

Table S1 Representative morphologies of MOF derived carbons

S. No	Material	Carbonization Temperature/Time/atmosphere	Morphology	Reference
1	Electrospun Zn-MOF	1000C/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 C/ 5 hours/ Argon	hollow carbon nanospheres	5
6	metal @ZIF-8	600 to 900 C/ 4 hours/ 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 1000C/ 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 MOF	Microwave/ 45 seconds/ Air	NCNT on rGO/ NCNT on Carbon fiber	

Materials and Methods

Materials:

99.5% pure graphite (grade-QSG) was purchased from Samjung (C & G, Korea) whereas reagent grade sulphuric acid (H_2SO_4), hydrochloric acid (HCl), sodium nitrate ($NaNO_3$), hydrogen peroxide, potassium permanganate ($KMnO_4$), 1,4-diazabicyclo[2.2.2]octane (DABCO) and iron(III) acetate 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, Model number: KR-B202WL with output power of 700 W operating at 2450 MHz.

Methods:

Field-emission scanning 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. Energy-dispersive X-ray spectroscopy (EDS) scans were taken on TALOS F200x (FEI) using the in-built UltraFast mapping SDD-EDS using Mn-K α detector. Due to inherently excellent electrical conductivity of all the synthesized 3-D carbonaceous materials, viz. Fe@NCNT-rGO, Co@NCNT-rGO and Fe@NCNT-CF, there was no necessity of metal coating for SEM testing. Structural properties were studied by X-ray diffraction and Raman spectroscopy using Rigaku D/max-2550V, Cu-K α radiation and LabRAM HR evolution UV/vis/NIR spectrometer. High resolution X-ray photoelectron spectroscopy studies were carried out on a Sigma Probe Thermo VG spectrometer using Mg K α X-ray sources. The XPS spectra were curve fitted with a mixed Gaussian-Lorentzian shape using XPSPEAK version 4.1. BET (Brunauer-Emmett-Teller) surface area was measured by Nitrogen adsorption and desorption isotherms at 77K using a BEL Japan Inc. Belsorp Mini II Surface Area. Prior to testing, the sample was first degassed for 24 h at 250 °C.

Electro-chemical tests

All the electrochemical measurements were conducted on a CHI 660 electrochemical station (CH Instruments, Inc.) with a conventional three-electrode system. In a typical electrochemical measurement, a total of 5 mg of catalysts was dispersed by sonication in a mixture of 480 μL isopropanol (J&K Scientific LTD.) and 20 μL of Nafion aqueous solution (5 wt.%, DuPont) for 30 min. 12 μL of the above suspension was gently dropped onto a glassy carbon rotating disk electrode (RDE, 5 mm diameter) or rotating ring-disk electrode (RRDE, 4.93 mm inner diameter and 5.38 mm outer diameter) and dried naturally in air. The above procedure was repeated twice which results in a total loading mass of about 0.6 mg/cm². The electrolyte was 0.1 M KOH aqueous solution, and the reference and counter electrodes were saturated calomel electrode (SCE) and Pt wire, respectively. The electrolyte was saturated with O₂ before the experiment, and O₂ was continuously supplied during the experimental operation. All potential values reported in this study were converted to the reversible hydrogen electrode (RHE) scale, according to the equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.0591\text{pH} + 0.242$. For the stability test, the working electrode ran at - 0.7 V vs SCE for 60,000 s in O₂-saturated 0.1M KOH with a rotation rate of 1600 rpm. For comparison, commercial Pt/C (20 wt.% Pt) powder was tested under the same conditions, with a loading mass of 0.25 mg cm⁻². Linear sweep voltammetry (LSV) was measured by RDE/RRDE technique the with the scan rate of 10 mV/s at various rotating speeds from 400 to 2400 rpm.”

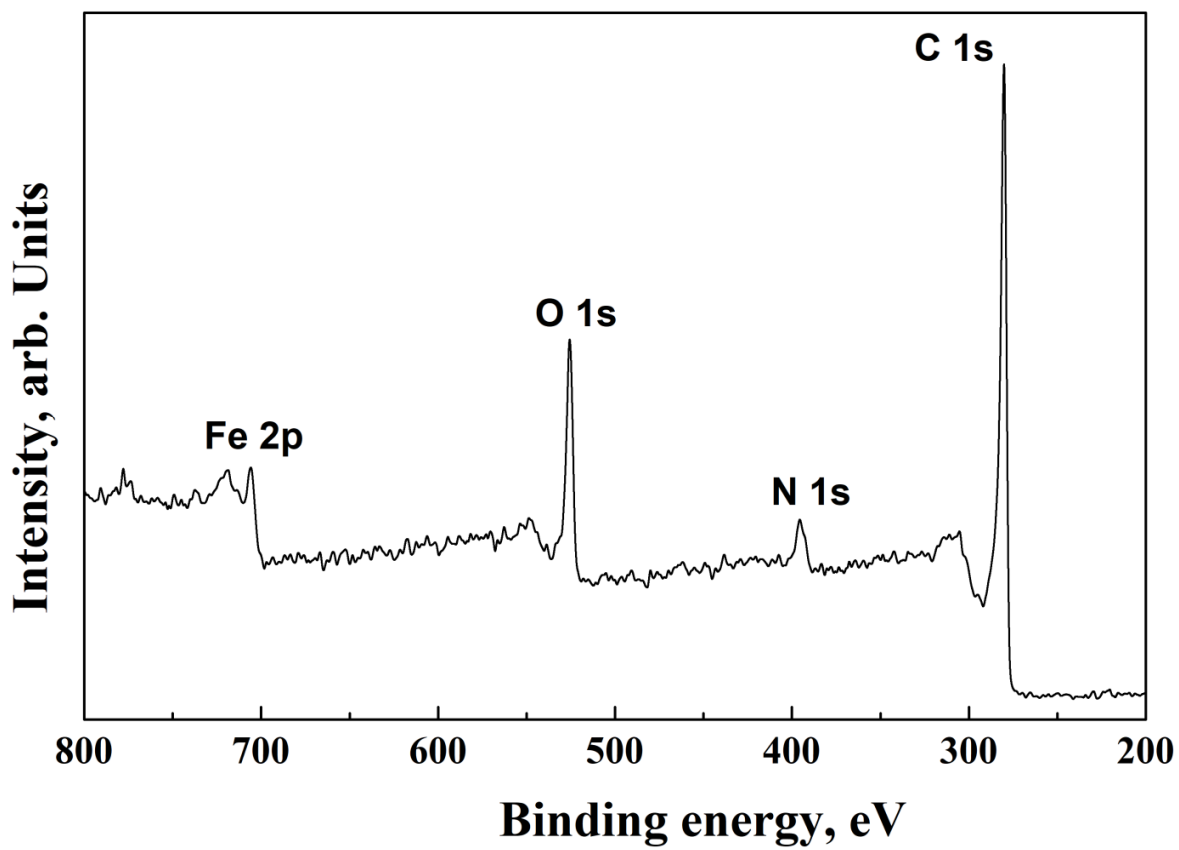


Figure S1: XPS survey scan of MDCNT@rGO.

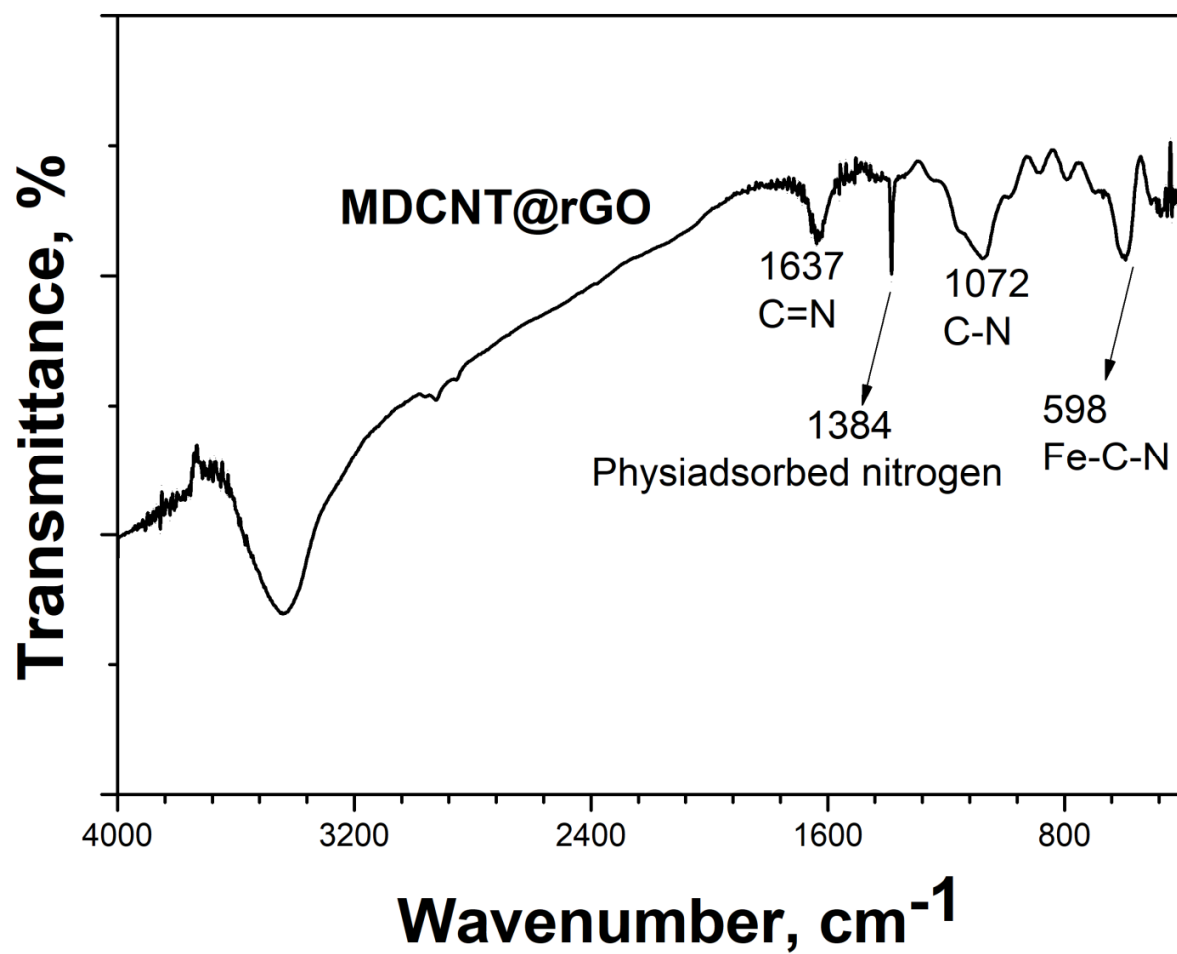


Figure S2. FTIR spectra of MDCNT@rGO indicating presence of nitrogen moieties

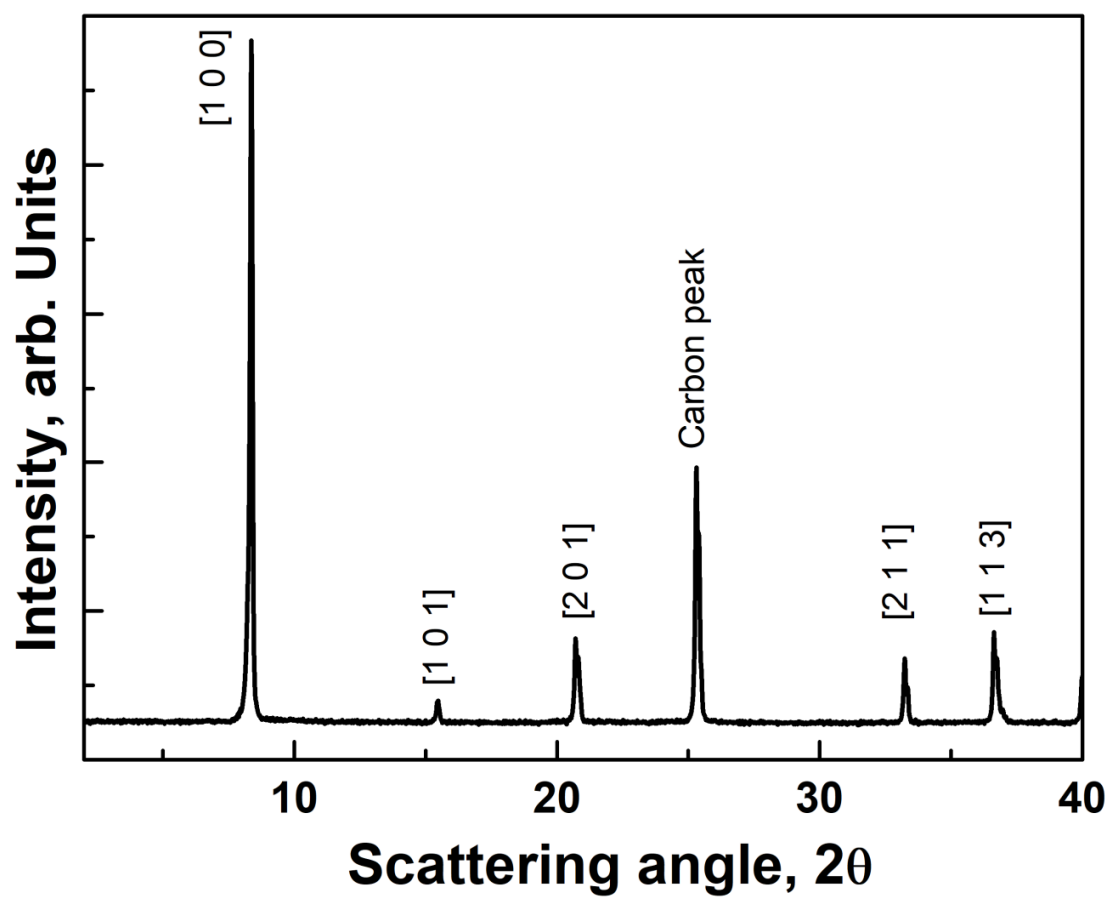


Figure S3: XRD of Fe-MOF synthesized on carbon fiber substrate.

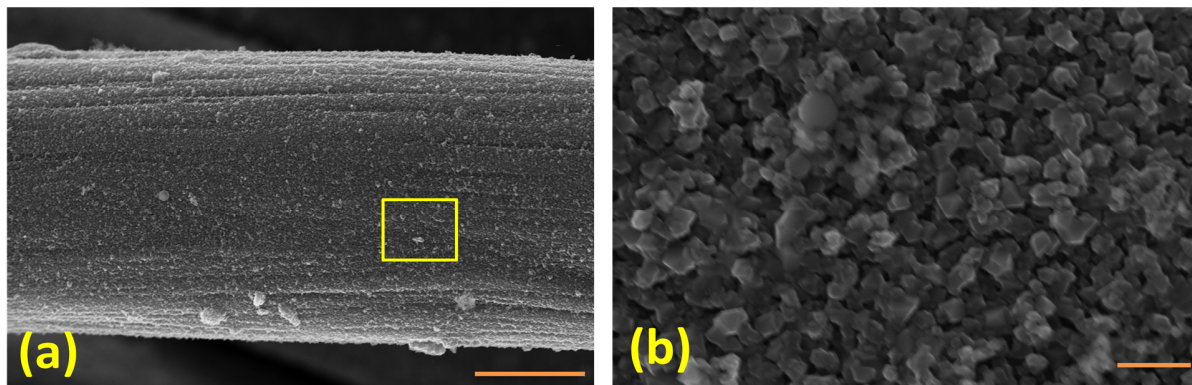


Figure S4 Representative SEM morphology of DABCO MOF decorated carbon fibers. Scale bars are 2 μm and 200 nm in (a) and (b), respectively.

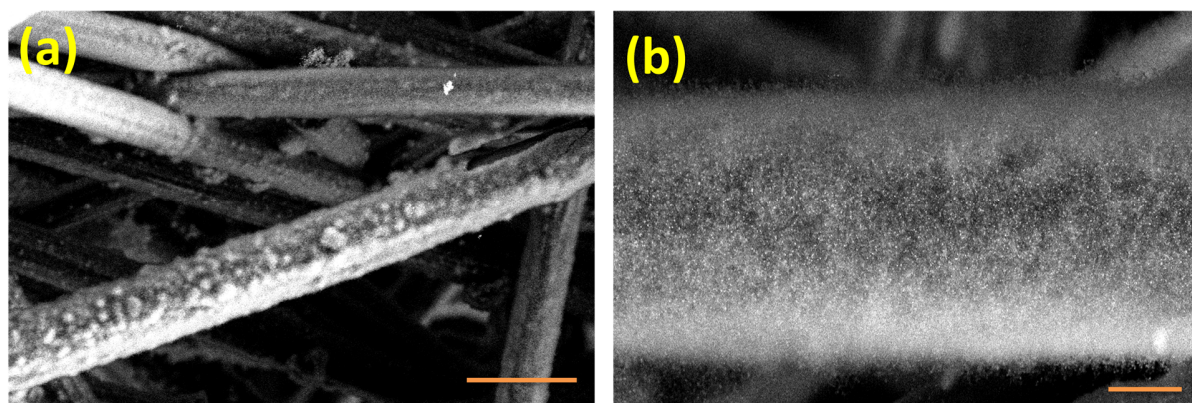


Figure S5 Secondary electron image corresponding to MDCNT@CF shown in Fig. 5(a) and 5(b) of the manuscript. Scale bars are 3 μm and 1 μm respectively.

References

1. 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.
2. 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.
4. 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.
5. 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.
6. 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.
7. 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.
8. 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.

9. 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.
10. 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.
11. 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.
12. 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.
13. 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.
14. 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.

16. 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.