Supporting Information:

Improving the Performance of Cobalt-Nickel Hydroxides-based Self-Supporting Electrodes for Supercapacitors using Accumulative Approaches

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1. EDS mapping of the mixed hydroxide composite.

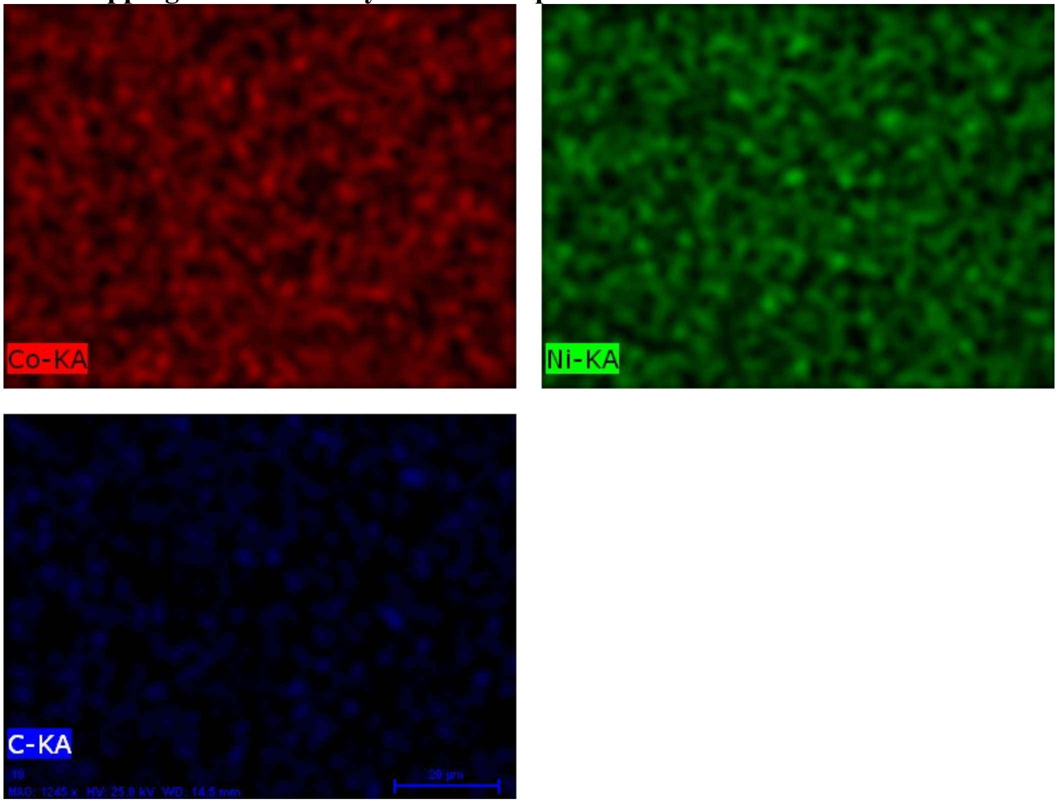

Figure S1: EDS elemental mapping of the $Co_{0.5}Ni_{0.5}(OH)_2$/graphene composite. Both nickel and cobalt appear distributed uniformly in the composite, no obvious phase segregation was observed.

2. Electrochemical behavior of an electrode fabricated without carbon nanotubes.

To study the effect of carbon nanotubes on improving the electrochemical performance of the fabricate electrode, a control electrode was fabricated without carbon nanotubes. In this case, the electrode was fabricated via casting the mixture of $Co_{0.5}Ni_{0.5}(OH)_2$/graphene composite, carbon black and PVDF with the mass ratio of 70:20:10 on nickel foam. The electrode was evaluated using galvanostatic charge-discharge technique at current densities ranging from 0.5 A/g to 10 A/g. The results, along with the specific capacitance, were shown and compared in Figure S2.

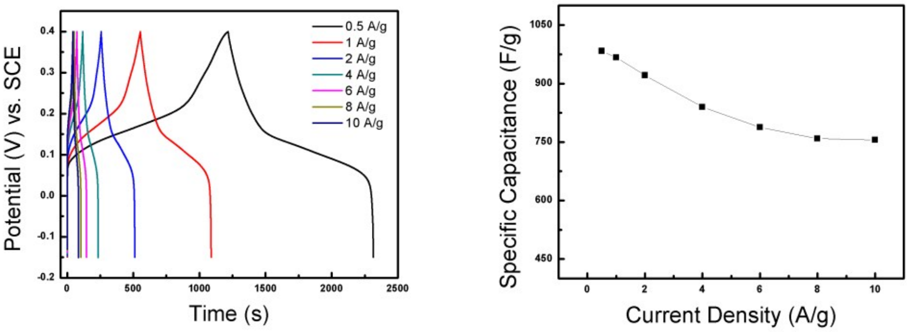

Figure S2: (left) galvanostatic charge-discharge curves at different current densities for the $Co_{0.5}Ni_{0.5}(OH)_2$/graphene composite without using nanotubes; (right) the corresponding specific capacitances.

3. Electrochemical behavior of an electrode fabricated without carbon nanotubes and graphene.

To study the effect of graphene on improving the electrochemical performance of the fabricate electrode, a control electrode was fabricated without graphene and carbon nanotubes. In this case, the active material was synthesized by co-precipitation of cobalt and nickel hydroxides without the presence of graphene. The electrode was also fabricated via casting the mixture of $Co_{0.5}Ni_{0.5}(OH)_2$, carbon black and PVDF with the mass ratio of 70:20:10 on nickel foam. The electrode was evaluated using galvanostatic charge-discharge technique at current densities ranging from 0.5 A/g to 10 A/g. The results, along with the specific capacitance, were shown and compared in Figure S3. The electrode delivered 850 F/g at 0.5 A/g and keeps 580 F/g at 10 A/g.

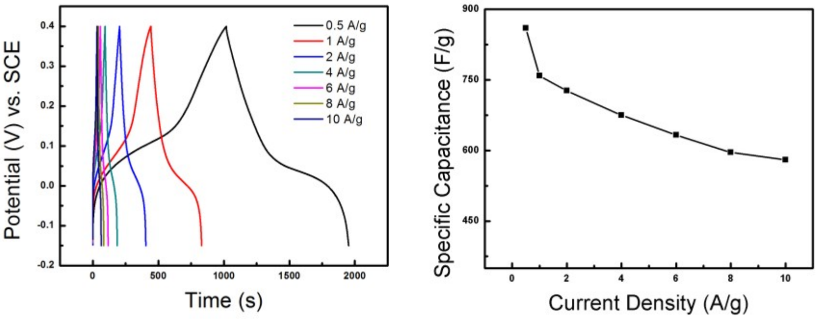

Figure S3: (left) galvanostatic charge-discharge curves at different current densities for the $Co_{0.5}Ni_{0.5}(OH)_2$ composite without using graphene and nanotubes; (right) the corresponding specific capacitances.

4. Cycle stability of Ni(OH)2 without the addition of cobalt.

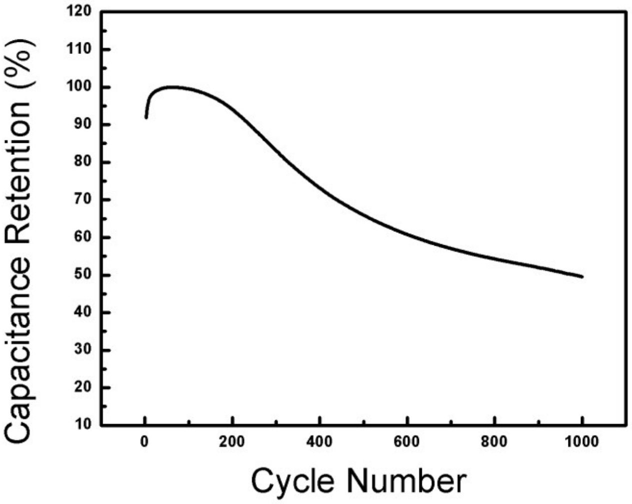

Figure S4: Cycle stability of a electrode fabricated with $Ni(OH)_2$/graphene composite and carbon nanotubes (without any cobalt additive). This electrode showed ~50% capacitance loss after 1000 charge-discharge cycles at 10 A/g.

5. Comparison of our results with typical results reported previously.

Table S1: Comparison of the performance metrics for electrodes made with our accumulative approach and with other typical approaches as reported in literature.

Ref.	electrode structure	specific capacitance	rate capacity	remarks
This work	Ni-Co double hydroxide/graphene/CNTs	2360 F/g at 0.5 A/g	86 % retention at 20 A/g	High areal density: 6 mg/cm^2. Freestanding electrodes without binder. High active material loading (~72 wt%)
J. Mater. Chem., 2012, 22, 23587	Ni-Co double hydroxide microspheres with hollow interior and hedgehog-like exterior structures	2275 F/g at 1A/g	44 % retention at 24 A/g.	Electrode made with traditional approach with binder and conducting additive and Ni foam as current collector
J. Power Sources, 209(2012), 141	Physical mixture of $Co(OH)_2$ and $Ni(OH)_2$	300~400 F/g		Traditional approach with binder and conducting additive and Ni foam as current collector
RSC Advance,	Aligned nickel-cobalt	456 F/g	70%	Nanorod arrays

2012, 2, 3190~3193	hydroxide nanorods		retention as scan rate increased by 10 times	directly grown on stainless steel as electrode. Active material loading was only 0.3 mg/cm^2
Adv. Mater. 2012, 24, 2148	Cobalt-nickel hydroxide nanocones	1580 F/g with 50% Co at 10 A/g		Traditional approach with binder and conducting additive and graphite as current collector
J. Am. Chem. Soc 2010, 132, 7472	Single-crystalline $Ni(OH)_2$ hexagonal nanoplates grown on graphene	1335 F/g at 2.8 A/g	71% retention at 46 A/g	Mass loading ~ 1.0 mg, electrode fabricated with Ni foam without binder
J. Power Sources 175 (2008) 680-685	Potentiostatically deposited CoNi layered double hydroxide	2104 F/g at 1 A/g	85% at 10 A/g	Active material loading ~0.2mg/cm^2 Electrodes were active materials deposited on stainless steel.
J Solid State Electrochem 2007, 11:571-576	$Co(OH)_2$-$Ni(OH)_2$/ultrastable Y zeolite composite	1710 F/g at 2 mA/cm^2		Electrode made with traditional approach with Ni foam Active material only ~28wt%
Electrochimica Acta 54(2009) 2737-2741	Mesoporous CoNi double hydroxide	1809 F/g at 1 A/g	86% at 10 A/g	Electrodes were fabricated using the traditional approach with Ni foam as the current collector

6. Fabrication and testing of asymmetric supercapacitors.

As for full supercapacitors, the mass of positive and negative electrodes need to be optimized in order to ensure efficient utilization of active materials. The charge stored by an electrode depends on its specific capacitance (C_{sp}), the potential range of the charge/discharge process (ΔE) and the mass of the electrode (m) following the Equation:

$$q = Csp * \Delta E * m$$

and in order to get equal charge flow (q_+ = q.), the mass ratio between the positive and negative electrodes need to follow:

$$\frac{m_+}{m_-} = \frac{C_- * \Delta E_-}{C_+ * \Delta E_+}$$

on the basis of the specific capacitance values and potential windows found for the double hydroxide electrode and the AC/CNTs, the optimal mass ratio between these two electrodes was determined. Prior testing, both electrodes were polarized to -0.1 V vs. SCE for 30 min.

Calculation of energy density and power density of the asymmetrical supercapacitor

Based on the galvanostatic charge/discharge results, the total capacitance C of the asymmetric supercapacitor was calculated by using

$$C = i/-[\Delta V/\Delta t]$$

where i is the current applied, and $\Delta V/\Delta t$ is the slope of the discharge curve after the iR drop.

Based on the capacitance calculated, the energy density and power density were calculated using equation:

$$E = \frac{CV^2}{2m}$$

where C is the capacitance of the full cell and V is the voltage difference between the voltage after the iR drop at the beginning of discharging and the voltage at the end of discharge, m is the total mass of the electrode material from both electrodes. The power density was calculated using:

$$P = \frac{E}{t}$$

where E is the energy density and t is the corresponding discharge time in hour.

Reference:

(1) Zhao, J. P.; Pei, S. F.; Ren, W. C.; Gao, L. B.; Cheng, H. M. *Acs Nano* **2010**, *4*, 5245.
(2) Qian, C.; Qi, H.; Liu, J. *J Phys Chem C* **2007**, *111*, 131.
(3) Brozena, A. H.; Moskowitz, J.; Shao, B. Y.; Deng, S. L.; Liao, H. W.; Gaskell, K. J.; Wang, Y. H. *J Am Chem Soc* **2010**, *132*, 3932.