Synthesis of Bismuth Vanadate by a Novel Process and Its Enhanced Photoelectrochemical Performance

Fengkai Yu¹, Yan Zhang¹,*, Xiangzhong Ren², Meijun Yang¹ and Jianqiang Yu¹, *

¹. School of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071, China.
². Jinan Institute of Chemical Engineering, Jinan 250000, China
Email: zhangyanchem@qdu.edu.cn, jianqyu@qdu.edu.cn

Abstract. Highly crystalline monoclinic scheelite BiVO₄ were synthesized by a hydrothermal process from strong redox reaction of VOC₂O₄ and NaBiO₃ solutions over a wide range of pH. A simple electrophoresis process was employed to fabricate the BiVO₄ thin films photoelectrochemical cell, which was used as photoanodes for water splitting. It can be found that the photoelectrochemical performance of the BiVO₄ thin-film is strongly dependent on the pH used in the synthesis. It demonstrated that the distortion and polarization of the local structure of the synthesized material dependent greatly on the pH condition during the synthesis. Moreover, upon pH = 1, the photocurrent density increase. While the Flat band of these bismuth vanadate shifts to positive as the pH decrease, which means the Fermi Energy Level (E₅) is risen as the pH decrease, as well as the conductive band (CB). Electrochemical impedance spectroscopy (EIS) measurements suggested that the sample of pH = 1 showed the highest rate of photogenerated charge transfer.

1. Introduction
Since photoelectrochemical water splitting was reported in 1972 [5], the development of n-type semiconductors that can serve as efficient photoanodes for solar water oxidation have attracted more and more attentions. n-type bismuth vanadate (BiVO₄) is one of the semiconductors [6]. It has been recently applied in many field, such as the water splitting [1, 2], CO₂ reduction [3], removal pollution [4]. BiVO₄ is a well-known photocatalytic material with a band gap nearly 2.4 eV and the appropriate valence band position for O₂ evolution [7, 8], outstanding light absorption edge up to 500 nm, and low cost of synthesis. Its conduction band located at ca. 2.4 V vs. RHE (reversible hydrogen electrode). However, its photocatalytic activity is usually low, because for water oxidation BiVO₄ suffer from excessive electron-hole recombination, poor charge transport properties. Some scientists have been focused on the synthesis method, which could enhance the activity of BiVO₄, such as morphology control [9]. Li et al. have investigated the activity of BiVO₄ with various facets [10], they find that the photogenerate electrons and holes occurred separately on the {010} and {110} facets under photo-irradiation.

In this study, we report a novel process for the synthesis of bismuth vanadate. The BiVO₄ was synthesized from aqueous VOC₂O₄ (Vanadyl oxalate) and NaBiO₃ (Sodium bismuthate dihydrate) solutions over a wide range of pH by a hydrothermal process. Vanadyl oxalate is organic vanadium source, the activity of organic compound is higher than that of inorganic compound. The C₂O₄²⁻ (oxalic ion) shows a high reducibility, which can be easily oxidized to carbon dioxide. Therefore we selected bismuth(V) salt as the vanadium source. The carbon dioxide generate from the reaction may
increase the pressure of the reactor, and thus to make the BiVO₄ has a smaller particle size. The pH of the synthesis is also has a great role on the controlling of the morphology [10]. The electrochemical and photoelectrochemical properties were studied to understand the surface state and to evaluate the potential of the electrodes for PEC cell application.

2. Experiment

2.1. Materials
V₂O₅ (99 %, AR), H₂C₂O₄·2H₂O (99 %, AR), NaBiO₃ (99 %, AR), HNO₃ (69 %, AR), ammonium solution (28 %, AR), Platinum foil auxiliary and Ag/AgCl reference electrodes were purchased from Tianjin Aida Hengsheng Technology. Deionized water was made by the Flom ultrapure water system.

2.2. Preparation of Materials
VOC₂O₄ solution is prepared by dissolving V₂O₅ and H₂C₂O₄ (\(M_{V_2O_5}/M_{H_2C_2O_4} = 1:2.12\)) in 100 ml deionized water, stirring under 50 °C for 2h. Then cool it down in temperature. It will be a transparent blue solution.

25ml above-mentioned VOC₂O₄ adjust various pH by adding 2 M HNO₃ and NH₃·H₂O, reacting with 0.1 M NaBiO₃. Then put this solution in 100 ml PTFE (Polytetrafluoroethylene) reactor in 180 °C for 24h. The production washed by centrifugation.

BiVO₄ films were electrophoresised on a conductive FTO glass.

2.3. Characterization
X-ray diffraction (XRD) spectra were obtained on a DX-2700 X-ray diffractometer using Cu-Kα radiation over the range from 5° to 60°. Scanning electron microscope (SEM) images were acquired on a JSM-6390F (JEOL, Tokyo, Japan) microscope by using an accelerating voltage of 20.0 kV. UV-visible diffuse reflectance spectra were obtained by a UV-vis diffuse reflectance spectrophotometer (U-41000, HITACHI, Tokyo, Japan). The photoelectrochemical measurements were carried out using a standard three-electrode cell and a electrochemical workstation (CompactStat.h10800).

3. Results and Discussion

3.1. Structure and Morphology of Material
To investigate the structure and morphology of BiVO₄, a variety of detection methods have been performed.

![Figure 1. XRD patterns of products synthesized in different pH.](image-url)
Fig. 1 shows X-ray diffraction patterns of samples synthesized in different pH. The peaks of 30.5, 35.2, 45.4, and 50.3˚ are observed corresponding to (004), (020), (-213) and (220) planes for the monoclinic phase of BiVO₄ (PDF#75-1866). That proved hydrothermal at 180 ˚C can make monoclinic phase of BiVO₄. The monoclinic BiVO₄ is known to show the highest photocatalytic effect than other crystal phases [11,12]. In the XRD, we can find the degree of crystallinity decreased firstly, and increase after pH5 as pH increased.

Fig. 2 presents scanning electron microscopy (SEM) images of samples. As shown in Fig. 2a, the sample (pH=1) powders show a morphology decahedron with the grain sizes of ca. 1 μm. The {010} and {110} facets separates obviously [10]. Compared with other samples, As the pH increase, morphology of BiVO₄ powders will change from sheet to rodlike grains. These long rods might be formed by the sintering of short rodlike grains in a one-dimensional fashion [9].

The UV-visible diffuse reflection spectra of samples were shown in Figure 3. The optical band gap was determined by the following equation (1): 
\[ \alpha h\nu = A(h\nu - E_g)^n \]

It was found that these samples displayed good photoabsorption properties ranging from ultraviolet to visible light with the wavelength shorter than 550 nm. There band gap energy is around 2.2eV.
3.2. Photoelectrochemical Measurements

Photoelectrochemical measurements were used to tested the photoactivity of these films. A beam of visible light was irradiated on the back (FTO) side of the film immersed in 0.1 M NaOH (pH = 13). To converting the obtained potential (vs. Ag/AgCl) to RHE (NHE at pH = 0), the following equation (2) were used.

![Figure 3](image)

**Figure 3.** UV-vis images of products synthesized in different pH.
- a. pH=1; b. pH=9; c. pH=7; d. pH=5; e. pH=3.

![Figure 4](image)

**Figure 4.** Photocurrent–potential curves of samples.
- a. pH=1; b. pH=3; c. pH=5; d. pH=7.
\[ E_{RHE} = E_{AgCl} + 0.059 \, pH + E_{AgCl}^0 \]  

(2)

Fig. 4 are the photocurrent–potential curves of BiVO₄ measured under visible light in 0.1 M NaOH. The photocurrents increased with increasing applied anodic potential representing a typical n-type semiconductor behaviour. Fig. 4 is a magnified view in 0.55–1.80 V (vs. RHE) of applied potentials to determine photocurrent onset potential. Onset potential is ca. (a) 0.55 V, (b) 0.7 V, (c) 0.8 V, (d) 0.85 V (vs. RHE). The onset potential shifted to negative potential by decreasing the synthesis pH. Thus, the fermi level is more positive with increasing of synthesis pH. The negative shift indicates there are larger accumulation of electrons in the BiVO₄ (pH=1) electrode and reflects decreased charge recombination [13]. However, due to the limitation of interfacial charge transport, we can’t find precise value of flat band. So we test the Mott–Schottky plot.

\[
\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_0 N_D} \left( E - E_{fb} - \frac{\kappa T}{e} \right)
\]  

(3)

The flat band potential of electrodes can be determined by the Mott–Schottky curve used the following equation (3):

The flat band potential of the thin-film synthesized at various pH can be calculated from Fig. 5. As we can find, the flat band potential of the sample synthesized at pH=1 is more negative than that of others. It demonstrated once again that we the dependence of flat band potential on the pH value used in the synthesis. Equation (3) also indicated that the slope is inversely proportional to the carrier concentration. Therefore, the carrier number in sample of pH=1 is higher.
Figure 6. photocurrent density of samples.
a. pH=1; b. pH=3; c. pH=5; d. pH=7.

Fig. 6 indicates that the photocurrent density curves of the samples synthesized at various pH conditions. The photocurrent over the sample synthesized at pH=1 is the most intensive one. This result relates to the distortion and polarization of the material itself. As shown in Fig. 2, the morphology can be controlled by adjusting the synthesis pH condition. Thus, lower pH value will result in a larger distortion of Bi and V atoms in the local structure, the particle size decreases as well.

Figure 7. Nyquist plots of EIS.

The electrochemical impedance spectroscopy (EIS) measurements were performed to evaluate the kinetics of charge transfer. The EIS is a powerful tool to research electrochemical behaviour, especially the charge transfer at the photoanodes and water oxidation kinetics at the interface of the photoanode/electrolyte [13]. As shown in the Nyquist plots in Figure 7, the photoanodes show semicircles with different radii. The fitting of the semicircles indicate that samples synthesized in pH=1 has the lowest Rct. In contrast, when pH increases to 7, it shows the highest Rct. The reverse
tendency of the change in Rct from that of the PEC performance strongly suggests that synthesis pH is a critical factor in determining the photogenerated charge transfer of BiVO₄.

4. Conclusions
In summary, we investigated a novel process for the synthesis of bismuth vanadate from VOCl₂O₄ and NaBiO₃ solutions by a hydrothermal process. Monoclinic BiVO₄ with various morphology can be synthesized by adjusting the pH condition. BiVO₄ sample synthesized at pH=1 shows the best photoelectrochemical water splitting performance. J-V plot suggests that BiVO₄ synthesized in pH=1 has a more negative onset potential, with a higher photocurrent. The EIS study demonstrated photogenerated charge transfer of pH=1 is the best, which were responsible for the distortion and polarization of the material itself.

5. References
[1] Kim, T. W.; Choi, K. S. 2014 Science 343 990
[2] Murciálopez, S.; Fábrega, C.; Monllorsatoca, D.; Hernándezalonso, M. D.; Penelaspérez, G.; Morata, A.; Morante, J. R.; Andreu, T. 2016 ACS Appl. Mater. Interfaces 8 4076
[3] Liu, Y.; Huang, B.; Dai, Y.; Zhang, X.; Qin, X.; Jiang, M.; Whangbo, M. H. 2009 Catal. Commun. 11 210-213
[4] Zhang, Y.; Yu, J.; Yu, D.; Zhou, X.; Lu, W. 2011 Rare Metals 30 192-198
[5] Fujishima, A.; Honda, K. 1972 Nature 238 37-38
[6] Kudo, A.; Omori, K.; Kato, H. 1999 Cheminform 121 137-138
[7] Berglund, S. P.; Flaherty, D. W.; Hahn, N. T.; Bard, A. J.; Mullins, C. B. 2014 J. Phys. Chem.C 115 3794-3802
[8] Iwase, A.; Kudo, A. 2010 J. Mater. Chem. 20 7536-7542
[9] Yu, J.; Kudo, A. 2006 Adv. Funct. Mater. 16 2163-2169
[10] Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C. 2013 Nat. Commun. 4 1432
[11] Kudo, A.; Omori, K.; Kato, H. 1999 J. Am. Chem. Soc. 121 11459-11467
[12] Tokunaga, S.; Kato, H.; Kudo, A. 2001 Chem. Mater. 13 4624-4628
[13] Hong, S. J.; Lee, S.; Jang, J. S.; Lee, J. S. 2001 Energy & Environmental Science 4 1781-1787