Supplementary Information

Epitaxial Growth of Hexagonal Pd on Co_3O_4/NC Heterostructures for High-Performance ORR Electrocatalysis

Fatima Nasim[1], Muhammad Sajid[1], Guobao Xu[*2,3], and Muhammad Arif Nadeem[*1,4]

[1]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

[2]State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun Jilin 130022, China

[3]School of Applied Chemistry and Engineering, University of Science and Technology of China,

[4]Pakistan Academy of Sciences, 3-Constitution Avenue Sector G-5/2, Islamabad, Pakistan.

Hefei 230026, China

*M. A. N; manadeem@qau.edu.pk

*G. X; guobaoxu@ciac.ac.cn

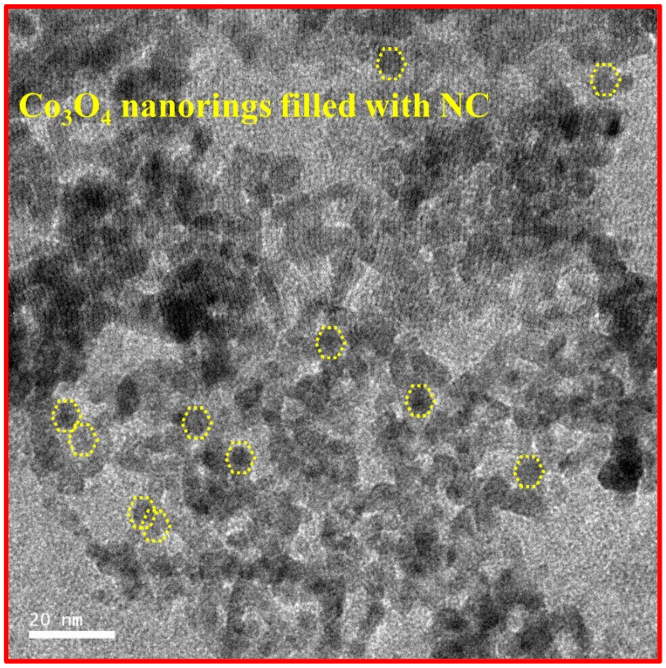

Figure S1: Visible nanosheets in the HRTEM image of $Pd_{2.43}$-O_x/Co_3O_4/NC at 20 nm covering large physical area

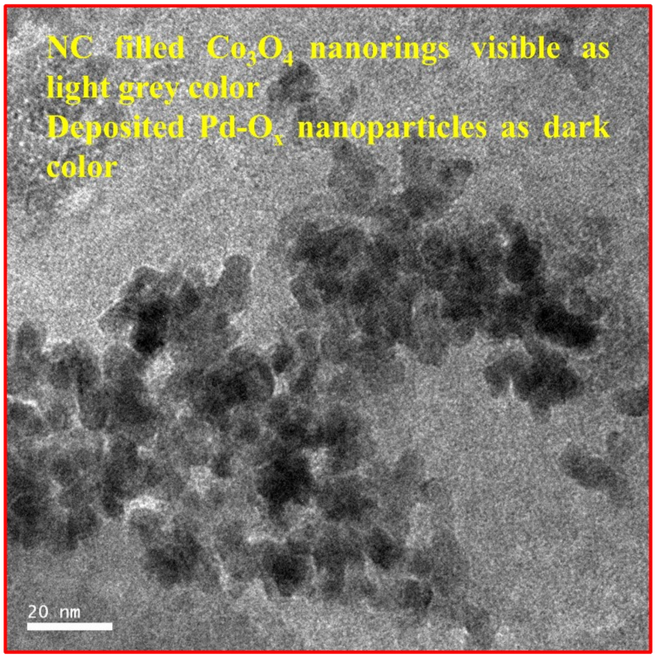

Figure S2: Large area HRTEM image of $Pd_{2.43}$-O_x/Co_3O_4/NC at 20 nm showing uniform deposition of Pd-O_x over NC filled Co_3O_4 nanorings

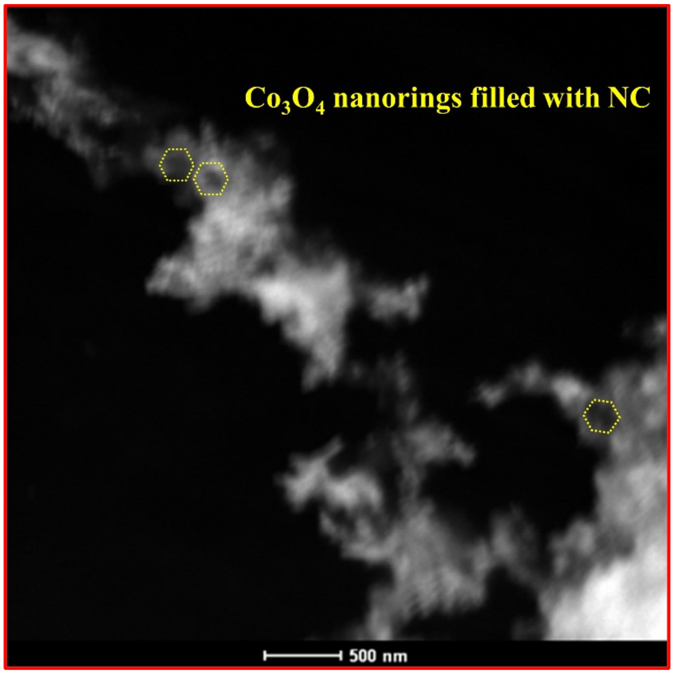

Figure S3: HAADT-STEM image of $Pd_{2.43}$-O_x/Co_3O_4/NC at 500 nm

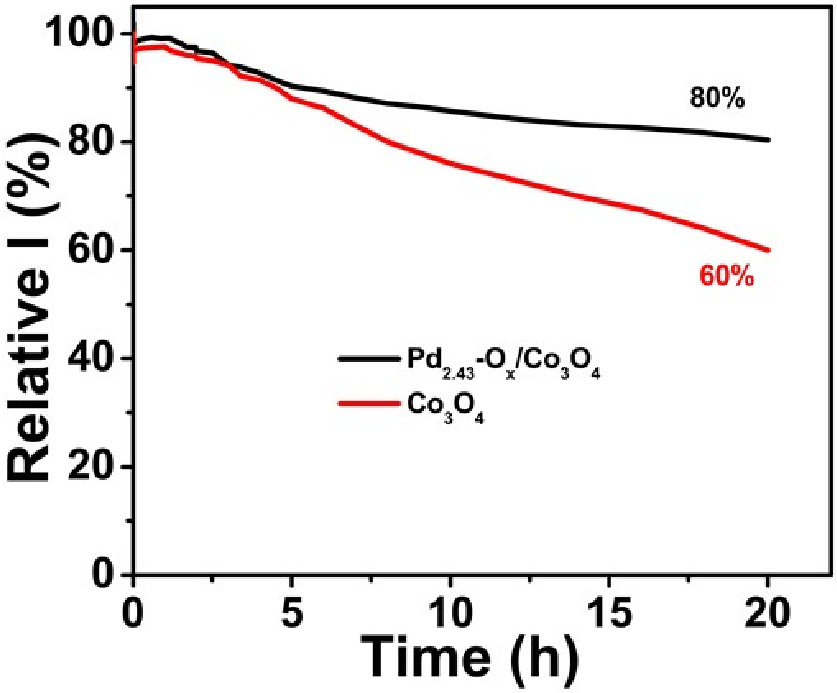

Figure S4: Chronoamperometric measurement of Co_3O_4 and $Pd_{2.43}$-O_x/Co_3O_4 over 20 hrs.

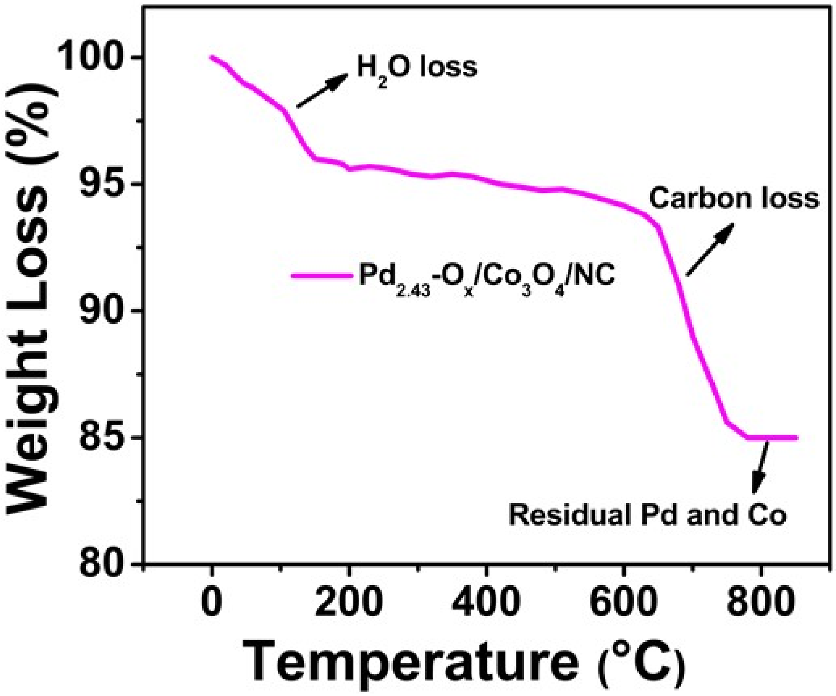

Figure S5: Thermogravimetric analysis of $Pd_{2.43}$-O_x/Co_3O_4/NC

Average crystallite size by using Debye-Sherrer equation

The crystallite size of the crystalline materials was estimated from X-ray diffraction patterns using the Debye-Scherrer equation.[1]

$$D = K\lambda / \beta \cos\theta$$

The Scherrer constant (K) was taken as 0.89, and the wavelength (λ) of the X-ray was determined by the X-ray source, which was Cu Kα radiation with a wavelength of 1.5406 Å. The FWHM (β) in radians was measured by determining the diffraction peak width at half of its maximum intensity, and the Bragg angle (θ) was obtained from the XRD pattern by locating the position of the diffraction peak.

Table S1: Crystallite size calculations of the synthesized materials

S.No	**Materials**	**Xc**	**FWHM (β) (degree)**	**D (nm)**	**Avg. Size (nm)**
1	**Co_3O_4**	18.9738	0.23126	36.39	27.318
		31.2606	0.27476	31.37	
		36.8364	0.3183	27.49	
		44.7430	0.34286	26.18	
		59.3634	0.4484	21.31	
		65.2508	0.46562	21.17	
2	**Co_3O_4/NC**	18.9460	0.20901	40.26	29.21
		31.2232	0.26118	33.00	
		36.8008	0.29217	29.94	
		44.7687	0.34176	26.27	
		59.3226	0.41889	22.81	
		65.2064	0.42878	22.98	
3	**$Pd_{2.43}/Co_3O_4$**	12.6685	0.78689	10.61	
		18.8872	0.26547	31.70	
		31.187	0.29723	28.99	
		36.7707	0.34061	25.68	

		39.6589	1.66343	5.30	20.48
		44.7528	0.38623	23.24	
		59.3185	0.50314	18.99	
		65.1937	0.50852	19.38	
4	**$Pd_{2.43}/Co_3O_4/NC$**	12.5430	0.91786	9.10	23.77
		18.9071	0.2151	39.12	
		31.1862	0.24175	35.65	
		36.7597	0.28011	31.23	
		39.4957	1.90671	4.63	
		44.7293	0.37689	23.82	
		59.3001	0.43069	22.18	
		65.1767	0.40339	24.43	

Determination of electron number

For the determination of electron number, Koutechy-Levich plots were drawn at different potentials from which electron number was calculated according to the formula given below.[2]

$$\frac{1}{j_L}=\frac{1}{j_d}+\frac{1}{j_k}$$

$$\frac{1}{j_L} = \frac{1}{B\sqrt{\omega}} + \frac{1}{j_k}$$

$$j_d = 0.62nFC_0\,(D_0)^{2/3}\,(V)^{-1/6}\omega^{1/2}$$

ECSA measurement

Electrochemical active surface area was calculated from palladium oxide layer reduction curve at potential limit of 1.4 V_{RHE} according to the following formula.[3]

$$ECSA = \frac{Q_0}{q^{\circ}}$$

$Q^0 = Charge\ contaimed\ in\ the\ CV\ curve$

$q^0 = standard\ value\ for\ Pd - based\ catalysts$

Determination of Electrochemical Surface Area (ECSA) from Pd–O Reduction

The ECSA of the synthesized catalysts was determined from cyclic voltammetry (CV) measurements recorded in Ar-saturated 0.1 M $HClO_4$ solution at a scan rate of 50 mV s^{-1}. The characteristic Pd–O reduction peak appearing during the cathodic sweep was used to quantify the ECSA of palladium.

To ensure accuracy and reproducibility, the ECSA was calculated using the following procedure:

1. **Baseline Determination**

   The capacitive background current was first established by identifying the potential regions immediately before the onset and after the completion of the Pd–O reduction process. These regions correspond to potentials where no faradaic reactions occur, and the current is primarily capacitive. A linear baseline was drawn by connecting the average current values of these two regions, representing the non-faradaic contribution beneath the Pd–O reduction peak.

2. **Integration of the Pd–O Reduction Peak**

   The area enclosed between the experimental CV curve and the constructed baseline was numerically integrated to obtain the total reduction charge (Q, in mC) associated with Pd–O to Pd^0 conversion

   Normalization and Conversion

   The integrated charge was converted to the ECSA, in $cm^2{}_{Pd}$, using the standard conversion factor of 0.420 mC cm_{Pd}^{2}, which corresponds to the charge required for monolayer reduction of Pd–O on polycrystalline Pd surfaces.[3] The obtained value was then normalized by the Pd loading (in mg) deposited on the glassy carbon electrode to yield ECSA ($cm^2\ mg_{Pd}^{-1}$). The obtained value was then converted to ($m^2\ g_{Pd}^{-1}$).

3. **Reproducibility Verification**

   Each measurement was repeated at least three times under identical conditions. The calculated ECSA values showed less than ±5 % variation, confirming the reproducibility of the method and stability of the electrode.

The high ECSA of $Pd_{2.43}$–O_x/Co_3O_4/NC ~ 13.6 $m^2\ g_{Pd}^{-1}$ can be attributed to the ultrafine dispersion of Pd nanoparticles, the presence of interstitially modified interfaces, and the porous nanostructure of the Co_3O_4/NC framework, which maximizes accessibility of active Pd sites and enhances charge transport.

References

1. Hameed, A.; Nasim, F.; Nisar, N.; Ali, H.; Qurashi, A.; Anjum, D. H.; Sohail, M.; Nadeem, M. A., Heterostructure NiCo-Alloy Nanosheet Embedded Ceria Nanorods: A Highly Efficient Bifunctional Electrocatalyst toward Oxygen Evolution Reaction and Oxygen Reduction Reaction. *Energy & Fuels* **2023,** *37* (22), 17605-17615.
2. Khan, I. A.; Qian, Y.; Badshah, A.; Nadeem, M. A.; Zhao, D., Highly porous carbon derived from MOF-5 as a support of ORR electrocatalysts for fuel cells. *ACS Appl. Mater. Interfaces* **2016,** *8* (27), 17268-17275.
3. Nasim, F.; Ali, H.; Nadeem, M. A., The pronounced effect of cobalt oxide on the electrocatalytic activity of palladium nanoparticles anchored on CoOx/NC towards the ORR with increased MA and ECSA. *Mater. Adv.* **2023,** *4* (2), 578-585.