Supporting Information

Editable Asymmetric All-Solid-State Supercapacitors Based on High-Strength,

Flexible, and Programmable 2D-Metal-Organic Frameworks/Reduced Graphene

Oxides Self-Assembled Papers

Junye Cheng,[†] ^a Shengmei Chen,[†] ^{a,b} Da Chen,^c Liubing Dong,^d Jinjie Wang,^d Taolin Zhang,^e Tianpeng Jiao,^a Bin Liu,^a Hao Wang,^{*,b} Ji-Jung Kai,^c Deqing Zhang,^f Guangping Zheng,^{*,g} Linjie Zhi,^e Feiyu Kang,^d Wenjun Zhang^{*,a}

^aCenter of Super-Diamond and Advanced Films, and Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong 999077, China

^bGuangdong Provincial Key Laboratory of Micro/Nano Optomechatronics Engineering, College of Mechatronics and Control Engineering, Shenzhen University, Shenzhen 518060, China

^cDepartment of Mechanical and Biomedical Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong, China

^dSchool of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

^eCAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China

^fSchool of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, China

^gDepartment of Mechanical Engineering, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

[†] These authors contribute equally to this work.

*E-mail: apwjzh@cityu.edu.hk; whao@szu.edu.cn; mmzheng@polyu.edu.hk

Experimental Section

Preparation of GO

In a typical procedure, GO was chemical exfoliated from natural graphite flakes via a modified Hummers method as reported in our previous research. [S1] Typically, graphite flakes (5.0 g) and sodium nitrates (2.5 g) were put into concentrated sulfuric acid (115 ml) at room temperature. The mixture was under ice bath for 25 mins with mild agitation. Potassium permanganate (15.0 g) was added gradually and the temperature of suspension was kept to below 10 °C for another 25 mins. Then, the mixed suspension was heated to 35 °C and kept for 45 mins until a thick paste was formed. Deionized water (140 ml) was added and the temperature of the solution was kept at 98 °C for 45 mins. When the brown mixture turned into yellow, the mixture solution was diluted to 700 ml, followed by adding 30 ml H₂O₂ (30%). The mixture was then filtered and washed with 50 ml of HCl solution. Finally, the solution was centrifuged for several times at 11000 rpm until the pH of the system was about 7. The resulting sample was dried in vacuum at 60 °C for 72 hrs. 1mg mL⁻¹ of GO solution was prepared by the sonication of 1.1 g graphite oxide in 1L DMF for about 2 hrs, after which the aggregates were removed by mild centrifugation (3000 rpm for 10 mins). The resulting dispersion was ready for further application.

Preparation of 2D Co-MOF sheets

 $Co(NO_3)_2 \cdot 6H_2O$ (4.4 mg), BPY (1.56 mg) and PVP (10.0 mg) were dissolved in 6 mL of the mixture of DMF and ethanol (V:V=3:1) in a 10 mL vial. Then the TCPP (4.0 mg) dissolved in 2 mL of the mixture of DMF and ethanol (V:V=3:1) was added dropwise into the aforementioned solution, which was then sonicated for 25 min. After that, the vial was capped and then heated to 80 °C. After the reaction was kept for 24 h, the resulting red product was washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 mins. Finally, the 2D Co-MOF sheets were obtained, which were re-dispersed in DMF.

Preparation of 2D Ni-MOF sheets

Ni(NO₃)₂·6H₂O (2.18 mg), BPY (0.78 mg) and PVP (10.0 mg) were dissolved in 6 mL of the mixture of DMF and ethanol (V: V=3:1) in a 10 mL vial. Then the TCPP (2.0 mg) dissolved in 2 mL of the mixture of DMF and ethanol (V: V=3:1) was added dropwise into the aforementioned solution, which was then sonicated for 25 min. After that, the vial was capped and then heated to 80 °C. After the reaction was kept for 24 h, the resulting red product was washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 mins. Finally, the 2D Ni-MOF sheets were obtained, which were re-dispersed in DMF.

Preparation of assembled 2D Co-MOF/rGO and 2D Ni-MOF/rGO hybrid papers

2D MOF/rGO hybrid electrode papers were prepared through an electrostatic self-assembly process. Typically, the dispersed GO suspension in DMF (1 mg mL⁻¹) was added into 20 mL of MOF (Co-MOF or Ni-MOF) suspension (1 mg mL⁻¹) drop by drop under stirring. Then the mixture was subjected to continuous magnetic stirring for 1 h. In the next step, the uniformly mixed GO-MOF solution was filtered with organic membrane filters under vacuum. After filtration, the paper was peeled off from the membrane and dried for 24 hours in a vacuum oven at 60 °C. Moreover, dried MOF/GO papers were reduced through immersion in the steam of hydroiodic acid (HI, 57%, Sigma Aldrich) in a sealed cuvette which was placed in a warm oil bath (80 °C) for 2-3 h to obtain MOF/rGO hybrid papers. Finally, the reduced hybridd papers were washed several times with water and ethanol to remove the excessive HI and were dried for further examinations. The Co-MOF based paper was denoted as C-M/G-*x*, and the Ni-MOF based paper was denoted as N-M/G-*x*, where *x* was the mass ratio of rGO in the hybrids. For comparison, rGO film was prepared without the addition of MOF.

Characterizations

Structural and phase characterizations of the as-prepared solid electrolytes film and paper electrodes were

performed by XRD using a Bruker D2 Phaser diffractometer with Cu K α irradiation ($\lambda = 1.54$ Å). The surface morphology of those samples was characterized by an environmental scanning electron microscope (ESEM, FEI/Philips XL30). The morphology and microstructure of the samples were revealed by a JEOL-2001F field-emission TEM. Tapping mode atomic force microscopy (AFM) measurement was performed with Nanoscope V controller (Veeco) equipped with an E-type vertical engage scanner at room temperature. The X-ray photon spectroscopy (XPS) examinations were carried out with a Sigma Probe and monochromatic X-ray source (XPS, K-Alpha, Thermo Scientific) to analyze the elemental compositions. The Raman spectroscopy technique (Renishaw) was used to analyze structural information with 532 nm Nd:Yag laser. Mechanical properties of samples were determined using a universal test machine (H5KT, Tinius Olsen) with a preload of 0.02 N at a controlled extension rate of 2 mm min⁻¹. The dc electrical conductivity was measured using four-pin probe (MCP-TP06P PSP) with Loresta GP meter (MCP-T610 model, Mitsubishi Chemical, Japan).

Assembly and performance tests of all-solid-state supercapacitors and in-plane flexible micro-supercapacitor

Aqueous symmetric supercapacitor with 2D Co-MOF/rGO paper electrodes or 2D Ni-MOF/rGO paper electrodes were assembled in a typical CR2032 coin cell to test the electrochemical performance of the obtained two kinds of electrodes. In this case, 1 M H₂SO₄ solution served as the aqueous electrolyte. Solid-state supercapacitors were assembled with PVA/H₂SO₄ gel electrolyte. The gel electrolyte was prepared by stirring a mixture of 2 g PVA, 2 g H₂SO₄ and 20 mL deionized water at 85 °C for 2 h. The electrodes and separator were immersed into the gel electrolyte for several minutes. Solid-state asymmetric textile supercapacitor was assembled with 2D Co-MOF/rGO paper as a positive electrode and 2D Ni-MOF/rGO paper as a negative electrode. Configuration design was described in detail in Figure S13. For

the in-plane flexible micro-supercapacitor, the produced rGO/MOF papers were first transferred on PET substrate. Subsequently, 30 nm of gold (Premion, 99.9985% metals basis, Alfa Aesar) was thermally evaporated (EDWARDS FL400) onto the rGO/MOF papers through a home-made 30-interdigital finger mask (widths of 210 mm, interspaces of 70 mm). The thermal evaporation rate of Au was controlled at 2.0 Ås⁻¹ and the chamber pressure was 3.75×10^{-6} Torr. The patterns of rGO/MOF papers microelectrodes on PET were then created by oxidative etching of the exposed graphene in an O₂-plasma cleaner (Plasma System 200-G, Technics Plamsa GmbH) for 2-5 min (dependent on the thickness) with 20 sccm O₂ flow (chamber pressure 0.15 Torr) and 100-200W rf power under the vacuum of less than 0.05 mbar. Subsequently, different rGO/MOF papers were transferred and integrated on the same substrate. Next, 5 ml H₂SO₄/PVA gel electrolyte was drop-casted onto the surface of interdigital electrode and solidified overnight. Finally, on-chip all-solid-state rGO/MOF -MSCs with an in-plane geometry was obtained. Two silver strings were connected to the pad of each microelectrode using silver paste to make a connection to the electrochemical instruments. Electrochemical properties of the assembled supercapacitors were evaluated through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements on a VMP3 electrochemical station.

Calculations

The area-specific capacitance (C) of the device can be calculated using

$$C=Q / (A \times \Delta V) = \int Idt / (A \times \Delta V) = 4 \times I \times t_{discharge} / (A \times \Delta V),$$
(1)

where A is the surface area of the device, I is the discharge current, $t_{discharge}$ is discharge time, ΔV is the potential drop during discharge (excluding the IR drop).

The energy density and power density of the device can be obtained from:

$$E=C\times(\Delta V)^{2}/8\times 3.6,$$
(2)

where E is the energy density of the device, ΔV is the potential drop during discharge (excluding the IR drop), t_{discharge} is the discharge time.



Fig. S1 Characterization of 2D Co-MOF nanosheets. (a) SEM image of 2D Co-MOF nanosheets with high TCPP addition amount of 2.5 mg; (b) SEM image of 2D Co-MOF nanosheets with high BPY addition amount of 1.0 mg. (c) SEM image of 2D Co-MOF nanosheets with higher BPY addition amount than that in (b).



Fig. S2 Characterization of 2D Ni-MOF nanosheets. (**a**) SEM image of 2D Ni-MOF nanosheets; The inset presents the side face of a 2D Ni-MOF nanosheet. (**b**) TEM image of 2D Ni-MOF nanosheets. (**c**) Annual dark-field TEM image of 2D Ni-MOF and the corresponding EDX elemental mapping images of elements C, N, and Ni. (**d**) XRD patterns of as-prepared Ni-MOF nanosheets.



Fig. S3 Characterization of graphene oxide (GO) sheets. (**a**) TEM image of as-exfoliated GO sheets; The inset presents statistical analysis of the diagonal sizes of GO sheets measured in TEM images. (**b**) A tapping mode AFM image of GO sheet on a mica surface; And AFM thickness analysis on the GO film along the red line. (**c**) XRD patterns of as-prepared GO sheets. (**d**) XPS high-resolution C 1s spectra of GO sheets.



Fig. S4 Characterization of GO papers. (a) GO papers obtained via a vacuum suction filter method. (b) Cross-sectional SEM image of the as-prepared GO papers. (c) XRD patterns of as-prepared the GO paper.



Fig. S5 Reduction process. The set up for the reduction of flexible and freestanding 2D MOF/GO hybrid paper by HI vapour.







Fig. S7 Preparation of samples for cross-sectional TEM analysis. (a) Top-view SEM image of Pt-plating (square area) of 2D-MOF/GO hybrid paper reduced by HI vapour. FIB–SEM analysis of Co-MOF/rGO hybrid paper. (b) SEM graph of the trench carved by FIB on the surface of Co-MOF/rGO hybrid paper. The green frame indicates that the region is selected to extract sample for further cross-sectional TEM analysis.



Fig. S8 (a) Cross-sectional TEM image of the 2D Co-MOF/rGO hybrid paper. (b) The line profile of the d-spacing of rGO nanosheets along the blue line in (a).



Fig. S9 N₂ adsorption/desorption isotherms of rGO papers, C-M/G-40 hybrid papers and N-M/G-40 hybrid papers.

	Table S	1 M	lechanical	properties	of free-	-standing	carbonaceous	papers
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Type of paper	Young's modulus	Ultimate tensile	Reference
	(GPa)	strength (MPa)	
Reduced graphene oxide paper	5.9	42.8	[S2]
Bucky paper	2.7	33.2	[S3]
Graphene paper	3.4	25	[S2]
Graphene oxide paper, Mg ²⁺ -modified	27.9	80.6	[S4]
Graphen oxide membrane,	12.7	70.0	[S5]
self-assembled			
Graphene-cellulose paper	Not	8.67	[S6]
	determinable		
rGO/2D-Co-MOF paper	34.4	89.9	This work

Simulation and Computation

We use Materials Studio (MS) to build the model crystal to do the calculation and simulation. Containing a MOF molecule and a graphene-oxide sheet in a primitive cell, the crystal is built with P1 space group. Volume of this primitive cell is 43*43*90 Å³. After constructing the primitive cell of crystal, we extend it in to 4*4*1 supercell (Fig. S10) and simulate it with the Forcite module in MS. to calculate the mechanical properties based on molecular mechanics (MM). It gives us reliable results for geometric optimization and energy calculation. In this case, we select COMPASS II, a force-field which can be used to deal with organic and inorganic molecular system. The un-bonded force consists of two terms: electrostatic item and Van de Waals item. Because separation between the same charge atoms (Co²⁺ and COO⁻ in this case) is far apart and all atoms are not exactly arranged uniformly in the crystal model, so we choose PPPM (for periodic system) in electrostatic item and atomic based (for non-periodic system) in Van de Waals item. Other settings for the model are treated as defaults, shown in Fig. S11.

According to:

$$S_i = C_{ij} * L_j$$

where S_i is the stress in i-direction, C_{ij} are the elastic stiffness constants and L_j is strain in j-direction. According to calculation, we can get C_{ij} (GPa):

47.1543	14.2036	32.4024	10.6163	3.3296	5.3852
14.2036	18.2862	30.2190	9.8540	3.3421	6.2303
32.4024	30.2190	2.0693	0.9002	-0.1379	0.0269
10.6163	9.8540	0.9002	2.0357	0.2188	-0.3098
3.3296	3.3421	-0.1379	0.2188	1.5782	0.0000
5.3852	6.2303	0.0269	-0.3098	0.0000	7.7015

and the elastic compliance constants E_{ij} (1/TPa):

26.6773	-28.8069	3.7637	-1.2079	5.2170	4.5884

-28.8069	28.9126	30.9330	-4.2453	2.8403	-3.5253
3.7637	30.9330	54.9338	-194.6037	-41.6678	-35.6749
-1.2079	-4.2453	-194.6037	618.4728	-91.2001	29.8341
5.2170	2.8403	-41.6678	-91.2001	625.5969	-9.4661
4.5884	-3.5253	-35.6749	29.8341	-9.4661	130.8127

The corresponging Young's modulus (GPa):

X=37.4850, Y=34.5870,

where X(Y) is the Young's modulus in x-(y-) direction.

By knowing the modulus X or Y, we can plot the stress-stain diagram, which is shown in Fig. S12.



Fig. S10 The model built after geometric optimization. A little change in the MOF structure after geometric optimization can be observed.

Setup Energy	Job Control		Forcefeld types	Caluffer
Forcefield:	COMPASSII	More	Name T Description mds thromtum, +4, in oxide thromtum, +4, in oxide tri2s thromtum, -4, in oxide	
Quality:	Pre 2	•	i m+2 anc. +2 ion yb3o ytterbum, +3 in oxides y3o ytterb, +3 in oxides xe xenon	
Summation meth	od		P Ust all forcefield types	Arright
Electrostatic:	PPPM	•	Bund order	Catalone
van der Waals:	Atom based	•	Charges	
		More	Forcefield assigned	Calculate
			F Calular administr	(Here)
	Run	* Help		Help

Fig. S11 Parameter setting for the Forcite calculation.



Fig. S12 Stress-strain diagram in the x- and y-directions.



Fig. S13 Schematic of preparation procedure for symmetric supercapacitors: (a) coin cell symmetric supercapacitors with paper electrodes; (b) flexible asymmetric supercapacitors with C-M/G-40 paper electrode (upper) and N-M/G-40 paper electrode (below). Coin cell supercapacitors and flexible supercapacitors have the same structures except for packing shells. Generally, coin cell supercapacitors have better sealing property and can effectively prevent the loss of electrolyte (1M H_2SO_4 aqueous solution) for a long time, and are employed for most of the electrochemical performance tests in this work. While flexible supercapacitors are mainly used for the measurements of electrode capacitances at different bending angles.



Fig. S14 (a) CV curves and (b) Galvanostatic charge/discharge curves for rGO paper assembled symmetric supercapacitors.



Fig. S15 (a) CV curves and (b) Galvanostatic charge/discharge curves for C-M/G-50 paper assembled symmetric supercapacitors.



Fig. S16 (a) CV curves and (b) Galvanostatic charge/discharge curves for C-M/G-40 paper assembled symmetric supercapacitors.



Fig. S17 (a) CV curves and (b) Galvanostatic charge/discharge curves for C-M/G-30 paper assembled symmetric supercapacitors.



Fig. S18 (a) CV curves and (b) Galvanostatic charge/discharge curves for N-M/G-40 paper assembled symmetric supercapacitors.

	2
n (mWh cm	m ⁻³) (mW
	cm ⁻³)
MoS_2 -rGO/ PVA-H ₂ SO ₄ 2 A cm ⁻³ 3.8 1	0.06 <i>Angew</i> .
MWCNT	Chem.Int. Edit
	2015, 127,4734.
	[S7]
PEDOT- PVA-H ₂ SO ₄ 0.5 115 1	0.05 Energy
cellulose A cm ⁻³	Environ.Sci.,
paper	2015,
	8, 1339. [S8]
VN/CNTs- PVA-H ₃ PO ₄ 0.025 7.9 0.54	0.4 Adv. Mater.,
SCs A cm ⁻³	2013, 25,
	5091. [S9]
G/PANI- PVA-H ₂ SO ₄ 0.05 3.55 0.32	0.05 Nano Energy
paper A cm ⁻³	2013,
	2, 107. [S10]
MnO ₂ /ZnO PVA-LiCl 10 0.52 0.234	0.13 <i>J. Mater. Chem.</i>
/rGO mV s ⁻¹	<i>C</i> , 2014,2, 133.
	[S11]
TiN-Fe ₂ N PVA-LiCl $1 \ 2 \ A \ g^{-1}$ 60 0.61	0.05 <i>Adv. Mater.</i>
	2015, 27,
	4566. [S12]
C-M/G-40/ PVA-H ₂ SO ₄ 1.2 mA 22.45 1.87	0.250 This work
/N-M/G-40 cm ⁻² E-SCs	

Table S2 Comparison of $C_{Volumetric}$, energy density and power density of the C-M/G-40//N-M/G-40asymmetric SCs with those of other state-of-the-art graphene based SCs.



Fig. S19 GCD curves for C-M/G-40//N-M/G-40 asymmetric supercapacitor under different bending states at 2.4 mA cm⁻².



Fig. S20 (**a**) Capacitance retention of C-M/G-40//N-M/G-40 asymmetric supercapacitor under different loads. GCD curves for (**b**) the SCs at their initial state, (**c**) the SCs under a weight of 30 g (3.75 g cm⁻²), (**d**) SCs under a weight of 60 g (7.5 g cm⁻²), and (**e**) SCs under a weight of 90 g (11.25 g cm⁻²).



Fig. S21 (a) Cutting tests for the all-solid-state SCs at their initial state. GCD curves for (b) the SCs at their initial state (current density: 2.4 mA cm^{-2}), and after the first (current density: 5.5 mA cm^{-2}), the second (current density: 7.4 mA cm^{-2}), and the third (current density: 9.5 mA cm^{-2}) cutting tests.



Fig. S22 The photographs showing editable SCs for complicated, and artistic patterns.

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