

Electronic Supporting Information for

Modulating Charge Transfer Dynamics for $g\text{-C}_3\text{N}_4$ through Dimension and Interface Engineered Transition Metal Phosphide co-catalyst for Efficient Visible-Light Photocatalytic Hydrogen Generation

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Figures

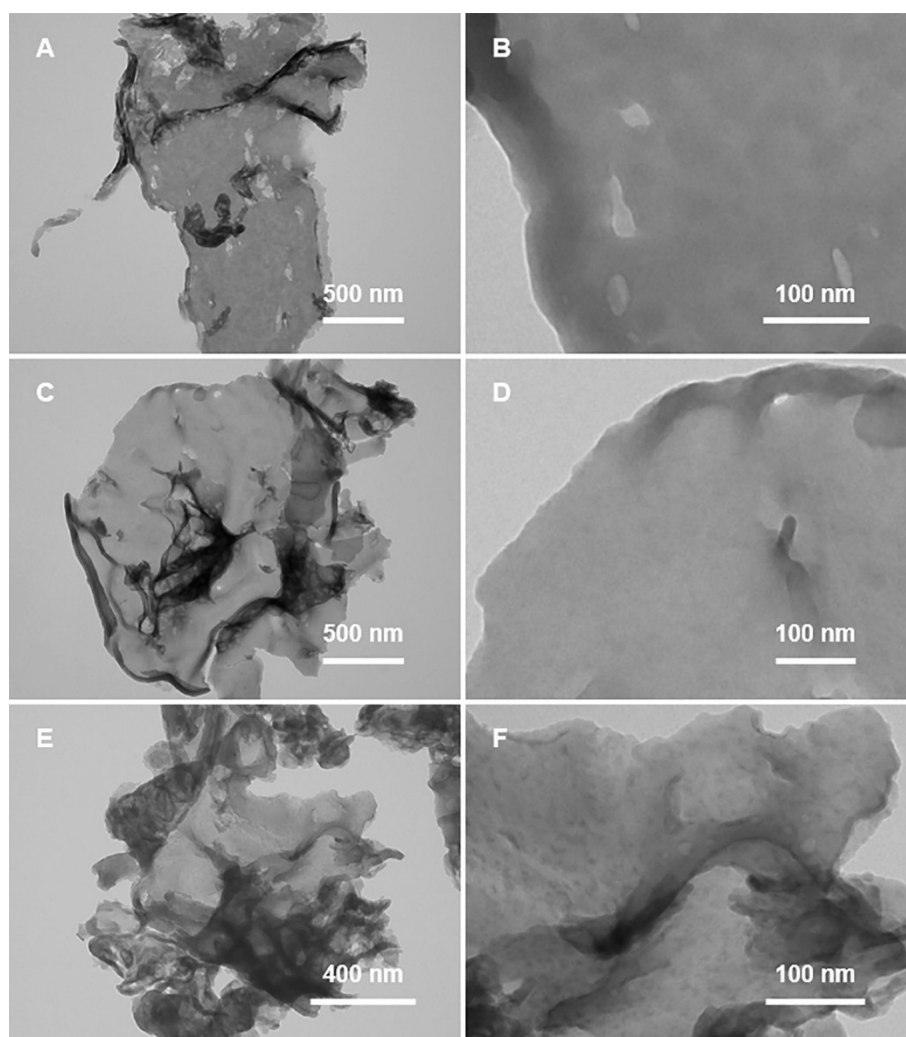


Fig. S1 Low-magnification and high-magnification TEM images of (A, B) pure $g\text{-C}_3\text{N}_4$, (C, D) Co-glycolate/ $g\text{-C}_3\text{N}_4$ composites and (E, F) the 2.5CP/CN sample.

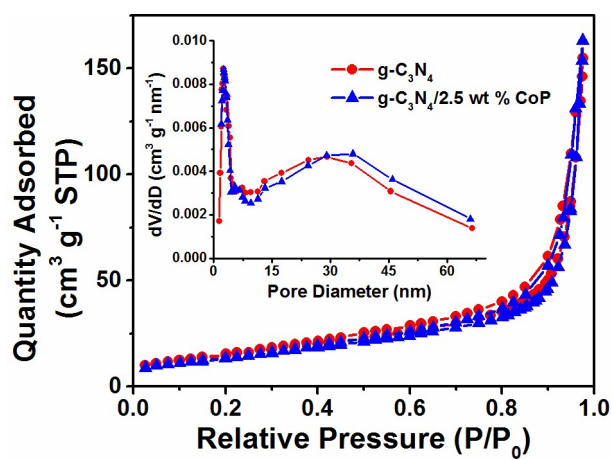


Fig. S2 Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of $g\text{-C}_3\text{N}_4$ and 2.5CP/CN samples.

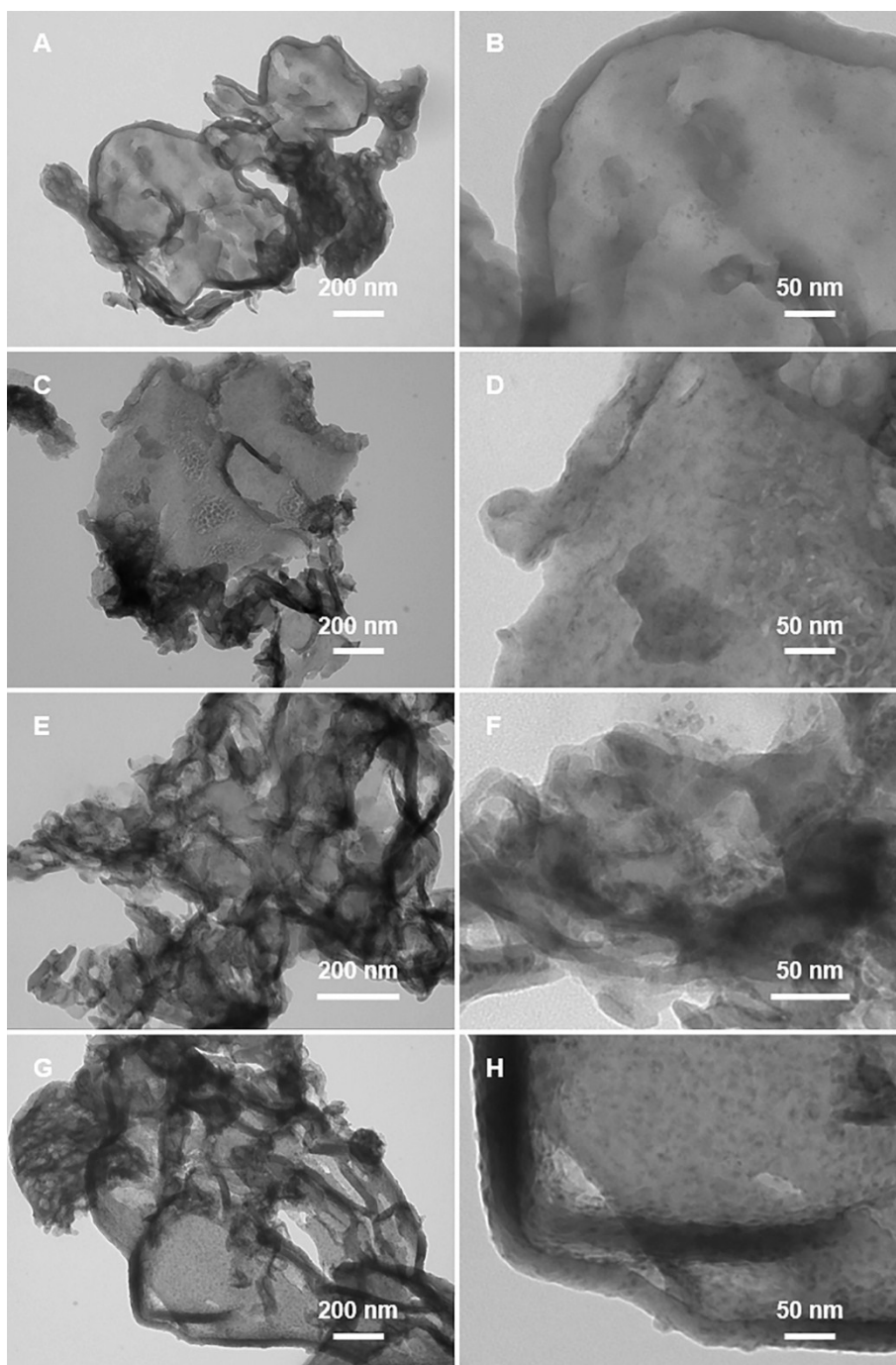


Fig. S3 Low-magnification and high-magnification TEM images of (A, B) 1.25CP/CN, (C, D) 5CP/CN, (E, F) 7.5CP/CN and (G, H) 10CP/CN.

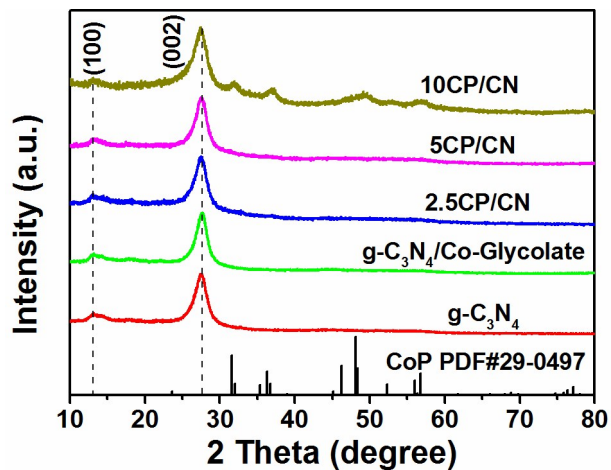


Fig. S4 XRD patterns of the pure $g\text{-C}_3\text{N}_4$, Co-Glycolate/ $g\text{-C}_3\text{N}_4$, CoP/ $g\text{-C}_3\text{N}_4$ composites with variable CoP mass contents (2.5, 5, 10 wt%).

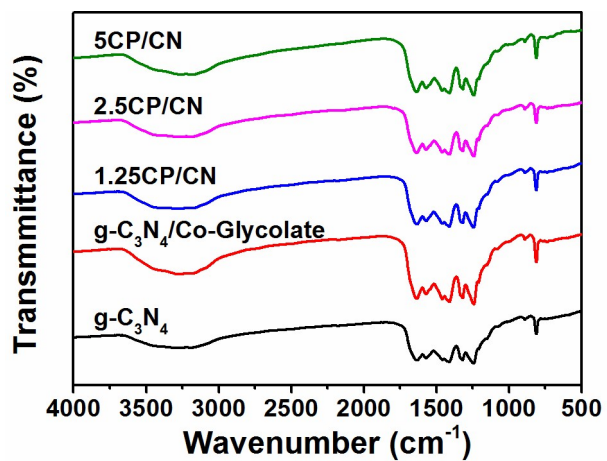


Fig. S5 FT-IR spectra of the pure $g\text{-C}_3\text{N}_4$, Co-Glycolate/ $g\text{-C}_3\text{N}_4$, CoP/ $g\text{-C}_3\text{N}_4$ composites with variable CoP mass contents (1.25, 2.5, 5 wt%).

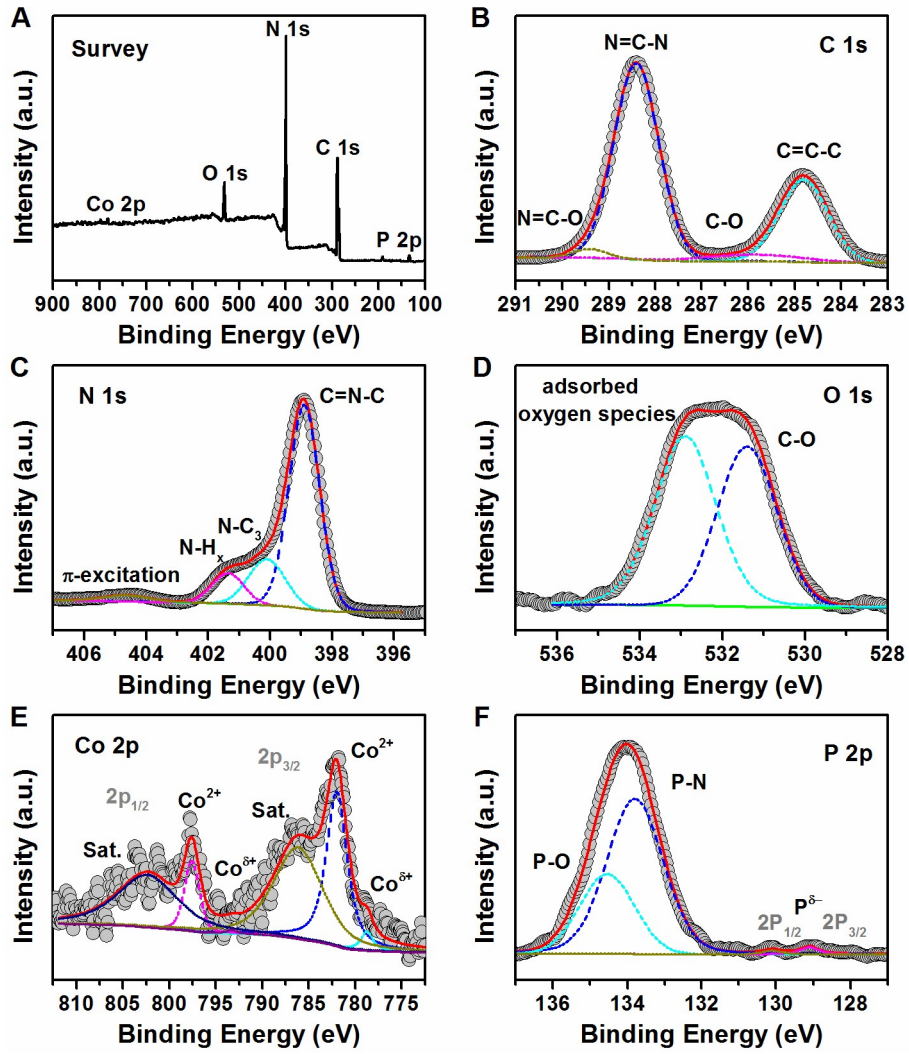


Fig. S6 XPS spectra for 2.5CP/CN sample.

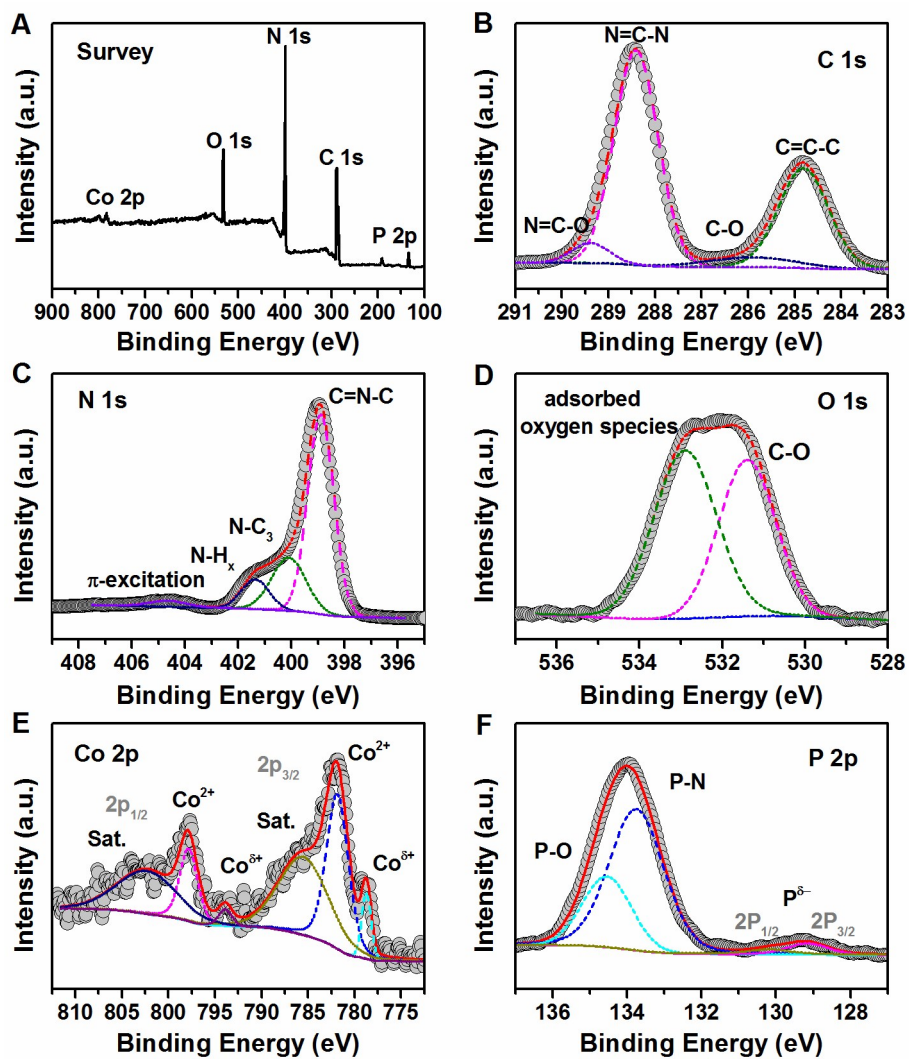


Fig. S7 High resolution XPS results of 7.5CP/CN sample.

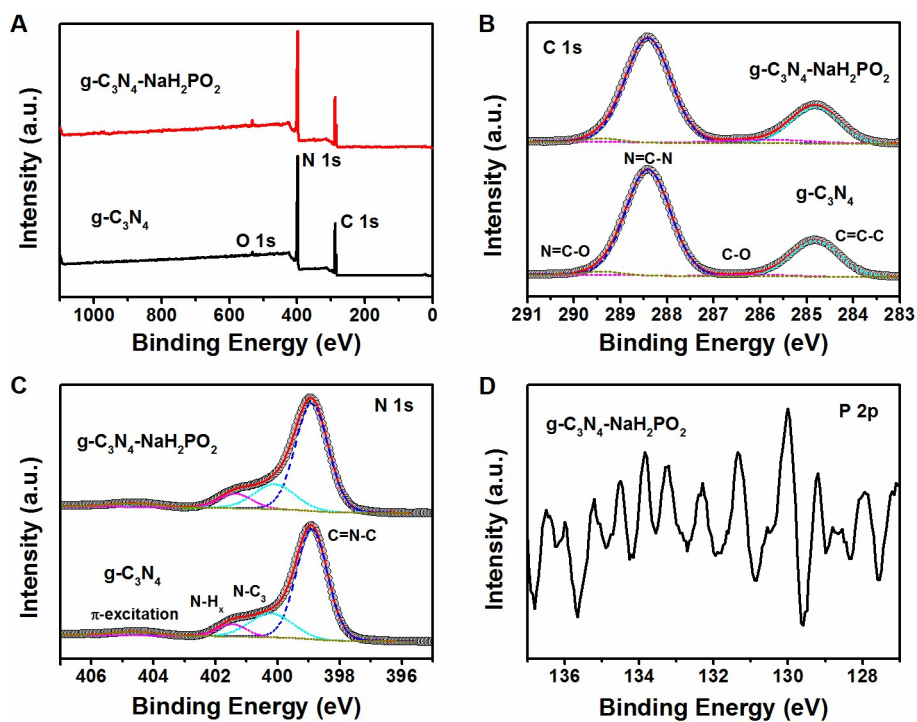


Fig. S8 XPS spectra for pristine $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4$ after heated with NaH_2PO_2 .

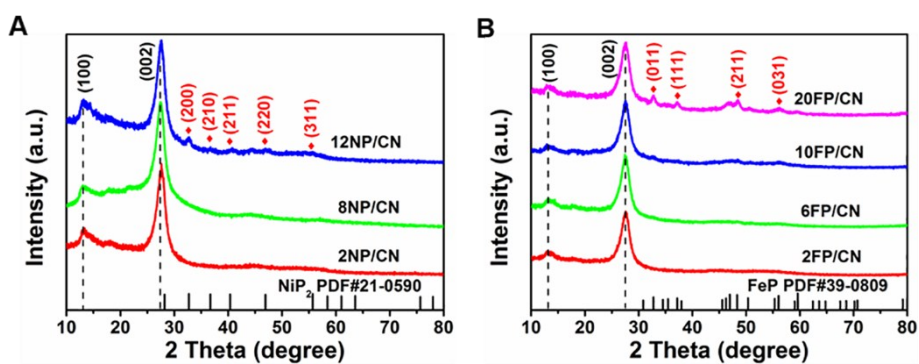


Fig. S9 XRD patterns of (A) the $\text{NiP}_2/g\text{-C}_3\text{N}_4$ composites with variable NiP_2 mass contents (2, 8, 12 wt%) and (B) the $\text{FeP}/g\text{-C}_3\text{N}_4$ composites with variable FeP mass contents (2, 6, 10, 20 wt%).

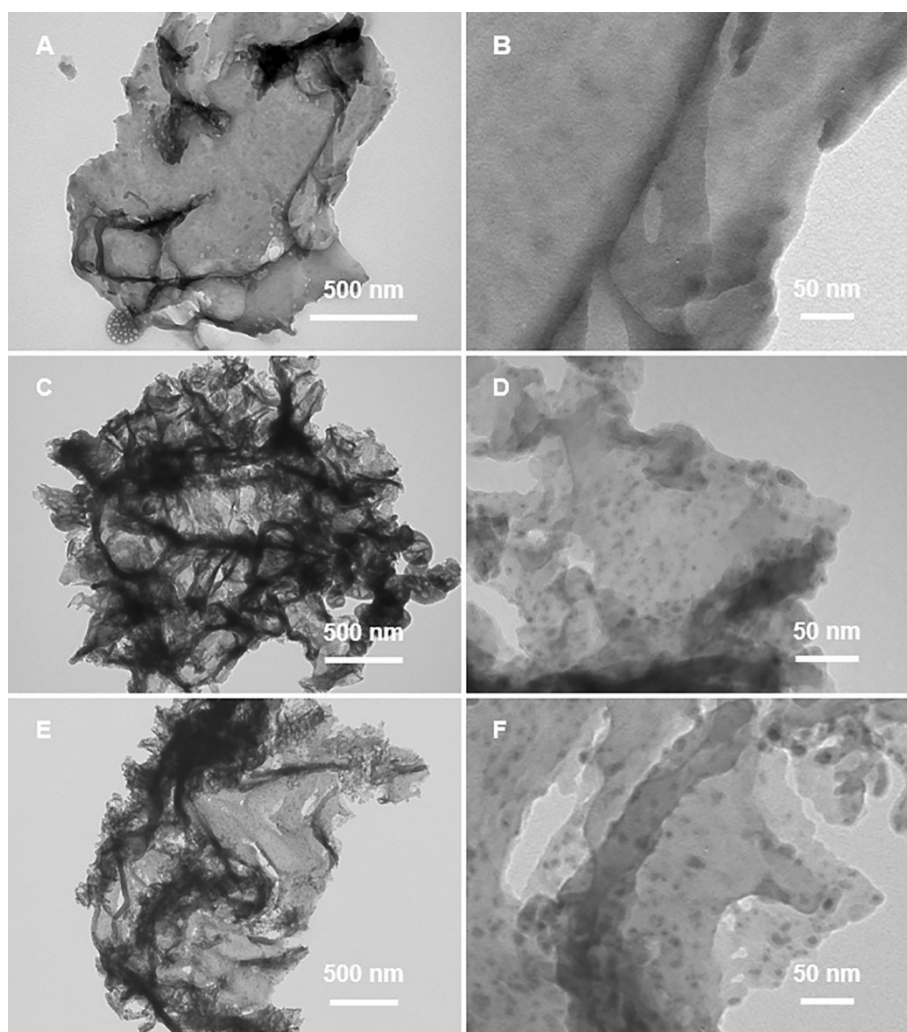


Fig. S10 Low-magnification and high-magnification TEM images of (A, B) 2 wt% NiP₂/g-C₃N₄, (C, D) 8 wt% NiP₂/g-C₃N₄ and (E, F) 12 wt% NiP₂/g-C₃N₄.

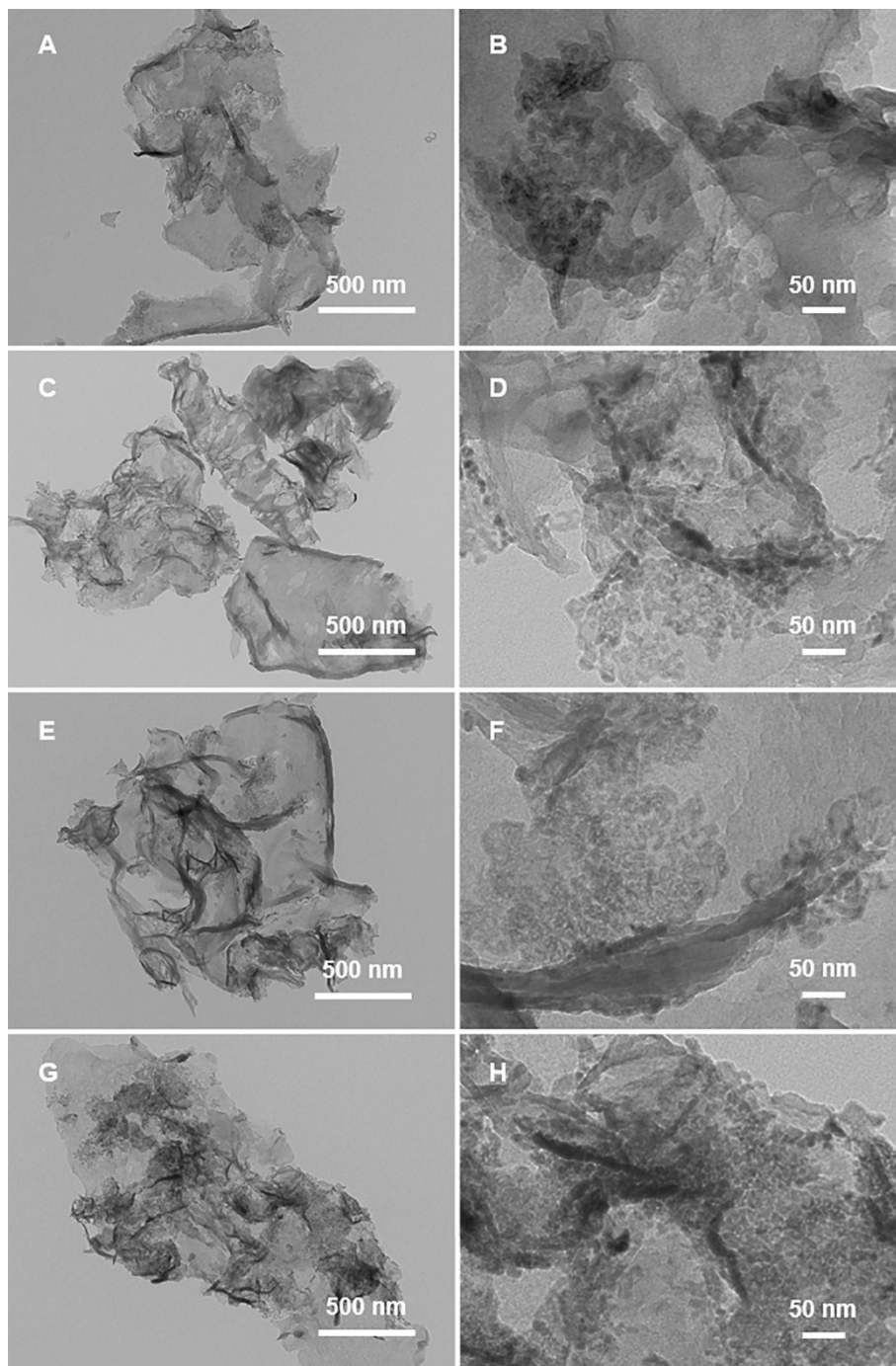


Fig. S11 Low-magnification and high-magnification TEM images of (A, B) 2 wt% FeP/g-C₃N₄, (C, D) 6 wt% FeP/g-C₃N₄, (E, F) 10 wt% FeP/g-C₃N₄ and (G, H) 20 wt% FeP/g-C₃N₄.

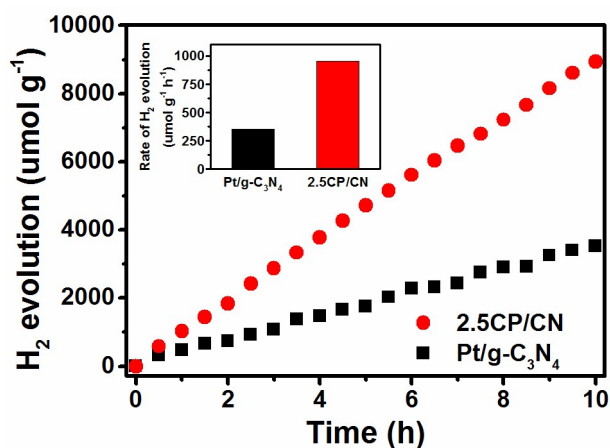


Fig. S12 Time course of photocatalytic H₂ production for 2.5 wt% Pt/g-C₃N₄ and 2.5CP/CN samples under visible light irradiation ($\lambda > 420$ nm) from 300 W Xe lamp using TEOA as the sacrificial agent.

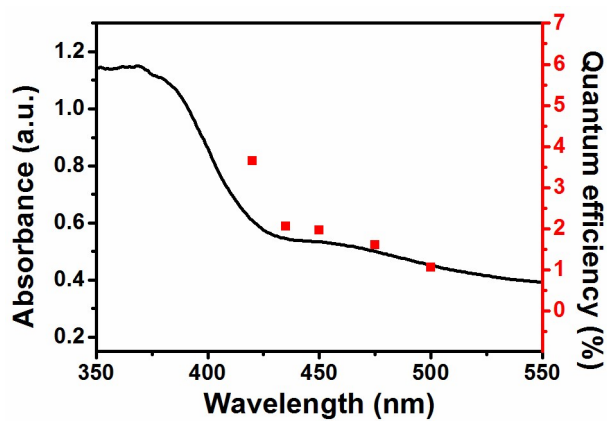


Fig. S13 The UV-vis diffuse spectrum (left axis) and wavelength-dependent quantum efficiency (right axis) of 2.5CP/CN for H₂ evolution (irradiation by a 300 W Xe lamp using a band-pass filter of full width at half maximum (FWHM) = 15 nm).

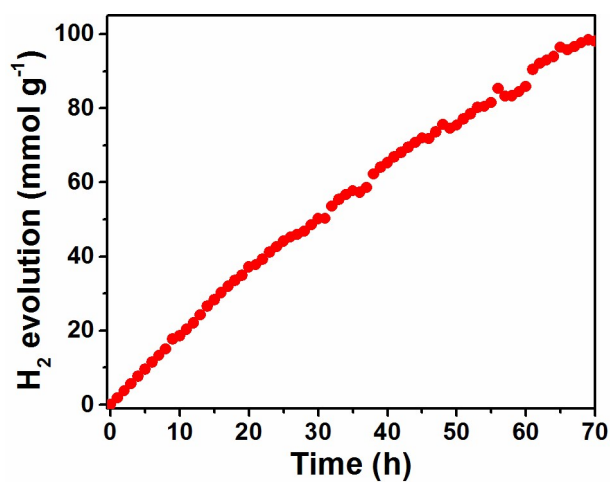


Fig. S14 Long-term photocatalytic H₂ evolution with 2.5CP/CN sample under simulated solar irradiation ($\lambda > 300$ nm) from 300 W Xe lamp using TEOA as the sacrificial agent.

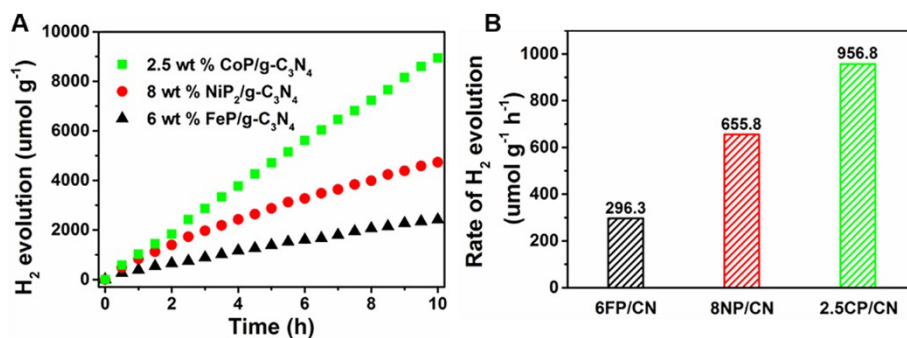


Fig. S15 (A) Time courses of photocatalytic H₂ evolution and (B) photocatalytic H₂ evolution rates over 2.5 wt% CoP/g-C₃N₄/, 8 wt% NiP₂/g-C₃N₄ and 6 wt% FeP/g-C₃N₄ hybrid photocatalysts in 10 vol% triethanolamine (TEOA) aqueous solution under visible light irradiation ($\lambda > 420$ nm).

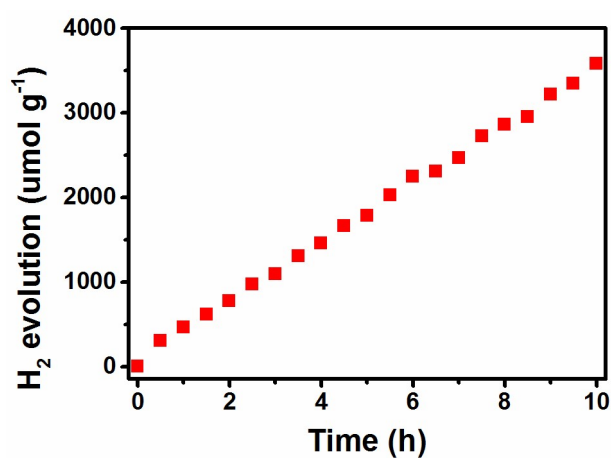


Fig. S16 Time course of H₂ production for 2.5 wt% Pt/g-C₃N₄-NaH₂PO₂ sample under visible light irradiation ($\lambda > 420$ nm) from 300 W Xe lamp using TEOA as the sacrificial agent.

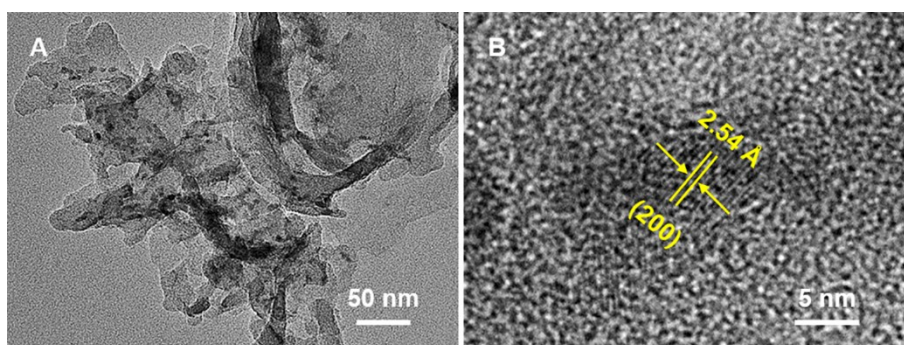


Fig. S17 TEM images of 2.5CP/CN sample after 70 h of continuous photocatalytic hydrogen production.

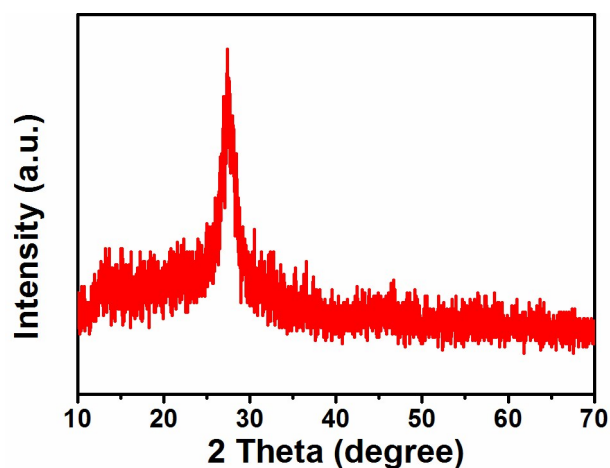


Fig. S18 XRD pattern of 2.5CP/CN sample after 70 h of continuous photocatalytic hydrogen production.

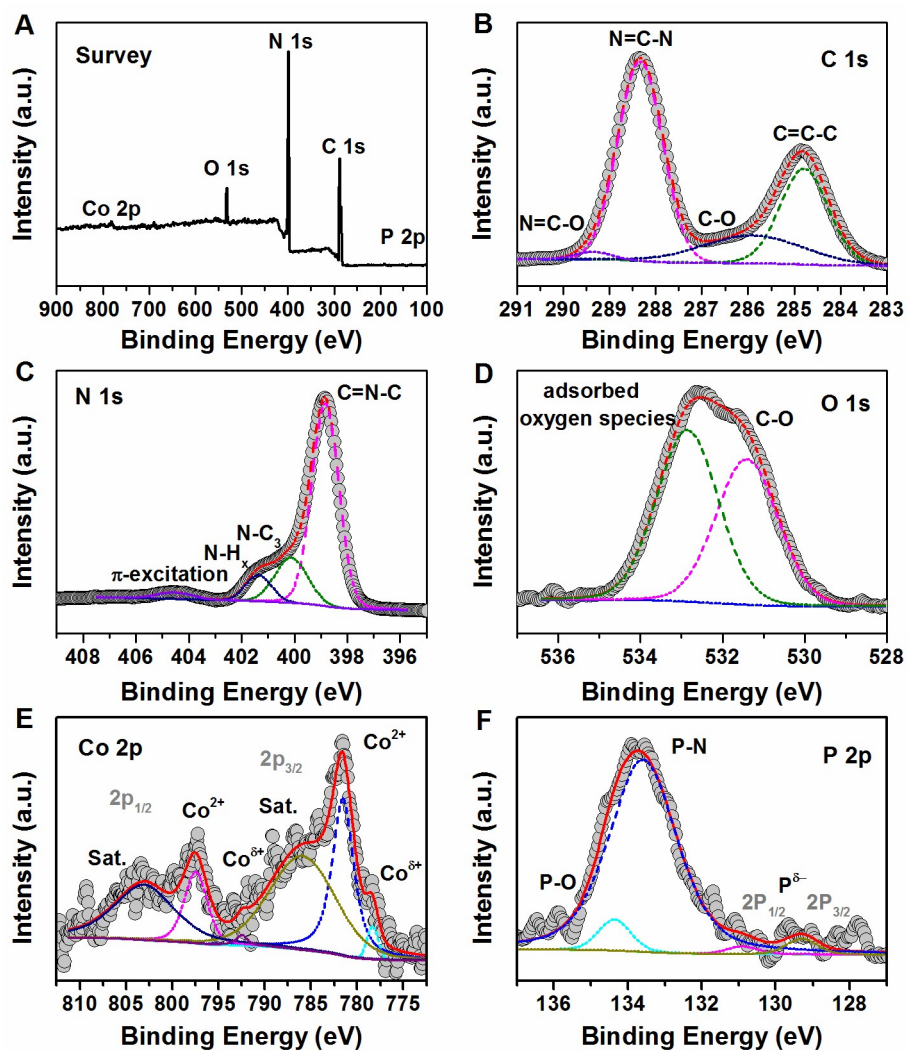


Fig. S19 (A) Co 2p and (B) P 2p XPS survey spectra of 2.5CP/CN sample after 70 h continuous photocatalytic hydrogen production.

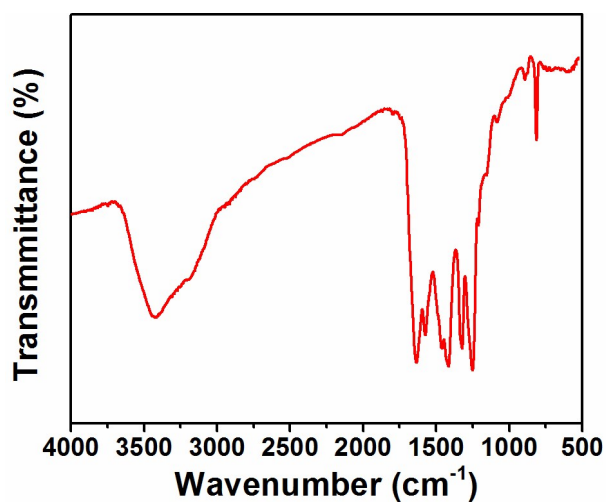


Fig. S20 FT-IR spectra of 2.5CP/CN sample after 70 h of continuous photocatalytic hydrogen production.

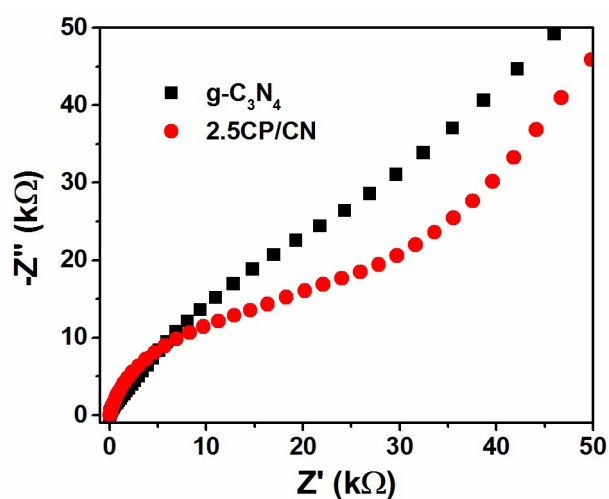


Fig. S21 EIS Nyquist plots of pure $g\text{-C}_3\text{N}_4$ and 2.5CP/CN samples.

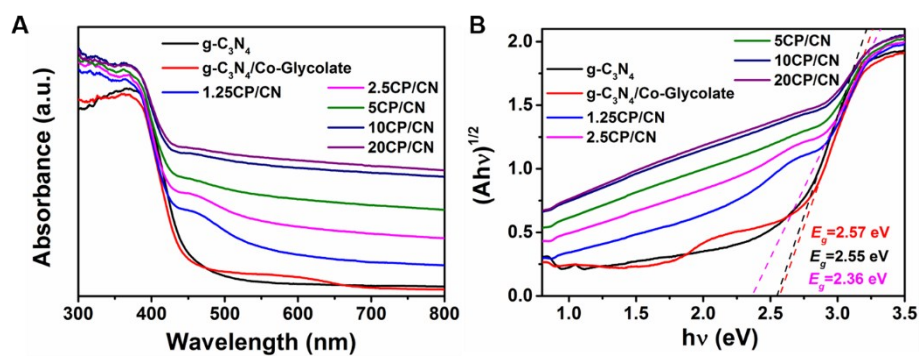


Fig. S22 (A) UV-vis diffuse reflectance spectra and (B) The Tauc plot of the pure $g\text{-C}_3\text{N}_4$, Co-Glycolate/ $g\text{-C}_3\text{N}_4$, CoP/ $g\text{-C}_3\text{N}_4$ composites with variable CoP mass contents (1.25, 2.5, 5, 10, 20 wt%).

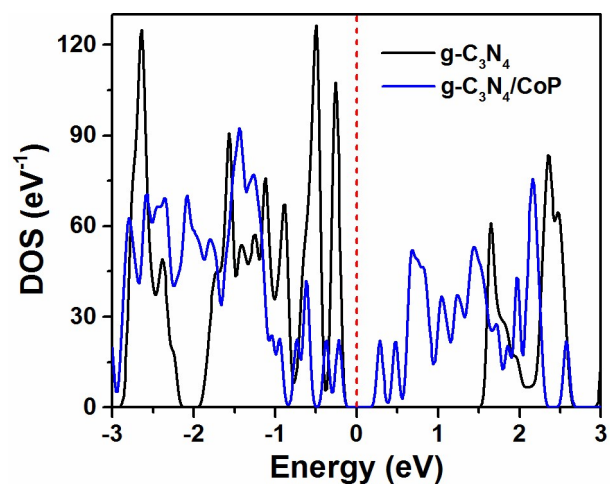


Fig. S23 Total density of states for pure $g\text{-C}_3\text{N}_4$ (black) and $\text{CoP}/g\text{-C}_3\text{N}_4$ (blue).

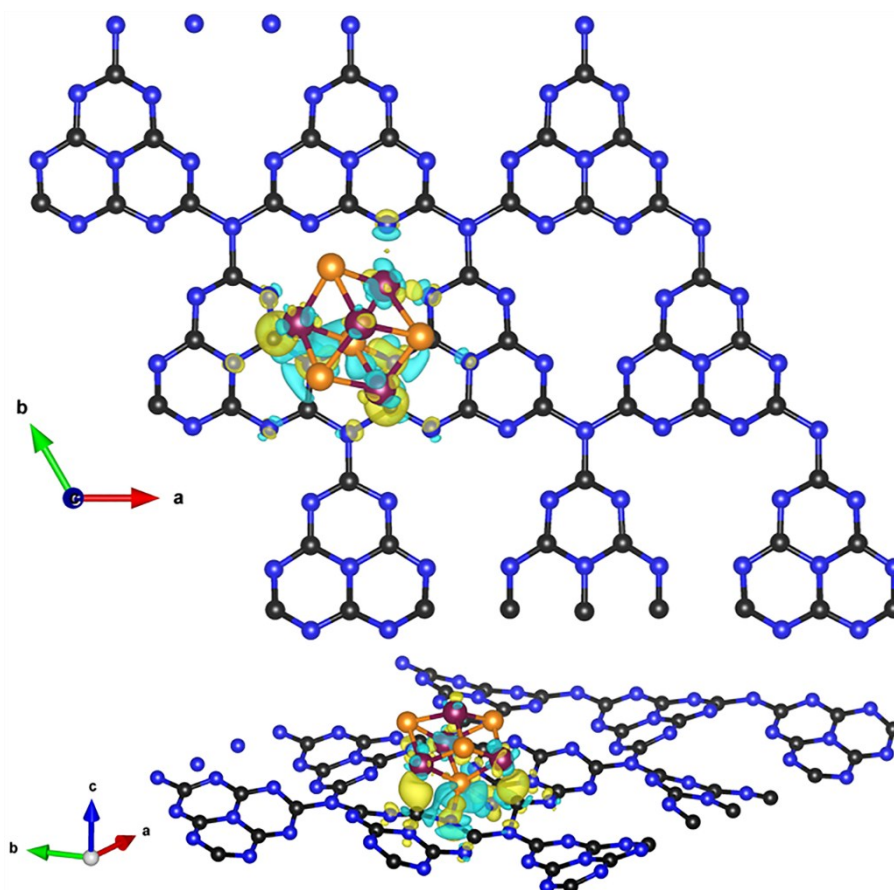


Fig. S24 Charge density difference isosurfaces of $\text{CoP}/g\text{-C}_3\text{N}_4$. The cyan region represents charge depletion, and the yellow region represents charge accumulation. The isosurface value is $0.05 \text{ e}/\text{\AA}^3$. The blue, black, orange and violet spheres represent N, C, P and Co atoms, respectively.

Table S1 ICP results of the as-prepared CoP/g-C₃N₄ samples with variable CoP mass contents (1.25, 2.5, 5, 7.5 and 10 wt%).

Sample	Content (wt%)
1.25CP/CN	1.17
2.5CP/CN	2.44
5CP/CN	4.16
7.5CP/CN	6.05
10CP/CN	6.48

Table S2 ICP results of the as-prepared NiP₂/g-C₃N₄ samples with variable NiP₂ mass contents (6, 8 and 10 wt%).

Sample	Content (wt%)
6NP/CN	4.44
8NP/CN	6.37
10NP/CN	8.05

Table S3 ICP results of the as-prepared FeP/g-C₃N₄ samples with variable FeP mass contents (2, 6 and 10 wt%).

Sample	Content (wt%)
2FP/CN	2.52
6FP/CN	6.83
10FP/CN	8.87

Table S4 The hydrogen production activity of as-prepared FeP/g-C₃N₄ and NiP₂/g-C₃N₄ samples with variable FeP and NiP₂ mass contents.

Sample	H ₂ production (umol g ⁻¹ h ⁻¹)
6NP/CN	480.1
8NP/CN	655.8
10NP/CN	580.5
2FP/CN	129.1
6FP/CN	296.3
10FP/CN	194.6

Table S5 Comparison of photocatalytic H₂ evolution activities of the non-noble-metal cocatalyst modified g-C₃N₄ photocatalysts.

Catalyst	Synthetic method	Electron donor	Light source	H ₂ production (umol g ⁻¹ h ⁻¹)	Ref.
Ni ₂ P/g-C ₃ N ₄	Mixing the Ni salt, NaH ₂ PO ₂ , g-C ₃ N ₄ and heating method	TEOA	≥ 420 nm	644	1
CoP/g-C ₃ N ₄	Grinding method	TEOA	≥ 420 nm	474.4	2
Ni ₁₂ P ₅ /g-C ₃ N ₄	Solution-phase self-assembly method	TEOA	≥ 420 nm	535.7	3
Ni(OH) ₂ /g-C ₃ N ₄	Precipitation method	TEOA	≥ 400 nm	152	4
NiS/g-C ₃ N ₄	Hydrothermal method	TEOA	≥ 420 nm	482	5
CoP/g-C₃N₄	Reflowing-phosphorization method	TEOA	≥ 420 nm	956.8 (3 h) 861.3 (24 h) 783.8 (70 h)	Our work

References

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4. J. Yu, S. Wang, B. Cheng, Z. Lin, F. Huang, *Catal. Sci. Technol.* 3 (2013) 1782-1789.
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