Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Diamond@Carbon-onion Hybrid Nanostructure as a Highly Potential Electrocatalyst in Oxygen Reduction Reaction

Jaekang Koh,[a] Sung Hyeon Park,[b] Min Wook Chung,[a] Seung Yong Lee,[a] and Seong Ihl Woo[a,b*]

[a] *Graduate School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea.*

[b] *Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea.*

* *Corresponding author, Tel: +82-42-350-3918, Fax: +82-42-350-3910,*

E-mail address: siwoo@kaist.ac.kr

Supporting Information

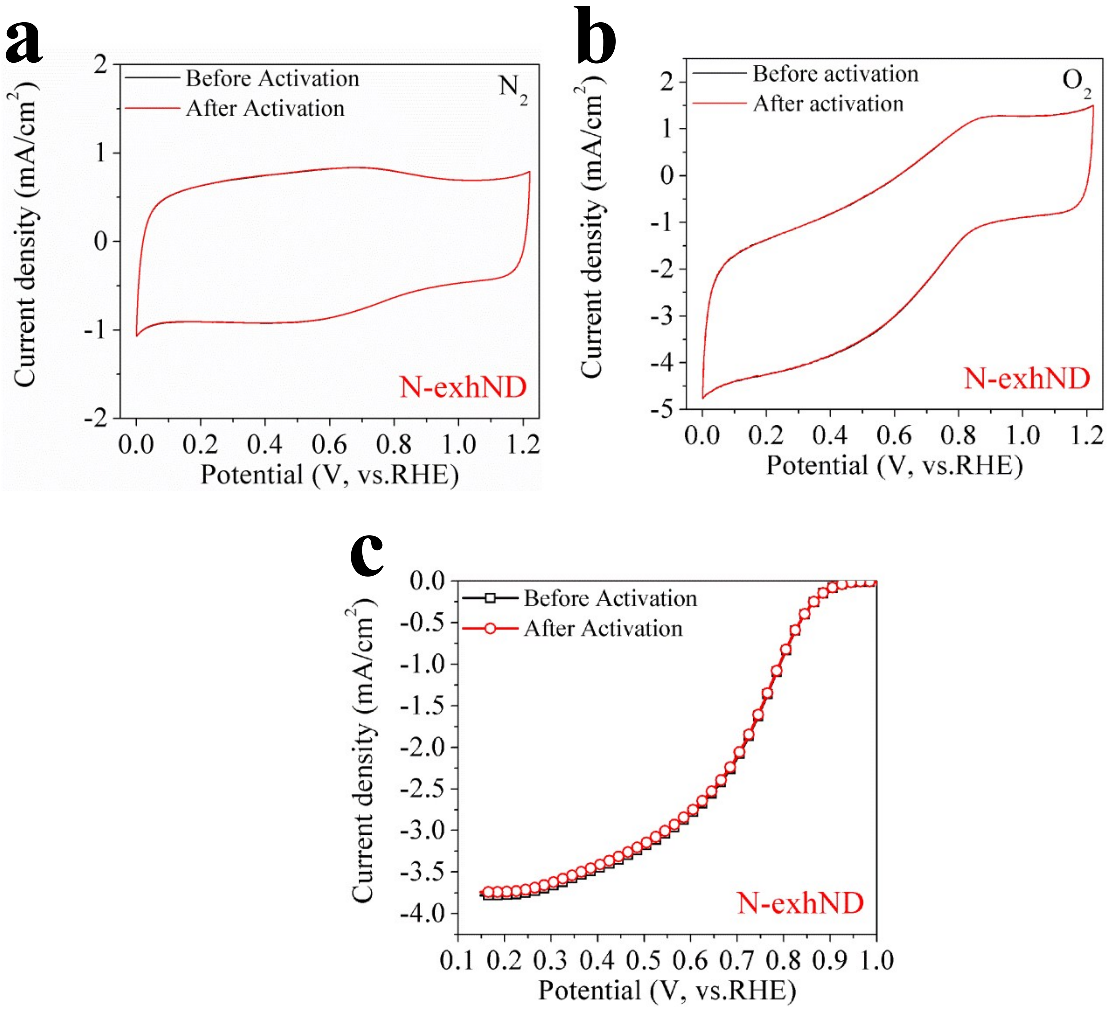
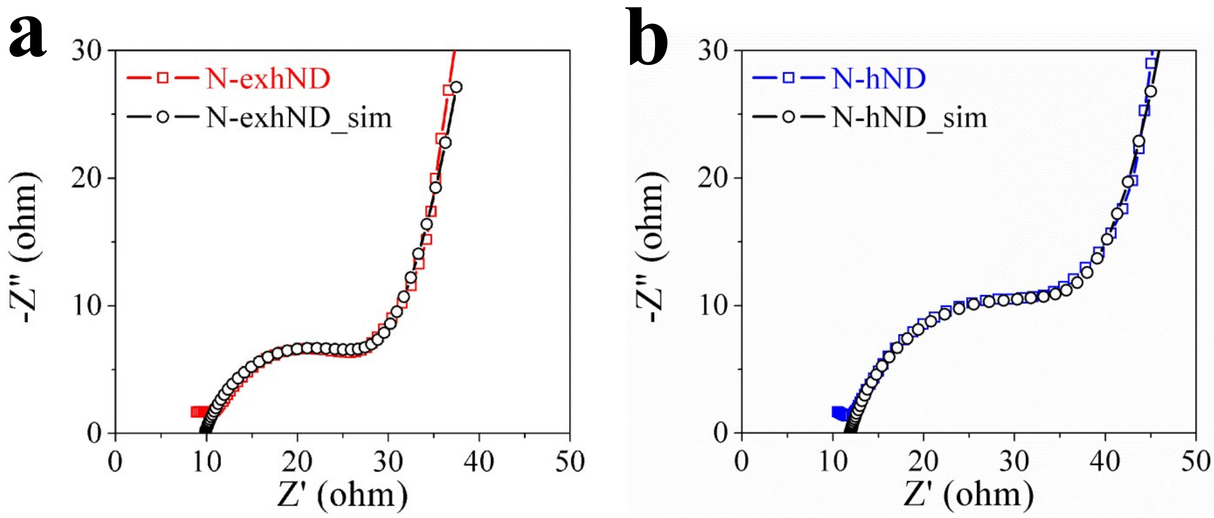


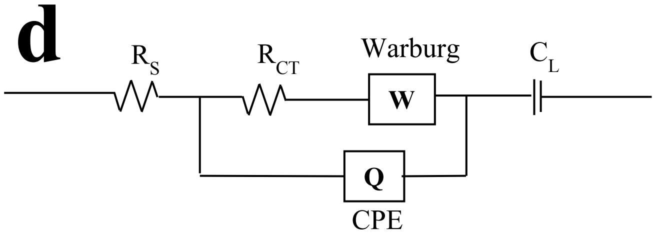
Fig. S1 Electrochemical results for before and after activation process. a) CV in N_2-purged b) CV in O_2-purged and c) ORR performance of N-exhND catalyst in 0.1 M $HClO_4$.



c

Parameter	N-exhND	N-hND
R_S (ohm)	9.80	11.9
R_{CT} (ohm)	18.8	25.8
Warburg (S-sec$^{1/2}$)	0.0868	0.0860
CPE (S-sec^n)	0.002346	0.003015
C_L (farad)	0.098	0.080

d



R_S	Solution resistance
R_{CT}	Charge transfer resistance
Warburg	Warburg element
CPE	Constant phase element
C_L	Low frequency mass capacitance

Fig. S2 EIS measurement and their simulation for a) N-exhND, and b)N-hND. c) Obtained parameter values by the simulations, and d) electric circuit model.

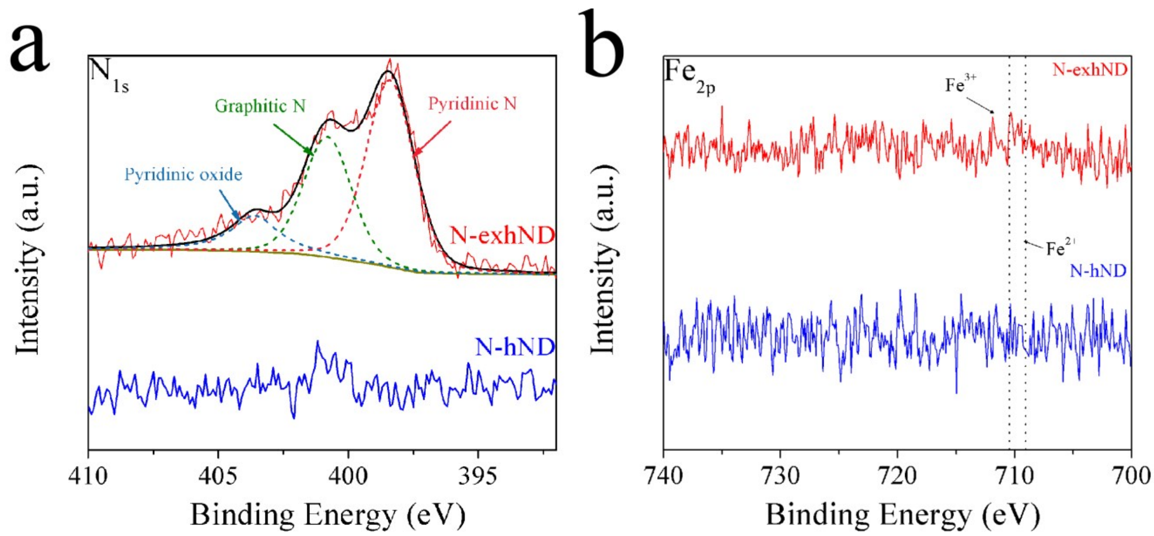


Fig. S3 XPS results of a) N_{1s} b) Fe_{2p} of N-exhND and N-hND catalysts.

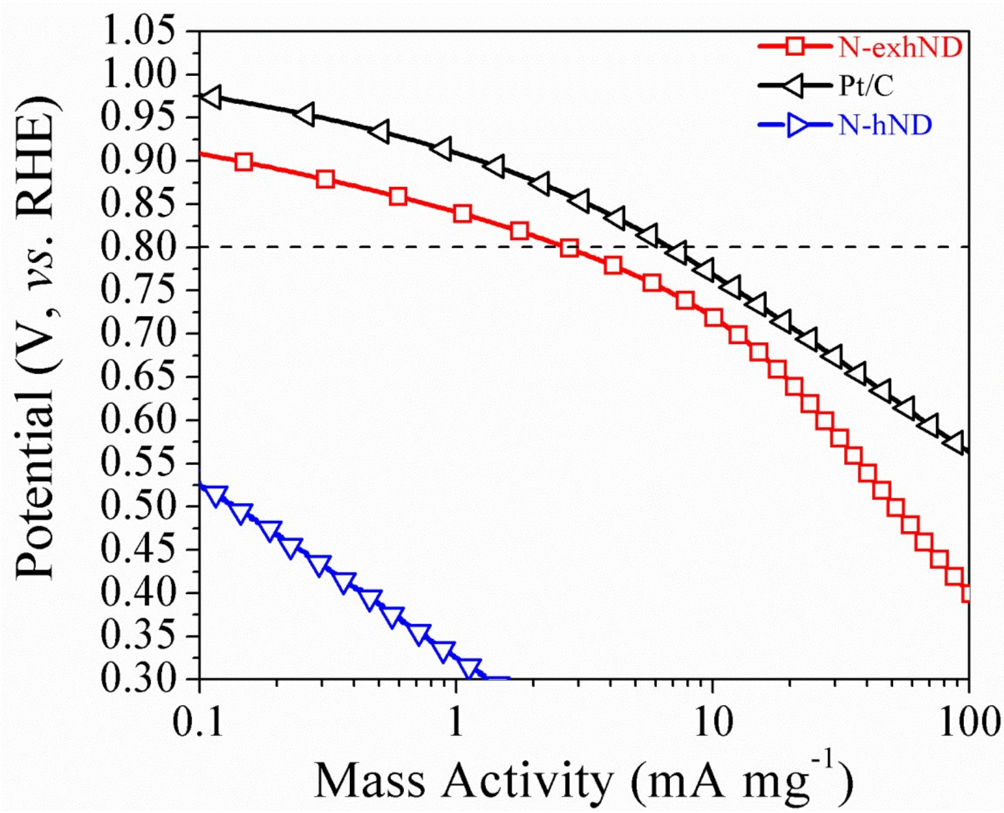


Fig. S4 Tafel plots calculated from the ORR current densities of the prepared catalysts.

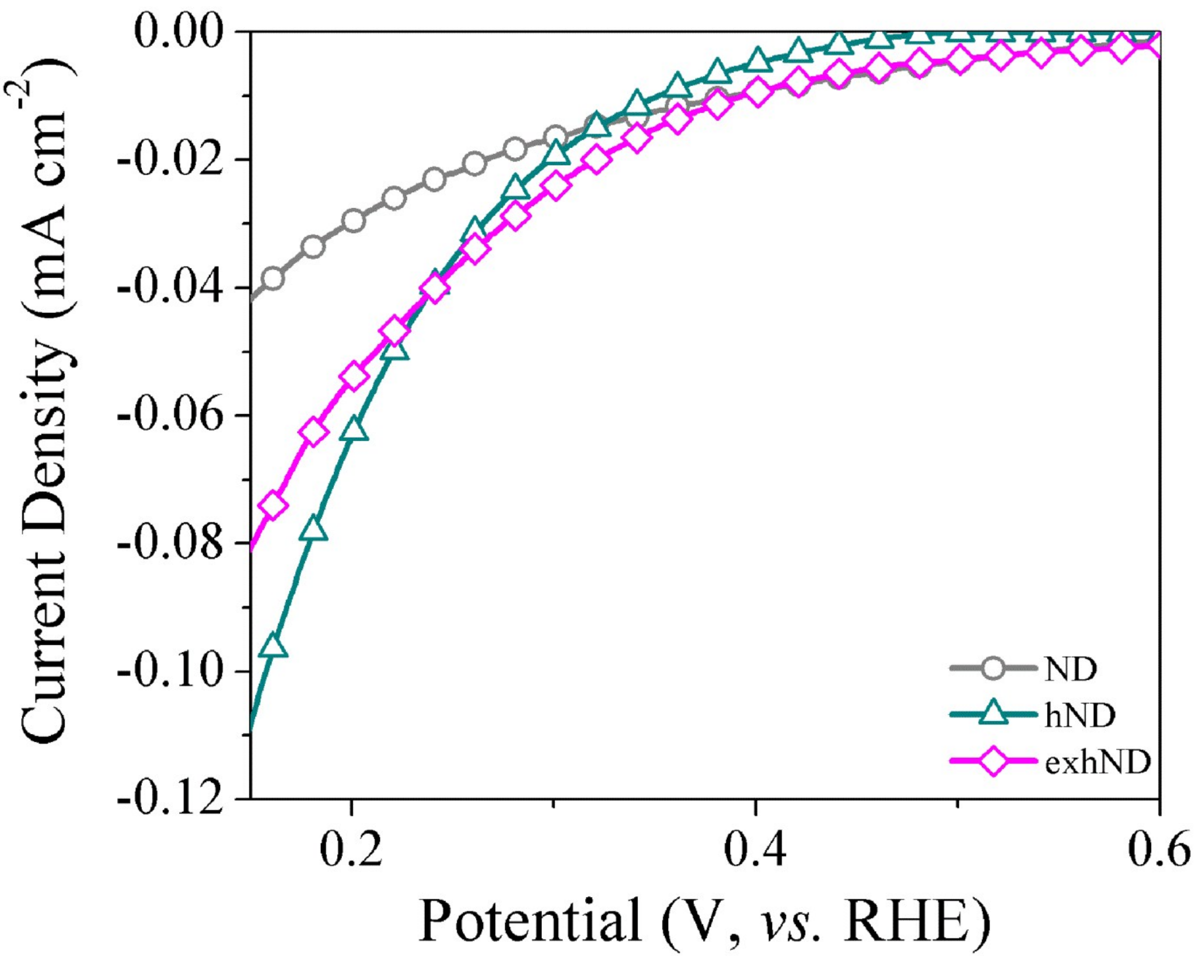


Fig. S5 Electrochemical results of the prepared catalysts: LSV analysis in O_2-purged 0.1 M $HClO_4$ at a scan rate of 5 mV s^{-1}.

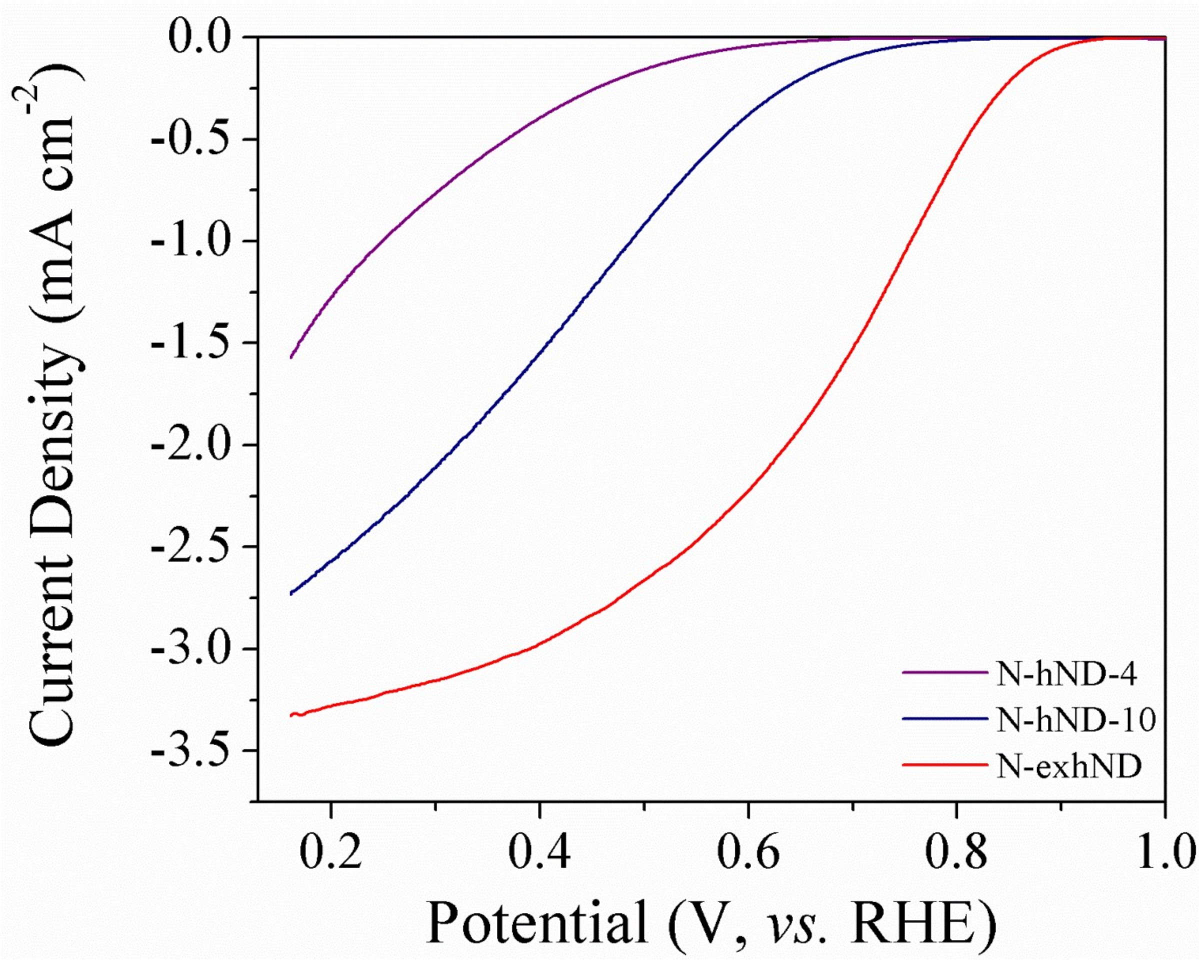


Fig. S6 Electrochemical comparison of the N-hND-4 and N-hND-10 with N-exhND catalyst: LSV analysis in O_2-purged 0.1 M $HClO_4$ at a scan rate of 5 mV s^{-1}.

Catalyst name	C^1	O^1	N^1	H^1	S^1	Fe^2	C^3	O^3	N^3
ND	84.63	2.38	1.81	11.17	N/A	0.01	92.94	5.46	1.6
hND	99.47	0.36	0.16	N/A	N/A	0.01	100	N/A	N/A
exhND	82.86	9.88	0.22	6.90	0.13	0.01	84.17	15.09	N/A
N-exhND	91.74	1.27	1.92	4.35	0.05	0.67	87.85	4.02	7.32
N-hND	99.18	0.24	0.46	N/A	N/A	0.12	100	N/A	N/A

All values are in atomic %.

[1]Results from an EA

[2]Results from an ICP analysis

[3]Results from an XPS analysis

Table S1. Compositions of the prepared catalysts from EA, ICP and XPS analysis.

Catalyst name	C	O	N	H	S
N-exhND	91.74	1.27	1.92	4.35	0.05
N-hND	99.18	0.24	0.46	N/A	N/A
N-hND-4	98.16	0.46	0.71	0.64	N/A
N-hND-10	96.59	0.78	1.64	0.45	N/A

All values are in atomic %.

Table S2. The elementary analysis of N-hND-4 and N-hND-10.

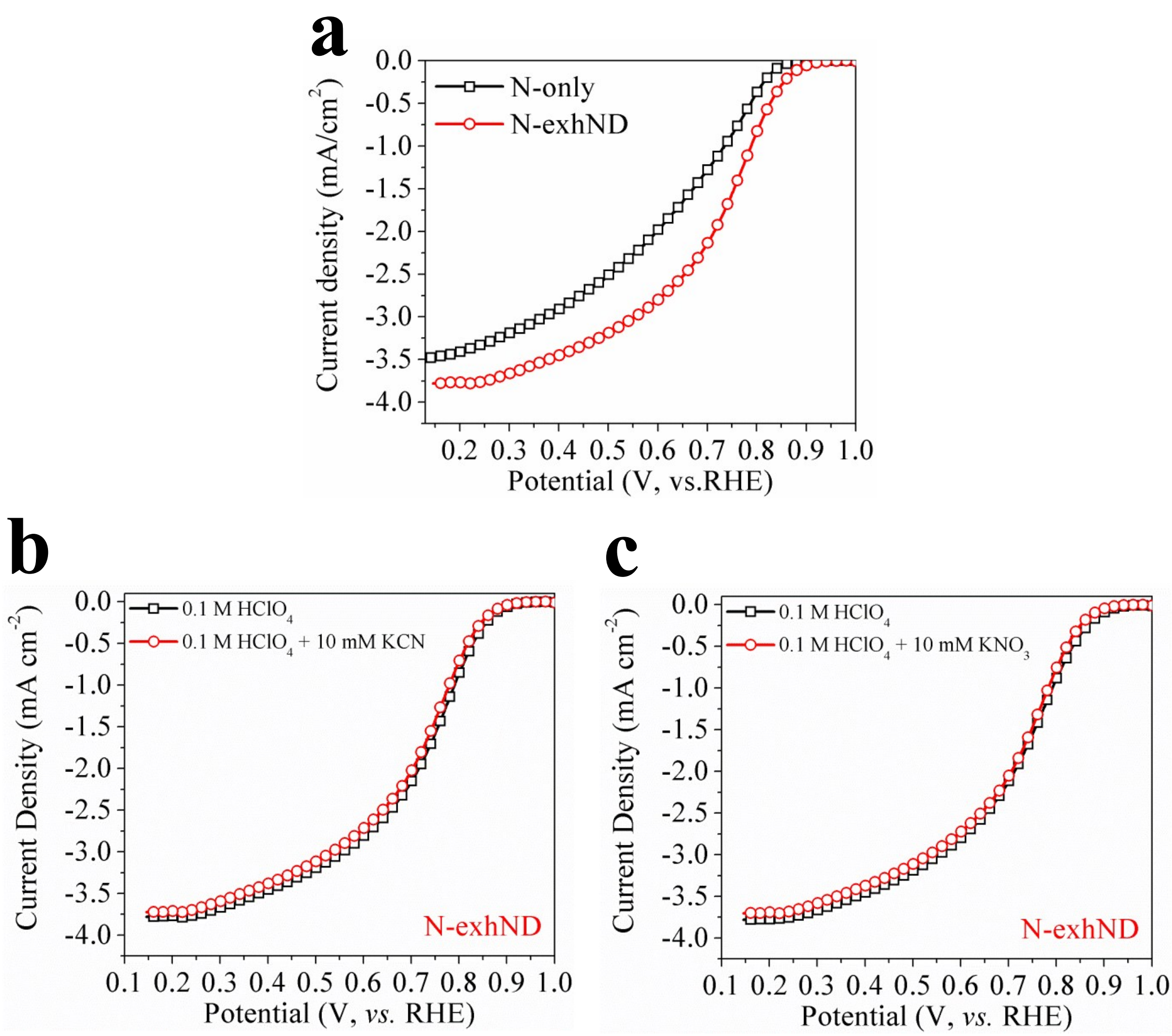


Fig. S7 ORR performance of a) N-only catalyst in 0.1 M $HClO_4$, b) N-exhND in 10mM KCN containing 0.1 M $HClO_4$, c) N-exhND in 10mM KNO_3 containing 0.1 M $HClO_4$.

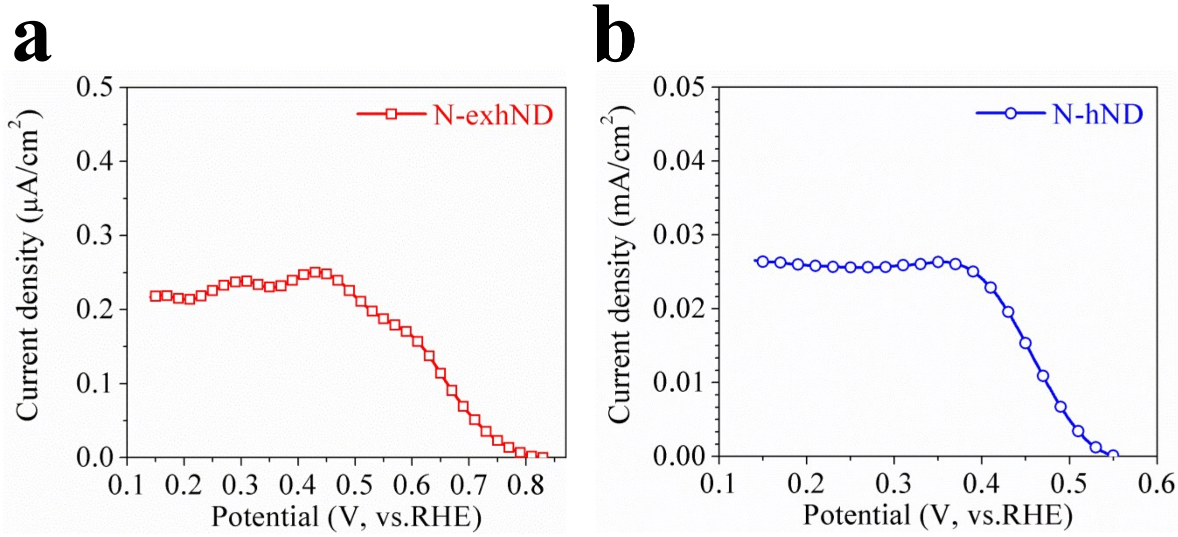


Fig. S8 H_2O_2 current densities from RRDE of a) N-exhND, and b) N-hND catalysts.

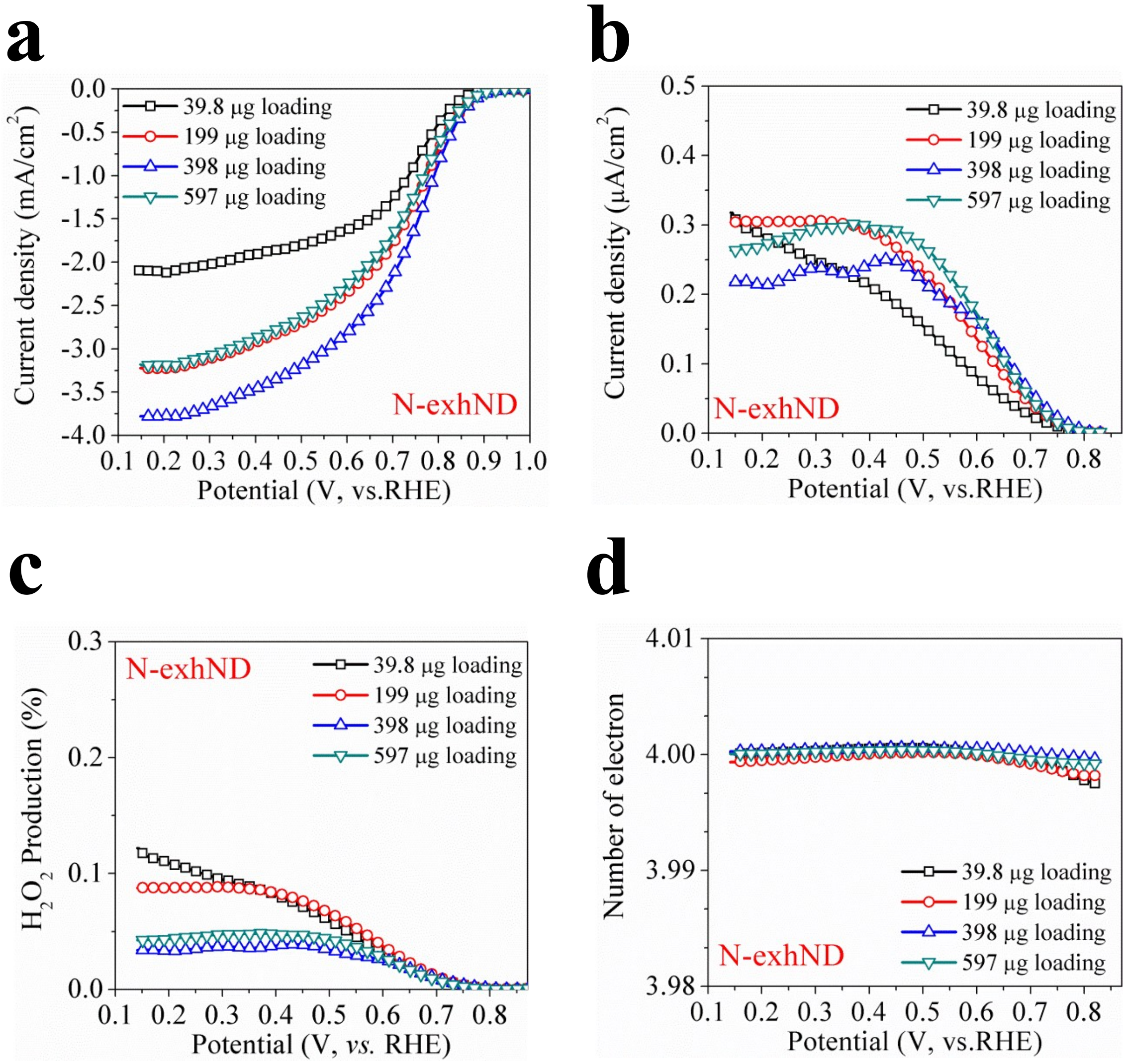


Fig. S9 Effect of various loadings on ORR and H_2O_2 production. a) LSV curves, b) H_2O_2 RRDE current densities, c) H_2O_2 production yield and d) number of electron transfer.

Source	Electrolyte	Range V	Scan Rate mV s^{-1}	Cycles	Loading mg cm^{-2}	$E_{1/2}$ mV
N-exhND (This Study)	**0.1 M $HClO_4$**	**0.6-1.4**	**500**	**5,000**	**0.398**	**31**
Angew. Chem. Int. Ed. 2014, 53, 3675	0.1 M $HClO_4$	0.6 – 1.0	10	4,500	0.6	22
Angew. Chem. Int. Ed. 2014, 53, 10673	0.5 M H_2SO_4	0.6 – 1.0	10	5,000	0.9	79
J. Am. Chem. Soc. 2013, 135, 16002	0.1 M $HClO_4$	0.6 – 1.0	50	10,000	0.6	9
J. Am. Chem. Soc. 2015, 137, 1436	0.5 M H_2SO_4	0.364 - 0.964	50	3,000	1.2	N/A
J. Mater. Chem. A, 2014, 2, 17047	0.5 M H_2SO_4	0 – 1.04	50	1,000	0.193	N/A (69.3% retention)
J. Mater. Chem. A, 2014, 2, 1242	0.1 M $HClO_4$	0 – 1.0	100	10,000	0.8	24
J. Mater. Chem. A, 2015, 3, 3343	0.1 M $HClO_4$	0.6 – 1.0	50	5,000	0.485	39
J. Mater. Chem. A, 2015, 3, 1752	0.1 M $HClO_4$	0.6-1.0	N/A	2,000	0.6	17

Table S3. ADT conditions from previously reported studies.

Source	Type of material	Loading mg cm^{-2}	Onset V	Mass activity mA mg^{-1} at 0.8 V	Electron transfer
N-exhND (This Study)	**Carbon Nano-onion**	**0.398**	**0.91**	**2.70**	**4**
Angew. Chem. Int. Ed. 2014, 53, 3675	Iron Carbide particles	0.6	0.90	0.50[1]	4
Angew. Chem. Int. Ed. 2014, 53, 10673	Fe-N Complex	0.9	0.83	-	3.8
J. Am. Chem. Soc. 2013, 135, 16002	Ordered mesoporous Co-N carbon	0.6	0.91	0.43[1]	3.8
J. Am. Chem. Soc. 2015, 137, 1436	Fe_3C/CNT	1.2	0.89	0.36[1]	4
J. Mater. Chem. A, 2014, 2, 17047	FeN_4-doped porous carbon	0.193	0.90	1.94[1]	3.9
J. Mater. Chem. A, 2014, 2, 1242	FeN_xC/C	0.8	0.92	0.68[1]	4
J. Mater. Chem. A, 2015, 3, 3343	N-doped 3D graphene	0.485	0.83	-	4
J. Mater. Chem. A, 2015, 3, 1752	Fe3C	0.6	0.81[2]	-	Mixed 2 and 4

[1] This value is not mentioned in the article but derived from LSV results at 0.8 V (vs. RHE)

Table S4. Comparison of ORR activity in acidic media from previously reported studies.