

Supporting Information

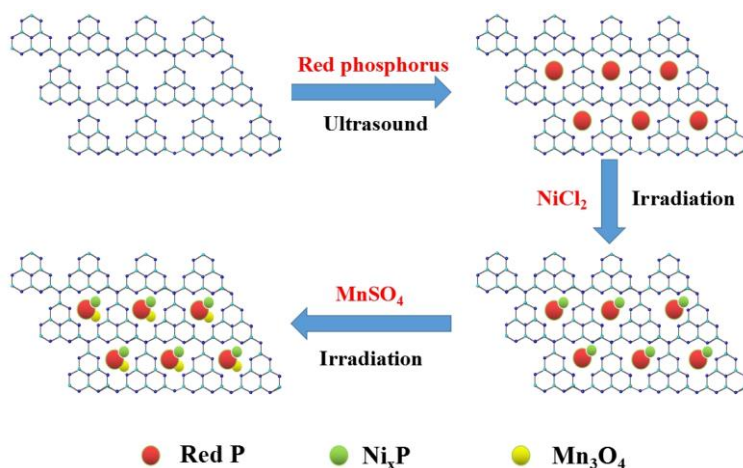
Ni_xP and Mn₃O₄ dual co-catalysts separately deposited on g-C₃N₄/red phosphorus hybrid photocatalyst for efficient hydrogen evolution

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Photochemical formation of CNP-Ni-Mn



Scheme S1. The proposed photochemical synthesis route of CNP-Ni-Mn.

CNP-Ni-Mn is prepared by a two-step photodeposition process (Scheme S1). The first step is to form reduction co-catalyst Ni_xP on the conduction band by adding NiCl_2 . During this process, P^0 at the conduction band is reduced to $\text{Ni}_x\text{P}^{+\delta}$ by photo-generated electron (eq 2), and P^0 at the valence band is oxidized to $\text{PO}_x^{+\delta}$ (eq 3).



The second step is to deposit the oxidation co-catalyst Mn_3O_4 at the valence band position. In this process, the product CNP-Ni of the first step was added as a carrier. After photo-excitation generates electrons and holes (eq. 4), hydrogen is producing at the conduction band position due to the presence of the reduction co-catalyst (eq. 5), and the generated hydrogen gas has been measured by gas chromatography. At the valence band position, Mn^{2+} is oxidized by photo-generated holes to form oxidation co-catalyst Mn_3O_4 (eq. 6).

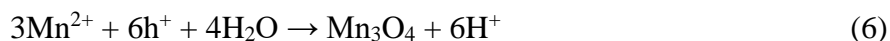
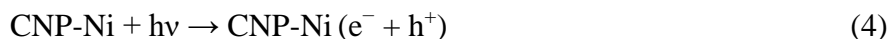


Table S1. Conditions of control experiments.

	CNP /mg	NiCl ₂ (0.1M) /mL	MnSO ₄ (0.1M) /mL	H ₂ O /mL	Irradiation time /min	Heating time (50°C) /min	Stirring time /min
A	30	-	1	9	50	-	-
B	30	1	-	9	50	-	-
C	30	1	1	8	50	-	-
D	30	-	1	9	50	-	-
	30(CNP-Mn)	1	-	9	50	-	-
E	30	1	-	9	50	-	-
	30(CNP-Ni)	-	1	9	50	-	-
F	30	1	-	9	-	50	-
	30(CNP-Ni)	-	1	9	-	50	-
G	30	1	-	9	-	-	50
	30(CNP-Ni)	-	1	9	-	-	50
H	30(P + CN)	1	-	9	50	-	-
	30(P/CN-Ni)	-	1	9	50	-	-

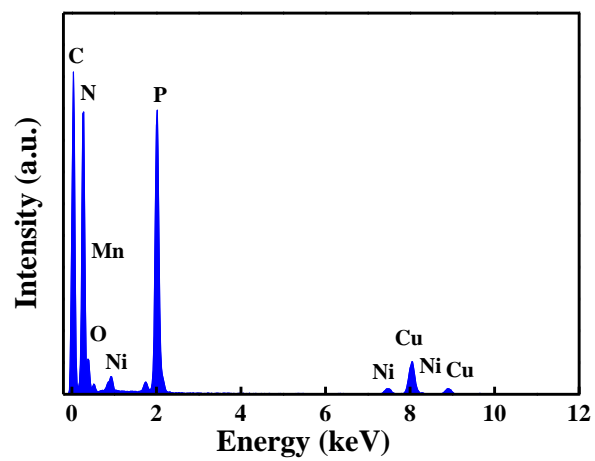


Fig. S1. TEM-EDX of CNP-Ni-Mn.

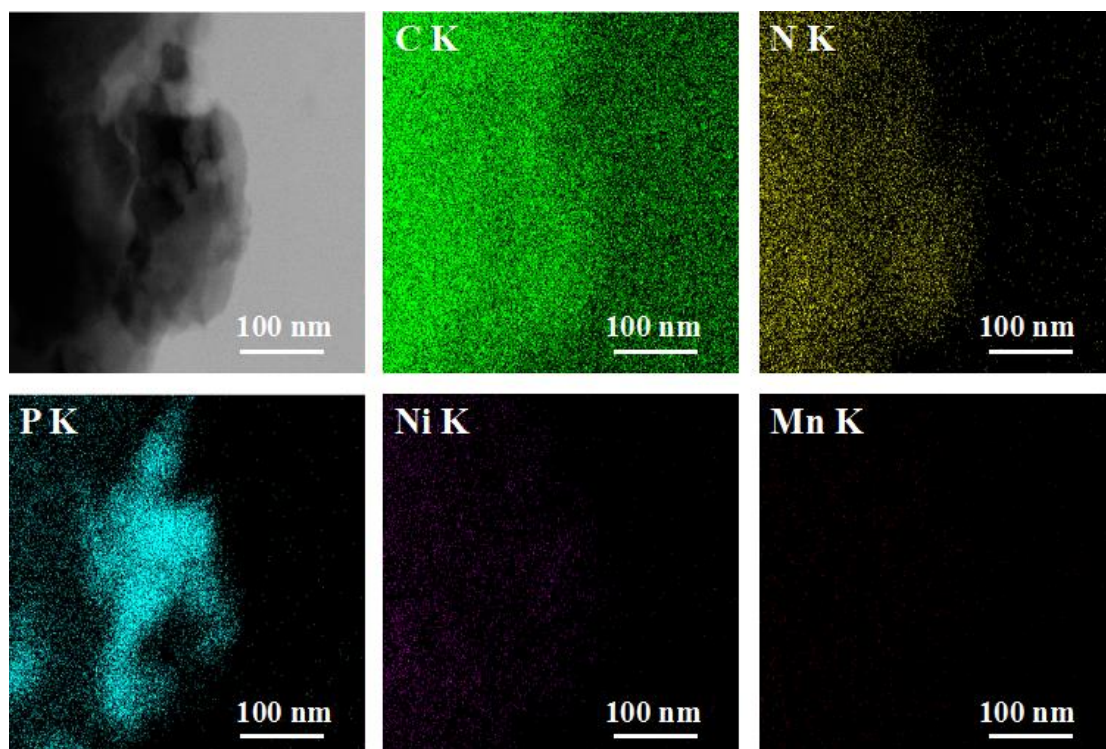


Fig. S2. EDX-Mapping images of C, N, P, Ni and Mn elements in CNP-Ni-Mn.

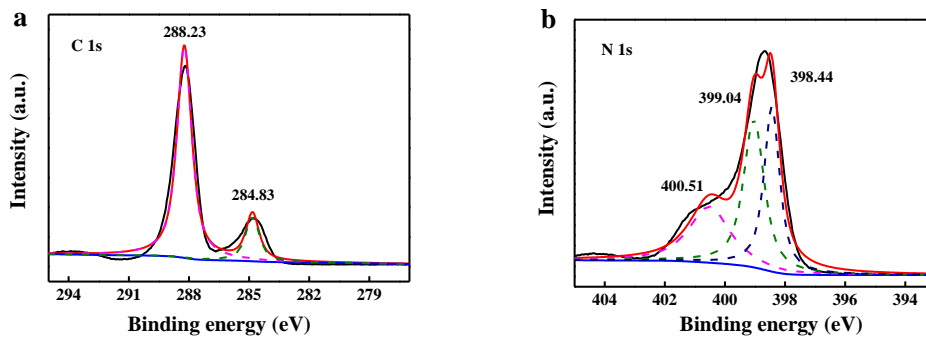


Fig. S3. The high-resolution XPS spectra of C 1s (a) and N 1s (b) in pure g-C₃N₄.

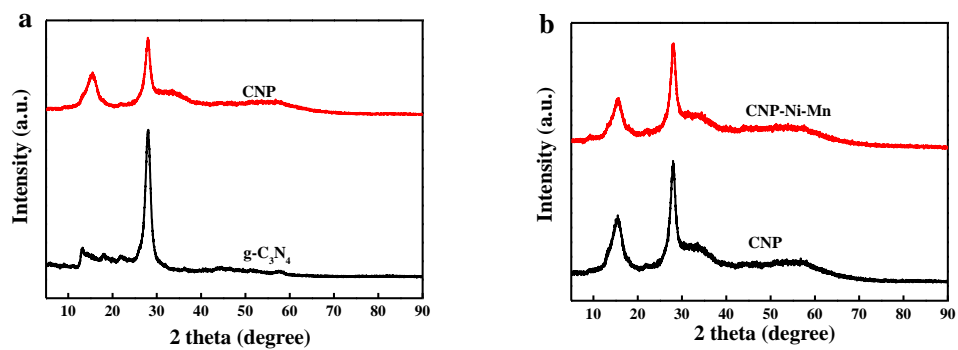


Fig. S4. The XRD patterns of $g-C_3N_4$ and CNP (a), CNP and CNP-Ni-Mn (b).

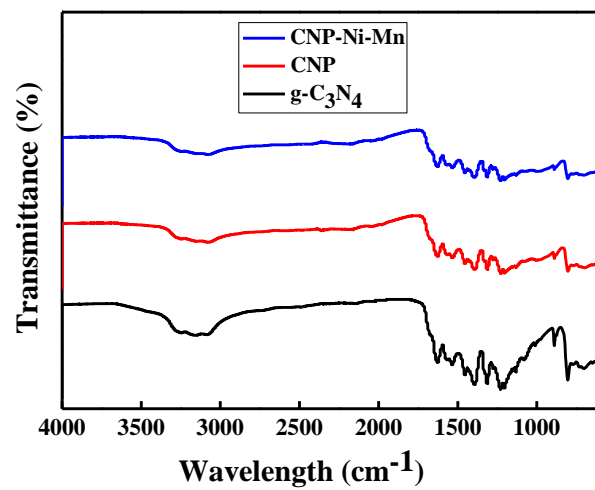


Fig. S5. FT-IR spectroscopy of g-C₃N₄, CNP and CNP-Ni-Mn.

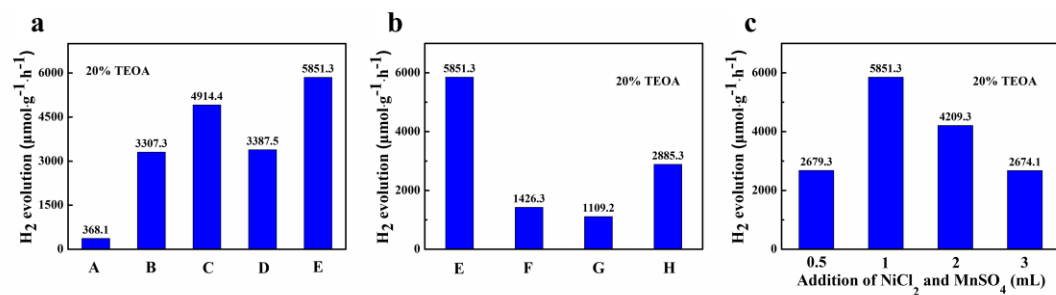


Fig. S6. (a) Photocatalytic hydrogen production activity of catalyst A-E in 20 vol% TEOA solution in Table 1. (b) Comparison of irradiation (E), heating (F), stirring (G) and red phosphorus (H) in 20 vol% TEOA solution. (d) Photocatalytic hydrogen production activity of different addition amount of NiCl₂ and MnSO₄ (1:1) in 20 vol% TEOA solution.

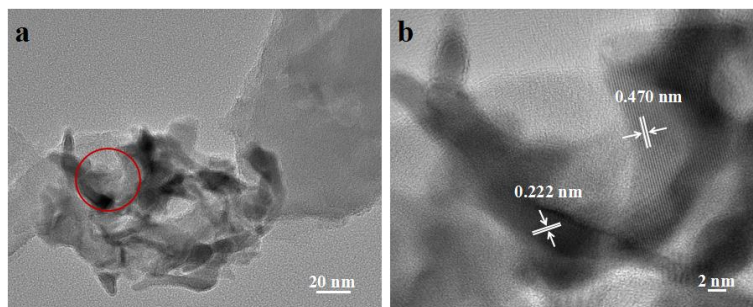


Fig. S7. TEM (a) and HR - TEM (b) of CNP-Ni-Mn after photocatalysis. The measured lattice fringes of 0.222 nm and 0.470 nm correspond to the (111) crystal face Ni_2P and the (200) crystal face of Mn_2O_3 .

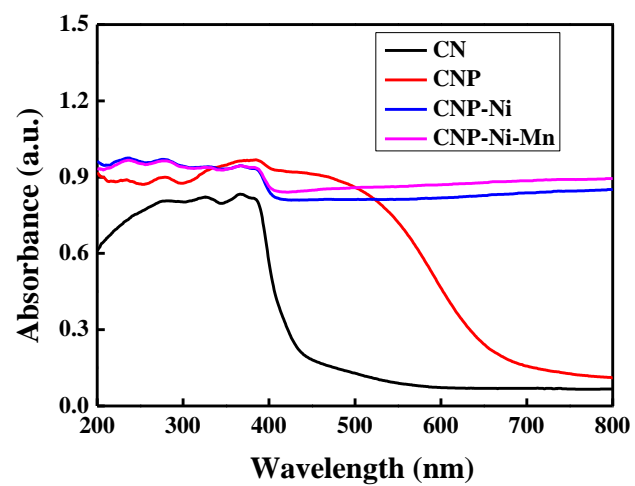


Fig. S8. UV-vis diffuse reflectance spectroscopy of pure g-C₃N₄, CNP, CNP-Ni and CNP-Ni-Mn.

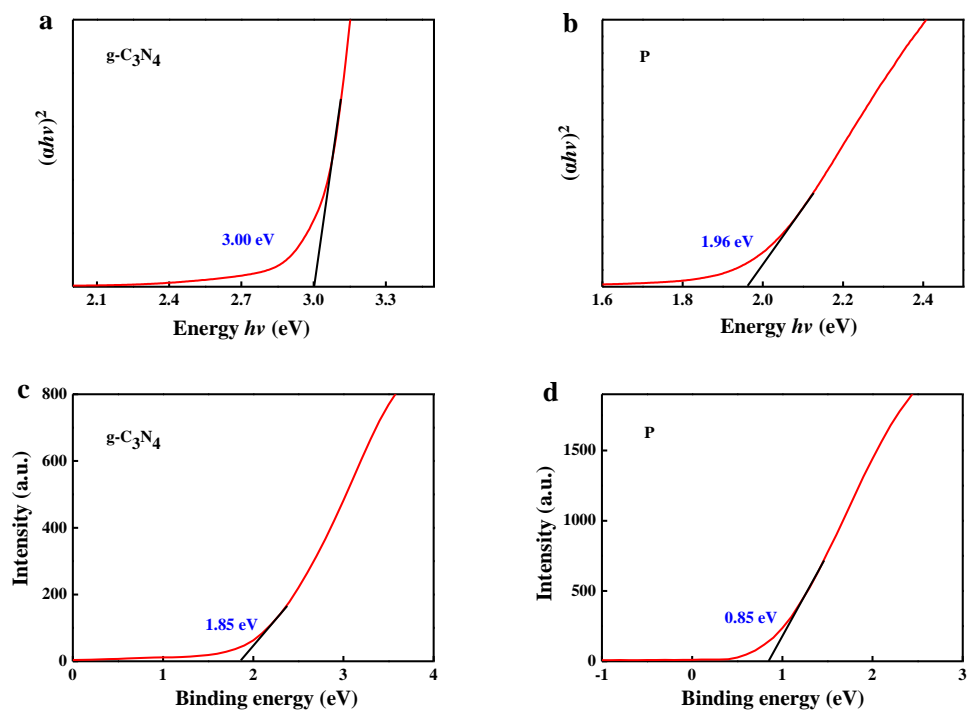


Fig. S9. Tauc plots of $g\text{-C}_3\text{N}_4$ (a) and red P (b). XPS spectra of $g\text{-C}_3\text{N}_4$ (c) and red P (d) for valence band offset determination.

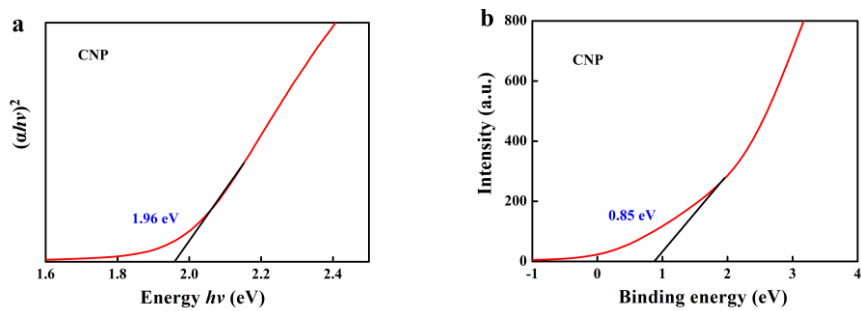


Fig. S10. (a) Tauc plots of CNP. (b) XPS spectra of CNP for valence band offset determination.

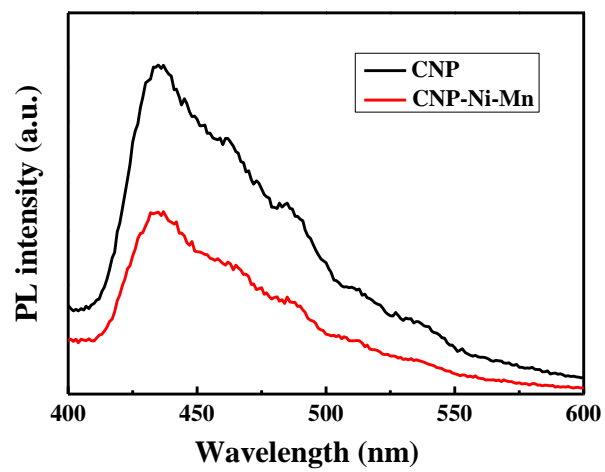


Fig. S11. PL spectra of CNP and CNP-Ni-Mn under the excitation wavelength of 375 nm.

Table S2. The co-catalysts for photocatalytic hydrogen evolution reaction.

Photocatalyst	Co-catalysts	Light source	Sacrificial agent	Activity ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	Stability at least (h)	Ref. (year)
g-C ₃ N ₄ /WO ₃	Ni(OH) _x	$\lambda > 400 \text{ nm}$ (Xe)	TEOA	576	12	¹ (2017)
g-C ₃ N ₄	Co	AM 1.5 (Xe)	TEOA	2296	48	² (2018)
g-C ₃ N ₄	MoS ₂	$\lambda \geq 400 \text{ nm}$ (Xe)	Lactic acid	660	9	³ (2018)
N-TiO ₂ /g-C ₃ N ₄	Ni _x P	$780 > \lambda >$ 350 nm (Xe)	TEOA	5438	10	⁴ (2018)
TiO ₂	CuO _x	AM 1.5G (Xe)	Methanol	407	—	⁵ (2018)
CaIn ₂ S ₄	MnO _x	$750 \text{ nm} \geq$ $\lambda \geq 420 \text{ nm}$ (Xe)	Na ₂ S + Na ₂ SO ₃	5520	—	⁶ (2019)
g-C ₃ N ₄	NiS, CoS _x , CuS _x	420 nm (LED)	TEOA	244	7.5	⁷ (2021)
g-C ₃ N ₄	Ni-Ag	$\lambda \geq 420 \text{ nm}$ (Xe)	Methanol	2137.5	16	⁸ (2022)
g-C ₃ N ₄ /red P	Ni _x P-Mn ₃ O ₄	AM 1.5 (Xe)	TEOA	5851.3	8	This work

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