

Supporting Information for

Three-dimensional low-defect carbon nanotube/nitrogen-doped graphene hybrid aerogel-supported Pt nanoparticles as efficient electrocatalysts toward methanol oxidation reaction

Minmin Yan^a, Quanguo Jiang^a, Tao Zhang^a, Jiayu Wang^b, Lu Yang^a, Zhiyong Lu^a,
Haiyan He^a, Yongsheng Fu^b, Xin Wang^b, and Huajie Huang^{a,*}

^aCollege of Mechanics and Materials, Hohai University, Nanjing 210098, China

^bKey Laboratory of Soft Chemistry and Functional Materials, Nanjing University of Science and Technology, Ministry of Education, Nanjing 210094, China

*Corresponding author. E-mail address: huanghuajie@hhu.edu.cn

Supplementary Results

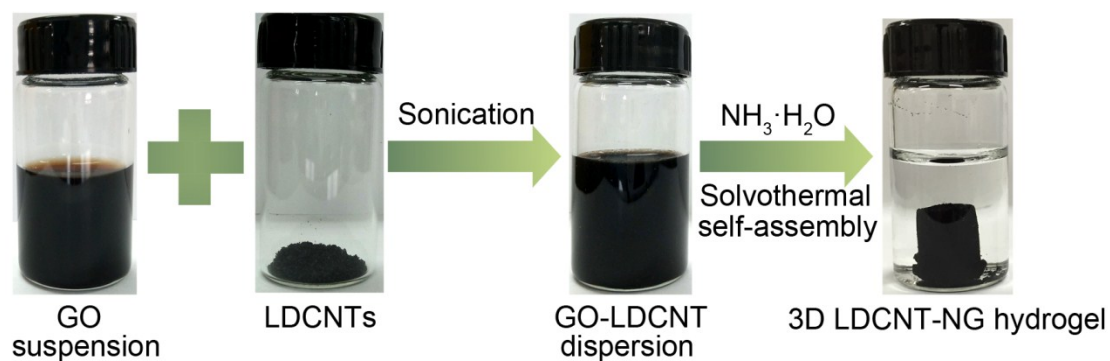


Fig. S1 The synthetic process for 3D LDCNT-NG hydrogel. It includes: (1) dispersion of low-defect CNTs in GO suspension via ultrasonic treatment; (2) formation of 3D LDCNT-NG hydrogel through a solvothermal reaction.

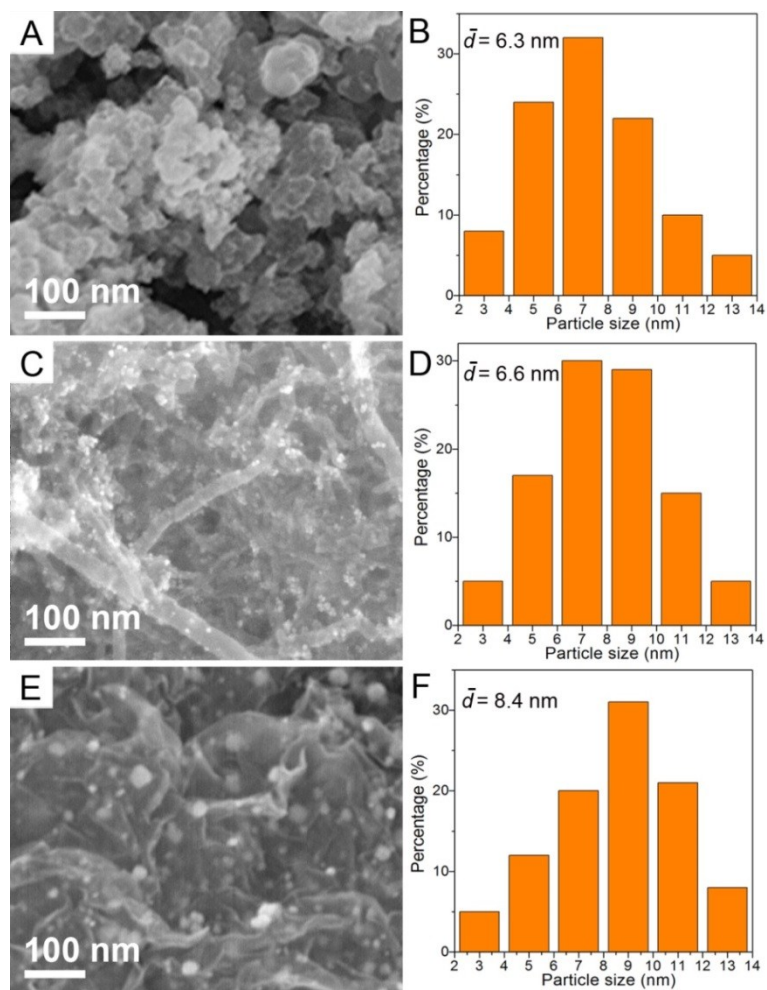


Fig. S2 Representative FE-SEM images and Pt particle size distribution of (A and B) Pt/C, (C and D) Pt/CNT, and (E and F) Pt/G, respectively.

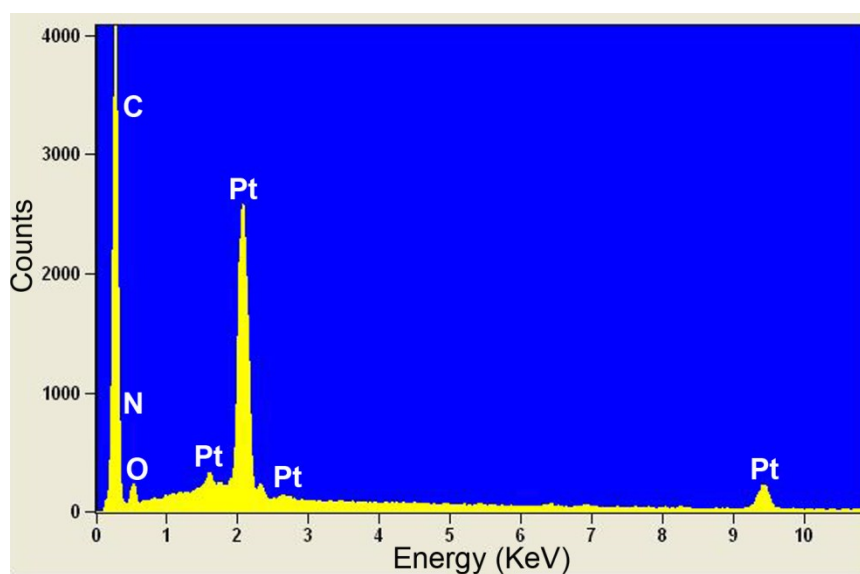


Fig. S3 EDX spectrum of the Pt/LDCNT-NG architecture.

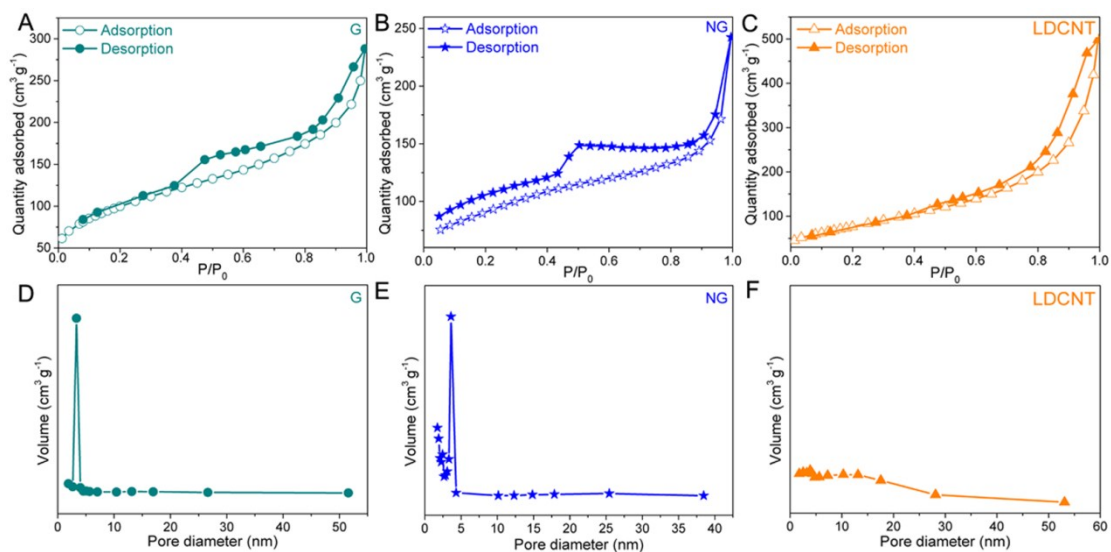


Fig. S4 Nitrogen adsorption–desorption isotherms and pore size distributions of (A and D) G, (B and E) NG, and (C and F) LDCNT samples, respectively.

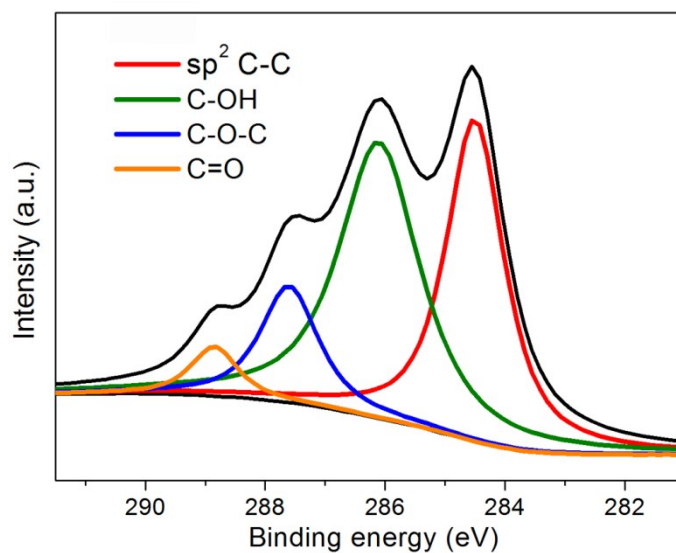


Fig. S5 C 1s core-level XPS spectrum of GO.

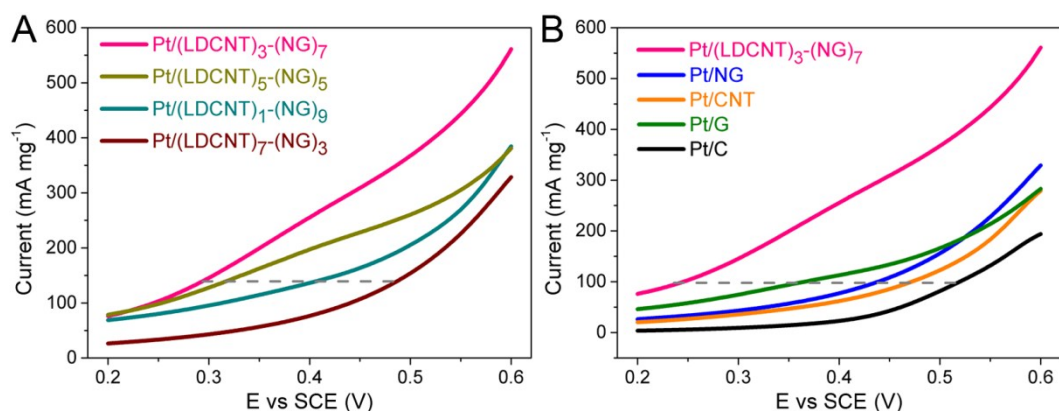


Fig. S6 Linear sweep voltammets of (A) the Pt/LDCNT-NG architectures with varying LDCNT/NG ratios, and (B) Pt/(LDCNT)₃-(NG)₇, Pt/NG, Pt/CNT, Pt/G and Pt/C in 0.5 M H₂SO₄ solution at 50 mV s⁻¹.

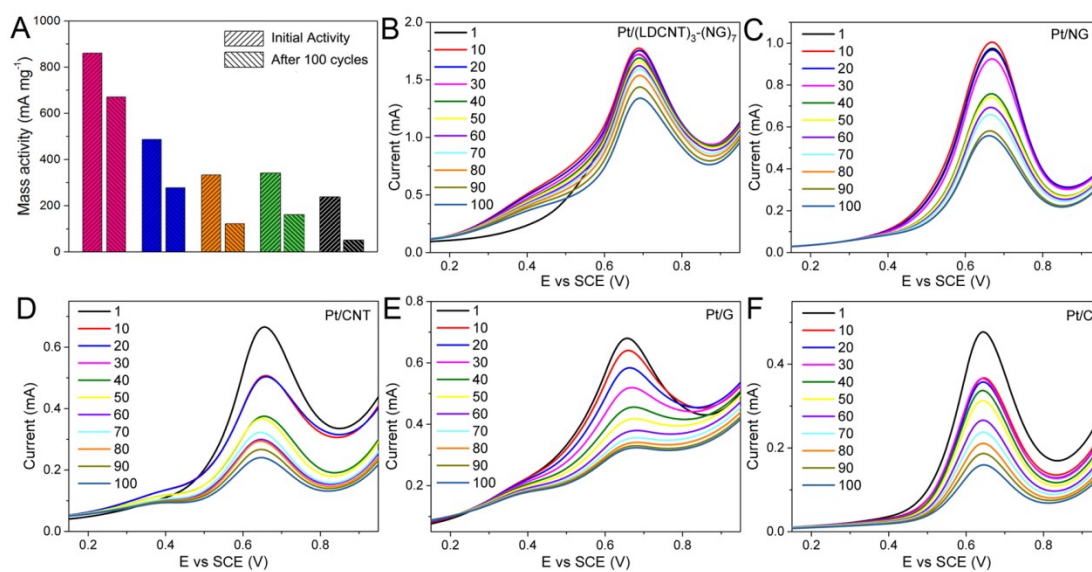


Fig. S7 (A) The mass activities of different catalysts before and after 100 cycles. 100 consecutive cycle scans of methanol oxidation obtained from (B) Pt/(LDCNT)₃-(NG)₇, (C) Pt/NG, (D) Pt/CNT, (E) Pt/G and (F) Pt/C.

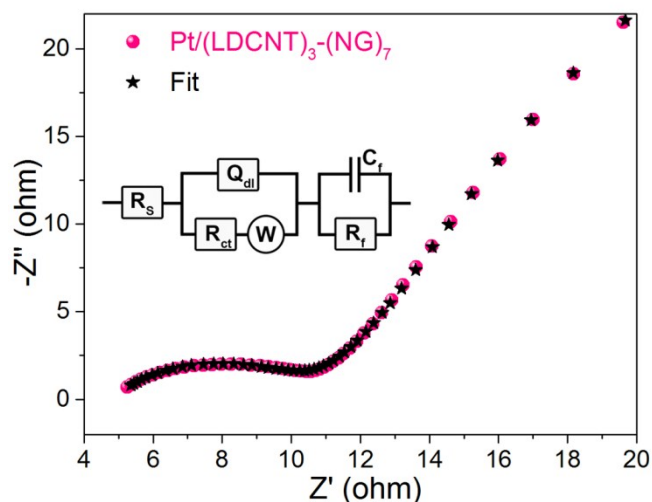


Fig. S8 Nyquist plots of Pt/(LDCNT)₃-(NG)₇ electrode and the corresponding fitting curve. The inset is the equivalent circuit.

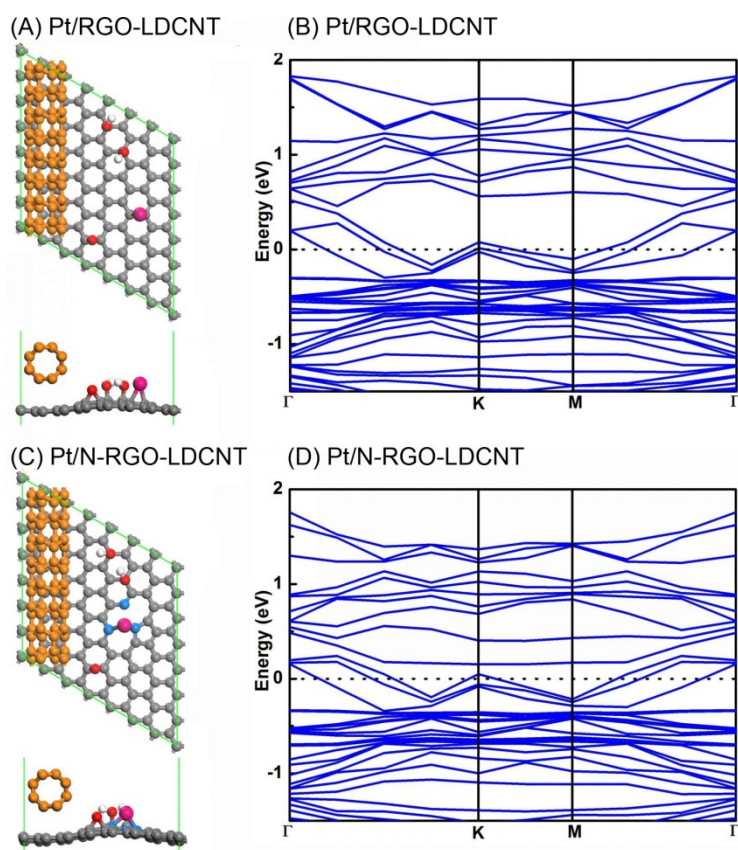


Fig. S9 The relaxed atomic structure of (A) Pt/RGO-LDCNT, and (B) the corresponding band structure. The relaxed atomic structure of (C) Pt/N-RGO-LDCNT, and (D) the corresponding band structure.

Table S1. Comparison of methanol oxidation activity for the 3D Pt/(LDCNT)₃-(NG)₇ hybrid and recent state-of-the-art Pt-based catalysts.

Catalyst	ECSA (m ² g ⁻¹)	Mass activity (mA mg ⁻¹)	Scan rate (mV s ⁻¹)	Electrolyte	Reference
3D Pt/(LDCNT) ₃ -(NG) ₇	132.4	871.9	50	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	This work
Pt/[BMIM]BF ₄ / CNT	N.A.	155.0	50	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	1
Pt/ionic liquid/ CNT	67.6	~410.0	50	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	2
Pt/low-defect graphene	63.0	203.8	20	1 M H ₂ SO ₄ + 2 M CH ₃ OH	3
Pt/graphene	101.3	333.3	50	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	4
Pt/exfoliated graphene	51.0	~300.0	50	0.5 M H ₂ SO ₄ + 2 M CH ₃ OH	5
Pt/CNT/graphene	95.6	617.9	20	1 M H ₂ SO ₄ + 2 M CH ₃ OH	6
Pt/N-doped graphene	N.A.	~400.0	200	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	7
Pt/N-doped graphene ribbon	64.6	~390.0	20	1 M H ₂ SO ₄ + 2 M CH ₃ OH	8
PtAu/N-doped graphene	60.9	417.0	50	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	9
Pt/B-doped graphene	58.8	~410.0	50	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	10
PtRu/N-doped CNT-graphene	N.A.	500.5	10	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	11
3D Pt/C ₃ N ₄ / graphene	69.0	612.8	20	1 M H ₂ SO ₄ + 2 M CH ₃ OH	12
Pt/mesoporous carbon	N.A.	~450.0	20	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	13
Pt/macroporous carbon	N.A.	81.6	50	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	14
Pt/N-doped porous carbon	24.6	343.0	50	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	15
3D Pt/RuO ₂ / graphene	122.7	646.5	20	1 M H ₂ SO ₄ + 2 M CH ₃ OH	16
AuPtCu nanowires	N.A.	~500.0	50	0.1 M HClO ₄ + 1 M CH ₃ OH	17

FePtPd nanowires	N.A.	488.7	50	0.1 M HClO ₄ + 0.2 M CH ₃ OH	18
PtPd dendrites	N.A.	490.0	50	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	19
PtPd dendrites/ graphene	81.6	647.2	50	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	20
PtAu dendrites/ graphene	100.8	365.0	50	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	21

Table S2. The charge-transfer resistance (R_{ct}) for different catalysts.

Electrode	R_{ct}	
	Value (ohm)	Error (%)
Pt/(LDCNT) ₃ -(NG) ₇	5.3	1.9
Pt/CNT	22.5	6.1
Pt/G	9.6	9.1
Pt/C	1.6×10 ³	4.8

Reference

- (1) H. Chu, Y. Shen, L. Lin, X. Qin, G. Feng, Z. Lin, J. Wang, H. Liu and Y. Li, *Adv. Funct. Mater.*, 2010, **20**, 3747-3752.
- (2) S. Guo, S. Dong and E. Wang, *Adv. Mater.*, 2010, **22**, 1269-1272.
- (3) H. Huang, H. Chen, D. Sun and X. Wang, *J. Power Sources*, 2012, **204**, 46-52.
- (4) S. Wu, J. Liu, Z. Tian, Y. Cai, Y. Ye, Q. Yuan and C. Liang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 22935-22940.
- (5) S. M. Choi, H. S. Min, H. J. Kim and W. B. Kim, *Carbon*, 2011, **49**, 904-909.
- (6) X. Zhang, J. Zhang, H. Huang, Q. Jiang and Y. Wu, *Electrochim. Acta*, 2017, **258**, 919-926.
- (7) B. Xiong, Y. Zhou, Y. Zhao, J. Wang, X. Chen, R. O'Hayre and Z. Shao, *Carbon*, 2013,

- 52**, 181-192.
- (8) H. Huang, G. Ye, S. Yang, H. Fei, C. S. Tiwary, Y. Gong, R. Vajtai, J. M. Tour, X. Wang and P. M. Ajayan, *J. Mater. Chem. A*, 2015, **3**, 19696-19701.
- (9) G. Yang, Y. Li, R. K. Rana and J. J. Zhu, *J. Mater. Chem. A*, 2013, **1**, 1754-1762.
- (10) Y. Sun, C. Du, M. An, L. Du, Q. Tan, C. Liu, Y. Gao and G. Yin, *J. Power Sources*, 2015, **300**, 245-253.
- (11) R. Lv, T. Cui, M. S. Jun, Q. Zhang, A. Cao, D. S. Su, Z. Zhang, S. H. Yoon, J. Miyawaki and I. Mochida, *Adv. Funct. Mater.*, 2015, **21**, 999-1006.
- (12) H. Huang, S. Yang, R. Vajtai, X. Wang and P. M. Ajayan, *Adv. Mater.*, 2014, **26**, 5160-5165.
- (13) H. Jiang, T. Zhao, C. Li and J. Ma, *Chem. Commun.*, 2011, **47**, 8590-8592.
- (14) X. Bo and L. Guo, *Electrochim. Acta*, 2013, **90**, 283-290.
- (15) F. Su, Z. Tian, C. K. Poh, Z. Wang, S. H. Lim, Z. Liu and J. Lin, *Chem. Mater.*, 2010, **22**, 832-839.
- (16) H. Huang, J. Zhu, D. Li, C. Shen, M. Li, X. Zhang, Q. Jiang, J. Zhang and Y. Wu, *J. Mater. Chem. A*, 2017, **5**, 4560-4567.
- (17) W. Hong, J. Wang and E. Wang, *Small*, 2014, **10**, 3262-3265.
- (18) S. Guo, S. Zhang, X. Sun and S. Sun, *J. Am. Chem. Soc.*, 2011, **133**, 15354-15357.
- (19) L. Wang, Y. Nemoto and Y. Yamauchi, *J. Am. Chem. Soc.*, 2011, **133**, 9674-9677.
- (20) S. Guo, S. Dong and E. Wang, *Acs Nano*, 2010, **4**, 547-555.
- (21) W. Yuan, X. Fan, Z. Cui, T. Chen, Z. L. Dong, C. Li, W. Yuan, X. Fan, Z. Cui and T. Chen, *J. Mater. Chem. A*, 2016, **4**, 7352-7364.