

Study of Thermal Conductivity of Fluorinated Graphene

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Abstract: With the rapid development of technology in recent years and the advent of the 5G era, the heat dissipation of electronic devices has received great attention. However, the high intrinsic conductivity of ordinary graphene materials limits their potential applications in electronic packaging materials due to poor thermal management. The results show that fluorinated graphene has excellent heat resistance, corrosion resistance, and strong wear resistance. It can also play a certain role in lubrication and be commonly used in high-temperature coatings, wear-resistant lubrication coatings, and corrosion-resistant coatings since it is not easy to react with other substances. . Fluorinated graphene is very stable and antioxidant under high temperature due to the strong electronegativity of fluorine. Therefore, in this paper, a highly compressible, thermally conductive, and electrically insulating fluorinated graphene was developed by hydrothermal method assisted by hydrofluoric acid, and the effect on the thermal conductivity of fluorinated graphene was investigated by varying the fluorine-to-carbon ratio (F/C) via adjusting the hydrofluoric acid content. The structure of fluorinated graphene was characterized by SEM and XRD to prove the porous structure which is a customized interconnected graphene network with adjustable fluorine coverage. The prepared fluorinated graphene has good insulating properties with a minimum conductivity of 4×10^{-7} S cm^{-1} and a thermal conductivity of $1.254 \text{ W m}^{-1} \text{ K}^{-1}$ as confirmed by the conductivity test results. Meanwhile, because of the porous structure of graphene fluoride, we prepared epoxy resin/fluorinated graphene nanocomposites by vacuum-assisted infiltration process with epoxy resin as the filler material. This material and fluorinated graphene showed outstanding thermal performance during typical cooling process. The conclusions indicate that graphene fluoride and epoxy resin/fluorinated graphene nanocomposites have a promising future in electronic packaging.

Keywords: fluorinated graphene; thermal conductivity; epoxy

I. INTRODUCTION

Nowadays, with the rapidly developing in 21st century, some of the technology about electronic devices is more and more flourishing. Electronic devices are widely used, and our reliance on them in daily life is also getting higher. The progress of technology has begun to affect the normal operation of the national economy. And due to the advent of the 5G era, the heat dissipation of electronic devices has received higher attention. The requirements for heat dissipation performance is increasing rapidly due the increase requirement of the performance of electronic devices.

Traditional thermally conductive materials with poor chemical resistance and electrical insulation properties are now unable to meet the requirements of applications such as electronic packaging preparation. Commonly, graphene has high thermal conductivity, however, its inherent high electrical conductivity greatly increases the difficulty of its application in electronic packaging materials. Therefore, it is urgent to investigate the thermal conductivity of graphene[1]. Currently, the introduction of thermally conductive and insulating carbon-based aerogels into polymers can result in low bulk resistivity, high dielectric constants, and high dielectric losses, which may negatively affect the performance and lifetime of electronic devices. Even with the use of boron nitride decorated aerogels with low dielectric constants, the improvement in electrical insulation properties is still limited. Therefore, the development of carbon-based aerogel materials with high insulating and heat dissipation properties and good structural stability remains a great challenge. In this work, we have successfully prepared a highly compressed, thermally conductive, and electrically insulating graphene fluoride. The epoxy resin/graphene fluoride nanomaterial was also synthesized, and this material and the graphene fluoride showed outstanding thermal performance during typical cooling processes in various tests, so both materials have a promising future for use in the field of electronic packaging.

A. Properties of fluorinated graphene

Fluorinated graphite with fewer layers or directly in the form of a single layer can usually be regarded as a two-dimensional nanomaterial. The ideal structure of a single-layer fluorinated graphene (FG) with an F/C ratio of 1 is shown in Figure 1. FG is a new material recently extracted from graphene materials and bonded several fluorides to carbon atoms through covalent, semi-ionic and ionic bonds without damaging the two-dimensional structure of graphene. Due to its unique framework structure and properties, FG can be used in many fields, such as cathode materials for batteries, lubricating materials, insulating materials and some other advanced materials, and it can also be used in electronic devices such as transistors and displays.

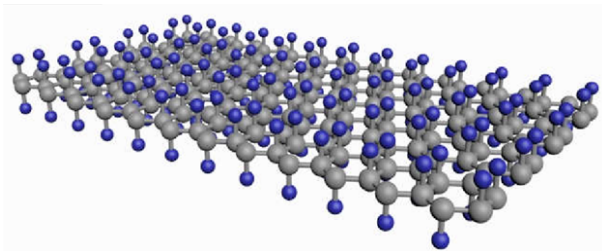


Fig.1 Structure of fluorinated graphene

The new substance, FG, retains the two-dimensional carbon structure of graphene and its chemical composition has similarities to polytetrafluoroethylene. Therefore, the overall properties of FG are similar to those of two-dimensional graphene and polytetrafluoroethylene. Fluoride is particularly important for its hydrophobicity, chemical stability and solvent strength, and has a certain strength at high temperatures, being decomposed only at temperatures greater than 2600 degrees Celsius, and more rapidly at temperatures greater than 400 degrees Celsius [1].

FG loses its pristine conductivity due to the introduction of fluorine atoms which is sufficient to compromise the highly interconnected two-dimensional structure, but it can be modulated to some extent by varying the content of fluorine in graphene [2]. Nair et al [1] found that the permeability gradually increased with increasing fluoride content [3], and the UV absorption of fluorinated graphene position lies at $e = 4.6$ eV. However, the absorption is still not higher than that of graphene, which indicates the promising application of FG in the field of optics [1].

In addition, FG has other special properties such as UV luminescence and fluorescence [4]. Due to the introduction of fluorine atoms, the sp^3 doping of carbon compounds in the structure is longer, resulting in a lower mechanical strength of fluorinated graphene than unfluorinated graphene, with a Young's modulus of 0.3 TPa and a fracture strength of 15 N/m [1]. Wang et al [5] found that compared to graphene, suitable bone marrow mesenchymal stem cells were more likely to be cultured on perfluorinated graphene with a 30% increase in culture density, thus inspiring researchers to focus on perfluorinated and partially fluorinated graphene in the field of tissue engineering [5]. Although FG is chemically inert, fluorine atoms can easily interact with other electron groups or atoms through hydrogen bonding [6].

II. EXPERIMENTAL SECTION

A. Preparation of fluorinated graphene using hydrothermal method

FG was prepared by hydrofluoric acid-assisted hydrothermal method. Typically, 350 mg of graphene oxide (GO) flakes were dispersed in 60 ml of water by sonication for 20 min[7]. Then, 0.75 ml of hydrofluoric acid was added as a fluorinating agent and stirred for 1 h at room temperature to obtain a homogeneous graphene oxide dispersion. The dispersion was added to a hydrothermal kettle with PTFE lining, screwed tightly to seal it, then placed in an oven and heat treated at 180 °C for 24 hours[8]. At the end of the

reaction, it was allowed to cool naturally to room temperature. The reaction solution was filtered and washed several times with ultrapure water until its pH reached neutral, and the resulting solid product was freeze-dried for 48 h to obtain a fluorinated graphene sample[9]. The FG_{0.09}, FG_{0.21}, FG_{0.25} and FG_{0.16} were prepared in the same way with different amounts of hydrofluoric acid as shown in Table 1.

Table.1 FGs prepared using different amounts of hydrofluoric acid ($R_{F/C}$)

Sample	$R_{F/C}$
FG (0.25 ml HF)	0.09
FG (0.5 ml HF)	0.21
FG (0.75 ml HF)	0.25
FG (1 ml HF)	0.16

B. Preparation of epoxy resin/fluorinated graphene nanocomposites

Epoxy resin/fluorinated graphene nanocomposites were prepared by a vacuum-assisted infiltration process. The epoxy resin monomer and DETD (Diethyltoluenediamine) (curing agent) were mixed at a weight ratio of 100/24 and stirred at 45 °C for 1 h. The FG was placed in a preheated mold, and then the resin mixture was slowly dripped onto the aerogel. After infiltration, the samples were transferred to a vacuum oven at 45 °C for 12 h to remove air bubbles[7]. Finally, the nanocomposites were dried at 80 °C for 6 h and at 150 °C for 3 h.

C. Characterization of fluorinated graphene and epoxy resin/fluorinated graphene nanocomposites

The prepared fluorinated graphene and epoxy resin/fluorinated graphene nanocomposites with different fluorine contents were used to test heat dissipation properties respectively after heating to a certain temperature using an infrared thermal sensing thermometer. Their thermal conductivity was also measured by TCi thermal conductivity tester to analyze their thermal conductivity principles[10].

III. RESULTS AND DISCUSSIONS

A. Morphology of fluorinated graphene and epoxy resin/fluorinated graphene composites

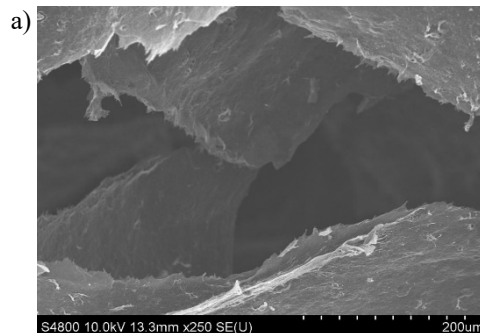


Fig.2a SEM image of FG_{0.75}

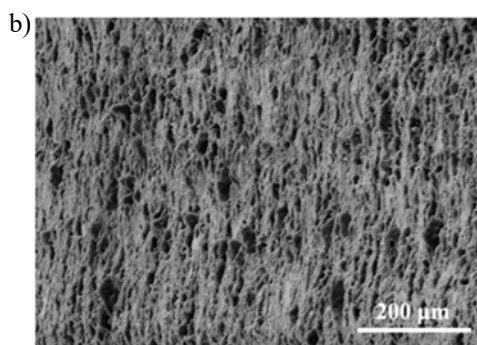


Fig.2b SEM image of Epoxy/FG_{0.75}

Fig. 2a shows that the FG has a highly porous cytosolic structure consisting of randomly oriented convoluted sheets with abundant micropores. Detailed observation revealed a variety of interconnections such as overlapping, folding, twisting and wrapping, which may contribute to the enhancement of the elasticity of the aerogel. Fig. 3b shows that the FG network is well maintained after epoxy resin infiltration, forming a neatly arranged lamellar structure.

B. X-Ray Diffraction Characterization

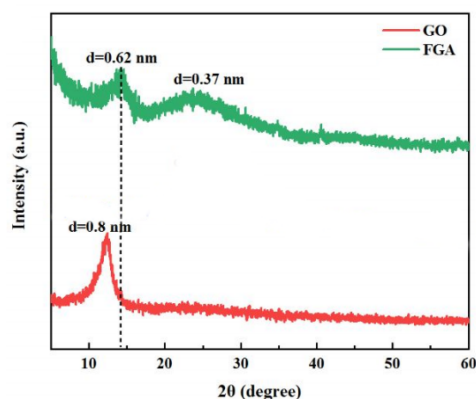


Fig.3a XRD patterns of graphene oxide and fluorinated graphene

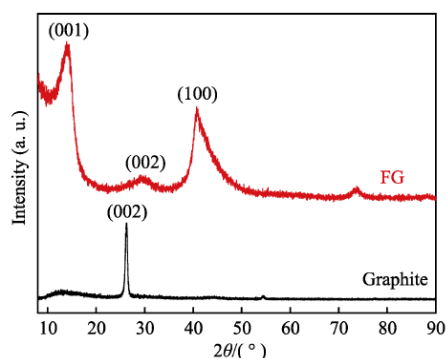


Fig.3b XRD patterns of graphene and fluorinated graphene

Firstly, as shown in Fig. 3a, the typical diffraction peak of graphene oxide is 11° and its interlayer distance is 0.8 nm.

After the hydrothermal treatment, the characteristic peak shown in 11° disappears and a broad peak appears around 24°. The interlayer distance of this broad peak is 0.37 nm, which confirms that the oxygen-containing group of graphene oxide is removed. After the addition of hydrofluoric acid in the later hydrothermal process, the obtained fluorinated graphene shows an additional peak at 14.3° with an interlayer distance of 0.62 nm, which may be a reflection of the high fluorine content level.

Secondly, as shown in Fig. 3b, the pure graphene shows a characteristic diffraction peak representing the graphite (002) crystal plane at an angle of 26.25°. After the hydrothermal reaction with the addition of hydrofluoric acid, the (002) crystallographic plane of fluorinated graphene is shifted to the right and the intensity of the diffraction peak is significantly reduced, which indicates the successful exfoliation of graphene after the fluorination treatment. Meanwhile, the characteristic diffraction peaks representing the (001) and (100) crystal faces of fluorinated graphene appear again at 14.23° and 41.07°, respectively, which indicate that the highly fluorinated graphene was indeed obtained after our novel hydrothermal fluorination treatment.

C. Electrical conductivity of fluorinated graphene

As shown in Table 2, even the weakly fluorinated FG_{0.09} has a high insulating property with a conductivity of $3.6 \times 10^{-5} \text{ S cm}^{-1}$. The graph (Fig. 4) shows the folding line graph of the change in conductivity of FGs at different F/C. The electrical insulating property of fluorinated graphene further improves when F/C increases from 0.09 to 0.25, the lowest conductivity is $4 \times 10^{-7} \text{ S cm}^{-1}$. This may be due to the introduction of fluorine atoms, which leads to a sharp decrease in the carrier density and a widening of the band gap.

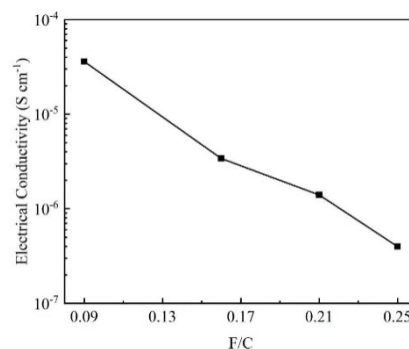


Fig.4 Schematic diagram of electrical insulation performance of FG with different fluorine content

Table 2 Electrical Conductivity of FG_{0.09}, FG_{0.16}, FG_{0.21} and FG_{0.25}

Sample	Electrical Conductivity ($\text{S} \cdot \text{cm}^{-1}$)
FG _{0.09}	3.6×10^{-5}
FG _{0.16}	3.4×10^{-6}
FG _{0.21}	1.4×10^{-6}

D. Effect of different HF contents on the thermal conductivity of fluorinated graphene and epoxy resin/fluorinated graphene nanocomposites

1) Fluorinated graphene with different HF contents

In order to study the effect of fluorine content on thermal conductivity, we chose to add different amount of hydrofluoric acid with 1 ml, 0.75 ml, 0.5 ml, and 0.25 ml. Fluorinated graphene was prepared by adding the same content of graphene oxide and using the same preparation conditions. The specific experimental design and the corresponding thermal conductivity of graphene fluoride are shown in Table 3.

Table 3 Effect of different hydrofluoric acid contents on the thermal conductivity of fluorinated graphene

Addition of HF (ml)	F/C	Thermal conductivity (W/(m•K))
1	0.16	1.254
0.75	0.25	1.074
0.5	0.21	0.963
0.25	0.09	0.891

From the above results, The decrease in the thermal conductivity of graphene is due to the hydrothermal process that first removes the oxygen-containing groups from graphene oxide and then introduces fluorine atoms. Some chemical defects were created in this process. Moreover, the lack of oxygen-containing functional groups in fluorinated graphene makes the interaction between graphene sheets weak, which makes fluorinated graphene unable to be a material with super high thermal conductivity like graphene. But because the thermal conductivity of resin is generally very low (less than 0.5 W/(m•K)). Epoxy resin material, its thermal conductivity is only 0.24 W/(m•K), while the thermal conductivity of fluorinated graphene can reach 1.254 W/(m•K) depending on the fluorine content, which is about 5 times higher than epoxy resin. The thermal interface materials used in chip packaging are composite materials based on resin materials, so FG can also be used as an excellent thermally conductive filler in resin-based thermal interface materials.

2) Epoxy resin/fluorinated graphene composites with different HF content

Table 4 Effect of different hydrofluoric acid contents on the thermal conductivity of epoxy resin/ fluorinated graphene nanocomposites

Addition of HF (ml)	F/C	Thermal conductivity (W/(m•K))
1	0.16	1.333

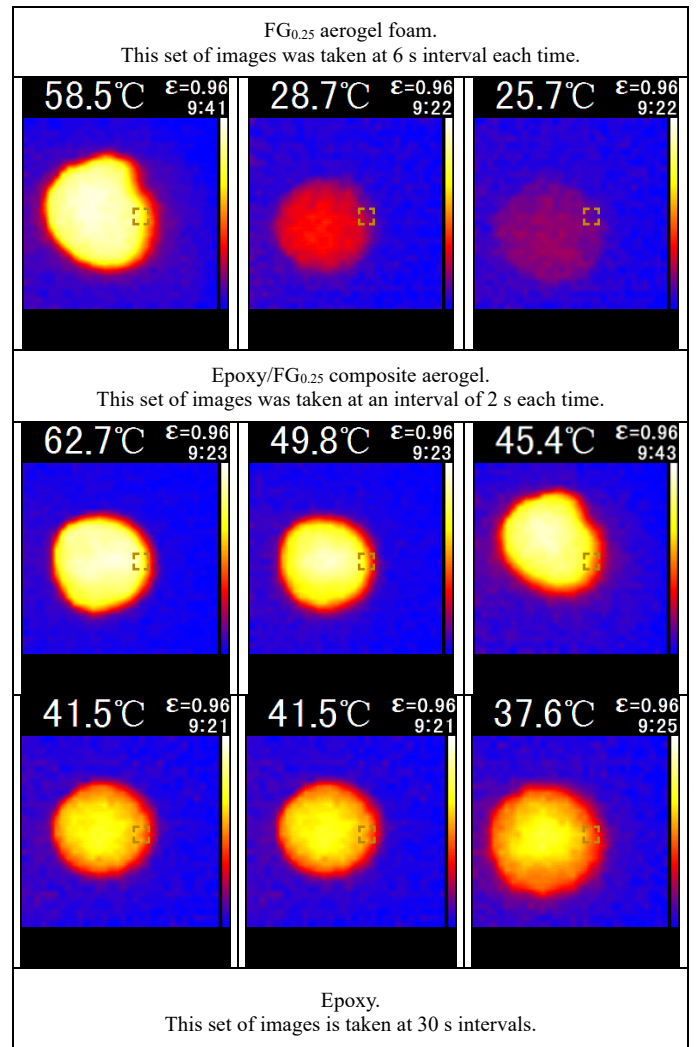
0.75	0.25	1.348
0.5	0.21	1.082
0.25	0.09	1.421

Table 4 shows the comparison of thermal conductivity of epoxy resin/fluorinated graphene nanocomposites with pure epoxy resin. The room temperature thermal conductivity of the pure epoxy resin was only 0.24 W/(m•K). However, after compositing with fluorinated graphene, the thermal conductivity of the epoxy resin was significantly improved. The thermal conductivity of FG_{0.09} can be improved to about 1.421 W/(m•K) at room temperature, which is about 6 times higher than that of pure epoxy resin.

This improvement in thermal conductivity is due to the fact that in the epoxy resin, the epoxy matrix can be uniformly distributed among the layered hollow network of fluorinated graphene aerogel. It is also possible that each layer of fluorinated graphene can be tightly stacked and adhered to the epoxy matrix at the edges of each layer, thus creating a large number of efficient heat transfer channels.

3) Heat dissipation performance test

Table 5 Heat dissipation performance test



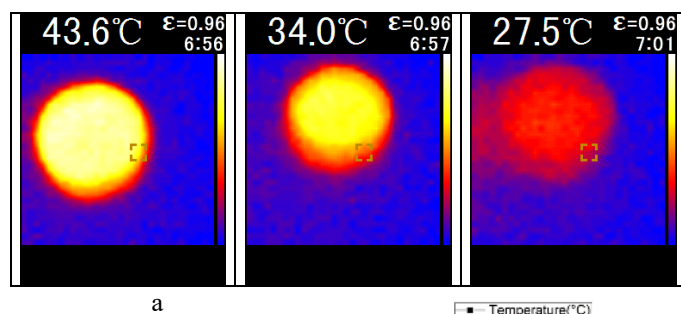


Fig.5a Infrared image and top temperature change during cooling of FG_{0.25}

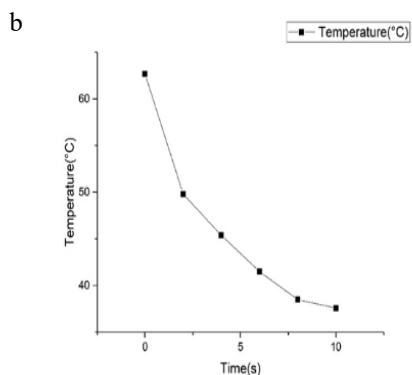


Fig.5b Infrared image and top temperature change during cooling of epoxy resin/FG_{0.25}

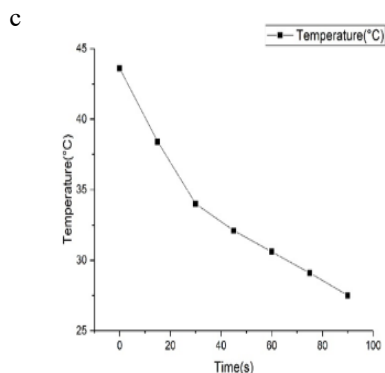


Fig.5c Infrared image of Epoxy cooling process and top temperature change

The thermal performance of the FGs was verified by comparing the surface temperature changes of the fluorinated graphene aerogel, the epoxy/graphene fluoride nanocomposite and the epoxy during a typical cooling process. To achieve this test, all samples were preheated in an oven at 180 °C and transferred to a stainless-steel plate located at room temperature after cooling to between 40 °C and 70 °C . The temperature changes of the aerogels were recorded with an infrared temperature camera. As shown in Table 5 and Fig. 5a-c, the top temperature of FG_{0.25} dropped rapidly from 58 °C to ambient temperature within 12 s. Such an efficient heat dissipation should be attributed to the 3D interconnected graphene network, which facilitates the heat flow from the top to the bottom of the aerogel. However, the epoxy/fluorinated graphene nanocomposite does not drop to room temperature very quickly within the same 12 s as shown in the second row of the table.

The surface temperature of epoxy/FG_{0.25} nanocomposites can drop to room temperature within 30 s, while the pure epoxy resin takes about 1 min to cool down as shown in the fourth row of the table. The great difference in the surface temperature change can be seen from Figure 5a to c which indicates that the thermal management capability of epoxy/FG_{0.25} nanocomposites has been greatly improved.

E. Conclusions

In this work, we prepared FG material by a novel hydrothermal reaction and compounded it with epoxy resin material to investigate its thermal conductivity. We have prepared a FG material with high thermal conductivity, excellent heat dissipation and electrical insulation, which consists of a three-dimensional interconnected network of aerogels. Based on our tests of the electrical conductivity of fluorinated graphene, the lowest electrical conductivity of our fluorinated graphene is $4 \times 10^{-7} \text{ S cm}^{-1}$, which shows that its excellent electrical insulation properties are maintained even after the introduction of fluorine atoms. The introduction of FG into epoxy resin can largely enhance its thermal properties, and FG itself also has excellent electrical insulation and heat dissipation properties. We mainly study the effects of different fluorine-to-carbon ratios on the thermal conductivity of graphene fluoride and its thermal conductivity after compounding with epoxy resin, and subsequently, other types of polymers can be compounded to maintain its good electrical insulation properties. Finally, we believe that this material will be of greater value in electronic devices and other fields after continuous research and improvement.

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