Supporting Information

Ordered ZIF-8-derived Layered Double Hydroxide Hollow Nanoparticles-Nanoflake Array for High Efficiency Energy Storage

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Experimental Section

Synthesis of zinc nitrate hydroxide nanoflake array (Zn-NFA)

Ni foam was first placed in 3 mol/L HCl solution with ultrasonic treatment for 30 min and washed with ethanol and water for several times. In a typical synthesis, 75 mmol/L of Zn(NO₃)₂·6H₂O (2.23 g) and 250 mmol/L of hexamethylenetetramine (3.5 g) was dissolved in 100 ml of methanol, and then 10 ml of 2 mol/L HNO₃ aqueous solution was added. The mixed solution was subsequently transferred to a glass bottle and Ni foam was sunk in the reactant solution. The bottle was finally sealed and heated in a 60 °C oven for 48 h. After cooling to room temperature naturally, a white-colored product was covering on the surface of Ni foam and Zn-NFA was obtained. For comparison, ZnO nanowires were also synthesized. Simply, 1.19 g of Zn(NO₃)₂·6H₂O, 0.16 g of NaOH, 0.14 g of hexamethylenetetramine and 0.34 g of NaF was dissolved in 40 ml of water at room temperature. After stirring for 1 h, the precursor solution was then transferred into 50 ml of Teflon-lined stainless steel
autoclave. The autoclave was heated at 120 °C for 10 h and cooled to room temperature naturally. The white precipitate was washed with water, collected by centrifugation and dried at 80 °C.

**Synthesis of ZIF-8 nanoflake array (ZIF-NFA)**

For the transformation from Zn-NFA to ZIF-NFA, the obtained Zn-NFA on Ni foam was simply immersed into 2-methylimidazole aqueous solution (5 g in 20 ml H2O) for 6 h at room temperature. After that, the white product on Ni foam was washed with water and ethanol for more than 5 times, and dried at 80 °C. The conversion from ZnO nanowires to ZIF-8 was carried out through the similar procedures, only the reaction time would last for 7 days.

**Synthesis of layered double hydroxide (LDH) hollow nanoparticle-nanoflake array (LDH-NFA)**

ZIF-NFA was used as the sacrificial template for the synthesis of LDH-NFA in the presence of Ni(NO3)2/Co(NO3)2 methanol solution. The ZIF-NFA was sunk in 0.5 M of Co(NO3)2, Ni(NO3)2 and Co(NO3)2+Ni(NO3)2 methanol solution for 24 h. After taking the Ni foam out of the vessel, it was further transferred into 1 M NaOH solution to remove unsatisfying Zn species. Finally, the resulting Ni foam was washed with water and ethanol, and dried at 80 °C for following characterizations. The mass of Co-NFA, Ni-NFA and NiCo-NFA was measured by calculating the increased mass of Ni foam, their mass loading was determined as 2.0, 2.2 and 2.1 mg/cm², respectively.

**Materials characterizations and electrochemical measurements**

The X-ray diffraction (XRD) analysis was conducted on a Rigaku D/MAX2500VL/PC X-ray diffractometer with Cu Kα radiation. The structure and component information of the materials was got through a field-emission scanning electron microscopy (SEM, SU8020) and a transmission electron microscopy (TEM, JEM-2100) operated at 200 KV. The as-prepared samples were analyzed by the nitrogen sorption technique using a Micromeritics ASAP 2020 instrument at 77 K, the surface area values were calculated by using the Brunauer-Emmett-Teller (BET) method in the relative pressure (P/Po) range of 0.002-0.3. The X-ray photoelectron
spectroscopy (XPS) analyses were examined on a Thermo Fisher X-ray photoelectron spectrometer system (ESCALAB250). Fourier transform infrared spectrum (FTIR) was recorded on a Perkin Elmer Fourier-Transform infrared spectrometer by using the KBr wafer technique. Raman spectrum was recorded from an Ar laser (Renishaw Invia) with an excitation line at 514 nm at room temperature. All the electrochemical measurements were tested on an Autolab 3 electrochemical workstation. A three-electrode system was used to investigate the electrochemical performances in 6 M KOH electrolyte solution. 4 cm² of Ni foam with active materials was directly used as the working electrode, KCl saturated Ag/AgCl as the reference electrode and Pt rod as the counter electrode. The electrochemical impedance spectroscopy (EIS) measurement was carried out in the frequency range from 0.1Hz to 100 kHz at open-circuit potential with an ac perturbation of 0.1 V. The area capacity (C cm⁻²) of the electrodes was calculated based on Equation 1 (CV plots) and Equation 2 (galvanostatic charge/discharge curves), and the specific capacity of the electrode was calculated by Equation 3:

\[
C_a = \frac{\int_{V_s}^{V_e} I(V) dV}{S \nu}
\]

Equation 1

where \(C_a\) is the area capacity (C cm⁻²), \(S\) is the geometrical area of the electrode (cm²) and \(\nu\) is the scan rate of CV curves (V s⁻¹).

\[
C_a = \frac{I \Delta t}{S}
\]

Equation 2

where \(C_a\) is the area capacity (C cm⁻²), \(I\) is the discharge current (A), \(S\) is the geometrical area of the electrode (cm²) and \(\Delta t\) is the total discharge time (s).

\[
C_s = \frac{I \Delta t}{m}
\]

Equation 3

where \(C_s\) is the specific capacity (C g⁻¹), \(I\) is the discharge current (A), \(m\) is the mass of the active materials (g) and \(\Delta t\) is the total discharge time (s).

The asymmetric supercapacitor was assembled and measured in a two-electrode system. A piece of NiCo-NFA (1 cm * 1 cm) was pressed onto Ni foam (1 cm * 3 cm) as the positive electrode. In the preparation of negative electrode, 90 wt% of
commercial active carbon was mixed with 10 wt% PVDF in addition of NMP to make a slurry, the mixed slurry was then cast a 1 cm$^2$ of area on a Ni foam (1 cm * 3 cm), dried at 80 °C for 12 h and pressed under 10 MPa of pressure. The two electrodes and a cellulose separator permeable to ion transport were placed into a test fixture consisting of two stainless steel plates, with 6 M KOH aqueous solution as the electrolyte. The specific capacitance (C, F g$^{-1}$), specific energy density (SE, Wh kg$^{-1}$) and specific power density (SP, W kg$^{-1}$) were calculated from chronopotentiometric curves by using following Equation 4-6, respectively.

\[ C = \frac{I \Delta t}{m \Delta V} \quad \text{Equation 4} \]

where C is the specific capacitance (F g$^{-1}$), I is the discharge current (A), m is the total mass of both positive and negative electrodes (g), \( \Delta t \) is the discharge time (s) and \( \Delta V \) is the window potential during the discharge process.

\[ SE = \frac{C \Delta V^2}{7.2} \quad \text{Equation 5} \]

where SE is the specific energy density (Wh kg$^{-1}$), C is the specific capacitance (F g$^{-1}$), \( \Delta V \) is the window potential during the discharge process.

\[ SP = \frac{3600 \cdot SE}{\Delta t} \quad \text{Equation 6} \]

where SP is the specific power density (W kg$^{-1}$), SE is the specific energy density (Wh kg$^{-1}$) and \( \Delta t \) is the discharge time (s).
Figure S1 XRD patterns of the resulting products at every step: Zn-NFA (a), ZIF-NFA (b), Co-NFA (c), Ni-NFA (d) and NiCo-NFA (e).

Figure S2 SEM images of ordered Zn-NFA aligned on Ni foam tightly.
Figure S3 SEM images of ZnO nanoparticles before (a) and after (b) placing in 2-methylimidazole aqueous solution for 7 days at room temperature; SEM images of ZnO nanowires (c), after immersing in 2-methylimidazole aqueous solution for 48 h at room temperature (d) and 90°C (e); XRD patterns of the samples (f): pure ZnO (1), ZnO in 2-methylimidazole aqueous solution for 7 days at room temperature (2), zinc nitrate hydroxide nanoflakes before (3) and after (4) placing in 2-methylimidazole aqueous solution for 6 h. The complete transformation from zinc nitrate hydroxide to ZIF-8 was much faster than the transformation from ZnO, the resulting product was pure ZIF-8 and no other peaks were detected. ZnO nanowires and nanoparticles lost their initial morphology in the transformation process.
Figure S4 Nitrogen adsorption-desorption isotherms of ZIF-8 nanoflake array synthesized at room temperature in aqueous media.

Figure S5 FTIR (a) and Raman spectra (b) of as-synthesized ZIF-8 nanoflake array. In FTIR spectrum, the bands at 3135 and 2929 cm\(^{-1}\) could be assigned to the aromatic and the aliphatic C–H stretch of the imidazole, respectively. The peak located at 1584 cm\(^{-1}\) was attributed the C═N stretch mode. Bands in the spectral region of 600–1500 cm\(^{-1}\) were associated with the entire ring stretching or bending. The peak at 421 cm\(^{-1}\) was due to Zn-N stretch, and the band at 3620 cm\(^{-1}\) could be ascribed to the free hydroxyl groups. In Raman spectrum, very strong bands were observed at 168 cm\(^{-1}\), 686 cm\(^{-1}\), 1146 cm\(^{-1}\), and 1458 cm\(^{-1}\), respectively corresponding to Zn-N stretching, imidazole ring puckering, C5-N stretching and methyl bending. In addition, the band located at 2931 cm\(^{-1}\) was originated from the C–H (methyl) stretching.
Figure S6 (a) XPS full spectra of ZIF-NFA after immersing into Co(NO₃)₂ (1), Ni(NO₃)₂ (2) and Co(NO₃)₂+Ni(NO₃)₂ (3) methanol solution; high-resolution XPS spectra of Co 2p₃/₂ (b) and Ni 2p₃/₂ (c) of sample 1; high-resolution XPS spectra of Ni2p₃/₂ of sample 2 (d); high-resolution XPS spectra of Co 2p₃/₂ (e) and Ni 2p₃/₂ (f) of sample 3. The peaks located at 779.1 eV and 785.8 eV for sample 1 and sample 3 corresponded to Co³⁺ and Co³⁺ satellite peaks; for Ni 2p₃/₂ spectra of sample 2 and sample 3, it was obvious to see two new peaks at 853.8 eV and 861.6 eV emerged in comparison with that of sample 1, which can be assigned to Ni³⁺ and Ni³⁺ satellite peak. The existence of Co³⁺ and Ni³⁺ valence states revealed that oxidization from Co²⁺/Ni²⁺ to Co³⁺/Ni³⁺ ions had already occurred by dissolved O₂ and NO₃⁻ ions in the solution, resulting from the hydrolization of Co²⁺/Ni²⁺ when ZIF-8 was introduced.
Figure S7 SEM images of ZIF-NFA before (a) and after immersing into 0.5 M of Co(NO$_3$)$_2$ (b), Ni(NO$_3$)$_2$ (c) and Co(NO$_3$)$_2$+Ni(NO$_3$)$_2$ (d) methanol solution.
Figure S8 EDX mapping of ZIF-NFA on Ni foam before (a, b) and after immersing into 0.5 M of Co(NO$_3$)$_2$ (c, d), Ni(NO$_3$)$_2$ (e, f) and Co(NO$_3$)$_2$+Ni(NO$_3$)$_2$ (g, h) methanol solution.
Figure S9 XRD of ZIF-NFA on Ni foam after immersing in 0.5 M of Co(NO₃)₂ (a), Ni(NO₃)₂ (b) and Co(NO₃)₂+Ni(NO₃)₂ (c) methanol solution.

Figure S10 SEM images of ZIF-NFA in 0.0625 M (a), 0.125 M (b), 0.25 M (c) and 0.5 M (d) of Co(NO₃)₂+Ni(NO₃)₂ methanol solution. The high concentration facilitates the formation of nanoparticles-nanoflake morphology due to the fast hydrolysis rate and more sufficient H⁺ protons produced.
Figure S11 EDX mapping of ZIF-NFA after immersing in 0.5 M of Co(NO₃)₂ (a, b), Ni(NO₃)₂ (c, d) and Co(NO₃)₂+Ni(NO₃)₂ (e, f) methanol solution following by rinsing with 1 M NaOH aqueous solution for 24 h. Zn could not be detected, implying the removal of Zn species.
Figure S12 SEM images of ZIF-NFA after immersing in 2 M of Co(NO$_3$)$_2$+Ni(NO$_3$)$_2$ methanol solution following by rinsing with 2 M NaOH aqueous solution for 24 h. No hollow structure but solid nanoflakes could be observed.
Figure S13 CV plots of Co-NFA (a), Ni-NFA (b) and NiCo-NFA (c) at the scan rate of 2, 5, 10, 20 and 50 mV/s; galvanostatic charge-discharge curves of Co-NFA (d) and Ni-NFA (e) at different current density.
Table S1 The electrochemical properties of layered double hydroxide materials in the recent literature.

<table>
<thead>
<tr>
<th>Active materials</th>
<th>Mass loading</th>
<th>Mass capacity (C/g)</th>
<th>Rate capability</th>
<th>Rate capability</th>
<th>Cycling retention</th>
<th>References</th>
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<tr>
<td>ZIF-67-derived LDH nanocage</td>
<td>_</td>
<td>601.5</td>
<td>78.1%</td>
<td>90.2%</td>
<td>11770</td>
<td>Nanoscale, 2013, 5,</td>
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<tr>
<td>Co-LDH</td>
<td>0.285</td>
<td>137.3</td>
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<td>85%</td>
<td>2014, 24, 4831</td>
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<td>CoO₆@NiAl-LDH nanowire array</td>
<td>1.2</td>
<td>886</td>
<td>61.4%</td>
<td>87.9%</td>
<td>7, 134</td>
<td>Nano Energy, 2014,</td>
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<td>NiCo-LDH</td>
<td>3.0</td>
<td>1341</td>
<td>63.6%</td>
<td>_</td>
<td>2014, 24, 934</td>
<td></td>
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<td>Carbonized bacterial cellulose@niCo-LDH</td>
<td>3.0</td>
<td>779.8</td>
<td>54.7%</td>
<td>74.4%</td>
<td>3235</td>
<td>Small, 2016, 12,</td>
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<td>ZIF-67-derived CoO₄ nanotube array</td>
<td>3.4</td>
<td>580</td>
<td>51.4%</td>
<td>96.9%</td>
<td>2015, 3, 16688</td>
<td>J. Mater. Chem. A,</td>
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<td>Prussian blue analogue-derived NiS</td>
<td>1.0</td>
<td>1013.7</td>
<td>33.6%</td>
<td>91.8%</td>
<td>Ed., 2015, 54, 1</td>
<td>Angew. Chem. Int.</td>
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<tr>
<td>ZIF-67-derived Co₃O₄-NiCo₂O₄ nanocages</td>
<td>1.0</td>
<td>408</td>
<td>63.2%</td>
<td>92.5% (12000)</td>
<td>2015, 137, 5590</td>
<td>J. Am. Chem. Soc.,</td>
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<td>NiCo-NFA</td>
<td>2.1</td>
<td>971.4</td>
<td>49.5 %</td>
<td>94.1%</td>
<td>This work</td>
<td></td>
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</table>
Figure S14 Nyquist plots of Co-NFA, Ni-NFA and NiCo-NFA at a range of 0.1 Hz ~100 kHz.

Figure S15 The resulting SEM images of Co-NFA (a), Ni-NFA (b) and NiCo-NFA (c) at the current density of 40 mA/cm² after 5000 cycles; and the resulting TEM images of Co-NFA (d), Ni-NFA (e) and NiCo-NFA (f). The nanoflake morphology of layered double hydroxides could be still retained after the cycling test, revealing their excellent electrochemical durability for energy storage application.
Figure S16 CV plots of positive electrode NiCo-NFA (+) and negative electrode AC (-) at a scan rate of 20 mV/s. As for a full supercapacitor cell, the charge balance followed the relationship \( Q_+ = Q_- \). The charge stored by electrodes depended on specific capacitance (\( C \)), potential range for the charge/discharge process (\( \Delta E \)) and the mass of the electrode (\( m \)), and the charge could be describe as: \( Q = C \cdot m \cdot \Delta E \), so the mass balancing of NiCo-NFA/AC (\( m_+/m_- \)) was calculated as:

\[
\frac{m_+}{m_-} = \frac{C_- \Delta E_-}{C_+ \Delta E_+} = \frac{158 \cdot 1}{641 \cdot 0.8} = 0.31.
\]
Figure S17 Cycling stability of the assembled asymmetric supercapacitor NiCo-NFA//AC measured at a current density of 5 A/g.