Supporting Information for

Covalent triazine-based polymers with controllable band alignment matched with BiVO₄ to boost photogeneration of holes for water splitting

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The number of tables: 6
Experimental Section

Preparation of BiVO₄ electrode

The BiVO₄ electrodes were prepared by improved electrodeposition and calcination processes, as reported by T. W. Kim and K. S. Choi. Generally, the BiOI nanosheets were firstly prepared by electrochemical deposition with a conventional three-electrode system. A 0.4 M KI solution was prepared in 50 mL of H₂O and its pH was adjusted to 1.7 by adding HNO₃, before a 0.04 M Bi(NO₃)₃ solution was prepared by dissolving Bi(NO₃)₃·5H₂O. This solution was mixed with 0.23 M p-benzoquinone in 20 mL of ethanol and was strongly stirred for 1 h. A fluorine-doped tin oxide coated glass substrate (FTO, ~7Ω, ~3 cm², Pilkington) served as the working electrode, an Ag/AgCl (4 M KCl) used as the reference electrode and a Pt wire electrode applied as the counter electrode. Cathodic deposition was implemented potentiostatically at -0.1 V vs. Ag/AgCl at room temperature (~ 25°C) for 200 s.

Then the pristine BiVO₄ electrodes were prepared by BiOI conversion. BiOI electrodes were impregnated in 0.2 mL of dimethyl sulfoxide (DMSO) with 0.2 M VO(acac)₂. Then pretreat by heating under 100°C with magnetic heated stirrer to ensure electrodes dry, before annealed in muffle furnace at 470°C for 2 h with a ramping rate of 2°C per min. After annealing, the BiVO₄ electrodes were obtained by soaking the excess V₂O₅ in 1 M NaOH with gentle stirring for 20 min, after rinsing with DI water and drying at room temperature.

Calculation

The potential vs Ag/AgCl (4 M KCl) was converted versus RHE using the following equation:

\[ E(\text{vs RHE}) = E(\text{vs Ag/AgCl}) + E_{Ag/AgCl}(\text{ref}) + 0.0591 \times \text{pH} \quad (S1) \]

\[ (E_{Ag/AgCl}(\text{ref}) = 0.1976 \text{ V vs RHE at 25°C}) \]

Light harvesting efficiencies (ηAbs) based on the light absorption abilities of the different electrodes, expressed using the following equation:

\[ \eta_{\text{Abs}} = 1 - 10^{-A(\lambda) \times 1.3} \quad (S2) \]

A (λ) is the absorbance, and λ is wavelength (nm).

Applied bias photo-to-current efficiency (ABPE) of the electrodes were calculated assuming Faradaic efficiency η_F=100% using the equation:

\[ \text{ABPE} = \frac{J_{\text{PEC}} \times (1.23 - V_{\text{app}}) \times \eta_F}{\eta_{\text{total}}^{1.4}} \quad (S3) \]

J_{PEC} is the measured photocurrent density under AM 1.5G illumination (mA cm⁻²),
is the applied potential of the working electrode vs RHE (V), and \( P_{\text{total}} \) is the total power density of the incident AM 1.5G illumination (100 mW cm\(^{-2}\)), \( \eta_F \) is Faradaic efficiency of H\(_2\) evolution.

Incident photon-to-current conversion efficiency (IPCE) is expressed using the following equation:

\[
\text{IPCE} = \frac{(1240 \times J_{\text{PEC}})}{(\lambda \times P_{\text{light}})} \quad (S4)
\]

\( P_{\text{light}} \) is the power density of monochromatic light (mW cm\(^{-2}\)).

Absorbed photon-to-current conversion efficiency APCE is obtained by dividing the IPCE by the \( \eta_{\text{abs}} \) at each wavelength using the following equation:

\[
\text{APCE} = \frac{\text{IPCE}}{\eta_{\text{abs}}} \quad (S5)
\]

The practical water oxidation photocurrent \( J_{\text{PEC}} \) can be expressed as:

\[
J_{\text{PEC}} \approx J_{\text{abs}} \times \eta_{\text{trans}} \times \eta_{\text{sep}} \quad (S6)
\]

Surface charge-transfer efficiency of water oxidation \( \eta_{\text{trans}} \) \((\text{H}_2\text{O})\) were calculated by equation:

\[
\eta_{\text{trans}} = \frac{J_{\text{PEC}}}{J_{\text{HS}}} \quad (S7)
\]

\( J_{\text{HS}} \) is the photocurrent density of the electrodes with Na\(_2\)SO\(_3\) as the hole scavenger.

Calculated photocurrent densities \( J_{\text{abs}} \) of the electrodes can be obtained by integrating the IPCE values with the standard solar spectrum (ASTMG-173-03) using the following equation:

\[
J_{\text{abs}} = \int \frac{\lambda \times \text{IPCE}(\lambda) \times E(\lambda)}{1240} \, d\lambda \quad (S8)
\]

Charge separation efficiency \( \eta_{\text{sep}} \) represents the yield of electron-hole pair separation can be calculated by the following equation:

\[
\eta_{\text{sep}} = \frac{J_{\text{HS}}}{J_{\text{abs}}} \quad (S9)
\]

According to the Mott-Schottky curves, charge carrier density \( N_D \) can be calculated using the following equation:

\[
N_D = \frac{2}{e \varepsilon \varepsilon_0} \times \left[ \frac{d(1/C^2)}{dE} \right]^{-1} \quad (S10)
\]

The electronic charge \( e \) is 1.6 \times 10^{-19} \text{C}, relative permittivity \( \varepsilon \) is 68 \text{F m}^{-1} for BiVO\(_4\) and vacuum permittivity \( \varepsilon_0 \) is 8.86 \times 10^{-12} \text{F m}^{-1}. C \) obtained from Mott-Schottky curves is the space charge capacitance in the semiconductor \( \text{(F cm}^{-2} \text{)}\), and \( E \) (V) is the applied potential for Mott-Schottky curves.

Faradaic efficiency \( \eta_F \) is the most valuable way to confirm that the generated photocurrent comes from water splitting rather than side reactions and photocorrosion.
of the samples. It is defined as:

$$\eta_F = \frac{\text{Gas}_{\text{experimental}}}{\text{Gas}_{\text{theoretical}}} = \frac{nO_2}{\left(\frac{J_{\text{PEC}} \times A \times T}{4 \times N_A \times e}\right) \times 100\%} \quad (S11)$$

T is the measurement time (s); A is the illumination area of the electrode (cm²); The electronic charge (e) is $1.6 \times 10^{-19}$ C and $N_A$ is the Avogadro constant ($6.02 \times 10^{23}$ mol⁻¹).
Figure S1. SEM images of different CTPs

Figure S2. FT-IR spectra of different monomer A for different CTPs

Figure S3. XPS spectra of C 1s and N 1s for different CTPs
Figure S4. Tauc plots of BiVO$_4$ and CTPs

Figure S5. (a) LSV curves and (b) J-t curves of different CTPs in 0.1 M phosphate buffer (pH=7) under AM 1.5G (100 mW cm$^{-2}$) illumination at 1.23 V vs. RHE
Figure S6. (a) Mott-Schottky plots of different CTPs in 0.1 M phosphate buffer (pH=7) with 1 M Na$_2$SO$_3$; (b) EIS plots under AM 1.5G illumination

Figure S7. PL emission spectra of different CTPs excited at 400 nm
Figure S8. SEM images of (a) BiVO₄, (b) BiVO₄/CTP1, (c) BiVO₄/CTP2 and (d) BiVO₄/CTP3.

Figure S9. XRD patterns of BiVO₄ and different BiVO₄/CTPs electrodes. Vertical lines indicate JCPDS diffraction peaks of monoclinic scheelite BiVO₄ (dark yellow, JCPDS #14-0688) and FTO (orange).
Figure S10. (a) LSV curves of BiVO₄/CTPs in 0.1 M phosphate buffer (pH=7) with 1 M Na₂SO₃ under AM 1.5G (100 mW cm⁻²) illumination or in the dark.

Figure S11. (a) $\eta_{sep}$ curves and (b) $\eta_{trans}$ of the BiVO₄ and different BiVO₄/CTPs electrodes.
Figure S12. (Right) Calculated photocurrent density curves corresponding to different wavelengths from (Left) the standard solar spectrum (ASTMG-173-03) of BiVO$_4$ (black), and BiVO$_4$/CTPs electrodes.

Figure S13. (a) $\eta_{\text{abs}}$ curves and (b) APCE spectra of BiVO$_4$ and different BiVO$_4$/CTPs electrodes.
Figure S14. XPS spectra of (a) Fe 2p and (b) Ni 2p peaks for the BiVO<sub>4</sub>/CTPs/FN electrode.

Figure S15. (a) LSV curves in 0.1 M phosphate buffer (pH=7) with 1 M Na<sub>2</sub>SO<sub>3</sub> under AM 1.5G (100 mW cm<sup>-2</sup>) illumination or in the dark, (b) η<sub>trans</sub> curves of BiVO<sub>4</sub>, BiVO<sub>4</sub>/CTP2, BiVO<sub>4</sub>/FN and BiVO<sub>4</sub>/CTPs/FN electrodes.
Figure S16. (a) $\eta_{abs}$ curves of BiVO$_4$ and BiVO$_4$/CTP2 electrodes and (b) APCE spectra of BiVO$_4$, BiVO$_4$/CTP2, BiVO$_4$/FN and BiVO$_4$/CTPs/FN electrodes.
Table S1. Charge carrier density \( (N_D) \) values of CTPs

<table>
<thead>
<tr>
<th>Samples</th>
<th>CTP1</th>
<th>CTP2</th>
<th>CTP3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_D \times 10^{17} \text{ cm}^{-3} )</td>
<td>5.32</td>
<td>10.02</td>
<td>6.74</td>
</tr>
</tbody>
</table>

Table S2. EIS Nyquist fitting values of CTPs in 0.1 M phosphate buffer

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>CTP1</th>
<th>CTP2</th>
<th>CTP3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_S \Omega \text{ cm}^2 )</td>
<td>404.1</td>
<td>98.44</td>
<td>153.6</td>
</tr>
<tr>
<td>( R_{\text{CT}} \times 10^6 \Omega \text{ cm}^2 )</td>
<td>2.65</td>
<td>1.02</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Table S3. Energy band positions of BiVO\(_4\) and CTPs

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>BiVO(_4)</th>
<th>CTP1</th>
<th>CTP2</th>
<th>CTP3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB/LUMO(eV)</td>
<td>-0.02</td>
<td>-0.35</td>
<td>-0.48</td>
<td>-0.43</td>
</tr>
<tr>
<td>VB/HOMO(eV)</td>
<td>2.45</td>
<td>1.62</td>
<td>1.38</td>
<td>1.84</td>
</tr>
<tr>
<td>Band gap(eV)</td>
<td>2.47</td>
<td>1.97</td>
<td>1.86</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Table S4. EIS Nyquist fitting values in 0.1 M phosphate buffer of BiVO\(_4\)-based electrodes

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>BiVO(_4)</th>
<th>BiVO(_4)/CTP1</th>
<th>BiVO(_4)/CTP2</th>
<th>BiVO(_4)/CTP3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_S \Omega \text{ cm}^2 )</td>
<td>61.7</td>
<td>51.9</td>
<td>44.1</td>
<td>56.4</td>
</tr>
<tr>
<td>( R_{\text{CT}} \Omega \text{ cm}^2 )</td>
<td>1063</td>
<td>886.9</td>
<td>576.8</td>
<td>779.6</td>
</tr>
</tbody>
</table>

Table S5. XPS contents of different elements for the BiVO\(_4\)/CTP2/FN electrode

<table>
<thead>
<tr>
<th>Elements</th>
<th>Bi 2p</th>
<th>V 2p</th>
<th>O 1s</th>
<th>C 1s</th>
<th>N 2p</th>
<th>Fe 3d</th>
<th>Ni 3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiVO(_4)/CTP2/FN (%)</td>
<td>0.21</td>
<td>0.25</td>
<td>15.65</td>
<td>65.01</td>
<td>12.10</td>
<td>3.68</td>
<td>3.10</td>
</tr>
</tbody>
</table>
Table S6 Summary of the BiVO$_4$-based photoanodes at 1.23 V vs. RHE for PEC water splitting.

<table>
<thead>
<tr>
<th>Samples</th>
<th>J (mA cm$^{-2}$)</th>
<th>$\text{H}_2$/O$_2$ evolutions (μmol cm$^{-2}$)</th>
<th>$\text{H}_2$/O$_2$ evolutions (μmol cm$^{-2}$ h$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Zr)BiVO$_4$/NiFePB</td>
<td>3.23</td>
<td>~1/16 for 1.8 h</td>
<td>~8.9</td>
<td>(6)</td>
</tr>
<tr>
<td>CoBi/ E-BiVO$_4$</td>
<td>3.2</td>
<td>28/13.8 for 1 h</td>
<td>28/13.8</td>
<td>(2)</td>
</tr>
<tr>
<td>NiOOH/BP/BiVO$_4$</td>
<td>4.48</td>
<td>~144/72 for 3.3 h</td>
<td>~43.6/22.8</td>
<td>(7)</td>
</tr>
<tr>
<td>BiVO$_4$/Ag/MoS$_2$</td>
<td>4.02</td>
<td>578/297 for 10 h</td>
<td>57.8/29.7</td>
<td>(8)</td>
</tr>
<tr>
<td>NFCB</td>
<td>5.99</td>
<td>664/330 for 10 h</td>
<td>66.4/33</td>
<td>(3)</td>
</tr>
<tr>
<td>ZBGC</td>
<td>5.03</td>
<td>882/440 for 10 h</td>
<td>88.2/44.0</td>
<td>(9)</td>
</tr>
<tr>
<td>2-BVO1.5h/FeOOH</td>
<td>5.87</td>
<td>498/247 for 5 h</td>
<td>99.6/49.4</td>
<td>(10)</td>
</tr>
<tr>
<td>/NiOOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo:BiVO$_4$/LBR</td>
<td>5.25</td>
<td>~200/100 for 2 h</td>
<td>~100/50</td>
<td>(11)</td>
</tr>
<tr>
<td>BiVO$_4$/CTP2/FN</td>
<td>4.05</td>
<td>676/338 for 10 h</td>
<td>67.6/33.8</td>
<td>This work</td>
</tr>
</tbody>
</table>

Referring to the comparison with other researches, the performance in this work is not very high, therefore, we consider that the structural design of the BiVO$_4$-based photoanodes is crucial for the PEC performance. As reported, the PEC performance of semiconductors depends on multifarious modification strategies mainly including morphology regulation, elemental doping, metal deposition, heterojunction construction and co-catalyst loading to synergistically boost the charge separation and transfer, and to broaden the light absorption and improve the oxygen evolution kinetics. On the other hand, the hybrid methods will influence the PEC performance of electrodes. As for this work, we deem that the hybrid method for BiVO$_4$ and CTPs can be further optimized in future. Hence, we will enhance the electrical conductivity between BiVO$_4$ and CTPs from the aspect of hybrid methods in the future work.
References: