Supplementary Data

Constructing a novel TiO$_2$/$\gamma$-graphyne heterojunction for enhanced photocatalytic hydrogen evolution

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1. Calibration details of X-ray photoelectron spectroscopy (XPS)

Au element was introduced as baseline for calibration. The peaks should not be adjusted by C 1s at 286.4 eV because γ-graphyne is carbon material. Thus, Au was deposited on sample to adjust the position of peaks. In a typical process, 20 mg of the photocatalyst was suspended in 0.1mL HAuCl₄·4H₂O (0.01mol/L) alcohol solution. After illumination under UV light for 0.5 h, Au was loaded onto the surface of the samples by a photo-deposition method.

2. The specific steps of adsorption experiment for methylene blue (MB)

Typically, 5 mg sample was introduced into 4 mL MB solution (5 mg L⁻¹) in a quartz container by ultrasonication for 0.5 h. The mixed suspension was stirred for 1 h at room temperature in dark to reach the adsorption equilibrium. Then, the powders were removed by centrifugation, and the residual MB concentration was determined by its absorption spectrum at 664.5 nm, which was recorded on a UV-2300 spectrophotometer. Thus, the equilibrium adsorption amount of MB was calculated according to Eq. (1).

\[
Q_e = \frac{(C_0 - C_e)V}{m}
\]

where \(Q_e\) (mg g⁻¹) is the equilibrium adsorption amount of MB, \(C_0\) and \(C_e\) (mg L⁻¹) is the initial and equilibrium centration of MB, respectively. \(V\) (L) is the volume of MB solution, and \(m\) (g) is sample mass. The equilibrium centration of MB (\(C_e\)) is calculated by a linear fit using five different concentrations of MB: 5 mg L⁻¹, 4.375 mg L⁻¹, 3.75 mg L⁻¹, 3.125 mg L⁻¹, 2.5 mg L⁻¹.
The detailed test conditions of Mott-Schottky plots

The corresponding electrodes of the as-prepared sample were fabricated on fluorine-doped tin oxide (FTO) conducting glasses. Electrochemical measurements were performed in a three-electrode cell, with the as-prepared corresponding electrodes as working electrode and Pt plate as counter electrode and saturated calomel electrode (SCE) as reference electrode.

Fourier transform infrared (FT-IR) spectra of TiO₂ and TiO₂/GY-5

For the pure TiO₂, the low-frequency band around 665 cm⁻¹ is ascribed to the Ti–O–Ti bonds. Two peaks around 1636 and 3435 cm⁻¹ correspond to O–H stretching vibrations of physically adsorbed water and hydroxyl group, respectively. Compared with the FT-IR spectrum of TiO₂, no obvious changes could be observed for the FT-IR spectrum of TiO₂/GY-5, which is because γ-graphyne is insensitive to infrared rays due
to the absence of C–H.

Fig. S2 Fourier transform infrared (FT-IR) spectra of TiO$_2$ and TiO$_2$/GY-5

5. **TEM image and EDS point-analysis spectrum of TiO$_2$/GY-5 sample**

The element composition of TiO$_2$/GY-5 was firstly characterized by the EDS spectrum. As shown in Fig.S2, carbon, titanium and oxygen were detected. The atomic ratio of oxygen is over twice as much as that of titanium, which might origin from the absorption of air and surface state.

Fig. S3 (a) TEM and (b) EDS spectrum of TiO$_2$/GY-5 sample
6. XPS spectra of γ-graphyne and TiO$_2$/GY-5 samples

XPS spectra of γ-graphyne and TiO$_2$/GY-5 are displayed in Fig. S4 and Fig. S5. Different from the isolated γ-graphyne mostly composed of carbon (Fig. S4), Ti, O and C elements were detected in the XPS spectra of TiO$_2$/γ-GY nanocomposite (Fig. S5).

![Fig. S4 XPS spectrum of γ-graphyne sample](image)

![Fig. S5 XPS spectrum of TiO$_2$/γ-GY-5 nanocomposite](image)

7. Photocatalytic H$_2$ evolution of TiO$_2$/GY-20 sample
Fig. S6 Hydrogen evolution of TiO$_2$/GY-20 nanocomposite

8. A comparison of the $\text{H}_2$ production rate

Table S1 A comparison of the $\text{H}_2$ production rate for the latest reported photocatalysts modified by other 2D materials.

<table>
<thead>
<tr>
<th>System</th>
<th>Sacrificial agent</th>
<th>Light source</th>
<th>$\nu(\text{H}_2)$ ($\mu$mol h$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/γ-graphyne</td>
<td>10% methanol</td>
<td>300 W Xe lamp</td>
<td>19.4</td>
<td>Our work</td>
</tr>
<tr>
<td>B-rGO/O-gC$_3$N$_4$/Pt</td>
<td>30% triethanolamine</td>
<td>500 W Xe lamp</td>
<td>8.30</td>
<td>[2]</td>
</tr>
<tr>
<td>TiO$_2$/graphene QDs</td>
<td>10% ethanol</td>
<td>250 W Hg lamp</td>
<td>2.20</td>
<td>[3]</td>
</tr>
<tr>
<td>CdSe QDs/graphdiyne</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>300 W Xe lamp</td>
<td>0.25</td>
<td>[4]</td>
</tr>
<tr>
<td>BCN/TiO$_2$</td>
<td>20% triethanolamine</td>
<td>300 W Xe lamp</td>
<td>3.01</td>
<td>[5]</td>
</tr>
<tr>
<td>GO/Ln/DPyE</td>
<td>16% triethanolamine</td>
<td>300 W Xe lamp</td>
<td>1.25</td>
<td>[6]</td>
</tr>
</tbody>
</table>

DPyE: 1,2-di (pyridine-4-ly) ethyne

9. XPS spectra of TiO$_2$/GY-5 sample after photocatalytic reaction.
Fig. S7 XPS spectra of the narrow scan for elemental C of TiO$_2$/GY-5 after photocatalytic reaction.

10. Raman spectra of TiO$_2$/GY-5 sample after photocatalytic reaction.
Fig. S8 (a) Raman spectra and (b) the corresponding magnified Raman spectra at 1200-2000 nm of TiO$_2$/GY-5 before and after photocatalytic reaction.

References


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