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Synthesis and characterization of nitrogen-doped graphene sheets by hydrothermal reduction method

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Abstract: Graphene, a single atom-thick sheet of hexagonally arranged sp^2 – bonded carbon atoms, shows extraordinary electronic, mechanical and optical properties for potential applications. Currently there are several methods like mechanical exfoliation, bottom-up synthesis and chemical reduction of graphene oxide (GO) suspension are used to prepare the reduced graphene sheets. Among them, the chemical reduction of GO is used to prepare the reduced graphene sheets. In this work, Graphene oxide was synthesized from graphite using Hummers method. Nitrogen-doped graphene sheets were prepared through hydrothermal reduction of graphene oxide in the presence of hydrazine and ammonia. The structure and morphology were investigated through X-ray Diffraction(XRD) and Scanning Electron Microscopy (SEM) techniques. Raman spectroscopy analysis was used to confirm the nitrogen doping and the optical properties of GO and reduced graphene sheets were studied using UV-Vis Spectroscopy.

Keywords: Graphene oxide, Reduced graphene sheets, Hummers method, Hydrothermal reduction.

Introduction

Graphene, a single atom-thick sheet of hexagonally arranged sp^2 – bonded carbon atoms, shows extraordinary electronic, mechanical, optical and potential applications because of its unique properties such as high surface area, high conductivity, mechanical strength. Graphene has potential applications in many fields, such as solar cells, sensors, fuel cells and drug delivery and biosensor¹⁻⁷⁷. Doping of graphene with elements like B, N, O and S can enhance the electronic properties and chemical reactivity⁸⁻¹⁰. In particular, nitrogen-doped graphene (NG) and boron doped graphene (BG) have been highly used in lithium-ion-batteries¹¹, supercapacitors¹², and catalysis for oxygen reduction reaction (ORR)¹³⁻¹⁵. Among these the most important applications of NG is electro catalyst of ORR, because it has ability to replace expensive Pt-based catalyst for fuel cells and metal-air batteries. It has high catalytic activity and superior reliability.

In order to optimize the materials such as supercapacitors, lithium ion batteries, a high percentage of N functionalities are very important to achieve. The schematic diagram of the bonding configuration of N atoms in graphene is shown in Fig.1 which determines the performance of NG. The configurations of typical N functionalities present in NG includes N atoms doped into graphene basal plane (quaternary N), N atoms in six-member ring (pyridinic N) and five member ring (pyrrolic N), among them Quaternary N is believed to be vital

to ORR catalytic activity and for enhancing the capacitance of graphene in supercapacitor^{16,12}. The recent theoretical study predicts that pyridinic N has higher reversible capacity in lithium ion battery¹⁷.

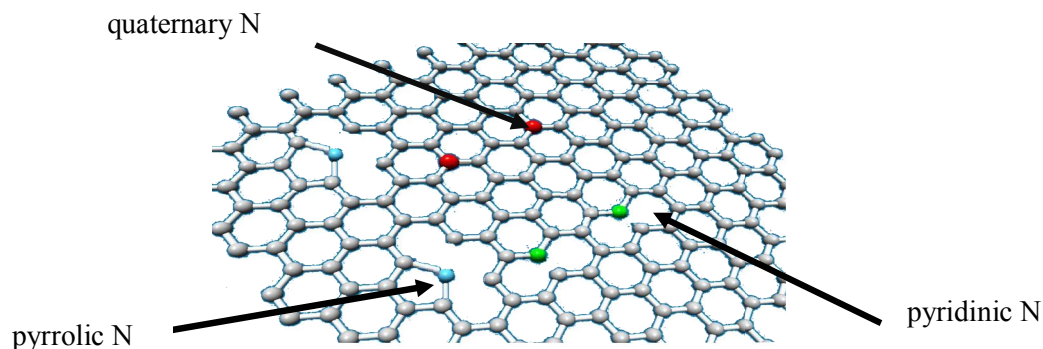


Fig. 1. Schematic diagram of the bonding configuration of N atoms in graphene.

Generally, there are several major methods like mechanical exfoliation¹⁸, epitaxial growth^{1,19}, bottom-up synthesis²⁰ and chemical reduction of graphene oxide (GO) suspension^{21,22,23,24}, which are used to prepare the reduced graphene sheets. Among them, the chemical reduction of GO is used here to prepare the reduced graphene sheets, in bulk quantity and at relatively low cost.

GO is mainly synthesized by the Brodie²⁵, Staudenmaier²⁶ or Hummers method²⁷. All of them produce GO by the strong oxidation of graphite with acid. GO is highly hydrophilic, and it can be easily exfoliated in aqueous media which are then be subjected to chemical reduction to obtain graphene as individual sheets. The reducing agents which are mainly used are hydrazine²⁴, sodium borohydride²⁸, hydroquinone²⁹, or strongly alkaline solutions³⁰. The chemical reduction of GO results in restoration of sp^2 carbon sites but not all the oxygen functionalities are removed completely and it also leaves a number of defects like vacancies, edge/cracks and adsorbed impurities.

Many methods have been successfully demonstrated to dope nitrogen atoms into graphene sheets such as thermal annealing of GO in ammonia^{31,32}, chemical vapor deposition by adding ammonia gas³³ (or other nitrogen precursor) and electrical joule heating in ammonia.

In this paper, nitrogen doping and reduction of GO was simultaneously done by simple hydrothermal reaction. Nitrogen doped graphene sheets prepared via reduction of GO colloidal solution in the presence of hydrazine and ammonia under hydrothermal temperature. Structure and morphology studies are investigated.

Experimental

Synthesis of graphene oxide(GO)

Graphene oxide (GO) was synthesized by hummers method. 2g of graphite powder, 1g of sodium nitrate and 46ml of conc. sulphuric acid were mixed together and stirred using magnetic stirrer. After 1 hour, 6g of $KMnO_4$ was added gradually to the above solution and keeping the temperature less than $20^\circ C$ to prevent overheating and explosion. The mixture was stirred at $35^\circ C$ for 30 min and then slowly added 92ml of water, the resulting mixture was maintained in $98^\circ C$ for 15 mins, then the heat was removed and additional 280 ml of water and 30% H_2O_2 were added. The final mixture was washed with HCl and DI water respectively and dried for overnight at $60^\circ C$.

Preparation of nitrogen-doped graphene sheets

GO was dissolved in water in the concentration of 2mg/mL to give a colloidal solution, and then sonicated for 1 h. The solution was then subjected to 10 min of centrifugation at 2000 rpm to remove unexfoliated GO particles. Chemical reduction of GO solution was achieved using ammonia and hydrazine hydrate (N_2H_4) as reducing agents under a hydrothermal environment. 70 mL of above GO solution was adjusted the pH value to 10 using 30% ammonia then 2 mL of hydrazine hydrate was added and stir for 15 min. The solution was then transferred into a Teflon-lined autoclave and heated at $80^\circ C$ and $130^\circ C$ for 3 h. The

nitrogen-doped graphene sheets were collected with centrifugation, followed by washing with de-ionized water several times. The collected samples were dried for overnight.

Characterization techniques

The structure of the GO and reduced graphene sheets were examined by X-ray diffraction PANalytical X'pert PRO, with Cu K α radiation ($\lambda=1.542 \text{ \AA}$). Morphology studies of GO and reduced graphene sheets were analyzed under a Field Emission Scanning Electron Microscope (FESEM) and Energy-Dispersive X-ray Spectroscopy (EDS) analysis were performed using FEI Quanta FEG 200. Raman spectroscopy was performed using Raman11, Nanophoton Corporation, Japan with 532 nm Nd-YAG excitation source. Optical absorption spectra were investigated using Analyticaljena, Specord 200 plus, Germany.

Result and Discussion

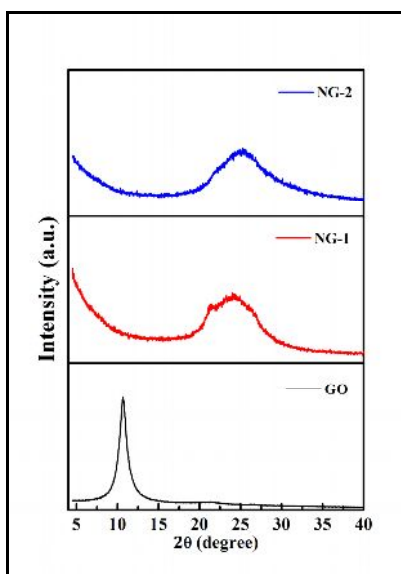


Fig. 2 XRD patterns of GO and nitrogen-doped graphene sheets at different hydrothermal temperature.

Fig. 2 shows the XRD patterns of GO and nitrogen-doped graphene sheets at different hydrothermal temperature. The GO has a sharp peak at 10.67° , corresponding to lattice distance of 0.83 nm. After hydrothermal reduction, this peak was disappears and to form broad peak at around 24° and lattice distance of 0.37 nm is observed for nitrogen-doped nitrogen sheets, which confirms the graphitic crystal structure. No other differences are observed in broadness in XRD peaks for reduced samples at various hydrothermal temperatures, stating the similar stacking thickness of graphene layers.

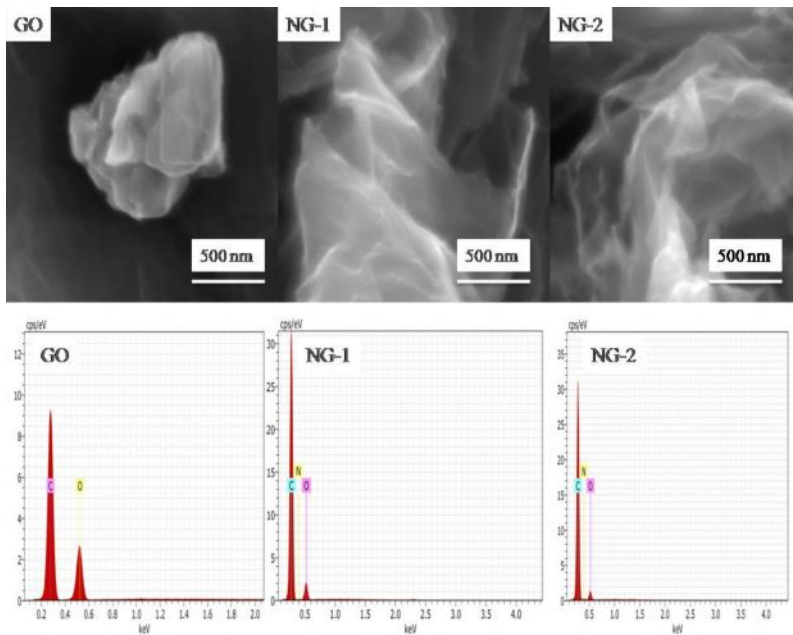


Fig. 3. SEM image and EDS spectra of GO and nitrogen-doped graphene sheets.

Fig. 3a shows the SEM image of GO and nitrogen-doped graphene sheets. The images demonstrate thin and wrinkled sheets. There are some differences noted for reduced graphene sheets at different temperatures. Doped nitrogen levels are shown in EDS graph fig. 3b. NG-1 and NG-2 has nitrogen atomic wt% of 2.70% and 5.04% respectively.

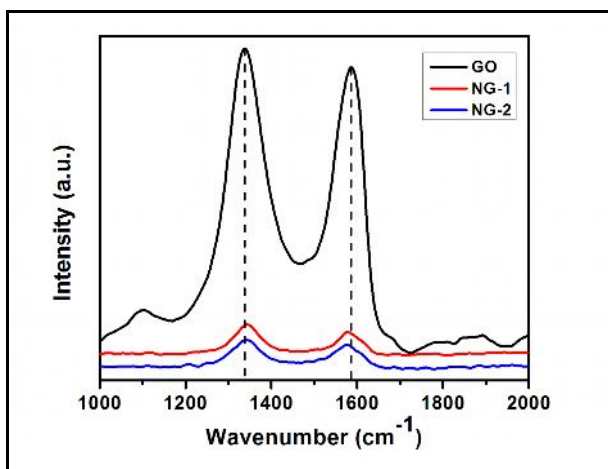


Fig. 4. Raman Spectra of GO, NG-1 and NG-2.

Raman spectroscopy is used to measure the structural disorder in graphene materials. Fig. 4 shows the Raman Spectra for GO and hydrothermally reduced graphene sheets at different temperatures 80°C and 130°C (NG-1 and NG-2). Raman Spectra of GO shows two primary peaks, G band at 1587 cm⁻¹ which corresponds to E_{2g} phonon of C atoms and D band at 1336 cm⁻¹, which corresponds to local defects and disorder at the edges of graphene sheets. The G band and D band for hydrothermally reduced Graphene sheets at various temperatures is known to be shifted. For reduced Graphene sheets (NG-1) at 80°C has G band at 1575 cm⁻¹ and D band at 1343 cm⁻¹, whereas reduced Graphene sheets (NG-2) at 120°C has G band at 1345 cm⁻¹ and D band at 1577 cm⁻¹.

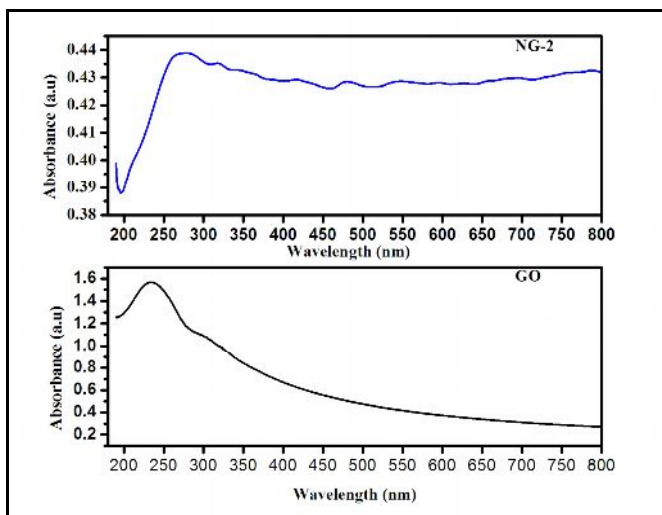


Fig. 6 shows UV-Vis spectrum of the GO and NG-2.

Fig. 6 shows UV-Vis spectrum of the GO and NG-2. The spectrum of GO has a peak at 235 nm which is related to $\pi-\pi^*$ electron transition in the polyene-type structure from the graphitic oxide. After hydrothermal reduction at 130°C, peak would be observed at 272 nm, which shows the electronic conjugation of GO was restored. Depending on hydrothermal temperature, the reduced graphene samples at low temperature could be easily dispersed in the water. But high temperature samples giving poor dispersion properties.

Conclusion

Chemical reduction and nitrogen doping were simultaneously achieved in graphene oxide using ammonia and hydrazine hydrate (N_2H_4) as reducing reagents by hydrothermal reduction reaction. The structure of the nitrogen-doped graphene sheets depends on hydrothermal temperature. Nitrogen-doped graphene were formed wrinkled sheets structure. With increasing of temperature, the nitrogen content increased gradually. The unique hydrothermal environment such as high self generated pressure should play a key role in nitrogen doping. We expect that nitrogen-doped graphene sheets may have good electrical properties and potential applications like supercapacitor and electrocatalyst for fuel cell.

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