nature portfolio

https://doi.org/10.1038/s41596-022-00718-2

Supplementary information

MOF-derived nanoporous carbons with diverse tunable nanoarchitectures

In the format provided by the authors and unedited

MOF-derived nanoporous carbons with diverse tunable nanoarchitectures.

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Supplementary Method 1 │ Device-level supercapacitor

Fabrication of symmetric supercapacitor cell

1. To prepare electrode dispersion, add 10.0 mg of active material, 1.25 mg of carbon black (CB), 1.25 mg of poly(vinylidine difluoride) (PVDF), and then 1 mL of 1-methylpyrrolidinone into a 4-mL glass vial. The ratio of NPC:CB:PVDF in the electrode dispersion is set at 8:1:1 (Fig. 1).

2. Tightly close the 4-mL glass vial with its cap and sonicate the mixture for 1 hour without stirring.

▲ **CRITICAL** Adsorbed active materials on the wall of the glass vial can lead to variation in the concentration of active material in the electrode dispersion, and eventually decrease in specific capacitance.

3. After sonication, carefully drop-cast first 100 µL of electrode dispersion onto the top side of two different current collectors, and dry them in a vacuum oven at 60 °C.

6. After drying, carefully drop-cast the second 100 µL of electrode dispersion onto the top side of the two different current collectors and dry them again in the vacuum oven at 60 °C for 3 h.

▲ **CRITICAL** The weight loading of active material is 2 mg per electrode.

▲ **CRITICAL** Homogeneous deposition of active material on the current collector must be ensured.

7. Unscrew and open HS test cell and carefully place one current collector with deposited electrode facing the top.

8. Wet glass microfiber filter paper cut into a circle with a diameter of 1.5 cm in 1 M H_2SO_4, and carefully place it on top of the electrode side of the current collector in the HS test cell.

9. Carefully place the other current collector with deposited electrode facing the glass microfiber filter paper in the HS test cell.

10. Carefully close the HS test cell and screw the pins to firmly fix the cell.

Equations for the capacitance of two-electrode symmetric supercapacitor cell

$$\boldsymbol{C_g} = \frac{\boldsymbol{I} \times \Delta \boldsymbol{t}}{\boldsymbol{M} \times \Delta \boldsymbol{V}}$$

where 'C_g' is gravimetric capacitance (F g^{-1}), 'I' is current (A), 't' is discharge time (s), 'M' is the total mass of active materials on both electrodes (g), 'V' is the potential window (V).

$$\boldsymbol{C_v} = \boldsymbol{C_g} \times \boldsymbol{\rho}$$

where 'C_V' is volumetric capacitance (F cm^{-3}), and '$\boldsymbol{\rho}$' is the density of active material (g cm^{-3}).

Supplementary Table 1 │ Summary of physical and electrochemical properties of the MOF-derived NPC

	Type of MOF-derived NPC								
Parameters	**NPC-700**	**NPC-800**	**NPC-900**	**NPC-1000**	**HNPC**	**NC@GC (0.05)**	**NC@GC (0.35)**	**HPC-2.5**	**HPC-5.0**
Surface Area (m^2 g^{-1})	1032	1678	1823	1591	788	1276	813	412	563
Pore volume (cm^3 g^{-1})	0.80	0.97	1.40	0.89	1.41	1.78	0.89	0.52	0.71
Nitrogen content (at. %)	14.2	13.6	11.9	3.5	2.7	10.6	8.5	7.8	7.7
Specific capacitance (F g^{-1})	16 (5 mV s^{-1})	165 (5 mV s^{-1})	217 (5 mV s^{-1})	153 (5 mV s^{-1})	113 (2 A g^{-1})	270 (2 A g^{-1})	149 (2 A g^{-1})	159 (2 A g^{-1})	271 (2 A g^{-1})

Supplementary Table 2 | Summary of previously reported MOF-derived nanoporous carbons and applications

Reference	Precursor	Carbon	Application
1	ZIF-8@ZIF-67	CoP nanoparticle embedded N-doped carbon nanotube hollow polyhedron	Hydrogen evolution reaction
2	SOM ZIF-67	3DOM $CoSe_2$@C	Aluminium ion battery
3	ZIF-8	Ni SAs/N-C	CO_2 reduction reaction
4	ZIF-8@ZIF-67	$ZnCo_2O_4$@N-doped carbon/carbon nanotube	Oxygen reduction reaction
5	Fe-doped ZIF	Fe/N-doped carbon	Oxygen reduction reaction
6	ZIF-8/PAN	N-doped carbon	Capacitive deionization
7	Fe-doped ZIF-8	Fe/N-doped carbon	CO_2 reduction reaction
8	ZIF-8/PS	M-PNC	Oxygen reduction reaction
9	Zn-ZIF-L	NGM	Oxygen reduction reaction
10	TPI@ZIF-8(SIO_2)	Fe/N-doped carbon	Oxygen reduction reaction
11	FePC@ZIF-8	FeSA/N-doped carbon	Oxygen reduction reaction
12	Bimetallic Zn/Co ZIF	Co/N-doped carbon	Oxygen reduction and evolution reactions
13	ZIF-8@PZS	Fe/SA-doped hollow carbon	Oxygen reduction reaction
14	ZIF-8	NPC	Supercapacitor
15	Bimetallic Zn/Co-ZIF	Co/Zn-ZIF-derived NPC	Supercapacitor
16	ZIF-8	NPC	Supercapacitor
17	ZIF-67@ZIF-8	N-CNT	Oxygen reduction reaction
18	ZIF-8/PAN	Hollow particle-based N-doped carbon nanofiber	Supercapacitor
19	ZIF-8	NPC	Supercapacitor
20	Bimetallic Zn/Co-ZIF@SiO_2	Co-N-doped carbon nanoframework	Oxygen reduction reaction
21	ZIF-67@AF	Hierarchical ZIF-67@PR composite carbon	Oxygen reduction reaction
22	Bimetallic Zn/Co-ZIF	Co-SAs/N-doped carbon	Oxygen reduction reaction
23	Bimetallic Zn/Co-ZIF	Co-N_x-doped carbon	CO_2 reduction reaction
24	ZIF-8	Cu-SAs/N-doped carbon	Oxygen reduction reaction
25	Bimetallic Zn/Co-ZIF	Fe/Co/N-doped carbon	Oxygen reduction reaction
26	ZIF-67	N-doped carbon nanotube framework	Oxygen reduction and evolution reactions
27	PS@ZIF-67	Co/N-doped carbon	Oxygen reduction reaction
28	ZIF-67	Co/P-doped carbon	Lithium ion battery and hydrogen evolution reaction
29	Co-ZIF-8@F127	Co/N-carbon@F127	Oxygen reduction reaction
30	ZIF	Hollow mesoporous carbon nanocube	Li-SeS_2 battery

References

1. Pan, Y. *et al.* Core–shell ZIF-8@ZIF-67-derived CoP nanoparticle-embedded N-doped carbon nanotube hollow polyhedron for efficient overall water splitting. *J. Am. Chem. Soc.* **140**, 2610-2618, (2018).
2. Hong, H. *et al.* Ordered macro–microporous metal–organic framework single crystals and their derivatives for rechargeable aluminum-ion batteries. *J. Am. Chem. Soc.* **141**, 14764-14771, (2019).
3. Zhao, C. *et al.* Ionic exchange of metal–organic frameworks to access single nickel sites for efficient electroreduction of CO_2. *J. Am. Chem. Soc.* **139**, 8078-8081, (2017).
4. Li, J. H. *et al.* ZIF-8@ZIF-67–derived $ZnCo_2O_4$@nitrogen–doped carbon/carbon nanotubes wrapped by a carbon layer: a stable oxygen reduction catalyst with a competitive strength in acid media. *Mater. Today Energy* **19**, 100574, (2021).
5. Zhang, H. *et al.* Single atomic iron catalysts for oxygen reduction in acidic media: particle size control and thermal activation. *J. Am. Chem. Soc.* **139**, 14143-14149, (2017).
6. Xu, X. *et al.* Ultrahigh capacitive deionization performance by 3D interconnected MOF-derived nitrogen-doped carbon tubes. *Chem. Eng. J.* **390**, 124493, (2020).
7. Huan, T. N. *et al.* Electrochemical reduction of CO_2 catalyzed by Fe-N-C materials: a structure–selectivity study. *ACS Catal.* **7**, 1520-1525, (2017).
8. Xia, W. *et al.* Highly ordered macroporous dual-element-doped carbon from metal–organic frameworks for catalyzing oxygen reduction. *Chem. Sci.* **11**, 9584-9592, (2020).
9. Xia, W. *et al.* Defect-rich graphene nanomesh produced by thermal exfoliation of metal–organic frameworks for the oxygen reduction reaction. *Angew. Chem. Int. Ed.* **58**, 13354-13359, (2019).
10. Wan, X. *et al.* Fe–N–C electrocatalyst with dense active sites and efficient mass transport for high-performance proton exchange membrane fuel cells. *Nat. Catal.* **2**, 259-268, (2019).
11. Jiang, R. *et al.* Edge-site engineering of atomically dispersed Fe–N_4 by selective C–N bond cleavage for enhanced oxygen reduction reaction activities. *J. Am. Chem. Soc.* **140**, 11594-11598, (2018).
12. Gadipelli, S., Zhao, T., Shevlin, S. A. & Guo, Z. Switching effective oxygen reduction and evolution performance by controlled graphitization of a cobalt–nitrogen–carbon framework system. *Energy Environ. Sci.* **9**, 1661-1667, (2016).
13. Chen, Y. *et al.* Enhanced oxygen reduction with single-atomic-site iron catalysts for a zinc-air battery and hydrogen-air fuel cell. *Nat. Commun.* **9**, 5422, (2018).
14. Salunkhe, R. R. *et al.* A high-performance supercapacitor cell based on ZIF-8-derived nanoporous carbon using an organic electrolyte. *Chem. Commun.* **52**, 4764-4767, (2016).
15. Kim, J. *et al.* CNTs grown on nanoporous carbon from zeolitic imidazolate frameworks for supercapacitors. *Chem. Commun.* **52**, 13016-13019, (2016).
16. Salunkhe, R. R. *et al.* Fabrication of symmetric supercapacitors based on MOF-derived nanoporous carbons. *J. Mater. Chem. A* **2**, 19848-19854, (2014).
17. Meng, J. *et al.* General oriented formation of carbon nanotubes from metal–organic frameworks. *J. Am. Chem. Soc.* **139**, 8212-8221, (2017).
18. Chen, L.-F., Lu, Y., Yu, L. & Lou, X. W. Designed formation of hollow particle-based nitrogen-doped carbon nanofibers for high-performance supercapacitors. *Energy Environ. Sci.* **10**, 1777-1783, (2017).
19. Wang, R. *et al.* Engineering metal organic framework derived 3D nanostructures for high performance hybrid supercapacitors. *J. Mater. Chem. A* **5**, 292-302, (2017).
20. Shang, L. *et al.* Well-dispersed ZIF-derived Co, N-Co-doped carbon nanoframes through mesoporous-silica-protected calcination as efficient oxygen reduction electrocatalysts. *Adv. Mater.* **28**, 1668-1674, (2016).
21. Kale, V. S. *et al.* Microporosity-controlled synthesis of heteroatom codoped carbon nanocages by wrap-bake-sublime approach for flexible all-solid-state-supercapacitors. *Adv. Funct. Mater.* **28**, 1803786, (2018).
22. Yin, P. *et al.* Single cobalt atoms with precise N-coordination as superior oxygen reduction reaction catalysts. *Angew. Chem. Int. Ed.* **55**, 10800-10805, (2016).
23. Wang, X. *et al.* Regulation of coordination number over single Co sites: triggering the efficient electroreduction of CO_2. *Angew. Chem. Int. Ed.* **57**, 1944-1948, (2018).
24. Qu, Y. *et al.* Direct transformation of bulk copper into copper single sites via emitting and trapping of atoms. *Nat. Catal.* **1**, 781-786, (2018).
25. Wang, J. *et al.* Design of N-coordinated dual-metal sites: a stable and active Pt-free catalyst for acidic oxygen reduction reaction. *J. Am. Chem. Soc.* **139**, 17281-17284, (2017).
26. Xia, B. Y. *et al.* A metal–organic framework-derived bifunctional oxygen electrocatalyst. *Nat. Energy* **1**, 15006, (2016).

27. Guan, B. Y., Yu, L. & Lou, X. W. Formation of single-holed cobalt/N-doped carbon hollow particles with enhanced electrocatalytic activity toward oxygen reduction reaction in alkaline media. *Adv. Sci.* **4**, 1700247, (2017).
28. Wang, X. *et al.* Phytic acid-assisted formation of hierarchical porous CoP/C nanoboxes for enhanced lithium storage and hydrogen generation. *ACS Nano* **12**, 12238-12246, (2018).
29. He, Y. *et al.* Highly active atomically dispersed CoN_4 fuel cell cathode catalysts derived from surfactant-assisted MOFs: carbon-shell confinement strategy. *Energy Environ. Sci.* **12**, 250-260, (2019).
30. Liu, C. *et al.* Hollow mesoporous carbon nanocubes: rigid-interface-induced outward contraction of metal-organic frameworks. *Adv. Funct. Mater.* **28**, 1705253, (2018).