Supporting Information

Coassembly and High ORR Performance of Monodisperse Pt Nanocrystals with a Mesopore-rich Nitrogen-Doped Graphene Aerogel

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Experimental Section

Materials

Graphite flakes (99.9995 %) with a lateral dimension of 2-15 μ m were purchased from Alfa Aesar (USA). Commercial Pt/C (20 wt.%) purchased from Aladdin Co., Ltd. Dopamine (DA) and Nafion solution (5 wt% in lower aliphatic alcohols (80-85 vol%) and water (15-20 vol%)) were purchased from Sigma-Aldrich Co. H₂PtCl₆·5H₂O, potassium permanganate (KMnO₄), sulfuric acid (H₂SO₄, 98 %), phosphate acid (H₃PO₄), hydrogen peroxide (H₂O₂, 30%), hydrochloric acid (HCl, 36-38 %), ethanol, methanol, ethylene glycol (EG), and tris(hydroxymethyl)aminomethane (Tris) were purchased from Sinopharm Chemical Reagents Co., Ltd. They were all analytical grade reagents and directly used without further purification. Pure water with a resistivity of 18.2 MΩ·cm at 25 °C was used in all experiments.

Preparation of GO nanosheets

The preparation of GO nanosheets can be referred to our previous work^[1] based on an improved Hummers's method with some modifications.^[2] Briefly, a 9/1 (volume ratio) mixture of concentrated H_2SO_4/H_3PO_4 (180 mL/20 mL) was added into the milled graphite flakes (1.0 g), followed by stirring for 12 h at 0 °C in an ice water bath. Sequentially, KMnO₄ (3.0 g) was slowly added into the mixture at 15 °C and then stirred at 40 °C for 6 h. Another portion of KMnO₄ (3.0 g) was added into the mixture followed by keeping stirring at 40 °C for 6 h and then at 85 °C for 30 min. The mixture was cooled down to room temperature (rt) in a beaker (500 mL) and dropped into H_2O_2 solution (85 mL, 30 %). The GO nanosheets in the mixture were thoroughly washed three times with HCl solution (5.0 wt%) to remove the metal ions, then repeatedly centrifuged (27530 g, 15 min) and washed with water until the pH value of the supernatant was neutral. The suspensions of GO nanosheets (2.0 mg/mL) were subject to sonication (KQ-600KDB, China, 40 kHz, 300 W) for 8 h. The temperature of sonication water bath was kept below 30 °C.

Preparation of PtNCs@NGA

The sonicated GO nanosheets (40-700 nm) were sedimented by a high speed centrifuge (Sigma 3-18K, Germany, 27530 g, 90 min). The sedimentation was dispersed in freshly prepared Tris-HCl buffer solution (10 mL, pH=8.5). To GO nanosheets dispersion (10 mL, 2.0 mg/mL), DA (20 mg), H₂PtCl₆ (2 mL, 10 mg/mL), EG solution (7.5 mL) for reducing H₂PtCl₆ to Pt were added under stirring, followed by sonication (300 W, 40 min). The mixture was then kept in a 25 mL Teflon-lined autoclave (180 °C, 12 h) to obtain graphene hydrogel. After naturally cooled down to rt, the hydrogel was carefully taken out, washed separately by water and ethanol, then freeze-dried. PtNCs@NGA was obtained after annealing at 800 °C for 3 h under an Ar atmosphere. The weight of PtNCs@NGA was obtained on an analytical balance (Al104, METTLER TOLEDO).

Preparation of PtNCs@GA

The preparation process of PtNCs@GA was similar to that of NGAs except that DA was not added as the N source.

Characterization

X-ray photoelectron spectroscopy (XPS) was taken on a Phi 5300 ESCA system (Perkin-Elmer, U.S.A) with the Mg (K α) radiation (X-ray energy 1253.6 eV). The analysis spot area was 1.0×3.5 mm². The XPS samples were prepared by using double-side tap to stick GO nanosheets (2 mg) or PtNCs@NGA powders (2 mg) onto silicon substrates. X-ray diffraction (XRD) patterns were collected through a D8 Advance diffractometer (Bruker, Germany) with the Cu target (K α , λ = 1.54184 Å) in an angular range of 8-90° at an interval of 0.02° and a scanning rate of 4°/min. Nitrogen (N₂) adsorption-desorption isotherms were recorded with an ASAP 2020 HD88 instrument (Micromeritics, USA). The specific surface area of PtNCs@NGA was obtained by calculating the adsorption branch (0.2-0.5 p/p₀) with a BET method. The pore size distribution of PtNCs@NGA was obtained by calculating the adsorption branch with a density functional theory (DFT) method, which is suitable for analyzing microporous and mesoporous pore. Scanning electron microscopy (SEM) observation was obtained out using a SU-8010 (Hitachi, Japan) instrument with an operating voltage of 3 kV. The elemental composition was obtained

from high resolution energy dispersive X-ray spectrometer (Bruker, Germany) attached to SEM. Transmission electron microscopy (TEM) images were obtained through a JEM-1011 TEM (JEOL, Japan) under an accelerating voltage of 100 kV. The TEM samples were prepared by dipping PtNCs@NGA dispersion (5 μ L, 0.5 mg/mL) into the lacey support films. High resolution TEM (HRTEM) images were obtained through a JEOL-2100F TEM (JEOL, Japan) with an acceleration voltage of 200 kV. Raman spectra were obtained using a LabRAM HR 800 system (Horiba Jobin Yvon, France) with a laser of 633 nm. Thermogravimetric curves of PtNCs@NGA were obtained from 25 to 800 °C in air at a heating rate of 10 °C/min with a TGA-50 thermal analyzer (Shimadzu, Japan).

Electrochemical measurement

The LSV curves and chronoamperometric responses of PtNCs@NGA and commercial Pt/C (20 wt% Pt) were investigated on a electrochemical work station (CHI770C, China) with a three-electrode system. PtNCs@NGA or commercial Pt/C (20 wt% Pt) or PtNCs@GA modified glassy carbon rotating disk electrode (RDE) of 5 mm in diameter, Ag/AgCl (sat. KCl) and Pt electrode were used as working, reference and counter electrodes, respectively. All the potentials reported were calibrated with respect to the reversible hydrogen electrode (RHE) according to the equation: $E(vs. RHE) = E(vs. Ag/AgCl) + 0.2223 V in 0.5 M H_2SO_4$. Before coating, the RDE was polished using Al₂O₃ powder of 0.3 µm in diameter and rinsed separately with water and ethanol, then sonicated for 15 min, and dried by high purity N₂ stream. PtNCs@NGA (2 mg) was purposely broken and separately dispersed in a mixture of ethanol (985 µL) and Nafion solution (15 µL). Subsequently, the above suspensions (10 µL) were cast onto the surfaces of RDE and dried under rt. The working electrode was scanned at a rate of 5 mV/s with varying rotating speed from 200 to 2000 rpm. Kouteckýe-Levich (K-L) plots were analyzed at various electrode potentials. The slopes of their linear fit lines were used to calculate the number of electrons transferred (*N*) on the basis of the K-L equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}} = \frac{1}{j_k} + \frac{1}{B(2\pi n)^{0.5}}$$

$$B=0.2NFv^{1/6}D^{2/3}C$$

where *j* is the measured current density (mA/cm²), j_K and j_d are the kinetic- and diffusion-limiting current densities (mA/cm²), ω is the angular velocity of the working electrode, *n* is the rotation speed of the working electrode (rpm), *N* is transferred electron number, *F* is the Faraday constant (*F*=96485 C/mol), *C* is the bulk concentration of O₂ in 0.5 M H₂SO₄ (1.1×10⁻⁶ mol/cm³), v is the kinematic viscosity of the electrolyte (0.01 cm²/s), and *D* is the diffusion coefficient of O₂ in 0.5 M H₂SO₄ (1.4×10⁻⁵ cm²/s). For the Tafel plot, the kinetic current density measured at a rate of 5 mV/s with a rotating speed of 1600 rpm was calculated from the mass-transport correction of the RDE data by:

$$j_k = \frac{j * j_d}{j_d - j}$$

The Pt loading and the total loading amount for PtNCs/NGA obtained from the product of volume and concentration of catalyst. The electrochemical surface area (ECSA) of the PtNCs/NGA was obtained through CV in N₂ saturated 0.5 M H₂SO₄ solution. The ECSA was calculated from the formula of ECSA = $Q_{H}/(0.21 M_{Pt})$ ^[3] where Q_{H} is the electrical charge due to hydrogen adsorption/desorption in the hydrogen region of the CV plots, 0.21 is the charge associated with a monolayer adsorption of hydrogen on Pt, and M_{Pt} is the mass of Pt loading on the working electrode.



Figure S1. The weighing photograph of PtNCs@NGA.



Figure S2. Comparison of the morphology, N content, and specific surface area among NGA and reported 3D N doped carbon including graphene materials ^[4].



Figure S3. SEM image of PtNCs@NGA and the corresponding elemental mapping images of C, N, O and Pt, respectively.



Figure S4. Thermogravimetric curve of PtNCs@NGA.



Figure S5. a) CV plot of PtNCs/NGA electrode in N2 saturated aqueous solution of 0.5 M H2SO4 at a scan rate of 50 mV/s (the shaded part corresponds to hydrogen desorption).

Sample	<i>E</i> _{1/2}	Ν	j_d / j_k at 0.45V (mA/cm ²)	Durability	Tafel slope (mV/dec)	Total loading of catalysts / Pt loading (mg)	Ref.
Pt/RGO/CB	0.84		5.0 / 29.0			0.02 / 0.0066	Li, Y. J.; Li, Y. J., et al., <i>J. Am. Chem. Soc.</i> 2012 , <i>134</i> , 12326.
Pt/graphene nanoribbons	0.90	3.91	5.7 / 27.3			0.016 / 0.005	Fortunato, G. V.; de Lima, F., et al., <i>J. Power Sources</i> 2016 , <i>302</i> , 247.
PtCo/RGO	0.93		4.6 / 17.3			0.01 /	Li, J.; Fu, X., et al., Nanoscale Res. Lett. 2016 , 11, 3.
Pt/GA	0.82		5.5 / 24.9		70	0.015 / 0.006	Huang, Q.; Tao, F., et al., <i>Electrochim. Acta</i> 2015 , <i>152</i> , 140.
CoO/NGHS	0.83	3.95	4.8 / 16.6	36000 s, 93.8 %	53.7	0.04 /	Jiang, Z. J.; Jiang, Z., Sci. Rep. 2016 , 6. 27081.
MnO-m-N-C	0.81	3.84	5.0 / 19.0	20000 s, 96 %	62	0.02 /	Tan, Y. M.; Xu, C. F., et al., <i>Adv. Funct. Mater.</i> 2012 , <i>22</i> , 4584.
rGO/(Co ²⁺ - THPP) ₇		3.85	4.0 / 30.5	20000 s, 80 %		0.02 /	Tang, H.; Yin, H., et al., Angew. Chem. Int. Ed. 2013 , 52, 5585.
GNC-Co		3.95	4.5 / 15.1				Li, S.; Wu, D., et al., Angew. Chem. Int. Ed. 2013 , 52, 12105.
PtNCs@NGA	0.89	3.95	6.5 / 32.7	20000 s, 97.2 % 30000 s, 96 % 43200 s, 96.5 %	57	0.02 / 0.0042	This work

Table S1. Catalytic data of PtNCs@NGA and reported catalysts supported on carbon materials for ORR.

RGO (rGO): reduced graphene oxide; CB: carbon black; GA: graphene aerogel;

NGHSs: Nitrogen doped graphene hollow microspheres; m-N-C: mesoporous nitrogen-doped carbon; THPP: 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin; GNC: N-doped carbon nanosheets.

References

- [1] B. B. Xie, X. D. Ren, X. B. Yan, Z. Y. Dai, W. G. Hou, N. Du, H. P. Li, R. J. Zhang, *RCS Adv.* 2016, *6*, 23012.
- [2] a) B. Xie, Y. Li, J. Shang, J. Xin, X. Yang, R. Zhang, Sci. Adv. Mater. 2014, 6, 2395; b) D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, ACS Nano 2010, 4, 4806.
- [3] D. Chen, Q. Tao, L. W. Liao, S. X. Liu, Y. X. Chen, S. Ye, *Electrocatalysis* 2011, 2, 207.
- [4] a) J. Meng, Y. Suo, J. Li, G. Zheng, Y. Liu, J. Zhang, X. Zheng, *Mater. Lett.* 2015, *160*, 392; b) Z. S. Wu, S. B. Yang, Y. Sun, K. Parvez, X. L. Feng, K. Mullen, *J. Am. Chem. Soc.* 2012, *134*, 9082; c) C. Xu, Y. Su, D. Liu, X. He, *Phys. Chem. Chem. Phys.* 2015, *17*, 25440; d) Z. X. Cai, X. H. Song, Y. Y. Chen, Y. R. Wang, X. Chen, *Sens. Actuators, B* 2016, *222*, 567; e) Z. J. Jiang, Z. Jiang, *Sci. Rep.* 2016, *6*, 27081; f) J. J. Duan, Y. Zheng, S. Chen, Y. H. Tang, M. Jaroniec, S. Z. Qiao, *Chem. Commun.* 2013, *49*, 7705; g) Y. M. Tan, C. F. Xu, G. X. Chen, X. L. Fang, N. F. Zheng, Q. J. Xie, *Adv. Funct. Mater.* 2012, *22*, 4584; h) J. Du, F. Y. Cheng, S. W. Wang, T. R. Zhang, J. Chen, *Sci. Rep.* 2014, *4*, 4386.