

Nitrogen-Doped Reduced Graphene Oxide Supported Pd_{4.7}Ru Nanoparticles Electrocatalyst for Oxygen Reduction Reaction

Gil-Ryeong Park ¹, Seung Geun Jo ¹, Anuraj Varyambath ¹, Jeonghyun Kim ^{2,*} and Jung Woo Lee ^{1,*}

¹ Department of Materials Science and Engineering, Pusan National University, Busan 46241, Korea;

rlffud1479@pusan.ac.kr (G.-R.P.); linkroot1128@pusan.ac.kr (S.G.J.); anurajvaryambath@gmail.com (A.V.)

² Department of Electronic Convergence Engineering, Kwangju University, Seoul 01899, Korea

* Correspondence: jkim@kw.ac.kr (J.K.); jungwoolee@pusan.ac.kr (J.W.L.); Tel.: +82-51-510-2898 (J.W.L.)

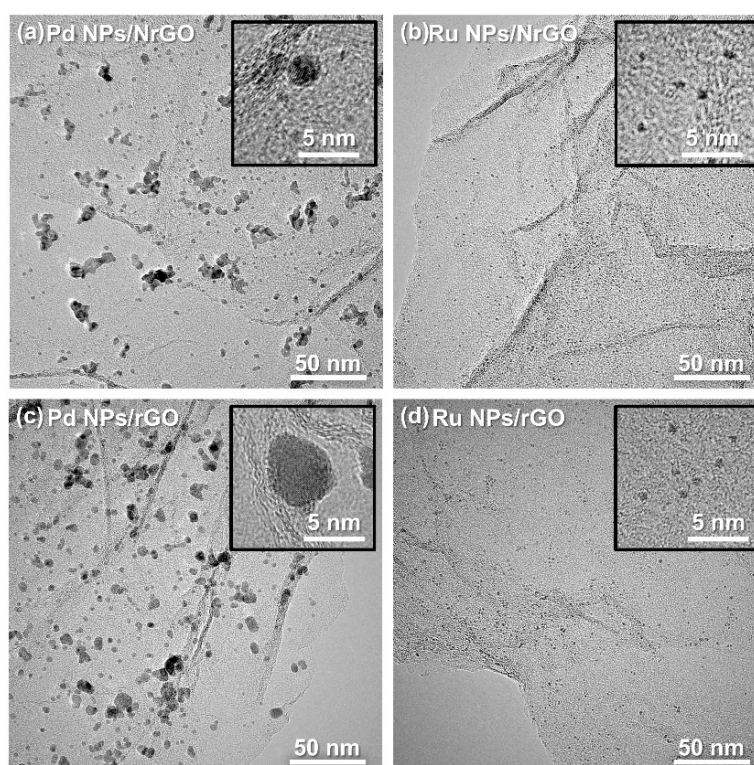


Figure S1. TEM images of the (a) Pd NPs/NrGO, (b) Ru NPs/NrGO, (c) Pd NPs/rGO and (d) Ru NPs/rGO.

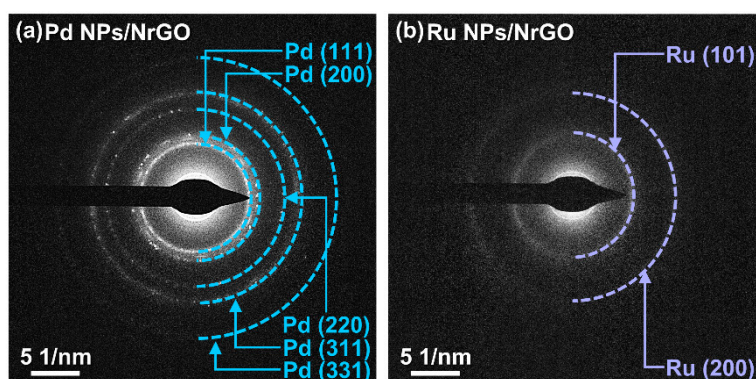


Figure S2. SAED patterns of the (a) Pd NPs/NrGO and (b) Ru NPs/NrGO.

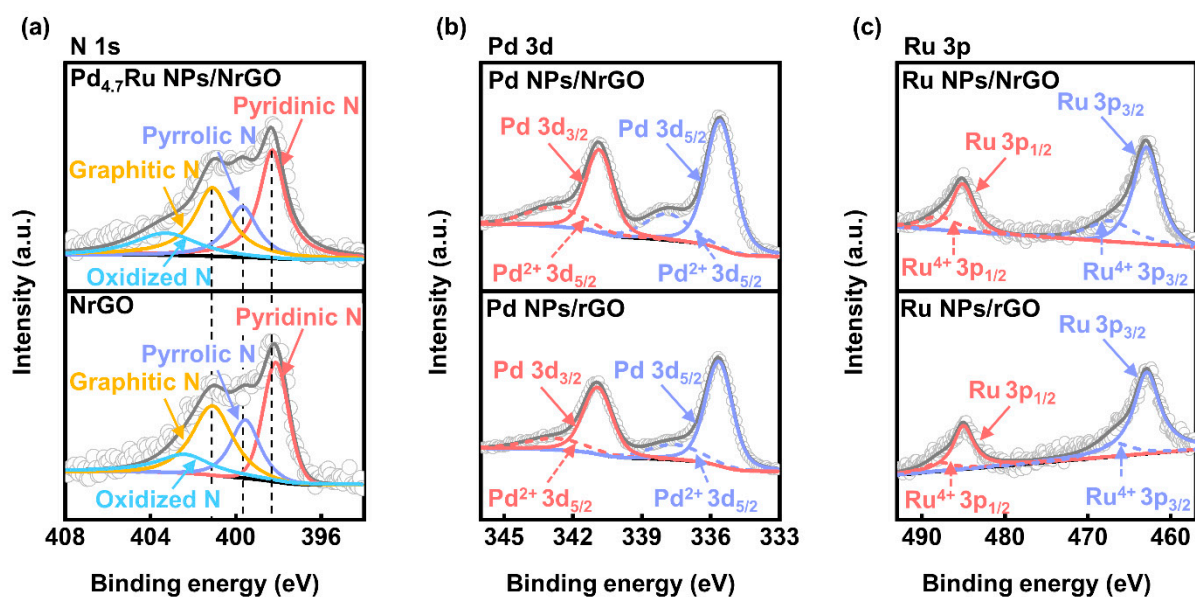


Figure S3. XPS survey spectra of (a) N 1s of the $\text{Pd}_{4.7}\text{Ru NPs/NrGO}$ and NrGO with dotted line for shifts comparison of pyridinic N, pyrrolic N, and graphitic N, (b) Pd 3d of the Pd NPs/NrGO and Pd NPs/rGO , and (c) Ru 3p of the Ru NPs/NrGO , Ru NPs/rGO .

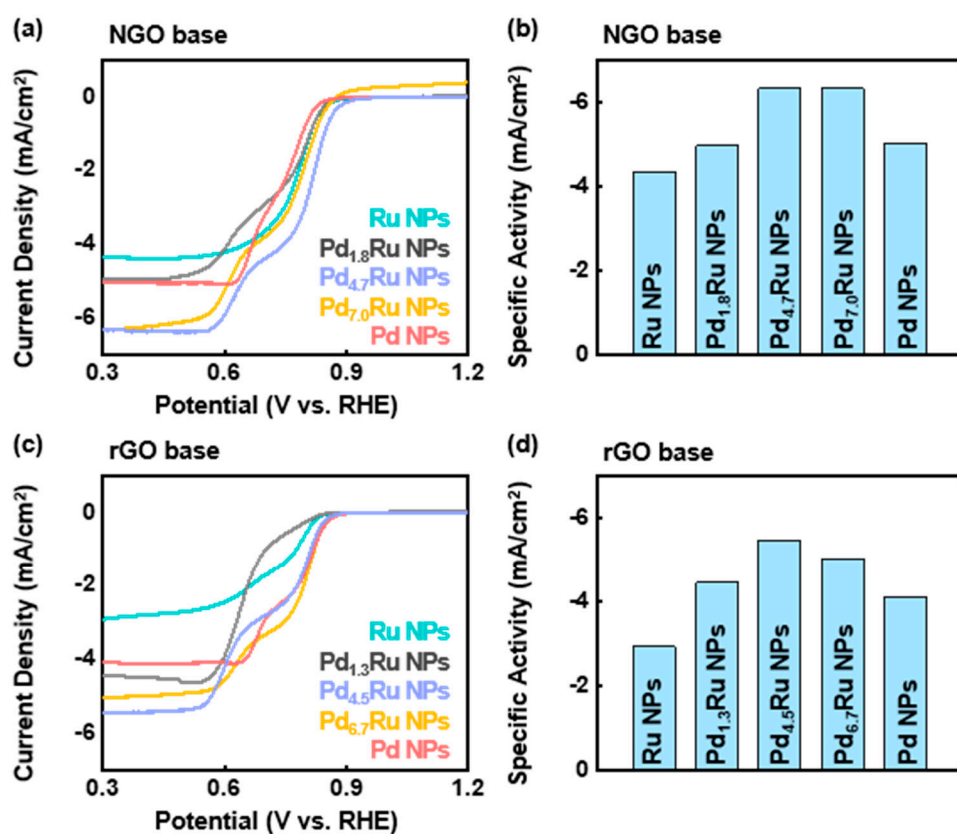


Figure S4. LSV curves of the (a) Pd-Ru NPs/NrGO catalysts, (c) Pd-Ru NPs/rGO catalysts and (b), (d) their corresponding specific activities at $0.3 V_{\text{RHE}}$.

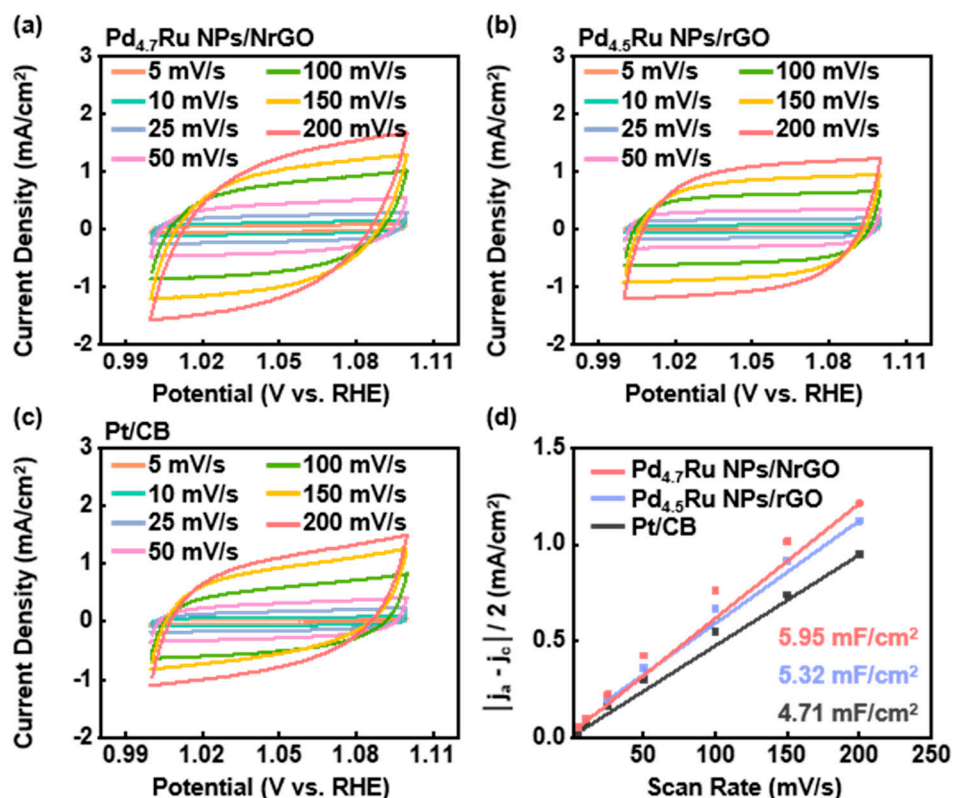


Figure S5. CV curves of the (a) $\text{Pd}_{4.7}\text{Ru}$ NPs/NrGO, (b) $\text{Pd}_{4.5}\text{Ru}$ NPs/rGO and (c) Pt/CB between 1.00 and 1.10 V_{RHE} at different scan rates of 5, 10, 25, 50, 100, 150 and 200 mV/s . (d) Linear fittings of current densities at 1.05 V_{RHE} versus scan rates for the CV tests.

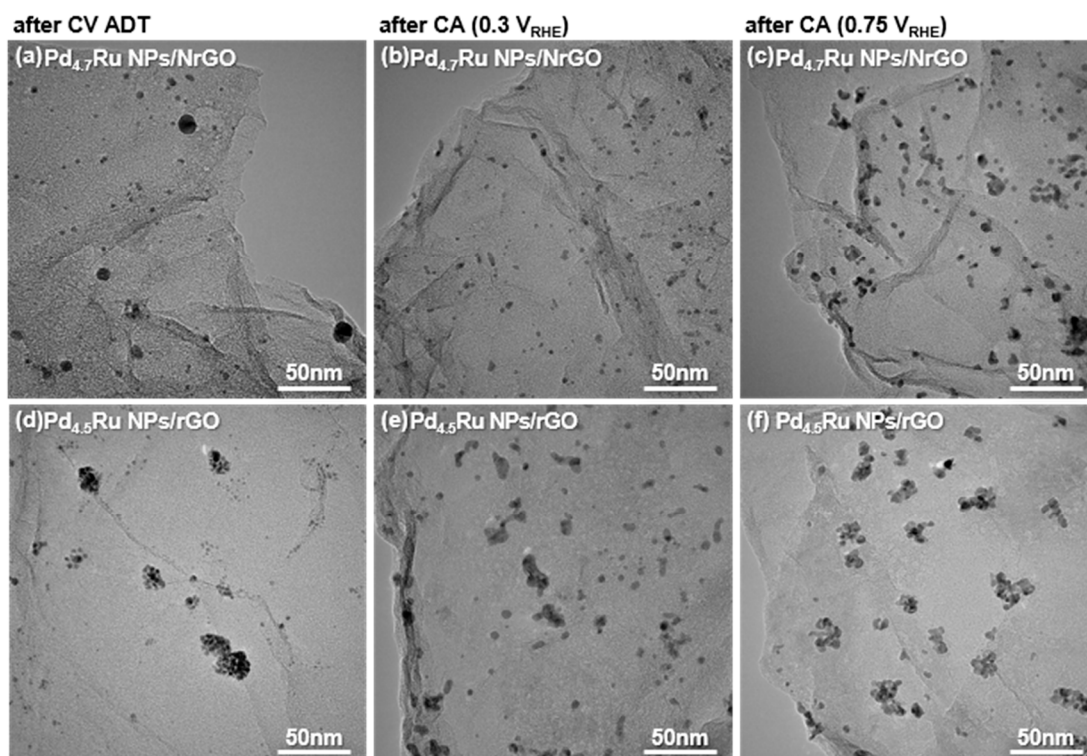


Figure S6. TEM images of $\text{Pd}_{4.7}\text{Ru}$ NPs/NrGO after (a) 1000 cycles CV ADT, (b) CA at 0.3 V_{RHE} , (c) CA at 0.75 V_{RHE} and of $\text{Pd}_{4.5}\text{Ru}$ NPs/rGO after (a) 1000 cycles CV ADT, (b) CA at 0.3 V_{RHE} , (c) CA at 0.75 V_{RHE} .

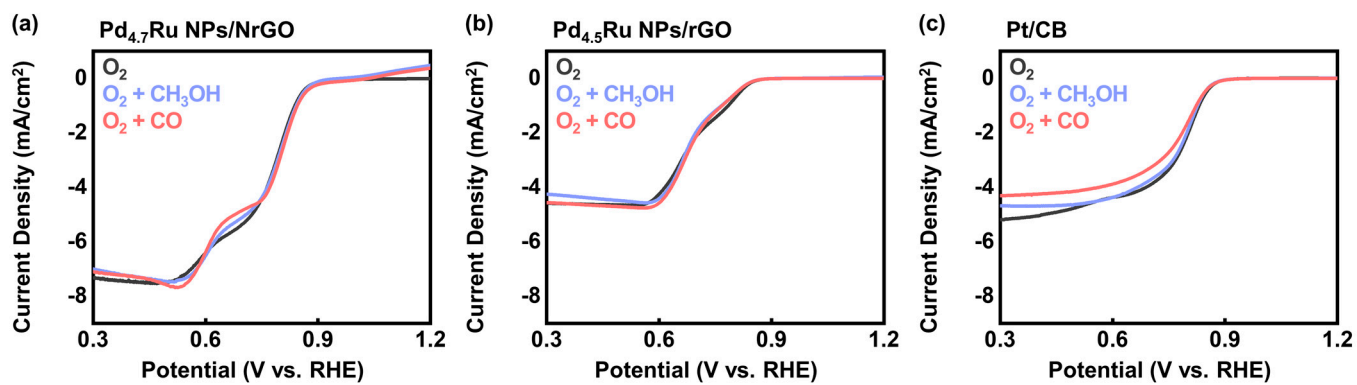


Figure S7. The response of (a) $\text{Pd}_{4.7}\text{Ru}$ NPs/NrGO, (b) $\text{Pd}_{4.5}\text{Ru}$ NPs/rGO, and (c) Pt/CB to CO saturation and 1 M CH_3OH in 0.1 M KOH.

Table S1. Elemental contents and of the Pd–Ru NPs/NrGO and Pd–Ru NPs/rGO determined from ICP-OES.

Sample	Atomic percent		Sample	Atomic percent	
	Pd (%)	Ru (%)		Pd (%)	Ru (%)
Pd_{1.8}Ru NPs/NrGO	64.5	35.5	Pd_{1.3}Ru NPs/rGO	57.2	42.8
Pd_{4.7}Ru NPs/NrGO	82.5	17.5	Pd_{4.5}Ru NPs/rGO	81.8	18.1
Pd_{7.0}Ru NPs/NrGO	87.5	12.5	Pd_{6.7}Ru NPs/rGO	87.0	13.0

Table S2. D-spacing values of the Pd_{4.7}Ru NPs/NrGO, Pd NPs/NrGO, and Ru NPs/NrGO calculated from SAED pattens.

Sample	Pd d-spacing (nm)					Ru d-spacing (nm)	
	(111)	(200)	(220)	(311)	(331)	(101)	(200)
Pd_{4.7}Ru NPs/NrGO	0.220	0.191	0.137	0.116	0.088		
Pd NPs/NrGO	0.223	0.198	0.140	0.119	0.090		
Ru NPs/NrGO						0.205	0.118

Table S3. Comparison of the onset potential of Pd_{4.7}Ru NPs/NrGO with previously reported Pd and Ru catalysts towards ORR.

Sample	E _{onset} (V _{RHE})	Reference
Pd_{4.7}Ru NPs/NrGO	0.913	This work
Pd-Cu NCs/RGOs	0.89	[1]
Pd-RGOs	0.86	[1]
rGO/Pd	0.85	[2]
Pd-tGO	0.89	[3]
Pd₁₀₀/CNS	0.89	[4]
N-rGO-Pd	0.91	[5]
Pd NP/MWCNT	0.85	[6]
Pd₃Co/C	0.85	[7]

References

1. Lv, J.-J.; Li, S.-S.; Wang, A.-J.; Mei, L.-P.; Feng, J.-J.; Chen, J.-R.; Chen, Z. One-pot synthesis of monodisperse palladium–copper nanocrystals supported on reduced graphene oxide nanosheets with improved catalytic activity and methanol tolerance for oxygen reduction reaction. *J. Power Sources* **2014**, *269*, 104–110.
2. Huang, Y.-X.; Xie, J.-F.; Zhang, X.; Xiong, L.; Yu, H.-Q. Reduced graphene oxide supported palladium nanoparticles via photoassisted citrate reduction for enhanced electrocatalytic activities. *ACS applied materials & interfaces* **2014**, *6*, 15795–15801.
3. Yun, M.; Ahmed, M.S.; Jeon, S. Thiolated graphene oxide-supported palladium cobalt alloyed nanoparticles as high performance electrocatalyst for oxygen reduction reaction. *J. Power Sources* **2015**, *293*, 380–387.
4. Yan, W.; Tang, Z.; Wang, L.; Wang, Q.; Yang, H.; Chen, S. PdAu alloyed clusters supported by carbon nanosheets as efficient electrocatalysts for oxygen reduction. *Int. J. Hydrogen Energy* **2017**, *42*, 218–227.
5. Ejaz, A.; Jeon, S. The individual role of pyrrolic, pyridinic and graphitic nitrogen in the growth kinetics of Pd NPs on N-rGO followed by a comprehensive study on ORR. *Int. J. Hydrogen Energy* **2018**, *43*, 5690–5702.
6. Jukk, K.; Alexeyeva, N.; Sarapuu, A.; Ritslaid, P.; Kozlova, J.; Sammelselg, V.; Tammeveski, K. Electroreduction of oxygen on sputter-deposited Pd nanolayers on multi-walled carbon nanotubes. *Int. J. Hydrogen Energy* **2013**, *38*, 3614–3620.
7. Rahul, R.; Singh, R.; Neergat, M. Effect of oxidative heat-treatment on electrochemical properties and oxygen reduction reaction (ORR) activity of Pd–Co alloy catalysts. *J. Electroanal. Chem.* **2014**, *712*, 223–229.