Electronic Supplementary Information

Donor-acceptor Covalent Organic Framework/g-C_3N_4 Hybrids for Enhanced Visible Light Photocatalytic H_2 Production

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Experimental Section

Materials

2,4,6-triformylphloroglucinol (TP) and 4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)dianiline (BTDA) were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co. Ltd. Chloroplatinic acid, 1,3,5-Trimethylbenzene, 1,4-dioxane, triethanolamine (TEOA), and ascorbic acid were obtained from Saan Chemical Technology Ltd. Urea and methanol was obtained from Sinopharm Chemical Reagent Company, Ltd. All commercial chemicals were used without further purification unless otherwise mentioned.

Characterizations

Powder X-ray diffraction (PXRD) data were collected on a TTR III multi-function X-ray diffractometer operated at 40 kV and 300 mA with Cu Kα radiation. FT-IR spectra were recorded as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. The transmission electron microscopy (TEM) was acquired on HITACHI HT7700 with an electron acceleration energy of 100 kV. The images of high angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and energy dispersive spectroscopy (EDS) mapping were observed by a JEM-ARM200F electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) data were collected on an ESCALAB 250Xi system. Al Kα X-ray (6 mA × 12 KV) was utilized as the irradiation source. All measurements were performed in the CAE mode with the reference of C 1s (284.80 eV). UV-vis diffuse reflectance

absorption spectra (DRS) were recorded on a Shimadzu UV-2600 UV-vis-NIR spectrophotometer with $BaSO_4$ as the reference. Steady-state PL spectra (excitation at 500 nm) were measured with a Hitachi F-4500 fluorescence spectrophotometer. Time-resolved photoluminescence spectra (TRPS) were obtained on an Edinburgh FLS 980 fluorescence spectrophotometer with excitation and detection wavelengths of 475 and 615 nm, respectively. Platinum contents were determined using inductively coupled plasma optical emission spectrometer (ICP-OES) with an Agilent ICP-OES 725 ES system, by digesting the hybrids in HNO_3/HCl (1:3, v/v).

Electrochemical measurement

Photoelectrochemical measurements were conducted on a CHI760E electrochemical workstation in a three-electrode cell. The counter electrode was a Pt wire, and the reference electrode was a Ag/AgCl electrode. For the preparation of the working electrodes, the as-synthesized 4 mg samples were added into a mixed solution of 10 μL Nafion and 200 μL ethanol, then the catalyst suspension (10 μL × 3) were dropped onto the ITO glass (0.7 cm × 0.7 cm) surface, forming a film after drying naturally for 12 h. An aqueous solution containing 0.2 M Na_2SO_4 was used as the electrolyte. The i-t measurements were performed with the light on and off conditions (300 W Xe-lamp, $\lambda > 420$ nm). The electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 10^{-1} to 10^5 Hz with a bias potential of +1.5 V. The Mott-Schottky plots were obtained with a bias potential that ranged from -1.6 to 1.0 V (vs Ag/AgCl) under the frequency of 1000, 1500, and 2000 Hz, respectively.[1,2]

Synthesis of g-C_3N_4 and C_3N_4-Pt

g-C_3N_4 was prepared according to a reported procedure.[3] C_3N_4-Pt was synthesized as follows:[3] g-C_3N_4 (0.6 g) was added to a mixed solvent of 150 mL deionized water and 60 mL methanol, and then ultrasonically dispersed for 5 min. After adding 1.2 mL of H_2PtCl_6 solution (0.0386 M in water) under stirring, the resultant suspension was irradiated for 3 h under a 300 W mercury lamp. After being cooled to room temperature, the product was separated by centrifugation and washed with water and EtOH, then dried at 70 °C overnight. The Pt content was 2.08% as determined by ICP-OES.

Synthesis of polymer TBTA

A Pyrex tube (10 mL) was charged with 2,4,6-triformylphloroglucinol (TP) (10.5 mg, 0.05 mmol), 4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)dianiline (BTDA) (24 mg, 0.075 mmol), mesitylene (0.6 mL), and ethanol (2.4 mL). The mixture was sonicated for 1 min, subsequently, 0.3 mL of acetic acid was added. The tube was flash frozen at 77 K using a liquid N_2 bath and degassed by three freeze-pump-thaw cycles, sealed under vacuum and then heated at 120 °C for 3 days. The red precipitate was collected by centrifugation and washed with 1,4-dioxane and anhydrous acetone. After drying at 50 °C for 24 h, the product was obtained as dark red powder (26 mg, 82.7%).

Synthesis of x-TBTA/g-C_3N_4 and 2.5-TBTA/g-C_3N_4-Pt (x refers to wt% of TBTA).

200 mg of g-C_3N_4 was dispersed in 4.5 mL of mesitylene/ethanol (4:1) in a Pyrex

tube by ultrasonication for 10 min. Subsequently, TP (1.7 mg, 0.008 mmol) and BTDA (3.8 mg, 0.012 mmol) were added and the mixture was sonicated for 5 min. Then, 0.15 mL of acetic acid was added. The tube was flash frozen at 77 K using a liquid N_2 bath and degassed by three freeze-pump-thaw cycles, sealed under vacuum and then heated at 120 °C for 3 days. The light red color precipitate was collected by centrifugation and washed with mesitylene and anhydrous acetone. After drying at 50 °C for 24 h, 2.5-TBTA/g-C_3N_4 was obtained as light red color powder (185 mg, 92.5%). Following the synthesis procedure of 2.5-TBTA/g-C_3N_4 with 0.0032 mmol TP and 0.0048 mmol BTDA, 0.016 mmol TP and 0.024 mmol BTDA, 0.024 mmol TP and 0.036 mmol BTDA, and 0.032 mmol TP and 0.048 mmol BTDA instead of 0.008 mmol TP and 0.012 mmol BTDA, respectively, as starting materials, 1.0-TBTA/g-C_3N_4, 5.0-TBTA/g-C_3N_4, 7.5-TBTA/g-C_3N_4, and 10.0-TBTA/g-C_3N_4 were prepared. In addition, 2.5-TBTA/g-C_3N_4-Pt was also prepared by using the synthesis procedure of 2.5-TBTA/g-C_3N_4 with g-C_3N_4-Pt instead of g-C_3N_4 as the starting material.

General procedure for photocatalytic hydrogen evolution

The measurements were performed in a gas-closed circulation system (AuLight, Beijing, China, CEL-SPH2N). A Xe-lamp (CEL-HXF300, 300 W) equipped with $\lambda \geq$ 420 nm cutoff filter was used as visible-light source, and the temperature was maintained at 5℃ using a homoeothermic cooling circulation pump. The H_2 evolution rate was quantified by an online gas chromatograph (GC7980, TCD detector, 13X molecular sieve columns, and Ar carrier). Typically, the photocatalysts (5 mg) was

dispersed in 20 mL deionized water with 0.1 M ascorbic acid as a sacrificial reagent. Before measurement, the reactor was sonicated for 5 min to obtain well-distributed suspension and then illuminated by $\lambda \geq 420$ nm light from its top after being thoroughly degassed.

Density functional theory computational methodology

The present first principle DFT calculations were performed by Vienna Ab initio Simulation Package(VASP)[5] with the projector augmented wave (PAW) method.[6] The exchange-functional was treated using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)[5] functional. The cut-off energy of the plane-wave basis was set at 450 eV for the calculations of atoms and cell optimization. The vacuum spacing in a direction perpendicular to the plane of the catalyst was at least 15 Å. The Brillouin zone integration was performed using 3×3×1 Monkhorst-Pack k-point sampling for a primitive cell.[7] The self-consistent calculations apply a convergence energy threshold of 10^{-5} eV. The equilibrium lattice constants were optimized with maximum stress on each atom within 0.05 eV/Å. Finally, the interface adhesion energy (E_{ads}) has been calculated as: $E_{ads} = E_{total} - E_{TBTA} - E_{g\text{-}C3N4}$, where E_{total} is the energy of TBTA/g-C_3N_4, E_{TBTA} is the energy of TBTA, $E_{g\text{-}C3N4}$ is the energy of g-C_3N_4.

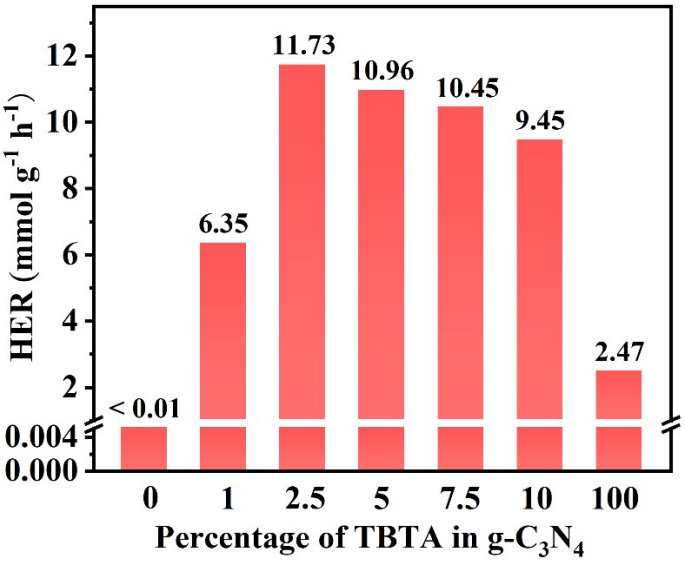

Fig. S1 The photocatalytic H_2 evolution activity of x-TBTA/g-C_3N_4 (x = 0, 1.0, 2.5, 5.0, 7.5, 10.0, 100). Note: 5.0 mg catalyst and 20.0 mL deionized water under $\lambda \geq 420$ nm light irradiation.

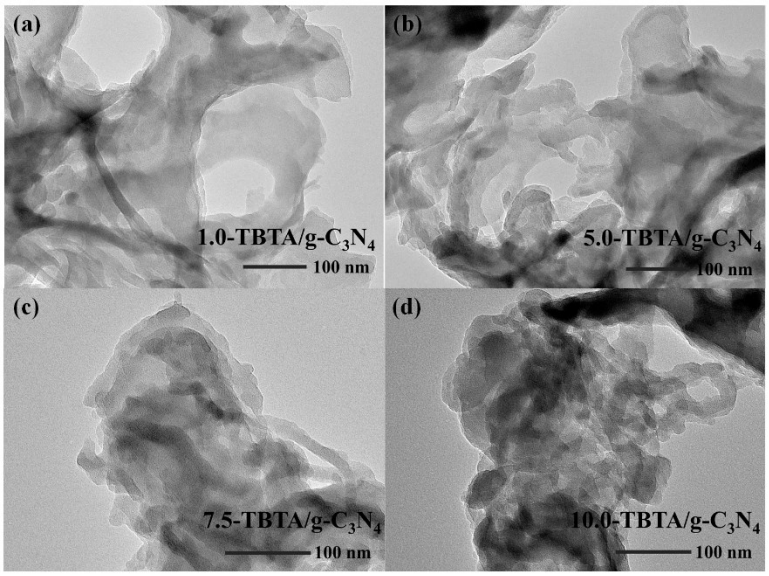

Fig. S2 TEM images of (a) 1.0-TBTA/g-C_3N_4. (b) 5.0-TBTA/g-C_3N_4. (c) 7.5-TBTA/g-C_3N_4 and (d) 10.0-TBTA/g-C_3N_4.

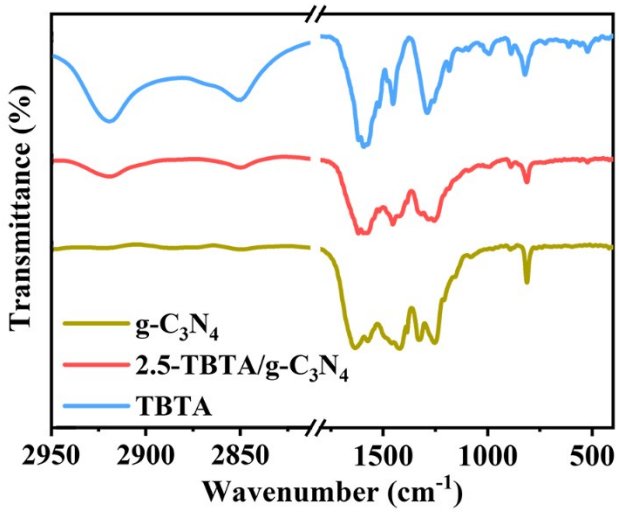

Fig. S3 FTIR spectra of TBTA, 2.5-TBTA/C_3N_4, and g-C_3N_4.

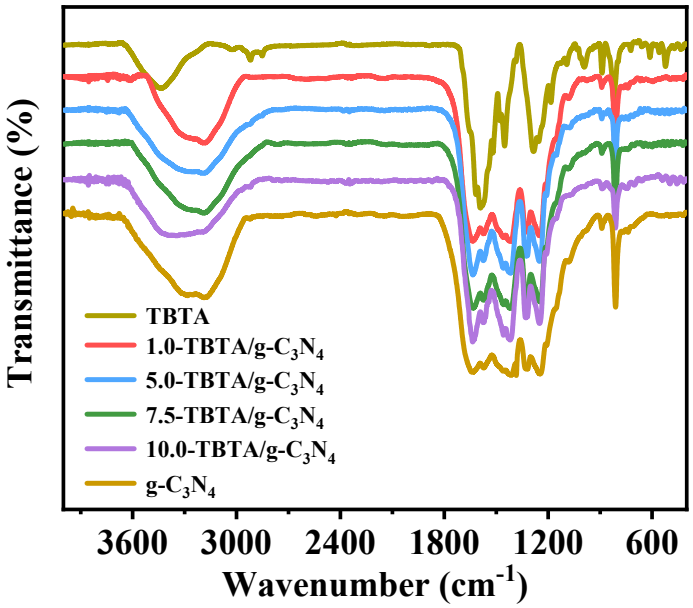

Fig. S4 FTIR spectra of as-synthesized samples.

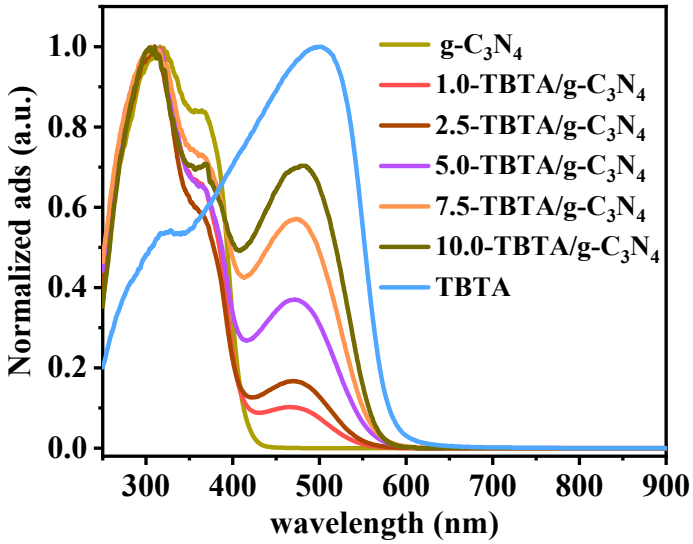

Fig. S5 The UV-vis diffuse reflectance absorption spectra (DRS) of samples.

Table S1. Absorption spectroscopic data and energy levels.

Sample	$\lambda_{abs\text{-}onset}$ [a] (nm)	E_{CB} [b] (V)	E_{VB} [c] (V)	E_g [d] (V)
$g\text{-}C_3N_4$	428	-1.26	1.64	2.90
TBTA	576	-1.45	0.70	2.15
$2.5\text{-}TBTA/g\text{-}C_3N_4$	538	-1.265	1.04	2.30

[a] Absorption onset. [b] Determined from Mott-Schottky plots. [c] $E_{VB} = E_g + E_{CB}$. [d] Determined by the absorption onset from DRS spectra: $E_g = 1240/\lambda_{abs\text{-}onset}$.

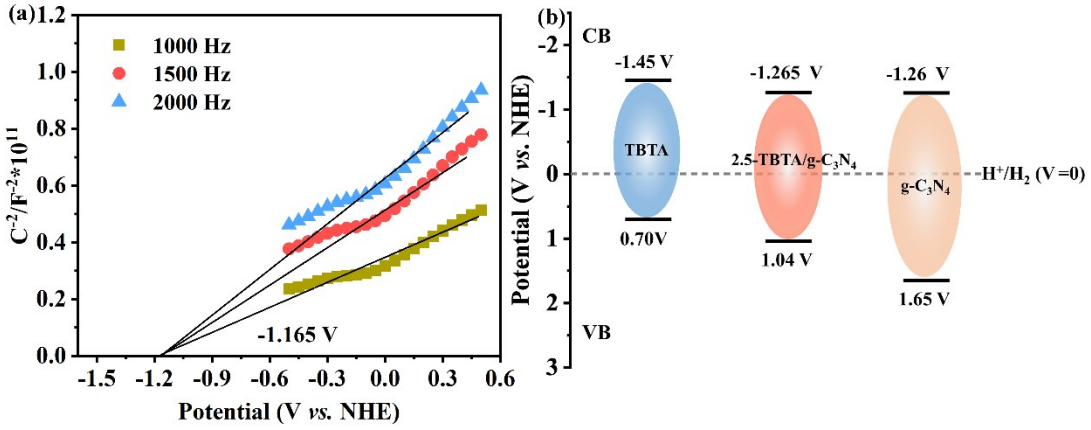

Fig. S6 (a) MS plots of 2.5-TBTA/g-C_3N_4 and (b) Energy levels of TBTA, 2.5-TBTA/g-C_3N_4 and g-C_3N_4.

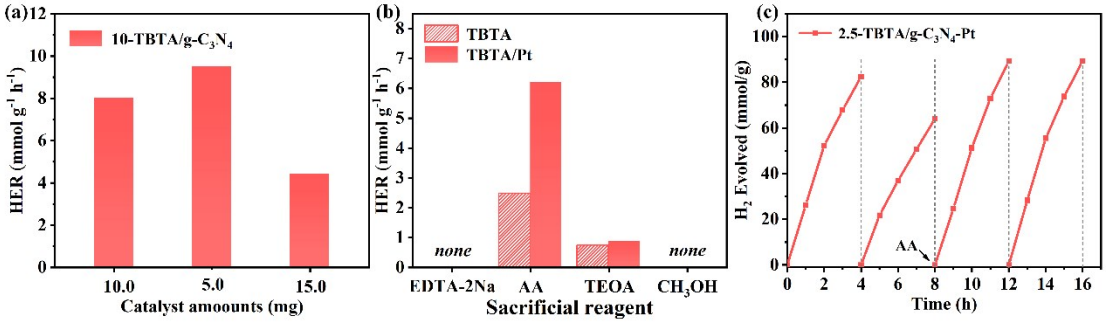

Fig. S7 (a) The photocatalytic H_2 evolution activity with different catalyst amounts of 10-TBTA/g-C_3N_4. (b) The photocatalytic H_2 evolution activity with different sacrificial reagants of TBTA. (c) Long-term stability for H_2 production of 2.5-TBTA/g-C_3N_4-Pt. Note: 5.0 mg catalyst and 20.0 mL deionized water under $\lambda \geq 420$ nm light irradiation.

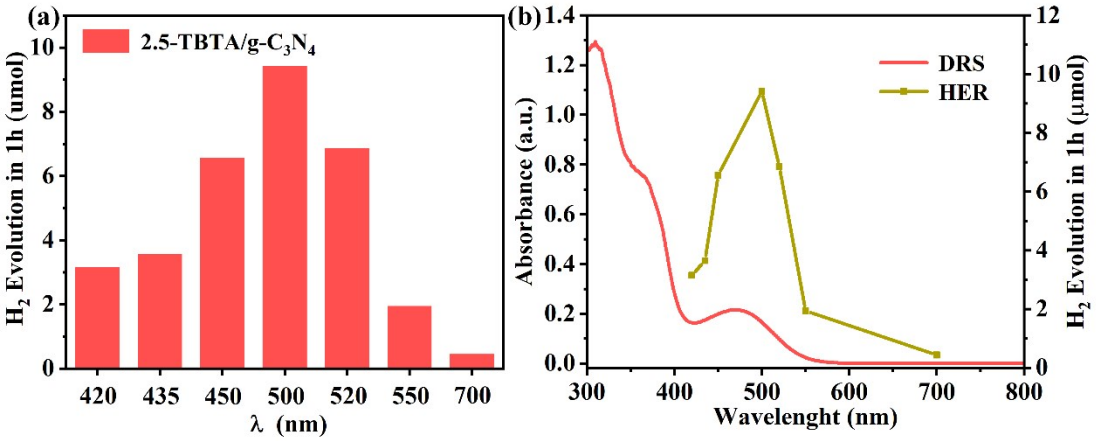

Fig. S8 (a) The photocatalytic H_2 evolution rate of 2.5-TBTA/g-C_3N_4 with monochromatic light irradiations. Note: 5.0 mg catalyst and 20.0 mL deionized water with 0.1 M AA as a sacrifice reagent. (b) Wavelength-dependent photocatalytic H_2 evolution rate and DRS spectrum of 2.5-TBTA/g-C_3N_4.

Table S2. Comparison of the performance of photocatalytic H_2 evolution rate of organic semiconductor/g-C_3N_4 hybrids with Pt as co-catalysts.

Photocatalyst	Co-catalyst	Sacrificial agent	Irradiation condition	Reaction rate (H_2 evolution)	Ref.
2.5-TBTA/g-C_3N_4	3.0 wt% Pt	AA	$\lambda \geq 420$ nm (300 W Xe lamp)	26.04 mmol/g/h	*This work*
Flu-DFBA/g-C_3N_4	1.0 wt% Pt	TEOA	$\lambda \geq 420$ nm (300 W Xe lamp)	14.85 mmol/g/h	7
P_3/g-C_3N_4	1.0 wt% Pt	TEOA	$\lambda \geq 420$ nm (300 W Xe lamp)	13.00 mmol/g/h	8
PFBT/g-C_3N_4	1.0 wt% Pt	TEOA	$\lambda \geq 420$ nm (300 W Xe lamp)	0.72 mmol/g/h	9
P3HT/g-C_3N_4	1.0 wt% Pt	AA	$\lambda \geq 500$ nm (300 W Xe lamp)	3.05 mmol/h	10
PPy/ g-C_3N_4	3.0 wt% Pt	without	$\lambda \geq 400$ nm (300 W Xe lamp)	0.39 mmol (25 h)	11
Pt/C_3N_4-P3HF	1.0 wt% Pt	Na_2S-Na_2SO_3	$\lambda \geq 400$ nm (300 W Xe lamp)	0.56 mmol/h	12

Table S3. Comparison of the performance of photocatalytic H_2 evolution rate of g-C_3N_4-based heterostructured photocatalysts without noble metal as co-catalyst.

Photocatalyst	Co-catalyst	Sacrificial agent	Irradiation condition	Reaction rate (H_2 evolution)	Ref.
2.5-TBTA/g-C_3N_4	none	AA	$\lambda \geq 420$ nm (300 W Xe lamp)	11.73 mmol/g/h	*This work*
Flu-DFBA/g-C_3N_4	none	TEOA	$\lambda \geq 420$ nm (300 W Xe lamp)	2.73 mmol/g/h	1
MG@hm-C$(CN)_3$	none	TEOA	300 W Xe lamp	1.01 mmol/g/h	13
CNPS-NH_2	3.0 wt% Ni	TEOA	$\lambda \geq 420$ nm (300 W Xe lamp)	1.23 mmol/g/h	14
Phosphorene/ g-C_3N_4	Phosphorene	lactic acid	$\lambda \geq 400$ nm (300 W Xe lamp)	0.57 mmol/g/h	15
C_3N_4/$(FeTPP)_2O$	none	TEOA	$\lambda \geq 420$ nm (300 W Xe lamp)	0.18 mmol/g/h	16
Black phosphorous/ g-C_3N_4	none	Methanol	$\lambda \geq 420$ nm (300 W Xe lamp)	0.43 mmol/g/h	17
C,N-TiO_2/g-C_3N_4	none	TEOA	$\lambda \geq 400$ nm (300 W Xe lamp)	0.039 mmol/g/h	18

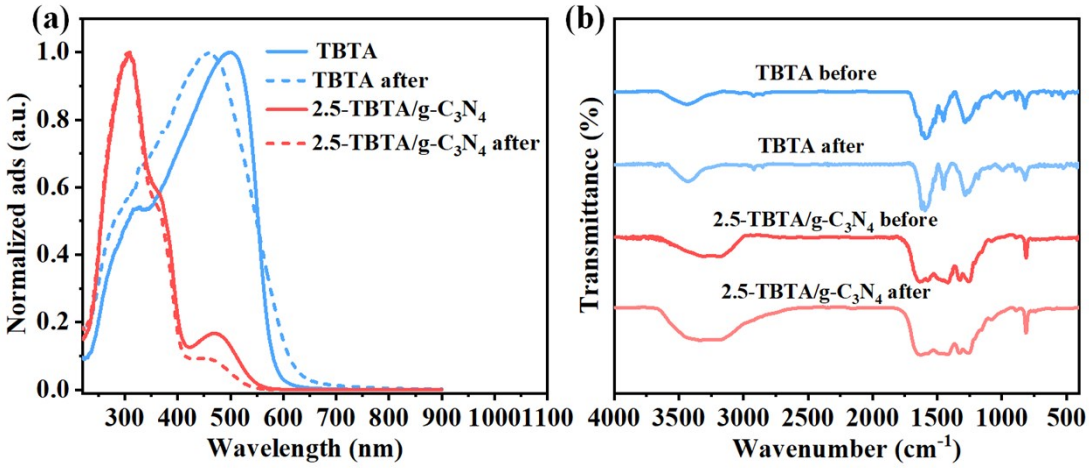

Fig. S9 Comparison of (a) DRS (b) IR before and after H_2 production process.

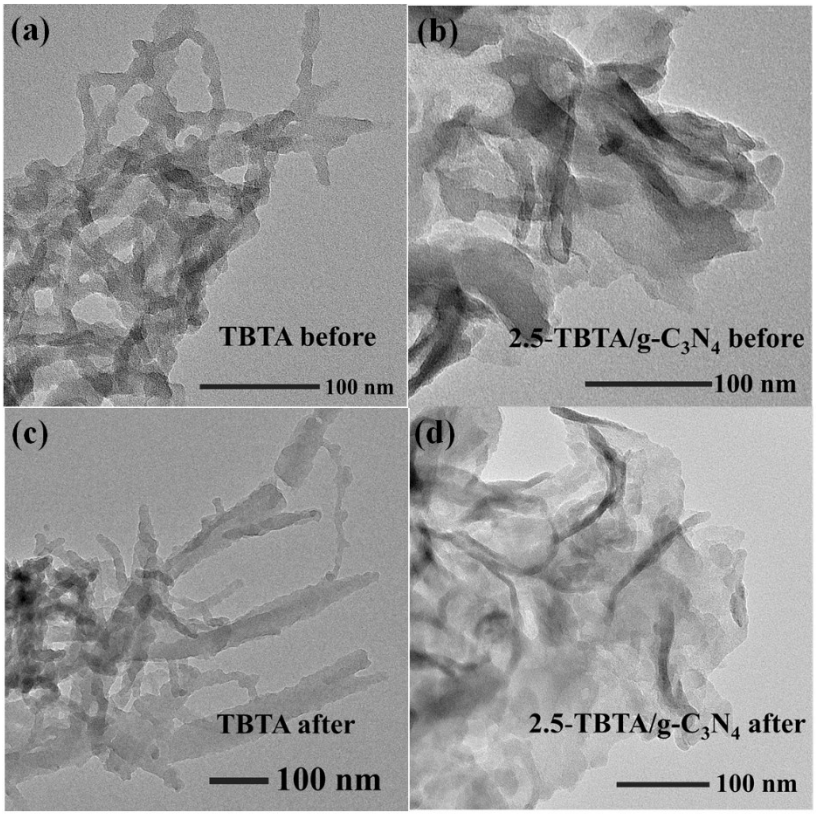

Fig. S10 Comparison of TEM images before and after H_2 production process.

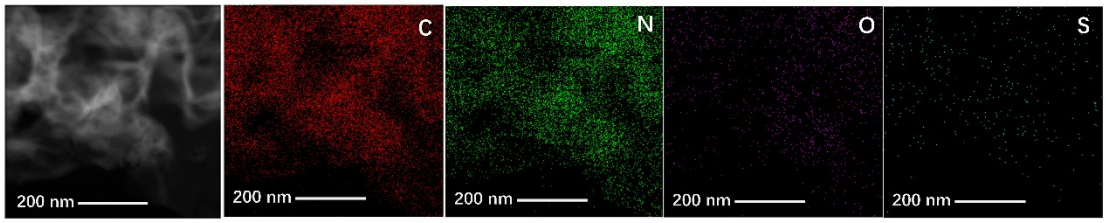

Fig. S11 HAADF-STEM image and elemental mappings of 2.5-TBTA/g-C_3N_4 after H_2 production process.

Table S4. PL Decay parameters.

Samples	Lifetime, τ (ns)	Pre-exponential fators, A%	Average lifetime, τ (ns)
TBTA	0.58	70.60	1.12
	2.43	29.40	
2.5-TBTA/g-C_3N_4	0.24	74.27	0.75
	2.23	25.73	

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