

## *Supporting information for*

# **Organic composite photocatalysts from g-C<sub>3</sub>N<sub>4</sub> and soluble dibenzothiophene-S-S'-dioxide-containing polymer for hydrogen generation under visible light**

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### **2.3 Characterizations**

The FT-IR spectra were collected in transmission on a Tensor 27 FT-IR spectrometer (Bruker) using KBr disks. The thermal properties of the polymer networks were evaluated using thermogravimetric analysis (TGA) with a differential thermal analysis instrument (Q1000DSC + LNCS + FACS Q600SDT) over the temperature ranging from 30 to 800°C under a nitrogen atmosphere with a heating rate of 10°C min<sup>-1</sup>. Solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) measurements were performed on a Bruker advance 400 Hz spectrometer. X-ray diffraction measurement (XRD) was carried out on X-ray Deffractometer (D/Max-3c). The morphology of the polymer networks were carried out on an environmental scanning electron microscope (FEI, Quanta 200) and transmission electron microscopy (JEOL, JEM-2100). Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using an ASAP 2420-4 (Micromeritics) volumetric adsorption analyzer. The surface

areas were calculated in the relative pressure ( $P/P_0$ ) range from 0.05 to 0.20. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory. Gas sorption isotherms were measured on an ASAP 2420-4. The samples were degassed at 120°C for 12 h under vacuum ( $10^{-5}$  bar) before analysis. The UV-vis diffuse reflectance spectra (DRS) were measured on a UV-Lambda 950(PerkinElmer, US) spectrophotometer and the absorption spectra were obtained by the conversion of Kubelka–Munk approach, using BaSO<sub>4</sub> as the reflectance standard. X-ray photoelectron spectroscopy (XPS) measurements were performed on an HI5700ESCA instrument with monochromatic Al K $\alpha$  (1486.6 eV) X-ray radiation. The fluorescent spectra of the polymer powders were measured with a Shimadzu F-7000 PC fluorescence spectrometer by using excitation wavelength of 365 nm at room temperature. Electrochemical measurements were performed on a CHI 660 C electrochemical instrument with a standard three-electrode system. The prepared electrodes act as working electrodes, using a Pt flake and calomel (saturated KCl) as counter electrode and reference electrode, respectively. The light source utilizes a 300 W Xe arc lamp. CV curve measurements were determined in tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) and acetonitrile solution under N<sub>2</sub> atmosphere with a scan rate of 100 mV s<sup>-1</sup> in the range of -2 V to 1 V. For the conversion from Hg/Hg<sub>2</sub>Cl<sub>2</sub> redox couple to the Normal Hydrogen Electrode (NHE), the equation  $E_{\text{NHE}} = E_{\text{SCE}} - 0.24$  V was applied. Electrochemical impedance spectroscopy (EIS) measurements were determined at an AC voltage magnitude of 5 mV with the frequency range of 10<sup>5</sup> to 10<sup>-2</sup> Hz in Na<sub>2</sub>SO<sub>4</sub> (0.5 mol/ L) aqueous solution. Working

electrodes were prepared as follows: FTO glass was washed sequentially with distilled water, ethanol and acetone in an ultrasonic cleaner for 30 min. Then, 0.05 g of g-C<sub>3</sub>N<sub>4</sub> or g-C<sub>3</sub>N<sub>4</sub>/PFSO photocatalyst was ground with 7  $\mu$ L of fluoride resin solution to obtain slurry, and then the slurry was coated onto 1 cm  $\times$  2 cm FTO glass electrode by the spin coater.

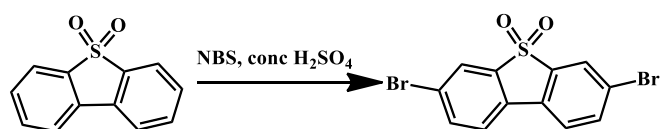
## 2.4 Photocatalytic Reactions

H<sub>2</sub> evolution reactions were carried out in a gas-closed circulation system with a side window by the photocatalyst. The photocatalyst (0.1 g) was suspended in 100 mL of aqueous solution which contain 20 vol % triethanolamine (TEOA) as a sacrificial agent for H<sub>2</sub> evolution and 1% H<sub>2</sub>PtCl<sub>6</sub> as co-catalyst. All photocatalytic experiments were performed in a double-walled glass reactor, where the outer compartment is circulated with water keeping a constant temperature (25°C) through a thermostat. The suspension was thoroughly degassed to remove air and irradiated by a 300 W Xe lamp (Beijing Perfect Light Co.). The yield of H<sub>2</sub> was measured by an online Agilent 7890 gas chromatography (TCD), using N<sub>2</sub> or Ar as the carrier gas.

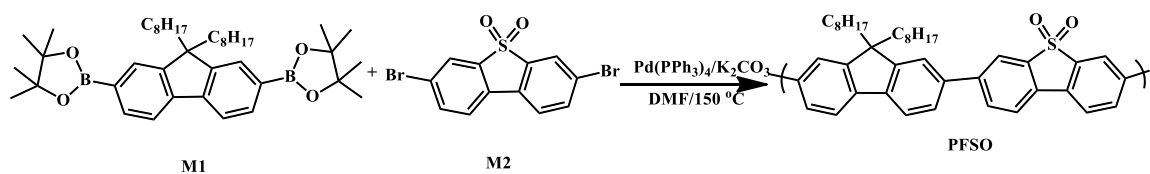
### Synthesis of 3,7-dibromodibenzothiophene-S, S-dioxide

To a solution of Dibenzothiophene-dioxide (2.00 g, 9.24 mmol) in conc H<sub>2</sub>SO<sub>4</sub> (60 mL) was added NBS (3.28 g, 18.48 mmol) and the resulting mixture was stirred at ice-water. After 24 h, the solution was poured into ice water carefully. Colorless solids were filtrated and washed with water and methanol. The obtained solids were recrystallized from trichloromethane to afford desired product (1.6 g, 46%) as colorless needles.

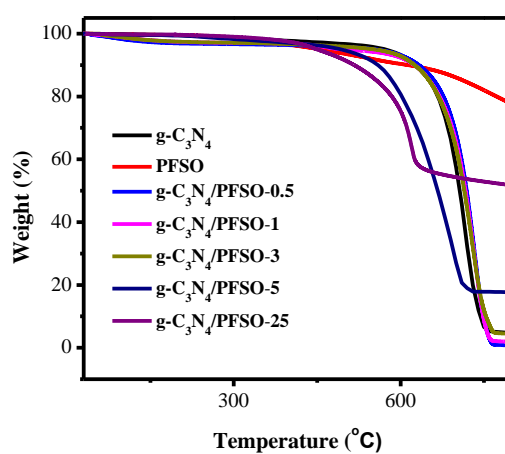
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (d, 2H), 7.79(d, 2H), 7.65 (d, 2H)[1].



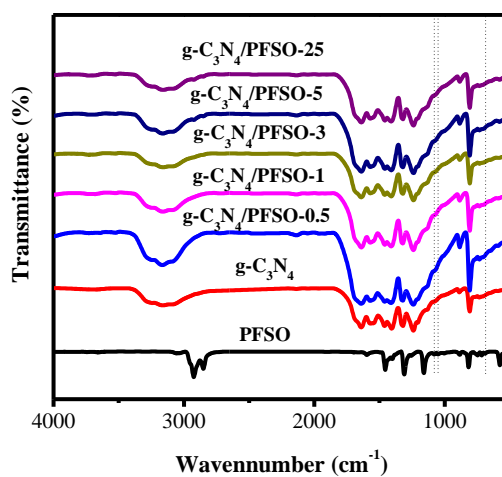
**Schematic S1.** Schematic illustration for the preparation of 3,7-dibromodibenzothiophene-S,S-dioxide.



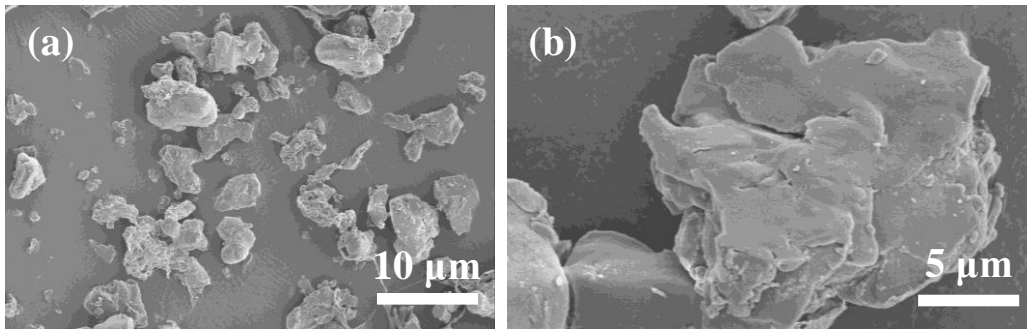
**Schematic S2.** Schematic illustration for the preparation of PFSO.



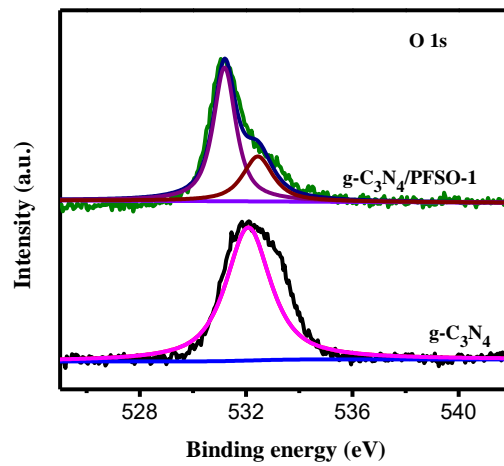
**Fig. S1.** Thermogravimetric analysis curve of  $g\text{-C}_3\text{N}_4$ , PFSO and  $g\text{-C}_3\text{N}_4/\text{PFSO}$  composites under  $\text{N}_2$  atmosphere.



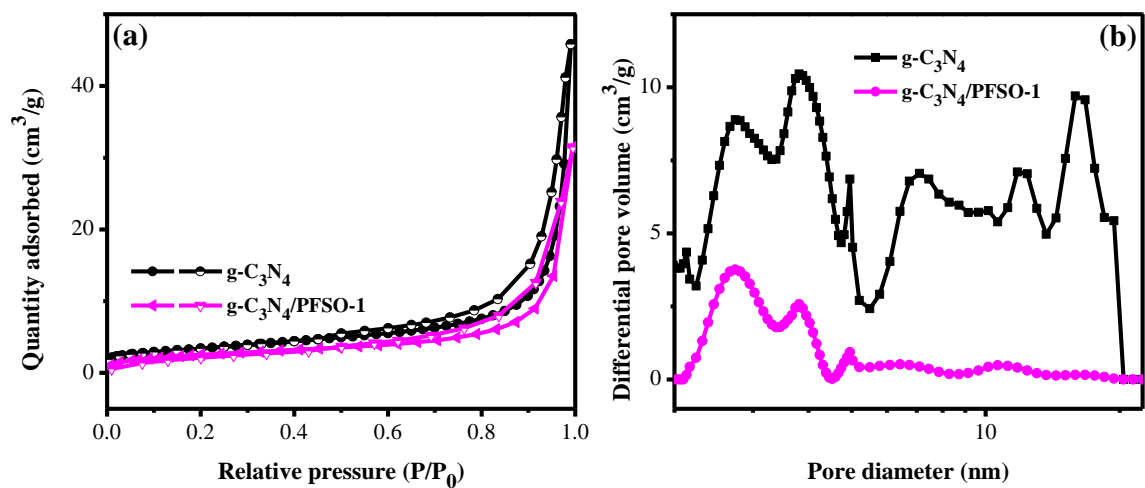
**Fig.S2.** FTIR of all samples  $g\text{-C}_3\text{N}_4$ , PFSO and  $g\text{-C}_3\text{N}_4/\text{PFSO}$  composites.



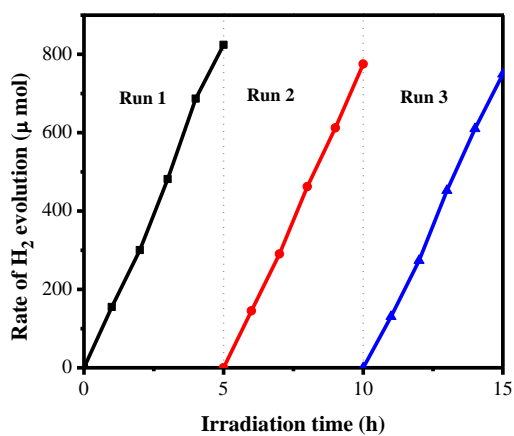
**Fig.S3.**TEM images of the pure PFSO



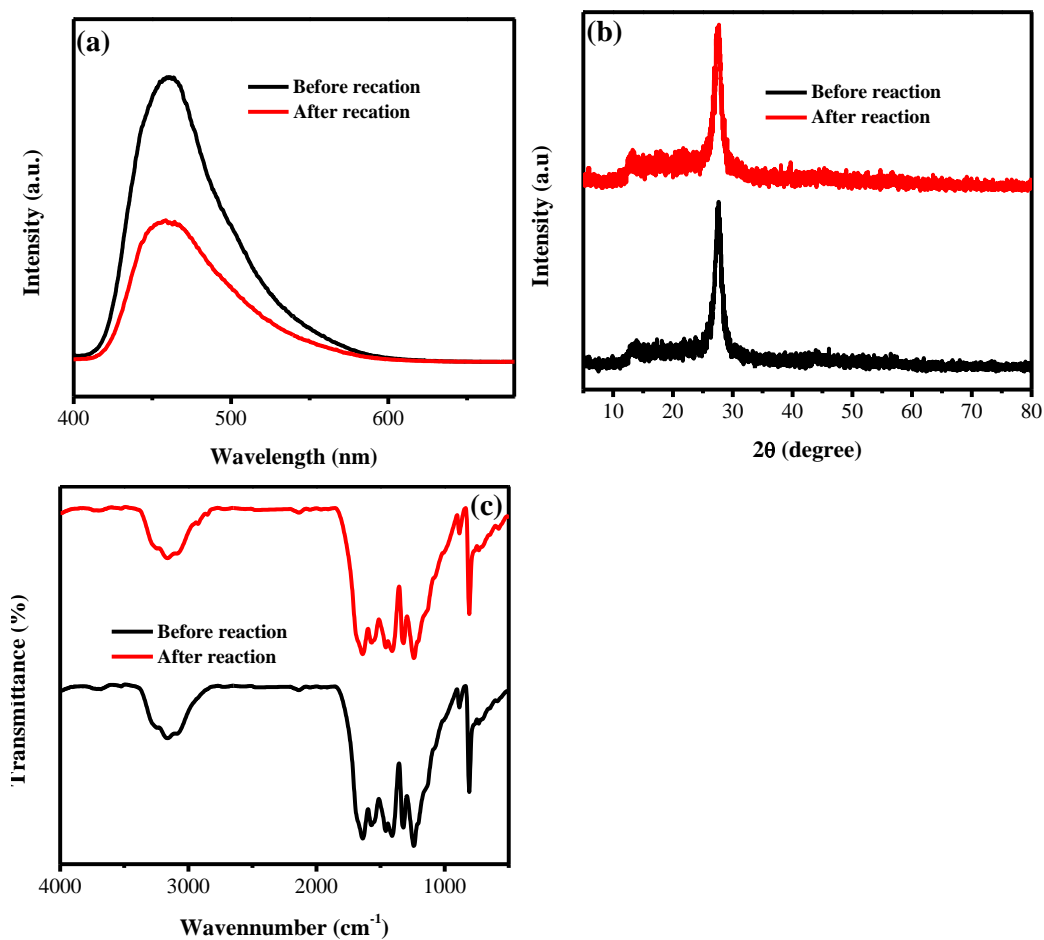
**Fig.S4** High-resolution analysis of O 1s for PFSO, g-C<sub>3</sub>N<sub>4</sub>/PFSO-1 composite.



**Fig.S5** (a) Nitrogen adsorption–desorption isotherms and (b) the corresponding pore-size distribution curves for pure g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/PFSO-1 composite samples.



**Fig.S6** Recyclability of g-C<sub>3</sub>N<sub>4</sub>/PFSO-1 photocatalyst for the photocatalytic H<sub>2</sub> evolution.



**Fig.S7.** (a) Photoluminescencespectra ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ); (b) Powder XRD spectra, (c) FT-IR spectra of g-C<sub>3</sub>N<sub>4</sub>/PFSO-1 composite before and after irradiation under visible light ( $\lambda > 400 \text{ nm}$ ) for 15 h in a triethanolamine/water mixture.

## References

[1] K. C. Moss, K. N. Bourdakos, V. Bhalla, K. T. Kamtekar, M. R. Bryce, M. A. Fox, H. L.

Vaughan, F. B. Dias, A. P. Monkman, *J. Org. Chem.* 2010, 75, 6771–6781.