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Supporting Information

Conductive polymer mediated earth abundant Z-scheme g-C_3N_4/Fe_2O_3 heterostructure with excellent photocatalytic activity

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1. Chemicals:

Melamine ($C_3N_3(NH_2)_3$, 99%, CAS: 108-78-1), $FeCl_3$ (99%, CAS: 7705-08-0), Na_2SO_4 (99%, CAS: 7757-82-6), pyrrole (99%, CAS: 109-97-7) are purchased from Shanghai Macklin Biochemical Technology Co., Ltd and used as received without further purification.

2. Sample preparation.

For the preparation of g-C_3N_4, 5 g of melamine ($C_3N_3(NH_2)_3$) in a crucible was processed at 650 °C for 2 h in argon atmosphere. After the ball-milling and freeze drying process, the obtained bulk g-C_3N_4 went through thermal exfoliation process at 550 °C for 2 h in argon atmosphere for yielding the g-C_3N_4 nanosheets.

In a typical synthesis procedure of g-C_3N_4-PPy-Fe_2O_3, 100 mg g-C_3N_4 and excess amount of ferric chloride (100 mg) to make sure the sufficient content of Fe_2O_3 was dissolved in 40 mL DI water, and then different volume of pyrrole (10, 20, 50 μL) was added into the abovementioned solution with ultrasound for 30 min, then the solution was magnetically stirred at 40 °C for 10 h. Afterwards, the solution was washed with DI water and ethanol for three times respectively, followed by drying at 60 °C for 12 h. The final g-C_3N_4-PPy-Fe_2O_3 was obtained after the post-annealing process at 350 °C for short time (1 h) in air to avoid the complete destruction of PPy. The g-C_3N_4-PPy was prepared using the ammonium persulfate to realize the formation of PPy, and the g-C_3N_4-FeP was prepared via the phosphating process over the mechanical mixture the g-C_3N_4 and $FeCl_3$.

The PPy with Fe ion was also prepared with ammonium persulfate as the control sample. Typically, 50 mg ammonium persulfate ($(NH_4)_2S_2O_8$) was dispersed into 30 mL deionized water, then different amounts 1 mL pyrrole was added dropwise into the aforementioned solution. The as-prepared solution was dispersed by ultrasound for 30 min and continuously stirred for 12 h, the dark grey dispersion was centrifuged and washed several times with deionized water and anhydrous ethanol, and then dried at 60 °C overnight in the oven. The P-doped g-C_3N_4 and PPy controll sample was prepared with the similar phosphating process using bare g-C_3N_4 and PPy derived from the ammonium persulfate as the precursors.

3. Characterization.

The powder X-ray diffraction (XRD) patterns were recorded on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54060$ Å). 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 BaSO4 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 Ω/square) with a geometrical area of 1.0 ± 0.1 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. Na_2S (0.1 M) and Na_2SO_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 Na_2S + 0.02 M Na_2SO_3 mixed solutions.

4. Photocatalytic Hydrogen Production.

The photocatalytic 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 $mW \cdot cm^{-2}$, which was measured by a FZ-A visible-light radiometer (CEAU-Light, China). In a typical photocatalytic H_2-production experiment, 20 mg of the as-prepared photocatalyst was suspended in 50 mL of mixed aqueous solution containing 5 ml $C_6H_{15}NO_3$ (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. H_2 content was analyzed by gas chromatography (GC-7900, CEAU-Light, China) under room temperature (about 25±5 °C) maintained by a cooling circulating water equipment. The evolved H_2O_2 was measured using the colorimetric titration method according to the previous publication (Appl. Catal., B 2014, 152, 383−389). All glass wares were carefully rinsed with DI water prior to usage. The photocatalytic stability was performed in the same processing parameters.

5. 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 Ω-2) as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode. 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 μL 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^{-2}. The electrolyte of transient photocurrent responses experiments, electrochemical impedance spectroscopy (EIS), and Mott-Schottky (M-S) was in 0.5 M Na_2SO_4 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.

6. Supporting Figures.

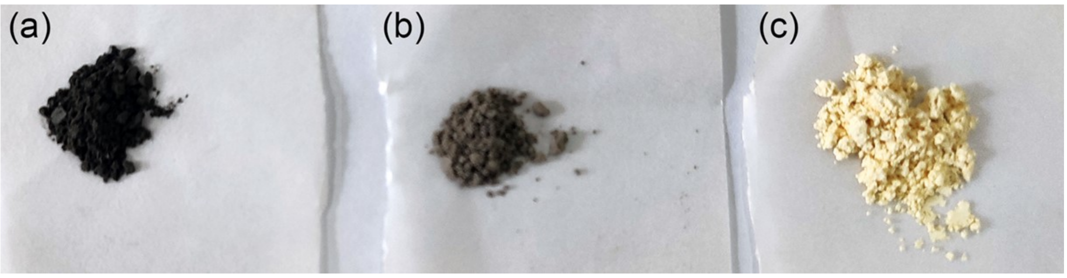

Fig. S1. The photographs of (a) g-C_3N_4-PPy-$FeCl_3$, (b) g-C_3N_4-PPy-Fe_2O_3 and (c) g-C_3N_4.

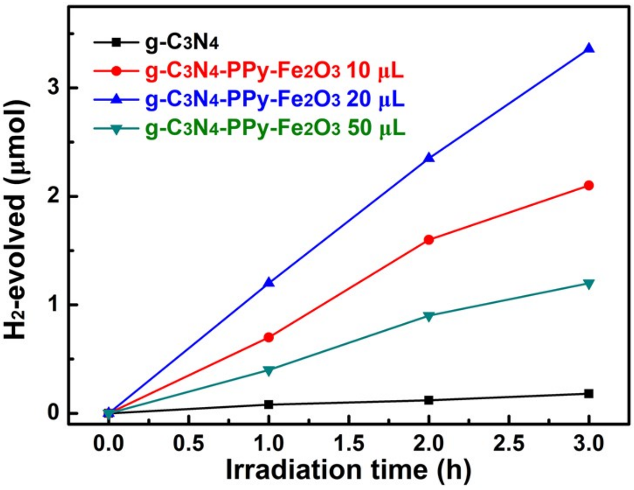

Fig. S2 The photocatalytic hydrogen production activity of g-C_3N_4 and g-C_3N_4-PPy-Fe_2O_3 with different volume of Py.

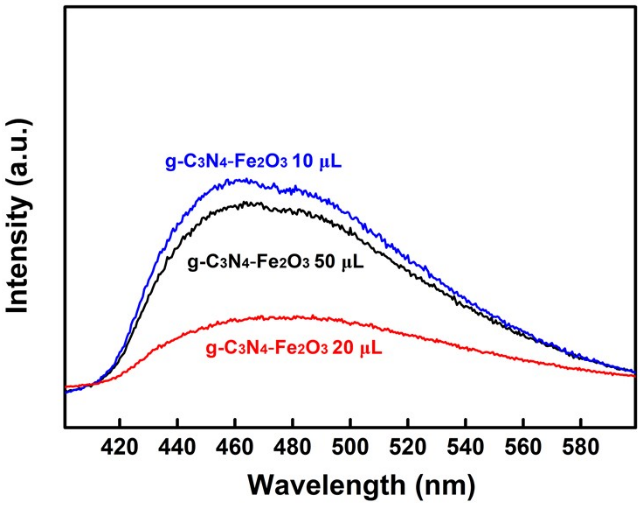

Fig. S3 The PL emission spectra of g-C_3N_4 and g-C_3N_4-PPy-Fe_2O_3 with different volume of Py.

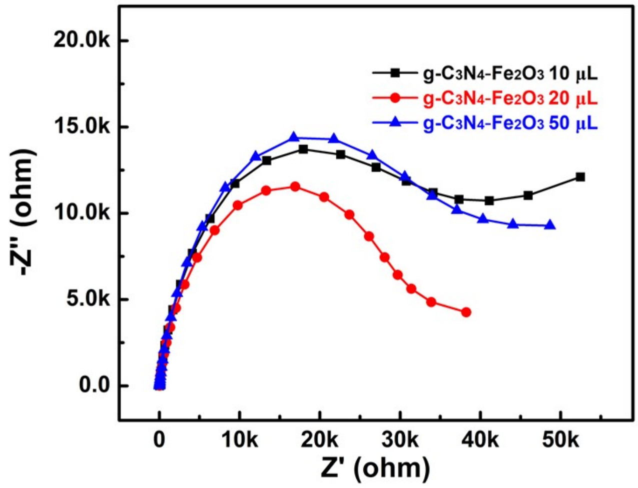

Fig. S4 The electrochemical impedance spectroscopy (EIS) spectra of g-C_3N_4 and g-C_3N_4-PPy-Fe_2O_3 with different volume of Py.