Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2020

Supplementary file for

<u>Microwave induced transformation of metal organic frameworks into defect rich carbon</u> <u>nanofibers</u>.

Vadahanambi Sridhar and Hyun Park *

Published in New Journal of Chemistry, dated 19th February, 2020.

Table T1 Representative morphologies of MOF derived carbons

| S. | Material | Carbonization | Morphology | Reference |
|----|---------------------------------|--|---|-----------|
| No | | Temperature/Time/atmosphere | | |
| 1 | Electrospun Zn-MOF | 1000 °C/6 hours/Argon | Carbon fiber web | 1 |
| 2 | MIL-101, Alumina template | 600 to 1000 °C/ 5 hours/ Argon | Honeycomb carbons | 2 |
| 3 | Zn MOF-74 | 600 to 1000 °C/ 5 hours/ Argon | Carbon nanorods | 3 |
| 4 | Co-MOF | 500 °C/ 2 hours/ Nitrogen | Disordered carbons | 4 |
| 5 | Basolite, F300 | 700 to 900 $^{\circ}C/5$ hours/ Argon | hollow carbon nanospheres | 5 |
| 6 | metal @ZIF-8 | 600 to 900 °C/ 4 hours/ $\rm H_2$ and Argon | Porous carbons | 6 |
| 7 | Cobalt-Melamine- BDC | 700 to 900 °C/ 4 hours/ Nitrogen | Disordered CNT carbons | 7 |
| 8 | Cobalt-triazine networks | 700 °C/ 3 hours/ Vacuum | Porous polyhedrons | 8 |
| 9 | Fe-MIL | 500 °C/ 2 hours in Argon; subsequent annealing in air for 2 more hours | Iron oxide@C | 9 |
| 10 | Ni-MOF | 500 °C/2 hours/Nitrogen | Nickel rich hollow carbons | 10 |
| 11 | ZIF-67 | 800 to 1000 °C/ 5 hours/ Nitrogen | Sodalite structured mesoporous carbons | 11 |
| 12 | Ti-amino BDC | 1000 °C/8 hours/Argon | 3D carbon cuboids | 12 |
| 13 | ZIF-67/LDH | 400 °C/ 3.3 hours/ Air | Hollow nanocages | 13 |
| 14 | ZIF-8 | 600 and 1000 °C/ 1 hour/ Nitrogen | Mesoporous carbons | 14 |
| 15 | ZIF-67 | 350 °C/ 2 hours/ Nitrogen | Cobalt rich carbon Hollow prisms | 15 |
| 16 | ZIF-8/MnO ₂ Nanorods | 700 °C/ 4 hours/ Argon | ZnMnO ₄ carbon rods | 16 |
| XX | DABCO based Co- MOF | Microwave/ 45 seconds/ Air | NCNF on rGO/ NCNF on Carbon fiber | |

Materials and Methods

High purity graphite was purchased from Samjung C & G, Korea whereas sulphuric acid (H₂SO₄), hydrochloric acid (HCl), sodium nitrate (NaNO₃), hydrogen peroxide, potassium permanganate (KMnO₄), Dabco(1,4-diazabicyclo[2.2.2]octane) and cobalt nitrate were purchased from Sigma-Aldrich, Korea and were used as received. Microwave irradiation was carried out in a domestic microwave oven manufactured by Daewoo Korea. Field-emissionscanning electron microscopy (FE-SEM, Nova NanoSEM 230 FEI operating at 10kV and TALOS F200X Transmission electron microscopy operating at 200 kV were used to study SEM and HRTEM morphology, respectively. Due to inherently excellent electrical conductivity of both MDNCNT-Co@rGO and MDNCNT-Co@CF, there was no necessity of metal coating for SEM test. The structural properties were studied by X-ray diffraction (XRD, Rigaku D/max-2550V, Cu-Ka radiation) and by Raman spectra (LabRAM HR UV/vis/NIR Horiba Jobin-Yvon, France). Chemical analysis was performed by X-ray photoelectron spectroscopy (Sigma Probe Thermo VG spectrometer using Mg Ka X-ray sources). The XPS spectra were curve fitted with a mixed Gaussian-Lorentzian shape using the freeware XPSPEAKversion 4.1. BET surface area was measured by Nitrogen adsorption and desorption isotherms at 77K using a BEL Japan Inc. Belsorp Mini II Surface Area.Electrochemical tests were conducted using CR2032 coin-type test cells assembled in argon-filled glove box. Working electrodes were prepared with active materials and poly(acrylic acid) as the binder (mass ratio of 90: 10) were added to ethanol and mixed into a homogeneous slurry. The slurry was cast on a glass plate cleaned with piranha solution and dried at 100 °C in vacuum for 5 h. The coin cells were assembled with pure sodium foil as counter electrode, a glass fiber as separator, 1M NaClO₄ in ethylene carbonate/propylene carbonate (1:1 v/v) as electrolyte. Galvanostatic charge-discharge cycling tests were performed using an WBCS 3000, Won-A-Tech, Korea battery testing system in the voltage range between 0.005–3 V). EMI testing in the 1 to 18 GHz range was carried out as reported in our previous papers [21].



Figure S1 Representative HRTEM morphology of carbon nanofibers in MDCNF-Co@rGO showing disordered turbostatic graphene layers are dominant and minor quantities of hollow free space.



 $\label{eq:Figure S2Carbon map of MDNCNF-Co@rGO corresponding to TEM image of Fig. 1(g) in the main manuscript. Scale bar is 1 \mu m.$



Figure S3Secondary electron back scattering image corresponding to Fig 5(a) and (b) of the manuscript. Scale bars in (a) and (b) are 5μ m and 1μ m, respectively.

References

- I. T. Kim, S. Shin, M. W. Shin. Development of 3D interconnected carbon materials derived from Zn-MOF-74@carbon nanofiber web as an efficient metal-free electrocatalyst for oxygen reduction. Carbon, 2018, 135, 35–43.
- Q.-L. Zhu, W. Xia, T. Akita, R. Zou, Q. Xu. Metal-Organic Framework-Derived Honeycomb-Like Open Porous Nanostructures as Precious-Metal-Free Catalysts for Highly Efficient Oxygen Electroreduction. Adv Mater., 2016, 28 (30), 6391–6398.
- 3. P. Pachfule, D. Shinde, M. Majumder, Q. Xu. Fabrication of carbon nanorods and graphene nanoribbons from a metal–organic framework. Nat. Chem., 2016, 8 (7); 718–724.
- B. Lin, A. Wang, Y. Guo, Y. Ding, Y. Guo, L. Wang, W. Zhan, F. Gao. Ambient Temperature NO Adsorber Derived from Pyrolysis of Co-MOF(ZIF-67)). ACS Omega, 2019, 4 (5); 9542– 9551.
- M. Klose, R. Reinhold, K. Pinkert, M. Uhlemann, F. Wolke, J. Balach, T. Jaumann, U. Stoeck, J. Eckert L. Giebeler. Hierarchically nanostructured hollow carbon nanospheres for ultra-fast and long-life energy storage. Carbon, 2016, 106, 306–313.

- Z. Qi, Y. Pei, T. W. Goh, Z. Wang, X. Li, M. Lowe, R. V. Maligal-Ganesh, W. Huang. Conversion of confined metal@ZIF-8 structures to intermetallic nanoparticles supported on nitrogen-doped carbon for electrocatalysis. Nano Research, 2018, 11 (6); 3469–3479.
- H. Zhong, Y. Luo, S. He, P. Tang, D. Li, N. Alonso-Vante, Y. Feng. Electrocatalytic Cobalt Nanoparticles Interacting with Nitrogen-Doped Carbon Nanotube in Situ Generated from a Metal–Organic Framework for the Oxygen Reduction Reaction. ACS Appl. Mater. Interfaces., 2017, 9 (3); 2541–2549.
- J.-D. Yi, R. Xu, G.-L. Chai, T. Zhang, K. Zang, B. Nan, H. Lin, Y.-L. Liang, J. Lv, J. Luo, R. Si, Y.-B. Huang, R. Cao. Cobalt single-atoms anchored on porphyrinic triazine-based frameworks as bifunctional electrocatalysts for oxygen reduction and hydrogen evolution reactions. J. Mater. Chem. A, 2019,7 (3), 1252-1259.
- K. Wang, M. Chen, Z. He, L. Huang, S. Zhu, S. Pei, J. Guo, H. Shao, J. Wang. Hierarchical Fe3O4@C nanospheres derived from Fe2O3/MIL-100(Fe) with superior high-rate lithium storage performance. J. Alloys Compd., 2018, 755, 154–162.
- X. Lin, S. Wang, W. Tu, Z. Hu, Z. Ding, Y. Hou, R. Xu, W. Dai. MOF-derived hierarchical hollow spheres composed of carbon-confined Ni nanoparticles for efficient CO₂ methanation. Catal. Sci. Technol., 2019, 9(3); 731–738.
- N. L. Torad, R. R. Salunkhe, Y. Li, H. Hamoudi, M. Imura, Y. Sakka, C.-C. Hu, Y. Yamauchi. Electric Double-Layer Capacitors Based on Highly Graphitized Nanoporous Carbons Derived from ZIF-67. Chem.: Eur. J., 2014, 20 (26); 7895–7900.
- A. Banerjee, K. K. Upadhyay, D. Puthusseri, V. Aravindan, S. Madhavi, S. Ogale. MOF-derived crumpled-sheet-assembled perforated carbon cuboids as highly effective cathode active materials for ultra-high energy density Li-ion hybrid electrochemical capacitors (Li-HECs). Nanoscale, 2014, 6 (8), 4387-4384.

- W. Kong, J. Li, Y. Chen, Y. Ren, Y. Guo, S. Niu, Y. Yang. ZIF-67-derived hollow nanocages with layered double oxides shell as high-Efficiency catalysts for CO oxidation. Appl. Surf. Sci., 2018, 437, 161–168.
- F. J. Martín-Jimeno, F. Suárez-García, J. I. Paredes, M. Enterría, M. F. R. Pereira, J. I. Martins, J. L. Figueiredo, A. Martínez-Alonso, J. M. D. Tascón. A 'Nanopore Lithography' Strategy for Synthesizing Hierarchically Micro/Mesoporous Carbons from ZIF-8/Graphene Oxide Hybrids for Electrochemical Energy Storage. ACS Appl. Mater. Interfaces, 2017, 9 (51), 44740–44755.
- 15. L. Yu, J. F. Yang, X. W. D. Lou. Formation of CoS2 Nanobubble Hollow Prisms for Highly Reversible Lithium Storage. Angew. Chem. Int. Ed., 2016, 55 (43); 13422–13426.
- M. Zhong, D. Yang, C. Xie, Z. Zhang, Z. Zhou, X.-H. Bu. Yolk-Shell MnO@ZnMn₂O₄/N-C Nanorods Derived from α-MnO₂/ZIF-8 as Anode Materials for Lithium Ion Batteries. Small, 2016, 12 (40); 5564–5571.
- 17. This work.