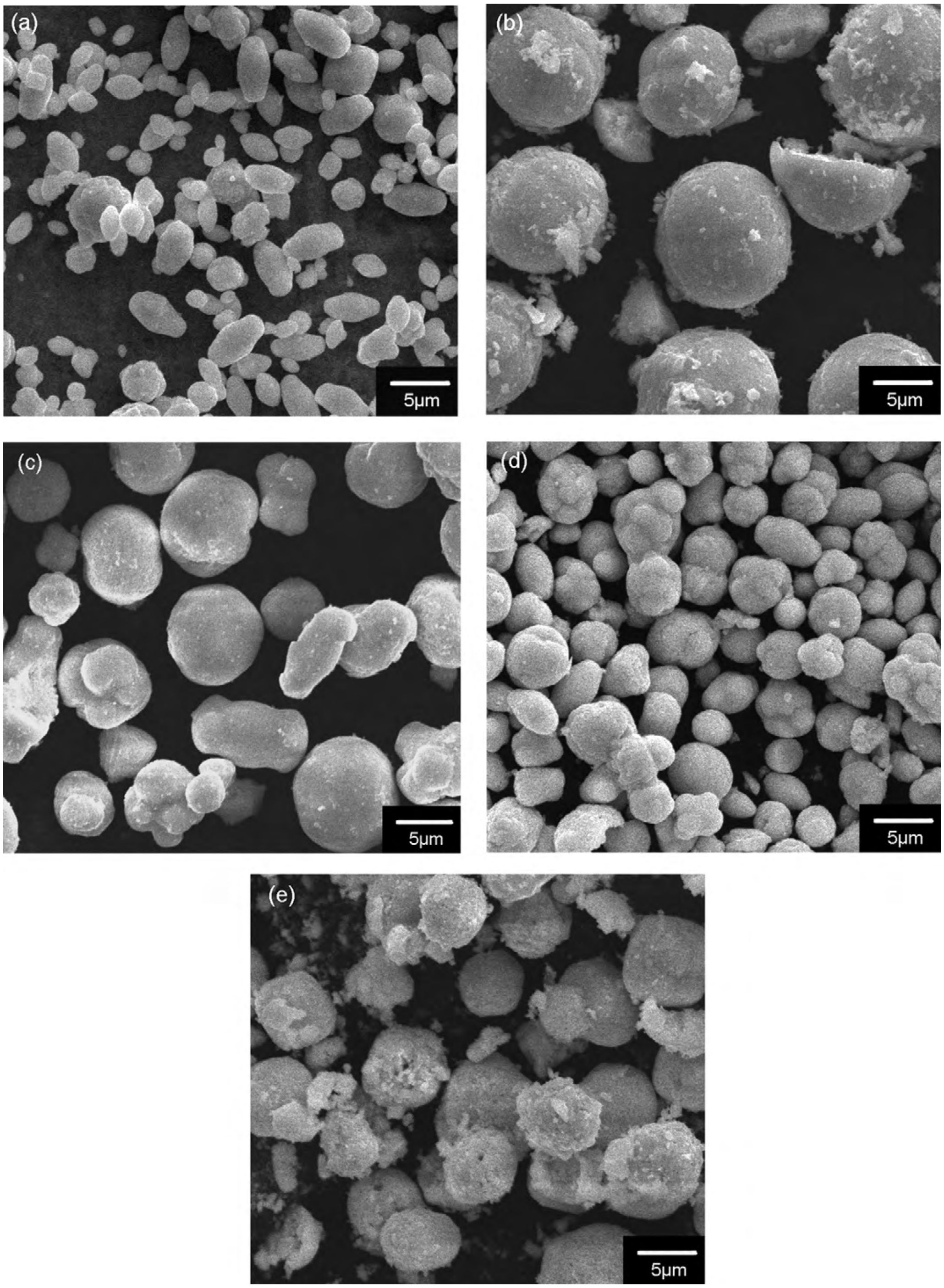

Fig. 3. SEM images of the precursor, and $BiVO_4$ crystallites prepared at different calcining temperatures for 8 h in a 1:8 weight ratio of the precursor to the salt: (a) precursor; (b) 200 °C; (c) 270 °C; (d) 340 °C; and (e) 410 °C.

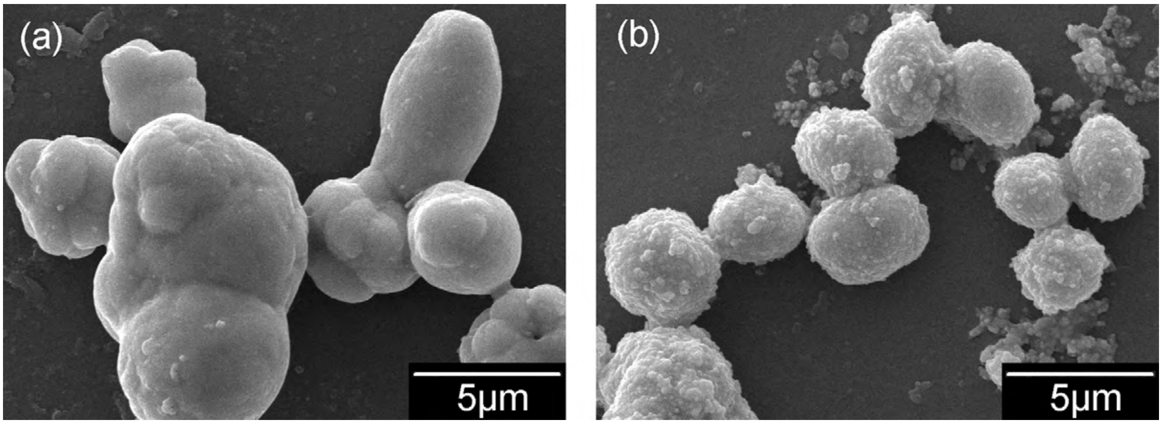

Fig. 4. SEM images of $BiVO_4$ crystallites prepared by calcining at 340 °C for 8 h in different weight ratios of the precursor to the salt: (a) 1:0 and (b) 1:8.

particles with smooth surface can be obtained even at 200 °C (Fig. 3(b)), having an average particle size of ca. 8 μm. It implies that the incorporation of the salt in the preparing process would be beneficial to $BiVO_4$ crystallization. Noteworthily, with the formation of monoclinic-phase, $BiVO_4$ crystallites in particle size progressively decrease (Fig. 3(b) to Fig. 3(c)), meaning that the appearance of the monoclinic-phase would inhibit the growth of $BiVO_4$ crystallites. The crystalline morphology of the pure monoclinic-phase of $BiVO_4$ crystallites is shown in Fig. 3(d) and Fig. 3(e). Although elevating the calcining temperature would also promote the growth of the monoclinic-phase $BiVO_4$ crystallites, it results in a low crystallinity (Fig. 3(e)) where the rough surface and a little loose microstructure can be observed. It is in agreement with XRD analysis in Fig. 1(d).

Fig. 4 displays the effect of the presence of the salt medium on the crystalline morphology of $BiVO_4$ crystallites under the same calcining condition (340 °C, 8 h). The remarkable difference in particle size and morphology between $BiVO_4$ crystallites prepared with and without using the salt can be found: (1) the incorporation of the salt in the preparing process results in reduced particle size; (2) the presence of the salt medium would make $BiVO_4$ crystallites more homogeneous in particle size, and the irregular-shaped particles like that in Fig. 4(a) (without using the salt) are hardly observed in the $BiVO_4$ sample prepared by the molten salt method (Fig. 4(b)).

In practice, the formation mechanism of $BiVO_4$ crystallites in present study should belong to dissolution-recrystallization. The molten salt (Complex-salt $LiNO_3$–$NaNO_3$ or $LiNO_3$) plays two important roles in the synthetic process: Firstly, it is a good solvent, but does not react with $BiVO_4$ precursor. Above the melting point of salts, the precursor can dissolve in the molten salt medium, which would greatly speed up the diffusing and transporting rates of components due to its low viscosity. Secondly, it can provide a homogeneous medium of recrystallization for $BiVO_4$ crystallites when their saturation is reached, favoring their nucleation and growth. Therefore, the as-prepared $BiVO_4$ crystallites possess a good crystallinity and crystalline morphology.

3.2. UV–vis analysis of $BiVO_4$ samples

Fig. 5 presents UV–visible absorption spectra of TiO_2-P25, and $BiVO_4$ crystallites prepared by the molten salt method at 200, 270, 340 and 410 °C for 8 h in a 1:8 weight ratio of the precursor to the salt, respectively. The UV–vis spectra of all the $BiVO_4$ samples can be divided into two types: one type includes (b), (c) and (d) in Fig. 5, and another one is (a). Their XRD analysis being taken into account (Fig. 1), $BiVO_4$ crystallites obtained by calcining at 340 and 410 °C (Fig. 5(c) and (d)) are assigned to monoclinic-phase, while the main phase of the sample prepared at 270 °C (Fig. 5(b)) is still monoclinic, only containing a trace amount of tetragonal-phase (Fig. 1(b)). The monoclinic-phase samples exhibit excellent light absorption, and their onset of the absorption appears at about 520 nm. Moreover, a little red-shift can be also found in the monoclinic-phase $BiVO_4$ sample (Fig. 5(c)) with better crystallization than

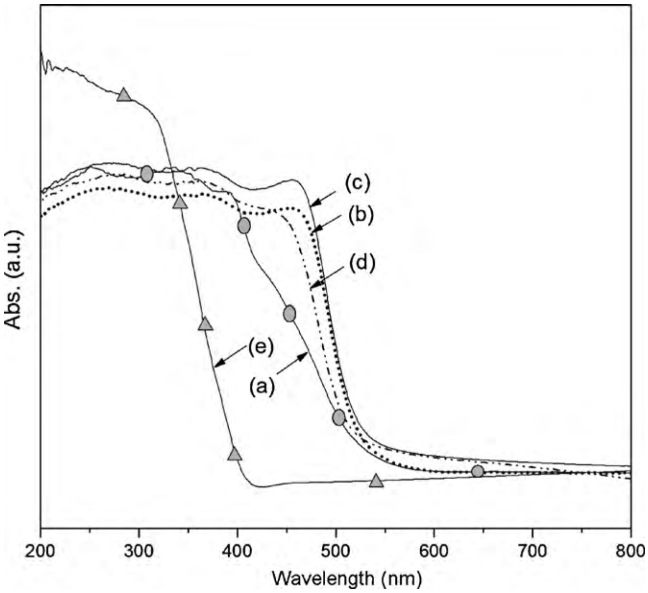

Fig. 5. UV–vis absorption spectra of TiO_2-P25, and $BiVO_4$ crystallites prepared at different calcining temperatures for 8 h in a 1:8 weight ratio of the precursor to the salt: (a) 200 °C; (b) 270 °C; (c) 340 °C; (d) 410 °C; and (e) TiO_2-P25 (using as reference).

that of Fig. 5(d). The similar results can be found in the reference [21], where the monoclinic-phase $BiVO_4$ crystallites were prepared by a hydrothermal process and exhibited the absorption onset of <520 nm (2.39–2.47 ev).

Fig. 5(a) corresponds the $BiVO_4$ sample with pure tetragonal-phase (Fig. 1(a)), showing an obvious blue-shift from that of the monoclinic-phase samples. It also verified that the monoclinic-phase $BiVO_4$ should have better photocatalytic activity in visible-light region than the tetragonal-phase. In addition, compared with TiO_2-P25 (Fig. 5(e)), $BiVO_4$ crystallites comprehensively exhibit better photocatalytic potential, especially in visible-light region.

4. Conclusion

A new technological route (low-temperature molten salt method) was proposed, where the monoclinic and tetragonal $BiVO_4$ crystallites could be easily prepared without using any template, surfactant, and other organic additives. The morphology and dimension of the products can be well controlled by varying such experimental conditions as the calcining temperature and the weight ratio of the precursor to the salt. The results also show that $BiVO_4$ crystallites comprehensively exhibit better photocatalytic potential than TiO_2-P25, especially in the visible-light region; and here the monoclinic-phase $BiVO_4$ should have better photocatalytic activity than the tetragonal-phase.

Compared with other methods, this approach is very simple in facility, easy in manipulation, environmentally friendly and available to a large-scale production, and has no special requirements for equipment.

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References

[1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37.

[2] Z. Zou, J. Ye, K. Sayama, H. Arakawa, Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst, Nature 414 (2001) 625.

[3] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 93 (1993) 341.

[4] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69.

[5] A. Mills, S. Le Hunte, An overview of semiconductor photocatalysis, J. Photochem. Photobiol. A: Chem. 108 (1997) 1.

[6] J.D. Bierlein, A.W. Sleight, Ferroelasticity in bismuth vanadate ($BiVO_4$), Solid State Commun. 16 (1975) 69.

[7] A.K. Bhattacharya, K.K. Mallick, A. Hartridge, Phase transition in $BiVO_4$, Mater. Lett. 30 (1997) 7.

[8] A. Kudo, K. Omori, H. Kato, A novel aqueous process for preparation of crystal form-controlled and highly crystalline $BiVO_4$ powder from layered vanadates at room temperature and its photocatalytic and photophysical properties, J. Am. Chem. Soc. 121 (1999) 11459.

[9] S. Tokunaga, H. Kato, A. Kudo, Selective preparation of monoclinic and tetragonal $BiVO_4$ with scheelite structure and their photocatalytic properties, Chem. Mater. 13 (2001) 4624.

[10] W.I.F. David, A.M. Glazer, A.W. Hewat, The structure and ferroelastic phase transition of $BiVO_4$, Phase Trans. 1 (1979) 55.

[11] A.W. Sleight, H.Y. Chen, A. Ferretti, D.E. Cox, Crystal growth and structure of $BiVO_4$, Mater. Res. Bull. 14 (1979) 1571.

[12] H. Tokomoto, H. Unoki, Investigation of structural phase transition of $BiVO_4$ by Brillouin-scattering measurements, Phys. Rev. 27 (1983) 3748.

[13] A.R. Lim, S.H. Choh, M.S. Jang, Feroelastic phase transition of $BiVO_4$ studied by 51V NMR, Ferroelectrics 94 (1989) 389.

[14] Bull. Bismuth Institute 70 (1997).

[15] A. Galembeck, O.L. Alves, $BiVO_4$ thin film preparation by metalorganic decomposition, Thin Solid Films 365 (2000) 90.

[16] Dingning Ke, Tianyou Peng, Liang Ma, Ping Cai, Ping Jiang, Photocatalytic water splitting for O_2 production under visible-light irradiation on $BiVO_4$ nanoparticles in different sacrificial reagent solutions, Appl. Catal. A 350 (2008) 111.

[17] A. Kudo, K. Ueda, H. Kato, I. Mikami, Photocatalytic O_2 evolution under visible light irradiation on $BiVO_4$ in aqueous $AgNO_3$ solution, Catal. Lett. 53 (1998) 229.

[18] S. Kohtani, S. Makino, A. Kudo, R. Nakagaki, et al., Photocatalytic degradation of 4-n-nonylphenol under irradiation from solar simulator: comparison between $BiVO_4$ and TiO_2 photocatalysts, Chem. Lett. 31 (2002) 660.

[19] M. Long, W.M. Cai, J. Cai, B.X. Zhou, X.Y. Chai, Y.H. Wu, Efficient photocatalytic degradation of phenol over $Co_3O_4/BiVO_4$ composite under visible light irradiation, J. Phys. Chem. B 110 (2006) 20211.

[20] L. Zhang, D.R. Chen, X.L. Jiao, Monoclinic structured $BiVO_4$ nanosheets: hydrothermal preparation, formation mechanism, and coloristic and photocatalytic properties, J. Phys. Chem. B 110 (2006) 2668.

[21] J.Q. Yu, A. Kudo, Effects of structural variation on the photocatalytic performance of hydrothermally synthesized $BiVO_4$, Adv. Funct. Mater. 16 (2006) 2163.

[22] L. Zhou, W.Z. Wang, S.W. Liu, et al., A sonochemical route to visible-light-driven high-activity $BiVO_4$ photocatalyst, Mol. Catal. A: Chem. 252 (2006) 120.

[23] K. Sayama, A. Nomura, Z. Zou, R. Abe, Y. Abe, H. Arakawa, Photoelectrochemical decomposition of water on nanocrystalline $BiVO_4$ film electrodes under visible light, Chem. Commun. 23 (2003) 2908.

[24] K. Sayama, A. Nomura, T. Arai, T. Sugita, R. Abe, M. Yanagida, T. Oi, Y. Iwasaki, Y. Abe, H. Sugihara, Photoelectrochemical decomposition of water into H_2 and O_2 on porous $BiVO_4$ thin-film electrodes under visible light and significant effect of Ag ion treatment, J. Phys. Chem. B 110 (2006) 11352.

[25] H. Liu, R. Nakamura, Y. Nakato, Promoted photo-oxidation reactivity of particulate $BiVO_4$ photocatalyst prepared by a photoassisted sol–gel method, J. Electrochem. Soc. 152 (2005) G856.

[26] M.C. Neves, T. Trindade, Chemical bath deposition of $BiVO_4$, Thin Solid Films 406 (2002) 93.

[27] F. Rullens, A. Laschewsky, Devillers, Bulk and thin films of bismuth vanadates prepared from hybrid materials made from an organic polymer and inorganic salts, Chem. Mater. 18 (2006) 771.

[28] E. Heymann, R.J.L. Martin, M.F.R. Mulcahy, Distribution equilibria between molten metals and molten salts, with reference to the stability of intermetallic compounds in the molten state, J. Phys. Chem. 47 (1943) 473.

[29] T.Y.R. Lee, Lyle F. Albright, Production of potassium monobasic phosphate using a molten salt technique, J. Agric. Food Chem. 26 (1978) 1267.

[30] Cheng-Yan Xu, Liang Zhen, Rusen Yang, Zhong Lin Wang, Synthesis of single-crystalline niobate nanorods via ion-exchange based on molten-salt reaction, J. Am. Chem. Soc. 129 (2007) 15444.

[31] H.J. Zhou, Y.B. Mao, Stanislaus S. Wong, Probing structure–parameter correlations in the molten salt synthesis of $BaZrO_3$ perovskite submicrometer-sized particles, Chem. Mater. 19 (2007) 5238.

[32] David Arney, Brittany Porter, Benjamin Greve, Paul A. Maggard, New molten-salt synthesis and photocatalytic properties of $La_2Ti_2O_7$ particles, J. Photochem. Photobiol. A 199 (2008) 230.

[33] Z.J. Dong, X.K. Li, G.M. Yuan, Y. Cong, N. Li, Z.J. Hu, Z.Y. Jiang, A. Westwood, Fabrication of protective tantalum carbide coatings on carbon fibers using a molten salt method, Appl. Surf. Sci. 254 (2008) 5936.

[34] Ruren Xu, Synthesis and Preparation in Inorganic Chemistry, Higher Education Press, 2001,, p. 199.