

Supporting Information for

Preparation of Preferentially Exposed Poison-Resistant Pt(111) Nanoplates with Nitrogen-Doped Graphene Aerogel

Beibei Xie¹, Yong Zhong¹, Na Du^{1,2}, Haiping Li³, Wanguo Hou^{1,2}, Renjie Zhang^{1,2,3,}*

¹ Key Laboratory of Colloid and Interface Chemistry of the Ministry of Education of the P. R. China, Shandong University, Jinan 250199, P. R. China

² Key Laboratory of Special Functional Aggregated Materials of the Ministry of Education of the P. R. China, Shandong University, Jinan 250199, P. R. China

³ National Engineering Technology Research Center for Colloidal Materials, Shandong University, Jinan 250199, P. R. China

*Corresponding author, Email: zhrj@sdu.edu.cn

Materials and methods

Materials

Graphite flakes (99.9995 %) with a lateral width of 2-15 μm were purchased from Alfa Aesar (USA). Dopamine (DA), Nafion solution (5 wt.%) and $\text{H}_2\text{PtCl}_6 \cdot 5\text{H}_2\text{O}$ were purchased from Sigma-Aldrich. Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4 , 98 %), phosphate acid (H_3PO_4), hydrogen peroxide (H_2O_2 , 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 M Ω ·cm at 25 °C was used in all experiments.

Preparation of GO nanosheets as precursor of NGA

The preparation of GO nanosheets can be referred to our previous work based on an improved Hummers's method with some modifications.^{1,2} Briefly, a 9/1 (volume ratio) mixture of concentrated H₂SO₄/H₃PO₄ (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 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 85 mL of H₂O₂ (30 %). The GO nanosheets in the mixture were thoroughly washed three times with HCl (5.0 %), 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 (1.0 mg/mL) were subject to sonication (KQ-600KDB, 40 kHz, 300 W) for 8 h. The temperature of sonication water bath was kept below 30 °C.

Preparation of NGA

The preparation of NGA can be referred to our previous work using GO nanosheets and DA as precursors.³ GO nanosheets were sedimented separately by a high speed centrifuge (Sigma 3-18K, Germany, 27530 g, 90 min). The sedimentation was dispersed in 20 mL of freshly prepared Tris-HCl buffer solution (pH=8.5). To GO nanosheets dispersion (20 mL, 1.0 mg/mL), DA (20 mg) was added under stirring, followed by sonication (300 W, 40 min). The mixture was then kept in a 50 mL Teflon-lined autoclave (180 °C, 12 h) to obtain N-containing graphene hydrogel. After naturally cooled down to rt, the hydrogel was carefully taken out, washed separately by water and ethanol, then freeze-dried. NGA was obtained after annealing at 800 °C for 3 h under an Ar atmosphere.

Preparation of Pt₍₁₁₁₎NPTs/NGA with different loading amount of Pt₍₁₁₁₎NPTs

10 mg of NGA was mixed with 1 mL (0.05, 0.25, 0.5, or 1.5 mL, respectively) of H₂PtCl₆ (10

mg/mL) and 15 mL (0.75, 3.75, 7.5, or 22.5 mL) of EG solution. The mixture was transferred to a flask after stirring for 1 h, and then heated at 130 °C for 3 h in oil bath under stirring. The Pt₍₁₁₁₎NPTs/NGA with 20 wt% (1.5, 6.4 11.0, or 28.2 wt%) of Pt₍₁₁₁₎NPTs was isolated by repeated centrifugation (1359 g, 10 min), then washed with water, and freeze-dried.

Characterization

Pt₍₁₁₁₎NPTs for the Atomic force microscopy (AFM) measurement were obtained from Pt₍₁₁₁₎NPTs/NGA after thermal decomposition of NGA through annealing at 450 °C for 2 h under an air atmosphere. The AFM samples were prepared by dropping 5 μL of Pt₍₁₁₁₎NPTs aqueous dispersion (0.2 mg/mL) on mica substrates followed by air drying. AFM height images and section analysis were obtained in tapping mode (Nanoscope IIIA, Digital Instruments Corp., USA). 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 sticking 2 mg of NGA or Pt₍₁₁₁₎NPTs/NGA powders onto silicon substrates. X-ray diffraction (XRD) patterns were collected through a D8 Advance diffractometer (Bruker, Germany) with the Cu K α target (λ = 1.54184 Å) in an angular range of 8-90° at 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 pore size distribution of PtNPTs/NGA was obtained by calculating the adsorption branch with a density functional theory (DFT) method. Scanning electron microscopy (SEM) observation was carried out using a SU-8010 (Hitachi, Japan) instrument with an operating voltage of 5 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. High resolution TEM (HRTEM) images were obtained on a JEOL-2100F TEM (JEOL, Japan) with an acceleration

voltage of 200 kV. Raman spectra were obtained using a LabRAM HR 800 system (Horiba JY, France) with a laser of 633 nm. Thermogravimetric analysis (TGA) of PtNPTs/NGA was carried out 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 electrochemical tests for Pt₍₁₁₁₎NPTs/NGA with different loading amount of Pt(111)NPTs and Pt/C (20 wt%) were investigated on a CHI440C electrochemical work station with a three-electrode system. Pt₍₁₁₁₎NPTs/NGA with different loading amount of Pt(111)NPTs and Pt/C (20 wt%) modified glassy carbon electrode (GCE), Ag/AgCl (sat. KCl) and Pt electrode were used as working, reference and counter electrodes, respectively. Before coating, the GCE was activated as follows. Firstly, the GCE was polished using Al₂O₃ powder of 0.3 μm in diameter and rinsed separately with ethanol and water, then sonicated for 15 min, and dried by high purity N₂. Secondly, the GCE was repeatedly scanned by cyclic voltammetry (CV) testing in H₂SO₄ solution (0.5 M), in a potential range of -1.0-1.0 V at a scan rate of 50 mV/s, until the CV plots were stable. Thirdly, the efficiency of the activation of GCE was tested by CV scanning in 0.20 M KCl containing K₃Fe(CN)₆ (1×10⁻³ M) and K₄Fe(CN)₆ (1×10⁻³ M), in a potential range of -1.0-0.6 V at a scan rate of 50 mV/s. It is efficient if the difference of peak potential is less 80 mV, otherwise, the GCE should be activated by repeating the last two steps until the difference of peak potential is less than 80 mV. 5 mg of PtNPTs/NGA was purposely broken and dispersed in a mixture of 1 mL of ethanol and 50 μL of Nafion solution (5 wt.%). Subsequently, 10 μL of the above suspensions were casted onto GCE surfaces and dried under rt. The electrochemical surface area (ESA) of the Pt₍₁₁₁₎NPTs/NGA was measured through CV in N₂ saturated 0.5 M H₂SO₄ solution. The ESA was calculated from the formula of $ESA = Q_H / (0.21 M_{Pt})$.⁴ Q_H is the charge due to hydrogen adsorption/desorption in the hydrogen region of the CV plots, 0.21 is the electrical charge associated with a monolayer adsorption of hydrogen on Pt, and M_{Pt} is the mass of Pt loading on the working electrode. To measure electrocatalytic oxidation of methanol, a solution of 0.5 M methanol in 0.5 M H₂SO₄ purged with N₂ before measurement was taken, and CV plots were recorded in a potential range of 0-1.0 V at a scan rate of 50 mV/s.

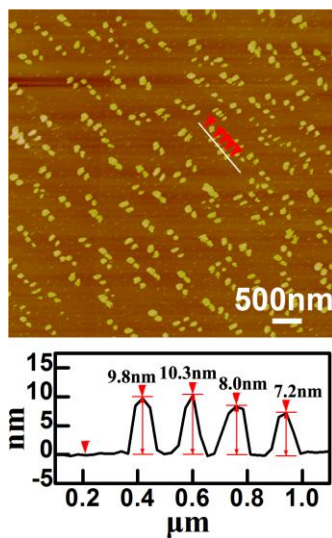


Figure S1. AFM height image and section analysis of Pt₍₁₁₁₎NPTs.

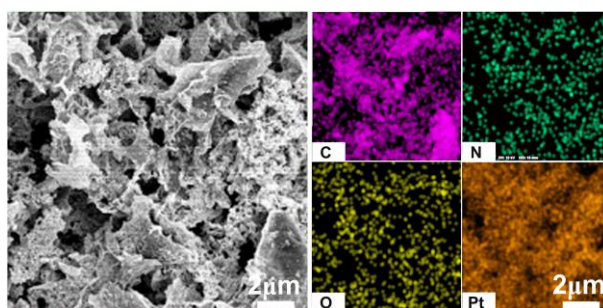


Figure S2. SEM image of Pt₍₁₁₁₎NPTs/NGA and the corresponding elemental mappings of C, N, O and Pt, respectively.

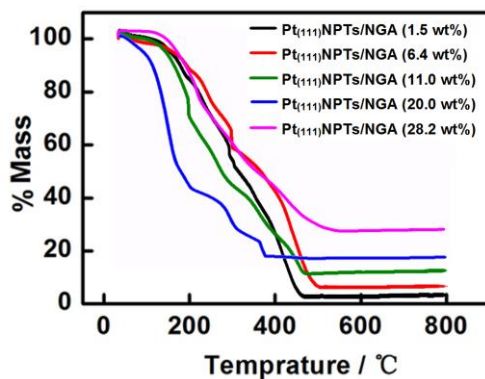


Figure S3. TGA curves of Pt₍₁₁₁₎NPTs/NGA with different loading amount of Pt₍₁₁₁₎NPTs.

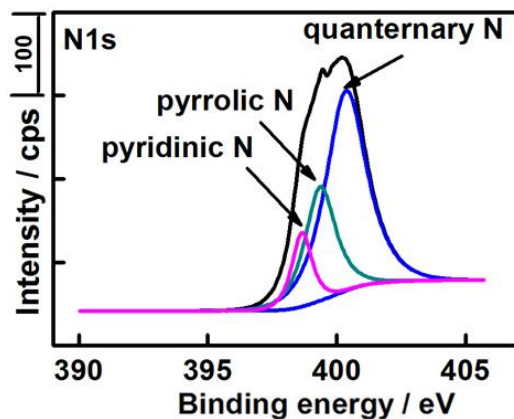


Figure S4. N1s XPS spectra of NGA.

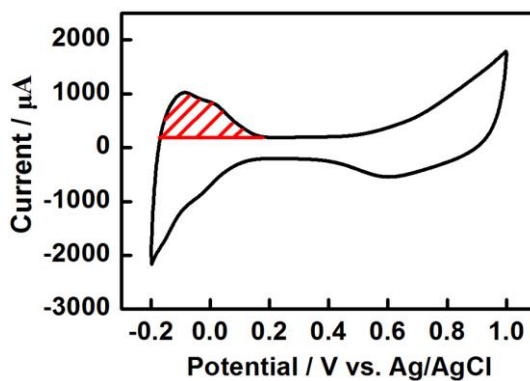


Figure S5. CV plot of $\text{Pt}_{(111)}\text{NPTs/NGA}$ electrodes in N_2 saturated aqueous solution of 0.5 M H_2SO_4 at a scan rate of 50 mV/s (the shaded part corresponds to hydrogen desorption).

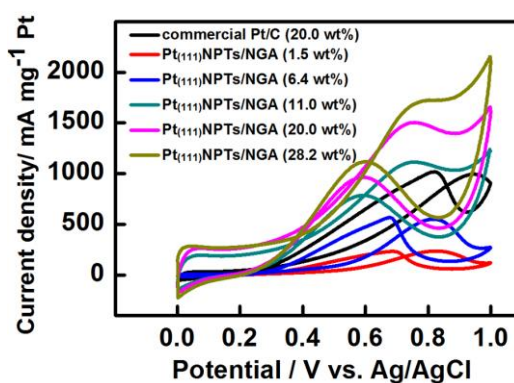


Figure S6. CV plots of $\text{Pt}_{(111)}\text{NPTs/NGA}$ with different loading amount of $\text{Pt}_{(111)}\text{NPTs}$ and that of commercial Pt/C (20 wt%) in N_2 saturated aqueous solution of 0.5 M H_2SO_4 containing 0.5 M CH_3OH at a scan rate of 50 mV/s.

Table S1. Comparison of onset potential, oxidation current, ability of poison-resistance (I_f/I_b) among Pt₍₁₁₁₎NPTs/NGA and reported graphene materials supported Pt catalysts.

Sample	Onset potential (V)	Oxidation current (mA mg ⁻¹ Pt)	I_f/I_b	Refs.
Pt/graphene	0.69	---	1.29	5
Pt/NG ^{a)}	0.71	376.17	---	6
Pt/NG	---	---	1.1	7
Pt/GOA ^{b)}	0.91	876	---	8
Pt/RGO ^{c)}	0.75	---	1.93	9
Pt ₍₁₁₁₎ NPTs/NGA	0.69	985	2.25	this work

a): nitrogen doped graphene, b): graphene oxide aerogel, c): reduced graphene oxide

Table S2. The catalytic data of commercial Pt/C and Pt₍₁₁₁₎NPTs/NGA with different loading amount of Pt₍₁₁₁₎NPTs for methanol electrochemical oxidation.

Sample	Onset potential (V)	Oxidation current (mA mg ⁻¹ Pt)	I_f/I_b
commercial Pt/C (20 wt%)	0.93	162.07	0.81
Pt ₍₁₁₁₎ NPTs/NGA (1.5 wt%)	0.81	179.3	1.19
Pt ₍₁₁₁₎ NPTs/NGA (6.4 wt%)	0.80	327.39	0.91
Pt ₍₁₁₁₎ NPTs/NGA (11.0 wt%)	0.74	485.67	1.61
Pt ₍₁₁₁₎ NPTs/NGA (20.0 wt%)	0.69	985.00	2.25
Pt ₍₁₁₁₎ NPTs/NGA (28.2 wt%)	0.72	1040.42	2.23

References and notes

- 1 B. Xie, Y. Li, J. Shang, J. Xin, X. Yang and R. Zhang, *Sci. Adv. Mater.*, 2014, **6**, 2395-2399.
- 2 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806-4814.
- 3 R. Zhang, B. Xie, X. Ren, X. Yan, Z. Dai, W. G. HOU, N. Du and H. Li, *RSC Adv.*, 2016, **6**, 23012-23015.
- 4 D. Chen, Q. Tao, L. W. Liao, S. X. Liu, Y. X. Chen and S. Ye, *Electrocatalysis*, 2011, **2**, 207-219.
- 5 M. La, X. Li, T. Sun, L. Qu, B. Zhou and F. Zhao, *Int. J. Electrochem. Sci*, 2015, **10**, 9539-9546.
- 6 B. Xiong, Y. Zhou, Y. Zhao, J. Wang, X. Chen, R. O'Hayre and Z. Shao, *Carbon*, 2013, **52**, 181-192.
- 7 L. Tao, S. Dou, Z. Ma, A. Shen and S. Wang, *Int. J. Hydrogen Energy*, 2015, **10**, 9539-9546.
- 8 J. Duan, X. Zhang, W. Yuan, H. L. Chen, L. Chang, Z. Sun and J. Du, *J. Power Sources*, 2015, **285**, 76-79.
- 9 H. Feng, Y. Liu and J. Li, *Chem. Commun.*, 2015, **51**, 2418-2420.