

## **K<sub>2</sub>HPO<sub>4</sub>-mediated Photocatalytic H<sub>2</sub> Production over NiCoP/RP Heterojunction**

Junfeng Huang<sup>1</sup>, Chenyang Li<sup>1</sup>, Xiaoyun Hu<sup>2</sup>, Jun Fan<sup>1</sup>, Binran Zhao<sup>1\*</sup> and Enzhou Liu<sup>1\*</sup>

<sup>1</sup>School of Chemical Engineering/Xi'an Key Laboratory of Special Energy Materials, Northwest University, Xi'an 710069, China

<sup>2</sup>School of Physics, Northwest University, Xi'an 710069, China

Corresponding authors. Emails: liuenzhou@nwu.edu.cn (Enzhou Liu) and zhaobr@nwu.edu.cn (Binran Zhao)

## n MATERIALS

Phosphorus red (RP, 99.0%) was purchased from Tianjin Damao Chemical Reagent Factory. Polyvinylpyrrolidone K.30 ((C<sub>6</sub>H<sub>9</sub>NO)<sub>n</sub>, 98.0%) was purchased from Shanghai Lanji Biological Reagent Co., Ltd. Cobalt chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O 98.0%) and cetyltrimethyl ammonium bromide (C<sub>19</sub>H<sub>42</sub>BrN 99.0%) were purchased from Tianjin kemio Chemical Reagent Co., Ltd. Nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O 98.0%) was purchased from Tianjin Shengao Chemical Reagent Co., Ltd. Sodium dodecyl benzene sulfonate (C<sub>18</sub>H<sub>29</sub>NaO<sub>3</sub>S 96.0%) was purchased from Tianjin Fuchen Chemical Reagent Factory. Ethylene glycol ((CH<sub>2</sub>OH)<sub>2</sub> 99.0%) and ethanol (C<sub>2</sub>H<sub>5</sub>OH 99.0%) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. And all chemicals are analytical reagent.

## n CHARACTERIZATION

A series of characterization methods, including scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), ultraviolet-visible-near-infrared diffuse reflectance spectroscopy (UV/VIS/NIR DRS), photoluminescence spectroscopy (PL), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Brunner-Emmet-Teller (BET) measurements, were conducted to analyze the morphology, crystalline structure, and optical properties of the different as-prepared samples in detail<sup>[1]</sup>.

To prepare the working electrodes, 3.0 mg catalyst was dispersed in 5 mL deionized water and then sonicated for 2 h. Subsequently, 1 mL of the solution was dropped homogeneously on a 2cm × 3cm fluoride-doped tin oxide (FTO) glass. After drying at ambient temperature, the FTO working electrodes were used without further processing. Transient photocurrent (i-t), Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were performed with the electrochemical workstation (CHI660E, Chenhua in Shanghai) in 0.5 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> electrolytes by employing Hg/HgO electrode as the reference electrode and Pt wire as the counter electrode. The bias of 0.5 V was used for the photocurrent tests. LSV was determined from 0 to 2 V at a scan rate of 10 mV/s<sup>[2]</sup>.

## n PHOTOCATALYTIC ACTIVITY MEASUREMENTS

The photocatalytic H<sub>2</sub> evolution experiments were conducted in a 250 mL Pyrex flask reactor at a constant temperature (30 °C). Specifically, 30 mg of sample was added to a reactor containing 100 mL of a mixed solution (0.35 M Na<sub>2</sub>S/0.25 M Na<sub>2</sub>SO<sub>3</sub>). The reaction was performed using a 300 W Xe lamp. The gas in the system was completely evacuated before the reaction until the vacuum meters stabilized. The lamp was placed 15 cm from the reactor. The amount of H<sub>2</sub> was determined through the gas chromatography every 1 h. The temperature of the vaporizer, column and thermal conductivity detector were 80, 100 and 120 °C, respectively. The carrier gas was N<sub>2</sub> with a flow rate of 30 mL/min and the separation column is 5 A molecular sieve<sup>[3]</sup>.

## n RECYCLE EXPERIMENTS

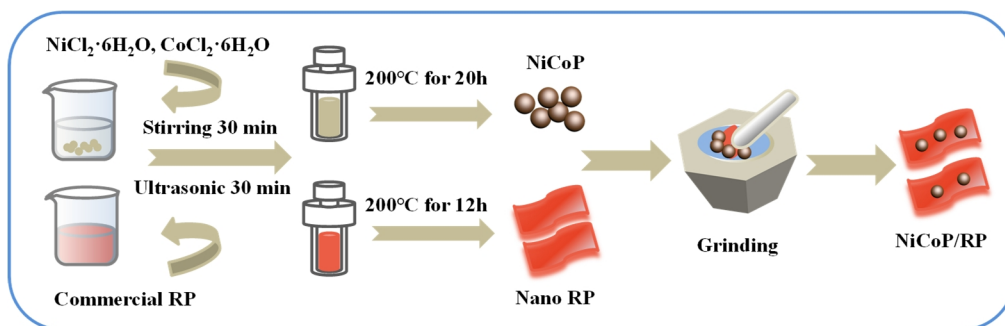
Photocatalytic H<sub>2</sub> evolution cyclic experiments were conducted in 20 v% TEOA aqueous solution as a hole sacrificial agent with 30 mg of prepared catalysts under a 300 W Xe lamp. The H<sub>2</sub> evolution was measured at the interval of 1 h for continuous 3 h via gas chromatography. Afterwards, the reaction system was connected to the atmosphere to remove obtained H<sub>2</sub> and a new round of photocatalytic experiment with the same sample was carried out in sealed vacuum environment.

## n PHOTOCATALYTIC MECHANISM SUPPLEMENT

Thank you for your valuable advice. To investigate the band structure of RP nanosheets, Tauc plots are obtained by converting the UV-vis diffuse reflectance spectra using the formula  $(ah\nu)^n = A(h\nu - E_g)$ , where  $a$  is absorption coefficient,  $h$  is Planck's constant,  $\nu$  is light frequency,  $E_g$  is band gap,  $A$  is a constant, and  $n$  is 2. As presented in Fig. 1a, the optical band gap ( $E_g$ ) is calculated to be 1.78 eV (vs RHE.). Meanwhile, the valence band minimum ( $E_{VB}$ ) is calculated to be 1.4 V (vs RHE.) by XPS. Consequently, the conduction band through  $E_{CB} = E_g - E_{VB}$  is calculated to be -0.38 V (vs RHE), which is similar with the previous reports<sup>[4]</sup>.

**Table S1.** Comparison of Hydrogen Evolution Performance of NiCoP in Recent Years

Materials	Preparation methods	Sacrificial agent	Experimental result	Ref.
NiCoP/g-C <sub>3</sub> N <sub>4</sub>	one-pot synthesis method	TEOA	The H <sub>2</sub> production rate can reach 1643 mmol·h <sup>-1</sup> ·g <sup>-1</sup> over NiCoP/g-C <sub>3</sub> N <sub>4</sub> .	[1]
ZnCdS-NiCoP	physical mixing method	lactic acid solution	The H <sub>2</sub> evolution of the composite ZnCdS-NiCoP with the highest H <sub>2</sub> evolution activity was 789.7 μmol in 5 h.	[2]
NiCoP@CdS	hydrothermal route and phosphidation process	formic acid	NiCoP@CdS nanorods reached 354 mmol·mg <sup>-1</sup> ·h <sup>-1</sup> under visible light irradiation.	[3]
MMT/g-C <sub>3</sub> N <sub>4</sub> /NiCoP	phosphating method	TEOA	The highest H <sub>2</sub> -evolution rate from water splitting under visible-light irradiation observed over MMT/g-C <sub>3</sub> N <sub>4</sub> /NiCoP was 12.50 mmol·g <sup>-1</sup> ·h <sup>-1</sup> .	[4]
NiCoP/C <sub>3</sub> N <sub>4</sub>	controllable alcoholothermal process	methanol	The highest photocatalytic H <sub>2</sub> evolution rate of composite NiCoP/C <sub>3</sub> N <sub>4</sub> was 159 μmol·g <sup>-1</sup> ·h <sup>-1</sup> .	[5]
NiCoP/Mn <sub>0.3</sub> Cd <sub>0.7</sub> S	calcination method	isopropanol	The NCP/MCS composite displays the optimum photocatalytic H <sub>2</sub> evolution rate of 118.5 mmol·g <sup>-1</sup> ·h <sup>-1</sup> under visible-light irradiation.	[6]
NiCoP/g-C <sub>3</sub> N <sub>4</sub>	annealed at 350 °C gradually in Ar	TEOA	The best photocatalytic performance of NiCoP/ g-C <sub>3</sub> N <sub>4</sub> catalyst is 1067.11 μmol·g <sup>-1</sup> ·h <sup>-1</sup> .	[7]
NiCoP/RP	physical grinding process.	TEOA	The optimum H <sub>2</sub> production rate is 1535.6 μmol·g <sup>-1</sup> ·h <sup>-1</sup> .	This work



**Figure S1.** Schematic diagram of preparation NiCoP/RP composites.

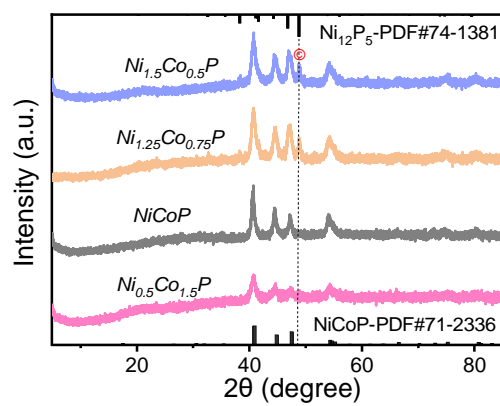
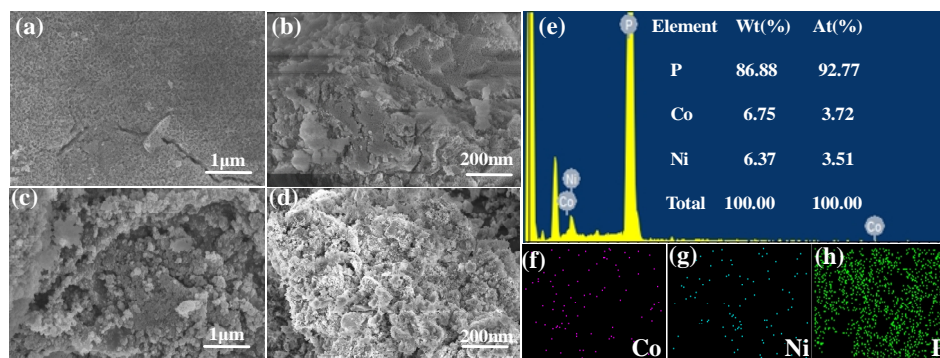
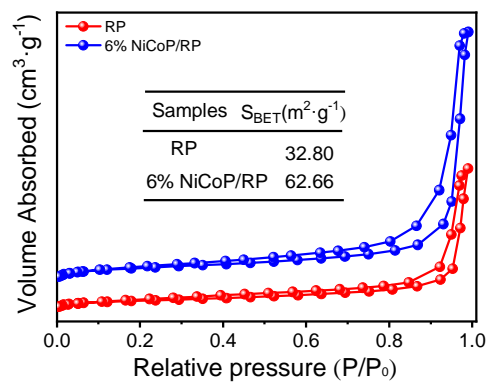


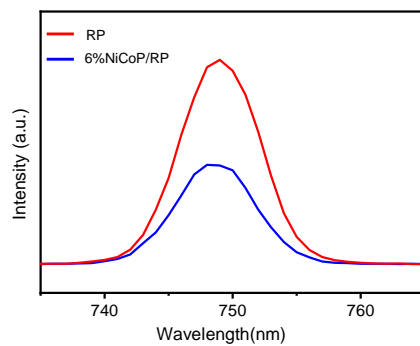
Figure S2. XRD patterns of  $\text{Ni}_x\text{Co}_{2-x}\text{P}$ .



**Figure S3.** SEM images of (a–b) RP, (c–d) 6% NiCoP/RP, (e–h) the EDS spectra and elemental mapping of 6% NiCoP/RP.

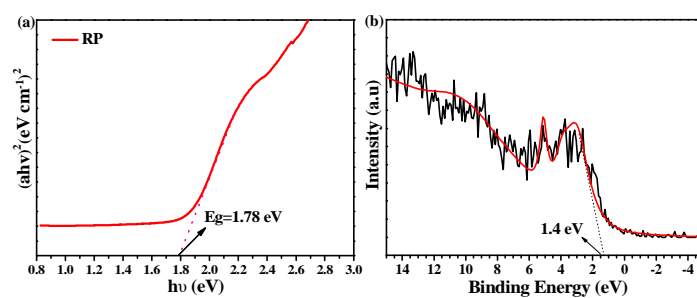


**Figure S4.** N<sub>2</sub> adsorption-desorption isotherm plots and BET of the samples.



**Figure S5.** PL spectra of the samples.





**Figure S6.** (a) Tauc plots for the band gap of RP. (b) Valence band of RP.

## n ACKNOWLEDGEMENTS

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