Hollow Co_2P nanoflowers organized by nanorods for ultralong cycle-life supercapacitors

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The theoretical capacity value of Co_2P and Ni_2P

The formula used to calculated theoretical capacity: C=n×F/(V×M), where n is the moles of charge transferred per mole of active material, F is Faraday's constant (96485.3383 C mol^{-1}), M is the molar mass of the active material, and V is the potential range.[1] For comparison, V is supposed to be 0.5 V for both sample here.

For Co_2P, $C_1=(4-\delta_1)$x2601 F g^{-1}, $(0<\delta_1<1)$;[2, 3]

For Ni_2P, $C_1=(3-\delta_2)$x2601 F g^{-1}, $(0<\delta_2<1)$;[2, 3]

So cobalt phosphides should have a higher theoretical capacity than nickel phosphides.

The details of the calculation methods

The electronic band structure of Co_2P is evaluated by the density functional theory calculations performed using CASTEP.[4] The OTFG ultrasoft pseudo-potentials and generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional are adopted. Plane-wave basis sets with the energy cutoff of 600 eV are used to expand the electronic wave-functions. The residual energy are less than 10^{-6} eV for each atom. A Γ center (9×13×7) Monkhorst-Pack grid of k points is used for the DOS calculations. Co_2P have the C_{23} orthorhombic structure with the space group D_{2h}^{16}(Pnma). The lattice constants and atomic positional parameters of Co_2P are shown in below.[3]

	a (nm)	b (nm)	c (nm)		x	y	z
Co_2P	0.5646	0.3513	0.6608	Co_I	0.8560	0.2500	0.0647
				Co_{II}	0.9685	0.2500	0.6657
				P	0.2461	0.2500	0.1249

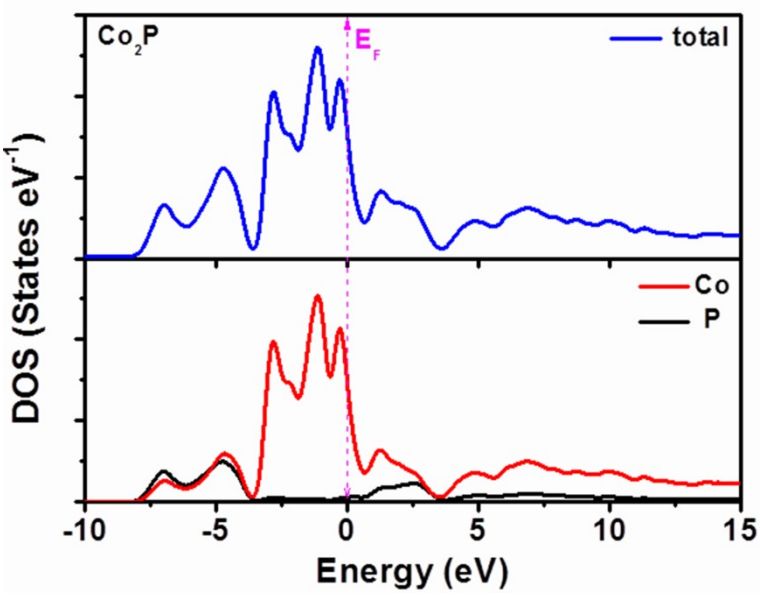


Fig. S1 Total densities of states and partial densities of states curves of Co_2P.

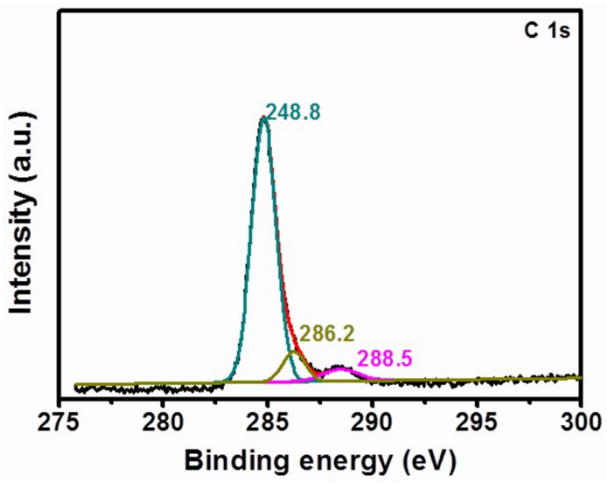


Fig. S2 High resolution XPS spectra of C 1s for Co_2P HNF.

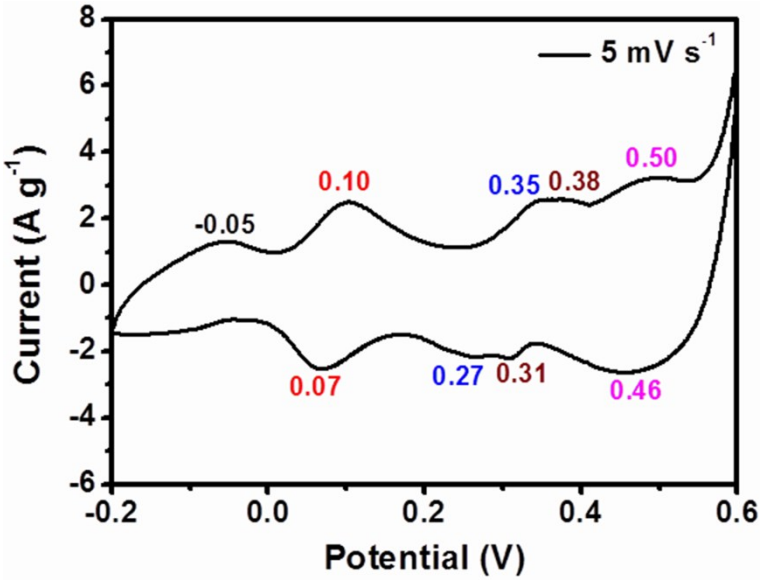


Fig. S3 CV curve of Co_2P HNF at a scan rate of 5 mV·s^{-1}.

Electrocatalytic Activity toward OER

OER activity was evaluated in a standard three-electrode cell with platinum foil as the counter electrode and Ag/AgCl (KCl saturated) as the reference electrode. To prepare the working electrode, 7.0 mg of Co_2P catalyst was dispersed in 2 mL of solution (1 mL of DI water, 0.88 mL of isopropanol and 0.12 mL of 5 wt.% Nafion solution) by ultrasonication. Then, 11 μL of the catalyst suspension was carefully pipetted onto the glass carbon (GC) electrode surface with a diameter of 5 mm. The coated electrode was dried in air. The catalyst loading amount is 0.2 mg cm^{-2} on the GC electrode. Potentials were referenced to a reversible hydrogen electrode (RHE): E(RHE) = E(Ag/AgCl) + (0.1976 + 0.059 pH). Linear sweep voltammetry (LSV) was recorded in O^2-saturated 1.0 M KOH (pH = 13.62) at a scan rate of 5 mV s^{-1} to obtain the polarization curves. The long-term stability tests were performed by continuous LSV scans at a sweep rate of 100 mV s^{-1}. The polarization curves were all corrected by 95% iR compensation. Cyclic voltammetry curves were conducted from 0.80 to 0.88 V (vs. RHE) without faradaic processes at different scan rates (5 to 12.5 mV/s). The I−t curve was measured under a fixed overpotential of 0.37 V.

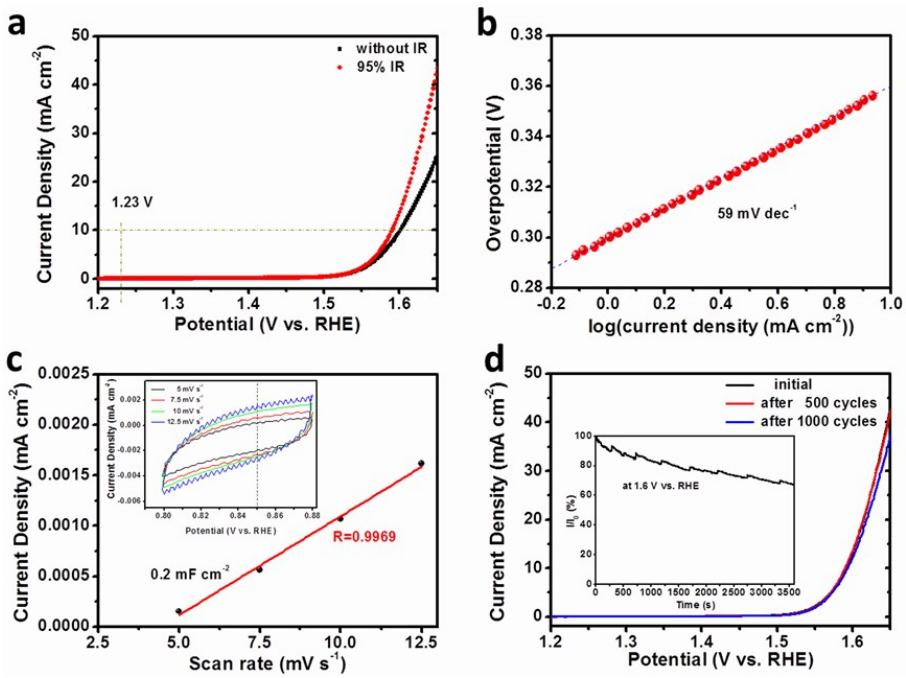
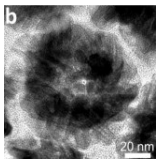
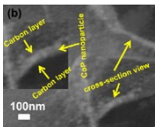
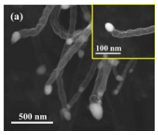
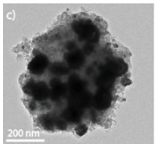
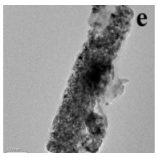
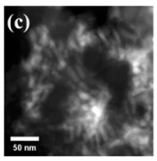
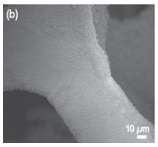
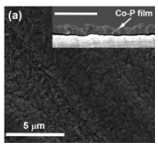
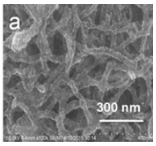
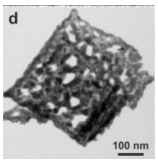
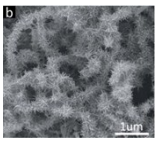


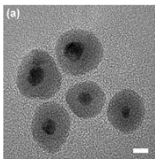
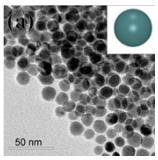
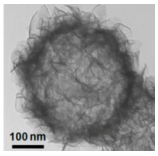
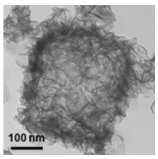
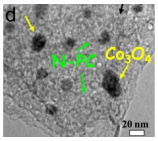
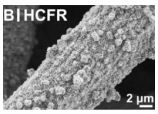
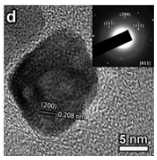
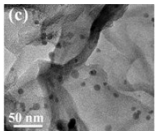
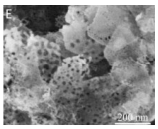
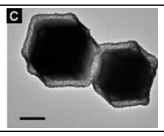
Fig. S4 Electrochemical performance of the OER catalysts in 1 M KOH: (a) The polarization curves of Co_2P HNF. (b) Tafel curves of Co_2P HNF. (c) Scan rate

dependence of the average apacitive currents at 0.85 V vs. RHE of Co_2P HNF. Inset is the cyclic voltammogram curves in a potential window without faradaic processes. (d) The stability of Co_2P HNF modified electrode before and after LSV testing for 500 and 1000 cycles, respectively. Inset is the current-time plot of Co_2P HNF electrode with a constant applied potential of 1.60 V vs. RHE.

The OER activities of Co_2P HNF were evaluated in a high pure O_2-saturated 1.0 M KOH solution using a standard three electrodes setup. As shown in Fig. S4a, Co_2P HNF affords a current density of 10 mA cm^{-2} at 1.590 V (vs. RHE). The Tafel slope of Co_2P HNF, which is usually used to evaluate the efficiency of the catalytic reaction,[5] is also determined to be 59 mV dec^{-1} (Fig. S4b). Furthermore, the electrochemically active surface area of Co_2P HNF can be estimated from the electrochemical double-layer capacitances of the catalytic surface by measuring the CV curves in the potential range of 0.80 − 0.88 V (vs. RHE) without redox process (Fig. S4c).[6] The capacitance of Co_2P HNF is measured to be 0.20 mF cm^{-2}. To assess the durability of Co_2P HNF electrocatalyst, continuous linear potential sweeps were conducted repeatedly on the electrode. Co_2P HNF exhibits inherent stability after 500 continuous cycles, and only a little anodic current loss is observed after 1000 cycles (Fig. S4d). The stability of the Co_2P HNF is further tested by using a chronoamperometric method at 1.60 V (vs. RHE), as shown in Fig. S4d. The OER activity retains 67% after 1 h, which could be ameliorated by improving adhesion of the powder to the electrode.[7] The OER activity of Co_2P HNF is also compared with the previoursly previously transition metal compounds (Table S1). Though our perpared Co_2P HNF is not as good as the reported transition metal phosphide, it outperforms many reported transition metal oxides or hydroxides.

Electrocatalysts	**Morphology**	**Electrolyte**	**Loading (mg cm^{-2})**	**η @10 mA cm^{-2} (mV)**	**Tafel slope (mV dec^{-1})**	**Ref.**
Co_2P HNF		1.0 M KOH	0.2	360	59	**This work**

Sandwich-like CoP/C nanocomposites		1.0 M KOH	0.36	330	53	8
Co_2P/CNT		1.0 M KOH	0.75	292	68	9
$Cu_{0.3}Co_{2.7}P$/NC		1.0 M KOH	0.4	190	44	10
CoP NR/C		1.0 M KOH	0.71	320	71	11
CoP nanoparticles		0.1 M KOH	0.4	360	66	12
CoP nanorod arrays on Ni foam		1.0 M KOH	6.2	290	65	13
Co-P film		1.0 M KOH	1.0	345	47	14
CoP/CNT		0.1 M NaOH	0.285	400	80	15
Carbon coated Ni-P		1.0 M KOH	0.20	300	64	**16**
FeP@CNT		1.0 M KOH	0.204	300	53	**17**

Au@$Ni_{12}P_5$		1.0 M KOH	0.13	340	49	7
$Ni_{12}P_5$		1.0 M KOH	0.13	380	43	
Hollow fluffy $Co(OH)_2$		PH 14 KOH	0.14	422	93	18
Hollow fluffy Co_3O_4		PH 14 KOH	0.14	409	70	
Co3O4/N-PC		0.1 M KOH	0.354	390	72	19
NiCo LDH		1.0 M KOH	0.17	370	40	20
Hollow CoO		1.0 M KOH	0.20	375	55	21
PGE-CoO		0.1 M KOH	0.524	348	79	6
Porous FeNi Oxides nanosheets		1.0 M KOH	0.254	213	32	22
$Co_3O_4/NiCo_2O_4$ DSNCs		1.0 M KOH	1.0	340	88	5

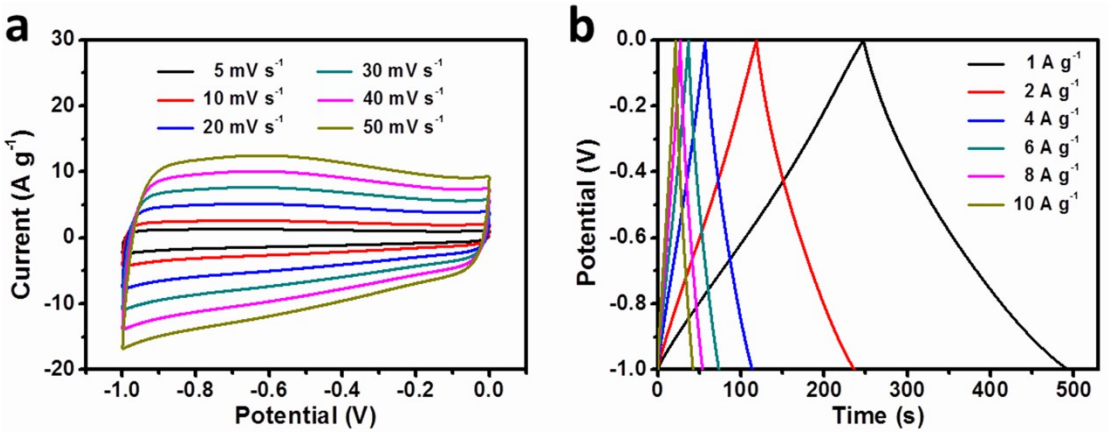


Fig. S5 (a) CV curves at different scan rates and (b) CP curves at different current densities of the active carbon (AC).

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