Electronic Supplementary Information (ESI)

Nano-sandwiched metal hexacyanoferrate/graphene hybrid thin films for in-plane asymmetric micro-supercapacitors with ultrahigh energy density

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Experimental section

Chemicals and materials:
All the reagents and solvents, such as graphite flakes, sodium nitrate (NaNO$_3$), sulfuric acid (H$_2$SO$_4$), potassium permanganate (KMnO$_4$), copper chloride dihydrate (CuCl$_2$·2H$_2$O), nickel chloride hexahydrate (NiCl$_2$·6H$_2$O), cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O), ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O), potassium hexacyanoferrate (K$_3$Fe(CN)$_6$), and dimethylformamide (DMF, GC, 99.9%), were purchased from commercial suppliers such as Sigma-Aldrich, Macklin, and Adams-beta. All the available chemicals were used without further purification.

Preparation of graphene suspension:
Graphene suspension (0.05 mg mL$^{-1}$) was prepared by dispersing graphene nanosheets into dimethylformamide (DMF) solvent under sonication-assisted procedure. Typically, graphene-oxide (GO) was synthesized from natural graphite flakes by a modified Hummers method, and then GO was reduced through hydrothermal method at 180 °C for 24 h to obtain graphene suspension. Next, graphene suspension was freeze dried and graphene nanosheets powder was achieved. After that, graphene powder (100 mg) was dispersed into DMF (200 mL), with sodium dodecyl benzene sulfonate (SDBS, 100 mg) added into graphene suspension as dispersant. High-power probe sonication was then carried out to make graphene nanosheets fully dispersed in the suspension.

Preparation of MHCF suspension:
MHCF (M=Cu, Ni, Co, Fe) nanoparticle powders were synthesized by chemical co-precipitation. In a typical procedure, CuHCF nanoparticles were prepared by dropwise addition of copper chloride (CuCl$_2$) aqueous solution (40 mM, 50mL) to potassium hexacyanoferrate (K$_3$Fe(CN)$_6$) aqueous solution (40 mM, 50 mL). The solution was stirred at 500 rpm and heated at 70 °C for 8h. Then, the solution was washed through centrifugation at 5000 rpm for two times and dried at 60 °C. After that, CuHCF powder was obtained. CuHCF suspension was further prepared via dispersing CuHCF powder (10 mg) into DMF (100 mL) with sonication assisted.
Similarly, NiHCF nanoparticles, CoHCF nanoparticles, and FeHCF nanoparticles were prepared by dropwise addition of nickel chloride (NiCl$_2$) aqueous solution (40 mM, 50 mL), cobalt chloride (CoCl$_2$) aqueous solution (40 mM, 50 mL), and ferric chloride (FeCl$_2$) aqueous solution (40 mM, 50 mL) into potassium hexacyanoferrate (K$_3$Fe(CN)$_6$) aqueous solution (40 mM, 50 mL), respectively, following by the same procedures in the preparation of CuHCF suspension to obtain NiHCF suspension, CoHCF suspension, and FeHCF suspension.

**Fabrication of MHCF/graphene hybrid thin films with interdigital patterns:**
MHCF/graphene hybrid thin films (M=Cu, Ni, Co, Fe) were prepared through a mask-assisted filtration method. Typically, a lab-made mask with 10 interdigital-fingers (width of 1.6 mm, length of 15 mm, and interspace of 1.6 mm) was covered on the a polytetrafluoroethylene (PTFE) membrane filter (pore size of 0.2 μm, diameter of 47 mm). Then, graphene suspension (2 mL) and MHCF suspension (2 mL) were alternately dropped on the mask and vacuum-filtrated, resulting in the formation of one layer graphene and one layer MHCF. By repeating such steps for ten times, MHCF/graphene composites with ten layers of graphene and ten layers of MHCF alternately stacked were obtained. Then, the resultant MHCF/graphene composites were directly transfer on the polyethylene terephthalate (PET) substrate to fabricate AMSCs with CuHCF/graphene served as one electrode and NiHCF/graphene, CoHCF/graphene, and FeHCF/graphene served as the other electrode, respectively.

**Materials characterization:**
Scanning Electron Microscopy (SEM) measurements and corresponding energy dispersive X-ray spectroscopy (EDX) elemental mapping were performed on field emission scanning electron microscope (FE-SEM) (Carl Zeiss Gemini 500). X-ray diffraction (XRD) patterns were measured on an X-ray diffractometer (D/max-2200/PC, Rigaku) using Cu-Kα radiation (λ = 1.5418 Å, voltage of 40 kV). Raman spectra were obtained using a Raman spectrometer (Renishaw inVia) with excitation laser wavelength of 532 nm at room temperature. Fourier transform infrared spectra (FTIR) were collected by Bruker Tensor 27 spectrometer. X-ray photoelectron
spectroscopy (XPS) measurements were conducted by AXIS Ultra DLD system from Kratos with Al Kα radiation as X-ray source (1486.6 eV), anode voltage/current of 15 kV/10 mA.

**Electrochemical characterization:**
LiCl/PVA gel (2.12 g LiCl and 5 g PVA mixed with 50 ml deionized water), serving as electrolyte, was dropped on the MHCF/graphene films carefully and solidified overnight before electrochemical measurements. Besides, Cu foil was adhered on the end of microelectrode by silver paste as connector during electrochemical measurements. All the electrochemical measurements were conducted using CHI760D electrochemical work-station.

**Electrochemical calculations:**
The specific capacitance values of the device can be calculated from CV curves according to the following equation (1) and (2):

\[
C_A = \frac{1}{2v \times A \times (V_f - V_i)} \int_{V_i}^{V_f} I(V) dV
\]  

\[
C_V = \frac{1}{2v \times V \times (V_f - V_i)} \int_{V_i}^{V_f} I(V) dV
\]

where \(C_A\) is donated as specific areal capacitance (mF cm\(^{-2}\)) of MHCF/graphene-based AMSCs, \(v\) is the scan rate (V s\(^{-1}\)), \(V_f\) and \(V_i\) are the integration voltage limits of the voltammetric curve, and \(I(V)\) is the voltammetric current with unit of ampere (A), \(A\) (cm\(^2\)) is the area of the entire device. \(C_V\) is donated as specific volume capacitance (F cm\(^{-3}\)) of MHCF/graphene-based AMSCs and \(V\) (cm\(^3\)) is the volume of the entire device.

The specific areal capacitance \((C_A, \text{ mF cm}^{-2})\) and specific volume capacitance \((C_V, \text{ F cm}^{-3})\) of the entire AMSC on the basis of GCD curves can be obtained according to the following equation (3) and (4):

\[
C_A = \frac{I \times \Delta t}{\Delta V}
\]  

\[
C_V = \frac{C_A}{d}
\]
where \( J \) is the current density (A m\(^{-2}\)) of charge/discharge, \( \Delta t \) is the discharged time (s), \( \Delta V \) is voltage output window (V), and \( d \) is the thickness of MHCF/graphene-based AMSCs.

The volume energy density \( (E, \text{Wh cm}^{-3}) \) and volume power density \( (P, \text{W cm}^{-3}) \) of the entire device in the Ragone plot were calculated from GCD curves referred the equations (5) and (6) as follows:

\[
E = \frac{1}{2} \times C_V \times \frac{(\Delta V)^2}{3600}
\]

(5)

\[
P = \frac{E}{\Delta t} \times 3600
\]

(6)

where \( C_V \) is specific volume capacitance of MHCF/graphene-based AMSCs, \( \Delta V \) is voltage output window (V), and \( \Delta t \) is the discharged time (s).
Fig. S1 Photograph of Cu-Fe-AMSC transferred on the substrate of SiO₂/Si wafer.

Fig. S2 Cross-sectional SEM images of (a) CuHCF/graphene and (b) FeHCF/graphene hybrid thin films.

Fig. S3 Cross-sectional SEM images and corresponding EDX elemental mapping of (a-c) CuHCF/graphene and (d-f) FeHCF/graphene.
**Fig. S4** Cross-sectional SEM images of (a) NiHCF/graphene and (b) CoHCF/graphene hybrid thin films.

**Fig. S5** Overall cross-sectional SEM images of (a) CuHCF/graphene, (b) NiHCF/graphene, (c) CoHCF/graphene, and (d) FeHCF/graphene hybrid thin films.
Fig. S6 Top-view SEM images of (a) CuHCF layer for CuHCF/graphene films, (b) NiHCF layer for NiHCF/graphene films, (c) CoHCF layer for CoHCF/graphene films, and (d) FeHCF layer for FeHCF/graphene films.

Fig. S7 Top-view SEM image of graphene layer of CuHCF/graphene films.
**Fig. S8** XRD patterns of as-prepared MHCF (M=Cu, Ni, Co, Fe) and standard face-centered-cubic Prussian blue crystal structure.

**Fig. S9** XPS wide spectra of (a) CuHCF/graphene, (b) NiHCF/graphene, (c) CoHCF/graphene, and (d) FeHCF/graphene.
Fig. S10 XPS survey spectra of (a) graphene and (b) original graphene-oxide with corresponding oxygen to carbon (C/O) atom ratios.

Fig. S11 FTIR spectra of MHCF/graphene (M=Cu, Ni, Co, Fe) hybrid thin films.

Fig. S12 CV curves of MHCF/graphene (M=Cu, Ni, Co, Fe) hybrid thin films measured by standard three-electrode system.
Fig. S13 GCD curves of Cu-Fe-AMSC at current densities of (a) 0.15 mA cm$^{-2}$, (b) 0.3 mA cm$^{-2}$, (c) 1.5 mA cm$^{-2}$, and (d) 3 mA cm$^{-2}$.

Fig. S14 GCD curves of (a) Cu-Co-AMSC and (b) Cu-Ni-AMSC at a current density of 1.5 mA cm$^{-2}$. 
**Fig. S15** CV curves of Cu-Fe-AMSC at scan rates of (a) 10 mV s\(^{-1}\), (b) 50 mV s\(^{-1}\), (c) 100 mV s\(^{-1}\), and (d) 1000 mV s\(^{-1}\).

**Fig. S16** CV curves of (a) Cu-Co-AMSC and (b) Cu-Ni-AMSC at a scan rate of 100 mV s\(^{-1}\).
**Fig. S17** CV curves of (a) Cu-Co-AMSC and (b) Cu-Ni-AMSC at a scan rate of 10 mV s$^{-1}$.

**Fig. S18** The capacitive behavior of Cu-Fe-AMSC under the voltage window of 1.8 V, including (a) CV curves at scan rates from 200 to 2000 mV s$^{-1}$ and (b) GCD curves at current densities from 3 to 30 mA cm$^{-2}$.

**Fig. S19** Nyquist plots of (a) Cu-Co-AMSC and (b) Cu-Ni-AMSC (inset shows the magnification of the high-frequency region).
Fig. S20 The impedance phase angle at different frequency and the corresponding RC time constant $\tau_0$ for (a) Cu-Fe-AMSC, (b) Cu-Co-AMSC, and (c) Cu-Ni-AMSC.

Fig. S21 Ragone plots of Cu-Co-AMSC and Cu-Ni-AMSC.

Fig. S22 The Nyquist plots before and after 5000 charge/discharge cycles of Cu-Fe-AMSC (The inset shows the magnification of the high-frequency region of corresponding Nyquist plots).
**Fig. S23** Cycling stability of Cu-Co-AMSC measured at 3 mA cm\(^{-2}\) under the voltage window of 1.4 V (inset shows the first five cycles and the last five cycles GCD curves).

**Fig. S24** Cycling stability of Cu-Ni-AMSC measured at 3 mA cm\(^{-2}\) under the voltage window of 1.4 V (inset shows the first five cycles and the last five cycles GCD curves).

**Fig. S25** Self-discharge curve of Cu-Fe-AMSC.
Table S1 The comparison of this work and previously reported MSCs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>Areal capacitance (mF cm(^{-2}))</th>
<th>Energy density (mWh cm(^{-3}))</th>
<th>Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Fe-AMSC</td>
<td>LiCl/PVA</td>
<td>19.8</td>
<td>44.6</td>
<td>Asymmetric</td>
<td>This work</td>
</tr>
<tr>
<td>Azulene-bridged coordination polymer framework</td>
<td>H(_2)SO(_4)/PVA</td>
<td>0.1</td>
<td>4.7</td>
<td>Symmetric</td>
<td>Angew. Chem. Int. Ed. 2017, 56, 3920</td>
</tr>
<tr>
<td>Phosphorene/graphene</td>
<td>Ionic liquid</td>
<td>9.8</td>
<td>11.6</td>
<td>Symmetric</td>
<td>ACS Nano 2017, 11, 7284</td>
</tr>
<tr>
<td>Laser-scribed graphene</td>
<td>H(_2)SO(_4)/PVA</td>
<td>2.32</td>
<td>0.4</td>
<td>Symmetric</td>
<td>Nat. Commun. 2013, 4, 1475</td>
</tr>
<tr>
<td>PANI nanowires</td>
<td>H(_2)SO(_4)/PVA</td>
<td>45.2</td>
<td>0.8</td>
<td>Symmetric</td>
<td>Adv. Energy Mater. 2014, 4, 1301269</td>
</tr>
<tr>
<td>TiO(_2)/reduced graphene-oxide</td>
<td>H(_2)SO(_4)/PVA</td>
<td>1.5</td>
<td>7.7</td>
<td>Symmetric</td>
<td>ACS Nano 2017, 11, 4283</td>
</tr>
<tr>
<td>d-Ti(_3)C(_2)/AC</td>
<td>K(_2)SO(_4) solution</td>
<td>-</td>
<td>1.0</td>
<td>Asymmetric</td>
<td>Science 2013, 341, 1502</td>
</tr>
<tr>
<td>graphene-FeOOH//graphene-MnO(_2)</td>
<td>H(_2)SO(_4)/PVA</td>
<td>934</td>
<td>2.4</td>
<td>Asymmetric</td>
<td>Adv. Mater. 2016, 28, 838</td>
</tr>
<tr>
<td>K(_2)Co(_3)(P(_2)O(_7))(_2)//graphene</td>
<td>KOH/PVA</td>
<td>1100</td>
<td>0.96</td>
<td>Asymmetric</td>
<td>Nano Energy 2015, 15, 303</td>
</tr>
</tbody>
</table>
Table S2 The comparison of this work and previously reported asymmetric supercapacitors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>Cycling stability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Fe-AMSC</td>
<td>LiCl/PVA</td>
<td>96.8% after 5000 cycles</td>
<td>This work</td>
</tr>
<tr>
<td>H-TiO$_2$@MnO$_2$/H-TiO$_2$@C</td>
<td>LiCl/PVA</td>
<td>91.2% after 5000 cycles</td>
<td>Adv. Mater. 2013, 25, 267</td>
</tr>
<tr>
<td>MnO$_2$ NW/graphene/graphene</td>
<td>Na$_2$SO$_4$ solution</td>
<td>79% after 1000 cycles</td>
<td>ACS Nano 2010, 4, 5835</td>
</tr>
<tr>
<td>MnO$_2$//graphene hydrogel</td>
<td>Na$_2$SO$_4$ solution</td>
<td>83.4% after 5000 cycles</td>
<td>ACS Appl. Mater. Interfaces 2012, 4, 2801</td>
</tr>
<tr>
<td>RuO$_2$/graphene/graphene</td>
<td>H$_2$SO$_4$/PVA</td>
<td>95% after 2000 cycles</td>
<td>Nanoscale 2012, 4, 4983</td>
</tr>
<tr>
<td>MnO$_2$//PPy</td>
<td>LiCl/PVA</td>
<td>~80% after 5000 cycles</td>
<td>J. Mater. Chem. A 2016, 4, 9502</td>
</tr>
<tr>
<td>VN//Co(OH)$_2$-PHMSs</td>
<td>KOH/PVA</td>
<td>~88% after 5000 cycles</td>
<td>npj 2D Materials and Applications 2018, 2, 7</td>
</tr>
<tr>
<td>K$_2$Co$_3$(P$_2$O$_7$)$_2$/graphene</td>
<td>KOH/PVA</td>
<td>94.4% after 5000 cycles</td>
<td>Nano Energy 2015, 15, 303</td>
</tr>
<tr>
<td>graphene quantum dots//MnO$_2$</td>
<td>Ionogels</td>
<td>80% after 3000 cycles</td>
<td>ACS Appl. Mater. Interfaces 2015, 7, 25378</td>
</tr>
<tr>
<td>VN//Co(OH)$_2$</td>
<td>KOH solution</td>
<td>86% after 4000 cycles</td>
<td>J. Mater. Chem. A 2014, 2, 12724</td>
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</tbody>
</table>