Preparation and Electro-thermal Properties of Low Voltage DC Driven Graphene Electro-thermal Film

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Abstract. Exfoliated graphene were prepared by supercritical carbon dioxide fluid stripping and electro-thermal film with graphite and exfoliated graphene were prepared and then studied by SEM and Raman spectroscopy. The results show the graphene sheets are exfoliated from the graphite blocks with a size of 3-10μm after stripping. The graphene existed in sheet in the electro-thermal film while graphite was blocks, which caused the graphene oriented and the conductive network more abundant and effective. The power of graphene electro-thermal film reduced by 22.5% compared with graphite electro-thermal film to reach the same space temperature under 12V, and the film temperature decreased by 9.623 °C, the comprehensive heat transfer coefficient is 2.60×10⁻³ W·cm⁻²·°C⁻¹, And the heating rate of the graphene electro-thermal film rapidly increase and the temperature rise time greatly decrease. The initial heating rate of graphene electro-thermal film is 19.3 times of that of the graphite electro-thermal film, and the temperature rise time decreased to 24.7%.

1. Introduction
Recently, electro-thermal materials such as nano-metal wires, carbon nanotubes, graphene and their composite materials have become the hotspots of research due to their feature of flexible, environment friendly, low working voltage, safe and efficient [1-4]. Among these electro-thermal materials, graphene has attracted much attention owing to its unique two-dimensional structure and excellent properties. Sun H et al. mixed the exfoliated graphene by electrochemical method with graphene oxide and annealed in HI vapour atmosphere at 800°C to obtain rGO/EEG film with a sheet resistance of 3kΩ/sq. When heating under the 10V, it took 60s to reached 35.7°C [1]. Tian S et al. stripped graphene from graphite electrode in the oxalic acid and hydrogen peroxide electrolyte, and then applied the graphene ink prepared to A4 paper with a sheet resistance of 49.7 Ω/sq. The paper reached 75.2°C under the 10V at the room temperature of 26.5°C, and the temperature rise time is only 30s, In contrast, the temperature was 2 times higher and had a faster increasing rate than graphite foil under the same voltage of 10 V [2]. Supercritical carbon dioxide fluid stripping used to prepare graphene due to its low viscosity, high diffusivity and small molecular size. Compared with oxidation-reduction method and electrochemical method, this method was environmentally friendly with neither various reagents nor oxidation and reduction of graphite, to ensure good performance of graphene by less defects of structure [5-6].
2. Experimental

2.1. Preparation of Exfoliated Graphene Coatings and Electro-thermal Films
20g of graphite powder (Qingdao Risheng Graphite Co., Ltd. China) was dispersed into 100mL DI water on a multifunction disperser for 30min at a speed of 800r/min assisted by dispersion agent, signed as coating D. Than they were transferred into a 200mL high-pressure stainless steel vessel whose temperature kept at 45℃ by water bath. After that, CO₂ was pumped into the vessel to reach 6MPa by a pump. After 150min exfoliation, the graphene coating was collected. Half of the coating was signed as coating EG-6 for use and other half coating was sonicated at 2000Hz for 120min than signed as coating EG-6u. The prepared coating was coated on non-woven substrate using the temperature control coating machine PF400-H (Jiangsu LEBO SCIENCE Co., Ltd.) and signed as electro-thermal films D, EG-6, EG-6u respectively. They were cut into 100mm×120mm after dried and Cu foils with width of 10mm were adhered as electrodes on both wider sides of electro-thermal films for test.

2.2. Characterization and the Test of Electro-thermal Properties of Electro-thermal Films
Scanning electron microscopes (SEM, Quanta 650 FEG) were used to examine the sample morphology and microstructure. The Raman spectra were measured at room temperature with an excitation wavelength of 532 nm. Electrical resistivity (ρ) and sheet resistance (Rs) of the films was measured by square resistance meter (DMR-1C, Nanjing Daming Instrument Co., Ltd.). The prepared electro-thermal film was placed in the system shown in figure 1 for testing the electro-thermal performance, including initial heating rate, average heating rate and temperature rise time. Several different voltages were applied between the two Cu foils using a DC power supply (KPS-6005DU, Shenzhen Zhaoxinyuan Electronic Technology Co., Ltd.). Then Record the voltage, current, and temperature of the thermocouple as a function of time during heating.

![Figure 1. Test system for performance of electro-thermal film: 2-test system, 21- measuring greenhouse for electro-thermal characteristics; 22 - top surface; 23- side surface;24- bottom surface; 25- prepared electro-thermal film samples; 26- K-type thermocouple; 27- first interface; 28- second interface.](image)

3. Results and Discussion

3.1. Characterization of Raw Material and Graphene Electro-thermal Film
As shown in figure 2, the raw material graphite powder is in the form of block with the size of 10~40μm. In addition, the scaly structure of graphite, which can be seen clearly, provided the basis for the exfoliated of the exfoliated of graphene. The typical G peak of 1575.95cm⁻¹, 2D peak of 2716.79cm⁻¹ in figure 3 indicated the raw material is defect free.
SEM was often used to observe the microscopic morphology of the material. As shown in figure 4, after supercritical carbon dioxide stripping, the graphene sheet with the size of 5~15 μm (figure 4b and 4e) was exfoliated from graphite. Then after the ultrasonic stripping process, the size of graphene was further reduced to 3-10 μm (figure 4c and 4f) and oriented. When it comes to the existence in electro-thermal film, the graphite particles were mainly connected by dots while the graphene sheet had a piece-to-piece connection. In addition, we can see in the electro-thermal film EG-6, beside the piece-to-piece connection, the connection between the two has a bit-to-point connection and in the electro-thermal film EG-6u, graphene sheet connected with others totally by piece-to-piece. This connection method makes the exfoliated graphene oriented and the conductive network more abundant.
For graphene and graphene related materials, the electrical conductivity is not only related to the sheet and size of the material, but also related to the defects of the material. Raman spectroscopy is a commonly used method to characterize the number and defects (figure 5). After supercritical carbon dioxide stripping, there was an obvious D peak at 1350.03 cm\(^{-1}\) arise. In addition, after sonicated, the intensity of D peak futurity increased. Compared with the graphite, the intensity of G peak of exfoliated graphene was increased while the frequency of G peak moved toward the high wavenumber direction [7-8]. The intensity ratio of $I_D/I_G$ of D peak and G peak was used to characterize the defect of the material. After supercritical stripping and future sonicated, the defects increased, $I_D/I_G$ were 0.27 and 0.30 respectively. Although the increase of defects may cause the decrease of electro-thermal performance, the defects was much less than that by oxidation-reduction graphene [9-10].

3.2. Performance of Electro-thermal Film during Working

Resistivity is the intrinsic property of a material, according to $\rho = R_s \cdot d$, where $\rho$ is the resistivity, $R_s$ is square resistance; $d$ is the thickness of the film layer. As shown in Table 1, the thickness of the electro-thermal film EG-6 and EG-6u were thinner than that of electro-thermal film D, and the resistivity reduced to 98.5%, 73.4% respectively, which making the electro-thermal film to consume less power to reach higher room temperatures (shown in figure 6). The room temperature is determined by the ambient temperature, the film temperature and the way of heat transfer. The value of the film temperature is equal to the average of the four film temperature measurement points (figure 6a). Compared with electro-thermal film D, the power and the film temperature of electro-thermal film EG-6 were reduced to reach the same room temperature under the voltage of 6, 9 and 12. Obviously, the power decreased from 5.328W to 4.128W, reduced by 22.5% to reach the same room temperature 42.4°C under 12V where the ambient temperature was about 20 °C and the film temperature was reduced from 70.45°C to 60.825°C, decreased by 9.623°C. This result indicates that the heat transfer mode has changed. The methods of heat transfer include conduction, convection and radiation. For films, the main method is convection and for graphene and related materials, the main methods changed to radiation, which was faster and more efficient. Comprehensive heat transfer coefficient (K) was usually used to characterize the combined effects during the heat transfer process. According to the Newton cooling formula $P = K S \Delta T \rightarrow \frac{P}{S} = K \Delta T$, The slope K value is obtained by linear fitting in graph "P/S-ΔT". As shown in Figure 7, the K of the electro-thermal film D is 0.00207 W·cm\(^{-2}\)·°C\(^{-1}\), while it was to 0.00260 W·cm\(^{-2}\)·°C\(^{-1}\) of the electro-thermal film EG-6, increased by 25.6%. The change of the main heart transfer method results in the rise of comprehensive heat transfer coefficient. In addition, we noticed the K of the electro-thermal film EG-6u decreased to 0.00181 W·cm\(^{-2}\)·°C\(^{-1}\), which was caused by the defects’ great increase on the graphene sheets during the ultrasonic process [11-12].
Table 1. The value of $R_s$, $d$ and $\rho$ of the electro-thermal film D, EG-6, EG-6u

| electro-thermal film | D   | EG-6 | EG-6u |
|----------------------|-----|------|-------|
| $R_s (\Omega \cdot \square)$ | 25.85 | 41.23 | 27.55 |
| $d (\mu m)$          | 136.6 | 80.1  | 89.2  |
| $\rho (\Omega \cdot cm)$ | 0.355 | 0.330 | 0.246 |

Figure 6. The power, film temperature, and space temperature of electro-thermal film D, EG-6, EG-6u under 6V, 9V, and 12V

Figure 7. Integrated heat dissipation coefficient of electro-thermal film D, EG-6 and EG-6u
3.3. Performance of Electro-thermal Film during Heating

As shown in figure 8, the performance of electro-thermal film during heating was analyzed by nonlinear fitting of "ΔT-t", the suitable formula is \( y = Ae^{-x/t} + y_0 \) (figure 8a). The initial heating rate is the slope of the fitted curve when \( x=0 \), calculated according to the formula \( y'=-A/t \). The heating time is the value of \( x \) and the average heating rate is the value of \( y/x \) when \( y=0.9y_0 \).

![Figure 8](image.png)

**Figure 8.** Initial heating rate, average heating rate and temperature rise time of electro-thermal film D, EG-6, EG-6u under 6V, 9V, and 12V

As shown in figure 8b-d, the initial heating rate and the average heating rate of the electro-thermal films increased as the voltage increases. In addition, the heating time decreased. This is the commonality of electro-thermal materials, the increase in power results in a shorter time. When focused on the index during heating at the same voltage, we can see clearly the competitive advantage of graphene. Compared with the electro-thermal film D, the initial heating rate of electro-thermal film EG-6 and EG-6u were greatly increased. Obviously under 12V, the initial heating rate of electro-thermal film EG-6 and EG-6u were 84.5°C/min and 129.8°C/min, while that of the electro-thermal film D was 6.72°C/min increased by 12.6 times and 19.3 times respectively. And the average heating rate also changed from 1.6°C/min to 4.97°C/min and 8.08°C/min, increased by 210.6%, 405%. The temperature rise time reduced from 7.9 min to 2.66 min and 1.95 min, shortened to 33.7% and 24.7%, respectively.

4. Conclusion

(1) Two different exfoliated graphene were prepared by supercritical carbon dioxide fluid stripping. The graphene sheet with the size of 5–15μm was exfoliated from graphite and the size of graphene was further reduced after sonicated. Meanwhile, defects of graphene increased.
(2) Graphene film has high electro-thermal conversion rate, which means spend less power to reach higher room temperature. The power decreased by 22.5% to reach the same room temperature. The comprehensive heat transfer coefficient of the electro-thermal film EG-6 is $0.00260 \text{ W} \cdot \text{cm}^{-2} \cdot \text{°C}^{-1}$, increased by 25.6%.

(3) The graphene electro-thermal film can rise to the working temperature faster. Compared with the electro-thermal film D, the initial heating rate of electro-thermal film EG-6 and EG-6u increased by 12.6 times and 19.3 times, the average heating rate also increased by 210.6%, 405% and the temperature rise time shortened to 33.7% and 24.7%, respectively.

5. References

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