

## Supporting Information

### **Design of the earth abundant g-C<sub>3</sub>N<sub>4</sub>/rGO/FeOOH Z-scheme ternary heterojunction with enhanced photocatalytic activity**

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## 1. Chemicals:

$C_3H_6N_6$ (99%),  $FeCl_3$ (CP,97%) and  $Na_2SO_4$ (AR,99%) (Shanghai Macklin Biochemical Technology Co., Ltd) are analytical grade and used as received without further purification.

### 1.1 Preparation Steps of graphene oxide (GO):

Graphite powder was prepared by a modified Hummer's method to obtain GO. Two grams of graphite and 1 g of sodium nitrate ( $NaNO_3$ ) were mixed in sulfuric acid ( $H_2SO_4$  of 50 mL) by rigorous stirring for 3 h in an ice bath at 0 °C. Eight grams of potassium permanganate ( $KMnO_4$ ) was then added slowly into the suspension, and the suspension was stirred until its color turned dark gray. Next, deionized (DI) water (96 mL) was slowly added to the suspension, and the suspension was maintained at 98 °C for 1 h. Finally, warm DI water (280 mL) and hydrogen peroxide solution ( $H_2O_2$ , 50 wt %, 20 mL) were slowly added to obtain a bright brown graphite oxide solution. This solution was filtered and washed with DI water several times, followed by a drying step to obtain “graphite oxide powder. The next step was to obtain GO solution from the graphite oxide powder by sonication. Typically, 4.2 g of the graphite oxide powder was added to 350 mL of DI water, and this solution was tip-sonicated at 80 W for 2 h. The sonicated solution was centrifuged for 1 h at 9500 rpm. The supernatant solution was dried, and the GO powder was obtained.

## 2. Characterization.

The powder X-ray diffraction (XRD) patterns were recorded on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized  $Cu K\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ). Corresponding work voltage and current is 40 kV and 100 mA, respectively. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on JEOL-2100F apparatus at an accelerating voltage of 200 kV. The atomic structure of the CdS phase junction was characterized using an ARM-200CF (JEOL, Tokyo, Japan) transmission electron microscope operated at 200 kV and equipped with double spherical aberration (Cs) correctors. Element content analysis was tested on an inductively coupled plasma (ICP) spectroscope (Prodigy, Leeman, America). The UV–Vis absorption and diffused reflectance spectra were recorded using a Cary 5000 UV-Vis spectrometer (Viarian, USA) with  $BaSO_4$  as a reflectance standard. The

transient photocurrent responses experiments were carried out at room temperature using a conventional three-electrode system with a glassy carbon electrode (3mm in diameter), (sheet resistance 20–25  $\Omega$ /square) with a geometrical area of  $1.0 \pm 0.1 \text{ cm}^2$  as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl electrode as the reference electrode. All the samples were dispersed in deionized water with a concentration of 1.5 mg/mL and deposited on the glassy carbon electrode and dried infrared light irradiation.  $\text{Na}_2\text{S}$  (0.1 M) and  $\text{Na}_2\text{SO}_3$  (0.02 M) mixture solution was used as the supporting electrolyte. The transient photocurrent responses measurements were performed with a CHI 660E electrochemical station (Shanghai Chenhua Co. Ltd, China) under 365 nm of irradiation in 0.1 M  $\text{Na}_2\text{S}$  + 0.02 M  $\text{Na}_2\text{SO}_3$  mixed solutions.

### **3. Photocatalytic Hydrogen Production.**

The photocatalytic  $\text{H}_2$  production experiments were performed in a 100 mL Pyrex flask at ambient temperature and atmospheric pressure, and the openings of the flask were sealed with silicone rubber septum. A 300 W xenon arc lamp through a UV-cutoff filter with a wavelength range of 420–800 nm, which was positioned 13 cm away from the reaction solution, was used as a visible light source to trigger the photocatalytic reaction. The focused intensity on the flask was about 200  $\text{mW}\cdot\text{cm}^{-2}$ , which was measured by a FZ-A visible-light radiometer (CEAU-Light, China). In a typical photocatalytic  $\text{H}_2$ -production experiment, 20 mg of the as-prepared photocatalyst was suspended in 50 mL of mixed aqueous solution containing 5 ml  $\text{C}_6\text{H}_{15}\text{NO}_3$  (TEOA, AR,98%). Before irradiation, the system was vacuumed for 5 min via the vacuum pump to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. A continuous magnetic stirrer was applied at the bottom of the reactor to keep the photocatalyst particles in suspension during the experiments.  $\text{H}_2$  content was analyzed by gas chromatography (GC-7900, CEAU-Light, China). All glass wares were carefully rinsed with DI water prior to usage. The photocatalytic stability was performed in the same processing parameters. All the electrochemical measurements were conducted by Bio-Logic SP150 electrochemical station using three-electrode system at room temperature with a glassy carbon electrode (3 mm in diameter), (sheet resistance 20–25  $\Omega$ -2) as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode. Moreover, Mott-Schottky (M–S) plots under dark conditions were also investigated to compare the charge carrier density of different samples in  $\text{Na}_2\text{SO}_4$  (0.5 M) mixed

solutions under 500, 1000 and 2000 Hz

#### **4. Electrochemical measurements**

All the electrochemical measurements were conducted by Bio-Logic SP150 electrochemical station using three-electrode system at room temperature with a glassy carbon electrode (3 mm in diameter), (sheet resistance 20–25  $\Omega$ -2) as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode. Moreover, Mott-Schottky (M–S) plots under dark conditions were also investigated to compare the charge carrier density of different samples in Na<sub>2</sub>SO<sub>4</sub> (0.5 M) mixed solutions under 500, 1000 and 2000 Hz. For the electrochemical measurements, 4 mg of the catalysts were dispersed in 2 mL of 9:1 v/v water/Nafion by sonication to form a homogeneous ink. Typically, 5  $\mu$ L well-dispersed catalysts were covered on the glassy carbon electrode and then dried in an ambient environment for measurements. The electrocatalyst was prepared with a catalyst loading of 0.14 mg cm<sup>-2</sup>. The electrolyte of transient photocurrent responses experiments, electrochemical impedance spectroscopy (EIS), and Mott-Schottky (M-S) was in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution, and the electrolyte of linear sweep voltammetry (LSV) was in 1 M KOH solution for the HER and OER results, respectively. EIS was performed at an impressed voltage of -0.3 eV, for voltage ranging from -2.5 V to 2.5 V. M-S was measured for a scan voltage ranging from -1 V to 0.5 V at 500-2000 Hz. The transient photocurrent responses measurement was performed under full light irradiation, and the LSV obtained at a scan rate of 1 mV/s.

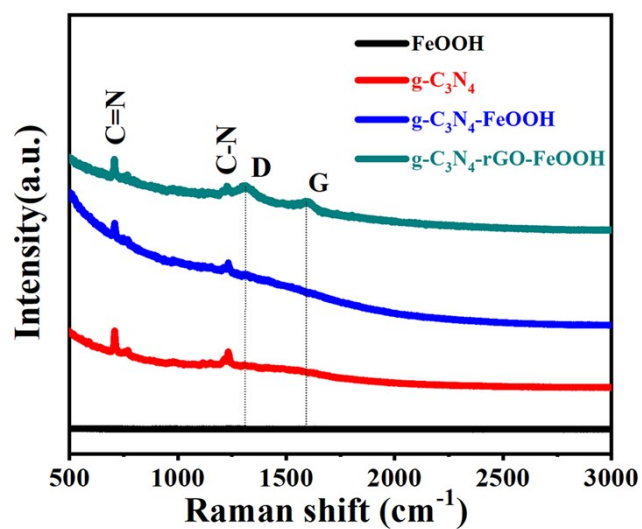


Fig. S1 Raman spectra of  $\text{g-C}_3\text{N}_4$ , FeOOH,  $\text{g-C}_3\text{N}_4/\text{FeOOH}$  and  $\text{g-C}_3\text{N}_4/\text{rGO}/\text{FeOOH}$ .

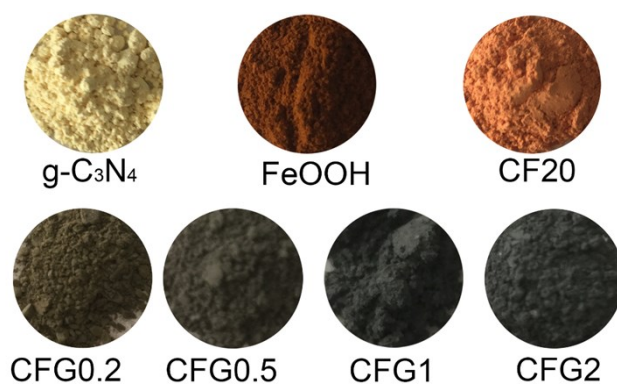
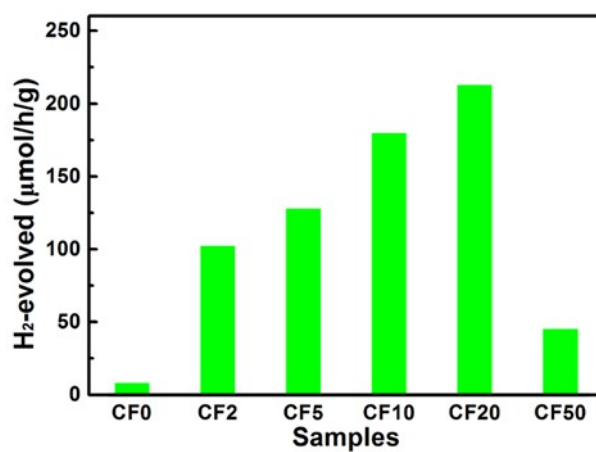
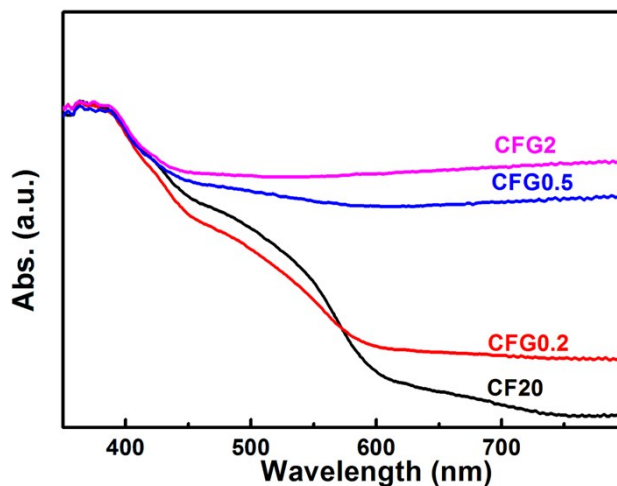


Fig. S2 The photographs of  $\text{g-C}_3\text{N}_4$ , FeOOH,  $\text{g-C}_3\text{N}_4/\text{FeOOH}$  and  $\text{g-C}_3\text{N}_4/\text{rGO}/\text{FeOOH}$ .



**Fig. S3.** The comparison results of the photocatalytic hydrogen production rate of CF all samples.



**Fig. S4** UV–visible diffuse reflection spectra of CF20, CFG2, CFG0.2 and CFG0.5

**Table S1.** Comparison of the photocatalytic H<sub>2</sub> generation activities of g-C<sub>3</sub>N<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> based composites

Photocatalyst	Dosage e /mg	Light source (nm)	H <sub>2</sub> -evolved	Year <sup>Ref.</sup>
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	10	$\lambda > 400$ nm	37.06 $\mu\text{mol h}^{-1} \text{g}^{-1}$	2018 <sup>1</sup>
2D/2D Fe <sub>2</sub> O <sub>3</sub> /g - C <sub>3</sub> N <sub>4</sub>	50	$\lambda > 420$ nm	398.0 $\mu\text{mol h}^{-1} \text{g}^{-1}$	2018 <sup>2</sup>
Mn-doped/Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	30	$\lambda > 400$ nm	51 $\mu\text{mol h}^{-1}$	2019 <sup>3</sup>
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	20	$\lambda > 420$ nm	31 $\mu\text{mol g}^{-1} \text{h}^{-1} \text{cm}^{-2}$	2020 <sup>4</sup>
g-C <sub>3</sub> N <sub>4</sub> / $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Co-Pi	20	$\lambda \geq 420$ nm	450 $\mu\text{mol h}^{-1} \text{g}^{-1}$	2020 <sup>5</sup>
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /MnO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	30	$\lambda > 190$ nm	124 $\mu\text{mol}^* \text{h}^{-1}$	2020 <sup>6</sup>
g-C <sub>3</sub> N <sub>4</sub> / $\beta$ -FeOOH	30	$\lambda > 420$ nm	9.62 $\mu\text{mol h}^{-1} \text{g}^{-1}$	2020 <sup>7</sup>
g-C <sub>3</sub> N <sub>4</sub> -Fe <sub>3</sub> O <sub>4</sub> / $\beta$ -FeOOH	30	$\lambda > 420$ nm	33.25 $\mu\text{mol h}^{-1} \text{g}^{-1}$	2020 <sup>7</sup>
<b>g-C<sub>3</sub>N<sub>4</sub>/rGO/FeOOH</b>	<b>20</b>	<b><math>\lambda \geq 420</math> nm</b>	<b>869.8 <math>\mu\text{mol/h/g}</math></b>	<b>This work</b>

## Supporting References

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