Supporting Information

Synthesis of Visible and Near Infrared Light Sensitive Amorphous Titania for Photocatalytic Hydrogen Evolution

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1. The mechanism of preparation of a-TiO$_{2-x}$

Fig.S1 Schematic illustration of the preparation of a-TiO$_{2-x}$

2. XRD analyses for hydrolytic products

Fig.S2 XRD patterns of hydrolytic products by repeating 120 h of water dissolving Ti$^0$ for three times in anaerobic environment

3. HRTEM analyses for final products
Fig. S3 (A) to (D) are the HRTEM images of the final products from 15 h, 30 h, 60 h, and 120 h of anaerobic hydrolysis, respectively.

4. XPS and EPR analyses for a-TiO$_{2-x}$

![XPS and EPR spectra for a-TiO$_{2-x}$](image)

Fig. S4 (A) and (B) are the Ti2p XPS spectrum and EPR test for a-TiO$_{2-x}$ after three months of storage.

5. XRD, XPS, EPR, and UV-vis analyses for c-TiO$_{2-x}$

![XRD, XPS, EPR, and UV-vis spectra for c-TiO$_{2-x}$](image)

Fig. S5 (A), (B), (C), and (D) are the XRD pattern, high resolution Ti2p XPS spectrum, EPR test, and UV-vis absorption spectrum for c-TiO$_{2-x}$, respectively.

6. Calculation of the bandgap

For a semiconductor, the optical absorption near the band edge follows the equation,

$$\alpha = A(hv - E_g)^{n/2}/hv$$

(1)

where $\alpha$, $v$, $E_g$, $A$, and $n$ are the absorption coefficient, incident light frequency, bandgap, constant, and an integer, respectively. $n$ depends on whether the transition is direct ($n=1$) or indirect ($n=4$). We use $n=4$ to calculate the mobility gap of as-synthesized a-TiO$_{2-x}$ by transforming equation (1) into the following equation: $(ahv/A)^{1/2} = hv - E_g$
**Fig. S6** Calculation of the mobility gap for a-TiO$_{2-x}$ based on the data shown in Fig. 6A

**Fig. S7** The calculation of the bandgap for c-TiO$_{2-x}$ based on the data shown in Fig. S5 D

**7. Calculation of the quantum yield**

The quantum yield was measured and calculated by the reported method.\(^2\) Irradiation was performed at room temperature by using a 750 W Xe arc lamp as the light source. The 488 nm single wavelength filter was used throughout the photocatalytic hydrogen evolution and the irradiation of iron (III) potassium oxalate trihydrate (IPOT) to get rid of the other wavelengths of incident light except 488 nm. The detailed measurement of the absorbance for IPOT at 510 nm wavelength is listed as follows:

Firstly, 25 ml 0.08 mol/l IPOT was irradiated by the incident light with 488 nm wavelength for 60 s, and then 1 ml of the irradiated IPOT was fetched and added into the stabilizing agent (containing 20 ml water, 4 ml 0.1% 1,10-Phenanthroline monohydrate, and 1 ml 7.6% sodium oxalate solution) under dark. Similarly, another two irradiated IPOT samples were prepared by repeating the above operations for two times.

Secondly, the unirradiated IPOT samples were prepared by adding 1 ml 0.08 mol/l unirradiated IPOT into the stabilizing agent (containing 20 ml water, 4 ml 0.1% 1,10-Phenanthroline monohydrate, and 1 ml 7.6% sodium oxalate solution) under dark. Similarly, another two unirradiated IPOT samples were prepared by repeating the above operations for two times.

Finally, the above irradiated and unirradiated IPOT samples were utilized as the samples to test their absorbances at 510 nm wavelength.

**Table S1.** The absorbances ($\Delta A$) at 510 nm wavelength for three IPOT samples via 488 nm light irradiation for 60 s and three IPOT samples without light irradiation

<table>
<thead>
<tr>
<th>Experiments</th>
<th>$\Delta A1$</th>
<th>$\Delta A2$</th>
<th>$\Delta A3$</th>
<th>Average ($\Delta \bar{A}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiation</td>
<td>0.1007</td>
<td>0.1023</td>
<td>0.0966</td>
<td>0.0999</td>
</tr>
<tr>
<td>Without</td>
<td>0.0754</td>
<td>0.0825</td>
<td>0.0805</td>
<td>0.0795</td>
</tr>
</tbody>
</table>
Table S2. The photocatalytic H₂ evolution of a-TiO₂₋ₓ and c-TiO₂₋ₓ irradiated by 488 nm incident light for 5 h and the calculated quantum yield

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Total H₂ produced (µmol)</th>
<th>H₂ produced (µmol h⁻¹)</th>
<th>Quantum yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-TiO₂₋ₓ</td>
<td>0.9104</td>
<td>0.182</td>
<td>4.57</td>
</tr>
<tr>
<td>c-TiO₂₋ₓ</td>
<td>0.0315</td>
<td>0.006</td>
<td>0.16</td>
</tr>
</tbody>
</table>

8. EPR analysis for a-TiO₂ from tetrabutyl titanate

![EPR spectrum](image1)

**Fig. S8** EPR (X-band) spectrum at 100 K in air for a-TiO₂ from hydrothermal decomposition of tetrabutyl titanate according to the reported method [3]

9. HRTEM analyses for final products

![HRTEM image](image2)

**Fig. S9** HRTEM analyses for final product by vacuum annealing the hydrolytic products at 400 °C for 5 h.

Reference