Supporting Information

Conductive polymer supported and confined iron phosphide nanocrystals for boosting the photocatalytic hydrogen production of graphic carbon nitride

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1. 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-FeP, 100 mg g-C_3N_4 and certain amount of ferric chloride to make sure the setting content of FeP of 10, 20, 50 wt% was dissolved in 40 mL DI water, and then appropriate pyrrole (5μL) was added into the abovementioned solution with ultrasound for 30 min, then the solution was magnetically stirred at 40 ^oC for 10 h. Afterwards, the solution was washed with DI water for three times, followed by drying at 60 ^oC for 12 h. Then the g-C_3N_4-PPy-Fe ion was collected and mixture with 20 mg sodium hypophosphite. The final g-C_3N_4-PPy-FeP was obtained after the post-annealing process at 350 ^oC for 2 h under Ar atmosphere. 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.

2. Materials and General Methods.

All chemicals were of analytical grade and used as received without further purification. 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), and the corresponding work voltage and current was 40 kV and 100 mA, respectively. Fourier transform infrared spectroscopy (FTIR) was collected on a Thermo Scientific Nicolet iS10 spectrometer. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on JEOL-2100F apparatus at an accelerating voltage of 200 kV, and the elemental mapping was performed with JSM-5160LV-Vantage typed energy dispersive X-ray spectroscopy (EDS) spectrometer. Surface morphologies of the g-C_3N_4-based heterostructures were examined by a scanning electron microscope (SEM, JSM-7600F) at an acceleration voltage of 10 kV. Element content analysis was tested on an inductively coupled plasma (ICP) spectroscope (Agilent ICP0ES730, America). The X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 Xi (USA)-ray photoelectron spectrometer using Al as the excitation source. 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. Nitrogen adsorption-desorption isotherms were measured at 77 K on a Quantachrome Instruments Autosorb AS-6B. The pore size distributions were measured by the Barrett-Joyner-Halenda (BJH) method. Steady photoluminescence (PL) emission spectra were tested by a luminescmce spectrophotometer (QM-400, PTI) with 350 nm excitation wavelength. The fluorescence decay times were measured using the Horiba Jobin Yvon Data Station HUB operating in time-correlated single photon counting mode (TCSPC) with the time resolution of 200 ps. Nano LED diode emitting pulses at 370 nm with 1 MHz repetition rate was used as an excitation source. Light-scattering Ludox solution was used to obtain the instrument response function (prompt). The time ranges are 0.055 ns/channel in 4096 effective channels.

3. Electrochemical measurements

All the electrochemical experiments were conducted on the electrochemical station (Bio-Logic SP-150) in a three-electrode system at room temperature with a glassy carbon electrode (3 mm in diameter), (sheet resistance 20−25 Ω/square) 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 (under visible light irradiation), electrochemical impedance spectroscopy (EIS), and Mott-Schottky (M-S) was 0.5 M Na_2SO_4 aqueous solution, and the electrolyte of linear sweep voltammetry (LSV) was performed in 1M KOH solutions for the HER result. 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, 1000 and 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. The contact angle of g-C_3N_4, g-C_3N_4-based binary and ternary heterostructures (coated on glass) by Contact angle measuring instrument (Shanghai Zhongchen Digital Technic Apparatus Co., Itd, JC2000D3A) using height measurement method. Before the measurements, 4 mg of the catalysts were dispersed in 2 mL of 5:5 v/v water/ethanol by sonication to form a homogeneous ink. Typically, 10 μL well-dispersed catalysts were covered on the glass and then dried in an ambient environment for measurements.

4. Photocatalytic Hydrogen Production

The photocatalytic H_2-production experiments were performed via a photocatalytic H_2-production activity evaluation system (CEL-SPH2N, CEAULight, China) in a 300 mL Pyrex flask, and the openings of the flask were sealed with silicone rubber septum. A 300 W xenon arc lamp, which was positioned 13 cm away from the reaction solution, was used as an all light source to trigger the photocatalytic reaction. A 300 W xenon arc lamp with and without 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 ~ 200 $mW\cdot cm^{-2}$, which was measured by a FZ-A visible-light radiometer (made in the photoelectric instrument factory of Beijing Normal University, 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, CEAULight, China). All glasswares were carefully rinsed with DI water prior to usage. The photocatalytic stability was performed in the same processing parameters. The apparent quantum yield of g-C_3N_4-PPy-FeP was measured using 300W xenon lamp equipped with monochromatic mass filter at 365, 420, 475, 550 filter. The AQY was calculated using the following equation: Apparent quantum yield (AQY) = (2 × the number of evolved H_2 molecules/the number of incident photons) × 100%.

5. Supporting Figures.

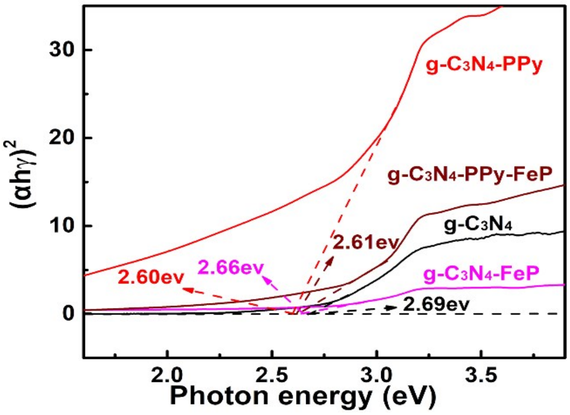

Fig. S1. The Kubelka-Munk plots curve of g-C_3N_4, g-C_3N_4-PPy, g-C_3N_4-FeP and g-C_3N_4-PPy-FeP.

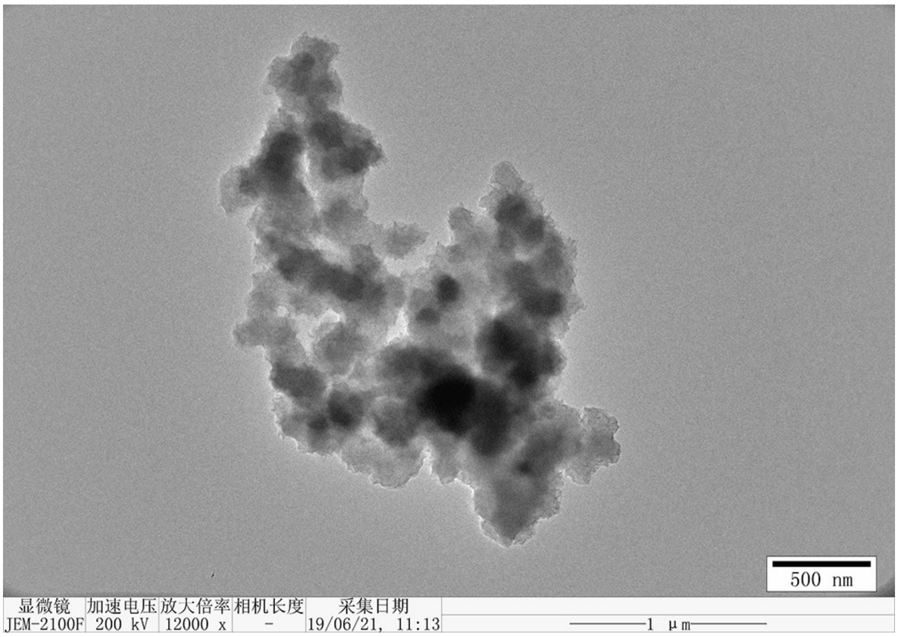

Fig. S2. Transmission electron microscopy (TEM) image of the g-C_3N_4-PPy-FeP.

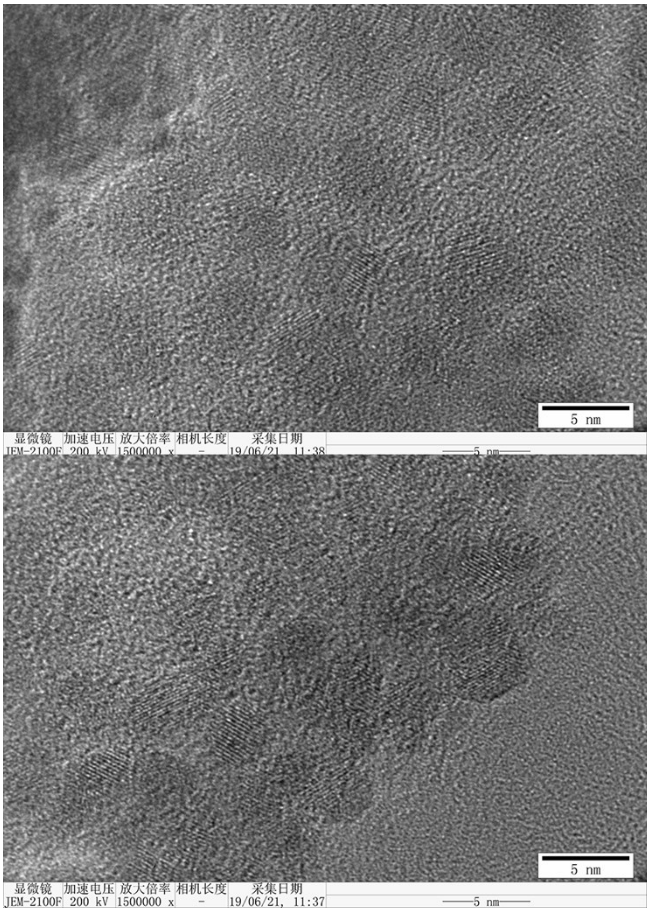

Fig. S3. High resolution TEM (HRTEM) image of the g-C_3N_4-PPy-FeP.

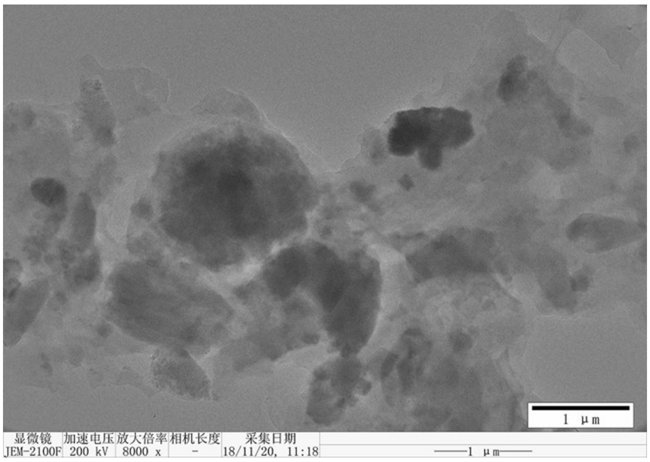

Fig. S4. Transmission electron microscopy (TEM) image of the g-C_3N_4-FeP.

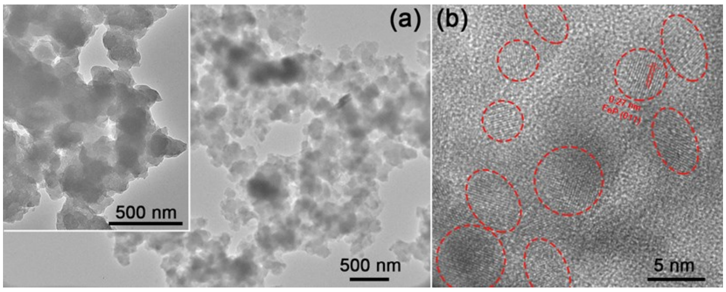

Fig. S5. The (a) TEM and (b) high resolution TEM (HRTEM) images of the PPy-FeP.

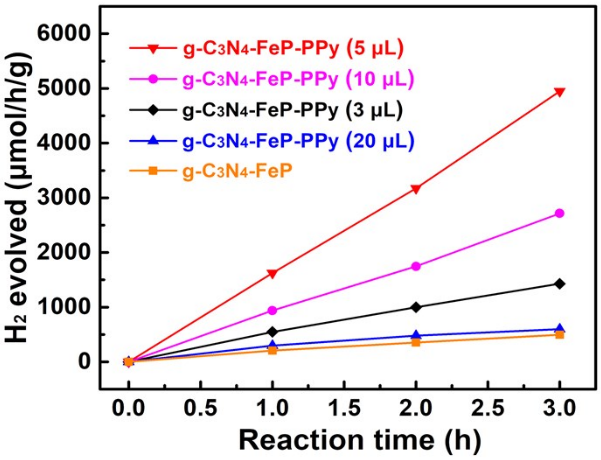

Fig. S6. Effect of volume of PPy on the photocatalytic hydrogen production activity of g-C_3N_4-PPy-FeP heterostructure under UV-vis light irradiation.

Fig. S7. The photograph of FeP-PPy.

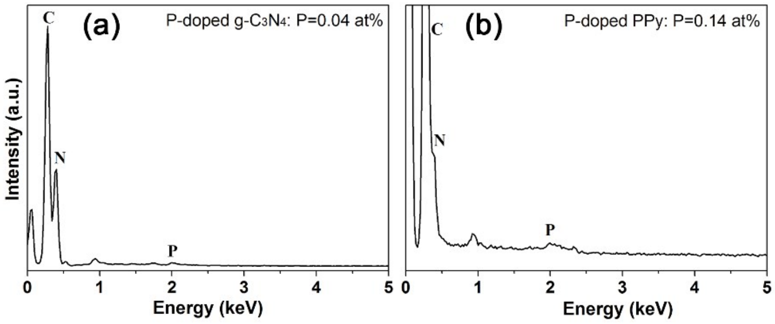

Fig. S8. The energy dispersive X-ray spectroscopy (EDS) spectrometer of (a) P-doped g-C_3N_4 and (b) P-doped PPy.

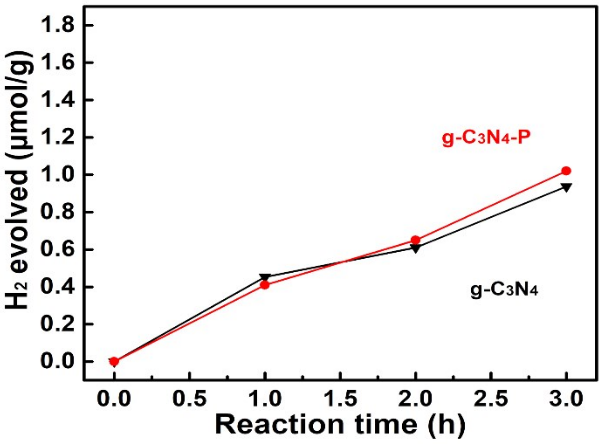

Fig. S9. Comparison of photocatalytic hydrogen evolution property between g-C_3N_4 and g-C_3N_4-P.

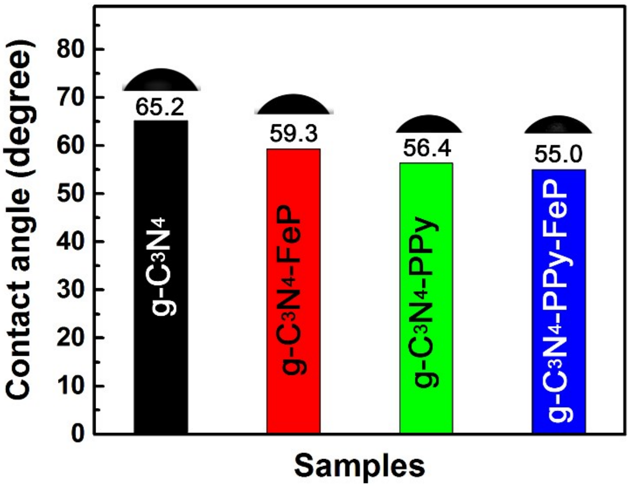

Fig. S10. The contact angle of g-C_3N_4, g-C_3N_4-FeP, g-C_3N_4-PPy, and g-C_3N_4-PPy-FeP.

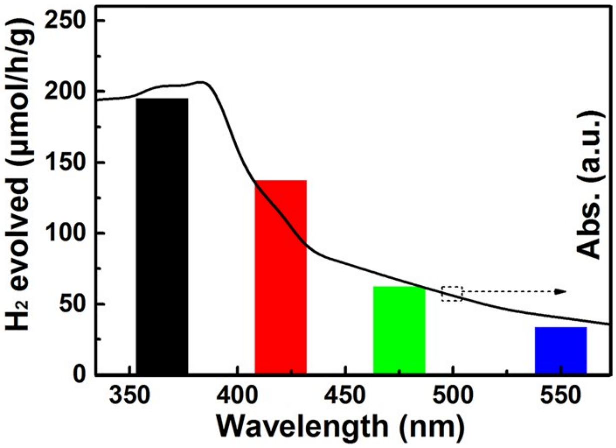

Fig. S11. Wavelength dependence of the hydrogen evolution rate for g-C_3N_4-PPy-FeP.

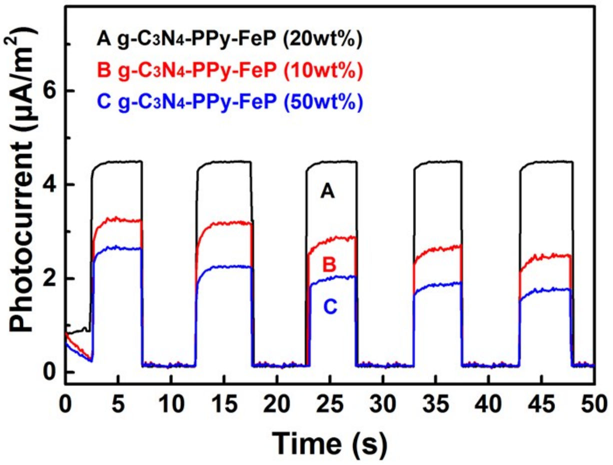

Fig. S12. Effect of amount of FeP on the transient photocurrent responses in g-C_3N_4-PPy-FeP.

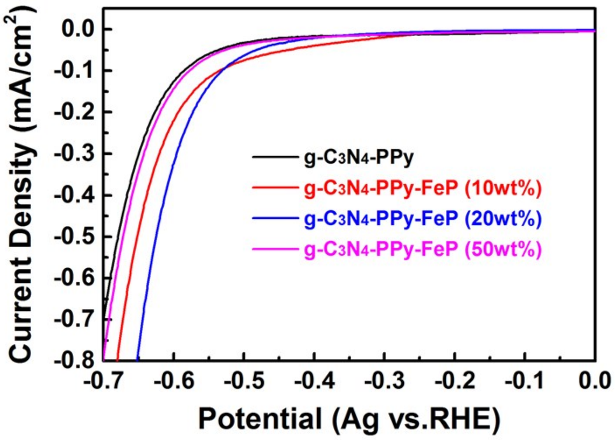

Fig. S13. Effect of amount of FeP on the electrocatalytic HER performance in g-C_3N_4-PPy-FeP.

6. Supporting Tables

Table S1. Comparison results of apparent quantum yield of g-C_3N_4-based heterostructures.

Photocatalyst	Reaction Conditions	AQY(%)	Ref.
g-C_3N_4/TiO_2-24	TEOA	0.31% at 420 nm	1
35%$Co_3(PO_4)_2$/g-C_3N_4	none	1.32% at 420 nm	2
$Ni_{12}P_5$- g-C_3N_4	TEOA	4.67% at 420 nm	3
Ni2P/ g-C_3N_4	TEOA	1.8% at 420 nm	4
5NiFeP/ g-C_3N_4	TEOA	4.98% at 420 nm	5
<5 nm FeP/ g-C_3N_4	TEOA	1.57% at 420 nm	6
Fe@ g-C_3N_4	TEOA	6.89% at 420 nm	7
g-C_3N_4-PPy-FeP	TEOA	10.01% at 420 nm	This work

Table S2. The detailed transient fluorescence properties of g-C_3N_4, g-C_3N_4 loaded with PPy and/or FeP.

Samples	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	A_3 (%)	τ_3 (ns)	Average lifetime τ (ns)
g-C_3N_4	0.38	2.33	0.54	0.61	0.08	10.11	5.16
g-C_3N_4-FeP	0.46	0.56	0.45	2.01	0.09	7.86	4.02
g-C_3N_4-PPy	0.41	0.52	0.47	1.79	0.12	7.06	3.99
g-C_3N_4-PPy-FeP	0.42	1.69	0.50	0.45	0.08	6.68	3.32

7. Supporting References

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