ABSTRACT: In view of the current high cost of graphene, the corn flour with rich sources was selected as the raw material to prepare nano-graphene by the hydrazine hydrate (Hummers) redox method. The elements, structure, and morphology of the obtained corn graphene (CG) were studied by the organic element analysis, X-ray photoelectron spectroscopy, X-ray diffraction, Raman spectroscopy, atomic force microscopy, and transmission electron microscopy. It was found that the carbon content of CG was increased by 37.8% from 57.4% (corn flour) to 95.2% (CG). There was a diffraction peak of graphene on the (002) crystal surface at 23.08°. The D and G peaks of the Raman test were present, and the $I_D/I_G$ of the peak intensity ratio was 1.19. The lattice distance of the CG sample was larger than that of the commercial graphene (GE), the CG was about three layers with a layer spacing of 1.21 nm, and the CG was thinner than the GE, which proved that the obtained CG was the nano-graphene.

INTRODUCTION

Graphene is composed of carbon atoms in a multiple hexagonal lamellar structure.1 Geim and Novoselov, physicists at the University of Manchester in the United Kingdom, had successfully separated graphene from graphite in their experiments in 2004.2,3 From then on, a lot of research has been carried out for more than a decade. Graphene has excellent thermal properties and other aspects of performance, and it has important application prospects in various fields such as energy, nanomanufacturing, biomedicine, micromaterials science, drug delivery, and so forth and is considered as a revolutionary material for the future.4,5 At present, the methods for preparing graphene mainly include chemical vapor deposition (CVD) and redox.

CVD is a process that takes gaseous alkane substances as carbon sources to deposit solid substances on the surface of metal or nonmetal solid substrates under high temperatures and produces solid products after removing the substrate.6 High-quality graphene can be produced by CVD in large quantities, which is an efficient method for the preparation of graphene.7 However, the reaction conditions of this method such as the carbon source, reaction temperature, matrix materials, and ventilation rate are harsh, and the process is expensive. Moreover, in the redox method,8 the graphite is treated by a strong oxidizer and strong acid, the oxygen-containing groups are introduced into the graphene sheets to bond with the $\pi$ electron cloud, the $\pi$ electron cloud of the graphite is damaged, the spacing between the layers is increased, and the hydrophilic graphite oxide is formed. Then, graphene oxide is exfoliated by ultrasonic treatment and it is treated by the Hummers method to obtain graphene. According to different oxidants, it can be divided into three methods to prepare graphene oxide, including the Staudenmaier method, Brodie method, and Hummers method.9,10 The easy-to-use Hummers method is now widely used by researchers. The graphene prepared by the redox method cannot fully restore the unique characteristics of graphene, but its experimental operation is simple, its yield is high, and it can be mass-produced, which is widely favored by research scholars; so, they use the redox method to prepare corn graphene (CG) in this work.

As described above, it is found that the traditional material for graphene preparation is usually the graphite powder,9 and it makes the graphene too expensive to be mass-produced in the industry.9 At present, the best method for graphene preparation is the preparation of biomass graphene with high carbon content, low price, and high reserves to prepare graphene instead of graphite in the world.10,11 After several...
hundred years of development, corn is now widely planted around the world and has the advantages of short regeneration cycle, green environmental protection, and no pollution. However, there are fewer impurities in the corn, which makes the raw material processing more convenient. In addition, the corn contains a lot of cellulose, which is an important prerequisite for the formation of graphene structures from biomass materials. Therefore, corn flour is used as a raw material to prepare CG in this work.

**RESULTS AND DISCUSSION**

**CG Component.** First, the carbon content of corn flour was studied in this work, as shown in Table 1. The carbon content in the corn flour was 57.6%, suggesting it to be very high, and so, it was selected as the raw material for preparing graphene. However, there were other organic elements in the corn flour, which needed to be purified. It could be seen that the carbon content of cornmeal graphite (Cg) was significantly increased to 82.9% by high-temperature carbonization and catalysis. Also, the carbon content of CG was increased to 95.1% by the Hummers-hydrazine hydrate method and the carbon content of CG was high. It indicated that the corn flour as a graphene material was preliminarily demonstrated to be feasible.

In addition, there are the C 1s peak and O 1s peak in the three spectra, as shown in Figure 1; it indicated that the corn flour, Cg, and CG samples contained C and O elements. There were the C 1s, O 1s, N 1s, P 2p, K 2p, Cl 2p, Ca 2p, and Si 2p peaks in the full spectrum of the corn flour, and it suggested that these elements were present in the corn flour. As the peak area represents the element content corresponding to the element, it could be seen from the corn flour curve that the peak area proportion of C 1s was 57.4% and that of O 1s was 22.21%, while other elements N 1s, P 2p, K 2p, Cl 2p, Ca 2p, and Si 2p were all from the corn flour. There were the C 1s, O 1s, and Si 2p peaks in the full spectrum of Cg, and the peak area of C 1s accounted for 82.43% and that of O 1s accounted for 15.55%; Si 2p was the residue of the corn flour after carbonization. It could be interpreted that the Cg obtained from the corn flour, after high-temperature carbonization, dialysis, and catalytic graphitization, had high ability to remove impurities and increase the content of graphite. There were the C 1s and O 1s peaks in the full spectrum of CG, C 1s was 95.2%, and O 1s was 4.3%, and the oxygen content decreased significantly. It can be explained that the most of the oxygen atoms could be removed by the Hummers-hydrazine hydrate reduction method. Due to certain limitations of hydrazine hydrate reduction method at present, it cannot be completely reduced to graphene structure, so a small amount of oxygen would be remained between the CG sheets. Compared with the analysis of organic elements, the data of the two groups were not much different; the carbon content was increased by 37.8% from 57.4% (corn flour) to 95.2% (CG).

**CG Microstructure.** In order to study the internal structure of Cg and CG, the X-ray diffraction (XRD) tests were carried out on the two carbon materials, as shown in Figure 2. The Cg curve showed a very strong diffraction peak at 2θ = 26.5°. This diffraction peak corresponded to the characteristic one of the graphite (002) crystal plane, and it indicated that the graphite prepared from corn flour possessed good crystallinity and relatively neat laminates. However, the (002) diffraction peak of CG prepared by the Hummers-hydrazine hydrate method shifted left to 23.08°, and the diffraction peak became wider and weaker. It could be attributed to the bonding action between carbon and oxygen atoms under the action of a strong oxidant, so that oxygen-containing groups were introduced into the graphite sheets and the crystal structure of graphite was destroyed. It suggested that the ability to reduce CG order degree was limited by the hydrazine hydrate method, and there are still some unreduced oxygen-containing groups in the carbon layer, which reduced the degree of crystallinity and increased the degree of structural disorder. The diffraction

---

**Table 1. Carbon Content of the Materials**

| sample      | weight (g) | content (%) |
|-------------|------------|-------------|
| corn flour  | 0.535      | 57.6        |
| Cg          | 0.406      | 82.9        |
| CG          | 0.362      | 95.1        |

---

**Figure 1.** XPS spectra of the corn flour, Cg, and CG.

**Figure 2.** XRD spectra of Cg and CG.
peak became wider and smaller, resulting in the smaller lattice size of CG and the larger spacing of crystal planes. Therefore, the diffraction peak of CG crystal planes (002) shifted left and the peak shape changed.

Raman spectroscopy is the most effective method for the characterization of carbon materials, which can analyze the degree of structural defects.\(^{18,19}\) In general, the Raman spectrum of graphite shows a D peak near 1351 cm\(^{-1}\) and a G peak near 1582 cm\(^{-1}\). The D peak can be regarded as a sp\(^3\) hybrid structure or sp\(^2\) bond hybrid defects of carbon atoms. In general, the D peak does not occur in graphite crystals with a complete structure. The G peak is generated by the stretching movement of the sp\(^2\) carbon atom, which represents the crystalline structure of the material. \(I_D/I_G\) is the intensity ratio of the D peak to G peak, which represents the disorder degree of carbon materials. There was a peak D near 1353 cm\(^{-1}\) in the Cg curve, as shown in Figure 3; it indicated that the structure of the obtained Cg had some defects. The G peak appeared near 1585 cm\(^{-1}\), and it can be seen that the sharp width of the G peak in the Cg was relatively narrow, suggesting that the crystallinity of Cg was high, which was consistent with the XRD spectrum results. The \(I_D/I_G\) of the Cg was 0.42, and it indicated that a few defects existed, the disorder degree was low, and the crystal structure was relatively complete. However, the positions of the D peak and the G peak in the CG curve moved to the higher wavenumber. The D peak appeared at 1368 cm\(^{-1}\), the G peak appeared at 1600 cm\(^{-1}\), and its peak shape and peak width changed obviously; the D peak became stronger and wider, the G peak became wider, and the \(I_D/I_G\) of CG was 1.19. It was considered that the crystal structure was destroyed, and the degree of disorder increased after oxidation and reduction of Cg, and parts of the sp\(^3\) hybridized carbon atoms were converted into the sp\(^3\) form, which enhanced the D peak and increased the defect degree. It also explained that the reduced oxide CG cannot be completely transformed into a complete graphene structure. According to the peak position and shape of the CG, the CG prepared from corn flour had a similar structure to reduction–oxidation graphene.\(^{20}\) Therefore, it can be considered that graphene prepared from corn flour was feasible, and the CG can be proved to be graphene.

**Morphological Structure of CG.** The CG and commercial graphene (GE) samples were compared by atomic force microscopy (AFM), as shown in Figure 4; the surface of the CG sample was a round and thin sheet, and its shape was relatively regular. The CG on the right has a thickness (layer spacing) of about 1.21 nm and diameter of 280 nm. It was a three-layer sheet, indicating that the CG prepared by the redox method was thin. The GE showed a more regular disc shape, and its thickness was about 0.49 nm; it could be seen that the layer spacing of the CG was greater than that of the GE. It indicated that the lattice spacing of the CG sample was larger than that of the GE sample.

At the same time, the transmission electron microscopy (TEM) analysis was also performed on the two samples. Both

![Figure 3. Raman pattern of the Cg and CG.](image)

![Figure 4. AFM images and thickness curves of CG and GE.](image)
CG and GE exhibited a relatively thin sheet structure, as shown in Figure 5. Compared with the GE, the CG showed a wrinkled sheet and a curled lamellar structure; it suggested that the sheet of CG was thinner than that of the GE, which further proved that the CG prepared from the corn flour possessed the graphene sheet structure and the interlayer distance was of nanometer size.

## CONCLUSIONS

In this work, the CG was prepared from corn flour by the Hummers redox method. The carbon content of CG was 95.2%, and oxygen content was 4.3%. The carbon content was increased by 37.8% from 57.4% (corn flour) to 95.2% (CG). The CG has a graphene diffraction peak on the crystal plane (002) at 23.08°. The D peak and G peak were presented by the Raman test, and the intensity ratio \( I_D/I_G \) of the D peak and the G peak was 1.19. It could be preliminarily judged to be graphene with an incomplete crystal lattice; the lattice spacing of the CG sample was greater than that of the GE, and the interlayer distance of CG was about 1.21 nm and has three layers. The thickness of the CG was thinner than that of GE. It proved that the prepared graphene was nano-graphene.

## EXPERIMENTAL SECTION

### Materials
Corn flour was obtained from edible corn at home. GE was supplied by Ningguo Longsciences Co., LTD. Potassium hydroxide (industrial grade) was supplied by Tianjin Kemiou Chemical Reagent Co., LTD. Absolute ethanol (industrial grade) was purchased from Tianjin Kaitong Chemical Reagent Co., LTD. Hydrazine hydrate (industrial grade) was obtained from Tianjin Fuchen Chemical Reagent Co., LTD. Other additives were commercially available in the chemical industry.

### Sample Preparation
First, 20 g of corn flour was placed into a beaker containing 100 mL of potassium hydroxide solution of 0.1 mol/L, stirred evenly with a glass rod, soaked for 12 h, and dried. Then, 10 g of the dried sample was placed into the quartz tube with an inner diameter of 25 mm. The temperature was elevated by a rate of 5 °C/min to 800 °C in the atmosphere of \( \text{N}_2 \) with a flow rate of 25 ml/min and kept constant for 1 h for the heat treatment to produce carbonized corn flour in a tube furnace (TNG1600-60) produced by Shanghai Shinbae Industrial Co., LTD.

Second, the carbonized corn flour was filtered by a dialysis bag for 24 h and dried to remove excess impurities in the carbonized corn flour. Then, 1 g of nickel powder was added into the sample in the quartz tube to recarbonize. The temperature was raised to 1500 °C with nitrogen gas and kept for 2 h, and the sample was taken out and cooled down. Then, 1 mol/L hydrochloric acid solution was added to the previous sample to make it neutral, and Cg was obtained.

Finally, 2 g of Cg and 1 g of sodium nitrate were filled into a 500 mL three-necked bottle, and 30 mL of concentrated sulfuric acid was slowly added with stirring for 20 min. Also, 6 g of potassium permanganate was added three times with stirring for 1.5 h, then deionized water was added until it was neutralized and dry, and then corn flour graphene oxide (CGO) was obtained. At last, the CGO was washed and dried with anhydrous ethanol and deionized water several times to obtain CG (yield 6.7%) with the Hummers-hydrazine hydrate method.17 The preparation process of the CG is shown in Figure 6.

### Characterization
The organic elements and contents of the samples were determined by the organic element analyzer (PE2400) (American Perkin Elmer Co., LTD) according to ISO 17973. The composition of the sample was analyzed by an X-ray photoelectron spectrometer (ESCALAB250X, American Thermo Co., LTD) according to ISO 19830. The aluminum Ka source was operated at 15 kV and 10 mA. The crystalline structure of the samples was observed by using an X-ray diffractometer (TDM-10, Japan Pigaku Co., LTD) according to ISO 9001. The diffraction angle (2θ) was from 5 to 90°, the operating voltage was 45 kV, and the electric current was 200 mA. The sample defects were studied by using a Raman spectrometer (China Zolix Co., LTD) according to ISO 9001. Power was set to 1–5 mW and the excitation ray wavelength to 532 nm with the continuous recording scan, and it was tested in the range of 500–3500 cm\(^{-1}\). Atomic force microscopy (AFM) analysis was carried out by a Multimode 8 AFM (Bruker Instruments Inc., Germany) in tapping mode at a scan rate of 0.7–1 Hz according to ISO 21222. The micro-morphology of the sample was determined by using TEM (H-7650, Japan Hitachi Co., LTD) at an accelerating voltage of 100 kV according to ISO 25498.

## AUTHOR INFORMATION

### Corresponding Author
Weili Wu — College of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, China; \( \text{orcid.org/0000-0001-9201-292X} \); Email: wuweili2001@163.com

### Author
Bowen Yu — College of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, China
Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.0c04722

Author Contributions
All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the Fundamental Research Funds in Heilongjiang Provincial Universities, China (no: YSTSXK201864).

ABBREVIATIONS
CG  corn graphene
Cg  cornmeal graphite
GE  commercial graphene
CVD  chemical vapor deposition
XPS  X-ray photoelectron spectroscopy
XRD  X-ray diffraction
TEM  transmission electron microscopy
AFM  atomic force microscopy

REFERENCES
(1) Alam, A.; Moussa, M. Preparation of graphene/poly(vinyl alcohol) composite hydrogel films with enhanced electrical and mechanical properties. Polym. Compos. 2020, 41, 809–816.
(2) Deacon, R. S.; Chuang, K. C.; Nicholas, R. J.; Novoselov, K. S.; Geim, A. K. Cyclotron resonance study of the electron and hole velocity in graphene monolayers. Phys. Rev. B: Condens. Matter Mater. Phys. 2007, 76, 081406R.
(3) Geim, A. K.; Novoselov, K. S. The rise of graphene. Nat. Mater. 2007, 6, 183–191.
(4) Ye, F.; Wang, Z.; Mi, Y.; Kuang, J.; Jiang, X.; Huang, Z.; Luo, Y.; Shen, L.; Yuan, H.; Zhang, Z. Preparation of reduced graphene oxide/titanium dioxide composite materials and its application in the treatment of oily wastewater. Colloid. Surface. A. 2020, 586, 124251.
(5) Zhou, Y.; Xie, C.; Su, L.; Han, X. Study of the risks of the graphene oxide preparation process by reaction calorimetry. J. Therm. Anal. Calorim. 2020, 139, 101–112.
(6) Marinoiu, A.; Mircea, R.; Mindaugas, A.; Asta, T.; Tomas, T.; Simona, N.; Daniela, B.; Mihai, V. Low-cost preparation method of well dispersed gold nanoparticles on reduced graphene oxide and electrocatalytic stability in PEM fuel cell. Arabian J. Chem. 2020, 13, 3585–3600.
(7) Padya, B.; Narasaiah, N.; Jain, P. K.; Rao, T. N. A facile co-solvent strategy for preparation of graphene nanoplatelet powder: An industrially viable innovative approach. Ceram. Int. 2019, 45, 13409–13413.
(8) Thamer, T.; Basma, H. A. T.; Saad, B. H. F. Preparation of graphene nano-sheets from graphite flakes via milling-ultrasonication promoted process. Mater. Today. 2020, 20, 579–582.
(9) Luo, Z.; Li, D. D.; Tan, S. Z.; Huang, L. H. Preparation and oil-water separation of 3D kapok fiber-reduced graphene oxide aerogel. J. Chem. Technol. Biotechnol. 2020, 95, 639–648.
(10) Hou, Y.; Lv, S.; Liu, L.; Liu, X. High-quality preparation of graphene oxide via the Hummers’ method: Understanding the roles of the intercalator, oxidant, and graphite particle size. Ceram. Int. 2020, 46, 2392–2402.
(11) Kudus, M. H. A.; Zakaria, M. R.; Akil, H. M.; Ullah, F.; Javed, F. Oxidation of graphene via a simplified Hummers’ method for graphene-diamine colloid production. J. King Saud Univ. Sci. 2020, 32, 910–913.