## **Supplementary Information**

## Thermally reduced mesoporous manganese MOF@ reduced graphene oxide nanocomposite as bifunctional electrocatalyst for oxygen reduction and evolution

Abdul Wahab,\*<sup>a</sup> Naseem Iqbal,\*\*<sup>a</sup> Tayyaba Noor,<sup>b</sup> Sheeraz Ashraf,<sup>a</sup> Muhammad Arslan Raza,<sup>a</sup> Awais Ahmad,<sup>a</sup> Usman Ali Khan,<sup>a</sup>

<sup>a</sup> U.S-Pakistan Center for Advanced Studies in Energy, National University of Sciences and Technology, Islamabad 44000, Pakistan.

<sup>b</sup> School of Chemical and Materials Engineering, National University of Sciences and Technology, Islamabad 44000, Pakistan.

Corresponding Authors

\*Email: <u>abdul\_che06@scme.nust.edu.pk</u> \*\*Email: <u>naseem@uspcase.nust.edu.pk</u>

Fig. S1: Optical images of prepared (a) MnBDC@75%rGO, (b) MnBDC@50%rGO, (c) MnBDC@25%rGO and (d) MnBDC annealed samples ready for electrochemical measurements.

Fig. S2: SEM micrographs of (a-d) graphene oxide prepared by improved Hummer's method.

Fig. S3: SEM micrographs of (a-h) MnBDC@75%GO nanocomposite.

Fig. S4: SEM micrographs of (a-h) MnBDC@75%rGO nanocomposite.

Fig. S5: XRD pattern of MnBDC@50%rGO nanocomposite.

Fig. S6: XRD pattern of MnBDC@25%rGO nanocomposite.

Fig. S7: FTIR spectrum of MnBDC@50%rGO nanocomposite.

Fig. S8: FTIR spectrum of MnBDC@25%rGO nanocomposite.

Table S1: ORR and OER electrocatalytic performance parameters of recently reported rGO composite catalysts.



Fig. S1: Optical images of prepared (a) MnBDC@75%rGO, (b) MnBDC@50%rGO, (c) MnBDC@25%rGO and (d) MnBDC annealed samples ready for electrochemical measurements.



Fig. S2: SEM micrographs of (a-d) graphene oxide prepared by improved Hummer's method.



Fig. S3: SEM micrographs of (a-h) MnBDC@75%GO nanocomposite



Fig. S4: SEM micrographs of (a-h) MnBDC@75%rGO nanocomposite



Fig. S5: XRD pattern of MnBDC@50%rGO nanocomposite



Fig. S6: XRD pattern of MnBDC@25%rGO nanocomposite



Fig. S7: FTIR spectrum of MnBDC@50%rGO nanocomposite



Fig. S8: FTIR spectrum of MnBDC@25%rGO nanocomposite

In Fig. S5 and Fig. S6, peaks of MnBDC, benzoic acid, benzophenone and rGO phases have been

Catalyst ID	Oxygen reduction reaction					Oxygen evolution reaction		
	E <sub>Pc</sub>	I <sub>pc</sub>	E <sub>onset</sub>	E <sub>1/2</sub>	Tafel	E <sub>onset</sub>	Tafel	Electrolyte
	V vs RHE	mA cm⁻²	V vs RHE	V vs RHE	mVdec <sup>-1</sup>	V vs RHE	mVdec <sup>-1</sup>	
					mvace		mvace	
NiCoMnO <sub>4</sub> /N- rGO [1]	0.75	0.84	0.92	0.75	38	1.5	128	0.1 M KOH
ZIF-8 derived N- PC @Graphene [2]	0.72	-	1.01	0.80	66	1.63	78	0.1 M KOH
Fe/Fe <sub>3</sub> C@ 3D N- Graphene [3]	0.77	-	-	-	62.2	1.487	30.1	0.1 М КОН 1 М КОН
CeO <sub>2</sub> /rGO [4]	0.74	0.76	0.761	-	-	1.33	138	0.1 М КОН
NiFe-LDH/rGO [5]	0.78	-	0.796	-	-	1.47	91	0.1 M KOH
S-Co <sub>9-x</sub> Fe <sub>x</sub> S <sub>8</sub> @rGO [6]	-	-	0.94	0.84	65	1.45 Approx.	66	0.1 M KOH
NiCo2S4@N/S- rGO [7]	0.76	-	0.91 approx.	0.79 approx.	-	1.61 approx.	-	0.1 M KOH
MnBDC@75%r GO (this work)	0.78	0.70	1.09	0.94	93.5	1.72	0.83	0.1 М КОН

Table S1: ORR and OER electrocatalytic performance parameters of recently reported rGO composite catalysts

designated with diamond ( $\diamond$ ), dot ( $\bullet$ ), circle (o) and asterick (\*) signs respectively.

## **References:**

[1] A. Pendashteh, J. Palma, M. Anderson, and R. Marcilla, NiCoMnO4 nanoparticles on N-doped graphene: Highly efficient bifunctional electrocatalyst for oxygen reduction/evolution reactions, *Applied Catalysis B: Environmental*, 2017, **201**, 241-252.

[2] S. Liu, H. Zhang, Q. Zhao, X. Zhang, R. Liu, X. Ge, G. Wang, H. Zhao and W. Cai, Metal-organic framework derived nitrogen-doped porous carbon@ graphene sandwich-like structured composites as bifunctional electrocatalysts for oxygen reduction and evolution reactions, *Carbon*, 2016, **106**, 74-83.

[3] L. Wei, H. E. Karahan, S. Zhai, H. Liu, X. Chen, Z. Zhou, Y. Lei, Z. Liu, and Y. Chen, Amorphous bimetallic oxide–graphene hybrids as bifunctional oxygen electrocatalysts for rechargeable Zn–air batteries, *Advanced Materials*, 2017, **29**, 1701410.

[4] L. Sun, L. Zhou, C. Yang, and Y. Yuan, CeO2 nanoparticle-decorated reduced graphene oxide as an efficient bifunctional electrocatalyst for oxygen reduction and evolution reactions. *International Journal of Hydrogen Energy*, 2017, *42*, 15140-15148.

[5] T. Zhan, Y. Zhang, X. Liu, S. Lu and W. Hou, 2016. NiFe layered double hydroxide/reduced graphene oxide nanohybrid as an efficient bifunctional electrocatalyst for oxygen evolution and reduction reactions. *Journal of Power Sources*, 2016, **333**, 53-60.

[6] T. Liu, F. Yang, G. Cheng and W. Luo, 2018. Reduced Graphene Oxide-Wrapped Co9–xFexS8/Co, Fe-N-C Composite as Bifunctional Electrocatalyst for Oxygen Reduction and Evolution. *Small*, 2018, **14**, p.1703748.

[7] Q. Liu, J. Jin and J. Zhang, NiCo2S4@ graphene as a bifunctional electrocatalyst for oxygen reduction and evolution reactions. *ACS applied materials & interfaces*, 2013, *5*, 5002-5008.