Zn:BiVO$_4$/Mo:BiVO$_4$ Homojunction as Efficient Photoanode for Photoelectrochemical Water Splitting

Jae Myeong Lee,$^{a,‡}$ Ji Hyun Baek,$^{a,b,‡}$ Thomas Mark Gill,$^b$ Xinjian Shi,$^b$ SangMyeong Lee,$^a$ In Sun Cho,$^c$ Hyun Suk Jung,$^{a,*}$ and Xiaolin Zheng$^{b,*}$

a. School of Advanced Materials Science & Engineering Sungkyunkwan University, Suwon 16419, Republic of Korea. *E-mail: hsjung1@skku.edu
b. Department of Mechanical Engineering Stanford University, Stanford California 94305, United States. *E-mail: xlzheng@stanford.edu
c. Department of Materials Science & Engineering and Energy Systems Research Ajou University, Suwon 16499, Republic of Korea.
‡ These authors contributed equally to this work.
Fig. S1. SEM images of Mo:BVO, Zn:BVO and undoped BVO photoanodes. All photoanodes have similar morphologies and thickness of 300 nm (scale bar = 400 nm).
Fig. S2. Raman spectra of the (a) symmetric stretching mode and (b) symmetric and antisymmetric bending modes of Mo:BVO, Zn:BVO and undoped BVO.
Fig. S3. Mott-schottky plots of Mo:BVO, Zn:BVO and undoped BVO photoanodes. All photoanodes indicate n-type semiconductor characteristics. The charge carrier concentrations of each photoanode were changed by doping and calculated using the following equation:\(^1\)

\[
\frac{1}{C^2} = \frac{2}{\varepsilon_0\varepsilon_r A^2eN_d} \left( E - E_{fb} - \frac{kT}{e} \right)
\]

where \(C\) is capacitance (F/cm\(^2\)), \(\varepsilon_0\) is permittivity (8.85 \times 10^{-14} \text{ F/cm})\(^1\), \(\varepsilon_r\) is relative permittivity (68), \(A\) is area (cm\(^2\)), \(e\) is elementary charge (1.602 \times 10^{-19} \text{ C}), \(N_d\) is donor concentration (cm\(^{-3}\)), \(E\) is applied potential (V vs. RHE), \(E_{fb}\) is flat band potential (V vs. RHE), \(k\) is Boltzmann constant (8.617 eV/K) and \(T\) is temperature (K).
Fig. S4. I-V curves of undoped BVO and Zn:BVO/Mo:BVO homojunction photoanodes measured in air under ambient conditions. (a) The I-V characteristic of undoped BVO shows ohmic behavior and (b) that of Zn:BVO/Mo:BVO shows rectification behavior, suggesting the formation of a n-n+ junction.
Fig. S5. (a) Thickness optimization process for Zn:BVO/Mo:BVO homojunction as we vary the total thickness and the component thickness. The thickness is quantified as numbers of spin coating layers. As a result, the junction with 9 layers of Zn:BVO and 5 layers of Mo:BVO (total 14 layers) has the best photocurrent density among all the conditions tested from total 6 to 16 layers. Dopant concentration optimization process for (b) Zn:BVO and (c) Mo:BVO, respectively. 1 % of Zn and 3 % of Mo were attained as the best condition in PEC performance at 1.23 V vs RHE.
Fig. S6. Optical properties (transmittance, reflectance, and light absorption efficiencies) of 14 layers of Zn: BVO/Mo: BVO homojunction photoanode for optimization process. 9 layers of Zn:BVO and 5 layers of Mo:BVO (Zn:BVO/Mo:BVO = 9:5) has slightly better light absorption efficiency.
Fig. S7. J-V curves of the (Zn, Mo) co-doped BVO and Zn:BVO/Mo:BVO photoanodes under 1 sun illumination. The PEC performance of the Zn:BVO/Mo:BVO homojunction photoanode was much better than that of the (Zn, Mo) co-doped BVO photoanode.
Fig. S8. Secondary ion mass spectrometry of (a) (Zn, Mo) co-doped BVO, (b) magnified plot from (a), (c) Zn:BVO/Mo:BVO homojunction photoanode and (d) magnified plot from (c).
Fig. S9. J-V curves of (a) Zn:BVO/Mo:BVO homojunction, (b) Mo:BVO, (c) Zn:BVO and (d) undoped BVO photoanodes with H₂O₂. Photocurrent density measured in the electrolyte with H₂O₂ can be assumed as all holes generated are used for water oxidation. The charge transfer and bulk transport efficiencies of four photoanodes were evaluated using the H₂O₂ hole scavenger method. The relationships between current density, light absorption, transfer efficiency and transport efficiency are as follows:

\[ J_{Ph} = J_{abs} \times \eta_{transfer} \times \eta_{transport} \]  \hspace{1cm} (2)

\[ \eta_{transfer} = \frac{J_{H_2O}}{J_{H_2O_2}} \]  \hspace{1cm} (3)

\[ \eta_{transport} = \frac{J_{H_2O_2}}{J_{abs}} \]  \hspace{1cm} (4)

, where \( J_{Ph} \) is the measured photocurrent density, \( J_{abs} \) is current density calculated from light absorption, \( \eta_{transport} \) is the charge transport efficiency, and \( \eta_{transfer} \) is charge transfer efficiency at the interface between the surface and electrolyte.
Fig. S10. (a) Transient photocurrent responses of Mo:BVO, Zn:BVO and undoped BVO photoanodes (b) Normalized plots of the current–time dependence of each photoanode at 1.23 V vs. RHE under illumination. $J_{\text{in}}$ and $J_{\text{st}}$ are the time-dependent, initial and steady-state photocurrent, respectively. Typically, the initial photocurrent, $J_{\text{in}}$, is attributed to bulk electron-hole separation under immediate illumination, which is followed by decay to the steady state photocurrent, $J_{\text{st}}$, due to surface charge recombination. In particular, Zn:BVO took approximately 5 sec when $\ln D=-1$ compared to Mo doped and undoped BVO (0.2 sec and 0.4 sec), suggesting dramatically improved carrier lifetimes with Zn doping.
Fig. S11. Two stability tests of Ni:FeOOH/Zn:BVO/Mo:BVO, Zn:BVO/Mo:BVO, Mo:BVO, Zn:BVO, and undoped BVO photoanodes. (a) with initial current density of 1 mA/cm$^2$ at 0.52 V, 0.85 V, 1.12 V, 1.34 V and 1.62 V vs. RHE, respectively. (b) with same applied bias of 1.23 V vs. RHE. Conditions: the phosphate buffer solution (pH ~ 7) for 1 hour under illumination.
Table S1. Specific EIS values at each region for undoped BVO, Zn:BVO, Mo:BVO and Zn:BVO/Mo:BVO.

<table>
<thead>
<tr>
<th></th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn:BVO/Mo:BVO</td>
<td>64.80</td>
<td>123.4</td>
<td>1062</td>
</tr>
<tr>
<td>Mo:BVO</td>
<td>62.58</td>
<td>361.7</td>
<td>2742</td>
</tr>
<tr>
<td>Zn:BVO</td>
<td>64.99</td>
<td>1376</td>
<td>2389</td>
</tr>
<tr>
<td>Undoped BVO</td>
<td>61.76</td>
<td>1720</td>
<td>3601</td>
</tr>
</tbody>
</table>
Table S2. Comparison of our Zn:BVO/Mo:BVO homojunction photoanode with different homojunction and heterojunction photoanodes.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Current Density (mA/cm²)</th>
<th>Thickness (nm)</th>
<th>Electrolyte</th>
<th>Process</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn:BVO/McBVO Ni:FeOOH/Zn:BVO/McBVO</td>
<td>2.5 at 1.23 V vs RHE 2.7 at 1.23 V vs RHE</td>
<td>300</td>
<td>0.5 M Kpi (pH=7)</td>
<td>Spin coating</td>
<td>This work</td>
</tr>
<tr>
<td>Co:BVO/McBVO</td>
<td>2.09 at 1.23 V RHE</td>
<td>200</td>
<td>0.1 M Kpi (pH=7)</td>
<td>Spin coating</td>
<td>Ref 5.</td>
</tr>
<tr>
<td>Zn:BVO/BVO</td>
<td>0.63 at 1.23 V vs Ag/AgCl</td>
<td>150</td>
<td>0.5 M Na2SO4</td>
<td></td>
<td>Ref 6.</td>
</tr>
<tr>
<td>BVO/McBVO</td>
<td>2.2 at 1.24 V vs RHE</td>
<td>-</td>
<td>Na2SO4 (pH=7)</td>
<td>Spin coating</td>
<td>Ref 7.</td>
</tr>
<tr>
<td>BVO/TiO2</td>
<td>0.8 at 1.23 V vs RHE 2.14 at 1.7 V vs RHE</td>
<td>600</td>
<td>0.5 M Na2SO4 + Kpi (pH=7)</td>
<td>Spin coating (BVO) Hydrothermal and CBD (TiO2)</td>
<td>Ref 8.</td>
</tr>
<tr>
<td>BVO/ZnO</td>
<td>1.75 at 1 V vs RHE</td>
<td>300 (BVO) 900 (ZnO)</td>
<td>0.2 M Na2SO4 (pH=6.5)</td>
<td>Spray pyrolysis (BVO) Hydrolysis condensation synthesis (ZnO)</td>
<td>Ref 9.</td>
</tr>
<tr>
<td>BVO/WO3</td>
<td>1.74 at 0.7 V vs Ag/AgCl</td>
<td>3000</td>
<td>0.5 M Na2SO4</td>
<td>Drop casting</td>
<td>Ref 10.</td>
</tr>
<tr>
<td>BVO/WO3</td>
<td>2.0 at 1.23 V vs RHE</td>
<td>400</td>
<td>0.1 M Kpi (pH=7)</td>
<td>Drop casting</td>
<td>Ref 11.</td>
</tr>
<tr>
<td>BVO/SnO2</td>
<td>0.95 at 1.23 V vs RHE</td>
<td>245</td>
<td>0.5 M Na2SO4 + 0.1 M Kpi (pH=7)</td>
<td>Drop casting</td>
<td>Ref 12.</td>
</tr>
</tbody>
</table>
References