

Highly Sensitive Multifilament Fiber Strain Sensors with Ultrabroad Sensing Range for Textile Electronics

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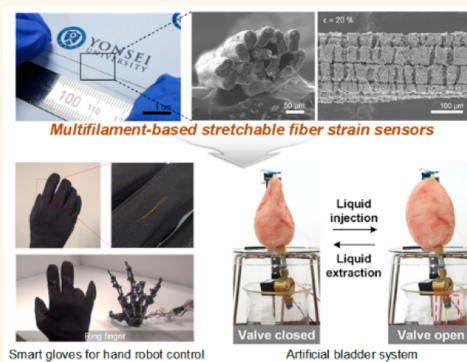
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S Supporting Information

ABSTRACT: Highly stretchable fiber strain sensors are one of the most important components for various applications in wearable electronics, electronic textiles, and biomedical electronics. Herein, we present a facile approach for fabricating highly stretchable and sensitive fiber strain sensors by embedding Ag nanoparticles into a stretchable fiber with a multifilament structure. The multifilament structure and Ag-rich shells of the fiber strain sensor enable the sensor to simultaneously achieve both a high sensitivity and largely wide sensing range despite its simple fabrication process and components. The fiber strain sensor simultaneously exhibits ultrahigh gauge factors ($\sim 9.3 \times 10^5$ and ~ 659 in the first stretching and subsequent stretching, respectively), a very broad strain-sensing range (450 and 200% for the first and subsequent stretching, respectively), and high durability for more than 10 000 stretching cycles. The fiber strain sensors can also be readily integrated into a glove to control a hand robot and effectively applied to monitor the large volume expansion of a balloon and a pig bladder for an artificial bladder system, thereby demonstrating the potential of the fiber strain sensors as candidates for electronic textiles, wearable electronics, and biomedical engineering.

KEYWORDS: fiber strain sensors, stretchable electronics, strain sensors, wearable electronics, biomedical engineering



Electronic devices with stretchable and wearable features have attracted tremendous attention as next-generation electronics because of their potential applications in wearable electronics, electronic skins, soft robotics, and biomedical electronics.^{1–8} Despite their several advantages and applications, conventional planar electronic devices have been limited to being woven into various flexible textiles or integrated onto complex nonplanar substrates, which has largely hindered their use in textiles, advanced wearable electronics, and biomedical applications.^{9–11} To this end, stretchable and wearable electronic devices in the form of fibers, such as fiber-shaped electrical conductors,^{12–14} energy devices,^{15–17} light-emitting devices,⁹ actuators,^{18,19} and sensors,^{20–22} have been intensively studied. In particular, fiber strain sensors, which can be woven into textiles or integrated onto nonplanar objects to monitor various human activities, are promising candidates for advanced wearable and stretchable electronics in the future.^{21–24}

For the development of fiber-based stretchable and wearable strain sensors, there have been various attempts to use conductive nanomaterials as a sensing element and polymeric elastomers as a stretchable scaffold. Several nanomaterials, including carbon nanotubes (CNTs),^{23,25–27} graphene,^{21,22,28,29} metallic nanoparticles,³⁰ and nanowires,^{24,27,31,32} have been widely explored for strain sensors because of their excellent flexibility and electrical properties. Nevertheless, it was difficult to simultaneously achieve high sensitivity and a broad sensing range for the vast majority of previous strain sensors; this limitation introduces a critical difficulty in various applications, including monitoring full-range human activities ranging from subtle physiological signals to vigorous motions. Wang *et al.* reported a highly elastic fiber strain sensor based on buckled

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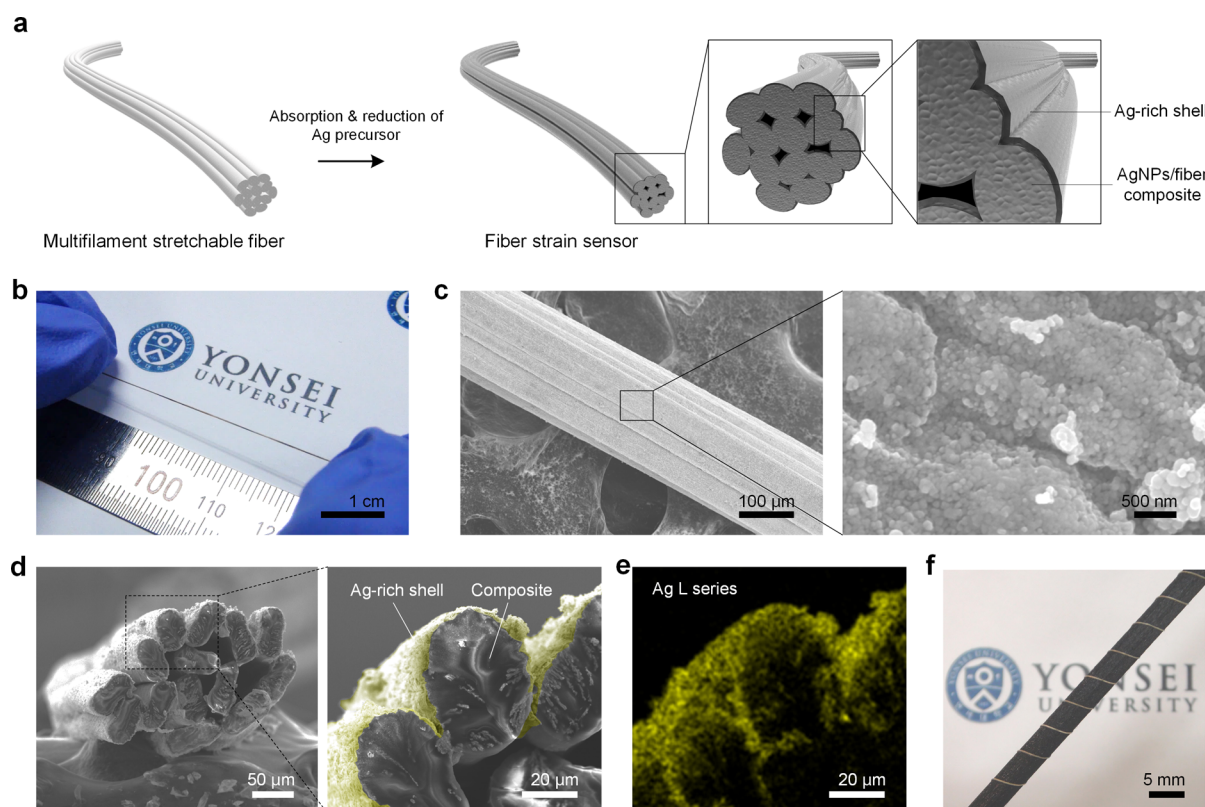


Figure 1. (a) Schematic illustration of the fabrication process for a fiber strain sensor. The higher-magnification illustrations of the cross-sectional fiber show the multifilament structure and Ag-rich shell of the fiber sensor. (b) Photograph of the fabricated fiber strain sensor. (c) Typical SEM images showing the surface of the fiber strain sensor. The fiber is uniformly coated with Ag nanoparticles (the corresponding higher-magnification image). (d) Cross-sectional SEM images of the fiber strain sensor. The fiber comprises a Ag-rich shell and a composite between the Ag and stretchable fiber (the corresponding higher-magnification image). (e) EDS mapping images showing the distribution of Ag nanoparticles in the fiber. (f) Photograph of the fiber strain sensor wound on the surface of a thin rod. Yonsei University logo used with permission.

CNT sheets.²⁵ Their sensor could be operated at strains as high as 600%; however, it exhibited a low gauge factor (GF) of only 0.5 in the strain range of 200%, limiting its ability to detect delicate deformations. To enhance the performance of fiber strain sensors, a Ag nanowire-based fiber strain sensor with a relatively high sensitivity of ~ 15 over a wide workable strain range as large as $\sim 100\%$ was reported; however, it is still insufficient for monitoring large deformations and includes high-cost conductive fillers which can hinder their use in industry.²⁴ Thus, the development of fiber strain sensors, which simultaneously exhibit high sensitivity and excellent strain-sensing range, remains a challenge for future technology.

Herein, we present an effective approach for fabricating highly sensitive and stretchable fiber strain sensors that simultaneously exhibit outstanding sensitivity and excellent sensing range, by incorporating only Ag nanoparticles into multifilament-structured stretchable fibers. The fiber strain sensors were fabricated by directly converting a large amount of Ag^+ ions into Ag nanoparticles inside a stretchable fiber comprising coalesced multi-microfilaments. The multifilament structure and Ag-rich shells of the fiber strain sensor enable the sensor to achieve outstanding sensitivity and wide sensing range at the same time despite the simple fabrication process and components of the sensor. The obtained fiber strain sensors exhibited a combination of ultrahigh sensitivity to tensile strain ($\sim 9.3 \times 10^5$ and ~ 659 in the first stretching and subsequent stretching, respectively), a largely wide strain-sensing range

(450 and 200% for the first and subsequent stretching, respectively), and high durability for more than 10 000 stretching cycles. In addition to the high performance, the fiber strain sensor can be successfully fabricated using commercialized stretchable fibers based on the absorption and reduction steps of Ag precursors, easily leading to the commercialization of the sensor. The absence of any high-aspect-ratio conductive fillers, which can limit the potential of the sensor because of their complicated synthesis and separation, is also beneficial in terms of the simplicity of the fabrication and cost. Additional elastomeric protection layers on the surface of the sensor could provide high biocompatibility for biomedical applications as well as high durability against the mechanical damages and humidity. The fiber strain sensor was fully integrated into a glove using a simple sewing method, demonstrating that the wearable sensor could be used to detect human motions precisely and to connect the human activities with robot movements as a smart textile. We also demonstrated that the fiber strain sensor could be used to fabricate an artificial bladder system by monitoring the large volumetric change of a balloon or pig bladder.

RESULTS AND DISCUSSION

Fabrication of Fiber Strain Sensor Using Multifilament Stretchable Fiber. Figure 1a presents a schematic illustration of the fabrication procedure and the structure of the highly sensitive and stretchable fiber strain sensors. The

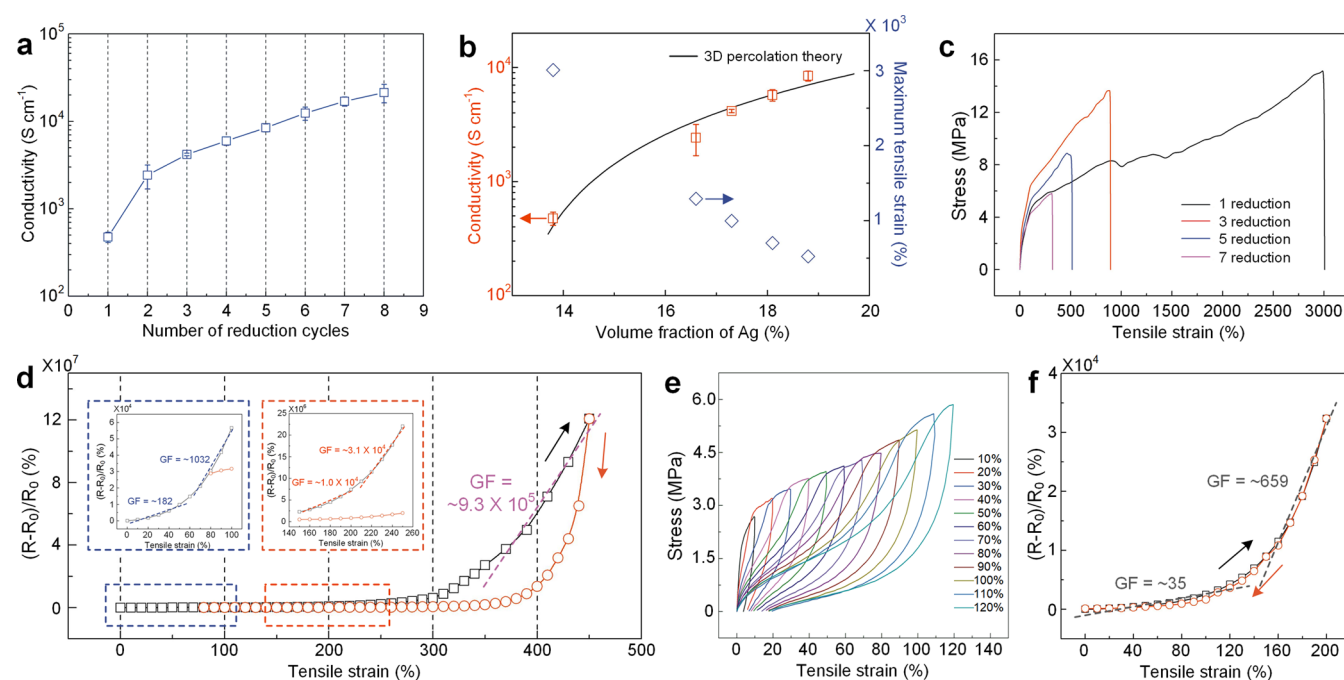


Figure 2. (a) Initial electrical conductivity of the fiber strain sensor according to the cycles of absorption and reduction of Ag^+ ions. (b) Dependence of the initial conductivity and maximum tensile strain of the fiber strain sensor on the volume fraction of Ag at $\varepsilon = 0\%$. The black line represents the calculated conductivity of the fiber based on the power-law relation and 3D percolation theory. (c) Stress-strain curve for fiber strain sensors fabricated with various numbers of cycles of absorption and reduction of Ag^+ ions. (d) Relative change in the electrical resistance of the fiber strain sensor as a function of the first applied and released maximal strain. Inset graphs show the relative change in the electrical resistance of the sensor versus the strain within the range of 0–100% and 150–250%, respectively. (e) Stress-strain curves of the fiber strain sensors for different strains, showing the mechanical hysteresis of the sensor according to the various applied strains. (f) Relative change in the electrical resistance of the sensor according to the subsequent stretching and releasing.

fabrication of the fiber strain sensors involved two main steps: the absorption of a Ag precursor into the stretchable fibers and reduction of the absorbed Ag precursor into Ag nanoparticles in the fibers. Here, a polyurethane-based commercialized stretchable fiber with a coalesced multi-microfilament structure resulting from its dry spinning process³³ was used as a highly elastic scaffold (Figure 1a and Figure S1). A large amount of Ag precursor was efficiently absorbed by immersing the stretchable fiber into a 40 wt % AgCF_3COO solution in ethanol for 30 min. In particular, because the trifluoroacetate anions (CF_3COO^-) induce an ion–dipole interaction with the hydroxyl groups ($-\text{OH}$) of the alcoholic solvent, which is easily absorbed into the fibers, the Ag precursors were rapidly and effectively absorbed into the fibers during the immersion step.^{4,34} To verify the successful absorption of the Ag precursor into the fibers, we carried out Fourier transform infrared spectroscopy (FTIR) measurements of the stretchable fibers with absorbed precursor; the results are shown in Figure S2. The specific peaks at 1145 and 1197 cm^{-1} , which represent the C–F stretching vibrations of the Ag precursor, in the FTIR spectra evidently reveal the successful absorption of the Ag precursor into the fibers.^{35,36} The Ag precursor absorbed into the fibers was easily converted into Ag nanoparticles using a solution of hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot 4\text{H}_2\text{O}$), completing the preparation of the Ag nanoparticle-based fiber strain sensors. Figure 1b and Figure S3 present photographs of the fabricated fiber strain sensors, showing the change in the color of the fiber due to the converted Ag nanoparticles on the surface of the fiber.

Typical scanning electron microscopy (SEM) images of the fiber strain sensors (diameter $\sim 206 \mu\text{m}$) reveal that the Ag nanoparticles were densely coated onto the surface of the fiber

without any damage to the fiber (Figure 1c). In addition, a substantial amount of Ag nanoparticles was effectively generated inside of the fiber sensor from the Ag precursor absorbed into the fiber, leading to excellent electrical connections between all the Ag nanoparticles (Figure S4). Despite the intensive incorporation of the Ag nanoparticles into the polymeric fiber, the multifilament structure of the fiber remained intact, as observed in the cross-sectional SEM images in Figure 1d. In particular, because the Ag precursors were gradually absorbed toward the center of the fiber during the absorption step of Ag precursors, the Ag nanoparticles were gradually distributed inside the fiber. This process resulted in the formation of a Ag-rich shell along the surface of the fiber (Figure 1a and the higher-magnification SEM image in Figure 1d). The gradual distribution of the Ag nanoparticles inside the fiber is clearly identified in the energy-dispersive X-ray spectroscopy (EDS) mapping image of the cross section of the fiber (Figure 1e). Although the Ag-rich shell of the fiber strain sensor was expected to behave like a bulk Ag shell because of the dense distribution of the Ag nanoparticles, X-ray photoelectron spectroscopy (XPS) clearly confirmed that the Ag-rich shell was a composite of Ag nanoparticles and the elastomeric polymer of the fiber (Figure S5). Therefore, the fiber strain sensors could retain the high flexibility of the fiber despite the fiber's relatively rigid Ag-rich shells, as shown in Figure 1f.

Electrical and Mechanical Properties of Fiber Strain Sensor. The initial electrical conductivity of the fiber strain sensor varied with the number of absorption and reduction cycles for the Ag precursors (Figure 2a). The initial electrical conductivity of the fiber strain sensor was substantially

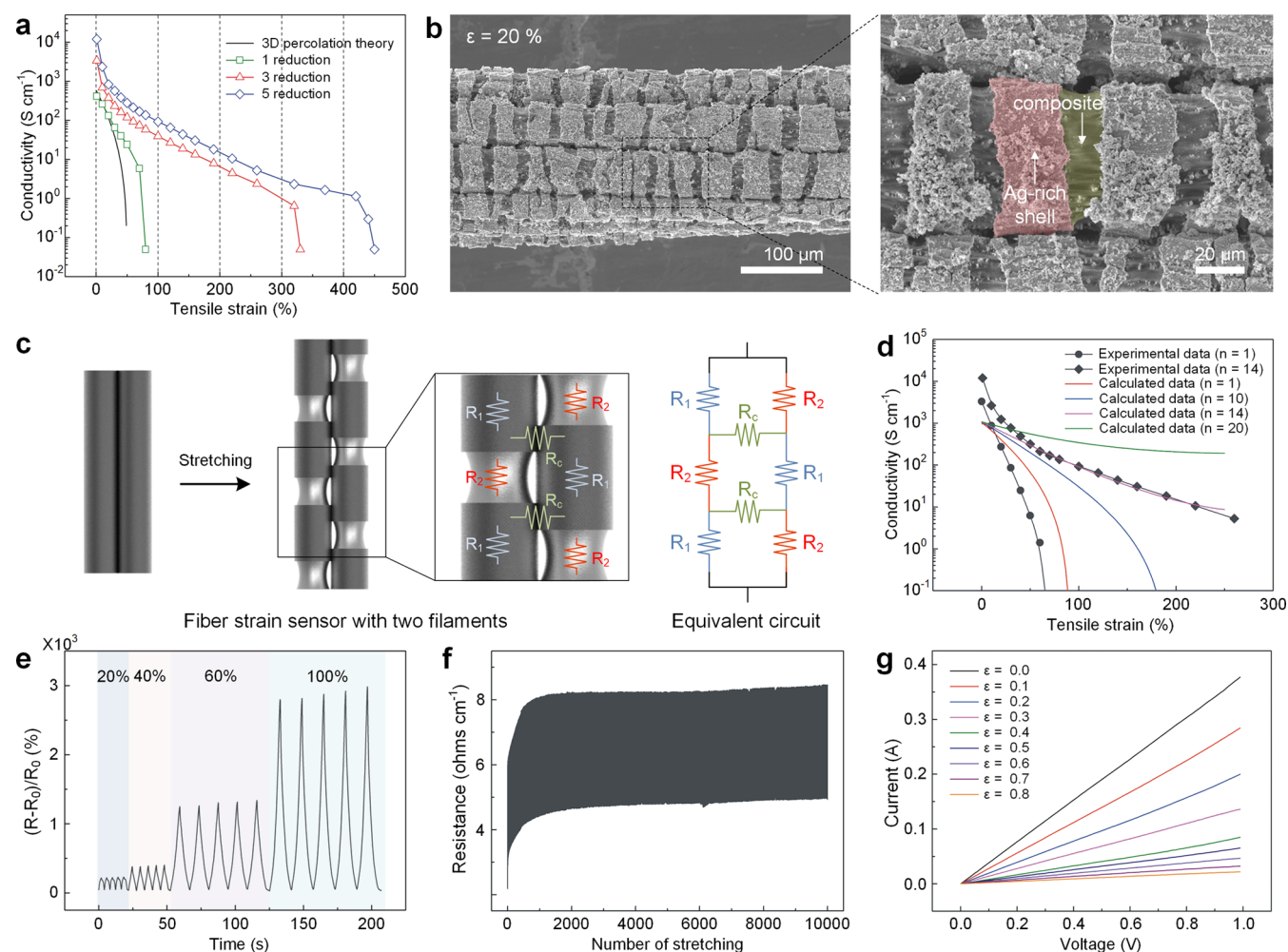


Figure 3. (a) Electrical conductivities of the fiber strain sensors under various conditions and calculated conductivity of the fiber sensor using the classical 3D percolation theory according to the applied strain. (b) SEM images showing the fiber strain sensor at $\epsilon = 20\%$. The corresponding higher-magnification image (right panel) shows that the fiber strain sensor exhibits a Ag-rich shell region that grabs the inner composite (highlighted in red) and an inner composite region that is exposed (highlighted in yellow). (c) Schematic illustrations showing the resistance model of the fiber strain sensor with two filaments and the corresponding equivalent circuit. (d) Conductivity dependence on tensile strain for fiber strain sensors with mono- and multifilaments; n represents the number of filaments in the fiber strain sensors. The solid line represents the calculated conductivity dependence on the applied strain for the fiber with various numbers of filaments based on the modified percolation theory for the fiber strain sensor with multifilament structure ($\alpha = 0.0036$). (e) Normalized resistance changes of the strain sensor against the repeated strains of 20, 40, 60, and 100%. (f) Stability of the resistive response of the fiber strain sensor to the repeated strains of 10% over 10 000 cycles. (g) I - V curves for the fiber strain sensor under various strains.

enhanced to $20\,964\text{ S cm}^{-1}$ by repeating the absorption and reduction steps of the Ag precursors. Because the repetitive steps lead to an increase in the amount of Ag nanoparticles inside the fiber, as demonstrated in the thermogravimetric analysis (TGA) results in Figure S6, the enhancement of the initial electrical conductivity of the fiber strain sensor is attributed mainly to the dense electrical connections between the greater number of Ag nanoparticles in the fiber. The electrical conductivity of conductive composites can be generally explained by the three-dimensional (3D) percolation theory and the classical power-law relationship as follows:

$$\sigma = \sigma_0(V_f^0 - V_c^0)^s \quad (1)$$

where σ is the electrical conductivity of the composites, σ_0 is the bulk conductivity of the filler, V_f^0 and V_c^0 indicate the volume fractions of the filler and percolation threshold without external strain, respectively, and s is the critical exponent.^{37,38} Figure 2b shows the initial electrical conductivity of the fiber

strain sensor as a function of the volume fraction of the Ag in the fiber; these results show excellent agreement with the calculation results based on the 3D percolation theory and eq 1. The detailed calculation of the conductivity of the fiber using the classical 3D percolation theory is described in Figure S7 and in the Supporting Information. Although the initial electrical conductivity of the fiber strain sensor was significantly improved with increasing number of absorption and reduction cycles for the Ag precursors, the mechanical rupture strain of the fiber strain sensor gradually decreased, as shown in Figure 2b,c. Because the elastic properties of composites between metal nanoparticles and elastomers depend strongly on the amount of nanoparticles embedded in the elastomer,^{13,39} the reduced mechanical rupture strain of the fiber strain sensor is attributed to the increase in the amount of Ag nanoparticles in the fiber sensor. Nevertheless, the mechanical stretchability of the fiber strain sensor is still sufficient to cover the strain-sensing range of the fiber strain sensor.

Figure 2d shows the relative changes in the electrical resistance of the fiber strain sensor fabricated through five reduction processes for the first application and consecutive release of the 450% strain. The fiber strain sensor exhibited a steep increase in electrical resistance with increasing strain; it also exhibited a highly wide strain-sensing range of 450%. The rapid increase in the electrical resistance of the fiber strain sensor is attributed to the loss of the electrical connections between the percolated Ag nanoparticles with increasing applied strain. The GF of the strain sensor, obtained as the slope of the graph in Figure 2d, is generally defined as $GF = \delta((R - R_0)/R_0)/\delta\epsilon$, where R and R_0 indicate the electrical resistance with and without tensile strain ϵ , respectively. Notably, the fiber strain sensors have a very low initial resistance (R_0) of $\sim 0.16 \text{ ohms cm}^{-1}$ because of the dense connections between Ag nanoparticles, which makes the fiber strain sensors exhibit a large relative change in resistance $((R - R_0)/R_0)$ and therefore an excellent GF. The fiber strain sensor roughly exhibited an outstanding GF of ~ 182 and ~ 1032 for the strain range within 100%, $\sim 1.0 \times 10^4$ and $\sim 3.1 \times 10^4$ for 150–250% and $\sim 9.3 \times 10^5$ for 300–450%, thereby demonstrating the high sensitivity and wide strain-sensing range of the fiber strain sensor. On the other hand, Figure 2d,e shows that the fiber strain sensor has electrical and mechanical hysteresis in the first stretching. The hysteresis and slight plastic deformation of the sensor can be attributed to the time-dependent behavior and stress relaxation of free chains in the network of the viscoelastic elastomer in the sensor.^{40–42} However, the sensor showed a negligible hysteresis in the subsequent stretching, demonstrating that the prestrained sensor has a high stability and elasticity (Figure 2f). The prestrained sensor simultaneously exhibited a high GF of ~ 35 and ~ 659 for the strain range within 100% and 150–200%, respectively. The GF and strain-sensing range of the sensor in the subsequent stretching decreased due to an increased base resistance and initial length of the sensor during the first stretching. However, the sensor still exhibited higher performance in comparison with the previously reported strain sensors (Figure S8). It is generally difficult to simultaneously achieve such a high GF and a wide sensing range in a strain sensor; nevertheless, the fiber strain sensor exhibited noteworthy performances, with a wide sensing range as well as an outstanding GF.

Analysis on Highly Broad Sensing Range of Fiber Strain Sensor. To analyze and understand the mechanism responsible for the wide sensing range of the fiber strain sensor, its electrical stretchability was evaluated on the basis of the classical 3D percolation theory. As shown in Figure 3a, it is hard for typical conductive composites following the 3D percolation theory to achieve such a wide strain-sensing range; however, the electrical stretchability of our fiber strain sensor is considerably higher than that of the typical conductive composites despite the much smaller aspect ratio of the conductive filler. In particular, the electrical stretchability of the fiber strain sensor was effectively increased as the reduction process of Ag precursors was repeated. The extraordinary capability of the fiber strain sensor can be attributed to its multi-microfilament structure and Ag-rich shells. When external strain was applied to the sensor, the Ag-rich shells, which behave similar to bulk Ag shells, cracked. This cracking led to the development of two main regions in the fiber strain sensor, as observed in Figure 3b: (i) a region in which the Ag-rich shell grabs the inner conductive composite between the Ag

nanoparticles and the polymeric fiber and (ii) a region where the inner conductive composite is exposed to the exterior. As described in Figure S9, the inner stress from the applied strain was mainly concentrated to the cracked Ag-rich shells in low strains. On the other hand, the stress was distributed to the region where the inner composite was exposed in high strains. Therefore, the Ag shells were mainly cracked at the relatively low strain ($\sim 150\%$), and the stretching of the inner composites was dominant in comparison to the cracking of the Ag-rich shells at high strain ($>150\%$), as shown in Figure S10. In addition, because the Ag-rich shells were composed of the composites of Ag nanoparticles and elastomeric polymers, the cracked Ag-rich shells can be stably preserved even after the fiber strain sensor was stretched to the high strain of 450% (Figure S11).

To understand how the fiber strain sensor exhibits such a wide sensing range, we developed a simple model using a fiber strain sensor comprising two filaments, as shown in Figure 3c. During the stretching of the fiber strain sensor, the cracks in the Ag-rich shells in each filament are assumed to form independently and randomly. On the basis of the equivalent circuit of the model shown in Figure 3c, the total electrical resistance of the stretched fiber strain sensor can be calculated as follows:

$$R_{\text{total}} = \frac{3R_1 \times R_2}{R_1 + R_2} + 2R_c \quad (2)$$

where R_1 , R_2 , and R_c represent the resistance of the region where the Ag-rich shell grabs the inner composite, the resistance of the region where the conductive composite is exposed, and the contact resistance between the Ag-rich shell regions in neighboring filaments, respectively. Here, because the inner conductive composite of the fiber strain sensor follows the 3D percolation theory, R_2 is expected to rapidly increase with increasing tensile strain compared that of R_1 and R_c because of the loss of connections between the Ag nanoparticles in the fiber sensor. The electrical resistance of the region for the Ag-rich shell (R_1) and the contact resistance (R_c), however, are expected to increase relatively slowly with increasing applied strain because the tight grip of the Ag-rich shell compensates for the tensile strain applied to the inner composites. Even if an external strain sufficiently high to break the electrical conduction of general conductive composites is applied to the fiber strain sensor, which induces an infinite increase in R_1 , eq 2 for the equivalent resistance of the fiber strain sensor becomes $R_{\text{total}} = 3R_1 + 2R_c$, and the fiber strain sensor can exceptionally retain the ability to transport electrons efficiently despite the high strain. Figure 3d presents the electrical conductivities of the fiber strain sensors comprising mono- and multifilaments with progressively increasing tensile strain. The results demonstrate the expected improvement in the electrical stretchability of the multifilament-based fiber strain sensor. In particular, because more contacts between the Ag-rich shells in neighboring filaments would be formed with increasing number of filaments, the strain-sensing range of the fiber strain sensor was effectively enhanced according to the number of the filaments in the fiber (Figure S12). Meanwhile, the number of the repeated reduction processes significantly affected the electrical stretchability of the fiber strain sensor (Figure 3a). As described in Figure 3c, the optimal cracking process of the Ag-rich shells is critical for the formation of electrical connections *via* the cracks, which lead to the high electrical stretchability. The cracking process is directly related

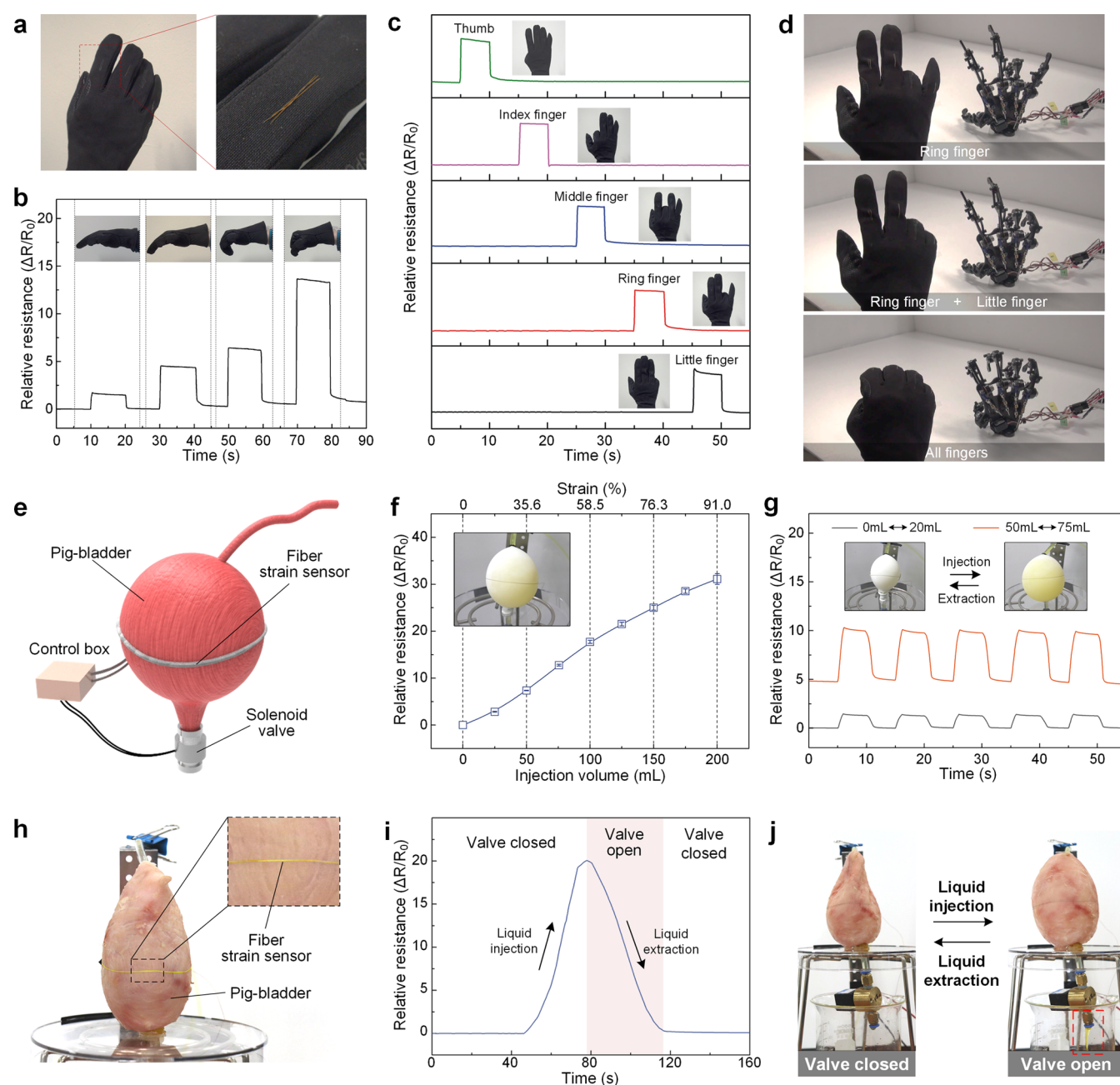


Figure 4. (a) Photograph showing the smart glove with the fiber strain sensors on the nodes of the five fingers. (b,c) Resistive responses of the fiber strain sensors in the smart glove for (b) various bending degrees of the fingers and (c) a full bending stimulation of each finger. (d) Photographs of a remotely operated hand robot controlled by the smart glove. (e) Schematic illustration of the artificial bladder system fabricated using the fiber strain sensor. (f) Change in resistive response of the fiber strain sensor on the rubber balloon according to the injection of yellow-dyed DI water (<200 mL). The inset image shows a photograph of the fiber strain sensor on the expanded rubber balloon. (g) Resistive response of the fiber strain sensor on the rubber balloon against the repeated injection of various amounts of liquid. (h) Photograph showing the fiber strain sensor on the pig bladder for the artificial bladder system. (i) Resistive response of the fiber strain sensor on the pig bladder and the operation of a solenoid valve according to the injection and extraction of liquid. (j) Photographs showing the operation of the artificial bladder system using the fiber strain sensor on the pig bladder.

to the appropriate fracture strengths of the Ag-rich shells, and the strength is determined by the contents of Ag nanoparticles. Thus, the optimized number of the reduction process is important for the high electrical stretchability of the sensor. If the reduction process was repeated for more than five cycles, which is the optimized condition for the sensor, the electrical stretchability of the sensor was gradually decreased, as shown in Figure S13. The decrease is attributed to the excessively high fracture strength of the cracked Ag-rich shells, resulting from

high contents of Ag nanoparticles in the sensor, which restricted the effective cracking process of the cracked Ag-rich shells. Consequently, on the basis of the multifilament structure and Ag-rich shell structure, our fiber strain sensor simultaneously achieved high sensitivity (*i.e.*, a high GF) and outstanding sensing range compared to that of previously reported strain sensors, as shown in Figure S8. For the fiber strain sensor comprising the monofilament, the electrical conductivity of the sensor decreased more dramatically with

increasing tensile strain than predicted on the basis of the classical power-law relationship (eq 1), leading to the diminished sensing range of the sensor (Figure 3d). Further degradation of the fiber strain sensor with the monofilament is attributed to the concentrated strain at the site where the inner conductive composite is exposed (a more detailed analysis is presented in Figure S14). As shown in Figure S15, the monofilament-based fiber strain sensor exhibited high gauge factors of ~ 406 and $\sim 7.0 \times 10^5$ for the strain range within 70%. Nevertheless, it is still limited as an advanced strain sensor for various applications due to its poor strain-sensing range.

Because the electrical stretchability of the fiber strain sensor is far superior to the calculated result (Figure 3a), the classical percolation theory cannot clearly explain the behavior of the fiber strain sensor with the multifilament structure. For our fiber strain sensor, the volumetric proportion of the conductive path in the fiber was reduced as tensile strain was applied to the fiber. Therefore, the percolation threshold (V_c^0), which represents the minimum volume fraction of Ag needed to obtain electrical conduction, can be decreased with increasing tensile strain. On the basis of the analysis, eq 1 for the classical power-law relationship was successfully modified for the multifilament-based fiber strain sensor by changing V_c^0 on the basis of the number of filaments in the fiber (n), a structural coefficient (α), and the square-root dependency of strain ε as follows:

$$V_c(\varepsilon) = \frac{V_c^0}{1 + \alpha n^2 \sqrt{\varepsilon}} \quad (3)$$

The structural coefficient α reflects the multifilament structure of the fiber that forms the conductive pathway under tensile strain. The modified percolation theory for our fiber strain sensor with multifilament structure exhibited excellent agreement with the experimental results, as shown in Figure 3d.

Stable and Reliable Operation of Fiber Strain Sensors.

Furthermore, we found that the fiber strain sensor exhibited stable and distinguishable responses with high repeatability for various tensile strains of 20, 40, 60, and 100% after an prestrain of 450% was applied to the sensor (Figure 3e). The response of the sensor for the various strains in Figure 3e are in excellent agreement with that of the sensor for the subsequent stretching in Figure 2f. The high durability of the fiber strain sensor was intensively investigated through repetitive stretch cycles, as shown in Figure 3f. Although the output signals of the strain sensor increased slightly in the early cycles because of the viscoelastic property of the elastomeric fiber, these output signals were stably maintained without considerable degradation despite the intensive 10 000 cycle tests with 10% strain. In addition, the resistive responses of the sensors under 10 000 cycle tests at various large strains of 50, 70, and 100% were also stably saturated, as shown in Figure S16. Although the saturated resistances of the sensors were increased with an increase in the applied strain due to the time-dependent behavior and the relaxation property of the elastomeric polymer in the sensor,^{40,41} the increased values could be effectively recovered if sufficient relaxation time was given even after the intensive cyclic tests (Figure S17). The high stability of the sensor can be attributed to the stable preservation of the cracked Ag-rich shells on the sensor despite the cyclic tests. As shown in Figure S11, the cracks of the Ag-rich shells on the fiber strain sensor were stably preserved despite the repeated stretching tests, leading the high stability of the sensor against the repeated

external strains. In addition, the fiber strain sensor can achieve high stabilities against external mechanical damages and humid conditions by uniformly coating the additional protection layers such as poly(dimethylsiloxane) (PDMS) or Ecoflex on the surface of the sensor (Figure S18). Figure 3g also presents I - V curves for the fiber strain sensors under various applied strains, showing the stably linear response under several conditions. These observations suggest that the fiber strain sensor has excellent stability for use as a high-performance wearable strain sensor.

Fiber Strain Sensor-Based Smart Glove for Controlling Hand Robot.

Given the excellent sensitivity, broad sensing range, high flexibility, and fibrous one-dimensional (1D) structure of the fiber strain sensor, it has tremendous potential for several applications in wearable and textile electronics. We first demonstrated that the fiber strain sensor could be applied for human-machine interfaces as a real-wearable sensor platform by simply sewing the fiber sensors onto the nodes of five fingers of a glove (Figure 4a). Because of the high sensitivity of the fiber strain sensor, the smart glove could easily monitor real-time motion of each finger. The bending degree of the fingers was precisely distinguished by monitoring the relative change in the resistance of the strain sensors in the smart glove, as shown in Figure 4b. Each strain sensor in the smart glove also exhibited a distinguishable response to the bending of the corresponding finger without any considerable interference between sensors (Figure 4c). On the basis of its performance, the smart glove including the wearable textile sensors was used to control a hand robot. To acquire output signals of each sensor, each fiber strain sensor in the smart glove was connected to a read-out circuit that included a driving circuit and microcontroller. While a constant voltage (5 V) was applied to each fiber strain sensor in the glove, the microprocessor unit measured the corresponding voltage change resulting from the resistance change of each sensor and transmitted the digital data to a computer (Figure S19). The responses of the five fiber strain sensors integrated onto the fingers of the smart glove were used to control the bending motion of the corresponding fingers of the hand robot. As demonstrated in Figure 4d and Movie S1, the various motions of the hand robot could be successfully controlled via the same motion of the smart glove system.

Artificial Bladder System Using a Fiber Strain Sensor.

As a further demonstration of the potential applications of the highly stretchable fiber strain sensor, we also developed an artificial bladder system, in which the sensor is used to monitor the volume of a bladder and control the extraction of the liquid in the bladder (Figure 4e). In general, a neurogenic lower urinary tract dysfunction resulting from spinal cord injury negatively affects a patient's quality of life and can lead to progressive renal failure.⁴³ Therefore, it is highly important for the patients to monitor the expansion of their bladder volume; however, methods for monitoring bladder volume are limited because of some restrictions such as the large stretching range of the bladder surfaces and the 3D curved surfaces of the bladder. To demonstrate the potential of our highly stretchable fiber strain sensor as a bladder sensor, we applied our sensor onto 3D curved surfaces of a rubber balloon and pig bladder. As shown in Figure 4f, the electrical resistance of the fiber strain sensor on the surface of the rubber balloon increased as yellow-dyed DI water was injected, which increased the strain of the balloon's surface (see Supporting Information for details). The fiber strain sensor could effectively detect the volumetric

change of the balloon despite the large amount of liquid injected. Figure 4g and Movie S2 present the resistive response of the fiber strain sensor against the repeated injection of the liquid, showing that the strain sensor has a stable and reliable continuous response for the various repeated volumetric changes. Moreover, the fiber strain sensor was used to realize an artificial bladder system with a pig bladder. For the fabrication of the artificial bladder system, we used a solenoid valve at the bladder outlet and automatically controlled the valve using a custom-made control circuit (see Figure 4e,g, Figure S20, and Methods section for details). Similar to that on the rubber balloon, the fiber strain sensor on the surface of the pig bladder exhibited a stable resistive response according to the injection and extraction of external liquids, as shown in Figure 4i. The solenoid valve was set to be closed before the resistive response of the sensor reached a certain threshold value and open until the response completely returned to its initial state from the threshold value (Figure 4i). Through the fiber strain sensor and solenoid valve, the artificial bladder system could be successfully operated against repeated injection and extraction of liquid (Figure 4j and Movie S3 and Movie S4). The pig bladder in the artificial bladder system was expanded until it reached 200 mL of liquid, similar to the general one-time urine volume of a normal adult. After the response of the sensor reached the threshold value corresponding to the injection of the 200 mL of liquid, the solenoid valve was opened and the stored liquid in the bladder was extracted until the bladder volume returned to its initial state. For the *in vivo* applications based on the fiber strain sensor, the limited biocompatibility of the Ag nanoparticles embedded in the sensor can be effectively improved by uniformly coating the additional protection layers such as PDMS or Ecoflex, which have excellent biocompatibility (Figure S21). In addition, the water-proof property of the sensor is also expected to be achieved by coating the protection layers or low-surface energy materials. These results imply that the fiber strain sensor shows strong potential as a powerful platform for smart wearable systems, textile electronics, and stretchable electronics.

CONCLUSIONS

In summary, using the multifilament structure of fibers and Ag-rich shells, we have developed highly sensitive and stretchable fiber strain sensors that simultaneously exhibit excellent sensitivity and outstanding strain-sensing range. The fiber strain sensors were successfully prepared by incorporating a large amount of Ag nanoparticles into elastomeric fibers comprising the coalesced multi-microfilaments. The sensors featured a high initial conductivity of $20\,964\text{ S cm}^{-1}$, high GF, and very broad strain-sensing range ($\sim 9.3 \times 10^5$ and 450% in the first stretching, ~ 659 and 200% in the subsequent stretching) and high durability over 10 000 cycles. Both experimental observations and theoretical analyses indicated that the multifilament structure and Ag-rich shell of the fiber strain sensor contributed to the outstanding sensing range of the sensor. We demonstrated that the fiber strain sensor is a promising candidate for wearable and textile electronics by readily integrating the sensors into a glove to detect hand motions and control a hand robot. In addition, the fiber strain sensor was used to develop an artificial bladder system by effectively monitoring the volumetric change of a pig bladder. Based on the high performance of the fiber strain sensor, we believe that it provides an innovative option for developing next-generation applications such as stretchable electronics,

biomedical engineering, textile electronics, and advanced wearable electronics.

METHODS

Fabrication of Fiber Strain Sensors. Polyurethane-based stretchable fibers (Creora, purchased from Hyosung) were cleaned via mild sonication in deionized (DI) water for 5 min. A large number of Ag^+ ions were absorbed into the fibers by immersing the stretchable fibers into a AgCF_3COO solution in ethanol (40 wt %) for 30 min. After the alcoholic solvent was evaporated from the fibers for 5 min, a mixture of hydrazine hydrate and ethanol (1:1 in volume ratio) was dropped onto the fibers to reduce the Ag^+ ions absorbed into the fibers to Ag nanoparticles. After 5 min, the reduction agent was washed from the fiber several times with DI water, and the residual water was completely evaporated in air to remove the reduction agent.

Smart Glove Test. A smart glove that can detect the motion of a hand was simply fabricated by sewing the fiber strain sensors at each node of the five fingers. To read the output signal of the fiber strain sensors in the glove, the commercialized read-out circuit including a resistor divider circuit and voltage measurement tools (Arduino Uno Rev3) was connected to both ends of each strain sensor at the five fingers. While a constant voltage (5 V) was applied to each fiber strain sensor in the glove, the voltage drop resulting from the electrical resistance of each fiber sensor in the glove was measured using the read-out circuit. The measured data were transmitted to a computer through serial communication, and the resistance change of the corresponding fiber strain sensor in each finger was calculated using the measured voltage values. Based on the resistance measurement of the fiber strain sensors in the smart glove, the movement of each finger in the smart glove was monitored and connected to the movement of the hand robot using the MATLAB program.

Artificial Bladder System. The fiber strain sensor was simply mounted along the central perimeter of the rubber balloon or pig bladder, and a solenoid valve was integrated at the outlet of the balloon and bladder for the fabrication of an artificial bladder system. Thirty milliliters and 50 mL of DI water were, respectively, injected into the rubber balloon and pig bladder beforehand to form and maintain their initial shape. To read the output signal of the fiber strain sensor, a commercialized read-out circuit (Arduino Uno Rev3) was connected to both ends of the strain sensor in the same manner as the smart glove. The read-out circuit was integrated with a power supply and driving circuit to control the operation of the solenoid valve according to the resistive response of the strain sensor (Figure S19). Using the custom-made control circuit, the solenoid valve was set to receive driving voltage (13 V) from the power supply only while the resistive response of the strain sensor above a certain threshold returned to its initial value.

Simulation Using Finite Element Method. Three-dimensional modeling and numerical simulations were performed using the COMSOL Multiphysics (version 5.0) software. We used a 2D axisymmetric model to simplify the model for a filament of the fiber. A linear elastic model was used for the Ag shell, and a Neo-Hookean hyperelastic model was used for the composite between Ag and the stretchable fiber. Finer meshes were used near the Ag-rich shell to increase the accuracy of the model. In particular, 1587 and 5419 triangular meshes were used for the simulation of the fibers with a 5 and 50 μm thick Ag-rich shell, respectively. One edge of the fiber was fixed, while the other edge was displaced with a prescribed value of $L_0 \times \text{strain}$ along the axial direction to stretch the fiber strain sensor. Axial symmetric boundary conditions were applied to the center axis of the fiber, and symmetric boundary conditions were applied to the fixed edge of the fiber.

Biocompatibility Test. C2C12 myoblasts (ATCC, USA) were used to evaluate the biocompatibility of the fibers. The cells (1×10^5 cells/mL) were seeded directly on the surface of the fiber samples and cultured in Dulbecco's modified Eagle's medium supplemented with 10% fetal bovine serum (Gibco) P/S. All cell culture experiments were performed in a humidified incubator with 5% CO_2 at 37 °C. The fiber samples were sterilized with ultraviolet light and 70% v/v ethanol

before the cell culture. The viabilities of the cells on the conductive fibers were characterized over time (days 1 and 3) using a live/dead viability/cytotoxicity kit (Invitrogen) according to the manufacturer's instruction. Live/dead images were taken using an inverted fluorescence microscope (Zeiss Axio Imager.A2 m; Zeiss, Göttingen, Germany).

Characterization. The electrical resistance of the fiber strain sensor was measured with a constant current of 0.1 mA using a Keithley 2400 sourcemeter after eliminating the contact resistances between the fibers and the device. The stretching experiment was carried out using a custom-made stretching machine. The surface morphologies were examined using a JEOL JSM-7001F field emission scanning electron microscope coupled with an EDS system, and the FTIR spectrum was obtained using a Bruker Vertex 70 FTIR spectrometer. The components of the Ag-rich shell in the fiber were measured using XPS (K-alpha, Thermo U.K.). The weight fraction of Ag in the fiber strain sensor was measured using thermogravimetry analysis (Q50, TA Instruments), and the stress-strain curves of the fibers were obtained using a custom-made tensile property tester.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.7b07795.

Movie S1: Operation of hand robot using smart glove (AVI)

Movie S2: Reliable train sensing of balloon using fiber strain sensor (AVI)

Movie S3: Artificial bladder system based on fiber strain sensor on pig bladder (AVI)

Movie S4: Artificial bladder system based on fiber strain sensor on balloon (AVI)

Theoretical calculations related to the conductivity of fiber strain sensors and the applied strain to the fiber strain sensor on the rubber balloon; photograph of the stretchable fibers and fiber strain sensors; FTIR analysis of the stretchable fiber before and after Ag precursor absorption; EDS mapping results of the fiber strain sensors; XPS spectra of the surface of untreated stretchable fibers and fiber strain sensors; TGA results of the fiber strain sensor; experimental Poisson ratios of the fiber strain sensors with various conditions; comparison of performances between the fiber strain sensors and previously reported strain sensors; computational simulations of cracking process of the Ag-rich shells on the fiber strain sensors; cracking process of the Ag-rich shells according to the applied strain; strain-sensing range of the fiber strain sensors with various numbers of the filaments and reduction processes; analysis for the fiber strain sensor composed of monofilament; stability of the fiber strain sensor against various repeated large strains, mechanical damages, and humidity; block diagrams of the custom-made circuits for measurement of the sensor signals; biocompatibility test for the untreated fiber strain sensor, PDMS-coated, and Ecoflex-coated sensor (PDF)

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Author Contributions

J.L. conducted the overall experiments, measurements, and analysis and wrote the manuscript. S.S. provided the assistance on the fabrication of the fiber strain sensors. S.L. performed the computational simulation for the cracking process of the Ag-rich shells on the fiber strain sensor under various strains. J.S. conducted the various stability tests of the fiber strain sensor, and S.K. supported the measurement and evaluation of the fiber strain sensors. H.H. assisted the experiments related to applications of the fiber strain sensors. S.G.K. designed and fabricated the circuits for the operation of the hand robot. S.K. performed the biocompatibility tests on the sensors. J.S. and D.E.K. provided helpful discussions on data analysis. T.L. supervised the project.

Notes

The authors declare no competing financial interest.

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