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Reversibly Stretchable Transparent Conductive Coatings of Spray-Deposited Silver Nanowires

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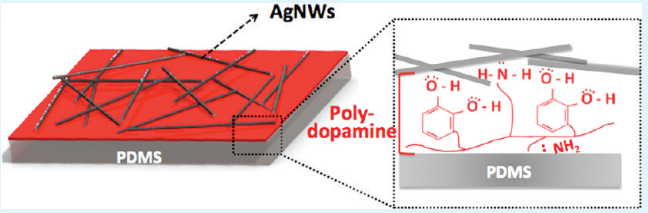
Supporting Information

ABSTRACT: Here, we report the creation of highly adhesive transparent and stretchable coatings via spray-deposition of solution-based silver nanowires (AgNWs). The AgNW dispersion was spray-deposited on a polydopamine-modified stretchable elastomeric substrate to prepare thin, stretchable, transparent, highly conductive films. The polydopamine layer on the elastomeric substrate created a highly hydrophilic surface, which facilitated the subsequent spraying of the AgNW solution. Additionally, the spray-deposited AgNWs demonstrated excellent adhesion to the substrate, which allowed the fabrication of stretchable electrodes with high conductivity. The AgNW-coated elastomeric substrate exhibited ~80% transmittance with an average sheet resistance of ~35 Ω/□, making it suitable for transparent electrode applications. The conductivity of the transparent electrode was maintained up to ~20% mechanical elongation, which demonstrated the stretchable characteristics of the AgNW-coated elastomeric substrate.



KEYWORDS: *silver nanowires, spray-deposition, stretchable electrode, polydopamine, hydrophilicity, surface adhesion*

INTRODUCTION

Transparent and conductive thin-film electrodes provide a low resistance electrical contact to the active layer of optoelectronic devices through which light must pass. These devices include touch panels,[1] liquid crystal displays (LCD),[2] solar cells,[3,4] light-emitting diodes (LED),[5] and others. The fabrication of transparent, conductive electrodes is largely dominated by metal oxides, such as tin-doped indium oxide (ITO).[6] The properties of the transparent electrodes are crucial to the performance of the device. Although metal oxides can display as high as 95% transmittance (T) with sheet resistance (R_s) as low as 3 Ω/□, the increasing cost of ITO and their brittle nature have limited their flexible applications.[7,8] Therefore, emerging research is looking for replacements for ITO for fabricating transparent electrodes using nanoscale materials. These studies include randomly distributed carbon nanotubes (CNTs),[9] graphene-based transparent electrodes,[10] and metallic nanowires.[2] Unfortunately, the transparency/sheet resistance (T/R_s) performances of CNTs and graphene-based electrodes do not match the minimum criteria for many low-cost applications.[2,7] Thus, metal nanowires are very important for achieving the best transparency and sheet resistance along with sufficient flexibility.

Copper-based metallic nanowires are very promising for fabricating low-cost transparent electrodes; however, they are limited by their low aspect ratio.[11] Electrospinning has been explored to produce continuous 1D copper nanofibers and requires complex fabrication methods, including high temperatures.[11] Conversely, silver nanowires (AgNWs) are an excellent candidate for transparent, highly conductive electrodes with mechanical flexibility.[12,13] Consequently, transparent AgNWs electrodes have been used recently to fabricate flexible and stretchable electronic devices.[14] AgNWs are usually synthesized by a low-cost, solution-based process through the reduction of silver nitrate in the presence of poly(vinyl pyrrolidone) (PVP) in ethylene glycol.[15,16] Additionally, the spray-deposition of AgNWs can facilitate the high-speed fabrication of transparent electrodes at room temperature with minimal material requirements. This technique involves an inexpensive, compatible, and easily scalable manufacturing process with higher efficiency.[17]

Although flexible electrode fabrication often involves polyethylene terephthalate (PET) substrates,[12,13] polydimethylsiloxane (PDMS) can contribute additional stretchiness for flexible electronics.[18] However, the hydrophobic surface of PDMS restricts its use in many applications. Oxygen plasma treatment has been used extensively to change the hydrophobic surface of PDMS to a hydrophilic surface.[19] Nevertheless, simple plasma-treated surfaces undergo hydrophobic recovery within minutes, while prolonged plasma treatment induces undesirable surface cracks.[20] Recently, the Messersmith group noticed the mussel's excellent adhesion on almost all types of surfaces and identified that the 3,4-dihydroxy-L-phenylalanine (DOPA) and lysine peptides in *Mytilus edulis* foot protein 5 (Mefp-5) in the mussel's adhesive threads are the origins of the extraordinary adhesive properties.[21] On the basis of these

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findings, researchers have used dopamine, a commercially available chemical containing the functional groups of both DOPA (catechol) and lysine peptides (amine), to modify various surfaces.[22−24]

In this study, we have fabricated stretchable, transparent, conductive coatings on PDMS substrates. The surface of PDMS was modified using mussel-inspired dopamine to create a hydrophilic surface. The AgNWs dispersion was deposited on the hydrophilic PDMS surface using the simple spray-deposition technique. Dopamine modification of the surface not only facilitated the spray-deposition of AgNWs but also demonstrated excellent adhesion of the wires to the modified PDMS surface. The sheet resistance variation of the AgNW transparent film was evaluated under stretching.

EXPERIMENTAL SECTION

Materials. The following materials were used in this study: anhydrous ethylene glycol (99.8%, Aldrich), copper chloride ($CuCl_2$) (97%, Aldrich), silver nitrate ($AgNO_3$) (Aldrich) and polyvinylpyrrolidone (PVP) ($M_w \approx 55\,000$, Aldrich), dopamine hydrochloride (Aldrich), tris(hydroxymethyl) aminomethane (Sigma-Aldrich), hydrochloric acid (HCl) (37%, Aldrich), silicone kit (SYLGARD 184), isopropyl alcohol (IPA) (Sigma-Aldrich), high-purity silver paint (SPI).

Synthesizing AgNWs. Silver nanowires were synthesized according to the literature using a polymer-mediated polyol process, which produces the nanostructures in large quantities with controlled morphologies.[16,25] In a typical synthetic process, a small glass vial containing anhydrous ethylene glycol was heated at 160 °C for 1 h. $CuCl_2$ solution in ethylene glycol was then added to the vial and heated for another 15 min to facilitate AgNW formation. Separate solutions of $AgNO_3$ and PVP in ethylene glycol were then simultaneously added dropwise for ∼20 min. The color of the hot solution turned to yellow as soon as the $AgNO_3$ and PVP solutions were introduced into the vial, indicating the formation of nanowires. The solution vial was heated for ∼1 h to complete the formation of AgNWs, indicated by a final opaque gray solution color. The reaction vial was then cooled by quenching it in a room temperature water bath.

Surface Treatment of PDMS with Dopamine. PDMS films were prepared using the silicone kit (w/w = 1:10). Ten mM Tris buffer solution was prepared using water, and the pH was maintained at ∼8.5 by adding HCl. Different amounts of dopamine hydrochloride (10, 20, and 50 mg) were dissolved in 10 mL of Tris-HCl solution to prepare solutions with different concentrations of dopamine. The PDMS films were then modified by simply soaking them in different concentrations of the dopamine solution for 24 h. The polydopamine-coated PDMS films were then air-dried using an air gun and were then spray-deposited with AgNWs.

Fabrication of AgNWs Spray-Deposited PDMS Film. Solutions of the AgNWs were centrifuged (IEC Centra CL2) at 2000 rpm for 20 min. The nanowire precipitates were collected and redispersed in IPA (7 wt %). The air-brush of the spray gun (Iwata 4292 HI-LINE KUSTOM) was set at 25 psi with a spraying distance of ∼3 cm from the surface of the modified PDMS film. The dispersions of the AgNWs were then evenly distributed for different time durations (2, 5, and 8 s, respectively). After spraying, the AgNWs films were heat treated at ∼200 °C for 20 min.

Experimental Analyses of the Spray-Deposited AgNWs Film. The transmittance values for the AgNW-deposited PDMS films were measured by a UV−visible spectrometer (Varian Inc., Cary 50). The surface morphology and the distribution of the nanowires were observed using a Scanning Electron Microscope (SEM) using Strata DB235 FESEM/FIB. The sheet resistance of the AgNW-deposited films was measured by a four point probe surface resistivity meter (Guardian Manufacturing, SRM-232). A mechanical stretching apparatus was custom-made (Figure 4a, b) and was used to measure the elongation of the nanowire-deposited PDMS films. 3 M scotch tape was used to monitor the adhesion of AgNWs to the dopamine modified PDMS substrates (Figure 2c). Patterned AgNW films were made by spray-deposition of the nanowires on the modified surface of PDMS and the circuit was completed by using a blue colored light emitting diode (LED) and a voltage source (Circuit Test Electronics, PSC-260) for demonstrating the conductivity of the circuit. The contact angles of the bare and polydopamine-coated PDMS surfaces were measured using a Digital AST Contact Angle System. The PDMS surface was plasma-treated using a Laboratory Corona Treater (BD-20AC).

RESULTS AND DISCUSSION

According to the literature, dopamine was self-polymerized in the buffer solution at pH ∼8.5, and the solution color changed to black-brown after 24 h of treatment.[22,24] The polydopamine surface modification resulted in the spontaneous deposition of a thin, adherent polymer layer on the surface of the immersed PDMS. The formation of the adherent polymer layer was likely due to the oxidation of dopamine, which led to bulk solidification of the adhesive through intermolecular cross-linking.[23] The lone pair electrons of the functional groups on the polydopamine layer cause a strong binding interaction with the subsequent inorganic or organic layers.[21] Figure 1a and 1b

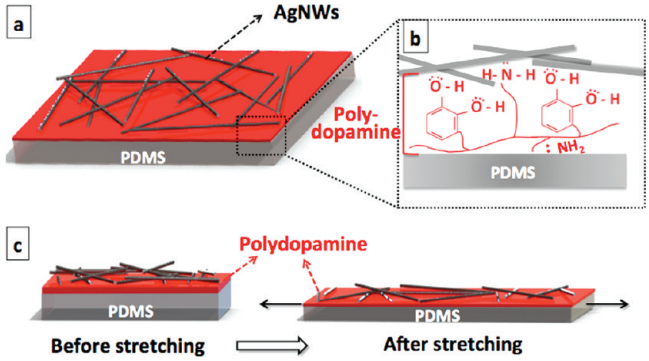

Figure 1. Schematic representation of (a) the spray-deposited AgNWs on dopamine-modified PDMS films, (b) the polydopamine interaction with AgNWs and the PDMS surface, and (c) the binding interaction of the polydopamine and the nanowires before and after stretching, respectively.

present a schematic for the interaction of the polydopamine layer on the PDMS surface and the subsequent spray-deposited AgNWs. While achieving homogeneous deposition of AgNWs was impossible on the bare PDMS, the nanowires were evenly distributed on the polydopamine-treated surfaces. As shown in Figure 1c, we expect that the strong binding interaction of the polymer layer and the AgNWs can also hold the nanowires during stretching.

The contact angle for bare PDMS was 115°, and it decreased to 25.7° for the polydopamine-coated PDMS surfaces (Figure 2a). This significant decrease in the water contact angle for polydopamine-coated PDMS surfaces indicated the formation of a strongly hydrophilic surface after modification. However, the formation of the black-brown solution changed the color of the PDMS surface, and the dopamine concentration seemed to affect the coated PDMS's transparency. Figure 2b shows the transmittance data for the AgNW-deposited PDMS films, which were modified with different concentrations of the dopamine buffer solutions. For all three films, the amount of AgNWs was kept unchanged by fixing the spray-deposition time at 2 s using 7 wt % AgNWs. As the concentration of the dopamine solution

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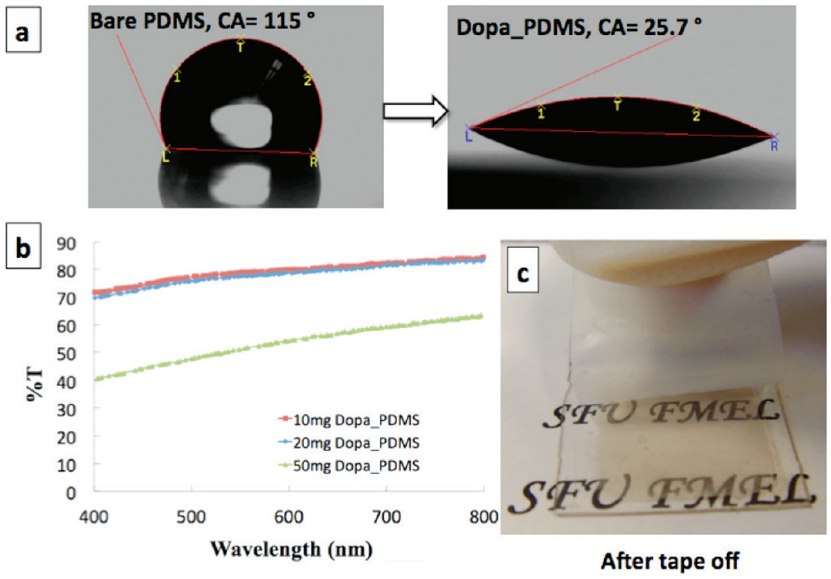

Figure 2. (a) Water contact angle measurements for bare and polydopamine-coated PDMS surface, (b) the transmittance data for AgNW-deposited PDMS films modified with different concentrations of dopamine buffer solutions, and (c) the enhanced adhesion of the AgNWs to the dopamine-modified PDMS surface was monitored using the taping test.

increased, the solution color became darker and the transparency decreased. However, the lowest amount of dopamine (10 mg) in Tris-buffer solution (10 mL) was sufficient to produce a hydrophilic surface on PDMS and to hold the nanowires on the surface. At 550 nm wavelength, the transmittance was ~80% for the AgNW-deposited PDMS, which was modified with 10 mg dopamine (in 10 mL Tris buffer). The 3 M scotch tape test was performed to monitor the adhesion of the deposited AgNWs to the modified surface. As shown in Figure 2c, no significant amount of AgNWs peeled off the surface, and the pattern maintained its conductivity even after the taping test, indicating the nanowires' excellent resistance to damage, such as scratching and peeling. Thus, the concentration of dopamine Tris buffer solution was kept constant at 1 mg/mL for the subsequent surface modification steps of the PDMS films.

The "SFU" pattern on the PDMS surface was made by modifying the letters with dopamine solution through a stencil mask. Figure 3a shows that the water droplets only resided on the hydrophilic letters, forming the "SFU" pattern. The patterned films in Figure 3b,c were obtained by spraying AgNWs on dopamine-treated PDMS through a PET mask. A blue LED lamp was connected with one end of the patterned AgNWs electrodes by conductive silver paint (Figure 3b). The film was then bent and the LED flashed on when the voltage source was connected to the other two ends of the pattern. This phenomenon demonstrated the excellent conductivity of the patterned nanowires, even under bending conditions, and their suitability as an electrode for flexible electronics. The SEM image (inset of Figure 3c) shows the homogeneous distribution of AgNWs on the polydopamine-coated PDMS surface. The diameters of the nanowires were 100−150 nm, while the lengths of the wires were ~20 μm on average. Thus, the spray-deposition technique can be used to easily fabricate large-scale coatings, as well as to create specific patterns.

Figure 4 shows the mechanical stretchability of the AgNW-deposited PDMS films. Initially, the AgNWs were spray-deposited for 2 s on the modified PDMS films and were then stretched with the mechanical stretching apparatus (Figure 4a,

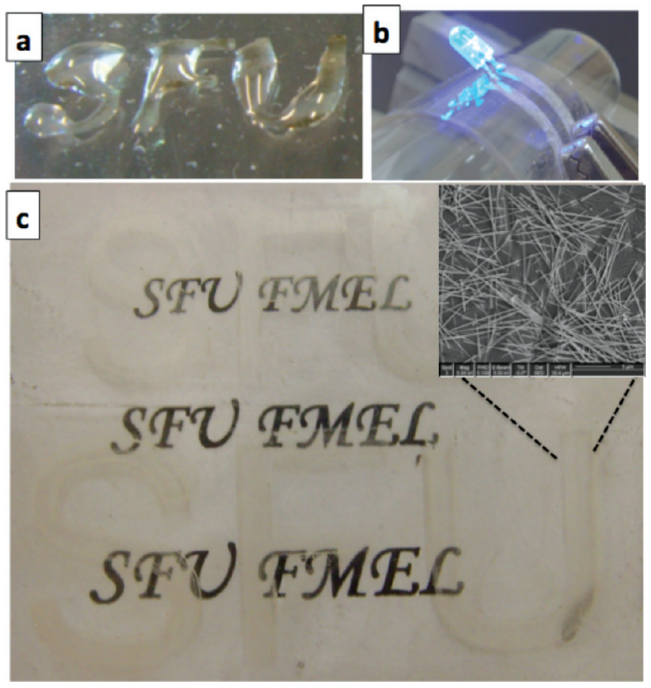

Figure 3. (a) Water droplets residing on the hydrophilic letters modified with dopamine buffer solution, (b) an image of patterned AgNWs with the blue LED lamp on dopamine-modified PDMS substrate during bending, and (c) the "SFU" pattern created by the spray-deposition of AgNWs on dopamine-modified PDMS; the inset is the SEM image of the distributed AgNWs.

b). The R_s values were monitored at different places on the nanowire-deposited films under stretching and the average was plotted against the elongation (Figure 4c). As shown in Figure 2a, the spray-deposited AgNWs film (2 s) showed ~80% transmittance and from Figure 4c shows that the average R_s for this film was ~35 Ω/□.. The average R_s remained almost unchanged up to ~15% elongation, whereas further elongation caused an increase in the R_s value, followed by cessation of

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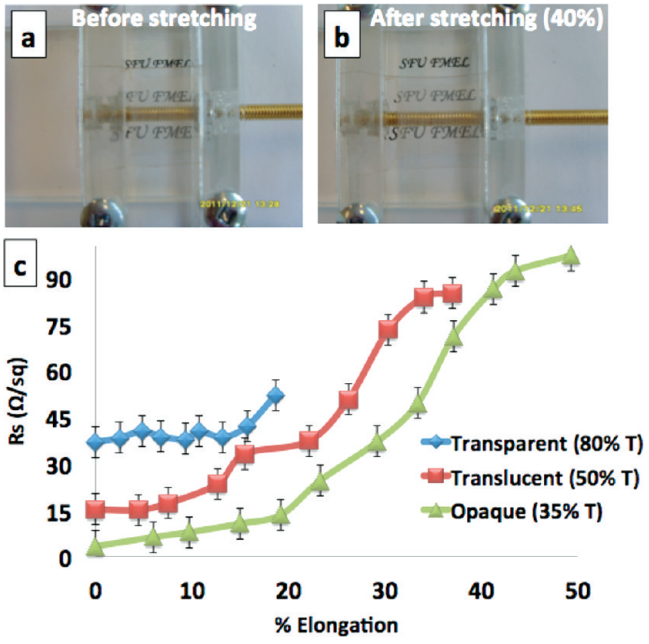

Figure 4. AgNW-spray-deposited PDMS film (a) before and (b) after stretching, (c) the change in the average sheet resistance with elongation for the 80, 50, and 35% transparent films, respectively.

conductivity. According to percolation theory,[7] the 80% transparent AgNWs film might have a conductive path for the electrons to pass with an initial R_s value of ~35 Ω/□. The R_s value should remain unchanged with stretching as long as the wires were connected through the conductive path (in our case, up to ~15% elongation). The increase in the average R_s with further elongation might be due to the increase in the length of the conductive path, causing difficulties for the electrons to pass through. Eventually, the conductive path broke (approximately 20% elongation) and resulted in the cessation of conductivity. Therefore, the more conductive paths that are formed by depositing more AgNWs, the more conductive the film should become[26,27] and thus, might be able to maintain its conductivity with greater elongation. However, the deposition of more nanowires is expected to decrease the transparency of the AgNW-deposited PDMS films.[1,28] The 50% and 35% transparent films (Figure 4c) were prepared by spraying AgNWs onto modified PDMS for 5 and 8 s, respectively. As expected, the transparency of the AgNWs films decreased with an increasing volume of nanowires. The average R_s decreased dramatically and the stretchability improved at higher depositions of AgNWs. The lowest R_s value and the highest stretching properties (over 30% elongation with less than 40 Ω/□) were obtained for the opaque film (8 s of spray-deposition of AgNWs). Although there was a hysteresis loss in the conductivity of the nanowire films during stretching and releasing (see the Supporting Information, Figure 2); the film was reversibly stretchable and maintained its conductivity, as long as the wires were connected through the conductive path.

The surface was also modified via plasma treatment to compare the stretching behavior of the plasma-treated film compared with that of the polydopamine-modified film. Plasma treatment produced a hydrophilic surface on the PDMS film; however, the hydrophilicity was not sufficient to hold the AgNWs homogenously on the surface after the subsequent spray-deposition. Conversely, the surface modification of the PDMS film with the dopamine buffer solution easily created stretchable electrodes with conductivity comparable to the other stretchable electrodes.[18,29]

CONCLUSION

In conclusion, we fabricated stretchable, transparent, conductive coatings by spray-deposition of AgNWs on dopamine-modified PDMS. The lowest amount of dopamine was sufficient to produce a hydrophilic surface, facilitating the subsequent spray-deposition of AgNWs. The spray-deposition technique created a homogeneous distribution of AgNWs on the surface and was also used to generate patterned structures. The nanowires adhered well to the polydopamine-coated PDMS film and the AgNW-coated film showed little change in the sheet resistance when stretched up to ~15%. Additionally, the stretchable and transparent AgNW-based electrode was conductive even under bending with a small bending radius. Thus, the AgNW-based spray-deposited films were suitable as an electrode material for stretchable electronic devices. Further, ongoing studies are exploring the possible applications of our transparent and conductive films to fabricate stretchable optoelectronic devices.

ASSOCIATED CONTENT

Supporting Information

SEM and EDS analyses of the bare PDMS, polydopamine-coated PDMS, and AgNW-spray-deposited PDMS (with polydopamine coating). The hysteresis behavior of the opaque (35% T) film during stretching and releasing is also included. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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