

K₂HPO₄-mediated Photocatalytic H₂ Production over NiCoP/RP Heterojunction

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n MATERIALS

Phosphorus red (RP, 99.0%) was purchased from Tianjin Damao Chemical Reagent Factory. Polyvinylpyrrolidone K.30 ((C₆H₉NO)_n, 98.0%) was purchased from Shanghai Lanji Biological Reagent Co., Ltd. Cobalt chloride hexahydrate (CoCl₂·6H₂O 98.0%) and cetyltrimethyl ammonium bromide (C₁₉H₄₂BrN 99.0%) were purchased from Tianjin kemio Chemical Reagent Co., Ltd. Nickel chloride hexahydrate (NiCl₂·6H₂O 98.0%) was purchased from Tianjin Shengao Chemical Reagent Co., Ltd. Sodium dodecyl benzene sulfonate (C₁₈H₂₉NaO₃S 96.0%) was purchased from Tianjin Fuchen Chemical Reagent Factory. Ethylene glycol ((CH₂OH)₂ 99.0%) and ethanol (C₂H₅OH 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^[1].

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⁻¹ Na₂SO₄ 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^[2].

n PHOTOCATALYTIC ACTIVITY MEASUREMENTS

The photocatalytic H₂ 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 Na₂S/0.25 M Na₂SO₃). 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 H₂ 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 N₂ with a flow rate of 30 mL/min and the separation column is 5 A molecular sieve^[3].

n RECYCLE EXPERIMENTS

Photocatalytic H₂ 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 H₂ 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 H₂ 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, ν 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^[4].

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

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

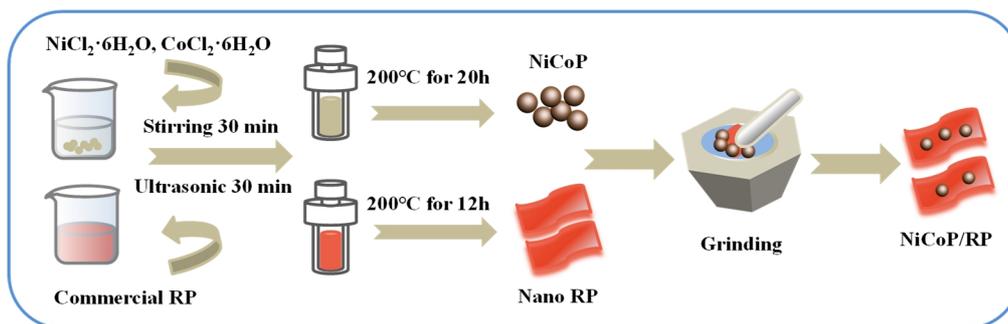


Figure S1. Schematic diagram of preparation NiCoP/RP composites.

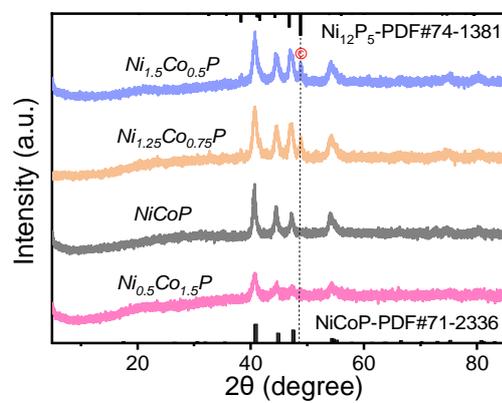


Figure S2. XRD patterns of $Ni_xCo_{2-x}P$.

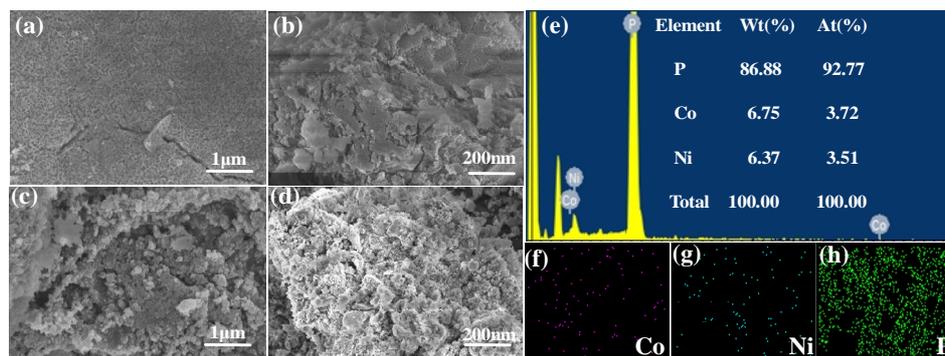


Figure S3. SEM images of (a–b) RP, (c–d) 6% NiCoP/RP, (e–h) the EDS spectra and elemental mapping of 6% NiCoP/RP.

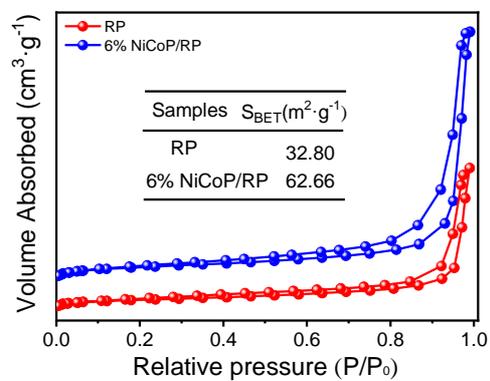


Figure S4. N₂ adsorption-desorption isotherm plots and BET of the samples.

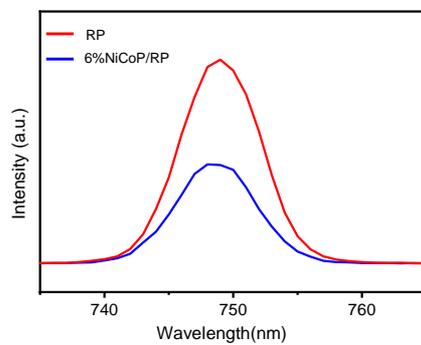


Figure S5. PL spectra of the samples.

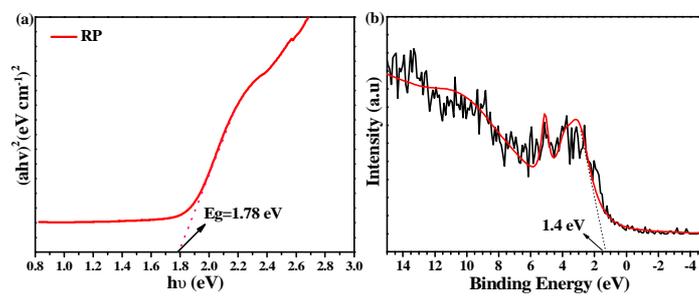


Figure S6. (a) Tauc plots for the band gap of RP. (b) Valence band of RP.

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