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Three Dimensional N-Doped Graphene/PtRu Nanoparticle Hybrids as High Performance Anode for Direct Methanol Fuel Cells

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Experimental Section

Materials:

Graphite powder (natural briquetting grade of 99.9995% purity), H_2PtCl_6•$6H_2O$ and $RuCl_3$•nH_2O were purchased from Alfa Aesar. Analytical grade $NaNO_3$, $KMnO_4$, ethylene glycol (EG), NaOH, 98% H_2SO_4, 30% H_2O_2 aqueous solution, and 30% HCl aqueous solutions were bought from Beijing Chemical Reagents Company and used directly without further purification. Ultrapure water (18 MΩ) was supplied by a Millipore System (Millipore Q, USA). Graphene oxide (GO) was prepared from the graphite powder according to Hummers' method.[S1]

Methods

Synthesis of three-dimensional (3D) architectures of N-Doped graphene aerogel (N-GA)

First, 60 mL GO aqueous solution (2 mg/mL) was mixed with 100 μL NH_3•H_2O under assistant of mild ultrasound. The mixture solution was then heated at 180 °C for 12 h, forming N-doped graphene. After the products were dialyzed with ultrapure water for one day at least, they were subjected to freeze-drying at -53 ^oC and -30 Pa for 12 h to generate 3D N-GA. The freeze-drying process was as following: First, the dialyzed products were put into a freeze-drying flask and kept at -20 ^oC in a refrigerator for 2 h. The frozen samples were subsequently transferred into a freeze-drying vessel (FD-1A-50, Boyikang experimental instrument LTD, China), which had been set at the temperature of -53 ^oC and vacuum pressure of -30 Pa. The samples were freeze dried for at least 12 h to remove both solvent and water completely. The aerogels produced were stored in a vacuum desiccator at room temperature until being used for characterization.

Synthesis of 3D architectures of N-free graphene aerogel (GA)

The procedure of preparing 3D GA was same as that of N-GA except for no addition of NH_3•H_2O.

Synthesis 3D Architectures of N-GA/PtRu catalyst

3D N-GA (20 mg) was dispersed in 30 mL EG followed by addition of 0.5 mL 80 mM H_2PtCl_6 and 0.5 ml 80 mM $RuCl_3$. After stirred for 1h, the pH value of the mixture solution was adjusted to 11 by adding 1 M NaOH solution drop wise. The mixture was then stirred for another 12 h. Next, the mixture was placed in a microwave oven (CEM Voyager, 800 W) and heated by microwave irradiation for 60 s. 3D catalyst materials were obtained via washed with ultrapure water followed by filtration. The products were dried in a vacuum oven at 60 °C for 12 h. The GA/PtRu samples were prepared via the same procedure as described above by using GA rather than N-GA as the starting materials.

Electrochemical Measurement

A conventional three-electrode system was used for electrochemical measurements. A mixture of 0.5 mL of deionized water, 0.5 mL alcohol, 3 mg of the N-GA/PtRu or other catalysts, and 0.05 mL Nafion solution was dispersed by ultrasonication for approximately 4 h to obtain a homogeneous suspension. Next, 10 μL of the dispersion was uniformly dropped onto the freshly polished glassy carbon electrode (Diameter = 0.5 cm and *ca.* 0.15 mg catalysts/cm^2). The electrode was then dried at room temperature and served as the working electrode. A Pt foil (1 cm × 1 cm) and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All electrolyte solutions were deaerated by Ar gas of high purity for 30 min prior to measurement. Cyclic voltammetry (CV) measurements on the electrochemical mass activity areas were recorded in the potential region from -0.25 to 0.85 V at a scan rate of 50 mV/s in 0.5 M H_2SO_4 solution. The CV experiments for evaluating methanol oxidation performance were performed in the solution containing 0.5 M H_2SO_4 and 0.5 M CH_3OH at a scan rate of 20 mV/s. The chronoamperometry (current *vs.* time response) tests were conducted in the solution containing 0.5 M H_2SO_4 and 0.5 M CH_3OH solution at 0.4 V for a period of 3600 s. The CO stripping voltammogram was performed with a three-electrode system in 0.5 M H_2SO_4 solution, and the experimental process was as follows: First, Ar gas was purged to 0.5 M H_2SO_4 solution for 30 min. Next, the CO gas was purged to the 0.5 M H_2SO_4 solution for 30 min by maintaining the electrode potential at -0.25 V. Subsequently, by bubbling Ar gas into the solution for 30 min, the dissolved CO in the H_2SO_4 solution was fully removed. Finally, the stripping voltammograms were collected between -0.25 V and 0.9 V with a scan rate of 50 mV/s under Ar atmosphere. All electrochemical tests were implemented at room temperature.

Construction and Performance Evaluation of Single Cell Direct Methanol Fuel Cell (DMFC)

The freestanding N-GA/PtRu products or other samples were directly used as the anode, while to prepare the cathode layer, the ink consisting of 20% (JM) C/Pt catalyst and Nafion ionomer was sprayed onto the carbon paper. The loading amount of PtRu in the N-GA/PtRu or other catalysts was set to be 2.5 mg/cm^2 at the anode, and the loading amount of Pt particles at the cathode was kept to be 2 mg/cm^2. The single cell was then constructed by sandwiching the Nafion 117 membrane between the anode and the cathode by hot pressing at 130 °C for 60 s. Single cell performance was tested by an Arbin FCTs instrument at 30 °C, 60 °C and 90 °C, respectively. 2 M methanol was pumped to the anode at a flux speed of 4.0 mL/min, while dry pure oxygen at a flux speed of 200 standard cubic centimeters per minute (sccm) was fed to the cathode. The fuel cell working conditions including the cell temperature, pressure, and reactant flux on the anode and the cathode were kept constant during the measurement.

Characterization

Transmission electron microscopy (TEM) imaging was performed on a FEI Tecnai G2 F20 electron microscope operated at 200 kV. The surface morphology was observed with a Hitachi S4800 scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) measurements were conducted by an ESCALAB 20 Xi XPS system, where the analysis chamber was 1.5×10^{-9} mbar and the size of

X-ray spot was 500 μm. X-ray diffraction (XRD) patterns were obtained by using a Panaltical X'Pert-pro MPD X-ray power diffractometer, with a Cu Kα irradiation source (λ =1.54056 Å), and a self-calibration process was performed with a SiO_2 internal standard sample prior to target measurement. The inductively coupled plasma-mass spectra (ICP-MS) were conducted with NEXION 300X. All the electrochemical data were measured in electrochemical station of Pine Instruments (Model: AFMSRCE).

Table S1. XPS analysis of N-GA and N-GA/PtRu.

	C (at.%)	N (at.%)	O (at.%)	Pt (at.%)	Ru (at.%)
N-GA	83.208	6.591	10.201	—	—
N-GA/PtRu	66.192	4.808	16.695	6.224	6.081

Note: H element is not considered in N-GA and N-GA/PtRu systems. The EDS can determine the total elemental composition in select areas, while the XPS can only detect a thickness of around 2-5 nm below the surface. For the supported catalyst, the EDS results suggest that elemental weight content of metal in the N-GA/PtRu is higher than that measured by the XPS results.[S2]

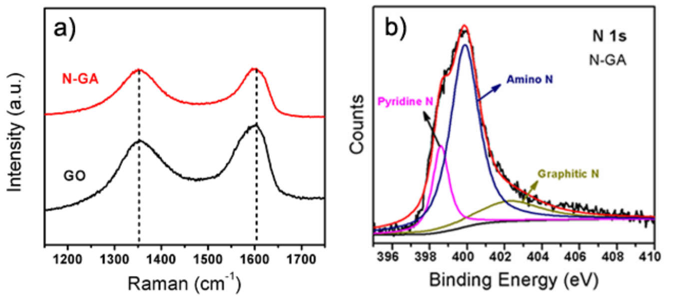


Fig. S1 a) Raman spectrums of GO and N-GA, D/G is 0.85 and 1.02 for GO and N-GA, respectively. b) XPS spectrum of N 1s of the pure N-GA.

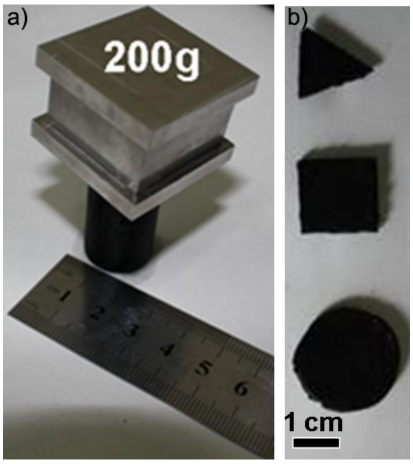


Fig. S2 a) and b) are remarkable mechanical property and easy shape control of N-GA/PtRu, respectively.

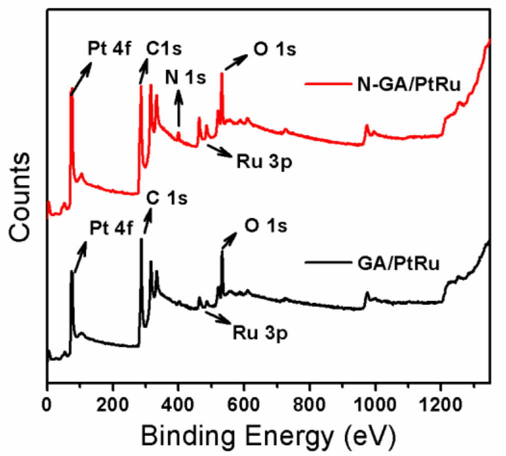
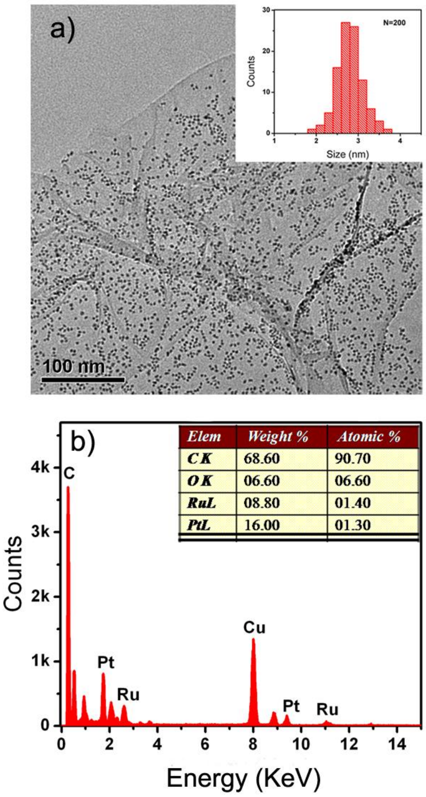


Fig. S3 XPS spectra of N-GA/PtRu and GA/PtRu.



Elem	Weight %	Atomic %
CK	68.60	90.70
OK	06.60	06.60
RuL	08.80	01.40
PtL	16.00	01.30

Fig. S4 a) TEM image of the GA/PtRu, and the insert is the size distribution of PtRu NPs on the surface of the GA. The PtRu alloy nanoparticles (NPs) with monodisperse sizes of 2.8 ± 0.4 nm are homogenously distributed on the surface of graphene sheets, and no free NPs are found outside the graphene sheets. b) EDX spectrum of the GA/PtRu, and the atom ratio of Pt/Ru is close to 1.

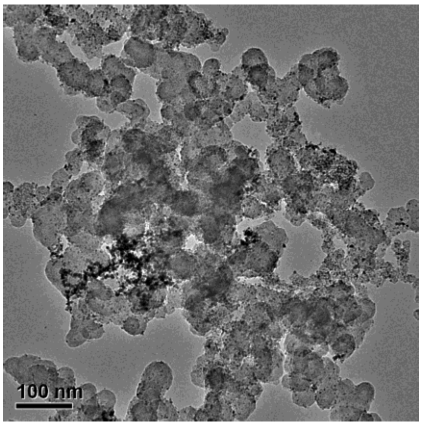


Fig. S5 TEM image of C/Pt (JM). The average sizes of Pt on carbon surface is 3.2 ± 0.8 nm and the loads of the metal is 20 wt%.

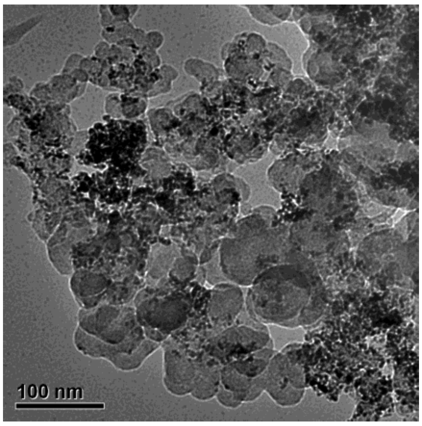


Fig. S6 TEM image of C/PtRu (E-TEK). The average sizes of PtRu on carbon surface is 3.2 ± 0.8 nm and loads of metal is 40 wt% (atom ratio of Pt to Ru is 1:1).

Table S2. Electrocatalyitic activity of the N-GA/PtRu compared with the previously-reported catalysts toward methanol oxidation.

Catalysts	Peak potential (V *vs*. Ag/AgCl)	Reference
N-GA/PtRu	0.48	Present work
PtRu/G	0.68	2012[S3]
PtRu/N-C-G	0.66	2011[S4]
PtRu/FGS	0.70	2012[S5]
PtRu/G-C	0.58	2013[S6]
Pt/C_{40}-CeO_2	0.68	2011[S7]
Pt/G-CeO_2	0.72	2012[S8]
Pt/N-G	0.63	2013[S9]
PtRu/CNTs	0.67	2012[S10]
Pt-Co/PZS-CNTs	0.55	2012[S11]
Pt-Ni NBS	0.56	2012[S12]
PtPd/G	0.69	2013[S13]
$PtCu_3$	0.61	2012[S14]
Pt-Ni/G	0.67	2013[S15]
PtCo NAWs	0.61	2012[S16]

Note: The reference electrodes are converted to Ag/AgCl.

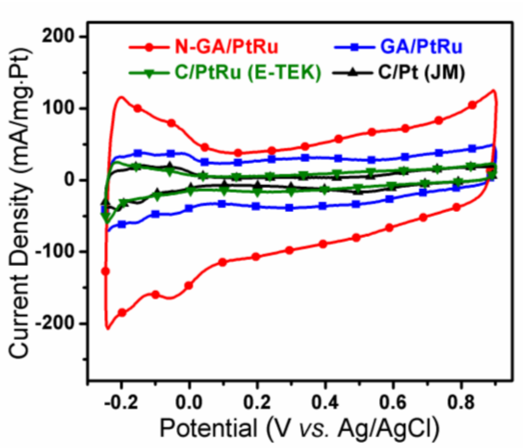


Fig. S7 Cyclic voltammetry measurement of the electrochemical surface activity (ECSA) of different catalysts at the scan rate 50 mV/s in 0.5 M H_2SO_4 solution.

Table S3. Electrochemical parameters in CO stripping voltammograms of different samples in 0.5 M H_2SO_4 aqueous solution at a scan rate of 50 mV/s.

Catalysts	Onset potential (V vs. Ag/AgCl)	Peak potential (V vs. Ag/AgCl)	Current density (mA/mg Pt)
N-GA/PtRu	0.12	0.44	306.3
GA/PtRu	0.34	0.60	157.1
C/PtRu (E-TEK)	0.36	0.56	130.4
C/Pt (JM)	0.53	0.64	110.6

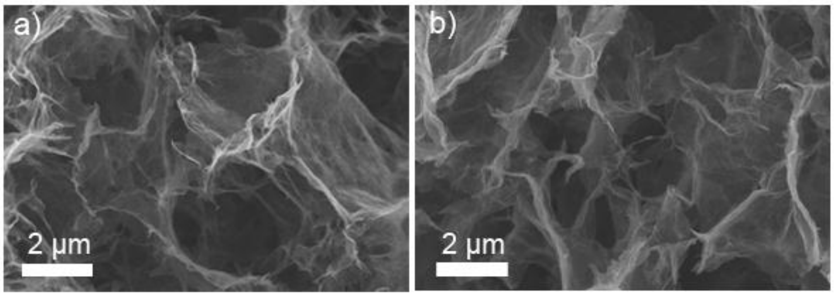


Fig S8 a), b) SEM images of N-GA/PtRu surface before (a) and after (b) pressing, respectively.

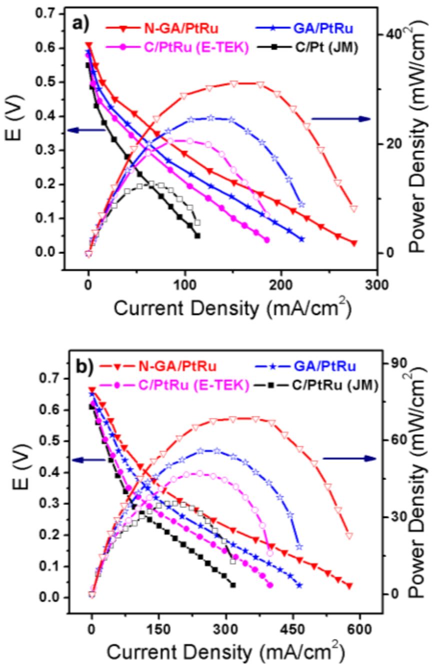


Fig. S9 a) DMFC single-cell performances based on different catalysts at 30 ^{o}C, b) DMFC single-cell performances based on different catalysts at 60 ^{o}C.

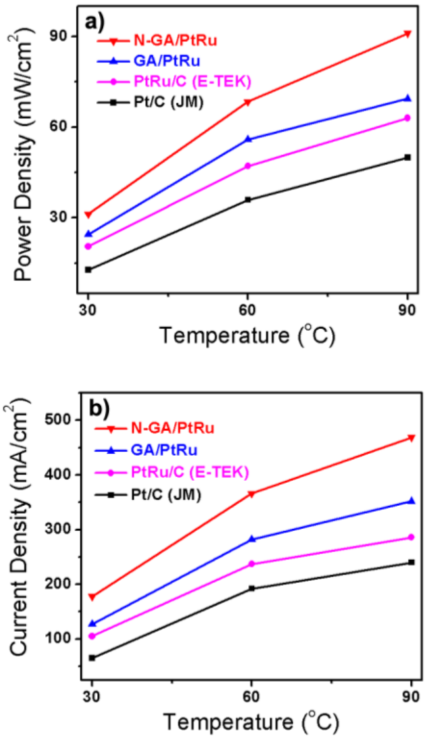


Fig. S10 a) Maximum power density of the DMFCs based on different catalysts at varying operating temperatures, b) Maximum current density of the DMFCs based on different catalysts at varying operating temperatures.

Reference

S1 W. Hummers, and R. Offeman, *J. Am. Chem. Soc.*, 1958, **70**, 1339.

S2 Z. Wen, S. Cui, H. Kim, S. Mao, K. Yu, G. Lu, H. Pu, O. Mao, and J. Chen, *J. Mater. Chem.*, 2012, **22**, 3300.

S3 H. Cong, X. Ren, and S. H. Yu, *ChemCatChem*, 2012, **4**, 1555.

S4 R. Lv, T. Cui, M. Jun, Q. Zhang, A. Cao, D. Su, Z. Zhang, S. Yoon, J. Miyawaki, I. Mochida, and F. Y. Kang, *Adv. Funct. Mater.*, 2011, **21**, 999.

S5 J. Zhao, H. Xue, L. Zhang, J. Yu, and H. Hu, *J. Nanopart. Res.*, 2012, **14**, 935.

S6 S. Woo, J. Lee, S-K. Park, H. Kim, T. Chung, and Y. Piao, *J. Power Sources*, 2013, **222**, 261.

S7 Y. Chu, Z. Wang, Z. Jiang, D. Gu, and G. P. Yin, *Adv. Mater.*, 2011, **23**, 3100.

S8 X. Wang, X. Li, D. Liu, S. Song, and H. Zhang, *Chem. Commun.*, 2012, **48**, 2885.

S9 B. Xiong, Y. Zhou, Y. Zhao, J. Wang, X. Chen, R. O'Hayre, and Z. Shao, *Carbon*, 2013, **52**, 181.

S10 B. Wu, Y. Zhang, Y. Kuang, Y. Yu, X. Zhang, and J. H. Chen, *J. Chem. Asian J.*, 2012, **7**, 190.

S11 J. Qian, W. Wei, X. Huang, Y. Tao, K. Chen, and X. Tang, *J. Power Sources*, 2012, **210**, 345.

S12 Z. Niu, D. Wang, R. Yu, Q. Peng, and Y. Li, *Chem. Sci.*, 2012, **3**, 1925.

S13 X. Chen, Z. Cai, X. Chen, and M. Oyama, *Carbon*, DOI: http://dx.doi.org/10.1016/ j.carbon.2013.09.014.

S14 B. Xia, H. Wu, X. Wang, and X. Lou (David), *J. Am. Chem. Soc.*, 2012, **134**, 13934.

S15 L. Li,Y. Wu, J. Lu, C. Nan, and Y. Li, *Chem. Commun.*, 2013, **49**, 7486.

S16 J. Xu. X. Liu, Y. Chen, Y. Zhou, T. Lu, and Y. Tang, *J. Mater. Chem.*, 2012, **22**, 23659.