Supporting Information

Ultrafine Pt Nanoparticles Stabilized by MoS₂ / N-doped Graphene as Durable Electrocatalyst for Alcohol Oxidation and Oxygen Reduction Reactions

S. Ramakrishnan^a, Mohanraju Karuppannan^b, Mohanraj Vinothkannan^c, K. Ramachandran^a, Oh Joong Kwon^b, Dong Jin Yoo^{a, c,*}

^aR&D Education center for whole life cycle R&D of fuel cell systems, Chonbuk National University, Jeollabuk-do 54896, Republic of Korea

^bDepartment of Energy and Chemical Engineering, Incheon National University, 119 Academyro, Yeonsu-Gu, Incheon 22012, Republic of Korea

^cDepartment of Life Science, Graduate School of Department of Energy Storage/Conversion Engineering, and Hydrogen and Fuel Cell Research Center, Chonbuk National University, Jeollabuk-do 54896, Republic of Korea

*Corresponding authors:

Email address: <u>djyoo@jbnu.ac.kr</u> (Prof. Dong Jin Yoo);

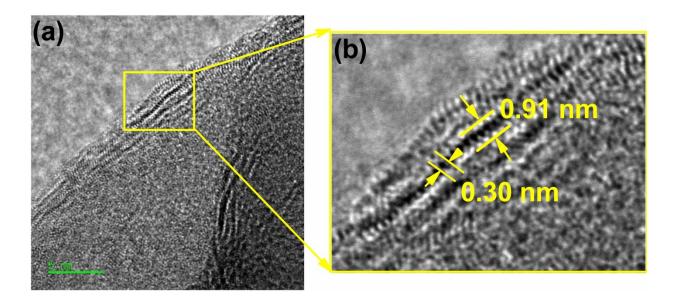


Figure S1. (a-b) HRTEM image and d-space value of $MoS_2/NrGO$.

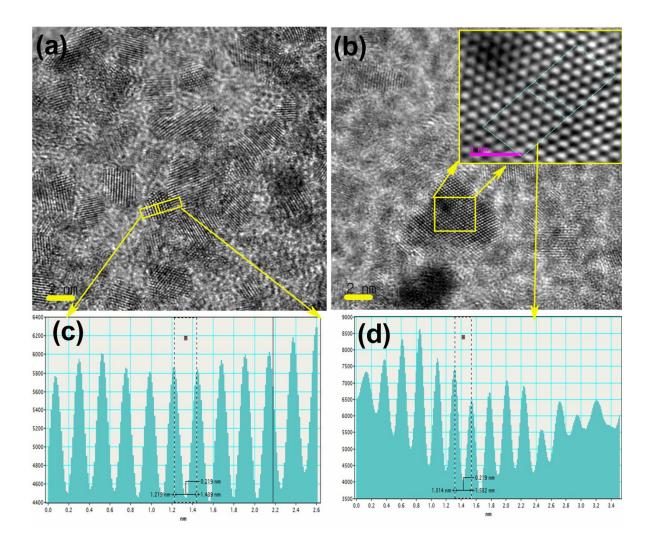


Figure S2. (a-b) HR TEM images and (c-d) d-space line profile for Pt@MoS₂/NrGO.

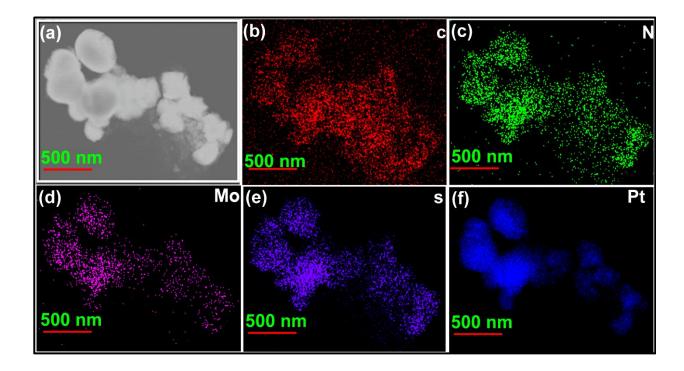


Figure S3. HAADF-STEM images of (a) Pt@MoS₂/NrGO and (b–f) the corresponding elemental mapping images.

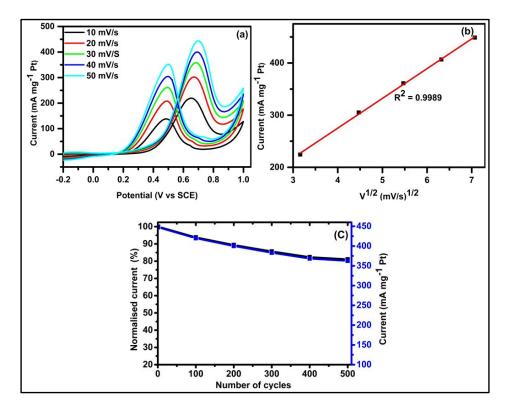


Figure S4. (a) CV curves of $Pt@MoS_2/NrGO$ as a function of different scan rate recorded in 1 M methanol and 0.5 M H_2SO_4 , (b) calibration plot of peak current density Vs square scan rate (c) Normalized current degradation as a function of cycles recorded in 1 M methanol and 0.5 M H_2SO_4 .

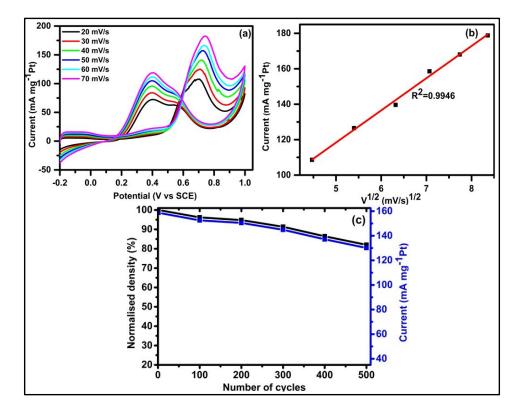


Figure S5. (a) CV curves of $Pt@MoS_2/NrGO$ as a function of different scan rate recorded in 1 M ethylene glycol and 0.5 M H_2SO_4 , (b) calibration plot of peak current density Vs square scan rate (c) Normalized current degradation as a function of cycles recorded in 1 M ethylene glycol and 0.5 M H_2SO_4 .

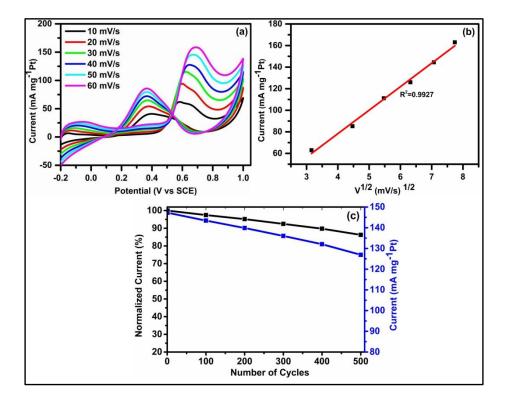


Figure S6. (a) CV curves of $Pt@MoS_2/NrGO$ as a function of different scan rate recorded in 1 M glycerol and 0.5 M H_2SO_4 , (b) calibration plot of peak current density Vs square scan rate (c) Normalized current degradation as a function of cycles recorded in 1 M glycerol and 0.5 M H_2SO_4 .

The Figure S4-S6(a-b) shows the plot between current density and square root of scan rates (V^{1/2}) of electro-oxidation of methanol, Ethylene glycol and glycerol using Pt@MoS₂/NrGO catalyst and its fitting sows good liner relationship with R² values are 0.9989, 0.9946 & 0.9927 corresponding to electro oxidation methanol, ethylene glycol and glycerol respectively. The

results are illustrates the alcohols oxidation reaction on $Pt@MoS_2/NrGO$ electrode is diffusion controlled process.

Electrode Materials	Fuel		Electrolyte		Current	
	Туре	Concentration (M)	Туре	Concentration (M)	density (mA mg ⁻¹ Pt)	Reference
Au@Pt/MoS ₂	Methanol	1	KOH	0.5	6240	1
Pd-MoS ₂	Methanol	1	KOH	0.5	433.5	2
Pt-MoS ₂ /N doped bio carbon	Methanol	0.5	H ₂ SO ₄	0.5	1030.2	3
Pt-Ce _{2-x} /GNS	Methanol	1	KOH	1	1159	4
	Ethylene Glycol	1	КОН	1	3260	
	Glycerol	1	KOH	1	2550	
PdPb alloy nanotubes	Ethylene glycol	1	КОН	1	4060	5
	Glycerol	1	КОН	1	2220	1
PdAu/NG	Ethylene glycol	1	КОН	1	12800	6
	Glycerol	1	KOH	1	8700	1
graphene– MWCNTs/Pt	Methanol	1	H ₂ SO ₄	0.5	168.41	7
	Ethylene glycerol	1	H2SO4	0.5	153.13	
Pd/RGO	Ethylene glycerol	0.5	КОН	0.5	33.7	8
	Glycerol	0.5	KOH	0.5	25.1]
Pt@MoS2/NrGO	Methanol	1	H ₂ SO ₄	0.5	448	Present work
	Ethylene glycol	1	H ₂ SO ₄	0.5	158	
	Glycerol	1	H ₂ SO ₄	0.5	147	

 Table S1. Comparisons of exiting electrocatalysts for alcohol oxidation.

Koutecky–Levich (K–L) plots

Using Equation (1) Koutecky–Levich (K–L) plots are derived from plots of inverse of current density (i_d^{-1}) and inverse of the square root of the rotation rate $(\omega^{-1/2})$

$$I_K = \frac{I_d I}{I_d - I} \tag{1}$$

Where I is experimentally measured current density

 I_K is Kinetic current density

I_d is Diffusion limited current density

Number of electron calculation

 $0.62nFAD^{2/3}Cv^{-1/6}\omega^{1/2}$ (2)

A is Geometric area of electrode (0.19625 cm-2

C -is bulk O_2 solubility of $1.18{\times}10^{\text{-6}}\ \mathrm{mol}\ \mathrm{cm}^{\text{-3}}$

 $D_{\rm O2}$ is diffusion co-efficient of oxygen of $1.9 \times 10^{-5} {\rm cm}^2 {\rm s}^{-1}$

V is Kinetic viscosity of $8.93 \times 10^{-3} \text{ cm}^2 \text{s}^{-1}$ in 0.1 M HClO₄

n is number of electron transfer per oxygen molecular during the ORR

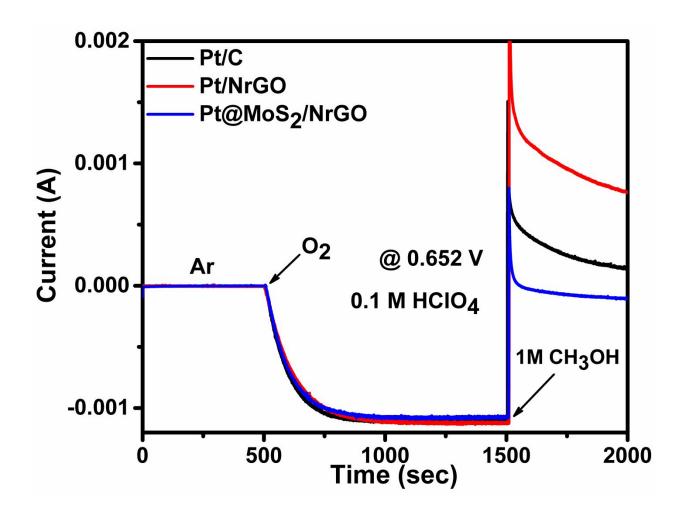


Figure S7. Chronoamperometry response of Pt@MoS₂/NrGO, Pt@NrGO and Pt/C electrode in presence of Ar / O_2 / O_2 + 1 M CH₃OH in 0.1 M HClO₄ at 1600 rpm.

Furthermore, the methanol tolerance study was also performed for Pt@MoS₂/NrGO, Pt@NrGO and Pt/C electrodes using chronoamperometry techniques. The modified electrodes were polarized with fixed potential of 0.652 V vs RHE upto 2000 s with rotation of 1600 rpm in 0.1 M HClO₄. The electrolyte was purged with argon upto 500 seconds and oxygen purged from 500 to 2000 seconds and then methanol introduced at 1500 seconds. In Figure S7, Pt@MoS₂/NrGO, Pt@NrGO and Pt/C electrodes shows almost similar oxygen reduction response from 500 to 1500 s, but once introduce the methanol at 1500 s, the ORR activity was significantly distrubed. It is identified that Pt@MoS₂/NrGO electrode has less disturbance than others and shows reduction current at 2000 s. This study reveals that Pt@MoS₂/NrGO has low methanol tolerance properties, even though it is better than commercial Pt/C and Pt/NrGO electrocatalysts.

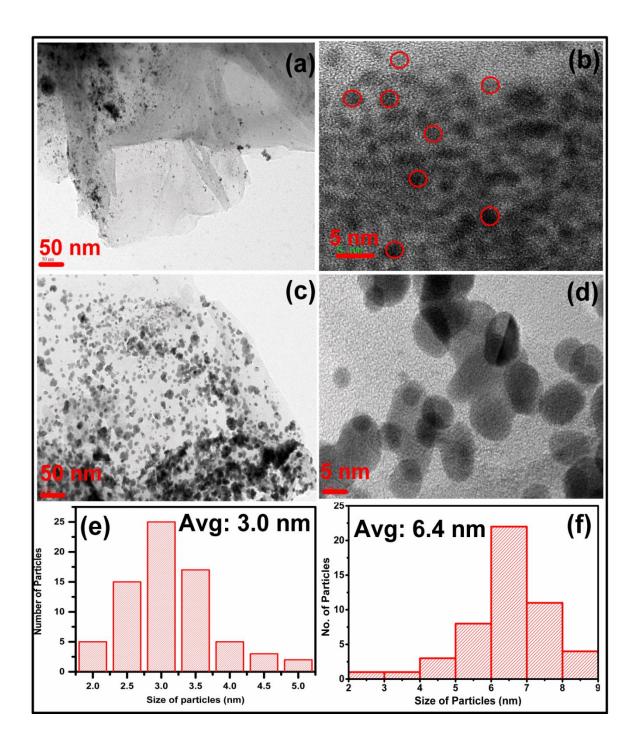


Figure S8. TEM images of Pt@MoS₂/NrGO (a and b) taken before 30000 potential cycles and (c and d) taken after 30000 potential cycles; corresponding particle size histograms of (e) before 30000 potential cycles and (f) after 30000 potential cycles.

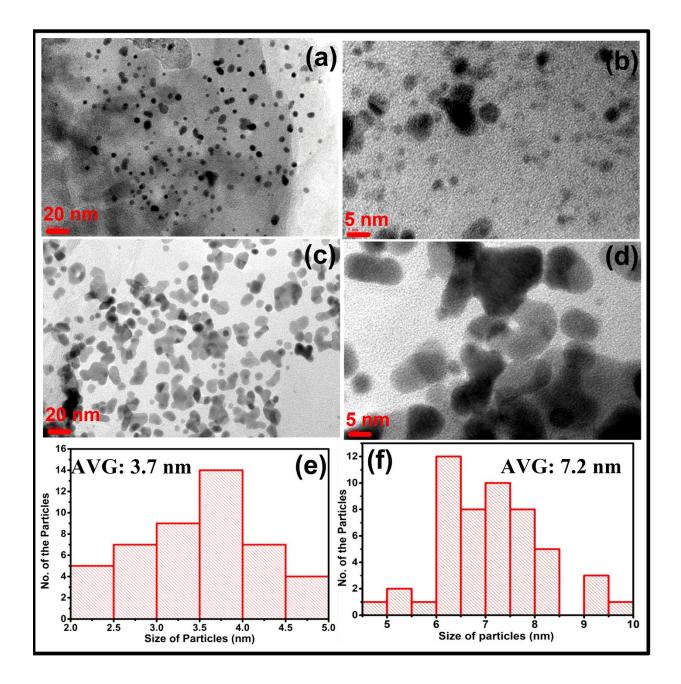


Figure S9. TEM images of Pt@NrGO (a and b) taken before 30000 potential cycles and (c and d) taken after 30000 potential cycles; corresponding particle size histograms of (e) before 30000 potential cycles and (f) after 30000 potential cycles.

References

- S1. Su, S.; Zhang, C.; Yuwen, L.; Liu, X.; Wang, L.; Fan, C.; Wang, L., Uniform Au@Pt core-shell nanodendrites supported on molybdenum disulfide nanosheets for the methanol oxidation reaction. *Nanoscale* 2016, 8 (1), 602-608.
- S2. Yuwen, L.; Xu, F.; Xue, B.; Luo, Z.; Zhang, Q.; Bao, B.; Su, S.; Weng, L.; Huang, W.; Wang, L., General synthesis of noble metal (Au, Ag, Pd, Pt) nanocrystal modified MoS2 nanosheets and the enhanced catalytic activity of Pd–MoS2 for methanol oxidation. *Nanoscale* 2014, 6 (11), 5762-5769.
- S3. Tang, B.; Lin, Y.; Xing, Z.; Duan, Y.; Pan, S.; Dai, Y.; Yu, J.; Zou, J., Porous coral reefs-like MoS2/nitrogen-doped bio-carbon as an excellent Pt support/co-catalyst with promising catalytic activity and CO-tolerance for methanol oxidation reaction. Acta .Electrochim 2017, 246, 517-527.
- S4. He, Q.; Shen, Y.; Xiao, K.; Xi, J.; Qiu, X., Alcohol electro-oxidation on platinum– ceria/graphene nanosheet in alkaline solutions. *Int. J. Hydrog. Energy* 2016, *41* (45), 20709-20719.
- S5. Xu, H.; Song, P.; Fernandez, C.; Wang, J.; Zhu, M.; Shiraishi, Y.; Du, Y., Sophisticated Construction of Binary PdPb Alloy Nanocubes as Robust Electrocatalysts toward Ethylene Glycol and Glycerol Oxidation. ACS Appl. Mater. Interfaces 2018, 10 (15), 12659-12665.
- S6. Zhai, C.; Hu, J.; Zeng, L.; Fu, N.; Du, Y.; Zhu, M., One-pot fabrication of Nitrogendoped graphene supported binary palladium-sliver nanocapsules enable efficient ethylene glycol electrocatalysis. *J. Colloid Interface Sci.* 2019, *535*, 392-399.
- S7. Gorle, D. B.; Kulandainathan, M. A., One-pot synthesis of highly efficient graphene based three-dimensional hybrids as catalyst supporting materials for electro-oxidation of liquid fuels. J. Mater. Chem. A 2017, 5 (29), 15273-15286.
- S8. Li, S.-S.; Hu, Y.-Y.; Feng, J.-J.; Lv, Z.-Y.; Chen, J.-R.; Wang, A.-J., Rapid roomtemperature synthesis of Pd nanodendrites on reduced graphene oxide for catalytic oxidation of ethylene glycol and glycerol. *Int. J. Hydrog. Energy* 2014, 39 (8), 3730-3738.