Synthesis of Graphene/Metal Nanocomposite Film With Good Dispersibility via Solvothermal Method

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This study present a general approach for the preparation of Ag-Grapheme nanocomposites in a water-ethylene glycol system using graphene oxide as a precursor and Ag as building blocks. The metal nanoparticles are adsorbed on graphene oxide sheets and play a pivotal role in catalytic reduction of graphene oxide with ethylene glycol, leading to the formation of Ag-Grapheme nanocomposites. The morphology and structure of the obtained material are examined by XRD, SEM, TEM and FT-IR. The size and morphology of the particles are influenced by the the concentration of $AgNO_3$ solution. Because of the existence of Ag particles, graphene sheets are well separated in the film obtained via vacuum filtration method. The electroconductibility of graphene/Ag film is investigated by four point resistivity test system. It is found that the electroconductibility of the film is increasing with the rising of the $AgNO_3$ solution concentration and the maximum value is 2.94scm^{-1} with the 0.15mol L^{-1}AgNO_3 solution.

1. INTRODUCTION

Graphene is a monolayer of carbon atoms that are tightly packed into a two-dimensional, honeycomb crystal structure [1]. Due to its astonishing properties including high thermal stability and mechanical strength and especially the highest natural mobility of all known materials at room temperature, graphene offers great opportunities in the areas of nanophotonics [2], nanoelectronics [3], nanosensor [4], supercapacitors [5], catalysis [6], and batteries [7]. Graphene can be obtained by many methods such as mechanical exfoliation of bulk graphite [8], epitaxial chemical vapor deposition on substrates [9] and chemical vapor deposition starting from carbon precursors [10]. Although the

graphene with the thickness control can be prepared by these methods, the large-scale preparation of the graphene is less effective and during the solution-phase preparation process of graphene, a challenge question is how to avoid the aggregation reaction of graphene nanosheets and obtain the graphene with high individual dispersion.

In order to reduce the aggregation reaction of the grapheme nanosheets and obtain the graphene with good electrical conductivity and high individual dispersion, some inorganic nanoparticals, such as metals or semiconductors have been intercalated into the interlayer of the graphene nanosheets [11–13]. On the other hand, hybrid nanomaterials provide an efficient strategy for promoting the functionality of materials. Many efforts have been done, which include graphene nanosheets and diverse metallic nanoparticles, like gold [14], silver [15,16] and platinum [17].

In this paper, electrically conducting particle, Ag, was selected to form graphene/Ag nanocomposite via solvothermal method. Results showed that graphene/Ag nanocomposite with good dispersity and electroconductibility was obtained.

2. EXPERIMENTAL

2.1. Sample preparation

Natural graphite (carbon content: 99.9%) was purchased from Qingdao Aoke Co., China. Analytical-grade reagents, including silver nitrate ($AgNO_3$), ethylene glycol and absolute ethanol, were purchased from Sinopharm Chemical Reagent Co., Ltd., China, in analytical purity and used without further purification.

Graphite oxide was prepared from purified natural graphite according to the method reported by Hummers and Offeman.[18] A 10 mg portion of graphite oxide powder was dispersed in 10 mL of water by sonication for 1 h, forming stable graphene oxide colloid. Then 20 mL of ethylene glycol and 100 mL $AgNO_3$ solution (0.03 mol L^{-1}, 0.06 mol L^{-1}, 0.09 mol L^{-1}, 0.12 mol L^{-1}, 0.15 mol L^{-1}) were added to the solution with magnetic stirring for 30 min. Subsequently, the mixture was put in an oil bath and heated at 100 °C for 6 h with magnetic stirring. The graphenes with Ag nanoparticles on them were then separated from the ethylene glycol solution in the centrifuge and washed with deionized water five times. The resulting products were dried in a vacuum oven at 60 °C for 12 h.

For film preparation, The graphenes with Ag nanoparticles on them were-dispersed in water with sonication at a concentration of 0.1 mg mL^{-1}. The dilute suspension was vacuumfiltrated using a mixed cellulose ester membrane with 25 nm pores (Millipore). The film was allowed to dry in a vacuum at 30∘C.

2.2. Characterization

The crystal structure of the composites was characterized by a Philips 1730 powder X-ray diffractometer (XRD) with Cu Kα radiation. The morphology and microstructures were observed by a JEOL 6460 scanning electron microscope (SEM). High resolution transmission electron microscopy

(HRTEM) was conducted on a JEOL 2011 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. Infrared (IR) spectra of the samples were collected on a Nicolet Avatar 360 FTIR Fourier transform infrared (FTIR) spectrometer. The film resistance was tested on RTS-9 four point resistivity test system at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 gives the XRD patterns of prepared samples. As shown in Fig. 2, there are some obvious diffraction peaks of graphite oxide or graphite were observed from the Graphene XRD pattern which can be assigned to the (1 0 2), (1 0 3) and (1 0 5) planes of the C crystal (JCPDS No. 79-1470). That perhaps owing to not completely exfoliated of graphite in preparing propress. Recent studies[19,20] have shown that, if the regular stacks of graphite oxide or graphite are destroyed, for example, by exfoliation, their diffraction peaks become weak or even disappear. It does not matter whether the existence state of the carbon sheets was graphene oxide or graphene in these composites; it was confirmed that the regular layered structure of graphite oxide or graphite was destroyed. After the chemical reduction by solvothermal method, the graphene/Ag composite showed characteristic peaks at $28.6°$, $32.2°$, $64.4°$ and $39.1°$ with high intensity, which can be assigned to the (2 2 0), (3 1 1) and (1 1 1) planes of the cubic Ag crystal (JCPDS No. 01-1167) indicating that graphene/Ag composite was successfully prepared during our experiments.
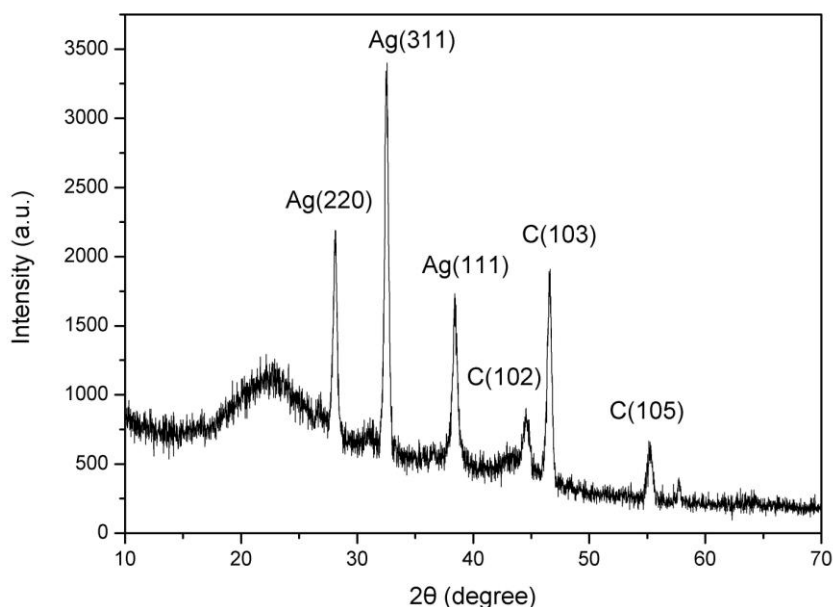

Figure 1. XRD patterns of Graphene/Ag composites

TEM images of Graphene/Ag composites with different concentration of $AgNO_3$ (Fig. 2) show the wide distribution of Ag particles ranging in the diameter of 10–30 nm. It can be observed that

graphene sheets are decorated by Ag particles which well separated with each other and distributed randomly. Fig. 2(a) shows that the smaller particles are spherical in shape where as the larger nanoparticles are in an elongated form in Fig. 2(c) . The elongated shape could be the result of the aggregation of the two or more particles together (Fig. 2(b)and(c)). The size and shape of the Ag nanoparticles are also influenced by the concentration of AgNO3 solution. Most of the nanoparticles are spherical in shape when synthesized using $0.09 molL^{-1}$ $AgNO_3$ solution. As observed in Fig. 2(b) and (c), the synthesis of the Ag nanoparticles using higher concentration of Ag salt ($0.15 molL^{-1}$) produces variable particle shapes.
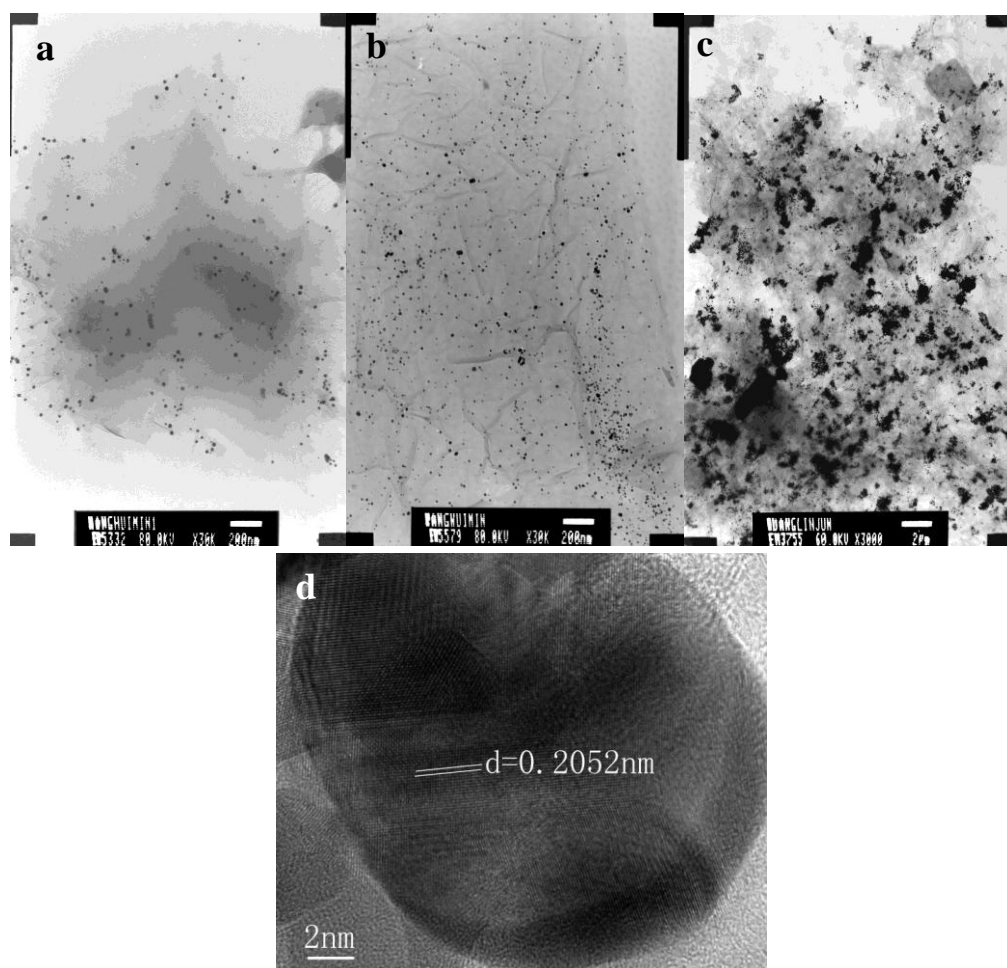

Figure 2. TEM images of Graphene/Ag composites with different concentration of $AgNO_3$ (a)$0.09 molL^{-1}$,(b)$0.12 molL^{-1}$,(c)$0.15 molL^{-1}$,(d)HRTEM image of Graphene/Ag composite

At this concentration nanoparticle with different shapes such as spherical, triangular, pentagonal, ellipsoid and rod are obtained. Nanoparticles are seen to be agglomerating when concentration of $AgNO_3$ solution used is higher than 0.12molL-1 resulting in formation of bigger particles. Fig. 2(d) is the high-resolution image of Ag particles reduced by ethylene glycol. The fringe

spacing shown in the image is about 0.2052 nm, which agrees well with the (2 0 0) lattice plane reported in the JCPDS (No. 04-0783).
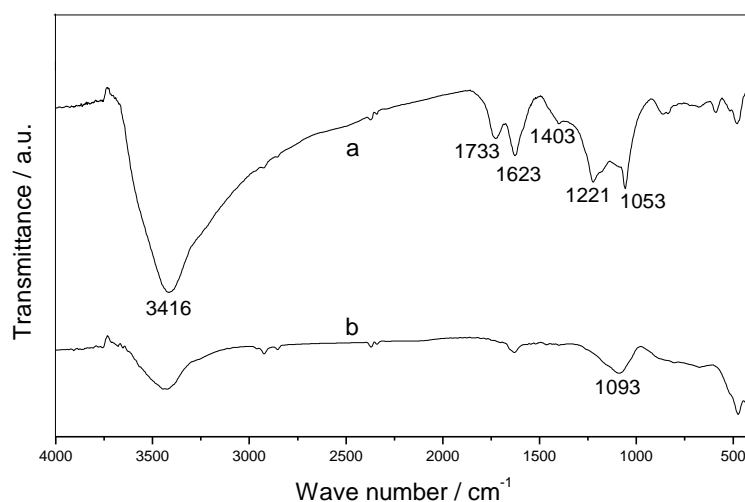

Figure 3. FTIR spectra of Graphene-oxide (a) and as-prepared Graphene/Ag composite(b)

There are few reports on the Ag nanoparticles decorated on the graphene sheets. Recently Pasricha et al. reported the solution-based synthesis of Ag nanoparticles into the graphene sheets without using any reducing agent [21]. In this report it is confirmed byTEM analysis that the Ag nanoparticles of size ranged 3–12nm were decorated on to the graphene sheets. Shen et al. also reported the solution based synthesis of Ag nanoparticles in CCG using mixed reducing agent and found the homogeneous distribution of Ag nanoparticles of size range 5–10nm on CCG [22]. Formation of bigger particle due to agglomeration of the smaller particles was also observed. Zhou et al. reported the single step in situ synthesis of Ag nanoparticles on single layer graphene surface under thermal condition without any surfactant or reducing agent [23]. This method resulted Ag particles in the size range of few nanometers to 1μm with non uniform size. Whereas the Ag noparticles, obtained by using solution phase synthesis, the method reported in this study, are about 5–25nm in size with variable shape. Lu et al. also reported a novel synthesis method for the decoration of aerosol Ag nanocrystals on the graphene sheet [24]. The aerosol Ag nanocrystals were synthesized using a mini-arc plasma reactor and subsequent deposition of as-synthesized nanocrystals onto a graphene. HRTEM analysis conformed that the Ag nanocrystals of about 5–10nm were attached to the graphene sheet. It is also observed that the shape of the nanoparticle is dependent on concentration of $AgNO_3$ solution.

The as-obtained Graphene-oxide and Graphene/Ag composite samples were preliminarily analyzed by means of FTIR spectroscopy and the results are shown in Fig. 3. The relatively broad peak at 3416 cm^{-1} and relatively sharp peak at 1623 cm^{-1} indicate that the samples contain adsorbed water. The peaks at 1403 cm^{-1} and 1053 cm^{-1} can be assigned to the deformation vibration of O–H and stretching vibration of C–O, respectively. Characteristic bands of C=O carbonyl stretching and C–O–C

vibration located at 1733 cm^{-1} and 1221 cm^{-1} are very weak, indicating the small amount of these two functional groups [25]. After the solvothermal reduction, removal of oxygen-containing groups is clearly indicated by the gradual disappearance of the most absorption bands as shown in Fig. 3.

In order to test the electroconductibility of the products, graphene film and graphene/Ag composite film were prepared via vacuum filtration method. Fig. 4 is The Graphene/Ag composite film obtained via vacuum filtration (a) and SEM image of the fracture surface (b). It can be seen that Ag particles are intercalated in the interlayer of grapheme sheets.
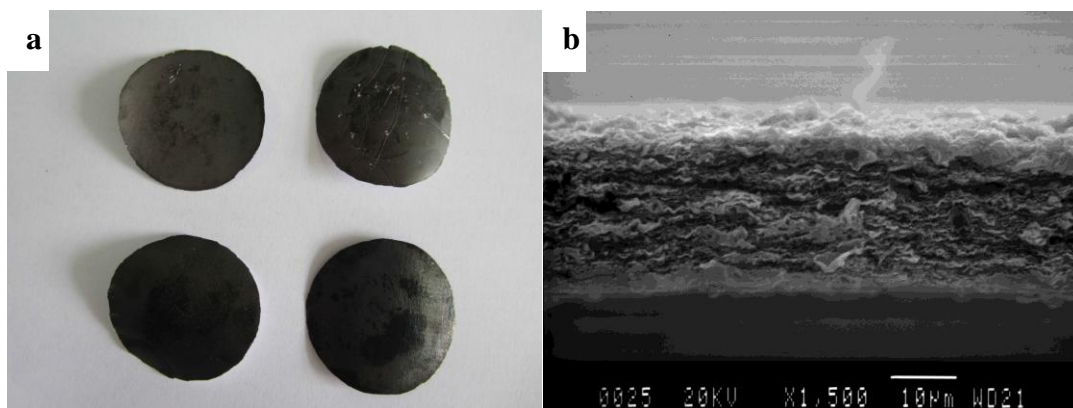

Figure 4. The Graphene/Ag composite film obtained via vacuum filtration (a) and SEM image of the fracture surface (b)
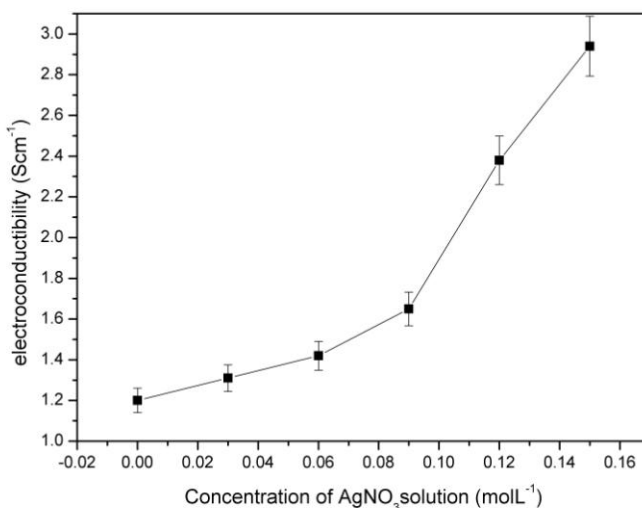

Figure 5. The electroconductibility of Graphene/Ag composite film with different concentration of AgNO$_3$ solution

Fig.5. show the electroconductibility of Graphene/Ag composite film with different concentration of AgNO$_3$ solution. It is observed that the electroconductibility of Graphene/Ag composite film is increasing with the rising of the AgNO$_3$ solution concentration and the maximum

value is 2.94scm^{-1} with the 0.15mol L^{-1}AgNO$_3$ solution, which is higher than that of the pure grapheme film with same carbon concentration, 1.21scm^{-1}. Although the density of the film is decreased by the intercalation of Ag particles(see Fig.5.b), but the good conductivity of Ag will make contribution to the excellent conductivity of graphene/Ag film. Recently Juan Yang et al. reported the synthesis of Graphene/Ag film using difderent reducing agent [26]. In this report the conductivity values are 1.18 scm^{-1} (using ethanol) and 1.67 scm^{-1}(using hydrazine).

4. CONCLUSIONS

Graphene/Ag nanocomposite with Ag particles randomly deposited on the graphene sheets was prepared by solvothermal method. The particle size and morphology of Ag were influenced by the reaction condition, especially the concentration of AgNO$_3$ solution.Graphene sheets were well separated by the deposition of Ag. The nanocomposite film of graphene deposited with Ag particles has good electroconductibility, which is possibly due to the peculiar conductivity of graphene sheets and the synergistic effect with the deposited Ag particles.

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