Electronic Supplementary Information

A Hybrid Bulk-Heterojunction Photoanode for Direct Solar-to-Chemical Conversion

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Contents

1. Supplementary Figures ...................................................................................................................................... S2
2. Supplementary Table ......................................................................................................................................... S14
3. Supplementary References .............................................................................................................................. S14
1. Supplementary Figures

Figure S1. Planar FTO/CPN photoanodes. a) shows photographs of the planar FTO/CPN photoanodes with different thickness of CPN prepared by depositing multiple layers. Three layers of CPN leads to a thickness of 120 nm on top of the FTO (as shown below in Figure S5). b) shows linear sweep voltammetry (LSV) of the planar FTO/CPN photoanodes in 1 M iodide electrolyte (pH 1) under intermittent simulated solar illumination as indicated by selected light on/off cycles shown. The minor difference in the current density, \( J \), between the light on and light off condition gives the photocurrent density \( J_{ph} \).

Figure S2. TEM image of SnO\(_2\) nanoparticles and SnO\(_2\) particle size distribution histogram extracted from the TEM image (accounting for overlapping).
Figure S3. Energy level diagram against vacuum energy level and NHE at pH = 0 of SnO$_2$ nanoparticles, CPN and I$^-$/I$_3^-$ redox couple.

Figure S4. Molecular structure and optimized geometry of PDI-DA and Triazine-TA. The equilibrium geometry is simulated by Spartan 14' software package using the B3LYP/6-31G* basis set and the distance of conjugated part is displayed in the image.

Figure S5. Cross sectional SEM image of CPN on FTO (3x monomer deposition/TAA). The scale bar is 200 nm.
Figure S6. Morphological characterization of bare FTO and CPN on FTO (prepared with 1x monomer deposition/TAAC). Height topography, KPFM potential image, and contact potential difference ($V_{\text{CPD}}$) are shown in the top, middle and bottom panel, respectively. All the measurements were performed under dark ambient condition. The scale bar of the images is 500 nm.

Figure S7. Comparison of the UV-vis absorption spectra of CPN:SnO$_2$ BHJ photoanode before and after chloroform (CF) washing (via a spin coating step). It can be seen that most of the absorption is kept after chloroform washing, indicating the TAAC reaction occurs after infiltrating PDI-DA and Triazine-TA into the SnO$_2$ nanoparticle film.
Figure S8. Cross-sectional SEM image of CPN:SnO$_2$ photoanodes. The scale bar in the images is 1 µm. The thickness is determined to be 480 nm (a), 770 nm (b), 1.77 µm (c), and 2.40 µm (d), respectively.

Figure S9. UV-vis absorption spectra of CPN:SnO$_2$ photoanode with SnO$_2$ nanoparticle thickness of 480 nm, 1.77 µm and 2.40 µm. PDI-DA and Triazine-TA were coated on top of SnO$_2$ nanoparticles with the same procedure. TAAC reaction was performed at 150 °C for 10 min to obtain CPN:SnO$_2$ BHJ.
Figure S10. LSV scans of CPN:SnO₂ BHJ photoanodes in 1 M iodide electrolyte (pH 1) under intermittent 1 sun illumination. The m-SnO₂ layers have the same thickness in all cases (480 nm) and the number of monomer deposition/TAAC cycles was changed.

Figure S11. LSV scans of FTO/SnO₂ nanoparticle film (480 nm) under dark and 1 sun illumination. The electrolyte is 1 M iodide (I⁻) at pH 1.
Figure S12. Comparison of LSV scans of CPN:SnO₂ BHJ (FTO/CPN:SnO₂) and SnO₂/CPN bilayer junction (FTO/SnO₂/CPN). 1x monomer deposition/TAAC was used for obtaining the CPN layer. The bilayer junction SnO₂ was prepared according to a previously-reported approach.¹ The SnO₂ thickness of both structures is 200 nm.

Figure S13. Performance of Triazine-TA and PDI-DA monomers:SnO₂ photoanode in 1 M iodide at pH 1. For the monomer:SnO₂ photoanode, the Triazine-TA:PDI-DA blend was coated onto SnO₂ nanoparticles (1.77 µm) with the same procedure but the heating to trigger TAAC reaction was not performed. a) LSV scans under intermittent illumination. b) CA test under continuous illumination at +0.75 V vs NHE. Illumination was switched on after 1 min stabilization in the dark.
Figure S14. Chronoamperometry of the optimal CPN:SnO$_2$ photoanode in 1 M iodide at pH 7 and pH 12 under continuous illumination at +0.75 V vs NHE. Illumination was switched on after initial stabilization in the dark.

Figure S15. LSV scans of CPN:SnO$_2$ photoanode with 480 nm SnO$_2$ nanoparticle film in 1 M iodide at different pH.
**Figure S16.** Polarization curves of bare FTO substrate after iR correction in 1 M iodide electrolyte at different pH (scan rate 1 mV s\(^{-1}\)).

**Figure S17.** Nyquist plots of impedance measurements. The potential scale for SnO\(_2\) and CPN is RHE and NHE, respectively. The equivalent circuit including series resistance \(R_s\), charge transfer resistance from bulk \(R_{CT,\text{bulk}}\), and bulk capacitance \(C_{\text{bulk}}\) was used to fit the impedance data. The fitted results were shown as the solid line in each graph.
Figure S18. a) Top-down SEM image of CPN:SnO₂ photoanode after 5 h operation in 1 M HI at +0.54 V vs NHE. EDX mapping displays the element distribution (tin, oxygen, carbon and iodine). The scale bar is 10 µm. b) Elemental composition map sum spectrum of the SEM image. The relative percentage contributions by weight % are listed. The result indicates in-situ I₂ deposition occurs at the photoanode surface, due to the poor solubility of I₂ in water.

Figure S19. IPCE of CPN:SnO₂ photoanode at +0.54 V vs NHE in 1 M HI electrolyte. The integrated Jph is shown with blue square markers.
Figure S20. Nyquist plots of (a) IMPS and (b) IMVS response of the optimal CPN:SnO₂ BHJ photoanode. Both IMPS and IMVS were conducted in 1 M HI. IMPS was recorded at +0.54 V vs NHE and IMVS was recorded under open-circuit condition. IMPS/IMVS analysis reveals an electron diffusion coefficient ($D_n$) of $4.87 \times 10^{-6}$ cm² s⁻¹ and an electron diffusion length ($L_n$) of 3.14 μm, according to the model developed for DSSCs.

Details on charge carrier dynamics: To evaluate the charge carrier dynamics of our hybrid photoanode, we performed light modulation techniques, including intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) on the optimal CPN:SnO₂ BHJ photoanode with m-SnO₂ thickness of 1.77 μm, using 1 M HI as electrolyte. IMPS and IMVS are spectroelectrochemical techniques to investigate carrier transport/recombination, and have been widely applied in photovoltaic devices, such as dye-sensitized solar cells (DSSCs), perovskite solar cells and organic solar cells. Recently, IMPS/IMVS have been considered as emerging techniques for revealing carrier dynamics of solar water splitting devices. The Nyquist plots of IMPS and IMVS response are shown in Figure S20. It can be observed that Nyquist plots of IMPS and IMVS of CPN:SnO₂ photoanode could follow the model that developed in DSSCs.² We suppose this is rational, as HI oxidation is a kinetic favorable two-electron transfer reaction, which is analogous with the case in DSSCs and different from the four-electron transfer OER. As highlighted in Figure S20a, the characteristic frequency ($f_{\text{min,IMPS}}$) at the minimal point of IMPS response is correlated to the mean transit time for photogenerated electrons:

$$\tau_d = \frac{1}{2\pi f_{\text{min,IMPS}}} = 1.61 \text{ ms}$$

Likewise, in Figure S20b the first-order electron lifetime ($\tau_n$) can be estimated from the characteristic frequency ($f_{\text{min,IMVS}}$) in IMVS response:

$$\tau_n = \frac{1}{2\pi f_{\text{min,IMVS}}} = 20.21 \text{ ms}$$

Combining the time constant obtained from IMPS and IMVS analysis, electron diffusion coefficient ($D_n$) and electron diffusion length ($L_n$) of CPN:SnO₂ photoanode can be estimated by:

$$D_n = \frac{d^2}{4\tau_d}$$

$$L_n = \sqrt{D_n \tau_n}$$

where $d$ is the film thickness (1.77 μm). $D_n$ and $L_n$ are found to be around $4.87 \times 10^{-6}$ cm² s⁻¹ and 3.14 μm, respectively. The value of $L_n$ is larger than $d$, ensuring the electron diffusion across the film.
Figure S21. PEC test of another individual CPN:SnO₂ photoanode in 1 M HI for the quantification of I³⁻ and H₂. a) LSV scan and b) 11.4 h CA test at +0.54 V vs NHE under 1 sun illumination.

Figure S22. The number of electrons (μmol) calculated from 11.4 h CA test as a function of time. The total electron amount is 260.6 μmol.

Figure S23. I³⁻ amount quantification. a) UV absorption spectra of standard I³⁻ solution with specific concentrations. b) Absorption intensity at 350 nm as a function of I³⁻ concentration. A linear regression was used to fit the results ($R^2 = 0.99$). The absorption intensity at 350 nm of the electrolyte with 1/50 dilution (shown in Figure 5c in the main text) is 1.664, corresponding to a concentration of 386.8 μmol L⁻¹.
Figure S24. Hydrogen amount (a) and hydrogen evolution Faradaic efficiency (b) as a function of operation time.

Figure S25. LSV scan of PTB7-Th:PDI-V photocathode and CPN:SnO$_2$ photoanode in 1 M HI under intermittent 1 sun illumination.


2. Supplementary Table

**Table S1.** Reported organic semiconductor photoanodes for solar-to-chemical conversion

<table>
<thead>
<tr>
<th>Publication</th>
<th>Starting material</th>
<th>Product</th>
<th>Photoanode structure</th>
<th>Initial (J_{ph}) @0.54 V vs NHE</th>
<th>Demonstrated operation time</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>This work</strong></td>
<td></td>
<td></td>
<td>FTO/CPN:SnO(_2)</td>
<td>3.3 mA cm(^{-2})</td>
<td>29 h @0.54 V vs NHE</td>
</tr>
<tr>
<td>Chem. Mater., 2018, 30, 324</td>
<td>H(_2)O O(_2)</td>
<td>FTO/ZnO/PC(_{32})/BM/(\text{ZnO})</td>
<td>(=60) (\mu)A cm(^{-2}) @1.23 V vs RHE</td>
<td>(\sim 940) s(^{[a]})</td>
<td></td>
</tr>
<tr>
<td>Mater. Chem. Front., 2018, 2, 2021</td>
<td>H(_2)O O(_2)</td>
<td>FTO/TiO(_2)/C12</td>
<td>(=30) (\mu)A cm(^{-2}) @1.2 V vs RHE</td>
<td>90 s(^{[a]}) @1.2 V vs RHE</td>
<td></td>
</tr>
<tr>
<td>ChemistrySelect, 2017, 2, 4522</td>
<td>H(_2)O O(_2)</td>
<td>ITO/PTEB</td>
<td>(=5) (\mu)A cm(^{-2}) @1.5 V vs RHE</td>
<td>Not reported</td>
<td></td>
</tr>
<tr>
<td>J. Am. Chem. Soc., 2015, 137, 15338</td>
<td>H(_2)O O(_2)</td>
<td>FTO/BBL/Ni–Co</td>
<td>(=30) (\mu)A cm(^{-2}) @1.23 V vs RHE</td>
<td>30 min(^{[a]}) @1.23 V vs RHE</td>
<td></td>
</tr>
<tr>
<td>ACS Appl. Mater. Interfaces, 2014, 6, 13367</td>
<td>H(_2)O O(_2)</td>
<td>ITO/PMPDI/CoO(_x)</td>
<td>(=150) (\mu)A cm(^{-2}) @1.56 V vs RHE</td>
<td>300 s(^{[a]}) @1.23 V vs RHE</td>
<td></td>
</tr>
<tr>
<td>Angew. Chem. Int. Ed., 2012, 124, 1943</td>
<td>H(_2)O O(_2)</td>
<td>ITO/PTTh(_2)-2:MnPor</td>
<td>(=20) (\mu)A cm(^{-2}) @1.51 V vs RHE</td>
<td>700 s(^{[a]}) @1.51 V vs RHE</td>
<td></td>
</tr>
<tr>
<td>Sci. China Chem., 2012, 55, 1953</td>
<td>H(_2)O O(_2)</td>
<td>ITO/PTCD(<em>{A})/PTCD(</em>{A}):P(<em>{C</em>{60}}BM/PC_{61})BM</td>
<td>(=160) (\mu)A cm(^{-2}) @1.16 V vs RHE</td>
<td>(\sim 1000) s(^{[a]}) @1.16 V vs RHE</td>
<td></td>
</tr>
<tr>
<td>Angew. Chem. Int. Ed., 2006, 45, 2778</td>
<td>H(_2)O O(_2)</td>
<td>ITO/PTC(_{B})/CoPc</td>
<td>(=20) (\mu)A cm(^{-2}) @1.2 V vs RHE</td>
<td>Not reported</td>
<td></td>
</tr>
<tr>
<td>J. Electroanal. Chem., 2006, 587, 127</td>
<td>H(_2)O O(_2)</td>
<td>ITO/PTC(_{B})/CoPc/CoPc/Nf</td>
<td>(=6) (\mu)A cm(^{-2}) @1.19 V vs RHE</td>
<td>1.5 h(^{[b]}) @1.19 V vs RHE</td>
<td></td>
</tr>
<tr>
<td>RSC Adv., 2015, 5, 46325</td>
<td>N(_2)H(_4) N(_2)</td>
<td>ITO/PTC(_{B})/CoPc/Nf</td>
<td>(=135) (\mu)A cm(^{-2}) @1.15 V vs RHE</td>
<td>1 h(^{[b]}) @1.15 V vs RHE</td>
<td></td>
</tr>
<tr>
<td>Chem. Commun., 2014, 50, 1950</td>
<td>N(_2)H(_4) N(_2)</td>
<td>ITO/C(_{60})/ZnPc/Nf</td>
<td>(=178) (\mu)A cm(^{-2}) @1.15 V vs RHE</td>
<td>1 h(^{[b]}) @1.15 V vs RHE</td>
<td></td>
</tr>
<tr>
<td>Chem. Commun., 2019, 55, 12491</td>
<td>RS(^{-}) RS(^{-})</td>
<td>ITO/ZnO/P3HT:PCBM/(\text{ZnPc})</td>
<td>(=32) (\mu)A cm(^{-2}) @0.85 V vs RHE</td>
<td>Not reported</td>
<td></td>
</tr>
<tr>
<td>Phys. Chem. Chem. Phys., 2008, 10, 1562</td>
<td>RS(^{-}) RS(^{-})</td>
<td>ITO/PTC(_{B})/H(_2)Pc</td>
<td>(=300) (\mu)A cm(^{-2}) @0.79 V vs RHE</td>
<td>12 min(^{[a]}) @0.79 V vs RHE</td>
<td></td>
</tr>
<tr>
<td>J. Electroanal. Chem., 2007, 599, 65</td>
<td>RS(^{-}) RS(^{-})</td>
<td>ITO/Co(_{61}/H(_2)Pc</td>
<td>(=530) (\mu)A cm(^{-2}) @1.09 V vs RHE</td>
<td>4 min(^{[a]}) @1.09 V vs RHE</td>
<td></td>
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</tbody>
</table>

\[^{[a]}\] The operation time is extracted from the I–t curve under illumination at the specific potential.

\[^{[b]}\] Overall product amount was checked after operation but I–t curve under illumination was not provided in the paper.

3. Supplementary References
