Research Article

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Synthesize and characterization of conductive nano silver/graphene oxide composites

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Abstract: To meet the high-precision needs of conductive ink in the field of microelectronic circuit printing, nano silver-coated graphene oxide (GO) composites were prepared as the conductive functional unit of the composites. The results show that compatibility of the GO grafted with ethylene glycol diglycidyl ether is better in the organic matrix than in the inorganic solvents. The nano silver particles attached to the surface of the grafted GO are evenly distributed and uniform in size. Moreover, the conductivity of grafted GO coated with silver particle composites is effectively improved. The composite conductivity is higher than 10^8 S/m, which is close to the electrical conductivity of silver.

Keywords: conductive composite ink, graphene oxide, surface grafting, nano silver

1 Introduction

As one of the key factors in printed electronics, conductive inks are increasingly used in the electronic field, such as printed circuit boards, full-motion membrane keyboards, membrane switches, flexible printed circuits, decorative art panels, electromagnetic shielding, fine printing, potentiometers, multilayer circuits, and wireless radio

frequency identification systems [1,2]. With the application of nanotechnology, composite conductive ink filled with nano-sized metal particles differ from traditional conductive inks in characteristics [3]. In particular, composite conductive ink has the advantages of good conductivity, strong process operability, and low curing temperature, and these characteristics make the composite conductive ink suitable for electrons transport. Typically, the composite conductive ink is composed of an inorganic conductive functional unit and an organic material. However, due to the poor interface between the particles and polymer materials, ensuring that the metal nanoparticles do not agglomerate and remain high content in the ink is necessary. The conductivity mainly depends on characteristics of these nanoparticles dispersed in the matrix. When particles disperse well and connect each other to form a bridge or a net, electrons can easily transport [3–10]. Silver, which is not easily disturbed by the environment, is the most conductive one among all metals. Therefore, it is particularly favored for use in preparing conductive materials [11–17]. Traditional micron silver powder conductive ink cannot easily meet the requirements of low processing temperature and small feature size, which are proposed for the development of miniaturization and flexibility of electronic products. However, nano silver which meets the requirements of low heat treatment temperature and small size processing technology has become an inevitable trend to be the filler of conductive ink. At present, the high-precision demand of microelectronic circuit printing and the emergence of direct writing have promoted research and development of silver ink [18]. However, silver particle will sink easily and quickly because of its high density.

Graphene oxide (GO), which is oxidation of graphene, is an important derivative of graphene. Electronic and dielectric properties of GO are higher than electrochemically reduced graphene papers by 2 orders of magnitude due to a higher percentage of interlayer O–H bonds [19]. However, sandwich structures made of GO-CuNPs-GO show long-term stable conductivity and high-temperature stability because the limited GO interlayer distance can protect CuNPs from oxidation [20]. Furthermore, the synthesized

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GO exhibited high values of dielectric constant $\varepsilon'(\omega)$ and low losses by fitting the theoretical approximations to the experimental results to show GO could be a good candidate for semiconductor compound [21]. The GO sheet contains many functional groups that provide a large number of active sites for modification. Thus, functional groups or segments can be introduced to provide good conditions for experimental research [22].

In this paper, the active groups on the surface of GO are grafted with small organic molecule ethylene glycol diglycidyl ether (EGDE) having epoxide group to improve the compatibility of GO in the organic matrix. Then nano silver particles were coated on the grafted GO to get rid of aggregation in organic matrix. Thus, the grafted GO enhances the dispersibility of the metal particles to perform the conductive functional unit of the composite conductive ink. On the other hand, silver particles will disperse evenly rather than sink because GO has enough big surface to float in the matrix. Once the nano silver particles connect each other, there will be a possible way for electrons to transport.

2 Experimental details

2.1 Materials and instrumentations

Natural flake graphite (NG) was supplied by Kuntai Graphite Co., Ltd. (China). And, the diameter of NG is around 1 mm. EGDE was supplied by Aladdin Industrial Corporation, Shanghai, China. All other reagents, such as 98% H_2SO_4 , KMnO_4 , H_2O_2 , lactic acid, AgNO_3 , $\text{NH}_3\cdot\text{H}_2\text{O}$, and glucose, were of analytical grade.

Fourier transform infrared (FTIR) spectroscopy was performed on an IR Prestige-21/FTIR-8400S FTIR spectrometer to characterize the EGDE before and after ring opening to certify the elimination of epoxide group. GO surface contact angle detection was tested by drop shape analyzer (DSA100, KRUS) to verify its compatibility changes with inorganic solvents. X-ray diffraction detection of GO, EGDE-grafted GO, and silver particles-coated GO was performed using an XRD-6000 instrument (SHIMADZU, Japan) to verify its structural changes. GO and the modified GO were morphologically characterized through transmission electron microscopy (TEM) (JEM-3010). TEM samples were dispersed in an ethanol solution and spooned out with a copper net for observation. Conductivity of GO was tested by RTS-8 four-probe which contains four thin collinearly placed tungsten wires probes which are made to contact the sample under test.

2.2 Composite fabrication

GO was prepared according to the improved Hummer's method [23,24]. First, 35 mL of H_2SO_4 was added to 1.5 g of NG in a 150 mL of three-necked round-bottomed flask and the mixture was stirred for 30 min at room temperature. 3 g of KMnO_4 was added slowly to the mixture, then the mixture was stirred for 2 h in an ice bath and then heated to 35°C under vigorous stirring for 30 min. After that, 150 mL of deionized water was gradually added to the reaction solution which had a temperature of 98°C under vigorous stirring for 15 min. Finally, 10 mL of H_2O_2 was added to the solution, which was stirred for 10 min. The reaction solution was centrifuged and then washed repeatedly with distilled water until the solution was almost neutral. The products were then immersed in 70% aqueous alcohol solution and treated in an ultrasonic bath for 2 to 3 days. After oxidization, epoxy, hydroxyl, and carboxyl were introduced on the surface of GO for further surface modification.

Lactic acid (2 mol) and EGDE (1 mol) were used for opening the epoxide group at 110°C under nitrogen protection for 8 h. The ring-opened EGDE was grafted with active groups on the GO surface at 80°C to achieve GO surface modification as shown in Figure 1. Silver mirror reaction, the aldehyde groups in glucose (9 g) reduced the silver ions in the silver ammonia solution which was made of AgNO_3 (4 g) and $\text{NH}_3\cdot\text{H}_2\text{O}$ (5 mL), made the nano silver particles coat the modified GO surface to enhance the dispersion of the metal particles in the matrix.

3 Results and discussion

3.1 Ring opening result of epoxide group of EGDE

First, the epoxide group in EGDE was confirmed by FTIR spectroscopy. Figure 2 shows an infrared spectrum of the epoxide group in EGDE. Before treatment, the characteristic peaks of ether bond appeared at 1,141/cm and the epoxide group appeared at 855 and 910/cm [25], and 1,254/cm [26]. After the ring opening reaction with lactic acid [27], the characteristic peaks of these three epoxide groups disappear, proving that the epoxide groups of EGDE successfully opened. Also, a peak of intramolecular association of hydroxyl groups was observed around 3,543/cm, which is the in-chain hydroxyl group proving

Figure 1: Surface modification process of GO.

Figure 2: Infrared spectrum of EGDE.

that lactic acid could open the epoxide group to generate a hydroxyl group easily [24]. Furthermore, the stretching peak of hydroxyl groups appeared at 3,290/cm and the peak of ether group at 1,141/cm became weaker at the same time.

3.2 GO surface contact angle detection

EGDE with hydroxyl group was connected with GO by condensation. Figure 3 demonstrates the surface contact angle of GO and grafted GO which was measured by the water drop measurement method. Figure 3a shows that the contact angle between GO and water is 57.5°. Figure 3b shows the contact angle between GO grafted with EGDE and water is 85°. The results showed that compatibility of grafted GO and inorganic solvents becomes poor. However, the compatibility of grafted GO with organic solvents and organic substances has been improved according

to the principle of similar miscibility. The results also indicated that the EGDE after treatment has been successfully grafted to the active group on the GO surface.

3.3 X-ray diffraction detection of GO

After improving the compatibility of GO, silver particles were evenly coated on the GO surface. Figure 4 indicates the XRD patterns of GO, EGDE-grafted GO, and silver particles-coated GO. As shown in the figure, the XRD curve of GO has a significant diffraction characteristic peak of (001) at $2\theta = 10.9^\circ$ [28]. The characteristic peak of GO around 11° significantly disappeared after being grafted with small organic molecules. With the condensation reaction between the organic molecules and the active groups on the GO surface, a large amount of $-OH$ and $-COOH$ has disappeared. At the same time, the inter-layer distance of GO has changed, which leads to the diffraction characteristic peak moving to left. The characteristic peak of graphite near 26° is strengthened, indicating that the active groups on GO have basically reacted. After silver ammonia reaction, there were not only the (002) peak of graphite, but the 38.1° , 44.3° , 64.4° , and 77.3° which stand for (111), (200), (220), and (311) of silver, respectively. That is to say, silver particle has coated on the GO surface.

3.4 GO morphology

Figure 5 illustrates the micromorphology of GO, EGDE-grafted GO, and silver-coated EGDE-grafted GO. The image proves that GO has been successfully prepared using the improved hummers method, as shown in Figure 5a. The GO is composed of 5–16 layers, as shown in HRTEM (High Resolution Transmission Electron Microscope) image (Figure 5b).

Figure 3: Contact angle with water of GO: (a) before grafting and (b) after grafting.

Figure 4: XRD of GO with different groups.

When the hydroxyl group in EGDE and the active groups $-OH$ and $-COOH$ on the surface of GO undergo a condensation reaction, the surface modification of GO by small organic molecules is achieved. As shown in Figure 5c, EGDE is scattered on the GO surface. The places where EGDE is present are wrinkled due to the formation of chemical bonds with GO. Moreover, the distribution of active groups on the surface of GO is highly random. The uncertainty of the reaction site leads to the irregular distribution of EGDE.

In Figure 5c and d, the shapes of EGDE particles are round and ellipse, which is because the $-OH$ groups of EGDE are at both ends of the segment after the epoxide group opening. The $-OH$ on the EGDE may react with $-OH$ group at the edge or on the surface of GO, as shown in Figure 1. Round particles are formed by the reaction between the $-OH$ at both ends of the EGDE segment and the active groups on the GO surface that are closely adjacent to one another. When the $-OH$ at both ends or one end of the segment reacts with the faraway active group, it easily forms an ellipse. After considering the adhering silver particles to the modified GO surface, it can be found that black silver particles and small gray organic molecules can be distinguished along with the silver particles attached to the modified oxide surface, as shown in Figure 5c. With increasing concentration of silver particles, the silver particles on the surface of GO can easily be distinguished from the gray organic molecules, as shown in Figure 5d. During the silver mirror reaction, the reduced silver particles tend to result in a rough surface. So, the silver particles can more easily attach to the surface of the grafted GO. Overall, the silver particles on the GO surface are evenly distributed and are uniform in size.

To observe the microstructure of the Ag-GO, TEM image was taken and shown in Figure 5e. The silver nanocrystals were coated on the GO surface evenly. The single crystal, as well as grains with diameters of ~ 10 nm, can be observed from the HRTEM of a silver nanoparticle in Figure 5f. Thus, silver particles can disperse evenly in organic matrix without precipitation and agglomeration.

3.5 Conductivity test

GO and modified GO were pressed, and the four-probe method was used to measure the square resistance of these samples. The resistivity ρ is calculated by formula (1), as follows:

Figure 5: Micromorphology of GO before and after grafting: (a) GO, (b) HRTEM of GO, (c and d) grafted GO, (e) GO coated with silver particles, and (f) HRTEM of silver particles.

Table 1: Conductivity of GO before and after the surface modification

Sample	Sheet resistance (Ω/sq)	Thickness (m)	Resistivity (Ω)	Conductivity (S/m)
GO	0.1336	3.2×10^{-4}	4.2×10^{-4}	2.3×10^4
Grafted GO	1.0052	2×10^{-4}	2.01×10^{-4}	5×10^3
Grafted GO with silver	$<10^{-4}$	3×10^{-4}	$<10^{-8}$	$>10^8$

$$\rho = RS \times t, \quad (1)$$

where ρ represents the resistivity, the unit of which is Ω . RS represents the measured sheet resistance value of the sample, the unit of which is (Ω/sq). t is the thickness of the measured sample block, the unit of which is m .

The conductivity σ is calculated by formula (2), as follows:

$$\sigma = 1/\rho, \quad (2)$$

where σ is the conductivity, the unit of which is S/m. The calculated results are shown in Table 1.

Although the surface of GO is modified with small organic molecules, the conductivity is reduced. However, after the silver particles have attached to the surface of GO, its conductivity is significantly improved.

4 Conclusion

Silver nanoparticles-coated GO which was grafted with EGDE was successfully synthesized. In this way, silver nanoparticles can evenly disperse in organic matrix without precipitation and agglomeration. At the same time, there will be a good interface between fillers and matrix because of the organic group. The composite conductivity is higher than 10^8 S/m, which meets the needs of conductive functional units as composite conductive ink.

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