Photocatalytic Activity of Hierarchically Nanoporous $BiVO_4/TiO_2$ Hollow Microspheres

Yang Zhou^a, Guohua Jiang^{a,b,*}, Rijing Wang^{a,b}, Xiaohong Wang^{a,b} Ruanbing Hu^{a,b}, Xiaoguang Xi^{a,b}

^aDepartment of Materials Engineering, College of Materials and Textile, Zhejiang Sci-Tech University Hangzhou 310018, China

^bKey Laboratory of Advanced Textile Materials and Manufacturing Technology (ATMT), Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China

Abstract

The hollow microspheres containing monoclinic scheelite BiVO₄ and anatase TiO₂ nanocrystals were easily prepared through a simple one-step template-free method. Bi(NO₃)₃·5H₂O and NH₄VO₃ were used as BiVO₄ precursor and (NH₄)₂TiF₆ as TiO₂ precursor to produce the target products in the presence of glucose under the high temperature pyrolysis. The products were characterized with SEM, XRD, TEM and UV-vis DRS. The as-prepared hollow microspheres showed high photocatalytic activity, which was demonstrated by degradation of acetic acid solution under visible-light irradiation ($\lambda > 420$ nm).

Keywords: Semiconductors; Photocatalytic Property; Hierarchically Structure; Hollow Microspheres

1 Introduction

TiO₂ is a very important multifunctional material because of its peculiar and fascinating physicochemical properties, and its wide variety of potential uses in diverse fields such as solar energy conversion, environmental purification, water treatment and antibacterial materials [1-4]. However, the large band gap of pure TiO₂ (E_g =3.0 eV for rutile, E_g =3.2 eV for anatase) limits its application as the electron-hole pairs can only be formed by UV light at wavelength shorter than 387 nm [5, 6]. Thus, only a small portion of the solar spectrum can be utilized for photo-oxidation reaction under the presence of TiO₂. The development of a general method for endowing TiO₂ with visible-light response and concomitantly increasing their UV-light activity should dramatically expand their viability [7-9]. To this end, doping of various transition metals and anions has been extensively studied [9-12]. Amongst different studies of oxides with activity under visiblelight irradiation, BiVO₄ has received special attention [13]. BiVO₄ crystallizes in three different polymorphs, i.e. tetragonal zircon, monoclinic distorted scheelite and tetragonal scheelite. Due to

^{*}Corresponding author.

Email address: polymer_jiang@hotmail.com (Guohua Jiang).

its relatively narrow band gap ($\sim 2.4 \text{ eV}$), the monoclinic form exhibits the higher photocatalytic activity for chemical reactions induced with visible-light irradiation [14, 15].

On the other hand, there has been considerable interest in the synthesis of micrometer and nanometer sized hollow spheres because of their widespread potential applications in catalysis, drug delivery, chromatography separation, chemical reactors, controlled release of various substances, and protection of environmentally sensitive biological molecules [16, 17]. Several micrometer and nanometer sized hollow spheres of transition metal oxides have been prepared due to researchers' unremitting effort using soft templating methods [18, 19] and mesoporous silica as hard template [20, 21]. However, such methods have disadvantages. Soft templating methods usually lead to the formation of mesoporous structure with amorphous walls, while the hard templating methods usually involve multistep processes and sometimes lead to the damage of pore structures during the removal of hard templates [22-24].

Monodisperse nanocrystals display novel properties which stimulated intensive research on the synthesis of monodisperse nanocrystals for their fundamental and technological importance [25, 26]. However, there are still problems with obtaining the mesoporous structure with monodisperse microspheres for the enhancement of the structural stability and photocatalytic property of BiVO₄ and TiO₂. With this in mind, we proposed one-step hydrothermal and pyrolysis treatment for the preparation of hierarchically nanoporous $BiVO_4/TiO_2$ hollow microspheres. One of the advantages of this method is that the nanoporous $BiVO_4/TiO_2$ hollow microspheres can be prepared without assistance of templates synthesized beforehand. High photocatalytic activity on the degradation of acetic acid is investigated for typical samples of $BiVO_4/TiO_2$ hollow microspheres under visible light.

2 Experimental

2.1 Materials

All chemicals were analytically graded and used as the starting materials without further purification. Glucose, $Bi(NO_3)_3 \cdot 5H_2O$, NH_4VO_3 and $(NH_4)_2TiF_6$ were purchased from East of China Chemical Regent Co.

2.2 Preparation of BiVO₄/TiO₂ Hollow Composite Microshperes

In a typical synthesis of colloidal carbon spheres, 4 g of glucose and 0.84 g of $(NH_4)_2 TiF_6$ were dissolved in 35 mL of distilled water to form a clear solution. 0.5 g of Bi $(NO_3)_3$ ·5H₂O and 0.7 g of NH₄VO₃ were dissolved in dilute HNO₃ and NaOH aqueous solution respectively. After stirring for 0.5 h, the three solutions were mixed. The mixture was then sealed in a 100 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 24 h. The products were washed by distilled water and ethanol three times each and dried in air at 60 °C for 8 h. The final products were obtained through a heat treatment at 400 °C in air for 4 h with a heating rate of 2 °C min⁻¹.

2.3 Characterization

The samples were characterized by powder X-ray Diffraction (XRD) performed on a Rigaku-Dmax

2500 diffractometer. Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA-DSC) data were recorded with a thermal analysis instrument (SDT 2960, TA Instruments, New Castle, DE) at a heating rate of 10 °C min⁻¹ in an air flow of 100 mL min⁻¹. The morphology and composition of the samples were inspected using a scanning electron microscope (SEM, JSM-5610) and transmission electron microscopy (TEM, JSM-2100) equipped with an energy-dispersive X-ray spectrum (EDX, Inca Energy-200) at an accelerating voltage of 200 kV. Diffuse Reflectance Spectroscopy (DRS) spectra were obtained with a UV-vis spectrometer (BWS003). The bandgap was calculated from the DRS of the samples.

2.4 Measurements of Photocatalytic Activity

Photocatalytic activity of the BiVO₄/TiO₂ hollow composite samples was evaluated by the degradation of acetic acid to produce carbon dioxide at atmospheric pressure under visible-light irradiation. The amount of CO₂ evolved resulted from the photocatalytic decomposition of acetic acid was analysized by a gas chromatographic (GC, Hewlett-Packard 5890II). A 300 W xenon lamp cooled with a water jacket was used as the irradiation source and placed 30 cm apart from the reactor. 0.05 g of BiVO₄/TiO₂ hollow composite samples were added into 100 ml acetic acid solution with a concentration of 0.9 M (C_{catalyst}=0.5 mg/mL). The 420 nm cutoff filter was placed under the reactor to completely remove all incoming wavelengths shorter than 420 nm to ensure irradiation occurs only with visible-light. Prior to irradiation, the suspensions were stirred in the dark for 1 h to reach an adsorption-desorption equilibrium between the pollutant and photocatalyst. Under irradiation, the suspensions were stirred continually and open to air. At irradiation time intervals of 20 min, 5 ml of the suspensions were collected, and then centrifuged (6000 rpm, 6 min) to remove the photocatalyst particles. In order to compare the photocatalytic activities, the equivalent weight of P-25 (pure TiO₂) and solid microsphere sample was carried out under same conditions for photolysis of acetic acid.

3 Results and Discussion

The formation of hierarchically nanoporous $BiVO_4/TiO_2$ hollow micro-spheres involves two steps (Fig. 1 (A)). First, monodisperse $BiVO_4/TiO_2/C$ composite microspheres are formed by hydrothermal method. Then, the microspheres with hollow structure are formed through aggregation and condensation of fine subunits under carbon pyrolysis. As shown in Fig. 1 (B)-(a), the XRD pattern of the hybrid microspheres before calcination treatment indicates that the peaks are in good agreement with the JCPDS (Joint Committee on Powder Diffraction Standards) No. 14-0133 for tetragonal BiVO₄ and No. 21-1272 for anatase phase of TiO₂. However, the signals of monoclinic BiVO₄ increased after high-temperature treatment, which indicates that BiVO₄/TiO₂ composites were successfully prepared.

The structure and morphology of $BiVO_4/TiO_2/C$ composites were characterized by their corresponding SEM and TEM images. As shown in Fig. 2 (A), the majority of highly uniformed microspheres with diameters ranging from 400 to 600 nm can be found. Moreover, the formation of spherical structure is strongly depended on the molar ration of precursor. The TEM images (Fig.2 (C)) show that the surface of the as-prepared samples is relatively smooth. The EDS analysis spectrum (Fig. 2 (D)) reveal that the as-prepared samples comprised of all the elements

C, O, Bi, V and Ti from the precursor materials.

A high-temperature treatment of $BiVO_4/TiO_2$ solid microspheres was applied to obtain $BiVO_4/TiO_2$ with a hollow structure. The successful preparation of hollow $BiVO_4/TiO_2$ mi-



Fig. 1: Schematic illustration of the formation process of hierarchically nanoporous $BiVO_4/TiO_2$ hollow microspheres (A) and XRD patterns of hybrid microspheres before (a) and after (b) calcination treatment (B)



Fig. 2: SEM ((A) and (B)), TEM (C) images and EDX analysis spectrum (D) of as-prepared $BiVO_4/TiO_2$ hybrid microspheres

crospheres was confirmed by their corresponding TEM images. The hollow spheres with diameter around 0.5 µm was still preserved after calcinations at 400 °C for 2 h, which can be found from Fig. 3 (A) compared to the SEM images (Fig. 2 (B)). It is clearly seen that the as-prepared samples are hollow and the shell was formed from the aggregation of nanoparticles ranging 20 to 40 nm in thickness. The possible formation process of hollow microspheres interiors can be well explained by the Ostwald ripening process. Usually, the time needed for structural evolution from solid to hollow structure by Ostwald ripening process is longer than 24 h [27, 28]. In the present work, we have obtained the hollow microspheres in a very short reaction time with calcination treatment. TGA curves reveal that these hollow microspheres show a high thermal stability. As shown in Fig. 3 (C)-(a), the solid microsphere shows a cumulative weight loss of about 5 wt% up to 100 °C caused by the loss of moisture, and a weight loss of about 20 wt% from 300 to 500 °C was associated with the carbon pyrolysis. Compared with these solid microspheres, the hollow microspheres only shows a weight loss 5 wt% from 100 to 500 °C, as shown in Fig. 3 (C)-(b), which indicates the carbon yielding for CO, CO_2 and steam after calcination treatment. The EDS analysis of as-prepared sample composed of the elements O, Bi, V and Ti (Fig. 3 (D)). The element of carbon disappeared, which is in alignment with the TGA results.

Diffuse Reflectance Spectroscopy (DRS) is a useful tool for characterizing the electronic states in semiconductor materials. Fig. 4 (A) shows the UV/Vis diffuse reflectance spectrum of hollow microsphere sample which showed absorption bands in the visible-light region. The absorption onset edge was estimated to be at approximately 550 nm, corresponding to a band-gap of 2.25 eV (Fig. 4 (B)), which is the characteristic absorption of monoclinic scheelite BiVO₄ [29, 30]. This result obviously reveals the band-gap of the hollow microsphere sample is narrower than that of



Fig. 3: TEM ((A) and (B)) images of $BiVO_4/TiO_2$ hollow microspheres, TGA curves of hybrid microspheres before (a) and after (b) calcination treatment (C) and EDX analysis spectrum (D) of as-prepared $BiVO_4/TiO_2$ hollow microspheres



Fig. 4: Diffuse reflectance spectrum (A) and band-gap energy (B) of hollow microsphere sample

the pure TiO_2 , which indicates that the hollow microspheres have a potential response to visible light.

Photocatalytic activity of the as-prepared BiVO₄/TiO₂ hollow microspheres was evaluated by the degradation of acetic acid to produce CO₂ at atmospheric pressure. As shown in Fig. 5 (A), the amount of CO₂ evolution increases linearly with irradiation time for the three samples under the UV irradiation. However, the BiVO₄/TiO₂ hollow microspheres exhibit superior photocatalytic activity, which is higher than BiVO₄/TiO₂ solid microspheres than P-25 due to its higher specific surface area and nanoporous properties which enables BiVO₄/TiO₂ hollow microspheres to have more accessible active sites for photocatalytic reaction [31]. And the irradiation light is extended into the visible light region ($\lambda > 420$ nm), the rate of the CO₂ production shows a very great variation for BiVO₄/TiO₂ solid microsphere sample, as shown in Fig. 5 (B). Both P-25 and BiVO₄/TiO₂ solid microsphere show similar photocatalytic activity. However, BiVO₄/TiO₂ hollow microsphere is still more efficient for degradation of acetic acid most likely because acetic acid is anchored to the Bi³⁺ sites through a weak Bi-O bond so that they can efficiently receive the photo-generated electrons from the V 3d-block bands of BiVO₄ [32]. The local environment around the Bi³⁺ ion is more strongly asymmetric in the monoclinic phase than in the tetragonal phase, so that the Bi³⁺ ion has a stronger lone pair character in the monoclinic phase and hence



Fig. 5: Photocatalytic acetic acid irradiated by Xe lamp (300 W) (A) and (B) equipped with optical cutoff filter ($\lambda > 420 \text{ nm}$)

has a stronger tendency to form a Bi-O bond with acetic acid. It will lead to a more efficient transfer of photo-generated electrons from the V 3d-block bands to the anchored acetic acid in the case of $BiVO_4/TiO_2$ hollow microsphere.

Using two semiconductors with different levels of redox energy of their corresponding conduction and valence band, and having them come in contact can actually be considered as one of the most promising methods for improving charge separations, increasing the lifetime of charge carriers, and enhancing the efficiency of the interfacial charge transfer to adsorbed substrate [16]. As the previous reported, the conduction band of $BiVO_4$ was more cathodic than that of TiO_2 [33]. In general, the difference in conduction bands between two semiconductors is the driving forces of electron injection. In the system of $BiVO_4/TiO_2$, the $BiVO_4$ can be excited and the excited electrons generate the conduction band of $BiVO_4$ which is quickly transferred to a TiO_2 particle under visible-light irradiation, since the conduction band of $BiVO_4$ is more negative than that of TiO_2 as show in Fig. 6. The anatase TiO_2 is coupled by interparticle electron transfer from irradiated BiVO₄ nanocrystals to its conduction band. The electrons are then scavenged by molecular oxygen O_2 to yield the superoxide radical anion O_2^- . Thus forming intermediates that can interreact to produce hydroxyl radical OH. In addition, the holes remaining in the BiVO₄ valence band after migration of excited electrons can also react with the hydroxyl groups (OH^{-}) to form OH. It is well known that the OH radical is a powerful oxidizing agent capable of degrading most pollutants. The transfer of charge should therefore enhance the photo-oxidation of the adsorbed organic molecules.



Fig. 6: Redox process of the valence and conduction bands of $BiVO_4/TiO_2$ hollow microsphere samples under visible-light irradiation

4 Conclusion

In summary, a simple one-step template-free method was applied to prepare $BiVO_4/TiO_2$ solid microspheres. Furthermore, the hollow microspheres can be obtained by pyrolysis of solid microspheres under high temperature. One of the advantages of this method is that the nanoporous $BiVO_4/TiO_2$ hollow microspheres can be prepared without assistance of templates. The asprepared hollow microspheres exhibit hierarchically nanoporous structures and a high photocatalytic activity in the degradation of acetic acid under visible light. The hierarchically $BiVO_4/TiO_2$ hollow microspheres should find various potential applications in photocatalysis, catalysis, solar cells, and separation and purification processes.

Acknowledgements

This work was financially supported by the Qianjiang Talents Project of Zhejiang Province (2010R10023), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, the State Education Ministry (1001603-C), the Natural Science Foundation of Zhejiang Province (Y4100045), the Key Bidding Project of Zhejiang Provincal Key Lab of Fiber Materials and Manufacturing Technology, Zhejiang Sci-Tech University (S2010002) and the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT: 0654).

References

- [1] Yu J., Liu W, Yu H. A one-pot approach to hierarchically nanoporous titania hollow microspheres with high photocatalytic activity. Crystal Growth and Design 2008, 8: 930-934.
- [2] Jiang G, Zeng J. Preparation of nano-TiO₂/polystyrene hybride microspheres and their antibacterial properties. Journal of Applied Polymer Science 2010, 116: 779-784.
- [3] Jiang G, Zheng X, Wang Y, Li T, Sun X. Photo-degradation of methylene blue by multi-walled carbon nanotubes/TiO₂ composites. Powder Technology 2011, 207: 465-469.
- [4] Ryu J, Choi W. Substrate-specific photocatalytic activities of TiO₂ and multiactivity test for water treatment application. Environmental Science and Technology 2008, 42: 294-300.
- [5] Zhou B, Zhao X, Liu H, Qu J, Huang CP. Visible-light sensitive cobalt-doped BiVO₄ (Co-BiVO₄) photocatalytic composites for the degradation of methylene blue dye in dilute aqueous solutions. Applied Catalysis B: Environmental 2010, 99: 214-221.
- [6] Choi W, Termin A, Hoffmann MR. The role of metal ion dopants in quantum-sized TiO₂: Correlation between photoreactivity and charge carrier recombination dynamics. Journal of Physical Chemistry 1994, 98: 13669-13679.
- [7] Ge L, Xu M, Fang H. Photo-catalytic degradation of methyl orange and formaldehyde by Ag/InVO₄-TiO₂ thin films under visible-light irradiation. Journal of Molecular Catalysis A: Chemical 2006, 258: 68-76.
- [8] Chen C, Ma W, Zhao J. Semiconductor-mediated photodegradation of pollutants under visiblelight irradiation. Chemical Society Reviews 2010, 39: 4206-4219.
- [9] Jiang G, Wang R, Jin H, Wang Y, Sun X, Wang S, Wang T. Preparation of Cu₂O/TiO₂ composite porous carbon microspheres as efficient visible light-responsive photocatalysts. Powder Technology 2011, 212: 284-288.
- [10] Tada H, Jin Q, Nishijima H, Yamamoto H, Fujishima M, Okuoka S, Hattori T, Sumida Y, Kobayashi H. Titanium (IV) dioxide surface-modified with iron oxide as a visible light photo-catalyst. Angewandte Chemie International Edition 2011, 50: 3501-3505.
- [11] Wang H, Lewis JP. Second-generation photocatalytic materials: anion-doped TiO₂. Journal of Physics: Condensed Matter 2006, 18: 421-427.
- [12] Reyes-Gil KR, Reyes-García EA, Raftery D. Photoelectrochemical analysis of anion-doped TiO2 colloidal and powder thin-film electrodes. Journal of the Electrochemical Society 2006, 153: 1296-1301.
- [13] Pérez UMG, Guzmán SS, Cruz AM, Méndez OU. Photocatalytic activity of BiVO4 nanospheres obtained by solution combustion synthesis using sodium carboxymethylcellulose. Journal of Molecular Catalysis A: Chemical 2011, 335: 169-175.

- [14] Cruz AM, Pérez UMG. Photocatalytic properties of BiVO₄ prepared by the co-precipitation method: Degradation of rhodamine B and possible reaction mechanisms under visible irradiation. Materials Research Bulletin. 2010, 45: 135-141.
- [15] Jiang H, Endo H, Natori H, Nagai M, Kobayashi K. Fabrication and photoactivities of sphericalshaped BiVO₄ photocatalysts through solution combustion synthesis method. Journal of the European Ceramic Society 2008, 28: 2955-2962.
- [16] Yu J, Yu X, Huang B, Zhang X, Dai Y. Hydrothermal synthesis and visible-light photocatalytic activity of novel cage-like ferric oxide hollow spheres. Crystal Growth & Design 2009, 9: 1474-1480.
- [17] Deng Y, Liu X, Shen B, Liu L, Hu W. Preparation and microwave characterization of submicrometer-sized hollow nickel spheres. Journal of Magnetism and Magnetic Materials 2006, 303: 181-184.
- [18] Hu CY, Xu YJ, Duo SW, Li WK, Xiang JH, Li MS, Zhang RF. Preparation of inorganic hollow spheres based on different methods. Journal of the Chinese Chemical Society 2010, 57: 1091-1098.
- [19] Tsai MS, Li MJ, Yen FH. Synthesis of nano grade hollow silica sphere via a soft template method. Journal of Nanoscience & Nanotechnology 2008, 8: 3097-3100.
- [20] Leidinger P, Popescu R, Gerthsen D, Feldmann C. Nanoscale La(OH)₃ hollow spheres and finetuning of its outer diameter and cavity size. Small 2010, 6: 1886-1891.
- [21] Meng Y, Chen D, Jiao X. Synthesis and characterization of CoFe₂O₄ hollow spheres. European Journal of Inorganic Chemistry 2008, 11, 4019-4024
- [22] Cao SW, Zhu YJ. Monodisperse α-Fe₂O₃ mesoporous microspheres: One-step NaCl-assisted microwave-solvothermal preparation, size control and photocatalytic property. Nanoscale Research Letters 2011, 6: 1.
- [23] Bai B, Wang P, Wu L, Yang L, Chen Z. A novel yeast bio-template route to synthesize Cr₂O₃ hollow microspheres. Materials Chemistry and Physics 2009, 114: 26-29.
- [24] Ai PF, Liu YL, Xiao LY, Wang HJ, Meng JX. Synthesis of Y₂O₂S: Eu³⁺, Mg²⁺, Ti⁴⁺ hollow microspheres via homogeneous precipitation route. Science and Technology of Advanced Materials 2010, 11, 035002.
- [25] Tian BZ, Yang HF, Liu XY, Xie SH, Yu CZ, Fan J, Tu B, Zhao DY. Fast preparation of highly ordered nonsiliceous mesoporous materials via mixed inorganic precursors. Chemical Communications 2002, 17: 1824-1825.
- [26] Wang R, Jiang G, Ding Y, Wang Y, Sun X, Wang X, Chen W. Photocatalytic activity of heterostructures based on TiO₂ and halloysite nanotubes. ACS Appl. Mater. Interfaces 2011, 3: 4154-4158.
- [27] Hu P, Yu L, Zuo A, Guo C, Yuan F. Fabrication of monodisperse magnetite hollow spheres. Journal of Physical Chemistry C 2009, 113: 900-906.
- [28] Luo B, Xu S. Ma WF, Wang WR, Wang SL, Guo J, Yang WL, Hu JH, Wang CC. Fabrication of magnetite hollow porous nanocrystal shells as a drug carrier for paclitaxel. Journal of Materials Chemistry 2010, 20: 7107-7113.
- [29] Khomenkova L, Fernandez P, Piqueras J. ZnO nanostructured microspheres and elongated structures grown by thermal treatment of ZnS powder. Crystal Growth & Design 2007, 7: 836-839.
- [30] Dong F, Wu Q, Ma J, Chen Y. Mild oxide-hydrothermal synthesis of different aspect ratios of monoclinic BiVO₄ nanorods tuned by temperature. Physica Status Solidi A 2009, 206: 59-63.
- [31] Cheng HF, Huang BB, Wang ZY, Qin XY, Zhang XY, Dai Y. One-pot miniemulsion-mediated route to BiOBr hollow microspheres with highly efficient photocatalytic activity. Chemistry- A European Journal 2011, 17: 8039-8043.

190

- [32] Liu Y, Huang B, Dai Y, Zhang X, Qin X, Jiang M, Whangbo MH. Selective ethanol formation from photocatalytic reduction of carbon dioxide in water with BiVO₄ photocatalyst. Catalysis Communications 2009, 11: 210-213.
- [33] Sayama K, Wang N, Miseki Y, Kusama H, Onozawa-Komatsuzaki N, Sugihara H. Effect of carbonate ions on the photooxidation of water over porous BiVO₄ film photoelectrode under visible light. Chemistry Letters 2010, 39: 17-18.