Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

High performance bifunctional electrocatalytic activity of a reduced graphene oxide - molybdenum oxide hybrid catalyst

Sundaram Chandrasekaran[a], Eui Jung Kim[a], Jin Suk Chung[a], Chris R Bowen[b], Balasubramaniyan Rajagopalan[a], Vaia Adamaki [b], R.D.K. Misra[c], and Seung Hyun Hur[a]*

[a]School of Chemical Engineering, University of Ulsan, Daehak-ro, 102, Nam-gu, Ulsan 680-749, South Korea.

[b] Department of Mechanical Engineering, University of Bath, Bath, BA2, 7AY, U.K

[c] Department of Metallurgical, Materials and Biomedical Engineering, University of Texas at El Paso, TX, 79968-0521, USA

corresponding author*: **shhur@ulsan.ac.kr

1. Electrochemical Measurements

1.1. RHE conversion

A saturated silver chloride electrode was used as the reference electrode in all measurements. The measured potentials versus Ag/AgCl reference electrode were converted to the reversible hydrogen electrode (RHE) scale via the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.241\ V + 0.0591 \times pH \text{ at } 25\ °C \quad (1)$$

1.2. Rotating disk electrode (RDE) measurement

The rotating disk electrode (RDE) measurement was carried out to study the kinetics of electrochemical catalytic ORR of the prepared catalyst. The electron transfer number per oxygen involved in the oxygen reduction currents was obtained and evaluated according to changes in the rotating speed of the RDE. The electron transfer number (n) of all samples according to the slopes of the linear fitted using Koutecky-Levich (K–L) plot on the basis of K–L equation is given,

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{0.5}} + \frac{1}{J_K} \quad (2)$$

$$B = 0.62nFC_o(D_o)^{\frac{2}{3}}v^{\frac{-1}{6}} \quad (3)$$

$$J_K = nFkC_o \quad (4)$$

For the Tafel plot, the kinetic current was calculated from the mass -transport correction of RDE by,

$$J_K = \frac{(J * J_L)}{(J_L - J)} \quad (5)$$

where J, J_K, and J_L are the ORR, kinetic limiting, and diffusion limiting currents, respectively. F is the Faraday constant, and n is the electron transfer number per oxygen molecule involved in the ORR. ω is the angular velocity of the disk. C_0 and D_0 are the bulk concentration of O_2 and the diffusion coefficient of O_2 in 0.1 M KOH, respectively, and v is the kinematic viscosity of 0.1 M KOH.

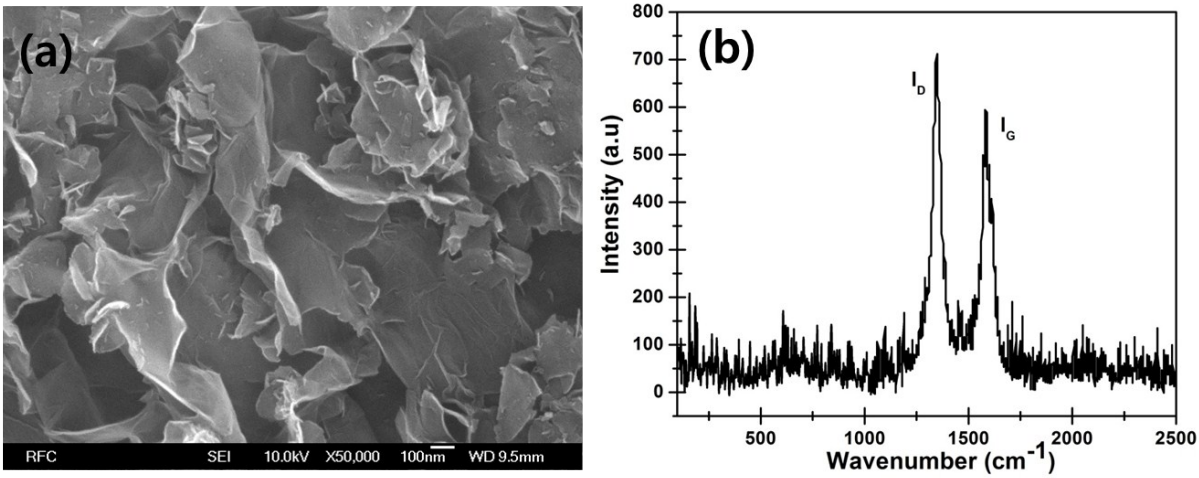

Fig. S1 (a,) FE-SEM image and (c) Raman spectra of the pristine rGO

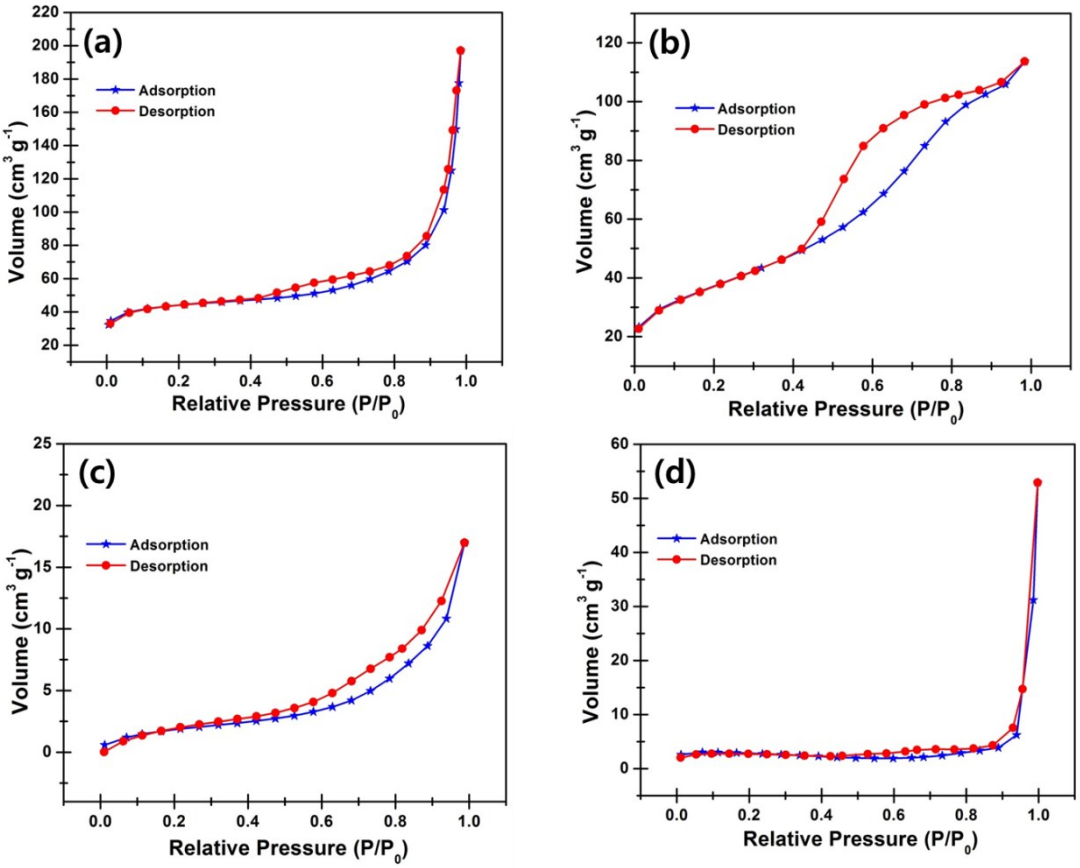

Fig. S2 Nitrogen adsorption/desorption isotherms of (a) high quality Pt/C, (b) GMR, (c) MR and (d) MS samples

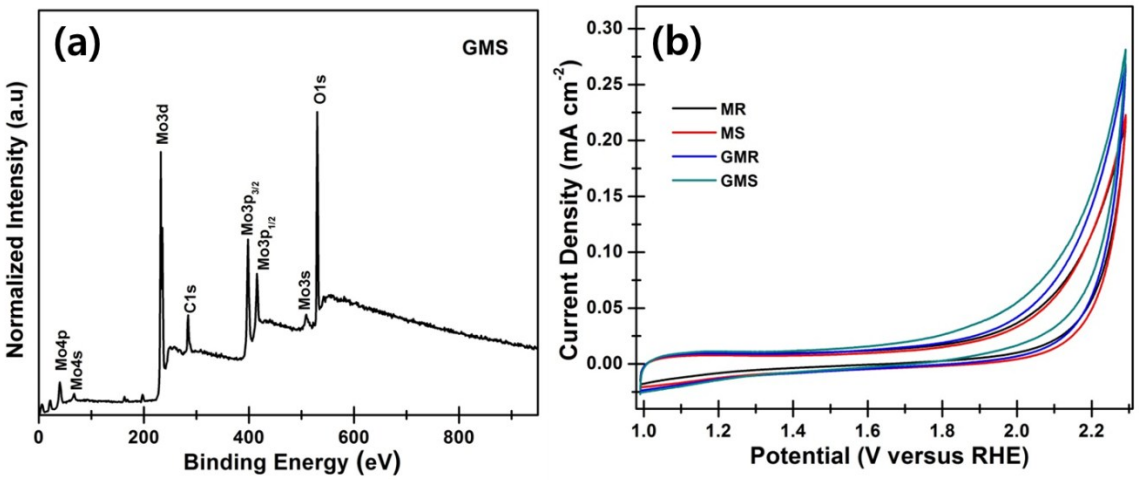

Fig. S3 (a) XPS analysis of GMS hybrid sample and (b) Oxygen evolution CV curves of all prepared samples in 0.1 M KOH with a sweep rate of 10 mV s^{-1}.

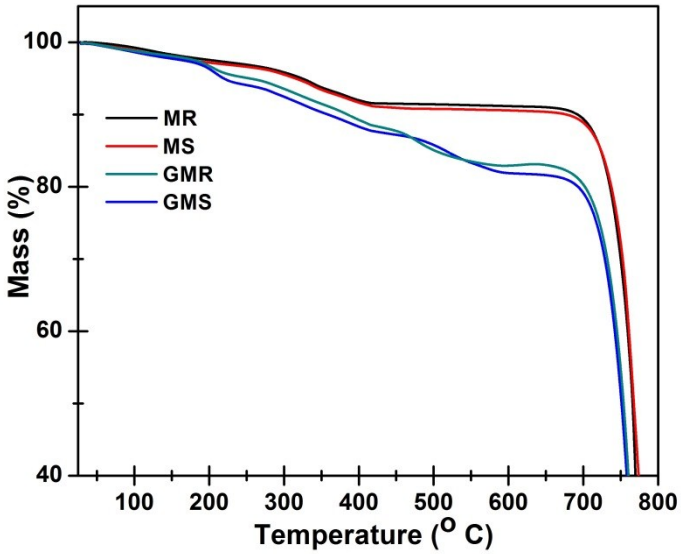

Fig. S4 TGA analsysis of prepared samples

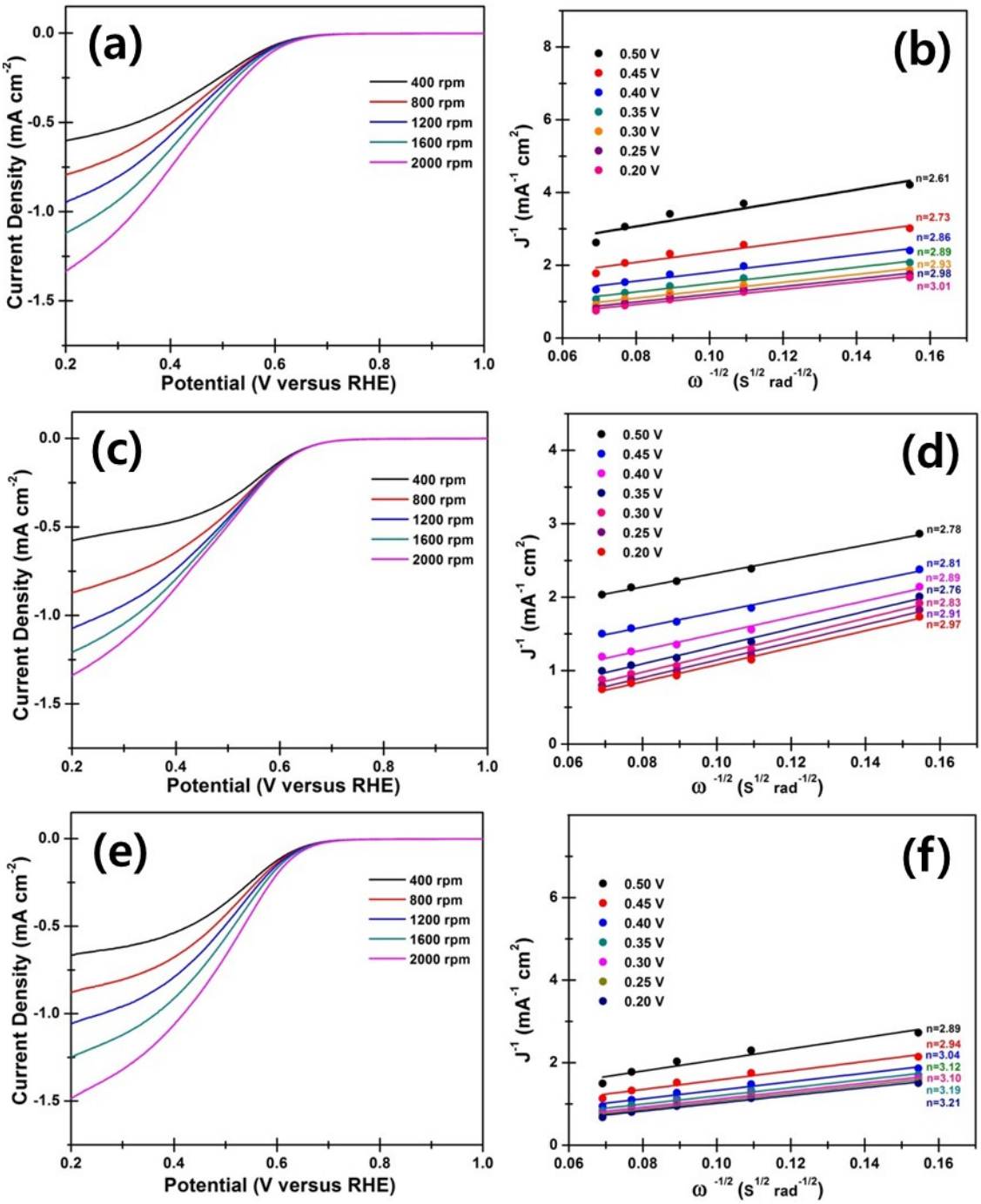

Fig. S5 Rotating-disk voltammograms of (a, c and e) MR, GMR and MS samples in an O_2-saturated 0.1 M KOH with a sweep rate of 10 mV s^{-1} at various rotation speeds indicated. (b, d and f) show corresponding Koutecky–Levich plots (J^{-1} versus $\omega^{-0.5}$) at different potentials.

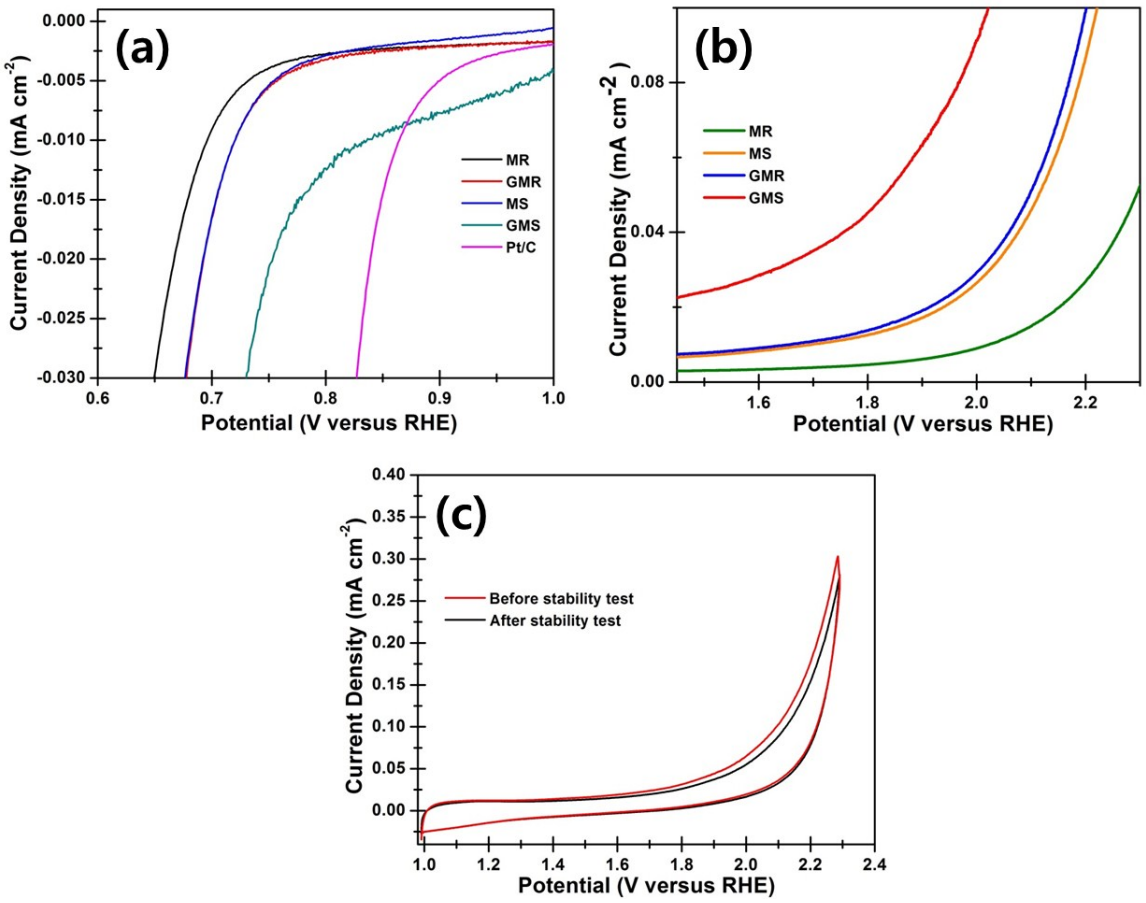

Fig. S6 One set potentials during (a) Oxygen Reduction Reaction (b) Oxygen Evolution Reactions and (c) CV curves of before and after durability test for GMS hybrid sample.

Table S1. Summarized electrochemical parameters of some previously reported high performance ORR and OER catalysts

Catalyst	ORR onset potential (V vs RHE)	Tafel slope	OER onset potential (V vs RHE)	Tafel slope
H_2-CoCat ***Cobo et al. in Nature Materials***[1]	-	-	1.775	-
GO (8 wt.%) Cu-MOF ***Jahan et al. in Advanced Functional Materials***[2]	0.29	69	1.19	65
CG-CoO ***Shun Mao et al. in Energy and Environmental science***[3]	0.86	56	-	75
Co_3O_4-RGO ***Yongye Liang et al. in Nature Materials***[4]	0.88	50	1.54	68
Co_3O_4/2.7Co_2MnO_4 Co_3O_4 Co_2MnO_4 Co_3O_4 + Co_2MnO_4 20 wt% Pt/C ***B. B. Li et al. in Nanoscale***[5]	0.68 0.49 0.59 0.55 0.80	-	1.77 1.83 1.92 1.86 2.08	-
Commercial MoO_2 ***B. B. Li et al. in Nanoscale***[6]	-	-	1.63	-
20 wt % Ir/C 20 wt % Ru/C Mn oxide ***Yelena Gorlin et al. in Journal of American Chemical Society*** [7]	0.69 0.61 0.73	-	1.61 1.62 1.77	-
Co1−xS/rGO ***Hailiang Wang et al. in Angewandte Chemie International Edition***[8]	0.73	-	-	-
Graphene-Co_3O_4 ***Yufei Zhao et al in Scientific Reports***[9]	-	-	0.446 V vs. Ag/AgCl	67
NG-NiCo ***Sheng Chen et al. ACS Nano***[10]	-	-	0.340 V vs. Ag/AgCl	-
Mn_xO_y/NC Ni_xO_y/NC Co_3O_4 ***Justus Mas et al. in Angewandte Chemie International Edition***[11]	0.81 0.71 0.27	-	1.68 1.64 1.68	-
GMS ***This work***	0.754	56	1.768	47

This overall summarized results showing that the electrocatalytic performance of our GMS hybrid catalyst toward ORR and OER are comparable and even better than some of the best bi-functional catalysts previously reported.

References

[1] S. Cobo, J. Heidkamp, P.-A. Jacques, J. Fize, V. Fourmond, L. Guetaz, B. Jousselme, V. Ivanova, H. Dau and S. Palacin, *Nat. Mater.*, 2012,**11**, 802.

[2] M. Jahan, Z. Liu and K. P. Loh, *Adv. Funct. Mater.*, 2013, **23**, 5363.

[3] S. Mao, Z. Wen, T. Huang, Y. Hou and J. Chen, *Energy Environ. Sci.,* 2014, **7**, 609.

[4] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat. Mater.*, 2011, **10**, 780.

[5] D. Wang, X. Chen, D. G. Evans and W. Yang, *Nanoscale*, 2013, **5**, 5312-5315.

[6] B. Li, Y. Liang, X. Yang, Z. Cui, S. Qiao, S. Zhu, Z. Li and K. Yin, *Nanoscale*, 2015, **7**, 16704.

[7] Y. Gorlin and T. F. Jaramillo, *J. Am. Chem. Soc.,* 2010, **132**, 13612.

[8] H. Wang, Y. Liang, Y. Li and H. Dai, *Angew. Chem., Int. Ed.,* 2011, **50**, 10969.

[9] Y. Zhao, S. Chen, B. Sun, D. Su, X. Huang, H. Liu, Y. Yan, K. Sun and G. Wang, *Sci. Rep.*, 2015, **5**, 07629.

[10] S. Chen and S.-Z. Qiao, *ACS Nano*, 2013, **7**, 10190.

[11] J. Masa, W. Xia, I. Sinev, A. Zhao, Z. Sun, S. Grützke, P. Weide, M. Muhler and W. Schuhmann, *Angew. Chem., Int. Ed.,* 2014, **53**, 8508.