# **Supporting Information**

# Engineering NiCoP nanosheet/ZnSe nanoparticle heterostructures

# for enhanced photocatalytic hydrogen production

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# Experimental

#### Preparation of bimetallic phosphides nanosheets

NiCo LDH (the precursors of NiCoP) were synthesized by common methods at 80 °C for 12 h.<sup>1</sup> The as-prepared NiCo LDH formed an uniformly nanosheets morphology. NiCoP nanosheets was obtained through the phosphating treatment for NiCo LDH by NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O (in mass ratio 1:10). Specifically, NiCo LDH was heated at 320 °C for 1 h with a heating rate of 2 °C/min under an argon atmosphere. Similarly, Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub> were synthesized without adding Co<sup>2+</sup> and Ni<sup>2+</sup> in the reaction, respectively, phosphating under the same conditions to get Ni<sub>2</sub>P and CoP-Co<sub>2</sub>P.

#### **Preparation of ZnSe nanoparticles**

ZnSe nanoparticles were synthesized through a simple solution-phase approach. In a typical process, zinc chloride (ZnCl<sub>2</sub>) (3.5 mmol) and selenlum (Se) powder (3.5 mmol) were put into 18 ml of oleylamine in a three-neck flask. Then the mixture was kept at a temperature of 300°C for 1 h under an argon atmosphere. After the precipitate was cooled down to room temperature and washed by ethanol and n-hexane for 3 times, the product was collected by drying 6 h under a vacuum at 60°C. Afterward, the as-prepared nanoparticles were treated using toluene and 3-mercaptopropionic acid (MPA) to exchange the surface oleylamine, according to previous reports.<sup>2,3</sup>

#### Preparation of NiCoP/ZnSe nanoparticles

In a typical procedure, at room temperature, a certain mass ratio of NiCoP and ZnSe was added into ethanol, and then ultrasonically treated 10 min until the mixture was uniformly dispersed. Subsequently, it was stirred at 1000 r/min for 12 h and vacuum-dried for 6 h to obtain NiCoP/ZnSe nanocomposite. X% refers to the loading amount of NiCoP by weight. Ni<sub>2</sub>P/ZnSe and CoP-Co<sub>2</sub>P/ZnSe were prepared the same way.

### Characterization

The crystalline phases were studied by an X-ray diffractometer (XRD, Smartlab-3KW (Rigaku Ltd., Japan)). The SEM images were recorded on a scanning electron microscope (SEM, Hitachi SU8220). The TEM images were obtained from a Titan G260-300 transmission electron microscopy. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were obtained from a Lambda-750 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were identified by a Thermo Fisher Scientific K-Alpha system. Time-resolved photoluminescence (TRPL) spectra were derived from an FL3C-111 (HORIBA Instruments Inc.).

#### Photocatalytic H<sub>2</sub> evolution tests

The H<sub>2</sub> evolution measurements of the photocatalyst were performed on a sealed Pyrex flask reaction system. In a typical experiment, 30 mg of the photocatalyst was dispersed in 60 mL of 0.35 M Na<sub>2</sub>S/0.25 M Na<sub>2</sub>SO<sub>3</sub> aqueous solution. Then the mixture was degassed for 30 min by a vacuum pump to remove the dissolved gas. After that, the reactor was vertically irradiated by a 300 W Xe lamp equipped with a 420 nm UV cut-off filter. The generated H<sub>2</sub> was detected by online gas chromatography (GC-7920, N<sub>2</sub> as the carrier gas, TCD). The 3% Pt/ZnSe sample was prepared by an in situ photodeposition approach, using H<sub>2</sub>PtCl<sub>6</sub>·xH<sub>2</sub>O as the precursor. For the photocatalytic H<sub>2</sub> evolution cycling experiments, the system was evacuated to remove residual gas before the cycling tests. The apparent quantum yield (AQY) was calculated using the following equation:

$$AQY (\%) = \frac{number \ of \ evolved \ H_2 \ molecules \ \times \ 2}{number \ of \ incident \ photons} \times 100\%$$

### Photoelectrochemical measurements

The photoelectrochemical (PEC) measurements were conducted on a VSP-300 (Biologic)

electrochemical workstation. The working electrodes were prepared as follows: the photocatalyst (5 mg) was dissolved in ethanol (0.5 mL) containing Nafion (10  $\mu$ L) and ultrasonicated for three hours. Then the ink was deposited on a 2.0 cm<sup>2</sup> ITO glass. The Ag/AgCl (3.5 M KCl) electrode, Pt sheet, and 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution served as the reference electrode, counter electrode, and electrolyte, respectively. The photocurrent responses were tested under several visible-light on-off cycles at an applied potential of 0.5 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) was measured over a frequency range from  $10^{-1}$  to  $10^5$  Hz. Mott-Schottky plots were determined at frequencies of 500, 1000, and 1500 Hz.

#### **Density functional theory calculations**

All Spin-polarization density functional theory (DFT) calculations were employed through the first-principles<sup>4,5</sup> using the Perdew-Burke-Ernzerhof (PBE)<sup>6</sup> formulation within the generalized gradient approximation (GGA). The projected augmented wave (PAW) potentials<sup>7,8</sup> are chosen to describe the ionic cores, and a plane wave basis set with a kinetic energy cutoff of 450 eV was used to account for the valence electrons. Van der Waals interactions have been considered using the DFT-D3 method of Grimme.<sup>9,10</sup> The electronic energy and geometry optimization were considered self-consistent and convergent when the energy change was smaller than  $10^{-5}$  eV and 0.02 eV Å<sup>-1</sup>, respectively. The Brillouin zone with a 2×2×1 Gamma-centered grid was used during the relaxation. The 13 Å vacuum layer was normally added to the surface to eliminate the artificial interactions between periodic images. Spin-polarized calculations were executed for this calculation.

For each elementary step, the Gibbs reaction free energy  $\Delta$  G is defined as the difference between free energies of the initial and final states and is given by the following expression:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S$$

where  $\Delta E$  is the reaction energy of reactant and product molecules adsorbed on the catalyst surface, obtained from DFT calculations;  $\Delta ZPE$  and  $\Delta S$  are the change in zero-point energies and entropy because of the reaction.



Fig. S1. (a) XRD pattern and (b) SEM image of NiCo(OH)<sub>2</sub>/NiCo LDH.



Fig. S2. (a) XRD patterns of Ni<sub>2</sub>P/ZnSe composites.



Fig. S3. (a) XRD patterns of CoP-Co<sub>2</sub>P/ZnSe composites.



Fig. S4. (a) XRD patterns of NiCoP/ZnSe composites.



**Fig. S5.** (a) Tauc plots of ZnSe, Ni<sub>2</sub>P/ZnSe, CoP-Co<sub>2</sub>P/ZnSe, and NiCoP/ZnSe. (b) Tauc plots of Ni<sub>2</sub>P, CoP-Co<sub>2</sub>P, and NiCoP. The corresponding Tauc plots were transformed by Kubelka-Munk.

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Fig. S6. UV-vis spectra of Ni<sub>2</sub>P/ZnSe.



Fig. S7. (a) UV-vis spectra of CoP-Co<sub>2</sub>P/ZnSe.



Fig. S8. UV-vis spectra of NiCoP/ZnSe.



**Fig. S9.** The high-resolution XPS spectra of (a) Zn 2p and (b) Se 3d of ZnSe, Ni<sub>2</sub>P/ZnSe, CoP-Co<sub>2</sub>P/ZnSe, and NiCoP/ZnSe.



**Fig. S10.** The high-resolution XPS spectra of (a) Ni 2p, (b) Co 2p, and (b) P 2p of ZnSe, Ni<sub>2</sub>P/ZnSe, CoP-Co<sub>2</sub>P/ZnSe, and NiCoP/ZnSe.



Fig. S11. (a) SEM and (b) TEM of  $Ni_2P/ZnSe$ .



**Fig. S12.** (a) SEM, (b) TEM, (c) HRTEM, (d) HADDF image and (e-h) corresponding element of CoP-Co<sub>2</sub>P/ZnSe.



Fig. S13. (a) SEM, (b-c) TEM, and (d) HRTEM of NiCoP.



**Fig. S14.** Particle size distribution of ZnSe nanoparticles in (a) pure ZnSe and (b) NiCoP/ZnSe.



**Fig. S15.** Photocatalytic H<sub>2</sub> production rate of different contents of (a) Ni<sub>2</sub>P in Ni<sub>2</sub>P/ZnSe composites, (b) CoP-Co<sub>2</sub>P in CoP-Co<sub>2</sub>P/ZnSe composites, and (c) NiCoP in NiCoP/ZnSe composites.



Fig. S16. Average H<sub>2</sub> evolution rate curve.



Fig. S17. XRD pattern of (a) Ni<sub>2</sub>P/ZnSe, (b) CoP-Co<sub>2</sub>P/ZnSe, and (c) NiCoP/ZnSe before and after 18 h irradiation.



**Fig. S18.** The high-resolution XPS spectra of (a) Zn 2p and (b) Se 3d of 18% NiCoP/ZnSe after 18 h irradiation.



**Fig. S19.** The high-resolution XPS spectra of (a) Co 2p, (b) Ni 2p, and (c) P 2p of 18% NiCoP/ZnSe after 18 h irradiation.



**Fig. S20.** (a) TEM, (b) HRTEM, (c) HADDF images and (e-h) corresponding element of NiCoP/ZnSe after 18 h irradiation.



**Fig. S21.** (a) The photocurrent responses and (b) EIS Nyquist plots of ZnSe, 8% Ni<sub>2</sub>P/ZnSe, 18% CoP-Co<sub>2</sub>P/ZnSe and 18% NiCoP/ZnSe.



Fig. S22. (a) PL and (b) TRPL spectra of ZnSe and 18% NiCoP/ZnSe composites.



Reaction coordinates Fig. S23. Gibbs free energy.



Fig. S24. Mott-Schottky plots of (a) ZnSe, (b) NiCoP and (c) 18% NiCoP/ZnSe.

Photo- catalyst	Additives	Light source	Scavenger	Activity (µmol·h <sup>-1</sup> ·g <sup>-1</sup> )	Refs
ZnSe	Cu <sub>2-x</sub> Se	420 W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	1846	11
		(λ> 420 nm)			
ZnSe	TiaCa	300 W Xe lamp	H <sub>2</sub> PtCl <sub>6</sub>		
	11302		(1 mg/mL)	765	12
	MXene		Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>		
ZnSe	ZnO	300 W Xe lamp	PET	3081	13
		(λ> 420 nm)			
ZnSe	CdS	LED lamp	/	$145.04 \pm 4.15$	14
		(λ>460 nm)			
ZnSe	Co <sub>3</sub> O <sub>4</sub>	300 W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	4197	15
ZnSe	ZnIn <sub>2</sub> S <sub>4</sub>	300W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	1297	16
		(λ> 420 nm)			
ZnSe	Cu <sub>0.08</sub> Zn <sub>0.92</sub> S	300W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	3587	17
		(320-780 nm)			
ZnSe	Co <sub>9</sub> S <sub>8</sub>	300W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	968	18
		(λ> 420 nm)			
ZnSe	FeSe <sub>2</sub>	300 W Xe lamp	methanol	1228	19
		(λ>420 nm)			
ZnSe	NiCoP	300 W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	4271	This
		(λ> 420 nm)			work

**Table S1.** Photocatalytic  $H_2$  evolution activity of ZnSe-based photocatalysts.

Photocatalyst	Light source	Scavenger	Activity (µmol·h <sup>-1</sup> ·g <sup>-1</sup> )	Refs
$Mn_{0.67}Co_{1.33}P/g-C_3N_4$	300 W Xe lamp	TEOA	2262	20
Mo-Ni <sub>2</sub> p/g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp	TEOA	1352	21
NiFeP/g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp	TEOA	3549	22
g-C <sub>3</sub> N <sub>4</sub> -NiCoP <sub>2</sub> -PC	300 W Xe lamp	TEOA	290	23
NiCoP/ ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp	TEOA	3840	24
Ni <sub>2</sub> P/N-TFMs	300W Xe lamp	Methanol	368	25
MoP-Cu <sub>3</sub> P	300W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	855	26
B-Cu <sub>3</sub> P	300W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	1040	27
CoP/CdS/rGO	500 W Xe lamp	TEOA	1104	28
Co <sub>2</sub> P/BP	300W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	202	29
7	300 W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	4271	This
Luse	$(\lambda > 420 \text{ nm})$			work

Table S2. Photocatalytic  $H_2$  evolution activity of transition metal phosphides.

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