

Supporting Information

In-situ synthesis of Co₂P decorated red phosphorus nanosheets for efficient photocatalytic H₂ evolution

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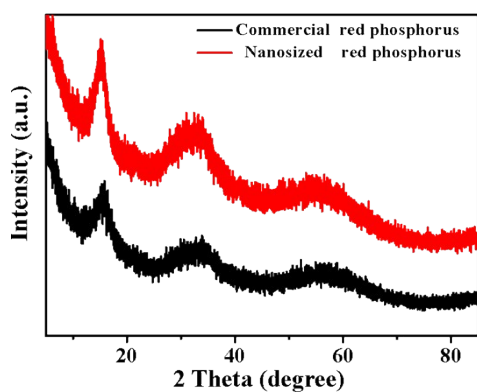


Fig. S1 XRD of different kinds of red phosphorus.

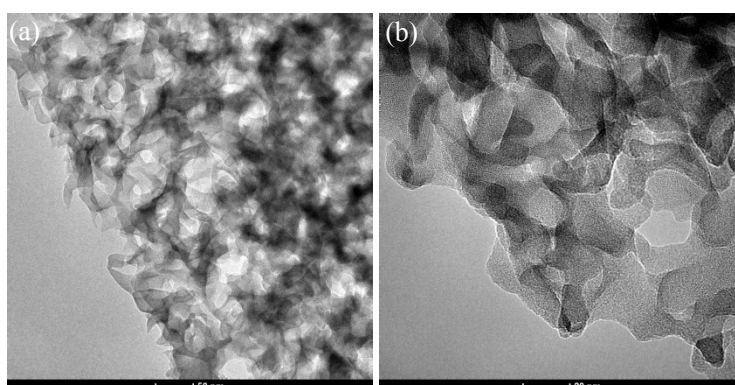


Fig. S2 (a)~(b) Nanostructure of two-dimension honeycomb red phosphorus.

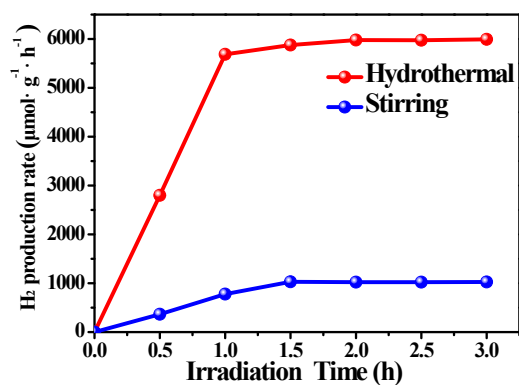


Fig. S3 The rate of photocatalytic H₂ evolution of 2% Co₂P/RP synthesized by different methods.

Characterization techniques

The crystalline structures were identified by a Shimadzu XRD-6000 powder diffractometer. Morphological and structural of the samples were investigated using scanning electron microscopy (SEM, Carl Zeiss SIGMA) and transmission electron microscopy (TEM, Tecnai G2 F20 STWIN). UV-vis diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-3600 UV/vis/NIR spectrophotometer using BaSO₄ as reference. Photoluminescence (PL) spectra were

recorded on a Hitachi-F 7000 fluorescence spectrophotometer. The specific surface areas were surveyed by N₂ adsorption/desorption in the instrument (Quantachrome, SI). X-ray photoelectron spectroscopy (XPS) were carried out using a Kratos AXIS NOVA spectrometer.

Photocatalytic hydrogen production

Photocatalytic hydrogen production was carried out in a top-irradiated reaction vessel connected to an on-line analysis system (Beijing Perfect Light Technology Co. Ltd., China, LabSobar-IIIAG). A 300W Xe lamp equipped was employed as the light source. In a typical process, 30 mg of photocatalyst powder was dispersed in the reactor with 100 mL of aqueous solution, containing 0.35 mol L⁻¹ Na₂SO₃ and 0.15 mol L⁻¹ Na₂S as the sacrificial agent. The temperature of the reaction solution was carefully maintained at 6 °C by a low constant temperature bath (Shanghai hengpin Technology Co. Ltd., China, DC-0506). Prior to irradiation, the reaction system was evacuated for 30 min to eliminate dissolved oxygen. The produced hydrogen was in-situ obtained every 30 min using an online gas chromatograph (GC 7900, Techcomp Shanghai Co. Ltd., China). The photocatalytic hydrogen evolution of Pt/RP was conducted by photo-decomposition. In detail: certain volume of H₂PtCl₆·6H₂O (1 g/L) was added to reaction vessel containing 100 ml sacrificial agent, then 30 mg RP was dispersed the mixed solution followed by irradiation for 3 h. To test the stability of the samples, a cycling experiment was performed in which after 3 hours testing, the vacuum was re-extracted and maintained in the same conditions as at the beginning of the experiment, repeat the above measurement activity. More importantly, the residual H₂ was removed by purging with nitrogen gas for 30 min before starting every new cycle.

Photoelectrochemical analyses

Photoelectrochemical analyses, including transient photocurrent (I-t curve, at 0.5 V potential vs. SCE), electrochemical impedance analysis (EIS, at 0.5 V potential vs. SCE), were conducted on an electrochemical workstation (CHI660E) equipped with a typical three electrode cell under 300W Xenon lamp and bubbling with N₂ before measurement, in which the working electrode, counter electrode and reference electrode were photoanode, Pt, and saturated calomel electrode,

respectively. Typically, the working electrodes were fabricated by dripping the mixed solution directly onto an FTO conductive glass surface and naturally drying at 25 °C; that is, 3 mg of sample was added into 3 mL of mixed solution (the volume ratio of ethanol/water is 1:1) and ultrasonically treated several times. Besides, the electrolyte solution and irradiation area was Na₂SO₄ solution (0.5 mol/L, pH = 7.0) and 0.785 cm², respectively.

Table S1 The photocatalytic systems containing Co₂P as a cocatalyst that have been reported in the literature.

Materials	Preparation method.	Phosphorus source.	Application	Sacrificial agent.	AQY [%]	Results	Ref.
Co ₂ P/CdS	Solvotherma l method.	Tri-n- octylphosphine (TOP) and tri- n- octylphosphine oxide (TOPO).	Photocatalytic water splitting under visible light rradiation.	DL-mandelic acid.	No	The H ₂ production rate can reach up to 19.3 μmol·h ⁻¹ g ⁻¹ after 10 h of LED light irradiation and shows a possibility for the utilization of the holes in VB to synthesize benzoylformic acid from DL- mandelic acid.	¹
O-Co ₂ P/CdS	Simple calcination method.	NaH ₂ PO ₂	Photocatalytic water splitting under visible light rradiation (λ > 420 nm).	Lactic acid	22.17 (420nm)	The optimal adding amount of o-Co ₂ P exhibits the highest H ₂ evolution rate of 184.48 mmol g ⁻¹ h ⁻¹ , which is 1.43 times higher than CdS/Co ₂ P.	²
Co ₂ P/CdS	One-step hydrotherma lmethod	NaH ₂ PO ₂ ·H ₂ O	Photocatalytic water splitting under visible light irradiation (λ ≥ 420 nm)	Na ₂ S and Na ₂ SO ₃ .	23.6 (420nm)	The CdS/Co ₂ P nanocomposites have a mass of active sites and high- efficiency photocatalytic splitting water ability.	³
H-Co ₂ P-CdS	One-step hydrotherma lmethod	Red phosphorus	Photocatalytic water splitting under visible light irradiation (λ ≥ 420 nm)	Lactic acid and K ₂ HPO ₄	13.88 (420nm)	The highest photocatalytic H ₂ evolution rate of 0.356 mmol·h ⁻¹ with a good photocatalytic stability was obtained by the sample of 1.2 mol% H-Co ₂ P-CdS, which is 41 times higher than pure CdS	⁴
M ₂ P (M = Fe, Co, and Ni) hybridized on S-C ₃ N ₄ .	Hydrotherm al and ultrasound assisted methods.	(NH ₄) ₂ HPO ₄	Photocatalytic water splitting under visible light irradiation (λ = 400, 440, 480, or 520 nm).	TEOA	No.	Three as-prepared M ₂ P can serve as an efficient non-noble metal co- catalyst for improving the H ₂ generation on S-C ₃ N ₄ .	⁵
Co ₂ P nanocrystals	Wet- chemical	Tri-n- octylphosphine	Electrocatalysts for H ₂ evolution in both	In 1 M KOH (or 0.5	No	The HB-Co ₂ P NCs act as efficient HER electrocatalysts, and perform	⁶

with 3D morphology	method.	oxide (TOPO).	alkaline and acidic media.	M H ₂ SO ₄)		well in both of alkaline and acidic media.
1D/2D Co ₂ P/g-C ₃ N ₄ heterojunction.	A two-step ultrasonic irradiation method.	Tri-phenylphosphine (TPP).	Photocatalytic water splitting under visible light irradiation ($\lambda > 420$ nm)	TEOA	No	The optimal 3% Co ₂ P/g-C ₃ N ₄ sample reveals the best performance for H ₂ generation, attaining a rate of 53.3 $\mu\text{mol h}^{-1} \text{g}^{-1}$.
Co ₂ P/g-C ₃ N ₄	A simple grinding method.	Na ₂ HPO ₂	Photocatalytic water splitting under visible light irradiation,	TEOA and K ₂ HPO ₄	No	The maximum H ₂ evolution rate of the g-C ₃ N ₄ -Co ₂ P-0.1M K ₂ HPO ₄ photocatalyst was 27.81 $\mu\text{mol h}^{-1}$, furthermore, the optimized contents of 2 wt % Co ₂ P and 0.1 mmol K ₂ HPO ₄ , which was about 561 times higher than that of pure g-C ₃ N ₄ nanosheets.

Table S2 The pore diameter and pore volume of different samples.

composites	pore diameter (nm)	pore volume (cm ³ g ⁻¹)
RP	2.586	0.262
2% Co ₂ P/RP	6.308	0.632

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