One-pot formation ultra-thin Ni/Co hydroxides with sheet-like structure for enhanced asymmetric supercapacitor

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Fig. S1 (A) Ni foam; (B, C, D and E) represent Ni3, Ni2Co1, Ni1Co2 and Co3 on the Ni foam, respectively.



Fig. S2 (A and B) The FESEM figures of Ni foam before and after treatment with 3 M HCl solution.

After treatment with 3 M HCl solution for 10 minutes, the Ni foam still preserves the original microstructure.



Fig. S3 (A and B) FESEM figures of Co3 sample; (C and D) TEM figures of Co3 sample.

In Fig. S3, severely cracked nanosheets with low crystallinity can be found.



Fig. S4 (A and B) FESEM figures of Ni1Co2 sample; (C and D) TEM figures of Ni1Co2 sample.

In Fig. S4, ultra-thin nanosheets can be found. The overlap, ripple or wrinkle of Ni1Co2

nanosheets in Fig. S4C and S4D originate from ultra-thin structure.



Fig. S5 (A and B) FESEM figures of Ni2Co1 sample; (C and D) TEM figures of Ni2Co1 sample.

In Fig. S5, Ni2Co1 nanosheets become thicker compared with Ni1Co2 nanosheets.



Fig. S6 (A and B) FESEM figures of Ni3 sample; (C and D) TEM figures of Ni3 sample.

In Fig. S6, Ni3 sample presents thicker multi-layer nanosheets compared with Ni1Co2 nanosheets.



Fig. S7 (A and B) FESEM figures of AC sample; (C and D) TEM figures of AC sample.

In Fig. S7, AC sample presents porous microstructure.



Fig. S8 (A) TEM figure of Ni1Co2 nanosheets and (B) the corresponding C elemental mapping.



Fig. S9 N_2 adsorption–desorption isotherms and corresponding BJH pore-size distribution curves in their insets: (A) Ni1Co2; (B) Ni2Co1; (C) Ni3; (D) Co3. All these curves are available according to the total materials containing Ni foam and active materials.

In Fig. S9, the BET values of Ni1Co2, Ni2Co1, Ni3 and Co3 samples (based on their total materials) are 2.68 m² g⁻¹, 1.79 m² g⁻¹, 2.90 m² g⁻¹ and 0.61 m² g⁻¹. Thanks to Ni foams are covered with active materials in the Ni1Co2, Ni2Co1, Ni3, Co3 samples completely, so Ni foams

don't contribute to specific surface area in these samples. According to the following equation:

, where and stand for the BET values based on the masses of active materials and total materials of these samples. And the total masses of Ni1Co2, Ni2Co1, Ni3 and Co3 samples are 0.2418 g, 0.2593 g, 0.2788 g and 0.2690 g, respectively. Besides, active materials of Ni1Co2, Ni2Co1, Ni3 and Co3 samples are 6.8 mg, 11.2 mg, 16.5 mg and 2.5 mg, respectively. So the of Ni1Co2, Ni2Co1, Ni3 and Co3 samples are 84.7 m² g⁻¹, 41.4 m² g⁻¹, 49.0 m² g⁻¹ and 65.6 m² g⁻¹, respectively. In addition, all these samples have a narrow pore size distribution, and the average pore sizes of Ni1Co2, Ni2Co1, Ni3 and Co3 samples are calculated to be 4.0 nm, 3.1 nm, 3.2 nm and 5.6 nm, respectively. Among these samples, Ni1Co2 materials show their larger specific surfaces area.



Fig. S10 XRD figures of Co3, Ni2Co1 and Ni3 samples.

In the XRD patterns of Co3, Ni2Co1 and Ni3 samples, main peaks can be indexed to Ni(OH)₂ phase. Except those peaks, the weaker peak located at ca. 11° appearing in the XRD patterns of Co3, Ni1Co2, Ni2Co1 closely associates with an amorphous cobalt hydroxide phase

ACo. A trace of Ni(OH)₂ was formed in Co3, which is attributed to Ni foam to participate in the reaction. In the reaction, the mass ratio of Co/Ni is 3:0 and there is no Ni²⁺ ions in solution in the beginning. A small mass change of Ni foam after the hydrothermal process and the low peaks intensity of Ni(OH)₂ in the XRD pattern of Co3 indicate a low mass loading of Co3 on Ni foam. Thus, the reduction of Ni foam is relatively weaker. And the mass ratio of Co/Ni varies from 2:1, 1:2, 3:0, a pronounced Ni²⁺ concentration in the solution can effectively restrain the reduction of Ni foam in the hydrothermal process in the dynamics. Therefore, Ni foam is ignored to react with solution in the process of formation of Ni1Co2, Ni2Co1 and Ni3 samples. In view of this, the mass loadings of Ni1Co2, Ni2Co1 and Ni3 on Ni foam can be evaluated by mass change of Ni foam after the hydrothermal process.



Fig. S11 XPS spectra of the as-prepared Ni1Co2: (A) C 1s, (B) N 1s and (C) O 1s.



Fig. S12 Raman patterns of the as-prepared AC precursor and AC.

As shown in Fig. S11, 1379.3 cm⁻¹ of AC precursor Raman pattern and 1343.9 cm⁻¹ of AC pattern are attributed to D band, while 1591.1 cm⁻¹ of AC precursor Raman pattern and 1592.3 cm⁻¹ of AC Raman pattern are attributed to G band. The left shift of D band and slight right shift after calcination may be result from reduction from AC precursor to AC.¹ In addition, compared with AC precursor, lower intensity values of D band G band imply the formation of porous AC structure, and the increasing intensity ratio of the D and G band (I_D/I_G) is due to the decrease of the sp² in-plane domain induced by the introduction of defects and disorders of the sp² domain.^{2, 3}



Fig. S13 (A) CV curves of pristine Ni foam with a area of 1.5 cm² at various scanning rates; (B) CV curves of Ni1Co2, Ni2Co1, Ni3 and Ni foam with areas of 1.5 cm² at a scanning rate of 5 mV s⁻¹, where the mass loadings of Ni1Co2, Ni2Co1 and Ni3 on Ni foam are 1.1 mg cm⁻², 1.6 mg cm⁻²

and 2.3 mg cm⁻², respectively.

In Fig. S13A, even though at a high scanning rate of 100 mV s⁻¹ for pristine Ni foam, the peak current does not exceed 0.01 A. In order to evaluate the contribution of pristine Ni foam in Ni1Co2, Ni2Co1, Ni3 electrodes, the CV curves of pristine Ni foam and Ni1Co2, Ni2Co1, Ni3 electrodes at 5 mV s⁻¹ are shown in Fig. S13B. Compared with Ni1Co2, Ni2Co1 and Ni3 electrodes, a much lower hysteresis loop area for Ni foam indicates its negligible capacitance.



Fig. S14 (A) The first and last three cycles galvanostatic charge-discharge profiles of Ni1Co2 at a current density of 10A g⁻¹ for 1500 cycles; (B) FESEM figure of Ni1Co2 after cycles.



Fig. S15 (A and D) CV curves at different scanning rates in 3 M KOH electrolyte of the Ni2Co1 and Ni3 electrodes, respectively; (B and E) Galvanostatic charge-discharge profiles at different current densities of the Ni2Co1 and Ni3 electrodes, respectively; (C and F) Nyquist plot of the Ni2Co1 and Ni3 electrode in the frequency range 0.01 to 100 kHz before and after 1500 cycles at current density of 10 A g⁻¹ of the Ni2Co1 and Ni3 electrodes, respectively.



Fig. S16 (A, B and C) I_{ap} - v and I_{ap} - v ^{1/2} plots of Ni1Co2, Ni2Co1 and Ni3 electrodes.



Fig. S17 Electrochemical performances of the AC electrode in 3 M KOH aqueous solution: (A) CV curves at various scanning rates; (B) Galvanostatic charge–discharge curves at various current densities; (C) Specific capacitance at various current densities; (D) Cycle performance of AC electrode measured at a current density of 10 A g⁻¹ for 4000 cycles.



Fig. S18 Electrochemical performances of the Ni2Co1//AC and Ni3//AC ASCs (according to the total mass of the active materials in these devices, the mass loadings of Ni2Co1 and Ni3 are 1.6 mg cm⁻² and 2.3 mg cm⁻², so the applied AC on Ni foam in Ni2Co1//AC and Ni3//AC are 6.6 mg

cm⁻² and 6.9 mg cm⁻² referring to $m_+/m_-=C_-V_-/(C_+V_+)$): (A) and (C) CV curves at different scanning rates; (B) and (D) Galvanostatic charge-discharge profiles at different current densities.



Fig. S19 Nyquist plots of the Ni1Co2//AC, Ni2Co1//AC, Ni3//AC before cycles and Ni1Co2//AC after cycles. Inset is the magnification from 0 to 15 ohm for Z' value.

Notes and references

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- 2 M. Liu, L. Gan, W. Xiong, Z. Xu, D. Zhu and L. Chen, Journal of Materials Chemistry A, 2014, **2**, 2555-2562.
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