

Electrical properties of acrylic resin composite thin films with graphene/silver nanowires

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ABSTRACT: Silver nanowires and graphene were used to form networks within acrylic resin to improve its toughness and conductivity through silane coupling agent. Meanwhile, acrylic resin was favorable to the adhesion of graphene to glass substrates and the connection among graphene sheets to form films. Experimental results indicate that after annealing at 400°C, sheet resistances of graphene-silver nanowire films were lower than those graphene films without silver nanowires. The findings in this study provide helpful information on the fabrication of graphene-based electronic devices. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42387.

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INTRODUCTION

Due to high charge mobility, low mass density, and good chemical stability of graphene,¹ graphene and graphene-based materials are widespread investigated for electronic devices,^{2,3} such as batteries,^{4–6} supercapacitors,⁷ sensors,^{8,9} flexible touch screen display, and conductive pads.^{10,11} However in the process of manufacturing graphene devices, a key issue often encountered by researchers is how to make the films not easily removed from the substrates. Acrylic resin (AC) has been widely used in adhesives and coating owing to its good adhesiveness, high modulus, attractive strength, creep resistance, and high heat distortion temperature,^{12–14} so introducing AC in graphene or graphene-based thin films will be an effective method to improve their adhesion to substrates.^{15,16}

However, high electrical resistance and plastic deformation of highly crosslinked microstructure of AC impede its toughness and conductivity. Nanowires have been used to solve this difficulty. Metal nanowires can efficiently improve the toughness and conductivity of AC due to their high aspect ratios and high conductivity. Among them, silver nanowire (AgNW) is one of the most promising candidates,^{17,18} because it has many advantages compared to other metal nanowires, such as low cost, low resistivity, and high flexibility,^{19–22} which benefit physical properties of the films.

Herein, we fabricated AgNWs by solvothermal method and AC thin films with graphene or graphene and AgNWs (labelled as AC-G films and AC-G-AgNW films, respectively) by blade coating process. We used silane coupling agent (KH-570) as cross

linker. The sheet resistances of AC-G films and AC-G-AgNW films were measured, and AC-G-AgNW films exhibited lower resistance than AC-G films.

EXPERIMENTAL

Materials

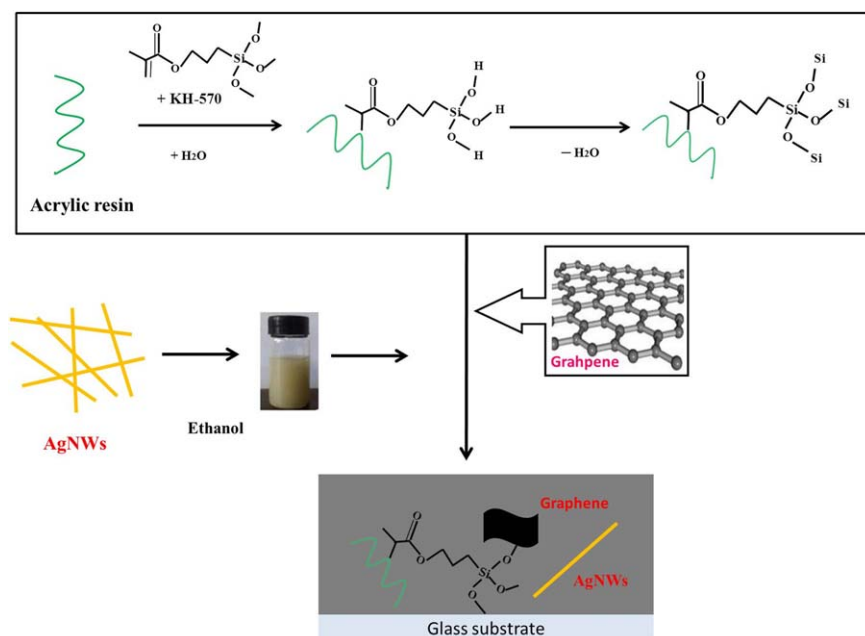
Silver nitrate (AgNO₃) and polyvinylpyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent. Ethylene glycol (C₂H₆O₂), iron chloride hexahydrate (FeCl₃·6H₂O), and KH-570 were purchased from Aladdin Reagent. Acrylic resin was purchased from Jinan Haoyao. Graphene was purchased from Skyspring Nanomaterials, Inc. (0541DX). The thickness of graphene sheets is 6–8 nm, and the dimension is about 15 μm). All chemicals were reagent grade.

Synthesis of AgNWs

AgNWs were synthesized by a solvothermal method.²³ 8 g of FeCl₃ ethylene glycol solution (6 × 10⁻⁴ mol/L), 0.54 g of silver nitrate (AgNO₃), and 0.49 g of PVP were added to 62.5 g of ethylene glycol (C₂H₆O₂). After the mixture reacted in an autoclave at 150°C for 1.5 h, the product was washed and filtered to remove residuals. The filtered AgNWs were dispersed in ethanol (the concentration was approximately 4 mg/mL) and stored at room temperature.

Preparation of Graphene Suspension

Graphene suspension was prepared with the following procedures.²⁴ 0.12 g of graphene and 0.04 g of sodium dodecyl sulfate (SDS) aqueous solution (1 mg/mL) were added to 0.8 g of deionized water. After the mixture was sonicated for 20 min, 1 g of AC (pH = 9, adjusted using ammonia), 0.16 g of



Scheme 1. Preparation procedure for AC-G-AgNW films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

KH-570, and 1.88 g of ethanol were added to the mixture solution and sonicated for another 40 min to obtain homogeneous graphene suspension.

Preparation of Composite Thin Films

The size of glass substrates was 18×18 mm. Glass substrates were cleaned by sonicating the substrates in water (20 min), acetone (20 min), ethanol (20 min), and deionized water (40 min), respectively, and then dried in oven at 60°C for 6 h.

Hybrid suspensions were formed by simply mixing graphene suspension with different weight fraction of AgNW suspension (5 wt %, 15 wt %, and 30 wt %). Thin films of AC-G-AgNWs were fabricated using these hybrid suspensions by blade coating method. The films were dried at room temperature for 2 h, and then annealed at different temperature (i.e., 25°C , 80°C , 120°C , 150°C , 200°C , 250°C , 300°C , 400°C , 450°C , and 500°C) for 1 h.

Characterization and Measurements

The morphology of AgNWs and AC-G-AgNW films was observed by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F), and their compositions were analyzed by energy-dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) measurements of AgNWs and composite films were taken on a Rigaku D-MAX 2500/PC using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The thermal analysis of crosslinked AC was carried out using a differential scanning calorimetry (DSC) (STA449C, Netasch Corp.) in air with a scanning rate of $10^\circ\text{C}/\text{min}$. Fourier-transform infrared (FT-IR) spectra of AC with KH-570 modification and composite films were measured by a Nicolet-510P Fourier transform infrared spectrometer (Nicolet Corp.) in the range of $450\text{--}4000 \text{ cm}^{-1}$. Raman spectra of samples were measured using a LabRAM HR confocal Raman system with 532 nm diode laser excitation at room temperature.

Sheet resistances of thin films were examined in ST-2258A multifunction digital four-probe tester (Suzhou Jingge Electronic).

RESULTS AND DISCUSSION

Thin films were synthesized according to Scheme 1. As we know, graphene films without AC easily break even with a touch, however the carboxyl of AC can crosslink with ethenyl group of KH-570 and interact with abundant hydroxyl groups on graphene surface, which can improve mechanical and conductivity performance of films. That is, the utilization of AC and KH-570 can enhance the adhesion of graphene or AgNWs onto glass substrates and the miscibility between graphene sheets and AgNWs. For example, as shown in Figure 1, whether the films were annealed or not, after immersing in three different solutions: deionized water, pH = 7; hydrochloric acid solution, pH = 2; and sodium hydroxide solution, pH = 10 for 24 h, the films modified with AC and KH-570 remained completeness, however, the films without modification fell off from the substrates and broke. The phenomenon above even started after immersing in the solutions for several minutes. This is because a network was formed by KH-570 modified AC, which went through hydrolysis, dealcoholization, and dehydration processes, and then contributed to the hydrophobicity of thin films in aqueous solution. Such high adhesion and completeness can meet diverse application requirements in electronic devices. In addition, as shown in Figure 1, for graphene films, the films immersed in hydrochloric acid kept more integrated compared to those in sodium hydroxide, which indicates that graphene films are more stable in acid and neutral solutions.

Thermal analysis and FT-IR were measured to understand the process of AC modified by KH-570. Figure 2(a) shows the DTA and TG analysis data of the crosslinked AC. The DTA (A) result

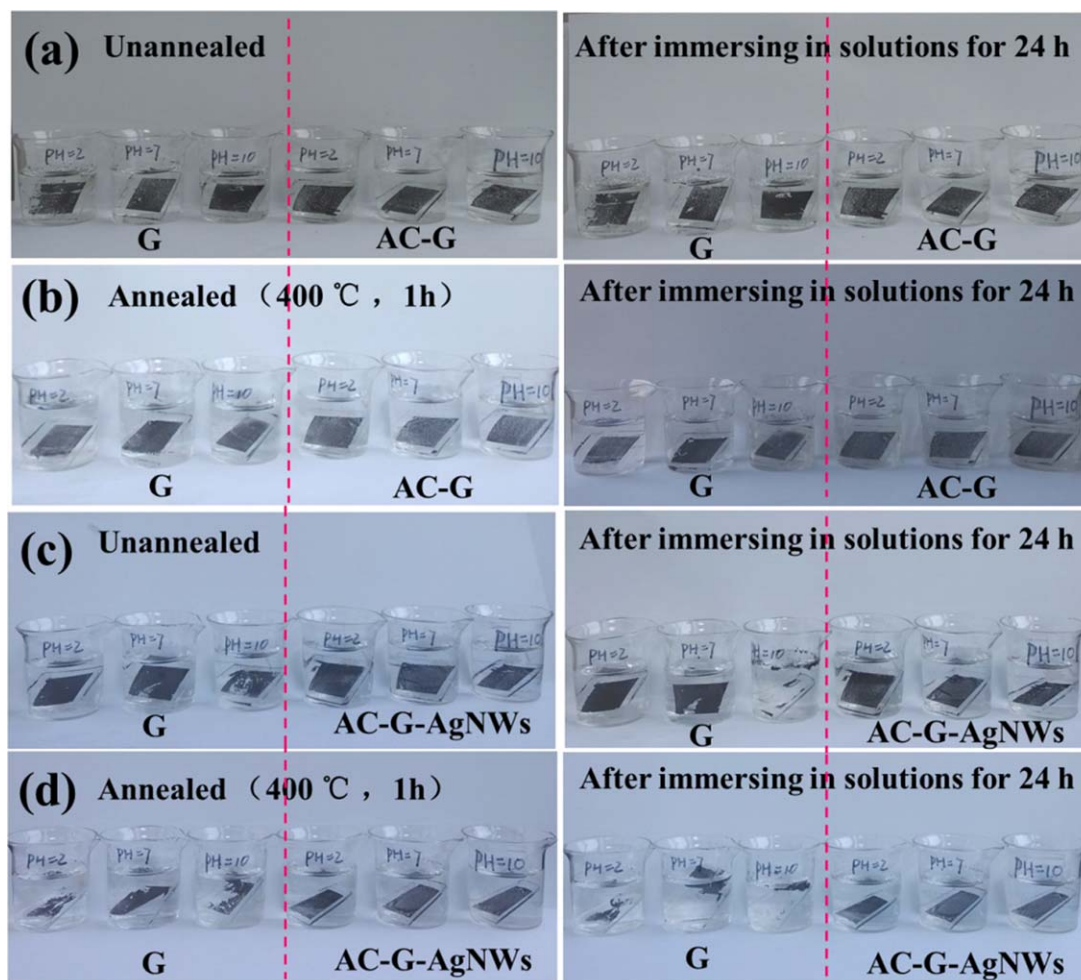


Figure 1. Photographs of un-annealed graphene films, AC-G films (a) and AC-G-AgNW films (15 wt %) (c) vs. annealed (400°C, 1h) graphene films, AC-G films (b) and AC-G-AgNW films (15 wt %) (d), immersed in hydrochloric acid solution (pH = 2), deionized water (pH = 7), and sodium hydroxide solution (pH = 10) for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shows two strong endothermic peaks at about 100°C and 112.8°C with a dramatic weight loss of about 60.83%. This corresponds to the evaporation of unreacted KH-570 and AC. With increase of temperature polymers started to decompose and lose weight. The FT-IR spectra proved that KH-570 was successfully grafted to AC. As shown in Figure 2(b), four samples of KH-570 modified AC (25°C) (C), KH-570 modified AC (400°C) (D), AC-G (400°C) (E), and AC-G-AgNWs (15 wt %, 400°C) (F) were investigated. The bands at 2930 cm^{-1} and 1453 cm^{-1} can be assigned to asymmetric stretching vibration of C—H bond in $-\text{CH}_2-$ and asymmetric bending vibration of $-\text{CH}_3$ in the AC, respectively. The bands at 1719 cm^{-1} and 1295 cm^{-1} are the stretching vibrations of C=O and C—O—C in ester compounds. Furthermore, the band at 700 cm^{-1} is the $-\text{CH}_2$ rocking vibration of butyl acrylate. The groups mentioned above nearly disappeared at 400°C due to the decomposition of polymers. The band at 1637 cm^{-1} is the stretching vibration of C=C which disappeared due to the polymerization.^{25,26} The bands at 3500–3200 cm^{-1} indicate that carboxyl groups existed as dipolymer or polymer using hydrogen bonds. As the temperature increased, the peak between 3500–

3200 cm^{-1} became wider due to higher degree of association of AC and KH-570 (as showed in D). E and F have similar variations due to small concentration of AgNWs. In comparison E, F to D, signals at 1090, 1577, 1384, and 800 cm^{-1} became clearer, which can be attributed to Si—O—C vibration, asymmetric stretching vibrations of O=C—O, in-plane vibration of $-\text{CH}_3$, and stretching vibrations of Si—C, respectively. As well known, there were many hydroxyl groups on the surface of graphene and AgNWs prepared through solution methods. When graphene or graphene and AgNWs were added, intermolecular association using hydrogen bond could take place among graphene, AgNWs, KH-570, and AC,^{27,28} so the peak between 3500–3200 cm^{-1} disappeared due to the fact that -OH of carboxyl group was mainly used to react (as showed in E and F). The bands at 1168 cm^{-1} and 1121 cm^{-1} correspond to Si—OH stretching vibration and Si—O—Si bond, respectively,^{25,28} which indicates the condensation reaction between silanol groups, and with increase of temperature the peak became wider due to higher degree of condensation (as showed in D). At 400°C, the Si—O—C vibration became clear (1090 cm^{-1}). In view of the results above, it is clear that polymerization reaction occurred

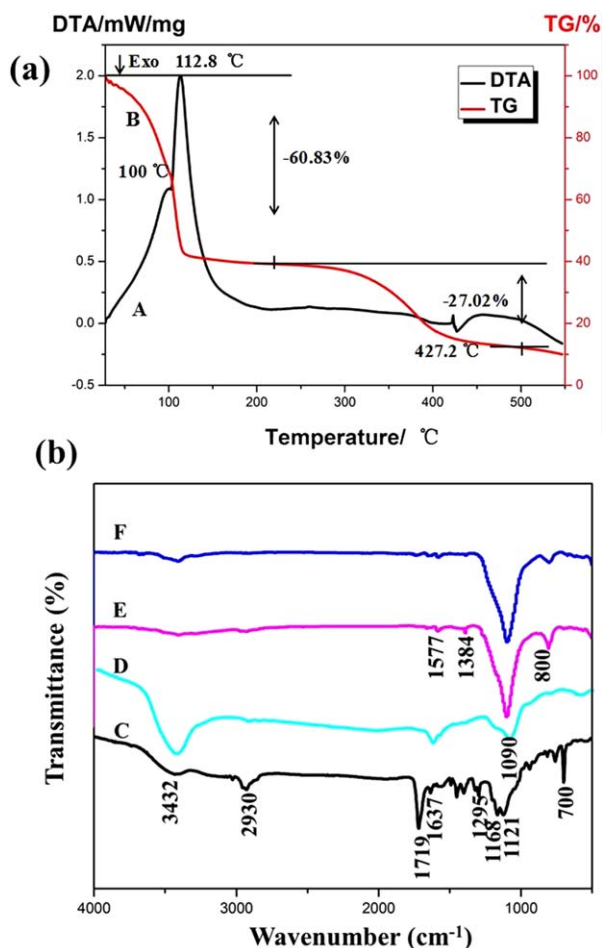


Figure 2. (a) DTA (A) and TG (B) results of silane coupling agent modified AC. (b): FT-IR spectra of KH-570 modified AC (25°C) (C), KH-570 modified AC (400°C) (D), AC-G (400°C) (E), and AC-G-AgNWs (15 wt %, 400°C) (F). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in AC and KH-570 at the temperatures of 25°C and 400°C, and the network structure of KH-570 modified AC was formed.

Raman spectroscopy is one of the most suitable techniques to characterize carbon materials. Figure 3 shows typical Raman spectra of graphene [Figure 3(a)], AC-G-AgNWs (25°C) [Figure 3(b)], and AC-G-AgNWs (400°C) [Figure 3(c)] with characteristic D band at around 1340 cm^{-1} (breathing mode related to defects and disorders) and G band at around 1590 cm^{-1} (the first-order scattering of E_{2g} phonons related to graphitization). The intensity ratio of I_D/I_G is an important indicator to evaluate the quality of graphene materials. The I_D/I_G intensity ratios are 0.15 for pure graphene, 0.20 for AC-G-AgNW films (25°C), and 0.19 for AC-G-AgNW films (400°C), respectively. When AC and AgNWs were introduced, graphene sheets were linked with them through hydrogen bond and dangling bond, acting as defects were introduced into graphene sheets, so the composites have a little higher I_D/I_G intensity ratio. With the increasing of annealed temperature, some defects of graphene sheets disappeared as indicated by the slightly decrease of the I_D/I_G intensity ratio.²⁹

Figure 4(a,b) show that AgNWs have high aspect ratio, tens of micrometers in length and about 50–100 nm in diameter. XRD patterns [Figure 4(c)] indicate typical peaks of FCC structure of Ag (JCPDS File 04–0783) for both samples of AgNWs and AC-G-AgNWs. For the AC-G-AgNW composite (15 wt %, 400°C), peaks in 26.4° and 54.5° can be indexed as (002) and (004) of graphite structure, respectively. As shown in Figure 4(d), the graphene sheets were wrapped with AC, and AgNWs were not observed probably due to their surface covered with AC; whereas in Figure 4(e), several AgNWs were observed within graphene sheets because of the decomposition of AC during annealing process. Chemical compositions of the composites were determined by EDS [Figure 3(f)]. Ag element was detectable although the concentrations were only 1.42 wt % and 1.13 wt % for un-annealed and annealed AC-G-AgNW films (15 wt %), respectively. Signals of Na and Ca came from glass substrate, and Si was from both the composite and substrate. The thickness of AC-G-AgNW thin films was about 5.5 μm after annealed at 400°C [Figure 4(g)].

After annealing, even though most of AC decomposed, a polymer matrix formed during thermal process,^{30,31} which benefits the contact among graphene sheets and thereby, enhances the conductivity of films. This may partly be proved by the fact that annealed films (400°C, 1h) with AC remained completeness after being immersed in solution for 24 h while graphene films without AC tended to easily break down. As we know, the AC films without graphene or AgNWs have no conductivity, but the electrical conductivity of films with graphene or graphene and AgNWs can be significantly improved. The sheet resistances of films made by different suspensions were measured by four-probe tester. In Figure 5, the sheet resistances decreased with the increase of annealing temperature from 25°C to 450°C, but increased at a temperature of 450°C or 500°C. At the temperature of 80°C and 120°C, curves became fluctuations due to evaporation of water, KH-570 and AC, even the degree of cross-link. The sheet resistance of AC-G films was lower than AC-G-AgNW films when the temperature below 300°C, while this

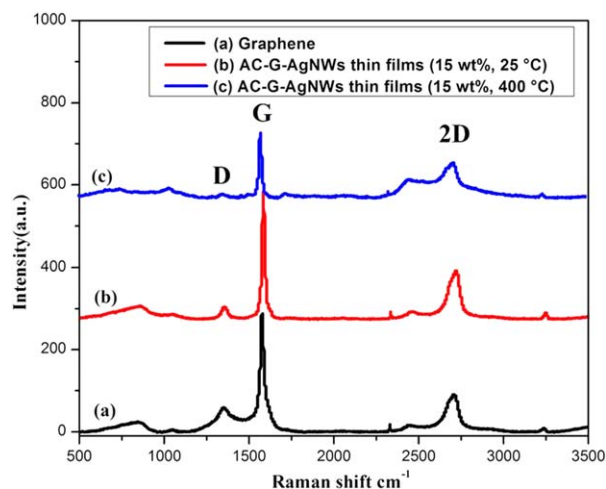


Figure 3. Raman spectra of graphene (a), AC-G-AgNW films (25°C) (b), and AC-G-AgNW films (400°C) (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

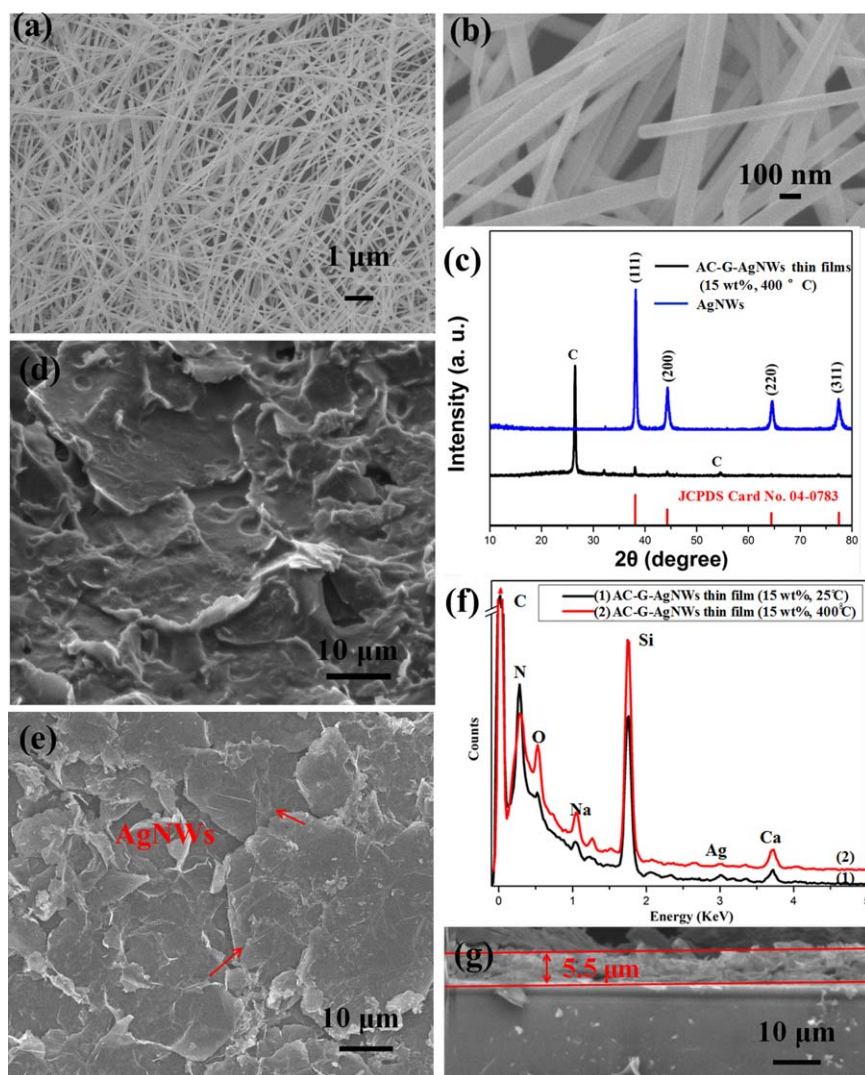


Figure 4. SEM images (a, b) and XRD pattern (c) of AgNWs and AC-G-AgNW film (15 wt %, 400°C). SEM images demonstrate the surface (d) of AC-G-AgNW films (15 wt %, 25°C), the surface (e) and cross-section (g) of AC-G-AgNW films (15 wt %, 400°C) on glass substrate. (f) EDX spectra of AC-G-AgNW film (15 wt %, 25°C) and AC-G-AgNW film (15 wt %, 400°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

value became higher for AC-G films compared to AC-G-AgNW films above 300°C, and at the temperature of 500°C, AC-G films had the highest value in the four samples. This phenomenon demonstrates non-conductive polymer could obviously upgrade adhesion to substrates and cohesion of graphene sheets while reducing the conductivity of films. At the temperature of below 300°C, AgNWs were wrapped by non-conductive polymer in the films which could act as new obstacles for the conducting of current. The more weight fraction of AgNWs in the hybrid suspensions, the more obstacles formed in thin films, so AC-G-AgNW films synthesized with 30 wt % silver suspensions have the highest sheet resistivity. Whereas 5 wt % and 15 wt % AC-G-AgNW films did not completely follow the rule, the reason might come from different distributions of AgNW films. With the quantity of polymer continually decreased because of decomposing above the temperature of 300°C, “bridges” effects of AgNWs between graphene sheets became obvious and started

to play critical roles, so the sheet resistance of AC-G-AgNW films became lower than graphene films. At temperature of 500°C, AC-G-AgNW films had lower sheet resistances than graphene films, which mean when non-conductive polymer decomposed, conductive AgNWs play a major role in the films. The inset in Figure 5 further illustrates effects of annealing temperature from 300°C to 450°C on sheet resistances of different films, and the sheet resistance of 15 wt % AC-G-AgNW films reached at 40.3 Ω/sq at 400°C, whereas 59 Ω/sq for AC-G films

CONCLUSIONS

High adhesion onto glass substrates of AC films with graphene or graphene and AgNWs was obtained by blade coating process, and sheet resistance of AC-G-AgNW films with 15 wt % AgNWs was 40.3 Ω/sq, which was lower than that of AC-G films. With the increase of annealing temperature, AC start to

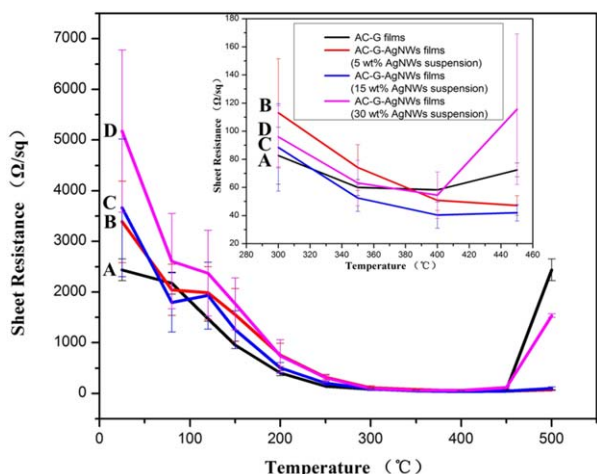


Figure 5. Effects of annealing temperatures from room temperature to 500°C on sheet resistances of different thin films: A, graphene; B, AC-G-AgNWs (5 wt %); C, AC-G-AgNWs (10 wt %); D, AC-G-AgNWs (30 wt %) . The inset is to further illustrate effects of annealing temperature from 300°C to 450°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decompose and AgNWs tend to act as “bridge” between graphene sheets to improve the conductivity of films. Different concentration and distribution of AgNWs in the films result in different values of sheet resistance of AC-G-AgNW films.

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