Electronic Supplementary Information (ESI)

Organophosphoric Acid-Derived CoP Quantum Dots@S, N-Codoped Graphite Carbon as Trifunctional Catalysts for Overall Water Splitting and Zn-air Batteries

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1. Supplementary Figures

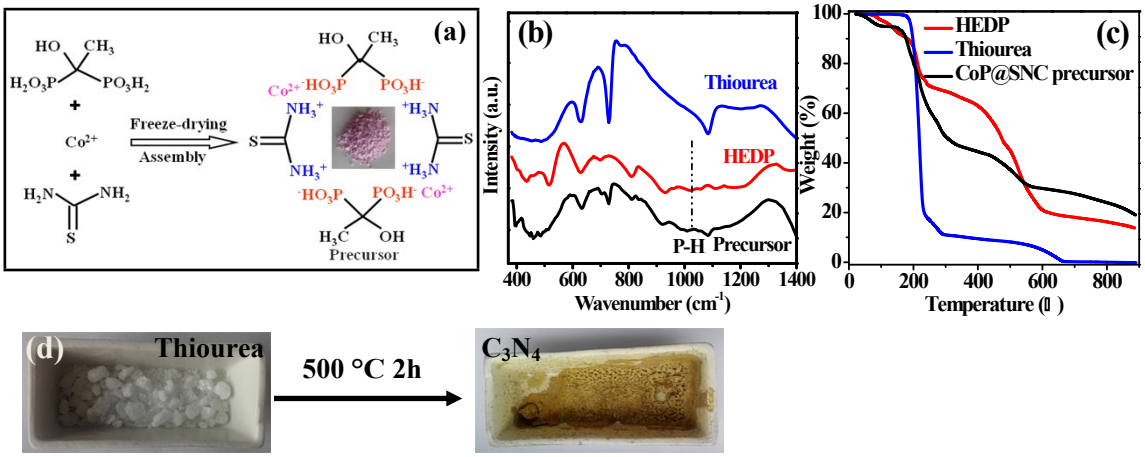

Fig. S1 (a) Illustration of the freeze-drying process and the cross-linking effect. (b) FT-IR spectra and (c) TGA curves for CoP@SNC precursor, HEDP, and thiourea. (d) Photograps of thiourea annealed before and after 500 ºC.

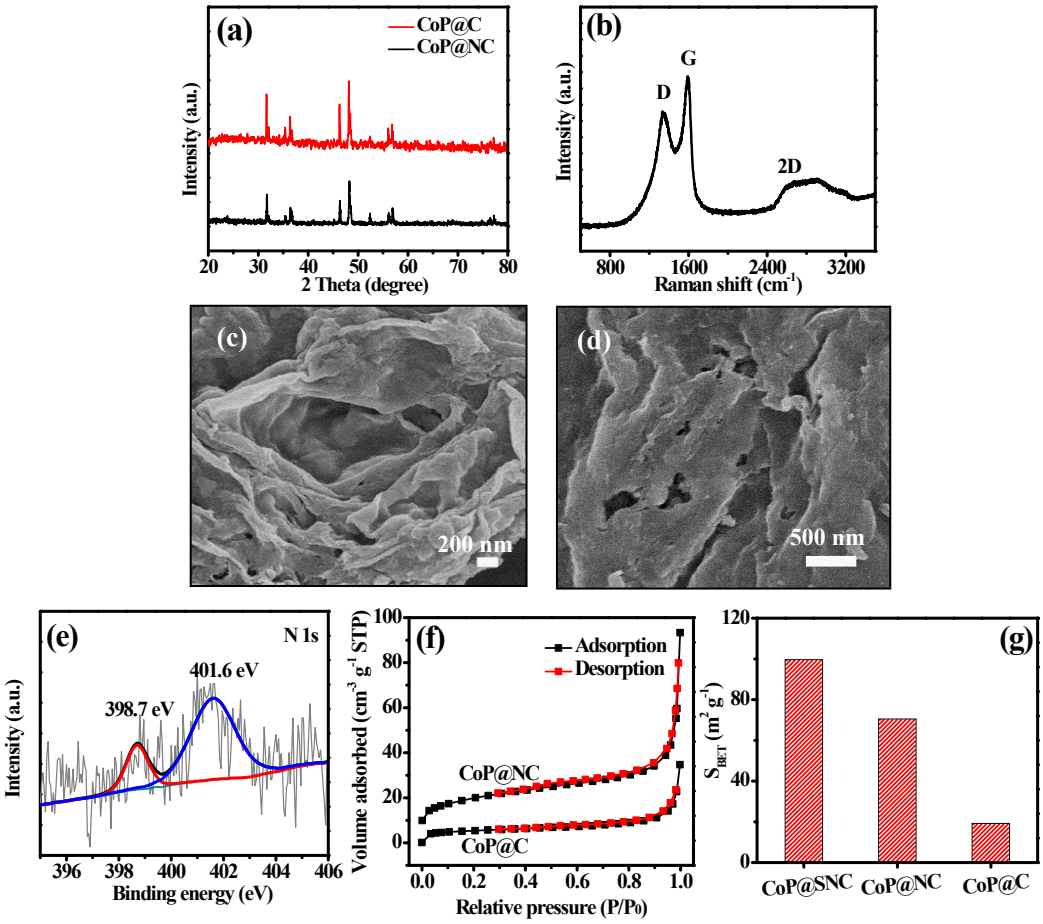

Fig. S2 (a) XRD patterns of CoP@NC and CoP@C. (b) Raman spectrum of CoP@NC. FE-SEM

images of CoP@NC (c) and CoP@C (d). XPS spectra of N1s (e). (f) N_2 adsorption-desorption curves of CoP@NC and CoP@C. (g) BET data for CoP@SNC, CoP@NC and CoP@C.

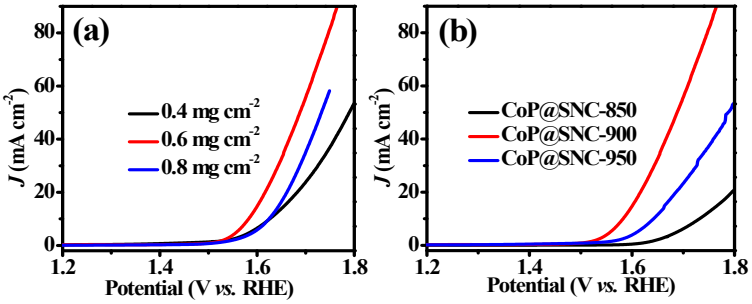

Fig. S3 OER LSVs in 1.0 M KOH for CoP@SNC with different mass loadings (a) and CoP@SNC catalysts prepared at different temperatures (b).

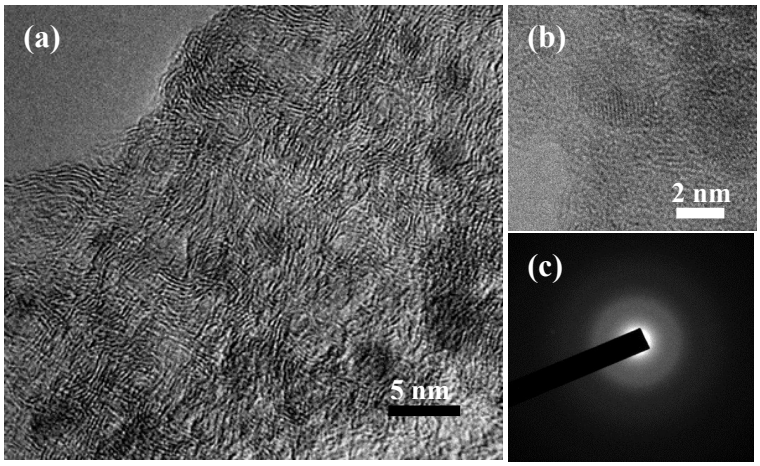

Fig. S4 TEM image (a), HRTEM image (b), and corresponding SEAD pattern of CoP@SNC after 10 h OER test at the potential of 1.58 V *vs.* RHE in 1.0 M KOH.

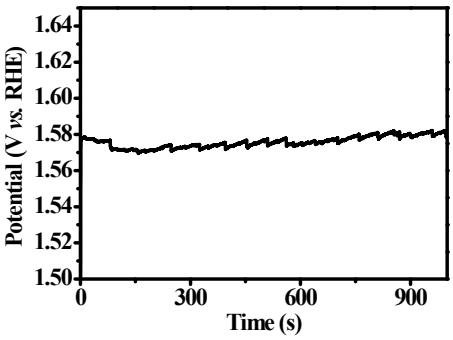

Fig. S5 Chronopotentiometric curve of CoP@SNC tested at the current density of 10.0 mA cm^{-2}

in 1.0 M KOH.

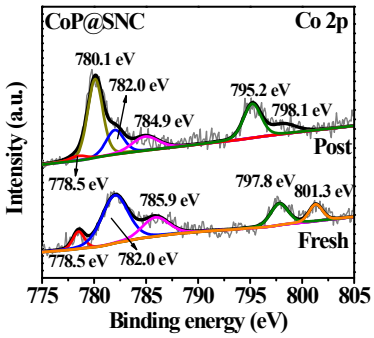

Fig. S6 High-resolution XPS spectra of Co 2p for CoP@SNC before and after OER test.

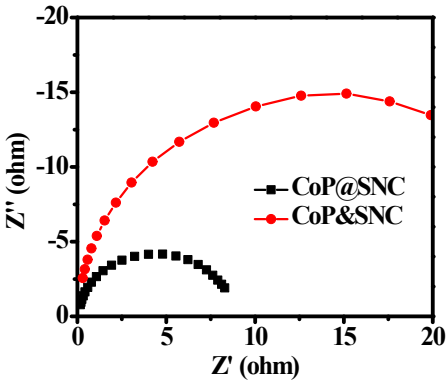

Fig. S7 EISs of CoP@SNC and CoP&SNC tested at 1.58 V *vs.* RHE.

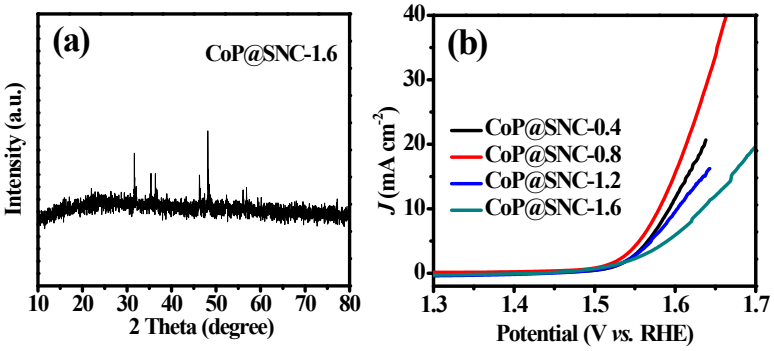

Fig. S8 (a) XRD pattern of CoP@SNC-1.6. (b) OER LSVs of CoP@SNC-X (X = 0.4, 0.8, 1.2, 1.6

mmol, stands for different molar amounts of Co salt).

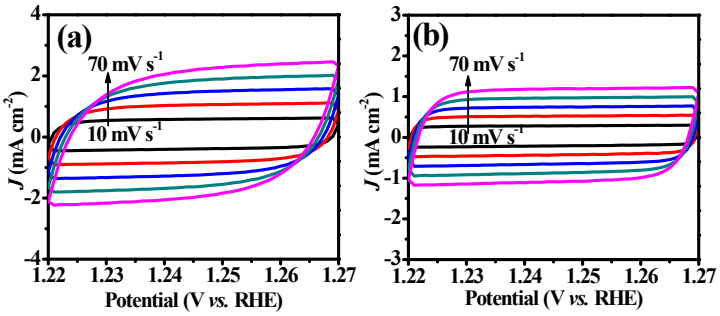

Fig. S9 CVs for (a) CoP@NC and (b) CoP@C tested at the potential range from 1.22 to 1.27 V *vs.* RHE under the scan rates from 10 to 50 mV s^{-1}.

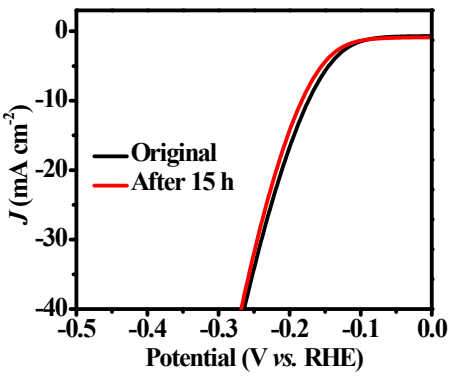

Fig. S10 HER LSVs tested before and after 15 h chronoamperometric response for CoP@SNC.

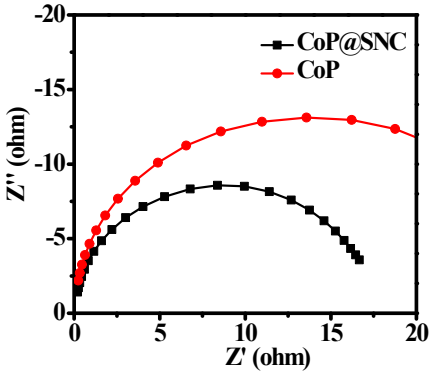

Fig. S11 EISs of CoP@SNC and CoP tested at -0.35 V *vs.* RHE.

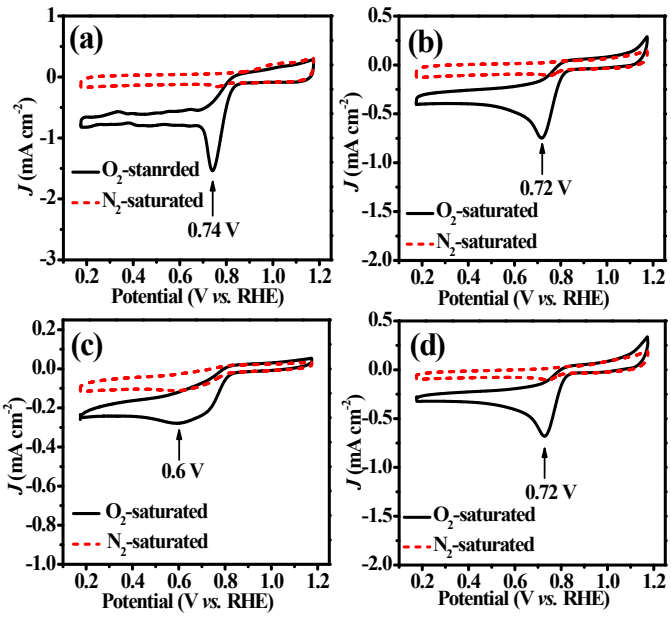

Fig. S12 CV curves of CoP@NC (a), CoP@C (b), CoP (c), and SNC (d) in 0.1 M KOH with a scan rate of 10 mV s^{-1}.

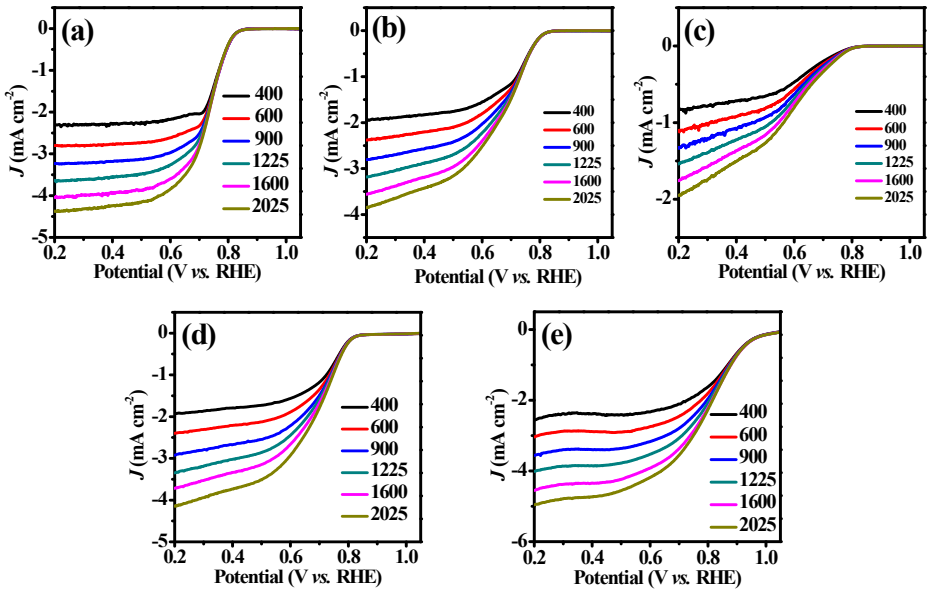

Fig. S13 LSV curves of CoP@NC (a), CoP@C (b), CoP (c), SNC (d), and Pt/C (e) in O_2-saturated 0.1 M KOH with a scan rate of 10 mV s^{-1}.

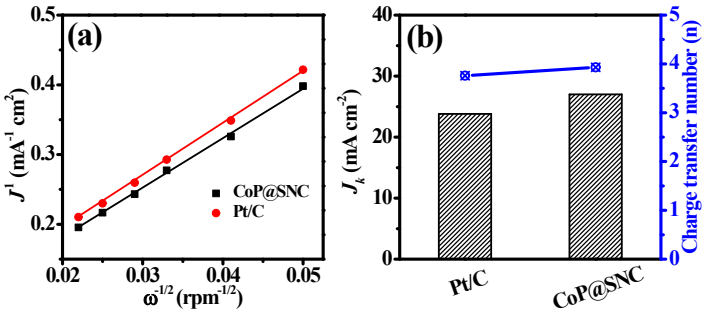

Fig. S14 (a) K–L plots obtained from the RDE data at 0.35 V *vs.* RHE for CoP@SNC and Pt/C. (c) Summary of the kinetic current (J_K) and the electron-transfer number (n) on the basis of RDE data at 0.35 V for CoP@SNC and Pt/C.

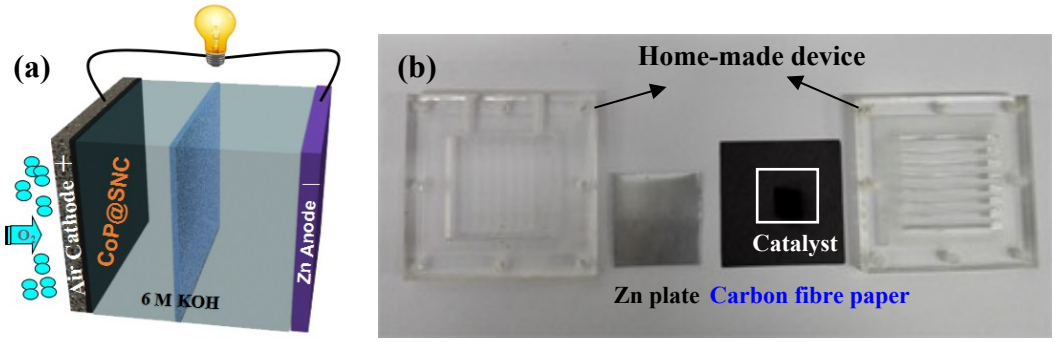

Fig. S15 (a) A schematic of the rechargeable Zn-air battery; (b) A representative photograph image of the home-made type Zn-air battery.

2. Supplementary Tables

Table S1 Comparison of the HER activity for our catalyst (CoP@SNC) with several recently reported highly active transition-/noble-metal and non-metal catalysts supported on different substrates in 1.0 M KOH.

Catalysts	Mass loading (mg cm^{-2})	Overpotential @ 10.0 mA cm^{-2} (mV *vs.* RHE)	Tafel slope (mV dec^{-1})	Substrate	Ref.
CoP@SNC	**0.6**	**174**	**82**	**Glassy carbon**	**This work**
CoP/CC	0.92	209	129	Carbon cloth	1
CoP/Ti	N.A.	108	52	Ti mesh	2
np-CoP /Ti	N.A.	150 [a]	71	Ti plate	3
CoP/MNA	6.2	54	51	Ni foam	4
FeP NAs/CC	1.5	218	146	Carbon cloth	5
CoO_x@CN	0.12	232	N.A.	Glassy carbon	6
MoP	0.86	~150	48	Glassy carbon	7
Co-NRCNTs	0.28	370	N.A.	Glassy carbon	8
MoC_x	0.8	151	59	Glassy carbon	9
MoB microparticles	N.A.	>210	59	Glassy carbon	10
MoS NAs	N.A.	190	100	Ti plate	11

Note: a at current density of 20 mA cm^{-2}.

Table S2. Comparison of the ORR activity for our catalyst (CoP@SNC) with previously reported materials in 0.1 M KOH.

Catalysts	Loading (mg cm^{-2})	ORR peak (V *vs.* RHE)	Onset (V *vs.* RHE)	Half-wave (V *vs.* RHE)	Ref.
CoP@SNC	**0.6**	**0.81**	**0.87**	**0.79**	**This work**
CoP NCs	0.286	N.A.	0.8	0.7	12
Co_xP-CNTs	N.A.	-0.24 [a]	N.A.	-0.2 [a]	13
Co_2P NRs	0.142	N.A.	N.A.	-0.196 [a]	14
Co_2P@CoNPG-800	2.0	0.78	0.87	0.8	15
Fe/Co-NpGr	0.71	0.80	0.93	N.A.	16
CoO/C	N.A.	N.A.	0.83	0.77	17
Co@Co_3O_4@C-CM	0.1	0.79	0.93	0.81	18
Co/N-HCOs	0.287	0.79	0.92	0.81	19
N,S,O-doped nanoporous carbons	0.203	0.753	~0.96	0.74	20
ZIF derived N-doped carbons	0.2	0.769	0.915	N.A.	21

Note: a, V *vs.* Ag/AgCl

Table S3 Comparison of the rechargeable Zn-air batteries based on CoP@SNC with several key parameters with several recently reported highly active transition-/noble-metal and non-metal catalysts.

Air catalyst used	Cycling conditions and stability	Voltage polarization V (@ *j*, mA cm^{-2})	Ref.
CoP@SNC	**10 mA cm^{-2}, 600 s per cycle periods for 180 cycles: polarization increased ~0.06 V at the end**	**0.83 (10)**	**This work**
MnO_2 nanotube and carbon nanotube composite	~8 mA cm^{-2}, 600 s per cycle periods for 50 cycles: polarization increased ~0.4 V at the end	1.5 (20)	22
Co_3O_4 nanoparticles decorated carbon nanofibers	2 and 20 mA cm^{-2}, 1 h per cycle periods for 160 and 55 cycles: polarization increased 0.09 V at the end for 20 mA cm^{-2}	0.7 (2) 0.85 (20)	23
Tri-electrode: CoO/N–CNT + NiFe LDH	20-50 mA cm^{-2}, 4-20 h per cycle period for >200 h: negligible voltage change at the end	0.7 (20)	24
Co_3O_4 NP modified MnO_2 nanotubes	15 mA cm^{-2}; 14 min per cycle period for 60 cycles; voltage gap increased ~0.3-0.4 V at the end	~0.85 (15)	25
$ZnCo_2O_4$/N–CNT	10-100 mA cm^{-2}, 20 min per cycle for 17 cycles (340 min); negligible voltage change at the end	0.84(10-100)	26
TCCN	20 mA cm^{-2}, 10 min per cycle for 15 cycles; negligible voltage change at the end	1.68 (20)	27

3. Supplementary video

Video S. CoP@SNC coated on nickel foam was used as the working electrode for overall water splitting powered by two series-connected home-made Zn-air batteries based on CoP@SNC as the air cathode. This video instinctively reflects that these two series-connected home-made Zn-air batteries can afford a large cell voltage to power water splitting device. And, CoP@SNC can also work as an efficient electro-catalyst for generating O_2 and H_2 gases, indicating its excellent overall water splitting performance. Both of these reveal that CoP@SNC can work as multi-functional catalysts for energy storage and conversion.

4. Supplementary references

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