Supplementary Information for

# Chemically converted graphene as substrate for immobilizing and enhancing the activity of a polymeric catalyst

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## 1. Experimental

**Chemicals.** Natural graphite powder (325 mesh) was bought from Qingdao HuaTai Lubricant Sealing S&T CO. LTD. (Qingdao, China). Melamine (99%) and Hydrazine monohydrate (98%) were purchased from Alfa Aesar. Hexachloroplatinic (□) acid hexahydrate (AR, $H_2PtCl_6 \cdot 6H_2O$) and Nafion (5 wt. %) were purchased from Sinopharm Chem. Reagent Co. LTD (Beijing, China). All reagents described above were used as received without further purification.

**Synthesis of CCG.** Graphite oxide (GO) was prepared by oxidation of natural graphite powder according to the method developed by Hummers and Offemann; the procedures of GO preparation and purification were reported previously.[1] CCG was prepared as follows. 100 mL (1 mg $mL^{-1}$) of purified GO dispersion was mixed with

1 mL of hydrazine monohydrate, and 50 mg of NaOH was added to adjust the pH value of the solution to 10. The mixture was stirred at 80 $^{o}$C for 24 h. After reduction, the product was filtrated and washed repeatedly with deionized water, and finally dried at 60 $^{o}$C for 24 h under vacuum.

**Synthesis of GCN**. GCN was prepared by polymerization melamine（2, 3, 6-triamino-1,3,5-triazine）under argon atmosphere by heating to 823 K at a rate of 2.2 K min$^{-1}$ and then kept at this temperature for 4 h.

**Synthesis of G-GCN.** 900 mg melamine was dissolved in 275 mL deionized water at room temperature to make a saturated solution. Then, 25 mL graphite oxide dispersion (4 mg mL$^{-1}$) was added under stirring. The pH value of the solution was adjusted to 10 by adding 100 mg NaOH. The mixture was reduced by adding 1 mL hydrazine monohydrate under stirring at 80 $^{o}$C for 24 h. Successively, the mixture was filtered though a porous polytetrafluoroethene membrane with pore diameter of 0.2 μm and washed repeatedly with deionized water. The resulting composite of CCG and melamine was dried at 60 $^{o}$C for 12 h under vacuum. Finally, it was heated at a rate of 2.2 K min$^{-1}$ to 823 K and then kept at this temperature for another 4 h to produce G-GCN.

**Synthesis of G-Pt.** To prepare G-Pt, a controlled amount of $H_2PtCl_6$ (containing 20 mg Pt) was added to 100 mL GO dispersion (1 mg/mL) under stirring and 50 mg

NaOH was used to adjust the pH value of the solution to 10. Then, the mixture was reduced at 80 $^{o}$C for 24 h by adding 1 mL hydrazine monohydrate. G-Pt composite was collected after washing with deionized water. Finally, it was dried at 60 $^{o}$C for 24 h under vacuum.

**Preparation of the Electrodes.** Glassy carbon electrode (surface area = 0.07 $cm^2$) was polished to a mirror using 0.5 μm and 50 nm alumina power. Then, the electrode was sonicated alternately in deionized water and ethanol for several times, and successively dried with nitrogen stream. 10 mg of catalyst was add to 0.5 mL aqueous solution containing Nafion (50 μL, 5%, by weight) and ethanol (50 μL). The mixture was sonicated for 30 min, and 2.5 μL of the solution was deposited on the glassy carbon electrode and dried at 60 $^{o}$C. For rotating disk electrode (RDE) voltammograms, 5 μL mixture was drop casted on the RDE (disk area = 0.20 $cm^2$) and dried at 60 $^{o}$C.

**Electrochemical Measurements.** All the electrochemical measurements were carried out in a conventional three-electrode system. Cyclic voltammetry (CV) was carried out using a CHI 440A potentiostat under computer control. The catalyst modified glassy carbon electrode was used as the working electrode, a Pt plate electrode and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. Aqueous solution of 0.1 mol $L^{-1}$ KOH was used as the electrolyte. For making $O_2$ or $N_2$ saturated electrolyte, pure $O_2$ or pure $N_2$ gas was

purged into the solution for 30 min before measurements and kept bubbling the corresponding gas during the tests. RDE voltammetry was recorded on a VersaSTAT 3 potentiostat and a CHI 616 (Princeton) electrode rotator. The 0.1 M KOH solution was purged with pure $O_2$ for 30 min before RDE voltammetry measurements and kept bubbling $O_2$ gas during the measurements. The potential scanning rate was 10 mV $s^{-1}$. Chronoamperometric response was measured by the use of a CHI 440A potentiostat. The electrodes were held at −0.4 V in 0.1 mol $L^{-1}$ KOH aqueous solution saturated with $O_2$ as described above and under magnetic stirring.

**Characterizations:** Scanning electron microscopy (SEM) images were taken out on a FEI Sirion 200 scanning electron microscopy. Thermo-gravimetric analysis (TGA) was performed by the use of a TGA 2050 thermal analysis system in air at a heating rate of 5℃ $min^{-1}$. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI 550 EACA/SAM photoelectron spectrometer (Perkin- Elmer PHI) with Al Kα (1486.6 eV) radiation. X-ray diffractions (XRD) patterns were recorded on a D8 Advance (Bruker) X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å). Conductivities were measured by pour-probe technique with the pressed pallets of the materials as the samples.

## 2. XPS spectra of G-GCN

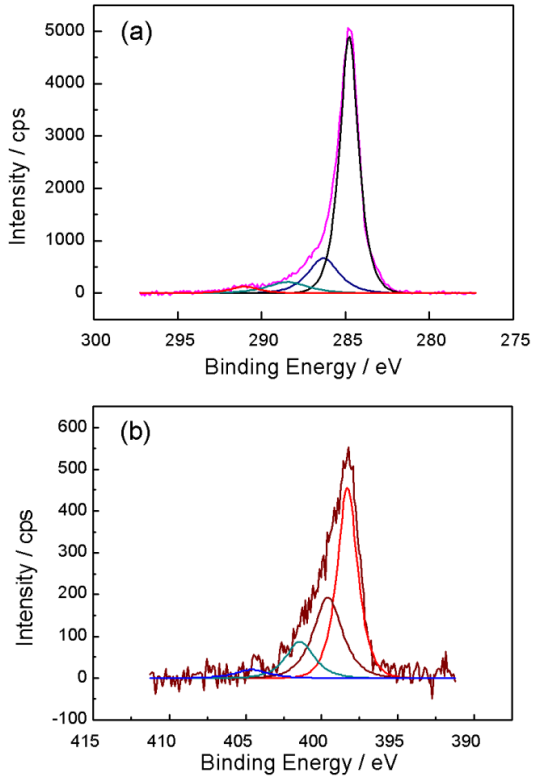


**Fig. S1.** C 1s (a) and N 1s (b) XPS spectra of G-GCN.

Fig. S1 shows the C1s and N1s XPS spectra of G-GCN composite. In the C 1s spectrum (panel a), the dominate peak at 284.7 eV is attributed to the $sp^2$ C-C bonds of graphene. The band at 288 eV is the characteristic of C-N-C bonds. XPS examinations also revealed that the ratio of nitrogen atoms to carbon atoms is about 0.1. This result is in agreement with that of elemental analysis described in the text. The N 1s XPS spectrum can be divided into four peaks at 398.3, 399.5, 401.4 and 404.4 eV, respectively (panel b). The strongest signal at 398.5 eV is related to the C-N=C groups and the weak peak at about 399.5 and 401.4eV are attributed to $N\text{-}(C)_3$

groups and amino functional groups carrying a hydrogen atom (C-N-H), respectively.[2,3] The existence of the N-$(C)_3$ confirms the polymerization of melamine and the intensity ratio of N-$(C)_3$/C-N-H peaks reflects the degree of condensation reaction. The peak at 404.4e V is assigned to N-O bonds, and this peak is so weak that comparable to noise. [2–4]

3. **Morphological studies of CCC, GCN, G-GCN, G-Pt.**

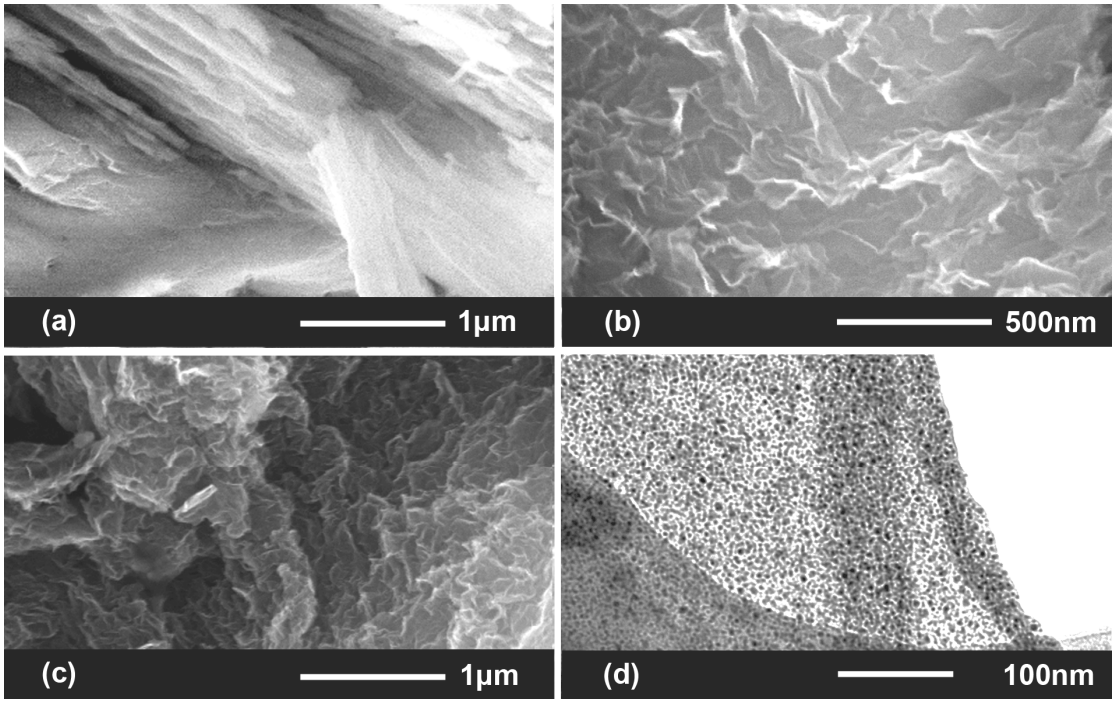


**Fig. S2.** SEM image of GCN (a), CCG (b), G-GCN (c), and TEM image of G-Pt (d).

Fig. S2 illustrates the SEM of GCN, CCG and G-GCN composite and transmission electron micrograph (TEM) of G-Pt composite. It is clear from panel a of Figure S2 that GCN has a layered structure similar to that of graphite, but some

disordered structures are also exist, indicating it is a polycrystalline material. The SEM image of CCG indicates that CCG is porous material and its sheets are curled with gauffers (panel b). In comparison with CCG, G-GCN composite has a more compact morphology (panel c). In this case, GCN component was sandwiched between graphene sheets through polymerization of melamine molecules adsorbed on CCG sheets. The TEM image of G-Pt composite (panel d) demonstrates that Pt nanoparticles uniformly immobilized on the surfaces of graphene sheets.

4. **The weight content and sizes of Pt nanoparticles in G-Pt composite.**

The weight content of Pt in G-Pt composite was tested to be about 23 wt. % by thermogravimetric analysis (TGA) in air (Fig. S3). Fig. S4a is a TEM image of Pt particles in G-Pt composite. According to this Figure, the Pt particles have sizes in the range of 2 to 10 nm and their average diameter was calculated to be 5.3 nm (Fig. S4b).

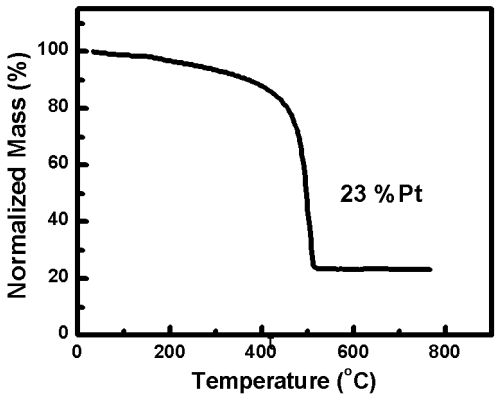


**Fig. S3.** TGA curve of Pt-G .

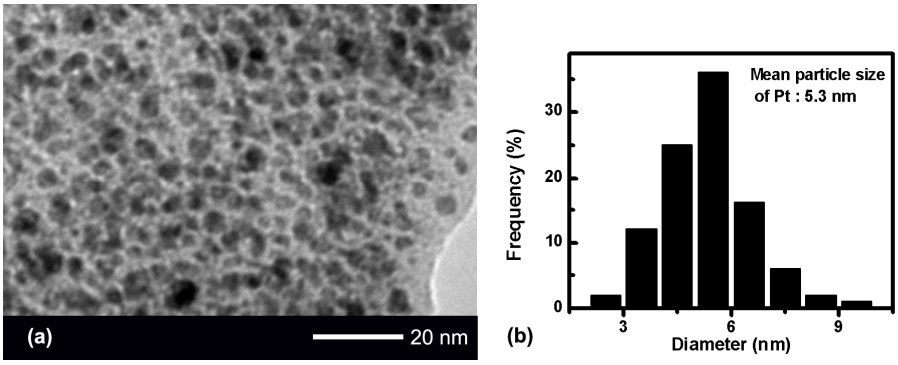


**Fig. S4.** TEM image of G-Pt (a), and the histogram of Pt metal particle diameters for G-Pt (b).

## 5. CVs of CCC, GCN, G-GCN or G-Pt modified electrode in $O_2$ or $N_2$ saturated electrolytes

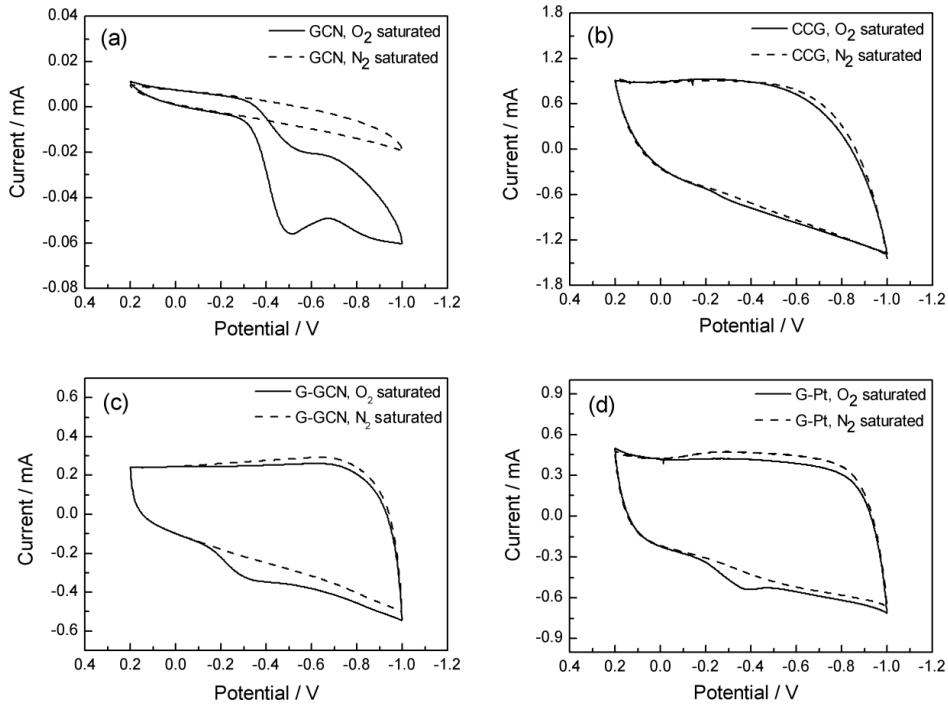


**Fig. S5.** Cyclic voltammograms of GCN (a), CCG (b), G-GCN (c) and G-Pt (d) modified glassy carbon electrodes in oxygen or nitrogen saturated 0.1 mol $L^{-1}$ KOH aqueous solutions. Scan rate = 100 mV $s^{-1}$.

## 6. Effect of GCN content on the electrocatalytic activity of G-GCN on ORR.

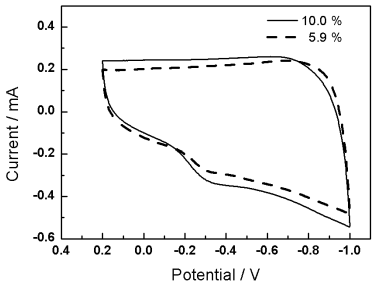


**Fig. S6.** Cyclic voltammograms of G-GCN with nitrogen contents 10.0 wt. % and 5.9 wt. %, respectively, in oxygen saturated 0.1 mol $L^{-1}$ KOH aqueous solutions. Scan rate =100 mV $s^{-1}$.

Fig. S6 indicates the CV wave current of ORR at G-GCN containing 5.9 wt. % nitrogen (90 μA) is about 75% of that at G-GCN containing 10.0 wt. % nitrogen (120 μA).

## References

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