Invariable resistance of conductive nanocomposite over 30% strain

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The dependence of the electrical resistance on materials’ geometry determines the performance of conductive nanocomposites. Here, we report the invariable resistance of a conductive nanocomposite over 30% strain. This is enabled by the in-situ-generated hierarchically structured silver nanosatellite particles, realizing a short interparticle distance (4.37 nm) in a stretchable silicone rubber matrix. Furthermore, the barrier height is tuned to be negligible by matching the electron affinity of silicone rubber to the work function of silver. The stretching results in the electron flow without additional scattering in the silicone rubber matrix. The transport is changed to quantum tunneling if the barrier height is gradually increased by using different matrix polymers with smaller electron affinities, such as ethyl vinyl acetates and thermoplastic polyurethane. The tunneling current decreases with increasing strain, which is accurately described by the Simmons approximation theory. The tunable transport in nanocomposites provides an advancement in the design of stretchable conductors.

INTRODUCTION

Stretchable conductive nanocomposites have received considerable attention for human-friendly soft electronic components such as wearable circuits, sensors, optoelectronic devices, and energy harvesters (1–4). The conductive nanocomposites are typically composed of conductive nanoparticulate fillers dispersed in a polymer matrix (5, 6). The electrical transport relies on conducting path construction by the fillers because most of the host polymers are intrinsically insulating. The electrical resistance, which is also dependent on materials’ geometry, determines the performance of conductive nanocomposites. The polymer matrix provides mechanical strength and stretchability to the nanocomposites. The invariable conductance of the nanocomposites over a wide strain range is required for stretchable electrode applications (1, 2), whereas strain-dependent conductance variation can be used for sensor devices (7, 8).

The electrical transport of the nanocomposites is governed by the percolation network of conductive fillers (9–12). It is desirable that metallic or carbonaceous fillers make direct physical contact with each other, decreasing interfacial contact resistance. Various methods have been proposed to decrease interparticle distances and to achieve direct physical contact more effectively. The particle size, length, aspect ratio, alignment, and distribution have been intensively investigated to achieve the percolation at a lower filler concentration (2, 11–17). These studies included one-dimensional carbon nanotubes and metallic nanowires (18–20). In addition to larger primary fillers, secondary fillers with substantially smaller nanoscale particles have also been added because the coalescence at the interfacial junction can be achieved at a lower curing temperature as the particle size is decreased (6, 20–22).

However, a substantial fraction of the fillers is still isolated and does not contribute to the electrical transport (11). Electron tunneling between noncoalesced particles can take place only when the particles are closely located in the highly insulating matrix polymer (11, 23, 24). The electron tunneling current depends on the width (i.e., interparticle distance) and height of potential energy barrier, and, in particular, the tunneling resistance exponentially increases with the tunneling width (11, 23, 25–26). The quantum mechanical tunneling has been extensively used for atomic-scale imaging in scanning tunneling microscopy (27) and semiconductor devices such as tunnel field-effect transistors, flash memories, field emission displays, and magnetic random access memories (28–30). In the case of a small tunneling barrier (<0.1 eV), thermionic emission with a controllable energy barrier height and charge depletion width at the junction between a metal electrode and semiconductor channel has also been reported (31). However, the electron tunneling has only been superficially explored in conductive nanocomposites although it is a major electrical transport mechanism in nanocomposites. A tunneling cutoff distance of 1 to 10 nm has been previously proposed in literature, without critically analyzing the barrier height between the matrix polymer and fillers, although it is a crucial parameter in nanocomposite percolation models (11, 12, 32).

Manipulation of the tunneling barrier height and width allows the ideal design of stretchable conductive nanocomposites. Here, we report the invariable resistance of a stretchable conductive nanocomposite over 30% tensile strain. The hierarchically structured silver nanosatellite (AgNS) particles with a bimodal size distribution (~3.47 and ~127 nm) are synthesized by the in situ etching and reduction reaction of Ag flakes (AgFLs) using tetrahydrofuran (THF) peroxide. With the optimized interparticle distance for electron tunneling transport (4.37 to 4.76 nm), the barrier height is deliberately controlled by using matrix polymers with different electron affinities: silicone rubber (SR; 4.76 eV), thermoplastic polyurethane (TPU; 4.21 eV), and ethyl vinyl acetates containing 25% vinyl acetate (EVA25; 4.35 eV) and 40% vinyl acetate (EVA40; 3.98 eV). The interparticle distance (i.e., barrier width) is further manipulated by stretching the nanocomposites. The resistances of the nanocomposites (TPU, EVA25, and EVA40) with non-negligible barrier heights increase with stretching, which follows the Simmons approximation model for tunneling (25). The energy barrier heights obtained by Kelvin probe force microscopy (KPFM) show excellent agreement with the
Simmons theory. In notable contrast, the resistance of the AgFL-AgNS-SR nanocomposite with a negligible tunneling barrier height remains constant over 30% tensile strain. There is a negligible change in the scattering of electrons over the initial (~4.37 nm) and elongated paths (<6 nm) in the matrix polymer of SR. Accordingly, our study provides a breakthrough on the basis of the tunable electron tunneling in stretchable conductive nanocomposites, which could be used for next-generation straintronics such as stretchable electrodes and ultrasensitive strain sensors.

RESULTS
Synthesis and characterization of AgFL-AgNS-polymer nanocomposites

The quantum tunneling occurs when two electrodes are separated by a sufficiently thin insulator (24). Figure 1A shows the schematic of quantum tunneling in Ag filler–polymer nanocomposites. The Ag fillers work as electrodes separated by a thin polymer barrier (width = d). The tunneling barrier height (λB) is determined by the difference between the work function of Ag (qφAg) and electron affinity of polymer (qχp; the energy difference between conduction band minimum and vacuum level) (24, 25). The Simmons approximation theory describes the electron tunneling current density (J) as a function of d and λB when the applied voltage across the electrodes (V) is sufficiently low (23, 25, 26)

\[ J = \frac{3(2m_ee^2)}{2\hbar d} V \exp\left(-\frac{4\pi d}{\hbar}(2m_ee^2)^{\frac{1}{2}}\lambda_B\right), \]

where \(m_e\) is the effective mass of electron, \(\hbar\) is Planck’s constant, and \(e\) is the elementary charge (see Supplementary Text for details). The tunneling barrier width (i.e., interparticle distance) can be continuously changed by stretching the nanocomposite. The barrier height can also be tuned by selecting polymer with different electron affinity. It is important to uniformly disperse fine conductive nanoparticles within the tunneling cutoff distance due to the exponential decrease in tunneling current with increasing barrier width. However, it is very challenging to achieve such dispersion by directly mixing nanoparticles with matrix polymer due to aggregation. In our previous study, we introduced the free radical and reactive oxygen species–mediated synthesis procedure is provided in Materials and Methods. Briefly, AgFLs (~4.3 μm) are reacted with THF peroxide in a polymer solution for 60 min. The surface of pristine AgFLs is smooth (Fig. 1E, inset). However, it becomes rough after the vigorous in situ etching and reduction reaction, generating hierarchically structured medium (~127 nm) and small (~3.6 nm) AgNS particles (Fig. 1E). The medium AgNS particles are observed in a scanning electron microscopy (SEM) image (Fig. 1E). High-resolution transmission electron microscopy (HRTEM) images also show the small AgNS particles (Fig. 1F). The particle size distribution is provided in fig. S2. The interparticle distance between AgNS particles is optimized for efficient electron tunneling, as will be discussed shortly. In the next step, the mixture is drop-casted and dried overnight to obtain an AgFL-AgNS-polymer nanocomposite. An optical image of a nanocomposite synthesized with EVA25 (AgFL-AgNS-EVA25 nanocomposite) is shown in Fig. 1D (top right). The AgFL-AgNS-EVA25 nanocomposite becomes brittle when the Ag filler concentration is greater than 40 volume %. Therefore, all the nanocomposites are synthesized using the identical Ag filler concentration of 40 volume % for property comparison.

Figure 1G shows small AgNS particles as a function of the THF peroxide concentration. The peroxidation of THF can be inhibited by a butylated hydroxytoluene (BHT) inhibitor (23). There is no AgNS particle generation when AgFLs are treated with THF containing the BHT inhibitor (15 ml of 0 M THF peroxide). In contrast, the population of small AgNS particles increases as the THF peroxide concentration increases. The densely distributed small AgNS particles are observed at 0.045 M (15 ml).

The work function of AgFLs and electron affinities of four matrix polymers (EVA40, TPU, EVA25, and SR) are measured by KPFM using a gold-coated silicon tip as shown in Fig. 1H (see Methods for details). The electron affinity is measured using pure polymer films (fig. S3). We note that the electron affinity of an insulating polymer can be measured by KPFM, as the charge transfer between the tip and specimen (making the contact potential difference) would be dominated by the charges in the conduction band minimum of the insulating polymer with the assumption of few gap states. The λB is then obtained from the difference between the work function of Ag and the electron affinity of polymer. This assumption could be further supported by the separately conducted Simmons approximation analysis, as will be discussed later. The λB obtained by the Simmons approximation model fitting precisely matches the λB obtained by the KPFM analysis.

The energy barrier height (\(\lambda_B\)) is directly obtained from the difference between the work function of AgFLs and the electron affinity of polymer, measured by KPFM. Therefore, the different electron affinities of matrix polymers provide a chance to tune \(\lambda_B\) and transport...
in conductive nanocomposites (Fig. 1H). In the case of SR, the surface potential (i.e., electron affinity = 4.76 eV) overlaps with the work function of AgFLs (4.71 eV). The $\lambda_B$ is almost zero, resulting in an efficient charge transport. The electron affinities of EVA25 (4.35 eV), TPU (4.21 eV), and EVA40 (3.98 eV) are smaller than the work function of AgFL. Accordingly, the $\lambda_B$ increases to 0.36, 0.50, and 0.73 eV, respectively.

Figure 1l shows the average particle sizes ($s$) and interparticle distances ($d_0$) of small AgNS particles in four different matrix polymers. The distribution data are also provided in figs. S4 and S5. There is no noticeable difference in $s$ (3.40 to 3.56 nm) and $d_0$ (4.37 to 4.76 nm) in the AgFL-AgNS-polymer nanocomposites. This indicates that the AgNS particle generation and dispersion are determined solely by the THF peroxide concentration rather than the type of matrix polymer. The volume fractions of medium and small AgNS particles in the SR matrix could be estimated using $s$ and $d_0$. The volume fractions of AgFLs and polymer, before the THF peroxide reaction, were made to be 40 and 60 volume %. For simplicity, the small spherical AgNS particles ($s$ = 3.47 nm, $d_0$ = 4.37 nm) are assumed to be arranged in a simple cubic structure in the polymer matrix after the reaction (fig. S6). This results in 2.72 volume % for small AgNS particles in the entire nanocomposite. Similarly, the volume fraction of medium AgNS particles ($s$ = 127 nm, $d_0$ = 221 nm) is estimated to be 1.53 volume % in the entire nanocomposite. Then, the volume fraction of AgFLs is calculated to be 35.75 volume %. Note that the in situ THF peroxide reaction does not change the total Ag concentration (40 volume %), because AgNS particles are generated from AgFLs.

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Electrical transport in AgFL-AgNS-polymer nanocomposites

Figure 2A shows the electrical resistivity of the AgFL-AgNS-SR, AgFL-AgNS-EVA40, AgFL-AgNS-TPU, and AgFL-AgNS-EVA25 nanocomposites as a function of THF peroxide concentration. The nanocomposite specimens are molded into a rectangular shape with a similar size (length = 20 mm, width = 5 mm, thickness = 0.4 to 0.42 mm) for the resistivity measurement, as shown in fig. S7. The resistivity is measured by the four-point probe method, and the slight thickness difference is corrected using the geometric factor for the resistivity calculation (19, 20). The electrical resistivity decreases with increasing THF peroxide concentration because of the active AgNS particle generation (Fig. 1G). The AgFL-AgNS-EVA25 nanocomposite shows the lowest resistivity compared with the AgFL-AgNS-TPU and AgFL-AgNS-EVA40 nanocomposites. This is due to the smaller $\lambda_B$ in the AgFL-AgNS-EVA25 nanocomposite (0.36 eV) compared with the AgFL-AgNS-TPU ($\lambda_B = 0.50$ eV) and AgFL-AgNS-EVA40 ($\lambda_B = 0.73$ eV) nanocomposites under a similar tunneling distance. However, the resistivity of the AgFL-AgNS-SR nanocomposite is higher even with the negligible $\lambda_B$. This is due to the viscoelastic playdough-like nature of SR. The linear polymer chains of SR are connected by the relatively weak hydrogen bonding, and different shapes are easily formed by the simple molding process (fig. S8A) (23). The hydrogen bonding also enables healing of the nanocomposite by slight pressurization, after breaking, as shown in fig. S9A. In contrast, the polymer chains of the other nanocomposites are connected by the strong C–C covalent bonding, exhibiting elastic stretching property. The AgFL-AgNS-EVA25, AgFL-AgNS-TPU, and AgFL-AgNS-EVA40 nanocomposites are not moldable and healable (figs. S8, B to D, and S9, B to D). The weak hydrogen bonding inevitably generates small voids in the AgFL-AgNS-SR nanocomposite during the bifurcation, reattachment, and molding process, decreasing conducting cross section and increasing resistivity. The cross-sectional SEM analysis shows the small voids (<10 µm) in the AgFL-AgNS-SR nanocomposite (fig. S10A). The other nanocomposites do not show these voids (fig. S10, B to D). The existence of the voids is also confirmed by density analysis (fig. S11). The experimentally measured density of the AgFL-AgNS-SR nanocomposite is 8.1% lower than the theoretical density, calculated by the rule of mixture, because of the voids. There is a close agreement (<1.3%) between the experimental and theoretical densities of the other nanocomposites without void. The resistivity of the nanocomposites synthesized using 0.045 M THF peroxide is also shown as a function of $\lambda_B$ in fig. S12.

Figure 2B shows the strain-dependent normalized current in the AgFL-AgNS-polymer nanocomposites (AgFL-AgNS = 40 volume %) measured using the two-probe method. The specimens with a similar size (length = 20 mm, width = 5 mm, thickness = 0.4 to 0.42 mm) are stretched using a universal testing machine (load cell = 50 N, crosshead speed = 1 mm/min). The Poisson’s ratios of the AgFL-AgNS-SR (0.39), AgFL-AgNS-EVA25 (0.34), AgFL-AgNS-TPU (0.24), and AgFL-AgNS-EVA40 (0.38) nanocomposites are measured during stretching. A low-bias voltage (10 mV) is used to avoid
any artifact that can modify the energy barrier alignment with Ag electrodes (25). The tunneling current critically depends on the interparticle distance (i.e., barrier width) under a given $\lambda_B$, as discussed in Eq. 1. However, the current is invariant for the AgFL-AgNS-SR nanocomposite over 30% tensile strain (black square in Fig. 2B). This indicates that the transport through the AgFL-AgNS-SR nanocomposite is not governed by the Simmons approximation theory, unlike the other nanocomposites. The exceptional transport feature originates from the close match between the work function of Ag (4.71 eV) and electron affinity of SR (4.76 eV), resulting in a negligible $\lambda_B$ (~0 eV). This allows an efficient electron flow via the conduction band of SR. Moreover, the short traveling distance between the AgNS particles (4.37 nm) enables the electron flow without additional stretching-induced scatterings in SR, which is interpreted as ballistic-like transport behavior. Thus, we achieve invariable resistance of the conductive nanocomposite over 30% strain, which deviates from the conventional Drude model. The Drude model links microscopic electron dynamics to macroscopic resistivity, where the resistivity is described by the scattering of electrons in materials (37). Therefore, the Drude model describes the resistance linearly proportional to the length of the specimen and follows Ohm’s law. It will be interesting to investigate energy quantization at low temperatures in the future. The necking of the AgFL-AgNS-SR nanocomposite occurs rapidly when the strain is further increased beyond 30%, and the specimen ruptures at ~33% strain (fig. S13). The current decreases rapidly with the mechanical rupture process.

In contrast, the currents of three other nanocomposites (AgFL-AgNS-EVA25, AgFL-AgNS-TPU, and AgFL-AgNS-EVA40) show exponential decay with increasing strain. The strain-induced modulation of tunneling distance is visualized in HRTEM images (Fig. 2C, AgFL-AgNS-TPU nanocomposite). The average interparticle distance between small AgNS particles (i.e., tunneling width) is increased from 4.48 nm (0% strain) to 5.36 nm (20% strain) by stretching. This leads to a rapid decrease in current. Note that the nanocomposite with a larger $\lambda_B$ results in a faster current decrease (EVA25 < TPU < EVA40) in Fig. 2B.

Figure 2D compares the experimentally measured current-strain data with the Simmons approximation theoretical model for electron tunneling. The detailed model fitting method is provided in Supplementary Text. The experimentally measured current of the AgFL-AgNS-SR nanocomposite is invariant over 30% strain, which deviates from the theory. The Simmons approximation model predicts a continuous decrease in tunneling current with increasing strain even in the case of $\lambda_B = 0$. As a control experiment, the ratio of AgFLs to AgNS particles is changed by using different THF peroxide concentrations (0 to 0.045 M). The nanocomposite without THF peroxide (0 M) has only AgFLs with an average interparticle distance of 1.31 μm (fig. S14). There is no AgNS particle generation at low THF peroxide concentrations (0.01 and 0.02 M). The current decreases rapidly with stretching if the nanocomposites have only AgFLs (fig. S15). An increase in the THF peroxide concentration to 0.026 M generates AgNS particles, and the interparticle distance between AgNS particles is decreased to 16.11 nm. The mixture of AgFLs and AgNS particles exists in the nanocomposite. Nevertheless, the current decreases with stretching, resulting in a negligible value at a strain of 3.3%, because the interparticle distance is still too long. A further increase in the THF peroxide concentration to 0.035 M generates more AgNS particles and decreases the interparticle distance to 10.04 nm. The current is invariant up to 8.1% strain and starts to decrease with further stretching. The interparticle distance is decreased to 4.37 nm, when the THF peroxide concentration is 0.045 M, resulting in invariable resistance over 30% strain. Apart from the negligible $\lambda_B$ in the AgFL-AgNS-SR nanocomposite, the short interparticle distance between AgNS particles (<6 nm even after 30% stretching) plays a vital role to realize the unique transport behavior.

In contrast, the transport is dominated by electron tunneling when $\lambda_B$ is not negligible, although the interparticle distance is short. The AgFL-AgNS-EVA25, AgFL-AgNS-TPU, and AgFL-AgNS-EVA40 nanocomposites with the non-negligible $\lambda_B$ and short interparticle distance (≤4.76 nm) show a nonlinear current decrease with increasing strain. This is accurately described by the Simmons approximation tunneling model (Eq. 1).

Figure 2E shows the energy band alignment diagram of the Ag, SR, EVA25, TPU, and EVA40. The Fermi levels are aligned in the diagram. The work function of Ag ($\phi_A = 4.71$ eV) and the surface potential (interpreted as electron affinity) of polymer ($\chi_p$), measured by KPFM, are shown in the diagram. The $\lambda_B$ values directly obtained using the KPFM measurements ($\lambda_B = \phi_A - \chi_p$) are denoted in red. The bandgap of the polymer is estimated from the ultraviolet-visible spectroscopy and Tauc plot analysis (fig. S16). The $\lambda_B$ values can also be obtained from the Simmons approximation model fitting of the current-strain data. These values are also shown using blue dashed lines. There is an excellent agreement between the $\lambda_B$ values obtained by the two independent methods. The KPFM analysis indicates that the $\lambda_B$ in the SR matrix is negligible (~0 eV) because of similar $\phi_A$ (4.71 eV) and $\chi_{SR}$ (4.76 eV). The Simmons approximation fitting also indicates a negligible $\lambda_B$. In such case, the Fermi level also aligns with the electron affinity in the SR matrix. The $\lambda_B$ values are also tabulated in table S2. This analysis supports the hypothesis of measuring the electron affinity of insulating polymers by KPFM.

The current-voltage ($I-V$) characteristics of the AgFL-AgNS-polymer nanocomposites are investigated using Ag electrodes (fig. S17). The AgFL-AgNS-SR nanocomposite with a negligible barrier height shows a linear $I-V$ characteristic. In contrast, the AgFL-AgNS-EVA25, AgFL-AgNS-TPU, and AgFL-AgNS-EVA40 nanocomposites with non-negligible barrier heights show nonlinear $I-V$ characteristics. To further validate the tunneling transport mechanism, the electrical resistivity of the AgFL-AgNS-polymer nanocomposites is investigated as a function of temperature (Fig. 2F). The electrical resistivity increases with increasing temperature in all the nanocomposites, excluding other transport mechanisms such as hopping and thermionic emission (38). Note that the hopping and thermionic emission exhibit decreasing resistivity with increasing temperature (39).

Note that the major focus of our previous publication was healing property investigation of nanocomposites, although the in situ generation of AgNS particles was introduced (23). The conductance of the nanocomposites was not previously investigated as a function of tensile strain (23). This study leads to the notable observation of invariable resistance upon stretching when the tunneling barrier height is negligible. Furthermore, the systematic strain-dependent conductance variation is achieved by adjusting the electron affinity of matrix polymer, which shows an excellent agreement with the Simmons approximation model for quantum tunneling (25, 26). This work provides notable insights for the mechanism analysis and design of stretchable conductors.
Applications of tunable transport in the nanocomposites

The tunneling barrier–dependent transport can be used for various practical applications. The invariable conductance of the nanocomposite can be used for a stretchable electrode. As shown in Fig. 3A, a light-emitting diode (LED) is connected to the AgFL-AgNS-SR nanocomposite ($\lambda_B \approx 0$ eV) using copper wires. The tensile strain is applied using a laboratory-built stretching device equipped with a stepper motor (19, 20). There is a negligible change in $I-V$ characteristics before and after stretching, confirming the invariable resistance. The brightness of the LED is also unchanged during the stretching (Fig. 3A, inset). In contrast, the current decreases after stretching for the nanocomposites with non-negligible barrier heights (Fig. 3B). It is noteworthy that the current decrease is larger for the nanocomposite with a larger $\lambda_B$ [EVA25 (0.36 eV) < TPU (0.50 eV) < EVA40 (0.73 eV)]. Accordingly, the brightness of the LED is decreased after stretching (fig. S18).

The exponentially varying tunneling current with distance has been used to observe surface atoms in scanning tunneling microscopy. It can also be used for the development of strain sensors. Figure 3C compares the apparent stress-strain characteristics of the nanocomposites. The AgFL-AgNS-TPU nanocomposite shows the highest tensile strength (2.02 MPa) compared with the AgFL-AgNS-EVA40 (1.60 MPa) and AgFL-AgNS-EVA25 (0.30 MPa) nanocomposites. This is due to the intrinsically stronger mechanical strength of TPU. Note that the tensile strength (0.02 MPa) of the AgFL-AgNS-SR nanocomposite is smaller than the other nanocomposites. The linear polymer chains of the viscoelastic playdough-like SR are connected by the relatively weak hydrogen bonding, resulting in small voids in the nanocomposite. The voids can be removed by introducing stronger covalent bonding between the linear polymer chains using cross-linkers. This will increase tensile strength and decrease resistance. We leave the cross-linking study for future work because it will also alter the electron affinity of the matrix polymer (40). The inset in Fig. 3C shows the relative resistance change ($\Delta R/R_0$) as a function of strain, which is simultaneously measured during the stress-strain experiment. There is a negligible change in the resistance of the AgFL-AgNS-SR nanocomposite. This is consistent with the observation in Figs. 2B and 3A. Again, the strain-induced resistance variation increases as the $\lambda_B$ increases [EVA25 (0.36 eV) < TPU (0.50 eV) < EVA40 (0.73 eV)]. The gauge factor $|(\Delta R/R_0)/\Delta \varepsilon, \varepsilon = \text{strain}|$ (41, 42) of the AgFL-AgNS-EVA40 nanocomposite is as high as 673 at $\Delta \varepsilon = 15\%$. This is comparable with those of highly sensitive metal or carbon-based strain sensors in literature (fig. S19) (43–47).

Figure 3D shows the cyclic resistance change of the AgFL-AgNS-TPU nanocomposite, which has the highest tensile strength. It shows a nearly perfect reversibility during 30 cycles. The tensile stress-strain data of the AgFL-AgNS-TPU nanocomposite are also shown in fig. S20. There is a hysteresis between stretching and releasing cycles due to the intrinsic nature of TPU. However, the nanocomposite is still reversible because the hysteresis pattern is repeatable without deviation for 30 cycles. Note that this study is primarily focused on the tunneling barrier–dependent transport physics of...
DISCUSSION
In summary, the invariable resistance of the AgFL-AgNS-SR nanocomposite is achieved over 30% tensile strain, which deviates from the conventional Drude model for resistivity and Simmons approximation theory for quantum tunneling. The unique transport behavior is achieved by the short interparticle distance and negligible barrier height. The hierarchically structured AgNS particles with a bimodal size distribution (~3.47 and ~127 nm) result in the short interparticle distance of 4.37 nm. Moreover, the barrier height between SR and Ag is negligible, which is independently confirmed by KPFA measurements and Simmons approximation model fitting. The transport can also be changed to quantum tunneling with tunable barrier heights by using different matrix polymers with smaller electron affinities. The resistance increases in order with stretching as the barrier height increases [EVA25 (0.36 eV) < TPU (0.50 eV) < EVA40 (0.73 eV)], which is accurately described by the Simmons approximation theory. Our study provides notable insight into the transport physics and future design of stretchable conductive nanocomposites.

MATERIALS AND METHODS
Synthesis of the AgFL-AgNS-SR, AgFL-AgNS-EVA25, AgFL-AgNS-TPU, and AgFL-AgNS-EVA40 nanocomposites
THF (Sigma-Aldrich, 401757) is air-bubbled for 72 hours to prepare THF peroxide (0.045 M). The AgFL-AgNS-SR nanocomposite is then synthesized following a previously published protocol (23). Briefly, SR [15 weight % (wt %); Wacker Chemie, ELASTOSIL R 401/10] is dissolved in THF with a BHT inhibitor (Sigma-Aldrich, 186562) to prepare a polymer solution. In the next step, AgFLs (40 volume %; Metalor, SA-31812) are dispersed in the SR polymer solution (2 g) with additional THF peroxide (15 ml, 0.045 M) by tip sonication (420 W, 10 min). The mixture is further stirred for ~60 min (300 rpm) to generate AgNS particles. Last, the mixture is drop-cast and dried overnight to obtain the AgFL-AgNS-SR nanocomposite (23). The AgFL-AgNS-EVA25, AgFL-AgNS-TPU, and AgFL-AgNS-EVA40 nanocomposites are synthesized using EVA25 (7 wt %; Sigma-Aldrich, 437220), TPU (7 wt %; Songwon Industrial, P-3185A), and EVA40 (15 wt %; Sigma-Aldrich, 340502), respectively. The other procedures are identical.

Characterization
The $^1$H NMR (700 MHz; Bruker, AVANCEIII700) analysis is carried out using CDCl$_3$ ($\delta = 7.26$ ppm; Sigma-Aldrich, 151858) (23). The microstructure is investigated by HRTEM (JEOL, Cs-corrected JEM-ARM 200F) and SEM (JEOL, JSM-7600F). The resistivity is measured by the four-point probe in-line method using a laboratory-built device (19, 20, 23). The distance between tungsten probes is 1 mm. The stress-strain characteristics are measured using a universal testing machine (Instron, 3343). The current change of the nanocomposite is also measured as a function of strain using a digital multimeter (Agilent, E3648A) and a data acquisition software (Keysight BenchVue). The resistance change of the specimen is measured during the stress-strain experiment using a digital multimeter (Fluke, 289 True-RMS multimeter). A laboratory-built stretching device is used for the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20). The surface potential is measured by the LED demonstration (19, 20).

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