The Photocurrent Response in the Perovskite Device Based on Coordination Polymer: Structure, Topology, Band Gap and Matched Energy Level

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Fabrication of Device Based on FTO/ Compact TiO₂ (cTiO₂)/ Perovskite CH₃NH₃PbI₃/ CP 2

The fabrication of device based on FTO/compact TiO₂ (cTiO₂)/perovskite CH₃NH₃PbI₃/ CP 2 is according to the literature method. ¹

Firstly, fluorine doped tin oxide (FTO, 12-14 μS/m) glass substrate was ultrasonic bath washed successively in acetone, ethanol and deionized water for 10 min each.

Secondly, a compact TiO₂ blocking layer was prepared with sol-gel method. The TiO₂ sol-gel used here was prepared by mixing titanium tetraisopropoxide (TTIP) contained solution A (TTIP, ethanol) and acid solution B (ethanol, HCl, H₂O). 0.1 mL of the sol-gel was dropped onto FTO with the effective area of the TiO₂ film maintained at 1.0 × 1.0 cm² through a Scotch tape mask. Then the substrate was calcined at 450 °C for 1 hour in
air. After cooling to room temperature, the surface of the TiO$_2$ film was further deposited by 0.1 mL of a 40 mM aqueous solution of TiCl$_4$. Then the TiCl$_4$ treated substrate was again calcined at 500 °C for 15 min to obtain the compact TiO$_2$ layer (cTiO$_2$).

Thirdly, 2 mg perovskite (CH$_3$NH$_3$PbI$_3$) (homemade and characterized by powder X-ray diffraction, please see Fig. S1) was dissolved in 2 mL N, N’-dimethylformamide (DMF), then 0.1 mL of the perovskite solution was dropped onto the compact TiO$_2$ surface. The substrate was then dried by an IR lamp on to remove the remaining solvent.

The fourth step is to deposit CP 2 on the above perovskite layer. 2 mg CP 2 was ultrasonicated in 2 mL ethanol, then 0.4 or 0.1 mL of the mixture (CP 2 mass loading: 0.4 mg or 0.1 mg) was dropped on the perovskite and dried by an IR lamp.

The above fabricated FTO/ cTiO$_2$ / perovskite / CP 2 device was used as the working electrode from the back side for the detection of the photocurrent generation with a platinum foil and a AgCl/Ag electrode as the counter electrode and the reference electrode, respectively. 0.2 M Na$_2$SO$_4$ solution (80 mL) was used as the electrolyte.

**Table S1** Selected bond lengths (Å) and angles (º) for CPs 1-3

<table>
<thead>
<tr>
<th>CP 1</th>
<th>Bond Length/Angle</th>
<th>CP 2</th>
<th>Bond Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(1)-O(4)#1</td>
<td>2.140(2)</td>
<td>Cd(1)-O(5)</td>
<td>2.274(4)</td>
</tr>
<tr>
<td>Mn(1)-O(2)#2</td>
<td>2.163(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(4)#1-Mn(1)-O(3)#3</td>
<td>96.85(10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(3)#3-Mn(1)-O(6)</td>
<td>177.80(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(1)-O(6)</td>
<td>2.263(3)</td>
<td>O(4)#1-Mn(1)-O(5)</td>
<td>84.03(9)</td>
</tr>
<tr>
<td>Mn(1)-O(1)</td>
<td>2.177(3)</td>
<td>O(1)-Mn(1)-O(3)#3</td>
<td>92.21(10)</td>
</tr>
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</tbody>
</table>

Cd(1)-O(4)#4         2.330(3)  
O(2)#5-Cd(1)-O(3)#6  173.35(11) 
O(3)#6-Cd(1)-O(3)#4  97.38(12)  
O(2)#5-Cd(1)-O(2)    105.03(12) 

**CP 3**

Mn(1) - O(1)           2.127(3)  
Mn(2)-O(4)#7           2.072(3)  
O(10)-Mn(1)-O(9)      82.23(12)  
O(4)#7-Mn(2)-O(8)     101.09(11) 

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z         #2 -x,-y+1,-z+1        #3 -x,y+1/2,-z+1/2     #4 x-1/2,y+1,-z+1/2
#5 –x+1/2,y+1/2,z    #6 –x+1,y+1/2,-z+1/2    #7 x-1,y,z

(a)

As-synthesized

Simulated

Intensity

Degree (2θ)

5  10  15  20  25  30  35  40
(b) After immersion in Na$_2$SO$_4$ aqueous solution for 6h

As-synthesized

Simulated

(c)

As-synthesized

Simulated
**Fig. S1** The PXRD patterns of CPs 1 (a), 2 (b), 3 (c) and the perovskite CH$_3$NH$_3$PbI$_3$ (d).

**Fig. S2** Thermogravimetric curves of CPs 1 (red), 2 (green) and 3 (pink).
(a)

(b)
Fig. S3 The SEM images of CP 2 before (a, b) and after immersion in Na$_2$SO$_4$ aqueous
solution (c, d).

**Fig. S4** UV-vis absorption spectra at room temperature for the free organic ligand $\text{H}_2\text{L}$ and CPs 1-3.
Fig. S5 The diffuse reflectance spectra (DRS) for CPs 1-3 in the transformed Kubelka–Munk functions.
**Fig. S6** CVs of 1-GCE in a 0.2 M Na$_2$SO$_4$ solution (80 mL) in the potential range from -1.6 to 1.2 V vs SCE at different scan rates.
Fig. S7 CVs of 3-GCE in a 0.2 M Na$_2$SO$_4$ solution (80 mL) in the potential range from -1.6 to 1.2 V vs SCE at different scan rates.
Fig. S8 CVs of 2-GCE in a 0.2 M Na$_2$SO$_4$ solution (80 mL) in the potential range from -1.6 to 1.2 V vs SCE at different scan rates.
Fig. S9 Solid-state emission spectra at room temperature for the free ligand \( \text{H}_2\text{L} \) and \( \text{CP} \ 2 \).
Fig. S10 Nyquist plots ($Z'$ vs. $-Z''$) of the three-electrode system at $E = 0$ V vs AgCl/Ag in Na$_2$SO$_4$ aqueous solution (0.2 M, 80 mL) in the absence and presence of visible light illumination ($650$ nm $> \lambda > 350$ nm) with the CP 2-modified FTO slide as working electrode.
Fig. S11 Cross-section (a-b) and oblique-view SEM images of FTO / TiO$_2$ / CH$_3$NH$_3$PbI$_3$ / CP 2 device (c-d).
Fig. S12 Top-view SEM images of the compact TiO$_2$ layer (a, b); the perovskite CH$_3$NH$_3$PbI$_3$ on the top of the compact TiO$_2$ layer (c, d) and CP 2 (e, f) on the top of the perovskite CH$_3$NH$_3$PbI$_3$. 
Fig. S13 Elemental mapping and total element amount of the perovskite CH$_3$NH$_3$PbI$_3$ on the top of the compact TiO$_2$ layer (a) and CP 2 (b) on the top of the perovskite
Fig. S14 CVs of CP 2- or PbI₂-modified FTO slices in a 0.2 M Na₂SO₄ solution (80 mL) in the potential range from -1.0 to 1.0 V vs AgCl/Ag at a scan rate of 0.01 V·s⁻¹ with (solid line) and without (dotted line) the visible light illumination (650 nm > λ > 350 nm).
**Fig. S15** CVs of FTO/cTiO$_2$/perovskite/CP 2 in a 0.2 M Na$_2$SO$_4$ solution (80 mL) from -1.0 to 1.0 V vs AgCl/Ag at 0.01 V·s$^{-1}$ with (solid line) and without (dotted line) the visible light illumination (650 nm > λ > 350 nm) at 100 mW·cm$^{-2}$. CP 2 mass loading: 0.4 mg (sapphire) or 0.1 mg (blue).

**Reference**