NiFe layered double hydroxide/BiVO4 photoanode based dual-photoelectrode photocatalytic fuel cell for enhancing degradation of azo dye and electricity generation

He, Yun; Zhang, Chengxu; Hu, Jue; Leung, Michael K.H.

Published in:
Energy Procedia

Published: 01/02/2019

Document Version:
Final Published version, also known as Publisher's PDF, Publisher's Final version or Version of Record

License:
CC BY-NC-ND

Publication record in CityU Scholars:
Go to record

Published version (DOI):
10.1016/j.egypro.2019.01.619

Publication details:
NiFe layered double hydroxide/BiVO₄ photoanode based dual-photoelectrode photocatalytic fuel cell for enhancing degradation of azo dye and electricity generation

Yun He¹, Chengxu Zhang¹,², Jue Hu², Michael K.H Leung²,³,∗

¹ Ability R&D Energy Research Centre, School of Energy and Environment, City University of Hong Kong, Hong Kong, China
² The City University of Hong Kong Shenzhen Research Institute, Shenzhen, Guangdong, China
³ The Engineering Laboratory of Advanced Battery and Materials of Yunnan Province, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, China

Abstract

Photocatalytic fuel cell (PFC) has recently emerged as a promising technology for simultaneous solar photocatalytic degradation of organic compounds and recovery of chemical energy stored in the organic compounds. Enhanced PFC using NiFe layered double hydroxide (LDH)/BiVO₄ photoanode and Cu₂O/Cu photocathode is first reported in this paper. The experimental results obtained show that the heterojunction photoanode can extend the spectrum of visible light absorption and effectively increase the photocurrent density. The superior characteristics are attributed to the heterojunction which decreases the interface recombination at the NiFe-LDH/BiVO₄ junction and allows favorable Helmholtz layer potential drop. The short-circuit current, open-circuit voltage and maximum power density of the NiFe-LDH/BiVO₄-Cu₂O/Cu PFC are 0.196 mA cm⁻², 0.647 V and 74 µW cm⁻², respectively, in photocatalytic degradation of methylene blue dye.

© 2019 The Authors. Published by Elsevier Ltd.
This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/)
Peer-review under responsibility of the scientific committee of ICAE2018 – The 10th International Conference on Applied Energy.

Keywords: Ni-Fe layered double hydroxide; Bismuth vanadate; Photocatalytic fuel cell; Heterojunction photoanode; Dual-photoelectrode cell

* Corresponding author. Tel.: +852-3442-4626; fax: +852-3442-0688
E-mail address: mkh.leung@cityu.edu.hk

1. Introduction

Recent research effort on photocatalytic fuel cell (PFC) has led to significant improvement in the PFC system performance. Previous experimental studies covered four main PFC configurations, namely, dual-photoelectrode...
PFC, air-breathing cathode PFC, optofluidic PFC, and rotating-disk PFC. The dual-photoelectrode PFC configuration was an important breakthrough to the boost in solar utilization efficiency for the PFC photoelectrochemical processes. Most dual-photoelectrode PFC systems were designed based on TiO$_2$ and its composite materials as the photoanode, but the activating spectral range was narrow and the composite materials were commonly unstable in water upon illumination. The PFC system could be effectively enhanced by improving the stability and efficiency of the visible light response of the photoanode [1].

Bismuth vanadate (BiVO$_4$) is regarded as a promising photoanode material for the PFC system due to its narrow band gap and excellent stability against photocorrosion [2]. With regard to the bifunctional PFC photoanode, we attempt to develop an eco-friendly, low-cost, and large-scale production method for BiVO$_4$ films and composites. Moreover, layered double hydroxides (LDH) are identified as a class of promising photocatalyst owing to their unique layered structure, tuneable band gaps, intensive photocatalytic activity for PEC, low cost and ease of scale-up [3]. In addition, new photocathodes, such as Cu$_2$O/Cu [4], are proposed in place of the expensive Pt cathode for the development of dual-photoelectrode-based solar responsive PFC system.

In this research, the NiFe-LDH/BiVO$_4$ heterojunction was fabricated for the first time as the photoanode in PFC. The BiVO$_4$ and NiFe-LDH/BiVO$_4$ photoanodes were prepared by a hydrothermal method. With the addition of NiFe-LDH, the heterojunction photoanode could enhance the photogenerated electron-hole separation resulting in better light harvesting. The photoelectrochemical properties were measured and analyzed for the NiFe-LDH/BiVO$_4$ photoanode coupled with a Cu$_2$O/Cu photocathode.

2. Experimental

2.1 Synthesis of NiFe-LDH/BiVO$_4$/FTO photoanode

The precursor for a solvothermal reaction was prepared by dissolving 0.07 mol L$^{-1}$ bismuth nitrate (Bi(NO$_3$)$_3$·5H$_2$O) and 0.07 mol L$^{-1}$ 1-hexadecyl-3-methylimidazolium bromide (CTAB) in ethylene glycol (EG) with vigorous stirring, till the mixture became transparent. FTO glasses were ultra-sonically cleaned using acetone, ethanol and DI water for 30 minutes each. A piece of cleaned FTO glass along with the precursor was placed together in a Teflon-lined stainless steel autoclave. The autoclave was then sealed and kept in a 160 °C oven for 2 hours. After cooling down to room temperature, the precursor BiOBr deposited FTO glass was rinsed with ethanol and DI water, then air dried for further use.

The BiOBr deposited FTO-glass was placed in a Teflon-lined stainless steel autoclave, in which a 0.2 mol L$^{-1}$ Ammonium vanadate (NH$_4$VO$_3$) aqueous solution was added. The autoclave was heated to 180 °C and kept for 24 hours. After cooling down to room temperature, the glass was rinsed using DI water and dried in air and then calcined at 450 °C for 2 hours in a muffle furnace with heating and cooling rates of 2 °C min$^{-1}$.

The NiFe-LDH layer was prepared by microwave hydrothermal method, which was a modified solvothermal method [5]. We first added 2.4 ml of 1.0 mol L$^{-1}$ nickel nitrate (Ni(NO$_3$)$_2$) and 0.48 ml of 1.0 mol L$^{-1}$ ferrous nitrate (Fe(NO$_3$)$_3$) aqueous solution into a mixture of 10 ml N, N-dimethylformamide (DMF) and 8 ml DI water. After sonication for 10 minutes, the solution was transferred to a 40 ml Teflon autoclave for microwave hydrothermal reaction at 120 °C for 60 minutes, followed by another microwave hydrothermal treatment at 160 °C for 30 minutes. The sample was washed with DI water and dried at room temperature.

2.2 Preparation of Cu$_2$O/Cu photocathode

A Cu mesh was immersed into 2.5 mol L$^{-1}$ NaOH aqueous solutions with 0.125 mol L$^{-1}$ ammonium persulphate, which was prepared using deionized water, for 30 minutes. Then the etched Cu mesh was annealed at 450 °C in the air atmosphere for 2 hours with heating and cooling rates of 2 °C min$^{-1}$. The Cu mesh was washed by acetone, ethanol and DI water for 30 minutes each.

2.3 Characterization methods

The crystal phase of the samples was characterized with X-ray diffraction (XRD) patterns by a PANalytical X'
Pert3 Power X-ray Diffractometer. The morphology of the sample was characterized by scanning electron microscopy (SEM) by using an EVO-MA10 (ZEISS). Optical absorption measurements were carried out in a SHIMASZU UV-2600 UV-vis diffuse reflectance spectra (UV-vis DRS). The band gap energy \( (E_g) \) of the samples can be estimated by

\[
\alpha h\nu = A(h\nu - E_g)^n
\]

where \( \alpha, h\nu \) and \( A \) are the absorption coefficient, photon energy and a constant, respectively. The value of \( n \) depends on the type of optical transition of the semiconductor (\( n = 1 \) for a direct transition and \( n = 4 \) for an indirect transition) [6].

### 2.4. Photoelectrochemical measurements

The photoelectrochemical characteristics of the bare BiVO\(_4\) and NiFe-LDH/BiVO\(_4\) were obtained using a three-electrode system with Ag/AgCl electrode as the reference electrode, platinum foil as the auxiliary electrode and the samples as the working electrode. The working electrode potential and current were controlled by a Solartron (ModuLab PhotoEchem). A 300W Xe lamp (Newport, Model 67005) was used for light irradiation with an AM 1.5G filter. The electrolyte was 1 M Na\(_2\)SO\(_3\) and 0.5 M phosphate buffer solution (pH 7) and the reaction solution was 80 mL during the experiment. The PFC was set up using two-electrode configurations according to the previous report [7]. The open-circuit voltage \( (V_{oc}) \), short-circuit current density \( (J_s) \), and current-voltage \( (J-V) \) characteristics of the PFC system were achieved by using the Solartron (ModuLab PhotoEchem) in a two-electrode system in which the photoanode served as the working electrode and the Cu\(_2\)O/Cu photocathode as the counter and reference electrodes. The photoanode and photocathode were immersed in the solution and then illuminated with the same light intensity on both electrodes. All runs were repeated at least three times at ambient temperature to check their reproducibility. For light measurements, the lamp was positioned to provide 100 mW cm\(^{-2}\) irradiation on the film as measured by a thermopile detector (Newport, Model 67005). Degradation of organic compounds was also carried out in a quartz reactor under AM 1.5G (light intensity of 100 mW cm\(^{-2}\)) solar light irradiation. The model organic compound was methylene blue (MB, 10 mg L\(^{-1}\)), and 0.5 M Na\(_2\)SO\(_4\) was used as the supporting electrolyte. The concentration of MB in the reaction solution was determined by monitoring the intensity change of the absorption peak at 664 nm every 30 minutes using the same UV-vis spectrophotometer (SHIMASZU UV-2600).

### 3. Results and discussion

#### 3.1 Characterization and optical measurements of the photoanode

The as-synthesized BiVO\(_4\) has flower-flake morphology (Fig. 1(a)). The NiFe-LDH layer structure (Fig. 1(b)) enhanced the coverage of the film and, thus, photoexcited electron loss could be reduced. Clearly, almost all the X-ray diffraction peaks of the as-prepared samples were indexed as monoclinic BiVO\(_4\) (JCPDS 14-0688) (Fig. 1(c)). The changes in the XRD pattern of BiVO\(_4\) indicated that modified semiconductors and bare BiVO\(_4\) were successfully combined and formed composites [8]. In the XRD pattern of NiFe-LDH/BiVO\(_4\), new crystal peak at 27.9° and emerge peaks at 46.9° and 47.2° could be assigned to NiFe-LDH. In Fig. 1(d), the absorption range of NiFe-LDH/BiVO\(_4\) has significant red-shift indicating a much larger visible light absorption region in comparison with bare BiVO\(_4\). In addition, the extrapolation of the Tauc plot on x-intercepts results in band gap energies of 2.30 eV and 1.85 eV for bare BiVO\(_4\) and NiFe-LDH/BiVO\(_4\), respectively (Fig. 1(e)). As there are a substantial number of photons in the 2.0-2.5 eV region of the solar spectrum, a reduction in bandgap by even 0.1-0.3 eV could yield a significant increase in the photonic efficiency [9]. The results indicate that the NiFe-LDH/BiVO\(_4\) heterojunction not only effectively reduces the bandgap but also increases the majority carrier density and mobility, resulting in enhanced electron-hole separation.

The prepared NiFe-LDH/BiVO\(_4\) heterojunction nanostructures are n-type semiconductors that are connected in series with reversible redox shuttles. The reduction of water to hydrogen and oxidation by reduced redox mediators occur on BiVO\(_4\) while the reduction of oxidized redox mediators and oxidation of water to oxygen take place on NiFe-LDH. Fig. 1(f) shows the mechanism of the band structures of the composite photoanode. The valence band (VB) position and conduction band (CB) positions of NiFe-LDH and BiVO\(_4\) can be calculated by the following...
equations:

\[ E_{vb} = X - E_g + 0.5E_g \]  
\[ E_{cb} = E_{vb} - E_g \]

where \( E_{vb} \) is the valence band gap potential; \( E_{cb} \) is the conduction band gap potential; \( X \) is the electron negativity of the constituent atoms (6.04 eV for BiVO\(_4\)) and \( E_g \) is the energy of free electrons on the hydrogen scale (about 4.5 eV). The bandgap energy values of BiVO\(_4\) and NiFe-LDH are 2.4 eV and 2.2 eV, respectively. According to the above equations, the CB potential of NiFe-LDH is -0.02 eV, which is more negative than that of BiVO\(_4\) (0.46 eV). Therefore, the electrons on the conduction band of NiFe-LDH move to the conduction band of BiVO\(_4\). The holes on the valence band of BiVO\(_4\) are transported to the valence band of NiFe-LDH since the valence band potential of BiVO\(_4\) is more positive than that of NiFe-LDH. Thus, the photogenerated electrons and holes pairs are effectively separated at the heterojunction, and more holes are available to oxidize organic matters.

Fig. 1. SEM images of (a) bare BiVO\(_4\) and (b) NiFe-LDH/BiVO\(_4\); (c) XRD patterns of bare BiVO\(_4\) and NiFe-LDH/BiVO\(_4\); (d) UV-vis absorption spectra of the BiVO\(_4\) and NiFe-LDH/BiVO\(_4\); (e) Determination of indirect interband transition energies of the samples; (f) Mechanism for the composite photoanode process.

Fig. 2. Working principle of the NiFe-LDH/BiVO\(_4\)-Cu\(_2\)O/Cu PFC system.
3.2 Establishment of the PFC

In the NiFe-LDH/BiVO₄-Cu₂O/Cu PFC PFC system (Fig. 2), photoanode is composed of an n-type semiconductor, and the Fermi level (\(E_f\)) is located near the conduction band (CB) edge. On the contrary, the \(E_f\) is located near the valence band (VB) edge of the p-type semiconductor, which is used as photocathode in the PFC system. The photoelectrons travel from the photoanode of higher Fermi level to photocathode of lower Fermi level through an external circuit to generate electricity and then combine with the holes of the photocathode under illumination \[10\]. Finally, the excited holes on the valence band of the photoanode act as strong oxidants to oxidize organic matters in the wastewater. In the proposed PFC system, the Fermi level of the NiFe-LDH/BiVO₄ photoanode is more negative than that of the Cu₂O/Cu photocathode, so this dual photoelectrode PFC system could be driven by interior bias under visible light illumination. The remaining holes on the NiFe-LDH/BiVO₄ photoanode and electrons on the Cu₂O/Cu photocathode could be used for organic matter degradation and energy recovery \[7\].

The operation reactions of the PFC system have been summarized with the following equations:

\[
\text{Photoanode} + h\nu \rightarrow h^+ + e^- \\
\text{H}_2\text{O} + h^+ \rightarrow \cdot\text{OH} + \text{H}^+ \\
\cdot\text{OH} + \text{R} \rightarrow \text{CO}_2 + \text{R}' + \text{H}_2\text{O} \\
\text{O}_2 + 4e^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} (+1.23 \text{ V})
\]

where R and R’ represents organic compounds and oxidized organic compounds, respectively.

![Fig. 3](image)

Fig. 3. (a) Photoelectrochemical response of bare BiVO₄ and NiFe-LDH/BiVO₄ under back illumination of AM 1.5G illumination (electrolyte: 1 M Na₂SO₄ and 0.5 M phosphate buffer solution (pH 7)); (b) \(V_{oc}\) and \(J_{sc}\) of NiFe-LDH/BiVO₄-Pt, Cu₂O/Cu-Pt and NiFe-LDH/BiVO₄-Cu₂O/Cu recorded without external bias (electrolyte: 0.5 M Na₂SO₄); (d) \(J-V\) characteristic curve (solid) and power density curve (dashed) of PFC under AM 1.5G illumination.
organic matters in the wastewater. In the proposed PFC system, the Fermi level of the NiFe-LDH/BiVO₄
be driven by interior bias under visible light illumination. The remaining holes on the NiFe-LDH/BiVO₄ photoanode
illumination [10]. Finally, the excited holes on the valence band of the photoanode act as strong oxidants to oxidize
through an external circuit to generate electricity and then combine with the holes of the photocathode under
system. The photoelectrons travel from the photoanode of higher Fermi level to photocathode of lower Fermi level
semiconductor, and the Fermi level (Ef) located near the valence band (VB) edge of the p-type semiconductor, which is used as photocathode in the PFC

The operation reactions of the PFC system have been summarized with the following equations:

\[
\text{NiFe-LDH} + \text{BiVO}_4 + \text{H}_2\text{O} \rightarrow \text{NiFe-LDH-BiVO}_4 + 2\text{H}^+ + 2e^- + \text{O}_2
\]

\[
\text{Cu}_2\text{O} + \text{Cu} + 2\text{H}^+ + 2e^- \rightarrow 2\text{Cu}^{2+} + \text{H}_2
\]

3.2 Establishment of the PFC

In the NiFe-LDH/BiVO₄-Cu₂O/Cu PFC system (Fig. 2), photoanode is composed of an n-type
substrate and 0.5 M Na₂SO₄ as the supporting electrolyte are plotted in Fig. 3(d). The open-circuit voltage, short-
characteristic curve (solid) and power density curve (dashed) of PFC under
AM 1.5G illumination.

As shown in Fig. 3(b), the open-circuit voltages (Voc) of the two photoelectrodes have opposite polarities. Thus, the photoanode provides a negative bias for the photocathode and the photocathode provides a positive bias for photoanode. As a result, the dual-photoelectrode PFC system can be driven easily by the interior bias between the two photoelectrodes. As the light is switched on, the short-circuit photocurrent density (Jsc) of the PFC system climbs up to 300 μA cm⁻² and gradually decreases to a steady value of 100 μA cm⁻² (Fig. 3(c)). In contrast, for a single photoelectrode system, Jsc is trivial since the unfavourable band voltage cannot reduce or oxidize water [7]. The higher photocurrent and better electrical conductivity resulted in achievement of higher Jsc for the PFC. The measurements reveal that the proposed dual-photoelectrode PFC enables efficient light harvesting and faster charge transport, resulting in Voc and Jsc that is higher than previous reports [11, 12].

The J-V curve and power density curve of the NiFe-LDH/BiVO₄ and Cu₂O/Cu PFC system using glucose as the substrate and 0.5 M Na₂SO₄ as the supporting electrolyte are plotted in Fig. 3(d). The open-circuit voltage, short-circuit current, maximum power density and fill factor (FF) of the dual-photoelectrode PFC system are 0.647 V, 0.196 mA cm⁻², 74 μW cm⁻² and 58.4%. The fill factor is an important value to examine the characteristics of the PFC. The results indicate that the PFC system is applicable to decompose organic matters and generate electricity using organic substrate as fuel. As shown in Table 1, the PFC performance varies with the substrate of the different molecular structure due to the variation in degradation rate [7, 13]. The results indicate that the PFC system is applicable to decompose organic matters and generate electricity using organic substrate as fuel.

![Fig. 4. (a) Degradation of MB (10 ppm) in NiFe-LDH/BiVO₄-Cu₂O/Cu system, and (b) the corresponding kinetics curves.](image-url)
3.3 Degradation of methylene blue in dual-photoelectrode PFC

Figure 4 presents the degradation of methylene blue (MB) by the NiFe-LDH/BiVO₄-Cu₂O/Cu PFC system. After 6 hours of irradiation, 81% of MB was effectively removed. In the photocatalytic degradation process, MB was first adsorbed by the photoanode [14]. As shown in Fig. 4(a), the dark adsorbed of the MB dye solution reached a stable stage after 30 minutes. Subsequent photocatalytic reaction generated electron-hole pairs and they were separated for distinct functions. The photogenerated holes oxidized surface adsorbed hydroxyl groups and water to generate -OH radicals as active ingredients for decomposition of the MB into CO₂ and H₂O [15]. Consequently, the recombination of the photogenerated electron and hole was suppressed by the self-generated bias. This photocatalytic oxidation of organic pollutants followed first-order kinetics [24] and the equation can be expressed as follows:

\[
\ln \left( \frac{C_0}{C} \right) = kt
\]

where k is the photocatalytic reaction rate constant [16], and \( C_0 \) and \( C \) are the dye concentrations in solution at times 0 and \( t \), respectively. The k value of the NiFe-LDH/BiVO₄-Cu₂O/Cu PFC system could be calculated from plots of \( \ln(C_0/C) \) vs \( t \), and the results are given in Fig. 4(b). It can be seen that the k value of PFC system was 0.0044 min⁻¹. The results prove that there was a synergistic effect between the two photoelectrodes because the electrons were preferentially stored on the photocathode and thus enhanced separation of photogenerated electron and hole pairs and production of holes on the photoanode for pollutant degradation [1].

4. Conclusions

In summary, a solar-light responsive dual-photoelectrode PFC system using a highly efficient NiFe-LDH/BiVO₄/FTO heterojunction photoanode and Cu₂O/Cu photocathode is reported. The dual-photoelectrode PFC system has mismatched Fermi levels of each photoelectrode and produces an interior bias to migrate the electrons of the NiFe-LDH/BiVO₄ photoanode to combine with the holes of the photocathode through an external circuit. The hole generated at the photoanode can decompose organic matters. The new dual-photoelectrode PFC enhances the performance of PFC for simultaneous organic matter degradation and energy generation.

Acknowledgments

This research was financially supported by the Hong Kong General Research Fund (GRF CityU 11207414), CityU Strategic Research Grant (Project 7004476), Shenzhen Knowledge Innovation Program (Basic Research, JCYJ20160428154632404) and the Hong Kong Scholars Program and China Postdoctoral Science Foundation Funded Project (No. 2015M582021).

Reference

organic pollutants followed first-order kinetics [24] and the equation can be expressed as follows:

radicals as active ingredients for decomposition of the MB into \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) [15]. Consequently, the recombination of the photogenerated electron and hole was suppressed by the self-generated bias. This photocatalytic oxidation of the NiFe-LDH/BiVO4 photoanode to combine with the holes of the photocathode through an external circuit. The
dual-photoelectrode PFC system has mismatched Fermi levels of each photoelectrode and produces an interior bias to migrate the electrons of the NiFe-LDH/BiVO4/Cu2O/Cu PFC system for simultaneous wastewater treatment and electricity generation, J. Hazard. Mater. 311 (2016) 51-62.


G. Tan, L. Zhang, H. Ren, S. Wei, J. Huang, A. Xia, Effects of pH on the hierarchical structures and photocatalytic performance of BiVO4 powders prepared via the microwave hydrothermal method, ACS Appl. Mater. Inter. 5 (2013) 5186-5193..

