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Research Article

Structural Defects of Graphene Oxidation Reduction and Its High-Efficiency Structural Reforming Technology

Junwei An,[1] Chen Wen,[2] Chuping Chen,[3] and Xiaolin Qiu[1]

[1]*Nanchang Institute of Technology, Nan Chang, China 330013*
[2]*Beijing Spacecrafts, China Academy of Space Technology, Beijing, China*
[3]*School of Material Science and Engineering, Beijing Institute of Petrochemical Technology, Beijing, China*

Correspondence should be addressed to Chen Wen; 13552907280@163.com

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The Hummers' method is used to prepare graphene oxide and graphene powder, and the obtained powder material contains a large amount of oxygen-containing groups. Due to the effect of strong oxidants, there are many defects on the graphene body. Although a large number of oxygen-containing groups are reduced by the reduction reaction, the defects of the graphene body are numerous, which has a great influence on the conductivity of graphene and also limits the high carrier transport capability and application of graphene itself. Using industrial means, the graphene powder is highly reduced, and the ultrathin graphene powder is obtained, the graphene powder has extremely low impurity content, and the defects are substantially completely reduced. Then, these lay the foundation for its application in the battery industry.

1. Introduction

Graphene is a two-dimensional crystal composed of closely packed carbon atoms. It was taught by Prof. A. Geim and Novoselov of the University of Manchester in the UK. A single layer of graphene was obtained by stripping off the graphite [1]. At the same time, graphene has also become a research hotspot in the field of materials and physics. With the "Graphene+" strategic platform, it can provide strong support for the performance improvement and application expansion of a large number of traditional materials, and at the same time, a series of new generation functional components with excellent performance will be derived [2], and the application in many traditional fields and emerging fields will cause revolution in related industries and become a strategic emerging industry leading a new generation of industrial technology. Graphene is the most disruptive new material in the 21st century. At present, the graphene industry is in a critical period of evolution from technology to business, and large-scale application is coming soon.

Graphene is a honeycomb two-dimensional crystal composed of a single layer of hexagonal cellular carbon atoms. Due to the special structure of graphene, it also exhibits specific property that many other materials do not have. In excellent electrical conductivity [3], carrier electrons and holes in graphene are continuous, and the mobility can reach $1 \times 10^5\ cm^2 \cdot Vs^{-1}$. In ultrahigh transmittance [4], the transmittance of single-layer graphene reaches 97.7%. In ultrahigh strength, graphene was found to be the material with the highest modulus of elasticity and strength after carbon nanotubes. Its strength is 100 times stronger than the best steel in the world. The hardness is higher than the hardest diamond in nature, and it has excellent flexibility and can be bent at will. In ultrahigh thermal conductivity, because of its low-dimensional physics and unique honeycomb structure [5, 6], graphene also has a very high thermal conductivity. The free-state single-layer graphene has a thermal conductivity of $5000\ W \cdot mK^{-1}$ at room temperature. Graphene is the currently known material with the highest thermal conductivity. In ultralarge specific surface area, since the thickness of graphene is only one carbon atom thick, single-layer graphene has an ultralarge specific surface area, which can reach $2630\ m^2 \cdot g^{-1}$ [7], which is much larger than the specific surface area of ordinary activated carbon. If

you look at these properties alone, graphene is simply perfect. But the only imperfection is that there are more defects on the graphene body, and properties of graphene can be significantly changed by defects [6].

At present, the preparations of graphene are mainly based on graphite. The main preparation methods include mechanical exfoliation method [8], liquid phase stripping [9], oxidation-reduction method [10], and chemical vapor deposition [11], and oxidation reduction is one of the most widely used methods. The main idea of oxidation reduction is to treat graphite with strong oxidant, such as sulfuric acid and potassium permanganate, adding a large amount of oxidizing groups between the graphite layer and the layer, so that the spacing between the layers is increased to form graphite oxide. Then, by reducing means, such as hydrazine hydrate [12], sodium borohydride [13], and other reducing agents or heat treatment under protective or reducing atmosphere, the surface groups are removed, making it a single layer of graphite, which is graphene. Commonly used preparation methods for graphene oxide are the Brodie method [14], the Staudenmaier method [15], and the Hummers' method [16]. The Hummers' method, named after the inventor Hummer, was reported as early as the middle of the last century and has been used by people until now. However, the biggest problem with this method is that chemical means cannot completely separate the single layer of graphite. It is not possible to remove the surface groups 100% and leave more lattice defects, thereby affecting the electrical and thermal properties of graphene. Therefore, graphene made by this method is difficult to apply to devices. In this paper, the graphene powder material was prepared by the modified Hummers' oxidation method, and then, the ultrathin graphene powder was obtained by industrial reduction method. The impurity content was extremely low, and the defects were almost completely reduced, and the conductivity was improved, which lay the foundation for its application in the battery industry.

2. Experimental Part

2.1. Preparation of Experimental Materials. Hummers' redox method graphene powder manufacturing method is a modification of the Hummers' method. The typical method is the first stage: 5.5 kg of 1000 mesh high-purity flake graphite (99.95%) is put into the reaction kettle, and then, 3 kg industrial sodium nitrate is added in 210 L of concentrated sulfuric acid, keep stirring at equal speed, use the coolant to the reaction kettle, and lower the temperature to below 10°C; continue to maintain the stirring, then add 2.42 kg of potassium permanganate in batches; when the temperature reaches below 10°C, start to add potassium permanganate to the reactor in batches, and put it into the reactor every 5 minutes, each time to put 96.68 g, 25 times in total; keep the temperature not exceeding 15°C, keep the temperature below 10°C, and keep the temperature constant for 2 hours. First, the temperature of the reaction kettle is raised to 35°C and then constant temperature for 0.5 hours; after the end of the constant temperature, add water in three stages: add 89.6 L water in one hour; add 89.6 L water in half an hour; add 179.2 L water in half an hour; first, raise the temperature to 93°C, then keep the temperature constant for 2 hours; raised to 98°C and then constant temperature treatment for 2 hours; discharged the slurry in the reactor, naturally cooled for 0.5 hours; discharged the slurry in the reactor, naturally cooled for 0.5 hours; added concentrated hydrochloric acid 136.25 L and then reacted for 1 hour. Tap water is 1692 L, settling for 12 hours. The second stage is drain the supernatant of the liquid after standing, add 4241.67 L of water, stir evenly, put the 320 mesh filter cloth into the centrifuge, rinse with a proper amount of water, and then add the feed liquid several times. Until there is no filtration droplets, take the liquid, put the 380 mesh filter cloth into the centrifuge, rinse with a proper amount of water, and then add the liquid several times until no liquid droplets are removed, and the liquid is taken; the filtrate is poured along in a three-reactor, electric heating, reflux with a condenser until the liquid boils for 150-300 min; place the 2000 mesh filter cloth in the centrifuge, rinse with a proper amount of water, and then add the liquid several times until there is no filtrate. Drip out, take the filter cake, scrape the filter cake on the filter cloth, add 121 L hydrochloric acid in the container, stir evenly, pour into the three-reactor, heat it, condense and reflux, monitor the liquid temperature until the temperature of the liquid after reaching 85°C, and continuing the reaction for 2 h; add the purified slurry to 2401.67 L of water, stir evenly, then put the 2000 mesh filter cloth into the centrifuge, rinse with a proper amount of water, and then add the feed solution several times. Until there is no filter drop out, cake. For the third stage, first take the filter cake into the tray, then put the tray into the oven, set the temperature of the oven to 80°C, and dry for 12 h; pulverize the dried material with a pulverizer and put it into a closed device. The fourth stage is weigh the crushed graphite oxide to 100 g per bag; cut the graphite paper according to the crucible structure and lay it into the crucible, cover it, and transfer the graphite paper paved crucible to the workshop carbonization Kiln production line; use the robot hand, take off the lid of the crucible, and spread the graphite oxide of the good bag evenly to the middle of the crucible; cover the lid and restore it to the kiln for 24 hours; after the carbonization treatment, take off the crucible the lid; the product was collected, and the graphene oxide powder was obtained by the Hummers' method, followed by test preparation.

The preparation process of graphitized graphene is as follows: The Hummers' method graphene powder prepared above is placed in a special graphite crucible; each crucible is filled with 800 g of graphene powder and then placed in a graphitization furnace. The reaction temperature curve is increased from 20°C to 2000°C at a rate of 15°C/hour, then from 2000°C to 2800°C at a rate of 10°C/hour, held for 48 h, and then increased from 2800°C at 5°C/hour to 3200°C, hold for 48 h, then reduce the temperature to 50°C at 10°C; open the crucible, take out the material powder, get graphene powder, and test.

2.2. Test Procedure. The surface structure of graphene and graphitized graphene was characterized by HITACHI S4800

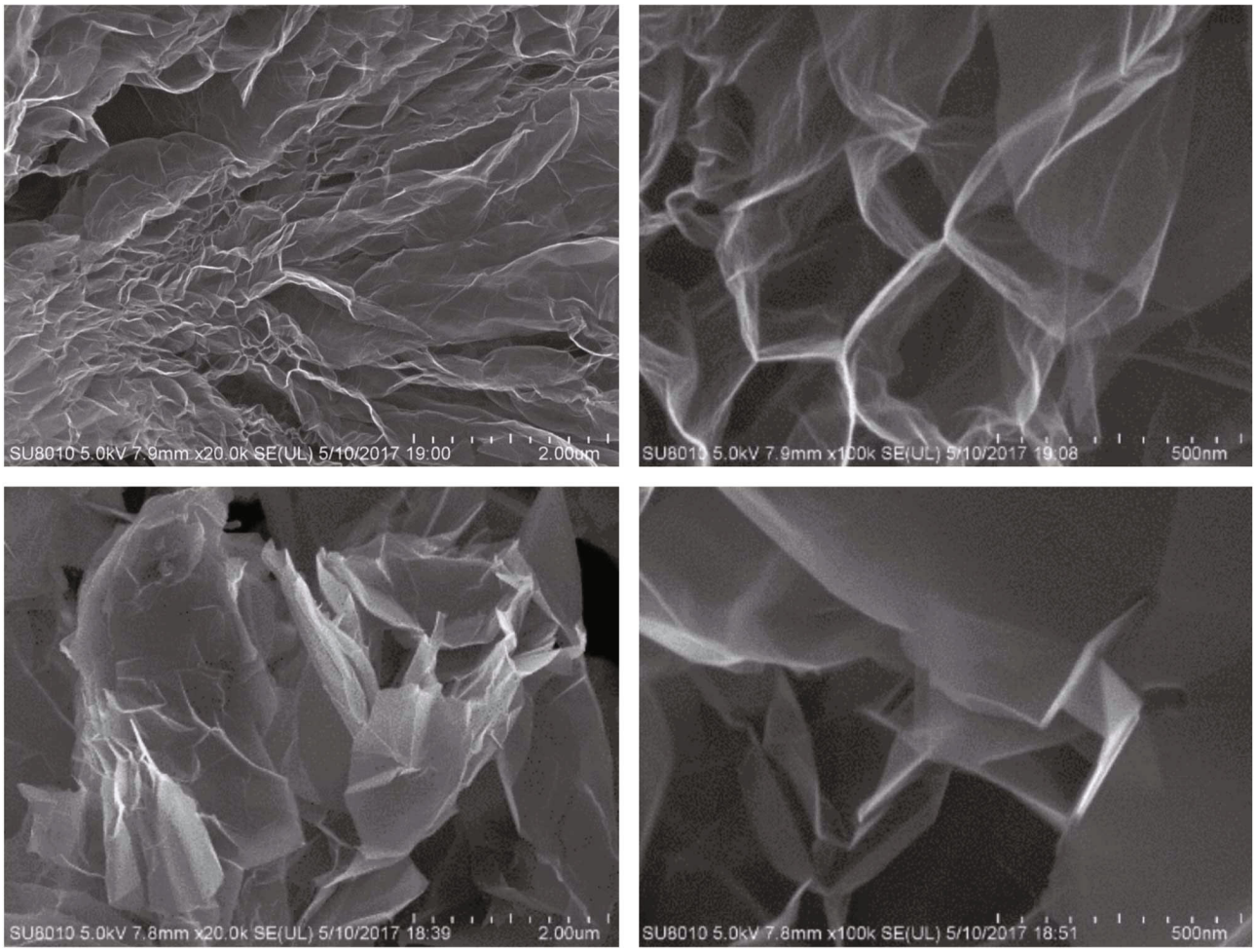
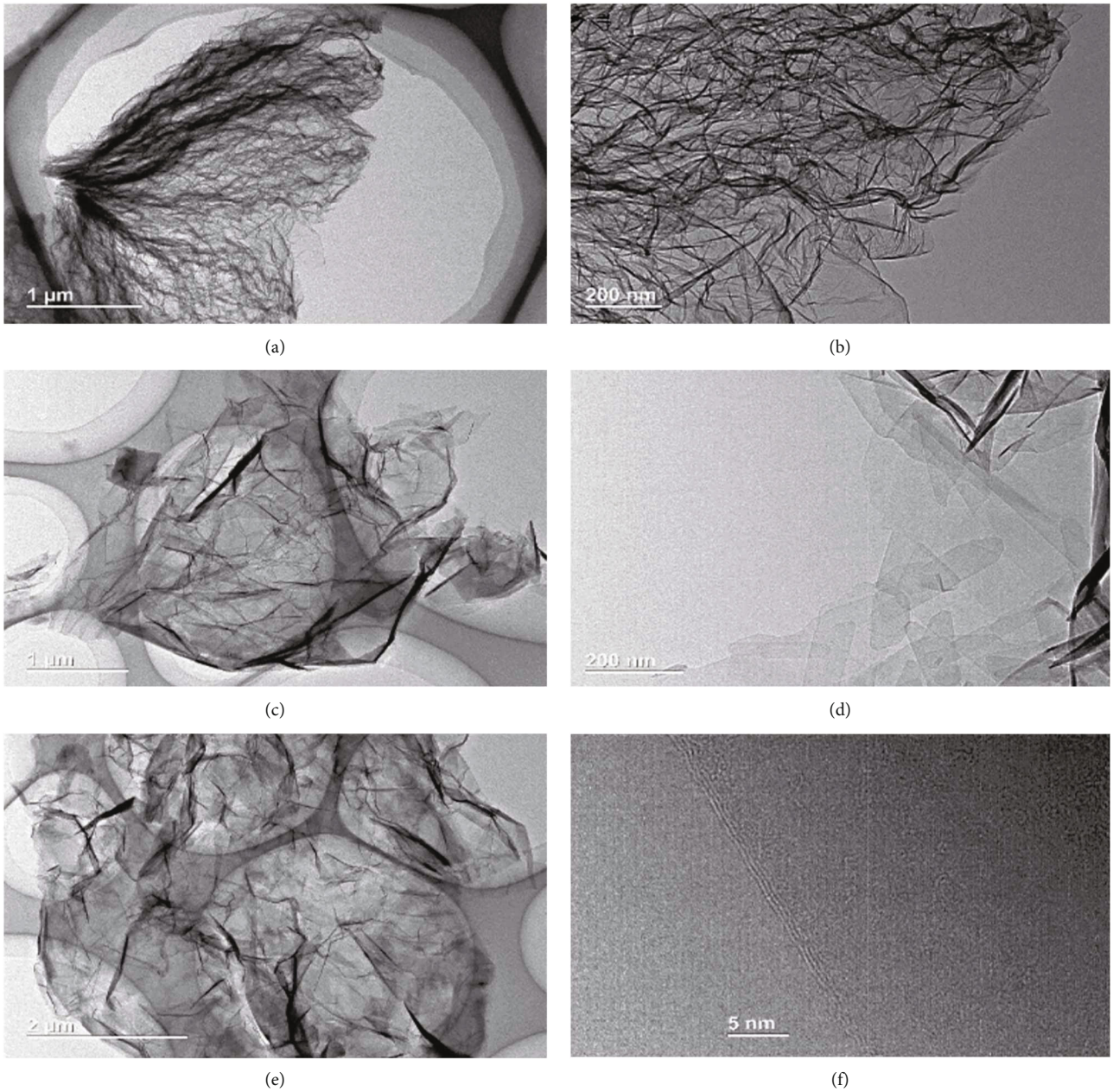


Figure 1: SEM surface topography of graphene and graphitized graphene.

field emission scanning electron microscope according to JY/T010-1996 analytical scanning electron microscopy method; using FEI Tecnai G2F30 transmission electron microscope, the structure and high resolution morphology of graphene and graphitized graphene were characterized by the JY/T011-1966 transmission electron microscopy method. Graphene and graphitized graphite were prepared according to the conventional treatment method using HORIBA LabRAM HR800 Raman spectrometer. The Raman spectrum structure of the olefin was characterized; the specific surface area of graphene and graphitized graphene was determined by using the Micromeritics ASAP2020 surface porosity and chemisorber according to the GB/T19587-2004 gas adsorption BET method for determining the specific surface area of solid materials. The RIGAKU D/max2500 X-ray diffractometer was used to test the layer spacing unit cell parameters of graphene oxide, graphene, and graphitized graphene; using Thermo Nicolet iS50 FTIR infrared spectrometer, according to GB/T 6040-2002 Infrared Spectroscopy General Rules for Graphene and Graphitized Graphene Infrared, band organic functional groups were analyzed; using Perkin Elmer Optima 7300 DV inductively coupled plasma spectrometer, according to GB/T 23942-2009 chemical reagent inductively coupled plasma atomic emission spectrometry for graphene, graphitized graphene metal and nonmetal elemental content was analyzed. The MCP-PD51 powder conductivity test systems were used to test the conductivity of graphene and other conductive materials.

The main equipments used for graphene and graphitized graphene are as follows: 5 1000 liter reactors, Zhejiang Wenzhou Zhao Flulon Co., Ltd., lined with PTFE; 1 chiller, Nanjing Hengbiao Srei Refrigeration Machinery Manufacturing Co., Ltd.; 20 sets of transfer pumps, Zhejiang Ligao Pump Industry Technology Co., Ltd.; 6 centrifuges, model SS600, Jiangsu Zhangjiagang Weilong Machinery Equipment Manufacturing Co., Ltd.; 4 plate rolling roller kiln, China Electronics Technology Group Co., Ltd. Forty-eighth Research Institute; Acheson Graphitization Furnace 1, Homemade; High Purity Water Water Machine, Qingdao Haiyue Company; and oven, CT-C-1, Nanjing Zhuoxin Drying Equipment Co., Ltd.

Drugs used in the experimental preparation are as follows: flake graphite, 1000 mesh, carbon content 99.96%, Inner Mongolia Ruisheng New Energy Co., Ltd.; concentrated sulfuric acid, 98%, industrial grade; potassium



(a) (b) (c) (d) (e) (f)

Figure 2: TEM morphology and HRTEM structure of graphene and graphitized graphene.

permanganate, Tianjin company; sodium nitrate, industrial grade, a company in Tianjin; concentrated hydrochloric acid, 35%, Tianjin Membrane Company; hydrogen peroxide, 30%, a company in Tianjin; and high purity water, 17 megohms.

3. Results and Discussion

The surface morphology of graphene and graphitized graphene was characterized and compared by field emission electron scanning microscopy. It is found from Figure 1 that the surface of graphene manufactured by the modified Hummers' method exhibits a remarkable wrinkle morphology, which may be related to its chemical oxidation and reduction during chemical separation and stripping, and the porous structure indicates that it is significantly high. The specific surface area is similar to the surface structure of the graphene powder prepared by the typical chemical method reported in the literature. The surface morphology of the graphene powder after graphitization is observed, and the structure is found to exhibit less obvious folds. At the same time, its high-magnification photographs show that its structure is thicker than the graphene produced by the redox chemistry of the Hummers' method, suggesting that it may undergo significant agglomeration and back-up and also indicates that it has a small specific surface area.

The structure of graphene powder and graphitized graphene powder produced by Hummers' redox chemical method was characterized by high-rate field emission

transmission electron microscopy, as shown in Figure 2. Observations show that Figures 2(a) and 2(b) show a typical pleat structure feature, corresponding to the surface topography in Figures 1(a) and 1(b), showing a thinner sheet structure, indicating that the peeling is more thorough; the layer is thinner, indicating a larger specific surface area. Figures 2(c) and 2(d) are structural diagrams of graphitized graphene. It is found by Dolby that the structure of graphene which has been graphitized by high temperature has no obvious wrinkles, and the higher magnification of the transmission electron micrograph is shown in Figure 2(d), showing that it is relatively transparent. The characteristics of the graphite sheet layer indicate that the thickness may be thicker than the thickness of the graphene method for the Hummers' method redox chemistry. By high magnification of the portion of Figure 2(e), as shown in Figure 2(f), it can be found that the thickness of the thinnest portion is about 1.5 nm, indicating that the overlap between the graphene sheets occurs, and the thickness may be between 3and 5 layers.

Figure 3 is the XRD spectrum of the graphene precursor graphene oxide powder, graphene, and high temperature graphitized graphene powder in the Hummers' process redox chemistry. The Hummers' method redox chemical method graphite can be seen from the figure. The precursor graphene oxide powder of the olefin powder has a 2θ angle of 11°, a layer spacing of 0.804 nm, and a graphite layer spacing of 0.35 nm. Bragg equation is as follows: $2d \sin \theta = n\lambda$, where d is the crystal plane distance (that is, the layer spacing you want), θ is the readout on the graph (note that 2θ is on the graph), λ is the X-ray wavelength, and $n = 1$ (first order diffraction) Cu target Ka ray ($\lambda = 0.15406$ nm).

The 2θ angle of graphene and graphitized graphene in the Hummers' method is 26.5°, and the layer spacing is 0.336 nm, indicating that the interlayer spacing has been consistent with the graphite layer spacing, indicating that it is not a single layer of graphene.

Figure 4 is a Raman spectrum of the Hummers' method redox method graphene powder and graphitized graphene. Figure 4(a) shows the Raman spectrum of the redox method graphene showing a distinct D peak and a weak 2D peak with a small G/D peak, showing the redox method of graphene powder, the structure being strongly oxidized. Destruction, this structural damage may affect the π-π conjugated structure of the redox graphene of the Hummers' method, which affects the transport of free electrons therein and has a decisive influence on its conductivity. The Raman spectrum of graphene produced by high-temperature graphitization is shown in Figure 4(b). In the structure, the D peak disappears almost completely, the G peak is sharp, and the 2D peak is more obvious and significant, indicating that the π-π conjugate structure has been fixed. This will better embody the intrinsic properties of the prepared graphene, so that it can be applied to fields requiring high conductivity properties such as lithium ion battery conductive agents and conductive inks.

The electrical conductivity comparison in Table 1 shows that the electrical conductivity of the graphitized graphene sheet powder is not improved but is slightly lower than that of the original nongraphitized graphene. This seems unreasonable, but from its tap density, it can be found that the tap density of graphene after graphitization is only 0.0505, and the tap density of graphene without graphitization is 0.0768. This low tap density may be due to its larger specific surface area and repulsion of electrostatic charges, which makes its density lower under the same pressure, and the contact between the lamellae is not close, which affects its powder conductivity lower than the conductivity of ordinary graphene powder that has not been graphitized. In addition, it can be seen from the element content in Table 2 that it

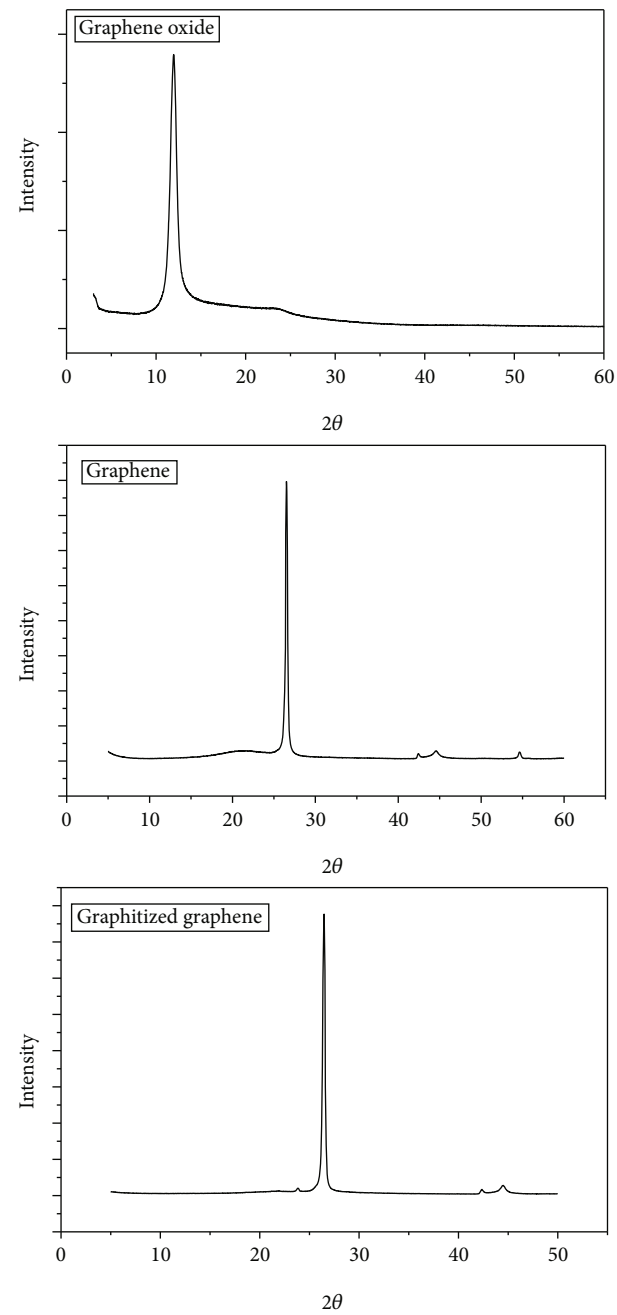


Figure 3: XRD structure of graphene oxide, graphene, and graphitized graphene.

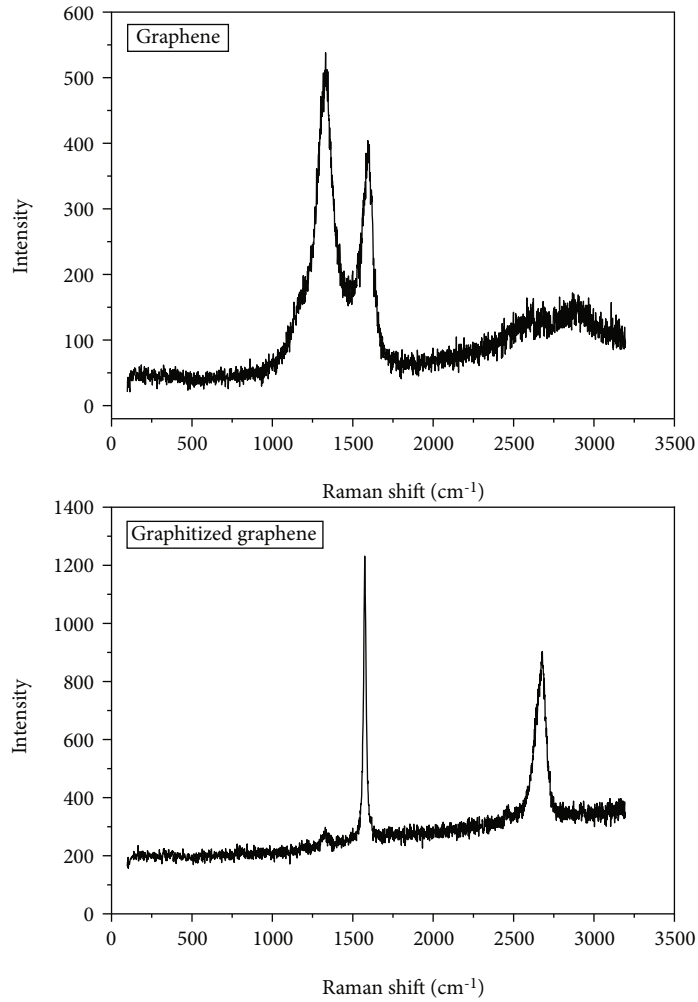


Figure 4: Raman spectrum of graphene and graphitized graphene.

Table 1: Comparison of conductivity between graphene and other conductive agents.

Sample	Conductivity (S/cm)	Conductivity (g/cm^3)
Graphitized graphene	587.3	0.0505
Graphitized graphene-purification	427.3	0.0539
Graphene	858.7	0.0768
BTR-1	400	
GC-325	773.6	0.6335
CNT	95	
KA	1210	0.4121
SP-1	20.07	0.4454
SP-2	35	0.4454

may also be due to the large amount of metal ions contained in ordinary graphene, which causes the overall conductivity of ordinary graphene powder to show greater conductivity, but its electrical conductivity may contribute more to the influence of a large amount of metal or metal oxide impurities.

Table 2: Element content in graphene powder.

Sample	Content	
	Graphene	Graphitized graphene
Fe	452.8	42.22
Mn	17730	1.19
Cu	7210	0.24
Ni	8448	1.9
Cr	103.3	3.79
Co	0.875	0.24
Mo	0	0.24
Zn		8.3
S		184.04
Cl		8

4. Conclusion

The structure and morphology of Hummers' graphene were studied by SEM, TEM, XRD, Raman, and FTIR methods. At the same time, the graphene after industrialization was compared, and the treated graphene was found to have reduced defects. Big tests on its conductivity and impurity content

show that it has high purity and impurity content, which has great prospects for its application in the battery field.

Data Availability

All data in this paper are true and valid and has not been published in other journals.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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