Supporting Information for

Ultrafine Co_2P Nanoparticles Encapsulated in Nitrogen and Phosphorus Dual-doped Porous Carbon Nanosheet/Carbon Nanotube Hybrids: High-Performance Bifunctional Electrocatalyst for Overall Water Splitting

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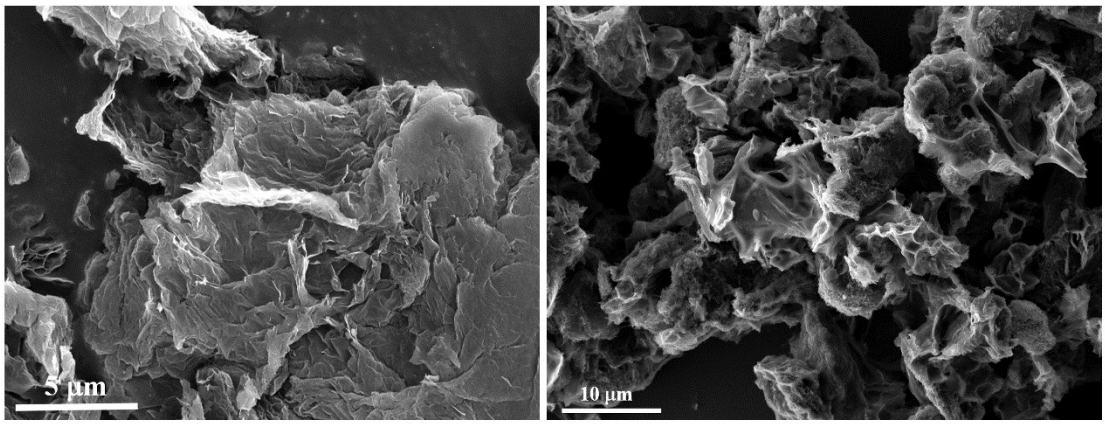

Fig. S1 SEM images of (a) Co_2P@N, P-PCN and (b) Co_2P@N, P-PCN/CNTs.

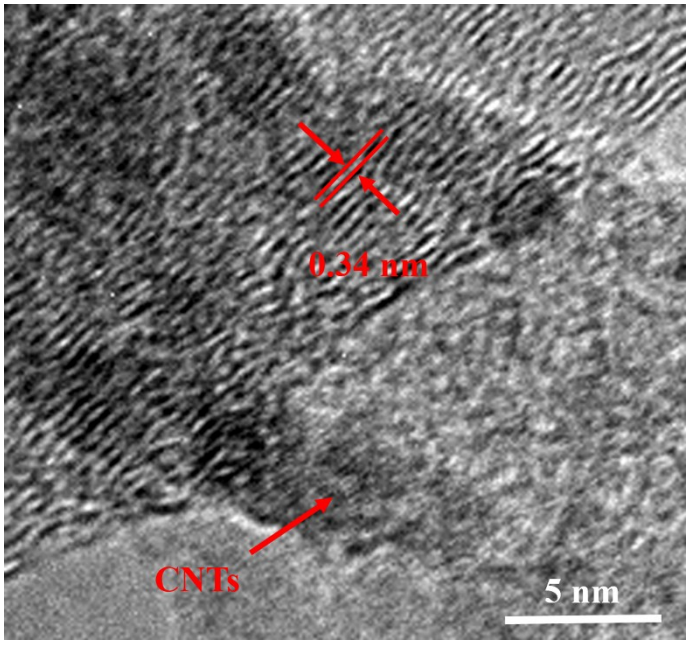

Fig. S2 HRTEM image of Co_2P@N, P-PCN/CNTs.

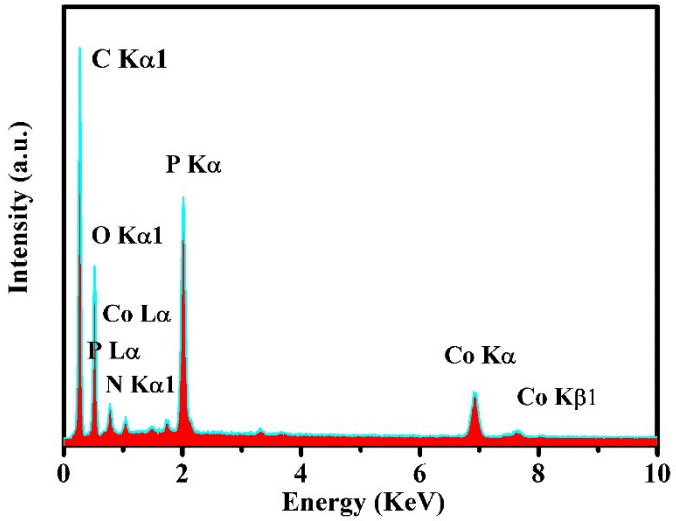

Fig. S3 EDX spectrum of Co_2P@N, P-PCN/CNTs.

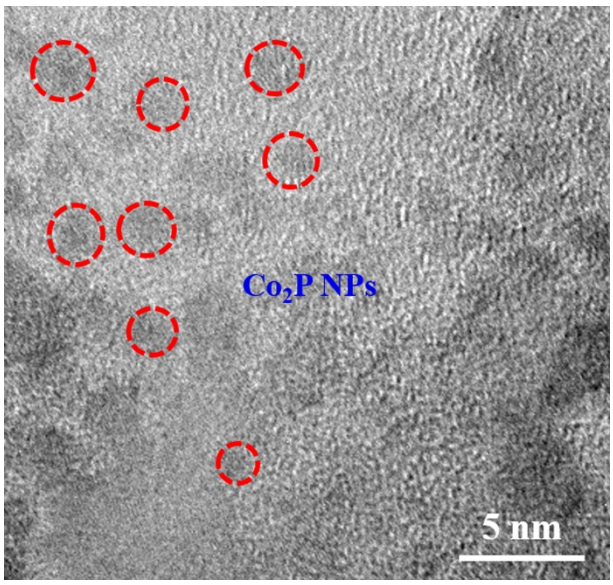

Fig. S4 TEM image of Co_2P@N, P-PCN/CNTs.

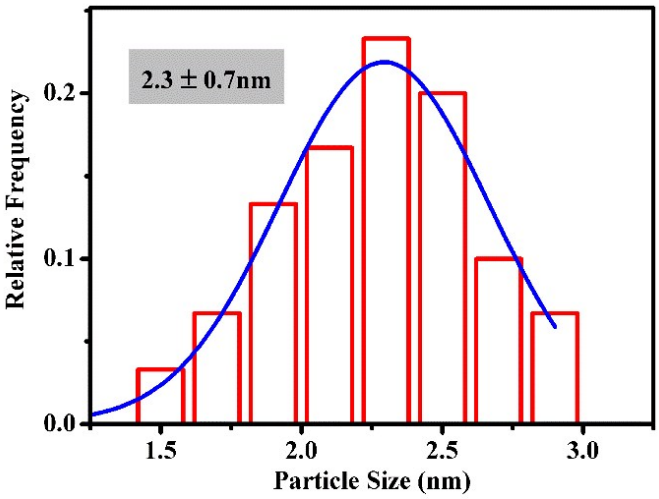

Fig. S5 Size distribution histograms of Co_2P NPs.

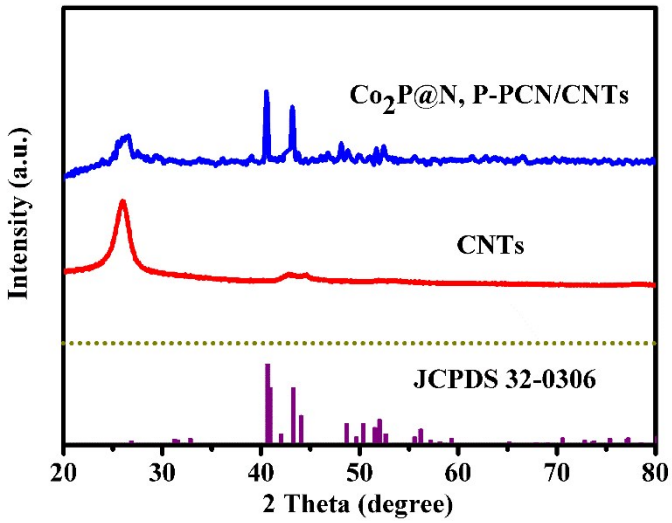

Fig. S6 Wide-angle XRD patterns of CNTs and Co_2P@N, P-PCN/CNTs.

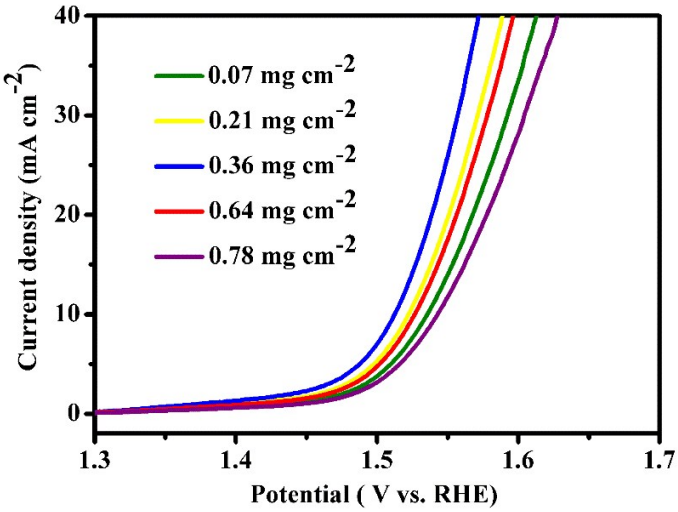

Fig. S7 LSVs curves for Co_2P@N, P-PCN/CNTs at five different mass loadings in O_2-saturated 1.0 M KOH solution.

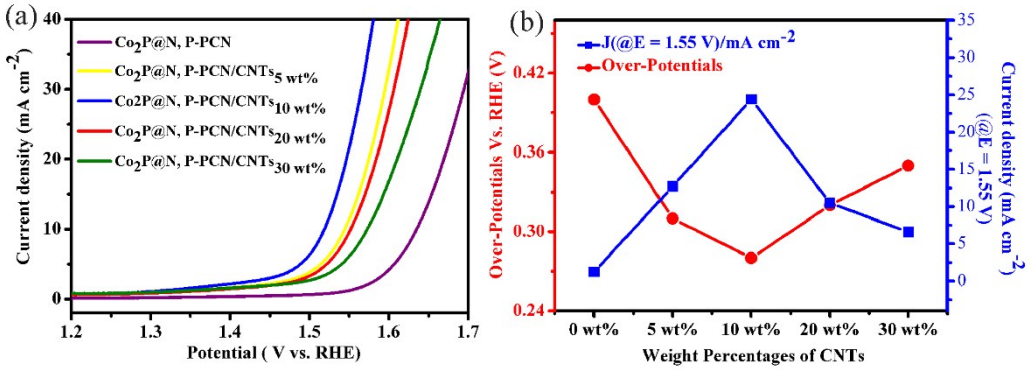

Fig. S8 (a) LSVs curves of Co_2P@N, P-PCN, Co_2P@N, P-PCN/$CNTs_{5\ wt\%}$, Co_2P@N, P-PCN/$CNTs_{10\ wt\%}$, Co_2P@N, P-PCN/$CNTs_{20\ wt\%}$ and Co_2P@N, P-PCN/$CNTs_{30\ wt\%}$ in an O_2-saturated 1.0 M KOH solution (scan rate 0.5 mV s^{-1}). (b) CNTs weight percentage-dependent over-potential (10 $mAcm^{-2}$) and current density (E = 1.55 V) plots of the products.

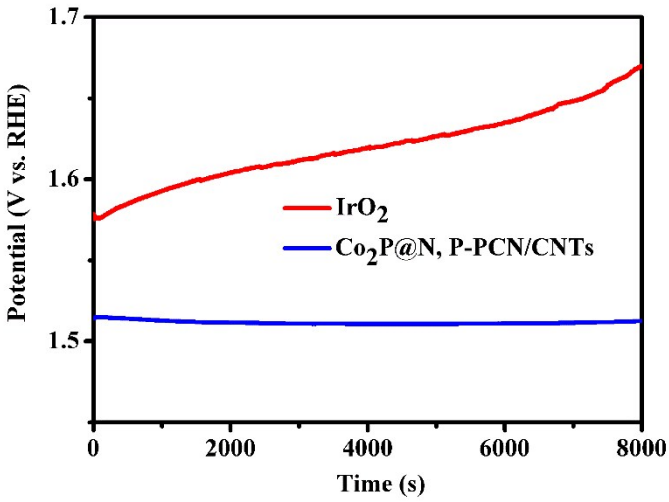

Fig. S9 Chronopotentiometric response at a constant current density of 10.0 mA cm^{-2} recorded for Co_2P@N, P-PCN/CNTs and commercial IrO_2 catalyst.

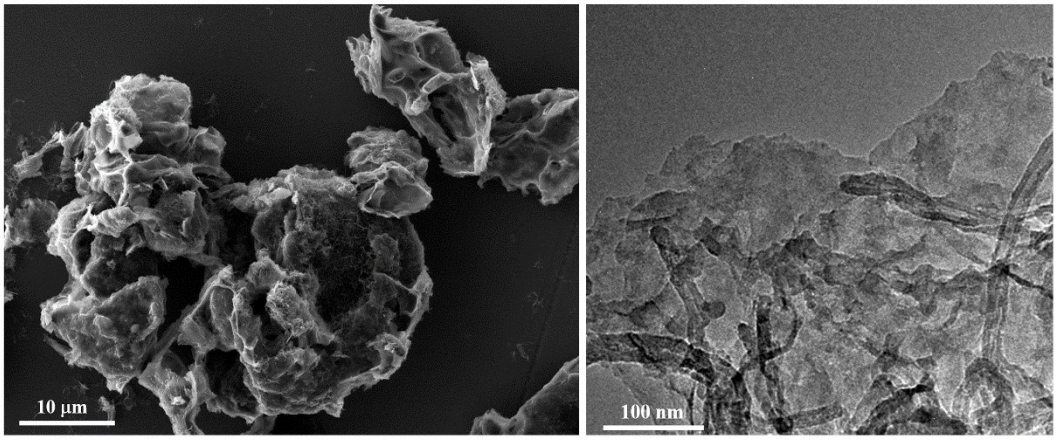

Fig. S10 SEM and TEM characterizations of Co_2P@N, P-PCN/CNTs after the chronopotentiometry test.

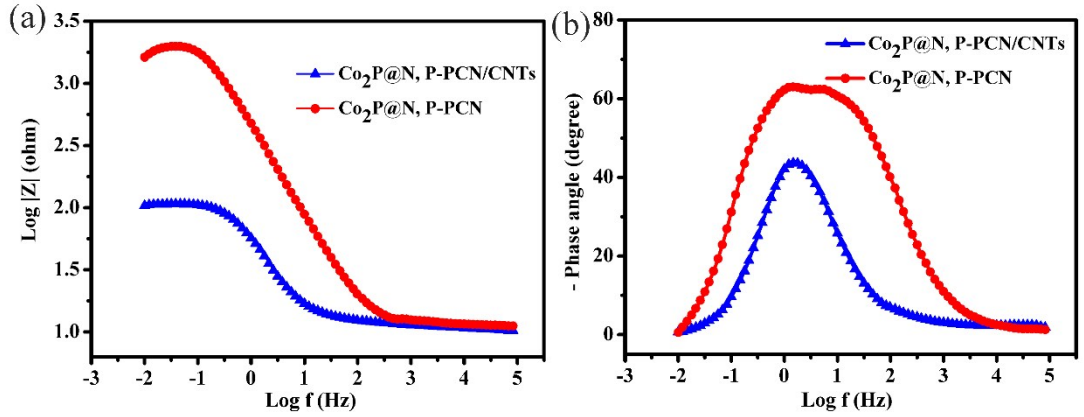

Fig. S11 EIS Bode plots for Co_2P@N, P-PCN and Co_2P@N, P-PCN/CNTs. Bode plots show the information of impedance, frequency and phase angle. Fig. S11 were the Bode plots for the data in Fig. 5a. The axes of both impedance modulus |Z| and frequency (f) were logarithmic. The impedance of the system measured in the low frequency range is closely related to the polarization resistance (or R_{ct}), which is affected by the kinetics of the electrode reactions. As can be seen, the impedance at low-frequency range (10^{-2} Hz) increased in the order CNTs-

Co_2P@N, P-PCN/CNTs < Co_2P@N, P-PCN, which in accordance with the Nyquist plots.

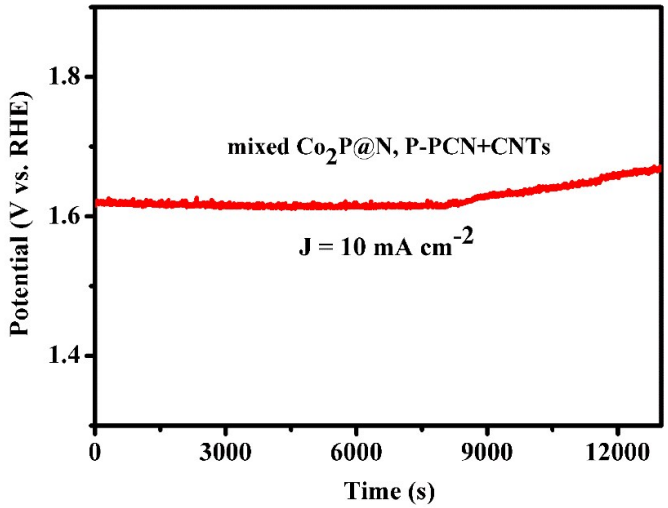

Fig. S12 Chronopotentiometry curve of physically mixed Co_2P@N, P-PCN+CNTs at a current density of 10 mA cm^{-2} in 1.0 M KOH.

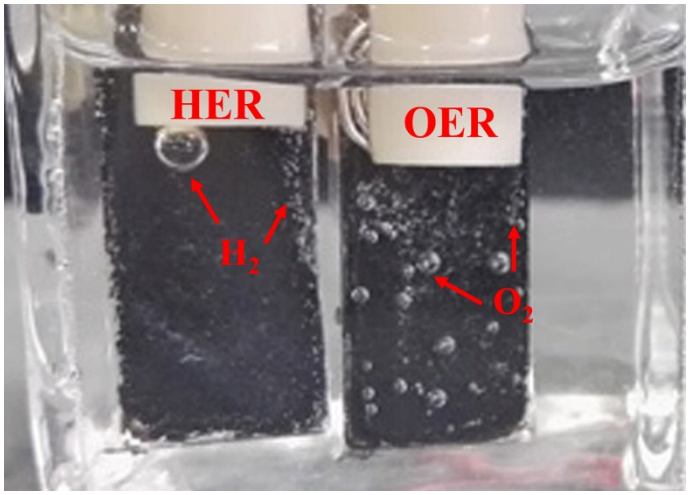

Fig. S13 The photograph of overall water splitting powered by a battery with a nominal voltage of 1.5 V.

Table S1 XPS results of Co_2P@N, P-PCN/CNTs on the atomic percentages of C, O, N, P and the Co distributions.

C (%)	O (%)	N (%)	P (%)	Co (%)	N distribution (%)			
					pyridinic N	pyrrolic N	graphitic N	oxygenated N
74.91	3.27	9.43	9.38	3.01	38.74	27.17	28.58	5.51

Table S2 Comparison of the OER activity for several recently reported high performance OER catalysts.

Catalyst	**Onset potential (V)**	**η@10.0 mA cm^{-2} (V)**	**Tafel slope (mV dec^{-1})**	**Electrolyte**	**Reference**
Co_2P@N, P-PCN/CNTs	1.46	0.28	49	1.0 M KOH	This work
Ni–Co ADHs nanocages	1.50	0.35	65	1.0 M KOH	[1]
Co-P/NC	~ 1.50	0.35	52	1.0 M KOH	[2]
N-doped graphene-CoO	~ 1.52	0.34	71	1.0 M KOH	[3]
CQDs/SnO_2–Co_3O_4	1.51	~0.33	60	1.0 M KOH	[4]
$CuCo_2O_4$/NrGO	~1.50	0.36	64	1.0 M KOH	[5]
Co_3O_4@C-MWCNTs	1.50	0.32	62	1.0 M KOH	[6]
$Co_{0.5}Fe_{0.5}S$@N-MC	1.6	0.64	159	1.0 M KOH	[7]
CNTs-Au@Co_3O_4	1.52	0.35	68	1.0 M KOH	[8]
Au@Co_3O_4/C	1.52	0.38	60	0.1 M KOH	[9]
$Zn_xCo_{3-x}O_4$ nanowire array	~ 1.50	0.32	51	1.0 M KOH	[10]

$Ni_xCo_{3-x}O_4$ nanowire	~ 1.58	~ 0.37	64	1.0 M KOH	[11]
$Mn_3O_4/CoSe_2$	/	0.45	49	0.1 M KOH	[12]

Notes: For the convenience of comparison, the measure potentials vs. Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale accorting to the Nerst equation ($E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.198$).

Table S3 Comparison of HER performance in 1.0 M KOH solution for Co_2P@N, P-PCN/CNTs with other non-noble metal electrocatalysts.

Catalyst	**Onset potential (V)**	**η@10.0 mA cm^{-2} (V)**	**Tafel slope (mV dec^{-1})**	**Reference**
Co_2P@N, P-PCN/CNTs	33	154	52	This work
MoC_x	25	151	59	[13]
CoNi@NC	~ 0	142	104	[14]
Cu_3P NW/CF	/	143	67	[15]
CoP/RGO	/	~ 250	104.8	[16]
Co_2P nanorods	70	134	71	[17]
CoO_x@CN	85	232	/	[18]
MoS_{2+x}/FTO	/	310	/	[19]
CoP/CC	/	209	129	[20]
Co-NRCNTs	100	370	/	[21]
FeP NAs/CC	~ 20	218	146	[22]

Table S4 Comparison of OER and HER performance in 1.0 M KOH solution for Co_2P@N, P-PCN/CNTs with other non-noble metal bifunctional electrocatalysts.

Catalyst	H_{OER}@10.0 mA cm^{-2}	H_{HER}@10.0 mA cm^{-2}	E (V)[1]	Reference
Co_2P@N, P-PCN/CNTs	280	154	1.64	This work
Ni_5P_4	340	150	~ 1.7	[23]
CoO_x@CN	260	235	~ 1.3	[18]
NiFe LDH/Ni foam	240	210	1.7	[24]
PCPTF	~ 310	~ 380	/	[25]
CoP/rGO	340	150	1.7	[26]
Co-P film	345	94	~ 1.64	[27]
Co-P/NC	319	154	~ 1.71	[2]
NiSe/Ni foam	/	96	1.63	[28]
PNC/Co	~ 370	298	1.64	[29]

Notes: [1] represents the overall water splitting overpotentials at 10 mA cm^{-2}.

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