Rare Metal Materials and Engineering
Volume 48, Issue 7, July 2019
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2019, 48(7): 2107-2111.

ARTICLE

Effect of Reduced-Graphene Oxide on Flexible Transparent Films Composed of Reduced Graphene Oxide and Silver Nanowires

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Abstract: We fabricated flexible transparent conductive films composed of silver nanowires (AgNWs) and reduced graphene oxide (rGO) as hybrid transparent electrode and mixed cellulose eater (MCE) as substrate by a vacuum-filtrating method. Effect of rGO on the electrical, optical and mechanical properties of the flexible transparent films were studied. The results show that with the increase of rGO deposition density, the optical transmission at 550 nm has a little decrease, while the sheet resistance (R_s) gradually decreases. Tape tests up to 200 cycles and bending fatigue tests up to 200 cycles were performed by monitoring the in-situ resistance change. The film sustains excellent reliability of the AgNWs/rGO hybrid conductive networks, where the fractional resistance change is little overt increase after tape tests and less than 3% after bending test. The excellent mechanical properties of the AgNWs/rGO film can be attributed to the burying of the AgNWs and RGO film at the surface of mixed cellulose eaters(MCEs).

Key words: silver nanowires; reduced-graphene oxide; flexible transparent conductive film; mixed cellulose eater film

There is an increasing demand for suitable flexible transparent electrodes due to the technological developments in flexible displays. Indium tin oxide (ITO) is the most widely used transparent conductive material because of its high transmittance (T>90%) and low sheet resistance. However, ITO cannot be used as transparent conductive materials on flexible substrates due to its brittleness. In the recent years, silver nanowires (AgNWs) used for fabricating flexible transparent conducting films (FTCFs) for flexible electronics and transparent heater have attracted significant attention for their excellent mechanical, optical, thermal and electrical properties[1-5]. However, the AgNWs networks still suffer from a relatively higher resistance because of the weak bonding between AgNWs [6-12].

As a new class of two-dimensional carbon nanostructure, graphene is considered as one of candidates in flexible electronics [6-15]. It is cheaper than AgNWs and has an abundant material source, greatly improving its feasibility for practical applications. Unfortunately, the value of figure of merit of graphene is usually less than 10, even when synthesized by chemical vapor deposition. For low-cost production of graphene films, reduced grapheme oxide (rGO) sheets are considered as a candidate, which are synthesized by reducing of grapheme oxide (GO) prepared from natural graphite sheet. Films produced with these rGO sheets are low cost but have poor uniformity and high resistances due to the presence of some the oxygen functional groups, which seriously impedes the industrialization of graphene transparent conductive film. Some attempts have been made to blend rGO with AgNWs to increase the number of electrically conductive tunnels or to lower the percolation limit by virtue of increasing the connectivity between the rGO and wires[16-23]. Meenakshi et al[18] fabricated AgNW-rGO hybrid electrode by a dip-coating method. AgNW-rGO transparent conductive electrodes (TCEs) show excellent optoelectrical properties of 27 Ω/sq with T=72% (at 550 nm). The silver nanowires modified by cysteamine were combined graphene nanosheets to form AgNW-graphene hy-

Received date: June 25, 2018
Foundation item: National Natural Science Foundation of China (61302044, 61671140); Zhongshan Science and Technology Projects (2015B2312, 2015B2300)
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brid nanomaterials[19]. AgNW-grap- hene hybrid nanomaterial films show a sheet resistance of 86 Ω/sq with 80% light transmittance. Lee et al[21] fabricated a sandwich-structured graphene/AgNW/graphene transparent conductive film by embedding AgNW network with chemical vapor deposition-grown graphene layers. The graphene/AgNW/graphene TCF exhibits excellent optical and electrical properties (light transmittance is 88.6% at 550 nm and a sheet resistance is (19.9±1.2) Ω/sq.

In previous work, we fabricated the flexible transparent film with AgNWs as conductive materials and mixed cellulose eater (MCE) as matrix[5]. In this work, the flexible transparent AgNWs/rGO hybrid films with the mixed cellulose eater (MCE) as matrix were prepared by the vacuum filtration process[5], and the effect of rGO on electrical and optical and mechanical properties of the AgNWs/rGO films were investigated.

1 Experiment

Silver nitrate (≥99.8%) was purchased from Guangdong Guanghua Chemical Reagent Co., Ltd, poly(vinylpyrrolidone) (PVP, K30, Mw≈10 000) was purchased from Guoyao Group Chemical Reagent Co., Ltd, and ferric chloride (≥99.5%) and sodium nitrate (99.5%) were purchased from Chengdu Kelong chemical Co., Ltd. Ethylene glycol (EG, ≥99.7%), ethanol absolute (≥99.7%), sulfuric acid (98%), hydrazine hydrate (98%) and hydrogen peroxide (30%), potassium permanganate (99.3%), and hydrochloric acid (85%) were purchased from Tianjin Yongda chemical Co., Ltd. Natural graphite flakes were purchased from Nanjing Xianfeng Nanomaterials Co., Ltd. 125 μm-thick polyethylene terephthalate (PET) film were purchased from Shanghai Fei Xia Plastic Hardware Co., Ltd. Water mixed cellulose esters membrane (MCE, *Φ*50, 0.4 μm) were purchased from Tianjin Jin Teng experimental equipment Co., Ltd. Silver nanowires and reduced grapheme oxide were synthesized in our laboratory. All the chemicals were used as received.

Silver nanowires with 90~150 nm in diameter and 20~50 μm in length were synthesized by our reported polyol process [6]. GO was prepared from natural graphite flakes by a modified Hummers method [17]. The rGO was prepared by chemical reduction of graphene oxide with the hydrazine hydrate as the reducing agent. Graphene oxide was dispersed to deionized water by ultrasonic treatment for 2 h. Then the dispersed graphene oxide solution was added into the flask, and hydrazine hydrate was added into the above solution with an electric mixer. The rGO solution was obtained after the reaction solution was kept for 3 d at room temperature. The reaction solution was vacuum filtered with organic cellulose filter. Then the solution was washed with deionized water by vacuum filter until the pH=7.0 of the filtrated solution and then washed 3 times with ethanol absolute. The purified rGO was dispersed into ethanol absolute to ultrasonic treatment for 2 h.

The flexible transparent AgNWs/rGO films with using the mixed cellulose eater (MCE) as matrix were prepared by the improved vacuum filtration process [5]. The fabrication process of AgNWs-MCE film is schematically illustrated in Fig.1.

All scanning electron microscopy (SEM) images were taken on a FE-SEM (Field emission scanning electron microscopy, Hitachi, S3400 N). The sheet resistance of the FTCFs was measured using a ST2263 four-point probe instrument (Suzhou Jingge Co., LTD). Optical transmittance (T_s) spectrum was measured using ultraviolet-visible light detector (UV-1800 SHIMADZU). 3 M tape with finger pressure as a method of mechanical tape test was adopted to evaluate AgNWs/rGO adhesion property to the substrate. The bending test was carried out with lab-made apparatus with software recording film resistance and cycle number.

2 Results and Discussion

SEM images of AgNWs (Fig.2a) and rGO (Fig.2b) are shown in Fig.2. The inserted are the photos of AgNWs and rGO synthesized. Seen from Fig.2a, the diameter of AgNWs is about 90~150 nm and the range of the length is 20~50 μm. rGO sheets with folding structure are observed in Fig.2b. The colors of AgNWs and rGO solution are gray and black, respectively, due to the effect of nano-materials on the light.

Fig.3 shows photos of AgNWs/rGO films with 220 mg·m^{-2} AgNWs and 88, 77, 66 , 55, 38, and 22 mg·m^{-2} rGO. Seen from Fig.3, there is not obvious difference in the transmittance of samples, indicating that rGO sheets have little effect on the transmittance of AgNWs/rGO film under the experimental conditions.

Fig.4 shows T_s spectra of the AgNWs/rGO films with 220 mg·m^{-2} AgNWs and 88, 77, 66, 55, 38, and 22 mg·m^{-2} rGO. The T_s was measured with a transparent MCE film as the reference. The T_s of AgNWs/rGO films at 550 nm is slightly reduced with the increase of rGO deposition density. When the deposition density of rGO is 22, 66, and 88 mg.m^{-2}, the T_s of

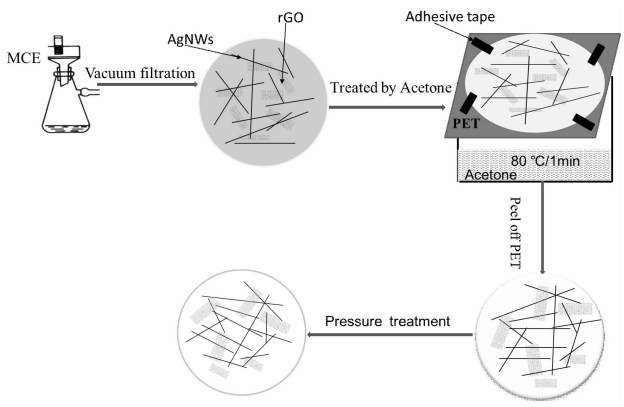

Fig.1 Schematic of fabrication process of AgNWs/rGO-MCE film

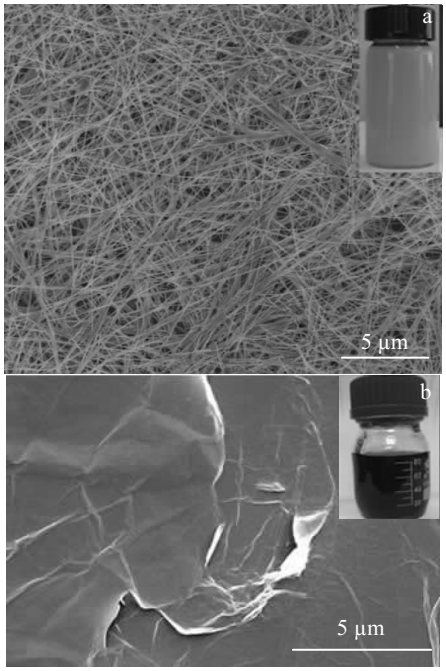

Fig.2 SEM images of AgNWs (a) and rGO (b); inserts are photos of AgNWs and rGO synthesized

film at 550 nm is 82%%, 80%, and 79%, respectively. The result is consistent with Fig.3, indicating that rGO has little effect on the T_s of film. However, when the deposition density of rGO is 77 and 88 mg·m^{-2}, the T_s increases at over 650 nm. This may be associated with the agglomeration of graphene because the agglomeration occurs with the increase of particle content.

Fig.5 shows SEM images of AgNWs/rGO films with 220 mg·m^{-2} AgNWs and 77, 55, 38, and 22 mg·m^{-2} rGO. It is clear that AgNWs and rGO adhere to the MCE, and connect to form conductive network. The rGO sheet is two-dimensional layer nanostructure, so that rGO may cover and connect some discrete AgNWs and prompt closer contact of overlapped AgNWs [15]. However, the agglomeration of rGO sheets is observed in Fig.5, which results in the non-uniform dispersion. We mixed the rGO which was not modified with the AgNWs in the aqueous solution. rGO sheets are difficult to disperse evenly into the water, because of the hydrophobicity of graphene sheets.

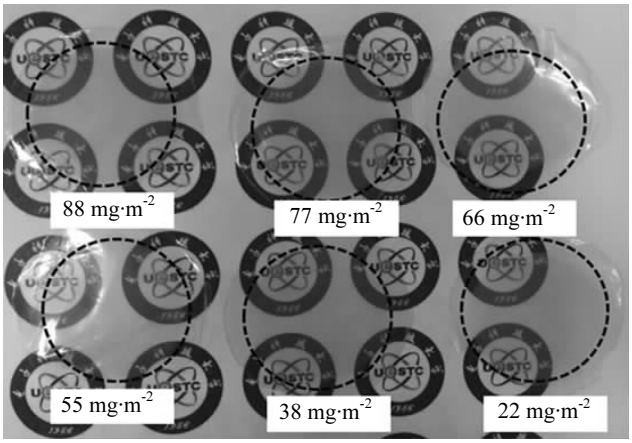

Fig.3 Photos of AgNWs/rGO films with 220 mg·m^{-2} AgNWs and different deposition densities of rGO

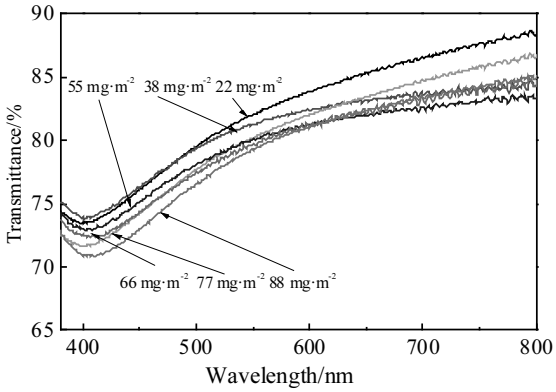

Fig.4 Optical transmittance spectra of AgNWs-rGO films with different rGO deposition densities

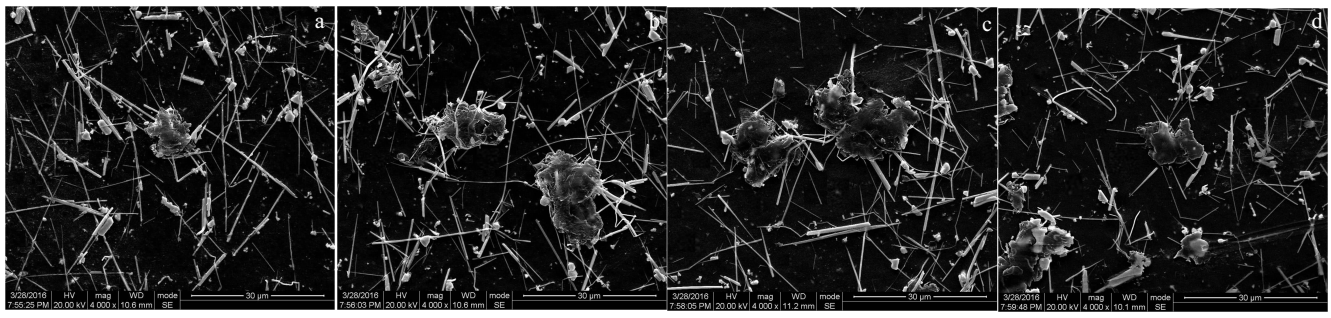

Fig.5 SEM images of AgNWs/rGO films with different rGO deposition densities: (a) 22 mg·m^{-2}, (b) 38 mg·m^{-2}, (c) 55 mg·m^{-2}, and (d) 77 mg·m^{-2}

Fig.6 shows R_s versus rGO deposition density of AgNWs/RGO films with 220 mg·m^{-2} AgNWs and 88, 77, 66, 55, 38, and 22 mg·m^{-2} rGO. With the increase of rGO deposition density, R_s of the film decreases. When the deposition density of rGO is 22, 38, and 88 mg·m^{-2}, the R_s of the film is 129, 83, and 55 Ω·sq^{-1}. The results indicate that rGO may improve the conductivity of AgNWs film [13, 14]. With the mixed AgNWs and rGO as conductive materials, the conductive paths are formed mainly by AgNWs. The rGO is a connection linking discrete AgNWs and a clipper inducting closer contact of overlapped AgNWs so the rGO can improve the conductivity of the film and has litter effect on the transmittance of film.

Three samples with 220 mg·m^{-2} AgNWs and 88, 55, and 22 mg·m^{-2} rGO were used to perform taping test. Fig.7 shows the relationship of R_s of AgNWs/rGO film to test time. As shown in Fig.7, there are little change in R_s after tape tests for 200 times. Fig.8 shows the relationship of R_s of AgNWs/rGO film to cycles of folding up. Seen from Fig.8, the bending test indicates that the change in R_s of AgNWs/rGO film is about 3% even after 200 cycles of compressive or tensile bending when the deposition densities of rGO is 22 mg·m^{-2}; while the change in R_s of AgNWs-rGO film is little even after 200 cycles of compressive or tensile bending when the deposition densities of rGO is 55 and 88 mg·m^{-2}. The results indicate that rGO may improve the mechanical robustness of the film.

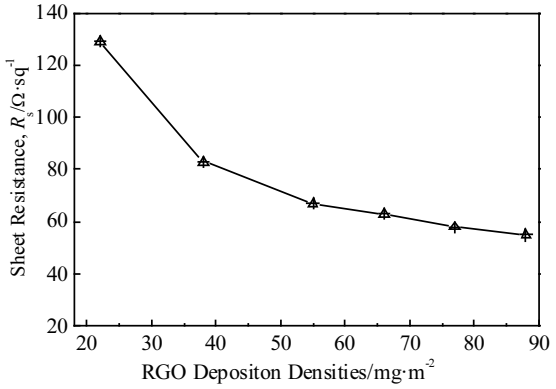

Fig.6 R_s versus rGO deposition density of AgNWs/rGO films

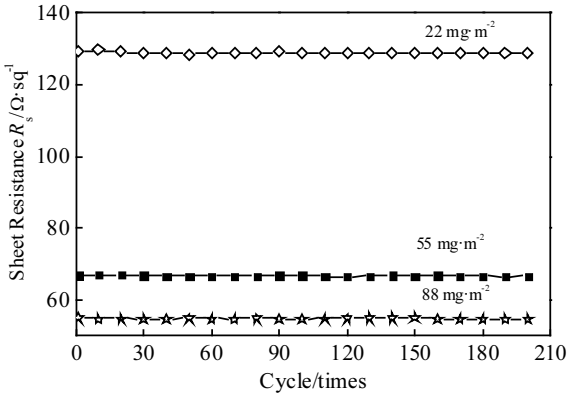

Fig.7 R_s of AgNWs-rGO films after taping test

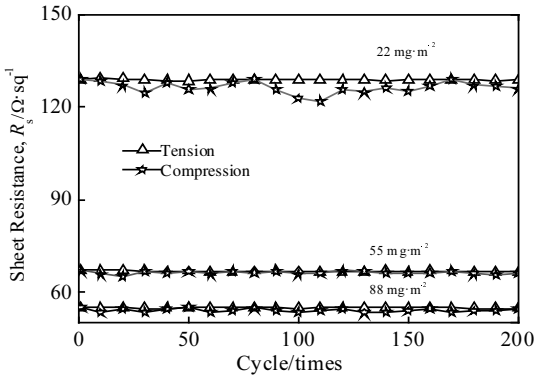

Fig.8 R_s of AgNWs-rGO films after cycles of folding up

3 Conclusions

1) With the increase of the rGO deposition density, the optical transmission of the AgNWs at 550 nm has a little decrease, indicating that rGO has little effect on the transmittance of the film. However, R_s gradually decreases with rGO deposition density increase. The film produced with the deposition density of 22 mg·m^{-2} rGO shows the optical transmission at 550 nm 82.0% and R_s around 129 Ω·sq^{-1}, whereas at deposition density of 88 mg·m^{-2} rGO, the optical transmission is 79% at 550 nm and R_s around 55 Ω·sq^{-1}.

2) the change in R_s of AgNWs/rGO film is about 3% even after 200 cycles of compressive or tensile bending when the deposition densities of rGO is 22 mg·m^{-2}; while the change in R_s of AgNWs-rGO film is little even after 200 cycles of compressive or tensile bending when the deposition densities of rGO is 55 and 88 mg·m^{-2}. The results indicate that rGO may improve the mechanical robustness of the film.

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还原氧化石墨烯对纳米银线/还原氧化石墨烯复合柔性透明导电薄膜影响

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摘 要：纳米银线和还原氧化石墨烯为导电相，混合纤维素膜为基底，采用真空抽滤法制备了柔性透明导电薄膜。研究了还原氧化石墨烯对柔性透明导电薄膜的光电及机械性能的影响。结果表明，随着还原氧化石墨烯含量的增加，导电薄膜的透过率变化不大，但薄膜的方阻逐渐下降。通过胶带测试 200 次原位监控方阻变化以及弯曲疲劳 200 次测试原位监控方阻变化，研究纳米银线和石墨烯导电相在混合纤维素膜表面的附着力和薄膜的弯曲疲劳特性。结果表明，经过 200 次的胶带测试，薄膜的方阻几乎没有改变。弯曲测试结果表明，薄膜方阻约有 3%的改变，说明薄膜具有良好的稳定性。分析认为，纳米银线-石墨烯复合薄膜具有良好的稳定性与纳米银线和石墨烯埋在混合纤维素膜表面有关。

关键词：纳米银线；还原氧化石墨烯；柔性透明导电薄膜；混合纤维素膜

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