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Gumsong Choe
Faculty of Mining Engineering, Kim Chaek University of Technology, Pyongyang, Democratic People's Republic of Korea

Changil Kim
Faculty of Mining Engineering, Kim Chaek University of Technology, Pyongyang, Democratic People's Republic of Korea

Songok Jang
Faculty of Mining Engineering, Kim Chaek University of Technology, Pyongyang, Democratic People's Republic of Korea

Chang Nam
Faculty of Mining Engineering, Kim Chaek University of Technology, Pyongyang, Democratic People's Republic of Korea

Correspondence
Gumsong Choe
Faculty of Mining Engineering, Kim Chaek University of Technology, Pyongyang, Democratic People's Republic of Korea

Synthesis route of few-layer graphene for additives of functional composite electrothermal coatings

Gumsong Choe, Changil Kim, Songok Jang and Chang Nam

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Abstract
Graphene preparation by electrochemical exfoliation of graphite is a promising preparation method for low cost and high yield.
In this paper, we have investigated the preparation of multilayer graphene/water-borne polyurethane (FLG/WPU) composite coatings with good electrical and mechanical performance using water-borne polyurethane (WPU) as a binder, and the preparation of graphene-based multilayers by simultaneous electrochemical activation of persulfate.
Physical activation by ultrasound treatment and electrochemical activation in aqueous systems improve the oxidation and dispersion of graphene.
Conductive composite coatings prepared by mixing FLG powder with waterborne polyurethane form a mechanically well-bonded FLG/WPU electrothermal film on PET matrix, with surface resistance of about $1.03\times10^4\Omega/m^2$ and exothermic temperature of 50~80 °C, which are applicable to electrothermal devices.

Keywords: Electrochemical exfoliation, few-layer graphene, electrothermal coatings

Introduction
Nowadays, Graphene is a two-dimensional nanomaterial of a single layer structure with sp^2 bonds between carbon atoms, has attracted a lot of attention due to electrical, mechanical and optical properties. Hence, there have been many studies on improving the properties of composite substrates by using functional additives in different industry fields, and new innovations are being made in the preparation methods and applications.
In particular, the unique physical and chemical properties, electrical conductivity [1], corrosion resistance [2], and good mechanical properties [3, 4], have been widely applied in electromagnetic shielding [5], energy storage [6], electrochemical sensors [7], and attempts to produce graphene in large amounts as functional additives have become an important research focus.
In graphene synthesis, the conventional method of graphene oxide (GO) by the modified Hummers method and reduction using different reducing agents to obtain reduced graphene oxide (rGO) is still widely used [8-9].
However, GO obtained by this method is limited by the low C/O ratio, the use of a reducing agent with high reducing power is harmful to the environment because it is a toxic, and the low electrical conductivity, complicated processing, and the poor mechanical adhesion with the substrate material in practical applications for the addition of composites.
Also, the thermal reduction of GO prepared by Hummers method is limited by the choice of high temperature resistant binder and matrix material.
Recently, attempts as are being made to improve the yield with the quality of graphene [10-12].
The liquid exfoliation method of exfoliating graphite by sonication in water or organic solution is an effective method to obtain graphene easily [13].
Liquid phase methods of graphene synthesis are cheap and scalable, and the product in a liquid suspension allows easy and defect-free transfer of graphene to the application substrate.
Among the liquid-phase exfoliation methods, Electrochemical exfoliation, has better electrical conductivity due to the high C/O ratio and low defect degree [14].
However, this method has the drawback of its low yield, during dispersion in solvent the surface size of graphene decreases due to the excessive ultrasound-assisted treatment.

Zaw Lin studied the ultrasonic dispersion of natural graphite in water using ozone gas.

It has been reported that the method is a method of preparing multilayer graphene (MLG) that is well dispersed in water without using chemical and organic solvents, and the obtained graphene can be applied to composite materials, conductive coating materials, energy storage materials, and various electronic devices [15].

Electrochemical exfoliation has been initiated by an attempt to prepare graphene sheets by electrochemical treatment of graphite rods in mixtures of water and ionic solutions [16].

The products obtained by this method can be an effective additive to overcome the above mentioned difficulties, because of the high C/O ratio and the simple operation that can be achieved.

Liqiong Wu *et al*. studied the preparation of graphene powder with several layers in high yield by electrochemical exfoliation of expanded graphite in sulfuric acid solution [17].

Sulphuric acid-graphite intercalation compounds are used as key intermediates in electrochemical exfoliation process to achieve effective exfoliation.

Destiarti, L et. al. studied the effect of electrolytes on electrochemical exfoliation using ammonium sulfate, sodium sulfate, ammonium oxalate, hydrogen peroxide and ammonium persulfate as electrolytes [18].

A. Mir et. al. studied the effect of the synthesis parameters on the size distribution and size of particles during electrochemical exfoliation and ultrasonic assisted-dispersion [19- 20].

The low dispersion in the matrix material is a limitation for applications when the products obtained by electrochemical exfoliation are used as conductive additives in composites.

To improve the dispersibility of multilayer graphene, it is necessary to enhance the oxidation of exfoliated products during the fabrication process.

Fabrication of electrothermal films with good mechanical, electrothermal, and environmentally friendly performance is still a subject of interest to ensure practical application of functionalized composite heating.

In this paper, we have prepared and characterized FLG/WPU composites by simultaneous electrochemical activation of persulfate and electrochemical exfoliation of multilayer graphene.

In the first step, the electrochemical oxidation at the graphite anode and the insertion of a graphite layer of anions in the electrolyte resulted in the formation of sulfuric-graphite interlayer compounds (GIC), sonicated to prepare FLG and used as an additive in the conductive composite.

The waterborne polyurethane(WPU) emulsions as binders to improve the dispersibility and conductive chain structure of conductive nanoparticles [23-28].

We have investigated the possibility of dispersing FLG in WPU to improve electrical conductivity and obtain electrothermal coatings with good electrothermal performance.

2. Experimental

2.1. Materials

Natural graphite plates (99.5% purity, 200 mm × 140 mm × 10 mm) used as anodes for electrochemical exfoliation was provided by Korea Natural Graphite Trading Co. Ltd

Sulfuric acid (95%) and ammonium sulfate (99.5%) were purchased from Aladdin Chemicals.

WPU suspension (PU116) was purchased from Hefei Anke Fine Chemicals.

All chemicals were used as received without further purification.

2.2. Synthesis of FLG

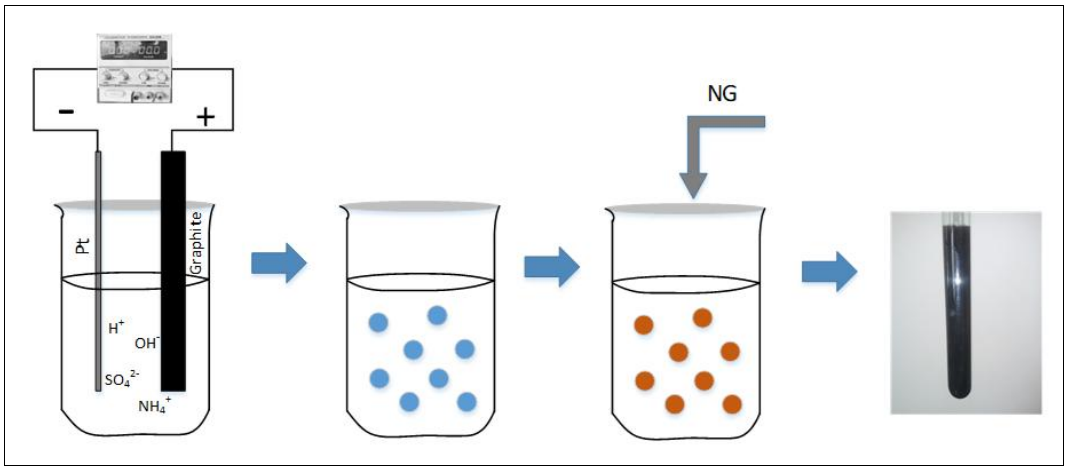

Fig 1: Preparation sets of expandable graphite

First, the graphite electrode was cut to a suitable sample size (100 mm × 20 mm × 10 mm, and then placed in contact with the copper plate, as the anode for electrochemical exfolation, and the platinum plate as the cathode, with a distance of 2 cm.

A mixture of 0.2 M ammonium sulfate and 5 M sulfuric acid solution was used as the electrolyte.

Initially, a pre-treatment was performed to ensure that the graphite electrode was fully wetted.

After 5 min of electrochemical pre-treatment with +2V using a DC power supply, electrochemical reactions were carried out to ensure the exfoliation of the graphite electrode by a DC current at +10 V.

Electrochemical reactions for 2 h resulted in colloidal EG suspensions.

The EG suspension was filtered and repeatedly washed with deionized water (DI) to separate the dispersed FLG in the undissolved EG and ethanol by dispersing the resulting EG

powder in 95% ethanol solution for 1.5 h using an ultrasonic disperser (sonic, Ultrasonic Vivracell, 750 W) and then treating it at 3000 rpm for 5 min at a rotational speed.
Then, the FLG dispersion was filtered using tetrafluoroethylene (PTFE) membrane and dried at 80 °C for 20 min to prepare FLG powder.

2.3. Fabrication of FLG/WPU/PET exothermic films

Water-borne polyurethane (WPU) was mixed with FLG powder and spin-coated on PET plastic sheets to prepare electrothermal films, cut to a suitable size and then tested for characterization.

2.4. Characterization

Scanning electron microscopy (SEM, Quanta 2000, FEI, Netherland) was used to characterize the electrochemical exfoliation process and the surface morphology of the films.
The FLG samples were characterized using X-ray diffraction (XRD, Cu Kα 1.5406 Å, Bruker D8ADVANCE, Germany) and Raman analysis (Raman, Renishaw, with excitation wavelength at 532 nm).
The surface resistance of the films was measured using a four-probe measurement method.
The temperature of the exothermic film was measured by an infrared camera (IRC, R500Ex-Pro-D, Japan).

3. Results and Discussion

3.1. Preparation characteristics of FLG

The process of obtaining expanded graphite (EG) from natural graphite in a mixed electrolyte solution of ammonium sulfate and sulfuric acid is schematically depicted in Fig. 2.

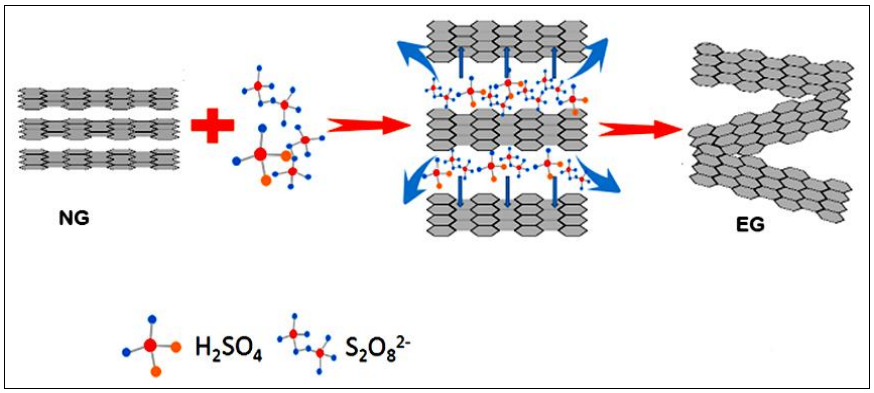

Fig 2: Schematic diagram of electrochemical insertion/exfoliation process.

The surface and rim of graphite showed obvious swelling (Fig. 3a-c).
This is because the OH^- ions present in the electrolyte polarize the carbon atoms between the graphite layers at the edges of the graphite, the SO_4^{2-} ions intercalate between the layers, and the anodic oxidation of SO_4^{2-} ions produces SO_2 and O_2 gas, which causes swelling between the layers forming graphite.

$$S_2O_8^{2-} \rightarrow 2SO_4^{2-} \cdot \quad (1)$$

$$2SO_4^{2-} \cdot + OH^- \rightarrow \cdot OH + SO_4^{2-} \quad (2)$$

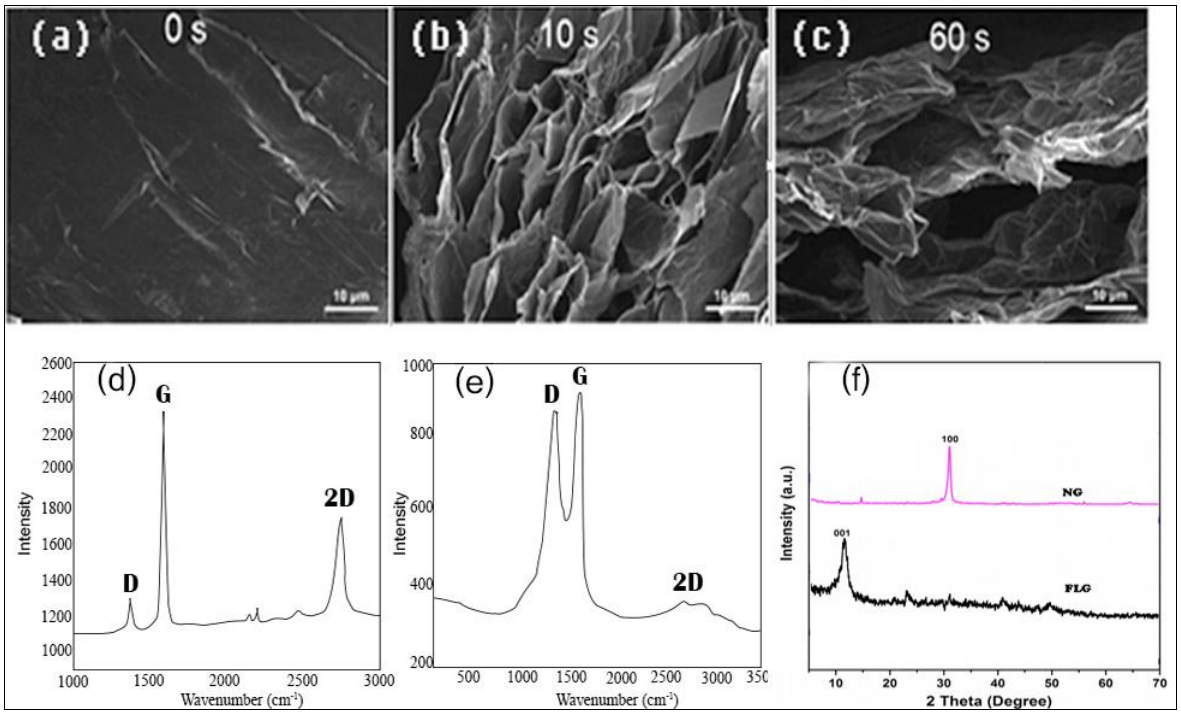

Fig 3: SEM of graphite electrodes between 0 and 60 s under 10 V(a-c), (d-e) Raman spectra, XRD of NG(e) and FLG(f).

It can also be concluded that the anodic oxidation of ammonium sulfate with sulfuric acid produces ammonium persulfate, which acts as an oxidant to further improve the colloidal stability of EG that has been removed from the electrode [8].

Next, comparing the Raman spectra of FLG samples obtained by ultrasonic dispersion treatment of EG powder in ethanol with NG, it can be seen that there was a clear expansion between the graphite layer and the layer [Fig. 3d,e].

The X-ray diffraction patterns of NG and FLG clearly show that FLG powder has a crystalline structure as graphene (Fig. 3f).

3.2. Surface properties of FLG/WPU composite electrothermal films: Graphene/polyurethane blends were prepared using a propeller-type mixer with 0, 4, 8 and 16 wt.% graphene addition.

The above prepared hybrid solution was prepared on PET resin by electrospun film samples with areas of 10.0 cm × 10.0 cm, 7.5 cm × 7.5 cm, 5.0 cm × 5.0 cm and 2.5 cm × 2.5 cm.

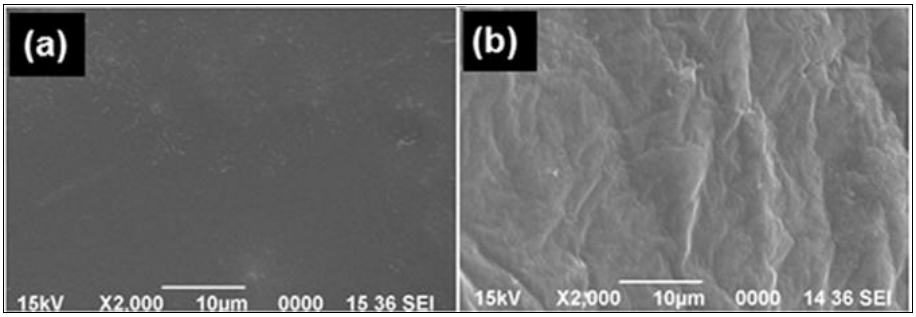

Fig 4: Scanning electron micrograph of electrospun paint on glass substrate: (a) pure waterborne polyurethane, (b) WPU doped with 4 wt.% FLG.

3.3. Surface resistance characteristic

The FLG/WPU composite with respect to graphene content was coated on PET resin to calculate the surface resistance by dividing the measured resistance by the thickness of the coated coating layer [4].

For comparative analysis, FLG/PVA composites were prepared with the same thickness.

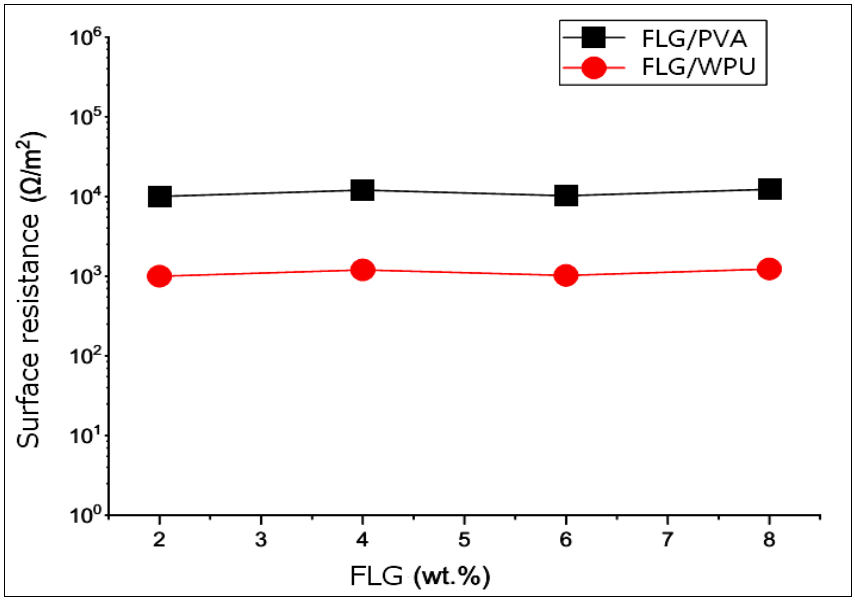

Fig 5: Surface resistance versus graphene doping.

As the graphene content increased, the surface resistivity decreased and the conductivity increased.

This is due to the fact that the conductive nanoparticles form a network structure inside the polymer blend as the content of conductive nanoparticles increases [18].

3.4. Electrothermal performance

The electrothermal performance of the sample is shown in Fig. 5 when the FLG/WPU was spin-coated on PET resin with a thickness of 0.5 mm and dried for 10 h and applied at a voltage between 0 and 50 V.

Table 1: Classification code of samples with different FLG contents.

No	FLG contents, wt.%	Sign
1	0	C-0
2	2	C-2
3	4	C-4
4	6	C-6
5	8	C-8
6	10	C-10

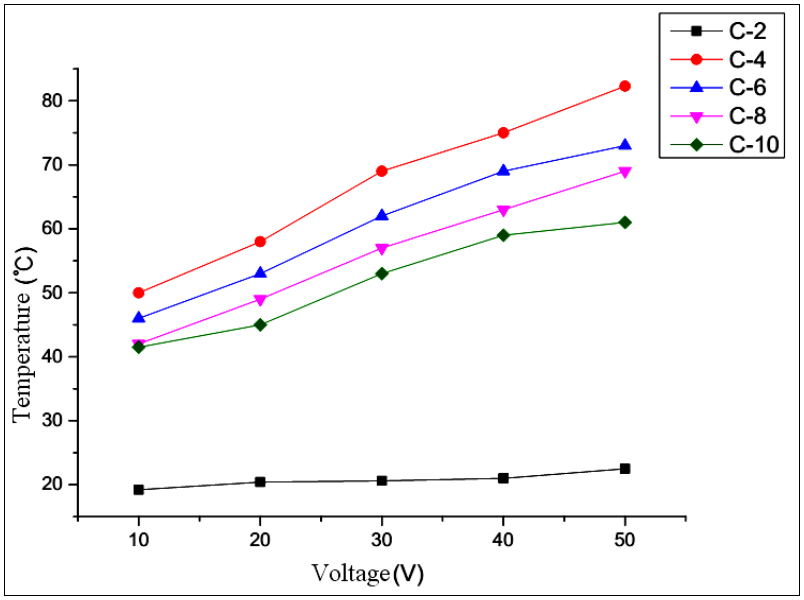

Fig 6: Temperature profile under voltage.

In the case of the C-2 sample, the maximum surface temperature is 22.5±0.5°C when applied at voltages up to 50 V.

For the C-4 sample, the temperature distribution showed a value of 50 °C at 20 V and 82.3 °C at 50 V.

At C-6, the exothermic performance decreased with decreasing temperature, while at 50 V, the heat distribution was not uniform.

3.5. Stability of electrothermal membranes

During the measurements, the films were evaluated by measuring the change in surface resistance after 100 bending cycles at different bending radii of 50-10 mm.

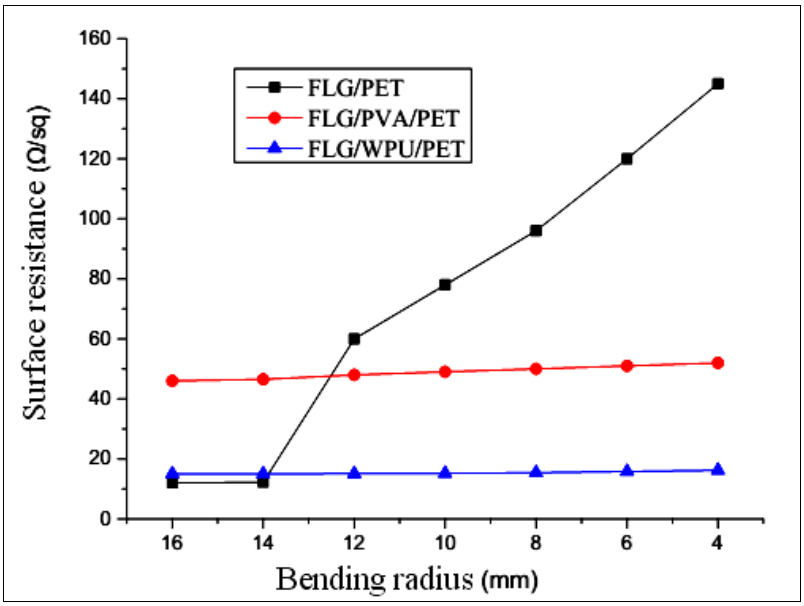

Fig 7: Surface resistance of transparent conductive films after 100 bending cycles at different bend radii.

The FLG/PET film used as reference resulted in a sudden decrease in surface resistance at radii below 15 mm, whereas the FLG/WPU/PET film maintained a constant initial conductivity even at a bending radius of 15 mm.

4. Conclusion

In this paper, a simple and novel conductive additive, graphene dispersions, combined with electrochemical intercalation/exfoliation and ultrasonic dispersion, was prepared by coating the PET resin with waterborne polyurethane as a binder to prepare composite electrothermal coatings.

The prepared solution was coated on PET resin to prepare 0, 2, 4, 6, 8, and 10 wt.% FLG/WPU composite electrothermal coatings with graphene content to examine the surface properties, electrothermal performance, and mechanical damage stability.

Surface characterization showed no significant change in adhesion properties for PET resin with increasing graphene content.

Surface resistance measurements showed that with increasing graphene doping, electrical conductivity improved and exothermic performance decreased.

The exothermic behavior was relatively uniform in C-6,

with a good exothermic performance at a temperature value of 65 °C when applied at a voltage of 50 V.

Excessively low graphene doping leads to the formation of a conductive network, which leads to a loss of electrical conductivity, whereas excessively high graphene doping leads to an increase in electrical conductivity, which leads to a decrease in the exothermic performance and, in turn, an unbalanced thermal distribution.

The mechanical stability of the electrospun film was analyzed and the mechanical stability was good even at bending radius less than 5 mm.

The above results would be a good experimental data for the preparation of conductive films using electrothermal coatings.

WPU improves the adhesion of functionalized graphene nanoparticles to various substrate materials and significantly improves the stability.

This conductive composite coating can be an excellent candidate for the fabrication of low-cost and flexible electrothermal thin films.

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