Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 38 (2012) 4827–4834
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

An EDTA-assisted hydrothermal synthesis of $BiVO_4$ hollow microspheres and their evolution into nanocages

Zhenfeng Zhu *, Juan Du, Junqi Li, Yanli Zhang, Dianguang Liu

School of Materials Science and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, PR China

Received 16 December 2011; received in revised form 23 February 2012; accepted 24 February 2012
Available online 20 March 2012

Abstract

$BiVO_4$ hollow microspheres have been synthesized in the presence of ethylenediaminetetraacetic acid (EDTA) by a microwave hydrothermal method. The as-prepared hollow microspheres were composed of hundreds of nanorods. Increasing the amount of EDTA produced a new nanocage structure. The evolution process of $BiVO_4$ with different microstructures indicated that the amount of EDTA added played a crucial role in determining the shape of the samples. Additionally, it was found that the existence of EDTA was vital to mediate the crystal growth, and the hydrothermal time and temperature were key parameters in determining the $BiVO_4$ morphologies. A possible formation mechanism is proposed.

Keywords: A. Powders: Chemical preparation; $BiVO_4$; Microwave hydrothermal synthesis

1. Introduction

Bismuth vanadate ($BiVO_4$), a non-titania based photocatalyst, has attracted increasing attention due to its narrow band gap and effective photocatalytic activities for water splitting [1–3] and pollutant decomposing [4–8] under visible-light irradiation. Recently, interest in developing morphologically controllable synthesis of $BiVO_4$ microstructures has been aroused by the recent success in the fabrication of various morphologies, such as nanosheets [7], microtubes [9], dendrites [4,10], and pyramidal-shaped nanowire arrays [11]. As the material's properties hugely depend on its morphology [9,10,12–16], it is of great importance to develop methods for controllable synthesis of desired structures of $BiVO_4$. Until now, various methods have been utilized to prepare $BiVO_4$, among which an additive-assisted solution method has been widely accepted as the most cost-effective and convenient way to prepare some novel morphologies.

Ethylenediamine tetraacetic (EDTA), a chelating agent and surfactant, has been used to synthesize various $BiVO_4$ morphologies. Sun et al. [17] reported that nanoplate-stacked starlike $BiVO_4$ was prepared by a hydrothermal method, using water/ethanol mixture as the solvent and EDTA as a chelating agent. Neves et al. [18] reported that $BiVO_4$ microrectangles were grown on glass substrates via a chemical bath deposition method, in which Bi^{3+} could coordinate with EDTA to form complex $[Bi(EDTA)^{-}]$, avoiding spontaneous precipitation. Therefore, EDTA has great influences on the formation of these unique morphologies.

Herein, hollow microspheres and nanocages self-assembled from $BiVO_4$ nanorods were successfully synthesized by a microwave hydrothermal method, in which EDTA was the chelating agent and assembly reagent. The key to the controllable synthesis was the use of EDTA to mediate the crystal growth, and the morphology evolution was investigated by tailoring the amount of EDTA added. Through time-dependent and temperature-dependent experiments, a possible growth mechanism for the $BiVO_4$ microspheres and nanocages was explored in detail.

2. Experimental

2.1. Preparation of $BiVO_4$ hollow microspheres

For the preparation of hollow spherical $BiVO_4$, a typical experiment was as follows: aqueous solutions of $Bi(NO_3)_3{\cdot}5H_2O$ (5 mmol) and NH_4VO_3 (5 mmol) in 1:1 molar

* Corresponding author. Tel.: +86 29 86168331; fax: +86 29 86177108.
E-mail addresses: zhuzf@sust.edu.cn, nmlab@sust.edu.cn (Z. Zhu).

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2012.02.071

ratio were mixed together to get the yellow suspensions. After being stirred for 30 min, and then left to stand, the supernatant was removed. Subsequently, 30 mL H_2O and 1.0 g EDTA were added into the above yellow precipitates and stirred with a magnetic bar for about 30 min. The microwave hydrothermal growth was carried out at 180 °C for 3 h in a 100 mL Teflon-lined autoclave. The equipment that we used to run is MDS-8 closed vessel microwave chemistry workstation. It is manufactured by Shanghai Sineo Microwave Chemistry Technology (China) Co., Ltd. and we mainly use it for microwave digestion. This workstation is suitable for supporting high-strength frame closed reaction vessel with 10 rotors. The temperature and pressure are controlled by high-precision resistance temperature sensor and piezoelectric crystal pressure sensor. After cooling down to room temperature, the samples were taken out and washed with de-ionized water and absolute ethanol several times, and then were dried in vacuum at 60 °C for 12 h.

To confirm the effect of the addition of EDTA on the formation of the structure of $BiVO_4$, the addition of EDTA was varied to 1.5 g and 2.0 g: these produced $BiVO_4$ nanocages. In addition, a comparative experiment without surfactant was also carried out. In order to reveal the formation process and the

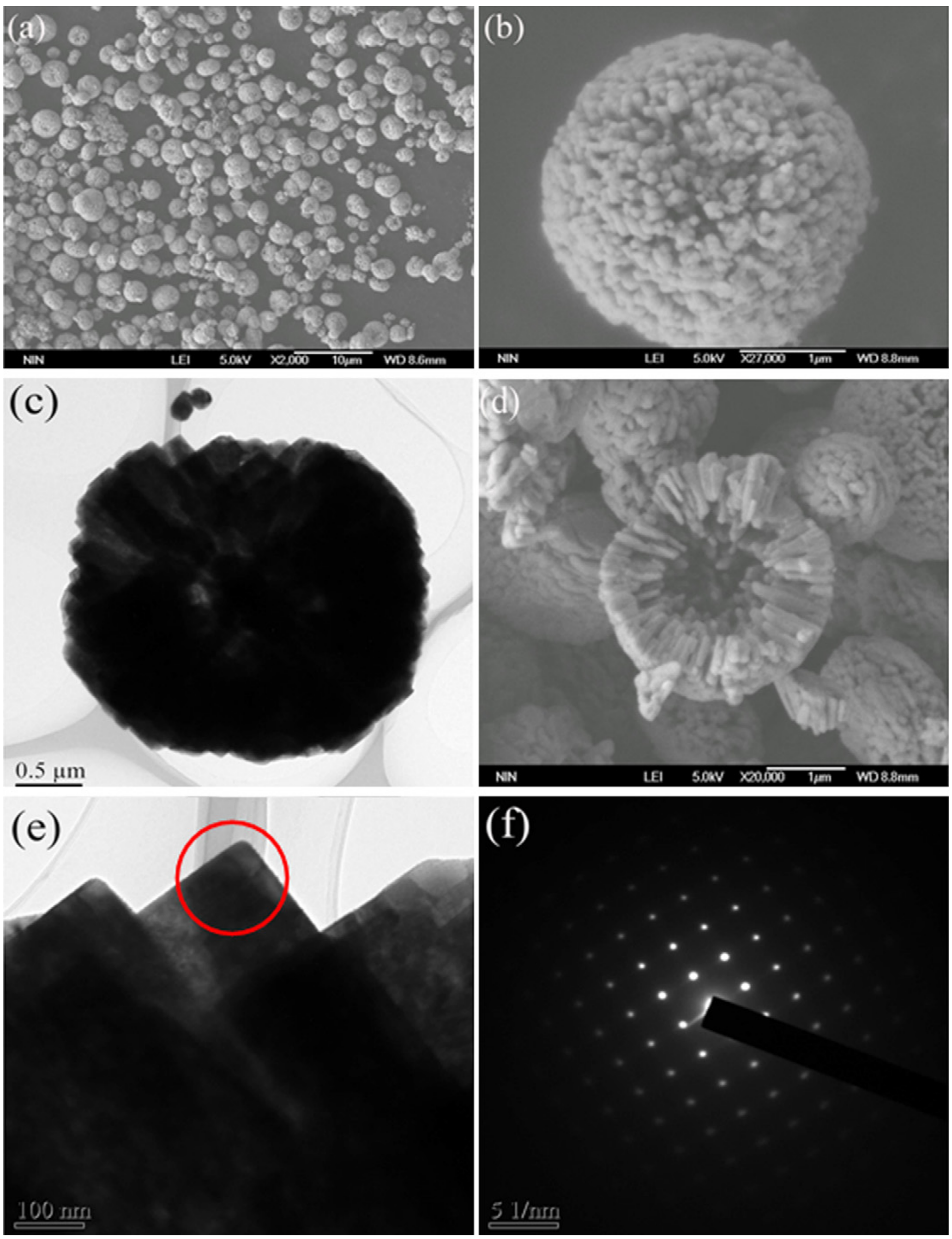


Fig. 1. FE-SEM images of $BiVO_4$ hollow microspheres obtained by the microwave hydrothermal treatment for 3 h at 180 °C with the addition of 1.0 g of EDTA: (a) low-magnification product morphology; (b) detailed view of an individual sphere; (c) high-magnification TEM image of an individual sphere; (d) one cracked sphere, showing the hollow interior structure; (e) HRTEM images of a hollow microsphere; (f) SAED pattern of the marked region.

growth mechanism of these special structures, the time-dependent and temperature-dependent experiments were carried out.

2.2. Characterization

X-ray powder diffraction (XRD) was carried out with a Japan Rigaku D/max 2200 X-ray diffractometer using a high-intensity Cu Kα radiation ($\lambda = 0.154$ nm). Field-emission scanning electron microscopy (FE-SEM, JSM-6700F) was applied to examine the morphology. The microstructure of the sample was investigated by transmission electron microscopy (TEM, JEM-3010) with an acceleration voltage 200 kV. Absorption spectrum was measured on a UV–vis spectrophotometer (UV-2550) in the wavelength range of 250–800 nm.

3. Results and discussion

3.1. Morphology and crystal phase of $BiVO_4$ hollow microspheres

The morphology and microstructures of the obtained $BiVO_4$ hollow microspheres were investigated by field-emission scanning electron microscopy (FE-SEM), as shown in Fig. 1. Fig. 1a exhibits a low-magnification FE-SEM image of $BiVO_4$ hollow microspheres derived from 180 °C and 3 h microwave hydrothermal process, and shows that an EDTA-mediated synthetic method can lead to well dispersed $BiVO_4$ microspheres. It also displays that the diameter of the microspheres ranged from 1 μm to 4 μm. Fig. 1b is the magnified image of an individual microsphere, revealing that the microspheres were composed of assembled nanorods, which were grown in high density with the addition of 1.0 g of EDTA. TEM image of a random sphere is shown in Fig. 1c. In addition, one partially broken or cracked sphere further indicated that there was a hollow interior structure, as presented in Fig. 1d. Close observation shows that the hollow microspheres were hierarchically assembled from hundreds of rods with lengths in the range of 0.3–1 μm, and diameters of about 80–150 nm. Similar hollow spheres have been reported with titania in some previous work. Komarneni et al. reported that hollow TiO_2 spheres were prepared by microwave-hydrothermal process [19,20] or sol–gel combined with microwave technology [21].

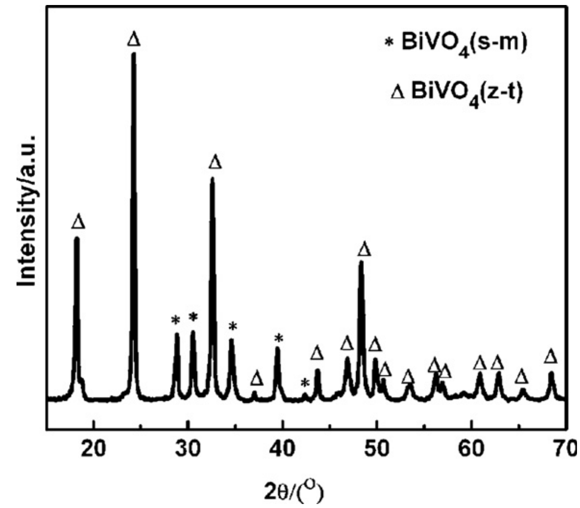


Fig. 2. XRD pattern of the as-prepared $BiVO_4$ hollow microspheres obtained by the microwave hydrothermal process.

An X-ray diffraction pattern of the as-prepared $BiVO_4$ microspheres is presented in Fig. 2, and the diffraction peaks can be indexed to the mixed crystal consisting of tetragonal and monoclinic phases. For the hollow microspheres, the corresponding selected area electron diffraction (SAED) pattern taken from the remarked area in Fig. 1e revealed the single-crystalline nature of the rod, as depicted in Fig. 1f.

3.2. Variation of $BiVO_4$ morphologies with EDTA addition

In order to investigate the contribution of EDTA to the growth of rod-assembled microspheres, a controllable experiment without EDTA was carried out while the other conditions remained unchanged. Fig. 3 presents the FE-SEM images of the $BiVO_4$ obtained by the microwave hydrothermal treatment without EDTA. The $BiVO_4$ samples possessed well dispersed spheres with diameters of 1–4 μm, which were shaped by self-assembled nanoparticles with the size of 100–200 nm, as seen

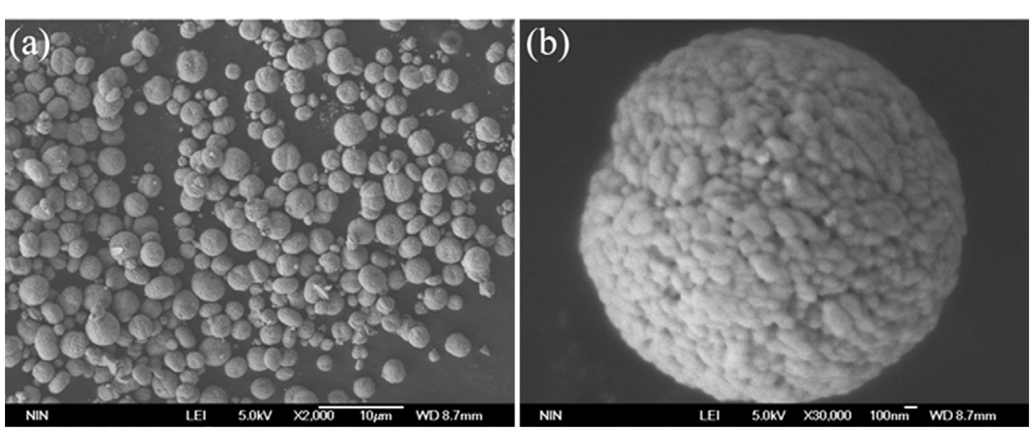


Fig. 3. FE-SEM images of $BiVO_4$ microspheres obtained by the microwave hydrothermal treatment for 3 h at 180 °C without EDTA: (a) overall view of the microspheres; (b) a magnified image of the $BiVO_4$ microspheres, while other conditions were kept the same.

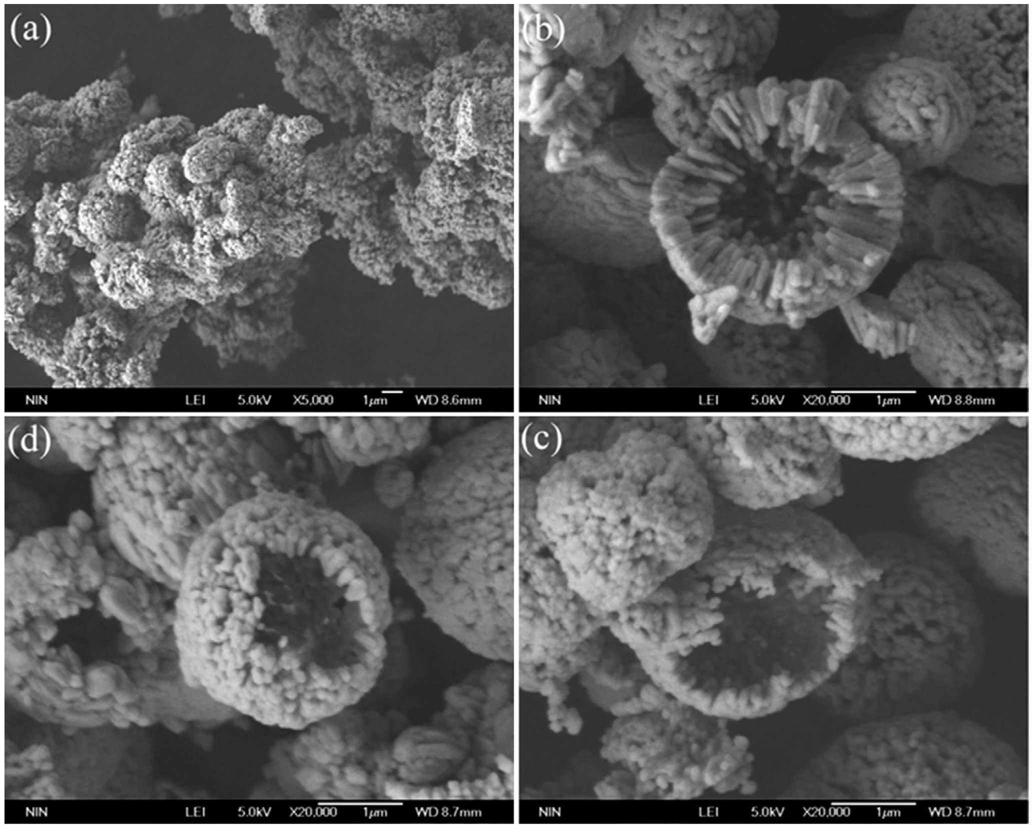


Fig. 4. FE-SEM images of $BiVO_4$ hollow microspheres obtained by the microwave hydrothermal process with the addition of EDTA: (a) 0.5 g; (b) 1.0 g; (c) 1.5 g; (d) 2.0 g while other conditions kept unchanged.

from Fig. 3a and b. By comparison, the presence of EDTA brought significant improvements in the microstructures. Therefore, more systematical experiments were carried out below in order to further investigate the influences of EDTA on the growth of the $BiVO_4$ hollow microspheres.

To investigate the effect of the amount of EDTA on the morphology, experiments involving different amounts of EDTA were carried out. Fig. 4 shows the results with different addition of EDTA while other experimental conditions were kept the same. As seen from Figs. 1a and 4b, relatively well dispersed $BiVO_4$ microspheres could be obtained when the addition of EDTA was 1.0 g. However, when the addition of EDTA was 0.5 g, no $BiVO_4$ microspheres were obtained, but loosely aggregated $BiVO_4$ particles appeared. In addition to the shapeless ones, a few aggregates exhibited a premature morphology as sphere structure (Fig. 4a). When the amount of EDTA was 1.0 g (Fig. 4b), hollow spherical structure formed as explained above. With the addition of 1.5 g EDTA, it was found that the hollow structure of the microspheres was more obvious, forming a nanocage structure built by nanorods. The size of the spheres was nearly the same but the length and the diameter of the rods decreased (~200–340 nm and ~70–80 nm respectively), as shown in Fig. 4c. A further increase to 2.0 g, shown in Fig. 4d, produced a similar nanocage structure to what was shown in Fig. 4c, but the subunits (nanorods) increased in diameter. The results indicated that $BiVO_4$ with different microstructures can be selectively synthesized by simply changing the amount of EDTA.

3.3. UV–vis diffuse reflectance spectra of different $BiVO_4$ samples

The UV–vis diffuse reflectance spectra of different $BiVO_4$ samples obtained by the microwave hydrothermal process (the amount of EDTA: (a) 0.5 g, (b) 1.0 g, (c) 1.5 g, (d) 2.0 g) are displayed in Fig. 5. The absorption edges of different $BiVO_4$ samples ranged from 525 nm to 435 nm with the increase of

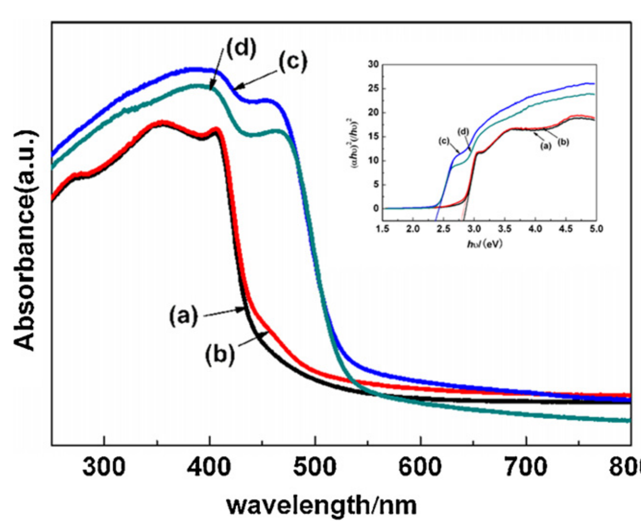


Fig. 5. UV–vis diffuse reflectance spectra of the $BiVO_4$ samples synthesized by the microwave hydrothermal treatment for 3 h at 180 °C by adding different amounts of EDTA: (a) 0.5 g; (b) 1.0 g; (c) 1.5 g; (d) 2.0 g.

EDTA addition. As a crystalline semiconductor, the optical absorption near the band edge is based on the equation $\alpha h\upsilon = A(h\upsilon - E_g)^{n/2}$ [22]. For $BiVO_4$, the value of n is one. From the curve of the $(\alpha h\upsilon)^2$ vs. photon energy ($h\upsilon$), the band gaps of the samples were estimated to be 2.5 eV, 2.84 eV, 2.94 eV and 3.0 eV, corresponding to the sample (a), (b), (c) and (d), respectively. The blue shift in the band gap transition occurs, that is, the band gaps become bigger with the increase of adding amount of EDTA. Such differences could be attributed to changes of crystalline phase, crystal structure, and so on.

3.4. Investigation on the growth mechanism of well dispersed $BiVO_4$ rod-assembled microspheres

In order to understand the growth mechanism of the hollow sphere and nanocage, a careful time-dependent experiment was carried out. And the morphology evolutions of the $BiVO_4$ samples obtained at different microwave hydrothermal time, with the addition of 1.0 g of EDTA, are shown in Fig. 6. The FE-SEM observation of the sample microwave-hydrothermal treated for 0 min revealed that spherical $BiVO_4$ assembly of nanoparticles existed (Fig. 6a). When the hydrothermal time was 5 min, the high-magnification image (Fig. 6b and c) showed that $BiVO_4$ hollow microspheres self-assembled from nanorods formed. As the growth time was prolonged to 10 min (Fig. 6d), the structures of hollow microspheres tended to improve. Subsequently, with the increase of the reaction time (Fig. 6e–g), the subunits (rods) of the hollow spheres grew to form thicker rods. At last, extending the growth time to 3 h (Fig. 6h), the typical $BiVO_4$ hollow microspheres with better crystal quality were formed perfectly. The self-assembled nanorods with length in the range of 0.3–1 μm, and diameter of about 80–150 nm could be observed. Interestingly, with further increase to 1.5 g EDTA, the hollow microspheres evolved into nanocage structure assembled by shorter rods. After adding 2.0 g EDTA, it was clearly seen that the nanocage architecture further developed. The results indicate that evolution of these morphologies is relevant to the amount of EDTA. It is only 5 min that rod-assembled spheres have shaped, indicating that the transition of particles to rods is done instantly. So series of

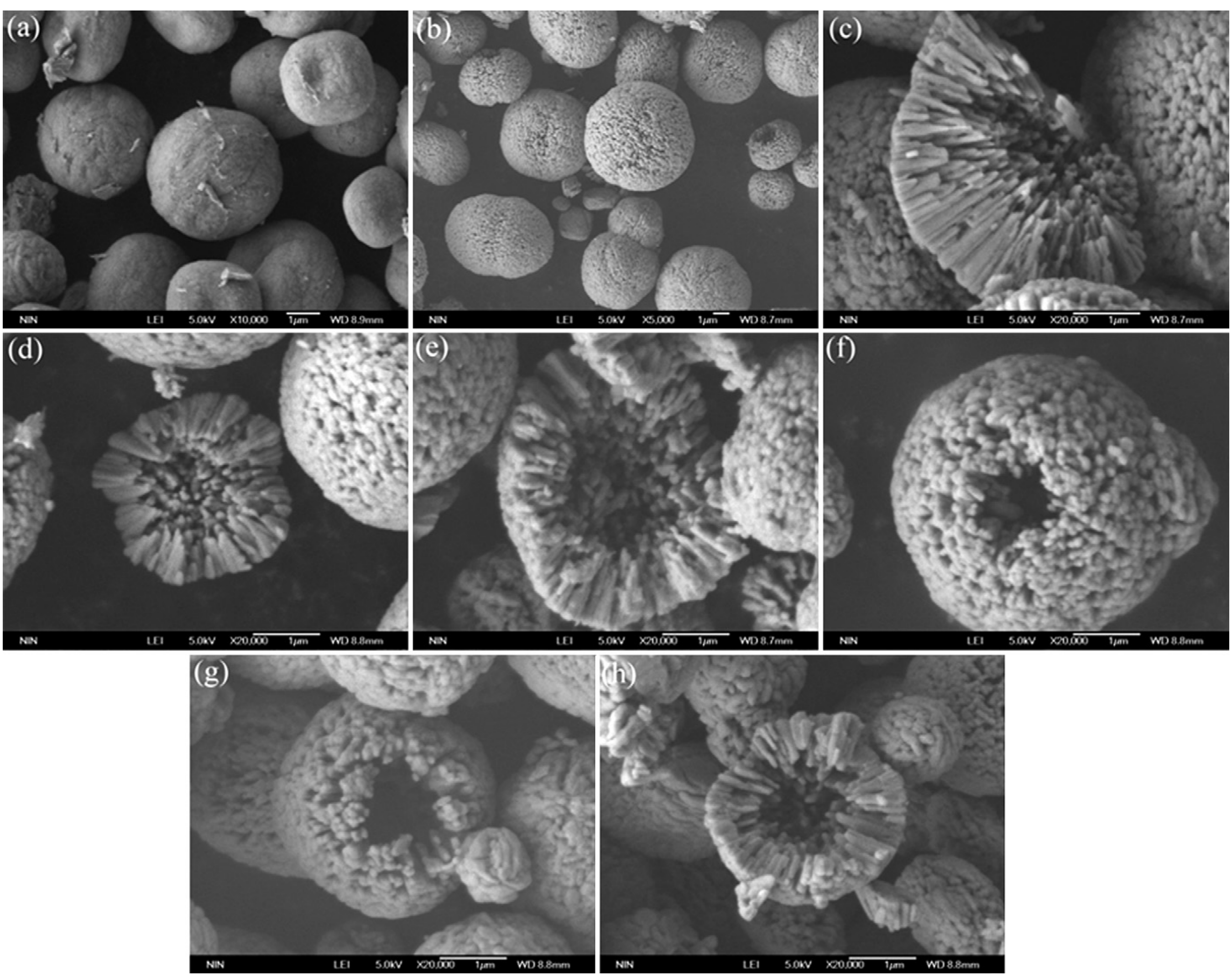


Fig. 6. FE-SEM images of $BiVO_4$ samples obtained at different microwave hydrothermal time: (a) 0 min; (b and c) 5 min; (d) 10 min; (e) 20 min; (f) 1.5 h; (g) 2.0 h; (h) 3.0 h with the addition of 1.0 g of EDTA.

time-experiments may not fully explain the formation of such hollow microspheres, it is necessary to investigate the effect of hydrothermal temperature on the morphology of the samples.

A series of temperature-dependent experiments were carried out by varying the microwave hydrothermal temperature from 80 °C to 180 °C, as shown in Fig. 7. Well-dispersed microspheres with diameters from 1 to 4 μm were obtained when the hydrothermal temperature was 80 °C (Fig. 7a). From the enlarged FE-SEM image (Fig. 7b), it was found that the subunits of the spheres were vaguely rodlike crystals. When the reaction temperature was varied from 100 °C to 160 °C (Fig. 7c–f), the vague rods gradually converted to crystallize in well formed crystal structures. During the hydrothermal treatment at relatively low temperature (e.g., 80–160 °C), the premature morphology of rodlike structures tended to be perfect. Once the hydrothermal temperature increased to 180 °C (Fig. 1d), hollow microspheres with better rods' quality perfectly formed due to the thermodynamic factor. Therefore, hydrothermal temperature is of great importance in forming the hollow microspheres assembled by fine crystalline rods.

As seen from the controllable experiments, the reaction time and hydrothermal temperature are also the key parameters in determining the $BiVO_4$ morphologies. In addition, during the hydrothermal process, EDTA is vital to the formation of hollow rod-assembled microspheres, and the probable formation mechanism of the hollow microspheres structure may be ascribed to a dissolution–recrystallization process through Ostwald ripening [23,24] under the microwave hydrothermal

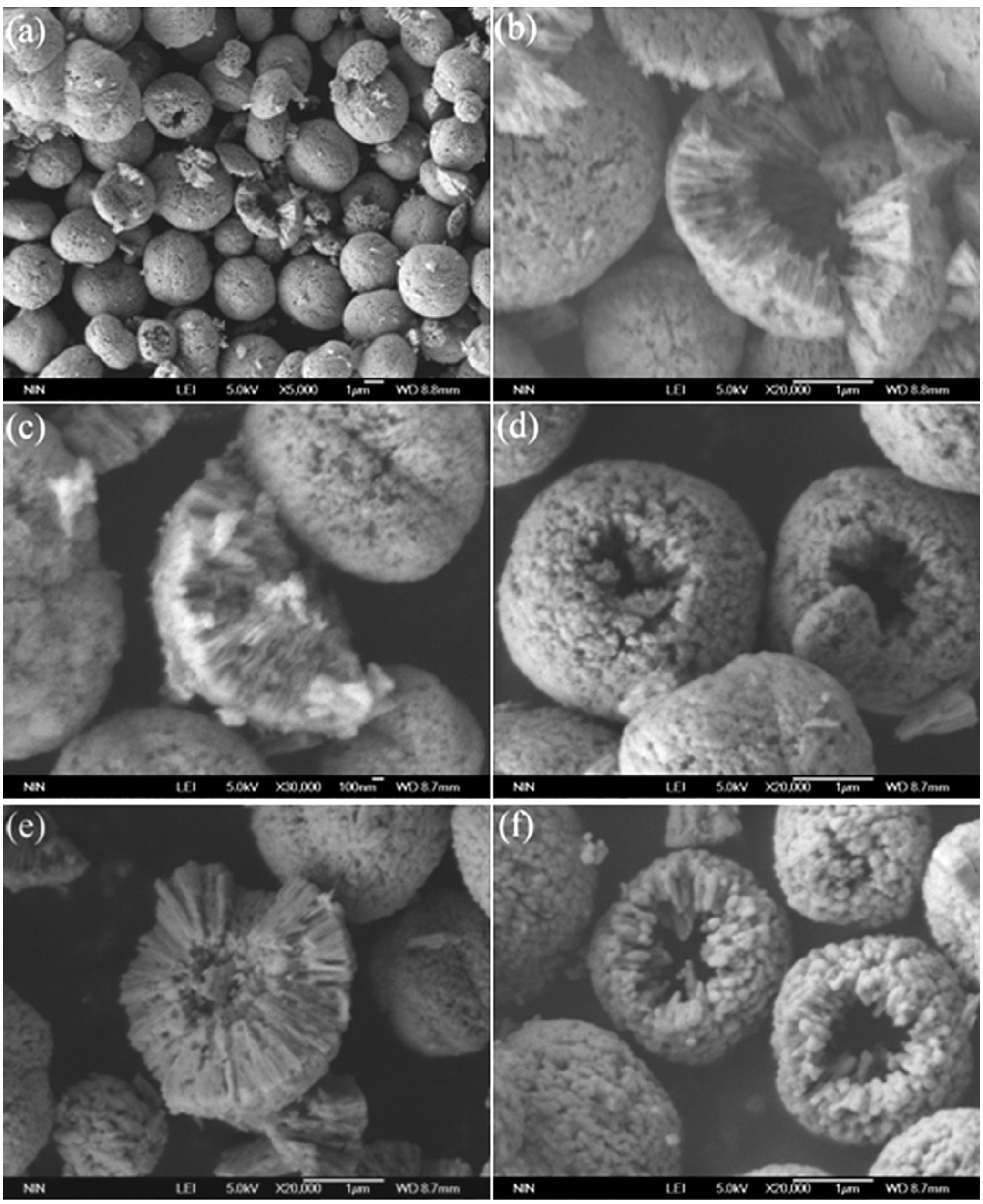
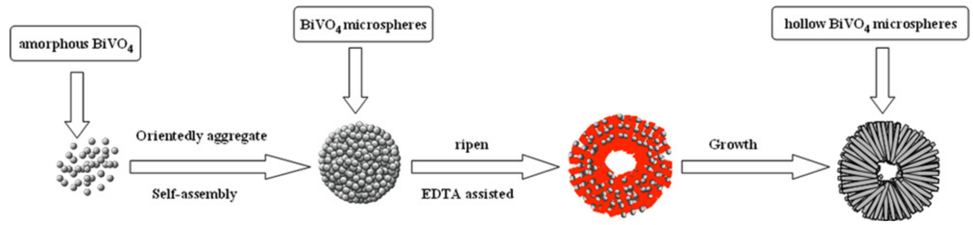


Fig. 7. FE-SEM images of $BiVO_4$ samples obtained at different microwave hydrothermal temperature: (a and b) 80 °C; (c) 100 °C; (d) 120 °C; (e) 140 °C; (f) 160 °C with the addition of 1.0 g of EDTA.



Scheme 1. The formation mechanism of hollow $BiVO_4$ microspheres.

conditions. In this process, large crystallites grow at the expense of small ones' dissolving, diffusing, and recrystallizing. Before the hydrothermal process, the tiny particles tend to aggregate and finally crystallize into spherical $BiVO_4$ structures. However, during the continuous microwave hydrothermal process, these tiny particles could dissolve and regrow to rod-assembled spheres through Ostwald ripening process. Usually, as a sphere composed of numerous particles, the inner crystallites can be visualized as smaller spheres because of their higher curvature. Thus, they can easily dissolve and diffuse to the outer surface owing to their higher surface energies, and finally result in the formation of hollow interior structures. In our case, EDTA is usually considered as an excellent chelating agent that slows down the nucleation rate and prevents further aggregation of the particles [25,26]. As a consequence, during the diffusion process of the inner particles, the tiny particles could regrow to rod structures gradually due to the effect of EDTA. The schematic illustration for the formation of hollow microspheres is shown in Scheme 1.

4. Conclusions

In conclusions, $BiVO_4$ hollow microspheres and nanocages have been synthesized by a microwave hydrothermal process. EDTA is found to play a crucial role in the formation of $BiVO_4$ hollow microspheres and nanocages assembled by hundreds of nanorods. As-obtained hollow microspheres construct from the assembly of rods with the length in the range of 0.3–1 μm and diameter of about 80–150 nm. A possible morphological evolution mechanism for the formation of these special structures from hollow spherical structure to nanocage structure has been proposed. Ostwald ripening process is responsible for the formation of the hollow microsphere. With further increase of EDTA addition, hollow microspheres can evolve into new nanocage structure. The controllable experiments also imply that the hydrothermal time and temperature are the key parameters in determining $BiVO_4$ morphologies. Moreover, the results of UV–vis diffuse reflectance spectra indicate that the blue shift occurs with the increase of adding amount of EDTA.

Acknowledgments

This work was financially supported by the China Postdoctoral Science Foundation Founded Project (Nos. 20080440185 and 200902584), the Special Found from Shaanxi Provincial Department of Education (09JK355), and the Postgraduate Innovation Fund of Shaanxi University of Science and Technology.

References

[1] K. Sayama, A. Nomura, T. Arai, et al., 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) 11352–11360.
[2] 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) 4624–4628.
[3] 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) 11459–11467.
[4] X. Zhang, Z.H. Ai, F.L. Jia, et al., Selective synthesis and visible-light photocatalytic activities of $BiVO_4$ with different crystalline phases, Mater. Chem. Phys. 103 (2007) 162–167.
[5] W.Z. Yin, W.Z. Wang, L. Zhou, et al., CTAB-assisted synthesis of monoclinic $BiVO_4$ photocatalyst and its highly efficient degradation of organic dye under visible-light irradiation, J. Hazard. Mater. 173 (2010) 194–199.
[6] H.Q. Jiang, H. Endo, H. Natori, et al., Fabrication and photoactivities of spherical-shaped $BiVO_4$ photocatalysts through solution combustion synthesis method, J. Eur. Ceram. Soc. 28 (2008) 2955–2962.
[7] 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) 2668–2673.
[8] L. Zhou, W. Wang, S. Liu, et al., A sonochemical route to visible-light-driven high-activity $BiVO_4$ photocatalyst, J. Mol. Catal. A: Chem. 252 (2006) 120–124.
[9] L. Zhou, W.Z. Wang, L.S. Zhang, et al., Single-crystalline $BiVO_4$ microtubes with square cross-sections: microstructure, growth mechanism, and photocatalytic property, J. Phys. Chem. C 111 (2007) 13659–13664.
[10] L. Zhou, W.Z. Wang, H.L. Xu, Controllable synthesis of three-dimensional well-defined $BiVO_4$ mesocrystals via a facile additive-free aqueous strategy, Cryst. Growth Des. 8 (2008) 728–733.
[11] J.Z. Su, L.J. Guo, S. Yoriya, et al., Aqueous growth of pyramidal-shaped $BiVO_4$ nanowire arrays and structural characterization: application to photoelectrochemical water splitting, Cryst. Growth Des. 10 (2010) 856–861.
[12] T. Yang, D.G. Xia, G. Chen, Y. Chen, Influence of the surfactant and temperature on the morphology and physico-chemical properties of hydrothermally synthesized composite oxide $BiVO_4$, Mater. Chem. Phys. 114 (2009) 69–72.
[13] H.B. Li, G.C. Liu, X.C. Duan, Monoclinic $BiVO_4$ with regular morphologies: hydrothermal synthesis, characterization and photocatalytic properties, Mater. Chem. Phys. 115 (2009) 9–13.
[14] S.S. Dunkle, R.J. Helmich, K.S. Suslick, $BiVO_4$ as a visible-light photocatalyst prepared by ultrasonic spray pyrolysis, J. Phys. Chem. C 113 (2009) 11980–11983.
[15] F.X. Wang, M.W. Shao, L. Cheng, et al., The synthesis of monoclinic bismuth vanadate nanoribbons and studies of photoconductive, photoresponse, and photocatalytic properties, Mater. Res. Bull. 44 (2009) 1687–1691.

[16] W. Liu, L.X. Cao, G. Su, et al., Ultrasound assisted synthesis of monoclinic structured spindle $BiVO_4$ particles with hollow structure and its photocatalytic property, Ultrason. Sonochem. 17 (2010) 669–674.
[17] S.M. Sun, W.Z. Wang, L. Zhou, H.L. Xu, Efficient methylene blue removal over hydrothermally synthesized starlike $BiVO_4$, Ind. Eng. Chem. Res. 48 (2009) 1735–1739.
[18] M.C. Neves, T. Trindade, Chemical bath deposition of $BiVO_4$, Thin Solid Films 406 (2002) 93–97.
[19] S. Komarneni, R. Roy, Q.H. Li, Microwave-hydrothermal synthesis of ceramic powders, Mater. Res. Bull. 27 (1992) 1393–1405.
[20] S. Komarneni, R.K. Rajha, H. Katsuki, Microwave-hydrothermal processing of titanium dioxide, Mater. Chem. Phys. 61 (1999) 50–54.
[21] S. Komarneni, R. Roy, Titania gel spheres by a new sol–gel process, Mater. Lett. 3 (1985) 165–167.
[22] M.A. Butler, Photoelectrolysis and physical properties of the semiconducting electrode WO_2, J. Appl. Phys. 48 (1977) 1914–1920.
[23] L. Zhou, W.Z. Wang, H.L. Xu, S.M. Sun, Template-free fabrication of $CdMoO_4$ hollow spheres and their morphology-dependent photocatalytic property, Cryst. Growth Des. 8 (2008) 3595–3601.
[24] X.F. Qu, Q.Z. Yao, G.T. Zhou, et al., Formation of hollow magnetite microspheres and their evolution into durian-like architectures, J. Phys. Chem. C 114 (2010) 8734–8740.
[25] F. Luo, C.J. Jia, W. Song, et al., Chelating ligand-mediated crystal growth of cerium orthovanadate, Cryst. Growth Des. 5 (2005) 137–142.
[26] Z.H. Xu, X.J. Kang, C.X. Li, et al., Ln^{3+} (Ln = Eu, Dy, Sm, and Er) ion-doped YVO_4 nano/microcrystals with multiform morphologies: hydrothermal synthesis, growing mechanism, and luminescent properties, Inorg. Chem. 49 (2010) 6706–6715.