

Communication

# NiFeO<sub>x</sub> co-catalyzed BiVO<sub>4</sub> photoanode for improved photoelectrochemical water splitting

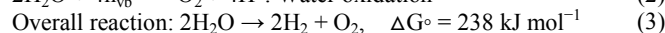
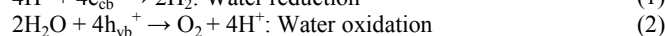
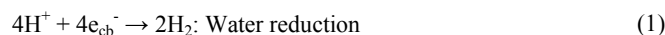
Jin Hyun Kim<sup>a</sup>, Hyun Joon Kang<sup>a</sup>, Ganesan Magesh<sup>b</sup> and Jae Sung Lee<sup>b\*</sup>

<sup>a</sup>Pohang University of Science and Technology (POSTECH), Pohang, 790-784, Republic of Korea

<sup>b</sup>Ulsan National Institute of Science and Technology (UNIST), Ulsan, 689-798 Republic of Korea

**ABSTRACT:** PEC (photoelectrochemical) water splitting for O<sub>2</sub>/H<sub>2</sub> production is one of the promising but difficult way to utilize solar energy. Among photocatalytic materials for PEC water oxidation, BiVO<sub>4</sub> (E<sub>g</sub> = 2.4 eV) has been recently intensively studied since it has various advantageous properties. But its maximum efficiency has not been realized owing to kinetic factors – slow water oxidation at surface & insufficient stability. These problems can be simultaneously solved by application of oxygen evolution catalyst (OEC) such as CoO<sub>x</sub>, Co-Pi, IrO<sub>x</sub> etc. Herein we report the first successful application of NiFeO<sub>x</sub> OEC on BiVO<sub>4</sub>, showing good performance compared to other effective OEC applied on BiVO<sub>4</sub> under basic conditions. The enhanced activity of OEC loaded BiVO<sub>4</sub> has been supported by the surface charge separation efficiency and electrochemical impedance studies.

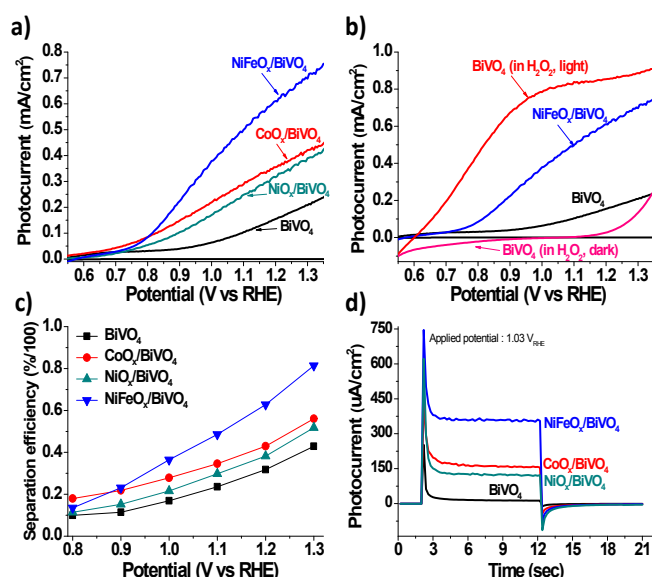
Solar energy utilization has been considered as the ideal way to cope with the energy and environmental crisis<sup>1-3</sup>. Among technologies for this, PEC (photoelectrochemical) water splitting and CO<sub>2</sub> reduction has been studied as one of the interesting but challenging technologies to realize because of many reasons. Owing to its ability to produce chemical fuel (H<sub>2</sub>, CH<sub>4</sub>, CO, etc.) directly instead of electricity using solar energy, PEC cell can function very similar with plants and its process is also called as artificial photosynthesis<sup>4</sup>. The photoelectrochemical water splitting involves the following reactions, equations (1)-(3)<sup>5</sup>.



The performance of the PEC system depends on the individual components used for the system. Photoelectrochemical water oxidation is an important part in the realization of the artificial photosynthesis. Herein, we studied photoanode – electrocatalyst counter electrode system for water oxidation reaction.

BiVO<sub>4</sub> (Bismuth vanadate) is n-type semiconductor, having modest 2.4 eV direct energy band gap and is stable in neutral and basic pH<sup>1,6</sup>. BiVO<sub>4</sub> has been recently intensively studied as photoanode material, and shows one of the highest PEC performance known for photoanode. But just like most of photoanode materials, BiVO<sub>4</sub> also suffers two major drawbacks – poor water oxidation kinetics and low surface

charge separation. Along with that, stability is also issue for long term application. Poor surface charge separation can be mitigated by surface modifications and application of OEC (water oxidation catalyst) is one of the most common and effective way to promote water oxidation kinetics and stability. Since the discovery of the functionality of Co-Pi to improve surface charge separation, many species of OEC (Ag<sup>+</sup> treatment, Pt, CoO<sub>x</sub>, IrO<sub>x</sub>, RhO<sub>x</sub>, NiO<sub>x</sub>, RuO<sub>x</sub>, MnO<sub>x</sub>, PdO<sub>x</sub>, FeOOH, NiOOH, Co-Pi, Co-Bi, Ni-Bi etc) have been found to show good water oxidation catalytic performance<sup>1,7,8</sup>. For the first time, we report NiFeO<sub>x</sub> as an efficient electrocatalyst for BiVO<sub>4</sub>, which outperformed CoO<sub>x</sub> and NiO<sub>x</sub>. NiFeO<sub>x</sub>, CoFeO<sub>x</sub>, NiCeO<sub>x</sub> are known to have very good OEC property and have low onset and good stability in basic pH<sup>9</sup>. Since BiVO<sub>4</sub> has modest stability in basic condition, these OECs are good candidates for BiVO<sub>4</sub>. BiVO<sub>4</sub> photoanode was prepared by a metal organic decomposition (MOD) method we reported previously<sup>1,3,10,11</sup>. Deposition of CoO<sub>x</sub>, NiO<sub>x</sub> and NiFeO<sub>x</sub> co-catalysts were made by spin coating the precursor solution on the BiVO<sub>4</sub> film. Experimental details are described in supplementary information.



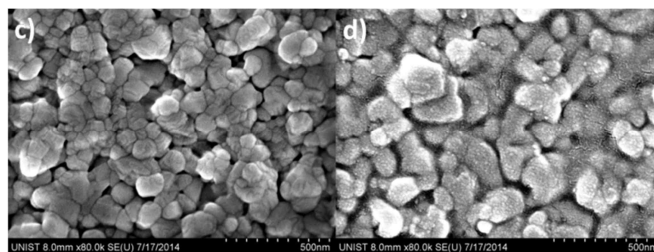
**Figure 1.** a) I-V curve of BiVO<sub>4</sub> and surface modified BiVO<sub>4</sub>, b) I-V curve of BiVO<sub>4</sub> in 0.5 ml H<sub>2</sub>O<sub>2</sub> + 100 ml 1 M NaOH, c) surface charge separation efficiency for BiVO<sub>4</sub> and surface modified BiVO<sub>4</sub>, d) photocurrent at constant potential (1.03 V<sub>RHE</sub>) of BiVO<sub>4</sub> and surface modified BiVO<sub>4</sub>. (Measurement condition: 1 sun, 1M NaOH, 20 mV/sec, back illumination)

\*To whom correspondence should be addressed.  
E-mail: jlee1234@unist.ac.kr

Figure 1 shows I-V curve of BiVO<sub>4</sub> with surface modifications. Bare BiVO<sub>4</sub> showed 0.15 mA/cm<sup>2</sup> while CoO<sub>x</sub> (0.33 mA/cm<sup>2</sup>), NiO<sub>x</sub> (0.29 mA/cm<sup>2</sup>) and NiFeO<sub>x</sub> (0.6 mA/cm<sup>2</sup>)/BiVO<sub>4</sub> showed much greater photocurrent at 1.23 V<sub>RHE</sub>. Calculation of η<sub>surf</sub> (surface charge separation efficiency) using photocurrent comparison of water oxidation and H<sub>2</sub>O<sub>2</sub> oxidation showed that PEC performance agrees with surface charge separation efficiency (Figure 1b & c). NiFeO<sub>x</sub> showed 60% of efficiency at 1.23 V<sub>RHE</sub> while bare BiVO<sub>4</sub> showed only 25%. This is modest efficiency for metal oxide but not better than other OEC with metal-ligand (ex: Co-Pi, FeOOH, near 100% of η<sub>surf</sub>)<sup>3, 7</sup>. Calculation of η<sub>surf</sub> was made according to the equation (4). Detailed description of the surface charge separation efficiency (η<sub>surf</sub>) can be found in earlier report or elsewhere<sup>1, 3, 7</sup>.

$$\eta_{surf} = J_{PEC} / J_{H2O2} \quad (4)$$

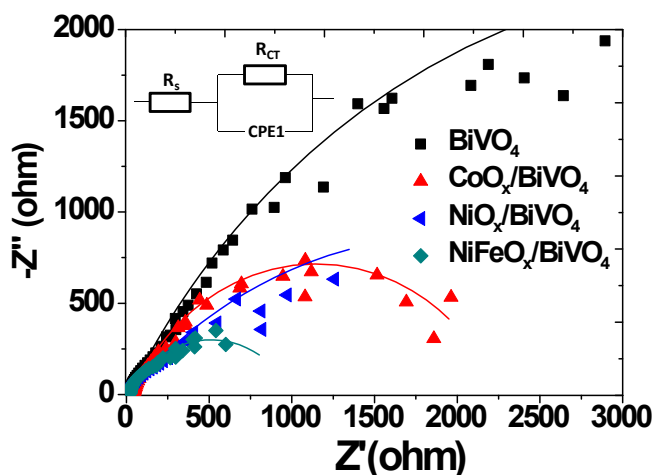
Recent report of ferrihydrite/Ta<sub>3</sub>N<sub>5</sub> showed that capacitive behavior of surface modification and electrocatalyst might be the key factor to improve performance of photoanode. Capacitance indicates charging via hole intake which is necessary for later discharging via hole transfer to water (hole going through semiconductor|electrocatalyst|electrolyte interface)<sup>12</sup>. Figure 1d shows photocurrent at constant potential where the photocurrent reached a peak upon light illumination, which later decreased rapidly and stabilized. The photocurrent turned cathodic when the irradiation was stopped and then slowly reached zero. This suggests that the surface is charged with holes during illumination and passed backward when illumination stopped. The released charge was calculated from the negative current and the values are BiVO<sub>4</sub> (0.339 mC), CoO<sub>x</sub>/BiVO<sub>4</sub> (1.21 mC), NiO<sub>x</sub>/BiVO<sub>4</sub> (2.80 mC) and NiFeO<sub>x</sub>/BiVO<sub>4</sub> (1.983 mC). All electrocatalyst loaded BiVO<sub>4</sub> showed larger capacitive behavior than bare BiVO<sub>4</sub> suggesting that electrocatalysts have hole charging ability before hole transfer through water. But the amount of charging is not proportional to PEC performance since capacitance of NiFeO<sub>x</sub> is not the highest. This indicates that hole charging property is necessary for hole/electron separation at semiconductor|electrocatalyst interface but discharging property is also important at electrocatalyst|electrolyte interface. Indeed, from other results related to Co-Pi loaded on BiVO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, Co-Pi had charging and discharging property but it did not show large capacitive behavior at constant potential mode. This means Co-Pi can be charged but also discharged fast enough to leave minor amount of residual holes during their transfer, and hence doesn't undergo severe kinetic bottleneck<sup>13, 14</sup>.



**Figure 2.** a) Diffuse reflectance UV-vis absorbance, b) XRD patterns (● - peaks of BiVO<sub>4</sub>) and SEM images of c) bare BiVO<sub>4</sub> and d) NiFeO<sub>x</sub>/BiVO<sub>4</sub>. Inset at a) is picture of BiVO<sub>4</sub> and NiFeO<sub>x</sub>/BiVO<sub>4</sub>.

UV-vis absorbance spectrum showed typical light absorption of BiVO<sub>4</sub> with threshold of ~520 nm (Figure 2a). Modification with NiFeO<sub>x</sub> showed little difference in absorption as loading amount was rather small. XRD patterns (Figure 2b) also showed pure monoclinic BiVO<sub>4</sub> phase but no obvious signal of NiFeO<sub>x</sub>. Similar phenomena is observed in our earlier reports and various other works as loaded electrocatalyst is often amorphous and the quantity is very small<sup>1, 10, 15</sup>. SEM image (Figure 2c) showed typical morphology of bare BiVO<sub>4</sub>. Deposition of NiFeO<sub>x</sub> (Figure 2d) showed small agglomerated particles covering the entire surface of BiVO<sub>4</sub>, suggesting that some small amount of Ni+Fe oxide is loaded. Exact composition is not yet known but it is in progress using XPS and other methods.

To further identify effect of electrocatalysts, EIS (Electrochemical impedance spectroscopy) was used. For fitting, simple Randles equivalent circuit model was introduced containing R<sub>s</sub> for electrolyte resistance, R<sub>CT</sub> is resistance at electrolyte|semiconductor interface, and CPE as capacitance of photoanode (Figure 3 inset). EIS results (Figure 3) showed a R<sub>CT</sub> of 7601 Ω, 2220 Ω, 3360 Ω and 991 Ω for BiVO<sub>4</sub>, CoO<sub>x</sub>/BiVO<sub>4</sub>, NiO<sub>x</sub>/BiVO<sub>4</sub> and NiFeO<sub>x</sub>/BiVO<sub>4</sub> respectively. These results show that R<sub>CT</sub> decreased upon loading the electrocatalysts and the lower the R<sub>CT</sub> the higher the photocurrent, with NiFeO<sub>x</sub>/BiVO<sub>4</sub> showing the lowest R<sub>CT</sub> and the highest photocurrent. This shows that the surface charge transfer was boosted by the electrocatalysts.



**Figure 3.** EIS (symbols: measured, line: fitted) of BiVO<sub>4</sub> and surface modified BiVO<sub>4</sub>. Inset is equivalent circuit used for fitting. (Measurement condition: 1 sun, 1 M NaOH, 20 mV/sec, back illumination, 1.23 V<sub>RHE</sub>)  
In summary, we applied NiFeO<sub>x</sub> OEC on BiVO<sub>4</sub> and observed improved PEC performance for water oxidation.

Characterization indicates that NiFeO<sub>x</sub> suppresses surface recombination and improves surface charges transfer resistance. Capacitance behavior was increased by introduction of electrocatalysts, but not necessarily had proportional relationship. This report shows that NiFeO<sub>x</sub> is good choice as OEC for photoanodes under basic conditions.

**KEYWORDS:** OEC, BiVO<sub>4</sub>, PEC

Received June 1, 2014; Accepted June 10, 2014

#### ACKNOWLEDGEMENT

This work was supported by grants from the BK+ Program (10Z20130011057) and Basic Science Research Program (No. 2012-017247) and the Korea Center for Artificial Photosynthesis (KCAP) funded by the National Research Foundation of Korea (No. 2012M1A2A2671779).

#### REFERENCES AND NOTES

1. J. H. Kim, J. W. Jang, H. J. Kang, G. Magesh, J. Y. Kim, J. H. Kim, J. Lee and J. S. Lee, *Journal of Catalysis*, 2014, **317**, 126-134.
2. A. Fujishima and K. Honda, *Nature*, 1972, **238**, 1.
3. D. K. Zhong, S. Choi and D. R. Gamelin, *J. Am. Chem. Soc.*, 2011, **133**, 18370-18377.
4. G. Magesh, E. S. Kim, H. J. Kang, M. Banu, J. Y. Kim, J. H. Kim and J. S. Lee, *J. Mater. Chem. A*, 2014, **2**, 2044-2049.
5. A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253-278.
6. M. F. Lichterman, M. R. Shaner, S. G. Handler, B. S. Brunschwig, H. B. Gray, N. S. Lewis and J. M. Spurgeon, *J. Phys. Chem. Lett.*, 2013, **4**, 4188-4191.
7. T. W. Kim and K.-S. Choi, *Science*, 2014, **343**, 990-994.
8. T. Hisatomi, J. Kubota and K. Domen, *Chem. Soc. Rev.*, 2014.
9. L. Trotochaud, T. J. Mills and S. W. Boettcher, *J. Phys. Chem. Lett.*, 2013, **4**, 931-935.
10. S. K. Pilli, T. E. Furtak, L. D. Brown, T. G. Deutsch, J. A. Turner and A. M. Herring, *Energy Environ. Sci.*, 2011, **4**, 5028-5034.
11. K. Sayama, A. Nomura, T. Arai, T. Sugita, R. Abe, M. Yanagida, T. Oi, Y. Iwasaki, Y. Abe and H. Sugihara, *J. Phys. Chem. B*, 2006, **110**, 11352-11360.
12. G. Liu, J. Shi, F. Zhang, Z. Chen, J. Han, C. Ding, S. Chen, Z. Wang, H. Han and C. Li, *Angew. Chem. Int.*, 2014, **53**, 7295-7299.
13. M. Dincă, Y. Surendranath and D. G. Nocera, *PNAS*, 2010, **107**, 10337-10341.
14. D. K. Zhong and D. R. Gamelin, *J. Am. Chem. Soc.*, 2010, **132**, 4202-4207.
15. W. Luo, Z. Yang, Z. Li, J. Zhang, J. Liu, Z. Zhao, Z. Wang, S. Yan, T. Yu and Z. Zou, *Energy Environ. Sci.*, 2011, **4**, 4046-4051.