Supporting Information

Hierarchical Glucose-intercalated NiMn-G-LDH@NiCo$_2$S$_4$ Core-Shell Structure as Binder-Free Electrode for Flexible All-Solid-State Asymmetric Supercapacitors

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FT-IR was performed to further verify the glucose intercalation. As shown in Fig. S2, the strong and broad absorption in the range of 3400-3600 cm⁻¹ and the peak at 1632 cm⁻¹ was observed in both samples, which can be ascribed to -OH and interlayer H₂O of LDH. The peaks in the range of 400-800 cm⁻¹ are mainly assigned to the vibrations of Ni-O and Mn-O bonds in the LDHs. And the peaks centered at 1336 cm⁻¹ and 1193 cm⁻¹ are assigned to CO₃²⁻ and C-O, suggesting the CO₃²⁻ intercalation in both NiMn-LDH and NiMn-G-LDH, which is consistent with the XRD results. Specially, the double peaks around 2868
cm$^{-1}$ and the obviously discerned peaks at 1042 and 985 cm$^{-1}$ in the NiMn-G-LDH are due to stretching vibration of C-H, C-OH and CH$_2$, respectively, verifying the successful intercalation of glucose into the interlayer of NiMn-G-LDH. The result is consistent with the previous literatures.\textsuperscript{2,3}

\textbf{Fig. S3.} SEM images of NiMn-G-LDH@CFC.

\textbf{Fig. S4.} EDS mapping images of S and C on NiMn-G-LDH@NiCo$_2$S$_4$ that were scratched from the CFC.
Fig. S5. XPS survey spectra of NiMn-G-LDH@NiCo$_2$S$_4$@CFC.

Fig. S6. (a)Ni 2p (b) Co 2p and (c) S 2p spectrum of NiCo$_2$S$_4$@CFC and (d) Mn 2p of NiMn-G-LDH@NiCo$_2$S$_4$@CFC.
Fig. S7. (a) Mn 2p and (b) C 1s spectrum of of NiMn-G-LDH@NiCo$_2$S$_4$@CFC.

Fig. S8. N$_2$ adsorption-desorption isotherm and pore size distribution of the NiMn-G-LDH that were scratched from the CFC.
Fig. S9. CV curves of the pristine CFC at 20 mV s\(^{-1}\).

Fig. S10. (a) CV curves, (b) GCD curves and specific capacity at various current densities of NiCo-OH@CFC and (c) CV curves, (d) GCD curves and specific capacity at various current densities of NiCo\(_2\)S\(_4\)@CFC.
The electrochemical performance of NiCo-OH@CFC and NiCo$_2$S$_4$@CFC were investigated in a three-electrode configuration. Fig. S10a and S10c show the CV curves of the NiCo-OH@CFC and NiCo$_2$S$_4$@CFC electrodes at different scan rates ranging from 5 to 50 mV s$^{-1}$, respectively. Obviously, two pairs of similar well-defined redox peaks can be observed and the integrated CV area of NiCo$_2$S$_4$@CFC is much larger than that of the NiCo-OH@CFC, suggesting the improved specific capacitance by the sulfurization. Moreover, the calculated specific capacity based on the GCD of NiCo-OH@CFC and NiCo$_2$S$_4$@CFC are 130 C g$^{-1}$ and 561 C g$^{-1}$ at 1 A g$^{-1}$, respectively. With the increase of current density, the specific capacitance retention of 58.5% for the NiCo-OH@CFC electrodes is lower than that of 67.1% for the NiCo$_2$S$_4$@CFC. The enhanced specific capacitance and rate retention can be attributed to the better electronic conductivity and faster redox reactions of NiCo$_2$S$_4$@CFC.

Fig. S11. IR drop of NiMn-G-LDH@CFC, NiCo$_2$S$_4$@CFC, and NiMn-G-LDH@NiCo$_2$S$_4$@CFC under various current densities.
Fig. S12. (a) CV curves, (b) GCD curves and specific capacity at various current densities of NiMn-LDH@NiCo$_2$S$_4$@CFC and (c) EIS of NiMn-LDH@NiCo$_2$S$_4$@CFC and NiMn-G-LDH@NiCo$_2$S$_4$@CFC.

The corresponding electrochemical tests of NiMn-LDH@NiCo$_2$S$_4$@CFC were conducted as a control. As displayed in Fig. S12a, the CV curves deformed when the scan rate increased to above 30 mV s$^{-1}$, suggesting an inferior specific capacity retention. The calculated specific capacity based on the GCD of NiMn-LDH@NiCo$_2$S$_4$@CFC is 783 C g$^{-1}$ at 1 A g$^{-1}$, which is lower than that of NiMn-G-LDH@CFC (1018 C g$^{-1}$). Additionally, NiMn-LDH@NiCo$_2$S$_4$@CFC also exhibit lower specific capacitances retention of 53.6% than that of NiMn-G-LDH@NiCo$_2$S$_4$@CFC (68.4%) at 20 A g$^{-1}$ (Fig. S12b). In order to better understand the improved ionic diffusion and charge transfer after glucose intercalation, the Nyquist plots of NiMn-LDH@NiCo$_2$S$_4$@CFC and NiMn-G-LDH@NiCo$_2$S$_4$@CFC were compared and fitted with the equivalent circuit model (Figure S12c). Upon glucose intercalation, NiMn-G-LDH@NiCo$_2$S$_4$@CFC
possess smaller charge transfer resistance \((R_{ct}, 0.37 \, \Omega)\) and higher Warburg slope \((W_o, 0.467)\) than those of NiMn-LDH@NiCo$_2$S$_4$@CFC \((R_{ct}, 0.88 \, \Omega \text{ and } W_o, 0.452)\).\(^4\,5\)

**Fig. S13.** (a) CV curves, (b) GCD curves and specific capacity at various current densities of NiMn-LDH@CFC and (c) CV curves, (d) GCD curves and specific capacity at various current densities of NiMn-G-LDH@CFC.

The electrochemical performance of NiMn-LDH@CFC and NiMn-G-LDH@CFC were also measured in a three-electrode system. The CV curves of the NiMn-LDH@CFC and NiMn-G-LDH@CFC electrodes also exhibit two pairs of similar well-defined redox peaks and the integrated CV area of NiMn-G-LDH@CFC is much larger than that of the NiCo-OH@CFC, implying the improved specific capacitance by the glucose intercalation (shown in Fig. S13a and S13c). Thus, the calculated specific capacity based on the GCD of NiMn-G-LDH@CFC is 666 C g\(^{-1}\), which is much higher than that of 384 C g\(^{-1}\) for the NiMn-LDH@CFC at 1 A g\(^{-1}\). Moreover, NiMn-G-LDH@CFC yield similar specific capacitance retention
of 78.1%, compared with that of 80.1% for NiMn-LDH @CFC at 20 A g\textsuperscript{-1} even at a much higher initial capacitance.

Fig. S14. Capacitive and diffusion-controlled contribution to the charge storage of NiCo\textsubscript{2}S\textsubscript{4}@CFC.

Fig. S15. (a) CV of AC negative electrode at different scanning rates and (b) GCD curves at different current densities.
Fig. S16. Electrochemical performance of NiMn-G-LDH@NiCo$_2$S$_4$@CFC//AC assembled in aqueous system (a) CV and (b) GCD curves; (c) specific capacitances of the SASC device at various current densities; (d) cycling stability at a current density of 10 A g$^{-1}$.

Fig. S17. LED lighting test with two device connected in series
**Table S1.** Comparison of intercalated and un-intercalated LDH electrodes in the three-electrode system.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Specific capacity (1 A g$^{-1}$)</th>
<th>Specific capacity (20 A g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMn-LDH@CFC</td>
<td>384 C g$^{-1}$</td>
<td>308 C g$^{-1}$</td>
</tr>
<tr>
<td>NiMn-G-LDH@CFC</td>
<td>666 C g$^{-1}$</td>
<td>520 C g$^{-1}$</td>
</tr>
<tr>
<td>NiMn-LDH@NiCo$_2$S$_4$@CFC</td>
<td>783 C g$^{-1}$</td>
<td>420 C g$^{-1}$</td>
</tr>
<tr>
<td>NiMn-G-LDH@NiCo$_2$S$_4$@CFC</td>
<td>1018 C g$^{-1}$</td>
<td>696 C g$^{-1}$</td>
</tr>
</tbody>
</table>

**Table S2.** Comparison of electrochemical performance of LDHs-based electrodes in the three-electrode system.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Electrolyte</th>
<th>Specific capacitance</th>
<th>Rate capability</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMn-G-LDH@NiCo$_2$S$_4$@CFC</td>
<td>6 M KOH</td>
<td>2036 F g$^{-1}$ (1 A g$^{-1}$)</td>
<td>68.4% at 20 A g$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>NiMn-LDH/rGO</td>
<td>2 M KOH</td>
<td>1635 F g$^{-1}$ (1 A g$^{-1}$)</td>
<td>71.0% at 10 A g$^{-1}$</td>
<td>6</td>
</tr>
<tr>
<td>Glucose-intercalated NiMn-LDH</td>
<td>6 M KOH</td>
<td>1464 F g$^{-1}$ (0.5 A g$^{-1}$)</td>
<td>59.4% at 10 A g$^{-1}$</td>
<td>2</td>
</tr>
<tr>
<td>(Ni,Co)Se$_2$/NiCo-LDH@CFC</td>
<td>3 M KOH</td>
<td>1224 F g$^{-1}$ (2 A g$^{-1}$)</td>
<td>71.0% at 20 A g$^{-1}$</td>
<td>7</td>
</tr>
<tr>
<td>KCu$_2$S$_4$@NiMn LDH</td>
<td>1 M LiOH</td>
<td>734 F g$^{-1}$ (1 A g$^{-1}$)</td>
<td>76.9% at 30 A g$^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$@CNT</td>
<td>2 M KOH</td>
<td>1596 F g$^{-1}$ (1 A g$^{-1}$)</td>
<td>88.1% at 10 A g$^{-1}$</td>
<td>8</td>
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</tbody>
</table>

**Table S3.** The energy density and power density of various electrodes in an ASC system in references.

<table>
<thead>
<tr>
<th>Asymmetric supercapacitor</th>
<th>Energy density</th>
<th>Power density</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMn-G-LDH@NiCo$_2$S$_4$@CFC//AC</td>
<td>60.3 Wh kg$^{-1}$</td>
<td>375 W kg$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>Core-shell NiCo-LDH/NiCoP@NiMn-LDH</td>
<td>42.2 Wh kg$^{-1}$</td>
<td>750 W kg$^{-1}$</td>
<td>9</td>
</tr>
<tr>
<td>Core-shell NiCo$_2$S$_4$@Ni(OH)$_2$@PPy</td>
<td>34.7 Wh kg$^{-1}$</td>
<td>120 W kg$^{-1}$</td>
<td>10</td>
</tr>
<tr>
<td>NiCo$_2$S$_4$ nanopetals//AC</td>
<td>35.6 Wh kg$^{-1}$</td>
<td>820 W kg$^{-1}$</td>
<td>11</td>
</tr>
<tr>
<td>Core-shell (Ni,Co)Se$_2$/NiCo-LDH//AC</td>
<td>39.0 Wh kg$^{-1}$</td>
<td>1650 W kg$^{-1}$</td>
<td>7</td>
</tr>
<tr>
<td>Core-shell CoS$_x$/Ni-Co LDH//AC</td>
<td>35.8 Wh kg$^{-1}$</td>
<td>800 W kg$^{-1}$</td>
<td>12</td>
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References:


