Highly sensitive electronic whiskers based on patterned carbon nanotube and silver nanoparticle composite films

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Mammalian whiskers present an important class of tactile sensors that complement the functionalities of skin for detecting wind with high sensitivity and navigation around local obstacles. Here, we report electronic whiskers based on highly tunable composite films of carbon nanotubes and silver nanoparticles that are patterned on high-aspect-ratio elastic fibers. The nanotubes form a conductive network matrix with excellent bendability, and nanoparticle loading enhances the conductivity and endows the composite with high strain sensitivity. The resistivity of the composites is highly sensitive to strain with a pressure sensitivity of up to ~8%/Pa for the whiskers, which is >10x higher than all previously reported capacitive or resistive pressure sensors. It is notable that the resistivity and sensitivity of the composite films can be readily modulated by a few orders of magnitude by changing the composition ratio of the components, thereby allowing for exploration of whisker sensors with excellent performance. Systems consisting of whisker arrays are fabricated, and as a proof of concept, real-time two- and three-dimensional gas-flow mapping is demonstrated. The ultrahigh sensitivity and ease of fabrication of the demonstrated whiskers may enable a wide range of applications in advanced robotics and human-machine interfacing.

Significance

Whiskers are hairlike tactile sensors used by certain mammals and insects to monitor wind and navigate around local obstacles. Here, we demonstrate artificial electronic whiskers that can respond to pressures as low as 1 Pa with high sensitivity. The active component is based on composites of carbon nanotubes and silver nanoparticles that are patterned on high-aspect-ratio fibers. The resistivity of the composite films is highly sensitive to mechanical strain and can be readily tuned by changing the composition ratio of the components. As a proof of concept, arrays of electronic whiskers are fabricated for real-time two- and three-dimensional gas-flow mapping with high accuracy. This work may enable a wide range of applications in advanced robotics and human-machine interfacing.
design of the devices along with the high strain sensitivity of the CNT–AgNP composite films provides ultrasensitive pressure sensors with a sensitivity of up to ∼8%/Pa, which is essential for whisker applications.

To form the CNT–AgNP composites, commercially available AgNP ink (Paru Company, Ltd.) and CNT paste (SWeNT Inc.; ∼50 wt % CNT in a polymer binder) are mixed with tunable component concentrations. After mixing the inks thoroughly, the composite mixture is patterned onto a polydimethylsiloxane (PDMS) substrate of desired shape and geometry by either painting or printing (see Supporting Information and Fig. S1 for details). This is followed by a thermal anneal at 70 °C for 1–2 h to remove the residual solvents and enhance the mechanical and electrical interfacing of the components.

Electrical characterization of CNT–AgNP composite films as a function of mechanical stress for different AgNP loadings (0–30 wt %) is shown in Fig. 1. Here, CNT–AgNP films (thickness of ∼2 μm) are patterned as lines (width of ∼2 mm; length of ∼1 cm) on the surface of a PDMS substrate (thickness of ∼250 μm) as illustrated in Fig. 1A and B. The resistivity of the CNT–AgNP films is then measured as a function of strain by bending the substrate. Fig. 1C shows the observed resistivity of the composites as a function of tensile and compressive stress conditions. Adding AgNPs to the composite has two effects. First, the resistivity of the printed films is reduced from ρ ∼ 5.4 × 10⁻² to ∼3.4 × 10⁻⁴ Ω cm as the AgNP loading is increased from 0 to 30 wt %. This is because AgNPs reduce the resistivity of nanotube–nanotube junctions by providing more transport pathways through tunneling and hopping (22). Second, the strain sensitivity is enhanced by increasing the weight content of AgNPs. Without AgNP incorporation, the CNT film shows minimal resistance change (<10%) when strained to ±2.4%. On the other hand, by adding 10 wt % AgNPs, resistance increases (decreases) by ∼260% (63%) under 2.4% tensile (compressive) strain. At high AgNP loadings, the current path is mostly dominated by tunneling through the
neighboring conductive NPs (22). The strain sensitivity in the CNT–AgNP composite films is thus caused by the distance change between the AgNPs, which affects the electron tunneling probability. To estimate the sensitivity merit, a gauge factor is defined by the ratio of relative resistance change and strain as:

$$g = \frac{d\left(\frac{\rho}{\rho_0}\right)}{de},$$

where $\rho_0$ is the resistivity of the film in the relaxed state, $\rho$ is the resistivity under a given strain, and $e$ is strain. For samples without AgNPs, the gauge factor is $<4$ for induced tensile strain up to $\sim2.4\%$. On the other hand, gauge factors of $\sim24$ and $95$ are obtained as the AgNP content is increased to 5 and 10 wt %, respectively, for the same tensile strain of $\sim2.4\%$. Notably, the tensile and compressive stress responses are near identical in magnitude, but opposite in sign (Fig. 1D). This trend is expected because compressive and tensile stresses induce smaller and larger gaps between AgNPs, respectively, compared with the relaxed state. This behavior allows the subsequently fabricated e-whisker to detect the direction of bending.

To examine the mechanical robustness of this composite material system, the resistance of the films after multiple cycles of bending, up to 500 times, was examined for films consisting of 5 and 30 wt % AgNPs (Fig. 1D). In each cycle, the samples were strained by $\sim2\%$ and relaxed. This was followed by resistance measurements at the relaxed state. Fig. 1D indicates that the CNT–AgNP composite films exhibit no measurable change of electrical properties up to 500 bending cycles, exhibiting superb mechanical reliability. This is essential for their use in practical whisker devices. It should be noted that for AgNP composite films without nanotubes, the films exhibit poor mechanical robustness with applied strains of $\sim0.5\%$ resulting in irreversible degradation of the film conductance caused by cracks and fractures. This highlights the importance of nanotubes in the composite films for providing a conductive matrix with excellent mechanical bendability needed for tolerating large strains.

Next, we focus on the use of CNT–AgNP composite films for e-whisker devices. Fig. 2A illustrates the schematic of an e-whisker device. The device consists of a thin PDMS fiber (width and thickness of $\sim250$ μm; length of $\sim15$ mm) with CNT–AgNP lines painted on the top and bottom surfaces and electrically shorted at the tip of the fiber. The resistance of the device is then monitored by applying a voltage between the top and bottom surfaces at the base of the fiber. The AgNP loadings for the painted lines are asymmetric between the top and bottom surfaces. On the top side, 5 wt % AgNP composite is used to serve as the active component for strain detection. On the bottom side, a 30 wt % AgNP composite is used as an interconnect electrode because its resistivity is $\sim2$ orders of magnitude lower than that of the top electrode (5 wt % AgNP composite), regardless of the strain magnitude. The use of asymmetric top and bottom electrodes is essential in this device configuration as the two electrodes are always under opposite strain (tensile vs. compressive) when the e-whisker is bent. Therefore, a symmetric device does not detect strain (Fig. S2). Because the top electrode is significantly more resistive than the bottom, only the resistance change of this electrode affects the output of the sensor (Fig. 2D). This presents a unique feature of the CNT–AgNP composites that enables a broad tunability in the resistivity with excellent mechanical flexibility.

The fabrication process of an array of e-whiskers is depicted in Fig. 2B. In brief, a silicon mold was first fabricated by using deep reactive ion etching, consisting of trenches with dimensions of 15 mm long, 250 μm wide, and 250 μm deep. The surface of the Si mold was coated by a fluorinated organosilane monolayer.

Fig. 3. Electrical characterization of e-whiskers. (A) The $\Delta R/R_0$ as a function of compressive and tensile stress induced by gas flow for a representative whisker, where $\Delta R = R_0 - R$. The bottom x axis displays the gas-flow velocity used to induce displacement and the top x axis displays the corresponding pressure. (B) Time-resolved resistance change by displacing a whisker upward and downward ($\sim2$ mm displacement) by applied pressure. (C, D) Response time of a whisker when bent downward and relaxed, respectively.

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using a molecular vapor deposition system. Elastomeric PDMS precursor was poured into the mold and cured at 70 °C in an oven for ~2 h. After curing, PDMS is mechanically detached from the mold. Oxygen plasma (30 W, 1 min) was applied on both top and bottom surfaces of PDMS to enhance the subsequent surface adhesion of CNT–AgNP composite inks. The composite mixture is then painted onto the molded PDMS fibers using the pattern shown in Fig. 2A followed by a thermal anneal at 70 °C for 1 h. Fig. 2C shows an optical image of a fully fabricated e-whisker that consists of an array of six fibers.

Next, we examine the sensitivity of the fabricated e-whiskers to airflow. The sensing properties of an individual e-whisker are depicted in Fig. 3. Here, the e-whisker is 15 mm long and is held stationary at one end with the rest of the device being suspended in air. The suspended side of the whisker is displaced up- or downward upon exposure to a directional airflow with controlled direction and velocity (i.e., applied pressure). Fig. 3A shows the normalized resistance change of the device as a function of the exposed airflow speed (bottom axis) and the corresponding applied pressure (top axis) at the tip of the whisker. The conversion of airflow speed to applied pressure is calibrated using a force sensor. The device exhibits a large modulation of the output resistance of ΔRR0 ∼ 40% for an airflow velocity of v ∼ 3 m/s corresponding to a small applied pressure of P ∼ 5 Pa. The resistance increases when the whisker is bent down (i.e., tensile stress for the top electrode) and decreases when bent upward, which is consistent with the observation in Fig. 1C. The response is near linear for a flow velocity up to ~3 m/s, which is highly desirable for sensing applications. The sensitivity of the e-whiskers are measured to be d(ΔR)/dP = 8%/Pa. This pressure sensitivity is ~10–350x higher than the state-of-the-art capacitive or resistive pressure sensors fabricated using microstructured PDMS (2, 26) and ~250x higher than silicon-based cantilever sensors (27). The sensitivity to airflow is ∼13.5%/m/s up to ~3 m/s flow rate, a range comparable to the one from an average human exhalation. The high sensitivity of our whiskers can be mainly attributed to (i) a strain-sensitive CNT–AgNP composite film with a relatively high gauge factor (~95), and (ii) the use of a high-aspect-ratio hairlike PDMS substrate with a low spring constant that deforms easily under applied pressure (see Supporting Information and Fig. S3 for details).

Time-resolved measurements of the e-whiskers were also conducted as 4-Pa pressure was applied upward and downward on the tip of a device in multiple cycles. Fig. 3B shows that the device consistently detects both compressive and tensile stresses (corresponding to upward and downward motions, respectively) with reproducible output signal. Fig. 3C and D depict that the response time of the sensor is ~100 ms for both pressure detection and recovery, which is governed by the elastic nature of the PDMS fiber. These results point to a maximum response speed of ~10 Hz, which is high enough for most sensing applications.

Next we examine the electrical response of an array of individually addressable e-whiskers. Four parallel e-whisker fibers with ~1.5 mm spacing are fabricated and electrically connected to a readout system consisting of a Wheatstone bridge circuit, a multiplex voltage reader, and a computer for data processing as shown in Fig. 4A. A directional flow of nitrogen gas is then used to simulate a wind flow. Each whisker independently responds with a clear increase or decrease in the output voltage as the gas flow is introduced from the bottom or top, respectively (Fig. 4B). The results clearly depict the consistent and reproducible response of the whiskers and the ability to perform 2D mapping of the gas flow.

Three-dimensional (3D) mapping of wind flow is also feasible by strategically positioning an array of whiskers on the desired surface. As a proof of concept, seven e-whiskers are mounted on a PDMS hemisphere with a diameter of ~2.5 cm as shown in Fig. 5A. Each whisker is mounted normal to the surface of the PDMS hemisphere and distributed with equal spacing. Silver interconnect lines are painted on the surface of the PDMS for reading out signals from individual pixels (i.e., whiskers) by an external electronic board. A nitrogen gas line set ~4 cm away from the PDMS substrate with a directional flow velocity of ~5 m/s is used to simulate wind. The direction of the gas line is manipulated to control the wind direction. Fig. 5C shows the real-time voltage output signal from the e-whiskers as the “wind” flows toward the front side of the PDMS hemisphere, facing whiskers 5–7 (as marked in Fig. 5A and B). Whiskers 5–7 clearly exhibit the highest voltage drops corresponding to the largest displacements because they are in the direct path of the gas flow. In contrast, whiskers 2–4 show smaller voltage drops because they are in indirect path of the flow. Finally, whisker 1, which is fully shadowed from the gas flow, exhibits nearly no response. The whiskers exhibit high sensitivity and small fluctuations in the gas flow over the structure are clearly mapped by the output voltage signal. A 3D airflow map at a fixed time is obtained and plotted as Fig. 5D by converting the output voltage drop (i.e., resistance change) of each whisker to gas velocity according to Fig. 3A. The results demonstrate the ability to map airflow in real time with high sensitivity, and provide just one example system which these e-whiskers could be used for monitoring the environment.

In summary, we have developed highly sensitive electronic whiskers by painting CNT–AgNP composite films onto hairlike PDMS fibers. The devices exhibit large resistance modulation...
upon pressure-induced bending with a sensitivity of $\sim8\%$/Pa, which is the highest for all reported tactile sensors. E-whisker arrays with different configurations were designed and successfully demonstrated for 2D and 3D mapping of wind flow. The work here represents a type of highly responsive tactile sensor networks for real-time monitoring of environmental effects. The ease of fabrication, light weight, and excellent performance of the e-whiskers may enable a wide range of applications for advanced robotics, human–machine user interfaces, and biological applications.

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Supporting Information

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**CNT–AgNP Patterning on PDMS Substrates**

CNT–AgNP lines were patterned on the PDMS substrates by either a painting (i.e., dip-pen writing) or printing (i.e., silk printing) approaches. The two techniques resulted in similar performance in terms of resistivity and strain sensitivity of the obtained films. The sample in Fig. 1 was made by printing and the other data were obtained by the painting approach. The detailed procedure for each technique is summarized below and depicted in Fig. S1.

**Approach 1: Printing (Fig. S1A).**

i) The surface of the PDMS substrate is oxygen plasma treated (40 W, 1 min).

ii) A shadow mask with the desired pattern is prepared using a Kapton substrate (~70 μm in thickness) and brought in contact on the PDMS substrate.

iii) The CNT–AgNP mixture ink is poured over the PDMS substrate with the mask on top.

iv) A glass blade is swept on the surface of the substrate at ~45° angle to remove the extra ink.

v) The mask is removed the PDMS surface, leaving behind ink that is deposited only in the patterned regions.

vi) The sample is baked at 70 °C for 1–2 h.

**Approach 2: Painting (i.e., Dip-Pen Writing; Fig. S1B).**

i) The surface of the PDMS substrate is oxygen plasma treated (40 W, 1 min).

ii) A sharp plastic tip (~160 μm in diameter) is dipped into the ink mixture and dragged on the surface of the PDMS substrate to write the desired pattern.

iii) The sample was baked at 70 °C for 1–2 h.

**Control Experiment—Devices with Symmetric CNT–AgNP Composite Films**

Symmetric CNT–AgNP (30 wt % AgNP loading) composite films were painted on the top and bottom of a PDMS fiber to serve as a control device as shown in Fig. S2A. Fig. S2B shows the output signal of this device, exhibiting no resistance change as the fiber is bent up and down, corresponding to ~1.5% strain. This is expected because the films exhibit resistivity change that is nearly identical in magnitude but opposite in sign in response to compressive and tensile strain. Because under bending conditions, the top and bottom surfaces exhibit opposite strain (Fig. S3), the resistance change of the films cancels out, resulting in no net response. The results highlight the importance of using asymmetric composite films on top and bottom surfaces to obtain maximum device sensitivity for e-whisker applications.

**Mechanical Simulations of E-Whiskers**

To understand the stress distribution over the e-whisker structure, mechanical simulations were conducted by using a finite-element method (Comsol Multiphysics 4.2) as shown in Fig. S3. In this simulation, the tip of the e-whisker is displaced downward by 1 mm and holding the base at a fixed location. Here, the active layer is assumed to be a pure AgNP film for simplicity. Young’s moduli of 40 GPa and 0.75 MPa were used for AgNP (1) and PDMS (2) layers, respectively. The structure assumes 2-μm-thick AgNP layers on the top and bottom surfaces of PDMS (thickness of 250 μm; and length of 15 mm). The simulation depicts the highest tensile and compressive stresses are in the Ag layers at the base of the e-whisker (Fig. S3B). The stress strength at the top and bottom surfaces is symmetric with tensile and compressive strains, respectively.

**Spring Constant of E-Whisker**

The e-whiskers can be viewed as highly elastic cantilevers. From our experiments, the displacement of the PDMS whiskers is linearly proportional to the applied force, for the explored range of up to $F \sim 50 \mu N$. Specifically, a force of $\sim 22.5 \mu N$ leads to a tip displacement of $d \sim 3 \text{ mm}$. The experimentally extracted spring constant, $k = F/d$, is $\sim 7.5 \text{ mN/m}$. This value is consistent with that obtained from Comsol simulations. From simulation, we obtained spring constants between 2 and 5.4 mN/m according by using PDMS Young’s modulus in the range of 0.75–3 MPa. It should be noted that the small spring constant of the PDMS fibers is essential in obtaining high sensitivity because minimal force leads to large displacement and thereby strain.


Fig. S1. Patterning techniques for CNT–AgNP composite films used in this work. (A) Silk printing using a line-patterned plastic mask. (B) Painting (i.e., dip-pen writing) using a sharp (~160 μm in diameter) plastic tip.

Fig. S2. (A) Schematic of a symmetric device where the same CNT–AgNP (30 wt % AgNP loading) composite film is patterned on the top and bottom surfaces of a PDMS fiber; (B) \( \Delta R/R_o \) by applying compressive and tensile strains (~1.5%) on the device, showing minimal response.

Fig. S3. Mechanical simulation of stress distribution for the e-whisker structure. (A) Stress distribution through the entire e-whisker structure with 15 mm length and 250 μm thickness with 2-μm-thick AgNP film for top and bottom PDMS surfaces. (B) Zoomed-in image of the root of AgNP film area.