DOI: 10.1002/ ((please add manuscript number))

Article type: Full Paper

Vastly Enhanced BiVO₄ Photocatalytic OER Performance by NiCoO₂ as Cocatalyst

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Keywords: (BiVO₄, photoelectrocatalyst, Ni-Co oxides, cocatalyst, oxygen evolution reaction)

Abstract: Here, a simple and efficient preparation of NiCoO₂ nanoparticle modified nanoporous bismuth vanadate (BiVO₄) thin film and its application to photoelectrocatalytic (PEC) oxygen evolution reaction (OER) is demonstrated. The role of NiCoO₂ in the composite electrode (BiVO₄/NiCoO₂) is two folds: OER cocatalyst and band structure adjustment. The dual-role on single-component NiCoO₂ improves surface reaction kinetics for PEC OER and enhances charge separation on the surface BiVO₄ simultaneously, which we believe to be a determining factor for the unprecedentedly PEC OER performance by BiVO₄/NiCoO₂. The photocurrent density of 3.6 mA cm⁻² at 1.23 V *vs* RHE in 0.1 M potassium phosphate buffered (pH=7) electrolyte by BiVO₄/NiCoO₂ is three times that of BiVO₄ and significantly higher than the majority of literature values. The BiVO₄/NiCoO₂ delivers charge separation efficiency (η_{surface}) of ~ 72 % as compared to 23% for BiVO₄ at 1.23 V *vs* RHE, which demonstrates convincing role of NiCoO₂ in the composite electrode. Both the excellent photocurrent density and great operational stability displayed by the BiVO₄/NiCoO₂ makes it a promising photocatalytic material for practical applications.

1. Introduction

Water splitting by photo(electro)catalysis (PEC) is believed to be a unique way to generate chemical fuels by solar energy, which is abundantly and freely available and is considered the most renewable energy source.^[1, 2, 3] Not surprisingly, water oxidation half reaction (*i.e.* oxygen evolution reaction, OER) in water splitting gains considerable more attention than the other half water reduction reaction (*i.e.* hydrogen evolution reaction, HER) as the OER involves kinetically unfavourable four electron transfer to produce one O₂ molecule as opposed to two electron transfer in the HER. OER is a generally limiting factor in many full water splitting processes.^[4] Among the popular metal-oxide based semiconductors being used as photoanodes for PEC OER (TiO₂,^[5] Fe₂O₃,^[6] WO₃,^[7] bismuth vanadate (BiVO₄)), BiVO₄ has distinguished itself due to its visible-light absorption capability and its suitable band edge positions which comfortably accommodate oxygen generation potential.^[8] The narrow band gap of BiVO₄ (~2.4 eV) facilitates the light absorption up to 11 % of the solar spectrum, moderately higher than ~4% by TiO₂.^[9] However, the inherently poor hole transfer at BiVO₄ and water interface leads to its sluggish water oxidation kinetics, promotes electron-hole recombination, and thus results in its unsatisfactory overall quantum efficiency.^[10] The conventional strategies to overcome these limitations of BiVO₄ are morphology control^[11] and doping with foreign atoms (metals^[12,13] and non-metals^[14,15]). However, getting popular nowadays is modification of BiVO₄ with OER electrocatalyst,^[16, 17] which are referred to as cocatalyst in photocatalysis. The roles of cocatalyst in photocatalytic OER are as follows: (1) cocatalyst lowers activation overpotential in photocatalytic OER by serving as favorable active site for O₂ generation;^[18] (2) cocatalyst provides suitable trapping sites for the photo generated charges and thus improves electron-hole separation; (3) suitable cocatalyst, by selectively and timely removing the photo generated charges, particularly the holes, decreases the photo corrosion, particularly oxidation of some unstable photocatalysts, for example MoS₂

for Cu_2O ,^[19] cobalt phosphate (Co-Pi) for CdS .^[20] Thus rational selection of an appropriate electrocatalyst to serve as a performing cocatalyst in photocatalytic OER can be vital for an effective water splitting where OER half reaction is the limiting factor.

In literature, there exists a wide range of electrocatalysts (e.g., FeOOH ,^[21] FeOOH/NiOOH ,^[22] Co_3O_4 ,^[23] layered double hydroxide^[24], FeSe_2 ^[25]) (Table S1) which has been investigated as cocatalysts along with BiVO_4 in photocatalytic OER. In particular, Co-Pi, first reported by Nocera *et al* in 2008, is considered as the first generation of photocatalytic OER cocatalyst for BiVO_4 .^[26,27,28] However, the dissolution of Co-Pi in phosphate buffer (pH-7) seriously dampers its application perspective.^[29] Modification of BiVO_4 with individual layers of NiO and Co_3O_4 has recently shown improved photocatalytic OER performance.^[29] Nowadays, multi-metal oxides (e.g., binary/tertiary metal oxides) are being intensively investigated in various fields. More specially, nickel-cobalt (Ni-Co) oxides have recently gained considerable amount of attention in energy applications, including supercapacitors,^[30] Li-ion battery,^[31] OER^[32] and photocatalysis.^[33] In fact, Ni-Co oxides provide rich redox chemistry compared to the individual component oxides of NiO and CoO_x arguably due to synergistic effect among atomically adjacent Ni and Co atoms^[34] and nano-sized Ni-Co oxides are believed to provide rich electrochemical active surface area toward desired reactions.^[35] Moreover, Ni-Co oxides have a hole conductivity (300 S cm^{-1}) almost two orders of magnitude higher than either NiO or Co_3O_4 and they have better chemical stability than the CoO_x in basic medium.^[36, 37] All these attractive properties promise Ni-Co oxides potentially effective cocatalysts for BiVO_4 based photocatalytic OER.

Herein in this work, NiCoO_2 nanoparticles are synthesized and are modified onto nanoporous BiVO_4 thin film. The structure of nanoporous thin film is rationally chosen for BiVO_4 in this study given the short hole diffusion length of BiVO_4 and more importantly the mismatch between its hole diffusion length and light penetration depth and the chosen structure allows for the hole diffusion and light absorption occurring on different axes. The role of NiCoO_2 in

the composite electrode is two folds: OER cocatalyst and band structure adjustment, both contributing to facilitated electron-hole separation photogenerated by BiVO_4 . The NiCoO_2 modified BiVO_4 exhibits vastly improved photocatalytic OER performance relative to pure and unmodified BiVO_4 . The maximum photocurrent density of the NiCoO_2 modified BiVO_4 in this study is 2.0 mA cm^{-2} at a bias at 0.6 V and 3.6 mA cm^{-2} at 1.23 V vs. RHE in 0.1 M potassium phosphate buffer (KPi) ($\text{pH}=7$), which makes it among the state-of-the-art materials in photocatalytic OER. It is our belief that the design concept of multiple-role on single-component cocatalyst provides significant insight into further improvement of PEC performance by many commonly investigated photocatalysts.

Scheme 1. (a-e) Scheme of the synthesis process of the $\text{BiVO}_4/\text{NiCoO}_2$ composite for photocatalytic OER.

2. Results and Discussions

Scheme 1 presents the synthetic route of $\text{BiVO}_4/\text{NiCoO}_2$ composite in this study. In more details, the porous BiVO_4 film was synthesized through electrochemical deposition of bismuth (III) oxyiodide (BiOI) onto an fluorine doped tin oxide plate (FTO) substrate by p-

benzoquinone reduction, followed by annealing with vanadium precursors (*i.e.*, vanadium acetyl acetonate). The detailed preparation procedure is given in the experimental method section in electronic supporting information (ESI). Figure 1a and b present the scanning electron microscopy (SEM) images of surface morphology of the as-synthesized BiOI and BiVO₄ on FTO, respectively. As can be seen, the synthesized BiOI is comprised of vertically placed 2-dimensional (2D) plate like structures (Figure 1a and Figure S2). After annealing with vanadium salts, the BiOI is completely converted to BiVO₄ film with nanoporous cavities on its surface [22] (Figure 1b and Figure S3).

Figure 1. SEM images of (a) BiOI, (b) BiVO₄, (c-d) HRTEM images BiVO₄, (e) fringe pattern image which shows a d-spacing ($d=0.36$ nm) corresponding to the (200) plane of BiVO₄. (f) HAADF STEM image and (g) EELS elemental mapping of the BiVO₄.

Figure 1c and 1d are the high resolution transmission electron microscopy (HRTEM) images of the BiVO₄, indicating its high crystallinity. The inter layer distance (d-spacing) calculated from the lattice fringes pattern in Figure 1e is 0.36 nm, which corresponds well to the d-spacing value of (200) plane of BiVO₄.^[38] The high angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) image of the BiVO₄ (Figure 1f and Figure S4a) and the *in situ* energy dispersive X-Ray spectroscopy (EDS) spectrum (Figure S4b) all validate the existence of bismuth (Bi), vanadium (V) and oxygen (O) atoms in the synthesized BiVO₄ nanostructures. Moreover, the elemental mapping acquired in electron energy loss spectroscopy (EELS) spectrum (Figure 1g) elucidates the even distribution of aforementioned atoms in the BiVO₄ nanostructures. The synthesis method allows for control over the thickness of the synthesized nanoporous BiVO₄ film by tuning electrodeposition time of BiOI in the first step. The optimum deposition time is found to be 300 s and the thickness of the resulting BiVO₄ film is 600 nm $\pm$ 50 nm (Figure S5).

Figure 2. (a-b) TEM images of NiCoO₂ in different magnifications; (c) HAADF-STEM image of NiCoO₂, (d) fringes pattern of NiCoO₂ in Figure 2b which shows a d-spacing value of 0.24 nm corresponding to the (311) plane of NiCoO₂, (d) HAADF-STEM image of NiCoO₂, (e) EELS spectrum of NiCoO₂ with background correction and (f) its elemental mapping (red-Ni, green- Co and blue-oxygen).

On the other hand, the NiCoO₂ nanoparticles in this study are synthesized by hydrothermal method. Briefly, nickel acetate and cobalt acetate are dissolved in ethanol in presence of ammonia and treated at 120 °C for 12 h. The resulted precipitates are subsequently annealed at 450 °C for 2 hours. The HRTEM images of the NiCoO₂ nanoparticles show their generally irregular shape (**Figure 2a**) and indicate their high crystallinity (Figure 2b and S6). The calculated d-spacing is 0.24 nm which corresponds to the (311) planes of NiCoO₂, confirming the formation of NiCoO₂ (Figure 2d). The HAADF-STEM images (Figure 2c and S7) further corroborate nano size range of the synthesized NiCoO₂. The EELS spectrum (Figure 2e) and elemental mapping show the atomically uniform distribution of Ni, Co and O (Figure 2f and Figure S7) in the nanoparticles. The above results all together confirm a successful synthesis of binary NiCoO₂, instead of separate NiO and CoO_x.

Figure 3. (a-b) SEM images of BiVO₄/NiCoO₂ in different magnifications. (c) TEM image of BiVO₄/NiCoO₂, (d) HAADF-STEM (dark field) image of BiVO₄/NiCoO₂, (e) and (f) respective EELS mapping and spectrum of BiVO₄/NiCoO₂ magnified in Figure 3d under dark condition. In Figure 3e, the interface between BiVO₄ and NiCoO₂ is represented by yellow dashed line.

The synthesized NiCoO₂ nanoparticles are then carefully deposited onto the pre-formed nanoporous BiVO₄ film by electrodeposition method and the composite material is denoted as BiVO₄/NiCoO₂. All of the SEM (**Figure 3a** and 3b) and TEM images (Figure 3c and 3d) of the BiVO₄/NiCoO₂ show uniform distribution of the NiCoO₂ nanoparticles on the surface of and across the entire profile of the BiVO₄ film. The high magnification image at the interface of BiVO₄/NiCoO₂ reveals the uniform distribution of nano sized (Figure S9) particles on the surface of BiVO₄. The SEM mapping (Figure S10) and EELS mapping (Figure 3e) along with its spectrum (Figure 3f) further validate the elemental composition of BiVO₄/NiCoO₂ and uniform distribution of the NiCoO₂ on BiVO₄ surface. Most importantly, a continuous interface between BiVO₄ and NiCoO₂ could be clearly identified from Figure 3e (marked with yellow dashed line), which can greatly enhance the rate of movement of holes coming from BiVO₄ to NiCoO₂ during PEC, reduce electron-hole recombination, and

ultimately lead to improved photocatalytic OER performance. Moreover, the HRTEM image (Figure S11) measured in dark field pronounces the higher crystallinity of NiCoO₂ at the interface of BiVO₄/NiCoO₂ and shows the retention of the higher crystalline feature after annealing with BiVO₄. X-ray diffraction (XRD) patterns show a high crystallinity of BiVO₄ with monoclinic structure (JCPDS No 14-0688) (Figure S12a).^[23] Although the XRD patterns of BiVO₄/NiCoO₂ composite do not show the characteristic peaks of NiCoO₂ due to the nano sized particles, the existence of NiCoO₂ in the composite can be confirmed with the SEM and HRTEM analyses (Figure 3). NiO (JCPDS No: 47-1049) and Co₃O₄ (JCPDS No: 43-1003)^[39, 40] are also synthesized in this study (Figure S12b) and are to be used as OER cocatalysts for the purpose of comparison.

Moreover, XPS analysis is carried out to get additional insights about interaction between BiVO₄ and NiCoO₂ and the results are represented in Figure 4. The spectrum of BiVO₄ in Figure 4a provides an indication for the presence of Bi, V and O. The binding energies of Bi 4f_{7/2} (158.5 eV), V 2p_{3/2} (516.3 eV) and O 1s (529.3 eV) in BiVO₄ are well in accordance with literature reports.^[41] In Figure 4b, the peaks at 158.6 and 163.8 eV are found to be splitting signals of Bi 4f_{7/2} and Bi 4f_{5/2}, respectively, which are characteristics of Bi³⁺. Similarly, the peaks at 524.0 (V 2p_{1/2}) and 516.3 eV (V 2p_{3/2}) in Figure 4c are the splitting signals of V 2p, assignable to the surface V⁵⁺ species. Moreover, the major peaks at 529.3 and 531.1 eV in O 1s spectrum (Figure 4d) are assigned to O bonded within a regular oxide crystal (O²⁻) in BiVO₄ and that of adsorbed hydroxyl groups on the surface, respectively.^[42]

Figure 4. (a) Large scan XPS spectrum of BiVO_4 and $\text{BiVO}_4/\text{NiCoO}_2$, (b) comparison of Bi 4f spectra, (c) comparison of V 2p spectra, (d) comparison of O 1s spectra, (e) deconvoluted spectra of Co 2p and (f) Ni 2p of NiCoO_2 .

In fact, the XPS spectra of Bi (Figure 4b), V (Figure 4c) and O (Figure 4d) in $\text{BiVO}_4/\text{NiCoO}_2$ are different from those of BiVO_4 , with a significant shift towards higher binding energies in Bi 4f, V 2p, and O 1s peaks in the composite sample. This indicates the stronger interaction of NiCoO_2 with BiVO_4 . The higher binding energy shift is presumably due to the doping of metal ions into the VO_4^{3-} tetrahedral sites of BiVO_4 ,^[43] which is supported by Raman spectroscopy result (Figure S13).^[44]

Upon confirming successful formation of a uniform interface between BiVO_4 and NiCoO_2 , efforts are then made to investigate the performances of BiVO_4 and its composite ($\text{BiVO}_4/\text{NiCoO}_2$, BiVO_4/NiO , and $\text{BiVO}_4/\text{Co}_3\text{O}_4$) towards PEC OER. In all cases, AM 1.5G simulated solar light (one sun with light intensity of 100 mW cm^{-2}) is irradiated on the backside of the electrode, which is immersed in 0.1 M potassium phosphate (KPi) electrolyte buffered to pH-7. The front side illumination scheme is also tested with $\text{BiVO}_4/\text{NiCoO}_2$ and is found to produce significantly lower photocurrent densities than the backside illumination for

both water oxidation and sulfite oxidation (Figure S14). Supposedly, the backside illumination generates electron-hole pairs near the back contact (*i.e.*, between FTO and BiVO₄) while the front-side illumination generates electron-hole pairs near the photoanode and the electrolyte interface. The highly nanoporous structure of the BiVO₄ film in this study allows for easy access of the photoanode/electrolyte interface by the holes in both illumination schemes. However, in the front-side illumination case, the photogenerated electrons will have to reach the back contact (*i.e.*, between FTO and BiVO₄) first and then transport all the way to the counter electrode, leading to a longer electron transport distance.^[42] The elongated electron transport distance would encourage electron-hole recombination and thus result in a lower photocurrent density. Based on the result, the backside illumination is used throughout this work.

Figure 5. j - V characteristics of BiVO₄ and its composites towards (a) PEC OER in 0.1 M potassium phosphate (KPi) buffer (pH= 7), (b) PEC sulfite oxidation in 0.1 M KPi containing

1 M Na₂SO₃, and (c) OER under dark condition in 0.1 M KPi. (d) BiVO₄ with Ni-Co oxides with different molar ratios towards PEC OER in 0.1 M KPi.

Figure 5a presents the j-V plots of PEC OER by BiVO₄ and its composites. As seen, both the onset potential (0.46 V *vs* RHE) and photocurrent density of the unmodified BiVO₄ (*e.g.*, ~1.4 mA cm⁻² at 1.23 V *vs* RHE) are unsatisfactory, which is reportedly due to the sluggish hole transfer kinetics at the unmodified BiVO₄ and water interface.^[8] To confirm this is the case in this work, a PEC sulfite oxidation by the unmodified BiVO₄ is then conducted. It is well known that photocatalytic oxidation of sulfite, a popular hole scavenger, is very kinetically favourable where surface charge recombination due to interfacial hole transfer kinetics is literally negligible.^[45, 46] The results show that the photocurrent density of the unmodified BiVO₄ is increased tremendously for sulfite oxidation (*i.e.*, 5.2 mA cm⁻² at 1.23 V *vs* RHE), with an onset potential at 0.08 V *vs* RHE (Figure 5b). The results in turn imply that it is the slow interfacial hole-to-oxygen transfer kinetics with the unmodified BiVO₄ that limits its PEC OER performance. The holes, once generated on the unmodified BiVO₄ under light illumination, cannot be consumed quickly enough by OER and thus tend to accumulate on the BiVO₄ electrode surface, resulting in enhanced hole and electron recombination and consequentially reduced photocurrent density. This finding serves as a rationale of selecting an appropriate electrocatalytic OER catalyst, which, by design, facilitates interfacial hole-to-oxygen transfer, to serve as PEC cocatalyst to promote the overall PEC OER performance by the BiVO₄ composite.

First, to confirm electrocatalytic activities of the OER catalysts (*i.e.*, NiCoO₂, Co₃O₄, and NiO), linear sweep voltammetry (LSV) is measured in the absence of light illumination for all the BiVO₄-cocatalyst composites (*i.e.*, BiVO₄/NiCoO₂, BiVO₄/Co₃O₄ and BiVO₄/NiO) along with the unmodified BiVO₄. The results show that all the composites show cathodic shift in their electrocatalytic OER onset potentials relative to the BiVO₄, with the onset

potentials being 1.68, 1.73, 1.78 and 2.14 V *vs* RHE for BiVO₄/NiCoO₂, BiVO₄/Co₃O₄, BiVO₄/NiO, and BiVO₄ respectively, which confirms the considerably electrocatalytic OER activities of these cocatalysts, with the NiCoO₂ being the best (Figure 5c).

Thus, not surprisingly, among all three BiVO₄-cocatalyst composites, BiVO₄/NiCoO₂ delivers the best PEC OER performance (Figure 5a). The PEC OER photocurrent density of BiVO₄/NiCoO₂ is ~3.6 mA cm⁻² at 1.23 V and ~2.0 mA cm⁻² at 0.6 V *vs* RHE, with an OER onset potential of 0.26 V *vs* RHE. The performance by the BiVO₄/NiCoO₂ in this study compares very favourably against many BiVO₄-cocatalyst composites in literature (Table S1). The half-cell photoconversion efficiency was calculated using j-V curves (Figure S15), and it is found that, among all, the BiVO₄/NiCoO₂ exhibits the best photoconversion efficiency with a maximum of 1.4 % at 0.6 V *vs* RHE. The fact that the maximum photoconversion efficiency occurs at 0.6 V on BiVO₄/NiCoO₂ is significant and it highlights the great potential of NiCoO₂ in promoting photocatalyst's OER performance. It also makes the BiVO₄/NiCoO₂ potentially favourable candidate in constructing photoelectrochemical diode.^[47]

The other composites (*i.e.*, BiVO₄/NiO and BiVO₄/Co₃O₄) (Figure 5a), although represent enhanced PEC OER performances in relation to the unmodified BiVO₄, they are all inferior to the BiVO₄/NiCoO₂. The photocurrent density obtained at 1.23 V *vs* RHE and the OER onset potentials are 2.2, 2.6 mA cm⁻² and 0.44 V, 0.27 V *vs* RHE for the BiVO₄/NiO, BiVO₄/Co₃O₄, respectively. The improved PEC OER performances of BiVO₄ in the presence of these OER cocatalysts are also confirmed under chronoamperometric conditions (*i.e.*, alternating light-on and light off) (Figure S16). **Figure 6** compares the incident photon-to-current conversion efficiency (IPCE) curves of the BiVO₄ and BiVO₄/NiCoO₂, with BiVO₄/NiCoO₂ showing much higher (~45%) IPCE than BiVO₄ (~23%) up to around 520 nm, beyond which the IPCE drops sharply to almost zero. This result is expected and is in a good agreement with the UV-Vis adsorption spectra by these materials (Figure S17).

In all, the results confirm that these OER electrocatalysts improve the photocatalytic OER of BiVO_4 , with the NiCoO_2 being the best among all. However, it is worth pointing out that the PEC OER photocurrent density of $\text{BiVO}_4/\text{NiCoO}_2$ is still lower than the photocurrent density of sulfite oxidation by $\text{BiVO}_4/\text{NiCoO}_2$ or BiVO_4 , which suggests that electron-hole recombination is still happening to some degree during the PEC OER. On the other hand, irrespective of the nature of the cocatalysts, no significant change in the photocurrent densities and no noticeable shifts in onset potentials are observed for the sulfite oxidation (Figure 5b), insinuating equally fast sulfite oxidation kinetics on the surface of BiVO_4 and their composite electrodes. This finding implies that BiVO_4 is indeed an effective photocatalyst and also demonstrates the inability of these OER cocatalysts in improving photocatalytic sulfite oxidation by BiVO_4 , which is expected as they are not sulfite oxidation catalyst by design.

In an extension, the effect of molar ratio of Ni and Co in the Ni-Co oxides is examined by preparing two additional Ni-Co oxides with differed metal ratios: NiCo_2O_4 (Ni:Co =1:2) and $\text{NiCo}_{0.5}\text{O}_2$ (Ni:Co=1:0.5),^[48] whose crystalline nature is analyzed and confirmed with XRD (Figure S18). It turns out that the $\text{BiVO}_4/\text{NiCo}_2\text{O}_4$ and $\text{BiVO}_4/\text{NiCo}_{0.5}\text{O}_2$ composites both show improved photocatalytic OER performances (Figure 5d) relative to the BiVO_4 , but their performances are poorer than the $\text{BiVO}_4/\text{NiCoO}_2$.

Figure 6. IPCE of BiVO_4 and $\text{BiVO}_4/\text{NiCoO}_2$ electrodes measured at 1.23 V vs RHE (a) in 0.1 M phosphate buffer solution without and (b) with 1 M sodium sulfite solution.

In order to further elucidate the origin of the improved photocatalytic OER activity of the $\text{BiVO}_4/\text{NiCoO}_2$, efforts are made to measure the optical band gap and flat band potential of BiVO_4 and $\text{BiVO}_4/\text{NiCoO}_2$. The optical band gap, which is measured by using Tauc plots derived from the UV plot (Figure S19), for BiVO_4 and $\text{BiVO}_4/\text{NiCoO}_2$ are 2.51 eV and 2.50 eV, respectively (Figure S19a and b) and almost no difference can be identified between the two. On the other hand, the flat band potential (E_{FB}), measured by Mott-Schottky plots, for BiVO_4 and $\text{BiVO}_4/\text{NiCoO}_2$ are 0.16 and 0.18 vs RHE, respectively (Figure S19c and d). In theory, onset potential is directly related with the flat band potential of a PEC electrode. The flat band potential for BiVO_4 (0.16 V vs RHE) is too far from its PEC OER onset potential (0.46 V vs RHE) (Figure 5a), dictating the poor photocatalytic OER kinetics by BiVO_4 . In a sharp contrast, the flat band potential of $\text{BiVO}_4/\text{NiCoO}_2$ (0.18 vs RHE) is much closer to its photocatalytic OER onset potential (0.26 V vs RHE) (Figure 5a), which validates the significantly better PEC OER performance by $\text{BiVO}_4/\text{NiCoO}_2$ than the unmodified BiVO_4 .

Figure 7. Charge separation efficiency (a) in the bulk and (b) on the surface of the BiVO_4 and $\text{BiVO}_4/\text{NiCoO}_2$ electrodes.

In order to quantify the role of NiCoO₂ towards the charge separation and surface reaction kinetics, the efficiency of charge separation in the bulk (η_{bulk}) and on the surface (η_{surface}) is determined and presented in **Figure 7**. The detailed calculation of charge separation efficiency is given ESI. Interestingly, the BiVO₄/NiCoO₂ electrode has a η_{surface} around 71.4 %, which is three times η_{surface} of the BiVO₄ electrode (23.2 %) at 1.23 V *vs* RHE. Moreover, the η_{surface} of the BiVO₄/NiCoO₂ electrode in this study is significantly higher than the values reported in literature.^[23] On the other hand, the η_{bulk} shows no significant difference (76%) between the BiVO₄/NiCoO₂ and BiVO₄, indirectly pointing out the active role of NiCoO₂ nanoparticles in promoting effective charge separation on the BiVO₄ surface. As can be seen, η_{bulk} is consistently higher than η_{surface} , which may be due to the poor hole diffusion on BiVO₄ surface.

BiVO₄ typically suffers from a mismatch between its electronic and optical properties, *i.e.*, the minority-carrier diffusion length is shorter than the light penetration depth (references) and thus an effective hole diffusion leads to an effective charge separation for BiVO₄. In this work, the hole diffusion length (L_D) is calculated for both BiVO₄/NiCoO₂ and BiVO₄ using Gartner Model,^[49] whose details are given in the supporting information. It turns out that, at $\lambda=450$ nm, the calculated L_D is 56 nm and 62 nm for BiVO₄ and BiVO₄/NiCoO₂ respectively, which agree somewhat with the L_D values for BiVO₄ in literature (*i.e.* ~100 nm).^[50] We believe that the variation of the L_D values in this work from the literature one may be a result of differed light absorption coefficient due to different film thickness of BiVO₄.

The light penetration depth, a measure of how deep light or any electromagnetic radiation can penetrate into a material, is a useful parameter in PEC field. The light penetration depth is calculated to be 3.25 and 2.00 μm for BiVO₄ and BiVO₄/NiCoO₂.^[51] The detailed calculation procedure and the results are represented in Figure S20. The shorter light penetration depth of

BiVO₄/NiCoO₂ is presumably due to its larger light absorption coefficient, which results in its light absorption within a shorter distance. Moreover, the sharp mismatch between the calculated hole diffusion length (<100 nm) and light penetration depth (> 2.00 μm) in BiVO₄ serves as a great justification for the selection of the nanoporous thin film of BiVO₄ in this work, which allows for two parameters to be orthogonalized, meaning that the carrier transport and light absorption can occur on different axes.

Furthermore, photoluminescence (PL) emission spectroscopy analysis is carried out to further study charge separation on the surface. A higher PL emission intensity indicates a faster recombination of electron hole pairs and thus a reduced PEC catalytic activity.^[52] under excitation at 450 nm, the PL spectra of BiVO₄ and BiVO₄/NiCoO₂ are shown in Figure S21 and, as can be clearly seen, BiVO₄ produces strong emission peak around 600 nm and BiVO₄/NiCoO₂ shows an emission peak around 680 nm. The relative PL intensity of BiVO₄ is greater than that of BiVO₄/NiCoO₂, implying that NiCoO₂ suppresses the recombination of electrons and holes.^[53] Putting all together, we believe that the larger hole diffusion length and shorter light penetration depth of BiVO₄/NiCoO₂ presumably are conducive to its more effective charge separation than BiVO₄ on the surface and result in its higher PEC OER performance.

The electrochemical impedance spectroscopy (EIS) measurements are carried out for BiVO₄, BiVO₄/NiCoO₂ and NiCoO₂ at 0.6 V *vs* RHE. From EIS spectra (Figure S22a), single semicircles are observed for all the samples, which can be fitted with Randles equivalent circuit model (Figure S22b). In this model, R_Ω indicates the resistance related to the charge transport including the resistance of FTO substrate, electrode and electrolyte in the whole circuit. The R_Ω value measured for BiVO₄/NiCoO₂ (32.9) is relatively low compared to BiVO₄ (36.3) indicating the higher conductivity of the composite electrode and thus its better PEC OER performance.

Figure 8. *j-t* curve for $\text{BiVO}_4/\text{NiCoO}_2$ and BiVO_4 , measured at 0.6 V vs RHE for 10,000 s. The inset images are the optical images of $\text{BiVO}_4/\text{NiCoO}_2$ and BiVO_4 showing accumulation of oxygen bubbles on the electrode surface.

In addition to photocatalytic OER performance, the operational stability of a PEC OER electrode is another important parameter to evaluate towards practical application. As seen in **Figure 8**, the photocurrent densities of both $\text{BiVO}_4/\text{NiCoO}_2$ and BiVO_4 remain relatively stable throughout, retaining 90% of their initial currents at the end of 10,000 seconds in both cases. The fluctuation in the photocurrent observed for $\text{BiVO}_4/\text{NiCoO}_2$ is presumably due to accumulation of oxygen bubbles transiently adhering on the electrode surface (Inset of Figure 8). In general, a cocatalyst with appropriate band structure may provide additional benefit in photocatalytic OER. If the valence band of cocatalyst is energetically aligned with or lie higher than that of photoanode, facilitated transfer of photo-generated holes from the photoanode material to the cocatalyst can thus be expected.^[54] The

valance band potential of NiCoO₂ (2.38 V) ^[55] is negative compared to the valance band potential of BiVO₄ (2.77 V),^[23] thus, the photo-generated holes on BiVO₄ could easily travel to NiCoO₂ (shown in Scheme 1), as NiCoO₂ resulting in a higher photocatalytic OER performance by BiVO₄/NiCoO₂. Besides, the very high hole conductivity (300 S cm⁻¹) of NiCoO₂ is also a contributing factor for facilitated hole transfer. ^[56]

Previously, Domen *et al.* have demonstrated the construction of p-n junction of BiVO₄ with individual layers of NiO and Co₃O₄ by expensive atomic layer deposition method for photocatalytic OER, where the p-type semiconductor (*i.e.* NiO) extract the photo-generated holes from the n-type photoanode surface and restrict the surface trapped electrons for the reduced charge recombination while the another electrocatalyst (*i.e.* Co₃O₄) leads to increase the OER kinetics.^[29] In contrast, in our case, NiCoO₂ is a p-type semiconductor, confirmed by Mott-Schottky plot in Figure S23, and it leads to the formation of a p-n junction and thus extraction of hole from the BiVO₄ surface while its inherent OER catalytic property results in improved photocatalytic OER kinetics by BiVO₄/NiCoO₂. It is worth mentioning that the photocatalytic OER performance exhibited by BiVO₄/NiO and BiVO₄/Co₃O₄ in this study is found to be comparable to literature values.^{[29], [23]} Therefore, the dual role of NiCoO₂ in our design is superior to the two-component of NiO and Co₃O₄ in the previous case and can be the reason for the unprecedentedly high photocatalytic OER performance of the BiVO₄/NiCoO₂ due to the synergy of high surface OER kinetics and improved charge separation served by the same single-component NiCoO₂ in our system.

Conclusion

In this work, NiCoO₂ nanoparticles modified porous BiVO₄ film has been rationally designed and fabricated as effective and stable photoanode for PEC OER. The NiCoO₂ in the BiVO₄/NiCoO₂ serves as an effective cocatalyst for OER and at the same time provides suitable band structure that facilitates photo-generated hole transfer and thus charge separation, leading to vastly enhanced PEC OER performance by the BiVO₄/NiCoO₂

photoelectrode. The PEC OER photocurrent density of 3.6 mA cm⁻² achieved at 1.23 V vs. RHE by the BiVO₄/NiCoO₂ compares very favourable again literature values and makes it among the state-of-the-art materials in photocatalytic OER.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the King Abdullah University of Science and Technology (KAUST) CCF fund awarded to Water Desalination and Reuse Center (WDRC). The authors are grateful to the other members of the KAUST Environmental Nanotechnology group for the helpful discussions.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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