

Stretchable conductive films based on carbon nanomaterials prepared by spray coating

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ABSTRACT: Stretchable conductive films consisting of a layer of carbon nanomaterials, that is, carbon nanotubes (CNTs), mechanically exfoliated graphene (GE), or chemically reduced graphene oxide (rGO), deposited on polydimethylsiloxane (PDMS) films were prepared by spray coating. The correlations among the concentration of the carbon nanomaterials, the electrical resistance and the optical transmittance of the spray-coated films were investigated. The results show that the conductivity of the CNT coatings was better than that of the GE-based coatings. When the CNT concentration of the dispersion for spraying increased from 0.01 to 0.075 mg/mL, the surface electrical resistance decreased from 7.8×10^3 to $6.7 \times 10^2 \Omega$, whereas for the GE or rGO coatings, the electrical resistance was several orders higher than that of the CNT coatings. The CNT spray-coated films exhibited an optical transmittance of about 60% at a wavelength of 550 nm; this was higher than that of the GE or rGO spray-coated films. The electric heating behaviors of the stretchable conductive films as functions of the applied voltage and the concentration of carbon nanomaterials and the electrical conductivity under tensile and bending strains were also investigated. The surface temperature of the CNT-coated films rose rapidly up to 200°C within about 40 s when the applied voltage was 110 V. The stretchable conductive films have potential as electric heating elements because of their excellent conductive properties. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43243.

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INTRODUCTION

Conductive films are currently used in optoelectronic devices, such as liquid crystal displays, touch screens, organic light-emitting diodes, printable electronics, and thin photovoltaic films. Indium tin oxide (ITO) with a sheet resistance of 10–25 Ω /square at about 90% transparency has been widely used. However, because of the rapidly growing market for flexible or even wearable and stretchable conductive films, the selection of ITO as a main conductive material has several limitations. ITO is expensive because it is a limited resource. Also, the traditional conductive film preparation based on vacuum deposition procedures is complex and time consuming and often requires a high temperature. Moreover, ITO is not flexible, and its conductivity decreases significantly on bending; this makes it unsuitable for the growing market of flexible electronics.¹ Therefore, the development of new materials and technologies to overcome the limitations exhibited by ITO films has become a strategic new research field. Carbon nanomaterials, including carbon nanotubes (CNTs) and graphene (GE), have aroused intense interest for flexible conductors because of their fascinating electronic,

mechanical, and thermal properties.^{2,3} CNTs and GE are mechanically stronger and chemically more inert than ITO; this makes them valuable alternatives to ITO for flexible electronics production.^{4–9} Furthermore, CNTs and GE exhibit a neutral color and the wide transmittance spectrum range used for most electronic devices.

Usually, conductive films based on carbon nanomaterials are fabricated through direct chemical vapor deposition (CVD)^{10–14} or, alternatively, through solution techniques, including spray coating,^{15–18} dip coating,^{6,19,20} vacuum filtration,^{21–27} and spin coating.^{28–32} Films prepared by CVD display good transparency and electrical conductivity, but the CVD process is complex and expensive. On the other hand, films prepared by solution processes rely on the effectiveness of the dispersion of CNTs or GE in water suspensions. Many efforts have been made to select solvents that can counterbalance the attractive interactions between nanotubes or GE nanoplatelets and attain a good dispersion of carbon nanomaterials.³³ Among solution approaches, spray coating is relatively simple and cost effective. This method was proposed as a valuable approach for the coating of the vast

majority of plastics and inorganic substrates, and it has been used promisingly in the preparation of stretchable conductive films on a large scale.^{15–18}

In this study, three different types of stretchable conductive films based on CNTs, chemically reduced graphene oxide (rGO), and mechanically exfoliated GE were prepared by spray coating on polydimethylsiloxane (PDMS) substrates. PDMS, as a kind of silicon-based elastomer with a low surface energy, has been widely used in many devices because of its excellent optical transparency, chemical/biological inertness, nontoxicity, gas permeability, and flexibility.^{34–36} There have been a few reports on stretchable conductive films prepared by the deposition of carbon nanomaterials on PDMS films.^{10,11,35} However, to the best of our knowledge, reports on spray-coating methods are scarce. The properties of stretchable conductive films obtained with different carbon nanomaterials have also not been compared. The influence of the concentration of carbon nanomaterial dispersions on the electrical resistance and visible-light transmittance of spray-coated PDMS substrates was investigated. The electric heating behavior of the stretchable conductive films as a function of the applied voltage and the concentration of carbon nanomaterials was examined.

EXPERIMENTAL

Materials

Flake graphite, with an average particle size of about 75 μm , was obtained from Qingdao Tianhe Graphite Co., Ltd. (China). CNTs (multiwalled, NC7000), with a diameter of 9.5 nm, were kindly provided by Nanocyl (Belgium). Mechanically exfoliated GE was kindly provided by Jinlu Group Co., Ltd. (China). Hydrazine hydrate was purchased from Chendu Kelong Chemical Reagent Co. (China). Liquid silicone rubber was purchased from Shenzhen Kuwart Silicone Materials Co., Ltd. (China, K-1008, two-part system: A/B = 1:1). Part A consisted of vinyl-terminated silicone oil and platinum catalyst, and part B consisted of methyl vinyl silicone oil and a crosslinking agent. The curing temperature was about 120°C. *N*-Hexane was purchased from Chengdu Kelong Chemical Reagent Co. (China). Sodium dodecyl sulfate (SDS) was purchased from Tianjin Bodi Chemical Industry Co., Ltd (China). All reagents and materials were used without any preliminary purification treatment.

Preparation of the PDMS Films

The PDMS films were prepared from liquid silicone rubber by a film casting method. Parts A and B of the two components of liquid silicone rubber were added to *n*-hexane (weight ratio of part A to part B to *n*-hexane = 1:1:5) and stirred vigorously. Then, the resulting mixture was poured into a round mold. After the removal of *n*-hexane solvent at 60°C in a dry oven, the temperature was raised and maintained at 100°C for 30 min to allow the curing of the silicone rubber. The diameter and thickness of the PDMS film were 75 and 0.5 mm, respectively. The as-prepared PDMS films were transparent and flexible.

Preparation of rGO-Based Coatings on the PDMS Films

Graphene oxide (GO) was produced from the natural graphite flakes by the Hummer method.^{8,38,39} Brown GO aqueous solutions with concentrations in the range between 0.075 and

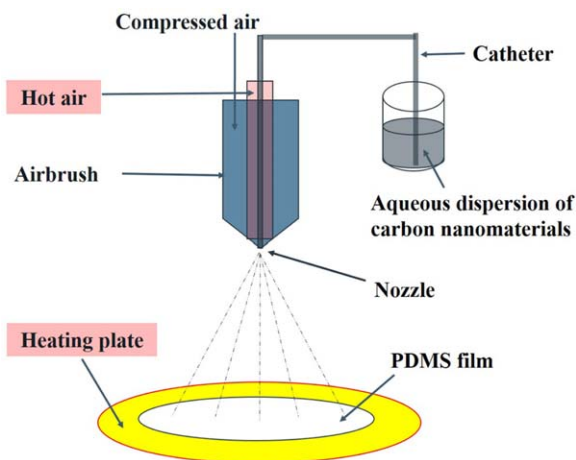


Figure 1. Schematic view of the spray coating process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0.125 mg/mL were obtained by the sonication of the prepared GO powder in water at 40°C for 1 h using a bath ultrasound machine (KQ-250DE, 40 KHz, Kunshan Ultrasonic Instrument Co., Ltd., China). The prepared GO dispersion was stable for several weeks. The GO dispersion was sprayed onto a preheated PDMS film with a laboratory-scale spray dryer. Figure 1 shows the schematic view of the spraying technology. Both the PDMS film and the air in the airbrush were preheated to 150°C. The rate of hot air and the spraying rate were selected to guarantee optimum deposition conditions. The flowing rate of hot air was about 5 m/s, and the spraying rate was 10 mL/min. The distance between the nozzle and the PDMS film was 15 cm. When the temperature of the heating plate and hot air reached the setting values, the peristaltic pump was opened, and the aqueous dispersion of carbon nanomaterials was transported to the airbrush. The dispersion was atomized into water sprays and sprayed out onto the preheated PDMS film via the nozzle. The sprayed volume for each deposition was 50 mL. The thickness of the stretchable conductive films was controlled by the adjustment of the concentration of the carbon nanomaterial dispersion.

After spraying, the PDMS films coated with GO were rinsed in a hydrazine hydrate solution (weight ratio of hydrazine hydrate to water = 1:5) to promote the chemical reduction of GO to obtain rGO at 60°C for 2 h.

Preparation of GE-Based and CNT-Based Coatings on the PDMS Films

The mechanically exfoliated GE powder was dispersed in an aqueous SDS solution (1 wt %). Then, the suspensions at GE concentrations of 0.01–0.075 mg/mL were sonicated for 30 min at 750 W using an ultrasonic immersion probe (Sonic & Materials, Inc., VC-1500, 20 kHz). The obtained dispersions were sprayed onto PDMS films with the procedure described previously. The GE-coated PDMS films were rinsed in deionized water for several minutes to remove excess of SDS and then dried in a vacuum oven at 60°C. The spray coatings for the

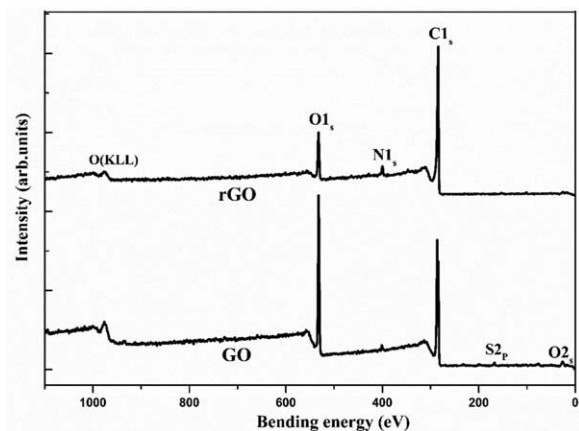


Figure 2. XPS spectra of the surfaces of the films coated with GO and rGO nanoparticles.

CNT dispersions at CNT concentrations of 0.01–0.075 mg/mL on the PDMS films were similar to those used for GE.

For a comparative purpose, we also prepared PDMS films coated with rGO, GE, and CNT nanoparticles by dip coating. Briefly, the PDMS film was glued smoothly to the bottom of a Petri dish. The carbon nanomaterial suspension was poured onto the PDMS film and then dried in an oven at 150°C to allow water evaporation and deposition of the solid nanoparticle layer on the PDMS film.

Characterization

The compositional and morphological analyses of GO and rGO were carried out with X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). XPS measurements were carried out with an XSAM800 (Kratos, Britain) with a pressure of 2×10^{-7} Pa in the analysis chamber during the measuring time. The XPS core-level spectra were collected with a nonmonochromated X-ray source powered by 12 kV of tension and 15 mA of emission current. The electron analyzer was operated in the fixed analyzer transmission mode. All of the spectra were calibrated to binding energies for $\text{Cu}^{2p_{3/2}}$ (932.67 eV), $\text{Ag}^{3d_{5/2}}$ (368.30 eV), and $\text{Au}^{4f_{7/2}}$ (84.00 eV) levels. Charge effects were compensated with the assumption of a carbon C_{1s} peak at a 284.8-eV position. SEM was performed with an Inspect F model FEI apparatus at an accelerating voltage of 20 kV.

The electrical resistance of the coated films was measured at room temperature by a two-point measurement with a standard potentiometer (Keithley 2400). Rectangular specimens were cut from films and coated with conductive silver pulp on both ends of surface to allow better adhesion of the measurement electrodes. Five different samples were measured for each concentration point, and the electrical resistance was the average value for five samples.

The optical transmittance of visible light of the coated films was measured with an ultraviolet–visible spectrophotometer (Unic 2800), and it was determined as the percentage transmittance at a wavelength of 550 nm.

The assessment of the electric heating behavior of the films was carried out with a thermal IR camera (Thermo Vision A40-M). The surface temperature of the coated samples under an electrical voltage was measured with a constant-current, direct-current switching power supply (YK-AD15010). The temperature was monitored during heating for about 60 s until the equilibrium temperature was reached through the application of voltages in the range between 10 and 110 V.

Finally, the measurements of the electrical conductivity of the samples subjected to strain cycles were performed with a fatigue tester (MTS 810), whereas the changes in the electrical resistance of the stretchable conductive films were recorded with a standard potentiometer. In particular, two different configurations were applied: tensile deformation and bending deformation. In the first case, the samples were subjected to tensile stress–strain cycles, where the linear strains were 10 and 20% (Tensile strain = $\Delta L/L_0$, where L_0 is the length of the sample). In the second case, the samples were subjected to a bending deformation cycle with a bending strain of 40% (Bending strain = $\Delta L/L_0$).

RESULTS AND DISCUSSION

Figure 2 shows the XPS spectra of the surfaces of the films coated with GO and rGO nanoparticles. The ratio of the atomic number of O to C (O/C) was obtained from the ratio of the peak areas corrected with the empirical sensitivity factors. The

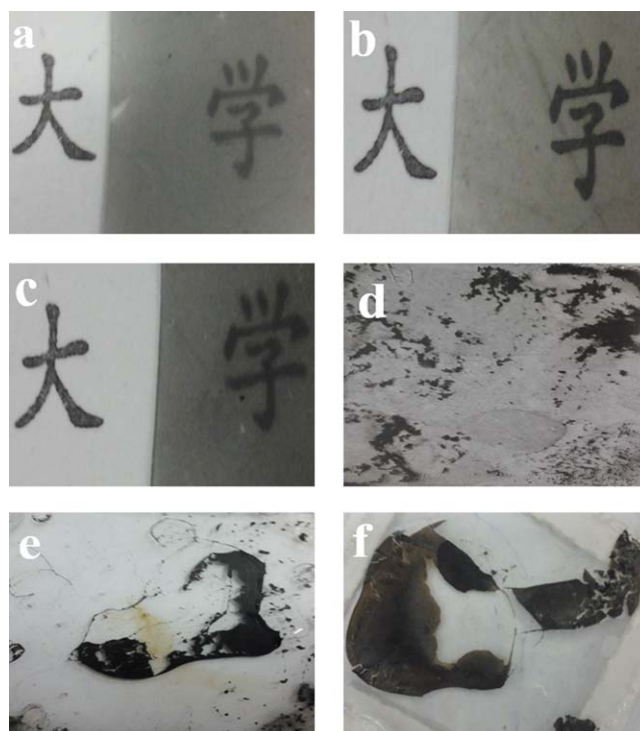


Figure 3. Digital images of the PDMS films coated with (a) GE, (b) CNTs, and (c) rGO prepared by spray coating without carbon nanomaterials (left) and with carbon nanomaterials (right). Digital images of PDMS films coated with (d) GE, (e) CNTs, and (f) rGO prepared by dip coating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

O/C ratio for GO was about 0.34, whereas the same ratio for rGO was about 0.13. The significant decrease in the oxygen content suggested that GO was chemically reduced to rGO and proved the effectiveness of the hydrazine treatment.

Figure 3(a–c) shows digital images of the PDMS substrate coated with GE, CNTs and rGO by spray coating. As shown in the right part of each digital image, the films were coated with a carbon nanomaterials layer. The left part of each image shows the film with no carbon coating exist. The uniformity and transparency of the films were fairly good. For sake of comparison, Figure 3(d–f) shows digital images of films with GE, CNTs and rGO by the dip-coating approach. In the dip-coating approach, serious agglomerations of carbon nanomaterials on the PDMS films were observed. The differences in the macroscopic appearance for different methods was ascribed to the different water evaporation rates. When the carbon nanomaterial aqueous dispersion was sprayed onto the substrate, the water evaporated quickly and left a homogeneous and uniform layer of carbon nanomaterials on the PDMS film. In contrast, in dip-coating deposition, the water evaporated slowly and, thus, generated carbon nanomaterial agglomerates on the PDMS substrates.

The morphologies of the layers of carbon nanomaterials deposited onto the surface of PDMS films by spray coating were observed by SEM (Figure 4). The carbon nanomaterials appeared to be uniformly distributed on the PDMS substrate. The film coated with rGO was smoother than the films coated with GO.

The electrical resistance and optical transmittance of the coated PDMS films obtained by spray coating are shown in Figure 5(a,b) as a function of the concentration of aqueous carbon nanomaterial dispersions. Both the resistance and transmittance depended strongly on the concentration of carbon nanomaterials in the dispersions. As for the CNT-coated films, when the con-

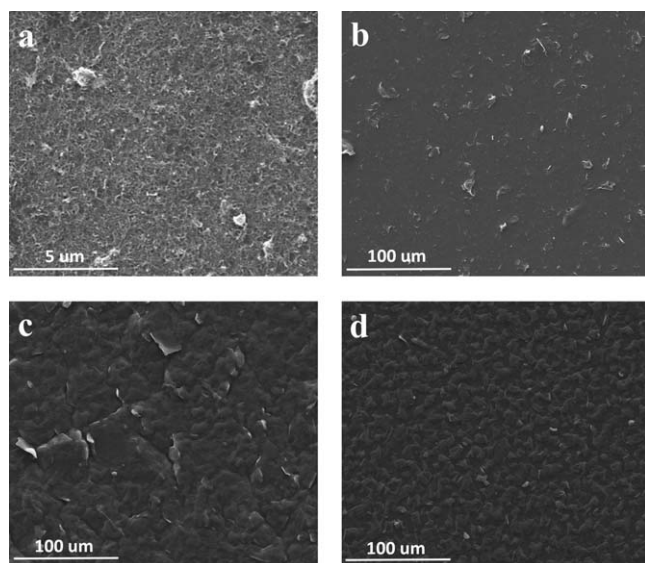


Figure 4. SEM images of the surfaces of PDMS films coated with (a) CNTs, (b) GE, (c) GO, and (d) rGO by spray coating. The carbon nanomaterial concentration for all of the spraying dispersions was 0.075 mg/mL.

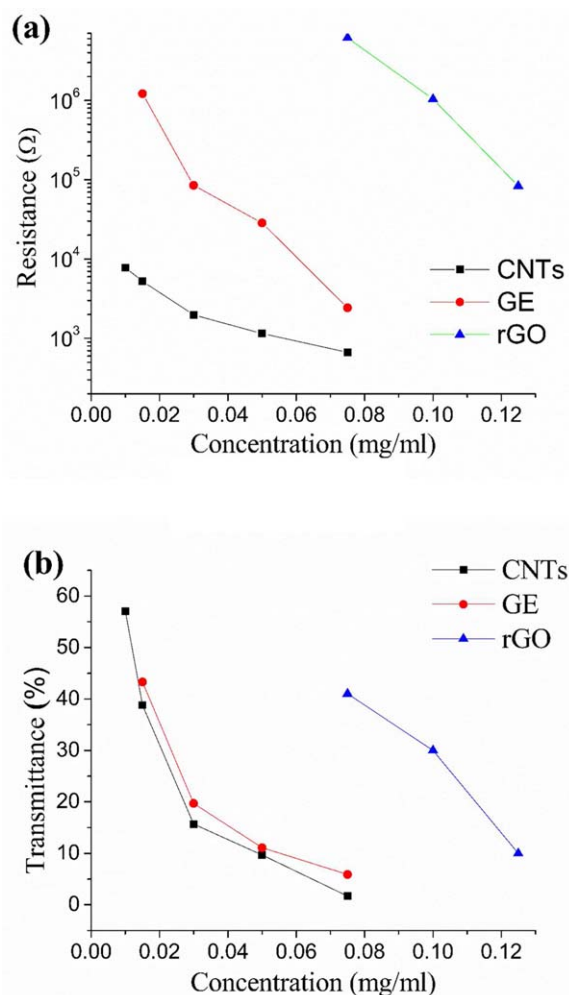


Figure 5. Plots of the (a) electrical resistance and (b) optical transmittance at 550 nm of the coated PDMS films as a function of the concentration of carbon nanomaterials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

centration of CNTs increased from 0.01 to 0.075 mg/mL, the resistance decreased from 7.8×10^3 to $6.7 \times 10^2 \Omega$. In a comparison of the electrical resistance of the different coatings, it appeared that the CNT-coated films exhibited much lower electrical resistances than the other two films spray-coated with GE and rGO. This was ascribed to the ability of the CNTs to form an homogeneous conductive network on the surface of the PDMS substrate because of their one-dimensional structure and higher aspect ratio compared to other fillers.⁴⁰ In fact, the CNTs exhibited an aspect ratio equal to about 700, whereas the GO and rGO presented an aspect ratio of about 170, as determined by some of the authors in the previous work.⁴⁰ As for the rGO-coated films, the higher electrical resistance was possibly due to its lower intrinsic electrical conductivity. The presence of a residual amount of oxygen-containing groups, such as hydroxyl and carboxyl groups, on the surface of the GE sheet after chemical reduction decreased the electrical conductivity of the rGO nanoplatelets. When the concentration of rGO was less than 0.075 mg/mL, the film was not conductive.

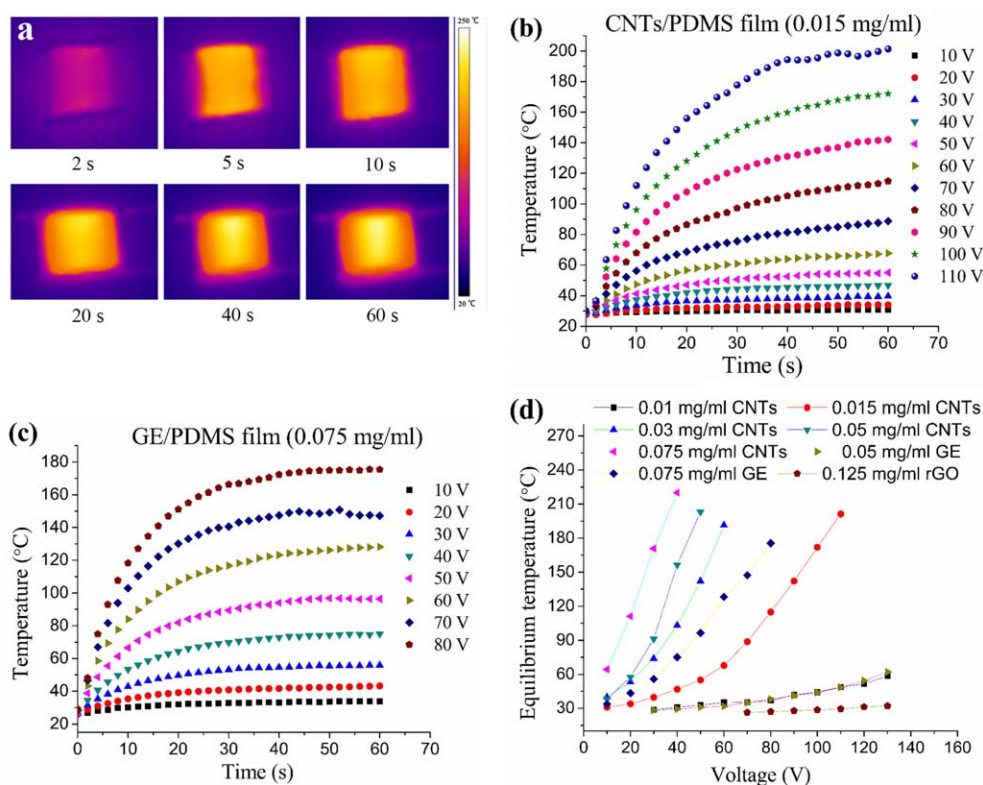


Figure 6. (a) IR thermal images of a PDMS film coated with CNTs (0.015 mg/mL) within 60 s at a voltage of 110 V. (b,c) Temperature changes of the PDMS film coated with CNTs (0.015 mg/mL) and GE (0.075 mg/mL) as a function of the time at different voltages. (d) Changes in the equilibrium temperature of different conductive PDMS films as a function of the applied voltage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The optical transmittance of the PDMS films coated with carbon nanomaterials was lower compared to the pristine PDMS substrates. Regardless of the concentration of the dispersion, all of the samples exhibited an optical transmittance lower than 60%. Only the CNT-coated film obtained from the 0.01 mg/mL dispersion exhibited a transmittance of about 57% at a wavelength of 550 nm; this was higher than those of all of the other GE-based coatings.

The electrical resistance and visible-light transmittance at a 550-nm wavelength are important performance measures for conductive films. The materials developed in this study exhibited a surface electrical resistance that was quite comparable to most of the conductive films developed in the literature and obtained with CNTs and GE derivatives.^{15,16,41} However, the achieved visible-light transmittance was lower than that developed by dry or alternative wet processes,^{10,19,23} and this may have limited the application of these conductive films in optoelectronic devices. The sheet resistance of the ITO films was about $10 \Omega^{-1}$ when the transparency was 90% at a wavelength of 550 nm.¹⁶ The comprehensive performance in terms of the electrical resistance and visible-light transmittance of the carbon nanomaterials films was not as good that of the ITO films.¹⁵

We monitored the electric heating behavior of the PDMS films spray-coated with CNTs, GE, and rGO by monitoring the temperature increase of the sample surface under different voltages in the range from 10 to 130 V. Joule's law⁴² is reported in eq. (1):

$$Q = I^2 R t = \left(\frac{U}{R} \right)^2 R t = \frac{U^2}{R} t \quad (1)$$

where Q is the heat produced by an electric current, I is the current intensity, R is the resistance value, U is the voltage applied on the conductor, and t is the time of application of voltage on the conductor. When the applied voltage is constant, the resistance of the material is smaller, and more heat is produced at a certain time.

Figure 6(a) shows the IR thermal images of the surface of the PDMS film spray-coated with CNTs (CNT concentration in spraying dispersion = 0.015 mg/mL) when a voltage of 110 V was applied, as a function of the time. The IR images of the conductive film changed from light yellow to white gold with time as a consequence of the electric heating of the conductive film. Figure 6(b,c) shows the changes in the surface temperature of the PDMS films spray-coated with CNTs (CNT concentration in the spraying dispersion = 0.015 mg/mL) and GE (GE concentration in the spraying dispersion = 0.075 mg/mL), respectively, as functions of the time and applied voltage. The results show that there were no apparent temperature changes when the applied voltage was below 30 V for the CNTs and GE-coated films. When the value of the applied voltage increased, the temperature of the coated surface rose with time. As for the CNT-coated films, when the applied voltage was above 80 V, the temperature rose rapidly over time. In particular, the maximum equilibrium temperature reached about 200°C in 40 s

when the voltage applied on the film was 110 V. Once the equilibrium temperature was reached, the heat generated by the electric power was equal to the heat dissipated into the air by radiation. For the GE-coated films, the temperature reached a maximum value at 180°C when the applied voltage was 80 V [see Figure 6(c)]. The CNT-coated film obtained by spraying a dispersion with a concentration of 0.015 mg/mL showed higher electrical resistance than those of the GE-coated films obtained from a deposition concentration of 0.075 mg/mL [see Figure 5(a)].

Figure 6(d) shows the changes in the equilibrium temperature of the PDMS films coated with carbon nanomaterials deposited with dispersions with different concentrations as a function of the applied voltage. The equilibrium temperature of the conductive films depended on the applied voltage; that is, the higher the voltage was, the higher the equilibrium temperature was. As for the PDMS films spray-coated with rGO at a concentration of 0.125 mg/mL, the surface temperature remained nearly constant at about 30°C because of its very high electrical resistance. Similar results were also observed for the PDMS film coated with GE at a concentration of 0.05 mg/mL and CNTs at a concentration of 0.05 mg/mL. For PDMS films coated with 0.075 mg/mL CNTs, the equilibrium temperature rose from 65 to 220°C when the applied voltage was increased from 10 to 40 V. When the concentration of carbon nanomaterial increased, consequently, the equilibrium temperatures increased. These results show that the electric heating behavior of the conductive films could be fine-tuned easily.

The flexibility of the conductive films is an important property because it can be used in flexible electronic devices. The electrical properties of the conductive films under tensile and bending deformation were measured with the two-probe conductivity measurement method. Figure 7(a) shows the normalized resistance, expressed as the ratio of the resistance of the sample under strain to the initial resistance (R/R_0 , where R_0 is the initial resistance), for the PDMS film coated with CNTs of 0.075 mg/mL as a function of the time or number of deformation cycles. During tensile tests, the strain was changed from 0 to 10% and back to zero again; the cycle was repeated four times, and the electrical resistance was simultaneously monitored. During the first cycle, the resistance of the conductive films increased slowly with strain and reached the maximum value when the strain was 10%. The normalized resistance increased from 1 to 1.6 in the first cycle; this meant that the conductivity of the conductive films was sensitive to strain within a small tensile strain. When the deformation was released, the resistance nearly recovered to R_0 when the tensile strain returned to zero. Similar behavior was observed during the following three stress-release cycles. The normalized resistance changes for the PDMS films coated with 0.075 mg/mL GE as a function of the time are shown in Figure 7(b). In this case, the tensile strain increased from 0 to 20% and then back to 0%. The normalized resistance increased from 1 to about 3.8 when the strain increased from 0 to 20% and decreased to nearly 1.5 when the strain returned back to 0%. The results were similar to those of the PDMS film coated with CNTs (0.075 mg/mL). These results confirmed that when the samples were stretched, the conductive network of the carbon nanomaterials may be

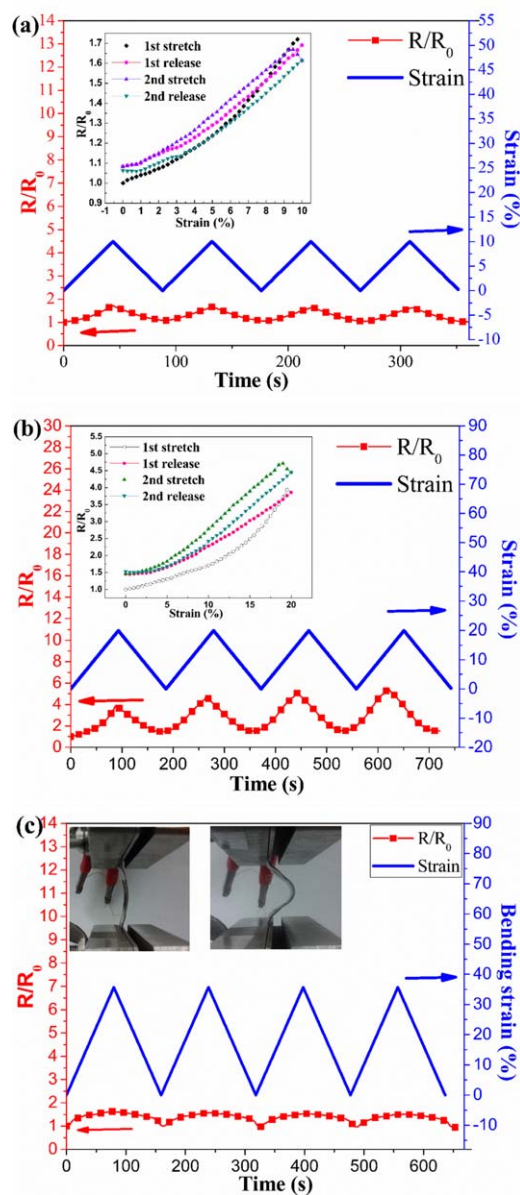


Figure 7. Normalized resistance of the PDMS films coated with (a) CNTs (0.075 mg/mL) and (b) GE (0.075 mg/mL) as a function of the uniaxial tensile strain. The insets show the normalized resistance of conductive films as a function of the uniaxial tensile strain for the first two stretch–release cycles. (c) Normalized resistance changes in the PDMS films coated with CNTs (0.075 mg/mL) as a function of the bending strain. The inset shows the bending process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

broken; this induced an increase in the electrical resistance. Moreover, as the strain returned to zero, the conducting network of carbon nanomaterials recovered to the initial one. The normalized resistance changes of the PDMS film as a function of the bending strain were also studied. The resistance changes of the PDMS film coated with 0.075 mg/mL CNTs as a function of the time and bending strains from 0 to 35% are shown in Figure 7(c). Contrary to the tensile tests, the resistance did not change significantly during the bending cycles. The results show

that in contrast with conventional materials used in flexible devices,⁴⁻⁶ the conductive films of the carbon nanomaterials prepared in this study had better flexibility and deformability than those prepared in previous studies.^{10,15,16,43}

CONCLUSIONS

Stretchable conductive films were prepared by the deposition of CNTs, GE and rGO conductive on PDMS films by spray coating. The correlations between the carbon nanomaterial concentration in the aqueous dispersion, electrical resistance, and optical transmittance of the coated films were investigated. The results show that the CNT-coated PDMS films possessed better electrical conductivity and optical transmittance than the GE- and rGO-coated PDMS films. The electric heating behavior of the conductive films and the electrical properties under tensile and bending strains were also examined. Under an electrical voltage, the conductive films were heated, and an equilibrium temperature was reached; this depended on the nature of the carbon nanomaterials, their deposition concentration, and the applied voltage. Stretchable conductive films of carbon nanomaterials can be used as flexible electric heating elements in some applications.

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