Electronic supplementary information

A bifunctional NiCoP-based core/shell cocatalyst to promote separate photocatalytic hydrogen and oxygen generation over graphitic carbon nitride

Zhixiao Qin, Yubin Chen*, Zhenxiong Huang, Jinzhan Su, and Liejin Guo*

International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Shaanxi 710049, P. R. China.

*Corresponding author information:

E-mail: ybchen@mail.xjtu.edu.cn; lj-guo@mail.xjtu.edu.cn.

Synthesis of Pt/g-C_3N_4. In a typical synthesis of Pt nanoparticles, 105 mg of polyvinyl pyrrolidone (PVP) and 60 mg of ascorbic acid (AA) were dissolved in 8 mL of deionized water and heated at 90 °C for 10 min under magnetic stirring. Then, 3 mL of 0.067 M K_2PtCl_4 aqueous solution was rapidly injected into the above solution. The mixture was maintained at 90 °C for 3 h. The product was centrifuged at 10,000 rpm for 10 min and washed with deionized water several times. The obtained sample was dispersed into 5 mL of deionized water for further use. The Pt/g-C_3N_4 photocatalysts were prepared by grinding the as-prepared g-C_3N_4 and Pt nanoparticles. Typically, appropriate amounts of Pt and g-C_3N_4 were dispersed in 0.5 mL deionized water, and

then thoroughly ground to further increase their contact areas. After the volatilization of water, another 0.5 mL deionized water was added, and the mixture was ground for another 15 min. The obtained Pt/g-C_3N_4 sample was dried under vacuum at 50 °C. The loading amount of Pt was 1.0 wt%.

Synthesis of NiCoP. Pure NiCoP particles were successfully prepared *via* a temperature-programmed reduction (TPR) of the NiCoP@NiCo-Pi in 5%H_2/Ar. The NiCoP@NiCo-Pi was annealed at 500 °C for 1 h in a quartz tube with a heating rate of 2 °C min^{-1} under 5%H_2/Ar flow. After cooling down in room temperature, the obtained products were NiCoP particles.

Electrochemical and photoelectrochemical measurements. The NiCoP, NiCoP@NiCo-Pi, g-C_3N_4, and NiCoP@NiCo-Pi/g-C_3N_4 films were prepared by the electrophoretic deposition (EPD) of the as-prepared powders onto fluorine-doped tin oxide (FTO) coated glass substrates. 30 mg of the prepared sample was first dispersed in 50 mL of acetone, and then two pieces of FTO glass were immersed into the suspension solution with a separation distance of 1 cm. Subsequently, a DC voltage of 50 V was applied for 10 min and then the glass electrodes were rinsed with ethanol, dried at 50 °C for 12 h under vacuum.

Electrochemical and photoelectrochemical measurements were carried out using a CHI 760D electrochemical workstation (CH Instruments, Inc., USA) in a three-electrode system. The reference electrode was a Ag/AgCl electrode, and the counter electrode was a platinum foil. Electrochemical impedance spectroscopy (EIS) was measured in N_2-saturated 0.5 M Na_2SO_4 electrolyte when the working electrode was

biased at a constant potential of -0.6 V *vs.* RHE. The frequency was from 100 kHz to 1 Hz with a 5 mV AC dither. The measured potentials *vs.* Ag/AgCl were converted to reversible hydrogen electrode (RHE) scale via the Nernst equation. Photocurrent density was measured at 0.4 V *vs.* RHE in N_2-saturated 0.5 M Na_2SO_4 electrolyte, and a 500 W Xe lamp coupled with an AM 1.5 filter was used as the light source. LSV curves of g-C_3N_4 and NiCoP@NiCo-Pi/g-C_3N_4 were conducted in N_2-saturated 0.5 M Na_2SO_4 electrolyte at a scan rate of 10 mV/s. Mott-Schottky plots of NiCoP, NiCoP@NiCo-Pi, g-C_3N_4, and NiCoP@NiCo-Pi/g-C_3N_4 were measured in 0.5 M Na_2SO_4 solution.

Table S1. The BET specific surface areas of g-C_3N_4 and NiCoP@NiCo-Pi/g-C_3N_4.

Sample	g-C_3N_4	NiCoP@NiCo-Pi/g-C_3N_4
Specific surface area /$m^2 \cdot g^{-1}$	10.4	11.5

Table S2. Fitted values of all parameters in the equivalent circuit for the Nyquist impedance plots of g-C_3N_4 and NiCoP@NiCo-Pi/g-C_3N_4.

Electrode	R_s ($\Omega \cdot cm^2$)	R_{ct} ($\Omega \cdot cm^2$)	R_{rec} ($\Omega \cdot cm^2$)	CPE1 ($S \cdot cm^{-2} \cdot s^{-n1}$)	CPE2 ($S \cdot cm^{-2} \cdot s^{-n2}$)
g-C_3N_4	30	120	961	1.537×10^{-6}	9.392×10^{-6}
NiCoP@NiCo-Pi/g-C_3N_4	32	62	482	1.408×10^{-6}	7.288×10^{-6}

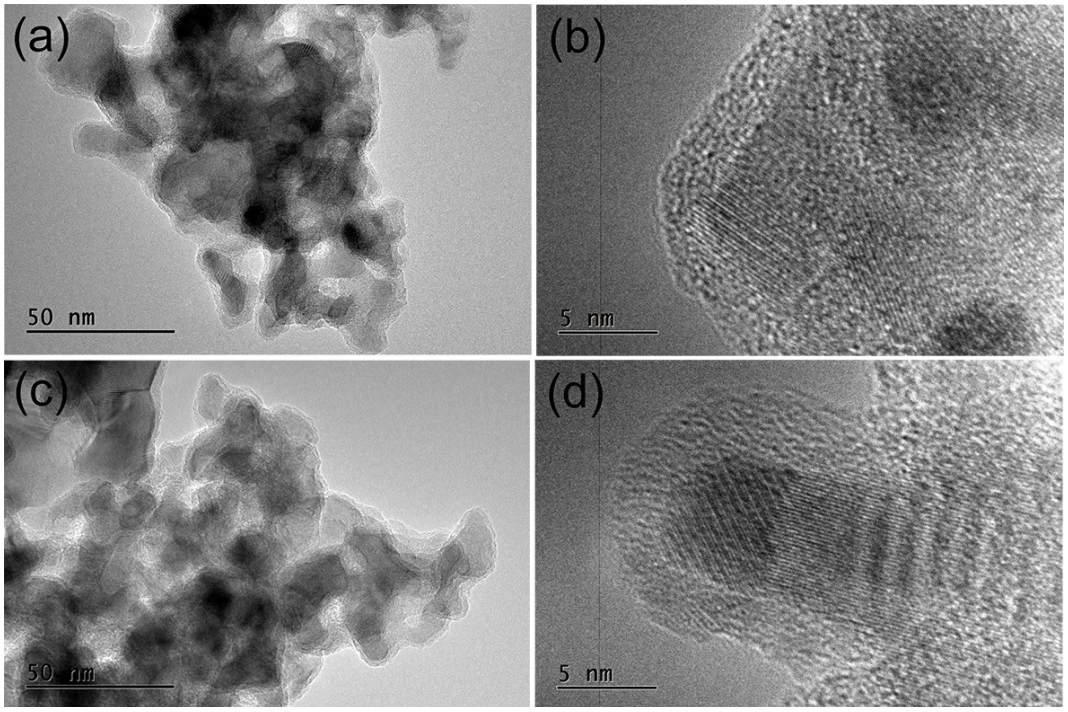

Fig. S1 (a, b) TEM and HRTEM images of NiCoP@NiCo-Pi core/shell nanoparticles just after the solid-state reaction. (c, d) TEM and HRTEM images of NiCoP@NiCo-Pi core/shell nanoparticles after placed in the air for 3 days.

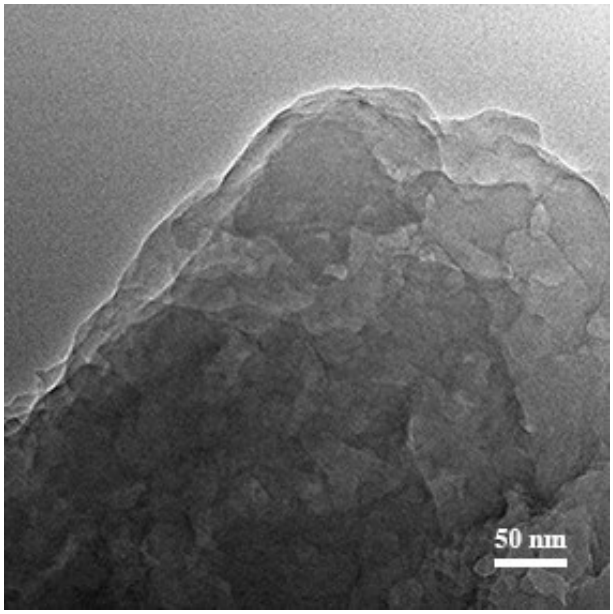

Fig. S2 TEM image of g-C_3N_4.

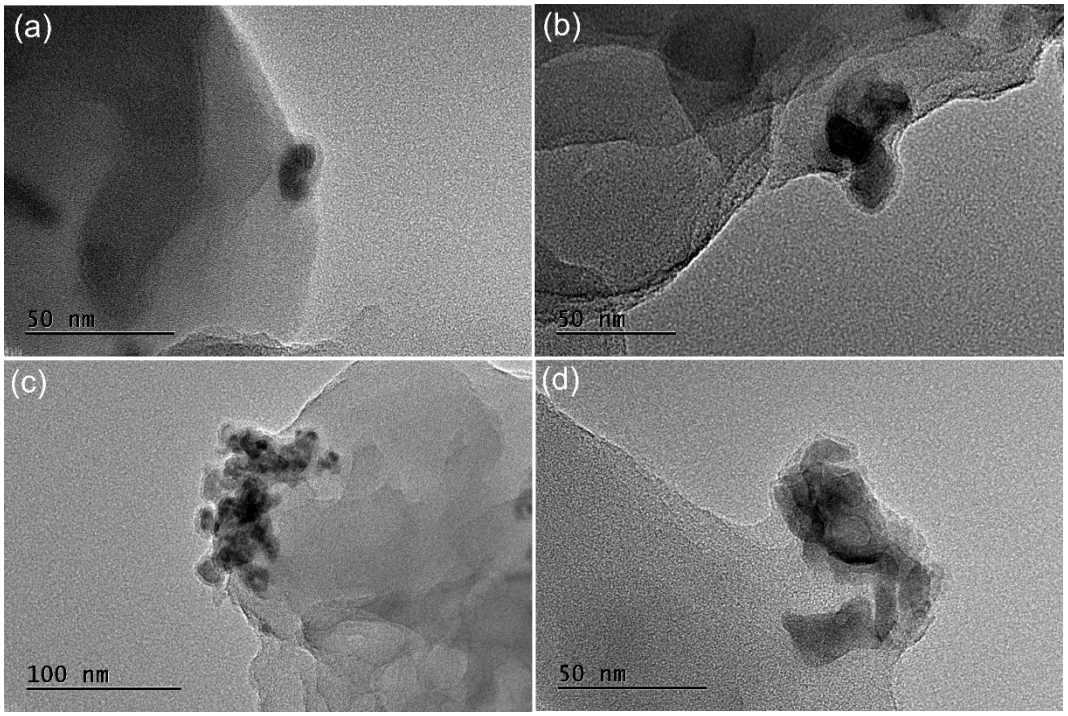

Fig. S3 HRTEM images of NiCoP@NiCo-Pi/g-C_3N_4.

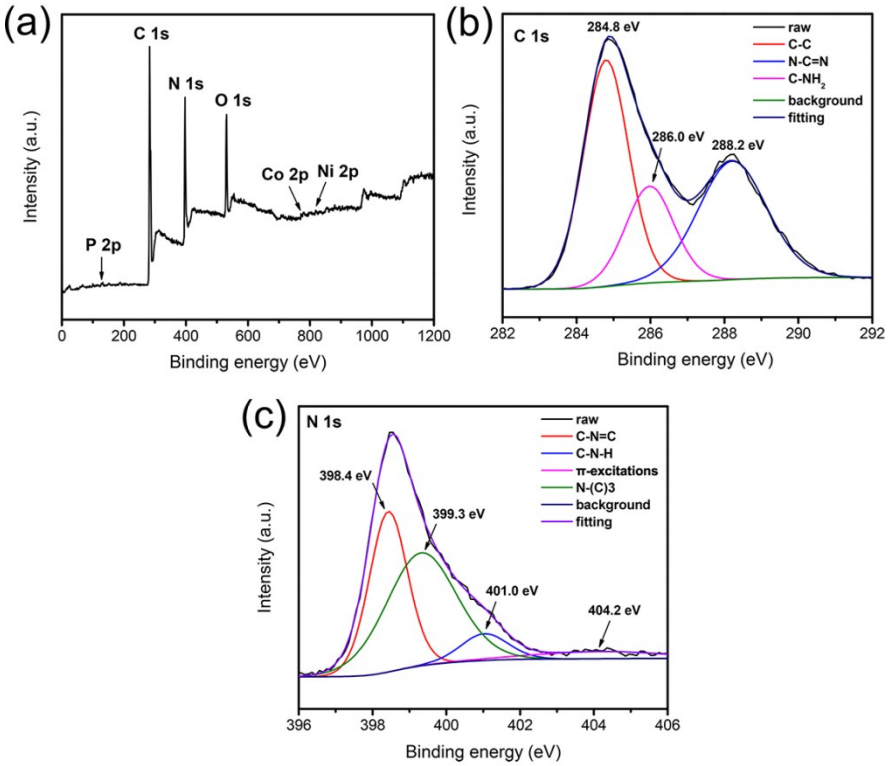

Fig. S4 (a) The survey XPS spectrum of NiCoP@NiCo-Pi/g-C_3N_4. The XPS spectra of (b) C 1s and (c) N 1s.

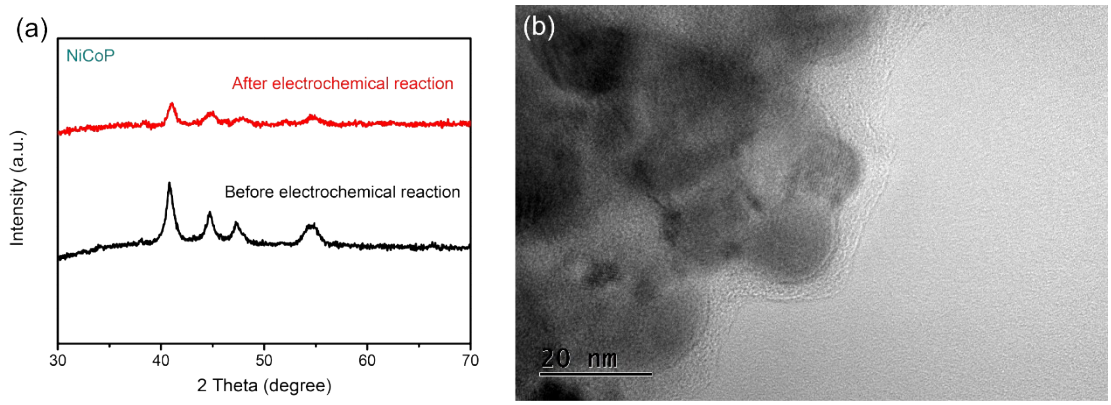

Fig. S5 (a) The XRD patterns of NiCoP@NiCo-Pi/g-C_3N_4 before and after electrochemical reaction in Na_2SO_4 solution. (b) HRTEM image of NiCoP@NiCo-Pi/g-C_3N_4 after electrochemical reaction in Na_2SO_4 solution.

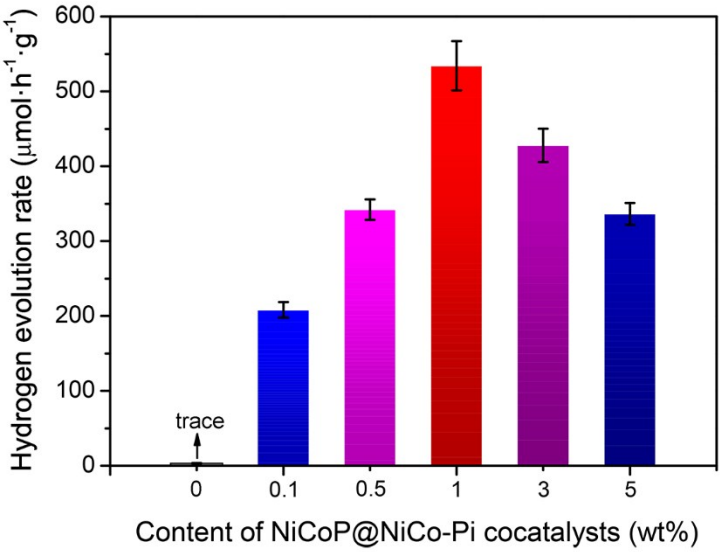

Fig. S6 Photocatalytic hydrogen evolution rates over NiCoP@NiCo-Pi/g-C_3N_4 with different contents of NiCoP@NiCo-Pi (0, 0.1, 0.5, 1, 3, 5 wt%). Reaction conditions: 50 mg of photocatalysts, 80 mL of aqueous solution containing 10 vol% TEOA, 300 W Xe lamp equipped with a cutoff filter ($\lambda \geq 420$ nm).

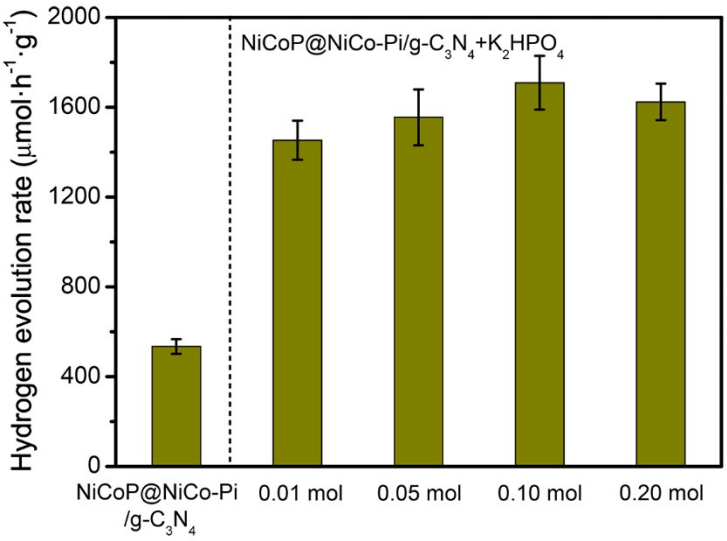

Fig. S7 Photocatalytic hydrogen evolution rates over NiCoP@NiCo-Pi/g-C_3N_4 with different amounts of K_2HPO_4 in the reaction solution. Reaction conditions: 50 mg of photocatalysts, 80 mL of aqueous solution containing 10 vol% TEOA with different amounts of K_2HPO_4. 300 W Xe lamp equipped with a cutoff filter ($\lambda \geq 420$ nm).

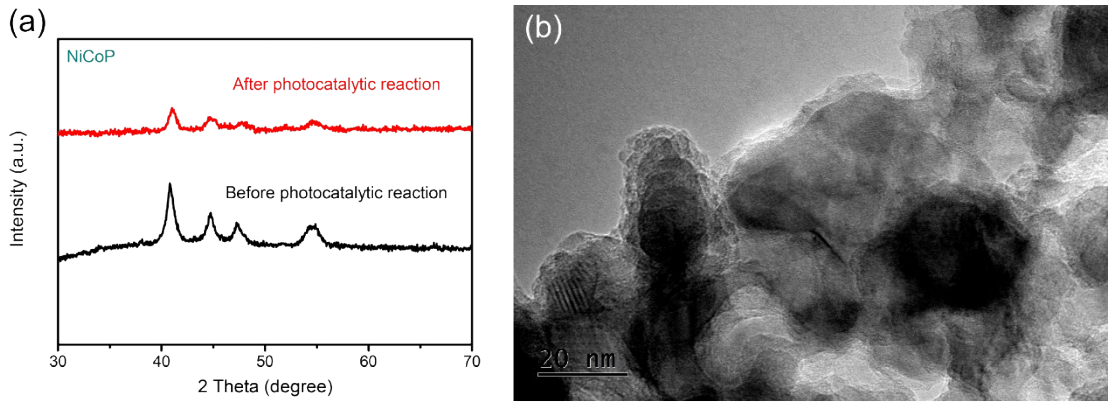

Fig. S8 (a) The XRD patterns of NiCoP@NiCo-Pi/g-C_3N_4 before and after photocatalytic reaction in TEOA and K_2HPO_4 solution. (b) HRTEM image of NiCoP@NiCo-Pi/g-C_3N_4 after photocatalytic reaction in TEOA and K_2HPO_4 solution.

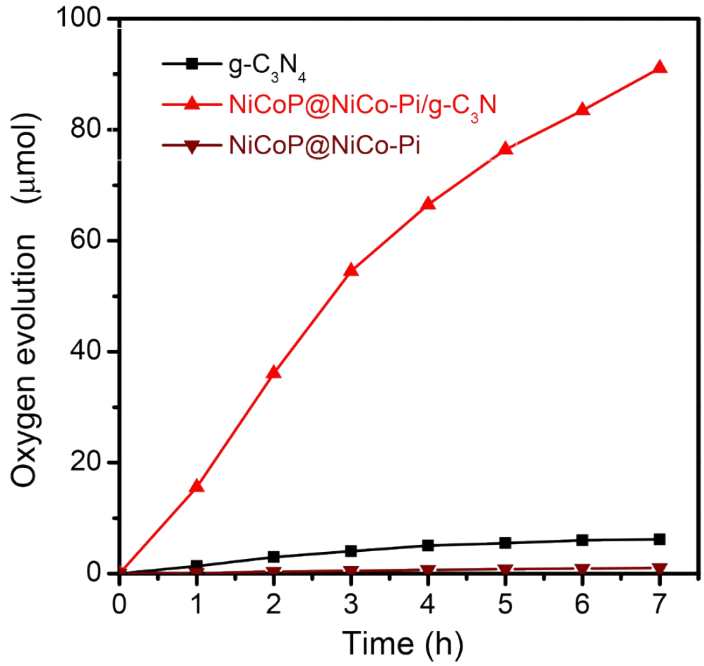

Fig. S9 Time courses of oxygen evolution over g-C_3N_4, NiCoP@NiCo-Pi, and NiCoP@NiCo-Pi/g-C_3N_4. Reaction conditions: 50 mg of g-C_3N_4 and NiCoP@NiCo-Pi/g-C_3N_4, 0.5 mg of NiCoP@NiCo-Pi (the same amount equal to NiCoP@NiCo-Pi in 50 mg of NiCoP@NiCo-Pi/g-C_3N_4), 80 mL of 0.02 M $AgNO_3$ aqueous solution containing 0.2 g of La_2O_3 as a pH buffer agent, 300 W Xe lamp.

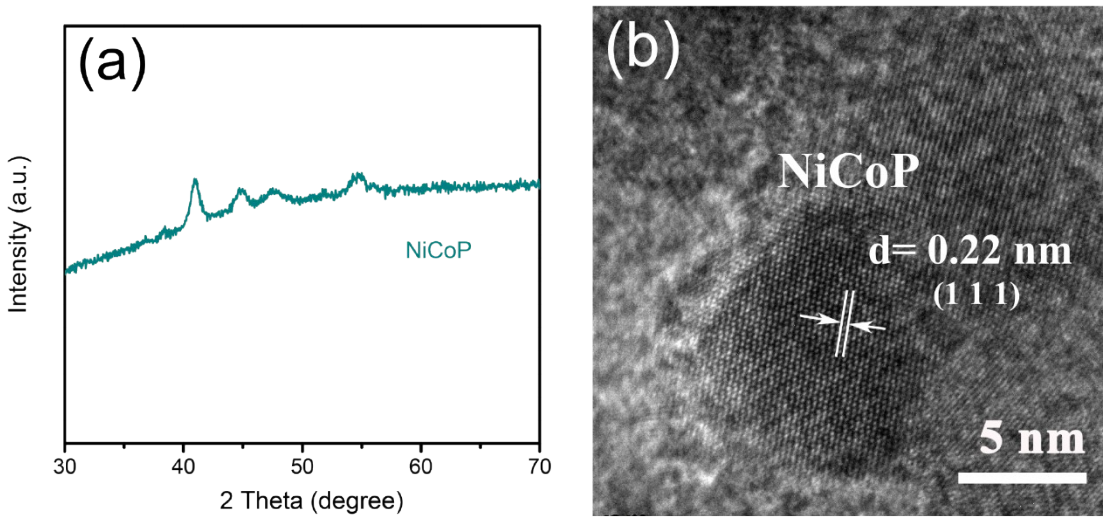

Fig. S10 (a) XRD pattern and (b) TEM image of NiCoP particles.

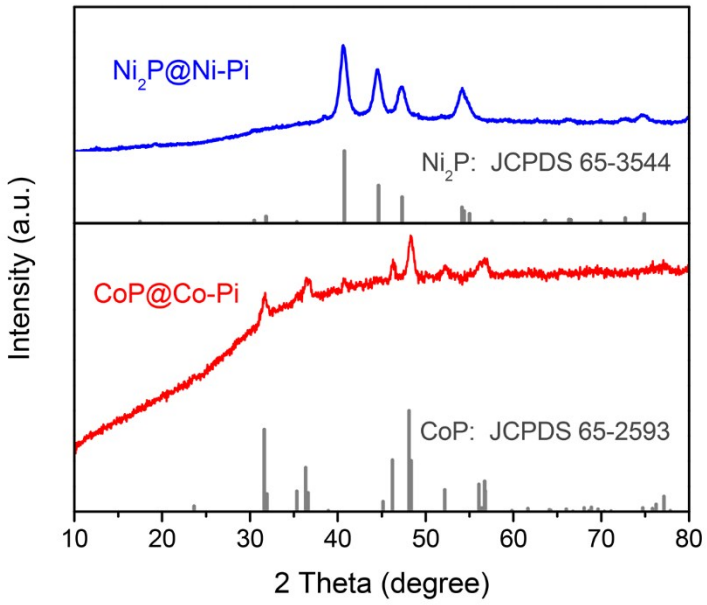

Fig. S11 XRD patterns of Ni_2P@Ni-Pi and CoP@Co-Pi samples.

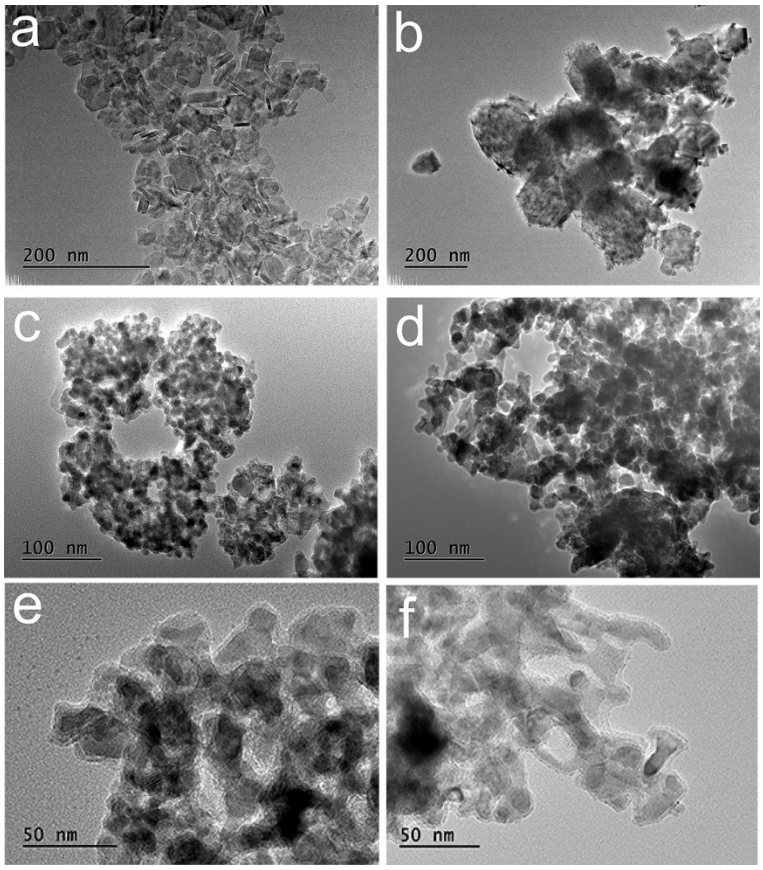

Fig. S12 TEM images of (a) $Ni(OH)_2$ precursors, (b) $Co(OH)_2$ precursors, (c) Ni_2P@Ni-Pi nanoparticles, and (d) CoP@Co-Pi nanoparticles. (e, f) HRTEM images of Ni_2P@Ni-Pi and CoP@Co-Pi core/shell nanoparticles.

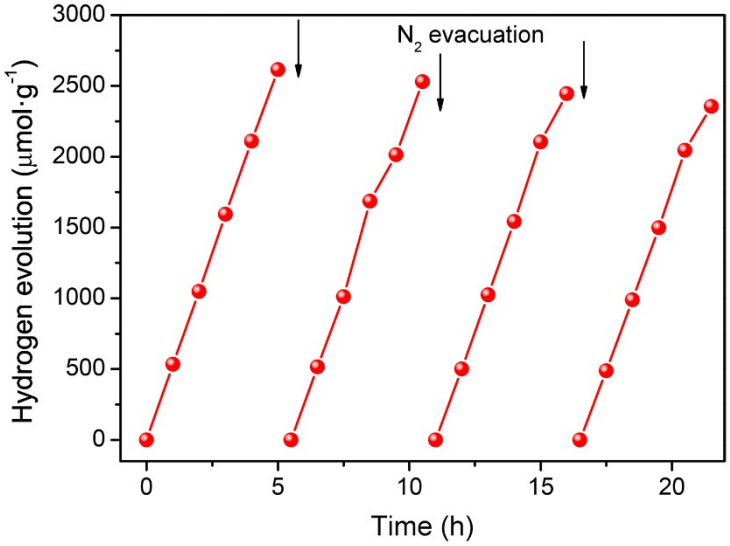

Fig. S13 Long-time photocatalytic hydrogen evolution test of NiCoP@NiCo-Pi/g-C_3N_4. Reaction conditions: 50 mg of photocatalysts, 80 mL of aqueous solution containing 10 vol% TEOA, 300 W Xe lamp equipped with a cutoff filter ($\lambda \geq 420$ nm).

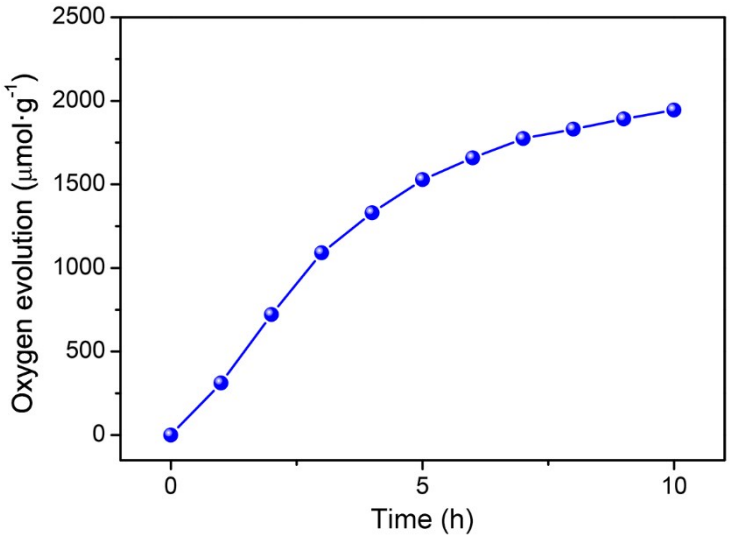

Fig. S14 Long-time photocatalytic oxygen evolution test of NiCoP@NiCo-Pi/g-C_3N_4. Reaction conditions: 50 mg of photocatalysts, 80 mL of 0.02 M $AgNO_3$ aqueous solution containing 0.2 g of La_2O_3 as a pH buffer agent, 300 W Xe lamp.

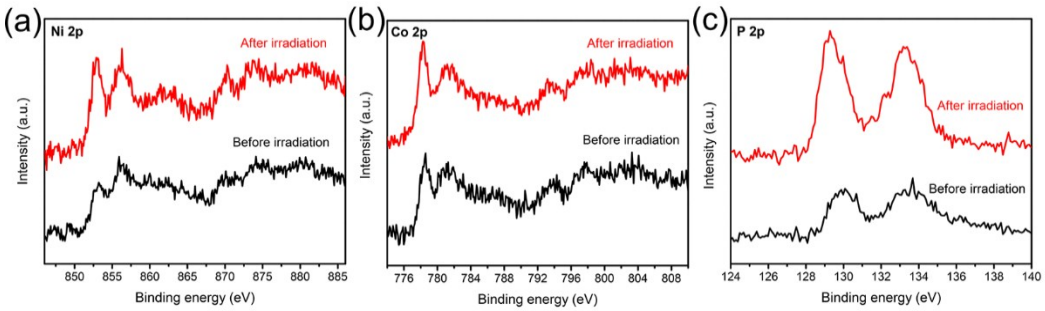

Fig. S15 XPS spectra of (a) Ni 2p, (b) Co 2p, and (c) P 2p in NiCoP@NiCo-Pi/g-C_3N_4 before and after photocatalytic reaction.

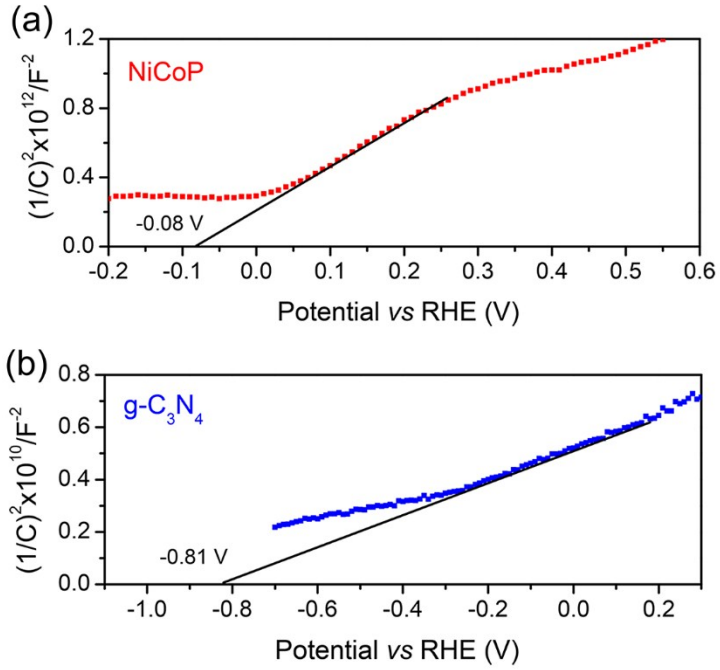

Fig. S16 Mott-Schottky plots of NiCoP and g-C_3N_4 in 0.5 M Na_2SO_4 solution.

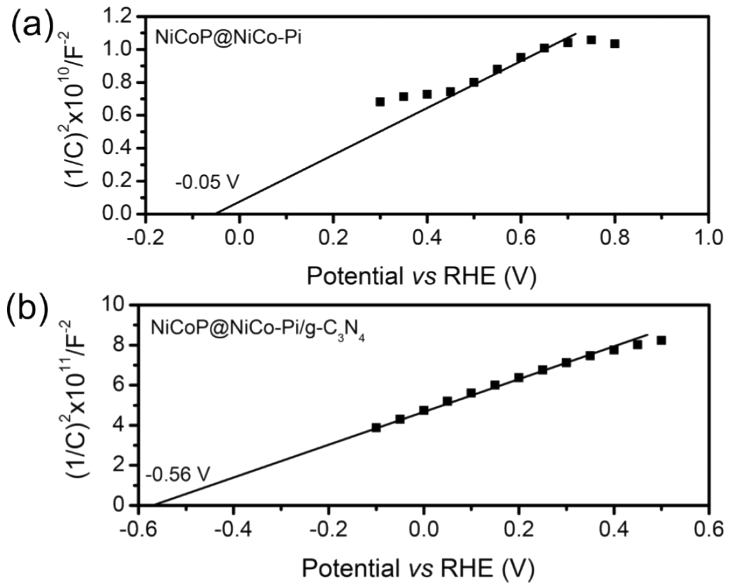

Fig. S17 Mott-Schottky plots of NiCoP@NiCo-Pi and NiCoP@NiCo-Pi/g-C_3N_4 in 0.5 M Na_2SO_4 solution.