

Supporting Information

Facile Synthesis of Covalently Connected rGO-COF Hybrid Material by In-situ Reaction for Enhanced Visible-light Induced Photocatalytic H₂ Evolution

Yu-Hao Yao,^a Jing Li,^a Hao Zhang,^a Hong-Liang Tang,^a Liang Fang,^a Gu-Dan Niu,^a Xiao-Jun Sun^a and Feng-Ming Zhang^{*a}

^a Key Laboratory of Green Chemical Engineering and Technology of College of Heilongjiang Province, College of Chemical and Environmental Engineering, Harbin University of Science and Technology, No.4, Linyuan Road, Harbin 150040, P.R. China.

Experimental Section

Materials and characterization. All of the reagents and solvents were commercially available and used without further purification besides Tp which was prepared from Phloroglucinol according to literature method.¹ The composition, structure and texture properties of the materials were investigated by Raman spectroscopy (WITec alpha 300 R), Fourier transform infrared (FT-IR) spectra (Spectrum 100), X-ray powder diffraction (XRD) patterns (Bruker D8 X-ray diffractometer), scanning electron microscopy (SEM) micrographs (Hitachi S-4800), transmission electron microscopy (TEM) experiment (JEM-2100 electron microscope), thermogravimetric analyses (TGA) (SDTA851e). N₂ adsorption-desorption isotherms were determined by MicroActive for ASAP 2460 analyzer at 77 K. Before the measurement, the catalysts were degassed at 120 °C for 12 h. The surface chemical states were study by XPS (ESCALAB 250). Optical properties were also studied by diffuse reflectance UV-vis spectroscopy (Lambda 35 spectrometer), photoluminescence spectrum (PL) (SPEX Fluorolog-3 spectrofluorometer with an excitation wavelength of 350 nm). The electrochemical impedance spectra (EIS), Mott-Schottky plot and photocurrent-time (I-T) profiles was recorded on the CHI660E electrochemical workstation with a standard three-electrode system with the photocatalyst-coated ITO as the working electrode, Pt plate as the counter electrode, and a saturated calomel electrode as a reference electrode. A 0.25 M Na₂SO₄ solution was used as the electrolyte. The as-

synthesized samples (2 mg) were added into 1 mL ethanol and 10 μ L Nafion mixed solution, and the working electrodes were prepared by dropping the suspension (200 μ L) onto an ITO glass substrate electrode surface and dried at room temperature. A 300 W Xenon lamp with a 420 nm cut-off filter was used as the light source during the measurement. The photoresponsive signals of the samples were measured under chopped light at 0.9 V.

Synthesis of graphene oxide (GO): For the preparation method of GO, we referred to the hummers method, and modified this method.^{2,3} First, 2 g of natural graphite and 1 g of sodium nitrate (NaNO_3) were added to a 250 mL three-necked flask and cooled to 0 $^\circ\text{C}$. Then, 50 mL of concentrated sulfuric acid (H_2SO_4) was slowly added to the three-necked flask and thoroughly stirred for 30 minutes, meanwhile, the temperature of the reaction system was not more than 5 $^\circ\text{C}$. Then add 0.3 g potassium permanganate (KMnO_4) to the three-necked flask and stirred for 30 minutes, meanwhile, the temperature of the reaction system was not more than 10 $^\circ\text{C}$. After the end, 7 g potassium permanganate (KMnO_4) was added to the three-necked flask in 4 batches within 1 hour and keeping stirring, meanwhile, the temperature of the reaction system was not more than 20 $^\circ\text{C}$. Then after stirring for 2 hours at about 35 $^\circ\text{C}$, And brown suspensions were obtained. After 2 hours, 90 ml of deionized water was slowly added to the three-necked flask, and the temperature of the system rapidly increased to 90 $^\circ\text{C}$, accompanied by a large amount of gas generation. The diluted suspensions were reacted at 90 $^\circ\text{C}$ for 15 minutes. Subsequently, A mixed solution of H_2O_2 (30%, 7 mL) and deionized water (55 mL, 45 $^\circ\text{C}$) was added to the suspension, and the bright yellow graphene oxide dispersion was obtained. The suspension was filtered while hot to give a yellow-brown filter cake. The filter cake was washed three times with 150 mL of dilute hydrochloric acid (3%, 45 $^\circ\text{C}$) and then dispersed in 600 mL of deionized water. Finally, the colloidal GO was separated from the filter cake dispersion using a centrifuge (4000 rpm, 20 min), transferred to a 40 $^\circ\text{C}$ vacuum drying box, and dried for 24 hours to obtain GO.

In order to obtain high-purity GO, the GO prepared for the first time needed to be dissolved into a suspension (0.01-1 mg/mL), and the remaining inorganic salts and

acids were removed by dialysis. Subsequently, the GO was stripped by ultrasonication (200 W) for 30 min, and the stripped solution was centrifuged (3000 rpm, 30 min) to remove graphite (precipitate) that had not been entirely oxidized. Finally, the obtained centrifugate (solution) was dried at 40 °C to obtain high purity GO.

Synthesis of TpPa-1-COF: The synthesis of TpPa-1-COF was according to the reported method and we made a little change to this method.⁴ 1,3,5-triformylphloroglucinol (Tp) (63 mg, 0.3 mmol) and p-phenylenediamine (PPD) (48 mg, 0.3 mmol) were added to a special tube containing DMF (3 mL) and then sonicated until get a homogeneous dispersion. Subsequently, 3M acetic acid (0.5 mL) was added to the tube, and sonicated 3 min. After this, the special tube was frozen by liquid N₂ and outgassed by freeze-pump-thaw for three times, then sealed the tube and heated at 120 °C for 72 h. After cooling down room temperature, the red product was collected by filtration and washed with tetrahydrofuran for several times, and dried at 60 °C under vacuum for 6 h before use.

Synthesis of reduced graphene oxide functionalized with PPD (PPD-rGO): In the preparation of TpPa-1 system, only GO (5.8 mg) and PPD (48 mg, 0.3 mmol) were added a special tube containing DMF (3 mL) and then sonicated until get a homogeneous dispersion. Subsequently, 3M acetic acid (0.5 mL) was added to the tube, and sonicated 3 min. After this, the special tube was frozen by liquid N₂ and outgassed by freeze-pump-thaw for three times, then sealed the tube and heated at 120 °C for 72 h. After cooling down room temperature, the resulting solid product was washed several times with alcohol and deionized water, respectively, and dried at 40 °C under vacuum for 12 h.

Synthesis of functionalized graphene oxide exposed amine groups (FGO-NH₂) and functionalized graphene oxide without exposed amine groups (FGO): The preparation methods of FGO-NH₂ and FGO refer to the preparation methods of GHPPD and GPPDH in the research of Lu et al.⁵, respectively.

Synthesis of reduced graphene oxide (rGO): The preparation method of rGO and PPD-rGO was the same, while the only difference was that PPD was not added to the reaction system.

Synthesis of rGO(5%)-TpPa-1-COF: 1,3,5-triformylphloroglucinol (Tp) (63 mg, 0.3 mmol) and p-phenylenediamine (PPD) (48 mg, 0.3 mmol) were grinded for 2 minutes until the mixture was changed into yellow to ensure them well mixed, and then GO was added and further grinding around 3 minutes improve the uniformity of GO. The mixture was then added to a special tube containing DMF (3 mL) and then sonicated until get a homogeneous dispersion. Subsequently, 3M acetic acid (0.5 mL) was added to the tube, and sonicated 3 min. After this, the special tube was frozen by liquid N₂ and outgassed by freeze-pump-thaw for three times, then sealed the tube and heated at 120 °C for 72 h. After cooling down room temperature, the red product was collected by filtration and washed with tetrahydrofuran for several times, and dried at 60 °C under vacuum for 6 h before use.

Synthesis of 5%rGO/TpPa-1-COF: The rGO prepared in advance was added to the monomers mixture of TpPa-1-COF synthesis system, And then the next method is similar to synthesis of rGO(5%)-TpPa-1-COF.

Photocatalytic hydrogen evolution: The photocatalytic performances were evaluated by the water splitting for hydrogen evolution in a 500 mL Pyrex reaction vessel using the 300 W Xenon arc lamp with a cut-off filter ($\lambda > 420$ nm) as the visible light source. In a typical experiment, 10 mg of TiO₂-TpPa-1-COF were suspended in 50 mL of PBS buffer solution (50 mL of 0.1 M solution at PH = 7) by sonication for 0.5 h. Afterword, 100 mg of sodium ascorbate (SA) as sacrificial electron donor and hexachloroplatinic acid as precursor for in situ formation of platinum (3 wt% Pt, which loaded by photodecomposition) as the co-catalyst was added and then the above mixed solution was dispersed under vigorous stirring at 4 °C in dark for 0.5 h. The above reaction solution was stirred for 5 h and irradiated. The hydrogen evolved was determined by a GC112A gas chromatograph with TCD detector. The determination of the apparent quantum efficiency (AQE) for hydrogen generation was performed using same closed circulating system under illumination of a 300 W Xe lamp with optical filter (420, 450, 500, 550, 600 and 650 nm) system. AQE was calculated under different wavelengths by the following equation:

$$AQE(\%) = \frac{2 \times \text{amount of } H_2 \text{ molecules evolved}}{\text{Total photons incident}} \times 100\%$$

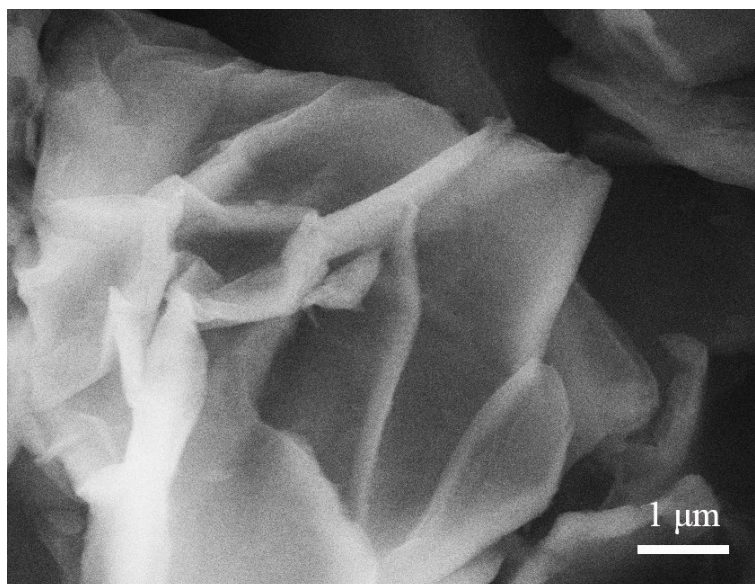


Figure S1. SEM image of GO. No gold sputter coating.

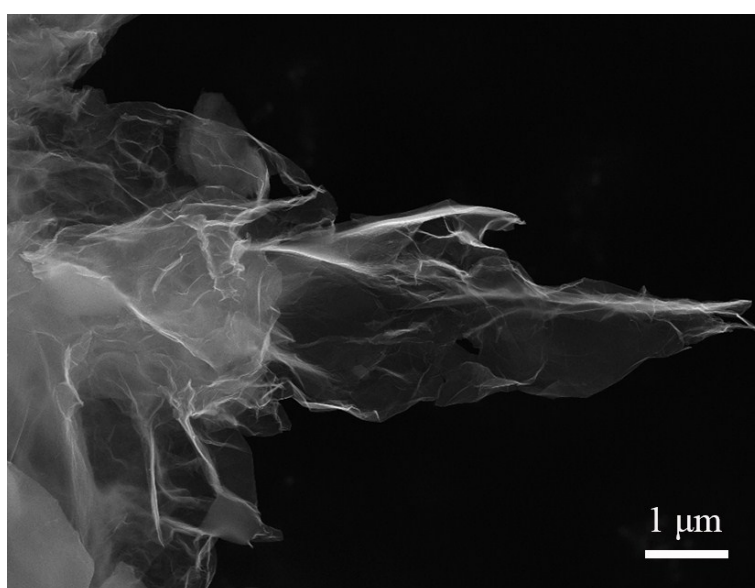


Figure S2. SEM image of rGO reduced by solvothermal reduction in DMF. No gold sputter coating.

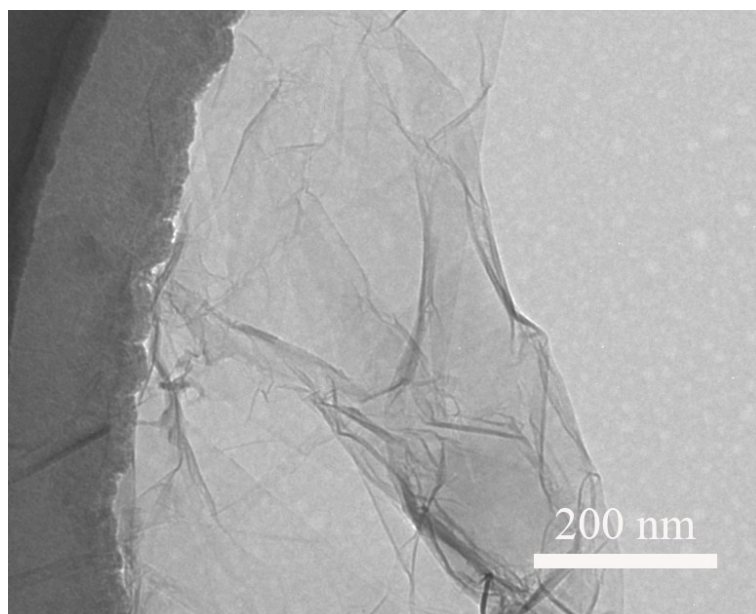


Figure S3. TEM image of reduced graphene oxide (rGO) reduced by solvothermal with DMF.

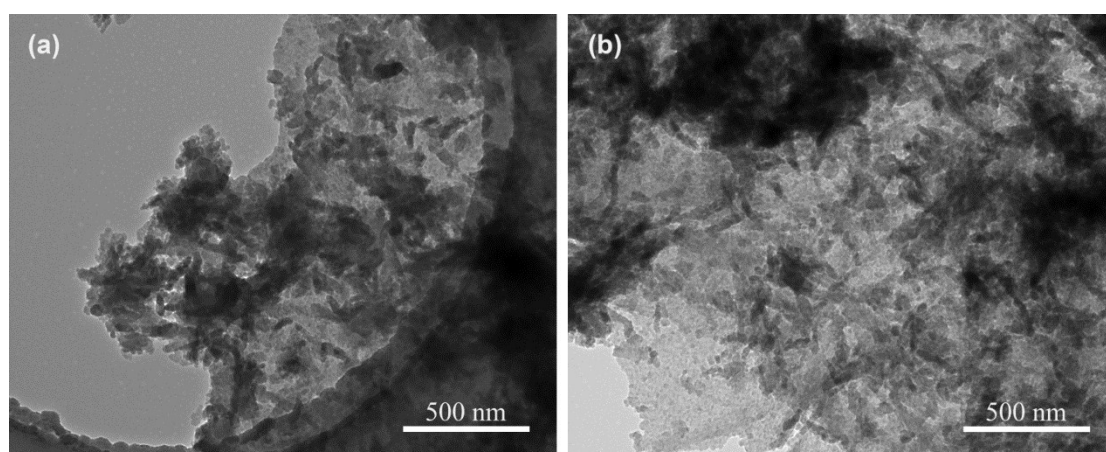


Figure S4. (a-b) TEM images of rGO(5%)-TpPa-1-COF.

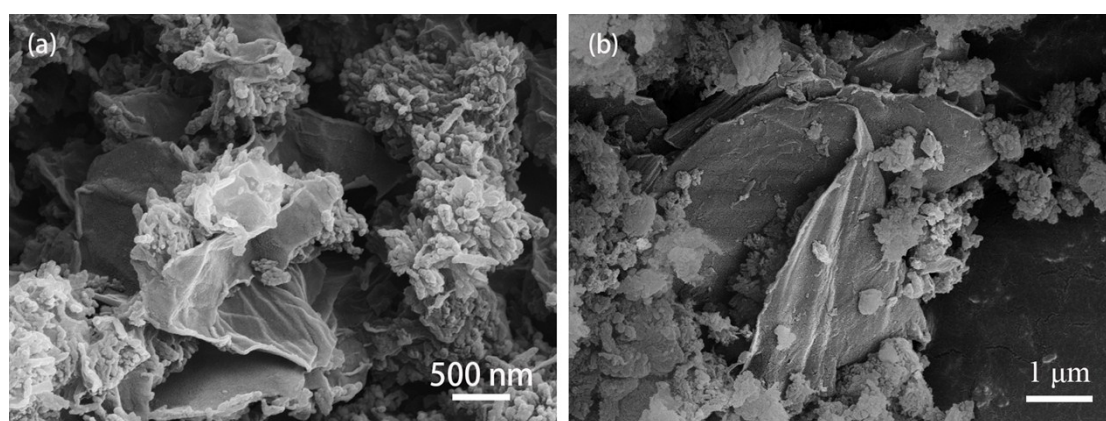


Figure S5. (a-b) SEM images of 5%rGO/TpPa-1-COF without covalent bond connection

between two components.

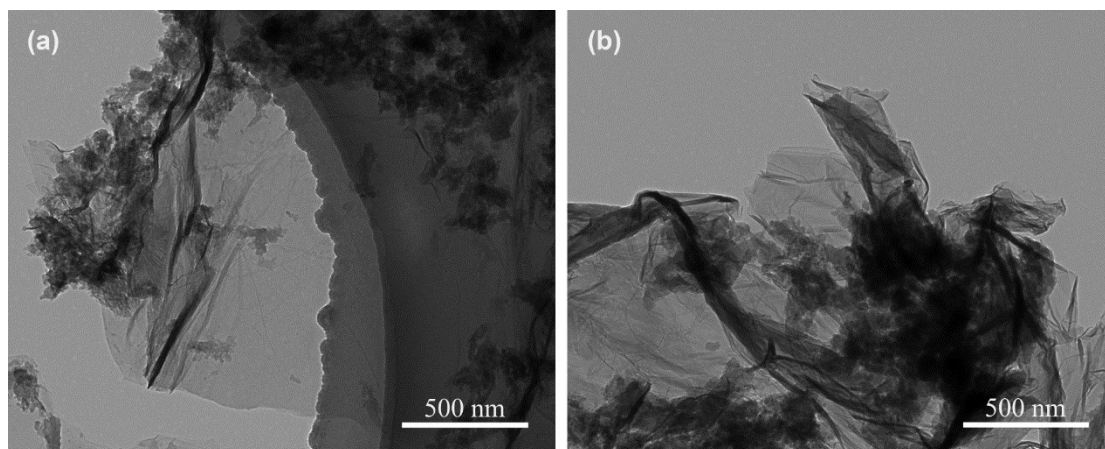


Figure S6. (a-b) TEM images of 5%rGO/TpPa-1-COF without covalent bonds without covalent bonds.

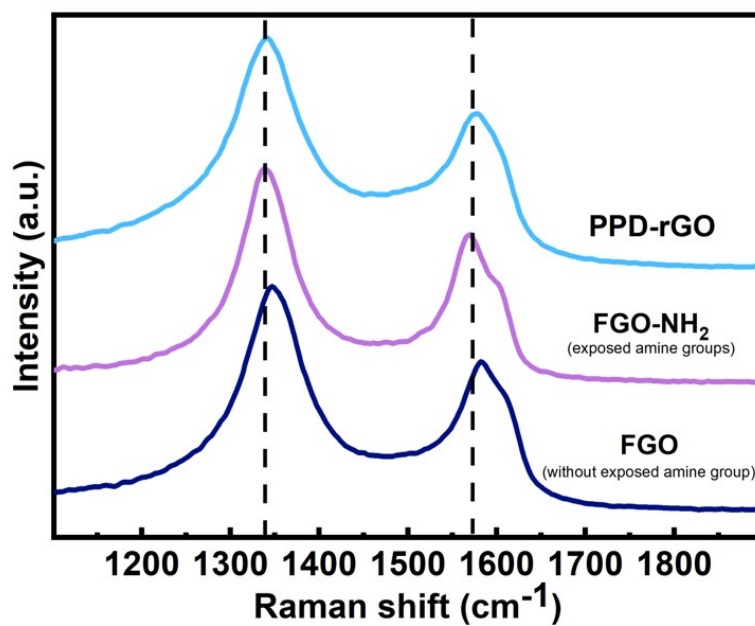


Figure S7. The Raman spectra of PPD-rGO, FGO-NH₂ and FGO with excitation wavelength of 532.5 nm.

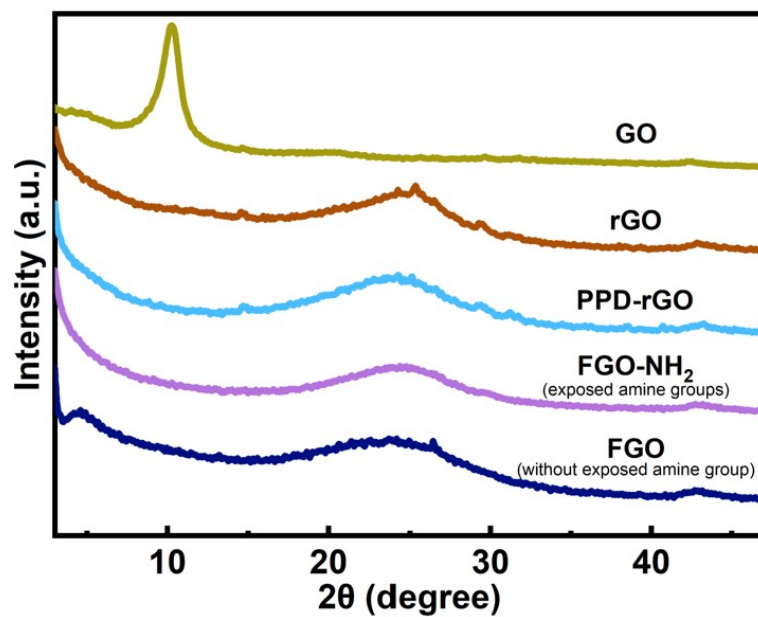


Figure S8. The XRD patterns of GO, rGO, PPD-rGO, FGO-NH₂ and FGO.

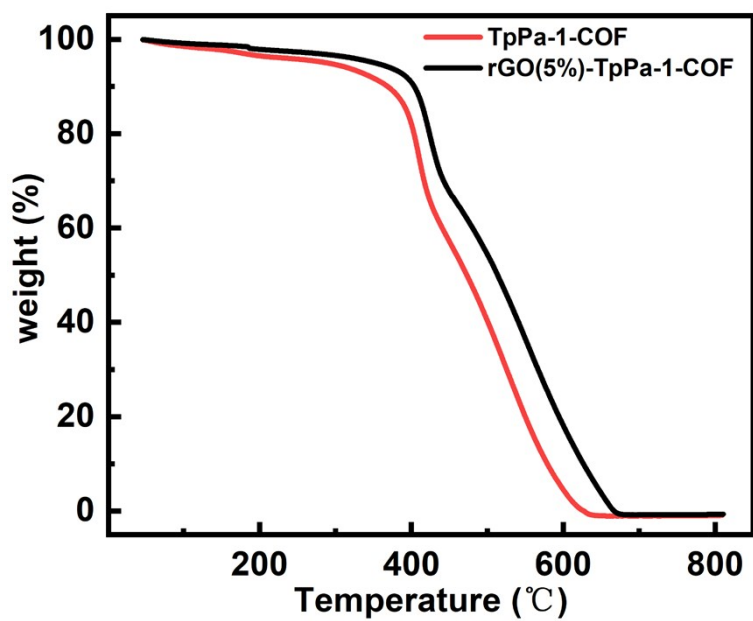


Figure S9. The TGA curves of TpPa-1-COF and rGO(5%)-TpPa-1-COF.

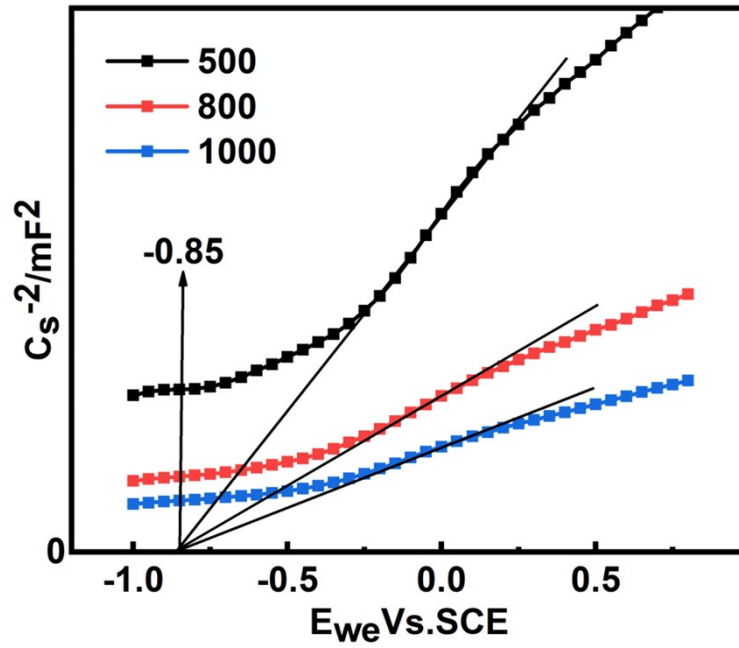


Figure S10. Mott-Schottky plots of TpPa-1-COF at three different frequencies.

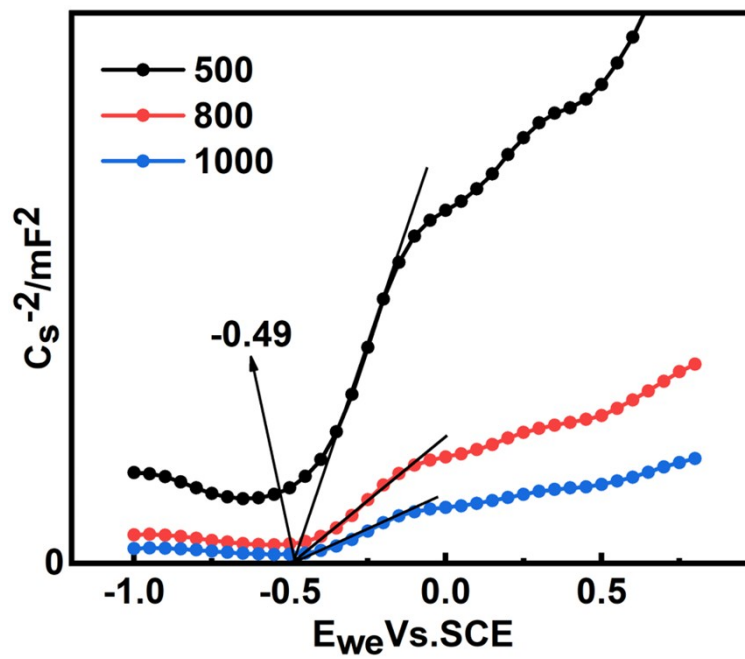


Figure S11. Mott-Schottky plots of rGO(5%)-TpPa-1-COF hybrid materials at three different frequencies.

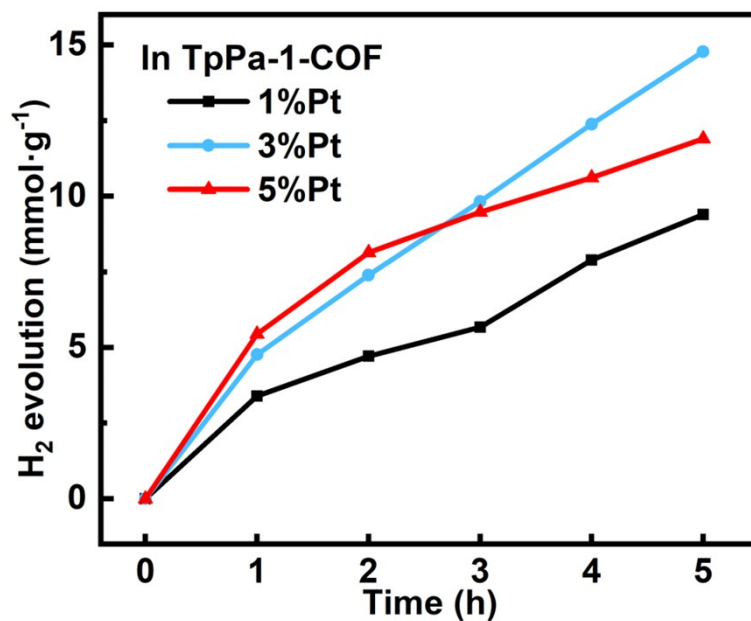


Figure S12. Comparison of photocatalytic H₂ evolution of 5 hours of TpPa-1-COF under different loads of Pt.

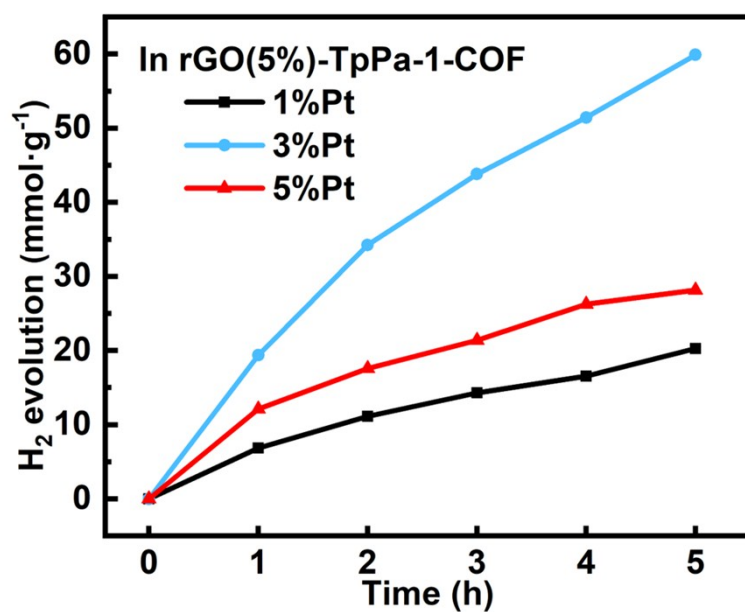


Figure S13. Comparison of photocatalytic H₂ evolution of 5 hours of rGO(5%)-TpPa-1-COF hybrid materials under different loads of Pt.

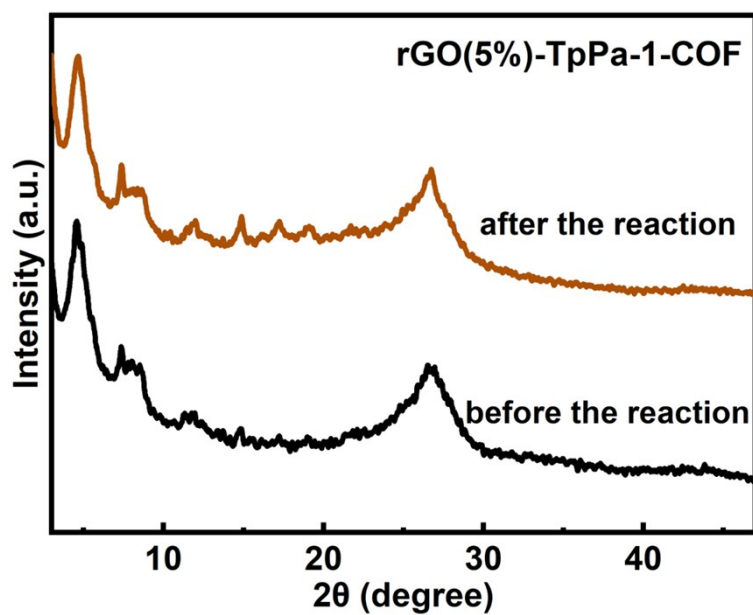


Figure S14. PXRD patterns of rGO(5%)-TpPa-1-COF hybrid materials before and after photocatalysis.

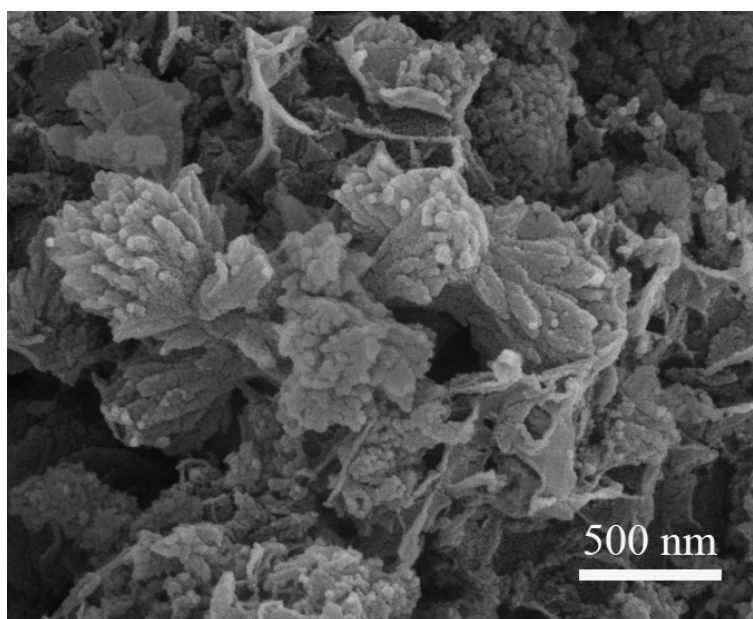


Figure S15. SEM of rGO(5%)-TpPa-1-COF hybrid materials after photocatalysis.

Table S1. Summary of H₂ evolution activity of photocatalysts.

| Catalyst | Co-catalyst | SED | Solvent | Illumination | Activity, $\mu\text{mol g}^{-1} \text{h}^{-1}$ | Ref |
|--|-------------------|-------------|----------------------|--------------|--|-----------|
| rGO-TpPa-1-COF | Pt | SA | PBS Buffer | >420 nm | 11980 | This work |
| TpPa-1-COF | Pt | SA | PBS Buffer | >420 nm | 2470 | This work |
| g-C ₃ N ₄ nanosheets | Pt | TEOA | H ₂ O | >420 nm | 1860 | 6 |
| rGO/g-C ₃ N ₄ | Pt | lactic acid | H ₂ O | >420 nm | 874.4 | 7 |
| g-PAN/g-C ₃ N ₄ | Pt | TEOA | H ₂ O | >400 nm | 370 | 8 |
| TFPT-COF | Pt | TEOA | Water | >420 nm | 1970 | 9 |
| N ₃ -COF | Pt | TEOA | PBS Buffer | >420 nm | 1703 | 10 |
| N ₂ -COF | Co-1 ^a | TEOA | ACN/H ₂ O | AM 1.5 | 782 | 11 |
| N ₂ -COF | Pt | TEOA | PBS Buffer | >420 nm | 438 | 10 |
| N ₂ -COF | Co-1 ^b | TEOA | ACN/H ₂ O | AM 1.5 | 414 | 11 |
| TP-BDDA | Pt | TEOA | Water | >395 nm | 324 | 12 |
| COF-42 | Co-1 | TEOA | ACN/H ₂ O | AM 1.5 | 233 | 10 |
| N ₃ -COF | Co-1 | TEOA | ACN/H ₂ O | AM 1.5 | 163 | 11 |
| N ₁ -COF | Co-1 | TEOA | ACN/H ₂ O | AM 1.5 | 100 | 11 |
| N ₁ -COF | Pt | TEOA | PBS Buffer | >420 nm | 90 | 10 |
| PTP-COF | Pt | TEOA | PBS Buffer | AM 1.5 | 83.83 | 13 |
| TpPa-COF-NO ₂ | Pt | SA | PBS Buffer | >420 nm | 220 | 14 |
| TFPT-COF | Pt | TEOA | Water | >420 nm | 1970 | 14 |
| MoS ₂ /G-CdS | MoS ₂ | lactic acid | Water | >420 nm | 9000 | 15 |
| GO-Sm-DPDP | Sm | TEOA | Water | >420 nm | 545 | 16 |

| | | | | | | |
|-----|------------------|------|-------|---------|-----|----|
| CGM | MoS ₂ | TEOA | Water | >420 nm | 317 | 17 |
|-----|------------------|------|-------|---------|-----|----|

^aCo-1: [Co(dmgH)₂pyCl]. ^bCo-2: [Co(dmgBF₂)₂(OH₂)₂]

Notes and references

1. J. H. Chong, M. Sauer, B. O. Patrick and M. J. MacLachlan, *Org. Lett.*, 2003, **5**, 3823-3826.
2. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.
3. S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature*, 2006, **442**, 282-286.
4. S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2012, **134**, 19524-19527.
5. X. N. Lu, L. Y. Li, B. Song, K. S. Moon, N. N. Hu, G. L. Liao, T. L. Shi and C. P. Wong, *Nano Energy*, 2015, **17**, 160-170.
6. S. B. Yang, Y. J. Gong, J. S. Zhang, L. Zhan, L. L. Ma, Z. Y. Fang, R. Vajtai, X. C. Wang and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 2452-2456.
7. Q. Sun, P. Wang, H. G. Yu and X. F. Wang, *J. Mol. Catal. A: Chem.*, 2016, **424**, 369-376.
8. F. He, G. Chen, Y. Yu, S. Hao, Y. Zhou and Y. Zheng, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7171-7179.
9. L. Stegbauer, K. Schwinghammer, B. V. Lotsch, *Chem. Sci.* 2014, **5**, 2789-2793.
10. V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld, B. V. Lotsch, *Nat. Commun.* 2015, **6**, 8508.
11. T. Banerjee, F. Haase, G. Savasci, K. Gottschling, C. Ochsenfeld, B. V. Lotsch, *J Am Chem Soc* 2017, **139**, 16228-16234.
12. P. Pachfule, A. Acharjya, J. Roeser, T. Langenhahn, M. Schwarze, R. Schomacker, A. Thomas, J. Schmidt, *J Am Chem Soc* 2018, **140**, 1423-1427.
13. F. Haase, T. Banerjee, G. Savasci, C. Ochsenfeld, B. V. Lotsch, *Faraday Discuss.* 2017, **201**, 247-264.
14. J. L. Sheng, H. Dong, X. B. Meng, H. L. Tang, Y. H. Yao, D. Q. Liu, L. L. Bai, F. M. Zhang, J. Z. Wei, X. J. Sun, *ChemCatChem* 2019, **11**, 2313-2319.
15. K. Chang, Z. W. Mei, T. Wang, Q. Kang, S. X. Ouyang and J. H. Ye, *ACS Nano*, 2014, **8**, 7078-7087.
16. L. X. Zhang, L. X. Qin, S. Z. Kang, G. D. Li and X. Q. Li, *ACS Sustainable Chem. Eng.*, 2019, **7**, 8358-8366.
17. Y. J. Yuan, Y. Yang, Z. J. Li, D. Q. Chen, S. T. Wu, G. L. Fang, W. F. Bai, M. Y. Ding, L. X. Yang, D. P. Cao, Z. T. Yu and Z. G. Zou, *ACS Appl. Energy Mater.*, 2018, **1**, 1400-1407.