Vastly Enhanced BiVO$_4$ Photocatalytic OER Performance by NiCoO$_2$ as Cocatalyst

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1. Experimental method

1.1 Preparation of BiVO$_4$

BiVO$_4$ was synthesized by electrodeposition of BiOI on FTO plate followed by annealing with vanadium precursor in air at 450 °C. Briefly, 25 ml of DI water containing 0.4 M of potassium iodide (KI) and 0.04 M of bismuth nitrate was mixed with 10 ml of ethanol solution with 1, 4 benzoquinone (0.23 M). Prior to that, the pH of KI aqueous solution was adjusted to 1.7 by using 2M HNO$_3$. The resulting dark transparent solution was mechanically stirred for 30 min to thus obtain a homogenous BiOI solution. Subsequently, in conducting the electrodeposition, FTO
plate, Ag/AgCl (3 M KCl saturated), Pt wire were used as the working, reference and counter electrode, respectively and the homogeneous BiOI solution was used as electrolyte solution. The electrodeposition of BiOI was carried out potentiostatically by applying potential at -0.1 V. To study an optimal thickness of BiVO₄ film on FTO, the electrodeposition time was varied and the optimal deposition time is found to be 300 s. The chronoamperometric response has been represented in the Figure S1. After the electrodeposition, the resulting BiOI coated FTO plate was dipped into DI water for 1 min, took out, and then dried in air for 12 h at room temperature. Subsequently, a 100 µl of vanadium acetyl acetonate (0.2 M) in dimethyl sulfoxide (DMSO) was drop casted on the surface of the BiOI coated FTO plate to ensure a full coverage before annealing at 450 °C for 2 h in a muffle furnace with a heating rate of 2 °C min⁻¹. Finally, the BiVO₄ coated FTO photoelectrode was dipped in to 1 M NaOH with gentle mechanical stirring to remove the unreacted V₂O₅. The resulting electrodes was washed with DI water, dried at 60 °C and preserved for further analysis.

1.2 Preparation of NiCoO₂ nanoparticles

The NiCoO₂ nanoparticles were synthesized by hydrothermal method. In a typical synthesis, 1 mmol Ni(NO₃)₂·6H₂O and 1 mmol Co(NO₃)₂·6H₂O (1 : 1 molar ratio) were dissolved in 50 ml of ethanol and sonicated for 10 min to get a clear solution. After being stirred gently for 30 min, 3 ml of ammonia was added to the mixture solution to increase the pH and the mixture was stirred for 10 min. Subsequently, the mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave. The temperature of the autoclave was increased to 120 °C and maintained there for 12 h. Then, the resulting precipitates were separated by centrifugation and washed thoroughly with DI water and ethanol three times before drying in air at 80 °C for 12 h. These grey color precipitates were calcined at 450 °C in air for 2 h with a slow heating rate of 1 °C min⁻¹ to obtain
NiCoO$_2$ nanoparticles. For comparison, NiCo$_2$O$_4$ and NiCo$_{0.5}$O$_2$ nanoparticles were prepared under otherwise the same experimental, and NiO and Co$_3$O$_4$ were synthesized as well.

1.3 Preparation of BiVO$_4$/NiCoO$_2$ composite

The NiCoO$_2$ slurry was prepared by dispersing 1 mg of NiCoO$_2$ in 1 ml ethanol/water mixture and sonicated for 30 min to form uniform slurry. Then 50 µL of slurry was then drop-casted onto the BiVO$_4$ electrodes. The resulting composites were dried at 60 ºC for 30 min and then annealed at 450 ºC with heating rate of 1 ºC min$^{-1}$ for 6 h. The final BiVO$_4$/NiCoO$_2$ composite electrode was used for PEC OER studies. For comparison, BiVO$_4$ electrodes were composited with NiO, Co$_3$O$_4$, NiCo$_2$O$_4$, and NiCo$_{0.5}$O$_2$ by following the same experimental procedures.

1.4 Material characterizations

XRD measurements were performed using a Bruker D8 Advance instrument (Cu K$\alpha$, 1.5406 Å. The morphologies of the BiVO$_4$ and composite electrodes were characterized by scanning electron microscopy (SEM, FEI, NovaNano). High resolution transmission electron microscope (HRTEM) images and energy-dispersive X-ray spectroscopy (EDS) were taken on a Titan Cs probe electron microscope operated at 300 kV. The diffuse reflectance UV-vis adsorption spectra were recorded on spectrophotometer (Shimadazu, UV 2550), with fine BaSO$_4$ powder as reference. All digital photos were taken by a Cannon EOS 7D.

1.5 Photoelectrochemical measurements

All photoelectrochemical studies were performed on an Autolab PGSTAT 302N (Metrohm) using conventional three electrode configuration. The scan rate of LSV was 10 mV s$^{-1}$. 0.1 M potassium phosphate buffer (KPi) (pH-7) with or without 1 M sodium sulfite (Na$_2$SO$_3$) was employed as the electrolyte. The simulated solar illumination was obtained by passing light from
a 300 W Xenon arc lamp (Beijing Perfectlight Technology Co. Ltd., Microsolar 300 UV) equipped with an AM 1.5 filter, and the power intensity of the incident light was calibrated to 100 mW cm\(^{-2}\) at the surface of the working electrode. Prior to the PEC measurements, the electrolyte was purged with N\(_2\) gas for 60 min to remove any dissolved oxygen from the electrolyte. The illuminated area was maintained as 1 cm\(^2\). The PEC measurements were done with backside illumination. During the stability test, the electrolyte was purged with N\(_2\) continuously with gentle rotation.

In measuring incident photon-to-current efficiency (IPCE), monochromatic light was produced using an Oriel Cornerstone 130 monochromator with a 10-nm bandpass and the output was measured with a photodiode detector. IPCE was consistently measured at 1.23 V vs RHE in 0.1 M KPi buffer (pH 7) with and without 1 M Na\(_2\)SO\(_3\) using the same three electrode setup described above. Chopped-light amperometric \(j-t\) characterizations were evaluated at different applied potential of 0.8 to 1.4 V vs. RHE under chopped light irradiation (light on or off cycles: 30 s). Electrochemical impedance spectroscopy (EIS) was carried out by applying an AC voltage amplitude of 10 mV within the frequency range from \(10^5\) to \(10^{-3}\) in 0.1 M KPi buffer solution under in 0.6 V vs RHE. The Mott-Schottky plots were measured in a 0.1 M KPi buffer (pH 7) at a frequency of 1000 Hz and amplitude of 10 mV under the dark condition. The measured potential against Ag/AgCl was converted against the reversible hydrogen electrode (RHE) using Nernst equation. The conversion was given as follows:

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{pH} + E^\circ_{\text{Ag/AgCl}} \tag{1}
\]

1.6 Calculation of charge separation efficiency

The photocurrent density from PEC measurement (\(J_{\text{PEC}}\)) can be expressed as follows\(^3\):

\[
J_{\text{PEC}} = J_{\text{abs}} \times \eta_{\text{bulk}} \times \eta_{\text{surface}} \tag{2}
\]
where $J_{\text{abs}}$ is the photocurrent density assuming a complete conversion of absorbed photons-to-current efficiency (APCE=100%). The addition of 1 M Na$_2$SO$_3$ to the electrolyte is assumed to completely suppress the surface charge recombination, namely full charge separation (i.e., $\eta_{\text{surface}} = 100\%$), but does not affect bulk charge separation in the electrode. Thus, $\eta_{\text{bulk}}$ and $\eta_{\text{surface}}$ can be determined:

$$\eta_{\text{bulk}} = \frac{J_{\text{sulfite}}}{J_{\text{abs}}} \quad (3)$$

$$\eta_{\text{surface}} = \frac{J_{\text{water}}}{J_{\text{sulfite}}} \quad (4)$$

where $J_{\text{water}}$ is the photocurrent density for PEC OER and $J_{\text{sulfite}}$ is the photocurrent density for PEC sulfite oxidation. By estimating the overlapped areas between the UV-vis absorbance spectrum (Figure S18) and the AM 1.5G solar spectrum and assuming APCE = 100%, the $J_{\text{abs}}$ of BiVO$_4$ is calculated and found to be 6.3 mA cm$^{-2}$. After the deposition of NiCoO$_2$, the ability of light absorption is enhanced slightly, which is reflected in the $J_{\text{abs}}$ of 6.52 mA/cm$^2$ for BiVO$_4$/NiCoO$_2$. Thus, the efficiency of charge separation in the bulk and on the surface of the photoelectrodes can be evaluated using the equation (2) to (4) and the data have been represented in Figure 7.

### 1.7 Determination of hole diffusion length

Hole diffusion length, $L_D$, is an important parameter for evaluating the hole transport property of a photoelectrode. The calculation procedure of $L_D$ is detailed as follows.

The $L_D$ is directly calculated from Equation (5):

$$\eta_{\text{sep}} = 1 - \frac{e^{-\alpha W}}{1 + \alpha L_D} \quad (5)$$
where $\alpha$ is the absorption coefficient, $W$ is the depletion layer width of photoelectrode, $\eta_{sep}$ is the quantum efficiency for the condition that all incident light is absorbed and that the generated electrons and holes transported to the surface are 100% converted.

The depletion layer width, $W$, is calculated by Equation (6):

$$W = \sqrt{\frac{2\varepsilon_0 \varepsilon (V - V_F)}{q N_d}} \quad (6)$$

where $\varepsilon_0$ is the vacuum dielectric constant ($8.85 \times 10^{-12} \text{ Fm}^{-1}$), $\varepsilon$ is the relative dielectric constant ($\sim 68$ for BiVO$_4$) and $V_F$ is the flat potential of the photoelectrode, which is taken as 0.18 $\text{V}_{\text{RHE}}$ for BiVO$_4$/NiCoO$_2$ composite and 0.16 $\text{V}_{\text{RHE}}$ for BiVO$_4$ according to Figure S19, $q$ is the electron charge ($1.6 \times 10^{-19} \text{C}$) and $N_d$ is the carrier concentration, which is calculated by Equation (7)

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon A^2 q N_d} \left( V - V_F - \frac{k_B T}{q} \right) \quad (7)$$

where $C$ is the space charge layer capacitance (from Figure S19), $A$ is the geometrical area exposed to electrolyte in cm$^2$, $k_B$ is the Boltzmann constant ($1.381 \times 10^{-23} \text{ JK}^{-1}$) and $T$ is the temperature in K (298K). As a result, $N_d$ for BiVO$_4$ is $1.08 \times 10^{18} \text{ cm}^{-3}$ and $N_d$ for NiCoO$_2$ is $1.25 \times 10^{18} \text{ cm}^{-3}$. Therefore, $W$ for BiVO$_4$ cm$^{-3}$ is 86.3 nm and $W$ for NiCoO$_2$ is 79.5 nm.

IPCE is measured and can also be expressed by taking into account of three processes as described in Equation (8)

$$\text{IPCE} = \eta_{abs} \times \eta_{sep} \times \eta_{int} \quad (8)$$

where $\eta_{abs}$ is the light harvesting efficiency, $\eta_{sep}$ is the separation efficiency for photogenerated carriers, and $\eta_{int}$ is interfacial charge transfer efficiency.
APCE (absorbed photon to current efficiency), or internal quantum efficiency, is determined by Equation (10)

\[ \text{APCE} = \frac{IPCE}{\eta_{abs}} = \eta_{sep} \times \eta_{int} \quad (10) \]

When IPCE is measured in KPi with 1 M sodium sulfite solution (hoe scavenger), the interfacial charge transfer efficiency \((\eta_{int}) = 1\), meaning completely suppressed surface recombination. Therefore, according to Equation (10), APCE in this case is the charge separation efficiency, \(\eta_{sep}\). At \(\lambda = 450\) nm, the absorption coefficient \(\alpha\) is \(0.19 \times 10^5\) cm\(^{-1}\) for BiVO\(_4\) and \(0.21 \times 10^5\) cm\(^{-1}\) for BiVO\(_4\)/NiCoO\(_2\). The charge separation efficiency for BiVO\(_4\) and BiVO\(_4\)/NiCoO\(_2\) are 0.57. As a result, at \(\lambda = 450\) nm and with back side illumination, the hole diffusion length of BiVO\(_4\) and BiVO\(_4\)/NiCoO\(_2\) is then calculated to be 56 nm and 62 nm, respectively.

1.8. Determination of light penetration depth

According to the thickness determined from SEM images (600 nm) (Figure S5) and the absorbance measured from UV-vis spectroscopy (Figure S17), the light penetration depth \(D_p\) (m) at each wavelength is calculated.

The absorption coefficient is obtained from Beer-Lambert Law (Equation 11):

\[ \alpha(\lambda) = \frac{abs(\lambda)}{l} \quad (11) \]

where \(\alpha(\lambda)\) is the absorption coefficient (m\(^{-1}\)), abs(\(\lambda\)) is the absorbance measured by UV-vis spectroscopy and \(l\) is the film thickness (m).
The light penetration depth, \( D_p(m) \), is then determined by Equation (12):

\[
D_p(m) = \frac{1}{\alpha(\lambda)} \quad (12)
\]

2. Results

**Figure S1.** \( j-t \) curve for electrodeposition of BiOI on FTO, measured at -0.1 V vs Ag/AgCl for 300 s.
Figure S2. SEM images of BiOI crystals in different magnifications.

Figure S3. SEM images of BiVO₄ crystals in different magnifications.
Figure S4. (a) High angle annular dark field (HAADF)-Scanning transmission electron microscopy (STEM) image of BiVO₄ and (b) energy dispersive X-Ray spectroscopy (EDS) spectra for BiVO₄.
**Figure S5.** Cross-sectional SEM image of BiVO$_4$.

**Figure S6.** HRTEM images of NiCoO$_2$ in different magnifications.
Figure S7. HAADF-STEM images of NiCoO$_2$ in different magnifications.
**Figure S8.** SEM image of BiVO₄/NiCoO₂ representing the uniform distribution of NiCoO₂ nanoparticles on the BiVO₄.
Figure S9. (a) HRTEM image of BiVO₄/NiCoO₂. (The interface between BiVO₄ and NiCoO₂ has been indicated by yellow dotted line and the NiCoO₂ nano particles are indicated by yellow arrow) (b) Particle size distribution chart of NiCoO₂ at the interface of BiVO₄/NiCoO₂.
Figure S10. SEM image and elemental mapping of BiVO$_4$/NiCoO$_2$ exhibiting uniform distribution of Bi, V, Ni, Co, O in the composite electrode.
Figure S11. (a) HAADF-STEM (dark field) image of BiVO$_4$/NiCoO$_2$, (b) fringes pattern of NiCo$_2$O$_4$ which shows a d-spacing value of 0.24 nm corresponding to the (311) plane of NiCoO$_2$. 

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Figure S12. XRD patterns of (a) BiVO$_4$ and BiVO$_4$/NiCoO$_2$ (the reflections corresponding to the BiVO$_4$ are represented by symbol in Figure S12a) and (b) XRD patterns of homemade NiO, Co$_3$O$_4$ and NiCoO$_2$.

Figure S13. (a) Raman spectra of BiVO$_4$ and BiVO$_4$/NiCoO$_2$ electrodes, (b) expanded view of Raman band at around 810 cm$^{-1}$ corresponding to V-O stretching of BiVO$_4$. 

Figure S14. j-V curves of BiVO$_4$ and BiVO$_4$/NiCoO$_2$ towards (a and b) water oxidation and (c and d) sulfite oxidation comparing the effect of the front side and back side illumination for PEC performances.
**Table S1. Summary of BiVO₄ with various electrocatalysts towards photocatalytic OER in literature.**

<table>
<thead>
<tr>
<th># Reference</th>
<th>Electrodes</th>
<th>Electrolyte</th>
<th>PEC OER onset potential (vs RHE)</th>
<th>Maximum photocurrent density at 0.6 V vs RHE</th>
<th>Maximum photocurrent density at 1.23 V vs RHE</th>
<th>Scan rate (mV s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>BiVO₄/rGO</td>
<td>0.1 M Na₂SO₄</td>
<td>-----</td>
<td>70 μA cm⁻² at 0.6 V vs SHE</td>
<td>~80 μA cm⁻² at 1 V vs SHE</td>
<td>***</td>
</tr>
<tr>
<td>3.</td>
<td>BiVO₄/MnOₓ</td>
<td>0.5 M Na₂SO₄</td>
<td>0.1 V</td>
<td>50 μA cm⁻² at 1 V vs SHE</td>
<td>~80 μA cm⁻² at 0.6 V vs SHE</td>
<td>***</td>
</tr>
<tr>
<td>4.</td>
<td>BiVO₄/CoOₓ</td>
<td>0.5 M KPi</td>
<td>0.5 V</td>
<td>0.25 mA cm⁻²</td>
<td>2.75 mA cm⁻²</td>
<td>50</td>
</tr>
<tr>
<td>5.</td>
<td>WO₃/WO/BiVO₄</td>
<td>0.5 M Na₂SO₄</td>
<td>-----</td>
<td>~2.5 mA cm⁻²</td>
<td></td>
<td>***</td>
</tr>
<tr>
<td>6.</td>
<td>BiVO₄/FeOOH/ NiOOH</td>
<td>0.1 M KPi</td>
<td>0.23 V</td>
<td>2.8 mA cm⁻²</td>
<td>4.2 mA cm⁻²</td>
<td>10</td>
</tr>
<tr>
<td>7.</td>
<td>CoPi/W:BiVO₄</td>
<td>0.1 M KPi</td>
<td>0.2 V</td>
<td>~1.0 mA cm⁻²</td>
<td>~1.5 mA cm⁻²</td>
<td>***</td>
</tr>
<tr>
<td>8.</td>
<td>CoPi/BiVO₄</td>
<td>0.1 M KPi</td>
<td>0.4 V</td>
<td>~0.7 mA cm⁻²</td>
<td>~1.5 mA cm⁻²</td>
<td>10</td>
</tr>
<tr>
<td>9.</td>
<td>NiO/CoOₓ/BiVO₄</td>
<td>0.1 M KPi</td>
<td>0.3 V</td>
<td>3.5 mA cm⁻²</td>
<td>3.5 mA cm⁻²</td>
<td>10</td>
</tr>
<tr>
<td>10.</td>
<td>BiVO₄/FeOOH</td>
<td>0.1 M KPi</td>
<td>0.2 V</td>
<td>~1.4 mA cm⁻²</td>
<td>~2.4 mA cm⁻²</td>
<td>10</td>
</tr>
<tr>
<td>11.</td>
<td>BiVO₄/SnO₂/WO₃</td>
<td>0.1 M Na₂SO₄</td>
<td>-----</td>
<td>~0 mA cm⁻²</td>
<td>~1.5 mA cm⁻²</td>
<td>10</td>
</tr>
<tr>
<td>12.</td>
<td>Co-Pi/SiO₂-BiVO₄</td>
<td>0.5 M Na₂SO₄</td>
<td>0.3 V</td>
<td>~0.25 mA cm⁻²</td>
<td>~1.2 mA cm⁻²</td>
<td>25</td>
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<tr>
<td>13.</td>
<td>Co-Pi/Mo-BiVO</td>
<td>0.5 M Na₂SO₄</td>
<td>0.4 V</td>
<td>0.4 mA cm⁻²</td>
<td>~0.9 mA cm⁻²</td>
<td>25</td>
</tr>
<tr>
<td>14.</td>
<td>RhO₂/Mo-BiVO₄</td>
<td>0.5 M K₂SO₄</td>
<td>0.4 V</td>
<td>~0.5 mA cm⁻²</td>
<td>2.7 mA cm⁻²</td>
<td>30</td>
</tr>
<tr>
<td>15.</td>
<td>MOF@Fe/W co-doped BiVO₄</td>
<td>0.1 M Na₂SO₄</td>
<td>-----</td>
<td>1.5 mA cm⁻²</td>
<td>3.4 mA cm⁻²</td>
<td>***</td>
</tr>
<tr>
<td>16.</td>
<td>BiVO₄/FeOOH</td>
<td>0.1 M KPi</td>
<td>0.2 V</td>
<td>1.17 mA cm⁻² at 0.55 V vs RHE</td>
<td>1.6 mA cm⁻²</td>
<td>10</td>
</tr>
<tr>
<td><strong>This study</strong></td>
<td>BiVO₄/NiCoO₂</td>
<td>0.1 M KPi</td>
<td>0.26 V</td>
<td>2.0 mA cm⁻²</td>
<td>3.6 mA cm⁻²</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure S15. Half-cell photoconversion efficiency of BiVO$_4$ and its composites.

Figure S16. Amperometric j-t curves of (a) BiVO$_4$ and (b) BiVO$_4$/NiCoO$_2$ in 0.1 M KPi measured at different potentials (0.8 to 1.4 V) vs RHE under chopped light illumination.
Figure S17. UV-Vis spectra of BiVO₄, BiVO₄/NiCoO₂ and FTO substrate.
Figure S18. XRD patterns of NiCo_{0.5}O_{2}, NiCoO_{2} and NiCo_{2}O_{4} prepared in this study.

Figure S19. (a and b) Tauc plot and (c and d) Mott-Schottky plot for BiVO_{4} and BiVO_{4}/NiCoO_{2}.
Figure S20. Light penetration depth of BiVO$_4$ and BiVO$_4$/NiCoO$_2$ as a function of wavelength.

Figure S21. Photoluminescence spectra of BiVO$_4$ and BiVO$_4$/NiCoO$_2$ indicating the efficient charge rectification by the junction.
Figure S22. Impedance spectra of (a) BiVO$_4$, (c) BiVO$_4$/NiCoO$_2$ measured at 0.6 V vs RHE and their Randles equivalent circuit (b and d). The tables on the right present the other parameters obtained in the impedance data fitting.
Figure S23. Mott-Schottky plot for NiCoO$_2$ nanoparticles indicating the p-type semiconductor behavior.

Reference


