

N- Graphene Derivatives from Papaya Seeds: Synthesis and Chemistry

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A two-step synthesis of nitrogen containing graphene (N-graphene) from papaya seeds is reported here. The preparation of N-graphene from a non-graphitic nitrogen containing precursor, without doping is really a challenging task. However, when papaya seeds were pyrolyzed at 250 °C temperature for 2 hrs, it led to the formation of N-GO without any additional oxidizing agent. Further, N-GO was converted to Nr-GO in presence of thiourea as a reducing agent. The synthesized N-GO was found to remove 82 % of iron from ground water.

Keywords: Papaya seeds, N-GO, Nr-GO, Pyrolysis, Thiourea

Introduction

The doping of nitrogen in pristine graphene has attracted considerable attention to control the physical, chemical, structural and electronic properties of graphene via manipulating the surface area and functional sites. It was earlier reported that the graphene oxide (GO), reduced graphene oxide and nitrogen doped graphene are promising candidate for biosensing and they are also capable of removing toxic chemicals from water due to the presence of hydroxyl and carboxyl groups which can adsorb the metal cations from water¹⁻³. In most of the cases, GO is the platform for preparing N-graphene using graphite powder via a two-step process, however the CVD technique is found to be common for single-step preparation of N-graphene till now⁴. In continuation of our recent research work on the synthesis of graphene derivatives from agrowastes⁵, we have now reported the preparation of N-graphene oxide (N-GO) and N- reduced graphene oxide (N-rGO) from papaya seeds, bypassing the use of graphite powder and other toxic chemicals. The papaya seeds were pyrolyzed at a temperature of 250 °C for 2 hrs in presence of trace amount of air, which initially produced nanosheets of N-GO. The N-GO was further subjected to reduction at 95 °C which resulted in the formation of N-rGO after 8 hrs. The N-GO obtained was used for the removal of iron from ground water collected from local area.

Experimental

Materials and method

Papaya seeds were collected from local market. FTIR spectra was observed on a Thermo Scientific TM Nicolet iS5 FTIR spectrometer at a scan range of 4000 – 600 cm⁻¹. *P*-XRD pattern was recorded by Bruker D8 advance diffractometer in the 2θ range of 5 – 60°. HRTEM images were collected using a JEOL JEM-2100 microscope at an acceleration voltage of 200 kV.

Preparation of nitrogen graphene oxide (N-GO)

The papaya seeds were washed thoroughly with deionized water for several times to remove dust, dried in sunlight for few days and finally dried at 70° C in vacuum oven for 24 hrs for removal of moisture content. It was finely grinded to give fine powders and subjected to pyrolysis at temperature 250 °C for 2 hrs. The brownish-black powder so obtained was washed with 2 M nitric acid to remove the impurities. The final product was filtered, washed and dried.

Preparation of reduced nitrogen graphene oxide (N-rGO)

1:10 ratio of N-GO and thiourea was stirred for 8 hrs at ~ 95 °C and the solution was filtered. The excess thiourea was removed by repeated washing with hot deionized water. The resultant black powder was dried at 80 °C for 24 hrs.

Studies on the removal of iron from water sample

The water sample was collected from the local area and tested for iron content. A glass column of 6 cm width and 20 cm length was taken which was kept

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open at one end and closed at the other end with a polythene cover having small pores for passing the water. The nitrogen containing graphene oxide was used as filter-bed material maintaining the height of 1 cm and 2 cm.

Results and Discussion

When papaya seeds were pyrolyzed at 250 °C temperature for 2 hrs, it initially gave brownish-black colored N-GO. Since the precursor contained carbohydrate and protein, the heating might have resulted in condensation and polymerization to form N-GO. It may be attributed to the fact that during pyrolysis, the presence of several hydroxyl groups in the precursor was responsible for the aromatization to develop graphitic planes in the product. The mechanism for the formation of N-GO from papaya seeds was proposed in figure 1.

The FTIR spectra showed the stretching frequency of the sp^2 hybridized C=C double bonds at 1648 cm^{-1} , which indicated the aromatization and condensation among the monomers present in papaya seeds. The N-GO also showed stretching frequency at 2914 cm^{-1} and 2847 cm^{-1} which suggested the presence of CH_2 and CH groups, respectively. A very sharp and intense peak was observed at 1742 cm^{-1} , confirming the presence of C=O group in N-GO. Moreover, the peaks of epoxy and C-O-C groups at around 1092 cm^{-1}

and 1159 cm^{-1} , respectively confirmed the proposed mechanism mentioned in figure 2 (a). The N-H stretching was observed as a hump at 3297 cm^{-1} which finally confirmed the formation of N-GO. The *p*-XRD pattern showed an intense peak at around 2θ of 12.3° confirmed the formation of N-GO from non-graphitic papaya seeds⁶. This suggested that the temperature of 250 °C can initiate the condensation, polymerization and aromatization as well as oxidation of the intermediates to give N-GO at the final stage (figure 2 b). The HRTEM images in figure 2 (c) confirmed the formation of nanosheets in case N-GO. The interlayer d-spacing corresponding to $\sim 3.14\text{ \AA}$ in figure 2 (d) also confirmed that the nanosheets were graphitic in nature.

When the 1:10 ratio of N-GO and thiourea was subjected to reduction at 95 °C, it resulted in the formation of N-rGO after 8 hrs (figure 1). Figure 3(a) showed the FTIR spectra of reduced N-rGO, which indicated that the intensity of the peaks of C=O and epoxy groups drastically reduced. It suggested that thiourea successfully reduced the N-GO to N-rGO. The formation of N-rGO was finally confirmed by *p*-XRD as shown in figure 3(b). The 001 peak at 2θ of 12.3° which was present in case of N-GO, found to be absent in N-rGO.

The amount of iron in the ground water sample was tested, which was found to contain 4.4 mg/L of iron.

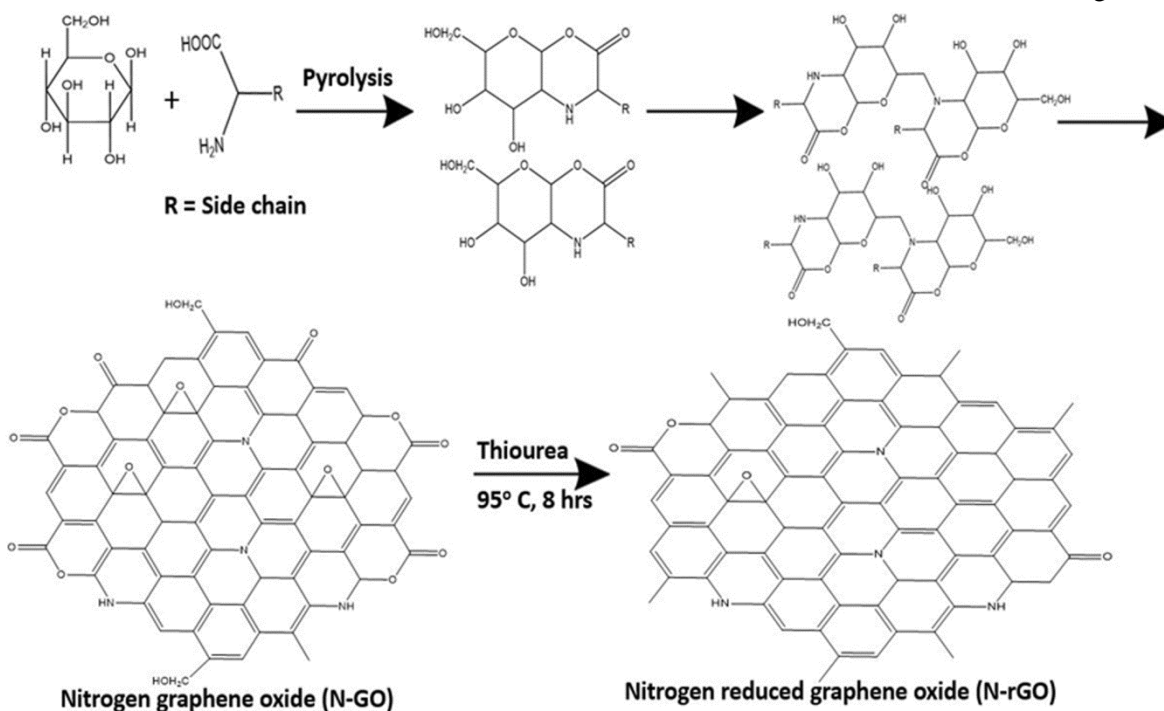


Fig. 1 — Proposed mechanism of formation of N-GO and N-rGO

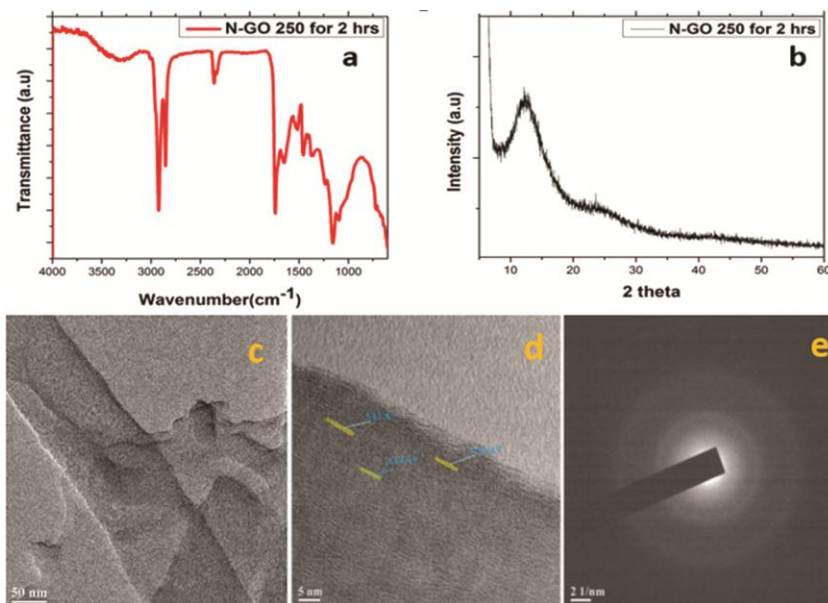


Fig. 2 — (a) FTIR spectra of N-GO, (b) XRD pattern of N-GO, (c) HRTEM image, (d) lattice fringes and (e) SAED patterns of N-GO at 250 °C

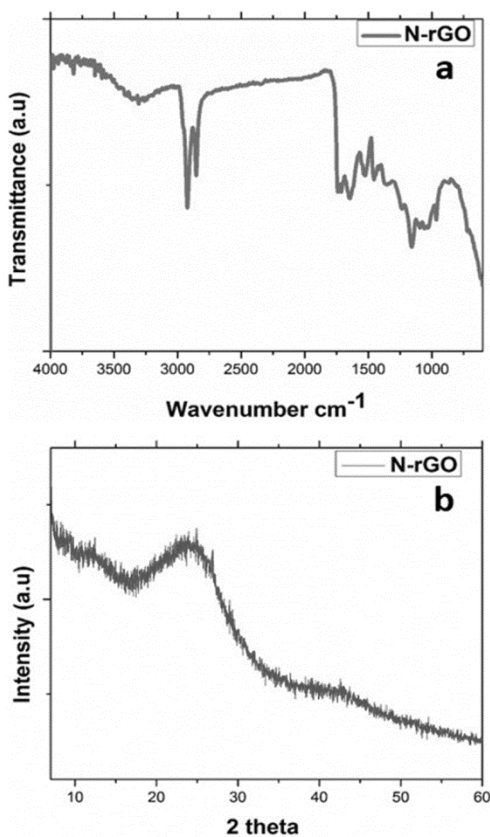


Fig. 3 — (a) FTIR spectra of N-rGO and (b) XRD pattern of N-rGO

The sample water was passed separately through the column containing N-GO as filter-bed material (1 cm and 2 cm of heights). It was observed that in case of 1 cm height of N-GO, the concentration of

iron which was initially 4.4 mg/L reduced to 2.3 mg/L after cycle 1. The filtered water sample was again passed through the same column which reduced the iron content upto 1.0 mg/L after cycle 2. In case of 2 cm height of N-GO, the amount of iron was drastically reduced to 1.8 mg/L from the initial value of 4.4 mg/L after cycle 1 and 0.8 mg/L after cycle 2. It can be clearly seen from the observation that 77.2 % and 81.8 % of iron can be removed from the water sample using 1 cm and 2 cm heights of N-GO, respectively.

Conclusion

In this paper, we have followed a simple approach to prepare N-graphene derivatives from papaya seeds without using graphite powder, oxidizing agent and other toxic chemicals. The results suggested that pyrolysis at 250 °C for 2 hrs is suitable for the formation of N-GO nanosheets. This further indicated excellent aromatization and condensation of the monomer moieties of the precursor. The *p*-XRD pattern confirmed the formation of N-GO which showed the characteristic peak at around 2θ of 12.3°. The reduction of N-GO to N-rGO using thiourea indicated drastic reduction in the intensity of C=O peak, retaining the aromaticity. This N-GO nanosheets was able to remove around 82 % of the iron successfully from the ground water sample.

Conflict of interest

The authors declare no conflict of interest.

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