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Research on the important properties of Graphene/AgNWs composites

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Abstract. Nano-material refers to small particles with a size within 100nm. It has received widespread attention from many industries because of its different performances of the light, electricity, heat and other industries that are different from conventional materials. In recent years, new nanomaterials such as AgNWs and graphene have attracted considerable attention worldwide due to their extremely high electrical conductivity and light transmission. However, AgNWs are less stable and graphene is less homogeneous in terms of resistance; thus, improving the performance by hybridizing the two composites has become a major research goal. In this paper, the synthesis methods of graphene and graphene/AgNWs composites are presented, and various properties of the composites, such as electrical conductivity, flexibility, and stress-strain capability, are also presented. The comparative analysis of these properties concludes that the excellent properties of graphene/silver nanowire composites have great potential for development and still need to be explored continuously.

Keywords: graphene, AgNWs, composites, properties.

1. Introduction

Graphene is a new two-dimensional material formed by the arrangement of sp2-hybridized carbon atoms, which is the basic unit constituting other stonewall materials. It was first obtained in 2004 by the Geim group at the University of Manchester, UK, by mechanical exfoliation with adhesive tape [1]. Since then, it has rapidly become a hot spot for research in materials, chemistry, and physics due to its unique mechanical-optical-chemical properties and other properties. Metal-graphene nanocomposites are formed by dispersing metal nanoparticles on graphene sheets. Currently, common loading metals include gold, silver, copper, etc., among which silver nanoparticles have unique properties, and thus the preparation and application of silver-graphene nanocomposites have received widespread attention. This paper introduces common methods for the preparation of graphene, including physical methods and chemical synthesis, and also introduces methods for the preparation of composites, including the one-step hydrothermal method, chemical reduction method, sol-gel method, electrochemical deposition method, and two-phase method. In addition, this paper integrates the experimental findings of previous work done to study the properties of graphene/silver nanowire composites. For example, in terms of electrical conductivity, Huiying Li* et al. found that the resistance was reduced from 650 Ω to 27 Ω after making the composites from a single layer of graphene, which improved the electrical conductivity of graphene films; in terms of flexibility, Jinlei Miao* et al. conducted a sandwich structure of graphene/silver nanowire composites that were subjected to up to 500 cycles of bending and found to

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still have good flexibility; In terms of stress-strain capability, Mohd Mustaqim Rosli* et al. found that the G and 2D bands of graphene shifted sharply to lower frequencies after the composite by analyzing Raman spectra, which improved the electrical conductivity, influenced by strain. This paper focuses on graphene fabrication methods and the synthesis of graphene/AgNWs composites, as well as investigating the electrical conductivity, flexibility and stress-strain properties of graphene/AgNWs materials.

2. Graphene preparation methods

Graphene has excellent optical, electrical, and mechanical properties and has important application prospects in materials science, micro and nano processing, energy, biomedicine, drug delivery, etc. It is considered the revolutionary material of the future.

There are two traditional methods to prepare graphene: one is the physical method, i.e., top-down size reduction process, mechanical exfoliation method, liquid phase exfoliation method, etc. The other is the chemical method, i.e., the bottom-up construction process: chemical vapor deposition, redox method, epitaxial growth method, etc.

2.1. Mechanical stripping method

The mechanical exfoliation method is a method that uses mechanical or ultrasonic forces to disrupt the van der Waals forces between graphite layers of bulk materials to exfoliate the nanolayer from the upper layer of the main body, which can be done by repeatedly taping the graphite material surface and exfoliating a single layer or few layers of graphene [2]. The advantages of this method are low cost and a simple process; the disadvantages are poor controllability and its unsuitability for mass production.

2.2. Liquid-phase exfoliation method

The liquid-phase method is a preparation method that takes graphite as raw material, disperses it in a specific solution, and uses oxidation, intercalation or thermal expansion to overcome the van der Waals forces between the layers of graphite flakes to obtain thin-layer graphene. The advantages of this method are simple preparation process and more complete graphene structure, and the disadvantages are high energy consumption and low yield.

2.3. Chemical vapor deposition method

Chemical vapor deposition is a process that uses vapor or gaseous substances to react at the gas-solid interface to produce solid deposits that can grow graphene materials on the surface of metal substrates. This method can increase the graphene area, high quality, controllable number of layers and adjustable band gap. However, this method is a high-temperature process with a complex transfer process and prone to defects.

2.4. Redox method

Graphene is prepared by reacting graphene with strong oxides to form graphene oxide, which weakens the van der Waals forces between graphite molecules, and then removing the oxygen-containing functional groups on the surface of graphene by adding reducing agents [3]. The advantages of this method are scalable production, simple process, low cost, and high controllability. However, the conductivity is poor due to the high number of oxygen-containing functional groups in the graphene structure.

2.5. Epitaxial growth method

This method involves heating single-crystal SiC at a high temperature (1000–1500 °C) to sublimate the silicon atoms on its surface, and the remaining carbon atoms can be rearranged on the surface of single-crystal SiC to form graphene. The graphene obtained by this method has a more complete crystal structure, but the high temperature environment required for the preparation process makes the preparation cost higher.

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3. Preparation of silver nanowire/graphene composites

Graphene/AgNWs composites have excellent properties. How to prepare such composites has also been much discussed, the most representative ones are the following five methods.

3.1. One-step hydrothermal method

This method is used to produce graphene/silver nanowire materials by solid deposition under high temperature and pressure. This method synthesizes graphene/silver nanowire composites in a one-step, green manner without any toxic solvents or chemicals to reduce graphite oxide. The composites produced by this method can be used as sensors with excellent sensitivity for electrochemical detection of hydrogen peroxide [4]. The one-step hydrothermal method has the advantages of low cost, simple preparation, environmental friendliness and greenness.

3.2. Chemical reduction method

Metal nanoparticles and their complexes were synthesized using plant-derived natural products, $AgNO_3$ as AgNPs precursor and gallic acid (GA) as reducing and stabilizing agent, and graphene/silver nanowire composites were synthesized by the 'one-pot cooking' method through the green reduction of silver nitrate precursor on the surface of graphene [5]. The AgNWs in the resulting composites were uniformly dispersed on the graphene lamellae with good surface-enhanced Raman spectral scattering effects.

3.3. Sol-gel method

It refers to the preparation of composite materials by a series of hydrolysis and condensation reactions using metal nitrides or metal alcohol salts as precursors. Graphene oxide nanoflakes were prepared by depositing SiO_2 on the surface of graphene oxide using a combination of ultrasound and sol-gel method, and silver nanoparticles were deposited onto this flake substrate to produce graphene/silver nanowire composites [6].

3.4. Electrochemical deposition method

It refers to the direct electrodeposition of silver nanoparticles on graphene substrates. Metal nanoclusters exhibit exceptionally high catalytic activity for oxygen reduction reactions due to their small size and unique electronic structure. Controlled electrochemical reduction of silver nanoclusters (agnc) (< 2 nm in diameter) on nitrogen-doped graphene (NG) can be performed using an effective single-stranded oligonucleotide sequence (ssDNA) as a template [7]. This method is green, environmentally friendly and efficient. It also shows very unique electronic and optical properties due to the specificity on the molecular scale. Because of their high specific surface area and unique electronic and catalytic properties, they are receiving increasing attention in the field of electrochemical catalysis.

3.5. Two-phase method

It refers to the preparation of graphene/silver nanowire composites at the interface of two different phases, such as in the toluene and aqueous phases [8]. Compared to the one-step synthesis method, the two-phase method is easier to control the degree of monodispersion and particle size of silver nanoparticles on the graphene sheet layer.

4. Characterisation of graphene/AgNWs composites

4.1. Electrical conductivity

The presence of vacancy defects in graphene films leads to high resistance values. In order to reduce the resistance, percolation theory is used to demonstrate that the combination of AgNWs with monolayer graphene can improve the electrical conductivity of graphene films [9]. Figure 1 shows electron micrographs of graphene and silver nanowire composites and two mechanisms of AgNWs reduce inter-sheet defects in graphene explained by Monte Carlo method of percolation [10,11]. According to Figure

1 (c) and (d), silver nanowires provide a superior electron transfer pathway than graphene inter-sheet hopping. The other is that silver nanowires provide new conducting bridges at graphene grain boundaries. As far as the present study is concerned, the good conductivity of graphene and silver nanowire composites can be applied to high-performance transparent conductive electrodes for flexible displays, solar cells and wearable electronic devices [12].

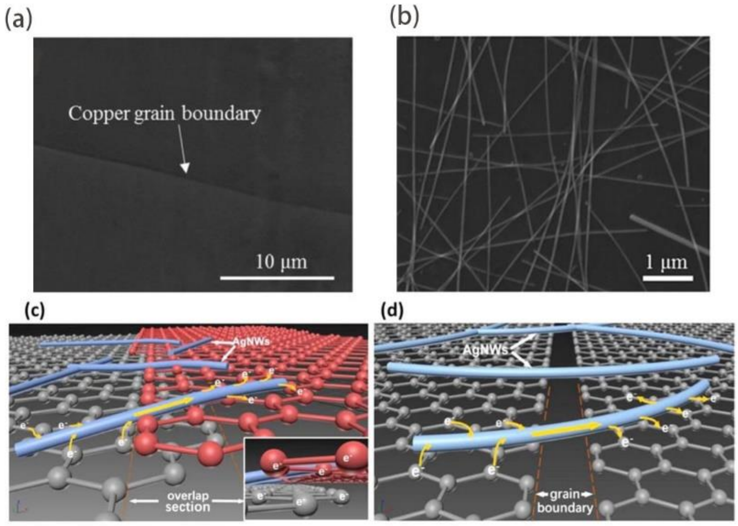

Figure 1. Relationship between graphene and AgNWs composites. (a) SEM image of graphene on copper. (b) SEM images of AgNWs on graphene at two different magnifications. (c) AgNWs provide a better skip Electron transfer path between Graphene sheets. (d) AgNWs provide a new conductive bridge at the grain boundary of Graphene.

Nowadays, some known conductive oxides such as N-type oxide semiconductor indium tin oxide ITO, although it has good electrical and optical properties, but ITO is mechanically brittle and prone to cracking during bending indium scarce resources [13]. That is why we are desperately looking for substances to replace conductive oxides. We have various ideas to reduce the resistance value of graphene, change the properties of AgNWs, or change the contact between graphene and AgNWs.

In order to reduce the resistance value of graphene and to better improve the conductivity of the composite, there are various ways, including chemical doping, nitrogen plasma treatment, double doping, and chemical deposition of ITO nanoparticles.

4.1.1. Chemical doping. Chemical doping is used to adjust and control the properties of graphene with chemical reagents, which lowers the sheet resistance value of graphene. We can use potassium doping of graphene with potassium nitrate (KNO_3) solution, which makes the potassium ions in the aqueous solution adsorbed to the surface of graphene to produce n-type doping to modify the electrical properties of monolayer, bilayer and trilayer graphene [14]. The biggest advantage of using potassium nitrate is that it does not cause graphene defects. According to Figure 2 (b), we can find that the absence of D-peak of mono, bilayer and trilayer graphene proves the high quality of graphene and the absence of defects.

4.1.2. Nitrogen plasma treatment. For nitrogen plasma treatment, we generally use a low-temperature method; the biggest advantage compared to other doping methods is that it does not need high temperature annealing. However, according to Figure 2 (c), we can see obvious D-peaks in Raman diagram, which indicates that the doping method with nitrogen plasma will make the graphene surface defective.

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4.1.3. Double doping. Double doping refers to adding different dopants to the top and bottom of graphene. The best result is p/p type double doping (p-type doping:HNO_3) [15]. According to the Raman plot in the Figure 2 (d), we can see that the G and 2D peaks are flattened after bottom and double doping, and no d-band peak is observed at any stage of doping, indicating that HNO_3 treatment does not break the chemical bonds of graphene and there are no defects on the graphene surface.

4.1.4. Chemical deposition of ITO nanoparticles. The chemical deposition of ITO nanoparticles was performed by depositing 10% tin-doped indium tin oxide nanoparticles on graphene, and the ITO solution was synthesized by an environmentally friendly aqueous sol-gel method. From the Raman spectra in Figure 2 (e), we see that the graphene has heterogeneous peaks, but the annealed graphene has good properties. According to Figure 2 (f), we can conclude that the red shift indicates the presence of electron doping, the blue shift indicates the presence of hole doping and the intensity of the D-peak and 2D-peak of the annealed graphene curve did not increase, indicating that the graphene has good properties after annealing, and there are no obvious vacancy defects and hybridization on its surface.

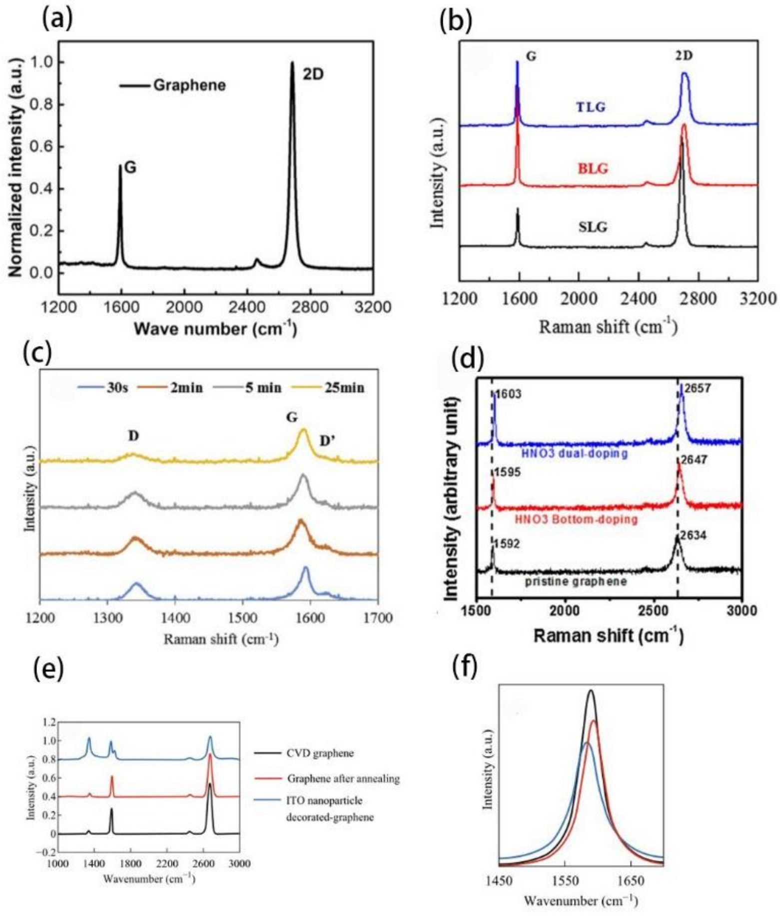

Figure 2. Different composite types of graphene films were analyzed by Raman spectroscopy: (a) silver nanowire binding: I2D/IG=2, indicating that the graphene films are monolayers (b) potassium nitrate doping: single, bilayer, and trilayer graphene films lack D peaks, and graphene has no defects (c) nitrogen plasma doping: there are obvious D peaks, and graphene has defects on the surface (d) double doping: G peaks and 2D peaks are flat-shifted, no D peaks, no defects in graphene (e) Chemical deposition of ITO nanoparticles: with heterogeneous peaks, unchanged intensity of D and 2D peaks after annealing, good performance (f) Chemical deposition of ITO nanoparticles: red-shifted, with electron doping; blue-shifted, with hole doping.

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4.2. Flexibility

Graphene and AgNWs can be attached to the filter membrane through electrostatic interaction, which in turn can form a sandwich structure of AgNWs/graphene/filter membrane as Figure 3 (a) shown. The composite membrane of this structure has good flexibility and can be bent within a certain angle. Based on this sandwich structure, we can lay the composite structure of AgNWs and graphene flat in the shape of paper, as shown in Figure 3 (b), to further explore its flexibility. Ultrathin AgNWs with a diameter of 20 nm were sandwiched between novel polydopamine functionalized graphene (PFG) and poly(3,4-ethylenedioxythiophene) (PEDOT) in Figure 3 (c) and (d) shows [16]. This sandwich structure not only induced effective welding of the AgNW network, but also enhanced the adhesion between the network and the substrate, leading to its effective load transfer during bending, stretching and scraping. After further investigation of its flexibility, it was found that this electrode maintained its excellent electrical conductivity even after 500 cycles of bending, and its surface has good flexibility.

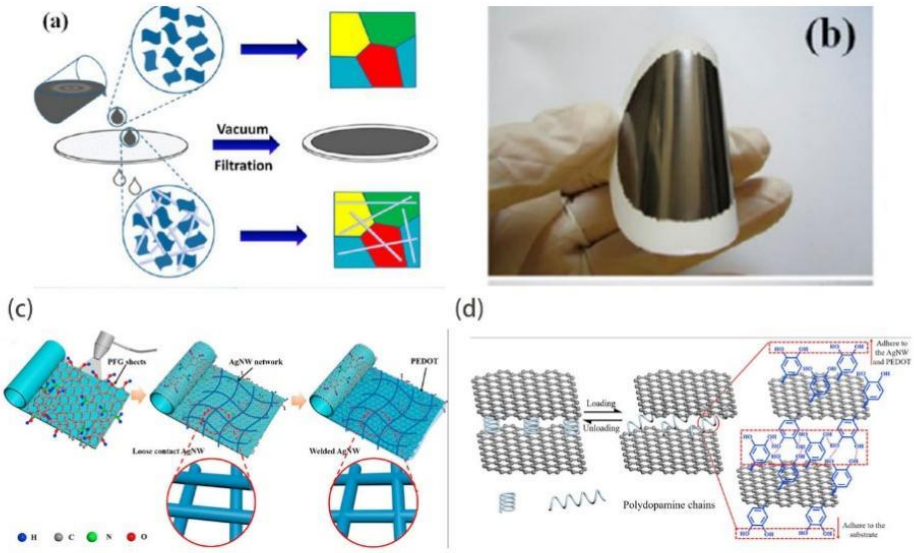

Figure 3. Mechanism and properties of graphene/AgNW (a) Graphene/silver nanowire composite on a filter membrane. (b) The graphene/silver nanowire composite bends a lot and does not break easily. (c) The mechanism of welding ultra-thin AgNWs with PFG and PEDOT to form a 3D interweave conductive network at low temperatures. (d) The mechanism of load transfer and adhesion of PEDOT/AgNW/PFG under bend and adhesion test.

4.3. Stress-strain analysis

Tensile test tests were performed by QuickTest QTS3 instrument with known size specimen area and strain rate at ambient temperature, and tensile stress was calculated by the equation s=F/A0, and stress-strain was applied at 15% MPa. According to Figure 4 (f), it was concluded that the incorporation of graphene and silver nanoparticles improved the stress-strain of the composites, probably because the two-dimensional structure of graphene cross-linked with silver nanoparticles strengthened the the structure of the composites [17]. In addition, the spectra of graphene under silver nanowire-induced strain were analyzed by Figure 4 (a), (d) and (e), it was found that the G and 2D bands of graphene shifted sharply to lower frequencies, yielding longer carbon-carbon bond lengths, and this shift was related to strain, enhancing surface interactions and charge transfer, and improving electronic conductivity [18].

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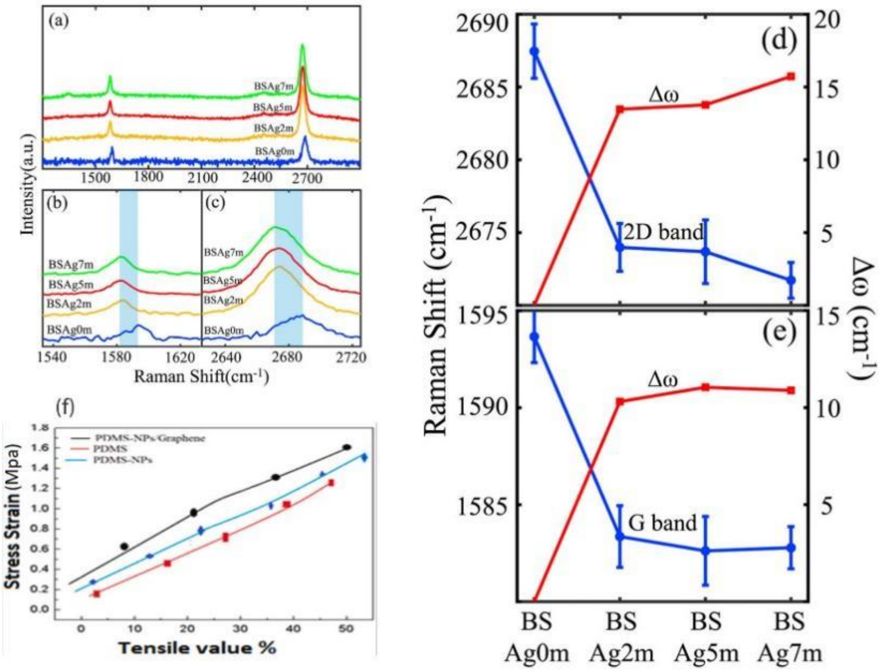

Figure 4. Raman spectra of the graphene on a blank quartz substrate and AgNWs decorated quartz substrate. (a) Full Raman spectra for graphene on blank quartz substrate and AgNWs decorated quartz with different AgNWs density. (b) Zoom in G band, Raman spectra of graphene on quartz substrate containing different AgNWs density. (c) Zoom in 2D band. (d) Shifting value (Δω) for Raman 2D band of graphene, respectively, under strain effect induced by AgNWs with different density. (e) the same for G band. (f) Tensile response of the fabricated composites of PDMS at applied stress at 15% strain.

5. Conclusion

Graphene/AgNWs composite is a promising new material with good electrical conductivity, flexibility and stress-strain properties. By summarizing the analysis and discussion of three typical properties of this composite material by previous authors, it is found that the addition of AgNWs to graphene materials can improve the electrical conductivity and reduce the surface defects of graphene in composites; transfer electrons more effectively during stretching and bending and form sandwich-type composites to improve electron conduction. Because there are many properties of graphene/AgNWs that are worthy of further exploration, such as sensitivity, repeatability, response time, etc., only three of these important properties are selected for discussion in this paper, and subsequent researchers can continue to study them in more depth on the basis of this paper.

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