In-situ C–H activation-derived polymer@TiO$_2$ $p$-$n$ heterojunction for photocatalytic hydrogen evolution

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Characterization

X-ray diffraction (XRD) was measured by Thermo Fisher NexsaI instrument. X-ray photoelectron spectroscopy (XPS) was measured by Thermo Fisher NexsaI instrument. Morphology of heterojunction photocatalysts was gained by scanning electron microscope (SEM, MLA650F, American) and transmission electron microscopy (TEM, FEI Tecnai G2 F20, American). Fourier transformed infrared (FTIR) spectra were performed on a FT-IR spectrometer (Bruker, ALPHA) in the range of 4000-500 cm$^{-1}$. UV-vis diffuse reflectance spectra were performed on UV-2600 scanning UV-vis spectrophotometer. Time-resolved fluorescence spectroscopy and photoluminescence (PL) spectra were carried out on HORIBA Instruments FL-1000 fluorescence spectrometer. Samples were degassed under vacuum at ambient temperature for 24 h. The volume of nitrogen adsorption was recorded over a relative pressure range between 0.01 and 0.99. 8 points in the relative pressure range of 0.05-0.2 were used for the calculation of the surface area according to the Brunauer-Emmet-Teller (BET) theory. Contact angle were obtained by JCY type measurement instrument (Shanghai Fang Rui Instrument Co. Ltd.).

Fig. S1 Hydrogen bond non-covalent interaction and structural illustration of PyOT@TiO$_2$s.
**Fig. S2** FT-IR spectra of pristine TiO$_2$, PyOT@TiO$_2$s, and PyOT.

**Fig. S3** SEM and TEM images of TiO$_2$ (a), PyOT (b), and 50% PyOT@TiO$_2$ (c).

**Fig. S4** EDS spectrum of 50% PyOT@TiO$_2$. 

S2
Fig. S5 (a-c) N\textsubscript{2} adsorption-desorption isotherms and (d) pore size distributions of 10\% PyOT@TiO\textsubscript{2}, 50\% PyOT@TiO\textsubscript{2} and 80\% PyOT@TiO\textsubscript{2}.

Fig. S6 XPS of TiO\textsubscript{2} (a), PyOT (b), and 50\% PyOT@TiO\textsubscript{2} (c).
**Fig. S7** Partial enlarged PL spectra of all samples (a), and PL spectra of in-situ synthesized 50% PyOT@TiO$_2$ and mechanically mixed 50% PyOT-TiO$_2$ composites (b).

**Fig. S8** EIS Nyquist plots 10% PyOT@TiO$_2$, 50% PyOT@TiO$_2$, 80% PyOT@TiO$_2$ under visible light irradiation ($\lambda \geq 420$ nm).

**Fig. S9** HERs of 50% PyOT-TiO$_2$ and 50% PyOT@TiO$_2$. 
Table S1. Comparisons of Photocatalytic HER of Various TiO$_2$-Based Photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Sacrificial agent</th>
<th>Light source</th>
<th>HER (µmol h$^{-1}$ g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyOT@TiO$_2$</td>
<td>AA</td>
<td>300 W Xe lamp</td>
<td>&gt;420</td>
<td>541</td>
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<tr>
<td>NiS/TiO$_2$ nanofibers</td>
<td>CH$_2$OH</td>
<td>350 W Xe lamp</td>
<td>&gt;420</td>
<td>655</td>
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<tr>
<td>TiO$_2$/CdS</td>
<td>CH$_2$OH</td>
<td>350 W Xe lamp</td>
<td>&gt;420</td>
<td>51.4</td>
</tr>
<tr>
<td>BE-TiO$_2$</td>
<td>TEOA</td>
<td>300 W Xe lamp</td>
<td>&gt;420</td>
<td>419.2</td>
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<tr>
<td>TiO$_2$(P25)-gC$_3$N$_4$</td>
<td>TEOA</td>
<td>150 W Hg Lamp</td>
<td>&gt;420</td>
<td>419</td>
</tr>
<tr>
<td>B-BT-1,4-E/TiO$_2$</td>
<td>TEOA</td>
<td>300 W Xe lamp</td>
<td>&gt;420</td>
<td>220.4</td>
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<tr>
<td>BBT/TiO$_2$</td>
<td>TEOA</td>
<td>300 W Xe lamp</td>
<td>&gt;420</td>
<td>30.0</td>
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<tr>
<td>FeS$_2$–TiO$_2$</td>
<td>CH$_3$OH</td>
<td>300 W Xe lamp</td>
<td>&gt;420</td>
<td>331</td>
</tr>
<tr>
<td>g-C$_3$N$_4$/TiO$_2$</td>
<td>TEOA</td>
<td>300 W Xe lamp</td>
<td>&gt;420</td>
<td>300</td>
</tr>
<tr>
<td>TiO$_2$@g-C$_3$N$_4$</td>
<td>CH$_3$OH</td>
<td>300 W Xe lamp</td>
<td>&gt;420</td>
<td>198</td>
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<tr>
<td>MoS$_2$/TiO$_2$</td>
<td>Na$_2$S+Na$_2$SO$_3$</td>
<td>300 W Xe lamp</td>
<td>&gt;420</td>
<td>143.32</td>
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<td>FH-TiO$_2$</td>
<td>CH$_3$OH</td>
<td>300 W Hg Lamp</td>
<td>&gt;420</td>
<td>566</td>
</tr>
</tbody>
</table>

4) P. Jiménez-Calvo, V. Caps, M. Ghazzal, C. Colbeau-Justin, V. Keller. Au/TiO$_2$(P25)-gC$_3$N$_4$ composites with low g-C$_3$N$_4$ content enhance TiO$_2$ sensitization for remarkable H$_2$ production from water under visible-light irradiation. 2020, 75, 104888.


**Fig. S10** Optical diagrams of H$_2$O droplets on samples TiO$_2$ (a), 10% PyOT@TiO$_2$ (b), 50% PyOT@TiO$_2$ (c), 80% PyOT@TiO$_2$ (d), and PyOT (e) surfaces, and their corresponding schematic interfaces and contact angles (f-j).
**Fig. S11** Cycling test of H\textsubscript{2} evolution (evacuation every 5 h) for catalyst/H\textsubscript{2}O/AA mixture (In the third run, AA was recharged).

**Fig. S12** Mott-Schottky (M-S) plots of TiO\textsubscript{2} (a), PyOT(b), 50% PyOT@TiO\textsubscript{2} (c).