Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Phosphorization Boosts the Capacitance of Mixed Metal Nanosheet Array for High Performance Supercapacitor Electrode

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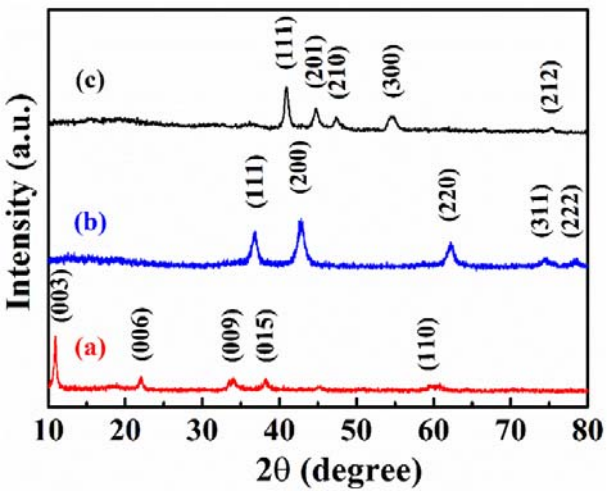

Figure S1. XRD patterns of (a) NiCo-LDH, (b) $NiCoO_2$ and (c) NiCoP nanopowders.

The diffraction peaks of the precursor (Fig. S1a) can be well indexed to NiCo-LDH with hydrotalcite-like LDH phase. After annealing treatment of the NiCo-LDH in Ar atmosphere, the sample shows five diffraction peaks located at 36.6, 42.6, 61.5, 73.7 and 77.7°, which can be assigned to the (111), (200), (220), (311) and (222) crystalline planes of face-centered cubic $NiCoO_2$ with a rock salt structure (PDF Card No. 10-0188). The NiCoP was chemically converted from NiCo-LDH precursor through thermal phosphorization treatment using $NaH_2PO_2 \cdot H_2O$ as phosphorus source. The corresponding XRD pattern (Fig. S1c) shows five diffraction peaks at 41.0, 44.8, 47.5, 54.4 and 75.3°, which can be well assigned to the (111), (201), (210), (300) and (212) crystalline planes of NiCoP with hexagonal structure. The XRD pattern of NiCoP matches well with JCPDS card No. 71-2336 with space group of *P-62m*.

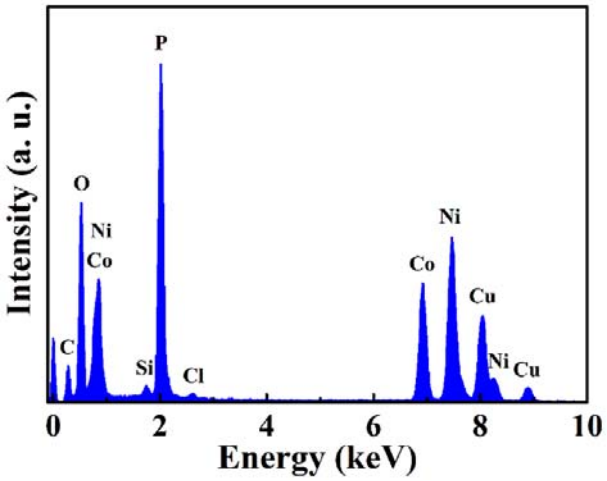

Figure S2. EDX spectra of the NiCoP@NF.

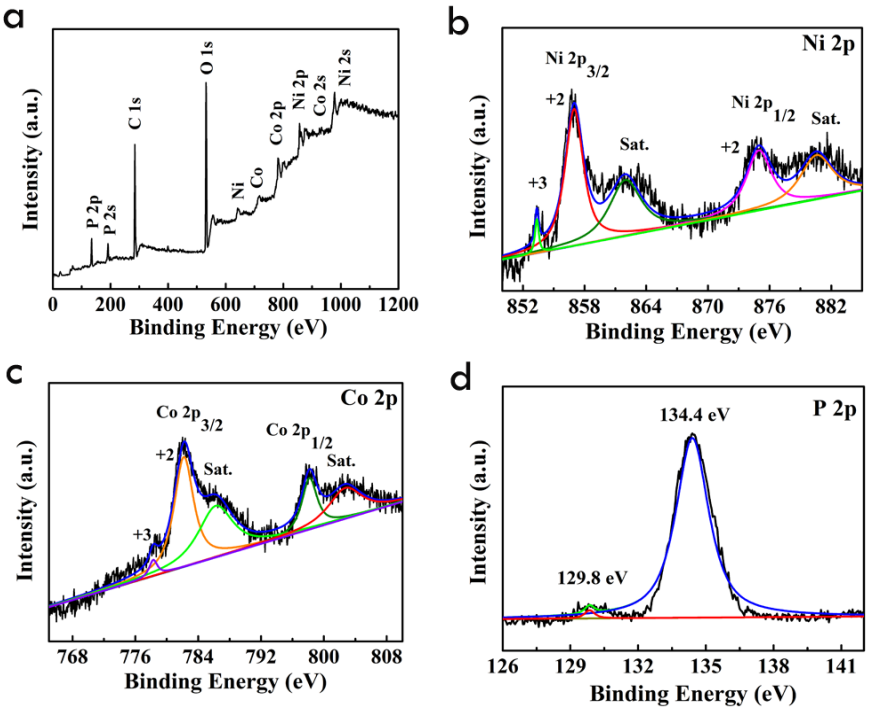

Figure S3. XPS spectra of NiCoP nanosheets: (a) wide scan, (b) Ni 2p, (c) Co 2p and (d) P 2p spectra.

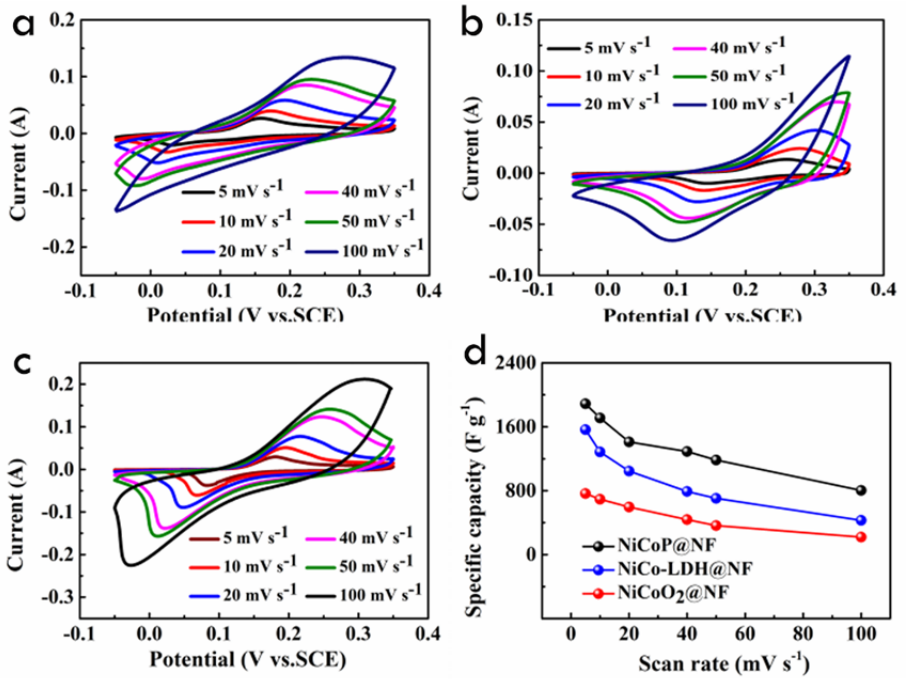

Figure S4. CV curves of (a) NiCo-LDH@NF, (b) $NiCoO_2$@NF, and (c) NiCoP@NF electrodes at different scan rates in 6 M KOH. (d) Comparison of the specific capacitances of NiCo-LDH@NF, $NiCoO_2$@NF, and NiCoP@NF electrodes at different scanning rates.

The CV curves of NiCo-LDH, $NiCoO_2$ and NiCoP@NF electrodes (Figure S4) show two distinct oxidation and reduction peaks. The peaks shown in the CV curves are correspond to the following redox reactions:

For NiCoP electrode:

$$NiCoP + 2OH^- \leftrightarrow NiP_{1-x}OH + CoP_xOH + 2e^- \quad (1)$$

$$CoP_xOH + OH^- \leftrightarrow CoP_xO + H_2O + e^- \quad (2)$$

For NiCo-LDH electrode:

$$NiCo(OH)_4 + 2OH^- \leftrightarrow NiOOH + CoOOH + 2H_2O + 2e^- \quad (3)$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \quad (4)$$

For $NiCoO_2$ electrode:

$$NiCoO_2 + 2OH^- \leftrightarrow NiOOH + CoOOH + 2e^- \quad (5)$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \quad (6)$$

The electrical double-layer capacitors have only physical charge accumulation happens at the interface of electrode and electrolyte during the charge/discharge processes. The pseudocapacitance electrode materials have reversible redox reactions at the surface and interior of electrodes in a certain voltage range, in addition to the physical charge accumulation at the interface. Therefore, the GCD curves show plateau.

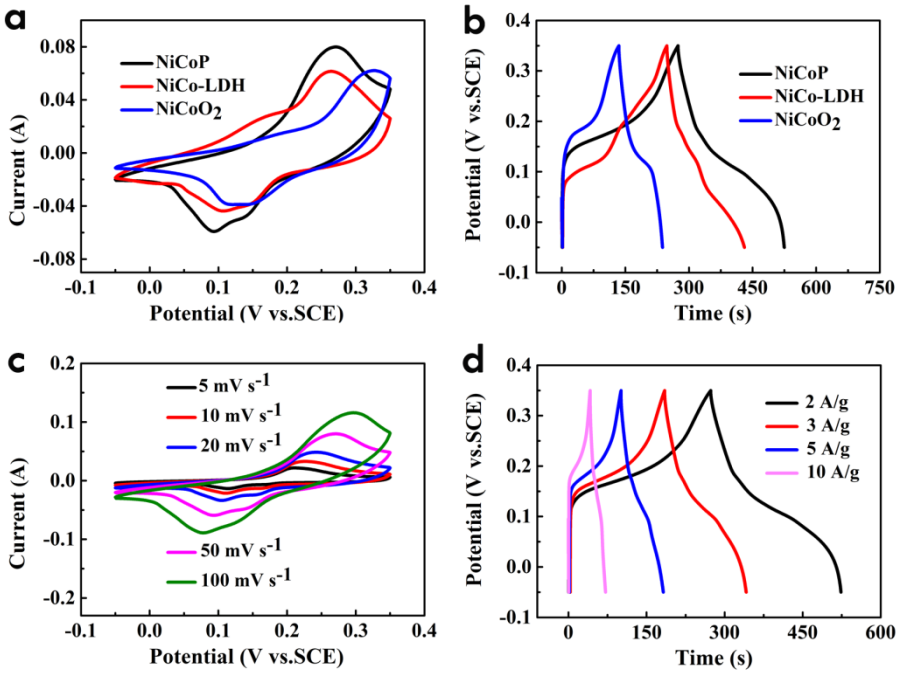

Figure S5. (a) The CV curves of NiCoP, NiCo-LDH and $NiCoO_2$ powders at a scan rate of 50 mV/s. (b) GCD curves of NiCoP, NiCo-LDH and $NiCoO_2$ powders at a current density of 2 A/g. (c) CV and (d) GCD curves of the NiCoP powders electrodes at different scan rates and current densities, respectively.

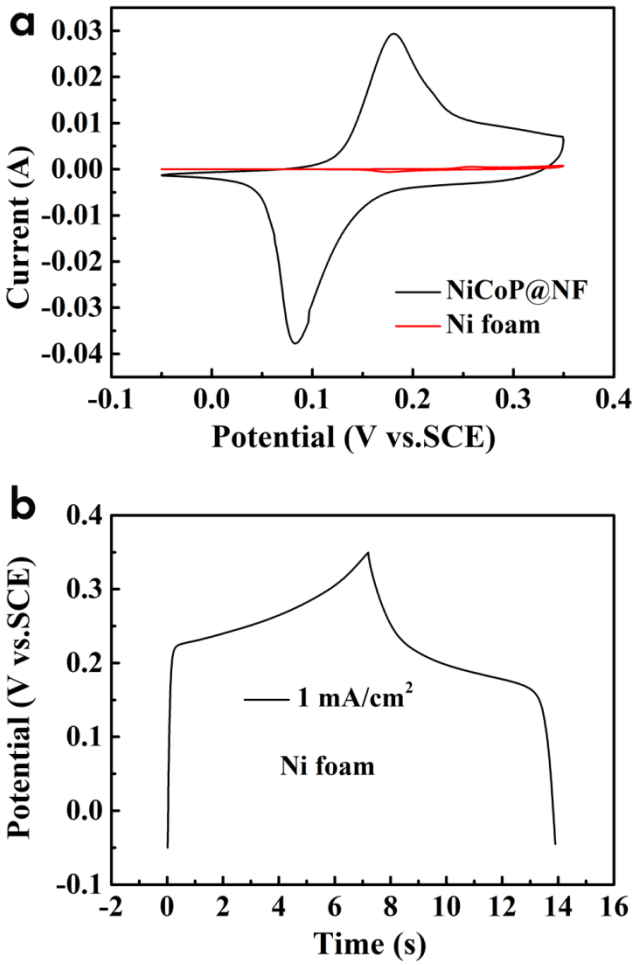

Figure S6. (a) CV curves of NiCoP@NF and Ni foam at the scan rates of 5 mV/s in 6 M KOH. (b) GCD curve of the Ni foam at the current density of 1 mA/cm^2.

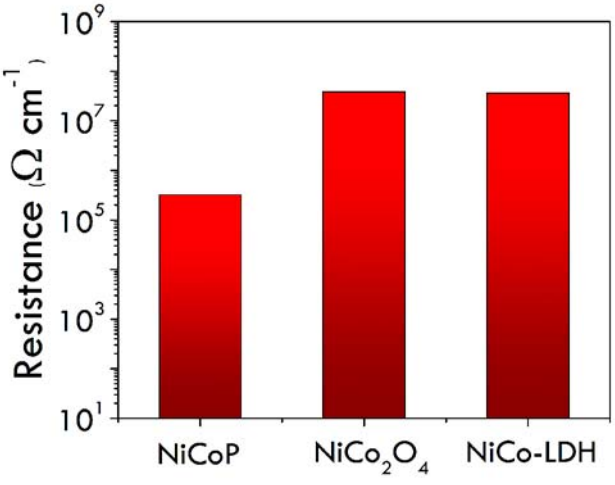

Figure S7. Comparison of resistance for NiCoP, $NiCoO_2$ and NiCo-LDH.

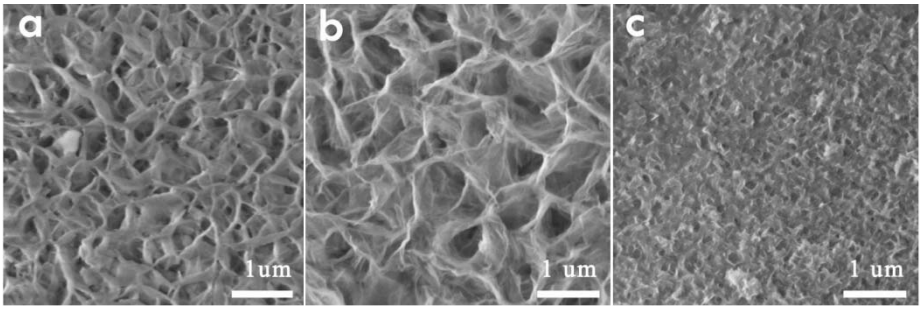

Figure S8. SEM images of (a) NiCoP@NF, (b) NiCo-LDH@NF and (c) $NiCoO_2$@NF after 2000 cycles.

Table S1 Specific capacitances of the Ni-based materials.

	Various materials	**Electrolyte**	**Current density**	**Specific capacitance**
This work	**NiCoP@NF**	**6 M KOH**	**1 A g^{-1}**	**2143 F g^{-1}**
[1]	NiCoP	2 M KOH	1 A g^{-1}	571 C g^{-1} (1427.5 F g^{-1})
[2]	NiCoP/carbon paper	1 M KOH	1 A g^{-1}	194 mAh g^{-1} (1396.8 F g^{-1})
[3]	NiCoP/G	2 M KOH	2 A g^{-1}	675 F g^{-1}
[4]	NiCoP/NF (2*3)	2 M KOH	2 mA cm^{-2}	9.20 F cm^{-2}
[5]	Ni_2P/GR	3 M KOH	1 A g^{-1}	672.4 F g^{-1}
[6]	Ni_2P	3 M KOH	1 A g^{-1}	799.2 F g^{-1}
[7]	$NiCoO_2$	3 M KOH	1 A g^{-1}	~ 700 F g^{-1}
[8]	$NiCoO_2$	2 M KOH	0.62 A g^{-1}	328 F g^{-1}
[9]	$NiCoO_2$/NF	1 M KOH	0.75 A g^{-1}	756 F g^{-1}
[10]	$NiCo_2O_4$	6 M KOH	1 A g^{-1}	1141 F g^{-1}
[11]	$NiCo_2O_4$/NF	3 M KOH	1 A g^{-1}	900 F g^{-1}
[12]	$NiCo_2S_4$ NS/NCF	6 M KOH	1 A g^{-1}	1231 F g^{-1}
[13]	$NiCo_2S_4$	2 M KOH	1 A g^{-1}	966.5 F g^{-1}
[14]	$NiCo_2S_4$	3 M KOH	1 A g^{-1}	744 F g^{-1}
[15]	NiCo-LDH	3 M KOH	2 A g^{-1}	~ 900 F g^{-1}

References

[1] Y. M. Hua, M. C. Liu, Y. X. Hu, Q. Q. Yang, L. B. Kong and L. Kang, *Electrochim. Acta*,

2016, **215**, 114-125.

[2] H. F. Liang, C. Xia, Q. Jiang, A. N. Gandi, U. Schwingenschlögl and H. N. Alshareef, *Nano Energy*, 2017, **35**, 331-340.

[3] C. Wang, Y. Y. Qian, J. Yang, S. Q. Xing, X. Ding and Q.Yang, *RSC Adv.*, 2017, **7**, 26120-26124.

[4] M. L. Kong, Z. Wang, W. Y. Wang, M. Ma, D. N. Liu, S. Hao, R. M. Kong, G. Du, A. M. Asiri, Y. D. Yao and X. P. Sun, *Chem. Eur. J.*, 2017, **23**, 4435- 4441.

[5] W. M. Du, S. H. Wei, K. K. Zhou, J. J. Guo, H. Pang and X. F. Qian, *Mater. Res. Bull.*, 2015, **61**, 333-339.

[6] H. Wu, Y. H. Ni, M. F. Wang and D. C. Lu, *CrystEngComm*, 2016, **18**, 5155-5163.

[7] X. N. Leng, Y. Shao, L. B. Wu, S. F. Wei, Z. H. Jiang, G. Y. Wang, Q. Jiang and J. S. Lian, *J. Mater. Chem. A*, 2016, **4**, 10304-10313.

[8] X. Zhang, Y. D. Xu, *Mater. Lett.*, 2017, **189**,78-81.

[9] X. Y. Xu, H. L. Zhao, J. K. Zhou, R. N. Xue and J. P. Gao, *J. Power Sources*, **329**, 2016, 238-246.

[10] L. F. Shen, L. Yu, X. Y. Yu, X. G. Zhang and X. W. (David) Lou, *Angew. Chem. Int. Ed.*, 2015, **54**, 1868-1872.

[11] W. W. Zhou, D. Z. Kong, X. T. Jia, C. Y. Ding, C. W. Cheng and G. W. Wen, *J. Mater. Chem. A*, 2014, **2**, 6310-6315.

[12] L. F. Shen, J. Wang, G. Y. Xu, H. S. Li, H. Dou and X. G. Zhang, *Adv. Energy Mater.*, 2015, **5**, 1400977.

[13] J. Q.Yang, W. Guo, D. Li, Q. Qin, J. Zhang, C. Y. Wei, H. M. Fan, L. Y. Wu and W. J.

Zheng, *Electrochim. Acta*, 2014, **144**, 16-21.

[14] Z. B. Wu, X. L. Pu, X. B. Ji, Y. R. Zhu, M. J. Jing, Q. Y. Chen and F. P. Jiao, *Electrochim. Acta*, 2015, **174**, 238-245.

[15] X. Q. Cai, X. P. Shen, L. B. Ma, Z. Y. Ji, C. Xu and A. H. Yuan, *Chem. Eng. J.*, 2015, **268**, 251-259.