Supplementary information

Pronounced effect of cobalt oxide on the electrocatalytic activity of palladium nanoparticles anchored on CoOx/NC towards ORR with increased MA and ECSA

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.¹

 $\frac{1}{j} = \frac{1}{jd} + \frac{1}{jk}$

 $\frac{1}{j} = \frac{1}{B\sqrt{W}} + \frac{1}{jk}$

$$jd = 0.62nFC_0 (D_0)^{2/3} (V)^{-1/6}$$

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.²

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

 $Q^0 = Charge \text{ contaimed in the CV curve}$ $q^0 = standard \text{ value for } Pd - based \text{ catalysts}$



Figure S1. XRD pattern of MWCNTs and Pd@MWCNTs



Figure S2. HRTEM image of CoOx/NC at 10nm





Figure S3. EDX analysis of Pd@CoOx/NC1

Figure S4. XPS spectrum of CoOx/NC (a) Co 2p (b) N 1s (c) O 1s (d) C $1s^3$



Figure S5. (a) K-L plot of Pd@CoOx/NC1 in 0.1M KOH (b) comparison of E_{onset} of the synthesized catalysts with 20 wt% Pt/C in 0.1M KOH (c) comparison of j_m of the synthesized catalysts with 20 wt% Pt/C in 0.1M KOH



Figure S6. (a) K-L plot of Pd@CoOx/NC1 in 0.1M HClO₄ (b) comparison of E_{onset} of the synthesized catalysts with 20 wt% Pt/C in 0.1M HClO₄ (c) comparison of j_m of the synthesized catalysts with 20 wt% Pt/C in 0.1M HClO₄



Figure S7. (b) ORR electrocatlytic performance of 20 wt% Pt/C in the presence of SO_3^{-2} , NO_3^{-1} , HPO₄⁻² anions in O₂ saturated 0.1M KOH at 10 mVs⁻¹ (b) LSV polarization curve of 20 wt% Pt/C in 0.1 M HClO₄ at 10 mV s⁻¹ (c) Pt-O layer reduction curve of 20 wt% Pt/C at 1.4 V_{RHE} in 0.1 M HClO₄ at a scan rate of 50 mV s⁻¹ in Ar saturated environment

Catalyst	Poisonous specie	$E_{onset}(V_{RHE})$		$E_{1/2}(V_{RHE})$		j (mA cm ⁻²)	
	50 mM	before	after	before	after	before	after
		addition	addition	addition	addition	addition	addition
Pd@CoOx/NC1	SO ₃ -2	1.07	1.06	0.95	0.941	6.65	6.19
	NO ₃ -1	1.07	1.06	0.95	0.948	6.65	6.27
	HPO ₄ -2	1.07	1.06	0.95	0.945	6.65	6.23
20 wt% Pt/C	SO ₃ -2	0.99	0.96	0.865	0.679	6.08	2.25
	NO ₃ -1	0.99	0.99	0.865	0.854	6.08	5.72
	HPO ₄ -2	0.99	0.99	0.865	0.856	6.08	5.78

Table S1. ORR evaluating parameters of synthesized catalysts in the presence of toxic species

References

- 1. I. A. Khan, Y. Qian, A. Badshah, M. A. Nadeem, and D. Zhao, ACS Appl. Mater. Interfaces, 2016, 8 (27), 17268-17275.
- 2. L.-I, Fang, Q. Tao, M.-f. Li, L.-w. Liao, D. Chen, and Y.-x. Chen, Chinese J. Chem. Phys., 2010, 23 (5),543-548.
- I. Khan, F. Nasim, M. Choucair, s. Ullah, A. Badshah and M. Nadeem, RSC Adv. 2016, 6 (2), 1129-1135.