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.**

![EDS mapping](image)

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 fabricated 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.

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

$$q = C_s p \Delta E \cdot m$$

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

$$ C = \frac{i}{-\Delta V/\Delta t} $$

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.