# Enhancement of Photoelectrochemical Oxidation by Amorphous Nickel Boride Catalyst on Porous BiVO<sub>4</sub>

Ke Dang, Xiaoxia Chang, Tuo Wang\* and Jinlong Gong\*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University; Collaborative Innovation Center of Chemical

Science and Engineering, Tianjin 300072, China

\* Corresponding author: jlgong@tju.edu.cn; wangtuo@tju.edu.cn; Fax: +86-22-87401818

## Contents

- 1. Experimental Section
- 2. Supplemental Figures and Tables
- 3. References

#### **Experimental section**

#### Materials

Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O, 99%), vanadium(IV)oxy acetylacetonate (VO(acac)<sub>2</sub>, 99%), and p-benzoquinone (98%) were supplied by J&K Scientific Ltd. Potassium iodide (KI, 95%) was purchased from Tianjin GuangFu Fine Chemical Research Institute. Nickel acetate (Ni(acac)<sub>2</sub>•6H<sub>2</sub>O), sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>, 98%), nitric acid (HNO<sub>3</sub>, 26-28%), acetone (GR), ethanol (GR) and dimethyl sulfoxide (DMSO, 99%) were supplied from Tianjin Kemi'ou Reagent Co. Ltd. Sodium borohydride (NaBH<sub>4</sub>) was purchased from Shanghai Taitan Scientific Ltd. High purity water (18.25 MΩ•cm) supplied by a UP Water Purification System was used in the whole experimental processes. All the reagents were used without any purification process. FTO substrates (F:SnO<sub>2</sub>, 14 Ω per square) were purchased from Nippon Sheet Glass, Japan. Before using, the FTO substrates were ultrasonically cleaned for 30 min each in acetone, ethanol, and deionized water respectively.

#### Synthesis of BiVO<sub>4</sub> electrodes

The synthesis of nanoporous BiVO<sub>4</sub> photoanode involves two steps electrodeposition of BiOI film on FTO substrates and conversion to the nanoporous BiVO<sub>4</sub> film, the approach which was reported previously.<sup>1</sup> Briefly, a 0.03 M Bi(NO<sub>3</sub>)<sub>3</sub> solution was prepared by dissolving Bi(NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O in 50 mL of a 0.8 M KI solution after its pH was adjusted to 1.7 by adding HNO<sub>3</sub>. This solution was mixed with 20 ml of absolute ethanol containing 0.4 M p-benzoquinone, and was vigorously stirred for a few minutes. Electrodeposition in the prepared electrolyte was carried out potentiostatically in the typical three-electrode system using a FTO substrate (2.5×1 cm<sup>2</sup>) as the working electrode (WE), a platinum foil (2×2 cm<sup>2</sup>) as the counter electrode (CE) and the saturated Ag/AgCl as the reference electrode (RE). As an optimized condition, electrodeposition was conducted at -0.1 V versus Ag/AgCl for 5 min. A BiOI film was deposited on the FTO substrate. Afterwards, the FTO substrate was rinsed with deionized water and dried in ambient air.

BiVO<sub>4</sub> electrodes were synthesized by placing 0.2 ml of a dimethyl sulfoxide (DMSO) solution containing 0.2 M vanadyl acetylacetonate (VO(acac)<sub>2</sub>) on each of the BiOI electrodes, followed by heating in a muffle furnace at 450°C (ramping rate 1°C/min) for 2 h. After cooling to room temperature the electrodes were soaked in 1 M NaOH solution for 1 h to remove the excess  $V_2O_5$  present in the BiVO<sub>4</sub> films. The obtained pure BiVO<sub>4</sub> electrodes were rinsed with deionized water and dried in ambient air.

#### Synthesis of amorphous nickel boride nanoparticles

The amorphous nickel boride (NiB) nanoparticle were synthesized by the chemical reduction of Ni(acac)<sub>2</sub> using NaBH<sub>4</sub>, in accordance with the reaction, 2 Ni(acac)<sub>2</sub> + 4 NaBH<sub>4</sub> + 9 H<sub>2</sub>O  $\rightarrow$  Ni<sub>2</sub>B + 4 Na(acac) + 12.5 H<sub>2</sub> + 3 B(OH)<sub>3</sub>. Briefly, an aqueous solution containing 1 M NaBH<sub>4</sub> and 0.1 M NaOH regarded as solution A were prepared and thoroughly saturated by N<sub>2</sub> for 30 min. Another aqueous solution containing 0.5 M Ni(acac)<sub>2</sub> regarded as solution B were also saturated by N<sub>2</sub> for 30 min. The solution A was slowly added to solution B by an injection pump under ice bath and in the atmosphere of N<sub>2</sub> purging. A dark precipitate formed immediately and was collected by centrifugal, washed several times with deionized water and ethanol, and stored in ethanol until use.

#### Preparation of nickel boride-decorated BiVO<sub>4</sub> photoanode

A drop-casting technique was used to prepare the NiB/BiVO<sub>4</sub> photoanode. Firstly, 23 mmol of NiB nanoparticles were ultrasonically dispersed in 1000 ml absolute ethanol for 30 min to form a uniform suspension. The suspension of 10  $\mu$ L was then drop-casted onto the BiVO<sub>4</sub> electrodes. The drop-casting area was controlled to be 1.5 cm<sup>2</sup> and the mass of NiB was adjusted by the concentration of the suspension. In order to optimized the load of NiB on BiVO<sub>4</sub> photoanode, the suspension was diluted to 1/2, 1/4, 1/8 and 1/16 of the original concentration, respectively.

#### *Preparation of nickel-borate-modified BiVO*<sub>4</sub> *photoanode*

The nickel-borate (Ni-B<sub>i</sub>) film was prepared on the BiVO<sub>4</sub> electrode by means of the electrodeposition methods previously reported by Chio et al.<sup>2</sup> A three-electrode system was used with an as-prepared BiVO<sub>4</sub> electrode (WE), the saturated Ag/AgCl (RE) and a platinum foil (2×2 cm<sup>2</sup>) (CE). Ni-B<sub>i</sub> complexes were electrodeposited by holding a constant potential of 1.24 V versus Ag/AgCl for varying times (10 seconds to 60 seconds) with a potentiostat (IVIUM technologies) in 0.1 M potassium borate (B<sub>i</sub> electrolyte) at pH 9.2 containing 1\_mM Ni(NO<sub>3</sub>)<sub>3</sub>. Following deposition, the film was rinsed by dipping it briefly in 0.1 M KB<sub>i</sub> (pH 9.2) solution to remove any adventitious Ni<sup>2+</sup>. After rinsing and drying, the electrodes were kept in the dark.

#### Physical Characterization

The morphology and microstructure of the sample were characterized by fieldemission scanning electron microscopy (FESEM) (Hitachi S-4800, 5 kV) with energy-dispersive X-ray spectrum (EDX). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images were obtained on a JEOL JEM-2100F microscope at 200 kV. Prior to the measurements, the Ni<sub>2</sub>B/BiVO<sub>4</sub> composites were detached from the FTO substrate and ultrasonically dispersed in ethanol, and dipped onto a copper grid with a carbon film and dried under ambient conditions. The crystal structure was determined by X-ray diffractometer (D/MAX-2500) with Cu Kα radiation ( $\lambda$ =1.5416 Å) at 40 kV and 140 mA. XRD spectra were collected over a 20 range of 20-80° at a scanning speed of 8° per minute. The X-ray photoelectron spectroscopy (XPS) analysis of the photoanodes was carried out on a Physical Electronics PHI 1600 ESCA system using an Al K $\alpha$  X-ray source (E = 1486.6 eV). The light absorption of as-prepared samples was obtained using a Shimadzu UV-2550 spectrophotometer equipped with an integrating sphere using BaSO<sub>4</sub> as the reflectance standard. The composition of NiB sample was measured using Agilent 7700X inductively coupled plasma mass spectrometry (ICP-MS). The 10 uL Ni<sub>2</sub>B suspension was dissolved in 5 mL diluted nitric acid solution before ICP-MS measurement.

#### Photoelectrochemical measurement

Photoelectrochemical measurement was performed with an electrochemical workstation (IVIUM CompactStat.e20250). A three-electrode configuration was used, with the BiVO<sub>4</sub> or NiB/BiVO<sub>4</sub> electrode as the working electrode, a platinum foil  $(2\times 2 \text{ cm}^2)$  as the counter electrode, and the saturated Ag/AgCl as the reference electrode. A 300 W Xenon arc lamp (Beijing Perfectlight Technology Co. Ltd., 300 UV) equipped with an AM 1.5G filter was used as the light source. Unless otherwise noted, all the tests were performed under front-side illumination with illumination area of 1 cm<sup>2</sup>, immersed in the electrolyte of 0.5 M potassium borate (KB<sub>i</sub>) buffer solution (pH 9.2) with and without 1 M Na<sub>2</sub>SO<sub>3</sub> as a hole scavenger. Prior to measurements, the electrolyte was thoroughly saturated by N<sub>2</sub> for 0.5 h. The longterm amperometric photocurrent density-time curves were measured under continuous irradiation and at a bias of 1.23 V versus reversible hydrogen electrode (RHE). The Electrochemical impedance spectra (EIS) were carried out in the range of 0.01 Hz to 100 kHz, with an AC voltage amplitude of 10 mV at a DC bias of 0.7 V versus RHE under sunlight irradiation (AM 1.5G, 100 mW cm<sup>-2</sup>). The Mott-Schottky plots were measured at a frequency of 100 Hz and amplitude of 10 mV under the dark condition. The incident-photo-to-current efficiency (IPCE) tests were performed as the function of wavelength from 400 nm to 650 nm at a bias of 1.23 V versus RHE. For the photovoltage measurement, each dark/light open circuit potential reading was obtained after a stabilization process (20-30 min) with constant stirring. The stabilization process was necessary for reproducible open circuit potential reading. The measured potentials versus saturated Ag/AgCl were converted to the RHE scales according to the Nernst equation: E (vs. RHE) = E (vs. Ag/AgCl) +  $0.0592 \times pH +$ 0.197. Onset potential of photocurrent is defined as the corresponding voltage when the photocurrent density reaches to 20 µA cm<sup>-2</sup> in current-voltage measurement.

#### **Supplemental Figures**



**Figure S1.** TEM image of NiB particles at (a) low and (b) high resolution. Inset of (a) is the particle size statistics of NiB nanoparticles. The average particle size is 10 nm. Inset of (b) is the SEAD pattern; XPS detailed spectra over the region of (c) Ni 2p, (d) B 1s and (e) O 1s.

The B exists in both an oxidized state and a metallic state. The oxidized state of B, proved by the peak located at 191.0 eV, may result from the  $B_2O_3$  and  $B(OH)_3$  on the surface (Figure S1c).<sup>3</sup> And the metallic state of B, proved by the peak located at 187.1 eV, may result from the Ni-B alloy.<sup>4</sup> Three distinct peaks of the Ni  $2p_{3/2}$  core level is also shown (Figure S1d). The peak at the low binding energy of 852.1 eV can be assigned to metallic Ni<sup>0</sup>, originating from the inner Ni<sub>x</sub>B nanoparticles in view of the sampling depth of XPS (about 10 nm).<sup>5</sup> Another peak at higher binding energy is close to the Ni<sup>2+</sup> signal, indicating the existence of Ni(OH)<sub>2</sub> or NiO.<sup>6</sup> The peak located at 860.3 eV belongs to the satellite of the Ni  $2p_{3/2}$ . Two distinct peaks located at 531.0 eV and 521.9 eV in O 1s spetra indicate the exsitance of NiOOH and absorbed water on the surface of NiB.



Figure S2. (a) Cross-sectional SEM of  $BiVO_4$  photoanode; (b) Top-sectional SEM of Ni- $B_i/BiVO_4$  photoanode.



Figure S3. XRD pattern of pure BiVO<sub>4</sub>, pure NiB and NiB/BiVO<sub>4</sub>.



**Figure S4.** (a) Raman spectrum of the NiB/BiVO<sub>4</sub> and BiVO<sub>4</sub> photoanodes; The inset is the magnification of the blue circle area in (a). XPS detailed spectra over the region of (b) Bi 4f, (c) V 2p and (d) O 1s of NiB/BiVO<sub>4</sub>.

The bare BiVO<sub>4</sub> and NiB/BiVO<sub>4</sub> exhibit Raman bands at 330, 365, and 826 cm<sup>-1</sup> (Figure S4a) which are characteristic of the monoclinic scheelite structure.<sup>7</sup> The single band at 826 cm<sup>-1</sup> is normally attributed to the symmetric V-O stretching mode ( $A_g$  symmetry). The band at 365 and 330 cm<sup>-1</sup> are attributed to the symmetric V-O ( $A_g$ ) bending mode and the antisymmetric V-O ( $B_g$ ) bending mode of the VO<sub>4</sub> units, respectively (Figure S4a, inset). Upon loading of NiB, all of the three bands mentioned above have a slight shift, indicating electron structure of VO<sub>4</sub> tetrahedra are affected. We further compare the XPS spectra of Bi 4f, V 2p and O 1s of BiVO<sub>4</sub> and NiB/BiVO<sub>4</sub>. While the Bi signal and V signal displays no change before and after loading (Figure S4b, 4c), the O 1s spectroscopic signals are affected. The O 1s peaks at 529.5 eV and 532.5 eV have been ascribed to lattice oxygen and non-uniform surface sites (such as dangling oxygen)<sup>8</sup>, respectively (Figure S4d). The 529.5 eV-XPS signal was significantly diminished for NiB-decorated BiVO<sub>4</sub>, partly due to the lack of electron of O element. The shift of O 1s peaks to higher binding energies suggest an effective electron transfer on the surface of NiB/BiVO<sub>4</sub>.



**Figure S5.** (a) Optimizations on the amount of NiB by different concentration of the suspension liquid; (b) Optimizations on the electrodeposition time of Ni-B<sub>i</sub>.



**Figure S6.** Time dependence of the photocurrent density of a NiB/BiVO<sub>4</sub> and BiVO<sub>4</sub> photoanodes, measured at 1.23 V vs RHE in 0.5 M KB<sub>i</sub> (pH 9.2) under continuous 1 sun, AM 1.5G simulated solar irradiation. The electrolyte was not stirred.



Figure S7. XPS detailed spectra over the region of Ni 2p and B 1s of NiB/BiVO<sub>4</sub> after 1 h stability test.



Figure S8. The J-V curves of bare  $BiVO_4$  before and after  $N_2$  annealing.

### References

- 1. T. W. Kim and K.-S. Choi, *Science*, 2014, **343**, 990-994.
- 2. S. K. Choi, W. Choi and H. Park, *Physical Chemistry Chemical Physics*, 2013, **15**, 6499-6507.
- 3. W. A. Brainard and D. R. Wheeler, *Journal of Vacuum Science and Technology*, 1978, **15**, 1800-1805.
- 4. J. A. Schreifels, P. C. Maybury and W. E. Swartz, *Journal of Catalysis*, 1980, **65**, 195-206.
- 5. L. Yanhui, S. Xuping, M. A. Abdullah and H. Yuquan, *Nanotechnology*, 2016, **27**, 12LT01.
- 6. D. He, L. Zhang, D. He, G. Zhou, Y. Lin, Z. Deng, X. Hong, Y. Wu, C. Chen and Y. Li, *Nat Commun*, 2016, **7**, 12362.
- 7. G. Li, D. Zhang and J. C. Yu, *Chemistry of Materials*, 2008, **20**, 3983-3992.
- 8. D. Li, W. Wang, D. Jiang, Y. Zheng and X. Li, *RSC Advances*, 2015, **5**, 14374-14381.