Electronic Supplementary Information

Sea-urchin-like nickel−cobalt phosphide/phosphate composites as advanced battery materials for hybrid supercapacitors

Hai Chao Chen,*[,a] Sipeng Jiang,[a] Binghui Xu,[a] Chenghao Huang,[a] Yuzhen Hu,[a] Yanliang Qin,[a] Maoxia He[b] and Haijie Cao*[,a]

[a]*Institute of Materials for Energy and Environment, School of Materials Science and Engineering, Qingdao University, Qingdao 266071, P. R. China.*

[b] *Environment Research Institute, Shandong University, Jinan, 250100, P. R. China.*

*Corresponding authors. E-mail: chenhchust@126.com, chenhc@qdu.edu.cn (H. C. Chen); caohj1582@hotmail.com (H. Cao)

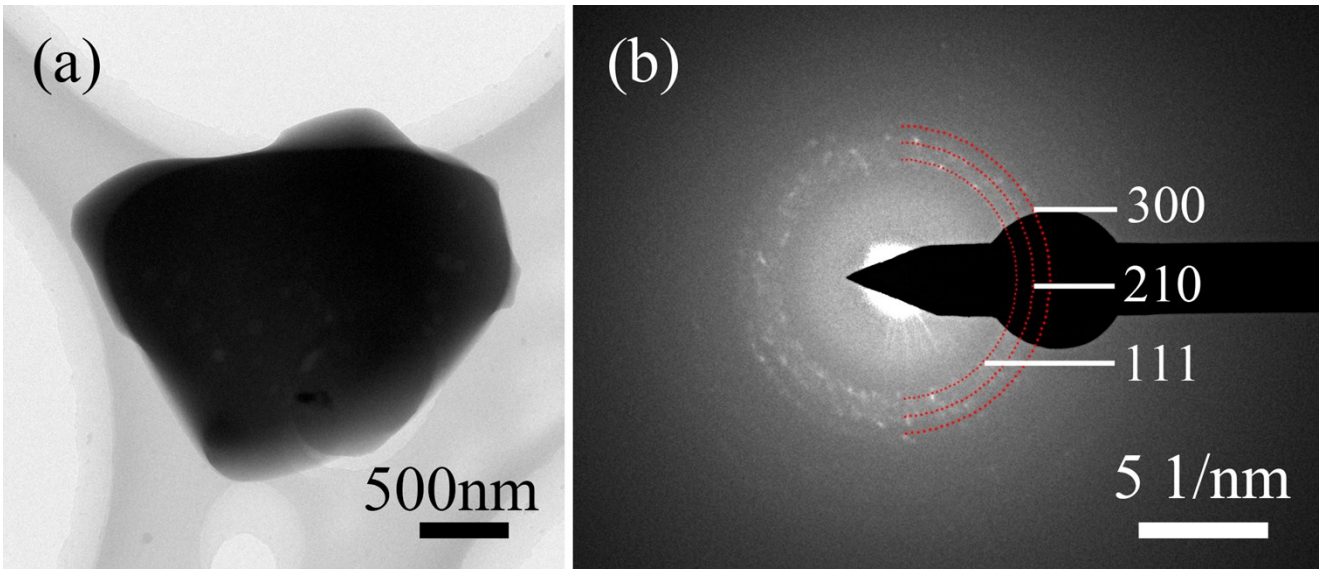

Fig. S1 (a) TEM image and (b) selected area electron diffraction pattern of the Ni−P/PO_x. The diffraction rings in the selected are electron diffraction pattern can be assigned to the 111, 210 and 300 crystal plane systems of Ni_2P.

For the theory calculations, all the calculations were carried out at Materials Studio program based on the density functional theory using the generalized gradient approximation (GGA) and following the Perdew-Bueke- Ernzerhof scheme (PBE) for the exchange–correlation potential. An energy cutoff of 350 eV is used for plane wave expansion. The energy and self-consistent field tolerances were 5.0×10^{-6} eV per atom and 5.0×10^{-7} eV per atom, respectively. The 5×5×8 Monkhorst-Pack grid of *k*-points was used. The optimized lattice parameters of Ni_2P are 5.869×5.869×3.383 Å which is in good agreement with the experimental values (5.867 × 5.867 × 3.389 Å).[S1]

Fig. S2 shows the colored maps of the electric density and its difference of a 2×2×2 supercell of Ni_2P bulk. The bulk compositions of Ni_2P is Ni_6P_3. Larger bond lengths are observed for P–Ni_B bonds (2.348 Å) compared to the P–Ni_A bonds (2.265 Å) in Ni_2P bulk, indicating stronger interaction of P atoms with the Ni_A than Ni_B. The electron density as well as its difference maps shown in Fig. S2 demonstrate that Ni_A has stronger covalent properties with P than Ni_B. It is found that the electrons slightly drift from the P 3*p* orbitals to Ni 3*d* orbitals (especially Ni_A) by analysis of the Hirshfeld charge.

As shown in Table S1, the volumes of bulks are slightly reduced when Ni ions are replaced by Co ions. Besides, Ni_BCo_AP has a lower cohesive energy (–5.31 eV) than Ni_ACo_BP (–5.22 eV), indicating that Ni_BCo_AP is more stable than Ni_ACo_BP. The formation energies of Ni_BCo_AP and Ni_ACo_BP are –1.00 and –0.24 eV, respectively. The result implies that cobalt ions are prior to replace the Ni_A ions.

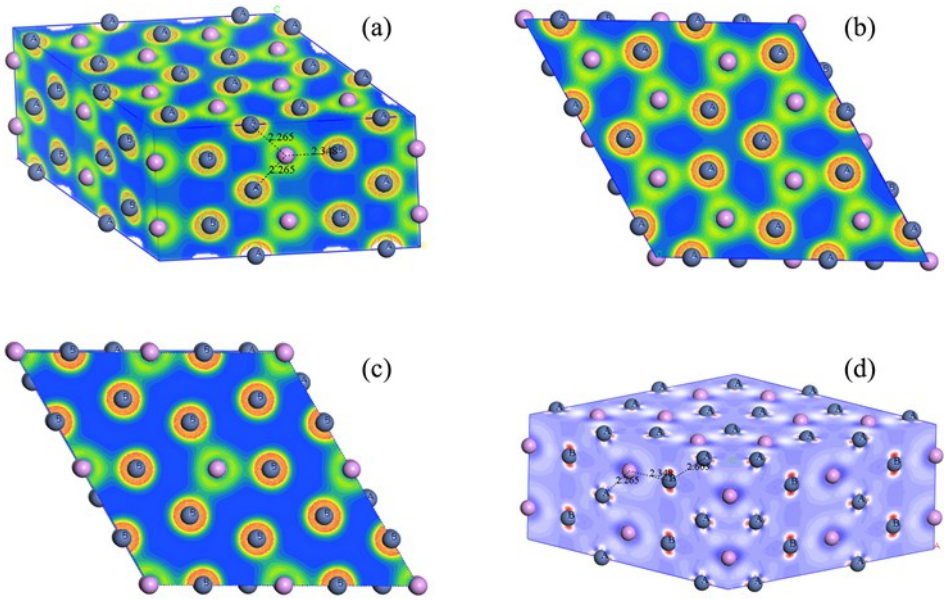

Fig. S2 Maps of electron densities for the (a) Ni_2P (2×2×2) bulks, (b) Ni_AP plane and (c) Ni_BP plane. (d) The electron density difference of Ni_2P (2×2×2) bulks.

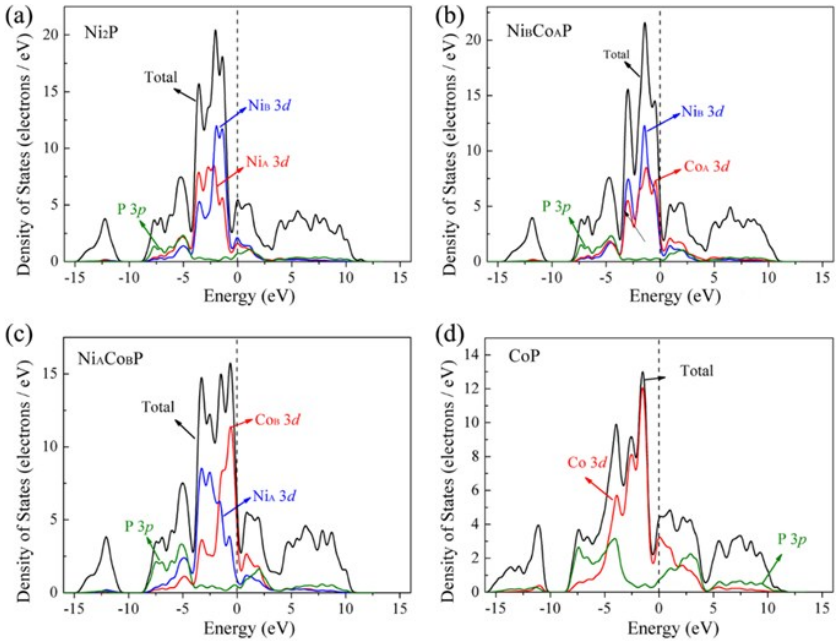

Fig. S3 Total and partial density of states of (a) Ni_2P, (b) Ni_BCo_AP, (c) Ni_ACo_BP and (d) CoP bulks.

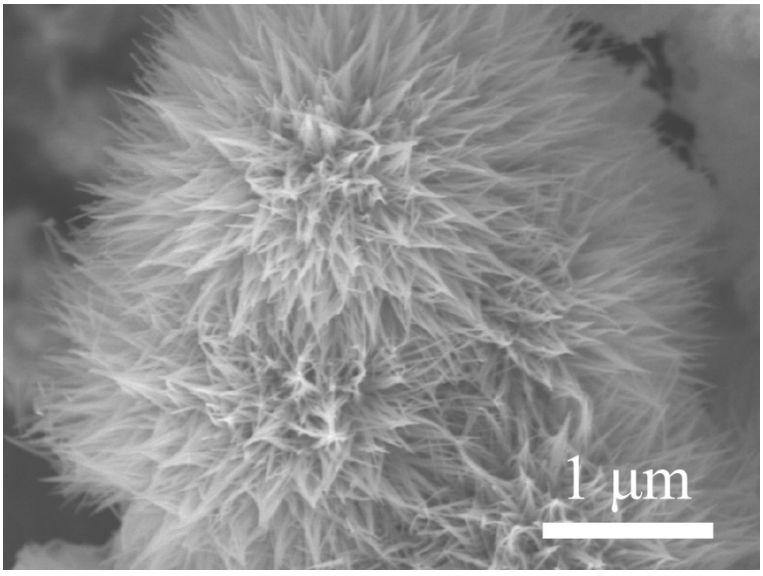

Fig. S4 SEM image of the Ni–Co oxide with a Ni to Co ratio of 1:1.

Table S1 Detailed parameters of Ni_2P, Ni_BCo_AP, Ni_ACo_BP and CoP bulks.

	Ni_2P	Ni_BCo_AP	Ni_ACo_BP	CoP
Composition	Ni_6P_3	Ni_3Co_3P	Ni_3Co_3P	Co_4P_4
Point group	P-62M	P-62M	P-62M	PNMA
Lattice parameters (Å)	5.87×5.87×3.38	5.82×5.82*3.33	5.81×5.81×3.35	5.05×3.27×5.53
Volume	116.528	112.824	112.826	91.369
N_e in -1~0 eV	4.2965	12.4002	12.6238	3.2012
N_e in -0.5~0 eV	2.0381	5.2224	5.3252	1.6624
Number of electrons around Fermi level (-0.5~0 eV)				
Ni-3*d*	1.4489	2.0294	0.8670	
Co-3*d*		2.7079	3.9974	1.2032
P-3*p*	0.3278	0.2065	0.2408	0.2426

Reference

S1 R. Fruchart, A. Roger, J. P. Senateur. Crystallographic and Magnetic Properties of Solid Solutions of the Phosphides M_2P, M = Cr, Mn, Fe, Co, and Ni. *J. Appl. Phys.*, 1969, **40**, 1250–1257.