

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

Kuniharu Takei^{1,2}, Zhibin Yu¹, Maxwell Zheng, Hiroki Ota, Toshitake Takahashi, and Ali Javey³

Department of Electrical Engineering and Computer Science, and Berkeley Sensor and Actuator Center, University of California, Berkeley, CA 94720; and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

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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 $\sim 8\%/Pa$ for the whiskers, which is $>10\times$ 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.

strain sensors | artificial devices | flexible electronics | nano materials

Functionalities mimicking biological systems are of tremendous interest in developing smart and user-interactive electronics. For example, artificial electronic skin (e-skin) (1–4) and electronic eye (e-eye) (5) have been developed recently by engineering novel material and device concepts on thin flexible substrates that give ordinary objects and surfaces the ability to feel and see the environment. Whiskers present yet another important class of sensor components that can monitor the air-flow, mediate tactile sensing for spatial mapping of nearby objects, and even enable balance during motion for advanced robotics with capabilities resembling those found in certain insects and mammals (6, 7). Several approaches to date have been explored to realize electronic whiskers (e-whiskers), among which bulky torque/force sensors placed at the base of micro-millimeter-scale fibers are most frequently used (8–12). However, the previously reported e-whiskers do not simultaneously offer lightweight, compact design, high sensitivity and dynamic range, and scalable processing scheme needed to enable large-scale integration for practical systems.

In essence, an e-whisker device consists of a highly sensitive tactile sensor that is mounted on a high-aspect-ratio hairlike structure. A promising approach for developing bendable strain sensors involves the use of thin films of conductive nanomaterials such as nanotubes (13–16), nanowires (17–19), nanoflakes (20), or nanoparticles (NPs) (21, 22). For instance, by using conductive NP thin films, strain is readily detected by measuring the resistance of the film as the spacing between the NPs changes due to bending or stretching of the substrate (21, 22). Although highly sensitive strain sensors based on conductive NP films have

been demonstrated, the irreversible breakage between the NPs when the substrate is bent or stretched to the extreme limits the reliability and active operation range of such sensors for e-whisker applications. Embedding the nanoparticles into an elastic polymer matrix can improve the stretchability of such electrodes, accompanied however with a sacrifice on the bulk conductivity, which leads to a high operation voltage. On the other hand, conductive nanotube/nanowire thin films exhibit excellent mechanical flexibility and stretchability (13–15, 23, 24), but lack high sensitivity to strain. Recently, Kim et al. also obtained highly conductive and stretchable nanoparticle/polymer composite electrodes through a layer-by-layer assembly process (25). In this work, we use composite thin films of carbon nanotube (CNT) paste and silver nanoparticles (AgNPs) as highly sensitive and mechanically robust sensors for e-whisker applications. The CNT paste forms a conductive network matrix with excellent bendability, and AgNP loading enhances the conductivity and endows the composite with high strain sensitivity. This composite is highly tunable, with strain sensitivity and resistivity modulated by the weight ratio of the two components. The composite can be readily painted or printed on high-aspect-ratio elastic fibers to form e-whiskers, and eventually be integrated with different user-interactive systems. Notably, the use of high-aspect-ratio elastic fibers with small spring constant (see *Supporting Information* for details) as the structural component of the whiskers provides large deflection and therefore high strain for smallest applied pressures. This architectural

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 painted 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.

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¹K.T. and Z.Y. contributed equally to this work.

²Present address: Department of Physics and Electronics, Osaka Prefecture University, Osaka 599-8531, Japan.

³To whom correspondence should be addressed. E-mail: ajavey@eecs.berkeley.edu.

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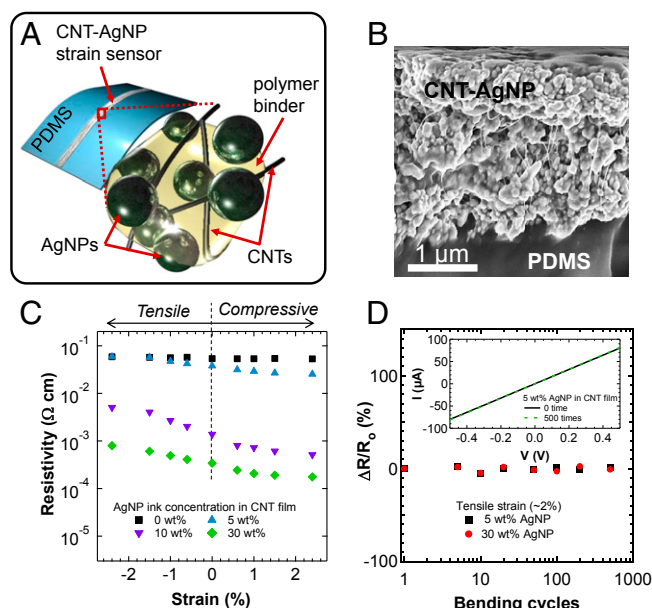


Fig. 1. CNT-AgNP composite films. (A) Schematic of a CNT-AgNP composite film patterned on a PDMS substrate. (B) Cross-sectional SEM image of a CNT-AgNP composite film on PDMS showing that CNTs are tangled in between AgNPs and polymer binders. (C) Resistivity as a function of strain for CNT-AgNP composites with different AgNP concentrations. (D) Resistance change ($\Delta R/R_0$) as a function of bending cycle ($\sim 2\%$ strain) for 5 and 30 wt % AgNP. Inset shows the current-voltage characteristics before and after 500 cycles.

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 $\sim 8\%/Pa$, 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 $70^\circ C$ 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 $\sim 2 \mu m$) are patterned as lines (width of ~ 2 mm; length of ~ 1 cm) on the surface of a PDMS substrate (thickness of $\sim 250 \mu m$) as illustrated in [Fig. 1 A](#) and [B](#). The resistivity of the CNT-AgNP films is then measured as a function of strain by bending the substrate. [Fig. 1 C](#) 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 $\rho \sim 5.4 \times 10^{-2}$ to $\sim 3.4 \times 10^{-4} \Omega cm$ 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 $\pm 2.4\%$. On the other hand, by adding 10 wt % AgNPs, resistance increases (decreases) by $\sim 260\%$ (63%) under 2.4% tensile (compressive) strain. At high AgNP loadings, the current path is mostly dominated by tunneling through the

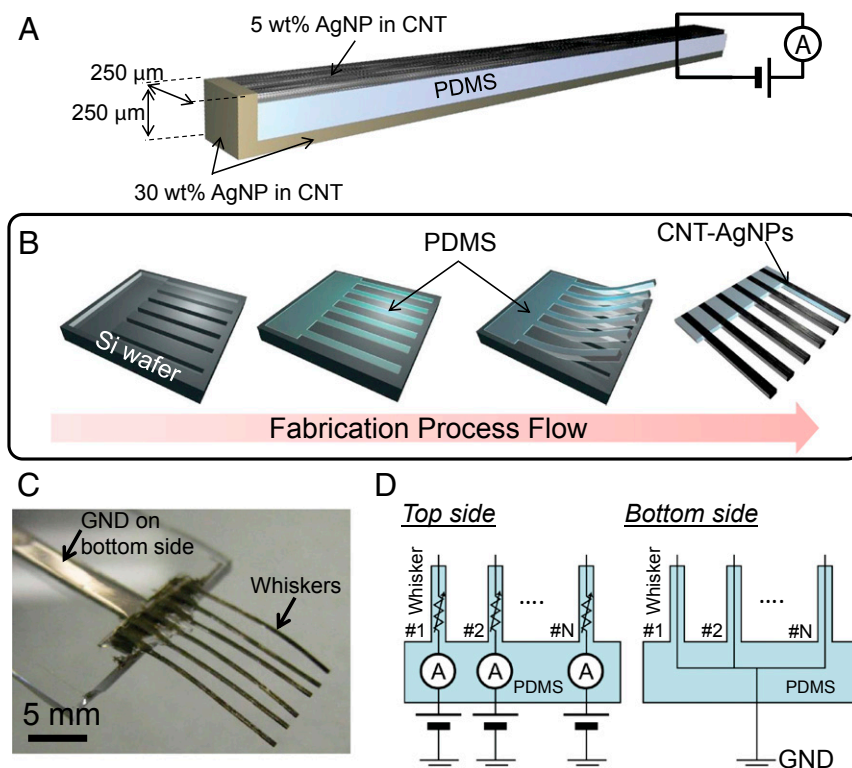


Fig. 2. Electronic whiskers. (A) Schematic showing the design of an e-whisker device with 5 and 30 wt % AgNP composite lines patterned on the top and bottom surfaces of a PDMS fiber, respectively. (B) Fabrication process scheme for an e-whisker array. (C) Optical image of a fully fabricated e-whisker array. (D) Circuit diagrams of the e-whiskers for the top and bottom surfaces of the fibers.

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:

$$g = \frac{d\left(\frac{\rho_s}{\rho_o}\right)}{d\varepsilon},$$

where ρ_o is the resistivity of the film in the relaxed state, ρ_s is the resistivity under a given strain, and ε is strain. For samples without AgNPs, the gauge factor is <4 for induced tensile strain up to $\sim 2.4\%$. On the other hand, gauge factors of ~ 24 and 95 are obtained as the AgNP content is increased to 5 and 10 wt %, respectively, for the same tensile strain of $\sim 2.4\%$. Notably, the tensile and compressive stress responses are near identical in magnitude, but opposite in sign (Fig. 1C). 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 $\sim 2\%$ 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 $\sim 0.5\%$ 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 $\sim 250\ \mu\text{m}$; length of $\sim 15\ \text{mm}$) 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 ~ 2 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, $250\ \mu\text{m}$ wide, and $250\ \mu\text{m}$ deep. The surface of the Si mold was coated by a fluorinated organosilane monolayer

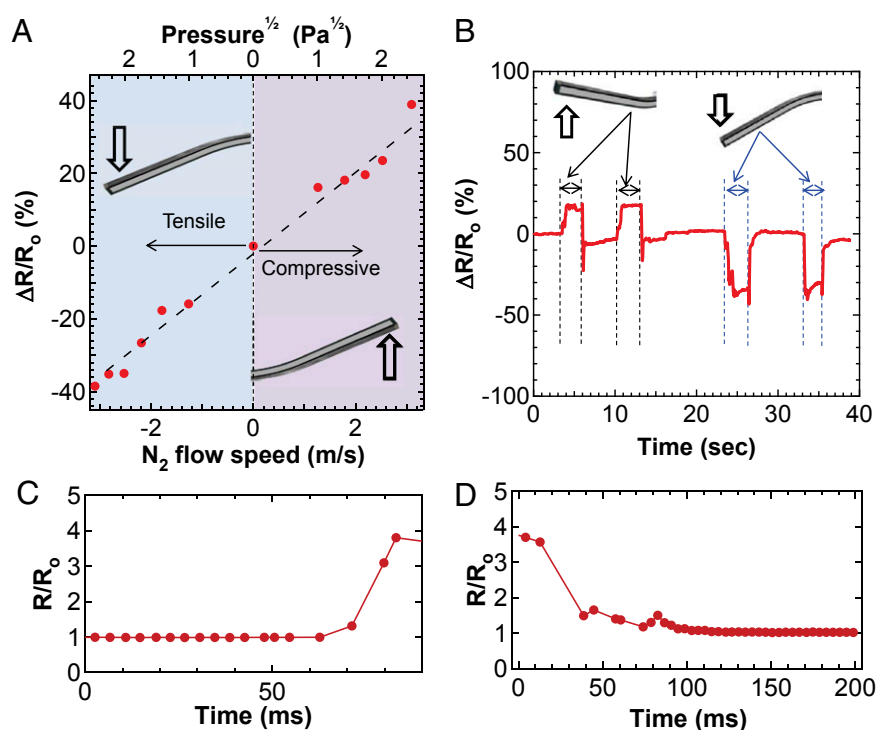


Fig. 3. Electrical characterization of e-whiskers. (A) The $\Delta R/R_o$ as a function of compressive and tensile stress induced by gas flow for a representative whisker, where $\Delta R = R_o - R$. The bottom x axis displays the gas-flow velocity used to induce displacement and the top x axis displays the corresponding pressure. (B) Time-resolved resistance change by displacing a whisker upward and downward ($\sim 2\ \text{mm}$ displacement) by applied pressure. (C, D) Response time of a whisker when bent downward and relaxed, respectively.

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 ($\sim 70\ \mu\text{m}$ 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 $\sim 45^\circ$ 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 ($\sim 160\ \mu\text{m}$ 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 $\sim 1.5\%$ 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 $250\ \mu\text{m}$; 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 $F \sim 50\ \mu\text{N}$. Specifically, a force of $\sim 22.5\ \mu\text{N}$ 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 $5.4\ \text{mN/m}$ 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.

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