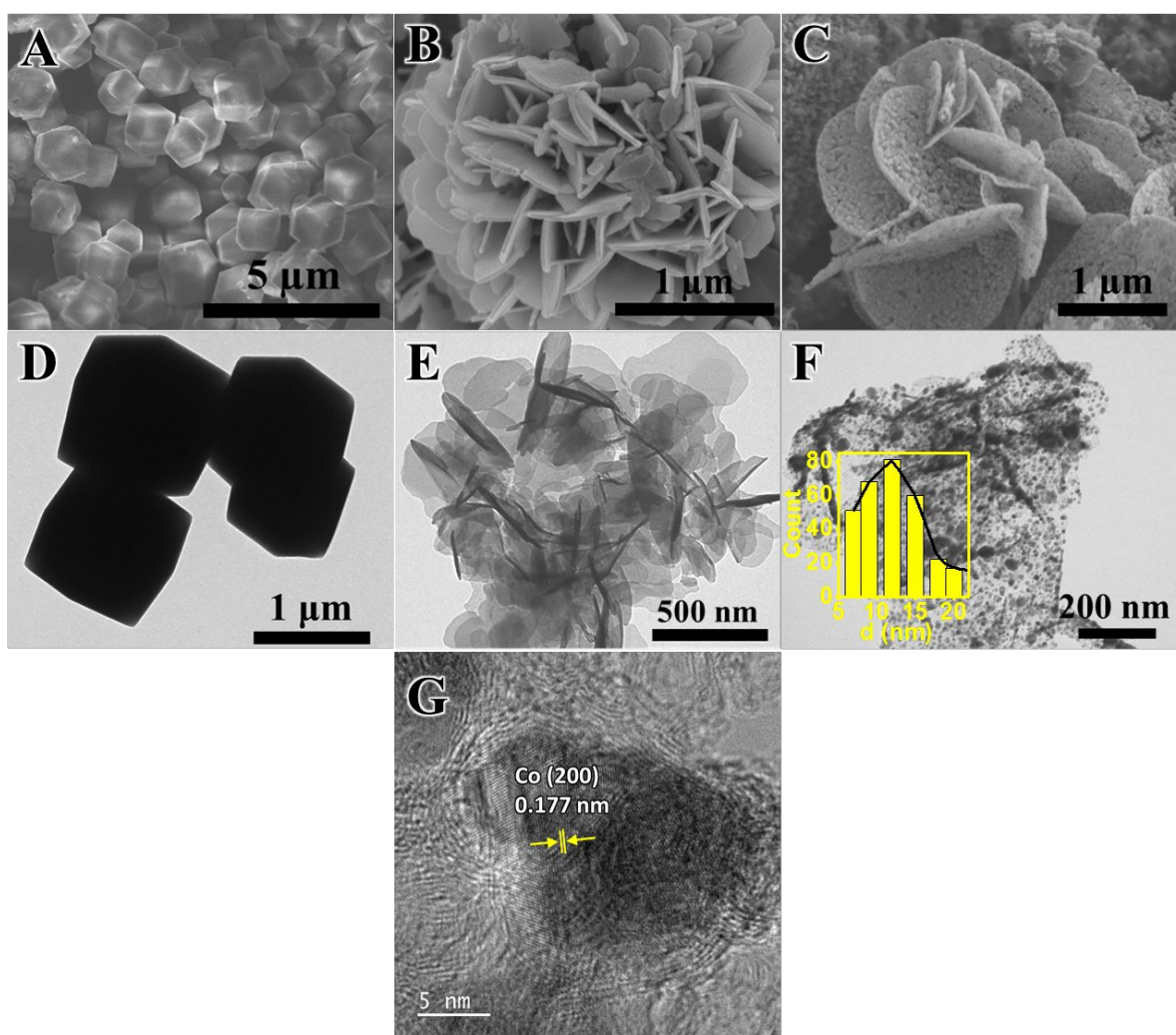


## **Supporting Information**

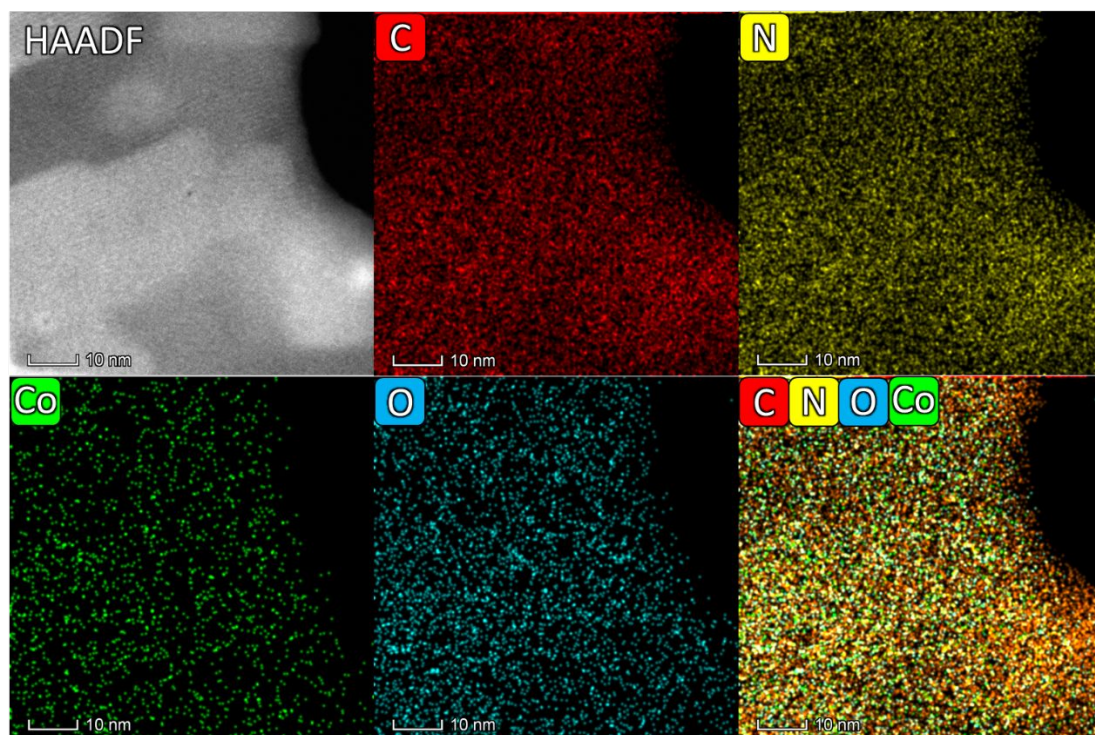
### **Synergistic CoN-Decorated Pt Catalyst on Two-Dimensional Porous Co-N-Doped Carbon Nanosheet for Enhanced Oxygen Reduction Activity and Durability**

*Thanh-Nhan Tran,<sup>#</sup> Ha-Young Lee,<sup>#</sup> Jong-Doek Park, Tong-Hyun Kang, Byong-June Lee,  
and Jong-Sung Yu\**

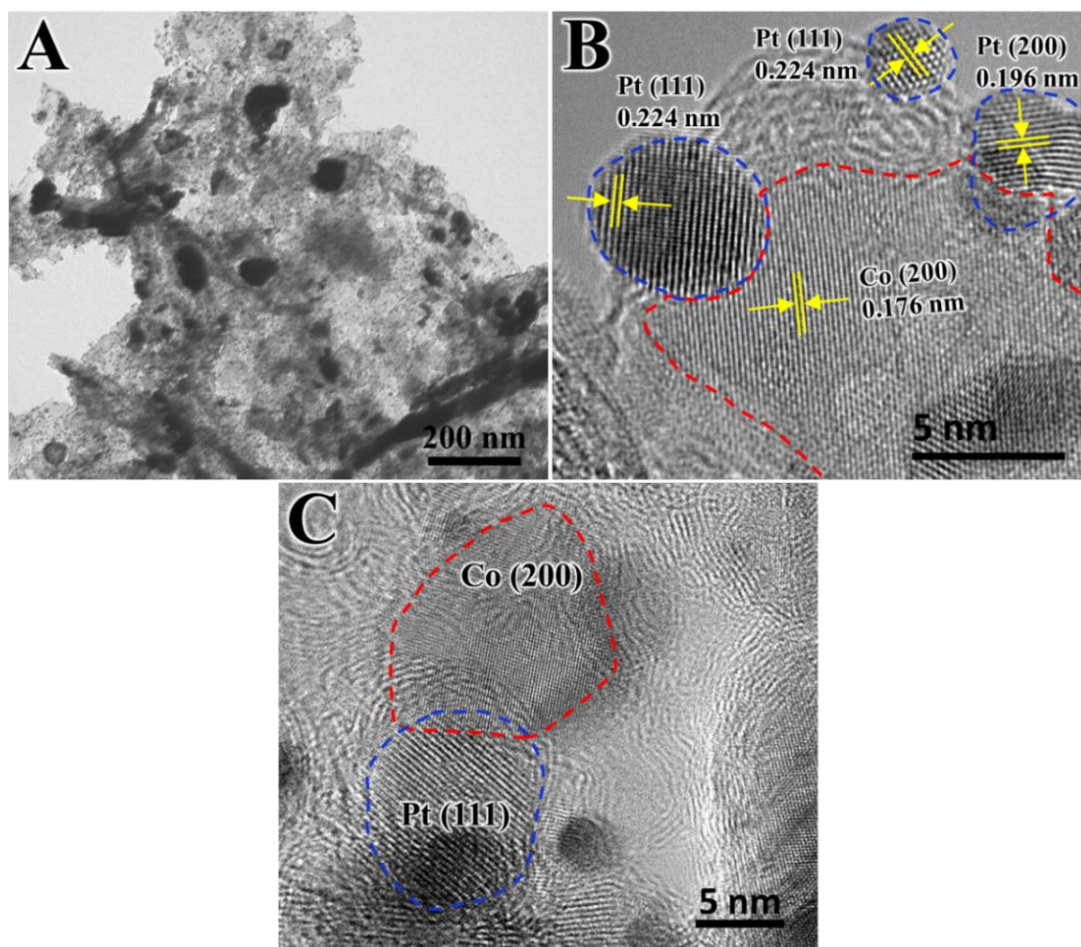
Email: jsyu@dgist.ac.kr



**Figure S1.** (A-C) SEM and (D-F) TEM images of as-prepared ZIF-67, NF-CoZIF and Co/CoNC-2D, respectively, and (G) HR-TEM image of Co/CoNC-2D along with Co lattice spacing.

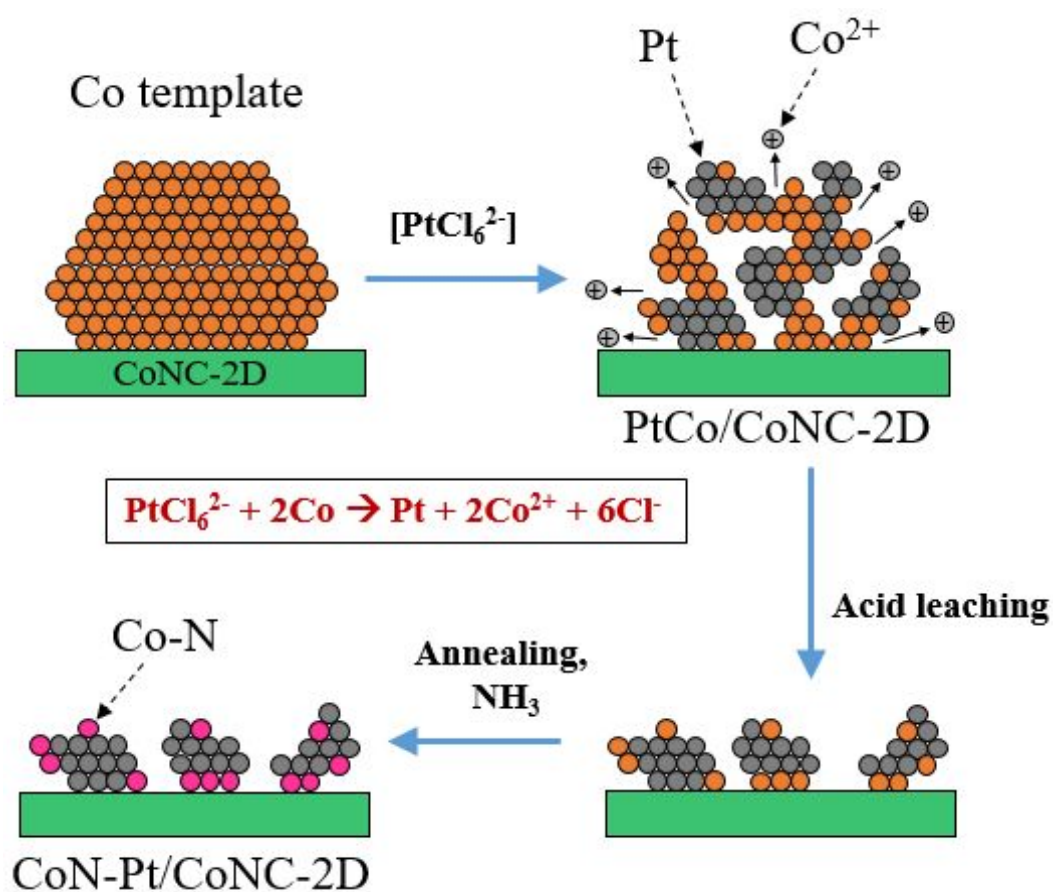


**Figure S2.** HAADF-STEM image of NF-CoZIF and EDS elemental mapping images for C, N, Co and O, and the merged image, respectively.

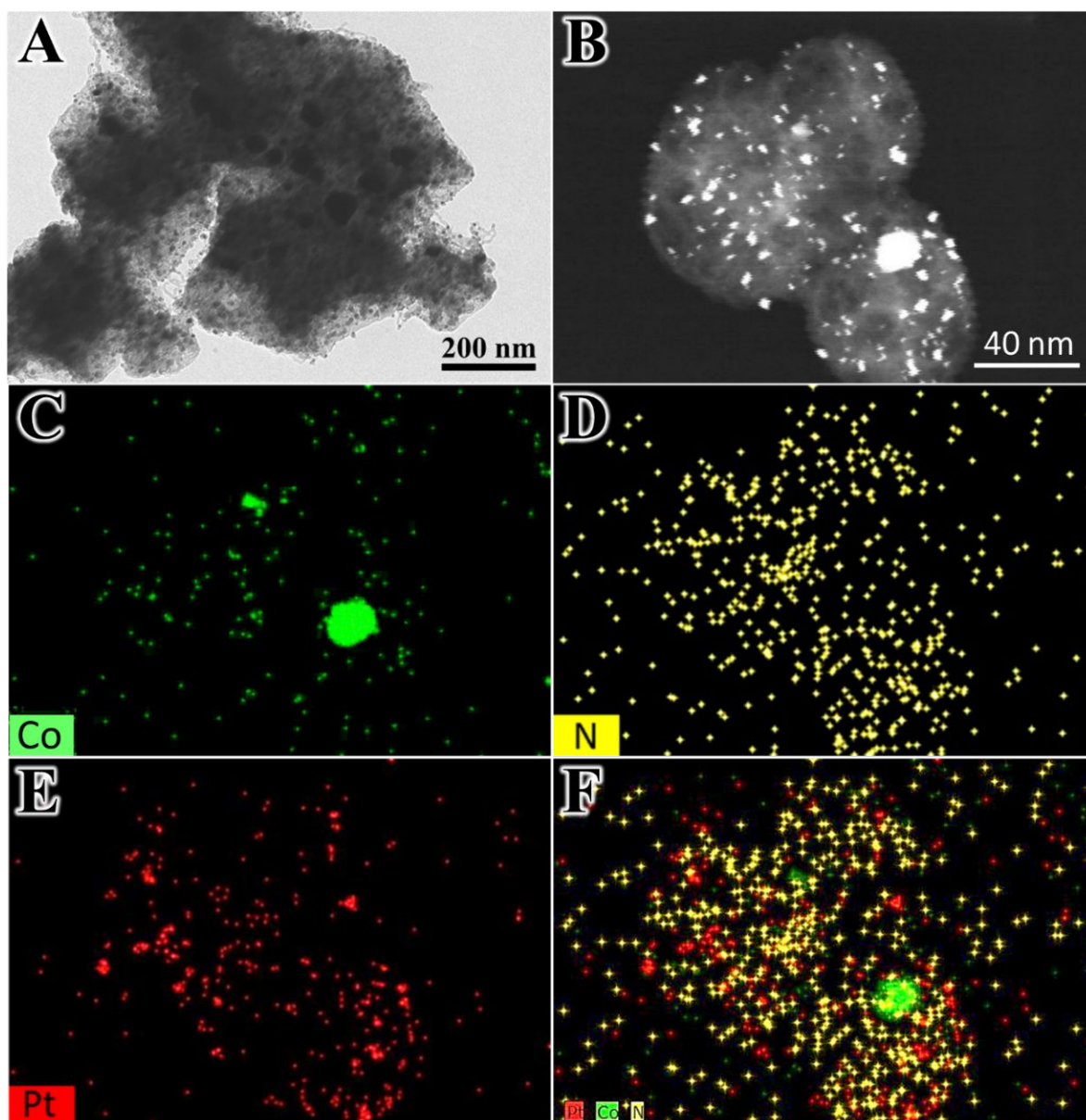


**Figure S3.** (A) TEM and (B, C) HR-TEM images for crystallite lattices of PtCo/CoNC-2D.

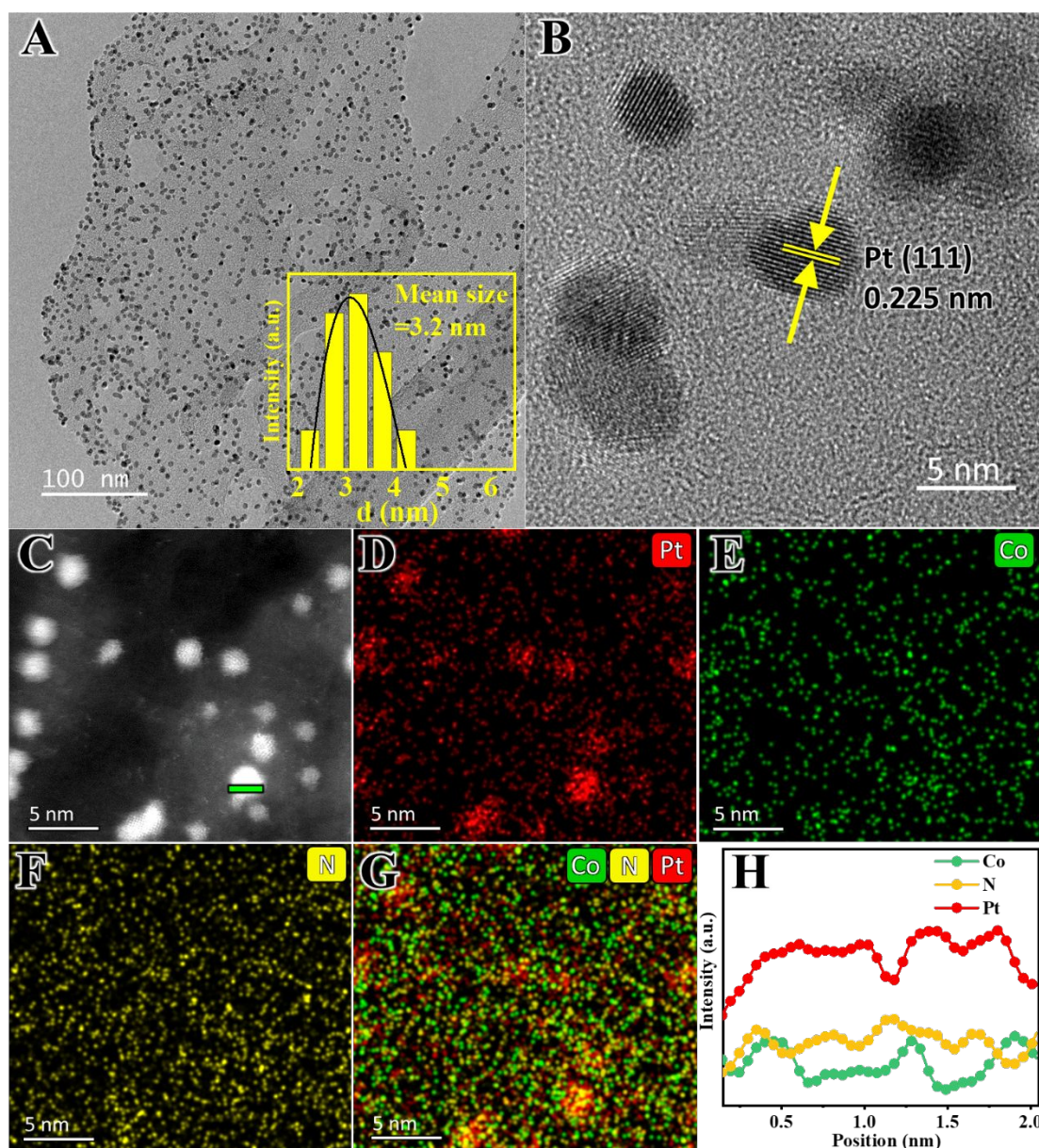




**Figure S4.** Schematic representation of Pt NPs growth pathway by galvanic replacement reaction on Co template. The undissolved Co traces on Pt surface are converted to CoN after  $\text{NH}_3$  heat treatment to generate CoN-Pt/CoNC-2D.

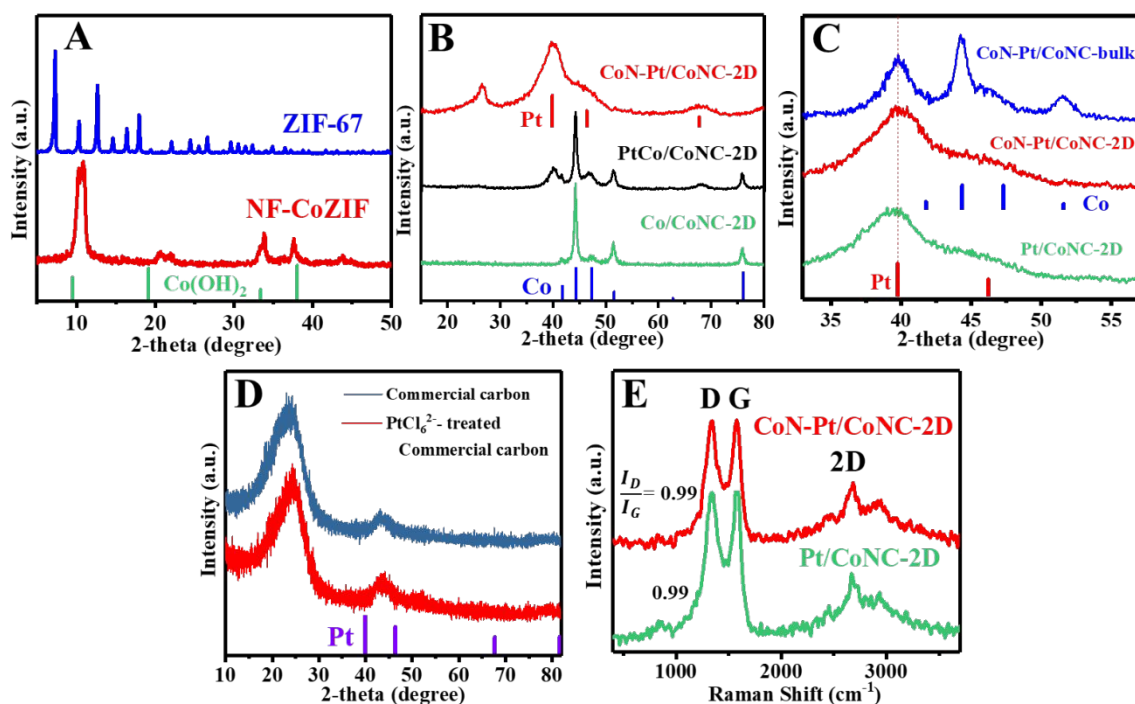


**Figure S5.** (A) TEM, (B) HAADF-STEM images of CoN-Pt/CoNC-bulk and (C-F) EDS elemental mapping images for Co, N and Pt, and the merged image, respectively.

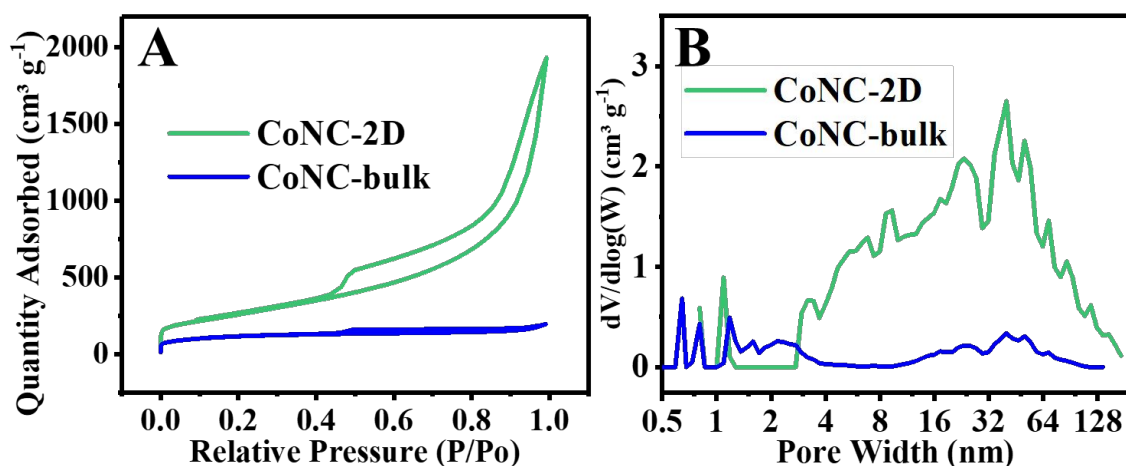


**Figure S6.** (A) TEM, (B) HR-TEM, (C) HAADF-STEM images of Pt/CoNC-2D and (D-G) EDS elemental mapping images for Pt, Co, N and the merged image, respectively. (H) Resulting element line profiles of a green line in image C with Pt, Co and N element signal intensity.





**Figure S7.** XRD patterns of (A) ZIF-67 and NF-CoZIF, (B) Co/CoNC-2D, PtCo/CoNC-2D, and CoN-Pt/CoNC-2D, (C) Pt/CoNC-2D, CoN-Pt/CoNC-2D, and CoN-Pt/CoNC-bulk and (D) commercial carbon before and after adding  $\text{PtCl}_6^{2-}$  into the carbon in EG at 80 °C for 4 h. (E) Raman spectra of Pt/CoNC-2D and CoN-Pt/CoNC-2D.

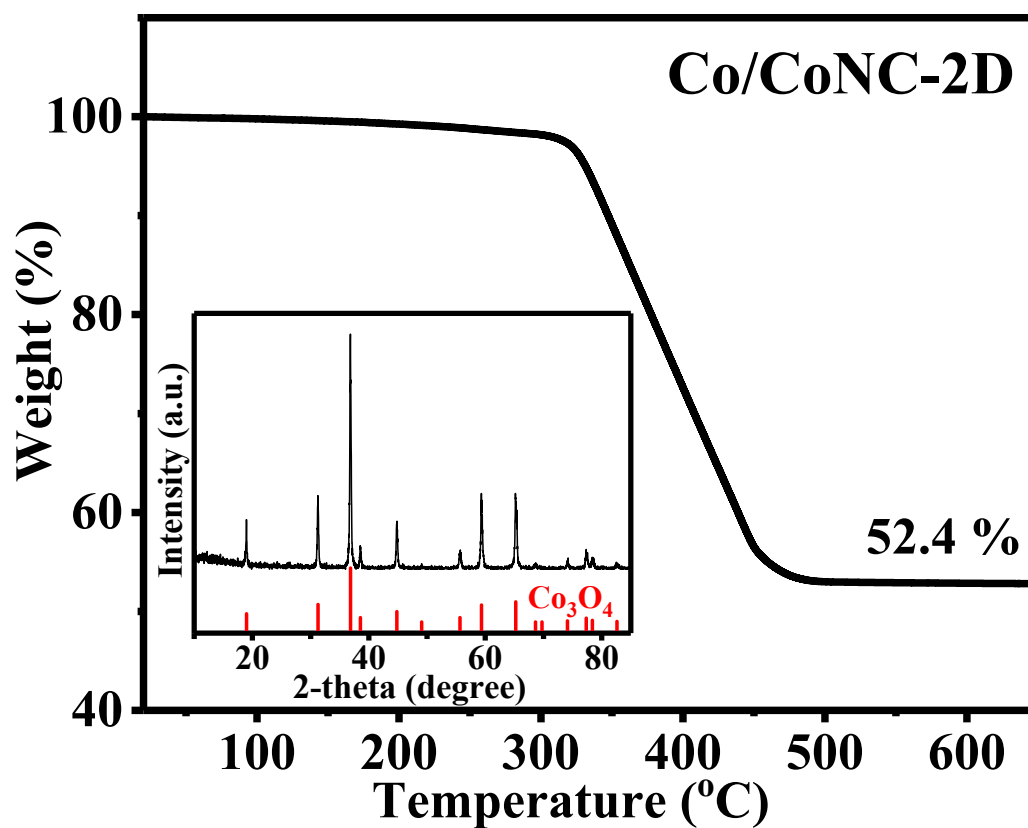


**Figure S8.** (A) nitrogen adsorption-desorption isotherms and (B) pore size distribution of CoNC-2D and CoNC-bulk samples.



**Table S1.** Physicochemical properties of as-prepared CoN-Pt/CoNC-2D, CoN-Pt/CoNC-bulk, CoNC-2D and CoNC-bulk samples.

Samples	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{micro}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{micro}}/S_{\text{BET}}$	$V$ ( $\text{cm}^3 \text{g}^{-1}$ )
CoN-Pt/CoNC-2D	288	54	18.8%	1.21
CoN-Pt/CoNC-bulk	202	164	80.9%	0.25
CoNC-2D	960	184	19.2%	3.00
CoNC-bulk	426	344	80.7%	0.30



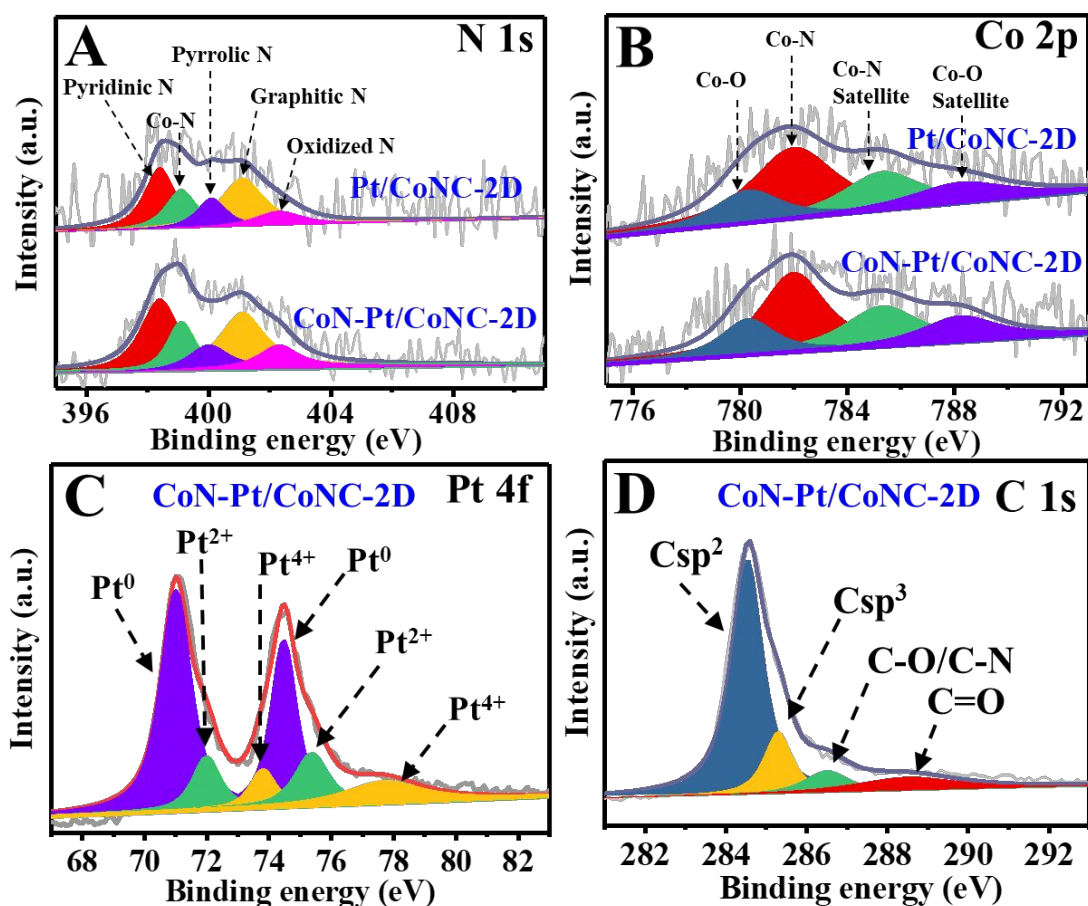
**Figure S9.** TGA plot of Co/CoNC-2D in air condition with a ramp of  $5\text{ }^{\circ}\text{C min}^{-1}$ . The inset shows XRD patterns of the Co/CoNC-2D residue after the TGA and  $\text{Co}_3\text{O}_4$  reference (ICDD 00-043-1003).

**Table S2.** ICP results of all the as-prepared samples.

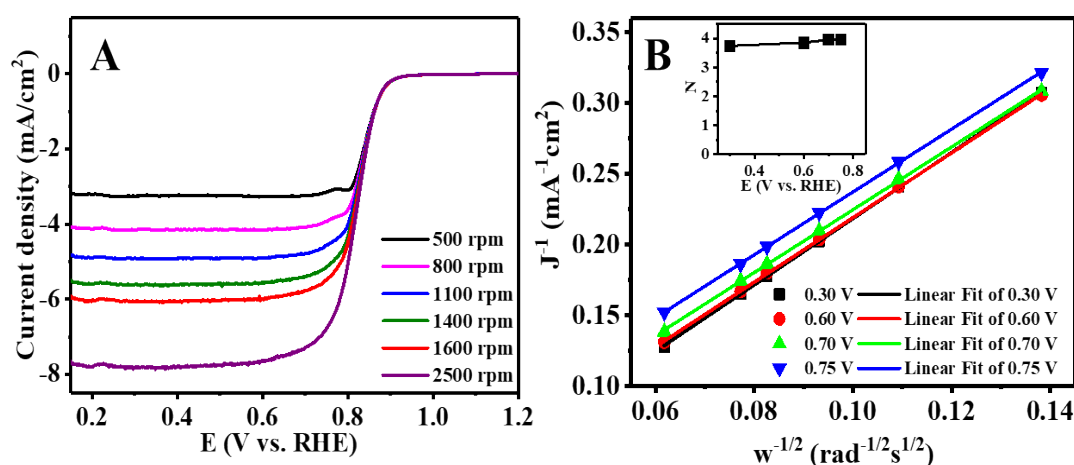
Material	$\rho_{\text{Pt}}$ ( $\mu\text{g/mL}$ )	$\rho_{\text{Co}}$ ( $\mu\text{g/mL}$ )	$C_{\text{Pt}}$ ( $\mu\text{mol/mL}$ )	$C_{\text{Co}}$ ( $\mu\text{mol/mL}$ )	Pt (wt%) in the sample	Co (wt%) in the sample
CoN-Pt/CoNC-2D	29.61	3.77	0.15	0.06	23.68	3.02
CoN-Pt/CoNC-bulk	26.19	15.47	0.13	0.26	20.95	12.38
Pt/CoNC-2D	30.10	2.51	0.15	0.04	24.08	2.01
PtCo/CoNC-2D	28.03	34.22	0.14	0.57	22.43	27.38
Co/CoNC-2D		49.10		0.83		39.28
CoNC-2D		2.91		0.05		2.32

**Table S3.** Atomic composition obtained from XPS spectra for as-prepared Pt/CoNC-2D, CoN-Pt/CoNC-bulk and CoN-Pt/CoNC-2D samples.

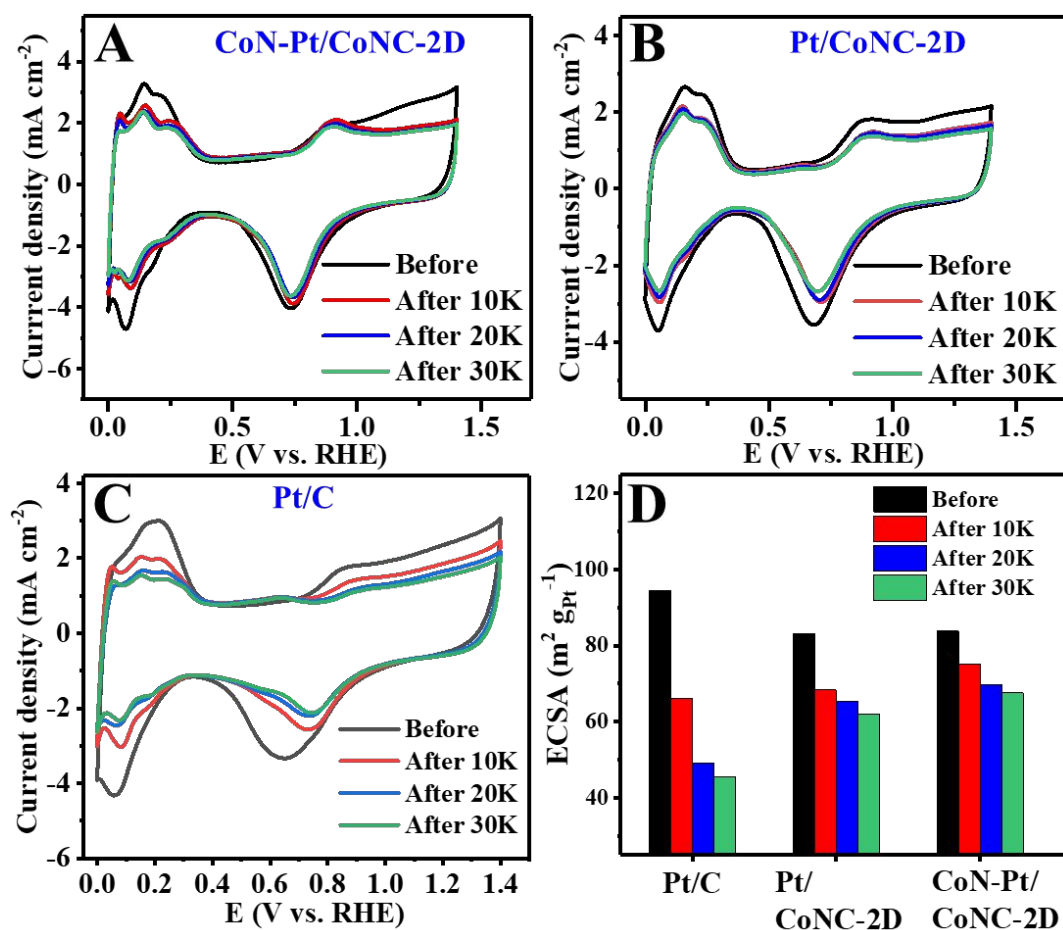
Samples	<b>C 1s</b> (at%)	<b>Pt 4f</b> (at%/wt%)	<b>Co 2p</b> (at%/ wt%)	<b>N 1s</b> (at%)	<b>O 1s</b> (at%)
CoN-Pt/CoNC-2D	87.98	2.06/ <b>24.50</b>	0.65/2.34	4.77	4.54
CoN-Pt/CoNC-bulk	86.52	1.88/ <b>21.36</b>	2.26/7.75	3.61	5.73
Pt/CoNC-2D	88.31	2.13/ <b>25.32</b>	0.32/1.14	3.30	5.94



**Figure S10.** High resolution XPS spectra of (A) N 1s, (B) Co 2p of Pt/CoNC-2D and CoN-Pt/CoNC-2D, and typical deconvoluted (C) Pt 4f and (D) C 1s XPS spectra of CoN-Pt/CoNC-2D.

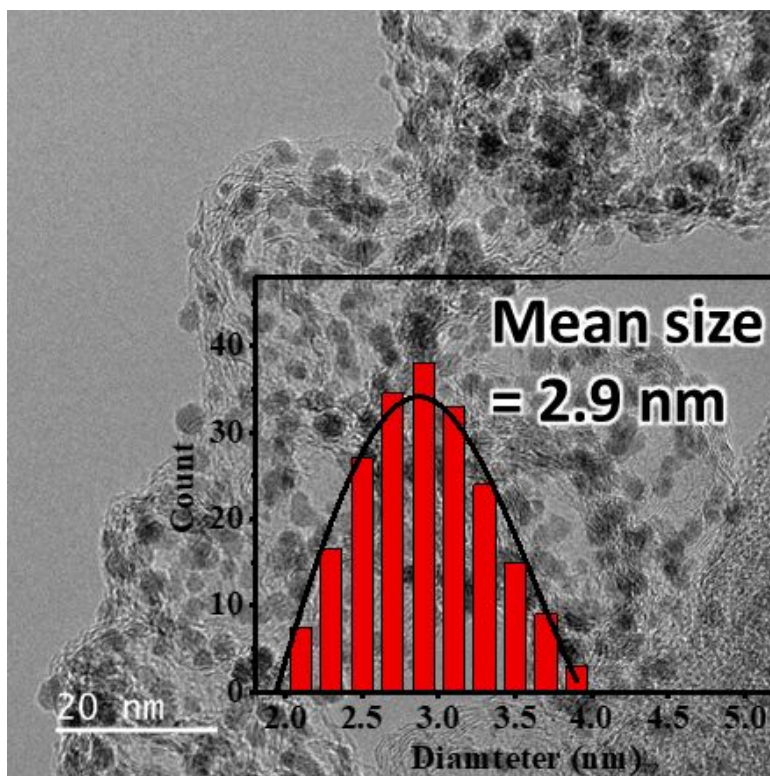


**Figure S11.** (A) LSV curves for different rotating speeds at 10 mV/s scan rate, (B) Koutecky-Levich plots at various potentials for the PtCo/CoNC-2D with inset for electron transfer number determined at various potentials.



**Figure S12.** Full CV curves in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> during ADT of (A) CoN-Pt/CoNC-2D, (B) Pt/CoNC-2D and (C) commercial Pt/C (20 wt%), and (D) changes in their ECSA during ADT.





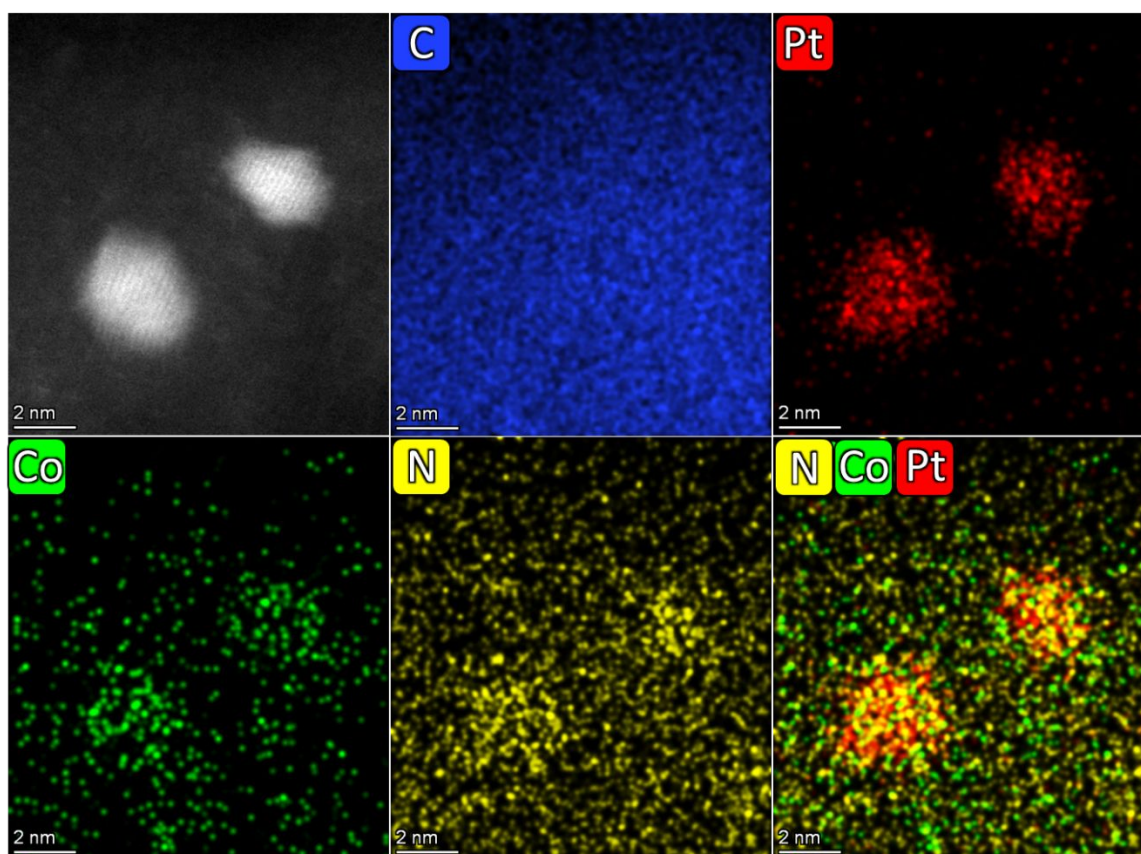
**Figure S13.** A typical TEM image of commercial Pt/C (20 wt%) before ADT.

**Table S4.** Comparison of the onset ( $E_{\text{onset}}$ ), half-wave potential ( $E_{1/2}$ ) and long-term durability for ORR of related PtCo/C catalysts from literature and this work.

Catalyst	$E_{\text{onset}}$ relative to Pt/C	$E_{1/2}$ relative to Pt/C	Durability	Ref.
Pt <sub>3</sub> Co/C	Similar	Positive shift ~ 50 mV	68% ECSA retention after 4000 cycles	1
Pt-Co/C	Similar	Positive shift ~ 17 mV	76% ECSA retention after 5000 cycles	2
PtCo/Co@NH PCC	Positive shift ~ 10 mV	Positive shift ~ 19 mV	70% ECSA retention after 5000 cycles	3
Pt <sub>3</sub> Co/C-700	Positive shift ~ 40 mV	Positive shift ~ 70 mV	70% ECSA retention after 5000 cycles	4
PtCoNW	Positive shift ~ 20 mV	Positive shift ~ 40 mV	75% ECSA retention after 1000 cycles	5
Dendritic PtCo	Similar	Positive shift ~ 49 mV	NA	6
Pt <sub>73</sub> Co <sub>27</sub> /C	Similar	Positive shift ~ 20 mV	NA	7
CoN-Pt/CoNC-2D	<b>Similar</b>	<b>Positive shift ~ 50 mV</b>	80.6 % ECSA retention after 30000 cycles	<b>This Work</b>

**Table S5.** The electrochemical results of  $E_{1/2}$ , electrochemical surface area (ECSA), specific activity (SA), mass activity (MA), and Tafel slope measured by half-cell for CoN-Pt/CoNC-2D and Pt/CoNC2D and Pt/C in  $O_2$ -saturated 0.1 M  $HClO_4$ .

Sample	$E_{1/2}$ (V)	ECSA ( $m^2/g_{Pt}$ )	SA (0.8V) ( $mA/cm^2_{Pt}$ )	MA (0.8V) ( $mA/mg_{Pt}$ )	Tafel slope (mV/dec)
CoN-Pt/CoNC-2D	0.83	83.8	0.059	49.72	49.5
Pt/CoNC-2D	0.81	83.1	0.045	37.06	65.8
Pt/C	0.78	94.5	0.033	31.25	89.9



**Figure S14.** HAADF-STEM and EDS mapping images for C, Pt, Co, N, and the merged image of CoN-Pt/CoNC-2D after 30,000 potential cycles.

## REFERENCES

- (1) Lee, J. D.; Jishkariani, D.; Zhao, Y.; Najmr, S.; Rosen, D.; Kikkawa, J. M.; Stach, E. A.; Murray, C. B. Tuning the Electrocatalytic Oxygen Reduction Reaction Activity of Pt–Co Nanocrystals by Cobalt Concentration with Atomic-Scale Understanding. *ACS Appl. Mater. Interfaces* **2019**, *11* (30), 26789–26797. <https://doi.org/10.1021/acsami.9b06346>.
- (2) Ma, Y.; Yin, L.; Yang, T.; Huang, Q.; He, M.; Zhao, H.; Zhang, D.; Wang, M.; Tong, Z. One-Pot Synthesis of Concave Platinum–Cobalt Nanocrystals and Their Superior Catalytic Performances for Methanol Electrochemical Oxidation and Oxygen Electrochemical Reduction. *ACS Appl. Mater. Interfaces* **2017**, *9* (41), 36164–36172. <https://doi.org/10.1021/acsami.7b10209>.
- (3) Ying, J.; Li, J.; Jiang, G.; Cano, Z. P.; Ma, Z.; Zhong, C.; Su, D.; Chen, Z. Metal–Organic Frameworks Derived Platinum–Cobalt Bimetallic Nanoparticles in Nitrogen-Doped Hollow Porous Carbon Capsules as a Highly Active and Durable Catalyst for Oxygen Reduction Reaction. *Appl. Catal. B Environ.* **2018**, *225*, 496–503. <https://doi.org/10.1016/j.apcatb.2017.11.077>.
- (4) Wang, D.; Xin, H. L.; Hovden, R.; Wang, H.; Yu, Y.; Muller, D. A.; Disalvo, F. J.; Abruña, H. D. Structurally Ordered Intermetallic Platinum–Cobalt Core–Shell Nanoparticles with Enhanced Activity and Stability as Oxygen Reduction Electrocatalysts. *Nat. Mater.* **2013**, *12* (1), 81–87. <https://doi.org/10.1038/nmat3458>.
- (5) Higgins, D. C.; Wang, R.; Hoque, M. A.; Zamani, P.; Abureden, S.; Chen, Z. Morphology and Composition Controlled Platinum–Cobalt Alloy Nanowires Prepared by Electrospinning as Oxygen Reduction Catalyst. *Nano Energy* **2014**, *10*, 135–143. <https://doi.org/10.1016/j.nanoen.2014.09.013>.
- (6) Wang, H.; Yuan, X.; Li, D.; Gu, X. Dendritic PtCo Alloy Nanoparticles as High Performance Oxygen Reduction Catalysts. *J. Colloid Interface Sci.* **2012**, *384* (1), 105–109. <https://doi.org/10.1016/j.jcis.2012.06.060>.
- (7) Loukrakpam, R.; Shan, S.; Petkov, V.; Yang, L.; Luo, J.; Zhong, C. J. Atomic Ordering Enhanced Electrocatalytic Activity of Nanoalloys for Oxygen Reduction Reaction. *J. Phys. Chem. C* **2013**, *117* (40), 20715–20721. <https://doi.org/10.1021/jp4067444>.