Supplementary Data

Constructing a novel TiO_2/γ-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 $HAuCl_4 \cdot 4H_2O$ (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). [1]

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

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}.

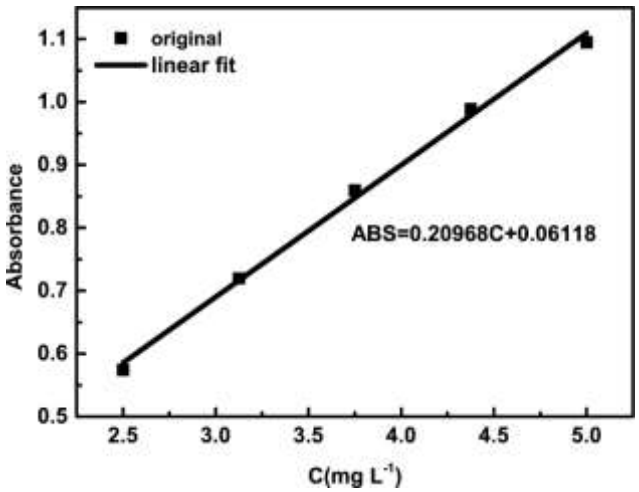


Fig. S1 A linear fit using five different concentrations of MB

3. 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.

4. Fourier transform infrared (FT-IR) spectra of TiO_2 and TiO_2/GY-5

For the pure TiO_2, 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 TiO_2, no obvious changes could be observed for the FT-IR spectrum of TiO_2/GY-5, which is because γ-graphyne is insensitive to infrared rays due

to the absence of C−H.

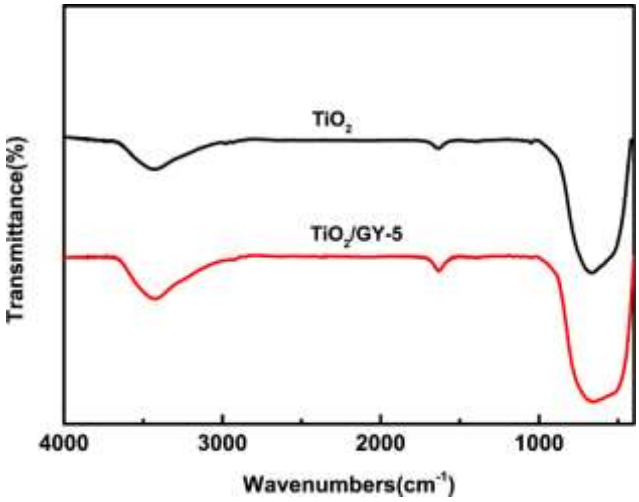


Fig. S2 Fourier transform infrared (FT-IR) spectra of TiO_2 and TiO_2/GY-5

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.

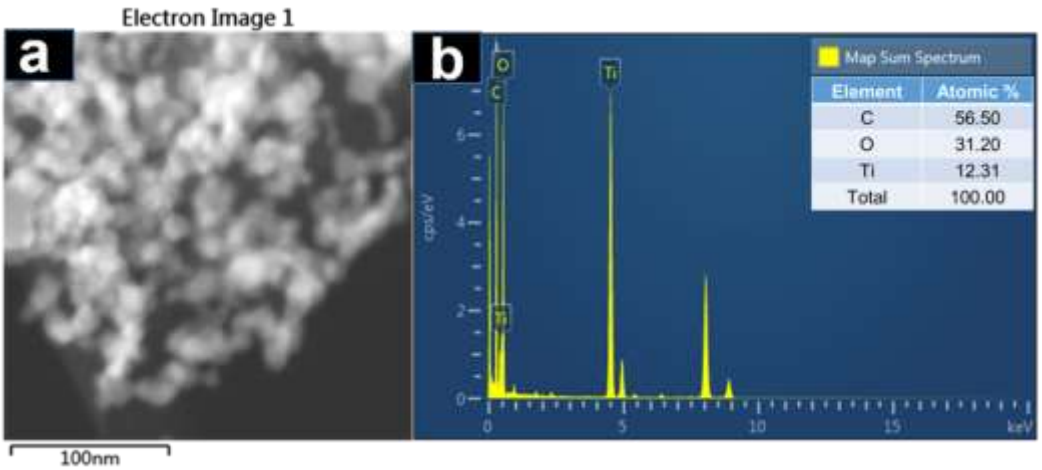


Fig. S3 (a) TEM and (b) EDS spectrum of TiO_2/GY-5 sample

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).

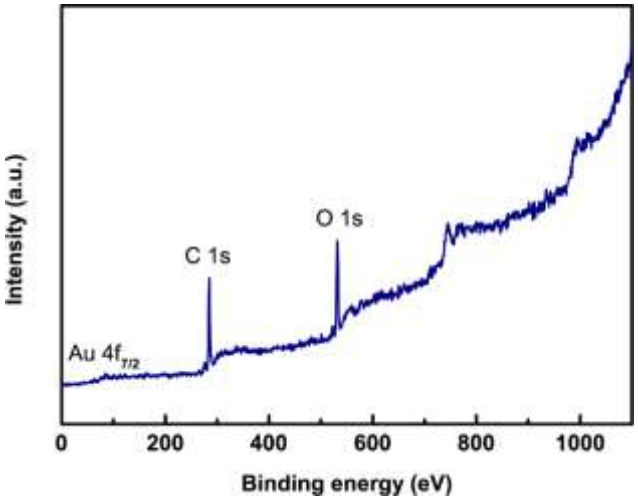


Fig. S4 XPS spectrum of γ-graphyne sample

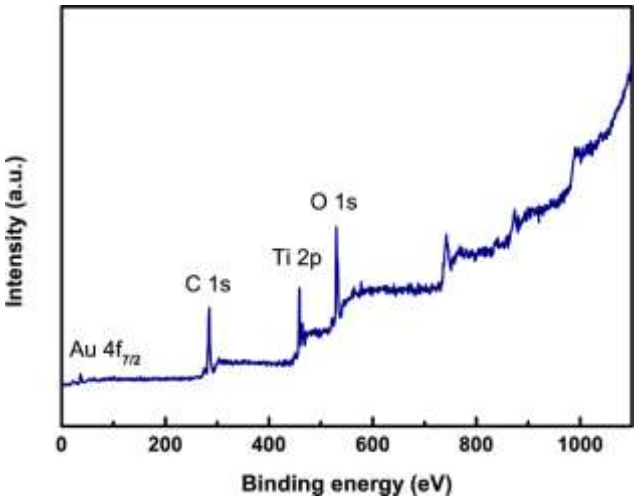


Fig. S5 XPS spectrum of TiO_2/γ-GY-5 nanocomposite

7. **Photocatalytic H_2 evolution of TiO_2/GY-20 sample**

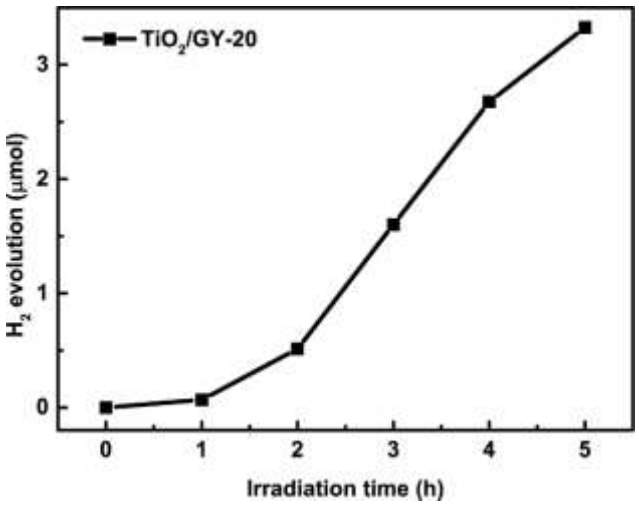


Fig. S6 Hydrogen evolution of TiO_2/GY-20 nanocomposite

8. A comparison of the H_2 production rate

Table S1 A comparison of the H_2 production rate for the latest reported photocatalysts modified by other 2D materials.

System	Sacrificial agent	Light source	$v(H_2)$ (μmol h^{-1})	References
TiO_2/γ-graphyne	**10% methanol**	**300 W Xe lamp**	**19.4**	**Our work**
B-rGO/O-gC_3N_4/Pt	30% triethanolamine	500 W Xe lamp	8.30	[2]
TiO_2/graphene QDs	10% ethanol	250 W Hg lamp	2.20	[3]
CdSe QDs/graphdiyne	0.1 M Na_2SO_4	300 W Xe lamp	0.25	[4]
BCN/TiO_2	20% triethanolamine	300 W Xe lamp	3.01	[5]
GO/Ln/DPyE	16% triethanolamine	300 W Xe lamp	1.25	[6]

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

9. XPS spectra of TiO_2/GY-5 sample after photocatalytic reaction.

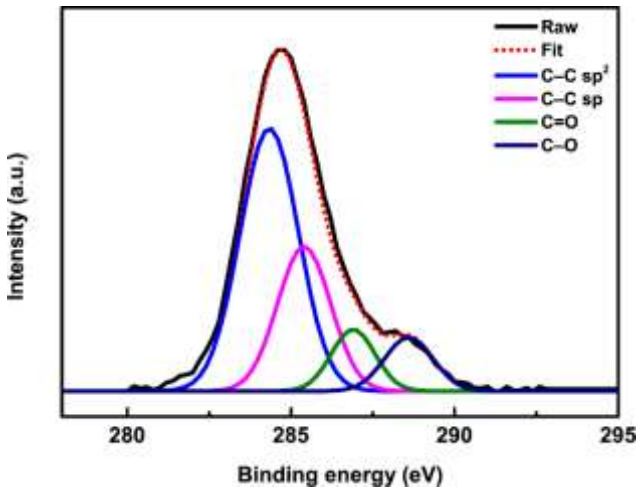
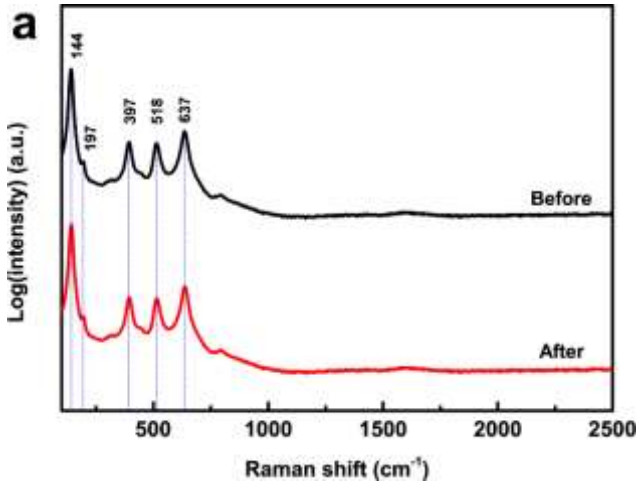


Fig. S7 XPS spectra of the narrow scan for elemental C of TiO_2/GY-5 after photocatalytic reaction.

10. Raman spectra of TiO_2/GY-5 sample after photocatalytic reaction.



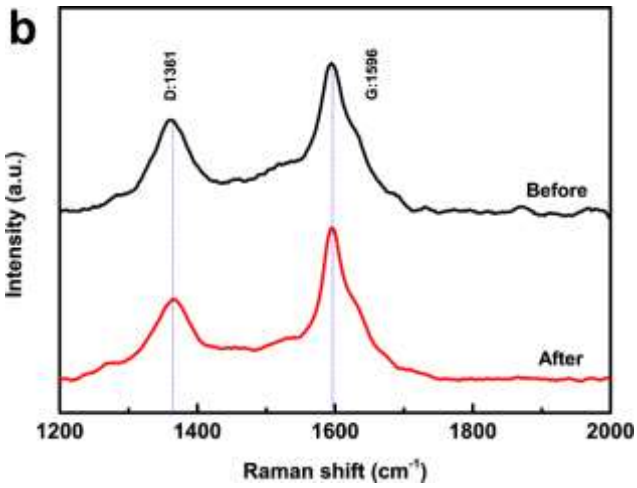


Fig. S8 (a) Raman spectra and (b) the corresponding magnified Raman spectra at 1200-2000 nm of TiO_2/GY-5 before and after photocatalytic reaction.

References

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