Supporting Information

A general route to the synthesis of layer-by-layer structured metal organic

framework/graphene oxide hybrid films: toward high-performance

supercapacitor electrodes

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Experimental section

Synthesis of metal ion sources: copper hydroxide nanowires (Cu-NWs), cobalt carbonate hydroxide nanowires (Co-NWs) and zinc nitrate hydroxide nanoflakes (Zn-NFs)

The prepartion of Cu-NWs were conducted at room temperature, 30 ml of 0.15 M ammonium hydroxide was transfered into 100 ml of 40 mM CuSO₄·5H₂O aqueous solution with magnetic stirring for 15 min, plenty of light blue suspended floccules could be observed. After that, 6 ml of 1.2 M NaOH was dropwise added, then continued stirring for another 15 min, at last the blue precipitates were collected by filtration and redispersed in water at a concentration of 2 mg ml⁻¹.

For synthesis of Co-NWs, 0.56 g of CoSO₄·7H₂O, 7 ml of glycerol and 33 ml of water was mixed and stirred for 10 min first, and then 0.1 g of urea was added with strring for another 30 min to prepare an uniform precursor solution. The mixture solution was thransferred into a Teflon-lined stainless steel autoclave with a capacity of 50 ml, the autoclave was sealed and heated at 170 °C for 24 h, then cooled to room temperature naturally. Finally, the pink precipitates were collected by filtration and redispersed in water at a concentration of 2 mg ml⁻¹.

The synthesis of Zn-NFs were also conducted at room temperature, 5 mmol g of 80 ml NaOH was added into 10 mmol of 50 ml $Zn(NO_3)_2 \cdot 6H_2O$ with stirring for 4 h. the white precipitates were collected by filtration and finally redispersed in water at a concentration of 2 mg ml⁻¹.

Synthesis of layer-by-layer metal oragnic framework/graphene oxide hybrid films: HKUST-1/graphene oxide hybrid (HKUST-1/GO), ZIF-67/graphene oxide hybrid (ZIF-67/GO) and ZIF-8/graphene oxide hybrid(ZIF-8/GO)

5 ml of metal ion source solution was mixed with 10 ml of graphene oxide aqueous solution (1 mg ml⁻¹). After treated with strong ultrasonic for 15 min, the suspending solution was filtrated, the initial layer-by-layer metal ion source/graphene oxide hybrid films were obtained such as Cu-NWs/graphene oxide hybrid film (Cu-NWs/GO), Co-NWs/graphene oxide hybrid film (Co-NWs/GO) and

Zn-NFs/graphene oxide hybrid film (Zn-NFs/GO). Subsequently, these hybrid films were immediately immersed into a bottle containing their corresponding organic linker solutions (0.3 g of 1,3,5-benzenetricarboxylic acid in 100 ml water/ethanol solution (v/v=1:1), 5 g of 2-methylimidazole in 20 ml water). The bottle was seeled and placed in a 80 °C oven for 7 days to start the transformation reaction from metal ion sources to metal organic frameworks. Finally, the starting Cu-NWs/GO, Co-NWs/GO and Zn-NFs/GO hybrid films were converted into HKUST-1/GO, ZIF-67/GO and ZIF-8/GO hybrids, respectively. The products were washed with water and ethanol, and dried at 70 °C. In order to offer larger space to process the next-step reaction and also create favorable interconnected networks as a high-efficiency electrolyte transfer pathway for supercapacitors, 10 ml of metal ion source solution and 10 ml of graphene oxide aqueous solution were used, and the synthesis of metal organic framework/graphene oxide hybrid films were following the similar preparation procedures.

Synthesis of layer-by-layer ZIF-67-derived NiCo layered double hydroxide nanoflakes/graphene oxide (ZIF-LDH/GO) and ZIF-8-derived nanoporous carbon/graphene (ZIF-C/G) hybrids

The as-synthesized ZIF-67/GO and ZIF-8/GO hybrids were used as the sacrificial template for the synthesis of ZIF-LDH/GO and ZIF-C/G hybrids, respectively. The ZIF-67/GO hybrid was placed in 0.5 M of Ni(NO₃)₂ methanol solution for 24 h, after that, the precipitates were filtrated, washed with water and dried at 70 °C for following characterizations, the ZIF-LDH/GO was prepared as the positive electrode material for supercapacitors. The ZIF-8/GO hybrid was heated in Ar atmosphere at 800 °C for 2 h, the heating rate was set at 2 °C min⁻¹. The resulting ZIF-C/G hybrid was then sunk in 2 M of HNO₃ for 24 h to remove the residual Zn species, and it was finally used as the active material for negative electrodes of supercapacitors.

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

phase information of the materials was characterized by 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 examined by the nitrogen sorption technique using a Micromeritics ASAP 2020 instrument at 77 K, and 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 analyzed on a Thermo Fisher X-ray photoelectron spectrometer system (ESCALAB250). All of 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. To prepare the working electrodes for electrochemical measurement, 80 wt% active materials, 10 wt% carbon black and 10 wt% PVDF in NMP solvent were mixed to make a slurry, the mixed slurry was then cast a 1 cm² of area on a Ni foam (1 cm * 3 cm), dried at 120 °C for 12 h and pressed under 10 MPa of pressure. The KCl saturated Ag/AgCl was used as the reference electrode and Pt rod was 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 specific capacitance (C_1) and capacity (C_2) of the electrodes were calculated by Equation 1 and Equation 2:

$$C_{1} = \frac{I\Delta t}{m\Delta V}$$
Equation 1
$$C_{2} = \frac{I\Delta t}{m}$$
Equation 2

Where C_1 is the specific capacitance (F g⁻¹), C_2 is the specific capacity (C g⁻¹), I is the discharge current (A), m is the mass of the active materials (g), ΔV is the potential drop excluding the IR drop (V) and Δt is the total discharge time (s).

The asymmetric supercapacitor was assembled and measured in a two-electrode system, the obtained ZIF-LDH/GO and ZIF-C/G hybrids on Ni foams were used as the positive and negative electrodes, respectively. 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 k g^{-1}) and specific power density (SP, W k g^{-1}) were calculated from chronopotentiometric curves by using following Equation 3-5, respectively.

$$C = \frac{I\Delta t}{m'\Delta V}$$
 Equation 3

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), Δt is the discharge time (s) and ΔV is the window potential during the discharge process.

$$SE = \frac{C\Delta V^2}{7.2}$$
 Equation 4

Where SE is the specific energy density (Wh kg⁻¹), C is the specific capacitance (F g^{-1}), ΔV is the window potential during the discharge process.

$$SP = \frac{3600 * SE}{\Delta t}$$
 Equation 5

Where SP is the specific power density (W kg⁻¹), SE is the specific energy density (Wh kg⁻¹) and Δt is the discharge time (s).



Figure S1 XRD patterns of original graphene oxide (a) and the hybrid products at every step (b): copper hydroxide nanowires/GO hybrid (1), cobalt carbonate hydroxide nanowires/GO hybrid (2), zinc nitrate hydroxide nanoflakes/GO hybrid (3), HKUST-1/GO hybrid (4), ZIF-67/GO hybrid (5), ZIF-8/GO hybrid (6), ZIF-67-derived NiCo layered double hydroxide nanoflakes/GO (7) and ZIF-8-derived nanoporous carbon/graphene (8).



Figure S2 SEM images of the starting metal ion sources: copper hydroxide nanowires (a), cobalt carbonate hydroxide nanowires (b), zinc nitrate hydroxide nanoflakes (c); TEM images of copper hydroxide nanowires (d), cobalt carbonate hydroxide nanowires (e), zinc nitrate hydroxide nanoflakes (f); TEM images of copper hydroxide nanowires/GO hybrid (g), cobalt carbonate hydroxide nanowires/GO hybrid (h), zinc nitrate hydroxide nanoflakes/GO hybrid (i).



Figure S3 TEM images of the Co-NWs/GO in 2-methylimidazole solution at 80°C for 3 days (a-b) and 7 days (c); TEM iamges of pure GO (d). The insets in a, c and d were their corresponding electron diffraction patterns.



Figure S4 The cross-section SEM images of the resulting materials by other methods: directly physical mixing ZIF-67 nanoparticles and graphene oxide (a-c), repeatedly pumping Co(NO₃)₂ solution and 2-methylimidazole solution through GO film (d-g). The physical mixing method led to laminated bulk mixture of ZIF-67 nanoparticles and graphene oxide, although we could see the layer-like accumulation (a), the thickness of each bulk layer was very big, the severe agglomerations of ZIF-67 nanoparticles could be seen, and the GO nanosheets actually presented in the messy and random arrangment (b, c); moreover, it was found that after annealing treatment at 800°C, the resulting product was almost in powder form, the layered architecture collapsed and it could not maintain the integrated sturtcure. In the second method, without the addition of spcacer materials, the reaction solutions hardly entered into

the interspacing of GO nanosheets, and these narrow interspacing coud not serve as the reservior to store more reaction solutions. Only at the defect voids during the nanosheet stacking process, some big ZIF-67 crystals generated (denoted by red arrows); in most of the cross-section area, no ZIF-67 was observed between the GO nanosheets (d-g). Therefore, these methods for the prepartion of layer-by-layer MOF/GO structure are not feasible, in contrast, our approach shows significant and effective advantages.



Figure S5 The high-resolution XPS spectra of Co $2p_{3/2}$ (a) and Ni $2p_{3/2}$ (b) of ZIF-LDH/GO; high-resolution XPS spectra of N 1s of ZIF-C/G (c); the Raman spectra (d): ZIF-LDH/GO (black line); ZIF-C/G (red line). The peaks located at 779.3 eV and 784.9 eV corresponded to Co^{3+} and Co^{3+} satellite peaks (a), and the peaks at 853.9 eV and 862.0 eV could be assigned to Ni³⁺ and Ni³⁺ satellite peaks (b), the co-existence of Co^{3+}/Ni^{3+} and Co^{2+}/Ni^{2+} valence states revealed the formation of NiCo layered double hydroxide. The high resolution N 1s spectra for ZIF-C/G were fitted with four peaks at about 398.3, 399.6, 400.9, and 404.1 eV, corresponding to pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen, and pyridinic N+-O-, respectively, the result revealed the successful N-dopping of ZIF-C/G which would benefit the excellent energy storage performances. The band ranging from 300 to 550 cm⁻¹ in Raman spectrum of ZIF-LDH/GO suggested the existence of Ni-O and Co-O bonds of layered double hydroxide; the negative shift of G band from 1600 cm⁻¹ to 1594 cm⁻¹ for ZIF-C/G indicated the typical characteristics of n-type doping of graphene.

Materials	C content (%)	O content (%)
GO	67.0	33.0
GO in 2-methylimidazole solution	89.4	10.6
GO in Ar at 800 °C	99.1	0.9

Table S1 The corresponding C/O content of the GO before and after treated with 2-methylimidazole solotion at 75 °C for 7 days or Ar gas at 800 °C for 2 h.



Figure S6 TEM images (a, b) and the high-resolution images (c, d) of ZIF-C/G. It could be clear to see the particle-like shape in the enclosed blue rectanglar area (a), the enlarged TEM image also denoted the ZIF-8-derived nanoporous carbon particles inside ZIF-C/G by red dashed line (b). The red arrows in d showed the parallel C(002) plans of graphene, the carbonized graphene presented the graphitized state ranther than the amorphous state of mesoporous carbon.



Figure S7 Nitrogen adsorption-desorption isotherms of the prepared ZIF-LDH+GO, ZIF-LDH/GO, ZIF-C+G and ZIF-C/G.



Figure S8 Galvanostatic charge-discharge curves of pure ZIF-LDH (a), ZIF-LDH+GO (b), ZIF-LDH/GO (c), ZIF-C (d), ZIF-C+G (e) and ZIF-C/G (f) at different current density.



Figure S9 Nyquist plots of pure ZIF-LDH, ZIF-LDH+GO, ZIF-LDH/GO, ZIF-C, ZIF-C+G and ZIF-C/G at a range of 0.1 Hz ~100 kHz.

Active materials	Loading	Mass Capacity	Capacity Rate Cyc		References
	(mg/cm ²)	(C/g)	capability	retention	
Co-LDH	0.285	137.3 (1 A/g)	54.1% (10 A/g)	85% (3000 cycles)	<i>Adv. Funct. Mater.</i> , 2014 , 24, 4831
Co ₃ O ₄ @NiAl-LDH nanowire array	1.2	886 (2 A/g)	61.4% (20 A/g)	87.9% (2000 cycles)	<i>Nano Energy</i> , 2014 , 7, 134
NiCo-LDH	3.0	1341 (3 A/g)	63.6% (20 A/g)	-	Adv. Funct. Mater., 2014 , 24, 934
Carbonized bacaterial cellulose@NiCo-LDH	3.0	779.8 (1 A/g)	54.7% (20 A/g)	74.4% (5000 cycles)	Small, 2016 , 12, 3235
ZIF-67-derived Ni _x Co _{3-x} O4 hollow nanocage	-	869 (1 A/g)	-	81% (5000 cycles)	Small, 2017 , 13, 1603102
Prussian blue analogue-derived NiS	1.0	1013.7 (1 A/g)	33.6% (20 A/g)	91.8% (4000 cycles)	Angew. Chem. Int. Ed., 2015 , 54, 1
ZIF-67-derived Co3O4-NiCo2O4 nanocages	1.0	408 (5 A/g)	63.2% (50 A/g)	92.5% (12000 cycles)	J. Am. Chem. Soc., 2015 , 137, 5590
Co-containing ZIF-derived NiCo-LDH nanoflake array	0.6	633.2 (4.2 A/g)	45.8 % (100 A/g)	-	Adv. Energy Mater., 2017 , 7, 1602391

Table S2 The electrochemical properties of MOF-derived materials in recent literature.

ZIF-67-derived Co ₃ O ₄ nanotube array	3.4	580 (1.18 A/g)	51.4% (11.8 A/g)	96.9% (5000 cycles)	J. Mater. Chem. A, 2015 , 3, 16688
ZIF-8-derived NiCo-LDH nanoflake array	2.1	971.4 (1.9 A/g)	49.5 % (19 A/g)	94.1% (5000 cycles)	J. Mater. Chem. A, 2016 , 4, 16953
ZIF-67-derived LDH nanocage	-	601.5 (1 A/g)	78.1% (10 A/g)	90.2% (1000 cycles)	Nanoscale, 2013 , 5, 11770
ZIF-LDH/GO	1.0	904.3 (1 A/g)	62.3% (10 A/g)	90.7% (5000 cycles)	This work

Table S3 The electrochemical properties of MOF-derived carbon materials in recent

literature.

Active materials	Loading	Mass Capacity	Rate capability	References
	(mg/cm ²)	(F /g)		
ZIF-8-derived nanoporous carbon	2.0	200 (0.25 A/g)	-	J. Am. Chem. Soc., 2011 , 133, 11854.
KOH treated ZIF-8-derived carbon	1.2	174.2 (1 A/g)	55.1% (10 A/g)	J. Mater. Chem. A, 2017 , 5, 292
ZIF-67-derived nanoporous -carbon	2.0	272 (5 mV/s)	59.9% (200 mV/s)	ACS Nano, 2015 , 9, 6288
ZIF-7-derived porous carbon	5.0	226.2 (0.2 A/g)	79% (10 A/g)	J. Mater. Chem. A, 2014 , 2, 12873
MOF-1-derived porous carbon	4.0 ~ 5.0	230 (1 A/g)	70% (20 A/g)	J. Mater. Chem. A, 2017 , DOI: 10.1039/C7TA00162B
ZIF-8/PAN-derived nanoporous carbon	1.0	332 (1 A/g)	-	Chem. Comm., 2017 , 53, 1751
ZnDTO-derived Fe-doped porous carbon	1.0	277 (5 mV/s) 128 (0.5 A/g)	115 (500 mV/s)	Adv. Energy Mater., 2017 , 7, 1602002
ZIF-8-derived N-rich carbon	5.0	285.8 (0.1 A/g)	72.7 % (2 A/g)	Carbon, 2015 , 85, 51
Carbonized ZIF-8-derived nanoporous carbon on 3D graphene monolith		238 (1 A/g)	84% (5 A/g)	Carbon, 2014 , 78, 231.

Core-shell ZIF-8@ZIF-67-derived	1.0	255 (2 A/g)	49.5 0% (10 A/g)	J. Am. Chem. Soc., 2015 , 137, 1572.
MOF-74-derived graphene nanoribbons	2.0	173 (0.5 A/g)	81.5% (10 A/g)	Nature Chem., 2016 , 8, 718
ZIF-C/G	1.0	317 (0.5 A/g)	60.8% (10 A/g)	This work



Figure S10 Cycling durability of pure ZIF-LDH, ZIF-LDH+GO, ZIF-LDH/GO, ZIF-C, ZIF-C+G and ZIF-C/G at a current density of 5 A g⁻¹.



Figure S11 Galvanostatic charge-discharge plots of the last 10 repeating cycles at a current density of 5 A g^{-1} : pure ZIF-LDH (a), ZIF-LDH+GO (b), ZIF-LDH/GO (c) , ZIF-C (d) , ZIF-C+G (e) and ZIF-C/G (f).



Figure S12 CV plots of positive electrode ZIF-LDH/GO (+) and negative electrode ZIF-C/G (-) at a scan rate of 5 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 (ΔE) and the mass of the electrode (m), and the charge could be describe as: $Q = C^*m^*\Delta E$, so the mass balancing of ZIF-LDH/GO(+)// ZIF-C/G(-) (m₊/m₋) was calculated as:

$$\frac{m_+}{m_-} = \frac{C_- *\Delta E_-}{C_+ *\Delta E_+} = \frac{265 * 0.9}{1357 * 0.6} \approx 0.3.$$



Figure S13 CV plots as a function of scan rate (a) and the cycling stability at a current density of 5 A/g (b) of the assembled asymmetric supercapacitor ZIF-LDH/GO(+)//ZIF-C/G (-).