Electronic supplementary information (ESI)

Nanoconfined nitrogen-doped carbon-coated MnO nanoparticles in graphene enabling high performance for lithium-ion batteries and oxygen reduction reaction

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Chemicals and Materials

Manganese(II) acetate (Mn(Ac)₂, Aladdin Reagent, AR), Oleylamine (Aladdin Reagent, AR), Oleic acid (Aladdin Reagent, AR), Xylene (Aladdin Reagent, AR), Cyclohexane (Aladdin Reagent, AR), Dopamine hydrochloride aqueous solution (25 wt%, Aladdin Reagent, AR), Igepal CO-520 (Aldrich), Ammonium hydroxide (28 wt%, Aladdin Reagent, AR), Graphite powders (325 mesh, Alfa Aesar, 99.8%), sulfuric acid (H₂SO₄, ≥98%, Beijing Chemical Works), Potassium permanganate (KMnO₄, Aladdin Reagent, AR), Phosphoric acid (H₃PO₄, ≥85%, Beijing Chemical Works), Hydrogen peroxide (H₂O₂, 30%, Aladdin Reagent), ethanol (≥99.7%, Beijing Chemical Works), Polyvinylidenefluoride (PVDF, DuPont Company, 99.9%), Acetylene black (Hong-xin Chemical Works), N-methyl-2-pyrrolidinone (NMP, Aladdin Reagent, AR), Separator (polypropylene film, Celgard 2400), Electrolyte for lithium ion batteries [1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) with the weight ratio of 1:1, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd], Nafion solution (5%, DuPont), Potassium hydroxide (KOH, 98%, Aladdin Reagent). All the reagents used in the experiment were of analytical grade purity and were used as received. De-ionized water with the specific resistance of 18.2 M Ω ·cm was obtained by reversed osmosis followed by ion-exchange and filtration.

Electrocatalysis measurements

For electrode preparation, the catalysts (5 mg) were dispersed in ethanol (1 mL) with adding Nafion solution (50 μ L), and sonicated for 2 h to obtain a well-dispersed ink. Catalyst ink was drop-casted onto the surface of the electrode with loading 0.2 mg cm⁻² and dried at room temperature. KOH (0.1M) aqueous solution was saturated with O₂ by bubbling oxygen for 20 min before testing.

The kinetics parameters can be analyzed with the K-L equations^[S1-S3] as following:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B \boldsymbol{w}^{1/2}}$$

Equation S1

$$B = 0.62 n F C_0 (D_0)^{2/3} n^{-1/6}$$

Equation S2

Where *j* is the measured current density, j_k is the kinetic current density, ω is the electrode rotating rate, *F* is the Faraday constant (96485 C mol⁻¹), C_0 is the bulk concentration of O₂ (1.2×10⁻⁶ mol cm⁻³), D_0 is the diffusion coefficient of O₂ (1.9×10⁻⁵ cm² s⁻¹), and *v* is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹).^[S4,S5]



Figure S1. TEM image of Mn₃O₄@PDA nanocrystals.



Figure S2. (a) Low and (b) high-magnification SEM images of GMNCs.



Figure S3. XRD patterns of Mn_3O_4 @PDA nanocrystals after annealing at 800 °C (a) and 900 °C (b).

 Mn_3O_4 is not stable in the presence of carbon under high temperature and could be transformed into different products depending on the use of temperature. The transformation process can be described as follows: ^[S6]

 $C + 2Mn_3O_4 \longrightarrow 6MnO + CO_2$

	Current			
	density	Cycle	Capacity	ref
Materials	(mA g ⁻¹)	number	(mAh g ⁻¹)	
GMNCs	50 (100)	180	994.3 (754.3)	this
		(350)		work
MnO/C nanotube	100	100	763.3	S6
MnO/C microspheres	100	50	702.2	S7
Manganese oxide/carbon yolk-				
shell nanorod	100	150	649	S 8
MnO/reduced graphene oxide	100	50	~650	S9
MnO /C composite	100	50	740	S10
Manganese oxide/carbon	50	50	597	S11
nanofibers				

 Table S1. Comparison of the capacity of present work with reported MnO/C composites.



Figure S4. (a) Discharge-charge profiles of Mn_3O_4 at 0.05 Ag⁻¹. (b) CV curves of Mn_3O_4 between 0 and 3.0 V at a potential sweep rate of 0.08 mV s⁻¹.

As shown in Figure S4a, in the first discharge curve, the first short plateau and the following sloped region may originate from the reduction of Mn_3O_4 to the intermediate composite manganese oxide phase and the formation of the SEI film on the electrode surface, respectively. The long and steady discharging plateau at ~0.3 V, followed by a gradual decrease to 0.1 V is mainly attributed to the reduction of Mn^{2+} to Mn^0 . In the first charge curve, two oxidation reactions at 1.2 and 2.5 V can be regarded as the oxidation reaction from Mn^0 to Mn^{2+} or Mn^{3+} . In the following cycles, the discharge plateau shifts to about 0.5 V, indicating that the irreversible formation of the crystalline metallic Mn and amorphous Li₂O matrix. The results are in good agreement with the CV curves in Figure S4b.



Figure S5. (a) CV curves of GMNCs between 0 and 3.0 V at a potential sweep rate of 0.08 mV s⁻¹. (b) Electrochemical impedance spectra. Nyquist plots before cycling of Mn_3O_4 and GMNCs by applying the AC voltage of 5 mV (amplitude) at frequencies from 0.1 to 700 kHz.

In order to investigate the effect of the N-doped double carbon coating, electrochemical impedance spectroscopy (EIS) measurements of Mn_3O_4 and GMNCs were performed. Both of the Nyquist plots include a depressed semicircle (at high frequency) ascribed to the charge-transfer reaction at the electrolyte/electrode interface and a linear Warburg part (at a low frequency) ascribed to the diffusion of the lithium ions in the bulk of the electrode. In comparison, the GMNCs show the smaller impedance than the bare Mn_3O_4 , which enables GMNCs with superior rate performance. The results demonstrate the important effect of carbon incorporation on increasing the electrical conductivity and reducing the charge-transfer impedance.



Figure S6. CV curves of Mn_3O_4 (a) and MnO (b) in Ar-saturated and O_2 -saturated 0.1 M KOH.

In order to show the superiority of the as-prepared GMNCs, the ORR catalytic activities of pure Mn_3O_4 and MnO are investigated. As shown in Figure S6, in an O_2 -saturated solution, well-defined cathodic peaks occurred at about 0.52 and 0.56 V, respectively, confirming their electrocatalytic activity towards ORR. But it is obvious that the GMNCs catalyst shows more positive ORR peak potential than that of pure Mn_3O_4 and MnO, highlighting the improved ORR catalytic activity.

Materials	$E_{\text{onset}}(\mathbf{V})$	$E_{\text{half}}(\mathbf{V})$	$J (\mathrm{mA \ cm^{-2}})$	п
GMNCs	0.98	0.76	-5.1	3.50
Mn ₃ O ₄	0.69	0.47	-3.0	3.30
MnO	0.73	0.58	-1.6	3.23
GNCs	0.86	0.70	-2.5	3.08
Pt/C	1.0	0.81	-4.2	4.00

Table S2. Summary of ORR catalytic performances of GMNCs, Mn_3O_4 , MnO, GNCs and Pt/C.

Herein, E_{onset} , E_{half} , J, and n represent onset potential, half-wave potential, current density and electron transfer number, respectively. It is obvious that the GMNCs catalyst shows significantly increased ORR onset potential, half-wave potential, current density and electron transfer number than that of pure Mn₃O₄, MnO catalysts, highlighting the improved ORR catalytic activity of GMNCs.



Figure S7. ORR polarization curves of Mn_3O_4 (a), MnO (c) and GNCs (e) at different rotating speeds. K-L plots of Mn_3O_4 (b), MnO (d) and GNCs (f) at different potentials.



Figure S8. Peroxide yields and electron transfer numbers of GMNCs at various potentials based on RRDE data.

To verify the ORR pathway, a rotating ring-disk electrode (RRDE) technique is carried out to monitor the formation of HO_2^- during the ORR process. Figure S8 reveals that the HO_2^- yields for GMNCs-800 is average 23.49% and the corresponding electron transfer number is calculated to average 3.53, which is well consistent with the result obtained from the Koutecky-Levich plots based on RDE measurements.

References

- [S1] S. C. M. Piana, H. A. Gasteiger, J. Electroanal. Chem. 2001, 495, 134.
- [S2] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nat. Mater.* 2011, 10, 780.
- [S3] Q. Li, S. Zhang, L. Dai, L. S. Li, J. Am. Chem. Soc. 2012, 134, 18932.
- [S4] S. J. Guo, S. Zhang, L. H. Wu, S. H. Sun, Angew. Chem. Int. Ed. 2012, 124, 11940.
- [S5] S. Wang, D. Yu, L. Dai, D. W. Chang, J. B. Baek, ACS Nano 2011, 5, 6202.
- [S6] G. L. Xu, Y. F. Xu, H. Sun, F. Fu, X. M. Zheng, L. Huang, J. T. Li, S. H. Yang,
- S. G. Sun, Chem. Commun., 2012, 48, 8502-8504.
- [S7] Y. Xia, Z. Xiao, X. Dou, H. Huang, X. H. Lu, R. J. Yan, Y. P. Gan, W. J. Zhu, J.
- P. Tu, W. K. Zhang, X. Y. Tao, ACS Nano 2013, 7, 7083.
- [S8] Z. Y. Cai, L. Xu, M. Y. Yan, C. H. Han, L. He, K. M. Hercule, C. J. Niu, Z. F.
- Yuan, W. W. Xu, L. B. Qu, K. N. Zhao, L. Q. Mai, Nano Lett., 2015, 15, 738.
- [S9] Y. J. Mai, D. Zhang, Y. Q. Qiao, C. D. Gu, X. L. Wang, J. P. Tu, J. Power Sources, 2012, 216, 201.
- [S10] W. J. Zhu, H. Huang, W. K. Zhang, X. Y. Tao, Y. P. Gan, Y. Xia, H. Yang, X.
 Z. Guo, *Electrochim. Acta*, **2014**, *118*, 112.
- [S11] L. W. Ji, A. J. Medford, X. W. Zhang, J. Mater. Chem., 2009, 19, 5593.