Electronic Supplementary Information (ESI)

Urchin-like NiCoP coated with carbon layer as high performance electrodes for all-solid-state asymmetric supercapacitors

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**Fig. S1.** High magnification SEM image of NiCo-ULAs precursor obtained from hydrothermal reaction for 2 h.

**Fig. S2.** (a) XRD patterns of as-prepared NiCo-NFAs, NiCo-ULAs and NiCo-HNSAs. The diffraction peaks of the three XRD patterns can be indexed to CoC$_2$O$_4$·2H$_2$O. (b) XRD patterns of Ni$_x$Co$_{1-x}$O@C-NFAs and Ni$_x$Co$_{1-x}$O@C-ULAs.

**Fig. S3.** (a) Low and (b) high magnification SEM images of Ni$_x$Co$_{1-x}$O@C-ULAs.
**Fig. S4.** SEM images of the hybrids (phosphides coated with carbon) obtained with the various glucose concentration of (a, c) 0.03 M and (b, d) 0.04 M.

**Fig. S5.** SEM images of (a) NiCo-NFAs, (b) NiCoP-NFAs, (c) Ni$_{1-x}$Co$_x$O@C-NFAs, and (d) NiCoP@C-NFAs.
Fig. S6. TEM images of (a) NiCo-NFAs, (b) NiCoP-NFAs, (c) NiCoP@C-NFAs, (d) NiCo-ULAs, (e) NiCoP-ULAs, and (f) NiCoP@C-ULAs.

Fig. S7. EDX spectrum of NiCoP@C-ULAs, and the inset of corresponding the element content.
Fig. S8. High-resolution XPS spectra of C1s and O1s for (a, b) NiCo-ULAs, and (c, d) NiCoP@C-ULAs.

Fig. S9. Nitrogen adsorption–desorption isotherms of the (a) NiCo-NFAs, (b) NiCoP-NFAs, and (c) NiCoP@C-NFAs. Insets of (a) and (b), and (c) are their pore size distributions.
Fig. S10. Electrochemical performance of NiCo-NFAs, NiCo-ULAs, and NiCo-HNSAs precursors. (a) CV curves at a scan rate of 10 mV s\(^{-1}\), (b) GCD curves at a current density of 1 A g\(^{-1}\), (c) rate performance, and (d) cycling performance at a constant current density of 8 A g\(^{-1}\).
Fig. S11. (a-d) CV curves with different sweep rates, (e-h) GCD curves with different current densities of NiCo-ULAs, NiCoP-ULAs, Ni$_x$Co$_{1-x}$O@C-ULAs, and NiCoP@C-ULAs electrodes, respectively.
Fig. S12. Logarithm relationship between anodic peak current and scan rate for ULAs series electrodes.

Fig. S13. The equivalent fitting circuit of ULAs series electrodes
Fig. S14. Electrochemical performance of electrodes. (a) CV curves at a scan rate of 10 mV s\(^{-1}\), (b) GCD curves at a current density of 1 A g\(^{-1}\), (c) the specific capacity at different current densities, and (d) cycling performance at a constant current density of 8 A g\(^{-1}\).

Fig. S15. SEM images of NiCoP-ULAs and NiCoP@C-ULAs after cycling for 5000 cycles.
Fig. S16. Electrochemical performance of the AC electrode: (a) CV curves at different scan rates from 5 to 50 mV·s⁻¹, (b) GCD curves at different current densities from 1 to 10 A·g⁻¹.

Fig. S17. (a) and (b) CV curves of the NiCoP@C-NFAs//AC ASC at different scan rates and voltage windows; (c) GCD curves of the NiCoP@C-NFAs//AC ASC at different current densities; (d) cycling performance of NiCoP@C-NFAs//AC at a current density of 8 A·g⁻¹. The inset shows the last 10 cycles of the GCD curves of the ASC device.
Fig. S18. The IR drop of the NiCoP@C-ULAs//AC device at different current densities.
Table S1. Textual parameters of the samples.

| Sample          | $S_{BET}$ (m$^2$ g$^{-1}$) | Average pore size (nm) | Total pore volume (cm$^3$ g$^{-1}$) |
|-----------------|-----------------------------|-------------------------|-----------------------------------|
| NiCo-ULAs       | 37.5                        | 16.8                    | 0.181                             |
| NiCoP-ULAs      | 139.1                       | 9.1                     | 0.306                             |
| NiCoP@C-ULAs    | 201.9                       | 4.4                     | 0.231                             |
| NiCo-NFAs       | 31.4                        | 21.3                    | 0.209                             |
| NiCoP-NFAs      | 123.7                       | 11.6                    | 0.312                             |
| NiCoP@C-NFAs    | 174.4                       | 6.1                     | 0.293                             |

Table S2. The electrochemical performances for as-prepared NFAs and ULAs series samples.

| Sample          | Specific capacity (C/g) | Rate capability | Cycle stability (5000 cycles) |
|-----------------|-------------------------|-----------------|-------------------------------|
|                 | 1A/g 2A/g 4A/g 6A/g 8A/g 10A/g 15A/g 20A/g |                 |                              |
| NiCo-NFAs       | 402 382 358 337 314 299 253 199      | 49.5%           | 87.9%                         |
| NiCoP-NFAs      | 662 634 606 570 536 512 399 264      | 39.9%           | 50.4%                         |
| Ni$_x$Co$_{1-x}$O@C-NFAs | 319 313 300 290 283 278 263 252 | 79.0%           | 103.4%                        |
| NiCoP@C-NFAs    | 934 903 864 837 810 782 733 690      | 73.9%           | 82.9%                         |
| NiCo-ULAs       | 424 402 375 354 341 322 298 272      | 64.2%           | 112.6%                        |
| NiCoP-ULAs      | 737 714 678 651 622 601 543 458      | 62.1%           | 55.1%                         |
| Ni$_x$Co$_{1-x}$O@C-ULAs | 349 343 333 323 315 310 292 273 | 78.2%           | 106.3%                        |
| NiCoP@C-ULAs    | 1046 1022 982 959 938 923 855 800    | 76.5%           | 86.3%                         |
Table S3. Comparison of our ASCs devices performances with reported literatures

| System | Device window (V) | Energy density (Wh kg⁻¹) | Power density (W kg⁻¹) | Cycle stability (cycles) | Ref. |
|--------|-------------------|--------------------------|-----------------------|--------------------------|------|
| AC//NiCoP | 0-1.4 | 32 | 351 | 91.8% (3000) | 1 |
| NiCoP/NiCo-OH30//PC | 0-1.6 | 34 | 775 | 92% (10000) | 2 |
| AC//CoP | 0-1.4 | 19 | 350.8 | 96.7% (5000) | 3 |
| AC//NiP@NiCoO₄ | 0-1.4 | 21 | 350 | 78.3% (10000) | 4 |
| NiCoP@NiCoP//AC | 0-1.5 | 34.8 | 750 | 81.2% (10000) | 5 |
| Ni₃P NS/NF//AC | 0-1.4 | 26 | 337 | 91.3% (5000) | 6 |
| NiCoP//graphene | 0-1.5 | 32.9 | 1301 | 83% (5000) | 7 |
| NiCoP//AC | 0-1.5 | 22.8 | 4320 | No decay (5000) | 8 |
| sandwich-like LDH/rGO/rGO | 0-1.6 | 34.5 | 772 | 86.7% (10000) | 9 |
| Ni-P//AC | 0-1.6 | 29.2 | 400 | 84.5% (10000) | 10 |
| Ni-Co-S//AC | 0-1.5 | 21.6 | 134.9 | 90.0% (3000 cycles) | 11 |
| NiCoO₄//AC | 0-1.5 | 27.4 | 493.2 | 79.2% (10000) | 12 |
| NiCoP@C-NFAs//AC | 0-1.5 | 32.9 | 871.3 | 87.4% (10000) | This work |
| NiCoP@C-ULAs//AC | 0-1.5 | 37.1 | 792.8 | 91.4% (10000) | 13 |

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