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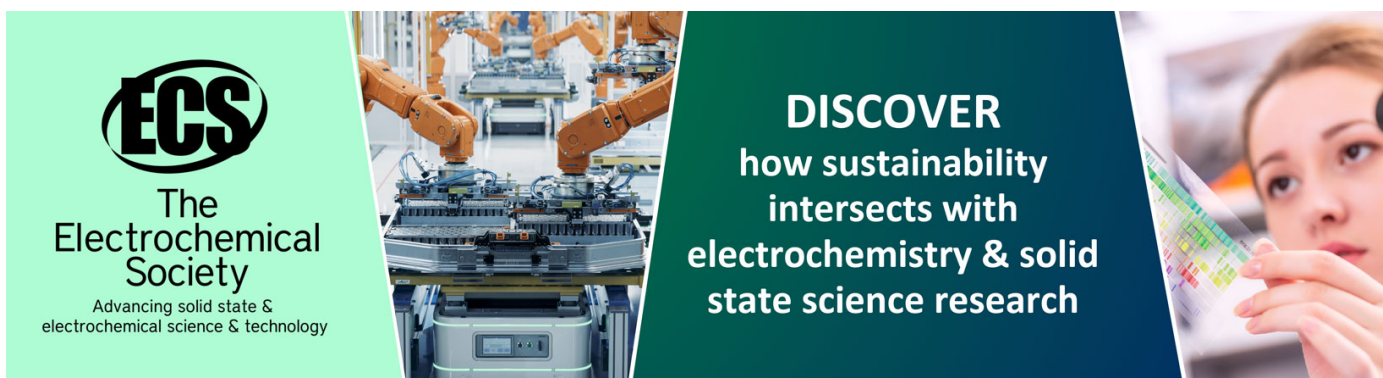
Visible Light Driven photocatalyst BiVO_4 for photocatalytic removal of NO

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Visible Light Driven photocatalyst BiVO₄ for photocatalytic removal of NO

Liang Wang, Ben Chong, Wentai Wang*, Xue Yu, Lijuan Feng, and Chunhu Li

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China.

Email: wentaiwang@ouc.edu.cn; Tel: +86-532-66783905

Abstract. BiVO₄ nanoparticles were synthesized through hydrothermal method, and characterized by XRD, SEM, FTIR and UV-Vis. The BiVO₄ were pure monoclinic scheelite type, with particle size around 300-500nm and band gaps around 2.34-2.45eV. The photocatalytic activity was evaluated by oxidation of NO under visible light irradiation. The hydrothermal temperature of 200 °C induced the best photocatalytic activity due to the fine crystalline phase, flower-like morphology and the stronger visible light absorbance.

1. Introduction

Semiconductor photocatalysts have attracted large attention due to the promising applications in decomposition of organic compounds^[1-3]. TiO₂ is one of the most widely applied photocatalyst as its high chemical stability, strong oxidizing power and nontoxicity^[4]. However, it only works with ultraviolet (less than 5% of whole sunlight) and is hard to meet the practical applications^[5]. Many efforts have been devoted to develop visible-light photocatalyst, such as Bi₂WO₆^[6], Bi₂MoO₆^[7], Bismuth oxyhalide compounds^[8] and BiVO₄^[9], etc. BiVO₄ has three crystalline phases, monoclinic scheelite, tetragonal scheelite and tetragonal zircon, among which BiVO₄ with monoclinic structure and discrete band gap of 2.3eV have been proven suitable for photocatalytic degradation of some harmful pollutants^[10-12]. Hence, it is desired to control the crystalline phases as monoclinic scheelite.

Hydrothermal method is a simple and effective way in generating monoclinic BiVO₄ with perfect crystal structures and regular morphologies^[13]. Meng et al.^[14] fabricated crystalline monoclinic BiVO₄ powders with polyhedral, rod-like, tubular, leaf-like and spherical morphologies through hydrothermal process, controlling pH values and using Pluronic P-123 as soft template. Zhu et al.^[15] obtained BiVO₄ with mixed structure of monoclinic scheelite and tetragonal zircon through hydrothermal method in the presence of EDTA. Xi^[10] prepared m-BiVO₄ nanoplates with preferential exposition of [001] facets by hydrothermal method, which lead to the enhanced photocatalytic activity for the degradation of organic contaminants. However, it still requires further exploration to obtain desirable micrometer architectures of BiVO₄ to achieve efficient visible-light harvesting and high photocatalytic activity^[2].

In this study, we prepared BiVO₄ nanoparticles by hydrothermal method and investigated their phase structures, morphologies and optical absorption properties. The photocatalytic activity was also evaluated by the oxidation of nitrogen monoxide (NO) under visible light irradiation.



2. Experimental

All chemicals were used without further purification. Typically, 0.5265g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved into 20mL of 2M HNO_3 solution (Suspension A), while 0.126g of NH_4VO_3 was dissolved in 20mL of 2M NaOH solution (Suspension B) under magnetic stirring. Then, Suspension B was dropped into A and stirred magnetically for 1h at room temperature. After adjusting the pH to 7.00, the mixture was transferred into a Teflon-lined stainless steel autoclave and maintained at certain temperature (140, 160, 180 and 200°C) for 24 h, named as T140, T160, T180 and T200, respectively. The sizes and morphologies were determined by scanning electron-microscopy (HITACHI S-4800). The phase composition was characterized by X-ray diffractometer (Bruker D8). The FT-IR spectra were recorded by Nicolet Nexus spectrometer. The UV-Vis diffusion reflectance spectra were collected on a UV-Vis spectrophotometer (UV-3600, Shimadzu, Japan). The photocatalytic removal of NO was carried out in an original designed reactor, using 50W xenon lamp with a cut-off filter of 420nm. The concentration of NO was continuously measured by combustion analyzer. The removal efficiency (η) of NO was calculated by $\eta = (C_0 - C) / C_0 * 100\%$, where C_0 and C are the concentrations of NO in the inlet and outlet stream, respectively.

3. Result and discussions

XRD was applied to investigate the phase structures of as-prepared BiVO_4 powders. The XRD patterns of different BiVO_4 samples were shown in Fig.1a. It is observed that all the diffraction patterns are almost same, no other peaks can be observed. These patterns can be assigned to monoclinic scheelite type structure according to the standard cards JCPDS14-0688^[16-17]. This result indicates that hydrothermal temperature (140~200°C) have no effect on BiVO_4 crystal structures, which is in agreement with the previous reports^[18-19]. The phase structures of BiVO_4 may be controlled both kinetically and thermodynamically. It is also observed that the intensity of diffraction peaks were slightly different. The intensity of diffraction peak of (121) plane, corresponding to monoclinic BiVO_4 , increased with the temperature. In the pattern of T200, the intensity of (121) planes of the monoclinic BiVO_4 was much higher than others, indicating the preferential growth of BiVO_4 crystal structures along (121) direction. Hence, the higher hydrothermal temperature can facilitate the growth of monoclinic BiVO_4 .

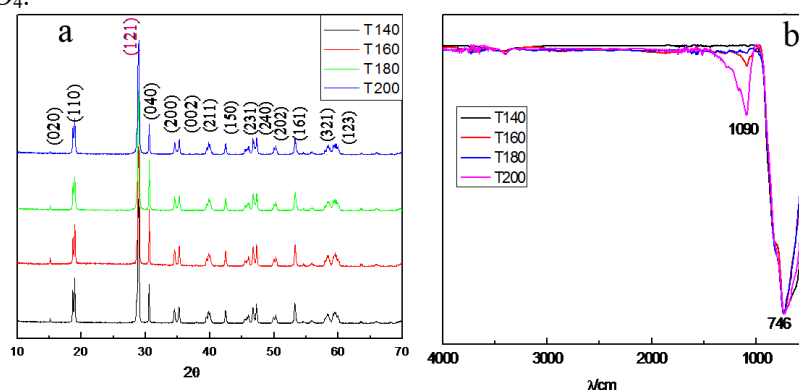


Fig.1. (a) XRD of BiVO_4 samples and (b) FTIR of BiVO_4 samples

FTIR was applied to investigate the chemical structure of BiVO_4 samples. As shown in Fig.1b, two typical absorption peaks can be observed, an unobvious peak at 830cm^{-1} is covered by the peak at 746cm^{-1} . The absorption peaks at 746cm^{-1} and 1090cm^{-1} can be attributed to the asymmetric stretching vibration of V-O band^[20], while the peak at 830cm^{-1} is the signal of the symmetric stretching vibration of V-O band. The intensity of the diffraction peaks at about 1090cm^{-1} become stronger with the increase of hydrothermal temperature. It can be concluded that the structures of the BiVO_4 samples change little in hydrothermal process, and higher hydrothermal temperature can facilitate the growth of monoclinic BiVO_4 , which further confirms the results of XRD.

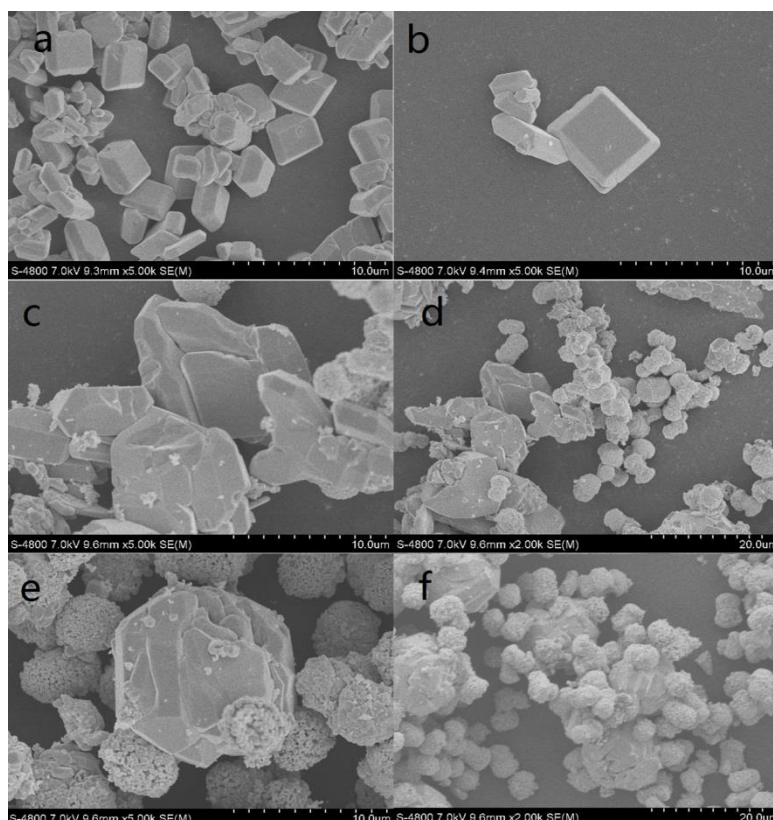


Fig.2. SEM images of BiVO_4 samples synthesized at different temperatures: (a) 140°C, (b) 160°C (c, d) 180°C and (e, f) 200°C

Fig.2 shows the morphologies and microstructures of BiVO_4 by SEM. Hydrothermal temperature greatly affects the morphologies of samples^[21]. T140 shows uniform crystal-like microstructures with particle size of 300~400nm as shown in Fig.2a. The morphology of T160 is similar to T140, but the average particle size increased to 500nm according to Fig. 2b. Fig.2c–f show the images of T180 and T200. The crystal-like microstructures sintered together and formed spherical structures with a rough surface^[22]. The surface of T200 shows flower-like structures, which may have higher surface area. These results reveal that the temperature is an important factor to control the morphology of BiVO_4 nanoparticles.

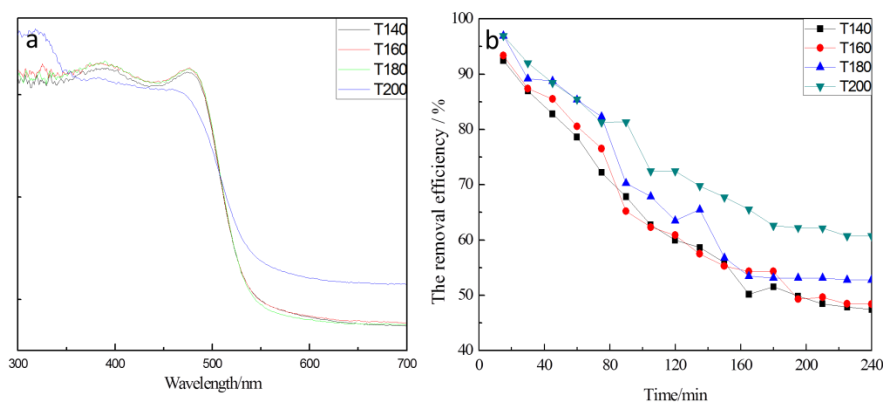


Fig.3. (a) UV-vis diffuse reflectance absorption spectra of BiVO_4 samples; (b) The removal efficiency of obtained samples under visible light Conditions: 5% of H_2O , 5% of O_2 , C_0NO 300ppm, $T=110^\circ\text{C}$.

The optical absorption of semiconductors are key factors in determining their photocatalytic activity^[23]. The UV–Vis spectrum of BiVO₄ in Fig.3(a) show strong adsorption in both UV and visible light region, indicating the potential as sunlight-driven photocatalysts. The absorbance of T140, T160 and T180 have no obvious difference, while T200, with absorption edge of 550nm, shows the best visible-light response. The absorption edge shows slightly red shift with the increase of hydrothermal temperature from 140 to 200°C. Band gap energy (E_g , eV) is used to evaluate the optical absorption performance of semiconductors. It can be calculated by $E_g = 1240/\lambda(eV)$. The band gaps of T140, T160, T180 and T200 were estimated to be about 2.45, 2.45, 2.44 and 2.34eV, respectively. The lower band gap energy of T200 makes it much easier to be excited by the light source, comparing with T140, T160 and T180. Meanwhile, the red shift of light absorption may also facilitate the utilization of light source.

The photocatalytic properties of BiVO₄ were evaluated by the removal of NO in simulated gas under visible light irradiation. Fig.3(b) shows the removal efficiency of NO over different catalysts against irradiation time. Hydrothermal temperature greatly affects the photocatalytic activities of BiVO₄, which is in accordance with previous study^[17]. T200 shows the highest activity with NO removal efficiency sustained over 60%, while other BiVO₄ can only achieve 45% removal efficiency after 240min. The difference in photocatalytic activity of BiVO₄ can be attributed to the crystalline phase, morphology and band gap, which has been proven greatly affected by the temperature, as confirmed by the XRD, SEM and UV-Vis results. Therefore, T200, which has monoclinic scheelite type and broader light absorption range, shows the best NO removal performance.

A possible formation mechanism of BiVO₄ was further discussed^[24], as shown in Fig.4. Bi³⁺ was released when Bi(NO₃)₃ was dissolved in HNO₃ solution (Eq.1), while VO₃⁻ was formed when NH₄VO₃ was dissolved in NaOH solution (Eq.2). Afterward, BiVO₄ formed immediately when above two solutions were mixed together (Eq.3)⁽¹⁶⁾. The crystallization process was conducted in hydrothermal autoclave at different temperature to form different phase structures and morphologies.

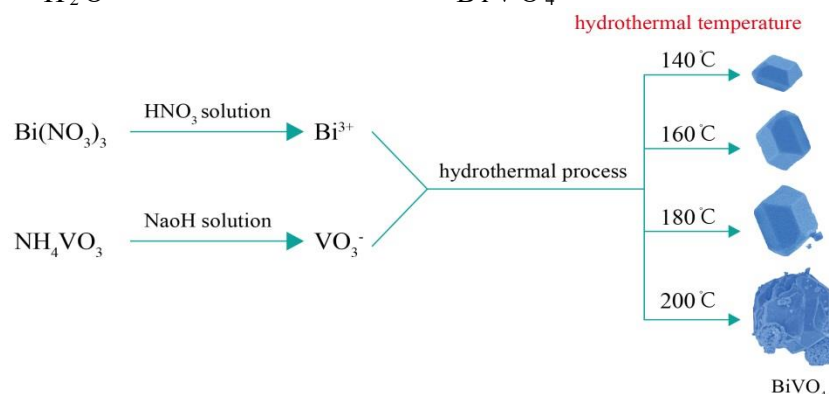
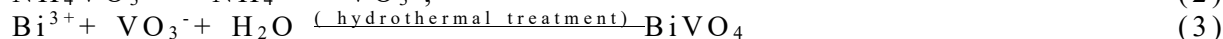
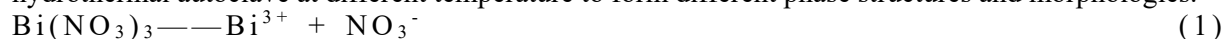


Fig.4. Schematic diagram of the formation mechanism of the BiVO₄ morphology

4. Conclusions

A facile hydrothermal route to synthesize BiVO₄ was reported. All the BiVO₄ samples derived at 140~200 °C are monoclinic scheelite type. Hydrothermal temperature has no effect on the crystal structure of BiVO₄, however, affect the morphology and optical absorption. Higher temperature induces the growth of BiVO₄ crystal structures along (121) direction and the formation of large particle size and rough surface. T200 shows the highest activity with NO conversion of 60% after 240min irradiation, due to better visible-light response and higher surface area.

Acknowledgement

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