Supporting Information (ESI)

Facile one-pot solvothermal preparation of two-dimensional Ni-based metal-organic framework microsheets as a high-performance supercapacitor material

Zhaohua Li,[a] Yuan Sun,[a] Rui Hu,*[a] Shuai Ye,[a] Jun Song,[a] Liwei Liu,[a] and Junle Qu[a,b]

[a] Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, P. R. China.

[b] National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 115409, Moscow, Russian Federation

*E-mail: rhu@szu.edu.cn

1. Experimental Section

Materials.

Nickel(II) chloride hexahydrate (NiCl$_2$·6H$_2$O, 99%) and trimesic acid (H$_3$BTC, 99%+) were purchased from Adamas. *N, N*-dimethylformamide (DMF, 99.5%) and ethanol (EtOH, 99.7%) were provided by Macklin. Terephthalic acid (H$_2$BDC, >99.0%) was obtained from TCI. Potassium hydroxide (KOH, 95%) and 2-methylimidazole (2-MI, 98%) were produced by Aladdin. All of these chemicals were used without further purification.

Preparation of Ni-MOFms.

DMF (32 mL), EtOH (2 mL) and H$_2$O (2 mL) were mixed in a 50 mL centrifuge tube followed by the sequential addition of NiCl$_2$·6H$_2$O (0.089 g, 0.375 mmol) and H$_3$BTC (0.158g, 0.75 mmol). The mixture was ultrasonicated and then transferred to a 50 mL Teflon-lined autoclave. After maintaining at 150 °C for 6 h, the product was separated by centrifugation, washed three times with DMF and EtOH, and finally dried in the vacuum oven.

Preparation of control samples.

One of the five factors, namely reaction time, reaction temperature, solvent, ligand addition amount and ligand type, was adjusted singly each time, while other conditions were kept unchanged.

Electrochemical measurements.

All electrochemical measurements were performed on a CHI-760E electrochemical workstation (Shanghai Chenhua) at room temperature in a three-electrode system, with Pt foil as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, a sample-coated carbon cloth as the working electrode, and 3 M KOH aqueous solution as the electrolyte. The working electrode was prepared as follows: Ni-MOFms (2 mg) was dispersed in EtOH (2 mL), and 0.1 mL of the mixture was dripped

on a carbon cloth (1 cm × 1 cm) and dried in an oven at 60 °C for 0.5 h. Cyclic voltammetry (CV) tests were performed between 0 and 0.4 V (vs. SCE) at different scan rates. Galvanostatic charge-discharge (GCD) curves were measured at different current densities in the potential range of 0 and 0.4 V (vs. SCE). The electrochemical impedance spectroscopy (EIS) test was conducted at an AC voltage of 5 mV amplitude in the frequency range from 0.01 to 100000 Hz at the bias potential of 0.4 V.

Calculation method of specific capacity and columbic efficiency.

The specific capacity C_s (C g^{-1}) and the columbic efficiency CE (%) of the Ni-MOFms are calculated according to previous literatures.[45,46] The specific formulas are as follows:

$C_s = (I \times \Delta t)/m$

where I (A) is the discharge current, Δt (s) is the discharge time, and m (g) is the mass of the active material on the test electrode.

CE = discharge capacity/charge capacity = discharge time/charge time

Characterizations.

The morphology and structure of the sample was characterized by transmission electron microscopy (TEM, Hitachi HT7700, 80 kV) and scanning electron microscopy (SEM, JSM-7800F, 5.0 kV). Energy dispersive spectroscopy (EDS) mapping was performed on JEM-F200 at 200 kV. The thickness of the sample was measured by atomic force microscopy (AFM, Dimension ICON). X-ray diffraction (XRD) patterns were obtained on an X'pertpro diffractometer with Cu Kα radiation at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was performed on a K-Alpha+ electron spectrometer (ThermoFisher Scientific) using Al kα radiation. The functional groups were characterized by Fourier transform infrared spectroscopy (FT-IR, Spectrum One Version B, USA PE).
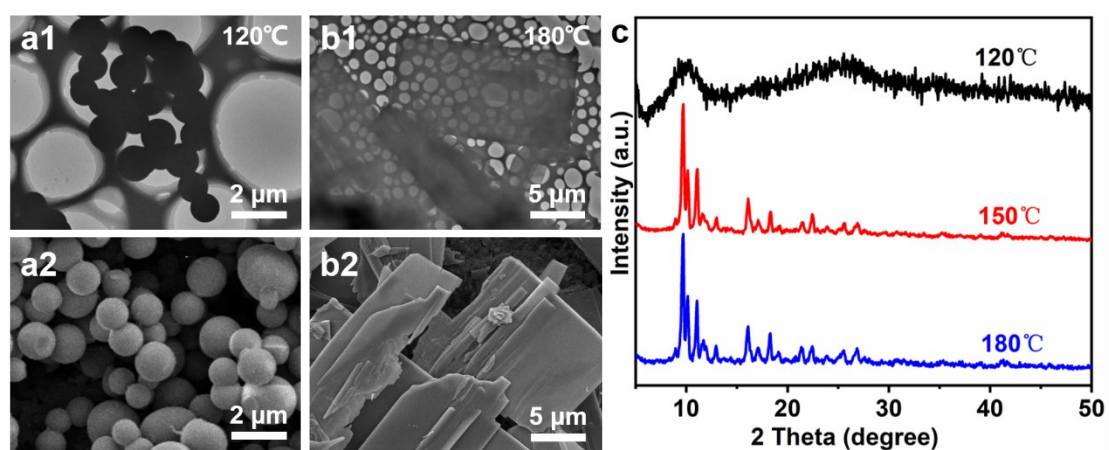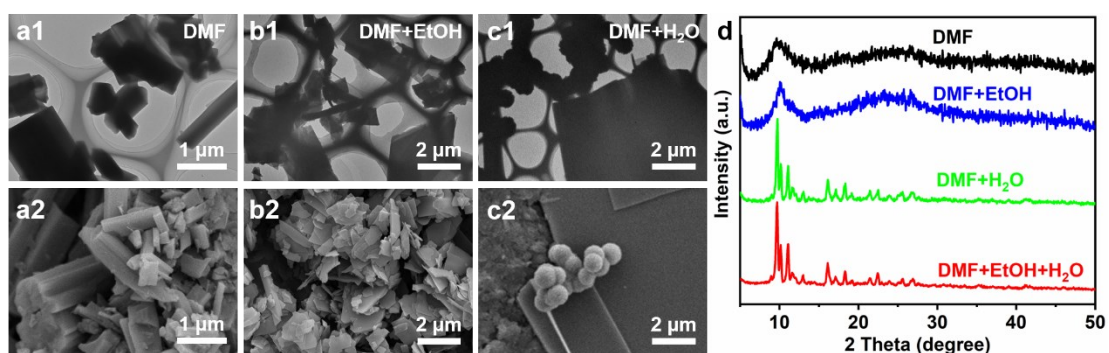
2. Supporting Figures and Tables
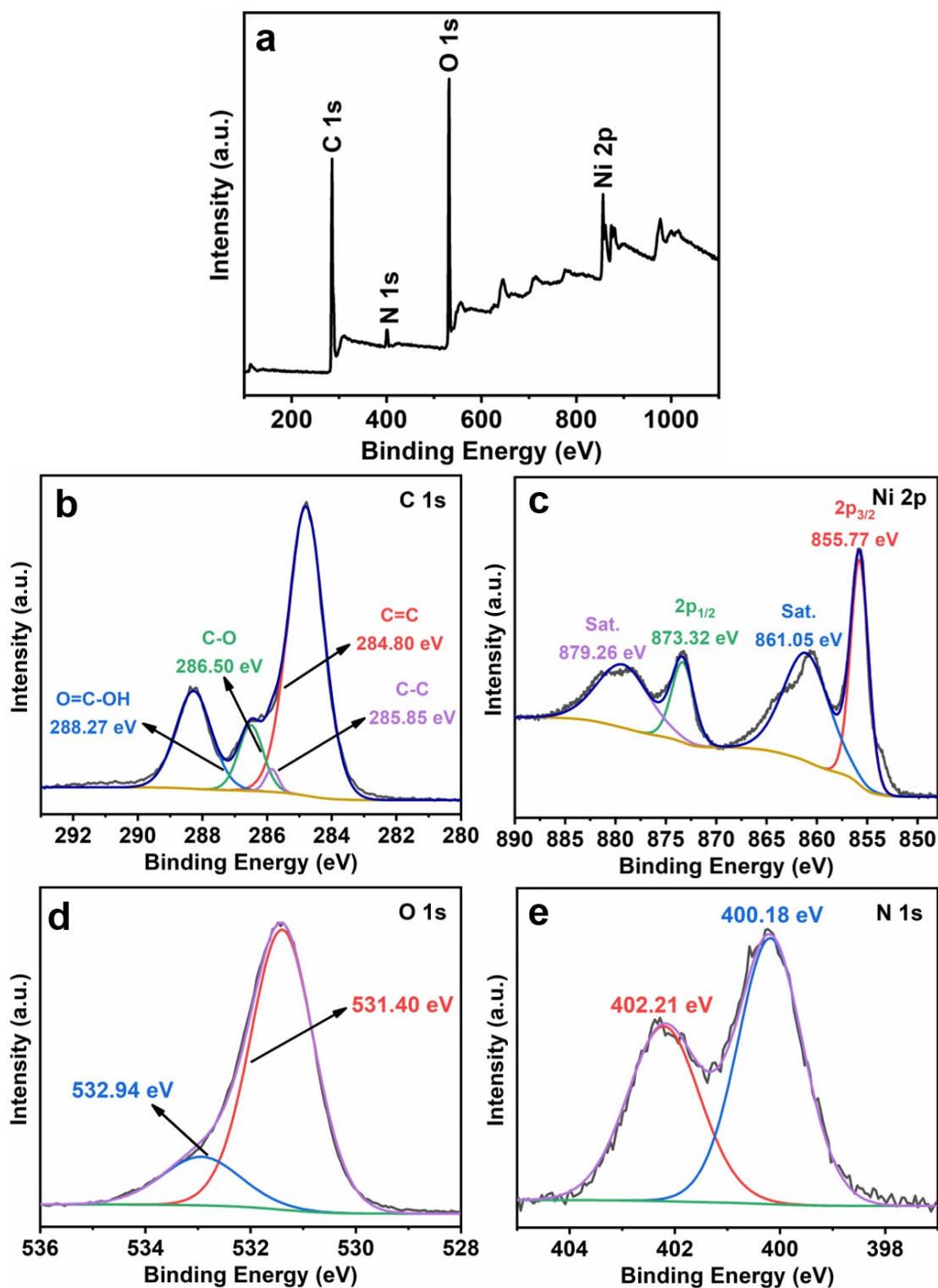
Figure S1. (a) XPS survey and high-resolution spectra of (b) C 1s, (c) Ni 2p, (d) O 1s, and (e) N 1s.
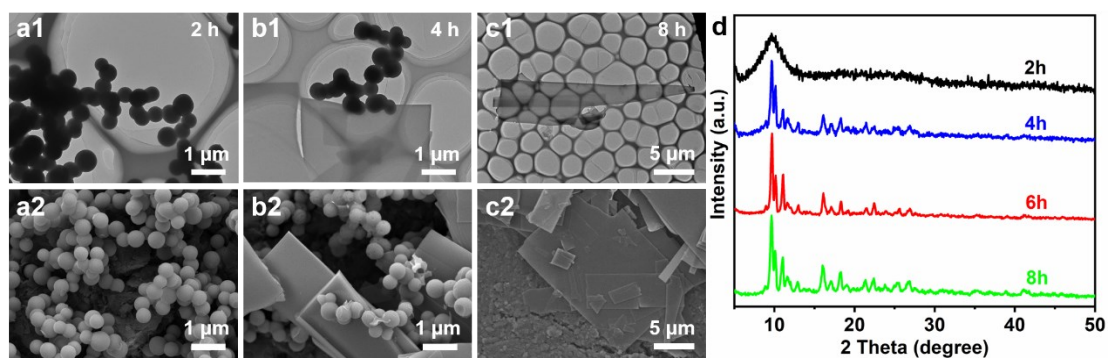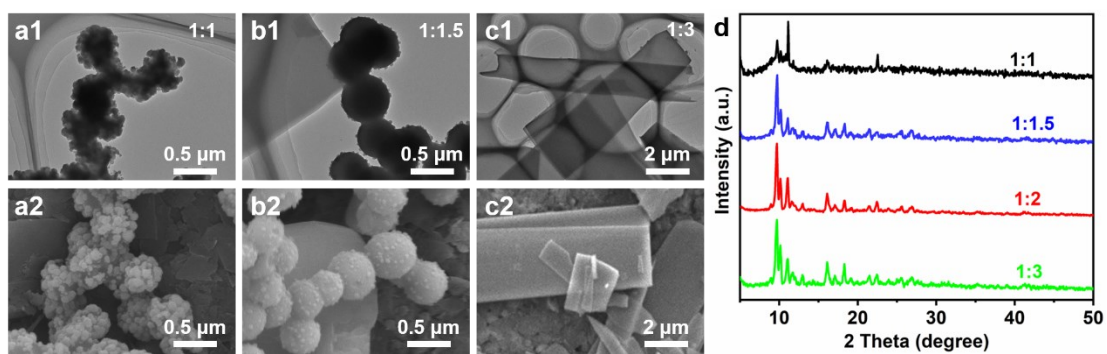
Figure S2. (a1, b1, c1) TEM images, (a2, b2, c2) SEM images and (d) XRD patterns of samples prepared at different reaction times.
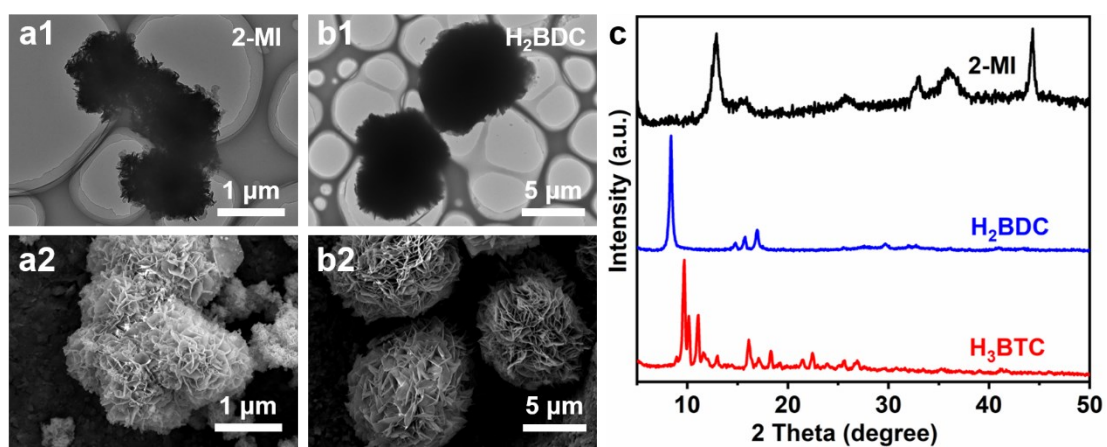

Figure S3. (a1, b1) TEM images, (a2, b2) SEM images and (c) XRD patterns of samples prepared at different reaction temperatures.

Figure S4. (a1, b1, c1) TEM images, (a2, b2, c2) SEM images and (d) XRD patterns of samples prepared in different solvents.

Figure S5. (a1, b1, c1) TEM images, (a2, b2, c2) SEM images and (d) XRD patterns of samples prepared with different H₃BTC addition amount.

Figure S6. (a1, b1) TEM images, (a2, b2) SEM images and (c) XRD patterns of samples prepared with different ligands.

Table S1. Specific capacity comparisons of Ni-MOFms in this study with other MOF materials in literatures

MOFs	Scan rate (mV s^{-1})	Current density (A g^{-1})	Specific capacity[a] (C g^{-1})	Ref.
Ni-MOFms	-	**2**	**91.4**	**This study**
Co-MOF-71	-	0.6	124.06 (206.76 F g^{-1})	47
Co-BDC	10	-	79.1 (131.8 F g^{-1})	48
Co-NDC	10	-	88.38 (147.3 F g^{-1})	48
Co-BPDC	10	-	107.5 (179.2 F g^{-1})	48
MIL-100(Fe)	5	-	50.7 (39 F g^{-1})	49
Co8-MOF-5	25	-	0.59 (0.49 F g^{-1})	50

[a]: Specific capacity (C g^{-1}) is adopted for comparison. For MOFs in literatures, this value is calculated by multiplying the specific capacitance (F g^{-1}, listed in the brackets) by the corresponding voltage.