

Electronic Supplementary Information (ESI)

Hydrogenated CoO_x nanowire @ $\text{Ni}(\text{OH})_2$ nanosheet core-shell nanostructures for high-performance asymmetric supercapacitors

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Preparation of H- Co_3O_4 NWs. First, self-supported Co_3O_4 NW arrays were prepared by a facile hydrothermal synthesis method.¹ The reaction solution was obtained by mixing 3 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 6 mmol of NH_4F , and 15 mmol of $\text{CO}(\text{NH}_2)_2$ in 80 mL of distilled water and then transferred into Teflon-lined stainless steel autoclave liners. Two pieces of nickel foam ($1.2 \times 6 \text{ cm}^2$ in sizes) were immersed into the reaction solution. Before use, Nickel foam ($1.2 \times 6 \text{ cm}^2$) was carefully cleaned with concentrated HCl solution (37 wt%) in an ultrasound bath for 5 min in order to remove the surface NiO layer, and then deionized water and absolute ethanol were used for 5 min each to ensure the surface of the Ni foam was well cleaned. The liner was sealed in a stainless steel autoclave and maintained at 120 °C for 5 h and then cooled down to room temperature. The samples were collected and cleaned with distilled water and ethanol in an ultrasound bath for 5 min each. Finally, the samples were annealed at 350 °C in normal purity argon for 2 h.

Preparation of graphite oxide (GO). GO was synthesized from purified natural graphite (SP-1, Bay Carbon, MI) by the modified Hummers method.² H_2SO_4 (75 mL) was added into the 250 mL flask filled with graphite (3 g) at room temperature, followed by addition of solid KMnO_4 (12 g) slowly at 0 °C (ice bath). After increase of temperature to 35 °C, the mixture was stirred by magnetic stirring bar for 15 h. Excess water was added into the mixture at 0 °C (ice bath), causing violent effervescence and an increase in temperature to 98 °C, maintained at this temperature for 15 minutes. And then H_2O_2 (30 wt% in water) was added until there was no gas producing. Filtration with glass filter afforded brown powder (GO) and the GO powder was dried in the vacuum at room temperature for 24 h.

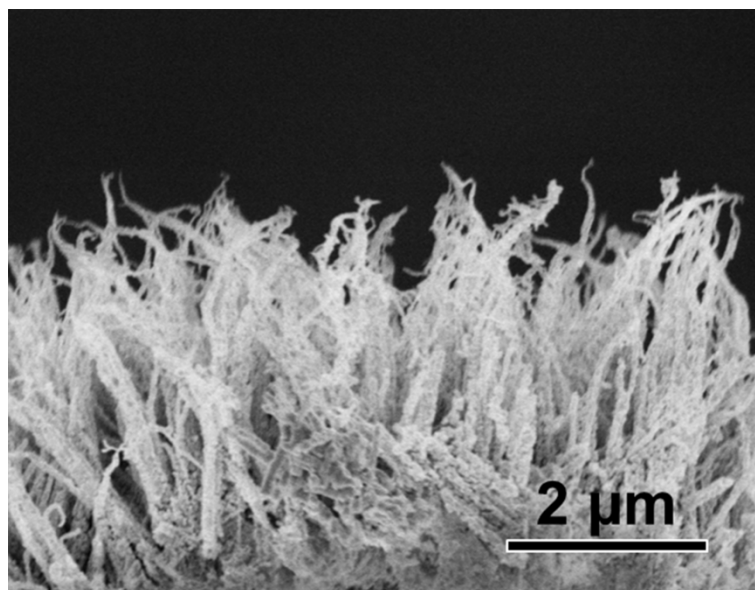


Fig. S1 FESEM cross section image of H-CoO_x NWs.

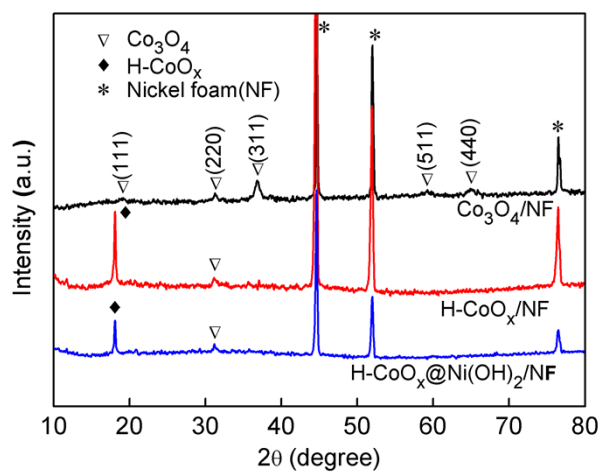


Fig. S2 XRD of Co₃O₄, H-CoO_x, H-CoO_x@Ni(OH)₂.

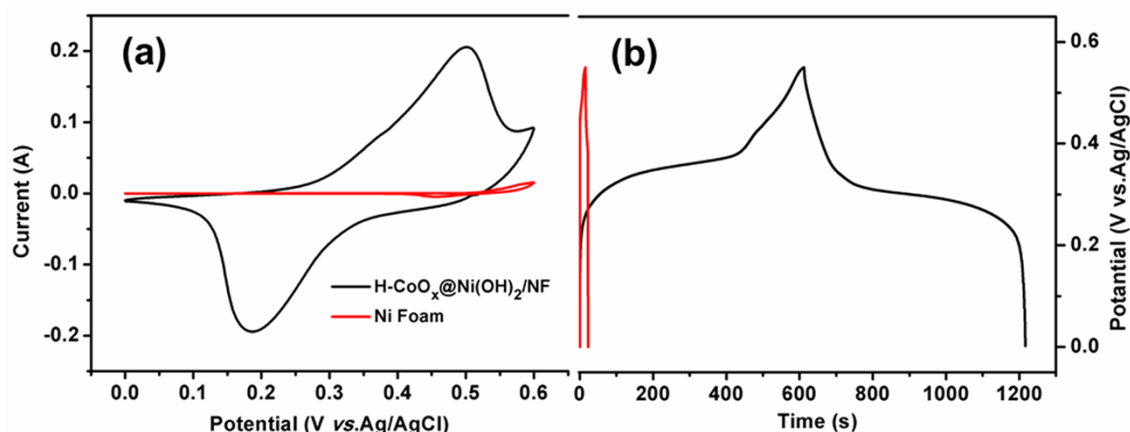


Fig. S3 (a) CVs of H-CoO_x@Ni(OH)₂ on nickel foam and bare nickel foam (underwent hydrothermal and high temperature postannealing processes) at scan rate of 10 mV s⁻¹ (b) Charge-discharge curves of H-CoO_x@Ni(OH)₂ on nickel foam and bare nickel foam at constant current of 7.52 mA.

Calculation of the specific capacitance of H-CoO_x@Ni(OH)₂.

C_{sp} (The specific capacitances) and C_A (the areal capacitance) were calculated from the galvanostatic discharge curves using Eq. (S-1) and Eq. (S-2), where I is the applied current, $V/\Delta t$ is the slope of the discharge curve, m is the mass of the samples on the electrode, and A is the geometrical area of the electrode (cm²):

$$C_{sp} = I\Delta t / (mV) \quad (\text{S-1})$$

$$C_A = I\Delta t / (AV) \quad (\text{S-2})$$

Considering that in our hybrid electrode with 1.44 cm² area, the mass of the mixture, H-CoO_x and Ni(OH)₂ is 3.76 mg, 2.01 mg and 1.75 mg, respectively, then, we obtained the capacitance of the hybrid:

$$C_{sp} = I\Delta t / (mV) = (0.00752 \text{ A} \cdot 604 \text{ s}) / (0.00376 \text{ g} \cdot 0.55 \text{ V}) = 2196 \text{ F g}^{-1} \quad (\text{At } 2 \text{ A g}^{-1} \text{ in Fig. 5e})$$

$$C_A = I\Delta t / (AV) = (0.00752 \text{ A} \cdot 604 \text{ s}) / (1.44 \text{ cm}^2 \cdot 0.55 \text{ V}) = 5.73 \text{ F cm}^{-2} \quad (\text{At } 2 \text{ A g}^{-1})$$

At the current density of 2 A g⁻¹, H-CoO_x and Ni(OH)₂ could obtain a capacitance of 944 F g⁻¹ and 1760 F g⁻¹, respectively. If we could simply add H-CoO_x and Ni(OH)₂ with the same mass ratio to that in the hybrid structure, the capacitance of the mixture (C) would be calculated as,

$$C = (944 \cdot 2.01 + 1760 \cdot 1.75) / 3.76 = 1324 \text{ F g}^{-1} < 2196 (C_{sp})$$

The result is poorer than the data we get from the hybrid structure, which may be attributed to synergistic effects of the atomic mixture of Ni(OH)₂ and H-CoO_x.

Table 1. The ESR (R_e) and the C_{sp} (at 2 A g⁻¹) of the different electrode materials.

Electrode	Co ₃ O ₄	H-CoO _x	Ni(OH) ₂	H-CoO _x @Ni(OH) ₂	H-CoO _x @Ni(OH) ₂ -5h
R_e	0.70 Ω	0.48 Ω	1.17 Ω	0.55 Ω	0.94 Ω
C_{sp}	486 F g ⁻¹	944 F g ⁻¹	1760 F g ⁻¹	2196 F g ⁻¹	1830 F g ⁻¹
$m_{\text{Ni(OH)}_2} : m_{\text{H-CoO}_x}$	--	--	1:0	1:0.87	1:1.3

RGO@Fe₃O₄ nanocomposites for negative electrode

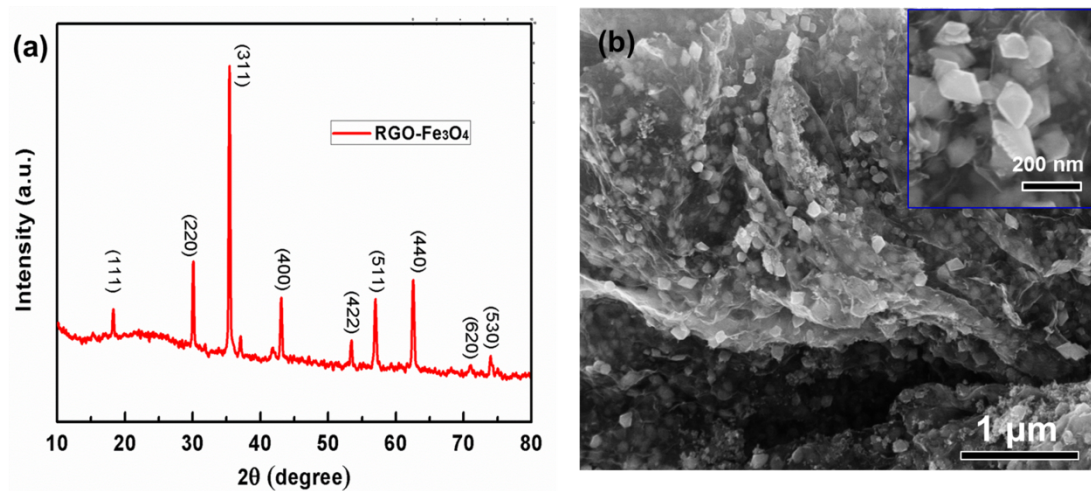


Fig. S4 (a) XRD of RGO@Fe₃O₄ nanocomposites. It shows the X-ray diffraction (XRD) of RGO@Fe₃O₄, which reveals that all the peaks of the RGO@Fe₃O₄ nanocomposites can be assigned to Fe₃O₄ (JCPDS no. 65-3107). Due to the little content of RGO, there are no obvious peaks in the range of 24–28 degree corresponding to graphene stacking. (b) FESEM of RGO@Fe₃O₄ nanocomposites (Inset is magnified SEM image). The SEM images show that the small Fe₃O₄ particles are spindle-like with sizes of 80-180 nm, and uniformly distributing in graphene nanosheets.

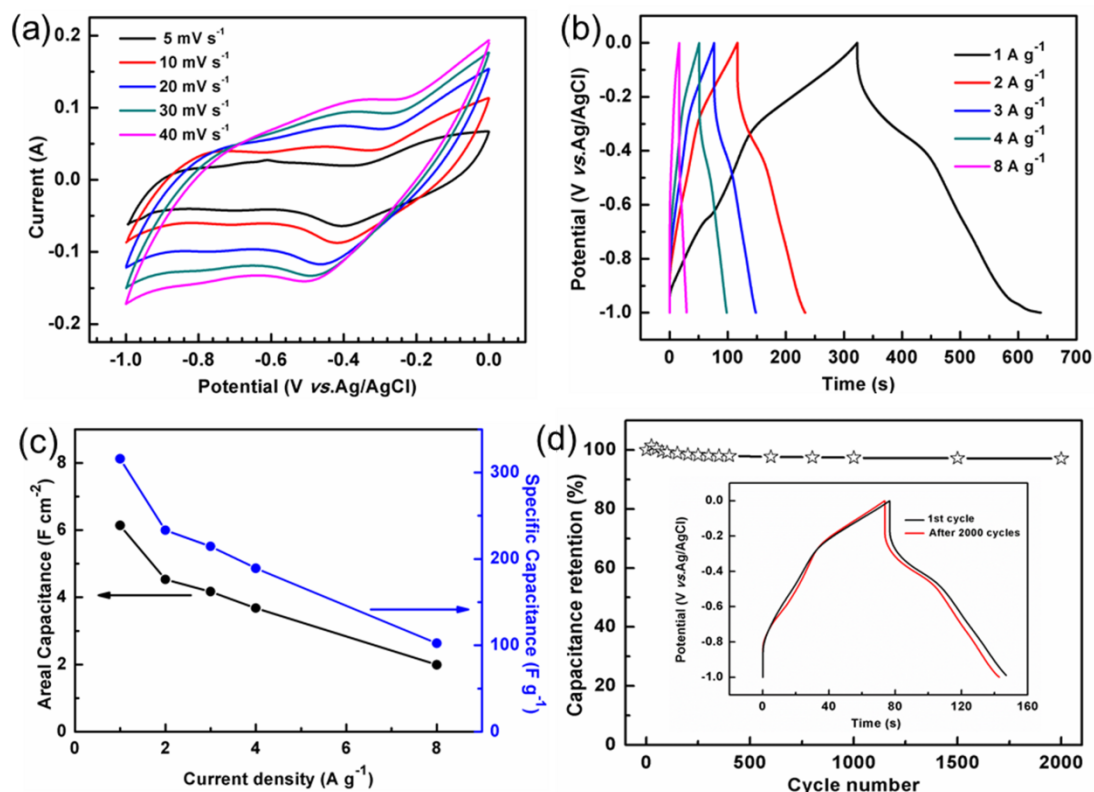


Fig. S5 (a) CV curves of RGO@Fe₃O₄ electrode at different scan rates. The CV curve of RGO@Fe₃O₄ shows a roughly rectangular shape with a pair of small peaks, suggesting that the capacitance of RGO@Fe₃O₄ electrode comes from not only electrical double-layer capacitance, but also faradaic pseudocapacitance. (b) Galvanostatic charge-discharge (GCD) curves of RGO@Fe₃O₄ electrode at different current densities. The GCD curves exhibits a similar symmetry charge-discharge curve with three voltage stages. (c) Areal capacitance and specific capacitance calculated for the RGO@Fe₃O₄ based on the galvanostatic charge-discharge curves as a function of current density. The RGO@Fe₃O₄ electrode shows a specific capacitance of 316, 233, 214, 189, and 102 F g⁻¹ at different densities of 1, 2, 3, 4, and 8 A g⁻¹, respectively (with high areal capacitance of 6.14 F cm⁻² at current density of 1 A g⁻¹). (d) Cycling performance of RGO@Fe₃O₄ electrode. Moreover, the RGO@Fe₃O₄ electrode exhibits an excellent long cycle life with only 3% capacitance loss after 2000 cycles.

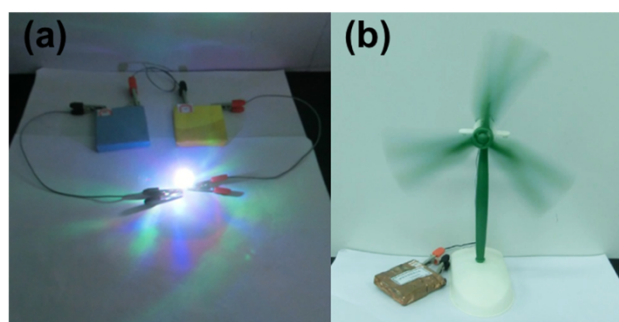


Fig. S6 (a) A picture showing that two ASCs in series can lighten up a 3.2 V seven-color LED brightly. (b) one 22 cm² ASC device can drive a small windmill for 20 min after 1 min of charging by a pair of AA battery.

References

- 1 X. H. Xia, J. P. Tu, Y. Q. Zhang, X. L. Wang, C. D. Gu, X. B. Zhao and H. J. Fan, *ACS Nano*, 2012, **6**, 5531.
- 2 S. Park, J. An, R. D. Piner, I. Jung, D. Yang, A. Velamakanni, S. T. Nguyen and R. S. Ruoff, *Chem. Mater.*, 2008, **20**, 6592.