

Supplementary Materials

Platinum Deposited Nitrogen-Doped Vertically Aligned Carbon Nanofibers as Methanol Tolerant Catalyst for Oxygen Reduction Reaction with Improved Durability

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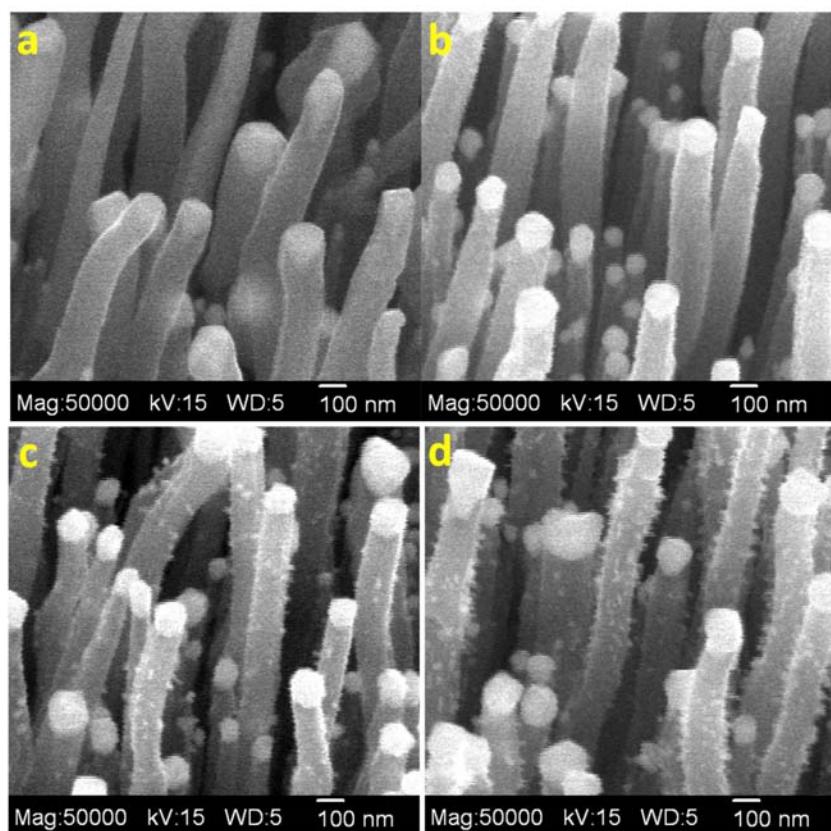


Figure S1. FESEM images of VACNFs (a) as-grown and plasma annealed for 5 min at (b) 550 °C, (c) 600 °C, and (d) 650 °C.

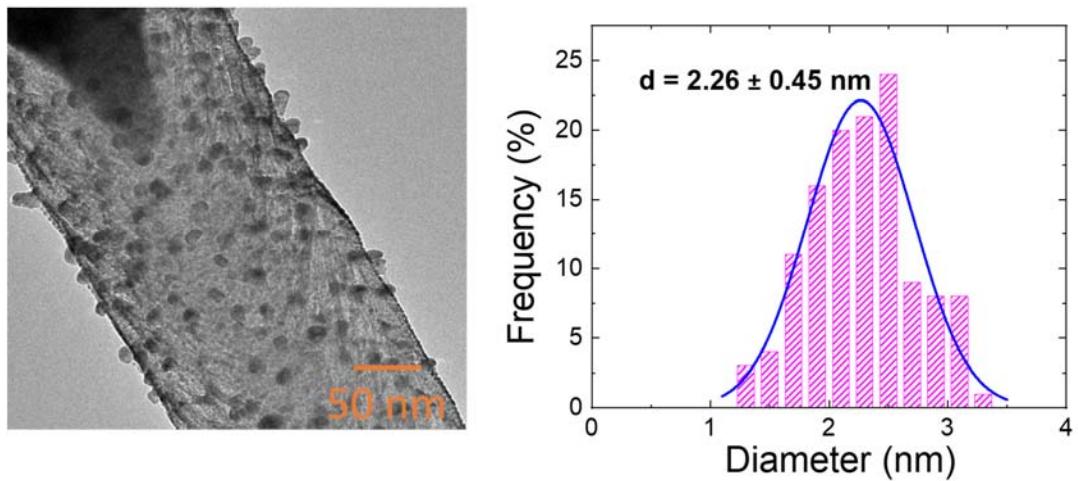


Figure S2. TEM image of Pt/N-VACNF PA 5 min ($43.0 \mu\text{g}/\text{cm}^2$) with the corresponding particle size distribution.

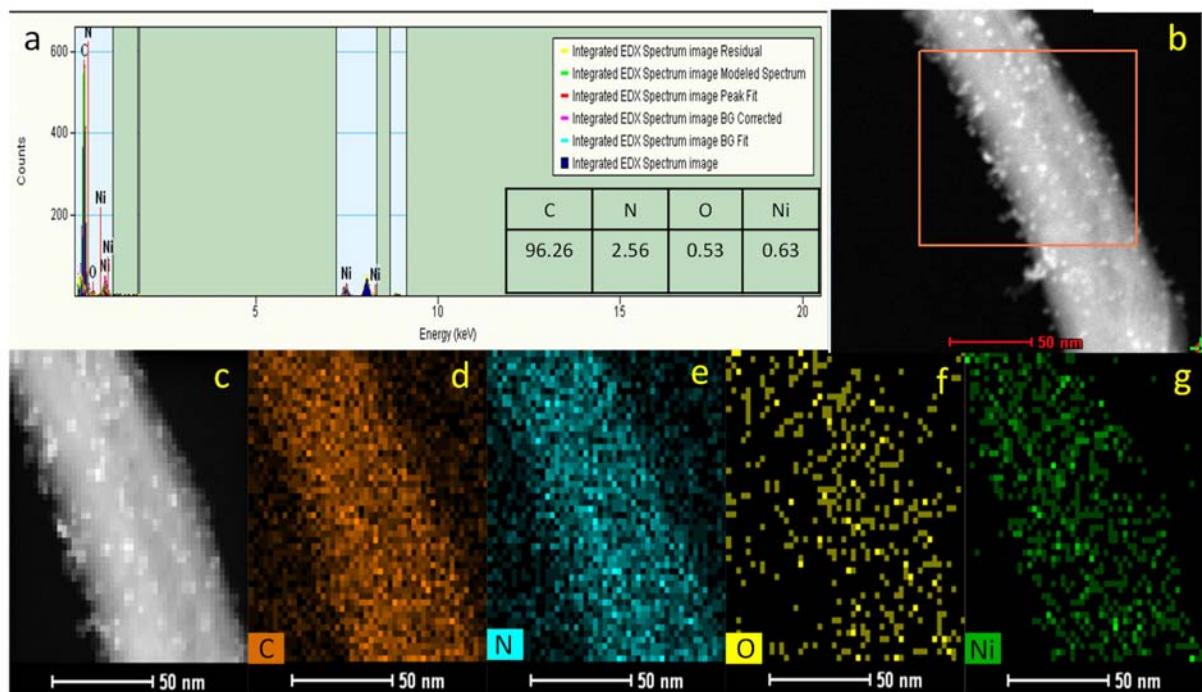


Figure S3. (a) TEM-EDS spectrum and (b) HAADF-STEM image showing the selected area for EDS analysis of N-VACNF PA 5 min; (c) HAADF-STEM image and (d-g) STEM-EDS mapping for all the elements of N-VACNF (PA 5 min). The inset table in (a) shows the atomic % of different elements.

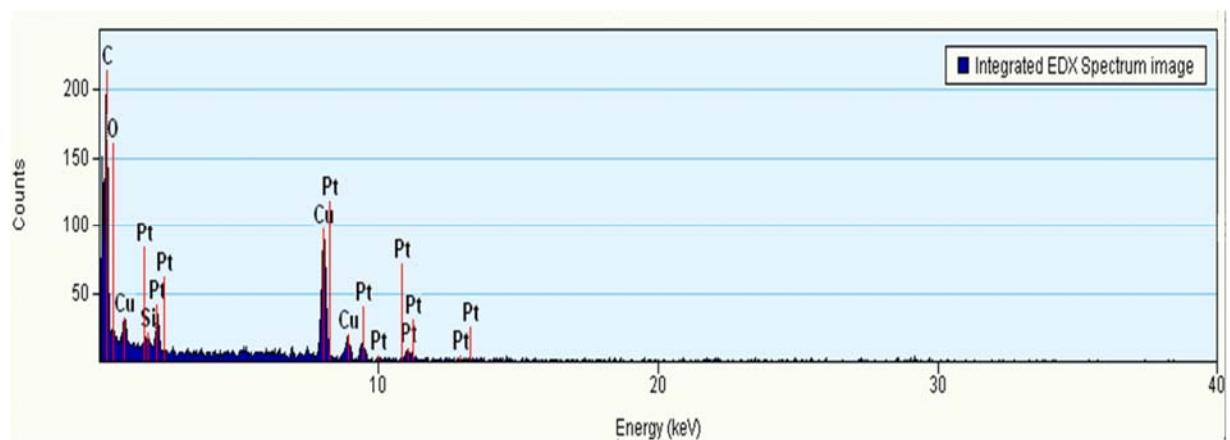


Figure S4. TEM-EDS spectrum of Pt/N-VACNF PA 5 min. The orange rectangle in inset HAADF-STEM image shows the selected area for EDS analysis. The inset table shows the weight % of different elements.

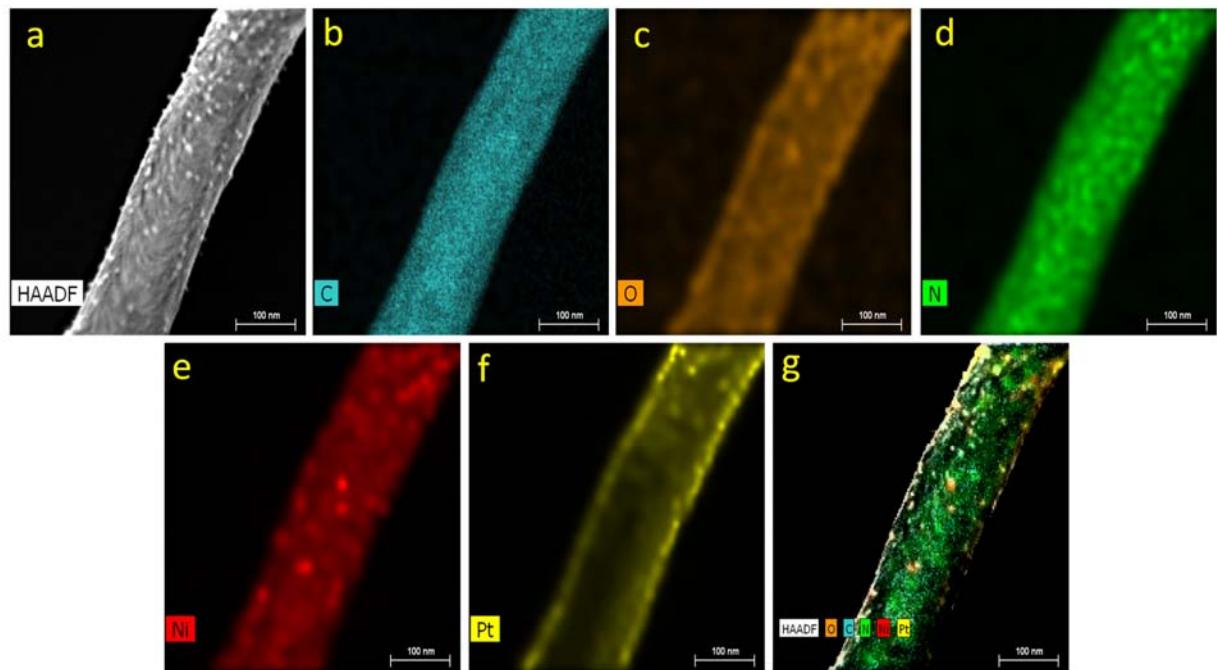


Figure S5. (a) HAADF-STEM image and (b-g) STEM-EDS elemental mapping of Pt/N-VACNF PA 5 min.

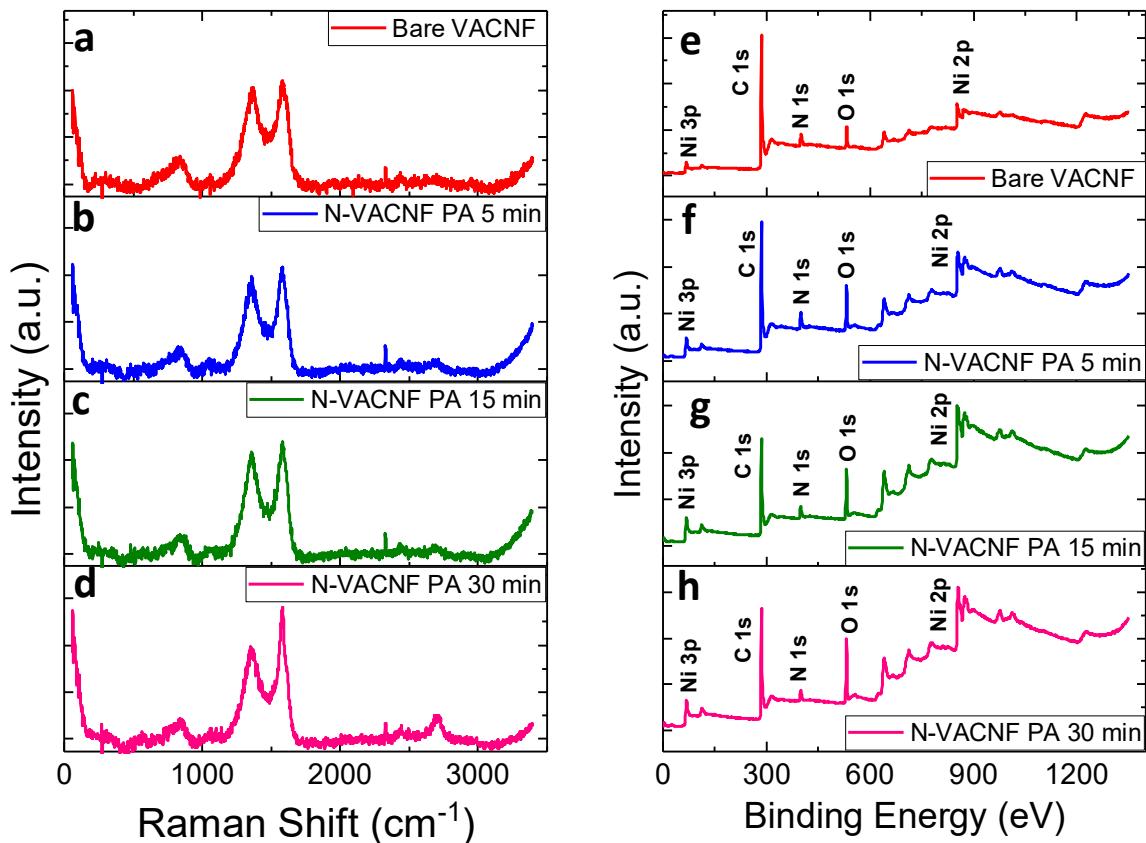


Figure S6. (a-d) Raman spectra and (e-h) XPS survey spectra of bare VACNF, N-VACNF PA 5 min, N-VACNF PA 15 min, and N-VACNF PA 30 min.

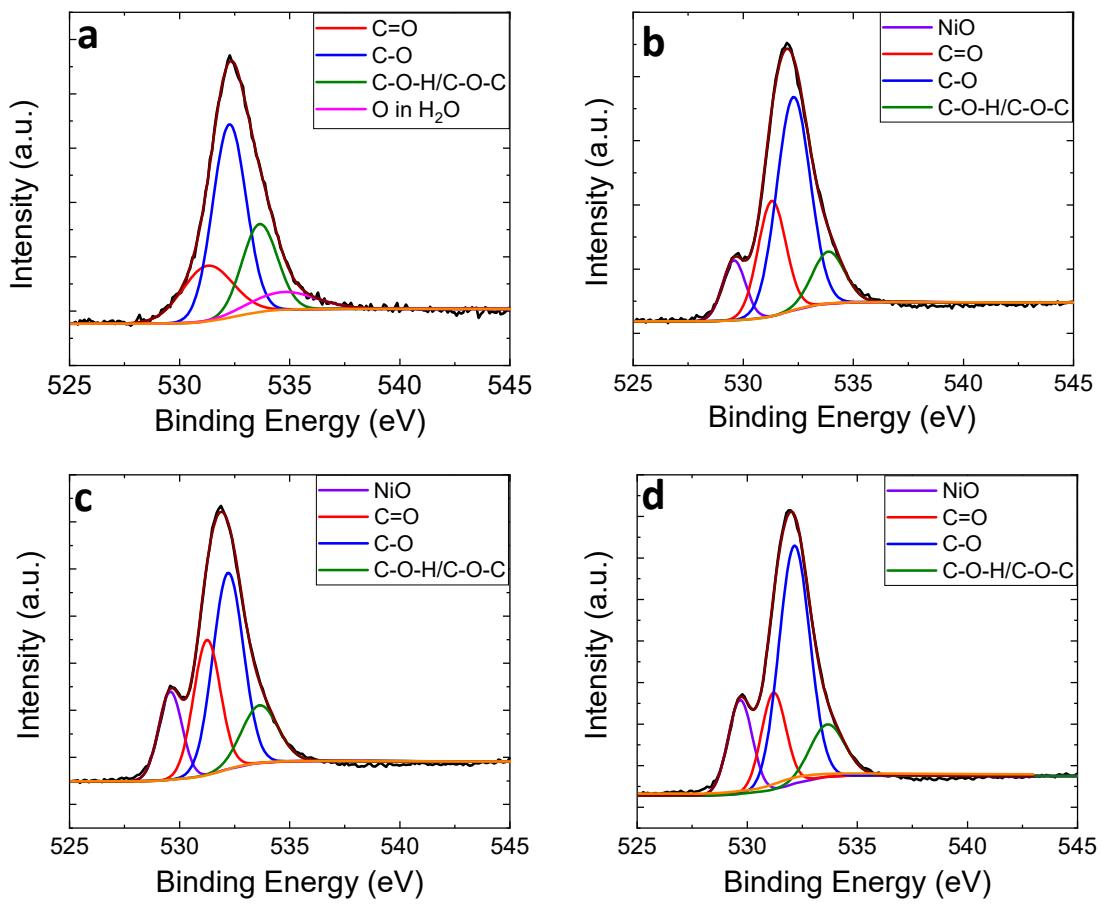
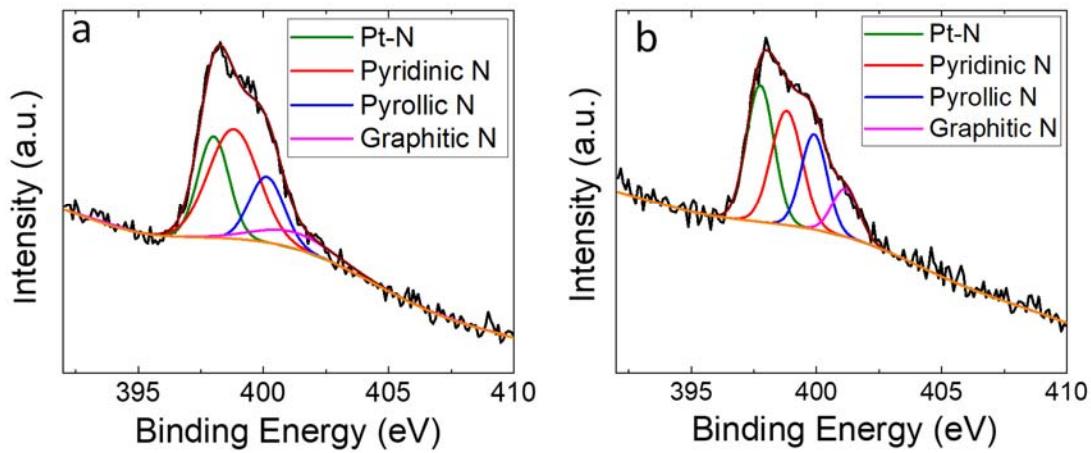


Figure S7. O 1s XPS spectra of (a) bare VACNF, (b) N-VACNF PA 5 min, (c) N-VACNF PA 15 min, and (d) N-VACNF PA 30 min.



Species	Pt/VACNF		Pt/N-VACNF	
	BE (eV)	Relative Area %	BE (eV)	Relative Area %
Pt-N	398.00	26.0	397.75	33.9
Pyridinic N	398.81	45.3	398.80	31.8
Pyrrolic N	400.13	17.6	399.90	22.5
Graphitic N	401.20	11.1	401.16	11.8

Figure S8. N 1s XPS spectra of (a) Pt/N-VACNF PA 5 min and (b) Pt/VACNF.

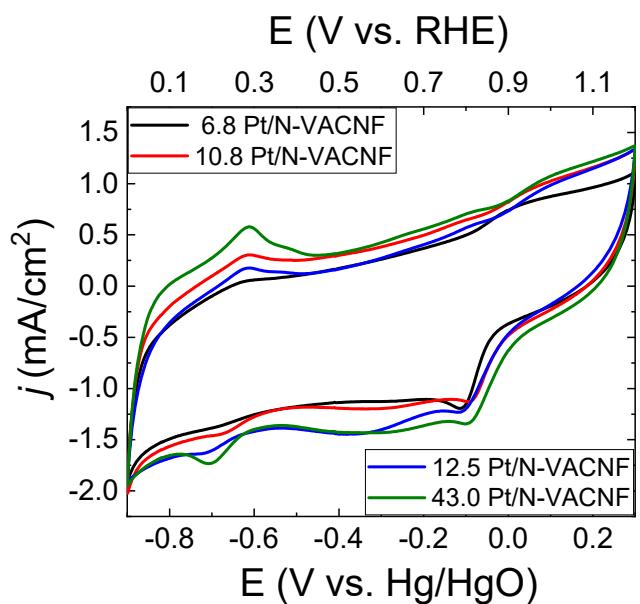


Figure S9. CV curves recorded at a scan rate of 50 mV/s in O_2 saturated 0.10 M KOH solution for N-VACNF PA 5 min catalysts with different Pt loadings (6.5, 10.8, 21.5, and 43.0 $\mu\text{g}/\text{cm}^2$).

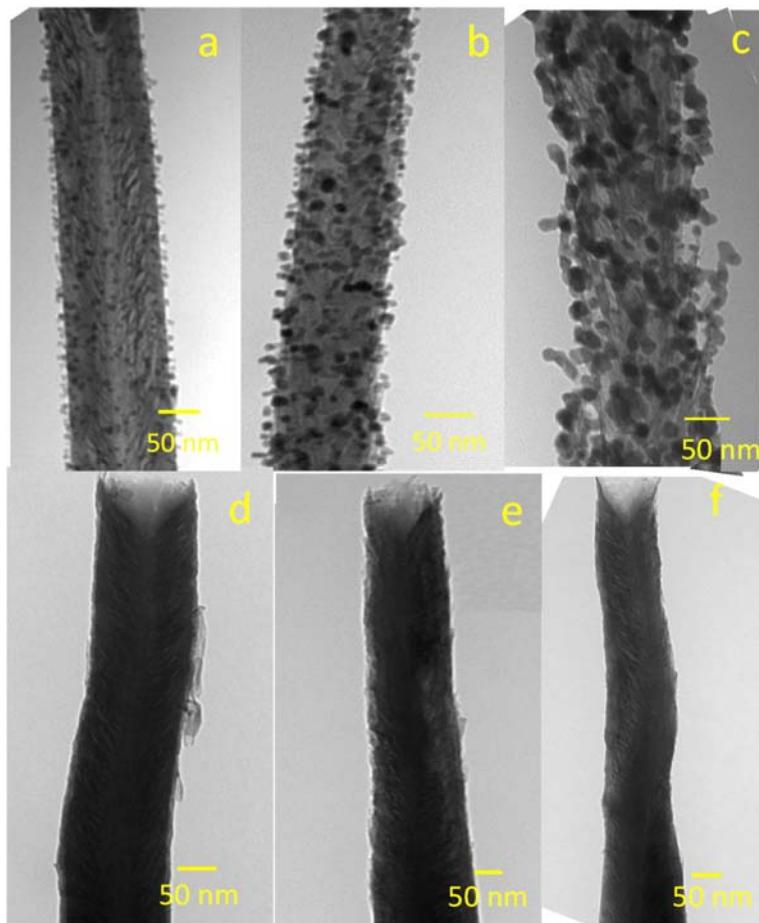


Figure S10. TEM image of (a) and (d) N-VACNF PA 5 min; (b) and (e) N-VACNF PA 15 min; (c) and (f) N-VACNF PA 30 min, where (a-c) are as-prepared and (d-f) are after treatment in 1.0 M HNO_3 .

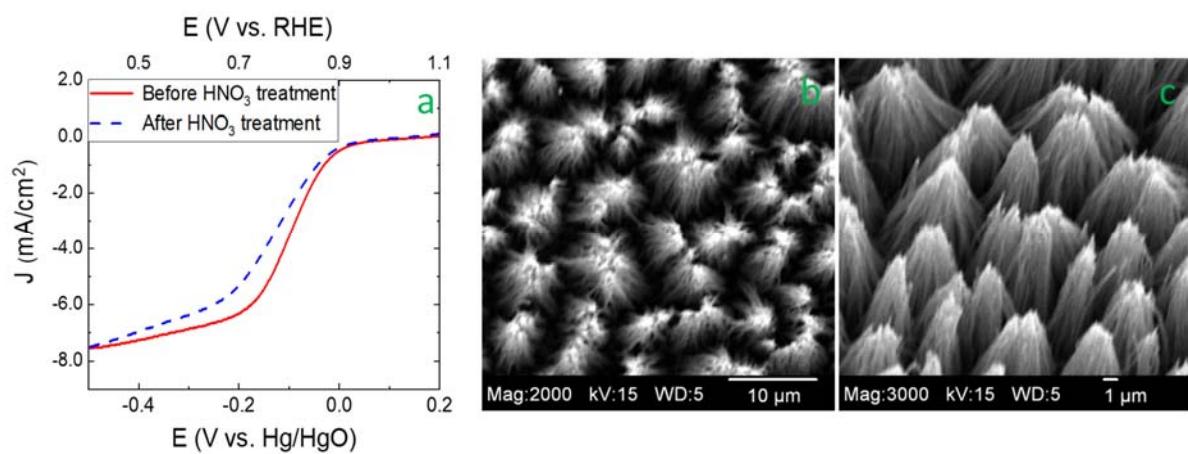


Figure S11. (c) LSV recorded at 1600 rpm in O_2 -saturated 0.10 M KOH solution with Pt sputtered without any treatment in HNO_3 and after treatment in HNO_3 for Pt/N-VACNF PA 5 min; (a and b) FESEM image of N-VACNF PA 5 min after contact with solution.

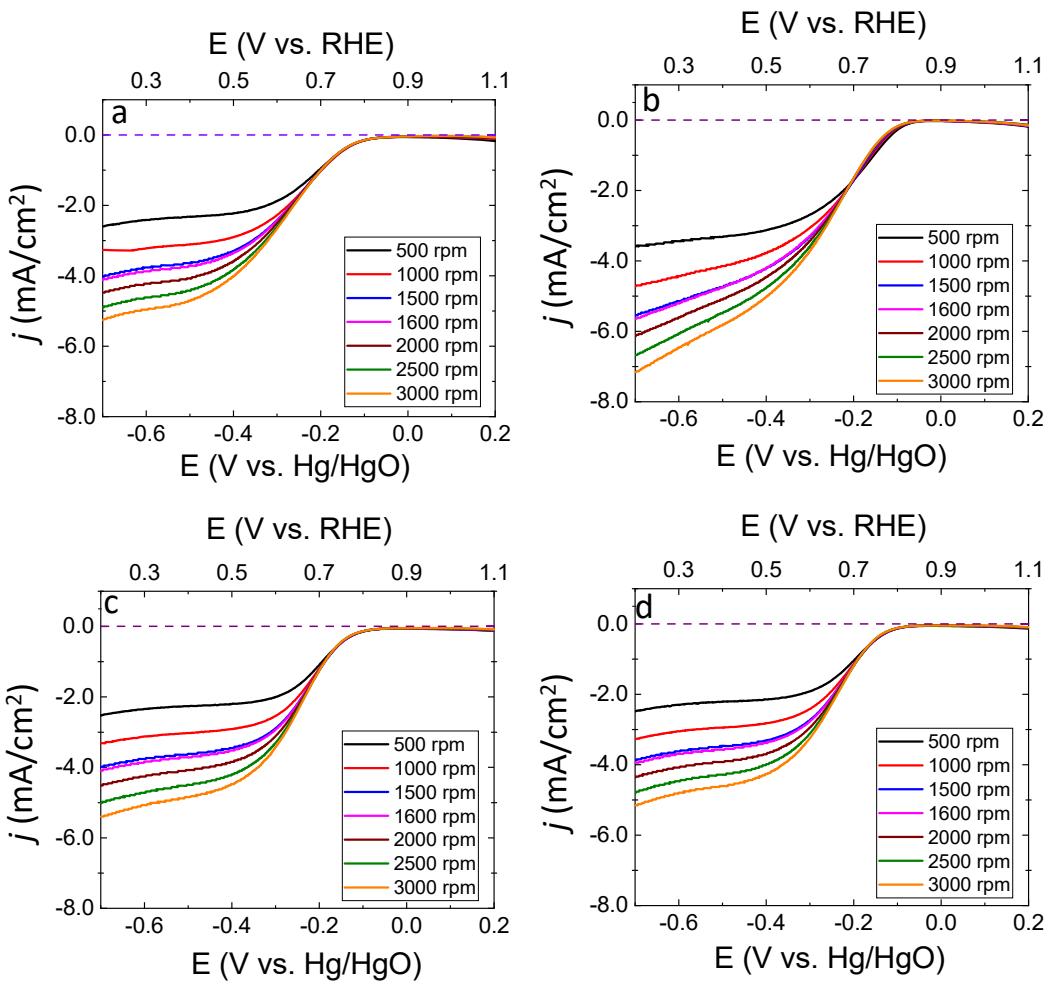


Figure S12. RDE LSV voltammogram of (a) bare VACNF, (b) N-VACNF PA 5 min, (c) N-VACNF PA 15 min, and (d) N-VACNF PA 30 min in O_2 -saturated 0.10 M KOH solution at a scan rate of 10 mV/s and at a rotation speed from 500 to 3000 rpm. The purple dash-line marks the zero-current density.

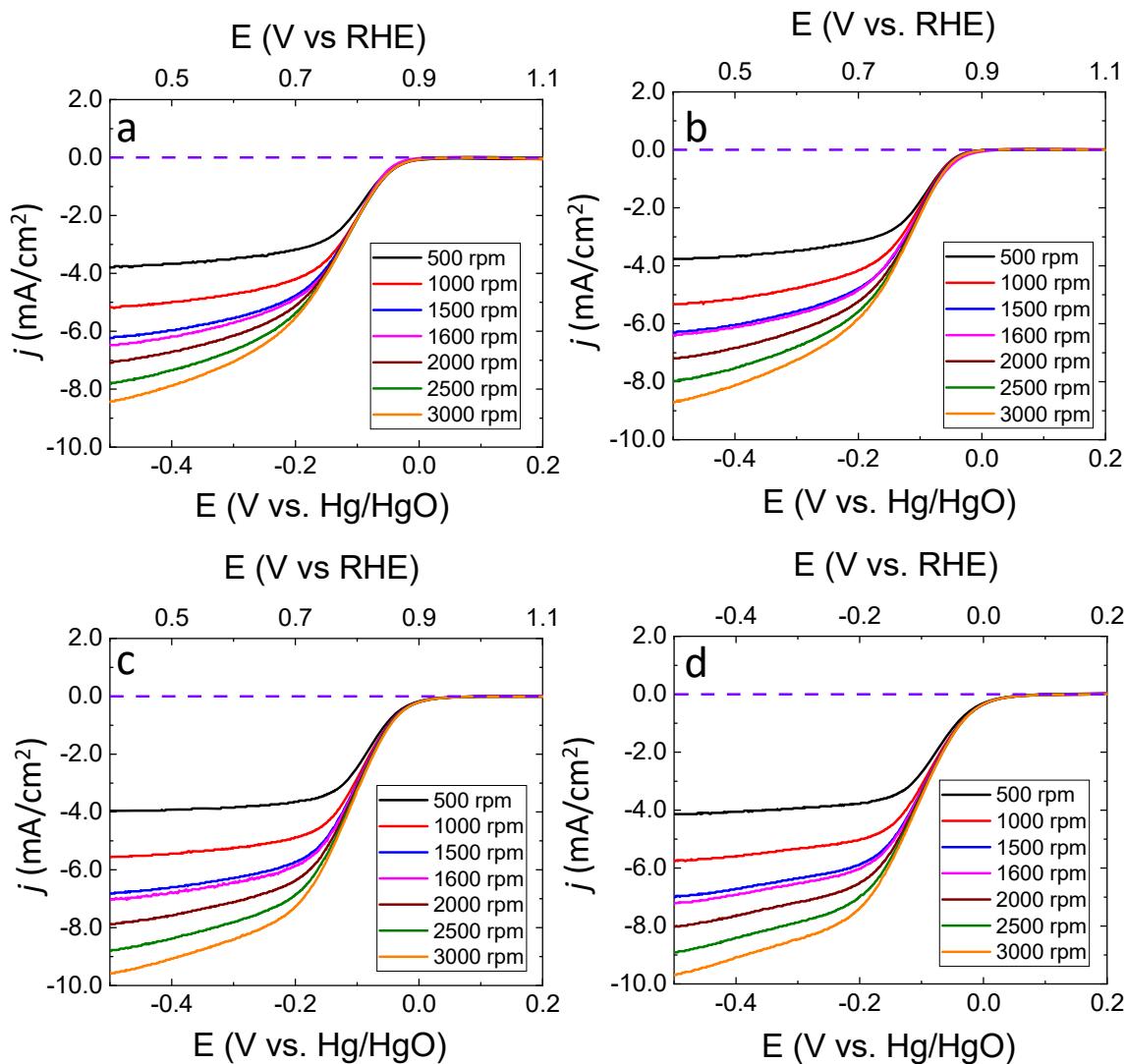


Figure S13. RDE LSV voltammogram of (a) Pt/N-VACNF PA 5 min ($6.5 \mu\text{g}/\text{cm}^2$ Pt), (b) Pt/N-VACNF PA 5 min ($10.8 \mu\text{g}/\text{cm}^2$ Pt), (c) Pt/N-VACNF PA 5 min ($21.5 \mu\text{g}/\text{cm}^2$ Pt), and (d) Pt/N-VACNF PA 5 min ($43.0 \mu\text{g}/\text{cm}^2$ Pt) in O_2 -saturated 0.10 M KOH solution at a scan rate of 10 mV/s and at a rotation speed from 500 to 3000 rpm .

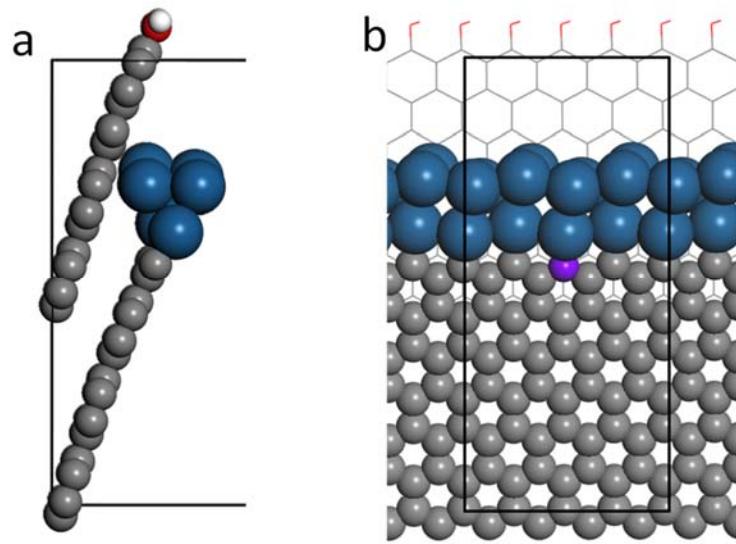


Figure S14. Side view (a) and front view (b) of molecular model for Pt/N_pVACNF model to represent Pt NPs supported by N_pVACNF edge. Color code: blue-Pt, gray-C, purple-N, red-O, white-H.

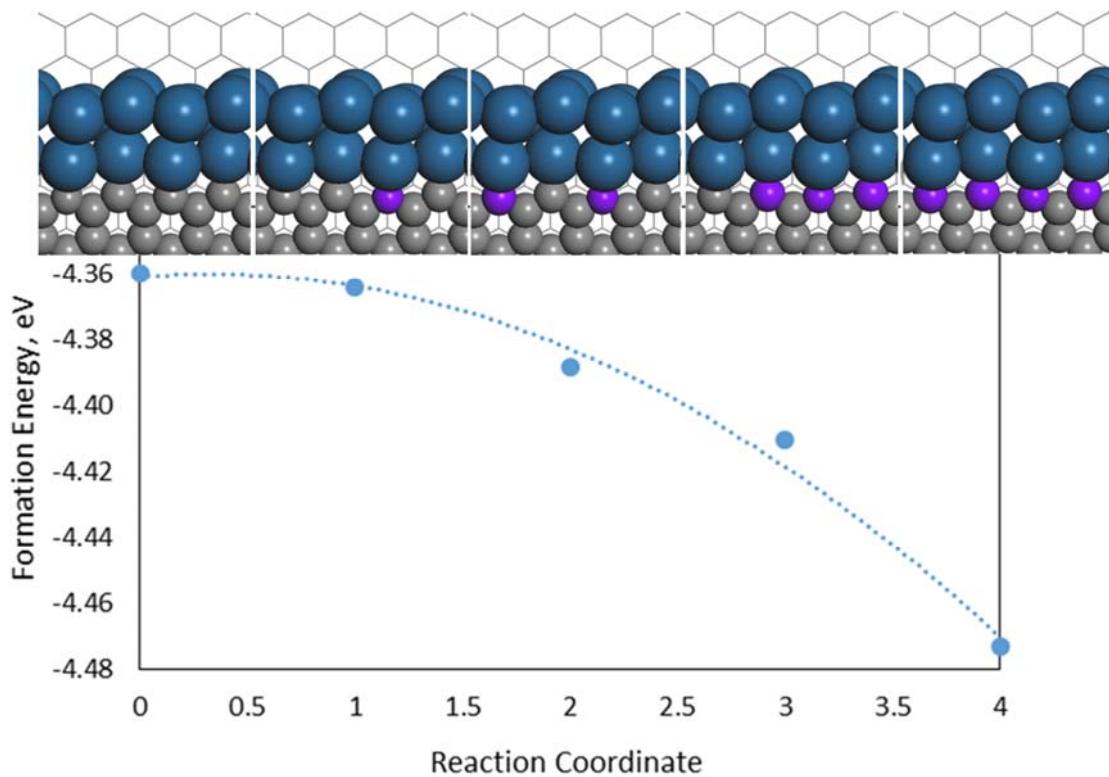


Figure S15. Stability analysis of Pt particles over pyridinic nitrogen (N_p) doped edge. Color code: blue-Pt, gray-C, purple-N

Table S1. Atomic Percentage (at %) of the elemental species from the XPS survey spectra.

Catalyst	at %			
	C	N	O	Pt
Bare VACNF	85.9	7.4	6.7	-
N-VACNF PA 5 min	78.9	8.5	12.6	-
N-VACNF PA 15 min	74.7	8.6	16.7	-
N-VACNF PA 30 min	73.6	7.4	19.0	-
Pt/N-VACNF PA 5 min	49.1	5.1	21.4	24.4
Pt/C	93.8	3.0	-	3.2

Table S2. Binding energies (BE) and integrated relative area % of individual chemical component from N 1s and O 1s XPS spectra of Bare VACNF, N-VACNF PA 5min, N-VACNF PA 15 min, and N-VACNF PA 30 min.

XPS Spectra	Species	Bare VACNF		N-VACNF PA 5 min		N-VACNF PA 15 min		N-VACNF PA 30 min	
		BE (eV)	Relative Area %						
N 1s	Pyridinic N	398.76	32.9	398.78	45.2	398.70	53.1	398.54	49.1
	Pyrrolic N	399.95	10.9	399.88	16.8	399.81	19.4	400.05	26.1
	Graphitic N	401.13	34.0	401.04	27.4	401.15	16.4	401.19	15.0
	Oxidic N	402.67, 405.13	22.2	403.46, 405.43	10.6	403.28	12.1	403.75	9.8
O 1s	NiO	-	-	529.58	10.3	529.58	15.0	529.68	16.4
	C=O	531.28	20.7	531.30	24.1	531.24	26.4	531.20	17.3
	C-O	532.26	47.7	532.28	53.1	532.20	43.6	532.14	53.2
	C-O-H	533.64	23.0	533.86	12.5	533.64	15	533.64	13.1
	O in H ₂ O	534.72	8.6	-	-	-	-	-	-

Table S3. Binding energies (BE) and integrated relative area % for each species of Pt/C and Pt/N-VACNF from Pt 4f XPS spectra.

Sample	Species	BE (eV)		Relative area %
		Pt 4f _{7/2}	Pt 4f _{5/2}	
Pt/C	Pt ⁰	71.32	74.63	45.6
	Pt ²⁺	72.47	75.59	41.1
	Pt ⁴⁺	77.70	79.90	13.3
Pt/N-VACNF	Pt ⁰	71.13	74.41	57.2
	Pt ²⁺	72.50	75.48	30.2
	Pt ⁴⁺	77.07	79.49	12.6