Electronic Supplementary Materials

Visual Observation of Hydrogen Bubbles Generation from Monodisperse CoP QDs on Ultrafine G-C_3N_4 Fiber under Visible Light Irradiation

Yunxiong Zeng,[†,‡,*] Yingchun Xia,[†,‡] Wenjia Song[†,‡] and Shenglian Luo[†,‡,*]

[†] State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, P. R. China

[‡] Department of chemistry, Hunan University, Changsha, 410082, P.R China

Corresponding authors

E-mail: yxzeng@hnu.edu.cn; sllou@hnu.edu.cn

1. Supplementary Figures:

Figure S1 SEM images of bare Co_3O_4 without CNF as a support (a, b).

Figure S2 XRD of bare Co_3O_4 and the Co_3O_4 standard card (JCPDS 42-1476).

Figure S3 XRD pattern (a) and EDS of 7-Co_3O_4/CNF (b).

Figure S4 SEM images of CoP without CNF as the support (a, b).

Figure S5 XRD of CoP and CoP standard card (JCPDS 29-0497).

Figure S6 (A) XRD of bare CoP, CNF, 1-CoP/CNF, 3-CoP/CNF, 5-CoP/CNF, 7-CoP/CNF and 10-CoP/CNF, (B) FT-IR spectrum of CoP, CNF and 7-CoP/CNF, (C) standard curve of cobalt ions determined at characteristic λ = 240.7 nm by atomic absorption spectrum (AAS) and (D) mass content of CoP in the CoP/CNF composites.

Figure S7 Photocatalytic hydrogen evolution rate of Pt/CNF under visible light.

Figure S8 PL spectra of CNF and CoP/CNF composites (A) and magnified PL spectrum of CoP/CNF (B). a: CoP, b: 1-CoP/CNF, c: 3-CoP/CNF, d: 5-CoP/CNF, f: 7-CoP/CNF and g: 10-CoP/CNF.

Figure S9 Nyquist plots (a) and visible light photocurrent density of CoP, CNF and 7-CoP/CNF (b).

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Figure S11 and long-term HER stability of 7-CoP/CNF (c). Condition: 15 vol% TEOA as hole sacrificial molecules under visible light and room temperature ($\lambda \geq$ 420 nm).

Figure S12 (a) TEM images of 7-CoP/CNF and (b) HR-TEM of CoP QDs in 7-CoP/CNF composite.

Figure S13 Co 2p XPS of 7-CoP/CNF before (a) and after reaction.

2. Supplementary Tables:

Table S1 C, N, P and Co atom and weight ratio of 7-CoP/CNF determined by energy dispersed X-ray spectrum (EDS).

Table S2 Comparison of various semiconductor composites for photocatalytic HER.

Table S3 Time-resolved photoluminescence (TR-PL) spectroscopy probed the specific charge carrier dynamics on the interface of CNF and 7-CoP/CNF.

Table S4 The charge-transfer resistance and ohmic resistance of CoP, CBF and 7-CoP/CNF.

Table S5 C, N, P and Co atom and weight ratio of 7-CoP/CNF after long-time cyclic HER determined by energy dispersed X-ray spectrum (EDS).

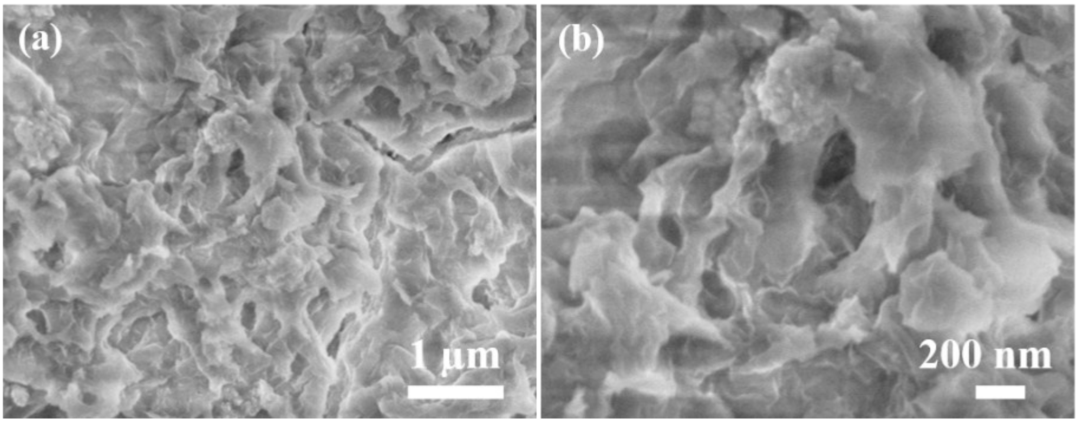

Figure S1 SEM images of bare Co_3O_4 without CNF as a support (a, b)

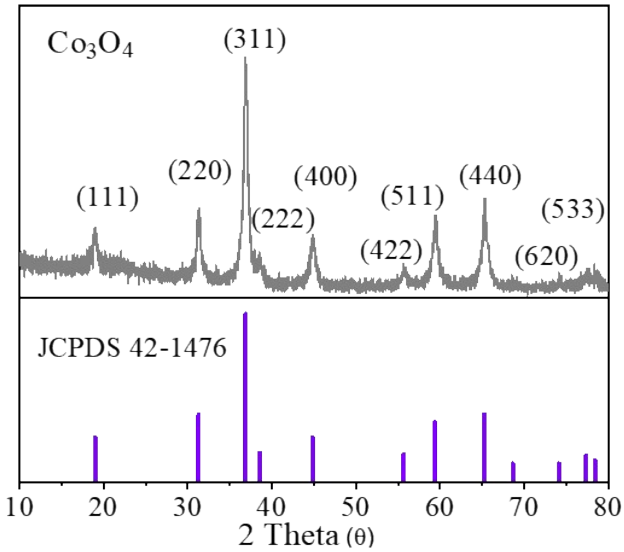

Figure S2 XRD of bare Co_3O_4 and the Co_3O_4 standard card (JCPDS 42-1476).

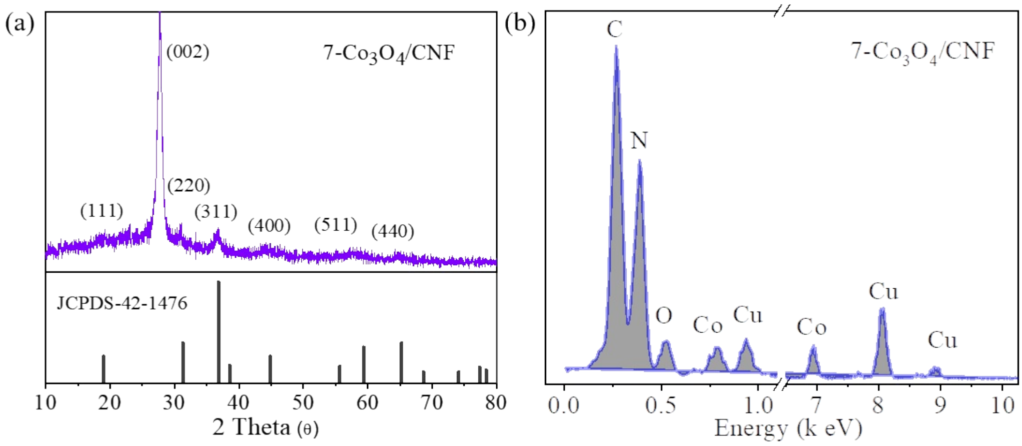

Figure S3 (a) XRD pattern and (b) EDS of 7-Co_3O_4/CNF.

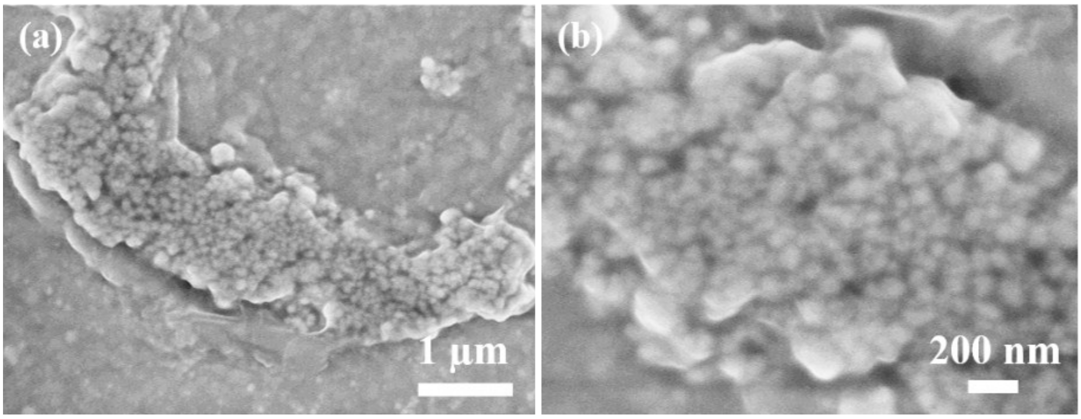

Figure S4 (a, b) SEM images of CoP without CNF as the support.

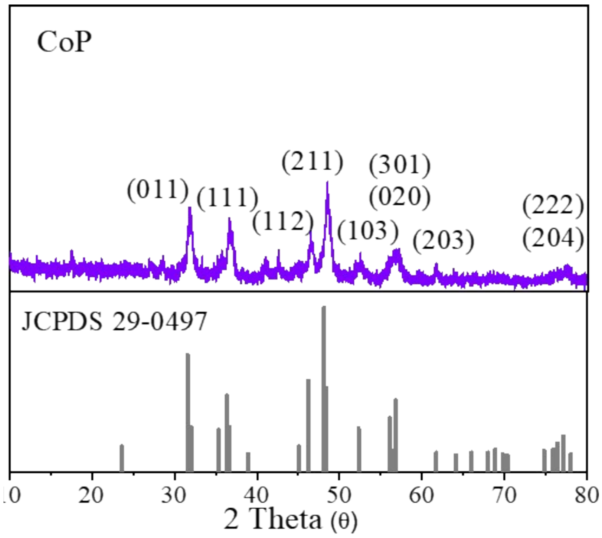

Figure S5 XRD of CoP and CoP standard card (JCPDS 29-0497).

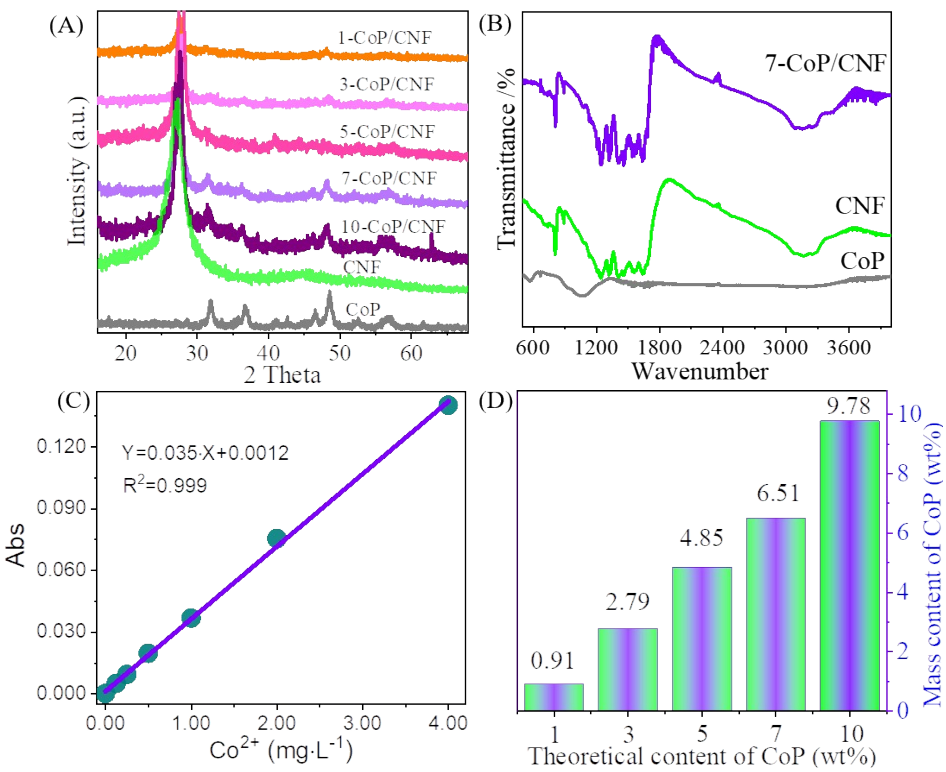

Figure S6 (A) XRD of bare CoP, CNF, 1-CoP/CNF, 3-CoP/CNF, 5-CoP/CNF, 7-CoP/CNF and 10-CoP/CNF, (B) FT-IR spectrum of CoP, CNF and 7-CoP/CNF, (C) standard curve of cobalt ions determined at characteristic λ = 240.7 nm by atomic absorption spectrum (AAS) and (D) mass content of CoP in the CoP/CNF composites.

Table S1 C, N, P and Co atom and weight ratio of 7-CoP/CNF determined by energy dispersed X-ray spectrum (EDS).

	C	N	P	Co	CoP
Weight (%)	34	58	3.9	4.1	6.32

Table S2 Comparison of various semiconductor composites for photocatalytic HER.

Photocatalysts	Light source Xe lamp (nm)	Reactant [a] solution	Activity (mmol/g/h)	AQE
Pt/g-C_3N_4 network [S1]	λ≧420 nm	10 vol% TEOA	1.36	12% (420 nm)
Pt/g-C_3N_4 nanofiber [S2]	λ≧420 nm	10 vol% TEOA	0.732	7% (420 nm)
Pt/O doped g-C_3N_4 [S3]	λ≧420 nm	10 vol% TEOA	0.375	-
Pt/g-C_3N_4 nanosheets [S4]	λ≧420 nm	10 vol% TEOA	1.15	-
Pt/g-C_3N_4 nanosheets [S5]	300W Xe lamp λ≧400 nm	10 vol% TEOA	0.64	-
Pt/g-C_3N_4 [S6]	300W Xe lamp λ≧420 nm	10 vol% TEOA	0.23	-
Pt/g-C_3N_4 nanosheets [S7]	300W Xe lamp λ≧420 nm	10 vol% TEOA	0.24	-
Pt/g-C_3N_4 [S8]	300W Xe lamp λ≧420 nm	10 vol% TEOA	0.098	0.6% (420 nm)
NiS/g-C_3N_4 nanosheets [S9]	300W Xe lamp λ≧420 nm	10 vol% TEOA	0.482	4.4% (440 nm)
Pt/g-C_3N_4 [S10]	300W Xe lamp λ≧420 nm	15 vol% TEOA	1.11	-
Pt/g-C_3N_4 [S11]	300W Xe lamp λ≧420 nm	10 vol% TEOA	0.37	-
Ag_2O/g-C_3N_4 [S12]	300W Xe lamp λ≧420 nm	10 vol% TEOA	0.33	-
Pt/g-C_3N_4 [S13]	300W Xe lamp λ≧400 nm	10 vol% TEOA	0.604	20 %
Pt/g-C_3N_4 [S14]	300W Xe lamp λ≧400 nm	10 vol% TEOA	1.510	5.7% (420nm)
Pt/g-C_3N_4 [S15]	λ≧420 nm	10 vol% TEOA	1.751	-
Pt/g-C_3N_4 [S16]	λ≧420 nm	15 vol% TEOA	3.446	32% (420 nm)
NiP/CdS [S17]	λ≧420 nm	$NaSO_3/Na_2S$	553	41% (450 nm)
MoS_2/CdS [S18]	λ≧420 nm	$NaSO_3/Na_2S$	17.2	24.2% (420 nm)
rGO/g-C_3N_4 [S19]	UV-Vis light	30 vol% TEOA	0.273	-
COFs/g-C_3N_4 [S20]	λ>420 nm	10 vol% TEOA	10.1	20.7% (425 nm)
C/g-C_3N_4 [S21]	λ>420 nm	TEOA	3.53	10.9% (420 nm)
C/g-C_3N_4 [S22]	λ>420 nm	-	0.11mol·h^{-1}	-
P/g-C_3N_4 [S23]	λ>420 nm	10 vol% TEOA		5.7% (420 nm)
ZnCdS/ZnO [S24]	λ>420 nm	$NaSO_3/Na_2S$	0.929	-
P/g-C_3N_4 [S25]	λ>400 nm	TEOA	28.6	-
FeS/$FeSe_2$ [S26]	UV-Vis light	$NaSO_3/Na_2S$	0.738	-

MoC/C [S27]	λ>400 nm	Lactic acid	2.071	-
$H_{0.53}WO_3/CdS$[S28]	λ>400 nm	Lactic acid	2.08	-
CdS [S29]	λ≧420 nm	Lactic acid	3.53	-
Pt/g-C_3N_4 [S30]	λ≧420 nm	10 vol% TEOA	0.916	6.52 (420 nm)
Pt/g-C_3N_4 [S31]	λ≧420 nm	20 vol% TEOA	1.596	3.56 (420 nm)
PDBTSO [S32]	λ>400 nm	20 vol% TEOA	44.2	8% (420 nm)
$MoSe_2$ [S33]	λ>400 nm	10 vol% TEOA	1.672	5.2% (520 nm)
Polymer Dots [S34]	λ>420 nm	ascorbic acid	0.84	0.9% (500 nm)
triazine polymers [S35]	λ>420 nm	10 vol% TEOA	6.60	7.3% (420 nm)
CdS/Ag_2S [S36]	λ≧420 nm	10 vol% TEOA	0.376	-
g-C_3N_4	λ>420 nm	10 vol% TEOA	1.619	-
CoP/g-C_3N_4 (this study)	λ≧420 nm	15 vol% TEOA	121	60% (420 nm)

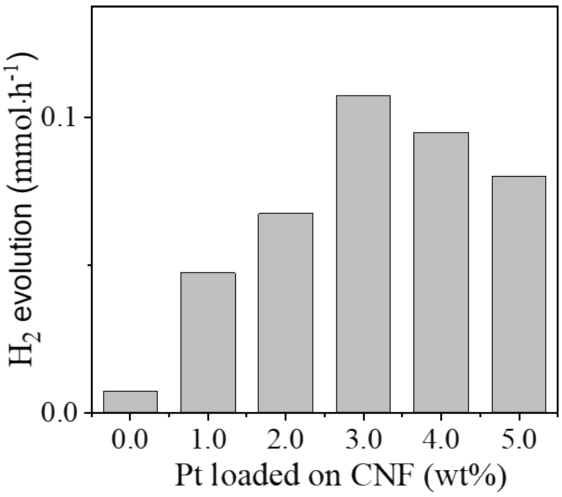

Figure S7 Photocatalytic hydrogen evolution rate of Pt/CNF under visible light.

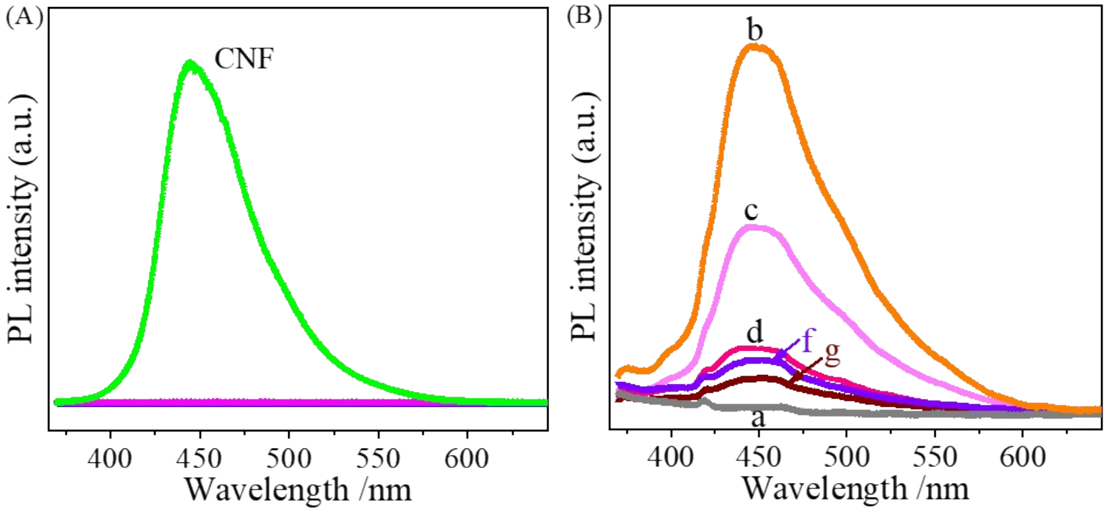

Figure S8 PL spectra of CNF and 7-CoP/CNF composites (A) and magnified PL spectrum of CoP/CNF (B). a: CoP, b: 1-CoP/CNF, c: 3-CoP/CNF, d: 5-CoP/CNF, f: 7-CoP/CNF and g: 10-CoP/CNF.

Table S3 Time-resolved photoluminescence (TR-PL) spectroscopy probed the specific charge carrier dynamics on the interface of CNF and 7-CoP/CNF.

Samples	A_1[%]	τ_1[ns]	A_2[%]	τ_2[ns]	A_3[%]	τ_3[ns]	τ_A[ns]
7-CoP/CNF	49.13	2.15	39.27	5.69	11.26	11.25	6.39
CNF	32.87	1.98	50.13	6.40	17.05	12.89	8.28

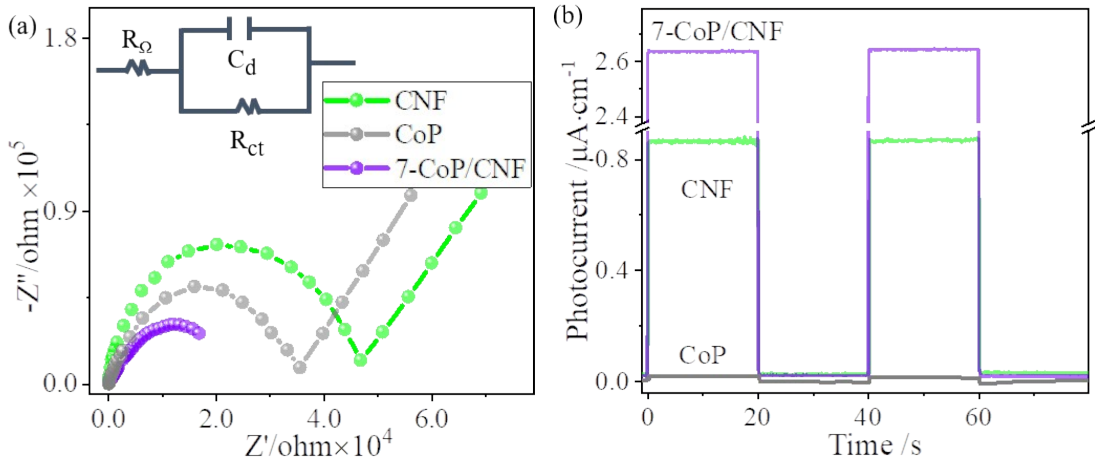

Figure S9 Nyquist plots (a) and visible light photocurrent density of CoP, CNF and 7-CoP/CNF (b).

Table S4 The charge-transfer resistance and ohmic resistance of CoP, CBF and 7-CoP/CNF fitted by Nyquist plots.

	CoP	CNF	7-CoP/CNF
R_{ct}	1.84 kΩ	23.9 kΩ	1.24 kΩ
R_s	0.16 kΩ	0.16 kΩ	0.16 kΩ

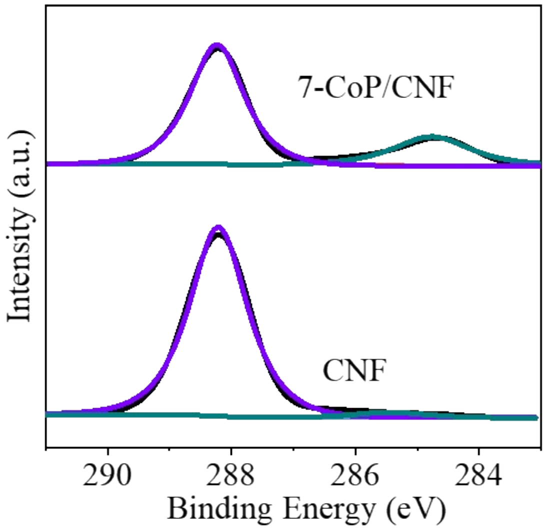

Figure S10 High-resolution C1 s XPS of CNF and 7-CoP/CNF.

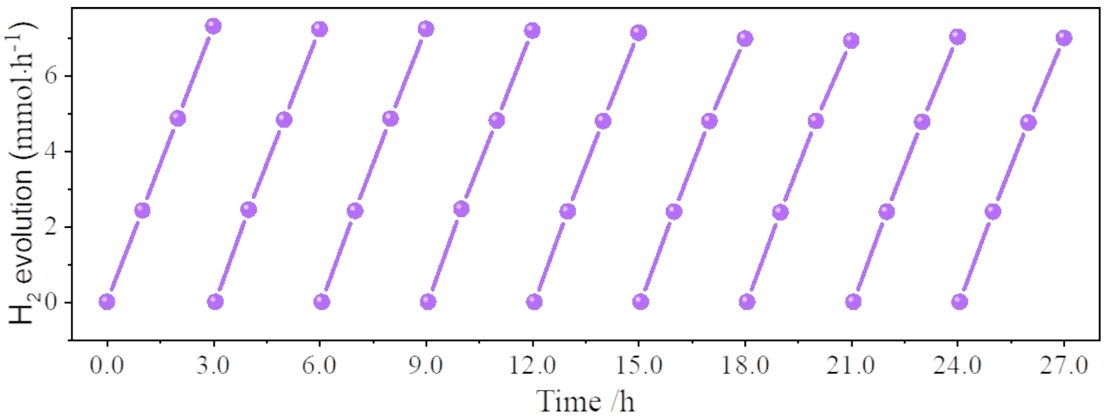

Figure S11 Photocatalytic HER rate comparation between Pt/CNF and CoP/CNF (a), HER activity of CNF loading various amount of Pt (b) and long-term HER stability of 7-CoP/CNF (c). Condition (a-c): 15 vol% TEOA as hole sacrificial molecules under visible light and room temperature (λ ≥ 420 nm).

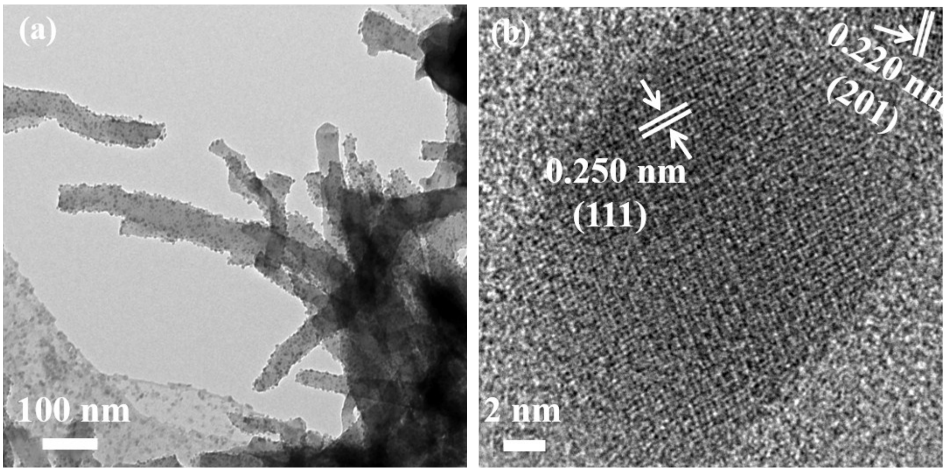

Figure S12 (a) TEM images of 7-CoP/CNF and (b) HR-TEM of CoP QDs in CoP/CNF composite.

Table S5 C, N, P and Co atom and weight ratio of 7-CoP/CNF after long-time cyclic HER determined by energy dispersed X-ray spectrum (EDS).

	C	N	P	Co	CoP
Weight (%)	35	57	3.8	4.0	6.2

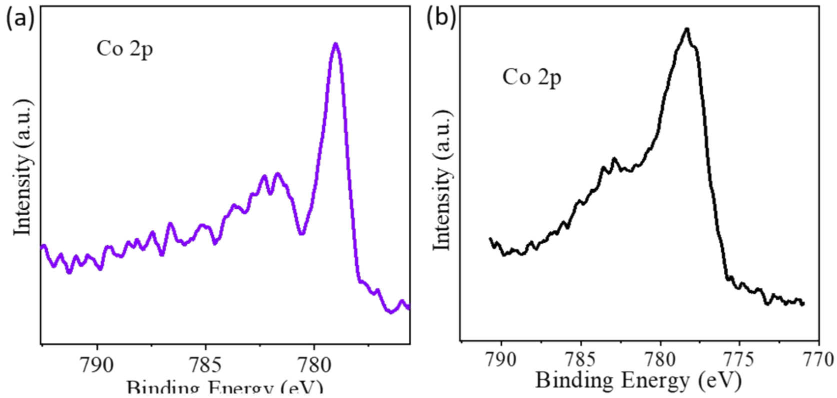

Figure S13 Co 2p XPS of 7-CoP/CNF before (a) and after reaction.

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