Mechanically Robust Silver Nanowires Network for Triboelectric Nanogenerators

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The authors develop a mechanically robust silver nanowires (AgNWs) electrode platform for use in flexible and stretchable triboelectric nanogenerators (TENGs). The embedding of an AgNWs network into a photocurable or thermocurable polymeric matrix dramatically enhances the mechanical robustness of the flexible and stretchable TENG electrodes while maintaining a highly efficient triboelectric performance. The AgNWs/polymeric matrix electrode is fabricated in four steps: (i) the AgNWs networks are formed on a hydrophobic glass substrate; (ii) a laminating photocurable or thermocurable prepolymer film is applied to the developed AgNWs network; (iii) the polymeric matrix is crosslinked by UV exposure or thermal treatment; and (iv) the AgNWs-embedded polymeric matrix is delaminated from the glass substrate. The AgNWs-embedded polymeric matrix electrodes with four different sheet resistances, controlled by varying the AgNWs network deposition density, are deployed in TENG devices. The authors find that the potential difference between the two contact surfaces of the AgNWs network-embedded polymeric matrix electrodes and the nylon (or perfluoroalkoxy alkane) governs the output triboelectric performances of the devices, rather than the sheet resistance. Both Kelvin probe force microscopy and numerical simulations strongly support these observations.

1. Introduction

Recent interest in wearable electronic devices has driven the development of applications in next-generation functional devices, such as flexible displays, stretchable circuits, artificial electronic skin, and sensors.[1–7] Consumer demand for wearable electronic devices has increased, with the goal of creating flexible and/or stretchable wearable devices.[8,9] Several clever strategies have been devised to achieve exquisite control over materials and micro/nanostructural features.[10–13] These approaches offer compelling advantages for achieving wearable devices; nonetheless, efficient and easily accessible power supplies for portable and everyday wearable devices remain obstacles in the social translation of the technology.[11,14,15] Currently, wearable devices that are used daily typically require frequent nontrivial power supply maintenance, such as the use of rechargeable batteries. Power sources capable of driving electronic devices have emerged as a critical issue for translating wearable electronic devices into common use. Mechanical energy is one of the most ubiquitous sources of energy and can be converted into electricity anytime and anywhere.[16,17] Recently, new types of mechanical power-generating devices called triboelectric nanogenerators (TENGs) were developed based on coupling between triboelectrification and electrostatic induction.[18–22] TENGs have a variety of advantages, including their low-cost, simple device fabrication, and their high output power density.[23–28] Most TENGs reported thus far have not been flexible or stretchable because nons stretchable metallic films, such as Au,[29] Al,[30] or Cu,[31] have been used as the conducting electrodes of TENGs. Large-area, solution-processable, and mechanically robust electrode materials must be developed to achieve flexible and stretchable TENGs.

Silver nanowires (AgNWs) show promise as a transparent, flexible, and stretchable conductive electrode platform due to their good optical transparency, high electrical conductivity, and high mechanical flexibility.[32–35] AgNWs dispersed in a solvent
can be readily deposited onto large-area flexible and stretchable substrates using simple solution-coating techniques, such as spin-coating, dip-coating, spray-deposition, and Meyer rod coating.\[36–38\] In addition, the sheet resistances of the electrodes could be precisely controlled by varying the deposition density of the AgNWs. The AgNWs platform is, therefore, appropriate for systematic studies of the effects of the electrode conductivity on the TENG performance, which have not been conducted to date.\[39–42\] The weak adhesion between the AgNWs network and the target substrate, however, provides for facile delamination of the nanowires from the substrate under the harsh external mechanical strain and stress conditions typical of triboelectric generators.\[43–48\] Mechanical durability issues must be addressed before AgNWs may be used as electrode materials in flexible and stretchable TENGs.

Here, we describe a mechanically robust platform of AgNWs electrodes for use in flexible and stretchable TENGs. The AgNWs were embedded in a polymeric matrix, which dramatically enhanced the mechanical flexibility and stretchability of the AgNWs. The TENGs were fabricated such that the bottom triboelectric layer of the AgNWs network-embedded polymeric matrix provided four different sheet resistances; the top triboelectric layer was nylon (or perfluoroalkoxy alkane (PFA)). The triboelectric potentials of the AgNWs network-embedded polymeric matrix were deterministically tuned by adjusting the fractional area of the AgNWs network that was exposed to the surface (i.e., the areal factor of the AgNWs network). The output voltage and current of the TENGs were governed by the triboelectric potential difference between the two contact surfaces rather than the sheet resistance. These experimental results agreed well with Kelvin probe force microscopy (KPFM) measurements and the numerical simulation results. The simple, inexpensive, and scalable fabrication of robust AgNWs network-embedded matrix electrodes provides a platform for the engineering of the translation-ready, flexible, and stretchable TENGs.

2. Results and Discussion

Figure 1a presents a schematic diagram of the process used to fabricate the AgNWs network-embedded polymeric matrix electrodes for use as flexible and stretchable TENGs. A uniformly distributed, large-area AgNWs network film was prepared on a hydrophobic octadecyltrichlorosilane (ODTS)-treated glass substrate using the Meyer rod coating technique. Four different Meyer rods (#2, 3, 14, and 28) were used to control the AgNWs deposition density. An ODTS film with a low surface energy\[49\] facilitated the transfer of the AgNWs networks from the mother substrate to the photocurable or thermocurable polymeric matrix. Separately, UV-curable SU8 or a thermocurable precursor of polydimethylsiloxane (PDMS) was spin-coated onto a polyethylene terephthalate (PET) substrate and then was conformally laminated onto the prepared AgNWs.
network/ODTS-glass substrate. The liquid state prepolymer easily penetrated the interstices among the individual AgNWs. Subsequent crosslinking by UV irradiation or thermal treatment yielded an interlocked network comprising the polymeric matrix and the AgNWs network. Finally, the fully-developed AgNWs network-embedded polymeric matrix electrodes were gently detached from the mother substrate. The weak adhesion between the polymeric matrix and the ODTS-treated substrate facilitated the clean delamination of the electrodes. The mechanical robustness of the interlocked AgNWs network contributed to the stable delamination process. Figure 1b displays photographic images of (i) the flexible AgNWs network-embedded SU8 matrix (AgNWs-SU8) and (ii) the stretchable AgNWs network-embedded PDMS matrix (AgNWs-PDMS). The two electrodes clearly displayed a high optical transparency at visible frequencies. For example, the optical transmittances of the AgNWs-SU8 and AgNWs-PDMS electrodes at 550 nm were 89.7% and 87.4%, respectively. The sheet resistances of the films were 11 Ω sq−1. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images revealed a conserved areal factor for the AgNWs network before and after embedding the AgNWs network in the polymeric matrix. These results indicated the successful transfer and embedding of the AgNWs in the matrix polymer films (see Figure 1c). The areal factor of the AgNWs network was controlled by varying the Meyer rod number (#2, 3, 14, and 28), as shown in Figure S1 in the Supporting Information. The spacing between adjacent metal coils in the Meyer rods increased with the number of rods, and a greater number of AgNWs were deposited. As the rod number increased from #2 to #28, the areal factor of the AgNWs network increased gradually, as shown in the inset of Figure 1d. The optical transmittance was inversely proportional to the areal factor of the AgNWs network (Figure 1d and Figure S2 in the Supporting Information), and the optical transmittance decreased from 96% to 82% as the areal factor increased from 0.18 to 0.59. Similarly, the sheet resistance was related to areal factor of the AgNWs network: sheet resistances of 5 and 406 Ω sq−1 were obtained for areal factors of 0.59 and 0.18, respectively. The inset of Figure 1e shows AFM images and the root-mean-square (RMS) roughness of AgNWs network-embedded polymeric matrices with four areal factors. The RMS values for all samples were found to be less than 1.2 nm. In general, the surface morphology (or roughness) can strongly affect the performance of a TENG. In our system, the contribution of the surface morphology to the TENG performance could be excluded because the surface roughness values of all electrodes were comparable within the margin of error. Therefore, we elucidated the contribution of the AgNWs areal factor to the triboelectric potential and sheet resistance in terms of the TENG performance.

The mechanical flexibility and robustness of the flexible AgNWs-SU8 and stretchable AgNWs-PDMS electrodes were investigated by monitoring the sheet resistance during fatigue cycles under a tensile bending strain of 3.0% (Figure 2a) and stretching strain of 15% (Figure 2b), respectively. The variations in the sheet resistance could be expressed as \((R - R_0)/R_0\), where \(R\) is the resistance at a certain cycle and \(R_0\) is the initial resistance. The values of the two AgNWs network-embedded polymeric matrix electrodes were compared with those obtained from the as-coated AgNWs mounted on PET or PDMS substrates, respectively. The lab-built bending test setup is illustrated in the insets of Figure 2a,b. Two edges of the films were loaded onto the bending machine and were connected with copper wires using silver paste. The resistances of the AgNWs films were monitored over time during the bending or stretching cycles. The as-coated AgNWs mounted on the PET substrate exhibited a gradual increase in resistance over 10 cycles due to the slipping or delamination of the AgNWs junctions. In stark contrast, the resistances of the AgNW-SU8 films remained constant, even after 1000 cycles, because the interlocked AgNWs network and the SU8 matrix minimized delamination or slipping of the AgNWs junctions. Similarly, a stretching fatigue test of the as-coated AgNWs and AgNWs-PDMS films indicated that the AgNWs embedded in
the crosslinked PDMS exhibited almost negligible variations in the sheet resistance over 1000 stretching cycles (Figure 2b). The hydrophobicity of the PDMS facilitated the detachment of the AgNWs from the PDMS surface after two cycles. 3M Scotch-tape detachment tests were performed on the as-coated AgNWs and the AgNWs network-embedded polymeric matrix electrodes (Figure 2c,d). The sheet resistance of the as-coated AgNWs increased dramatically over several detachment cycles; however, the AgNWs network-embedded films were found to be quite stable, and delamination was minimized. A slight increase in the sheet resistance values of the AgNWs-PDMS was observed at 100 stretching cycles. The relatively good stability of the AgNWs-SU8 could be attributed to a chemical reaction between the epoxy groups of SU8 and the polyvinylpyrrolidone present on the AgNWs surfaces. The insets of Figure 2c,d show the tape contact regions of the AgNWs films after full detachment from the PET and PDMS substrates after 50 or 10 detachment cycles, respectively. The AgNWs embedding technique used to prepare the flexible and stretchable electrodes provided mechanically stable electrode materials for use in TENG applications.

Two types of AgNWs network-embedded films were successfully used as electrodes in contact-mode double-electrode TENGs. Figure 3 presents the electrical performances of TENGs prepared using the AgNWs-SU8 with four different sheet resistances (5, 11, 75, and 406 Ω sq$^{-1}$). Nylon (with a strong positive triboelectric potential) and perfluoroalkoxy alkane (PFA, with a strong negative triboelectric potential)[53] films were attached onto Al tape and used as the top triboelectric layers (Figure 3a,b). The output curves obtained from a device prepared with a top PFA layer exhibited a positive voltage/current during pushing and a negative voltage/current during release. By contrast, the opposite voltage/current outputs were obtained from the top nylon devices, that is, negative values during pushing and positive values during release.

These results indicated that the triboelectric potential of the AgNWs-SU8 lie between that of the PFA and nylon devices. Figure 3c plots the voltage/current outputs produced by TENGs based on a top PFA layer and a bottom AgNWs-SU8 layer with various sheet resistances. The maximum voltage and current outputs of the devices are summarized in Figure 3d, revealing that the output performances increased as the AgNWs electrode sheet resistance increased from 5 to 406 Ω sq$^{-1}$. Interestingly, the output voltage/current decreased as the AgNWs electrode sheet resistance increased in the top nylon/bottom AgNW-SU8 devices (Figures 3e,f). The contradictory trends in the TENG performance as a function of the sheet resistance indicated that the electrode sheet resistance did not contribute significantly to the device performance. This issue was further probed by coating SU8 layers onto AgNWs networks with different sheet resistances, and these SU8-AgNWs films (distinct from the AgNWs-SU8 films described above) were used as bottom triboelectric layers (Figure S3, Supporting Information). In this system, SU8 was exposed to the surfaces of all four samples, and the bottom triboelectric layer surfaces (composed only of SU8) contacted the top triboelectric layers. The voltage/current outputs of the TENGs prepared using PFA or nylon top layers were independent of the AgNWs electrode sheet resistance. Given that the surface characteristics of the contact surfaces affected the TENG performances, we expected that the triboelectric potentials of the bottom surface could be tuned by varying the sheet resistance of the AgNWs-SU8 film. For example, a low AgNWs network areal factor compared to that obtained from the SU8 device (with a higher sheet resistance) yielded more positive triboelectric potentials. As a result, the triboelectric potential difference between the AgNWs-SU8 film and PFA (which has a strong negative triboelectric potential) was larger than that obtained from the AgNW-SU8 film paired with nylon (which has a strong positive triboelectric potential).

Figure 3. Schematic diagram illustrating the operation of the contact-mode TENGs based on AgNWs-SU8 electrodes prepared with top a) PFA or b) nylon layers. c) Output voltage and current of the TENGs based on top PFA and bottom AgNWs-SU8 layers. d) Maximum output voltage and current extracted from (c). e) Output voltage and current of the TENGs based on top nylon and bottom AgNWs-SU8 layers. f) Maximum output voltage and current extracted from (e).
The differences in the triboelectric potentials of the contact surfaces strongly affected the TENG performance. Variations in the triboelectric potential as a function of the AgNWs network areal factor at the bottom surface will be further explained. In addition, the mechanical durability test for the TENGs based on the AgNWs-SU8 and PFA was performed during 16,000 cycles (Figure S5, Supporting Information).

The AgNWs network embedded in the PDMS layer was used as an electrode in stretchable TENGs, as shown in Figure 4a,b. During the pushing/releasing cycle applied to the top PFA layer mounted on a bottom AgNWs-PDMS layer, the output voltage/current decreased as the sheet resistance of the AgNWs increased, as shown in Figure 4c-d. The TENGs based on a top nylon layer and a bottom AgNWs-PDMS layer, however, generated higher outputs at higher sheet resistances, as shown in Figure 4e-f. Note that the AgNWs-PDMS TENGs displayed the opposite trend compared with the AgNWs-SU8 TENGs, i.e., higher outputs were obtained from the device prepared with a top PFA layer and lower outputs were obtained from devices with a top nylon layer, at a given lower sheet resistance. As with the AgNWs-SU8 devices, this observation could be understood by the triboelectric potential differences between the contact surfaces. The lower areal factor of the AgNWs network exposed to the bottom contact surface (with a higher sheet resistance) yielded more negative triboelectric potentials. The reduced potentials produced a smaller triboelectric potential difference with the PFA layer, whereas a larger triboelectric potential difference was obtained in the presence of the nylon layer (as discussed below).

The triboelectric potential was measured as a function of the AgNWs network areal factor to compare the performances of devices prepared with SU8 or PDMS matrix polymers (the AgNWs are indicated in red in the SEM images shown in Figure 5a). KPFM measurements were collected in the noncontact mode using a Pt tip. Figure 5b plots the surface potential differences for the AgNWs networks embedded in SU8 or PDMS, as compared to the Pt tip. All AgNWs-SU8 films exhibited positive surface potentials, whereas all AgNWs-PDMS films showed negative surface potentials. These results revealed that the surface potential of the Pt tip occurred between the surface potentials of the AgNWs-SU8 and AgNWs-PDMS devices. The surface potentials of the AgNWs-SU8 films decreased from +154 to +50 mV as the areal factor of the AgNWs increased from 0 to 0.59. Furthermore, the surface potentials of the AgNWs-PDMS films decreased from −158 to −1397 mV as the AgNWs areal factor decreased from 0.59 to 0. These surface potential measurements and the triboelectric potentials of the AgNWs network-embedded films are summarized in Figure 5c. As the AgNWs network areal factor increased, the AgNWs-SU8 films exhibited smaller triboelectric potential differences in the presence of a top PFA layer, whereas larger triboelectric potential differences were obtained from a top nylon layer. A larger triboelectric potential difference resulted in better TENG output performances (see Figure 3). Among the AgNWs-PDMS films, a lower AgNWs network areal factor yielded a smaller triboelectric potential difference in the presence of a top PFA layer but a larger triboelectric potential difference in the presence of a top nylon layer. These triboelectric potential differences were also reflected in the output performances of the AgNWs-PDMS TENGs (see Figure 4). Consequently, the TENG device performances were mainly determined by the triboelectric potential difference between the contact surfaces and not by the sheet resistances of the electrodes.

The effects of the AgNWs network on the triboelectricity were analyzed by conducting finite element method simulations (using the COMSOL Multiphysics software) of the contacts between the AgNWs network embedded within a polymeric matrix and a PFA (or nylon) layer. Under open-circuit
conditions, the electric potential difference \( V_{oc} \) generated during contact-mode triboelectricity generation \(^{54} \) is defined as
\[
V_{oc} = \frac{\sigma \cdot x(t)}{\varepsilon_0}
\]  
where \( \varepsilon_0 \) is the permittivity in a vacuum, \( x(t) \) is the distance between two layers at a particular time. The symbol \( \sigma \) is the induced surface charge density, which can be expressed according to Equation (2) because the electrode surface was composed of a polymeric matrix (SU8 or PDMS) and an AgNWs network:

\[
\sigma = \sigma_{\text{polymer}} \cdot x_{\text{polymer}} + \sigma_{\text{AgNWs}} \cdot x_{\text{AgNWs}}
\]

where \( \sigma_{\text{polymer}} \) and \( \sigma_{\text{AgNWs}} \) are the surface charge densities of the polymeric matrix and the AgNWs network, respectively; and \( x_{\text{polymer}} \) and \( x_{\text{AgNWs}} \) are the areal factors of the polymeric matrix and the AgNWs network, respectively. We successfully simulated the triboelectric effect between bottom AgNWs-SU8 (or AgNWs-PDMS) layers characterized by different areal factors and top PFA (or nylon) layers, based on Equations (1) and (2). Figure 6a,b shows cross-sectional views of the 3D numerical simulation results obtained from the electric potential distribution of the TENGs prepared based on AgNWs-SU8/PFA or

**Figure 5.** a) SEM images of the AgNWs embedded in SU8 with different areal fractions. The regions occupied by the AgNWs are colored red in the image-mapping analysis. The areal fraction of the AgNWs varied from 0.59 to 0.18. b) The KPFM images and measured surface potentials of the AgNWs embedded in SU8 or PDMS, as a function of the AgNWs areal fraction. c) Triboelectric series in order of the surface potential polarities, based on the KPFM results.

**Figure 6.** Simulation schematics of the TENGs prepared with AgNWs-SU8 layers having one of three different areal fractions (from 0.6 to 0.2) and contacted with a top a) PFA or b) nylon layer. Comparison of the calculated and measured TENG potentials in devices prepared with AgNWs-SU8 contacted with top c) PFA or d) nylon layers.
AgNWs-SU8/nylon, respectively. A random AgNWs network embedded in a polymeric matrix was described simply as a mesh structure (see the insets of Figure 6a,b). The σ values were strongly related to the triboelectric characteristics of the contact materials, based on the location of the triboelectric series. The value of σ obtained from the AgNWs-SU8 TENGs prepared with PFA increased as the AgNWs areal factor decreased due to the increasing triboelectric potential difference with the top PFA layer, resulting in a higher simulated output voltage (Figure 6c). On the other hand, the simulated output voltages were generated between the AgNWs-SU8 and nylon showed the opposite tendency: the simulated output decreased as the areal factor of the AgNWs decreased (Figure 6d). These simulation results agreed well with the KPFM measurements and measured TENG performances. Numerical simulations were conducted to model the AgNWs-PDMS TENGs. The simulation results were also consistent with the corresponding experimental results (Figure S4, Supporting Information). The TENG outputs were in close relation to the triboelectric potential difference between contacts. Therefore, the rational selection of a contact surface is essential for achieving high-performance TENGs.

3. Conclusion

In conclusion, we have developed flexible and stretchable TENGs based on an AgNWs network embedded in a polymeric matrix. The interlocking structure of the AgNWs network within the polymeric matrix dramatically enhanced the mechanical stability during bending and stretching, which is an important requirement for achieving stable TENG operation. The areal factor of the AgNWs network exposed to the contact surface (sheet resistances of the electrodes) was systematically tuned by varying the Meyer rod number. The TENG performances were found to be governed mainly by the triboelectric potential difference between the contact surfaces rather than the sheet resistance of the electrodes, as supported by the KPFM and numerical simulation results. The proposed process for fabricating mechanically robust AgNWs electrodes is simple, inexpensive, scalable, and provides a novel approach to realizing next-generation flexible and stretchable TENGs.

4. Experimental Section

Fabrication of the Embedded AgNW Electrodes: AgNWs dispersed in isoproxy alcohol were purchased from Nanopixys Co. The AgNWs diameter and length were 27–37 nm and 20–30 μm, respectively. The glass was treated with hydrophobic OTDS using methods reported previously.[9] The AgNWs solution was coated onto the OTDS-treated glass substrate using the Meyer rod coating method. Four Meyer rods with #2, 3, 14, or 28 (RD Specialist Inc.) were used to control the deposition density. Separately, SU8 2005 (Microchem Co.) was spin-coated onto a PET substrate. The 5 μm-thick SU8 film prepared on a PET layer was laminated onto the preprepared Meyer rod-coated AgNWs/OTDS glass substrate. The AgNWs embedded in SU8 were exposed to UV light (365 nm and 25 mW cm⁻²) for 35 s to allow for SU8 cross-linking. The stretchable AgNWs electrodes were fabricated by spin-coating PDMS (Sylgard 184, Dow Corning) onto the PET film. This structure was then laminated onto the prepared AgNWs/OTDS glass substrate. The thickness of the PDMS film was 20 μm. The AgNWs embedded in the PDMS were crosslinked by heating on a hot plate at 80 °C over 30 min. Finally, the PET films were detached from the AgNWs-PDMS films. The AgNWs-SU8 film and AgNWs-PDMS film were released from OTDS-treated glass substrate smoothly.

Measurements: The surface morphologies of the AgNWs films were measured using a contact-mode AFM system (Park systems XE-100) equipped with Pt/Cr-coated silicon tips (radius < 25 nm) and by field-emission scanning electron microscopy (JSM-7600F, JEOL Ltd.). The sheet resistances of the AgNWs films were measured according to the four-point probe technique using Keithley 2182A and 6221 instruments. The optical transmittance was characterized using a UV-visible spectrophotometer (Agilent 8453). The KPFM images were measured using Park systems XE-100 with Pt/Cr-coated silicon tips. The scan area and scan rate were 5 μm × 5 μm and 0.3 Hz, respectively. The applied voltage, phase, and frequency were 2 V AC, –90°, and 17 kHz, respectively.

TENG Measurements: All device measurements were performed under ambient conditions (temperature = 23 °C and relative humidity = 25%–40%). All materials were first cleaned with ethanol and dried for 1 min to ensure electroneutrality. A Tektronix DPO 3052 Digital Phosphor Oscilloscope and a low noise current preamplifier (model no. SR570, Stanford Research Systems, Inc.) was used to measure the electric properties of the TENGs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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