



## Determination of *p*-Phenylenediamine Using Electrochemically Reduced Graphene Oxide

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In this communication, we report a green and effective approach to construct a sensitive detection platform based on electrochemically reduced graphene oxide modified electrode (EG@GCE). The surface morphology and structure of electrochemical reduction of graphene oxide were investigated by utilizing transmission electron microscope, FT-IR spectra, UV-visible spectra and X-ray diffraction. This EG@GCE exhibits sensitive current responses toward the electrooxidation of *p*-phenylenediamine (PDA) due to the excellent conductivity and large electroactive surface area of electrochemical reduction of graphene oxide and the strong  $\pi$ - $\pi$  stacking interactions between *p*-phenylenediamine and the electrochemical reduction of graphene oxide surface. Moreover, a low detection limit of 1.08  $\mu$ M (S/N = 3) with the linear range of 5 to 200  $\mu$ M is obtained. This new finding demonstrates that the electrochemical reduction of graphene oxide is a promising candidate of advanced electrode materials for electrochemical determination aromatic amines in environmental analysis.

**Keywords:** Determination, *p*-Phenylenediamine, Electrochemically reduced graphene oxide.

### INTRODUCTION

Graphene is a two-dimensional sheet of  $sp^2$  hybridized carbon atoms, which can be viewed as an extra-large polycyclic aromatic molecule. It has stimulated research interest owing to its ultralarge surface area, excellent conductivity, high mechanical stiffness, chemical inertness<sup>1-3</sup>, good biocompatibility<sup>4</sup> and low manufacturing cost<sup>5</sup>. These unique properties of graphene hold great promise for potential applications in various fields such as nanoelectronics<sup>6,7</sup>, nanocomposites<sup>8,9</sup>, supercapacitors<sup>10,11</sup>, electrochemical devices<sup>12</sup>, catalysis<sup>13</sup>, sensors<sup>14</sup>, batteries<sup>15</sup> and dye-sensitized solar cell<sup>16</sup>, etc.

Graphene-based applications undoubtedly need low-cost, high quality and large-scale production of graphene. Up to now, some approaches have been developed to prepare graphene, such as: micromechanical exfoliation of graphite with Scotch-tap<sup>1</sup>, chemical vapor deposition on metal substrates<sup>17</sup>, epitaxial growth on electrically insulating surface<sup>18,19</sup> and the reduction of graphene oxide (GO)<sup>20,21</sup>, which can be prepared from natural graphite by the modified Hummers' method<sup>22,23</sup>. Among these methods, the reduction from graphene oxide is the most realistic approach for low-cost and gram-level production of graphene. Especially, the electrochemical reduction of graphene oxide (EG) coated on glassy carbon electrode (GCE) surfaces is a promising route for preparing graphene-modified GCE because it is green, fast, low cost and more effective than chemical and

thermal reduction<sup>24-26</sup>. Recently, the electrochemical reduction of graphene oxide has successfully applied to the construction of a detection platform<sup>26,27</sup>. The prominent performance of electrochemical reduction of graphene oxide-modified GCE in discriminating target species is due to the excellent electrocatalytic activity and the large surface area of graphene sheets, which accelerate heterogeneous electron transfer.

Aromatic amine, as important organic intermediates, is widely applied in polymer materials, pesticides, dyes, etc. More and more containing aromatic amine with high mutagenic and carcinogenic activity is discharged into the water<sup>28</sup>. As a result, the pollution and damage to the environment endanger the survival of the organism. Therefore, it is necessary to develop effective methods to determine at very low concentrations before the discharge of effluents. Recently, Several enzyme-based detection procedures were reported for measuring aromatic amines<sup>29,30</sup>, however, the biggest defect of enzymatic sensors is that their stability is not good enough originating from their intrinsic dependence on enzyme activity<sup>31,32</sup>.

In this present work, we develop a simple, efficient and high sensitive method to detect a kind of aromatic amine *p*-phenylenediamine (PDA) based on the electrochemical reduction of graphene oxide modified glassy carbon electrode (EG@GCE) for the first time. After the surface morphology and structure of electrochemical reduction of graphene oxide were investigated by using TEM, FT-IR spectra, UV-visible

spectra and XRD, the electrochemical behaviours towards *p*-phenylenediamine at EG@GCE were studied. The result shows that the electrochemical reduction of graphene oxide exhibits sensitive responses toward the electrooxidation of *p*-phenylenediamine. This work demonstrates that the electrochemical reduction of graphene oxide has a perfect application prospect in determination aromatic amines in environmental analysis.

## EXPERIMENTAL

Graphite powder was obtained from Alfa Aesar (Shanghai Carbon Co., Ltd., China), with a particle size of 100  $\mu\text{m}$ . *p*-phenylenediamine and other chemicals were bought from Shanghai Chemical Factory (Shanghai, China) and used without further purification. All chemicals were of analytical grade and solutions were prepared with deionized water (DI) from a pure system (>18 MO, Purelab Classic Corp., USA).

**Synthesis of graphene oxide:** Graphene oxide was fabricated by a modified Hummer's method<sup>22,23</sup>. The process has been described in our previously work<sup>33</sup>. The as-prepared graphene oxide was dispersed in water and the homogeneous graphene oxide suspension was obtained and used in the following modification processes.

**Preparation of electrochemical reduction of graphene oxide modified glass carbon electrode (EG@GCE):** Glassy carbon electrode (GCE,  $\phi = 3 \text{ mm}$ ) was thoroughly polished with 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$   $\gamma$ -alumina slurry, then rinsed with ethanol and distilled water in an ultrasonic bath to remove any alumina residues. The cleaned GCE was dried with blowing  $\text{N}_2$  gas before modifications. The graphene oxide-modified GCE was prepared by dropping the graphene oxide aqueous suspension (10  $\mu\text{L}$ , 1 mg/mL) onto the pretreated bare GCE and dried in air. The electrochemical reduction of the graphene oxide film on the GCE was performed by cyclic voltammetry in 0.1 mol/L KCl solution. The electrochemical reduction of graphene oxide-modified GCE (EG@GCE) was directly used for the determination of *p*-phenylenediamine.

**Characterization:** The morphology of electrochemical reduction of graphene oxide layer on a GCE was characterized using a Hitachi-2100 TEM at a 200 kV accelerating voltage and The TEM samples were prepared by drying a droplet of the electrochemical reduction of graphene oxide suspensions on a Cu grid. FT-IR spectra with the range from 4000 to 500  $\text{cm}^{-1}$  were recorded on a Nicolet Nexus 470 spectrometer. UV-visible spectra were performed on a UV 3600 spectrophotometer (Shimadzu, Kyoto, Japan). The structure of the graphene oxide and electrochemical reduction of graphene oxide was examined by X-ray powder diffractometer (XRD, Shimadzu, X-6000,  $\text{CuK}\alpha$  radiation). Electrochemical measurements were carried out at a standard three-electrode cell on a CHI 842 electrochemical Station (CH Instrument, USA) with a modified glassy carbon electrode as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference.

## RESULTS AND DISCUSSION

**Preparation and characterization of electrochemical reduction of graphene oxide:** Fig. 1A shows that the cyclic

voltammetry for electrochemical reduction of graphene oxide in a potential range from 0.0 to -1.55 V. A large cathodic current peak appears at about -1.3 V in the first cycle, which is due to a decrease of oxygen functional groups of the graphene oxide surface. The reduction peak decreases obviously and disappears in the subsequent several cycles. This phenomenon indicates that the electrochemical reduction of oxygen groups on the surface of graphene oxide is rapid and irreversible. The morphologies of as-obtained electrochemical reduction of graphene oxide was characterized using TEM as shown in Fig. 1B, the electrochemical reduction of graphene oxide nanosheets are randomly compact and stacked together, showing uniform laminar morphology like crumpled silk veil waves. These electrochemical reduction of graphene oxide nanosheets with monolayer or double-layered nanostructure possess huge surface areas.

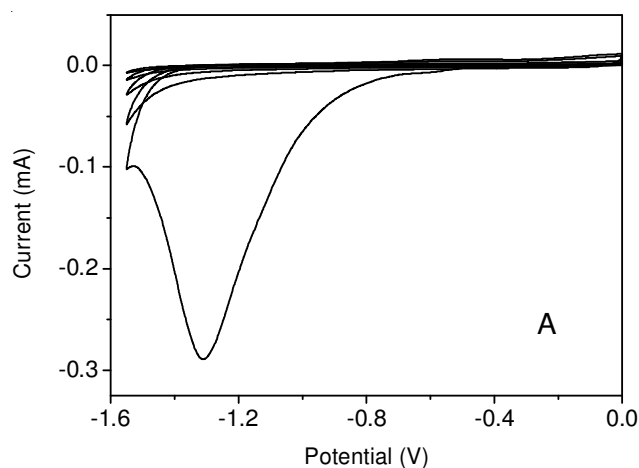


Fig. 1. (A) Cyclic voltammograms (CVs) of a graphene oxide-modified GCE in 0.1 mol/L KCl solution at a scan rate of 50 mV/s. (B) Typical TEM image of electrochemical reduction of graphene nanosheet electrochemical reduction of graphene oxide (EG)

In order to prove that the electrochemical reduction is an effective approach to produce high-quality graphene, several characterizations were carried out in detail. The FT-IR transmittance spectra (KBr) of graphene oxide (black line) and electrochemical reduction of graphene oxide (red line) as shown in Fig. 2A. The characteristic peaks of graphene oxide powder at 3420 (a broad band), 1680, 1400, 1140 and 1066  $\text{cm}^{-1}$  are

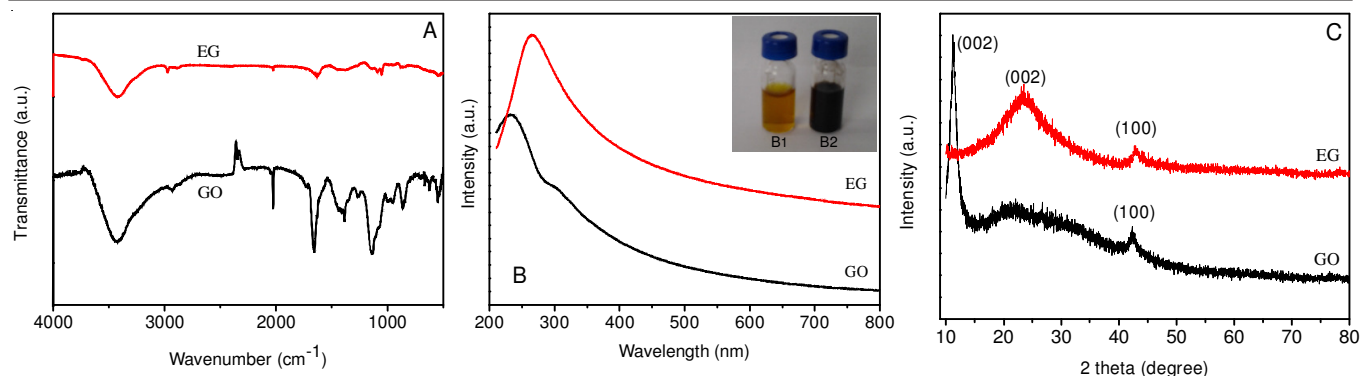


Fig. 2. (A) FT-IR spectra, (B) UV-visible spectra and (C) XRD patterns of graphene oxide and electrochemical reduction of graphene oxide (EG). The upright inset of (B) are digital photo of graphene oxide (B1) and EG (B2) dispersed in water (1 mg/mL), respectively

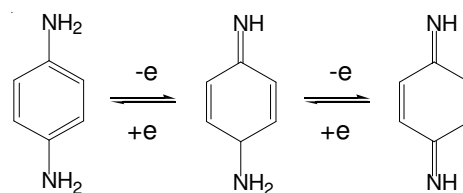
ascribed to O-H stretching mode of intercalated water, C=O stretching vibrations, O-H deformation, C-O stretching (epoxy or alkoxy) respectively. After the graphene oxide is electrochemically reduced, the broad O-H stretching bands remain and become small. The C=O vibration and the C-O stretching band become very small and almost disappear, demonstrating the removal of oxygen functional groups can be successfully reduced by electrochemical reduction.

Fig. 2B shows the UV-visible spectra of graphene oxide and electrochemical reduction of graphene oxide. The appearance of UV-vis absorption of graphene oxide at 232 nm (strong peak) and 305 nm (shoulder peak) could be ascribed to  $\pi$ - $\pi^*$  transition and  $n$ - $\pi^*$  transition. After the electrochemical reduction, the peak at 232 nm red shifts to 265 nm and the peak at 305 nm disappears, indicating that electronic conjugation within the graphene was restored<sup>34</sup> and graphene oxide was well reduced.

The X-ray diffraction patterns of as-obtained electrochemical reduction of graphene oxide (red line) compared with graphene oxide are shown in Fig. 2C. The sharp peak centered at  $2\theta = 11.2^\circ$  of graphene oxide corresponding to the C (002) average interlayer spacing of about 0.85 nm, which indicates the complete oxidation of graphite to graphene oxide. After reduction, the diffraction peak at  $11.2^\circ$  disappears, replaced by a broad peak at  $2\theta = 23.2^\circ$ , corresponding to an interlayer spacing of 0.35 nm, which is approximately the d-spacing peak of graphite. The shift in d-spacing peaks of the electrochemical reduction of graphene oxide is attributed to the removal of oxygen functional groups from the graphene oxide sheet surface.

**Electrochemical behaviours of *p*-phenylenediamine on EG/GCE:** The electrochemical behaviours of *p*-phenylenediamine (PDA) at bare GCE, GO@GCE and EG@GCE have been studied by cyclic voltammetry as shown in Fig. 3. It can be clearly seen that two strong anodic peaks with the potentials at 0.36V and 0.63V at the EG@GCE. This corresponds to the stepwise oxidation of two amino groups to the quinone diimine on the aromatic ring of *p*-phenylenediamine. The electrochemical mechanism is proposed in **Scheme-I**. At the same time, also two small well-defined reduction peaks appear, indicating that the electrochemical reaction of *p*-phenylenediamine is reversible<sup>35</sup>.

**Electrochemistry mechanism:** The efficient electrocatalytic activity of EG@GCE toward *p*-phenylenediamine mainly attributed to the unique electronic structure with a single



**Scheme-I:** Reversible single-electron catalytic mechanism toward *p*-phenylenediamine at EG@GCE

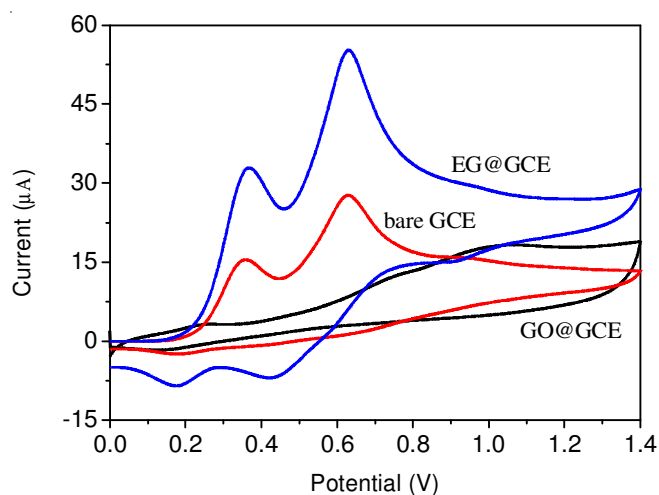


Fig. 3. Cyclic voltammograms of bare GCE, GO@GCE and EG@GCE in 0.1 M KCl solution containing 0.1 mM *p*-phenylenediamine at a scan rate of 100 mV/s

or a few layers of carbon atoms, thus making electrochemical reduction of graphene oxide as a promoter to enhance the electrochemical reaction. Besides the high density of localized  $\pi$  electrons in electrochemical reduction of graphene oxide surface would be beneficial for facilitating the accumulation of the aromatic species through the strong  $\pi$ - $\pi$  interactions. On the other hand, excellent conductivity, large electroactive surface area and a large number of edge-plane-like defective sites on electrochemical reduction of graphene oxide play significant roles in accelerating electron-transfer between the electrode and species in solution. Moreover, the theoretical calculations also revealed the surface of graphene has very strong adsorption affinity towards aminotriazines and aromatic molecules through hydrogen-bond and  $\pi$ - $\pi$  stacking interactions<sup>36,37</sup>.

Whereas, there are only two oxidation peaks at bare GCE, indicating that the electrochemical reaction of *p*-phenylene-

diamine is irreversible and undergoes sluggish electron transfer kinetic process. In addition, the electrical conductivity of graphene oxide is poor at GO@GCE, which almost fail to check signal.

The effects of different scan rates on the oxidation of *p*-phenylenediamine at the EG@GCE in 0.1 M KCl solution containing 0.1 mM *p*-phenylenediamine was also investigated using LSV as shown in Fig. 4A. The oxidation peak current increases along with scan rate from 5 to 500 mV/s, accompanied by the positive shift of the anodic peak. It is also apparent from Fig. 4B that the anodic current shows a good linear relationship ( $R^2 = 0.995$ ) with the scan rate in the scan rate range, which reveals that the oxidation of *p*-phenylenediamine at the EG@GCE is a surface controlled process.

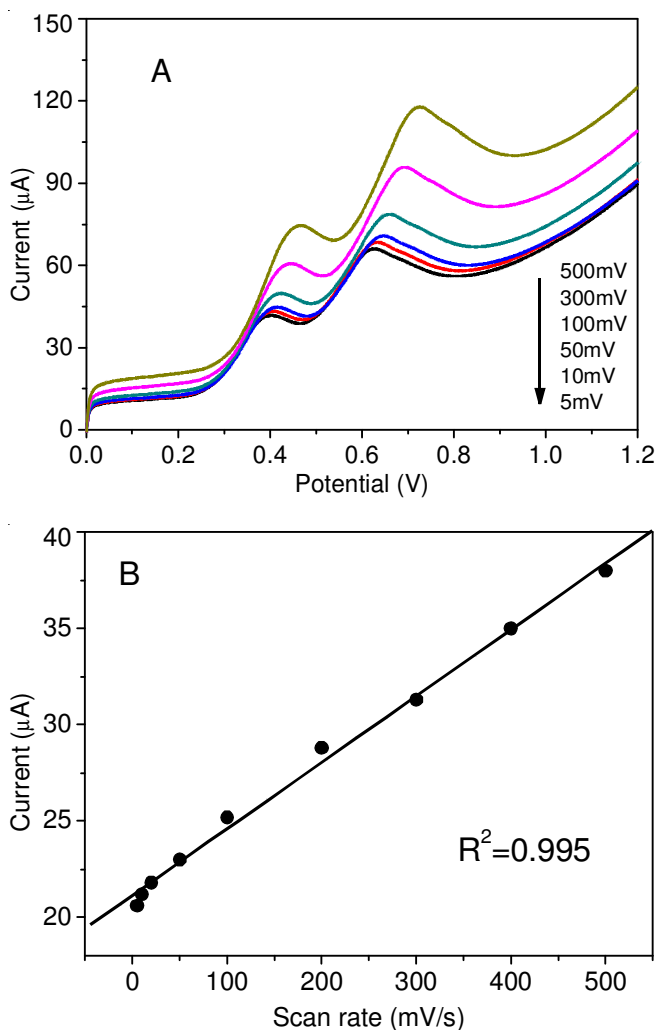


Fig. 4. (A) Linear sweep voltammetry (LSV) for the EG@GCE at different scan rate in 0.1 M KCl solution containing 0.1 mM *p*-phenylenediamine. (B) Influence of scan rate on the second oxidation peak current for *p*-phenylenediamine

Under the optimum conditions, *p*-phenylenediamine was detected at the different concentrations on the second oxidation peak are recorded in Fig. 5A. The anodic peaks at the potential of 0.63 V are observed and their peak currents increase with an increase in *p*-phenylenediamine concentration from 5 to 200  $\mu\text{M}$ . The second oxidation peak currents yield a linear calibration plot as shown in Fig. 5B. The current response of

EG@GCE exhibits a good linear dependence with correlation coefficient of 0.992 on *p*-phenylenediamine concentration and the detection limit can reach as low as 1.08  $\mu\text{M}$  (at signal/noise = 3). The reason is that the electrochemical reduction of graphene oxide has a large active surface area, excellent conductivity and a large number of edge-plane-like defective sites, which accelerate electron-transfer between the electrode and species in solution and facilitate high catalytic activity towards *p*-phenylenediamine.

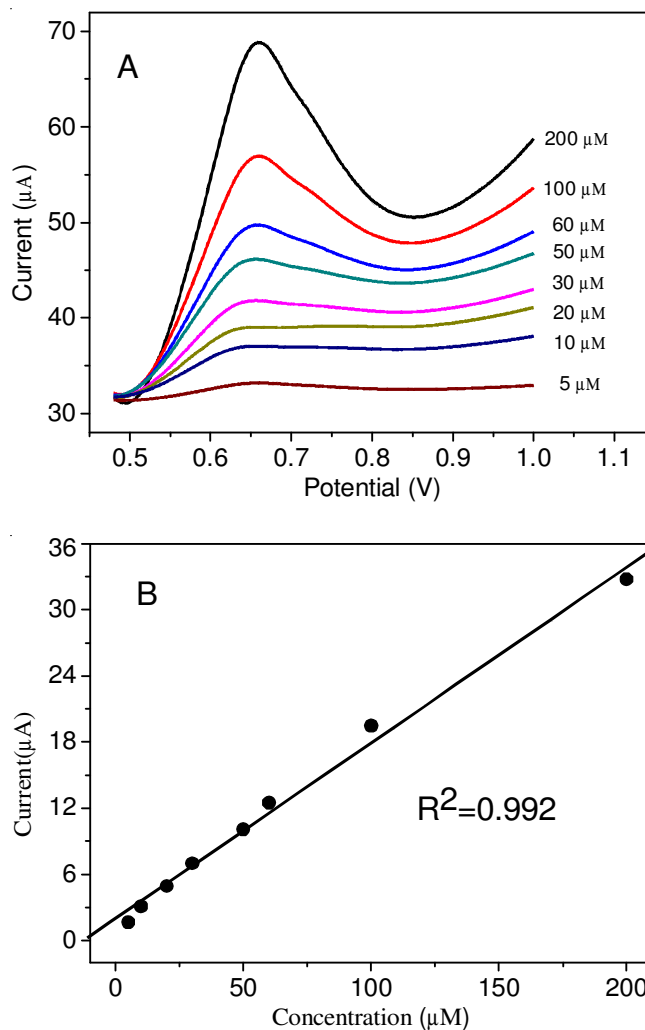


Fig. 5. (A) LSVs measured at the EG@GCE in various concentrations of *p*-phenylenediamine: 5, 10, 20, 30, 50, 60, 100, 200  $\mu\text{M}$ . (B) The plot displays the calibration curve for the detection of *p*-phenylenediamine on the second oxidation peak current

## Conclusion

In summary, we have developed a green and effective approach to elaborate a sensitive detection platform based on EG@GCE. The as-synthesized electrochemical reduction of graphene oxide was characterized by TEM, IR, UV-visible and XRD. The electrochemical detection of *p*-phenylenediamine was carried out at EG@GCE. The high sensitivity of the *p*-phenylenediamine detection could be ascribed to large surface area and enhanced electrocatalytic activity of the EG-modified surface. Moreover, the hydrogen-bond, electrostatic and  $\pi$ - $\pi$  stacking interactions between aromatic molecules and

graphene also play important roles. The low detection limit of 1.08  $\mu\text{M}$  ( $S/N = 3$ ) and the linear range of 5 to 200  $\mu\text{M}$  is obtained. The present work demonstrates that the electrochemical reduction of graphene oxide is a promising electrode materials for electrochemical determination aromatic amines in environmental analysis.

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