

Supporting Information for

Comparative studies of graphene oxide and reduced graphene oxide as carbocatalysts for polymerization of 3-aminophenylboronic acid

Lin Tan*, Bin Wang and Huixia Feng*

College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou, Gansu
730050, China

Email: tanlin@lut.cn; fenghx@lut.cn

Experimental Section

Materials

Graphene, 3-aminophenylboronic acid hemisulfate salt (ABA), potassium fluoride, fructose, were purchased from Aldrich and used as received. And other chemicals were used without further purification. All of the solutions were prepared using deionized water (18.2 MΩ).

General Methods

To identify the crystalline phase and the extent of surface functionalization of GO and RGO, X-ray diffraction (XRD) patterns and Elemental analyses data were collected using a Rigaku D/MAX 2400 diffractometer and an elementar analysensysteme GmbH varioEL cube analyzer, respectively. The conductivities of GO and RGO were also explored by the four-point probe system (ST2253, Suzhou Jingge Electronic Co., China). Electrochemical polymerization was performed with a CHI660B electrochemical workstation (CHI, USA) with a conventional three-electrode system, consisting of a glassy carbon working electrode (GCE, 3 mm diameter), a platinum foil counter electrode and a saturated calomel reference electrode (SCE). GCE was polished with alumina slurry of 50 nm diameter on a polishing cloth and then sonicated in a distilled water bath for 15 min before use. In situ polymerization was monitored by U-2001 UV-vis spectrophotometer.

Preparation of GO and reduced graphene oxide (RGO)

GO nanosheets were prepared from natural graphite powders by a modified Hummer's method¹. In the first step, preoxidized graphite powder was synthesized through reaction of natural graphite (1 g), sulfuric acid (4 mL), K₂S₂O₈ (0.8 g), and P₂O₅ (0.8 g), the reaction mixture was maintained at 80 °C for 5h and was terminated by adding 170mL deionized water. This preoxidized graphite powder (600 mg) was further oxidized by sulfuric acid (24 mL), KMnO₄ (3 g), the reaction mixture was stirred at 35 °C for 2h. In the end, the reaction mixture was maintained at 98 °C for 0.5h and was terminated by adding 50 mL deionized water. It was then further treated with H₂O₂ (30 wt %, 6 mL). The resulting GO solution was filtered and washed with deionized water several times, and complete remove of metal ions by dialysis membrane for a week, and vacuum dried overnight at 40 °C.

In a typical synthesis, GO (10 mg) were dispersed in deionized water to create 0.1 mg/mL dispersion with the aid of ultrasonication. Hydrazine monohydrate (0.1 mL, 98%) was then added, and the suspension was heated at 80 °C for 24 h. Finally, black RGO dispersion was obtained. In order to avoid agglomeration, RGO was used for further experiment as soon as possible.

GO exhibited a conductivity of 2.4×10^{-5} S/cm, and RGO exhibited an increased conductivity of

3.5 S/cm. Likewise, elemental analyses revealed deoxygenation of GO to form RGO. An increase in the C/O atomic ratio of RGO was found to be 2.66 compared to 1.08 in as-prepared GO (Table. S1).

	C (wt%)	N (wt%)	H (wt%)	O (wt%)	C/O
GO	43.30	0.24	3.06	53.39	1.08
RGO	62.58	4.03	1.99	31.4	2.66

Table S1 Elemental analysis results of GO and RGO

Figure S1 shows the XRD patterns of pristine graphite powder, GO and RGO. Graphite powder shows a sharp (002) peak at 26.4° with a typical d-spacing of 3.37 Å. GO exhibits a diffraction peak (002) at 2theta of 11.37° corresponding to a d-spacing of 7.82 Å, which suggests that graphite has been successfully oxidized by Hummers' method. It is also seen that the corresponding peak disappears after reduction, indicating the successful formation of RGO.

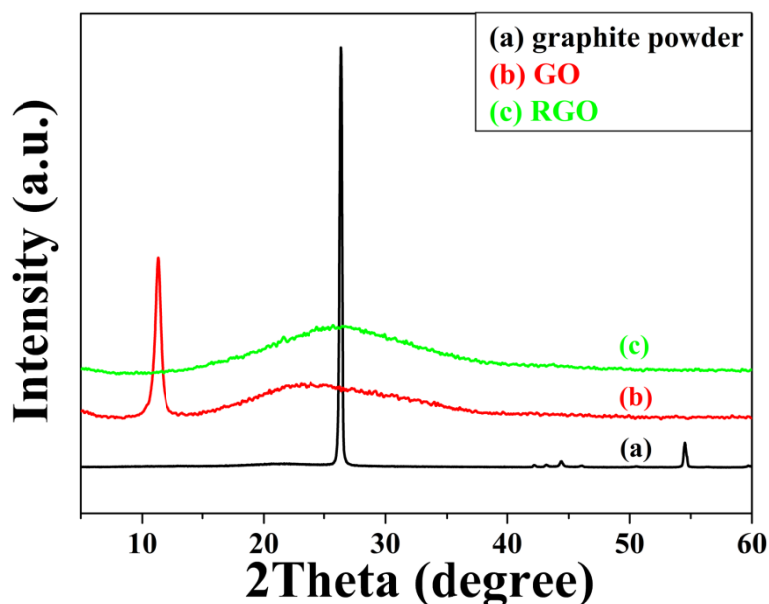


Fig. S1 XRD patterns of pristine graphite powder, GO and RGO

Preparation of GO modified GCE (GO/GCE) and RGO modified GCE (RGO/GCE)

Aqueous dispersion of pristine GO sheets (0.02 mg/mL) was prepared by sonicating for 90 min. A 5 μ L aqueous dispersion of GO was dropped on a GCE that was then allowed to dry at room temperature over night to form a GO deposited GCE (GO/GCE). To reduce GO, 0.10M phosphate buffer of pH 3.3 was deoxygenated by bubbling N_2 for 10 min. Fig. S2 shows a linear sweep voltammogram of a GO/GCE in the buffer solution. A reduction peak occurs at -1.14V, which is caused by GO reduction. Therefore, the GO/GCE were reduced 90 mins at -1.14 V in the buffer solution with bubbling N_2 to form RGO deposited GCE (RGO/GCE), which was used for the electrocatalytic oxidative polymerizations of ABA in the acidic solutions using cyclic voltammetry (CV) method.

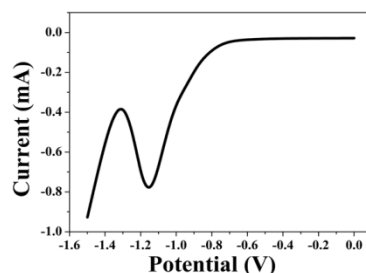


Fig. S2 linear sweep voltammogram of a GO/GCE in 0.1M phosphate buffer of pH 3.3

Electrochemical polymerization of ABA

Poly(3-aminophenylboronic acid) (PABA) was deposited onto the GCE, GO/GCE and RGO/GCE respectively by sweeping the electrochemical potential from -0.12 V to 1.3 V (versus SCE) in 40 mM ABA, 200 mM KF, 0.5 M HCl at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$. After the fifth cycle, the potential was decreased to 0.86 V in the subsequent forty cycles to reduce the possibility of overoxidizing the polyaniline backbone².

In Situ polymerization of ABA

ABA monomer (10 mM), KF (40 mM) and fructose (0.5 mM) were dissolved in 30 mL tris buffer solution (was prepared from tris 10 mM and EDTA 1 mM), and then 250 μL of RGO (or GO) 0.1 mg/mL was added to the prepared monomer solution. The mixture was bubbled with nitrogen for 30 min, after which the polymerization was started by adding 1.5 mL of 37.5 mM $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS) in tris buffer solution dropwise to the mixture. All of the experiments were performed under electromagnetic mixing at ice-bath. Control experiments were performed under the same conditions without RGO. Took 0.5 mL reaction solution were dissolved in 3.5 mL deionized water for every 15 mins and used UV-vis absorption spectroscopy obtained spectra. All of the spectra were obtained using a spectrophotometer.

Reference

- 1 W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* 1958, 80, 1339-1339.
- 2 Y. F. Ma, S. R. Ali, A. S. Doodoo, H. X. He, *J. Phys. Chem. B*, 2006, 110, 16359-16365.