Supporting Information

## Hydrothermal Synthesis of a New Kind of N-doped Graphene Gellike Hybrid as an Enhanced ORR electrocatalyst

Qin Xiang, Yuping Liu, Xuefeng Zou, Bingbing Hu, Yujie Qiang, Danmei Yu, Wei Yin, and Changguo Chen\*

College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, China.

\*Email: cgchen@cqu.edu.cn

## **Electrochemical Measurement.**

To prepare the working electrode, 5 mg of catalyst was ultrasonically dispersed in 450 µL of water, 50 µL of ethanol, and 125 µL of 0.05 wt.% Nafion solution to form a homogeneous ink. Then 10 µL of the resulting catalyst ink was dropped onto a prepolished rotating disk electrode (RDE,  $\Phi = 5$  mm, the loading of the catalysts was 0.407 mg cm<sup>-2</sup>) and allowed to dry in air naturally. For comparison, a 20 wt.% JM-Pt/C at loadings of 0.13 mg cm<sup>-2</sup>, was prepared in the same way. Electrochemical measurements were performed on an electrochemical workstation (CHI760E, CH Instrument, China) equipped with a conventional three-electrode electrochemical cell, and controlled at 25°C using a water-bath. The counter electrode was Pt wire, and the reference electrode was Ag/AgCl. All potentials were later converted to the RHE scale, the calibration was performed in the high-purity H<sub>2</sub> saturated electrolyte with Pt wires as the working and counter electrodes.<sup>1</sup>

The ORR was carried out in an N<sub>2</sub>- or O<sub>2</sub>- saturated 0.1 M KOH, including cyclic voltammetry (CV), rotating-disk electrode voltammograms, and chronoampero-metric response *i*–*t*. CV curves was typically carried out in the potential range from 1.2 to 0.0 V with 50 mV s<sup>-1</sup>. For the RDE measurements, the scan rate was 10 mV s<sup>-1</sup> and the disk rotation rate was from 400 to 2500 rpm. Afterwards, the durability of the catalyst was tested by cycling the potential from 0.6 V to 0.9 V (vs. RHE) with 50 mV s<sup>-1</sup>. For methanol tolerance test, methanol (5 mL) was added to the O<sub>2</sub> saturated 0.1 M KOH solution around 400 s and 700 s, respectively. The current was recorded at 0.4 V vs. RHE with 1600 RPM.<sup>1</sup>

Calculation of the kinetic-limiting current  $(j_k)$  and the electron transfer number (n).

According to the Koutecky-Levich equation given below:

$$j^{-1} = j_k^{-1} + B^{-1} \omega^{-1/2}$$

Where *j* is the measured current,  $\omega$  donates the rotation speed in RPM, and *B*, the reciprocal of the slope, could be determined from the slope of Koutecky-Levich plots based on Levich equation as follows:

$$B=0.2nFC_{\Omega 2} (D_{\Omega 2})^{2/3} v^{-1/6}$$

- *F*: The Faraday constant (96,485 C mol<sup>-1</sup>);
- $C_{O2}$ : The bulk concentration of  $O_2$  (1.2×10<sup>-6</sup> mol cm<sup>-3</sup>);
- $D_{02}$ : The diffusion coefficient of O<sub>2</sub> in 0.1 M KOH (1.9×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>);
- v: The kinetic viscosity (0.01 cm<sup>2</sup> s<sup>-1</sup>).

The constant 0.2 is adopted when the rotation speed is expressed in RPM.



Figure S1. Photographs for the preparation of catalyst NGS4-900.



Figure S2. SEM image of pristine GO (a) and hydrothermal GO (b,c) at different magnifications.

The pristine GO has a two-dimensional structure consisting of sheets with much wrinkles and fringes. After the thermal expansion process, the GO was assembled into a rich-edges volume-fluffy flower-like structure.



Figure S3. TEM images of g-C<sub>3</sub>N<sub>4</sub>@GO (a,b) and NGS4-900 (c,d) at different magnifications.

In g-C<sub>3</sub>N<sub>4</sub>@GO, the g-C<sub>3</sub>N<sub>4</sub> sheet was sandwiched between graphene sheets, forming a well-dispersed sheet-on-sheet structure, the sheets of NGS4-900 become thinner and transparent with many wrinkles and edge sites after removal of g-C<sub>3</sub>N<sub>4</sub>.



Figure S4. TGA of g-C<sub>3</sub>N<sub>4</sub> in N<sub>2</sub> with a temperature rise rate of 10 °C min<sup>-1</sup>.

The curve falls down (7%) prior to 100 °C is due to the moisture loss, and the weight loss (93%) between 350 and 680 °C is due to the decomposition of  $g-C_3N_{4.2}$ 



Figure S5. TGA of GO in N<sub>2</sub> with a temperature rise rate of 10 °C min<sup>-1</sup>.

The curve falls down prior to 100 °C is due to the moisture loss, and the weight loss between 150 and 300 °C is due to the CO, CO<sub>2</sub>, and steam release from the most labile functional groups. Between 650 and 800 °C, the mass loss can be attributed to the removal of more stable oxygen functionalities. <sup>3-4</sup>



Figure S6. XRD patterns of hydrothermal GO (a) and the prepared catalysts (b) with different mass ratio of  $g-C_3N_4$  to GO.

A broad peak centered at around 24° is observed for hydrothermal GO sample, confirming the recovery of graphitic crystal structure after hydrothermal process.



Figure S7. Raman spectra of pristine GO, hydrothermal GO and NGS4-900.



Figure S8. The possible structures of nitrogen atom and defective edges in the catalyst.



Figure S9. FT-IR spectra of pristine GO, g-C<sub>3</sub>N<sub>4</sub> and NGS4-900.

In the FTIR spectra of g-C<sub>3</sub>N<sub>4</sub>, the peak at 810 cm<sup>-1</sup> is attributed to the breathing mode of the triazine units, a series of peaks at the region of 1200-1650 cm<sup>-1</sup> are origin from the typical stretching vibrations of CN heterocycles; the broad bands at 3200-3400 cm<sup>-1</sup> ascribes to the N-H vibration of secondary, primary amines and the adsorbed H<sub>2</sub>O molecules.<sup>5</sup>As for GO, the peaks at 1068 and 1406 cm<sup>-1</sup> are corresponding to the C-O stretching vibrations and tertiary C-OH groups stretching, respectively; the 1631 and 1723 cm<sup>-1</sup> belong to the OH bending vibration of epoxide groups and skeletal ring and the C=O stretching of COOH groups, respectively.<sup>6</sup> Additionally, a new peak emerges at 1557 cm<sup>-1</sup>, can be assigned to the skeletal vibration of the graphene sheets.



**Figure S10.** (a) CV curves of **20 wt.% JM-Pt/C** in N<sub>2</sub> and O<sub>2</sub> saturated 0.1 M KOH at 50 mV s<sup>-1</sup>; (b) LSV curves of 20 wt.% JM-Pt/C at different rotating rates; (c) K-L plots at different potentials.



**Figure S11.** (a) CV curves of hydrothermal GO in  $N_2$  versus  $O_2$  saturated 0.1 M KOH at 50 mV s<sup>-1</sup>; (b) LSV curves of hydrothermal GO at different rotating speeds; (c) K-L plots at different potentials.



Figure S 12. SEM image of NGS2-900(a), NGS4-900(b), and NGS6-900(c).



**Figure S13.** (a) CV curves of **NGS2-900** in N<sub>2</sub> versus O<sub>2</sub> saturated 0.1 M KOH at 50 mV s<sup>-1</sup>; (b) LSV curves of NGS2-900 at different rotating speeds; (c) K-L plots at different potentials.



**Figure S14.** (a) CV curves of **NGS6-900** in  $N_2$  versus  $O_2$  saturated 0.1 M KOH at 50 mV s<sup>-1</sup>; (b) LSV curves of NGS6-900 at different rotating speeds; (c) K-L plots at different potentials.

Catalysts  $E_{1/2}(V)$  $J_{\rm L}({\rm mA~cm^{-2}})$  $E_{onset}(V)$ п NGS2-900 0.964 0.844 5.71 3.6 NGS4-900 0.984 0.859 5.98 3.9 NGS6-900 3.9 0.975 0.856 5.81 Pt/C 0.971 0.848 3.9 5.41

Table S1 Electroactivity of catalysts with different g-C<sub>3</sub>N<sub>4</sub>/GO mass ratio.



**Figure S15.** (a) CV curves of **NGS4-700** in N<sub>2</sub> versus O<sub>2</sub> saturated 0.1 M KOH at 50 mV s<sup>-1</sup>; (b) LSV curves of NGS4-700 at different rotating speeds; (c) K-L plots at different potentials.



**Figure S16.** (a) CV curves of **NGS4-800** in N<sub>2</sub> versus O<sub>2</sub> saturated 0.1 M KOH at 50 mV s<sup>-1</sup>; (b) LSV curves of NGS4-800 at different rotating speeds; (c) K-L plots at different potentials.



Figure S17. (a) CV curves of NGS4-1000 in  $N_2$  versus  $O_2$  saturated 0.1 M KOH at 50 mV s<sup>-1</sup>;

(b) LSV curves of NGS4-81000 at different rotating speeds; (c) K-L plots at different potentials.

The CV curves in N<sub>2</sub>-saturated 0.1 M KOH solutions for all catalysts were quasi rectangular without any oxygen reduction peaks, but in O<sub>2</sub> environment, the cathodic peaks were observed clearly for all catalysts, suggesting that the NGS shows significant ORR activities.



Figure S 18. SEM image of NGS4-700(a), NGS4-800(b), and NGS4-1000(c).

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