Photoelectric Characteristics of Reduced Graphene Oxide/Silver Nanoparticles Multilayer Films via Spin-Coating and Self-Assembly

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The graphene oxide/silver nanoparticles (GO/AgNPs) composite films were prepared by spin coating combined with electrostatic self-assembly technology, and the reduced graphene oxide/silver nanoparticles (RGO/AgNPs) composite films were finally obtained at 600°C under Ar/H₂ atmosphere for 2 h. With the increase of the number of film layers, the absorption characteristic peak intensity of reduced graphene oxide (RGO) also gradually increases, indicating that the composite film grew uniformly. The conductivity of graphene/silver nanoparticles composite films not only increased with the decreased of particle size, but also increased with the increased of self-assembly and spin-coating times. The lowest sheet resistance of RGO/AgNPs28-10 film was only 0.392 kΩ/sq, which showed excellent conductive performance.

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1. Introduction

As a new material of single-layer sheet structure with carbon atom thickness, graphene is a planar film of hexagonal honeycomb lattice composed of carbon atoms in sp² hybrid orbital.¹⁾ The unique structure of graphene determines excellent properties, including unique quantum Hall effect, high modulus of elasticity, ultra-high electron mobility, good light transmission, and low resistivity ($\sim 10^{-8} \Omega \cdot \text{m}$), the highest intensity, etc.^{2,3)} Absorbing about 2.3% of visible light, graphene with a light transmission rate of 97.7% has a single atomic thickness and is almost completely transparent.⁴⁾ Therefore, graphene, which has three major properties of transparency, conductivity, and flexibility, is expected to become an ideal substitute for the next generation of transparent conductive films.⁵⁻⁷⁾

Due to many defects caused by the preparation of the graphene film, the graphene film has a high electrical resistance. Silver nanoparticles with high surface energy and chemical activity exhibit unique thermal, electrical, optical, acoustic, magnetic, mechanical and catalytic properties, and have broad application prospects.⁸⁻¹¹⁾ The combination of silver nanoparticles and graphene can combine the excellent properties of these two materials, and the obtained nano-assembled materials have great application potential in the fields of optics, electricity and electrocatalysis.

The methods for preparing graphene oxide/metal nanoparticles composite materials in the currently reported literature mainly include drop coating, dipping, electrostatic self-assembly, suction filtration, Meyer bar coating, spin coating, and printing method.^{12,13)} Using the electrostatic interaction between positive and negative charges as the driving force, the "layer-layer" self-assembly technique of the multilayer film is constructed by alternate deposition of oppositely charged cells, which has the advantages of a simple preparation method, mild operating conditions, and rich in film formation.^{14,15)} This method has been widely

adopted in recent years and is considered to be an effective method for constructing a composite multilayer film.^{16,17)} In this experiment, a graphene oxide/silver nanoparticles composite film was formed on the surface of quartz substrate by spin coating method combined with electrostatic self-assembly method, and the reduced conductive composite film was obtained under Ar/H₂ atmosphere. At the same time, the effects of film thickness and particle size on the electrical conductivity of the composite film were also investigated.

2. Experimental Procedure

2.1 Materials

Silver nitrate, polyethyleneimine (PEI) and natural graphite (all purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.), hydrofluoric acid (purchased from Jinan Qiguang Electronics Co., Ltd.) were used in our experiment. All other chemicals and reagents were of analytical grade. All solutions were prepared using ultrapure water (Millipore, 18.2 MΩ/cm).

2.2 Preparation of aminated quartz substrates

The quartz substrates were first cleaned with Dicon 90 cleaning solution, and then immersed in sodium hydroxide alcohol solution for 24 hours. Subsequently, the substrates were taken out and immersed in H₂SO₄/H₂O₂ (30%) solution (v/v, 3:1) for 40 minutes. After they were taken out again, the substrates were heated in NH₃·H₂O (25%)/H₂O₂ (30%)/H₂O (v/v, 1:1:5) mixed solution for 20 minutes at 60°C, and then rinsed with deionized water 2 times, dried with air. The dried pretreated substrate were immersed in KH-550 silane (2%) alcohol solution for 2.5 h, and then rinsed with absolute ethanol, air-dried again. Finally, the substrates were immersed in hydrochloric acid solution (pH = 3) for 10 minutes and obtained quartz substrates with positive charges on the surface.

2.3 Preparation of GO/AgNPs films

Spherical Ag NPs/PEI was prepared according to the method described in the literature.^{18,19)} Two different sizes of

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silver nanoparticles were labeled as AgNPs28, AgNPs47. Graphene oxide was synthesized from natural graphite by modified Hummers method.^{20,21} First, the prepared graphene oxide solutions were dropped on an aminated quartz substrate, and spin-coated at 1000 rpm for 20 s and 2000 rpm for 30 s. Subsequently, the silver nanoparticle solutions were dropped on the quartz substrate with graphene oxide, and spin coating was performed in the same manner. Multilayer GO/AgNPs films were obtained by repeating these spin coating cycles and ensure that the outermost layer was graphene oxide. The prepared films were labeled as GO/AgNPs28-n (n is the number of graphene oxide layers), GO/AgNPs47-n.

2.4 Preparation of RGO/AgNPs films

The spin-coated film substrates were placed in a tube furnace and thermally reduced under Ar/H₂ atmosphere (volume ratio = 5/1) for 2 h at 600°C. After cooling to room temperature, the obtained films were labeled as RGO/AgNPs28-n (n is the number of graphene oxide layers), RGO/AgNPs47-n.

2.5 Characterization

A Shimadzu UV-3600 UV-V-NIR spectrophotometer was used to record the absorption spectra of the silver nanoparticle solution. The morphology and nanostructure of the prepared samples were observed by JEM-2100PLUS transmission electron microscopy (TEM). The electrical conductivity of the RGO/AgNPs films was measured using a ST2258C four point resistivity test system. XRD patterns were obtained using 3 Kw/PANalytical X-ray diffractometer. The zeta-potential was read on a US Malvern Zeta potential analyzer. Scanning electron microscopy (SEM) images of the films were taken on a JSM-6700F scanning electron microscope.

3. Results and Discussions

3.1 Characterization of silver nanoparticles and graphene oxide

Silver nanoparticles of different sizes were prepared by liquid phase reduction. The transmission electron microscope (TEM) was used to observe the morphology and size of the nanoparticles. The results are shown in Fig. 1(a) and (b). To quantitatively estimate the distribution of the particles, the frequency histograms of these two different size nanoparticles are shown in Figs. 1(c) and (d). The average size of the particles is about 28 nm and 47 nm, respectively.

The absorption spectra of nanoparticles with different sizes were measured, and the results are shown in Fig. 2. As shown in the absorption spectrum, the resonance absorption wavelength increases with increasing size of the nanoparticles, and the position of the absorption peak can be red-shifted from 400 nm to 425 nm. The full width at half maximum (FWHM) of absorption spectrum for the nanoparticles of these two sizes were measured, and their values were 53.5 nm and 77 nm, respectively. According to the latest TEM image (shown in Fig. 1), the morphology of the small-sized nanoparticles is more uniform and the shape is closer to a spherical shape. The morphology of large-sized nano-

Fig. 1 (a) TEM image of Ag NPs with smaller size (b) TEM image of Ag NPs with larger size (c) The particle size distribution for Ag NPs with smaller size (d) The particle size distribution for silver nanoparticles with larger size.

Fig. 2 Absorption spectra of silver nanoparticles with different sizes.

Fig. 3 (a) TEM image of graphene oxide (b) absorption spectrum of graphene oxide.

particles is not spherical enough, and the range of dimensional changes is slightly larger. The FWHM values of the absorption spectrum also better explain the phenomenon.

Graphene oxide was prepared by the improved Hummer method, and was also observed by transmission electron microscopy, and its absorption spectrum was measured. Figure 3(a) shows the TEM image of graphene oxide. The

Table 1 Zeta-potential of graphene oxide and silver nanoparticles.

Sample	GO	AgNPs(28nm)	AgNPs(47nm)
Zeta-potential(mV)	-37.6	54.3	57.9

typical two-dimensional fold sheet structure of graphene oxide can be seen from the figure, and its size is large, which has a good effect on its conductivity. Figure 3(b) shows the absorption spectrum of graphene oxide. A clear graphene oxide absorption peak can be seen at 231 nm, which is consistent with the results of previous literature.²²⁾ The absorption peak around 230 nm is the c-c* skeleton π - π^* transition peak of graphene oxide.²³⁾

Because of the repulsive interaction between the positive charges, PEI provides the existence of positive charges on the outer surface of silver nanoparticles and ensures the stability of the dispersion solution. More importantly, these positive charges provides polycations for electrostatic self-assembly process. The zeta potentials of graphene oxide and silver nanoparticles are measured, and the results are shown in Table 1. It can be seen that the nanoparticles have good positive electrical properties, while graphene oxide has good negative electrical properties, which provides a good basis for the electrostatic self-assembly.

3.2 Morphology and structural characteristics of graphene/silver nanoparticles composite films

Figure 4(a) shows the SEM surface morphology of the RGO-6 film without nanoparticles. The graphene film obtained after annealing still has a wrinkled state, good continuity, and no obvious defects. The SEM morphologies of RGO/AgNPs28-3, RGO/AgNPs28-6, and RGO/AgNPs47-6 composite membranes are shown in Fig. 4(b), (c), and (d), respectively. Graphene-silver nanoparticles composite films still exhibit obvious sheet graphene structure, and the nanoparticles are well embedded in the graphene film, which indicates that the graphene and nanoparticles are successfully compounded. By comparing

Fig. 4 SEM images of (a) RGO-6 film; (b) RGO/Ag NPs28-3 film; (c) RGO/AgNPs28-6 film; (d) RGO/Ag NPs47-6 film.

Fig. 5 XRD patterns of quartz substrate (black line), GO (red line) and RGO/AgNPs47-10 (blue line).

Fig. 4(b) and (c), it can be observed that, as selecting nanoparticles of the same size, the number of silver nanoparticles in the composite film increases with the increase of the number of film layers. Attribute to the aggregation of dimers or trimers of silver nanoparticles during the annealing process, the nanoparticles show a form similar to the island patterns.²⁴⁾ Figure 4(c) and (d) are composite films with the same number of coatings and different nanoparticle sizes. By comparing the two figures, the smaller of the nanoparticle size, the smoother of the annealed composite film surface; and the larger of the nanoparticle size, the more obvious structure of the island mold. The inset of Fig. 4(d) shows an enlarged SEM image of the composite film, the island-shaped mold structure is obvious and the film surface is rough and uneven.

Figure 5 shows the XRD patterns of GO (red line) and RGO/AgNPs47-10 (blue line). In order to distinguish the influence of the substrate, the XRD pattern of the quartz substrate (black line) was measured and also shown in Fig. 5. The angle of the diffraction peak of the quartz crystal is a broad peak at an angle of $2\theta = 21.20$ and also exists in the other two color diffraction images. The sharp diffraction peak of GO at an angle $2\theta = 10.60$ corresponds to the C (002) crystal plane.²²⁾ The Bragg formula shows that the interlayer spacing is 0.83 nm. After heat treatment reduction, the C (002) diffraction peak²⁵⁾ of the RGO/AgNPs47-10 film appeared at an angle of $2\theta = 26.20$ with an interlayer spacing of 0.33 nm. Contrast to graphene oxide, the interlayer spacing of graphene becomes smaller, which indicates that most of the oxygen-containing functional groups are removed by hydrogen during the heat treatment, the van der Waals interaction between layers is enhanced.²⁶⁾ At the same time, the XRD peaks of the nanoparticles are not observed in the diffraction pattern because fewer nanoparticles in the film have weaker diffraction signals.

Fig. 6 Absorption spectra of RGO/AgNPs28 composite films with different numbers of graphene layers.

Fig. 7 The relationships between the sheet resistance of RGO/AgNPs composite films and the number of RGO layers.

3.3 Optical and electrical properties of graphene oxide/silver nanoparticle composite films

3.3.1 Analysis of optical characteristics of composite films

Figure 6 shows the absorption spectrum of the RGO/AgNPs28 composite films. As shown in the absorption spectrum, the characteristic peaks of annealed RGO/AgNPs films were shifted to a longer wavelength (260 nm) than that of GO (231 nm), which indicated the reduction of GO under Ar/H₂ heat treatment at 600°C and the electron conjugate of the graphene sheet has been restored because of annealing. In addition, the charge transfer between silver nanoparticles and graphene was also considered to be the cause of the red-shift.²⁷⁾ With the increase of the number of film layers, the absorption characteristic peak intensity of RGO also gradually increases, indicating that the composite film grew uniformly.

3.3.2 Testing and analysis of the composite film sheet resistance

The surface resistances of films are listed in Table 2. Due to the flying out of the nanoparticles during the spin coating process, it was difficult to accurately control the number of nanoparticles deposited on the film. For keeping the number of particles as close as possible, the following preparations were made: First, in each process of preparing the film, the same volume of solution, the same spin coating time and spin coating speed were selected. Second, the conductivity of composite films with the same number of layers was compared. At the same time, the conductivity of five groups

of composite films with the same number of layers and different sizes was compared. Third, according to the SEM image, the number of small-sized nanoparticles was not more than the number of large-sized nanoparticles in the same layer composite films. It excluded the possibility that the large number of small-sized nanoparticles made their surface resistance smaller.

In order to compare the results more intuitively, Fig. 7 shows the relationship between the sheet resistance of RGO/AgNPs composite films and the number of graphene layers. Because of the decomposition of the oxygen functionalities via the thermal annealing treatment of GO film with Ar/H₂ gas, the RGO/AgNPs composite films display excellent electrical property than that of the unannealed GO films and GO/AgNPs composite films. By analyzing the surface resistance of RGO/AgNPs28-*n*, it can be seen that the sheet resistance of the films decrease from 7.086 kΩ/sq (*n* = 3) to 0.392 kΩ/sq (*n* = 10) with the increasing of assembly cycles. For the RGO/AgNPs47-*n* films, the sheet resistance decrease from 17.232 kΩ/sq (*n* = 3) to 1.514 kΩ/sq (*n* = 10). In other words, the electricity of film can be improved by increasing the thickness of film. At the same time, the square resistances of RGO-5 and RGO-6 without added silver nanoparticles are 102.15 kΩ/sq and 36.5 kΩ/sq respectively, which are much higher than RGO/AgNPs composite films. The higher resistance of graphene films is mainly due to the higher interface resistance and higher transport barriers of electrons between graphene sheets.²⁸⁾ At the same time, Fig. 4(a) shows the SEM surface morphology of the RGO-6 film without nanoparticles. By measuring the sheet resistance of

Table 2 Sheet resistances of the obtained films.

Samples	Square resistance(kΩ/sq)				
	<i>n</i> =3	<i>n</i> =4	<i>n</i> =6	<i>n</i> =7	<i>n</i> =10
GO	>10 ⁶	>10 ⁶	>10 ⁶	>10 ⁶	>10 ⁶
GO/AgNPs	>10 ⁶	>10 ⁶	>10 ⁶	>10 ⁶	>10 ⁶
RGO/AgNPs28- <i>n</i>	7.086	3.202	0.920	0.560	0.392
RGO/AgNPs47- <i>n</i>	17.232	10.743	3.225	2.416	1.514

the film, the electrical conductivity of the graphene film is illustrated. Figures 4(b), (c), and (d) shows the silver domain images formed by the nanoparticles after annealing, and the size of the silver domain is less than 1 μm . The four-probe resistance meter is used to measure the square resistance of the film surface, and the distance between the probes is 1 mm, which is much larger than the size of the silver domain. Therefore, the conductivity of the composite film cannot be the role of the individual AgNPs, which indicates that the silver nanoparticles embedded in the graphene film enhance the conductivity of the composite film. In the graphene/silver nanoparticle composite film, the conductivity of the film is mainly contributed by the electron transport in the following parts: electron transport in the graphene sheet, electron transport between the graphene sheet interface, and electrons in the nanoparticle and graphite transmission between olefin sheets.²⁹⁾ After the electrostatic self-assembly and spin-coating technology, the links between graphene and nanoparticles, and the links between graphene flakes are effectively strengthened, the transmission barrier of electrons in the network is greatly reduced to form a good conductive network channel. As the thickness of graphene increases, the coverage of graphene on the film surface increases, the concentration of nanoparticles also increases, the number of electron transmission channels increases, and the sheet resistance of the film decreases. Through the combination of cyclic self-assembly and spin-coating, sufficient and good contact between graphene and nanoparticles is achieved, and the electrical properties of the film are better optimized. By comparing the square resistances of RGO/AgNPs28-n and RGO/AgNPs47-n films, the conductivities of the films increase with the decrease of the size of the nanoparticles. The increase in conductivity is attributed to the contribution of the size effect of AgNPs to the RGO network. Uniform and small AgNPs are easily distributed on RGO flakes to form an AgNPs/RGO network. Compare with larger AgNPs, the small AgNPs can provide more contact area between AgNPs and RGO to improve electrical performance.

4. Conclusions

In summary, the electrostatic self-assembly and spin-coating technology was used to prepare the RGO/AgNPs composite transparent conductive film. According to this method, the links between graphene and nanoparticles, and the links between graphene flakes were effectively strengthened, and the conductivity of the films was greatly improved. The results showed that the conductivity of RGO/AgNPs composite films not only increased with the decreased of particle size, but also increased with the increased of self-assembly and spin coating times. The sheet resistance of RGO/AgNPs28-10 film was only 0.392 k Ω /sq, which showed excellent conductive performance. At the same time, the absorbance of the composite film increased as the film thickness increased. The composite film with excellent photoelectric performance and good stability can be used in high-performance photovoltaic devices.

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