Hierarchical Nickel/Phosphorus/Nitrogen/Carbon Composites

Templated by One Metal-Organic Framework as Highly-Efficient

Supercapacitor Electrode Materials

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Materials and General Methods

The organic ligand H₆L and other reagents for the syntheses were of analytical grade and used as received from commercial sources without further purification. Elemental analyses (C, H and N) were determined on a Perkin-Elmer 2400 analyzer. The IR spectra were recorded as KBr pellets on a 4000-400 cm⁻¹ Nicolet Avatar-360 spectrometer in the region. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from 25 to 800 °C under nitrogen atmosphere. Powder X-ray diffraction (PXRD) patterns for the as-synthesized samples were recorded on a X-ray diffraction meter (D/max 2500 PC, Rigaku) with Cu-Ka radiation (1.5406 Å). N₂ adsorption-desorption isotherms were measured using a Micromeritics ASAP 2020 system at 77 K for all of the samples that have been immersed in acetone for three days and activated at 120 °C for 10h. The morphologies of the hierarchical derivatives were observed by using a SU8020 Scanning Electron Microscope (SEM, Hitachi, Japan). Energy dispersive X-ray spectra (EDS) of different elements in different samples was recorded via SEM. X-ray photoelectron spectroscopy (XPS) carried was out on а VGESCALBMKII X-ray photoelectron system with an Al Ka radiation (1486.6 eV).

Synthesis of [Ni₃(H₂O)(bpy)₃(L1)] (1)

A mixture of Ni(NO₃)₂(17.5mg) , H₆L(9.6mg) and 4,4'-bipyridine(3.5mg),were dissolved in 5 mL of CH₃OH, then 0.1 mL DMF and 0.1 mL1,4-dioxane were added . The reaction mixture was sonicated for 5 minutes before heated in the 140°C isothermal oven for 2 days. Blue crystal sample was obtained in yield of 55%. Element analysis result for $C_{72}H_{50}N_9Ni_3O_{19}P_3$: Calcd (%):C, 53.57%, H, 3.12%, N, 7.81%; found C, 53.11%, H, 3.67%, N, 8.05%. IR(KBr,cm⁻¹): 1601, 1553.3, 1385.3, 1257.4, 1157.1, 962.7, 831, 784.6, 743.2, 693.1,636.7.

Single crystal X-ray diffraction

X-ray diffraction data of Ni-MOF **1** was collected via Bruker APEX-II CCD diffractometer using Cu-*K* α (λ = 1.54178 Å) and Mo-*K* α (λ = 0.71073 Å) radiation.

The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least squares procedure based on F^2 values. The *PLATON/SQUEEZE* routine was employed to calculate the diffraction contribution from the solvent molecules, and thereby to produce a set of solvent-free diffraction intensities. According to the results of EA and TGA, four methanol molecules have been squeezed for each formula. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. CCDC-1876561 for **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. A summary of the structural determination and refinement for compound **1** and **2** is listed in Table 1.

Electrochemical measurements

The working electrode was fabricated by the following procedure. The Ni-based MOFs or derivatives (2 mg), acetylene black, and poly(tetrafluoroethylene) were mixed in a mass ratio of 80 : 10: 10 and dispersed in ethanol to produce a homogeneous paste. Acetylene black and poly(tetrafluoroethylene) were used as the conductive agent and the binder, respectively. The slurry was coated on a nickel foam substrate (1 cm \times 1 cm) and dried at 60 °C for 8 h under vacuum. The as-formed electrode was then pressed at 10 MPa and further dried at 100 °C for 6 h. All electrochemical characterizations were evaluated using a CHI660E electrochemical workstation (Chenhua Instrument Co. Ltd., Shanghai, China), and a 6 M potassium hydroxide aqueous solution as an electrolyte with a three-electrode configuration at room temperature. The as-prepared nickel foam-based electrode was used as the working electrode, and the detailed electrode fabrication was described above. The platinum wire and Hg/HgO electrodes were employed as the counter and reference electrodes, respectively. Cyclic voltammograms (CV) were recorded in the range of 0 to 0.6 V at various scan rates with stirring at low speed. Galvanostatic charge-discharge (GCD) curves were obtained in the same potential range at different current densities. Moreover, the long-term cycle stability of the working electrode was determined by the GCD measurement at a current density of 1 A g⁻¹. **Table S1**. Crystal data and structure refinement for Ni-MOF 1.

	Ni-MOF
Empirical formula	C72H50N9Ni3O19P3
Formula weight	1614.19
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_{1}/c$
$a/{ m \AA}$	25.681(5)
$b/{ m \AA}$	17.209(3)
$c/{ m \AA}$	18.359(4)
$\alpha/^{\circ}$	90
$eta /^{\circ}$	99.51(3)
$\gamma/^{\circ}$	90
Volume/Å ³	8002(3)
Ζ	4
$\rho_{calc}g/cm^3$	1.340
μ/mm^{-1}	0.829
F(000)	4112.0
Crystal size/mm ³	$0.1 \times 0.1 \times 0.05$
Radiation	MoKa ($\lambda = 0.71073$)
Reflections collected	17828
Data/restraints/parameters	17828/0/956
Goodness-of-fit on F ²	1.010
Final P indexes [I>-2 (I)]	$R_1 = 0.0717, wR_2 =$
$\frac{1}{20} \left[1 - 20 \left(1\right)\right]$	0.2005
Final R indexes [all data]	$R_1 = 0.0802, wR_2 =$
	0.2105

 Table S2. Selected bond lengths for Ni-MOF 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni3	016 ¹	2.148(2)	Ni1	O1 ³	2.126(2)
Ni3	O17 ¹	2.277(2)	Ni1	$N1^4$	2.119(2)
Ni3	013	2.059(2)	O5	Ni1	2.195(2)
Ni3	N5	2.135(3)	O4	Ni1	2.273(2)
Ni3	N2	2.195(3)	O16	Ni3 ³	2.148(2)
Ni3	N4 ²	2.213(3)	O2	Ni2 ¹	2.087(2)

Ni2	019	2.221(2)	O17	Ni3 ³	2.277(2)
Ni2	O4	2.189(2)	08	$Ni2^1$	2.114(2)
Ni2	O10	2.075(2)	N6	Ni1	2.161(3)
Ni2	$O2^3$	2.087(2)	N1	Ni1 ⁴	2.119(2)
Ni2	O8 ³	2.114(2)	N4	Ni3 ²	2.213(3)
Ni2	N3	2.132(3)	01	$Ni1^1$	2.126(2)
019	Ni1	2.153(2)			

Asymmetric code: ¹+X,-1+Y,+Z; ²2-X,-1-Y,1-Z; ³+X,1+Y,+Z; ⁴1-X,-1-Y,1-Z.

Table S3. the XPS peak positions of hierarchical samples / eV

Sample	Ni 2p3/2	Ni 2p1/2	Ni 2p3/2 Sat.	Ni 2p1/2 Sat.
Ni/P/N/C-500	856.9	875.5	861.7	880.7
Ni/P/N/C-600	856.9	875.5	861.8	880.9
Ni/P/N/C-700	856.6	875.5	861.6	880.3
Ni/P/N/C-800	857.6	875.7	862.8	881.1

Table S4. the weight content (%) of nickel component in each derivative

Sample	Ni ^a	Ni ^b
Ni/P/N/C-500	23.43	19.98
Ni/P/N/C-600	26.72	22.46
Ni/P/N/C-700	32.95	28.67
Ni/P/N/C-800	40.01	31.06

^a determined by XPS

^b determined by ICP-OES

Table S5. the comparison of supercapacitive properties of reported pristine MOFs

 materials utilized as active electrode materials

Sample	Electrolyte	Current	Supercapa	References
		density(A g ⁻¹)	citor (F g ⁻¹)	
Ni/P/N/C-500	6M KOH	1 A g ⁻¹	2887.87	This work
Ni/P/N/C-600	6M KOH	1 A g ⁻¹	1430.5	This work

Ni/P/N/C-700	6М КОН	1 A g ⁻¹	1694.3	This work
Ni-MOF 1	6М КОН	1 A g ⁻¹	979.8	This work
Co-MOF	5М КОН	1 F g ⁻¹	2564	[1]
Ni-MOF	6М КОН	0.5 A g^{-1}	1127	[2]
Co-MOF film	1M LiOH	0.5A g^{-1}	206.7	[3]
Ni-MOF	2М КОН	1 A g ⁻¹	552	[4]
Zr-MOF ₁	6М КОН	$0.5 \mathrm{A g^{-1}}$	1144	[5]
Cu-MOF@C	6M KOH	$0.5 A g^{-1}$	138	[6]
Cu-LCP	1M LiOH	1 A g ⁻¹	1102	[7]
Zn-doped Ni-MOF	6 M KOH	0.25 A g^{-1}	1620	[8]
Ni-MOF	6 М КОН	0.5 A g ⁻¹	1127	[9]
Ni-doped MOF-5	1 M KOH	$0.05 \mathrm{A~g^{-1}}$	380	[10]
[Cu ₂ Br(OH)(L) ₂]·(CH ₃ OH) ₄	6 M KOH	0.5 A g ⁻¹	688	[11]
Ni-MOF	6 M KOH	0.5 A g ⁻¹	1127	[12]
[Ni ₂ (TATB) ₂ (bid) ₂ (H ₂ O)]·2H ₂ O	6 M KOH	1 A g ⁻¹	705	[13]
[Ni ₂ (TATB) ₂ (btd) ₂ (H ₂ O)]	6 M KOH	1 A g ⁻¹	666	[13]
Ni-DMOF-ADC	2 M KOH	1 A g ⁻¹	552	[14]
[Co(HTATB)(m-bib)]· 2H ₂ O	6 M KOH	2 A g ⁻¹	502	[15]
Zn-MOF/PANI	1M H ₂ SO ₄	1 A g ⁻¹	477	[16]
Ni-DMOF-TM	2 M KOH	1 A g ⁻¹	440	[14]
Ni-DMOF-NDC	2 M KOH	1 A g ⁻¹	410	[14]
Cu-MOF/GO	1M Na ₂ SO ₄	1 A g ⁻¹	385	[17]
Zr-MOF	6 M KOH	1 A g ⁻¹	207	[18]
Co-MOF	1 M LiOH	$0.6 \mathrm{A g^{-1}}$	207	[19]
[Ni(HOC ₆ H ₄ COO) _{1.48} (6 M KOH	1 A g ⁻¹	166	[20]
OH) _{0.5}]·1.1H ₂ O				
Ni ₃ (HITP) ₂	6 M KOH	0.5 A g ⁻¹	111	[21]
Ni ₃ (HITP) ₂	1M	0.5 Ag^{-1}	107	[22]
	TEABF ₄ /CA N/M			
Cu-MOF	1M Na ₂ SO ₄	1.6 A g ⁻¹	85	[22]
Al-MOF	6 M KOH	1 A g ⁻¹	84	[23]

[CoL(1,4-bdc)]· ₂ DMF	0.05M	0.2 A g ⁻¹	67	[24]
	NaNO ₃			
$[Cd2(TDC)_2(L)_2] \cdot {}_4H_2O$	1M Li ₂ SO ₄	2.5 m A g ⁻¹	22	[25]
CC@CoNi2O4	2 M KOH	2.5 mA cm^{-2}	1055.3	[26]

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	BET surface area $(m^2 g^{-1})$	Pore Size (Å)		
Ni/P/N/C-500	21.5	2.2		
Ni/P/N/C-600	26.6	2.4		
Ni/P/N/C-700	35.3	2.9		
Ni/P/N/C-800	247.2	4.5		

Table S6. The Summary of BET surface area and total N₂ uptake of MOFs



Figure S1. IR spectra of Ni-MOF 1



Figure S2. TGA curve of Ni-MOF 1



Figure S3. Pore size distribution profiles for Ni/P/N/C-500, 600, 700 and 800, respectively.



Figure S4. Cycling performances of Ni/P/N/C-500 electrodes measured at the current density of 10.0 A g^{-1} in 6 M potassium hydroxide aqueous solution for 5000 cycles.



Figure S5. SEM images of pristine MOF, along with the EDX mapping image of Ni, P, O and C elements



Figure S6. P XPS spectra of hierarchical derivatives along with the intensity comparison



Figure S7. C XPS spectra of hierarchical derivatives along with the intensity comparison



Figure S8. O XPS spectra of hierarchical derivatives along with the intensity comparison



Figure S9. XRD spectra of pristine Ni-MOF



Figure S10. TEM images of pristine MOF(a), Ni/P/N/C-500(b) and Ni/P/N/C-700(c).