Supporting Information

Diethylenetriamine (DETA) - Assisted Anchoring of Co_3O_4 Nanorods on Carbon Nanotubes as Efficient Electrocatalyst for Oxygen Evolution Reaction

Yu-Xia Zhang, Xin Guo, Xue Zhai, Yi-Ming Yan,** and Ke-Ning Sun *

Beijing Key Laboratory for Chemical Power Source and Green Catalysis, School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing, 100081,People's Republic of China.

Corresponding Authors.

Fax: +86-10-68918696;

[*] E-mail: bitkeningsun@163.com

[**]E-mail: bityanyiming@163.com ;

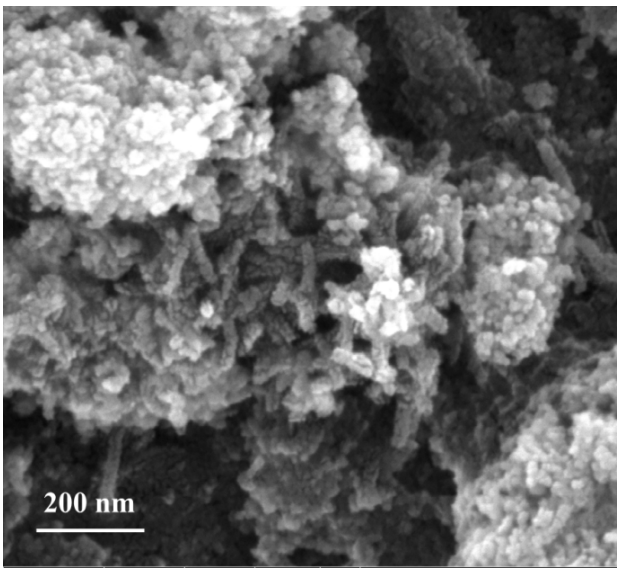

Figure S1 SEM image of the Co_3O_4- MWCNT hybrid synthesized with raw MWCNT.

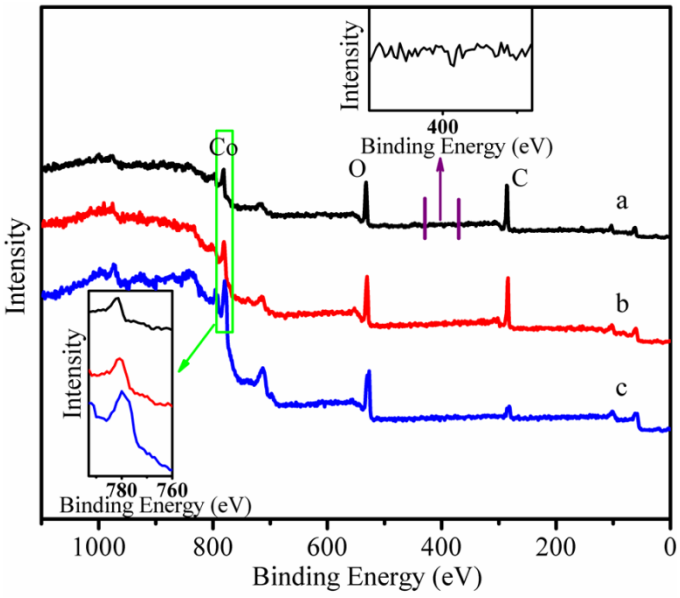

Figure S2 XPS spectrums of the Co_3O_4@MWCNT (black line a), Co_3O_4-MWCNT (red line b) and Co_3O_4 (blue line c). The inset of line a for Co_3O_4@MWCNT around 400 eV shows high resolution of the N region between two purple lines, and no significant signals are found in the N1s region, while another inset is the enlarged figure around 780 eV.

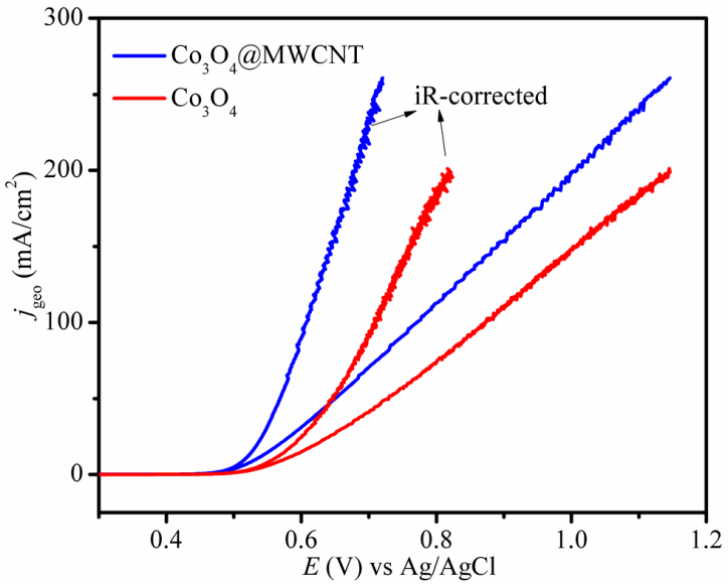

Figure S3 LSVs for modified GC electrodes comprising the Co_3O_4 nanorods and nanocubes, respectively, with and without iR correction. 1M KOH, $R_{Co3O4@MWCNT}$ = 6.2 Ω, R_{Co3O4} =6.6 Ω.

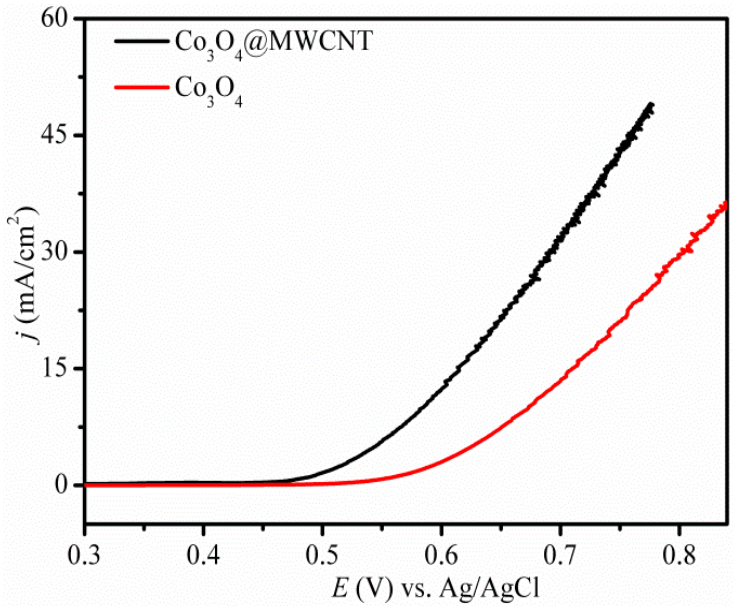

Figure S4 Linear sweep voltammetry curves (LSVs) obtained with RDE modified with Co_3O_4@MWCNT hybrid and Co_3O_4 respectively (after IR compensation) in 0.1 M KOH, Experimental conditions: the *j* (mA cm^2) is normalized by geometric area of the glassy carbon electrode, T: 298 K, glassy carbon electrodes of RDE at 2000 rpm, Scan rate: 1 mV s^{-1}.

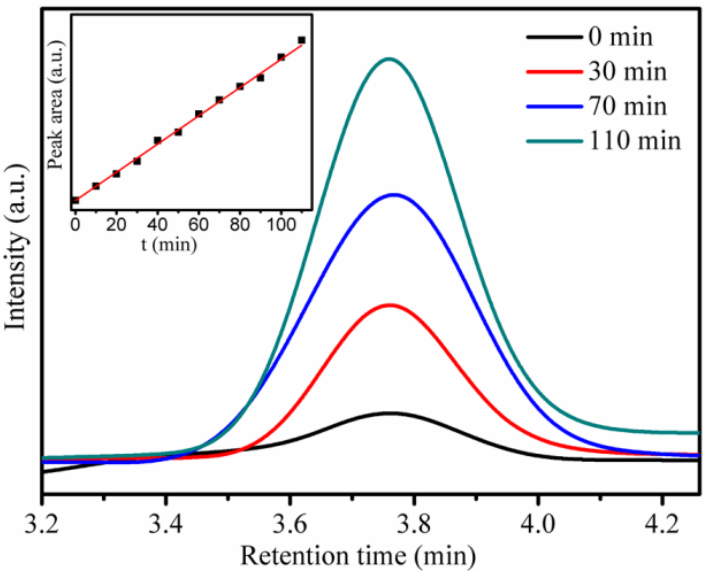

Figure S5 Gas chromatograph of oxygen obtained by ITO modified with Co_3O_4@MWCNT under electrolysis at 0.8 V vs. Ag/AgCl, the inset is the oxygen integral areas as a function of time.

Table S1. TOF of Co oxide materials at different overpotential reported in the literature (1M KOH, pH= 14)

Catalyst material	Overpotential η (mV)	TOF (s^{-1})	Catalyst loading (mg/cm^{-2})	Reference
Co_3O_4	300	0. 0075	0.05	This work
	500	0.433	0.05	
Co_3O_4@MWCNT	300	0.0533	0.05	
	500	1.91	0.05	
Co_3O_4	236	~0.007	3.0	[1]
Co_3O_4 / SWNT	500	~0.25	0.05	[2]
Co_3O_4 nanocubes	388	0.093	1.0	[3]
Co_3O_4 nanoparticles	507	0.04	1.0	[4]
Co_3O_4 /N-rmGO	310	0.003	1.0	[5]

Calculations for Turnover Frequencies (TOF)

In this work, the TOF is calculated on the basis of all Co atoms rather than the surface Co. TOFs were calculated by converting the measured charges to μ moles of oxygen using Faraday's Law, according to the formula TOF = n_{O2}/n_{Co} (n_{O2}=Q s^{-1}/4F= i/4F=j A/4F, Faraday constant F = 9.6×10^4 C mol^{-1}, A=2.475×10^{-5} m^2, j is read off directly from LSV curve which is after IR compensation, and the solution resistance was measured to be 4.9 Ω). According to the ICP results the Co content in Co_3O_4@MWCNT is 8.708 umol mg^{-1}, using 0.012 mg Co_3O_4@MWCNT offers 10.077e^{-8} mol Co atoms (8.708 umol mg^{-1} × 0.012 mg).

Overpotential (η) was calculated according to the equation: $\eta = E - E°$, where E is read off directly from LSV curve which is after IR compensation, $E°$ is the pH-dependent standard potential for H_2O oxidation, $E°$ (V) vs. Ag/AgCl (3 mol L^{-1} KCl) = 1.033 – 0.0591 × pH.

References

(1) R. N. Singh, D. Mishra, A. S. K. Sinha and A. Singh, *Electrochem. Commun.,* 2007, **9**, 1369-1373.

(2) J. Wu, Y. Xue, X. Yan, W. Yan, Q. Cheng and Y. Xie, *Nano Res.,* 2012, **5**, 521-530.

(3) A. J. Esswein, M. J. McMurdo, P. N. Ross, A. T. Bell and T. D. Tilley, *J. Phys. Chem. C,* 2009, **113**, 15068–15072.

(4) N. H. Chou, P. N. Ross, A. T. Bell and T. D. Tilley, *ChemSusChem* 2011, **4**, 1566-1569.

(5) Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat. Mater.,* 2011, **10**, 780-786.