



Efficient and Large Scale Synthesis of Graphene from Coal and Its Film Electrical Properties Studies

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Coal, which is abundant and has an incompact structure, is a good candidate to replace graphite as the raw material for the production of graphene. Here, a new solution phase technique for the preparation of graphene from coal has been developed. The precursor: graphene oxide got from coal was examined by atomic force microscopy, dynamic light scattering and X-ray diffraction, the results showed the GO was a small and single layer sheet. The graphene was examined by X-ray photoelectron spectroscopy, and Raman spectroscopy. Furthermore, graphene films have been prepared using direct solution process and the electrical conductivity and Hall effect have been studied. The results showed the conductivity of the films could reach as high as $2.5 \times 10^5 \text{ Sm}^{-1}$ and exhibited an *n*-type behavior.

Keywords: Graphene, Coal, Film, Conductivity.

1. INTRODUCTION

Graphene has attract world-wide attention after its discovery¹ for its unique structure and a many useful properties in chemistry, physics and mechanics: the excellent electronic transport properties;² the great strength and stiffness;^{3–6} and the good thermal conductivity.^{7–9} Large area sample preparation should be study on for the use of application or research. There are some methods to get graphene: micromechanical cleavage^{1,10} is not suitable for the large production. The growth on SiC wafer¹¹ or other substrates^{12,13} which can produce graphene with large area has the same problem of the low output. Arc-discharge method is considered a method for producing large-scale graphene sheets^{14,15} but it is not easy to get single layer graphene. Chemical exfoliation is an effective way of producing graphene in large quantity.^{16–22} However, it has a complicated process and costs a lot of time, what's more, great care should be taken for the use of KMnO_4 and H_2O_2 .

Coal may be a good candidate to replace graphite as the raw material of chemical exfoliation, for it is cheap and abundant. More importantly, the coal is a molecular solid which has an incompact structure while graphite is a lattice solid without weak bonds, so the process can be simplified and some dangerous medicines such as KMnO_4 and H_2O_2 can be avoided. Here we report a preparation

of graphene from coal in large quantity by a new solution phase technique.

2. EXPERIMENTAL DETAILS

Graphene oxide (GO) was synthesized in the concentrated sulfuric acid and was oxide by NaNO_2 . Briefly, 2.5 g of coal and 2 g of NaNO_2 (A.R.) were placed in a flask. Then, 120 ml of H_2SO_4 (A.R.) was added with stirring. The stirring was continued for 15.5 h at room temperature. Then the mixture was further stirred for 6 h at 80 °C. When temperature was reduced to room temperature, the solution was diluted by 1 M HNO_3 and GO was got as sedimentation by centrifugation at 10000 rpm for 15 min. To remove the ions of oxidant and other inorganic impurity, the sedimentation was dispersed in water and centrifuged at 12000 rpm for 15 min. The process was repeated for 5 times. A solution of GO was got after dissolving the sedimentation in the aqueous ammonia. For the graphene film fabricated from GO, we spin coated the GO solution on piranha-cleaned quartz surfaces. Then thermal treatment was taken under argon flow at 1100 °C for 3 h and the graphene film was got.

Typical tapping-mode atomic force microscopy (AFM) measurement was performed using Multimode SPM from Digital Instruments with a Nanoscope IIIa Controller. Samples for AFM images were prepared by spin-coating the dispersion of GO in water (0.5 mg/ml) onto a freshly cleaved mica surface (500 rpm, 18 s and then 1500 rpm,

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60 s) and allowing it to dry in air. The hydrodynamic radii (Rh) of the GO sheets were measured by dynamic light scattering (DLS) with a Brookhaven 90Plus laser particle size analyzer at a scattering angle of 90° . The sample temperature was controlled with a built-in Peltier temperature controller. X-ray diffraction (XRD) measurement was carried out on a Rigaku D/Max-2500 diffractometer with Cu-K α radiation. Raman spectra were measured with a Renishaw inVia Raman spectrometer using laser excitation at 514.5 nm. Electrical measurement was carried out, and the data was collected with a Keithley SCS 4200. X-ray photoelectron spectroscopy (XPS) was used to investigate defects in the few-layered graphene. XPS spectra were recorded using a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al-K α X-ray source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector.

3. RESULTS AND DISCUSSION

A typical tapping mode AFM image and the corresponding height cross-sectional profile of the as-prepared GO

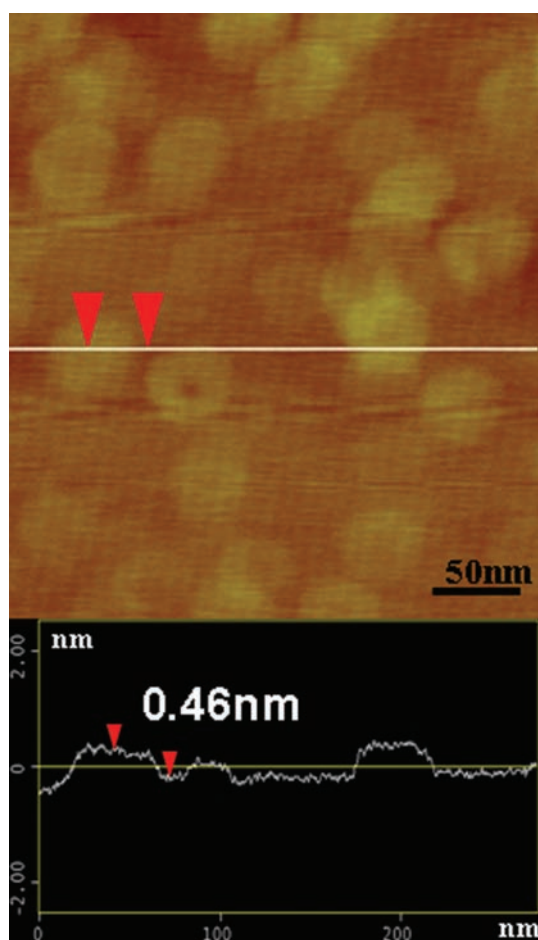


Fig. 1. AFM image of GO. The height profile reveals that the measured GO is single layer with a height of ~ 0.46 nm and a diameter of several decades nanometers.

sheets deposited on the quartz substrate was displayed in Figure 1. It revealed that the thickness of the GO sheets was uniform (~ 0.46 nm) and had a same disciform structure with a diameter of ~ 50 nm. The thickness is thinner than the GO got from chemical exfoliation of graphite, which indicates there are less functional groups for the less and weaker oxidizer.²³

XRD of GO was shown in Figure 2. The diffraction peak at $2\theta = 21.5^\circ$, came from the inter-GO diffraction, shows a d -spacing of 0.41 nm corresponding with the AFM result. The d -spacing is a little larger than that of the normal graphite for the present of functional groups but smaller than that of GO from graphite.

The DLS also showed that the small GO sheets had an Rh ranging from ~ 15 nm to ~ 35 nm (Fig. 3). The Rh of GO exhibited a Gaussian distribution and the maximum distribution is ~ 22 nm, the same as the result of the AFM results.

Raman spectroscopy is an efficient way to provide a quick and easy structural and quality characterization of the carbon material. Figure 4 shows the typical Raman spectra of GO and graphene got after thermal treatment.

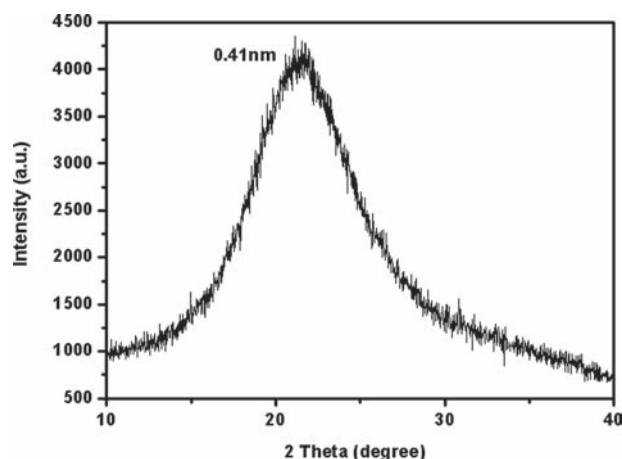


Fig. 2. XRD pattern of GO. The d -spacing of GO is 0.41 nm.

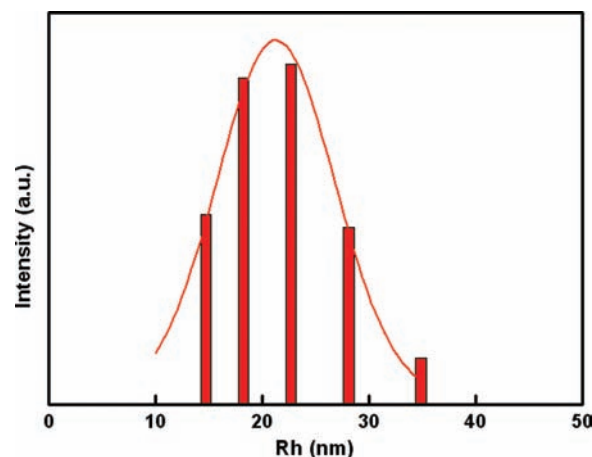


Fig. 3. The Rh distribution of GO got from DLS.

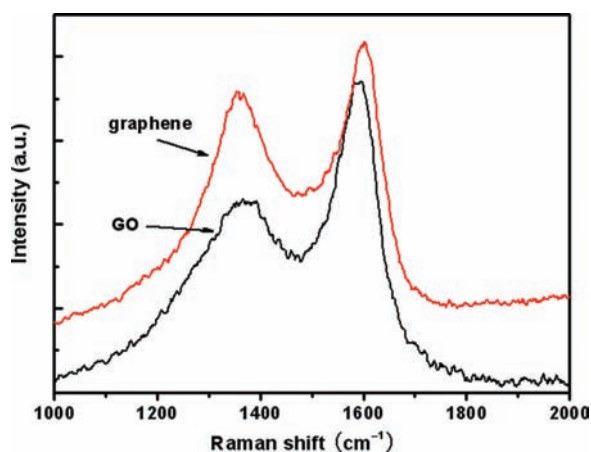


Fig. 4. Raman spectrum for GO and graphene.

The Raman spectrum of GO shows two peaks at 1365 and 1590 cm^{-1} , corresponding to *D* band and *G* band.²⁴ For the graphene got after thermal treatment, the *G* band shifts to higher wave numbers, reaching 1606 cm^{-1} , and the ratio $I(D)/I(G)$ increases from 0.63 to 0.87. The changes

in Raman spectra are characteristic of a phase transition for the thermal annealing to form a nanosized graphene network.²⁵

The graphene obtained after thermal treatment was a conductor comparing with GO as an insulator, for the thermal treatment could remove oxygenated functional groups from the GO. The electrical property of graphene was measured by the Kethelin after the gold evaporation on the graphene film supported by quartz. A good conductivity about $2.5 \times 10^5 \text{ Sm}^{-1}$ shows a perfect structure of the graphene. The conductivity is much higher than that of graphene got from chemical exfoliation due to less functionalization.²⁶

The XPS analysis of the graphene shows most of the carbon was sp^2 bonding. (The main peak at 284.5 eV) with a small amount of C–N (the peak at 285.7 eV) (Fig. 5(a)). Figure 5(b) is the high-resolution XPS spectra of N 1s. The small peaks at 398.8, 400.1 eV correspond to “pyridinic,” “pyrrolic” N, respectively. Hall measurements showed that the graphene exhibit an *n*-type behavior, which caused by the N atoms came from the ammonia or the coal’s own were doped into the graphene lattice.²⁷

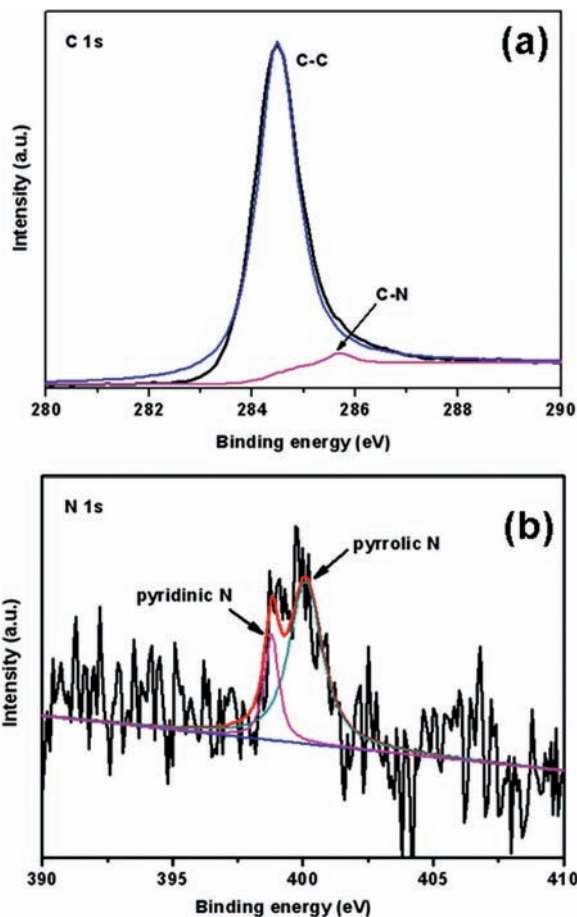


Fig. 5. (a) XPS C 1s spectrum and (b) XPS N 1s spectrum of the N-doped graphene. The C 1s peak can be split to two Lorentzian peaks at 284.5 and 285.7 eV. The N 1s peak can be split to two Lorentzian peaks at 398.8, 400.1 eV, correspond to “pyridinic,” “pyrrolic” N.

4. CONCLUSIONS

In summary, we demonstrated for the first time that high quality conducting graphene film can be got from the coal which is cheap and abundant by a simple process. We measured the electrical properties of the graphene. It has a high conductance and what’s more, it behaves as an *n*-type graphene because the N atoms doped into the graphene lattice which is not easy to be produced by other methods. This research provides a good way to the large scale production of *n*-type graphene that can be used in the electronic industry.

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