Discussing the Preparation Conditions of Graphene

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Abstract The oxide reduction process of preparation graphene always accompanies the stirring process. The stirring speed affects the efficiency of sulfuric acid to access the graphite sheet, but also affects the efficiency of potassium permanganate to oxide the graphite and affects the reducer to reduce graphene oxide. So the stirring speed has a non-negligible efficiency to control the synthesis of graphene. Focusing on this problem,this study uses oxidation reduction to compound the graphene, changing stirring speed in the process of synthetic experiment in order to prepare different graphene dispersions, then the samples are go through FT-IR, Raman spectrum, transmission electron microscopy (TEM) and resistivity test analysis. The experiment results express that graphene's conductivity is much better when stirring speed is 300 r/min than other speed (100 and 500 r/min) in preparation. In addition, the order degree and the flatness of graphene layers are more excellent. The graphene at 500 r/min stirring speed preparation contains less oxygen groups.

Keywords Graphene · Preparation conditions · Stirring speed · Test analysis

1 Introduction

Graphene is a two-dimensional (2D) crystalline material that consisted by a single atomic layer of carbon bonded all together in a honeycomb. Graphene has attracted a lot of attention and has been the subject of numerous theoretical and practical investigations owing to its extraordinary physical and chemical properties [1]. There are some methods for preparation of graphene, such as: mechanical peeling method, chemical vapor deposition method, liquid-phase stripping method, oxidation-reduction method and so on.

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This paper uses oxidation reduction to prepare graphene, so far, there is some literatures report that reducing agent dosage and reaction time have an impact on reduction effect [2]. Not only that, reaction temperature and pH value have an impact on reaction rate, product range [3]. As a result, researching the influence of reaction conditions the graphene sheets is very significance.

The oxide reduction process of preparation graphene always accompanies the stirring process. The stirring speed affects the efficiency of sulfuric acid to access the graphite sheets, but also affects the efficiency of potassium permanganate to oxide the graphene and affects the reducer to reduce graphene oxide. In this paper, we used the oxidation reduction to compound the graphene, setting the stirring speed of the reaction course to: 100, 300, 500 r/min (rest of the experimental conditions without changing) to prepare different graphene dispersion. Then the samples went through FT-IR, Raman spectrum, transmission electron microscopy and resistivity test analysis, exploring the impact of the preparation's condition on graphene's functional group, morphology, lamella, degree of order and resistivity.

2 Experiment

2.1 Experimental Materials

Graphite, 98% H_2SO_4, $NaNO_3$, $KMnO_4$, ionized water, H_2O_2, HCl, glucose, pH test paper.

2.2 Experimental Instrument

D2004 W electric mixer, HZ85-2 magnetic stirrer, RJ-TDL-60A low-speed large-capacity desktop centrifuge, BS244S electronic analysis The balance, KQ3200DE ultrasonic cleaner, DZF-6210 vacuum oven, RTS-9 four-probe tester, Renishaw in Via Raman spectrometer, Ncolet iS 50 infrared spectroscopy, CSPM5000 atomic force microscope, Tecnai G2 F20 S-TWIN transmission electron microscope, 200 ml beaker, 400 ml beaker, three-neck flask, glass rod.

2.3 Oxidation-Reduction Preparation of Graphene

2.3.1 Preparation of Graphene Oxide

Taking graphite powder 1, 0.5 g $NaNO_3$, 23 ml 98% H_2SO_4 at 0 °C mix, magnetic stirrer continue embrace mixing (respectively 100, 300, 500 r/min), and slowly add

6 g $KMnO_4$ with stirring for 2 h at 0 °C, then stirring for 4 h at 35 °C (respectively 100, 300, 500 r/min). Adding 138 ml deionized water to the resulting solution slowly for dilution, and raise the temperature to 95 °C for 0.5 h with stirring. In this case we add 130 ml deionized water and 20 ml H_2O_2 to the solution with stirring (respectively 100, 300, 500 r/min) 1 h and stand it overnight. After that we decant the upper clear liquid, then add 5% dilute HC1 for dilution, and then stand it overnight again, decanting the upper clear liquid again, repeating three times. Finally, the solution is placed in dialysis bag until the pH gets to 6. Take some solution to place into an ultrasonic cleaner (45 W, 50 Hz), ultrasound 1 h, then the graphene oxide dispersion was obtained [4].

2.3.2 Reduce Graphene Oxide to Prepare Graphene

Measuring 10 ml deionized water and oxide graphene formulated as 1 mg/ml solution of graphene oxide, adding ammonia so that the pH gets to 8–9 value. Adding 250 mg glucose to the reaction mixture with stirring (respectively 100, 300, 500 r/min). Furthermore, Stirring the solution at 95 °C in an oil bath (respectively 100, 300, 500 r/min),at the same time, making a reduction reaction reflux condenser for 12 h. Then using a centrifuge wash to the product (with deionized water washed six times) until pH value reaches 7. Finally, the product is washed and dried in a vacuum box for 48 h. At last, we get three groups of graphene which were prepared always at a stirring speed: 100, 300, and 500 r/min [4].

2.4 Sample Characterization and Test Methods

2.4.1 Resistivity Characterization

We press the graphene powder into a sheet, then using a four-probe resistivity tester to test each sample. To select three areas for measurement in each sample then calculate an average resistivity.

2.4.2 Infrared Spectroscopy Characterization

Using KBr tablet method, we take a small amount of graphene sample with KBr grinding evenly and placed in a tableting machine to tablet, then put it into the infrared spectroscopy for test [4, 5].

2.4.3 Raman Spectroscopy Characterization

Raman spectroscopy analysis is based on light scattering by the Raman scattering effect. Putting the graphene into the sample bottle and kept in a dark environment [3], moving the probe tip keep the distance to 2 mm, scanning graphene at an excitation wavelength of 514 nm [5].

2.4.4 Transmission Electron Microscopy (TEM) Characterization

Mixing the graphene sample with deionized water and taken an ultrasonic dispersion, drop it in the copper sulfate medium using a transmission electron microscope to observe the graphene surface morphology and measure graphene's structure and detail [6].

3 Results and Analysis

3.1 Resistivity Analysis

The graphene's slice thickness and quality have a causal relationship with graphene resistivity [7], so we use the four-probe tester at different speeds to test three sets of graphene samples' resistivity, data are as follows (Table 1).

As can be seen in the table, the resistivity of the graphene at 100 r/min stirring speed preparation is the biggest, which means the conductivity is worse than the graphene at 300 and 500 r/min stirring speed preparation obtained, which hints the graphene prepared at a low stirring speed contained more oxygen species or more hetero groups and the opening degree of the graphite sheets during the preparation of graphene is not complete, the reaction efficiency of oxidant and reductant with the reactant are relatively low. The resistivity of graphene at 300 r/min stirring speed preparation is smallest, which means the conductivity is the most.

3.2 Infrared Spectroscopy Analysis

In order to accurately analyze the influence of stirring speed on graphene molecular structure, we through infrared spectroscopy to characterize the three groups of

Table 1 Graphene resistivity prepared at different speeds

Rotate speed (r/min)	Resistivity (Ω m)
100	53.2
300	47.8
500	48.1

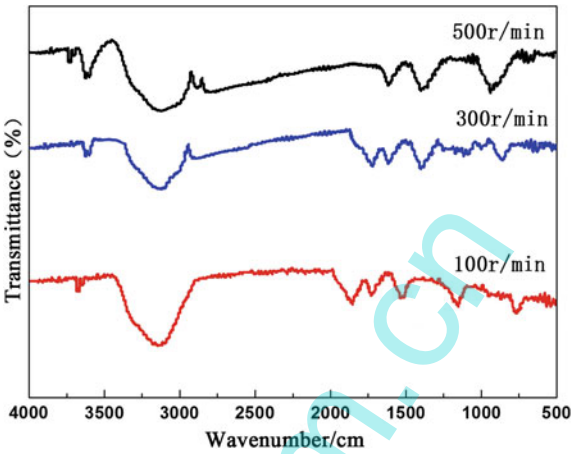

Fig. 1 IR spectra of graphene under different stirring speeds preparation

products and get Fig. 1 the IR spectra of graphene under different stirring speeds preparation, which is as follows.

Figure 1 can be seen that three curves all have the broad strong absorption peak and they appear in 3000–3200 cm^{-1} which means the water molecule stretching vibration of –0–H, 2800–3000 cm^{-1} is sp^2 hybridized C–H stretching vibration peak, 1550–1650 cm^{-1} is graphene stretching vibration of the C=C, 1300 cm^{-1} is C–O stretching vibration of the peak, in addition, there are smaller C=O (−1720 cm^{-1}) and the C–O–C (−1068 cm^{-1}) stretching vibration of three curves. The graphene at 500 r/min stirring speed preparation compare with the graphene at 100 and 300 r/min stirring speed preparation, the former contains less oxygen group peaks, while it has more C=C peak and sp^2 hybrid C–H stretching vibration peak [10].

3.3 Raman Spectroscopy Analysis

In order to explore influence of the stirring speed on graphene sheets regularity furtherly, under excitation wavelength of 514 nm to characterize the three groups of products through Raman spectrometer. We get the Raman spectra of graphene under different stirring speed as Fig. 2, the position of G peak and D peak and ratio of them as Table 2.

As we know that: D peak is characteristic defect peaks of graphene structures, G peak and D peak relative intensity ratio is an important parameter to characterize the degree of disorder and defects of the carbon material, the ratio is larger, the defects content is more. 2D peak occurs in the vicinity of 2700 cm^{-1}, and the peak 2D is stronger illustrates the graphene has fewer defects and fewer layers [9]. As can be seen from the above data, three groups of graphene have strong D peaks and weak 2D peaks, which describe the three groups of graphene were all flawed.

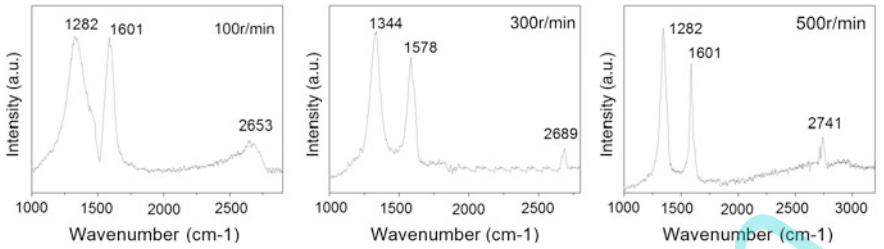

Fig. 2 Raman spectra of graphene under different stirring speed

Table 2 Position data of G peak, D peak and 2D peak; the I_D/I_G

Rotate speed (r/min)	D-band peak/cm	G-band peak/cm	I_D/I_G	2D-band peak/cm
100	1282	1601	1.216	2653
300	1344	1578	0.959	2669
500	1337	1585	1.074	2741

The graphene at 300 r/min stirring speed preparation compare with the graphene at 100 and 500 r/min stirring speed preparation, the former's I_D/I_G are smaller, which shows the graphene at 300 r/min stirring speed preparation has the greater grain size and the lower degree of disorder and defects as well. The graphene at 500 r/min stirring speed preparation has a largest 2D peaks which transfers that the thickness of graphene layers is thinnest.

3.4 Transmission Electron Microscopy Characterization

In order to observe the layer and the appearance of three groups graphene, we use the transmission electron microscopy to characterize graphene, and get the TEM of graphene under different stirring speed, which is as follows (Fig. 3).

The dark area of picture represents a lot of graphene layers, and the light area represents a small number of graphene layers [7]. From the chart we can see clearly the edges of graphene. There is little difference in thickness of each portion, showing the graphene dispersed uniform in a solution of copper mesh. At the same time, we can see the fold surface of the graphene, and the figure on the left has the most obvious situation. That means a lot of groups of the graphene at 100 r/min stirring speed preparation have been destroyed the structure of the carbon ring. And graphene sheets superposed with each other to form the folds. Learning from the shades of figures, three groups of graphene have fewer layers, but their edge has some defects. Among this, the graphene at 500 and 300 r/min stirring speed preparation have not obvious wrinkles, and a little overlap portion, what's more, their surface texture is clear, smooth and orderly.

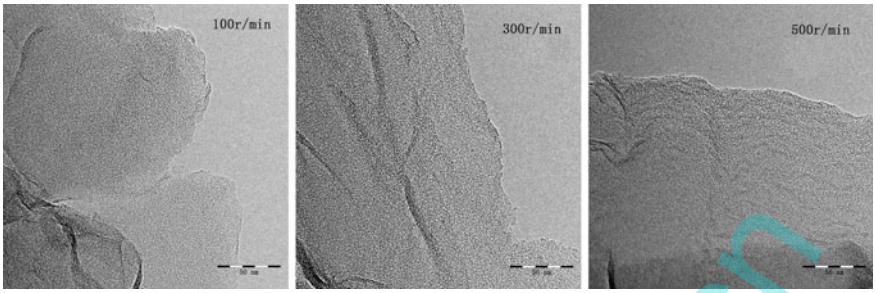

Fig. 3 TEM of graphene under different stirring speed

4 Conclusions

By comparison of the above experimental analysis, we find that the graphene at 300 r/min stirring speed preparation compare with that the graphene at 100 and 500 r/min stirring speed preparation, the former has the better conductivity, and the graphene has not obvious wrinkles, not too much overlap portion, the surface texture is clear, smooth and orderly state. The graphene at 500 r/min stirring speed preparation contains less oxygen groups.

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