

## Supplementary Information

### **One-pot hydrothermal synthesis of platinum nanoparticle- decorated on three-dimensional nitrogen-doped graphene aerogel as a highly efficient electrocatalyst for the methanol oxidation**

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## 1. Experimental section

### 1.1. Reagents and Chemicals

Graphite was purchased from Qingdao Tianhe Graphite Co., Ltd. Glycine (GLY), Methanol (CH<sub>3</sub>OH), Concentrated Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and the Chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) were purchased from Sinopharm. Graphite oxide (GO) was prepared using modified Hummers method from graphite powders.<sup>1</sup> Doubly distilled water was used throughout this work. All other reagents were of analytical reagent grade.

### 1.2. Apparatus

Scanning electron microscopy (SEM) images and energy-dispersive spectra (EDS) were performed on a Hitachi S4800 scanning electron. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were conducted using a JEOL 100 instrument (JEOL, Japan) with an accelerating voltage of 200 kV. X-ray diffraction (XRD) spectra was conducted on a Bruker D8 diffractometer. Raman spectra were performed on a Renishaw in plus laser Raman spectrometer with  $\lambda_{\text{ex}} = 633 \text{ nm}$ . X-ray photoelectron spectroscopy (XPS) was conducted on a VG MultiLab 2000 system with a monochromatic Mg-K $\alpha$  source operated at 20 kV. The surface area of catalyst was evaluated using the Brunauer-Emmett-Teller (BET) method. The content of element for different catalysts was measured by EDS method. Electrochemical impedance spectra (EIS) were conducted using ZENNIUM electrochemical workstation in 0.1 M KCl solution containing 5

mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  with the frequency range from 0.01 Hz to 100 kHz. The cyclic voltammetry (CV) measurements of the methanol electro-oxidation were done in a mixed solution containing 0.5 M  $\text{H}_2\text{SO}_4$  and 1 M  $\text{CH}_3\text{OH}$  within a potential range of 0~1.0 V (vs.SCE) with a scan rate of 50 mV/s. Prior to the CV measurements, the electrolytes were purged with pure  $\text{N}_2$  gas for 30 min in order to remove any dissolved oxygen. The conventional three-electrode system was employed with a modified glassy carbon electrode (GCE, 3 mm) as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl (saturated with KCl) as the reference electrode.

### 1.3. Preparation of composites

Preparation of PtNPs/3DNGA composites: typically, 160  $\mu\text{L}$  of 500 mg/mL  $\text{H}_2\text{PtCl}_6$  was added into 10 mL aqueous solution of 2.7 mg/mL GO and sonicated for several minutes. After 100 mg of glycine were added into the as-prepared solution, the mixture was sonicated for several hours and then poured into stainless-steel autoclave. The temperature of the mixture was heated to 180  $^\circ\text{C}$  for 12 h to prepare PtNPs/3DNGA composites. After cooled to room temperature, the obtained PtNPs/3DNGA composites were submerged in doubly distilled water overnight to remove all the unreacted chemicals. This process was repeated several times. Then all the obtained PtNPs/3DNGA composites were freeze dried for 2 days.

Preparation of PtNPs decorated graphene hydrogel (PtNPs/3DGA) composites: for comparison, the PtNPs/3DGA composites were synthesized with the same process except for the addition of glycine, respectively.<sup>2</sup>

Preparation of PtNPs decorated graphene (PtNPs/2DGR) composites: PtNPs were deposited on GO sheets by a chemical reduction of chloroplatinic acid in glycine water solution. The glycine was added into the aqueous solution of  $\text{H}_2\text{PtCl}_6$  and GO in a 25 ml flask. The mixture was first ultrasonically treated to ensure GO being uniformly dispersed. Then performed at high temperature for 24 h under constant stirring. The PtNPs/2DGR nanocomposites were finally separated by filtration and washed with doubly distilled water several times. The resulting product was dried in a vacuum desiccator at room temperature.<sup>3</sup>

## **2. Preparation of material electrodes**

To prepare the modified electrodes, a glassy carbon electrode was polished, sonicated and rinsed with doubly distilled water. Next 2 mg PtNPs/3DNGA, PtNPs/3DGA, and PtNPs/2DGR nanocomposites were diluted in 1 mL doubly distilled water, respectively. 6  $\mu\text{L}$  of these solutions were dropped onto a polished 3-mm diameter glassy carbon electrode and left to dry at room temperature, respectively.

## **3. Characterization**

X-ray diffraction (XRD) spectra was conducted on a Bruker D8 diffractometer. Raman spectra were performed on a Renishaw in plus laser Raman spectrometer with  $\lambda_{\text{ex}} = 633 \text{ nm}$ . X-ray photoelectron spectroscopy (XPS) was conducted on a VG MultiLab 2000 system with a monochromatic Mg-K $\alpha$  source operated at 20 kV.

### **3.1. XPS**

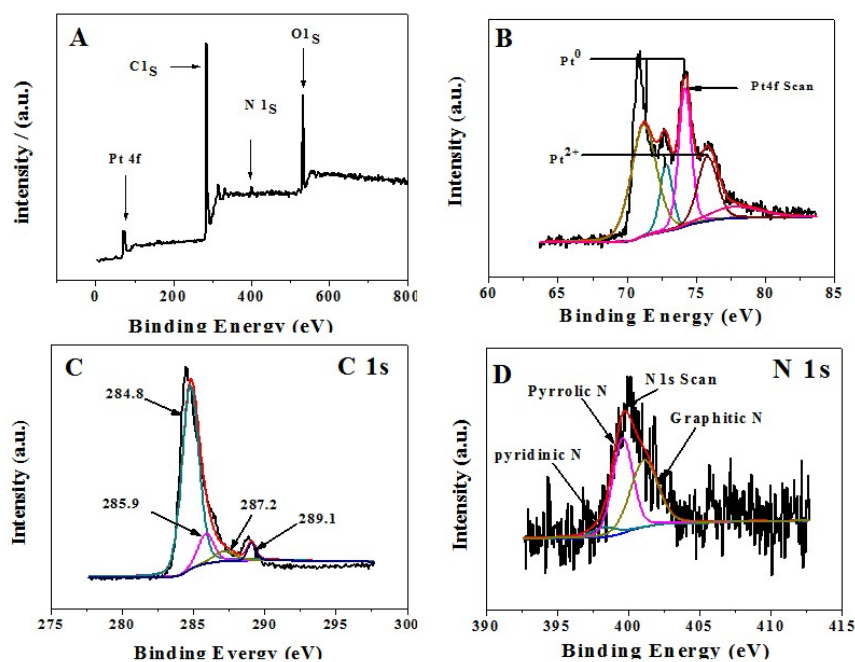


Figure S1. (A) XPS survey spectra of PtNPs/3DNGA composites. (B) Pt 4f XPS spectrum of the PtNPs/3DNGA composites. (C) The high-resolution XPS spectra of the C 1s region for PtNPs/3DNGA composites. (D) The high-resolution XPS spectra of the N 1s region for PtNPs/3DNGA composites.

Elemental analysis demonstrated that PtNPs/3DNGA nanoparticles had abundant N (3 wt%). The high resolution scan of Pt 4f showed two states of Pt in the compound: the dominant one was metallic Pt that showed two peaks appeared at 71.4 and 74.7 eV, and the other was the 2+ oxidation state of Pt with the couple of peaks at 71.8 and 76.0 eV, the third doublet of Pt showed the weakest intensity and was at even higher binding energies (75.6 and 78.1 eV), which were most likely from a small amount of Pt (IV) (Fig. S1B).<sup>4</sup> The C 1s XPS spectrum could be deconvoluted into (Fig. S1C) four peaks appeared at 284.8, 285.9, 287.2, and 289.1 eV, corresponding to  $sp^2$ - $sp^2$ C, N- $sp^2$ C, N- $sp^3$ C, and C-O type bonds, respectively.<sup>5</sup> The deconvoluted N 1s XPS spectrum showed three peaks at the binding energies of 398.3, 399.6, 401.1eV,

which were ascribed to the pyridinic, pyrrolic, and graphitic N, respectively (Fig. S1D).<sup>6</sup> As confirmed in the literature, the three types of N could form strong interactions with Pt atoms.<sup>7</sup>

### 3.2. TEM

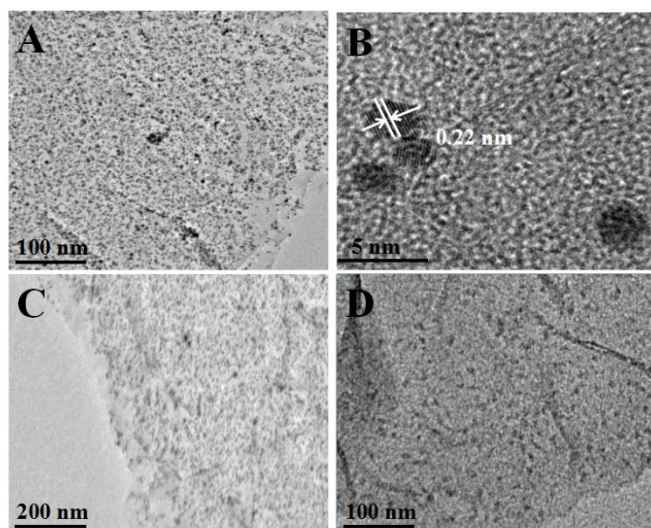


Figure S2. The low-resolution (A) and high-resolution (B) TEM images of PtNPs/3DNGA; (C), (D) TEM images of PtNPs/3DGA and PtNPs/2DGR, respectively.

### 3.3. The surface area

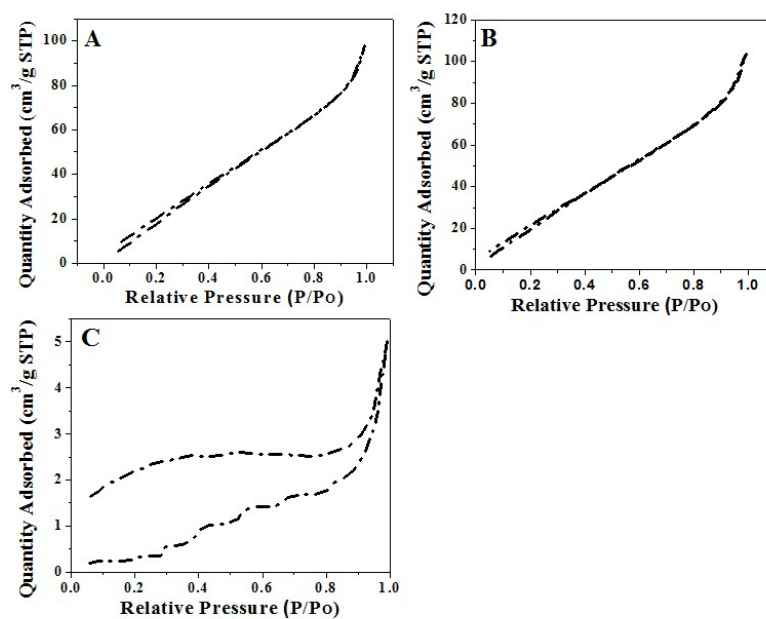


Figure S3. N<sub>2</sub> adsorption and desorption isotherm of PtNPs/3DNGA (A), PtNPs/3DGA (B) and

### 3.4. Elements content

Table S1. The content of different elements for the catalysts.

Catalysts	element content (mass%)	C	N	Pt
PtNPs/3DNGA		65.70	28.32	5.98
PtNPs/3DGA		66.23	0	3.08
PtNPs/2DGR		69.23	10.06	1.70

## 4. Electrochemical measurements

To evaluate the electrochemical properties of the resulting composites, the working electrodes were fabricated using the following procedure: a suspension with a concentration of  $2 \text{ mg mL}^{-1}$  was prepared by sonication to disperse the as-prepared samples. The suspension ( $6 \mu\text{L}$ ) was then drop coated onto a glassy carbon disk with a diameter of 3 mm and dried thoroughly at room temperature in air.

Cyclic voltammetry (CV) of the catalyst electrodes was performed in a conventional three-electrode system using a CHI 660B electrochemical workstation, which consists of the catalyst modified GCE as the working electrode, a platinum foil as the auxiliary electrode and a Ag/AgCl (saturated with KCl) as the reference electrode. The cycling potential was controlled in the range between -0.2 and 1.2 V at the scan rate of 50 mV/s in nitrogen saturated aqueous solution of 0.5 M  $\text{H}_2\text{SO}_4$ , or 0.5 M  $\text{H}_2\text{SO}_4$  containing 1 M  $\text{CH}_3\text{OH}$ . The electrochemical impedance spectroscopy (EIS) was conducted using ZENNIUM electrochemical workstation in 0.1 M KCl solution containing 5 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  with the frequency range from 0.01 Hz to 100

kHz. The electrochemical active surface area (ECSA) of the catalyst was determined using following equation:<sup>8</sup>

$$\text{ECSA [cm}^2\text{/g of Pt]} = \frac{\text{Charge [Q}_H\text{, uC/cm}^2\text{]}}{210 [\text{uC /cm}^2\text{]} * \text{electrode loading} * [\text{g of Pt /cm}^2\text{]}}$$

where  $Q_H$  was the total charge concerning  $H^+$  adsorption ( $\text{mC/cm}^2$ ); [Pt] was the platinum loading in the electrode ( $\text{mg/cm}^2$ ), and 0.21 was the charge required to oxidize the  $H_2$  monolayer on a bright Pt ( $\text{mC/cm}^2$ ).<sup>9-11</sup>

## References

1. S. Gilje, S. Han, M. S. Wang, K. L. Wang and R. B. Kaner, *Nano Lett.* 2007, 7, 3394.
2. Y. Qin, L. Chao, J. Yuan, Y. Liu, F. Chu, Y. Kong, Y.X. Tao and M.L. Liu, *Chem. Comm.* 2016, 52, 382.
3. Y. J. Li, W. Gao, L. J. Ci, C.M. Wang and P. M. Ajayan, *Carbon* 2010, 48, 1124.
4. Q. H. Huang, F. F. Tao, L. L. Zou, T. Yuan, H. Zhang and H. Yang, *Electrochim. Acta* 2015, 152, 140.
5. D. Jiang, Q. Liu, K. Wang, J. Qian, X. Y. Dong, Z. T. Yang, X. J. Du and B. J. Qiu, *Biosens. Bioelectron.* 2014, 54, 273.
6. Y. H. Li, T. H. Hung and C. W. Chen, *Carbon*, 2009, 47, 850.
7. G. Yang, Y. Li, R. K. Rana, J. J. Zhu, *J. Mater. Chem. A* 2013, 1, 1754.



8. G. Girishkumar, M. Rettker, R. Underhile, D. Binz, K. Vinodgopal, P. McGinn and P. Kamat, *Langmuir*, 2005, 21, 8487.
9. A. Pozio, M. D. Francesco, A. Cemmi, F. Cardellini and L. Giorgi, *J. Power Sources*, 2002, 105, 13.
10. J. Perez, E. R. Gonzalez and E. A. Ticianelli, *Electrochim. Acta*. 1998, 44, 1329.
11. K. Tao, J. Wang, Y. Li, D. Xia, H. Shan and H. Xu, *Sci. Rep.* 2013, 3, 2565.