Supporting Information

Single Atoms Anchored on Cobalt-based Catalysts Derived from Hydrogel Containing Phthalocyanine towards the Oxygen Reduction Reaction

Yuanyuan Fu,[†] Dawei Xu,[†] Yefei Wang,[†] Xuhui Li,[†] Zhengbo Chen,^{*, †} Kai Li,[†]

Zhongfeng Li,[†] Lirong Zheng, [‡] Xia Zuo.^{*,†}

[†]Department of Chemistry, Capital Normal University, Beijing, 100048, China

[‡]Dr. L. Zheng Department Beijing Synchrotron Radiation Facility Institute of High

Energy Physics, Chinese Academy of Sciences Beijing 100049 (P. R. China)

E-mail: czb979216@sina.com, zuoxia@mail.cnu.edu.cn

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Table	S1 .	Detailed	data	of	electrocatalytic	properties	for	the	all	as-prepared	samples
compa	red	with 20%	o Pt/C								

Catalysts	Eonset	E _{1/2}	J	Tafel plots
	(V vs. RHE)	(V vs.	$(mA cm^{-2})$	(mV dec ⁻¹)
		RHE)		
CoO _X /Co-N-C (700)	0.84	0.71	2.23	97.5
CoO _X /Co-N-C (800)	0.95	0.88	4.81	61.7
CoO _X /Co-N-C (900)	0.91	0.83	4.74	69.5
Co-N-C (700)	0.83	0.67	1.72	111.4
Co-N-C (800)	0.90	0.82	2.92	74.8
Co-N-C (900)	0.89	0.81	2.82	79.8
20% Pt/C	0.89	0.85	5.40	88.3

Table S2. Comparison of the ORR electrocatalytic data in 0.1 M KOH with catalysts

 using phthalocyanine as precursor reported previously.

Catalysts	E _{onset}	E _{1/2}	n	Tafel	references
	(V vs.	(V vs.		plots	
	RHE)	RHE)		(mV	
				dec ⁻¹)	
CoO _X /Co-N-C	0.95	0.88	3.97	61.7	This work
Co@G/N-GCNs	0.95	0.86	3.96	69.66	(1)
PcCu-O8-Co/CNT	-	0.83	3.93	≈60	(2)
FePcZnPor-CMP	0.936	0.866	≈4	33.3	(3)
FeCoPc-C	-	0.85	≈4	72	(4)
HS-Phth-Fe-900	0.964	0.823	3.86	-	(5)
SAFe-NDC-H	-	0.86	≈3.9	61.0	(6)
Cu-N ₄ -C	-	0.85	3.95	≈48	(7)
CAN-Pc(Fe/Co)	1.04	0.84	3.94	54	(8)
UiO-66-NO ₂ @CoCNT	-	0.86	3.90	-	(9)

Sample		Elec	trocataly	Conclusion		
	Hypothetical	Eonset	E _{1/2}	J	Tafel	
	synergistic effect	(V vs.	(V vs.	(mA	plots	
		RHE)	RHE)	<i>cm</i> ⁻²)	(mV	
					dec ⁻¹)	
CoO _X /Co-N-C	CoOx and Co	0.84	0.71	2.23	97.5	Poor
(700)	nanoparticles					
Co-N-C (900)	Co nanoparticles	0.89	0.81	2.82	79.8	Poor
	and single Co					
	atoms					
CoO _X /Co-N-C	CoOx	0.95	0.88	4.81	61.7	Excellent
(800)	nanoparticles and					(Better than 20%
	single Co atoms					Pt / C)
CoO _X /Co-N-C	CoOx& Co	0.91	0.83	4.74	69.5	Good
(900)	nanoparticles and					(Worse than 20%
	single Co atoms					Pt / C)

 Table S3. The explanation of the synergistic effect of different species.

We attribute the excellent catalytic performance to the following speculations:

- If we assume that the synergistic effect of CoOx and Co nanoparticles play a dominate role in ORR, it is easy to deduce <u>CoOx/Co-N-C (700)</u> should have the best performance. Because XRD confirms the existence of CoOx and Co nanoparticles, but there is no peak corresponding to Co-N in XANES.
- 2) If we assume that the synergistic effect of single Co atoms and Co nanoparticles play a dominate role in ORR, it is easy to deduce <u>Co-N-C (900)</u> should have the best performance. Because XRD confirms the existence of CoOx and Co nanoparticles and there is a peak corresponding to Co-N in XANES.
- 3) If we assume that the synergistic effect of single Co atoms and CoOX nanoparticles play a dominate role in ORR, it is easy to deduce <u>CoOx/Co-N-C</u> (800) should have the best performance. Because the HAADF-STEM, XANES and XPS results ironclad proves that the Co atoms anchor on the surface of the carbon layer. And XRD confirms the existence of CoOx.
- 4) If we assume that the synergistic effect of single Co atoms, CoO_X and Co nanoparticles make the contribution to the ORR in common, it is easy to deduce <u>CoOx/Co-N-C (900)</u> should have the best performance. Because the XRD and TEM proved that as the pyrolysis temperature increased, more crystalline CoO_X and Co nanoparticles appeared in the CoOx/Co-N-C (900) than CoOx/Co-N-C (800).

Obviously, it is only possible to attribute the good electrocatalytic performance to the synergistic effect of CoOx nanoparticles and single Co atom.



Figure S7. The i-t chronoamperometric curves of stability evaluation for Co/N/C (800) in O_2 -saturated 0.5 M H₂SO4 electrolyte with a rotation rate of 1600 rpm for 20000 s.

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