

Green synthesis of AgNPs/reduced graphene oxide nanocomposites and effect on the electrical performance of electrically conductive adhesives

Jinfeng Zeng^{1,2,3} · Xun Tian^{1,2,3} · Jingsi Song^{1,2,3} · Zhong Wei^{1,2,3} · Steven Harrington⁵ · Yagang Yao⁴ · Lei Ma⁵ · Yanqing Ma^{1,2,3}

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Abstract Here we report silver nanoparticles/reduced graphene oxide (AgNPs/rGO) nanocomposites were synthesized by a facile approach based on four green reductants using silver nitrate (AgNO_3) and graphene oxide (GO) as a precursor. Field Emission Scanning Electron Microscopy and High Resolution Transmission Electron Microscopy (HRTEM) have been employed to investigate morphological characteristics and exfoliation of reduced graphene oxide (rGO) sheets. The structure of AgNPs/rGO was determined by X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy. Electrical conductive adhesives (ECAs) were prepared by mixing the micro silver flakes, AgNPs/rGO nanocomposites and epoxy together. To achieve the best electrical conductance, the optimal average size of the silver nanoparticles (AgNPs) in AgNPs/rGO composites is found to be about 20.7 nm. The results show that the

resistivity of ECAs consisting of the AgNPs/rGO nanocomposites (0.2 wt% AgNPs/rGO and 69.8 wt% silver flake) was decreased compared with control sample (ECAs filled with 70 wt% silver flake). In particular, the resistivity of ECA filled with glucose-AgNPs/rGO (A-AgNPs/rGO) is $8.76 \times 10^{-5} \Omega \text{ cm}$. In summary, A-AgNPs/rGO was determined to be a promising candidate filler for conductivity improvement of ECAs.

1 Introduction

In the past decade, graphene sheet have attracted great attention due to its excellent mechanical, thermal [1], optical and electrical properties [2, 3], as well as the higher specific surface than single-walled carbon nanotubes [4]. To further exploit the advantages of graphene, a new type of materials, graphene composite, has been widely explored. Among these graphene composites used in ECAs filler, a great of efforts have been made to achieve a grafting Ag nanoparticales (AgNPs) decorated on graphene sheets. Usually graphene sheets are produced from graphene oxide (GO). However, oxygen-containing functional groups attached on GO sheets will make GO almost insulating [5]. Therefore, in order to achieve a good electric conductance, an effective deoxygenating process must be carried out to make the GO become conductive [6, 7] and also to guarantee that AgNPs efficiently grow on the reduced graphene oxide (rGO) sheets. High temperature thermal annealing is highly dioxygen approach, but the required temperatures is more than 900 °C [8–10]. Meanwhile, it is very difficult for AgNPs to grow on the surface of rGO sheets. Until now, many methods for synthesis of silver nanoparticles/reduced graphene oxide (AgNPs/rGO) nanocomposites have been studied. Manoj K. Singh and

✉ Lei Ma
maleixinjiang@tju.edu.cn

✉ Yanqing Ma
mayanqing@shzu.edu.cn

¹ School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, China

² Key Laboratory for Green Processing of Chemical Engineering of XinJiang Bingtuan, Shihezi, China

³ Engineering Research Center of Materials-Oriented Chemical Engineering of Xinjiang Bingtuan, Shihezi, China

⁴ Suzhou Institute of Nanotech and Nanobionics, Chinese Academy of Science, 398 Ruoshui Road, SEID, SIP, Suzhou, Jiangsu, People's Republic of China

⁵ Tianjin International Center of Nanoparticle and Nanosystems, Tianjin University, Tianjin 300072, People's Republic of China

co-workers [11] synthesized AgNPs/rGO by the concurrent reduction of Ag^+ and GO in the presence of hydrazine hydrate. Xiu Zhi Tang [12] reported a one-step method to synthesize AgNPs/rGO via using formaldehyde as the reductant and poly (N-vinyl 1–2 pyrrolidone) (PVP) as the surface-treating agent. Hassan [13] reported on the microwave irradiation treatment method to reduce the graphene oxide employing oleylamine as a reducing agent. Tao Long [14] also prepared AgNPs/rGO using the microwave assisted method. The reductants used in synthesis methods were formaldehyde or hydrazine. Use of these reductants is undesirable due to their being highly toxic, posing health risks, and necessitating complex manipulation.

Currently, methods by which to obtain AgNPs/rGO nanocomposites via one-step are garnering a great deal of interest [15–18]. This is because AgNPs/rGO could potentially exhibit not only the individual properties of AgNPs and rGO, but also other novel properties, such as distinctive and high catalytic activity, antibacterial and electrochemical properties, and strong surface enhanced Raman effect. There have been few similar studies have reported, which uses AgNPs/rGO as filler in ECAs, such as Xiao Peng [19] and Behnam Meschi Amoli [20] who prepared the mixture ECAs filled with silver-graphene nanocomposites and silver flakes. It effectively improved the conductivity of ECAs compared with conventional ECAs. However, AgNPs has fairly large size which show some inconvenience in term of cost and also quite high curing temperature will potentially lead to the method confront of extra industrial aspect challenge. Meanwhile, Cui [21] considered that the electrical performance of ECAs could be affected by the size and dispersion of conductive fillers.

In this report, four green reductants have been employed though facile approach to synthesize AgNPs/rGO nanocomposites. In which, the use of glucose as reductants leads to uniformly dispersed AgNPs with narrow size distribution nicely grafted on rGO sheets. The using of glucose owns dual advantages that both the products and reductant are environmentally friendly. Then AgNPs/rGO nanocomposite with silver flakes as conductive fillers are put into epoxy to prepare electrically conductive adhesives (ECAs). Higher conductivity was achieved compare to previous report results.

2 Experiments

2.1 Materials

Graphite flakes (natural, 325 mesh) were purchased from Alfa Aesar. Hydrochloric acid (HCl, 38 %), hydrogen peroxide (H_2O_2 , 30 %) and ethanol were supplied by

Tianjin Fuyu Fine Chemical Co. Ltd. Sodium nitrate (NaNO_3 , ≥ 99.0 %) was purchased from Aladdin Industrial Corporation. Concentrated sulfuric acid (H_2SO_4 , 95.0–98.0 %) and sodium borohydride (NaBH_4 , ≥ 97.0 %) were purchased from Chengdu area Kelong Chemical Co. Ltd. Silver nitrate (AgNO_3 , ≥ 99.8 %) was supplied by Xi'an Chemical Corporation. Potassium permanganate (KMnO_4 , ≥ 99.5 %), glucose, Trisodium citrate dehydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, ≥ 99.0 %), Sodium hydroxide (NaOH , ≥ 96.0 %) was supplied by Tianjin Shengyu Chemical Co. Ltd. Epoxy resin (862), used as an epoxy binder, was purchased from Guangzhou Topyon trade Co. Ltd. The catalyst 1-(2-Cyanoethyl)-2-ethyl-4-methylimidazole (2E4MZ-CN, ≥ 70.0 %) and 4-methylcyclohexane-1, 2-dicarboxylic Anhydride (MHHPA, ≥ 98.0 %) were supplied by TCI (Shanghai) Development Co. Ltd. The micro silver flakes were purchased from Strem Chemicals, Inc. All of the chemicals were used directly without further purification.

2.2 Synthesis of graphene oxide

Graphene oxide (GO) was prepared from natural graphite flake by employing a modified version of Hummers' method [22]. In brief, graphite powder (1 g) was added into an ice bath containing NaNO_3 (1 g), concentrated H_2SO_4 (100 mL) solution. KMnO_4 (6 g) was slowly added to the solution, while maintaining the temperature below 20 °C. The mixture was stirred in the ice bath for 2 h and then put in 35 °C water bath for 0.5 h. Water at a temperature of 70 °C (46 mL) was then added, followed by hydrogen peroxide (30 wt%, 20 mL) solution to terminate the reaction. The mixture was filtered and washed with distilled water several times to remove any excessive acid and inorganic salts. The resulting GO was dried overnight at 55 °C.

2.3 Synthesis of AgNPs/rGO nanocomposite by glucose (A-AgNPs/rGO)

The A-AgNPs/rGO was synthesized through one-step method according to the Ref. [23]. Briefly, glucose (7.5 g) was added into GO solution (150 mL, 1 mg mL^{-1}) which was stirring until the glucose dissolved. Meanwhile, 0.55 mol L^{-1} ammonia was added dropwise into 100 mL AgNO_3 aqueous solution (0.06 mol L^{-1}) until the precipitate disappeared. Then, the mixed solution was poured into the GO solution and stirred for 5 min. The solution was allowed to sit undisturbed at room temperature for 1.5 h. The product was centrifuged and washed with deionized water to remove any impurities. The obtained products were dried by lyophilization.

2.4 Preparation of the AgNPs/rGO nanocomposite using trisodium citrate dihydrate (B-AgNPs/rGO)

B-AgNPs/rGO was produced via the method in Ref. [21]. In short, 125 mg GO was dissolved in 200 mL deionized water and submitted to sonication for 2 h to form a stable solution. 82 mg AgNO_3 was dispersed into 200 mL of deionized water. The AgNO_3 aqueous solution was mixed with GO suspension and, after ultrasonic treatment for 45 min, was refluxed at 140 °C for 1 h. Trisodium citrate dehydrate solution (100 mL, 1 mmol L^{-1}) was added dropwise. The reaction was then maintained at 130 °C for 30 min. Finally, the product was centrifuged, washed with deionized water and dried by a freeze-drying method.

2.5 Synthesis of AgNPs/rGO nanocomposite using sodium hydroxide (C-AgNPs/rGO)

Synthesis of C-AgNPs/rGO employs the method developed by Lizhi Yuan [24]. 100 mg GO was dispersed in 200 mL deionized water with the aid of sonication for 2 h. Afterward, 315 mg AgNO_3 and 400 mg NaOH were added and stirred for another 10 min, and refluxed for 2 h at a temperature of 100 °C. The final product will be washed with deionized water and freeze dried.

2.6 Preparation of AgNPs/rGO nanocomposite using sodium borohydride (D-AgNPs/rGO)

Base on Sheng-Yun Huang's report [25], 50 mg GO dispersed in 25 mL distilled water with the aid of sonication for 2 h. Then AgNO_3 aqueous solution (1.18 mL, 0.05 mol L^{-1}) was added, further sonication was applied for 2 h, followed by a 6 h of stirring at room temperature. The solution was then poured into a culture dish, after which it was dried at 85 °C for 24 h. After that, the dried products were soaked in sodium borohydride ethanol solution (0.35 mol L^{-1}) at a temperature of 60 °C for 5 h. The final product was filtered and washed with deionized water.

2.7 Preparation of ECAs with silver flakes and AgNPs/rGO filler

The polymer matrix consisted of epoxy resin, HMMPA and 2E4MZ-CN with a weight ratio of 1:0.85:0.0185. The silver flakes were added into the polymer matrix mixed with AgNPs/rGO nanocomposite. Two strips of polyimide adhesive tape were placed on a cleaned glass slide separated by a distance of 3 mm. The mixed composite was bladed uniformly into the gap between the two strips. The

polyimide adhesive tape was removed from the glass slide after ECA has been cured at a temperature of 150 °C for 2 h.

2.8 Characterization of graphene oxide and AgNPs/rGO

The dispersion and morphology of the AgNPs were characterized by a Field Emission Scanning Electron Microscope (FESEM) from Hitachi Ltd, and High Resolution Transmission Electron Microscopy (HRTEM) from FEI Tecnai G20. The Raman spectra of nanocomposites were acquired using Laser confocal Micro-Raman Spectroscopy (LabRAM HR800). X-ray diffraction (XRD) (Bruker D8 advanced X-ray diffractometer) was used to detect the crystalline structure of the AgNPs/rGO. Quantitative surface analyses of AgNPs/rGO nanocomposites were characterized by X-ray photoelectron spectroscopy (XPS) (AMICUS/ESCA 3400, Shimadzu, Japan) with a monochromatic $\text{MgK}\alpha$ X-ray source ($h\nu = 1486.6$ eV). Particularly, all the as-synthesized samples were freeze-dried before testing except D-AgNPs/rGO. The curing film thickness was measured by a thickness gauge (Shanghai Chuanlu Measuring Tool Limited Liability Co.). Resistivity measurement was performed by using a RTS-8 4-point probe station system (Guangzhou four-probe electronic technology Limited Liability Co.).

3 Results and discussion

3.1 Morphology and structural characterization

The morphology of four AgNPs/rGO nanocomposites (A: A-AgNPs/rGO, B: B-AgNPs/rGO, C: C-AgNPs/rGO, D: D-AgNPs/rGO) were studied using FESEM. The results were shown in Fig. 1. It shows that AgNPs are evenly dispersed on the thin graphene layer. The size of the AgNPs in Fig. 1b (9.5 nm) are smaller than those of AgNPs in Fig. 1a (20.7 nm). Moreover, AgNPs were densely dispersed on the surfaces of rGO sheets as shown in Fig. 1c. Here, the existence of large size of AgNPs on the surfaces of rGO sheets could be the reason which causes the accumulation of rGO layers. Figure 1d shows that both large and small AgNPs can coexist on graphene sheets. The size and uniformity of AgNPs, as well as the approach of drying AgNPs/rGO nanocomposites have key effects on the morphology of the graphene sheets and, furthermore, influences the formation of conduction channel which direct to electrical performance of resultant ECAs [26]. Figure 2 shows the HRTEM images of AgNPs/rGO nanocomposites. The very nearly transparent rGO sheets were doped by the silver nanoparticles and only of few

Fig. 1 FESEM images of the AgNPs/rGO nanocomposites (**a** A-AgNPs/rGO, **b** B-AgNPs/rGO, **c** C-AgNPs/rGO, **d** D-AgNPs/rGO)

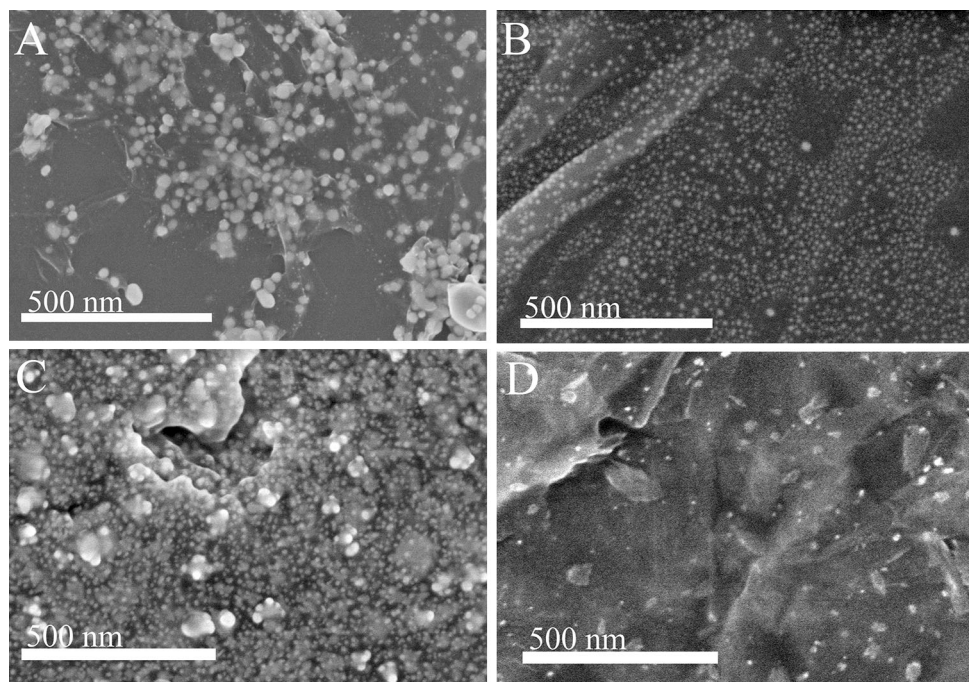
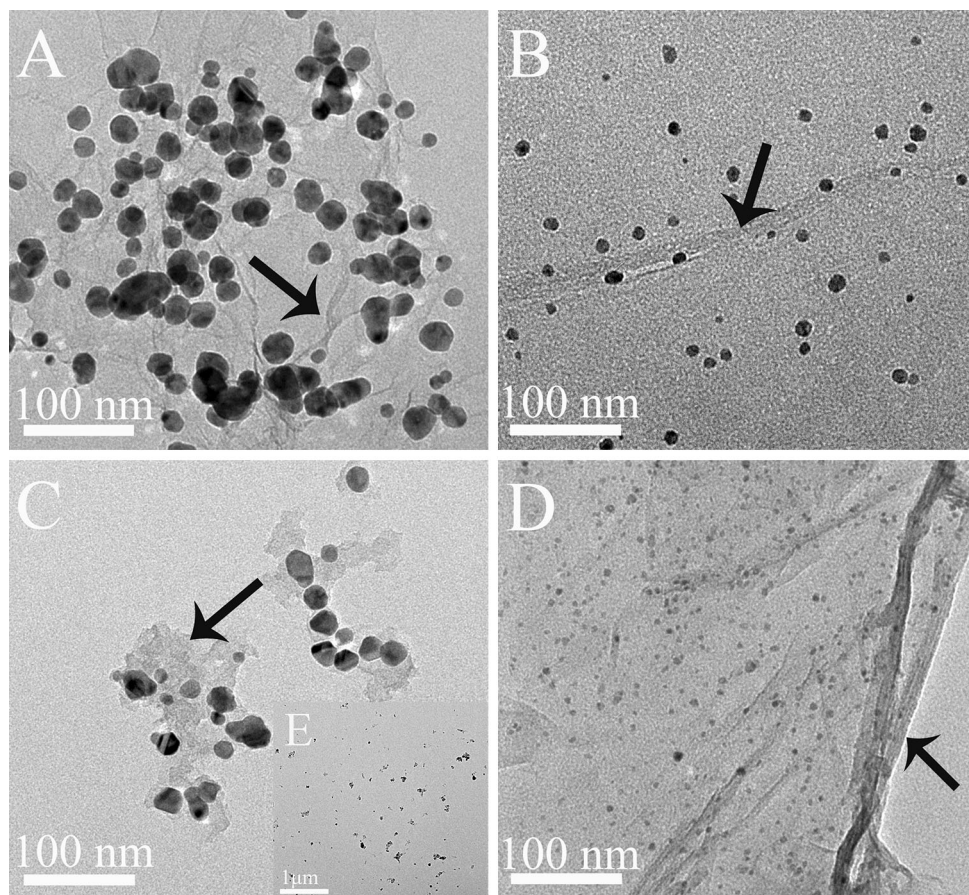


Fig. 2 HRTEM images of the AgNPs/rGO nanocomposites (**a** A-AgNPs/rGO, **b** B-AgNPs/rGO, **c** C-AgNPs/rGO, **d** D-AgNPs/rGO, **e** the overall appearance of the sample C)



AgNPs were scattered out of the rGO sheets. This revealed the strong grafting interaction between the rGO and AgNPs [27]. The GO sheets bear epoxy functional groups, carbonyl, carboxyl groups and hydroxyl on their basal planes which have been used as anchors for adsorption of AgNPs. Consequently the attached AgNPs may then prevent the crumpling together of rGO sheets. It was also found that a few layers of the rGO sheets were uniformly decorated with AgNPs on both sides. This also indicates that a certain amount of AgNPs decoration could efficiently prevent rGO sheets from stacking during the reduction [29].

Figure 3 shows XRD patterns of graphite, GO and four AgNPs/rGO nanocomposites. The diffraction peak at $2\theta = 26.68^\circ$ from the e line corresponds to (002) reflection of graphite [7, 30]. The distance between graphene layers was evaluated to be 0.33 nm by using Bragg's equation. The GO (f line) showed the 001 peak at around 11.09° . Line f shows that the d-spacing of the GO is increased to 0.80 nm. The d-spacing of GO is larger than graphite. This indicates that oxygen-containing groups were attached to rGO sheets [31]. There are no observable peaks of graphite or GO as there are expected to be at position a, c, or d lines in the XRD patterns. Some studies posit that the diffraction peaks of GO and graphite become weak or disappear after exfoliation. The attached particles may also prevent the restacking of these graphene sheets, and therefore the characteristic diffractions peaks of the layered structure disappears [28]. The peaks observed at about $2\theta = 38.0^\circ$, 44.2° , 64.5° and 77.4° are attributed to the (111), (200), (220) and (311) crystalline planes of face-centered cubic silver (corresponding to PDF2-2004 card). The above analysis confirmed that the AgNPs successfully decorated on the rGO sheet. However, there is little difference between the b line, the d line and the other two lines. The peak at $2\theta = 11.09^\circ$ can be assigned to the 001 crystalline plane of GO (Fig. 3b). The weak diffraction peaks of

AgNPs are caused by low loading of AgNPs [27]. Peak at $2\theta = 27.6^\circ$ comes from the diffraction indices of Ag (002) facet. This can be attributed to the preferred growth orientation adopted by silver when the sodium citrate was used as a reducing agent. The characteristic peak of Ag_2O (b and d line) at around 32.1° can be comes from deflection of the small size of AgNPs [32]. For AgNPs of smaller size, the concentration of the oxides becomes correspondingly greater due to the larger surface-volume ratio.

3.2 Raman analysis

The Raman spectra of AgNPs/rGO with 532 nm excitation are shown in Fig. 4. It shows that the Raman signals of AgNPs/rGO are stronger than that of GO. The reason for this is attributed to the different clustering of AgNPs [33], which corresponds to TEM images (Fig. 2), XRD patterns (Fig. 3) and XPS scans (Fig. 5). All samples show similar Raman features in the range of $800\text{--}3300\text{ cm}^{-1}$, where D band is ascribed to the sp^3 carbon of defective sites. The D band shifted to a lower wave number appearing near 1351 , 1344 , 1343 , and 1342 cm^{-1} for A-AgNPs/rGO, B-AgNPs/rGO, C-AgNPs/rGO and D-AgNPs/rGO, respectively. The G band is due to the plane vibrations with E_{2g} phonon [34]. The G band locates these wave number at 1587 , 1579 , 1583 and 1576 cm^{-1} , respectively. The 2D band is the second order mode of the D band [35, 36] and appears at 2682 , 2666 , 2706 , 2681 cm^{-1} . The shift of these wave numbers suggests charge transfers occurs between the AgNPs and rGO. This further indicates the interaction between them, actually evident the dopant of AgNPs to the graphene. This interaction shows the silver nanoparticles do indeed dock to graphene; in other words, the interaction between them implies the combination of these two materials. A very weak band around 2900 cm^{-1} is associated with the second-order of D + G [37]. The intensity ratio of the I_D/I_G is a

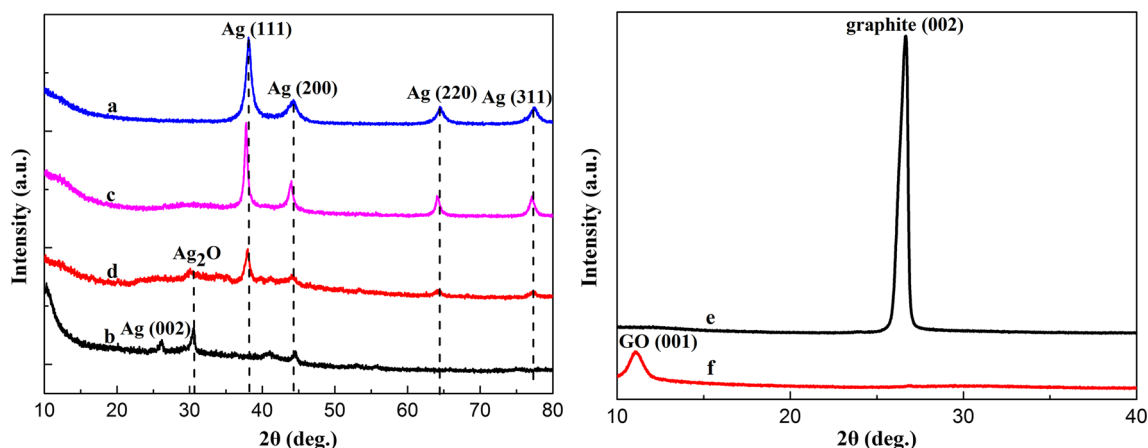


Fig. 3 XRD patterns of graphite, GO and AgNPs/rGO nanocomposites (a A-AgNPs/rGO, b B-AgNPs/rGO, c C-AgNPs/rGO, d D-AgNPs/rGO, e graphite, f GO)

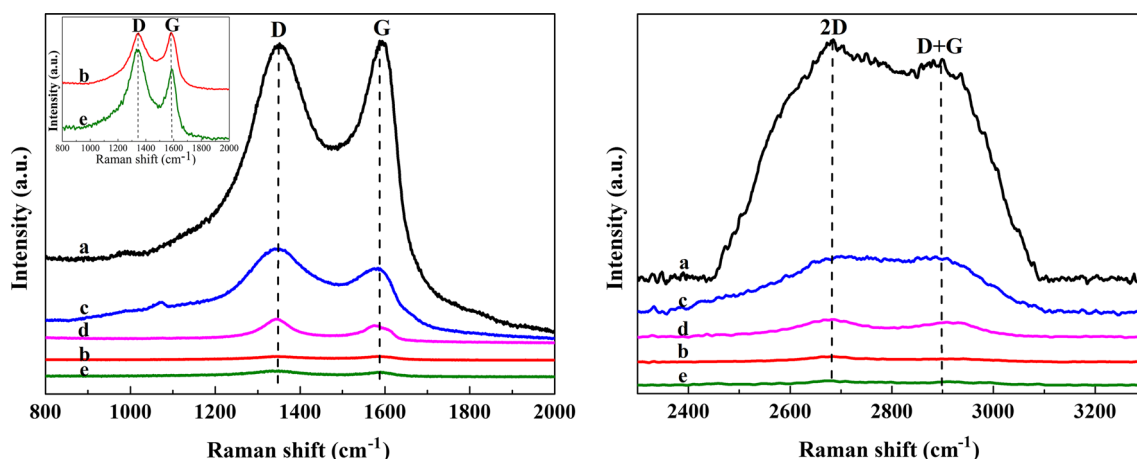


Fig. 4 Raman spectra of AgNPs/rGO nanocomposites and GO (a A-AgNPs/rGO, b B-AgNPs/rGO, c C-AgNPs/rGO, d D-AgNPs/rGO, e rGO), insert enlarged spectra of b and e lines

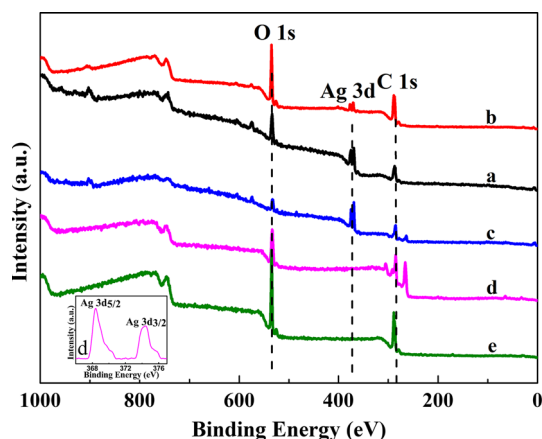


Fig. 5 XPS wide-scans of nanocomposites (a A-AgNPs/rGO, b B-AgNPs/rGO, c C-AgNPs/rGO, d D-AgNPs/rGO, e GO, insert Ag 3d XPS enlarged spectra of D-AgNPs/rGO)

significant parameter by which to evaluate the disorder of the crystal structure of graphene. It is 1.356, 1.851, 1.601 and 1.42 for A-AgNPs/rGO, B-AgNPs/rGO, C-AgNPs/rGO and D-AgNPs/rGO, respectively. Apparently, A-AgNPs/rGO has lower I_D/I_G value than all other nanocomposites and it is almost equal to that of reduced hydrazine hydrate rGO ($I_D/I_G = 1.340$). The significant drop of I_D/I_G of A-AgNPs/rGO is attributed to the decreased disorder and fewer defects in graphene after reduction using glucose compare to using other three different agents [38, 39]. Even though the ideal conductance of graphene requires no defects, these selfsame defects could practically provide ideal adsorption sites on the surface of rGO for nanoparticles. In our case, therefore a large number of AgNPs anchor on the surface of A-AgNPs/rGO though those defects and consequently significantly decreased the intensity ratio I_D/I_G in A-AgNPs/rGO from relatively strong bonding between AgNPs and rGO. In previous reported experiments

[40, 41], some researchers have confirmed that the change of shape of the 2D band from a sharp peak to flat peak indicates the number of graphene layers decreased from 10 to monolayer. It was found that the 2D band of AgNPs/rGO become wider and almost disappeared for C-AgNPs/rGO, A-AgNPs/rGO, B-AgNPs/rGO, D-AgNPs/rGO. This signifies that the number of rGO layers is less than ten. Additionally, Mohsen Forati-Nezhad [42] considered that the change of I_{2D}/I_D can be attributed to the surface defects caused by surface decoration of the nanocarbon materials. The I_{2D}/I_D values of AgNPs/rGO were 0.2007, 0.1408, 0.1233, 0.2075 corresponding to curve a to curve d in Fig. 4. Based on this, we can conclude that the loading rates of AgNPs in A-AgNPs/rGO (curve a) and D-AgNPs/rGO (curve d) are higher than those of C-AgNPs/rGO (curve c) and B-AgNPs/rGO (curve b). The ECA filled with A-AgNPs/rGO exhibited excellent conductivity of $8.76 \times 10^{-5} \Omega \text{ cm}$, which is lower than that of the other three composites fillers. The increase in conductivity results from the contributions of the attached AgNPs and rGO in creating conducting pathways.

3.3 Elements analysis by XPS

In order to determine the functional groups and decoration of AgNPs on the surface of rGO sheet, we carried out a further XPS measurement. In Fig. 5, the existence of the Ag 3d peak in the wide-scan spectra of AgNPs/rGO is clearly evident. Furthermore, the peaks with binding energies at 368.3 and 374.3 eV can be assigned to metallic Ag 3d_{5/2} and Ag 3d_{3/2} [43], respectively. Doublet components about spin-orbit splitting were measured to be 6 eV indicating the complete formation of metallic silver supported on rGO sheets. These observations are consistent with the XRD result.

The C 1s spectra of the A products (from Fig. 6a) can be deconvoluted into four peaks with binding energy 285.3, 286.3, 287.5 and 289.3 eV, with the associated bonds C–C, C–OH, C=O, and O=C–OH, respectively. The C 1s spectra of B product (Fig. 6B) can be deconvoluted into four peaks at around 284.8, 285.7, 287.4 and 289.0 eV, which corresponds to the bonds C–C, C–OH, C=O, and O=C–OH. The C 1s spectra of C product (Fig. 6c) were also deconvoluted into four peaks at around 285.0, 286.6, 288.1 and 289.6 eV. The last product (Fig. 6d) was deconvoluted into three peaks at around 284.5, 285.7 and 287.4 eV, with associated the bonds C–C, C–OH and C=O, respectively. The peak of D-AgNPs/rGO at 289 eV disappears, similar to what was reported in prior studies [44, 45]. The relative atomic content of C–C were 41.80, 31.06, 20.75 and 11.40 % for C-AgNPs/rGO, D-AgNPs/rGO, B-AgNPs/rGO and A-AgNPs/rGO, respectively [46]. Compare with Fig. 6e, the content of C–C (4.15 %) for pure GO, it can be clearly seen that GO is enriched with oxygen functional groups [47]. After chemical reduction, most chemically attached function groups are successfully removed and the portion of carbon species (C–C) clearly increases, suggestion the effective reduction of GO [48].

4 Measurements of electrical properties

Five identical specimens were made from each sample, and at least five different points were measured on each of the five specimens. The resistivity (ρ) of electrical conductivity adhesive was calculated by using the following formula:

$$\rho = \frac{RTW}{L} \quad (1)$$

where ρ is resistivity (Ω cm), R is resistance (Ω), T is the thickness of ECA layer (cm). L is the length (1.5 cm), and W is the width (0.3 cm).

As is well known, electrically conductive fillers are combined together by the bonding of matrix resin and forms electrically conductive channels to achieve electrical conductance. Figure 7a shows the relationship between AgNPs/rGO mass content and electrical resistivity when the total filler content remains 70 wt%. When the mass fraction of AgNPs/rGO reaches 0.2 wt%, the electrical resistivity of A-AgNPs/rGO, B-AgNPs/rGO, and D-AgNPs/rGO ECAs samples decrease to 8.76×10^{-5} , 8.91×10^{-5} and $9.42 \times 10^{-5} \Omega$ cm, respectively. These results show that the electrical resistivity of ECAs filled with AgNPs/rGO nanocomposites all decrease compared to silver flake filled ECAs ($1.75 \times 10^{-4} \Omega$ cm). In summary, AgNPs/rGO nanocomposites of graphene filled ECA exhibits marvelous improvement in conductivity compared to either pure AgNPs or pure graphene filled ECA. However, after with the increase of the concentration of AgNPs/rGO to reaches the maximum conductivity of ECA, the electrical resistivity starts to decreases with continuous increase AgNPs/rGO. This is because electrically conductive channels are formed between contacted Ag–Ag fillers on the surface of rGO sheets. Conductive fillers cannot contact with each other completely after only doped micrometer sized silver flakes in the conductive adhesive because silver flakes formed many gaps and voids. The number of electrically conductive channels is formed.

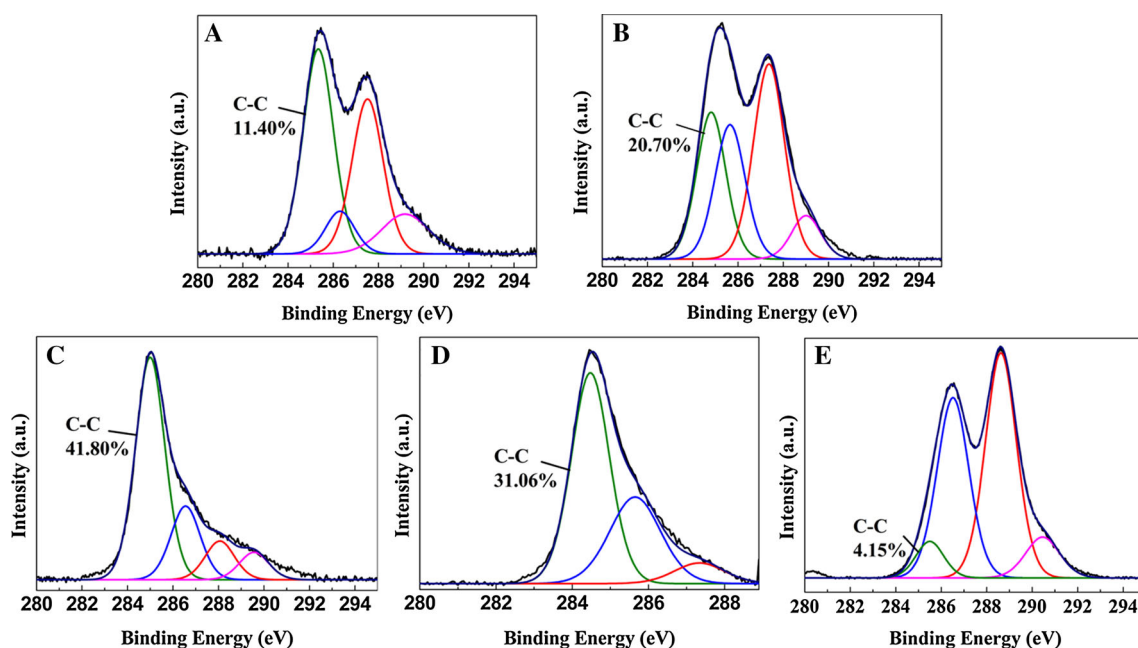


Fig. 6 C 1s narrow-scans XPS spectra of AgNPs/rGO and GO (a A-AgNPs/rGO, b B-AgNPs/rGO, c C-AgNPs/rGO, d D-AgNPs/rGO, e GO)

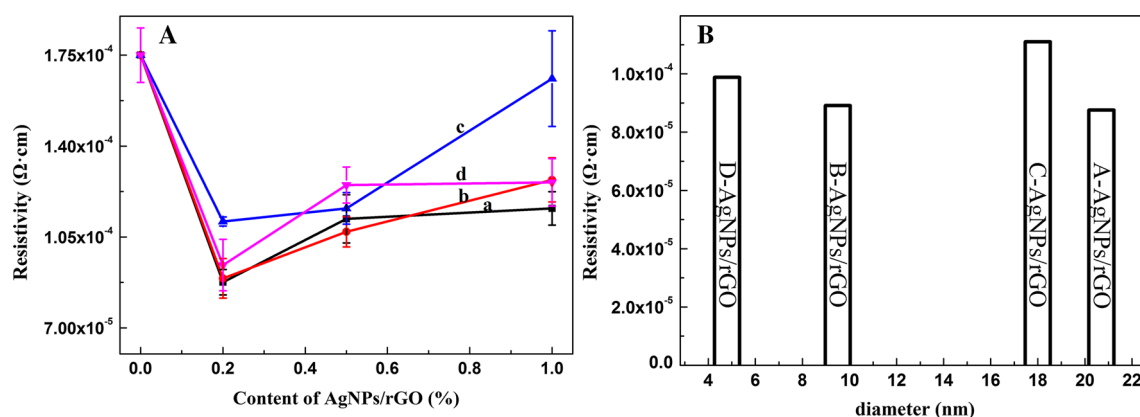


Fig. 7 Relationship between resistivity and the content of AgNPs/rGO nanocomposites (a), relationship between particle size of AgNPs and resistivity (b) (a A-AgNPs/rGO, b B-AgNPs/rGO, c C-AgNPs/rGO, d D-AgNPs/rGO)

AgNPs/rGO nanocomposites can fill in these gaps [49, 50]. Therefore, ECAs composed of AgNPs/rGO nanocomposites and micrometer silver flakes exhibit excellent electrical conductivity properties. The ECA filled with B-AgNPs/rGO nanocomposite has the resistivity lower than that of D-AgNPs/rGO doped with nanocomposite. Thus, the ECA filled with A-AgNPs/rGO has the lowest resistivity as the A-AgNPs/rGO contains a relatively higher content of AgNPs and graphene of lower defects as well as fewer defects after being reduced by glucose. The relationship diagram between the diameter of AgNPs and electrical resistivity is listed in Fig. 7b. The electrical resistivity of ECA filled with A-AgNPs/rGO is lower than the ECAs filled with the other three nanocomposites, and the diameter of AgNPs which on the surface of the A-rGO is the largest of all. Sodium borohydride resulted in AgNPs with the smallest diameters and produced Ag_2O . From the Fig. 1d, it can be seen that the accumulation of rGO layers and decreased the conductivity of ECA filled with D-AgNPs/rGO. Therefore, glucose is the optimal reducing agent, producing AgNPs of suitable diameter (20.7 nm).

5 Conclusions

AgNPs/rGO nanocomposites were successfully prepared by an environmentally friendly method via chemical reducing agents. TEM analysis of AgNPs/rGO showed AgNPs were successfully attached on the surface of rGO, the optimal average size of the AgNPs were about 20.7 nm with a narrow size distribution. Raman revealed low defects in graphene than other AgNPs/rGO nanocomposites after reduced by glucose. XPS shows the high loading of AgNPs on the surface of A-AgNPs/rGO. The conductivity of the ECA was improved by introducing A-AgNPs/rGO. When the mass fraction of A-AgNPs/rGO was

0.2 wt %, the resistivity of the ECAs reached its lowest value of $8.76 \times 10^{-5} \Omega \cdot \text{cm}$. The A-AgNPs/rGO can be a promising candidate filler to improve the conductivity of ECAs.

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