Short Communication

Detection of p-phenylenediamine Based on a Glassy Carbon Electrode Modified with Nitrogen Doped Graphene

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In this paper, nitrogen doped graphene (NG) was successfully synthesized via thermal annealing employing graphene oxide and urea as raw materials. The morphology and microstructure of NG was characterized by TEM, AFM, XRD and XPS, respectively. Due to its unique structure and properties originating from nitrogen doped in graphene frame, NG shows highly electrocatalytic activity towards the oxidation of p-phenylenediamine (PDA). A sensitive detection platform based on NG modified electrode (NG@GCE) was constructed. Moreover, a low detection limit of 0.67 μM (S/N=3) with the wide linear range of 2 to 500μM and fast response (within 3 s) are obtained. This new strategy opens a new facile and simple route to electrochemically determinate aromatic amines in environmental analysis and other electrocatalytic applications.

1. INTRODUCTION

Graphene has been attracting great deal of research interest due to its remarkable electronic, optical, and thermal properties, chemical and mechanical stability, and large surface area[1] for applications including field-effect transistors[2], electrochemical devices [3,4], electromechanical resonators[5], polymer nanocomposites [6], batteries[7], supercapacitors [8], and light emitting devices[9], catalysis [10], chemical sensor and biosensor [11-13], and many other areas [14,15].

Applications of graphene-based materials 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 [1], chemical vapor deposition (CVD) on metal substrates[16], epitaxial growth on electrically insulating surface [17, 18] and the chemical or electrochemical reduction of graphene oxide (GO) [19], which can be prepared from natural graphite by the modified Hummers'method [20, 21]. Among these methods, the reduction from GO is the most realistic approach for low-cost and gram-level production of graphene. Chemical doping with foreign atoms is a significant method to modify materials intrinsically, tailor electronic properties, manipulate surface chemistry, and produce local changes to the elemental composition of host materials [22, 23]. For carbon materials, chemical doping is also a leading potential strategy to enrich free charge-carrier densities and enhance the electrical or thermal conductivities [24, 25]. Recent studies have demonstrated efforts at chemical doping of graphene [26, 27].

P-phenylenediamine, an aromatic amine, is an important organic intermediate, which was widely used in polymer materials, pesticides, dyes and other substances. With more and more aromatic amine that can induce mutagenic and carcinogenic activity is difficult to be degraded under natural conditions being discharged into the water[28], a lot of national environmental organizations have to declare them as environmental pollutants which even threaten the survival of the organism. Accordingly, it is necessary to develop effective methods to determine p-phenylenediamine at very low concentrations before the discharge of effluents. Recently, several enzyme-based detection procedures were reported for measuring aromatic amines [29, 30], however, the defect of enzymatic sensors is that their stability is not good enough originating from their intrinsic dependence on enzyme activity [31,32].

Herein, we demonstrate the ability of NG as a platform for high sensitive detection a kind of aromatic amine based on electrochemical oxidation at NG modified glassy carbon electrode (NG@GCE) for the first time. After the surface morphology and structure of NG were characterized by TEM, AFM, XRD and XPS, the electrochemical behavior of p-phenylenediamine on the NG@GCE was studied. It is found that the NG shows excellent catalytic activity toward the oxidation of the aromatic amine. This work put forward the application prospects of graphene-based nanomaterials in determination of aromatic amines in environmental analysis.

2. EXPERIMENTAL

2.1. Raw materials

Graphite powder was obtained from Alfa Aesar (Shanghai Carbon Co., Ltd., China), with a particle size of 100 μm. Urea was bought from Sinopharm Chemical Reagent CO. Ltd (China), and recrystallized with water prior to use. P-phenylenediamine and other chemicals were bought from Shanghai Chemical Factory (Shanghai, China). All chemicals were of analytical grade and solutions were prepared with deionized water (DI) (>18 MΩ, Purelab Classic Corp., USA).

2.2. Synthesis of GO and NG

GO was fabricated by a modified Hummer's method [20, 21]. The process has been described in our previously work [33]. The mixture of as-prepared GO and urea with 1:5 (mass ratio) was placed in a quartz tube. Next the annealing temperature was increased to 700℃ at 10℃/min and kept for 1 h in argon atmosphere. The final product was taken out of the tube when the temperature was cooled down to room temperature. 3 mg NG was dispersed in DMF by ultrasonication, and 1 mg/mL NG suspension was acquired and used in the following modification processes.

2.3. Preparation of NG modified glass carbon electrode (NG@GCE)

GCE (φ=3mm) was thoroughly polished with 0.3μm and 0.05 mm γ-alumina slurry. The cleaned GCE was dried with blowing N_2 gas before modifications. The NG-modified GCE was prepared by dropping the NG suspension (10 μL, 1 mg/mL) onto the pretreated bare GCE and dried in air. The NG-modified GCE (NG@GCE) was directly used for the detection of p-phenylenediamine (PDA).

2.4. Characterization

NG was characterized using a Hitachi-2100 TEM at 200 kV and the samples were obtained by drying a droplet of the NG suspensions on a Cu grid. AFM image was recorded using an Agilent 5500 AFM/SPM system in the tapping mode. XPS (Kα) analyses were performed using a Thermo Fisher X-ray photoelectron spectrometer equipped with Al radiation as the probe, with a chamber pressure of 5 × 10^{-9} Torr. The power was 72 W, and the pass energies were 200 eV and 50 eV for survey scans and high-resolution scans, respectively. Electrochemical measurements were carried out at a standard three-electrode cell on a CHI 842 electrochemical Station (CH Instrument, USA) with a modified GCE as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference.

3. RESULTS AND DISCUSSION

3.1 Preparation and characterization of NG

The preparation of nitrogen doped graphene (NG) starts from graphene oxide (GO) and urea through thermal annealing at 700℃ in a tubular furnace. GO was synthesized by the modified Hummers' method. The process has been described in our previously work [33]. GO and urea were mixed together with a mass ratio of 1:5 by grinding. This mixture was then put into a quartz tube with high purity argon atmosphere and heated to 700℃ at a rate of 10℃/min. After the temperature was maintained for 2 hours, the furnace was stopped heating and cooled to room temperature. The product

was obtained from quartz tube. For comparison, thermal reduced graphene was also prepared using the similar process without urea into the GO sample.
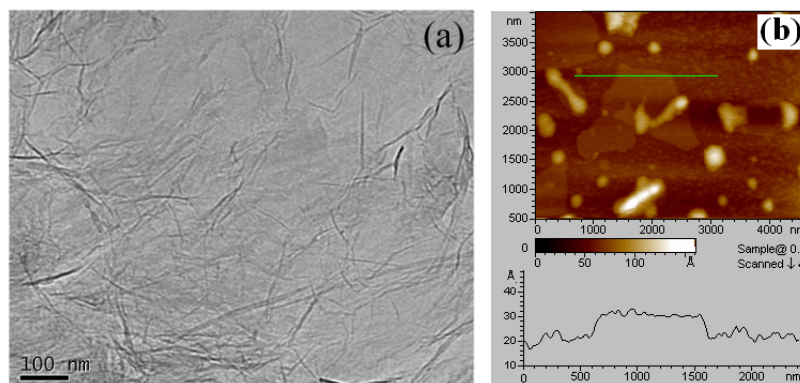

Figure 1. (a), (b) TEM and AFM image of nitrogen doped graphene.

Morphology of the as-obtained NG was characterized by TEM as shown in Fig. 1(a). It is clear that a layer of corrugated, thin paper-like materials are randomly compact and stacked together, showing uniform laminar morphology like crumpled silk veil waves. These NG nanosheets with monolayer or double-layered nanostructure possess huge surface areas. AFM can directly characterize the morphology and thickness of NG. Fig. 1(b) shows that a typical AFM image of NG dispersion was on freshly exfoliated mica through a drop-casting method. The average thickness of as-obtained NG, measured from the height profile of the AFM image is about 1 nm, corresponding to less than three single graphene layers by comparing with the theoretical thickness of a single-layer pristine graphene (about 0.34 nm) [34].
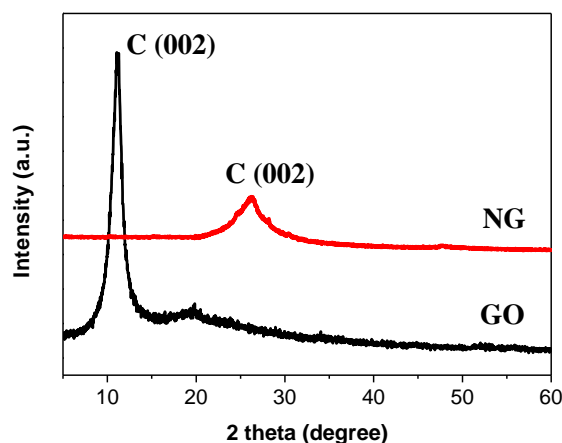

Figure 2. XRD patterns of graphene oxide (GO) and nitrogen doped graphene (NG).

The XRD patterns of NG (red line) compared with GO are shown in Fig. 2. The sharp peak centered at $2\theta = 11.2°$ (002) is observed with interlayer space (d-spacing) of about 0.79 nm, which shows the complete oxidation from natural graphite to GO. This value is larger than the d-spacing

(0.34 nm) of pristine graphite (2θ = 26.5°), as a result of the introduction of oxygen-containing groups on carbon sheets. After thermal annealing, the diffraction peak at 11.2° disappears, replaced by a broad peak at 2θ = 26.3° with an interlayer space of around 0.34 nm, which is approximately the d-spacing peak of graphite. This peak of the thermal reduction and nitrogen doping of GO is attributed to the removal of oxygen functional groups from the GO sheet surface.
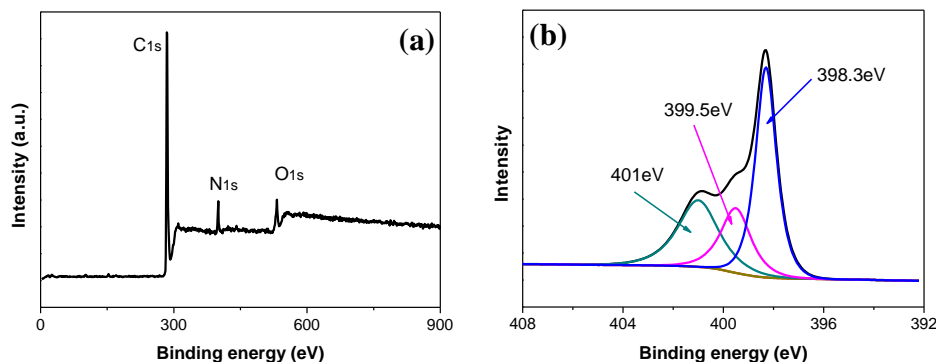

Figure 3. (a) XPS spectra of NG, The peaks located at 285, 399, and 534.0 eV indicate the carbon, nitrogen, and oxygen elements, respectively. (b) high-resolution scans for N1s.

To further demonstrate the formation of NG, XPS was carried out to analyze the composition and chemical configuration of nitrogen atoms in NG. Fig. 3(a) shows the XPS wide spectrum for NG. It is observed that the presence of principal C1s (285eV), N1s (399eV), and O1s (532eV) peaks clearly. The elemental content analysis from the XPS data reveals the mass composition of NG: C 91.3%, N 5.6%, O 3.1%. As for N1s, the peak can be fitted into three components (From Fig. 3b). The strong peaks locate at 398.3 eV and 399.5 eV is assigned to N atoms with "pyridinic" and "pyrrolic" chemical structures, and the peak at 401 eV corresponds to N atoms linked with three carbon atoms at the same ("graphitic" N atoms). These XPS analyses reveal that N atoms have been successfully incorporated into carbon frameworks and exist as three kinds of chemical status in NG.

3.2. Electrochemical behaviors of p-phenylenediamine on NG/GCE

The electrochemical behaviors of p-phenylenediamine (PDA) at bare GCE, G@GCE and NG@GCE have been studied by CVs as shown in Fig. 4. When graphene or NG was modified to the surface of GCE, the peak current is improved obviously compared with bare GCE. The efficient electrocatalytic activity at G@GCE and NG@GCE can be attributed to the as-prepared G or NG has the good conductivity and large electroactive surface area. Moreover, the theoretical calculations also revealed the surface of graphene possesses very strong adsorption affinity towards aminotriazines and aromatic molecules through hydrogen-bond and π-π stacking interactions [35]. In addition, the peak current at NG@GCE is larger than that of G@GCE. This phenomenon indicates that graphene doped

with nitrogen atoms has strong interaction with PDA molecules. It is beneficial for accelerating the electron transfer.
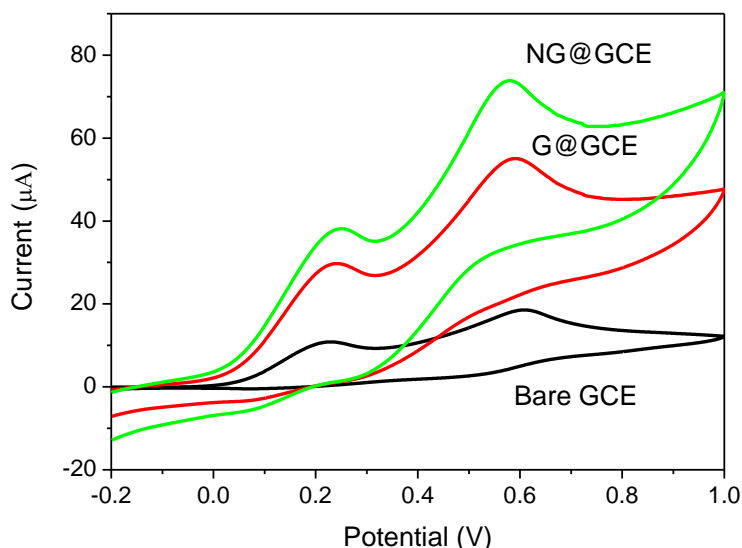

Figure 4. Cyclic voltammograms of bare GCE, G@GCE and NG@GCE in 0.1 M KCl solution containing 0.1 mM p-phenylenediamine at a scan rate of 100 mV/s.

It can be clearly seen that two strong anodic peaks with the potentials at 0.245V and 0.575V at the NG@GCE (in Fig 4). This corresponds to the stepwise oxidation of two amino groups to the quinone dimine on the aromatic ring of PDA. The electrochemical mechanism is proposed in Scheme1. At the same time, also two small well-defined reduction peaks appear, indicating that the electrochemical reaction of PDA is reversible.
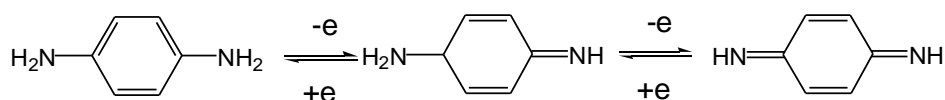
Scheme 1. Reversible single-electron catalytic mechanism toward PDA at NG@GCE.

The effects of different scan rates on the oxidation of PDA at the NG@GCE in 0.1 M KCl solution containing 0.1 mM PDA was also investigated using CV as shown in Fig. 5a. The oxidation peak current increases along with scan rate from 5 mV/s to 500 mV/s. In addition, the anodic response shifts positively with the increase of scan rate, while the cathodic peak moves negatively. It is also apparent from Fig. 5b that the anodic current shows a good linear relationship (R^2=0.9948) with the scan rate in the scan rate range, which reveals that the oxidation of PDA at the NG@GCE is a surface controlled process.
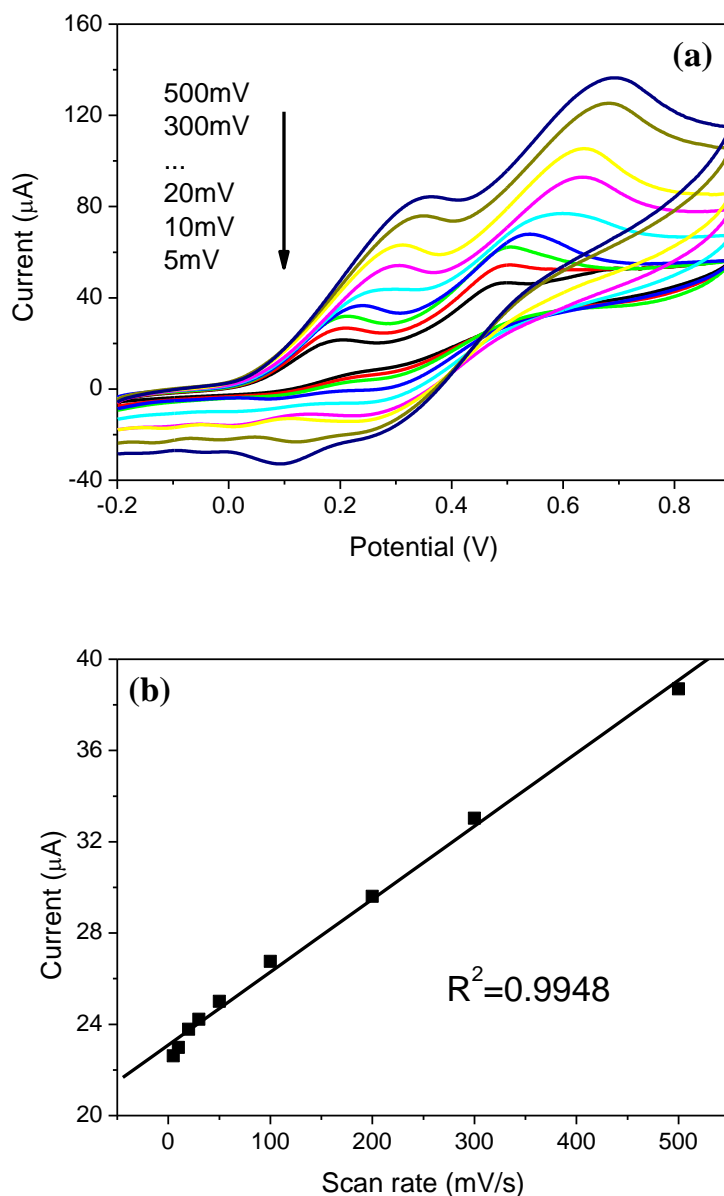
Figure 5. (a) Cyclic voltammograms (CVs) of bare GCE, G@GCE and NG@GCE in 0.1 M KCl solution containing 0.1 mM p-phenylenediamine at a scan rate of 100 mV/s. (b) Influence of scan rate on the second oxidation peak current for PDA.

Under the optimum conditions, PDA was detected at the different concentrations on the second oxidation peak are recorded in Fig. 6. The anodic peaks at the potential of around 0.60 V are observed and their peak currents increase with an increase in PDA concentration from 2 to 500μM. The second oxidation peak currents yield a linear calibration plot as shown in inset of Fig. 6. The current response of NG@GCE exhibits a good linear dependence with correlation coefficient of 0.9916 on PDA concentration and the detection limit can reach as low as 0.67 μM (at signal/noise =3). There are two main reasons for this excellent electrochemical activity. For one thing, the interaction between analytes and basal planes of NG plays an important role in electrocatalysis oxidation [36].
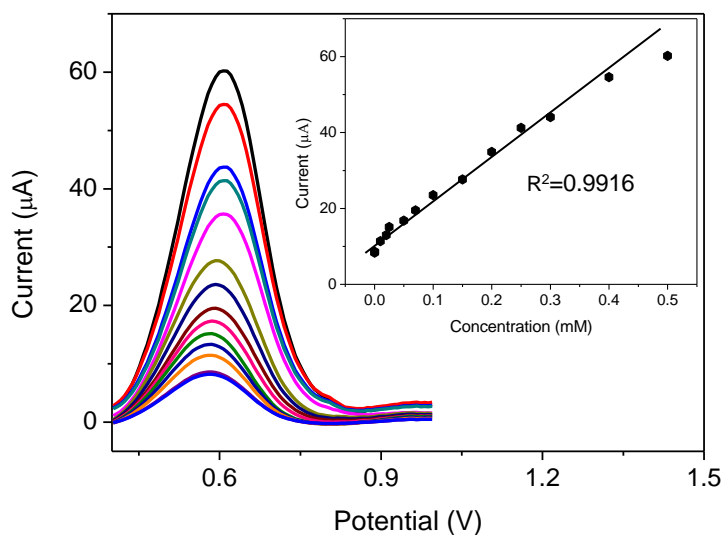
Figure 6. LSVs measured at the NG@GCE in various concentrations of PDA: 2, 5, 10, 20, 30, 50, 60, 100, 200, 300, 400 and 500μM. The inset plot displays the calibration curve for the detection of PDA on the second oxidation peak current.

For another, NG 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 PDA. Based on the higher electrocatalytic activities to the organic compounds [37], NG may be a good carbon material for constructing a novel and promising electrochemical sensing platform for detecting other pollutant.

4. CONCLUSION

In this work, we demonstrate the ability of NG as a platform for simple and effective detection a kind of aromatic amine based on electrochemical oxidation at NG@GCE. The as-prepared NG was characterized by TEM, AFM, XRD and XPS. The high sensitivity of the PDA detection could be ascribed to large surface area and enhanced electrocatalytic activity of the NG-modified surface. Moreover, the hydrogen-bond, electrostatic and π–π stacking interactions between aromatic molecules and graphene also play important roles. The low detection limit of 0.67μM (S/N=3) and the linear range of 2 to 500μM is obtained. The present work demonstrates that the NG is a promising electrode material for electrochemical determination aromatic amines in environmental analysis.

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