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Preparation of Graphene/Cellulose Composite Conductive Films

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Abstract

In this paper, carboxymethyl cellulose was used as matrix and graphene was used as conductive filler, compounding graphene with carboxymethyl cellulose. To prepare graphene/cellulose composite conductive film, the composite effect of it was discussed. Firstly, graphene was prepared by chemically reducing graphene oxide with ascorbic acid as reducing agent, and its conductivity was up to 110.2 S/cm. And then, graphene and carboxymethyl cellulose were composited by physical blending. When the mass ratio of graphene oxide to carboxymethyl cellulose was GO:CMC=1:6, the electrical conductivity of the composite film was 8.5×10-2 S/cm. Finally, graphene/cellulose composite conductive film was prepared by coating a graphene/cellulose composite system on a polytetrafluoroethylene substrate.

Keywords:*graphene, carboxymethyl cellulose, conductive film*

1. Introduction

With the development of printed electronics technology, electronic products tend to be personalized and intelligent. As a special functional ink, conductive inks rely on the market of various electronic products, and become thinner and more flexible. In the increasingly tense global energy demand, cellulose was favored by people as a natural material. Cellulose functional materials have great practical significance in today's increasingly scarce resources, and are widely used in many fields such as papermaking, medicine, food, and chemical engineering [1].

Graphene is the thinnest two-dimensional material that has been discovered today. Its thickness is only 0.34 nm. It is a perfect two-dimensional crystal structure consisting of a single layer of carbon atoms closely packed by hexagons [2]. At present, the conductive fillers of conductive inks studied are graphene [3,4], carbon nanotubes, carbon fibers, and composite functional fillers. Among them, some new materials such as graphene and carbon nanotubes are gradually applied.

Composite functional fillers have not been widely used because of their low affinity and poor dispersibility, but their excellent electrical properties and mechanical properties have attracted attention.

2. Experimental methods

2.1 Preparation of chemically reduced graphene oxide

At room temperature, 50 mg of graphite oxide was dissolved in 100 mL of distilled water, placed in a 250 mL volumetric flask, and sonicated (400 W) for 30 min to obtain a graphene oxide (GO) suspension. A certain amount of ascorbic acid was added to a suspension of 10 mL of graphene oxide (concentration: 0.5 mg/mL). After stirring for 10 min, the reaction system was heated to a certain temperature and reacted for a certain time to obtain reduced graphene oxide agglomerates.

2.2 Preparation of cellulose-graphene composites

Take appropriate amount of sodium carboxymethyl cellulose added to the graphene oxide suspension, fully stir and dissolve, add a certain amount of ascorbic acid according to GO:L-AA=1:10, control system temperature was 40°C, and stir at low speed for 36 hours. The graphene oxide was sufficiently reduced to give a composite product.

3. Experimental results and characterization

3.1 Observation of Micrograph Morphology of Graphene Oxide

After the graphite oxide was subjected to a certain degree of sonication, stripped graphene oxide sheets can be obtained. As can be observed from Fig.1, graphene oxide was a transparent sheet-like structure and has partial wrinkles or overlaps. The instantaneous implosion generated by the cavitation phenomenon has a strong shock wave and generates a transient high-energy environment. In such an environment, the van der Waals force between the graphite oxide layer and the layer was destroyed, and exfoliation of the flake graphite was promoted, thereby forming a graphene oxide suspension.

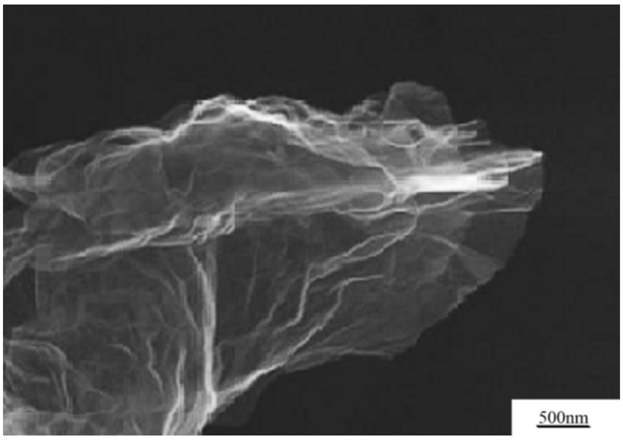


***Figure 1.** Scanning electron microscope image of graphene oxide*

In order to further confirm that the graphene oxide was exfoliated by graphene oxide, the two-dimensional structure of the graphene oxide was determined, and the experimental product was observed using an atomic force microscope.

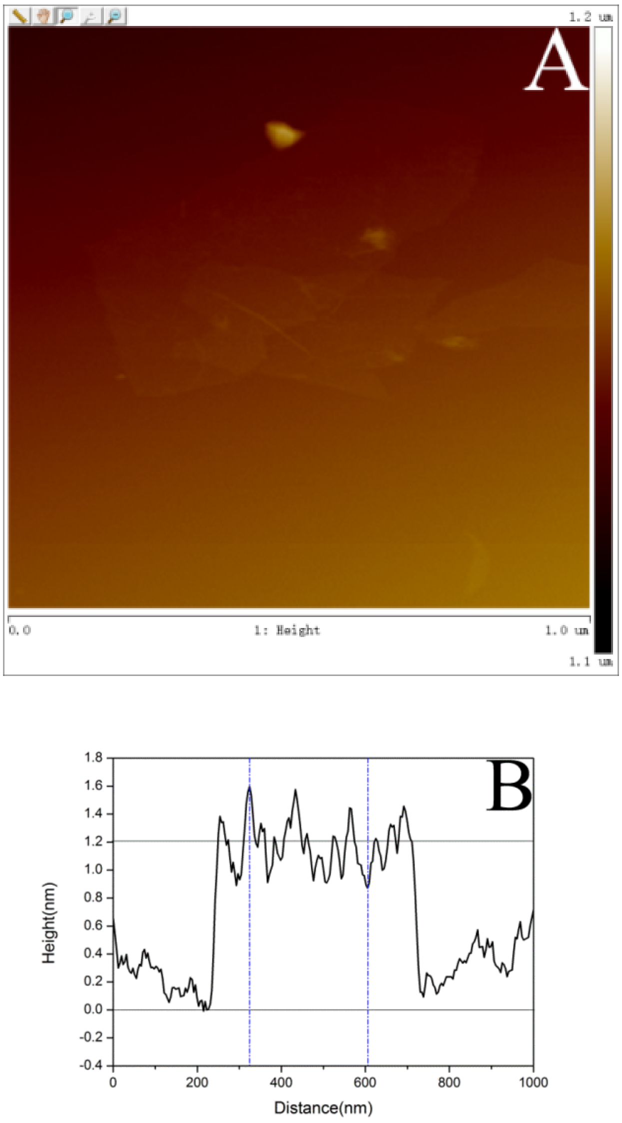


Figure 2. *Atomic force microscopy (A) and height (B) of graphene*

As shown in Fig. 2(A), the size of graphene oxide was about 700 nm, which shows a clear sheet structure with partial overlap, further confirming the transparent sheet structure of graphene oxide. Since the degree of oxidation of graphite oxide was between 45% and 50%, and the large π bond of some graphite was not oxidized, the van der Waals force between the layers was strong and was not destroyed in the ultrasonic treatment environment, causing the graphite layer to be only partially stripped or even not stripped. It can be seen from FIG. 2(B) that the thickness of the graphene oxide sheet was about 1.2 nm and the thickness of the single-layer graphene was about 0.34 nm. Therefore, the graphene oxide obtained by ultrasonic treatment of the graphite oxide was about 2-5 floor.

3.2 Discussion of reducing conditions

Temperature control was particularly important during the chemical reduction of graphene oxide. The appropriate temperature conditions can play a positive role in the chemical reduction of graphene oxide, and can also promote the chemical reaction of graphene oxide and ascorbic acid.

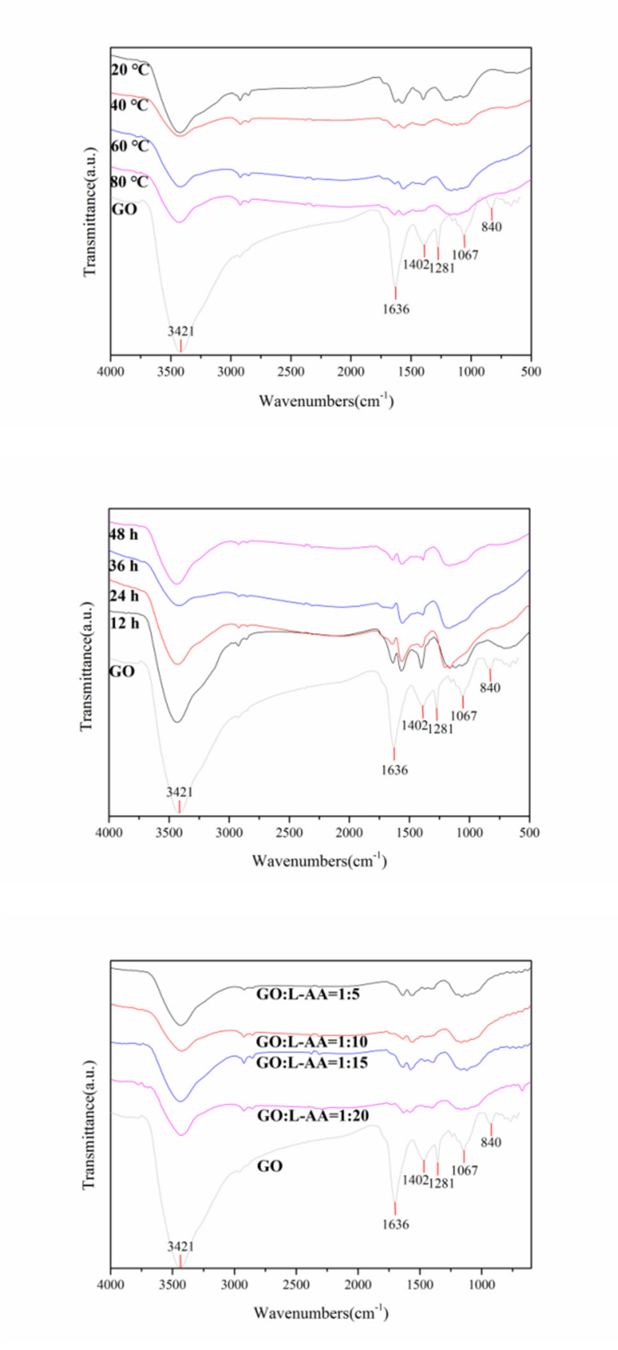


Figure 3. *Infrared spectrum of RGO prepared under different reducing conditions*

After GO was chemically reduced at 40 °C, the oxygen-containing functional groups on the surface produced obvious changes, deformation absorption peak at 1402 cm-1 hydroxyl OH, stretching peak of 1281 cm-1 epoxy C-O and 840 cm-1 The stretching vibration peak of the unsaturated carbon-hydrogen bond = C-H completely disappeared. When GO was chemically reduced for 36 h, the deformation vibration peak of the 1636 cm-1 adsorbed water molecule and the stretching vibration peak of the 840 cm-1 unsaturated carbon-hydrogen bond=C-H completely disappeared. When the mass ratio of GO to L-AA was 1:10, the characteristic peaks of RGO are obviously weakened or disappeared. The vibration absorption peak of 3421 cm-1 hydroxyl O-H, the deformation peak of 1636 cm-1 adsorbed water molecule and the intensity of the stretching vibration peak of 1067 cm-1 alkoxy C-O was significantly reduced.

3.3 Chemical Reduction Graphene Oxide Conductive Properties

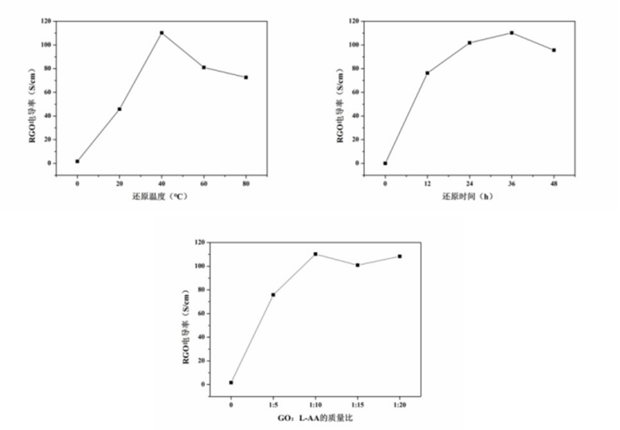
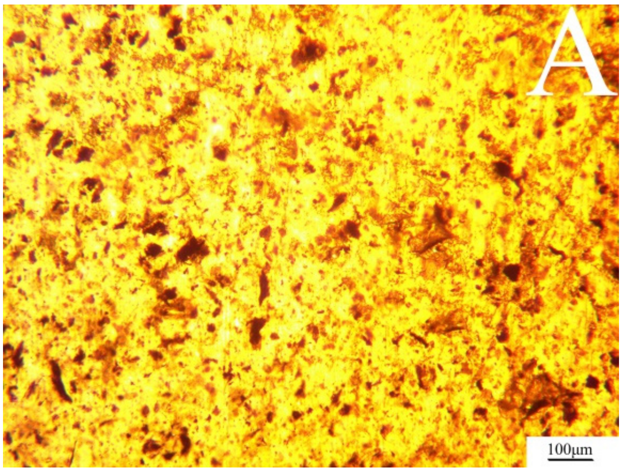


Figure 4. Conductivity of reduced graphene oxide under different reduction conditions

The graphene oxide produced by the experiment was not 1.7 S/cm when it was not reduced, and the reduced graphene oxide exhibits different electrical conductivity under different reducing conditions. When the reduction temperature was 40 °C, the conductivity of the reduced graphene oxide was the highest. When the graphene oxide was reduced for 36 h, the reduced graphene oxide reached the highest conductivity, the reaction time was not enough, resulting in the graphene oxide and reducing agent cannot fully react, the reaction time was too long, the conductivity of the reduced graphene oxide Slightly lower. When the GO:L-AA ratio was 1:10, the conductivity of the reduced graphene oxide reached the highest.

3.4 Effect of Compound Ratio on Dispersion of Composite Products



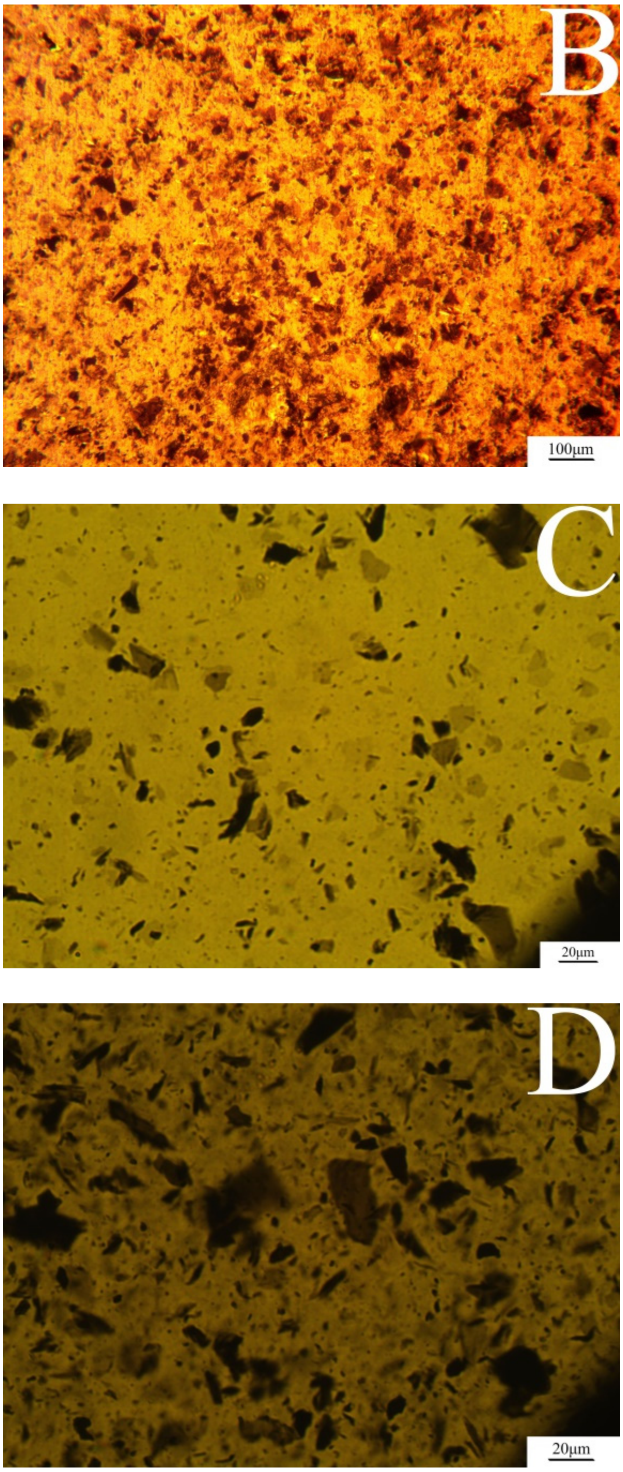


Figure 5. Dispersion effects of different content of graphene oxide (A and C: 0.5 g; B and D: 0.8 g)

It can be seen from Fig.5 that when the amount of graphene oxide added is 0.5 g, the sheet structure of the graphene oxide is clearly visible, and the graphene oxide is uniformly dispersed. When the addition amount of graphene oxide is 0.8 g, the content of graphene oxide is too large, resulting in uneven dispersion in the composite system, and agglomeration occurs, resulting in a decrease in the electrical conductivity of the composite product.

4. Conclusions

Graphene oxide was prepared by ultrasonic stripping to control the temperature at the time of ultrasonication to prevent graphene oxide from being reduced. The reduced graphene oxide was prepared by chemical reduction. The optimal conditions for the reduction were as follows: the reaction temperature was 40°C, the reaction time was 36 h, and the amount of reducing agent ascorbic acid was GO:L-AA=1:10. The conductivity of the reduced graphene oxide prepared under this condition can reach 110.2 S/cm. In the experiment of preparing composite materials, the composite ratio of GO:CMC=1:6 was selected as the mass ratio of graphene oxide and carboxymethyl cellulose, and the prepared composite film had higher conductivity of 8.5×10-2 S/cm. A graphene/cellulose composite conductive film was prepared by coating a graphene/cellulose composite system on a polytetrafluoroethylene substrate.

Acknowledgements

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Author Biography

Dr. Fuqaing Chu is a professor and the master student supervisor at the Qilu University of Technology, and also the Dean of the School of the Printing and Packaging Engineering. His main research interests include new materials of printing and packaging and their printability.