Electronic Supplementary Information (ESI)

Growth of ultrathin mesoporous Co$_3$O$_4$ nanosheet arrays on Ni foam for high-performance electrochemical capacitors

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Experimental

1. Materials synthesis

Nickel foam (approximately 1 cm × 4 cm) was carefully cleaned with 6 M HCl solution in an ultrasound bath for 30 min in order to remove the NiO layer on the surface, and then rinsed with deionized water and absolute ethanol, respectively. The electrodeposition was performed in a standard three-electrode glass cell consisting of the clean Ni foam working electrode, a platinum plate counter electrode and a saturated calomel reference electrode (SCE) at room temperature of 25 ± 1 °C. The Co(OH)$_2$ was electrodeposited upon Ni foam in a 0.05 M Co(NO$_3$)$_2$·6H$_2$O aqueous electrolyte using an IVIUM Electrochemical Workstation (the Netherlands). The electrodeposition potential is -1.0 V (vs. SCE). After electrodeposition for 20 min, the green Ni foam was carefully rinsed several times with deionized water and absolute ethanol with the assistance of ultrasonication, and finally dried in air. Then, the sample was put in a quartz tube and calcined at 250 °C for 2 h with a ramping rate of 1 °C min$^{-1}$ to transform into ultrathin mesoporous Co$_3$O$_4$ nanosheets. In average, about 1.4 mg of Co$_3$O$_4$ nanosheets was grown on the 1 cm$^2$ Ni foam, carefully weighted after calcination. For comparison, another heating rate of 10 °C min$^{-1}$ is also used.
2. Sample characterization

The morphologies and structures of the samples were characterized by scanning electron microscopy (SEM, LEO 1430VP, Germany), transmission electron microscope (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) (JEOL JEM 2100 system operating at 200 kV), powder X-ray diffraction (XRD) (Max 18 XCE, Japan) using a Cu Ka source (\(\lambda = 0.1542\) nm) at a scanning rate of 3 ° min\(^{-1}\) over a 2\(\theta\) range of 10 - 80°, and N\(_2\) adsorption-desorption measurements using an ASAP-2010 surface area analyzer. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area of samples. The pore size distributions (PSD) were derived from the desorption branch of the isotherm with the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analysis was performed on a TG instrument (NETZSCH STA 409 PC) with a heating rate of 10 °C min\(^{-1}\) from 30 to 600 °C under ambient atmosphere.

3. Electrochemical characterizations

The ultrathin mesoporous Co\(_3\)O\(_4\) nanosheet arrays supported on Ni foam were directly used as the working electrode. A platinum plate (1 cm\(^2\)) and a SCE were used as the counter and reference electrodes, respectively, for following electrochemical tests by cyclic voltammetry (CV) and chronopotentiometry (CP) performed with an IVIUM Electrochemical Workstation (the Netherlands). The electrolyte was a 2 M KOH aqueous solution. The specific capacitance of ultrathin mesoporous Co\(_3\)O\(_4\) nanosheets grown on Ni foam was calculated from the CP curves based the following equation:

\[
C = \frac{It}{\Delta V}
\]

where \(C\), \(I\), \(t\) and \(\Delta V\) are the SC (F g\(^{-1}\)), the discharging current density (A g\(^{-1}\)), the discharging time (s) and the discharging potential range (V), respectively.
From Figure S1, except the three peaks (2θ = 44.3°, 51.7° and 76.1°) ascribed to the Ni foam, other five obvious diffraction peaks of the as-synthesized green Co(OH)₂/Ni foam (the inset in Figure S1) can be easily identified for α-Co(OH)₂ crystalline structure,¹ which is consistent with the previous reports.

As seen from Fig. S2, the Co(OH)$_2$ obtained by electrodeposition undergoes a two step weight loss due to dehydration and deposition, rather than a single step weight loss for the β-Co(OH)$_2$.$^{2,3}$ Specifically, the weight loss below 155 °C is attributed to the removal of the absorbed water and the evaporation of the intercalated water molecules.$^3$ And the weight loss above 155 °C is associated with the loss of water produced by the decomposition and dehydroxylation of Co(OH)$_2$.$^3$ After thermally oxidative transformation into Co$_3$O$_4$, the net weight loss observed is ca. 23%, much larger than that of 13.6% of the β-Co(OH)$_2$.$^2$ These data further indicates the formed precursor is α-Co(OH)$_2$ phase rather than β-Co(OH)$_2$.

Fig. S3. XRD patterns of the pure Ni foam and Co$_3$O$_4$/Ni foam.
Fig. S4. TEM image of the Co$_3$O$_4$ nanosheets scratched down from the Ni foam.
Fig. S5. FESEM images of the precursor Co(OH)$_2$/Ni foam.
Fig. S6. FESEM images of the Co$_3$O$_4$/Ni foam obtained by calcination with a ramping rate of 10 °C min$^{-1}$. 
Table S1. Specific capacitances and area loading of the Co₃O₄/nickel foam in this study, compared with some other Co₃O₄/nickel foam electrodes reported in previous literature.

<table>
<thead>
<tr>
<th>Electrode structure</th>
<th>Specific capacitance</th>
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<tbody>
<tr>
<td>Ultrathin mesoporous Co₃O₄ nanosheet arrays/Ni foam (this study)</td>
<td>2735 F g⁻¹ at 2 A g⁻¹</td>
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<tr>
<td>Co₃O₄ nanosheets@nanowire arrays/Ni foam (ref. 4)</td>
<td>715 F g⁻¹ at ca. 0.67 A g⁻¹</td>
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<tr>
<td>Hollow Co₃O₄ nanowire arrays/Ni foam (ref. 5)</td>
<td>599 F g⁻¹ at 2 A g⁻¹</td>
</tr>
<tr>
<td>Mesoporous Co₃O₄ nanowire arrays (ref. 6)</td>
<td>1160 F g⁻¹ at 2 A g⁻¹</td>
</tr>
<tr>
<td>Co₃O₄ nanowire arrays/Ni foam (ref. 7)</td>
<td>754 F g⁻¹ at 2 A g⁻¹</td>
</tr>
<tr>
<td>Porous nanowall Co₃O₄ film/Ni foam (ref. 8)</td>
<td>325 F g⁻¹ at 2 A g⁻¹</td>
</tr>
<tr>
<td>Co₃O₄ nanoflowers/Ni foam (ref. 9)</td>
<td>1309.7 F g⁻¹ at 3 A g⁻¹</td>
</tr>
<tr>
<td>Co₃O₄ nanowire arrays/Ni foam (ref. 10)</td>
<td>746 F g⁻¹ at ca. 0.31 A g⁻¹</td>
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<tr>
<td>Net-like Co₃O₄ nanostructures/Ni foam (ref. 11)</td>
<td>1090 F g⁻¹ at 10 mV s⁻¹</td>
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