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Nitrogen-doped graphene/carbon nanotube/Co_3O_4 hybrids: One-step synthesis and superior electrocatalytic activity for oxygen reduction reaction

Hengyi Lu,[a] Yunpeng Huang,[a] Jiajie Yan,[a] Wei Fan*[b] and Tianxi Liu*[ab]

Electronic Supplementary Information (ESI)

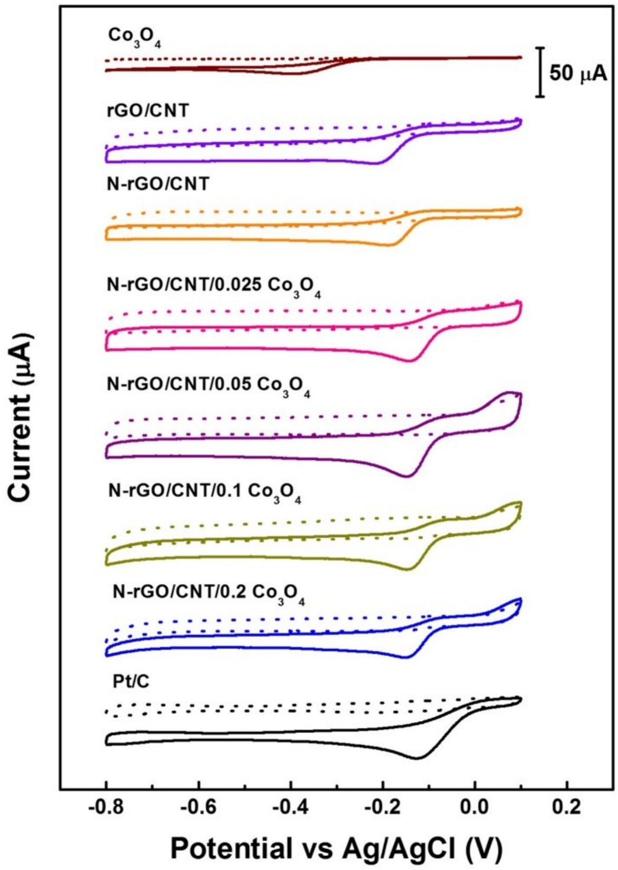

Fig. S1 CVs of pure Co_3O_4, rGO/CNT, N-rGO/CNT, N-rGO/CNT/Co_3O_4 hybrids (with different Co_3O_4 contents) and commercial Pt/C in N_2 (dot line) and O_2 (solid line) saturated 0.1 M KOH.

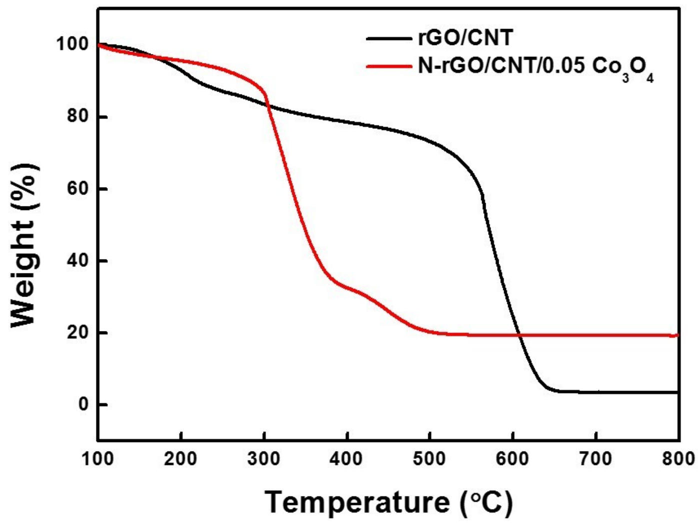

Fig. S2 TGA curves of N-rGO/CNT and N-rGO/CNT/0.05 Co_3O_4 hybrids in air.

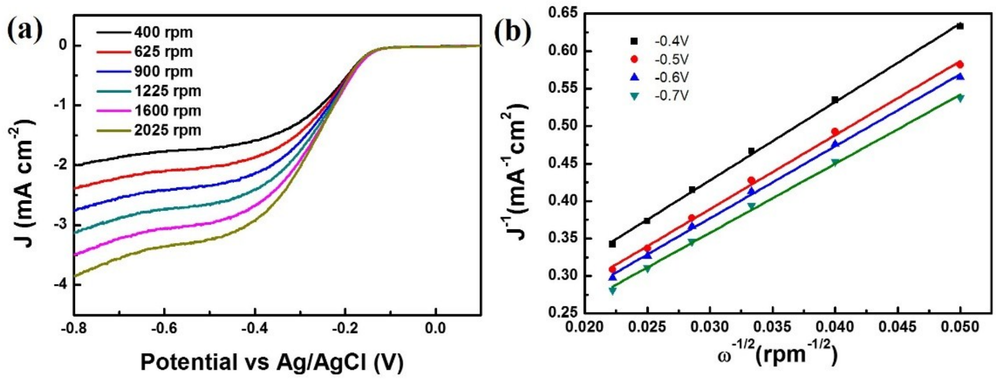

Fig. S3 (a) RDE voltammograms of rGO/CNT hybrid in O_2 saturated 0.1 M KOH at rotation rates from 400 rpm to 2025 rpm. (b) K-L plots of the rGO/CNT hybrid.

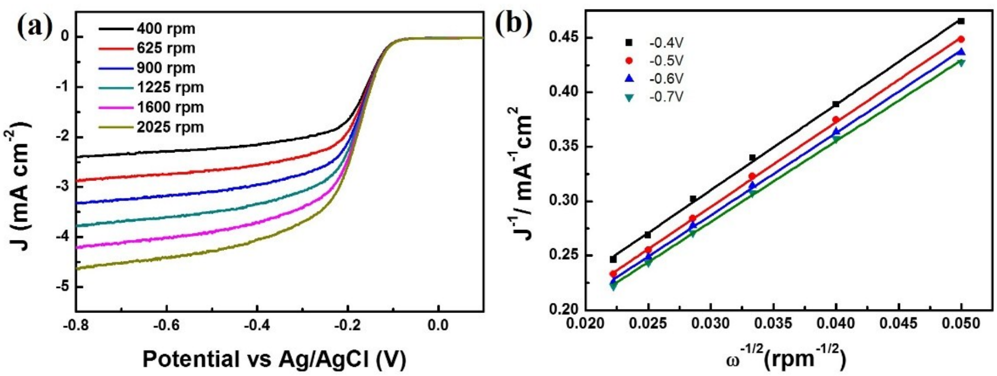

Fig. S4 (a) RDE voltammograms of N-rGO/CNT hybrid in O_2 saturated 0.1 M KOH at rotation rates from 400 rpm to 2025 rpm. (b) K-L plots of the N-rGO/CNT hybrid.

Table S1. Comparison of ORR catalytic performance between N-rGO/CNT/Co_3O_4 hybrid and previous reports.

Catalyst	Synthesis methods	Reference electrode	Peak Potential (V)	Onset Potential (V)	Electron Transfer Number	Ref.
N-rGO/CNT/ Co_3O_4	One step hydrothermal reaction	Ag/AgCl	-0.15	-0.09	3.98 at -0.4 to -0.7 V	This Work
Nitrogen-doped Graphene	CVD	Ag/AgCl	N.A.	~ -0.2	3.6 at -0.4 to -0.8 V	1
Nitrogen-doped graphene	High temperature treatment	Ag/AgCl	-0.32	-0.18	3.6 at -1.0 V 4.0 at -0.5 V	2
Nitrogen-doped graphene	High temperature treatment	Ag/AgCl	N.A.	~-0.1	3.4 - 3.6 at -0.3 to -0.8 V	3
Sulfur-doped graphene	High temperature treatment	Ag/AgCl	-0.32	N.A.	3.82 at -0.3 V	4
Nitrogen, sulfur-doped mesoporous graphene	High temperature treatment	Ag/AgCl	-0.24	-0.06	3.3 - 3.6 at -0.4 to -0.8 V	5
Vertically aligned nitrogen-containing CNT	pyrolysis of iron(II) phthalocyanine	Ag/AgCl	-0.15	-0.1	3.9 at -0.6 V	6
Nitrogen-doped graphene/CNT	Pre-oxidation followed by hydrothermal reaction	Ag/AgCl	~-0.3	-0.14	3.3 - 3.7 at -0.4 to -0.7 V	7
Graphene/ CNT	Hydrothermal reaction	Ag/AgCl	-0.22	N.A.	3.86 at -0.35 V	8
Nitrogen-doped graphene/ CNT/Co_3O_4 paper	Two step hydrothermal method grow Co_3O_4 on	Ag/AgCl	~-0.2	-0.06	3.97 at -0.7 V	9

	rGO/CNT paper					
Nitrogen-doped graphene/ Co_3O_4	Two step method	RHE	N.A.	~0.88	4.0 at 0.6 to 0.75 V	10
CoO/nitrogen-doped CNT	Two step method	RHE	0.86	0.93	3.9 at 0.4 to 0.9 V	11
Co_3O_4/nitrogen-doped mesoporous graphene	Two step method	RHE	0.82	0.93	~ 4 at 0.2 to 0.7 V	12
Nitrogen-doped SWCNT/ graphene	CVD	RHE	N.A.	0.88	3.3 at 0.47 V	13
Graphene-Co_3O_4	High temperature treatment and hydrotherm-al reaction	SCE	-0.23	-0.11	4 at -0.6 V	14
Nitrogen-doped CNT	High temperature treatment	Hg/HgO	~-0.25	N.A.	3.0 (the potential was not specified)	15
Co_3O_4 nano-octahedrons/ graphene	Reaction in solution and high temperature treatment	Hg/HgO	N.A.	-0.04	~3.8 at -0.3 to -0.5 V	16

References:

1 L. T. Qu, Y. Liu, J. B. Baek and L. M. Dai, *ACS Nano*, 2010, **4**, 1321-1326.

2 Z. Y. Lin, G. Waller, Y. Liu, M. L. Liu and C. P. Wong, *Adv. Energy Mater.*, 2012, **2**, 884-888.

3 Z. H. Sheng, L. Shao, J. J. Chen, W. J. Bao, F. B. Wang and X. H. Xia, *ACS Nano*, 2011, **5**, 4350-4358.

4 Z. Yang, Z. Yao, G. Li, G. Y. Fang, H. G. Nie, Z. Liu, X. M. Zhou, X. A. Chen and S. M. Huang,

ACS Nano, 2012, **6**, 205-211.
5 J. Liang, Y. Jiao, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2012, **51**, 11496-11500.
6 K. P. Gong, F. Du, Z. H. Xia, M. Durstock and L. M. Dai, *Science*, 2009, **323**, 760-764.
7 P. Chen, T. Y. Xiao, Y. H. Qian, S. S. Li and S. H. Yu, *Adv. Mater.*, 2013, **25**, 3192-3196.
8 W. Wei, Y. Tao, W. Lv, F. Y. Su, L. Ke, J. Li, D. W. Wang, B. H. Li, F. Y. Kang and Q. H. Yang, *Sci. Rep.*, 2014, **4**, 6289.
9 S. S. Li, H. P. Cong, P. Wang and S. H. Yu, *Nanoscale*, 2014, **6**, 7534-7541.
10 Y. Y. Liang, Y. G. Li, H. L. Wang, J. G. Zhou, J. Wang, T. Regier and H. J. Dai, *Nat. Mater.*, 2011, **10**, 780-786.
11 Y. Y. Liang, H. L. Wang, P. Diao, W. Chang, G. S. Hong, Y. G. Li, M. Gong, L. M. Xie, J. G. Zhou, J. Wang, T. Z. Regier, F. Wei and H. J. Dai, *J. Am. Chem. Soc.*, 2012, **134**, 15849-15857.
12 J. J. Xiao, X. J. Bian, L. Liao, S. Zhang, C. Ji and B. H. Liu, *ACS Appl. Mater. Inter.*, 2014, **6**, 17654-17660.
13 G. L. Tian, M. Q. Zhao, D. S. Yu, X. Y. Kong, J. Q. Huang, Q. Zhang and F. Wei, *Small*, 2014, **10**, 2251-2259.
14 C. W. Sun, F. Li, C. Ma, Y. Wang, Y. L. Ren, W. Yang, Z. H. Ma, J. Q. Li, Y. J. Chen, Y. Kim and L. Q. Chen, *J. Mater. Chem. A*, 2014, **2**, 7188-7196.
15 T. Sharifi, G. Z. Hu, X. E. Jia and T. Wågberg, *ACS Nano*, 2012, **6**, 8904-8912.
16 J. W. Xiao, Q. Kuang, S. H. Yang, F. Xiao, S. Wang and L. Guo, *Sci. Rep.*, 2013, **3**, 2300.