Rubbery electronics and sensors from intrinsically stretchable elastomeric composites of semiconductors and conductors

Hae-Jin Kim,1 Kyoseung Sim,2 Anish Thukral,1 Cunjiang Yu1,2,3,4*

A general strategy to impart mechanical stretchability to stretchable electronics involves engineering materials into special architectures to accommodate or eliminate the mechanical strain in nonstretchable electronic materials while stretched. We introduce an all solution–processed type of electronics and sensors that are rubbery and intrinsically stretchable as an outcome from all the elastomeric materials in percolated composite formats with P3HT-NFs [poly(3-hexylthiophene-2,5-diyl) nanofibrils] and AuNP-AgNW (Au nanoparticles with conformally coated silver nanowires) in PDMS (polydimethylsiloxane). The fabricated thin-film transistors retain their electrical performances by more than 55% upon 50% stretching and exhibit one of the highest P3HT-based field-effect mobilities of 1.4 cm²/V·s, owing to crystallinity improvement. Rubbery sensors, which include strain, pressure, and temperature sensors, show reliable sensing capabilities and are exploited as smart skins that enable gesture translation for sign language alphabet and haptic sensing for robotics to illustrate one of the applications of the sensors.

RESULTS

Intrinsically stretchable elastomeric composite conductors and semiconductors

Figure 1A shows a schematic illustration of sensors (upper) and TFTs (lower), which were constructed from AuNP-AgNW/PDMS elastomeric conductor, P3HT-NF/PDMS elastomeric semiconductor, and ion gel dielectric. We used AuNP-AgNW/PDMS composites as stretchable conductors to form an ohmic contact with P3HT-NF/PDMS because an energy barrier would exist for AgNW-based electrodes (28). We coated the AgNWs with AuNPs using a galvanic replacement process.
to form AuNP-AgNW (29). Comparison studies in transistor characteristics are described to further emphasize the necessity of developing these conductors. The detailed electrode preparation process is presented in Materials and Methods. Figure 1B shows the schematic illustrations of the AgNW before (upper left) and after (upper right) AuNP conformal coating. Note that only the exposed AgNWs will be coated with AuNPs. Scanning electron microscopy (SEM) images of AgNWs before (bottom left) and after (bottom right) conformal AuNP coating indicate the success of the galvanic replacement process (fig. S1). We performed stretching tests to examine the electrical characteristic change associated with the applied mechanical strain. Specifically, the AuNP-AgNW/PDMS electrode can be elastically stretched, and its sheet resistance increases from 2 to 5 ohms/□ upon 50% uniaxial stretching, as shown in Fig. 1C (upper). The SEM images in Fig. 1C (lower) revealed that no obvious crack was observed.

The stretchable elastomeric composite semiconductor is prepared by two major sequential steps: (i) forming the one-dimensional self-assembled π-conjugated P3HT-NFs in the solvent under a cooling process and (ii) blending the resulting P3HT-NFs with PDMS to yield percolated nanofibrils in a rubber matrix. This process not only forms percolated pathways for the carriers to transport but also results in P3HT-NFs that significantly improve crystallinity and therefore enhance the carrier mobility, as detailed in previous studies (22, 23, 30).

Specifically, P3HT was first dissolved in the m-xylene solvent at 60°C (fig. S2A, bright orange) and then cooled down and kept for 10 min at −20°C to form P3HT-NF (fig. S2A, dark purple). Transmission electron microscopy (TEM) and atomic force microscopy (AFM) images of the prepared P3HT-NF indicate that the diameter and length of P3HT-NF are 40 nm and 1.5 μm, respectively (fig. S2). The P3HT-NF solution was blended with a solvent (m-xylene−diluted PDMS [10:1 (w/w) prepolymer/curing agent]) to allow thorough mixing. A thin-film P3HT-NF/PDMS stretchable semiconductor is achieved by spin-coating, followed by solidifying at 60°C. We obtained the optimized weight composition of P3HT through systematic studies of the percolation behaviors, morphologies, and their electrical characteristics (fig. S3). The P3HT/PDMS weight ratio of 2:8 was chosen owing to the absence of microcracks and a moderate decrease in mobilities, as shown in fig. S4. We carried out AFM scanning to examine the microstructures...
of the nanofibrils and the detailed surface morphology of the P3HT-NF/PDMS thin film spin-coated on a PDMS substrate. The left AFM image in Fig. 1D with a scanning area of 1 μm × 1 μm shows the surface topography of the film. The right AFM image in Fig. 1D under phase mode illustrates the stiffness contrast between P3HT-NFs (~0.3 GPa) (31) and PDMS (~1 MPa) (32). The schematic illustration in Fig. S2E shows how the P3HT-NFs behave upon stretching at different extent. The P3HT-NFs first straighten and then eventually start to rupture, which can be seen from the AFM images in Fig. 1E. As the yellow arrows indicate, some P3HT-NFs rupture when stretched up to or beyond 50%. Nevertheless, majorities of the P3HT-NFs remain connected at 50%. Owing to the composite merits of elastomeric mechanical properties from the elastomer PDMS and the electrical conductance from the percolated P3HT-NFs, the P3HT-NF/PDMS can be stretched or twisted and return to its original state without any cracks, as shown in Fig. 1F. The stretchable ion gel dielectric was prepared by the solution-casting method. The detailed preparation can be found in Materials and Methods. The composite shows relatively stable electrical conductivity even after exposure in the environment (25°C, 75% relative humidity) for 600 hours (fig. S5). No obvious crack of the membrane was observed when it was stretched by 50%, as shown in Fig. 1G.

**Intrinsically stretchable rubbery transistors**

We constructed stretchable ion-gate TFTs by using these intrinsically stretchable electronic materials based on solution processes, including spin coating and stencil printing. Figure 2A shows the schematic structure of an ion gel-gated TFT. Specifically, the source and drain AuNP-AgNW/PDMS electrodes and P3HT-NF/PDMS composite semiconductor layer were patterned with a thin Kapton film-based stencil masks, which were generated by a cutting machine (Silhouette Cameo). A 140-μm-thick ion gel film was aligned and laminated on the source and drain electrodes to serve as ion-gated dielectric. The detailed fabrication process is described in Materials and Methods and fig. S6. Figure 2 (B and C) shows a photograph of fabricated TFT and an SEM image showing a channel length of 50 μm, respectively. The width of the channel was 5 mm. The thickness of the P3HT-NF/PDMS composite semiconductor and TFT were measured to be ~280 nm and ~430 μm, respectively (fig. S7).

To verify the feasibility and necessity of AuNP-AgNW/PDMS electrodes for the intrinsically stretchable rubbery TFT, we tested several different electrodes and carefully examined their corresponding characteristics. Specifically, we constructed TFTs and tested electron beam-evaporated Au and Ag electrodes and AgNW/PDMS- and AuNP-AgNW/PDMS-based electrodes. Only Au electrodes and AuNP-AgNW/PDMS-based TFTs showed transistor characteristics. The comparison results are presented in fig. S8. The results suggest that only Au or AuNP-AgNW can form an ohmic contact with the P3HT-NF/PDMS, and the Ag film or AgNW cannot (28).

Figure 2D shows the transfer $I_{ds} \sim V_{G}$ and corresponding $I_{ds}^{1/2} \sim V_{G}$ curves of the stretchable ion-gated TFT without any mechanical stretching. The drain current was obtained while the gate voltage ($V_{G}$) was swept from 0 to −4 V, with the drain voltage kept at ~0.5 V. The $I_{ON/OFF}$ was calculated to be $-5.6 \times 10^{5}$, which is comparable to other P3HT-NF-based stretchable TFTs (23). Figure 2E shows the sourcedrain $I_{DS} \sim V_{DS}$ characteristics of the TFT with a gate voltage decrease from −1.5 to −4 V at a voltage step of ~0.5 V. The drain voltage was decreased from 0 to −0.5 V. The drain current was as high as ~0.35 mA at $V_{G} = -4$ V and $V_{DS} = -0.5$ V.

To verify that the TFTs from P3HT-NF/PDMS composite semiconductor can offer enhanced device performance, we construct TFTs with a semiconductor from pristine P3HT and PDMS (p-P3HT/PDMS) composite on Au electrodes as a comparison. The TFTs from p-P3HT/PDMS and P3HT-NF/PDMS composite showed $\mu_{FE}$ of $4.5 \times 10^{-3}$ and 1.3 cm²/V·s and $I_{ON/OFF}$ of $1.68 \times 10^{2}$ and $3.82 \times 10^{2}$, respectively. Details are illustrated in fig. S9. Compared to p-P3HT, P3HT-NFs obtained through π conjugation of the thiophene rings yielded more efficient carrier transport and better device performance. These results are also consistent with the reported P3HT-NF–based devices (33).

To examine the transistor performances under mechanical strain, the characteristics of the fabricated TFT were measured while different levels of mechanical strain were applied using a custom-made stretcher. The strain was applied both along and perpendicular to the channel length directions. Because the TFT was constructed fully with elastomeric materials whose moduli are comparable and thus with no significant strain isolation effect (34, 35), the stretching strain applied is assumed to be evenly distributed across the whole device. Figure 2 (F and G) shows the transfer curves of the TFTs under 10, 30, and 50% mechanical strain along and perpendicular to the channel length directions, respectively. More detailed results are shown in fig. S10. On the basis of the linear regime of these transfer curves, the μ and threshold voltage ($V_{th}$) of the TFTs under different levels of mechanical strain were calculated (see the Supplementary Materials for details).

On one hand, once the TFT was stretched by up to 50% along the channel length direction, a moderate decrease in μ from 1.4 to 0.8 cm²/V·s and a slight increase in $V_{th}$ from −2.56 to −2.45 V were obtained (Fig. 2H). On the other hand, once it was stretched by up to 50% perpendicular to the channel length direction, a relatively larger decrease in μ from 1.4 to 0.4 cm²/V·s and a slight decrease in $V_{th}$ from −2.56 to −2.61 V were obtained (Fig. 2I). Note that owing to the gating effect, the TFT experiences less decrease in the channel current upon mechanical stretching compared with the devices without a gate, such as strain sensors, as described below. A similar phenomenon has been reported elsewhere (36). All these results suggest that the intrinsically stretchable rubbery transistors can maintain normal operation and relatively stable device performances while undergoing large mechanical stretching.

**Strain, pressure, and temperature sensors**

Various sensors, such as strain, pressure, and temperature sensors, were exploited by using intrinsically stretchable electronic materials. Figure 3A shows a schematic illustration of a strain sensor with a two-terminal configuration in which a P3HT-NF/PDMS stretchable semiconductor is connected at both ends with AuNP-AgNW/PDMS electrodes. The length and width of the channel were 50 μm and 5 mm, respectively. The thickness of the P3HT-NF/PDMS stretchable semiconductor was ~100 nm. The device was fabricated in a way similar to that of the transistor. Figure 3B presents a series images of a device stretched from 0 to 50% upon stretching, the electrical resistance increases. Figure 3C shows the plot of the measured electrical resistance versus the mechanical strain from 0 to 50% for both directions. When the applied strain was along the channel length direction, the resistance increased from 0.3 to 4.6 gigohms, and an approximately linear increase of resistance was obtained upon mechanical stretching. Note that the increase of resistance was mainly attributed to the semiconductor rather than to the conductor. The conductor contributes negligibly, as exhibited in Fig. 1G, compared with the overall resistance increase.

When the applied strain was perpendicular to the channel length direction, a much smaller increase in resistance from 0.3 to 0.64 gigohms was observed. Cyclic mechanical stretching and releasing of the strain sensor under a cyclic mechanical tester (CK-700FET, CKSI Co. Ltd.)
were performed to evaluate the stability of the sensor. The stretching increased from 0 to 50%, with a step increase of 10% along the channel length direction. Figure 3D shows the normalized electrical resistance during cyclic stretching and releasing at a rate of 1 Hz. These results agree with the measured resistance change, as shown in Fig. 3C. The inset in Fig. 3D shows a magnified resistance change of the sensor at 30% cyclic stretching, and stable and repetitive response was achieved. The calculated gauge factor (GF), defined as the ratio between the relative resistance change ($\Delta R/R_o$) and the extent of mechanical stretching, is shown in Fig. 3E. A GF of 33 is achieved for the 50% stretching. Note that this GF value is the highest, to our best knowledge, compared with GF values of other organic material– and inorganic material–based strain sensors that can be directly stretched to a similar extent, such as 50% (37, 38).

A similar two-terminal device configuration was adopted for pressure sensors because the applied pressure induces semiconductor deforming, which results in resistance change. Specifically, relative electrical resistance ($R/R_o$) was consecutively measured by applying different Hertzian contact pressures (see the Supplementary Materials for details). As shown in Fig. 3F, the applied pressure ranges from 0.66 to 1.2 MPa, and the resistance changes accordingly. With an increase of the applied Hertzian pressure from 0.66 to 1.2 MPa, the $R/R_o$ increases from ~0.98 to ~3.3. The change of $R/R_o$ corresponding to different applied pressures is plotted in Fig. 3G. The near hysteresis-less characteristic
for the loading/unloading cycle suggests that this device is a viable pressure sensor.

Temperature sensors were also exploited with the similar two-terminal device structure. The resistance changes of $R/R_o$ with respect to different temperatures were carefully examined. As shown in Fig. 3H, the $R/R_o$ decreased from 1.0 to 0.67 with an increase of temperature from 30° to 50°C. The experienced resistivity decrease is a major result of increased carrier concentration, which agrees with the reported work on P3HT from others (39–41). The measured temperature coefficients of resistance at 303 K (30°C), 313 K (40°C), and 323 K (50°C) are $-0.028/K$, $-0.023/K$, and $-0.016/K$, respectively (see the Supplementary Materials for details).

**Intrinsically stretchable rubbery sensors for robotic skins**

Owing to the simple form of rubber, the merits of great stretchability, and the retention of electrical functions, we applied our intrinsically stretchable rubbery device methods to construct smart artificial skins for robot hands, in which large deformations exist locally near the joints. As a demonstration, Fig. 4A presents arrays of strain, pressure, and temperature sensors mounted on a robotic hand (Star Wars Science, Darth Vader robotic arm). In particular, the temperature and pressure sensors were placed on the phalanges instead of the joints of the fingers to avoid coupled output from the finger motions. This artificial skin is implemented to impart capabilities, such as gesture interpretation and haptic sensing for robots. Specifically, the strain sensors directly translate the gesture into an electrical parameter, that is, resistance, which will facilitate the understanding of sign language. The strain sensor characteristics were calibrated for the finger subjected to different bending angles, wherein different mechanical strains are associated. As exhibited in Fig. 4 (B and C), the electrical resistances are 0.50, 0.78, 0.98, 1.35, and 1.57 gigohms corresponding to angles of 0°, 30° (that is, $\varepsilon = 8\%$), 45° ($\varepsilon = 10\%$), 60° ($\varepsilon = 13\%$), and 90° ($\varepsilon = 15\%$), respectively. These results are consistent with the aforementioned results in Fig. 3D. Direct linkage between the mappings of the resistance of the deformed strain sensor array with the specific gestures of the sign language alphabet has been built. A whole set of finger-based gestures of the sign language alphabet can be translated into letters by using 14 strain sensors that are mounted on all the joints of a robot finger. For example, to express the sign language alphabet “Y”, the index, middle, and ring fingers are completely folded (providing higher electrical resistance, >1.3 gigohms), whereas the thumb and pinky fingers were straightened (showing lower electrical resistance, <0.5 gigohms) (fig. S9). Figure 4D shows a set of letters, representing “YU LAB,” which was translated by configuring the hand into specific gestures correspondingly. The details of the sign language translation can be found in the Supplementary Materials and figs. S11 and S12. Although the sensors have shown the capability of translating the majority of the gestures in American Sign Language, note that integrating these sensors with other types of devices, such as accelerometers, suggests a possible approach to differentiating the letters (for example, I and J) with similar gestures but different motions.

To demonstrate its use as a temperature sensor, the skin with temperature sensors implemented on the robot hand was in contact with...

---

Fig. 3. Rubbery strain, pressure, and temperature sensors. (A) Exploded schematic illustration of the strain sensor. (B) Photographs of the sensors under different levels of mechanical strain. (C) Measured electrical resistance of the strain sensor under different levels of mechanical strain along the channel length direction (black) and perpendicular to the channel length direction (blue). (D) Relative change of the resistance ($\Delta R/R_o$) under cyclic stretching and releasing. (E) GF of the strain sensor with respect to the different strain. (F) Relative electrical resistance ($R/R_o$) change of the pressure sensor with respect to time under different levels of pressure. (G) Relative electrical resistance change of the pressure sensor under a loading (red) and unloading (blue) cycle. (H) Relative electrical resistance change of the temperature sensor with respect to the different temperature.
a cup filled with hot and cold (ice) water alternatively, as shown in Fig. 4E. The measured temperature response for two cycles of touching the hot and cold cup is shown in Fig. 4F. Governed by the geometries and materials of the skin and robot hand, the rise time (that is, the time required for the temperature to rise to 90% of its final temperature) is about 80 s and the fall time (that is, the time required for the temperature to fall to 10% of its final temperature) is about 50 s. Note that the speed of thermal response can be potentially improved through an amended thermal system, optimized geometries of the sensors, and enhanced thermal conductivity of the composites through inclusion of additives (such as graphene and carbon nanotubes).

**DISCUSSION**

The elastomeric composite semiconductors and conductors in this work enable a class of stretchable electronics and sensors that are intrinsically highly stretchable without any requirement for additional mechanical structure designs for traditional nonstretchable semiconductors. The elastomeric composite semiconductor of P3HT-NF/PDMS can all be created from common and commercially available materials. We demonstrate that stretchable electronics and sensors can also be created with simple fabrication steps by using these stretchable electronic materials. Our results show that intrinsically stretchable transistors remain functional while stretched by 50% and the elastomeric composite semiconductor achieves very high mobility while moderate mobility decrease is observed, that the strain sensors operate in a stable manner while achieving the highest GF for large level strains, that the pressure and temperature sensors show reliable performances, and that the intrinsically stretchable electronics and sensors can be used as smart skins for robotics. We foresee that this strategy of enabling elastomeric semiconductors by percolating semiconductor nanofibrils into a rubber will advance the development of stretchable semiconductors, and the approach to constructing electronics and sensors all from elastomeric electronic materials will move forward the advancement of stretchable electronics for a wide range of applications, such as artificial skins, biomedical implants, and surgical gloves.

**MATERIALS AND METHODS**

**Materials**

Anhydrous m-xylene (>99%), acetone (>99.9%), regioregular P3HT (rr-P3HT), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP;
Fabrication of elastomeric composite conductor

The fabrication of the conductor involves generating patterned AgNWs, embedding them into PDMS to form stretchable structures, and coating them with AuNPs using a galvanic replacement process. To pattern the electrodes, we first manufactured a shadow mask of 25-μm-thick Kapton film using a programmable cutting machine (Silhouette Cameo). AgNW solution (15 mg/ml) was drop-casted on a precleaned glass with Kapton film using a programmable cutting machine (Silhouette Cameo). To coat the exposed conductivity, a PDMS solution [10:1 (w/w) prepolymer/curing agent] was spin-coated on the patterned AgNWs at 300 rpm for 60 s followed by curing for 4 hours at 60°C to solidify. The PDMS was then peeled off from the glass to obtain patterned AgNWs embedded in PDMS. Owing to the high viscosity of the PDMS solution, this process results in AgNWs partially embedded within the PDMS. To coat the exposed AgNWs with AuNPs, the AgNW/PDMS sample was immersed in AgNW solution (~99.5%) solution (average diameter and length are 120 nm and 20 μm, respectively) was from ACS Material.

Fabrication of ion gel dielectric

The ion gel dielectric solution was prepared by blending PVDF-HFP, ionic liquid EMIM-OtF, and acetone at a weight ratio of 1:4:7 at 70°C. The ion gel membrane was achieved by casting the solution on a precleaned glass and cured to solidify under vacuum for 12 hours at 70°C (42, 43). The solidified membrane can be easily cut into different shapes and picked up from the glass (43). The capacitance of ion gel, which was obtained using an LCR meter (U1252B, Keysight) and an oscilloscope (DSO-X 2004A, Agilent), was 9.8 μF/cm² at 1 kHz, in agreement with the values in the literature (43–45).

Fabrication of stretchable TFTs

The fabrication of the TFTs involved generating source and drain electrodes, forming a thin-film composite semiconductor, and laminating the ion gel dielectric. The source and drain electrodes were fabricated in a way similar to that of the elastomeric conductor, as described before. A Kapton shadow mask was used to pattern the P3HT-NF/PDMS composite semiconductor. After the shadow mask was aligned and laminated on the electrodes, the P3HT-NF/PDMS solution was spin-coated at 2000 rpm for 60 s and dried for 30 min at 90°C. The patterned semiconductor film was fabricated by carefully removing the shadow mask. Finally, a piece of the 140-μm-thick ion gel was aligned and laminated on the device as a dielectric.

Characterization of stretchable electronic materials and devices

The surface morphology of the composite semiconductor was characterized using an AFM (Veeco Dimension 3000) under the tapping mode. The SEM (XL-30S FE, Philips) and TEM (JEM-2010, JEOL Ltd.) images were taken to examine the microstructures of the electronic materials. The I-V characteristics of the devices were measured by using a probe station (H100, Signatone) equipped with a semiconductor characterization system (4200-SCS, Keithley Instruments Inc.). Cyclic mechanical stretching and releasing tests were performed by using an IPC flexural endurance tester (CK-700FET, CKSI Co. Ltd.).


Acknowledgments
Funding: C.Y. acknowledges the partial financial support from the NSF (ECSS-1509763 and CMII-1554499), the Doctoral New Investigator grant from the American Chemical Society Petroleum Research Fund, and the Bill D. Cook faculty scholarship support from the Department of Mechanical Engineering at the University of Houston. Author contributions: H.-J.K. and C.Y. conceived and designed the experiments. H.-J.K., K.S., and A.T. performed the experiments. H.-J.K. and C.Y. analyzed the data. H.-J.K. and C.Y. wrote the paper.

Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 10 April 2017
Accepted 9 August 2017
Published 8 September 2017
10.1126/sciadv.1701114

Rubbery electronics and sensors from intrinsically stretchable elastomeric composites of semiconductors and conductors
Hae-Jin Kim, Kyoseung Sim, Anish Thukral and Cunjiang Yu

Sci Adv 3 (9), e1701114.
DOI: 10.1126/sciadv.1701114

ARTICLE TOOLS
http://advances.sciencemag.org/content/3/9/e1701114

SUPPLEMENTARY MATERIALS
http://advances.sciencemag.org/content-suppl/2017/09/01/3.9.e1701114.DC1

REFERENCES
This article cites 46 articles, 6 of which you can access for free
http://advances.sciencemag.org/content/3/9/e1701114#BIBL

PERMISSIONS
http://www.sciencemag.org/help/reprints-and-permissions

Use of this article is subject to the Terms of Service

Science Advances (ISSN 2375-2548) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. 2017 © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. The title Science Advances is a registered trademark of AAAS.