## **Supporting information**

## Unification of Catalytic Oxygen Reduction and Hydrogen Evolution Reactions: Highly Dispersive Co Nanoparticles Encapsulated inside Co and Nitrogen co-doped Carbon

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## **Experimental Section**

1.1. Synthesis of free Co(OH) (CO3)<sub>0.5</sub>.0.11H<sub>2</sub>O.

As described in ref [1], ethylene glycol (15-20 mL), concentrated NH<sub>3</sub>·H<sub>2</sub>O (10-15mL, 28 wt.%), 1 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (1-2 mL), 1 M Co(NO<sub>3</sub>)<sub>2</sub> aqueous solution (4-6 mL) were mixed step by step under vigorous stirring. After 2h vigorous stirring, the precursor was transferred into a Teflon-lined stainless steel autoclave; a thermal treatment was performed for the Teflon-liner in an electric oven at 170°C for 16h. After washed several times, the as-synthesized samples were then dried in a vacuum oven at 40°C overnight.

1.2. Synthesis of free Co(OH) (CO3)<sub>0.5</sub>.0.11H<sub>2</sub>O@PG.

Co(OH) (CO3)<sub>0.5</sub>.0.11H<sub>2</sub>O (100-300 mg) were ultrasonically mixed with glucose in D.I. water to form a homogeneous solution after 15 min. The above solution was introduced into a Teflon-lined autoclave and sealed tightly. Then the liner was heated in an electric oven at 180 °C for 6 h. After washed several times, the as-synthesized samples were then dried in a vacuum oven at 40°C overnight.

1.3. Synthesis of free Co@Co-N-C catalysts.

The as-prepared Co(OH) (CO3)<sub>0.5</sub>.0.11H<sub>2</sub>O@PG were mixed with melamine with mass ratio (1:5) by grind. After that, the mixed samples were loaded into the tube furnace and calcined in Ar atmosphere at 800 °C for 120 min, respectively.

1.3. Synthesis of free Co@Co-N-C-AT catalyst.

The as-prepared Co@Co-N-C catalyst was boiling in 0.5M sulfuric acid at 80 °C for 4h to acquire Co@Co-N-C-AT catalyst.

1.5. Synthesis of free Co@NCNT catalysts.

 $CoCl_2$  were mixed with melamine by grind with mass ratio (1:10). After that, the mixed samples were loaded into the tube furnace and calcined in Ar atmosphere at 900 °C for 30 min.

1.6. Characterization of catalysts

The morphology and structure of Co(OH) (CO3)<sub>0.5</sub>.0.11H<sub>2</sub>O, Co(OH) (CO3)<sub>0.5</sub>.0.11H<sub>2</sub>O@PG and Co@Co-N-C samples were observed under field emission scanning electron microscopy (FE-SEM, Hitachi S-4700) and transmission electron microscopy (TEM, Zeiss LIBRA 200 FETEM). The crystal structures of Co@Co-N-C catalysts were confirmed using the automated X-ray diffraction equipment (XRD, Rigaku D/MaXIIIA, Japan). TGA (NETZSCH TGASTA 409 PC analyzer) was carried out to investigate Co content. XPS was acquired using a Kratos XSAM800 spectrometer equipped with a monochromatic AI X-ray source (AI KR, 1.4866 keV). Raman spectrum was carried out using LabRam HR evolution, excited by a 532nm laser.

1.7. Electrochemical activity tests

Electrochemical measurements: All electrochemical experiments were performed in a standard three-electrode cell at room temperature on a Parstat 2273 potentiostat/galvanostat workstation assembled with a model 636 rotational system (AMETEK) at room temperature. The cell is consisting of a glassy carbon working electrode (GC electrode, 3 mm in diameter, PINE: AFE3T050GC), an Ag/AgCI (saturated KCI) reference electrode, and a platinum foil counter electrode. All potentials in this study, however, are given relative to the reversible hydrogen electrode (RHE). The working electrodes were prepared by applying catalyst ink onto glassy carbon (GC) disk electrodes. In brief, the electrocatalyst was dispersed in ethanol and ultrasonicated for 15 minutes to form a uniform catalyst ink. Well-dispersed catalyst ink was applied onto a pre-polished GC disk. After drying at room temperature, a drop of 0.05 wt. % Nafion solution was applied onto the surface of the catalyst layer to form a thin protective film.

The catalysts were characterized by a cyclic voltammetry (CV) test at room temperature in 0.1 M aqueous KOH. The linear sweep voltammetry(LSV) was obtained in an O<sub>2</sub>-saturated 0.1 M KOH electrolyte at a scan rate of 10 mV s<sup>-1</sup> in the potential range 0 to 1.2 V (ORR) or -0.8-0.1V (HER) in 0.1 M aqueous KOH. In the ORR experiment, the electrolyte was bubbled with high-purity  $O_2$  for 30 min before each test and maintained under atmospheric conditions with

constant  $O_2$  gas flow during the measurements.

The kinetic parameters can be analyzed on the basis of the Koutecky-Levich (K-T) equations:

 $1/J=1/J_{\rm k}+1/B\omega^2$ ; where  $B=0.62nFv^{-1/6} C_{\rm o} (D_{\rm o})^{2/3}$ 

where J is the measured current density,  $J_k$  is the kinetic current density,  $\omega$  is the angular velocity, n is the number of electrons transferred, F is the Faraday constant, v is the kinematic viscosity,  $C_o$  is the bulk concentration of  $O_2$ , and  $D_o$  is the diffusion coefficient of  $O_2$ .



Figure S1 TEM and HRTEM images of Co@Co-N-C catalyst.



Figure S2 a) HER LSVs for Co@Co-N-C, Co@NCNT catalyst in 0.1 M KOH with a sweep rate of 10 mV s<sup>-1</sup> at 1600 rpm; b) ORR LSVs for Co@Co-N-C, Co@NCNT catalyst in O<sub>2</sub>-saturated 0.1 M KOH with a sweep rate of 10 mV s<sup>-1</sup> at 1600 rpm. The loading of Co@Co-N-C and Co@NCNT catalyst is 0.6 mg cm<sup>-2</sup>.



Figure S3 SEM images of Co@NCNT.



Figure S4 Polarization curves illustrating (a) methanol tolerance and (b) ORR durability of the Co@Co-N-C catalyst. Methanol tolerance was examined in the oxygen saturated 0.1 M KOH containing methanol (1M). The loading of Co@Co-N-C catalyst is 0.6 mg cm<sup>-2</sup>.



Figure S5 Polarization curves illustrating HER durability of the Co@Co-N-C catalyst. The loading of Co@Co-N-C catalyst is 0.6 mg cm<sup>-2</sup>.



Figure S6 The plot of current percentage ( $j / j_{initial}$ ) vs. time at a constant potential of -0.3V (vs.RHE)



Figure S7 a, b) CVs for Co@Co-N-C, and Co@Co-N-C-AT in N2- and O2-saturated 0.1 M KOH; c, d) the corresponding ORR LSVs and HER LSVs in an O2-saturated 0.1 M KOH at 1600 rpm.



Figure S8 a) ORR LSVs for Co@Co-N-C-AT, Co@NCNT catalyst in 0.1 M KOH with a sweep rate of 10 mV s<sup>-1</sup> at 1600 rpm; b) HER LSVs for Co@Co-N-C-AT, Co@NCNT catalyst in O<sub>2</sub>-saturated 0.1 M KOH with a sweep rate of 10 mV s<sup>-1</sup> at 1600 rpm. The loading of Co@Co-N-C-AT and Co@NCNT catalyst is 0.6 mg cm<sup>-2</sup>.



Figure S9 TGA of Co@Co-N-C catalyst.

The TGA result reveals that the mass fraction of cobalt in Co@Co-N-C is about 42.31 wt. % (Fig. S2), which is much higher than that calculated from XPS (ca. 5.69 wt. % converted from the 0.76 at. % of Co, Table. S1-S2), that means most of the cobalt NPs of Co@Co-N-C are entirely encapsulated within graphitic carbon nanoshells.



Figure S10 K–L plots for Co@Co-N-C catalyst in 0.1 M KOH with a sweep rate of 10 mV s<sup>-1</sup>, respectively; the inset shows LSVs at different rotating speeds for Co@Co-N-C catalyst in 0.1 M KOH.

The average electron transfer number (n) of Co@Co-N-C was calculated to be 3.77 in 0.1 M KOH (Fig. S8) from the slopes of K-L plots, suggesting an apparent quasi-four-electron process on Co@Co-N-C, which is desirable for achieving high-efficiency ORR activity.

Sample	loading	Half-wave potential	ref	
		-0.18V (vs. Ag/AgCl)		
CoP-CMP800	0.6 mgcm <sup>-2</sup>	(10mV negative than	Adv. Mater. 2014, 26, 1450–1455	
		that of Pt/C)	, <u> </u>	
Co10–NMCV	0.15mgcm <sup>-2</sup>	(20mV negative than	L Mater, Chem, A 2014, 2, 11672–	
		that of Pt/C)	11682	
	0 /58 mg	25 mV negative than		
Co/N/C	cm <sup>-2</sup>	that of Pt/C	Sci Rep 2014, 4, 4386	
	CIII	2ml/ negative than		
Co@Co-N-C	0.6	that of Dt/C	This work	
	0.6mgcm -			
		0.8/9V (VS. RHE)		
Co/CoO/CoFe2O4/	0.28mgcm <sup>-2</sup>	50 mV negative than	Nanoscale 2014 6 203	
G		that of Pt/C	Nalloscale, 2014, 0, 205	
Fe-N/C-800	0.1mgcm <sup>-2</sup>	9 mV negative than	J. Am. Chem. Soc. 2014, 136,	
		that of Pt/C	11027-11033	
Fe3C/NG-800	0.4mgcm <sup>-2</sup>	0.86V (vs. RHE)	Adv.Mater.2015,	
			DOI:10.1002/adma.201500262	
Fe3C/C-800	0.6 mgcm <sup>-2</sup>		Angew. Chem. Int. Ed. 2014, 53, 3675	
		0.83 V (vs. RHE)	- 3679	
Fe-N-CNT-OPC	0.08 mgcm <sup>-2</sup>	Similar as Pt/C	Adv. Mater. 2014, 26, 6074–6079	

Table S1 Comparison of ORR performance in alkaline media for Co@Co-N-C with other non-noble-metal ORR electrocatalysts.

Sample	loading	Overpotential@10mAcm <sup>-2</sup>	ref	
Ni-Mo alloy/Ti foil	1mgcm <sup>-2</sup>	80	ACS Catal. 2013, 3, 166–169	
Ni@NC	0.4mgcm <sup>-2</sup>	177mV (IR-correction) R=40Ω	Adv. Energy Mater. 2014, 1401660	
FeP NAs/CC	1.5mgcm <sup>-2</sup>	218mV (IR-correction)	ACS Catal. 2014, 4, 4065–4069	
CoP/CC	١١	209mV	J. Am. Chem. Soc. 2014, 136, 7587–7590	
Co@Co-N-C	0.6mgcm <sup>-2</sup>	314mV	This work	
Co@NCNT	0.28mgcm <sup>-</sup> 2	370mV	Angew. Chem. 2014, 126, 4461 –4465	
N,P-graphen	0.25mgcm <sup>-</sup> 2	585mV@5mAcm <sup>-2</sup>	ACS Nano, 2014, 8, 5290	
C3N4@NG	0.1mgcm <sup>-2</sup>	Not given (~600 mV @6mAcm <sup>-2</sup> by estimating)	Nat. Commun., 2014, 5, 3783	
Со	١	Not given (~350 mV @5mAcm <sup>-2</sup> by estimating)	Energy Environ. Sci., 2013,	
Ni	Ni \ Ni \ estimating)		6, 1509–1512	
amorphous MoS2/FTO	\\	540mV	Chem. Sci., 2011, 2, 1262	

Table S2 Comparison of HER performance in alkaline media for Co@Co-N-C with other nonnoble-metal HER electrocatalysts ("\" polycrystalline disks; "\\" catalysts directly grown on current collectors)

Table S3 Elements content from XPS spectrum for Co@Co-N-C and Co@Co-N-C-AT catalysts.

	Co@Co-N-C	Co@Co-N-C-AT
C(wt.%)	78.87	84.18
Co(wt.%)	3.49	-
N(wt.%)	5.69	4.88
O(wt.%)	11.95	10.94

Table S4 The content of all kinds of N from N1s XPS spectrum for Co@Co-N-C and Co@Co-N-C-AT catalysts.

Sample	Pridinic N &Co-N	Pyrrolic N	Quaternary N	Oxidized N	Total N
Jampie	(%)	(%)	(%)	(%)	(%)
Co@Co-N-C	49.57	35.22	1.12	14.1	5.21
Co@Co-N-C-AT	42.91	46.85	2.13	8.11	5.69

Reference

1 Y. Wang, H. J. Zhang, L. Lu, L. P. Stubbs, C. C. Wong and J. Y. Lin, Acs Nano, 2010, 4, 4753-4761.