

The Catalysis of Ferric Chloride in the Preparation of Graphene Oxide Film

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ABSTRACT: *Accurate analysis of the catalysis of ferric chloride in the preparation of graphene oxide film can improve the performance of the finished product. The thermal conductivity of graphene film prepared by the original method is low, so a new catalytic analysis method is proposed. Firstly, the flake double-layer graphite oxide is prepared by the improved Hummers method. Under the catalysis of FeCl₃, different reaction temperatures and reaction times are set to get the finished products of graphene oxide under different conditions. The structure characteristics of the finished products are analyzed, and the structure of that the graphene oxide films prepared at 90 °C and 0.5h is determined to be the best. So far, the catalysis of ferric chloride in the preparation of graphene oxide film has been analyzed. The results show that the thermal conductivity of graphene oxide film prepared by catalysis is 900W/(m.K), which is higher than that of traditional products.*

KEYWORDS: *Catalysis; Preparation of graphene oxide film; Potential function; Thermal conductivity.*

INTRODUCTION

Carbon is one of the most abundant elements in nature, and also one of the earliest elements that humans contact and use. Carbon is widely distributed in the natural environment. Carbon materials generally have high thermal stability and carbon-carbon bond strength and show chemical inertia [1]. Therefore, the structural sequencing of carbon materials usually needs to provide high energy, and there are many kinds of allotropes, such as diamond, graphite, fullerene, graphene oxide, etc [2]. Before the appearance of graphene oxide, some scientists predicted theoretically that single-layer two-dimensional carbon atomic materials could not exist alone, even if they were prepared, they would decompose or curl up

quickly at room temperature. In early studies, the graphitization of carbon materials was achieved by high-temperature treatment. Until 2004, physicists Andre Heim and Constantine Novoselov of the University of Manchester in the United Kingdom succeeded in separating the oxidized graphene from graphite by micromechanical stripping. The graphene oxide has high-frequency characteristics and the frequency can reach 0.5-40 GHz [3], which can be used as an efficient intermediate connection material in the RF band. Highly ordered graphene oxide composites can be used as building blocks of artificial muscles. It has been proved that single-layer two-dimensional graphene oxide can exist

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Table 1: Main experimental drugs.

Name of drugs and reagents	Specifications	Supplier
expanded graphite	500 μ m	Nanjing Xianfeng Nano Materials Technology Co., Ltd
potassium permanganate	AR	Shanghai Guoyao Group Chemical Reagent Co., Ltd
concentrated sulfuric acid	98%	
Hydrogen peroxide solution	30%	
Ferric trichloride (FeCl ₃ · 6H ₂ O)	AR	
hydrochloric acid	AR	
Hydroiodic acid	AR	
Potassium persulfate	AR	
Polyvinyl alcohol	molecular weight : 18000-50000	Aladdin

alone. Until now, the research on graphene oxide in the scientific community has gradually become active, and graphene oxide is also known as the key of the fourth industrial revolution, known as "black gold" and "king of new materials". Many scholars have found that in addition to the type of catalyst, the particle size of the catalyst also has a different catalytic effect on the graphitization of carbon materials [4].

In addition, graphene oxide can also be used as the insulation layer of varistor memory and capacitor devices, and the research shows that the current switch ratio of the varistor memory prepared by graphene oxide can reach 103, showing excellent performance [5]. Ferric chloride (FeCl₃) plays an important catalytic role in addition reactions, substitution reactions, coupling reactions, cyclization reactions, oxidation-reduction reactions, and so on [6]. In this paper, based on the preparation of graphene oxide film in our earlier stage, FeCl₃ is used to catalyze the reaction of oxygen-containing functional groups such as via group, shuttle group, and carbon group in the graphene oxide film, so as to realize the connection of sheet-like oxyfossil graphene film, obtain large-area oxyfossil graphene (L-oxyfossil graphene) the film, and study the catalytic effect of ferric chloride on different temperatures and reaction times. According to the influence of the whole reaction, the connection mode of the graphene oxide film is predicted according to the morphology and infrared spectrum analysis, which provides a new basis for the preparation of graphene oxide film.

EXPERIMENTAL SECTION

Preparation of graphene oxide film

Selection of experimental materials

In this research, graphene oxide and graphene oxide film are prepared by the coating method. The main experimental drugs are as follows [7] (Table 1):

In the above table, the drugs and solvents used need not be further purified. The information on analysis and measurement equipment used in the structure analysis of graphene oxide film is shown in Table 2.

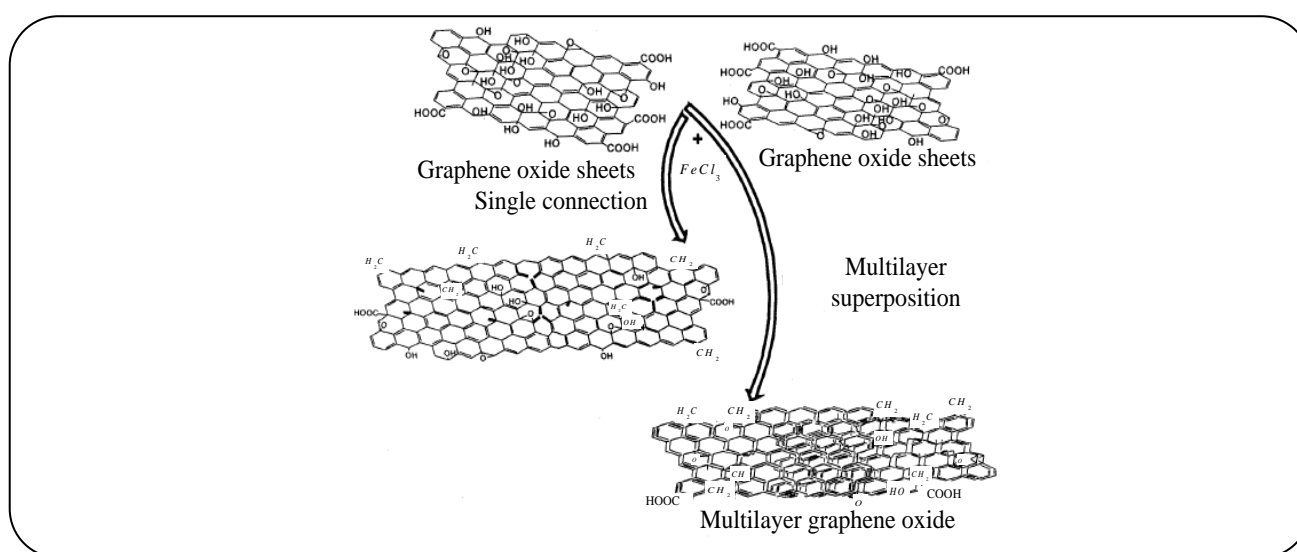
In this research, the graphene oxide films are prepared by using the above experimental materials and instruments and ferric chloride as a catalyst.

Preprocessing of raw material

In this research, the graphene oxide film is prepared by the improved Hummers method. After 1g of fine-scale graphite powder and 50 mL of 98% concentrated sulfuric acid s are fully mixed in an ice bath (below 5 °C), 4g of potassium permanganate K M n O₄ is slowly added in batches and stirred and kept at the temperature below 10 °C, reacting for about 1h until the solution is dark green; The water bath temperature is increased to 35 °C and stirred for 3 hours; then the reaction vessel is transferred to a 95 °C water bath. Adding 100 mL of deionized water, and taking out the solution brown after 30 minutes of reaction, a proper amount of deionized water is added to dilute, and then 20 ML30% H₂O₂ is added to remove the unreacted KMnO₄. Taking advantage of hot suction filtration, it is washed with 5%

Table 2: Main instruments and equipment used in the experiment.

Name of instrument	Model	Manufacturer
Constant temperature magnetic stirrer	DF-101S	Gongyi Yuhua Instrument Co., Ltd
Ultrasonic cleaning machine	KQ-500E	Kunshan Ultrasonic Instrument Co., Ltd
High speed centrifuge	TG-18G	Yancheng Kaite Experimental Instrument Co., Ltd
scanning electron microscope	S -4800	Hitachi Corporation of Japan
Fourier infrared spectrometer	-	SHIMADZU Japan
X-ray diffractometer	X'Pert PRO	PhilipsPhilips, the Netherlands
Universal testing machine	CMT-4304	Zhuhai Sansi Taijie company
Thermal conductivity meter	LF467	Germany fast

Fig. 1: Preparation of graphene oxide film under the catalysis of $FeCl_3$.

hydrochloric acid until SO_4^{2-} can not be detected, and finally, deionized water is used to make centrifugal washing until pH value is about 5 to obtain colloidal graphene oxide liquid for preparation [8].

The setting of catalytic conditions

In order to study the catalytic effect of ferric chloride on graphene oxide film under different conditions, different catalytic conditions need to be set by taking 210 mL of the above colloidal graphene oxide liquid and 90 mL of 1g/L $FeCl_3 \cdot 6H_2O$ aqueous solution and mixing them fully, and divide them into 6 parts on averagely; put the 6 parts of the mixed solution in a 98 °C water bath to react for 0.5h, 1.0h, 1.5h, 2.0h, 2.5h, and 3.0h respectively, then take them out; Finally, remove the catalyst by centrifugal cleaning; take 105 mL of colloidal graphene

oxide liquid and 45 mL of 1 g/L $FeCl_3 \cdot 6H_2O$ aqueous solution and mix them fully and divide them into three parts on average; place the three parts of the mixture in the water bath at 98, 90, and 80 °C for 2.0 hours, then take them out; finally, remove the catalyst by centrifugal cleaning; clean and dry SiO_2 substrate (Hui et al. 2018), and prepare the suspension of L-graphene oxide ethanol, and coat the suspension of l-graphene oxide ethanol on SiO_2 substrate (800 rpm, 10 s; 1900 rpm, 20 s) by ultrasonic at 53 kHz for 15 min. Finally, the samples are placed in an oven at 60 °C for 20 min to obtain graphene oxide film. The reaction process is as follows:

Graphene oxide films [9] are prepared under different catalytic conditions at different reaction times and these temperatures. temperatures. graphene oxide films are analyzed in-depth.

Table 3: Statistical data of defect structure under different catalytic conditions.

Temperature/K	With catalyst	No catalyst condition
1000	Carbon chain(5)	Carbon chain(5)
1600	Vacancy(1)	Vacancy(4)
	Carbon chain(1)	Carbon chain(4)
2000	Vacancy(0)	Vacancy(4)
2500	Vacancy(0)	Vacancy(1)

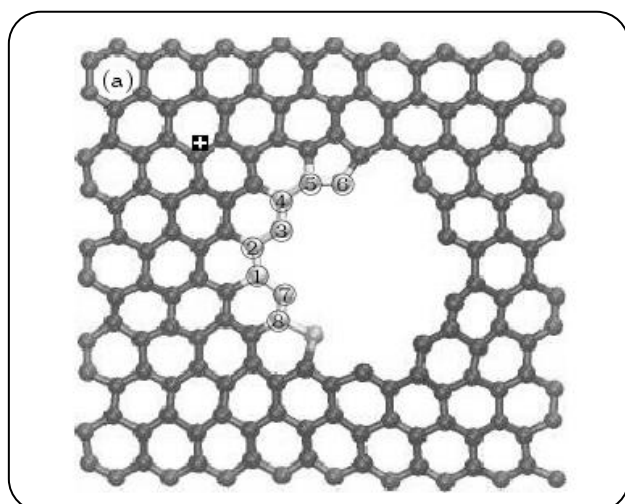


Fig. 2: Configuration of a carbon atom with hole defect.

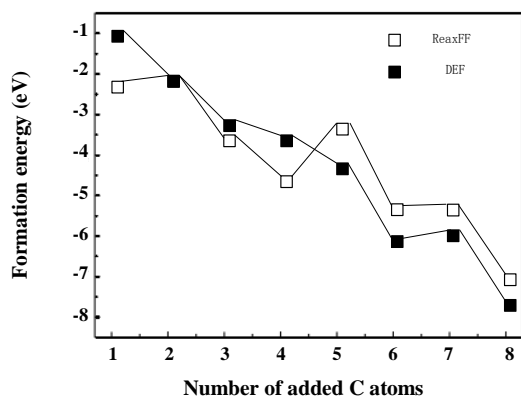


Fig. 3: Formation energy curve of carbon atom added by two methods.

Analysis of structural characteristics of the graphene oxide film

Analysis of potential function characteristics

In this paper, different ReaxFF potential functions are used to describe the C / Fe System in the preparation of graphene oxide film under FeCO_3 catalysis. For this system, the specific potential functions are accurately described

by fitting potential parameters. Firstly, the simplified process of metal atom catalyzing graphene oxide film is simulated. The simulation model is a single-layer graphene oxide sheet ($20 \times 20 \text{ \AA}$), with 180 original carbon atoms. 24 carbon atoms in the center of graphene oxide are removed to form pore defects, as shown in the following figure:

The carbon atom marked with the serial number in the above figure adds a carbon atom for repair every 50ps, and the serial number represents the order of addition. The formation energy of the added carbon atom is calculated by using the selected ReaxFF potential function, which is compared with the energy value obtained by DFT structure optimization [10]. Graphene itself has a strong ability for reconstruction, even if there is no catalytic atom, it is enough to achieve the full repair of graphene. However, in the temperature range (1600-2000 K) suitable for the repair of graphene, the repair effect of a catalytic atom is obvious without the effect of a catalyst. With the increase in temperature, the defect repair effect is also improved. Table 3 lists the statistical data of typical defect structures in the final structure obtained under different catalysis in this study:

The energy curve calculated by the two methods is shown in Fig. 3.

As can be seen from the above figure, the formation energy calculated by ReaxFF and DFT shows a very similar trend with the increase of carbon atom number [11], and the maximum difference is about 1eV. Therefore, we believe that the simulation results obtained by using the selected ReaxFF potential function are reliable and can reflect the kinetic process of catalytic repair of defective graphene oxide.

Analysis of the properties of graphene oxide films under a polarized microscope

With the help of a polarizing microscope, the products of graphene oxide prepared by Hummers method are observed at different reaction temperatures for 2 h, and the film

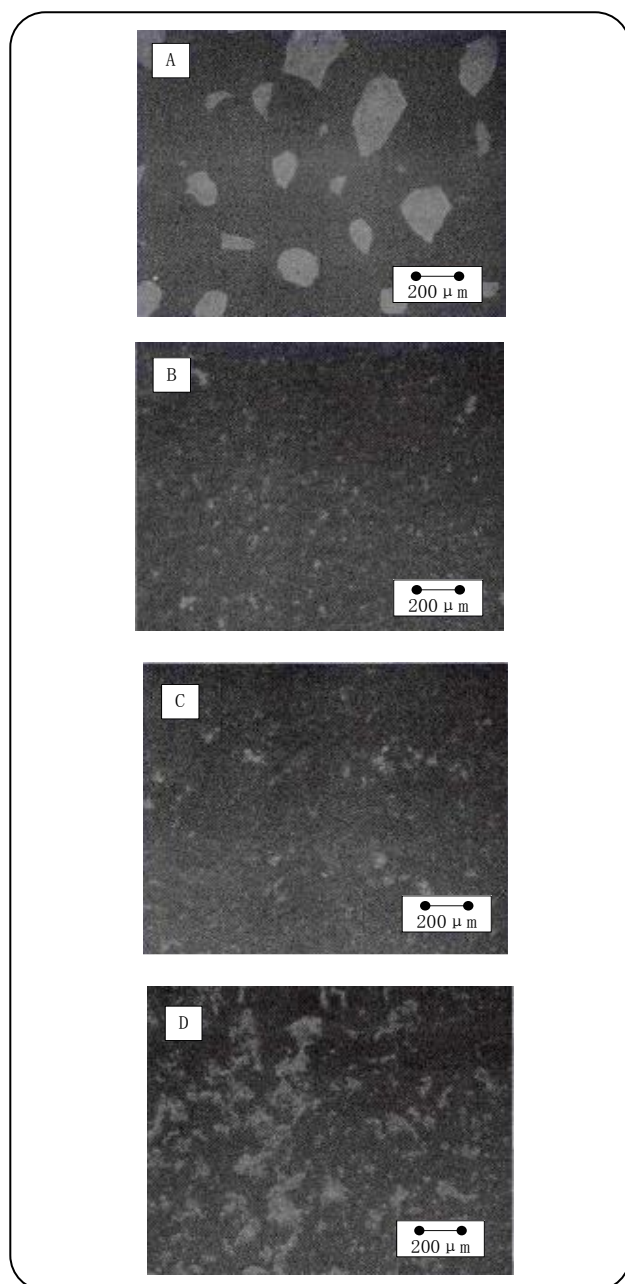


Fig. 4: Polarized micrograph of graphene oxide film prepared at different temperatures.

is formed by dropping it on the SiO₂ substrate. The picture of the polarizing microscope is as follows:

Fig. 4 A shows the graphene oxide film prepared in the presence of five catalysts. It is a block film with a similar hexagonal shape and different sizes and does not form a large area of the uniform graphene oxide film. There may be no physical connection between flake graphene oxide, and ethanol evaporation drives flake graphene oxide to aggregate, resulting in massive films [12]. B, C, and D in the

above figure are graphene oxide films at 80 °C, 90 °C, and 98 °C respectively. At different temperatures, graphene oxide films are formed. Figures B and C show that the film has good uniformity at low temperatures. When the temperature of Fig. 1D is high, the high and low irregular lines on the surface become prominent, which may be due to the catalytic reaction at the high reaction temperature. On the one hand, promoting the functional group reaction between flake graphene oxide, forming the interconnected graphene oxide film; on the other hand, the reaction between the functional groups of flake graphene oxide itself is strengthened, leading to the formation of uneven oxidation graphene film.

Analysis of the micromorphology of the graphene oxide film

In order to analyze the micromorphology of the film more carefully, AFM is used to analyze the morphology of graphene oxide film and the film at different catalytic temperatures. The photo of AFM is as follows:

As shown in Figure A, flake graphene oxide film without a catalyst is formed. It can be observed that most flake graphene oxide domains are distributed on the surface of the substrate. The size of flake graphene oxide film is much smaller than that of bulk film observed by polarized light micrograph, which shows that there is no large area of continuous film inside the flake graphene oxide film without a catalyst. It can be seen from B and C in the figure that large-scale domains appear in the reaction at 80 °C, 90 °C, and 98 °C for 2h under the catalysis of FeCl₃ catalyst. The size of continuous L-graphene oxide films at 80 °C and 90 °C is larger than that at 98 °C. There are obvious folds and agglomerations at the catalytic reaction temperature of 98 °C. The main reason may be that the edge functional groups of flake graphene oxide are connected with the surface, and the oxygen-containing functional groups also react, resulting in the increase of folding and agglomeration size of graphene oxide. At 98 °C, this serious phenomenon of folding and agglomeration will directly affect the transparency, uniformity, and flatness of the film, which is not conducive to integrated processing.

The A-D in the figure above corresponds to the height map of the A-D section of the atomic diagram. From the height map of the section, it is shown that the height of a corresponds to 1.4 nm, which is the double-layer graphene oxide. The corresponding heights of B, C, and D are 10.8nm, 7.5nm, and 8.4nm, Fig. B, C, and D are multilayer

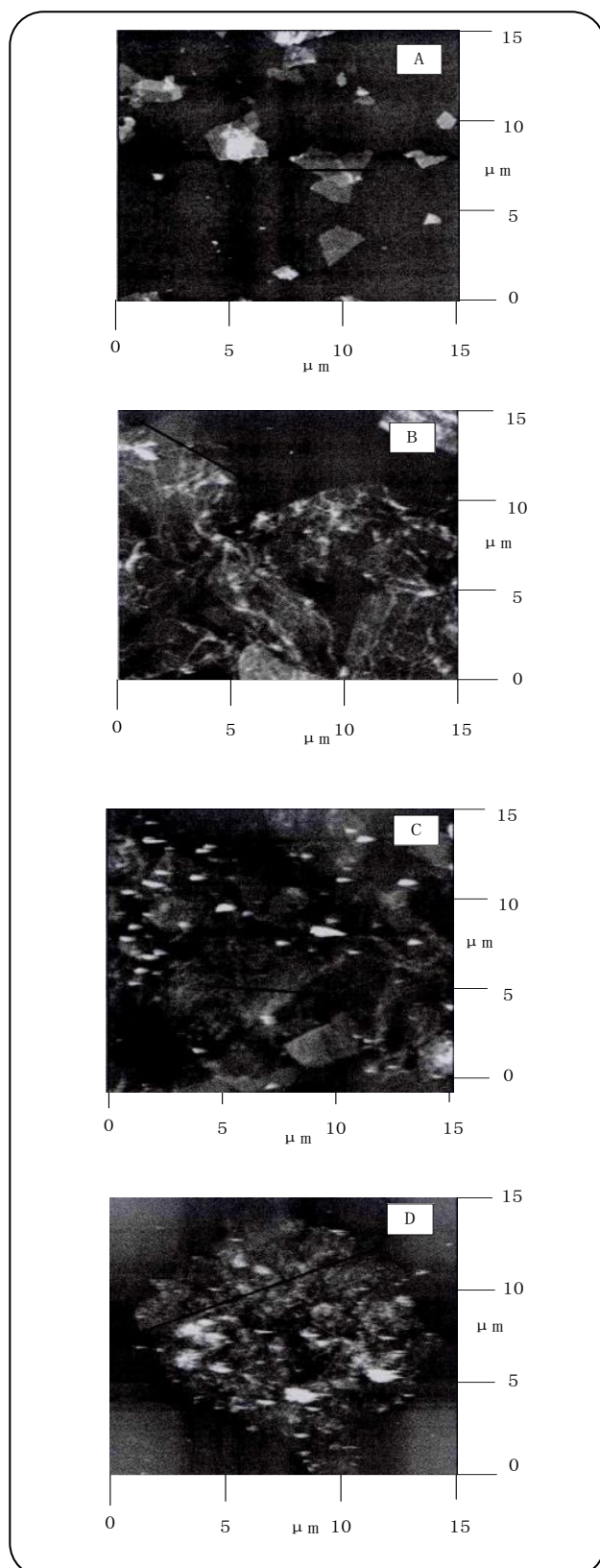


Fig. 5: AFM of graphene oxide films prepared at different temperatures.

graphene oxide and there are different degrees of wrinkles. According to the cross-section data in Fig. D, it can be shown that this phenomenon is more serious for the samples at 98 °C, but the thickness and size of the films prepared at 98 °C are slightly less than 80 °C and 90 °C, which may be due to the relatively high temperature of 98 °C, affecting the connection between the graphene oxide functional groups and intensifying the agglomeration of itself. It is further confirmed that the striation under the polarizing microscope is from the phenomenon of folding and agglomeration of the graphene oxide film.

Infrared spectrum analysis of graphene oxide film

In order to study the effect of FeCl₃ on the change of oxygen-containing functional groups in graphene oxide, the influence of catalytic reaction time on the preparation of graphene oxide at 98 °C is analyzed by infrared spectrum, the crystal sample is selected and the sample size is calculated and extracted according to the semi maximum value of diffraction peak [13,14]:

$$P = m \beta \cdot \alpha \sin \phi \quad (1)$$

In the formula, β is the wavelength of the X-ray (1.54056); α is the half-height width (radian) of the diffraction peak; m is the coefficient (0.89), ϕ is the maximum diffraction peak angle. According to the above formula, the crystal size is 3 μm × 3 μm. The prepared samples should be within the calculated crystal size range.

The infrared spectra of graphene oxide prepared under different reaction times are shown in the figure below:

Under the catalysis of FeCl₃, the IR spectra of graphene oxide with reaction times of 0.5h, 1.0h, 1.5h, 2.0h, and 3.0h are obviously different from those without catalysts. The absorption peaks of 2920 cm⁻¹ and 2850 cm⁻¹ in graphene oxide prepared under different catalytic reaction times are obvious. The absorption peaks near 2920 cm⁻¹ and 2850 cm⁻¹ correspond to the antisymmetric and symmetric stretching vibration of CH₂ respectively. The oxygen-containing functional group may be replaced by hydrogen under FeCl₃ catalysis, and the absorption peaks at 1735 cm⁻¹, 1224 cm⁻¹, and 1064 cm⁻¹ are weakened. The corresponding absorption peak at 1735 cm⁻¹ is from the C=O bond of hydroxyl group and carbonyl group. It is mainly attributed to the C-O-C stretching vibration near the 1224 cm⁻¹ position and the epoxy group (-O-) at the 1064 cm⁻¹ position. It shows that the oxygen-containing

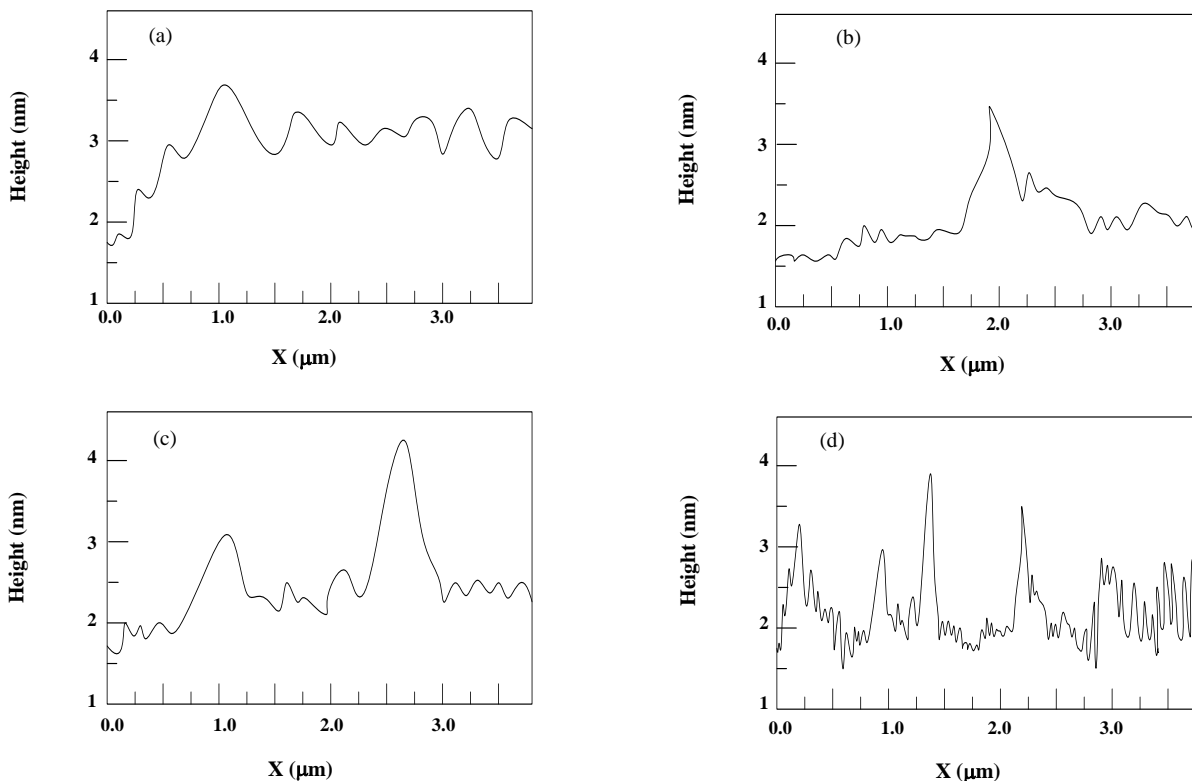


Fig. 6: Cross section at corresponding scanning line of atomic diagram.

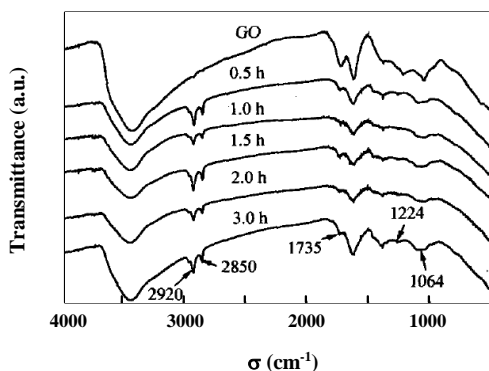


Fig. 7: Infrared spectrum of graphene oxide prepared at different reaction times.

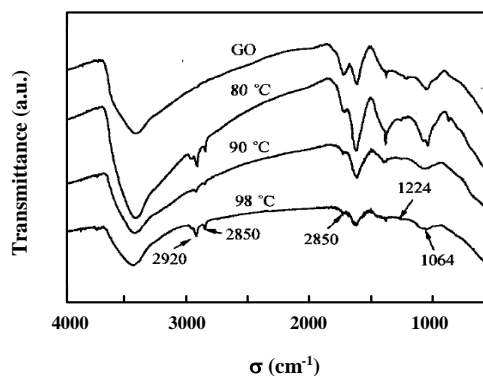


Fig. 8: Infrared spectrum of graphene oxide prepared at different reaction temperatures.

functional groups of graphene oxide decrease under the catalysis of FeCl₃. The infrared spectrum of the reaction time from 0.5h to 3.0h has no obvious change, so the reaction time has little effect on the whole reaction, which indicates that the reaction time of 0.5h at 98 °C may be due to the aggregation of graphene oxide, which results in the functional groups being wrapped up, so the catalytic effect is difficult to increase with the reaction time.

The above figure shows the infrared spectrum of graphene oxide under the catalysis of FeCl₃ at 80 °C, 90 °C and 98 °C for 2h. As a whole, with the increase in temperature, the absorption peak of oxygen-containing functional groups of graphene oxide gradually weakened, and a large-scale domain appears in the crystal, which is 10 μm × 10 μm, indicating that the heating up enhanced the catalysis. When the reaction temperature is 80 °C and 90 °C,

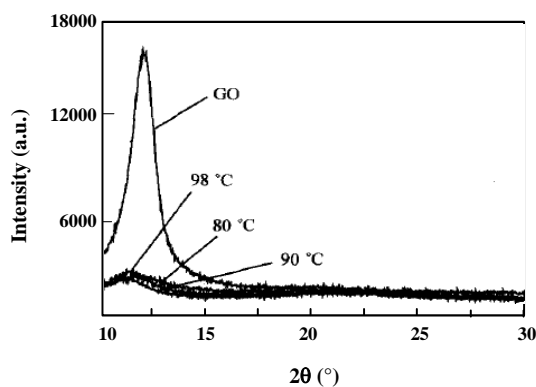


Fig. 9: XRD patterns prepared at different reaction temperatures.

the crystal size is generally larger than 98 °C degrees. At 90 °C, the two peaks at 2920 cm^{-1} and 2850 cm^{-1} are obviously smaller than those at 80 °C and 98 °C, and the crystal size is too large, which may be due to the decrease of oxygen-containing functional groups at the edge of oxyfossil marine at 90 °C, most of which form the transverse connection of lamellae, and only a few are replaced by hydrogen to form CH_2 . The size and thickness of graphene oxide film also confirm that the size of graphene oxide film formed at 90 °C is larger than that at other temperatures. However, at 80 °C and 98 °C, the reduced oxygen-containing functional groups form a CH_2 chemical bond which is not conducive to the lamellar film connection. It can be confirmed that graphene oxide will break chemical bonds under different catalytic temperatures, and the reaction and connection of active chemical bonds are temperature selective. 90 °C is more conducive to the formation of large-area films by the transverse connection between the films.

Analysis of crystal structure

The following figure shows the XRD images of graphene oxide at different reaction temperatures under the catalysis of FeCl_3 catalyst:

Graphene oxide has an obvious diffraction peak at $2\theta=12.3^\circ$. According to the Bragg equation:

$$2d \sin \theta = n\lambda \quad (n = 1, 2, 3 \dots) \quad (2)$$

The diffraction peak is obvious at $2\theta=12.3^\circ$, according to the calculation of Formula (2), the layer spacing d_{GO} of graphite oxide is 0.719 nm, which belongs to (001) diffraction peak, that is, the thickness of the graphene oxide monolayer is about 0.7 nm. It can be concluded that

the flake graphene oxide prepared by improved Hummers is about 1.4 nm, which is a double-layer graphene oxide structure. Compared with the diffraction peak intensity of graphene oxide at $2\theta = 12.3^\circ$, the diffraction peak of graphene oxide prepared by FeCl_3 catalysis at 80 °C, 90 °C, and 98 °C are obviously weakened, which may be due to the FeCl_3 catalytic action breaks some of the chemical bonds of the functional groups in graphene oxide, which leads to the occurrence of hanging, breaking and vacancy of graphene oxide, and reduces the regularity of the crystal structure of graphene oxide, which is basically consistent with the results of infrared spectrum analysis.

It can be concluded that under the catalysis of FeCl_3 , at 80 and 98 degrees of reaction, the oxygen-containing functional groups formed chemical bonds which were not conducive to the lamellar film bonding, the structure of graphene oxide film is the best when the reaction temperature is 90 °C and the reaction time is 0.5h. The film formed at 90 °C is larger in size and smaller in thickness than that at other temperatures, so it is more conducive to the transverse connection between thin films to form large-area films. So far, the catalysis of ferric chloride in the preparation of graphene oxide film has been analyzed.

Experimental comparison

In order to verify the accuracy of the catalytic action analysis method designed in this research, a comparative experiment was designed to prepare graphene oxide films by the catalytic method and the traditional preparation method. The thermal conductivity of the finished graphene oxide films was compared to verify the superiority of the method.

Experimental design

The graphene oxide film is prepared under the best experimental conditions obtained by the original catalytic action analysis method. The graphene oxide film obtained under the two reaction conditions is chemically reduced, and the mild chemical method is used to reduce the film. At 800°C, the vapor volatilized from the hydrogen iodide acid is used to reduce the film. After 24 hours, the film can be fully reduced. The obtained film is calendared by a calendar, so that the film has good flexibility, ductility, and orientation. The experimental process is as follows:

Netsch laser thermal conductivity instrument is used to study the thermal conductivity of the thin film.

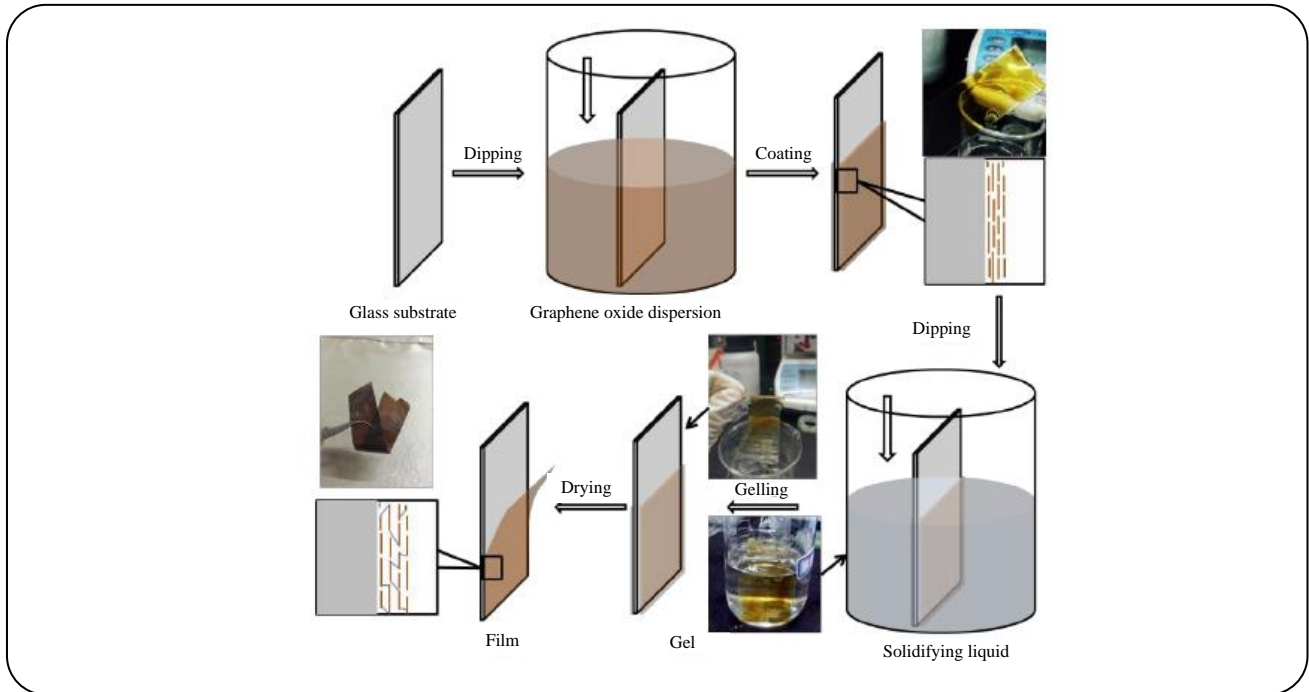


Fig. 10: Flow chart of the experiment.

The principle is the laser flash method. The sample size required by the laser flash method is small and the measurement range is wide. It can be used to measure most materials except for thermal insulation materials, especially for materials with medium and high thermal conductivity.

Experimental results and analysis

The thermal diffusion curve of the sample measured by laser flash method is shown in the following figure:

After the flash of the laser, the sample heats up rapidly. The first is the heating-up process. According to the above figure, we can see that the heating up time of the high thermal conductivity graphene film is significantly shorter than that of the reduced graphene oxide film, while the second half of the curve is the cooling process, and the heat dissipation time of the high thermal conductivity graphene film is also significantly shorter than that of the reduced graphene oxide film. According to the formula of heat transfer coefficient:

$$\lambda = - \frac{\varphi dx}{A dt} \tag{3}$$

Where, φ is the heat flow, λ is the heat transfer coefficient, A is the heat transfer area, dt is the temperature

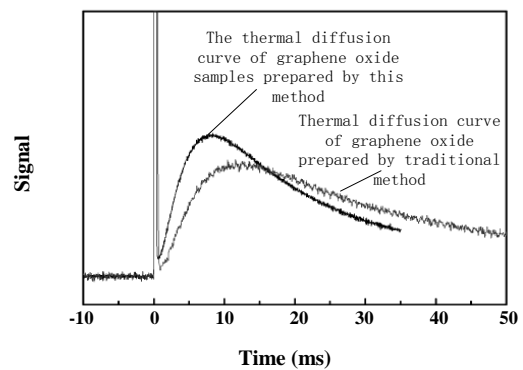


Fig. 11: Signal spectrum of two graphene film samples tested by heat conduction instrument.

difference between the two sides of the microelement thickness, dx is the microelement thickness. According to the above algorithm, the thermal conductivity formula is as follows:

$$\varphi = -A \lambda \frac{dt}{dx} \tag{4}$$

All of the above conditions are known, and the thermal conductivity of two kinds of graphene films can be calculated after being brought in. In this paper, the thermal conductivity of graphene films prepared under catalytic conditions is 1500 W/(m.K), and that of graphene films

prepared under traditional conditions is 600 W/(m.K). It is found that the graphene oxide film prepared under catalytic conditions has excellent thermal conductivity.

CONCLUSIONS

In this research, graphene oxide thin films are prepared under the catalysis of ferric chloride. The process is simple, the cost is low, the conditions are mild, and the energy consumption is small. Therefore, this kind of material is bound to shine brilliantly in the application of heat conduction. At present, the disadvantage is that graphene oxide cannot be mass-produced. With the efforts of researchers, if the mass production of graphene oxide becomes a reality, then our technology of preparing heat conduction film will also have a place in the field of heat dissipation.

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