Electronic Supplementary Information (ESI)

In-situ growth of Cu(OH)$_2$@FeOOH nanotubes arrays on catalytically deposited Cu current collector patterns for high-performance flexible in-plane micro-size energy storage devices

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Fig. S1 Surface SEM images of (a) PTFE, (b) cotton cloth and (c) waste paper. Digital photos of electroless deposited copper patterns on (d) PTFE, (e) cotton cloth and (f) waste paper. Surface SEM images of the electroless deposited copper on (g) PTFE, (h) cotton cloth and (i) waste paper.
Fig. S2 Surface SEM images of Cu coatings on PI (filled in epoxy resin) at ECD time of (a) 5 min, (b) 10 min, (c) 15 min and (d) 30 min.
Fig. S3 The variation of the surface resistivity of Cu coating with ECD time.

Fig. S4 Cross-sectional SEM images of Cu coatings on PI (filled in epoxy resin) at ECD time of (a) 1h, (b) 1.5h, (c) 3h and (d) 6h.
Fig. S5 (a) digital image, (b) Cross-sectional SEM image and (c-e) surface SEM images of the PI substrate.

Fig. S6 Contact angles between water and PI substrates (a) before and (b) after surface modification.
Fig. S7 Surface SEM images of interdigital electrodes: (a) Cu/PI and (b) Cu(OH)$_2$@FeOOH NTs array /Cu/PI.

Fig. S8 XRD patterns of the electroless deposited cooper before and after stability test.
Fig. S9 Cross-sectional SEM image of the Cu(OH)$_2$@FeOOH NTs array/Cu electrode.

Fig. S10 (a) Digital photo, (c-d) SEM images and (d) TEM image of Cu(OH)$_2$. (e) Digital photo, (f-g) SEM images and (h) TEM image of Cu(OH)$_2$@FeOOH-1. (i) Digital photo, (j-k) SEM images and (l) TEM image of Cu(OH)$_2$@FeOOH-2. (m) Digital photo, (n-o) SEM images and (p) TEM image of Cu(OH)$_2$@FeOOH-3. (q) Digital photo, (r-s) SEM images and (t) TEM image of Cu(OH)$_2$@FeOOH-4.
Fig. S11 (a) Cross-sectional SEM image and (b-d) SEM-EDS mapping of the Cu(OH)$_2$@FeOOH NTs array.

Fig. S12 Digital images of the as-fabricated interdigitated electrodes: (a) Cu/PI, (b) Cu(OH)$_2$ NWs array/Cu/PI and (c) Cu(OH)$_2$@FeOOH NTs array/Cu/PI.
Fig. S13 HRTEM images of (a) Cu(OH)$_2$ NWs and (b) FeOOH nanosheet.

Fig. S14 Structure illustration of the Cu(OH)$_2$ NWs and Cu(OH)$_2$@FeOOH NTs.
Fig. S15 The survey XPS spectra of the Cu(OH)$_2$ NWs and the Cu(OH)$_2$@FeOOH NTs.

Fig. S16 EDS spectra of (a) Cu(OH)$_2$@FeOOH-1 (b) Cu(OH)$_2$@FeOOH-2, (c) Cu(OH)$_2$@FeOOH-3 and (d) Cu(OH)$_2$@FeOOH-4.
Fig. S17 GCD curves of MSCs fabricated by Cu electrodes immersed in NaOH&\((\text{NH}_4)_2\text{SO}_3\) aqueous solution with different immersing time at 0.2 mA cm\(^{-2}\).

Fig. S18 Sectional SEM images of Cu(OH)_2 NWs array with immersing time at (a) 1 minute, (b) 2 minutes, (c) 3 minutes, (d) 4 minutes, (e) 5 minutes and (f) 6 minutes. (g, h) Surface SEM images of the structure with immersing time at 9 minutes.
Fig. S19 GCD curves of MSCs fabricated by Cu(OH)$_2$/Cu electrodes immersed in FeCl$_2$ aqueous solution with different immersing time at 0.2 mA cm$^{-2}$.

Fig. S20 The N$_2$ adsorption and desorption isotherms of Cu(OH)$_2$, Cu(OH)$_2$@FeOOH-1, Cu(OH)$_2$@FeOOH-2, Cu(OH)$_2$@FeOOH-3 and Cu(OH)$_2$@FeOOH-4.
Fig. S21 Contact angles between the electrolyte and (a) Cu, (b) Cu(OH)$_2$, (c) Cu(OH)$_2$@FeOOH-1, (d) Cu(OH)$_2$@FeOOH-2, (e) Cu(OH)$_2$@FeOOH-3 and (f) Cu(OH)$_2$@FeOOH-4.

Fig. S22 EIS curves of MSCs fabricated by different electrodes.
Table S1. Comparison of current collector, patterning technology, active materials, synthesis method and electrochemical performances of various MSCs.

<table>
<thead>
<tr>
<th>Current collector</th>
<th>Patterning technique</th>
<th>active materials</th>
<th>Synthesis/loading method</th>
<th>Areal capacitance (mF cm⁻²)</th>
<th>Areal energy density (μWh cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D graphene</td>
<td>Laser cutting and milling</td>
<td>3D graphene</td>
<td>Chemical vapor deposition</td>
<td>~10 (5mVs⁻¹)</td>
<td>0.38</td>
</tr>
<tr>
<td>Au/Ag ink</td>
<td>Ink-jet printing; magnetron sputtering</td>
<td>Ni@MnO₂ nanocoral</td>
<td>Electrodeposition</td>
<td>52.7 (5mVs⁻¹)</td>
<td>43.7 (0.54mA cm⁻²)</td>
</tr>
<tr>
<td>Carbon</td>
<td>Spin coating; photolithography</td>
<td>MoS₂ nanosheets @rGO-CNTs</td>
<td>Hydrothermal synthesis/spin coating;</td>
<td>13.7 (0.1 mA cm⁻²)</td>
<td>1.9</td>
</tr>
<tr>
<td>Au</td>
<td>Photolithography and magnetron sputtering</td>
<td>PPy film</td>
<td>Electrodeposition</td>
<td>47.42 (0.1mA cm⁻²)</td>
<td>4.0</td>
</tr>
<tr>
<td>Au</td>
<td>Magnetron sputtering via a printed mask</td>
<td>MnO₂</td>
<td>Electrodeposition</td>
<td>11.9 (0.5mA cm⁻²)</td>
<td>1.05*</td>
</tr>
<tr>
<td>Au</td>
<td>Magnetron sputtering Laser etching</td>
<td>rGO-PEDOT/PSS</td>
<td>Solution-based reaction/bar-coating</td>
<td>84.7 (T=58 μm; 5mVs⁻¹)</td>
<td>26.7 (T=12 μm; 5mVs⁻¹)</td>
</tr>
<tr>
<td>Ag nanowires ink</td>
<td>Ink-jet printing; Active carbon/carbon nanotubes</td>
<td>Ink-jet printing</td>
<td>~20 (0.2mA cm⁻²)*</td>
<td>11.1*</td>
<td></td>
</tr>
<tr>
<td>PPy NWs</td>
<td>Electrodeposition on customized fluorine-doped tin oxide pattern</td>
<td>PPy NWs</td>
<td>Electrodeposition</td>
<td>~11 (0.2mA cm⁻²)</td>
<td>0.38*</td>
</tr>
<tr>
<td>Ni</td>
<td>Electroless Ni deposition via a laser-etched mask (Kapton tape)</td>
<td>rGO</td>
<td>Hydrothermal synthesis/spontaneous assembly</td>
<td>8.19 (10 5mVs⁻¹)</td>
<td>5.75 (0.1mA cm⁻²²)</td>
</tr>
<tr>
<td>Material</td>
<td>Fabrication Method</td>
<td>Method</td>
<td>Specific Resistance</td>
<td>Conductance</td>
<td></td>
</tr>
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<td>---------------------------</td>
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<tr>
<td>3D porous graphene</td>
<td>Laser etching</td>
<td>3D porous graphene</td>
<td>2.47 (5mVs⁻¹)</td>
<td>0.22</td>
<td></td>
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<tr>
<td>Ni</td>
<td>Screen printing, Electroless Ni deposition and Electroplating Ni</td>
<td>MnO₂; PPy electrodeposition</td>
<td>25.8 (0.3mA cm⁻²)</td>
<td>8.05</td>
<td></td>
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<tr>
<td>rGO/Au</td>
<td>Laser writing on GO/HAuCl₄ mixture</td>
<td>rGO/Au</td>
<td>3.84 (1V s⁻¹)</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>MXenes (Ti₃C₂Tx)</td>
<td>Patterned by a 3D-printed stamp.</td>
<td>MXenes</td>
<td>15.25 (0.025 mA cm⁻²)*</td>
<td>0.63</td>
<td></td>
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<tr>
<td>Ti/Au</td>
<td>Vacuum evaporation with a shadow mask</td>
<td>VOₓ/rGO₃ graphene-vanadium nitride quantum dots/rGO</td>
<td>207.9 (T=412 μm)</td>
<td>73.9</td>
<td></td>
</tr>
<tr>
<td>Cu (This work)</td>
<td>Screening printing and Electroless cooper deposition</td>
<td>CuOH@FeOOH nanotubes</td>
<td>In situ conversion (solution immersion at room temperature)</td>
<td>58.0 (0.1mA cm⁻²)</td>
<td>18.07</td>
</tr>
</tbody>
</table>

* T: thickness of the active material.
* Calculated based on the dimensions given in reference if specific results were not given in literature.
Calculations:

The calculations of the areal capacitance \( C_A \) and the volumetric capacitance \( C_V \) based on discharging profiles were derived by the following equations:

\[
C_{\text{device}} = \frac{I t}{U} \quad \text{(S1)}
\]

\[
C_A = \frac{C_{\text{device}}}{A} \quad \text{(S2)}
\]

\[
C_V = \frac{C_A}{d} \quad \text{(S3)}
\]

where \( v \) is the scanning rate, \( U \) is the voltage window, \( I \) is the discharging current, \( t \) is the discharging time and \( A \) is the area of the MSC, \( d \) is the thickness of the device including thickness of both the active materials and the current collector.

The areal energy density \( E_A \) and power density \( P_A \) of the MSC were respectively calculated by the following equations:

\[
E_A = \frac{1}{2} \times C_A \times \frac{U^2}{3600} \quad \text{(S4)}
\]

\[
E_V = \frac{1}{2} \times C_V \times \frac{U^2}{3600} \quad \text{(S5)}
\]

\[
P_A = \frac{3600 \times E_A}{t} \quad \text{(S6)}
\]

\[
P_V = \frac{3600 \times E_V}{t} \quad \text{(S7)}
\]

References