

Rapid microwave-assisted synthesis of phase controlled BiVO₄ nanocrystals and research on photocatalytic properties under visible light irradiation

Hui Ming Zhang · Jing Bing Liu · Hao Wang ·
Wen Xiong Zhang · Hui Yan

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Abstract Pure tetragonal and monoclinic phases BiVO₄ were prepared from aqueous Bi(NO₃)₃ and NaVO₃ solutions by a rapid microwave-assisted method that employed accurate controlling of microwave irradiation time and power. The highly crystalline phase converted irreversibly from tetragonal to monoclinic BiVO₄ with gradually elongated irradiation time gradually, which is further proved by X-ray diffraction, UV–vis and Raman measurements. These variations of phase structures led to different photocatalytic properties under visible light.

Keywords BiVO₄ · Microwave · Phase transition · Photocatalytic · Nanostructure · Dispersion

Introduction

Bismuth (III) vanadate (BiVO₄) is a material that has recently attracted considerable attention for its exhibiting various interesting technological properties, such as ferroelasticity (David et al. 1983; Bierlein et al. 1975; Lu et al. 1986), ionic conductivity (Harota et al. 1992), and pigmentation (Wienand et al. 1998). Recently, the visible-light-responsive

property of BiVO₄ makes it worthy of consideration as an advanced material for photocatalytic applications (Kudo et al. 1999).

BiVO₄ appears in three main crystalline forms: tetragonal zircon, monoclinic scheelite, and tetragonal scheelite structures. It was reported that tetragonal BiVO₄ with a 2.9 eV band gap mainly possessing a UV absorption band, while monoclinic BiVO₄ with a 2.4 eV band gap had a characteristic visible light absorption band besides the UV band (Kudo et al. 1999; Bhattacharya et al. 1997). Thus, studying the relationship between some properties and different BiVO₄ phases is of interest. Over the last few years, it was reported that tetragonal BiVO₄ was prepared by a precipitation process from a Bi(NO₃)₃ nitric acid solution and an aqueous NH₄VO₃ solution at room temperature (Bhattacharya et al. 1997). Meanwhile, monoclinic BiVO₄ usually was obtained by solid state and melting reactions at a high temperature (Lim et al. 1995; Roth et al. 1963; Sleight et al. 1979), and hydrothermal method (Liu et al. 2004). Even more, tetragonal phase can transform into monoclinic at higher temperature by solid state method (Bierlein et al. 1975). Also, the phase transition has been studied by an aqueous process (Kudo et al. 1999) and precipitation method (Tokunaga et al. 2001). However, these techniques need long reaction time, high temperature treatment and complicated processing.

There is a considerable interest in evaluating new methods for the synthesis of very fine BiVO₄ powders

H. M. Zhang · J. B. Liu (✉) · H. Wang ·
W. X. Zhang · H. Yan
The College of Materials Science and Engineering,
Beijing University of Technology, Beijing 100022, China
e-mail: liujingbing@bjut.edu.cn

with high purity homogeneous and ultrafine size, which can improve their photocatalytic properties, regarded as not only the photocatalytic degradation organic compounds, but also photocatalytic O₂ evolution from aqueous AgNO₃ solution under visible light. Thus, an efficient, simple, and low temperature processing is required to synthesize high quality BiVO₄ powders. Microwave-assisted reactions are generally very fast and often occur at lower temperatures than the corresponding reactions in conventional heating procedures.

In this paper, microwave-assisted aqueous process generating phase controlled BiVO₄ powders is studied. The properties of the synthesized BiVO₄ powders were investigated by X-ray diffraction (XRD), UV–vis, Raman spectroscopies, and transmission electron microscopy (TEM). Meanwhile, the photocatalytic performances of the synthesized BiVO₄ powders were also studied.

Experiment

Synthesis

The vanadium compound, NaVO₃ stock solution, was used as vanadium source in this study. The NaVO₃ stock solution was prepared by stirring stoichiometric amount of V₂O₅ and NaOH in distilled water for 4 h while heating according to Na/V mole ratio being 1. Aqueous solutions of Bi(NO₃)₃ · 5H₂O dissolved in concentrated HNO₃ and NaVO₃ were prepared, respectively according to Bi/V molar ratio of 1. Then, cetyltrimethyl ammonium bromide (CTAB) was added to both of the above solutions by the concentration of 9.2×10^{-4} mol/L. After stirring the solutions for 10 min, the solutions were mixed together respectively. During the mixing, the clear solutions would immediately turn to an intensive orange–yellow colour. The pH value was measured as 1. Then, the beaker was placed in the center of a 2,450 MHz microwave oven (Galanz WP 700, 700 W) and was irradiated for 10, 20, 30, 35 and 40 min with power 17% (denoted to sample A, B, C, D and E). After irradiation, the samples were washed by water, filtered, and dried at 350 K for 12 h subsequently, respectively. In a similar way, the BiVO₄ powders were also obtained under microwave irradiation for 10 min with 37% and 40% power

export, respectively. In addition, it was observed that the solution mixtures were boiling after microwave irradiation for 15 min, which proved that the macroscopic temperature of the mixtures kept unchanged at about 100 °C in the further course of microwave treatment. Therefore, in comparison with the microwave method, the sample was also prepared by the traditional heating method that heated at 100 °C for 40 min.

Characterization

The produced phases were identified by X-ray diffraction (XRD, Germany Bruker D8-advance, Cu K α radiation). The UV–vis diffuse reflectance spectroscopy (DRS) studies were conducted by using a UV–vis–NIR spectrophotometer (Shimadzu UV-3101PC). Raman spectroscopy measurements were carried out on a Spex 1403 Raman Spectrometer under backscattering geometry. Excitation was taken as the 488 nm line of Ar⁺ laser. The morphology and particle sizes were determined by Transmission Electron Microscope (TEM, JEOL Ltd. JEM–2010).

Measurements of the photocatalytic properties

The photocatalytic properties of the powders were tested in our house-made instruments. At first, photocatalytic activities of the BiVO₄ powders were evaluated by degradation of N, N, N', N'-tetraethyl-rhodamine (RB) under the visible light irradiation (300 W–Xe). An aqueous BiVO₄ dispersion was prepared by adding 0.5 g BiVO₄ powders with different phases and components into a 100 mL RB solution (2.0×10^{-4} mol dm⁻³), adding aqueous silver nitrate solutions (AgNO₃) (0.05 mol/L) as the load, respectively. The solution was magnetically stirred and irradiated by visible light. During irradiation process for a designated time, the colour of RB solution turned lighter and lighter, and the RB absorption concentration was determined using the 7205 UV–vis spectrometer (Shanghai Xinmao Ltd.).

The photocatalytic O₂ evolution of the BiVO₄ powders was also evaluated under the visible light irradiation (300 W–Xe). An aqueous BiVO₄ dispersion was prepared by adding 0.5 g BiVO₄ powder with different phases and components into 150 mL

AgNO₃ (0.05 mol/L) as the load, respectively. The solution was magnetically stirred and irradiated by visible light. During irradiation for a designated time, the amount of O₂ evolution increased, and the amount of O₂ evolution was determined using GC-14C (SHIMADZU)

Results and discussion

Controlled phase transition

To investigate the formation process of BiVO₄ powders, a detailed time course experiment was carried out with power 17% (120 W). Figure 1 shows the XRD patterns of the as-prepared BiVO₄ powders obtained over different duration of microwave irradiation. It can be seen that the entire observed diffraction peaks for sample A obtained after microwave irradiation for 10 min match with those of tetragonal BiVO₄ (JCPDS card No. 14-0133). No peaks of any other phases or impurities were detected. As the microwave irradiation treatment was prolonged, the peaks corresponding to monoclinic BiVO₄ (JCPDS card No. 14-0688) appeared and became more and more dominant, and the peaks for tetragonal BiVO₄ gradually disappeared (sample B, C and D). After a reaction time of 40 min, all the peaks in the XRD pattern were indexed to pure monoclinic BiVO₄, while the tetragonal BiVO₄ peaks were disappeared completely (sample E). The percentile conversion of tetragonal to monoclinic form on irradiation time has been calculated from the normalized ratios of peak area corresponding to (121) peak of monoclinic BiVO₄ and that of (200) peak for tetragonal form in the manner of, i.e. $\alpha_{\text{mono}} = A_{\text{mono}(121)} / (A_{\text{mono}(121)} + A_{\text{tetra}(200)})$. The relationship between microwave irradiation time, temperature and the calculated fraction of monoclinic phase transformed are shown in Table 1. It was found that the as-synthesized monophasic tetragonal BiVO₄ underwent a phase transition and converted to its monoclinic form over a wide microwave irradiation time from 10 min to 40 min. And longer irradiation of the same sample for 40 min extended the conversion to as much as 100%. From these phenomena, it could be concluded that the precursor first crystallized in the form of tetragonal BiVO₄ powders, then transformed to monoclinic BiVO₄ gradually through

Table 1 Microwave irradiation time and the percentage of monoclinic BiVO₄ at 120 W power

| Sample | A | B | C | D | E |
|----------------------------|----|----|----|----|-----|
| Time (min) | 10 | 20 | 30 | 35 | 40 |
| α_{mono} (%) | 0 | 31 | 63 | 80 | 100 |

microwave irradiation. Further more, the preparative route employed in the present investigation to produce BiVO₄ was found to be sensitive to the reaction time. Therefore, the irradiation time of the microwave-assisted synthesis was clearly an important factor for controlling the phase structure of BiVO₄ powder.

In comparison with other soft chemical synthetic methods (Wienand et al. 1998; Kudo et al. 1999; Bhattacharya et al. 1997; Lim et al. 1995; Roth et al. 1963; Sleight et al. 1979; Liu et al. 2004; Tokunaga et al. 2001), this microwave irradiation method was a rapidly process that synthesized both tetragonal and monoclinic BiVO₄, and could control the phase transition conveniently only by changing the time of synthesis. The processing time was basically much shorter than the corresponding records reported by studies through other different methods (Wienand et al. 1998; Kudo et al. 1999; Bhattacharya et al. 1997; Lim et al. 1995; Roth et al. 1963; Sleight et al. 1979; Liu et al. 2004; Tokunaga et al. 2001). In order to understand the effect of microwave irradiation, a sample was prepared by traditional heating method,

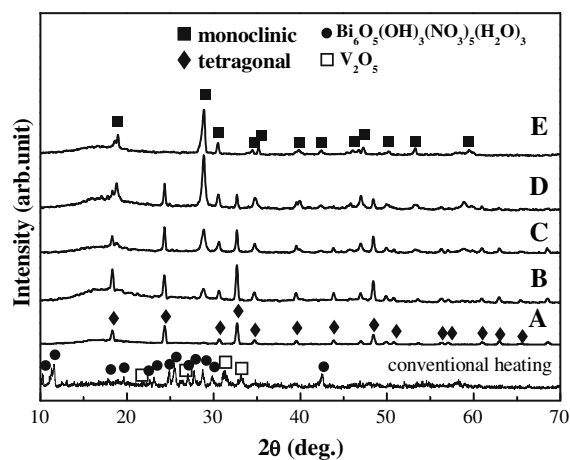


Fig. 1 XRD patterns of the BiVO₄ samples as-prepared by conventional heating method and microwave irradiation at different times (a) 10 min (b) 20 min (c) 30 min (d) 35 min (e) 40 min

which heated at 100 °C for 40 min. As seen from Fig. 1, bismuth oxide hydroxide nitrate hydrate ($\text{Bi}_6\text{O}_5(\text{OH})_3(\text{NO}_3)_5(\text{H}_2\text{O})_3$, JCPDS card No. 70-1226) and vanadium oxide (V_2O_5 , 76-1803) mixtures were obtained by using the traditional heating method. However, the clinobisvanate feature was observed in the XRD pattern for those synthesized by microwave irradiation for 40 min at almost the same temperature as that in the traditional way. In a word, it was proved that the microwave treatment led to acceleration of synthesizing the pure BiVO_4 powders.

Figure 2 shows the XRD patterns of the BiVO_4 powders as-prepared at different microwave irradiation powers. It can be seen that all the diffraction peaks of sample obtained after microwave irradiation for 10 min at 120 W can be indexed to tetragonal BiVO_4 . As microwave irradiation power was enhanced to a higher magnitude, such as 260 W and even higher power, 280 W, the peaks ascribed to monoclinic BiVO_4 can be seen along with the peaks representing tetragonal BiVO_4 . The percentage of monoclinic phase was calculated by the same formula as above. The 9% of monoclinic could be obtained at 260 W, while it would increase to 18% of monoclinic at 280 W under other similar conditions. The ratio of monoclinic phase BiVO_4 is increasing gradually with the powers enhancing. Thus, it would be concluded that the applied microwave powers also do affect the phase structure of BiVO_4 powders synthesized by microwave irradiation except the influence of irradiation time.

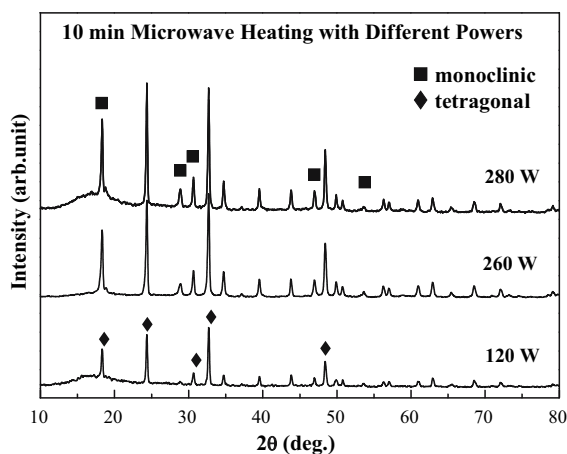


Fig. 2 XRD patterns of the BiVO_4 powders as-prepared at different microwave irradiation powers

Photophysical properties of BiVO_4 samples

The whole UV–vis DRS spectra of BiVO_4 samples prepared for various time are shown in Fig. 3. As can be seen from the figure, the absorption edges of BiVO_4 samples (Samples A–E) somehow varied in an orderly fashion. Different compositions of BiVO_4 powders result in different band gaps. With the phase transition from tetragonal to monoclinic phase, the band gaps tend to shift from UV region to the visible light region. The band gaps of sample A, B, C, D and E were estimated from the absorption edges to be 2.90 eV, 2.77 eV, 2.64 eV, 2.53 eV and 2.4 eV, respectively. These data clearly demonstrate that the electronic structures of BiVO_4 are also changed with the phase transition process which can be controlled by the duration of microwave irradiation.

Raman spectra of BiVO_4 samples

Raman spectroscopy is a useful technique for probing the local structure of materials. Figure 4 shows the Raman spectra over the 100 cm^{-1} – $1,000\text{ cm}^{-1}$ region for the series of BiVO_4 samples list in above in Table 1. For sample A, in accordance with the interpretation of Hardcastle et al. (1991), in the 750 cm^{-1} – $1,000\text{ cm}^{-1}$ region, the Raman spectrum of tetragonal phase BiVO_4 shows two intense bands at 850 cm^{-1} and 770 cm^{-1} , respectively, which separately attributes to the symmetric V–O stretching mode (A_g symmetry) and the antisymmetric V–O

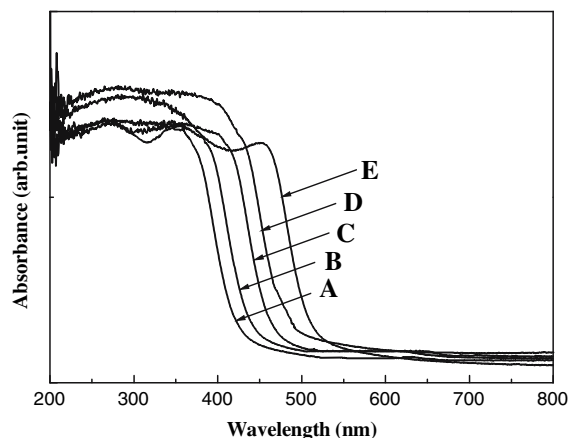


Fig. 3 The whole UV–vis DRS spectra of BiVO_4 sample A, B, C, D and E

stretching mode (B_g symmetry), similarly to the report (Frost et al. 2006). Compared with the Raman spectrum of tetragonal YVO_4 (Sun et al. 2006), that of the tetragonal $BiVO_4$ shows band at 380 cm^{-1} which is attributed to the O–V–O bending mode (A_g). And the band at 245 cm^{-1} can be assigned to the Bi–O stretching mode (E_g). With the increasing percentage of monoclinic phase in $BiVO_4$ powders (sample A–E), the Raman bands shift regularly, due to the different bond structure of V–O and Bi–O in monoclinic and tetragonal phases. During the phase transition process from tetragonal to monoclinic $BiVO_4$ (sample B–E), some Raman bands appear, such as 120 cm^{-1} , 208 cm^{-1} , 330 cm^{-1} , 365 cm^{-1} and 826 cm^{-1} , which are characteristic bands of monoclinic. Meanwhile, the Raman bands of tetragonal phase are weakened gradually. The spectrum of pure monoclinic $BiVO_4$ (sample E) shows a single band at around 826 cm^{-1} that is normally attributed to the symmetric V–O stretching mode (A_g symmetry). And the bands at around 365 cm^{-1} and 333 cm^{-1} are described as the symmetric V–O (A_g) bending mode and antisymmetric V–O (B_g) bending mode of VO_4 units, respectively. The external modes (rotation/translation) occur at 208 cm^{-1} and 120 cm^{-1} . These Raman results provide further evidence that the local structure transition of samples is taken place during the microwave irradiation.

From Fig. 4, it is noticed that the intensity of Raman band of monoclinic at around 826 cm^{-1} is not stronger than that of tetragonal at around 850 cm^{-1} ,

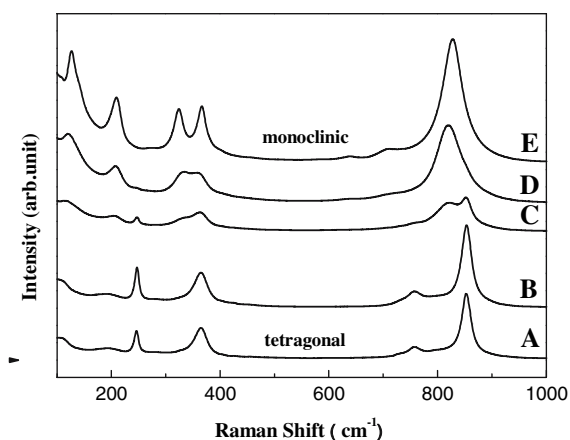


Fig. 4 Raman spectra of $BiVO_4$ sample A (pure tetragonal), B, C, D, and E (pure monoclinic) in the 100 cm^{-1} – $1,000\text{ cm}^{-1}$ region

although the percentage of monoclinic phase in sample C is 63%, which is even more than tetragonal. We can assume that the tetragonal bonds may be more sensitive than monoclinic.

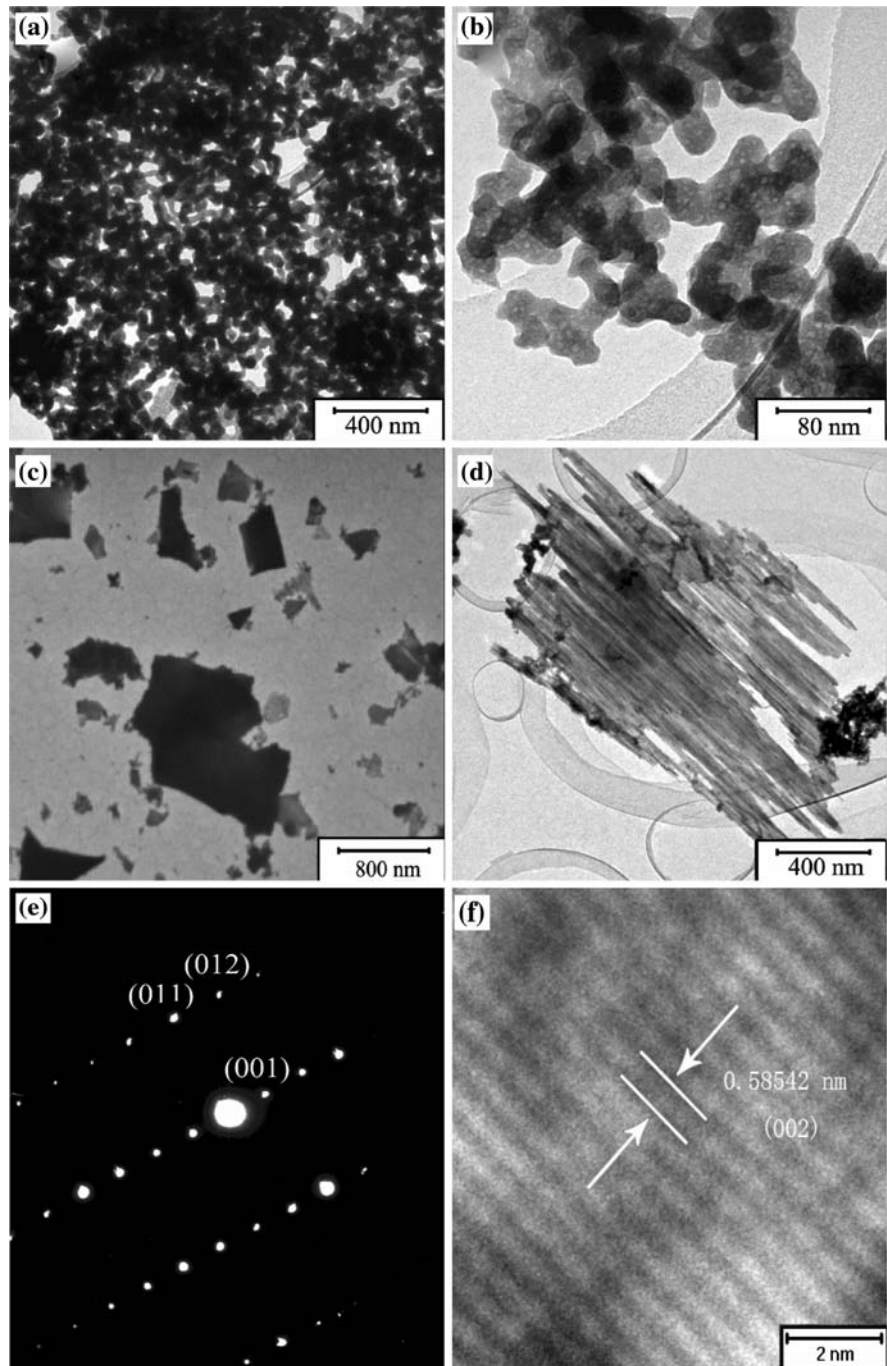
Morphology and microstructure of the $BiVO_4$ samples

The TEM images of pure tetragonal and monoclinic $BiVO_4$ samples prepared by microwave assisted process are shown in Fig. 5. Some significant differences are observed concerning the morphologies and particle sizes of the $BiVO_4$ samples. The pure tetragonal $BiVO_4$ (sample A) particles, synthesized by microwave irradiation for 10 min at 120 W, demonstrate small particle sizes. At low magnification (Fig. 5a), it is observed that the sample processes a large number of polydisperse nanoparticles. Furthermore, at higher magnification (Fig. 5b), each nanoparticle, with diameters of around 10–20 nm is clearly presented in the micrograph.

The monoclinic $BiVO_4$ (sample E), synthesized by microwave irradiation for 40 min at 120W, appears highly crystallized. At low magnification (Fig. 5c), large sheets (about 1–2 μm in size) and some strips are visible. At higher magnification, the nanostrips can be seen in Fig. 5d, normally 10–30 nm wide and 2–3 μm long. Careful observation shows that these nanostrips aggregate compactly together in parallel lines information.

More details about the structure of a nanostrip captured from a monoclinic $BiVO_4$ (sample E) are investigated by the selected-area electron diffraction (SAED) pattern. The corresponding SAED pattern of a single nanostrip (Fig. 5e) shows that the nanostrip is a single crystal of monoclinic $BiVO_4$, as the highly arrayed diffraction spots in the pattern reveal its single-crystalline nature of the monoclinic $BiVO_4$ nanostrips. In addition, Fig. 5f shows the high-resolution transmission electron microscope (HR-TEM) image taken from the nanostrip of the individual monoclinic $BiVO_4$ (sample E) shown in Fig. 5e. The clear lattice fringes are visible, and the regular spacing of the observed lattice interplanar is about 0.58542 nm, which is consistent with the (002) lattice spacing of monoclinic $BiVO_4$, showing that the nanostrip is of a uniform crystal structure.

Fig. 5 TEM images of tetragonal (sample A) and monoclinic (sample E) BiVO_4 . (a) low magnification image of sample A; (b) higher magnification of sample A; (c) low magnification image of sample E; (d) higher magnification of sample E; (e) SAED pattern of sample E; (f) HR-TEM image of sample E



However, the obvious difference in contrast and the defects at the light-colored area can be clearly observed, which might result from an oriented-attachment growth mode of the nanoplates (Kudo et al. 1999).

Photocatalytic properties of BiVO_4 samples

The photocatalytic performance of BiVO_4 powders synthesized by microwave irradiation for various time were examined in terms of the photodegradation

of RB and the photocatalytic O₂ evolution from an aqueous AgNO₃ solution under visible-light irradiation ($k \geq 420$ nm).

Figure 6 shows that the decrease in absorption intensity of RB, which has a strong absorption at 552 nm, by different BiVO₄ catalysts as a function of visible irradiation time. The employed catalysts are BiVO₄ powders heated over various microwave irradiation time, sample A, B, C, D and E, respectively. It is clear that the ratio of photodegradation with BiVO₄ powders is increasing with the increasing content of monoclinic phase. Moreover, compared sample A with sample B, only a few amounts of monoclinic BiVO₄ give great effect on photodegradation RB under visible light irradiation.

The photocatalytic activities of BiVO₄ samples for O₂ evolution under visible light irradiation are shown in Fig. 7. The amounts of O₂ evolution with BiVO₄ powders are increasing with the increasing contents of monoclinic phase. It has the same trend with the photodegradation of RB.

The obvious increase in the photocatalytic activity of BiVO₄ may result in the variation in phase composition and particle size. The absorption band of monoclinic BiVO₄ (sample E) in the visible light region was similar to that of tetragonal BiVO₄ (sample A), but monoclinic BiVO₄ (sample E) showed higher photocatalytic activity than tetragonal

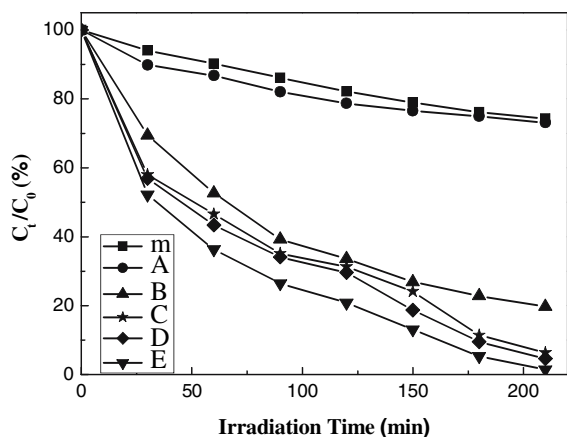


Fig. 6 Photodegradation RB under visible light irradiation with the role of 0.5 g BiVO₄ powders with 0.05 M aqueous AgNO₃ under the same condition. (m) blank experiment, 0.05 M aqueous AgNO₃ without BiVO₄ solution under visible light irradiation; (a) photodegradation RB by sample A with 0.05 M aqueous AgNO₃ solution; (b) sample B; (c) sample C; (d) sample D; (e) sample E

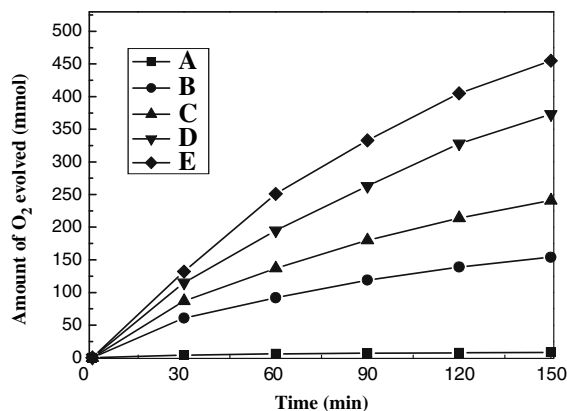


Fig. 7 Photocatalytic O₂ evolution from AgNO₃ solutions (0.05 mol/L, 150 mL) under visible light irradiation ($\lambda > 420$ nm) on sample A, B, C, D and E, respectively

BiVO₄. It is assumed that the high activity of monoclinic BiVO₄ is probably due to the distortion of the Bi–O polyhedron (Tokunaga 2001), because the major difference in photocatalytic properties between monoclinic BiVO₄ and tetragonal is only the distortion (Kudo et al. 1999). The distortion is attributed to 6s² lone pairs of Bi³⁺, whose effects have been reported for some bismuth oxide compounds (Jakubowicz 1998; Giraud 1999). It is supposed that the difference in the distortion leads to the different properties. In the present researches, it was found that the photocatalytic activity would also change because of the variations of monoclinic and tetragonal phases, which was also reported by Kudo and so on (Kudo et al. 1999).

Conclusion

To sum up, the phase transition from tetragonal to monoclinic BiVO₄ can be easily controlled by microwave irradiation method. With the time of microwave irradiation prolonging, the tetragonal phase transformed into monoclinic phase gradually. The XRD, Raman, TEM and UV–vis spectroscopic characterizations reveals that not only the macrostructure, such as the morphology, surface texture, and grain shape, but also the local structure of the synthesized BiVO₄ materials was significantly dependent on the microwave irradiation time and power.

The photocatalytic properties strongly depend on the phases and crystal forms. The photodegradation

RB activity and the photocatalytic O₂ evolution of monoclinic BiVO₄ are much higher than that of tetragonal under visible light irradiation, because of their internal structure, such as band gap, the 6s² lone pair of Bi³⁺, and so on.

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