

# Quasi In Situ Polymerization To Fabricate Copper Nanowire-Based Stretchable Conductor and Its Applications

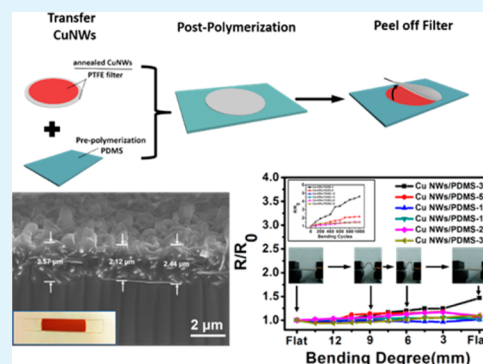
Tao Wang, Ranran Wang,\* Yin Cheng, and Jing Sun\*

The State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, University of Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, P.R. China

## S Supporting Information

**ABSTRACT:** Stretchable electronics have progressed greatly and have found their way into various applications, thus resulting in a growing demand for high-quality stretchable conductors. Poly(dimethylsiloxane) (PDMS) is the mostly frequently exploited elastomeric substrate for the construction of a stretchable and conductive platform because of its valuable features, such as superb stretch ability, high transparency, and reliable biocompatibility. However, the weak adhesion between the PDMS substrate and the conductive components has always been an intractable issue which undermines the good and stable performance of the resultant devices. We proposed a quasi in situ polymerization method to effectively build a tight and stable attachment between copper nanowire (Cu NW) and the PDMS substrate. The Cu NWs/PDMS conductors show excellent conductivity and antioxidation stability ( $R/R_0 < 1.4$  for 50 days in air), enhanced interface adhesion, and stretch ability (80% strain,  $R/R_0 \sim 5$ ), without any complicated preconfiguration of the PDMS substrates. For application demonstration, the Cu NWs/PDMS conductor was deployed as the stretchable electric wiring to illuminate a light-emitting diode. Furthermore, a stretchable capacitive strain sensor was fabricated using the Cu NWs/PDMS as electrodes. The sensor possessed a gauge factor of 0.82 and the minimum detection limit of 1% strain.

**KEYWORDS:** copper nanowires, PDMS, quasi in situ polymerization, stretchable electrode, strain sensor



## 1. INTRODUCTION

Stretchable electronics with unconventional mechanical performances are gaining numerous scientific and social interests in the last ~15 years.<sup>1,2</sup> Intensive efforts by material scientists and engineers have opened up a spectrum of sophisticated application fields, including elastomeric circuits,<sup>2,3</sup> flexible/stretchable displays,<sup>4</sup> flexible/stretchable energy-related devices,<sup>5,6</sup> electronic eye cameras,<sup>7</sup> smart skins,<sup>8</sup> muscle-like soft actuators,<sup>9,10</sup> implantable devices for human health monitoring,<sup>11</sup> pressure/strain sensors for human-motion detection,<sup>12,13</sup> and so on. Stretchable conductor with both high conductivity and stretch ability is one of the key building blocks of stretchable electronics.<sup>14,15</sup>

Stretchable conductors include two necessary motifs: electrical conductive components and stretchable substrates. To realize their wide applications for bending, stretching, twisting, and other deformation onto complex and nonplanar surfaces, flexible nanomaterials could be a suitable alternative as electrical conductive components due to their predominant compliance compared with their bulk counterparts.<sup>16,17</sup> Many efforts have been made to study a variety of new nanomaterials as electrical conductive components such as conducting polymers,<sup>18,19</sup> carbon nanotubes,<sup>12,13,20</sup> graphite,<sup>21</sup> and metal nanomaterials.<sup>2,17,22–24</sup> However, the instability and poor conductivity of conductive polymers and the relatively low electrical conductivity of carbon-based nanomaterials have

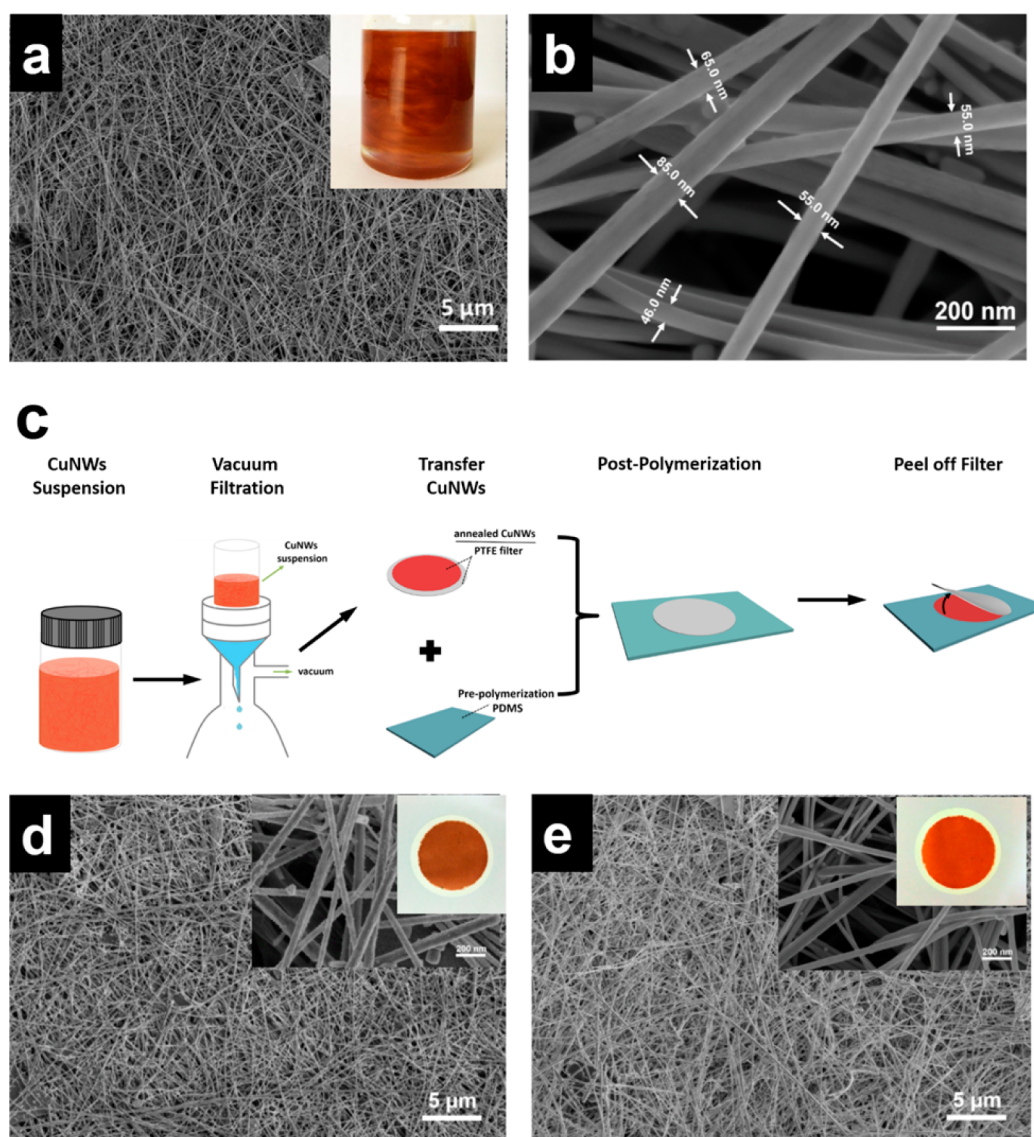
become the main limitations to their performance and applications. Among the nanomaterials, metallic nanowires (NWs) could be very promising candidates for electrical conductive components in stretchable conductors. Although silver nanowires (Ag NWs) have been intensively investigated for many years, the high price hinders their large-scale applications. Very recently, copper nanowires (Cu NWs) have become a research focus since copper possesses comparable conductivity with Ag, and is almost 100 times cheaper than Ag.<sup>25</sup>

Polydimethylsiloxane (PDMS) is a very common stretchable substrate and has been broadly investigated.<sup>15,17</sup> It possesses not only high stretch ability and durability but also good thermal stability, biocompatibility, and chemical inertness.<sup>26</sup> Additionally, transparency and cost-effective fabrication process could also be advantageous for PDMS.<sup>27,28</sup> Although PDMS possesses so many superior properties, the weak adhesion between PDMS and electrical conductive components is still a severe problem constraining its applications in stretchable electronics. This is attributed to the super hydrophobicity of its surface and fast recovery from hydrophilic to hydrophobic surface after being treated extensively by oxygen plasma.<sup>29</sup> The

Received: November 17, 2015

Accepted: February 19, 2016

Published: February 19, 2016



**Figure 1.** (a) SEM top view image of pristine Cu NWs coated on silicon. The inset shows a homogeneously dispersed Cu NW ink; (b) The magnified SEM image of pristine Cu NWs; (c) The schematic fabrication process of Cu NWs/PDMS; (d,e) SEM top view images and magnified SEM images of Cu NWs networks on PTFE filters before and after heat annealing at 230 °C. The insets show photographs of Cu NWs networks before and after heat annealing.

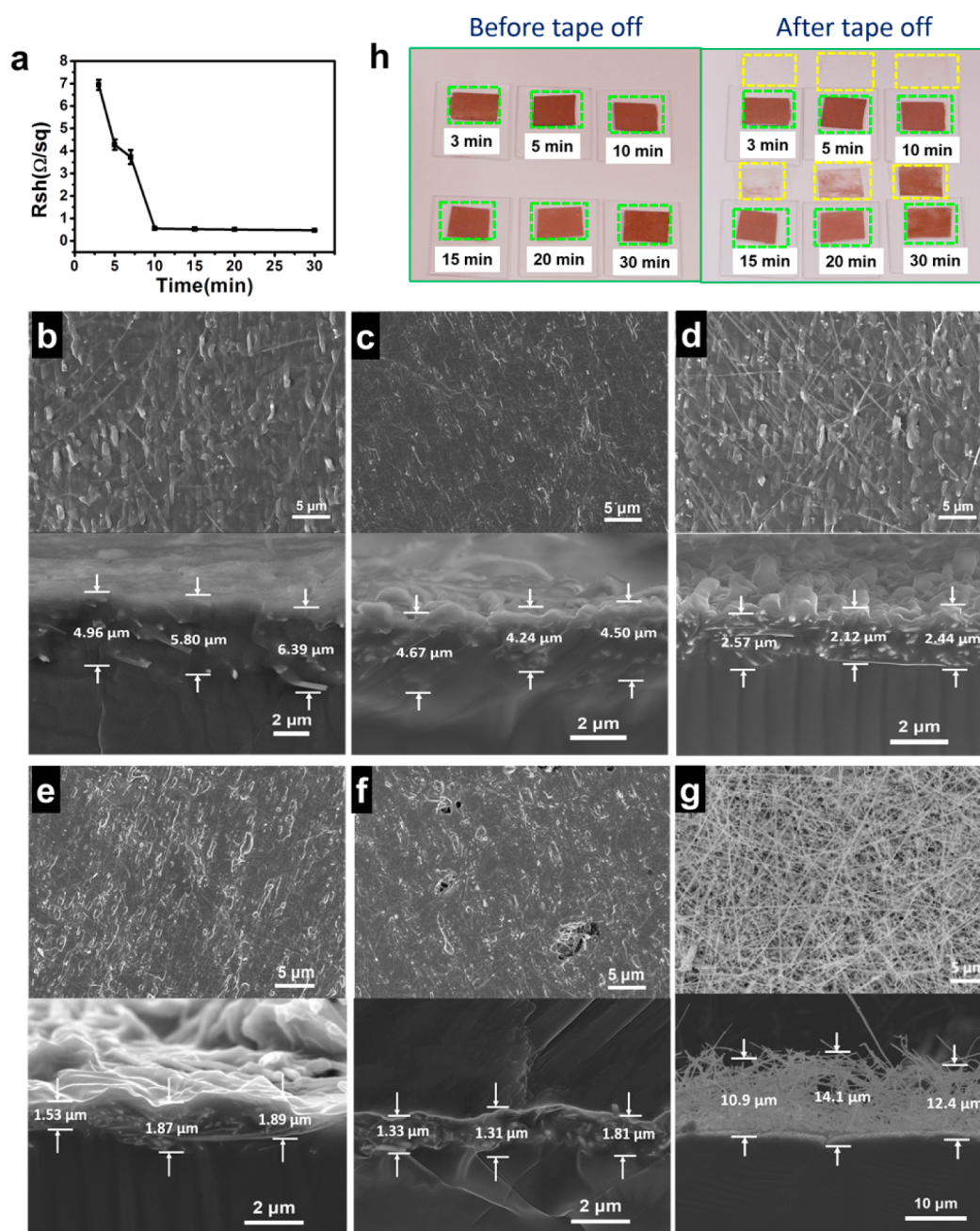
shortcomings of PDMS impair the electrical properties of stretchable conductors. Even worse, the conductive materials on PDMS could be detached easily from the surfaces when external force is applied.

With the purpose of enhancing adhesion of the various conductive materials with PDMS, a lot of measures have been adopted, such as surface functionalization and in situ polymerization. W. C. Kim et al. and W. S. Kim et al. modified the surface of PDMS using silane and polydopamine, respectively, and enabled the surface with hydrophilicity lasting for a long time. The method considerably improved the attachment of Ag NWs onto PDMS.<sup>30,31</sup> However, the process of chemical modification is rather complex and not easy to control. Zhu and co-worker reported that by in situ polymerization Ag NWs were embedded into PDMS substrates, obtaining Ag NWs/PDMS conductors with high stretch ability.<sup>32</sup> It can markedly improve the adhesion; unfortunately, it is difficult to be transplanted to the Cu NWs/PDMS system because Cu NWs would be fully embedded and lose their

conductance. To the best of our knowledge, there are no reports demonstrating good attachment of Cu NWs with PDMS yet, while only a little work is involved in the weak attachment of Cu NWs on PDMS substrates without any treatment.<sup>17</sup> Therefore, searching a facile, cost-effective, and scalable fabrication method to enhance the adhesion of Cu NWs on stretchable PDMS substrate is still urgent.

It was found that the stickiness of PDMS substrates varied with the polymerization time, which would affect the attachment of nanowires significantly. Enlightened by this phenomenon, herein, a novel, cost-effective, and easily scalable fabrication method, quasi in situ polymerization, composed of three main steps including prepolymerization, transfer of nanowire networks, and post-treatment were developed. Via regulating the prepolymerization time, part embedment of Cu NWs in PDMS substrates were realized, which endowed strong adhesion, excellent conductivity and stability ( $R/R_0 < 1.4$  for 50 days in air), enhanced stretch ability (80% strain,  $R/R_0 \sim 5$ ), and bendability of Cu NWs/PDMS composite conductors.





**Figure 2.** (a) Sheet resistance change of the Cu NWs/PDMS as the prepolymerization time is prolonged. The top view and cross-sectional SEM images of (b) Cu NWs/PDMS-3, (c) NWs/PDMS-5, (d) NWs/PDMS-10, (e) NWs/PDMS-15, (f) Cu NWs/PDMS-20, and (g) Cu NWs/PDMS-30. (h) Adhesive strength tests (3 M scotch tape test) of Cu NWs/PDMS-3, Cu NWs/PDMS-5, Cu NWs/PDMS-10, Cu NWs/PDMS-15, Cu NWs/PDMS-20, and Cu NWs/PDMS-30.

Stretchable light-emitting diode (LED) circuit and stretchable sensors with Cu NWs/PDMS conductors were fabricated to demonstrate the feasibility of this approach. The resulting capacitive sensor which can detect strain as low as  $\sim 1\%$  and has quite high sensitivity (gauge factor 0.82, close to the theoretical value of 1) surpasses the previous results. It is believed that the quasi in situ polymerization method can be extended to other materials and find more applications in flexible and stretchable devices.

## 2. EXPERIMENTAL SECTION

**Synthesis of Cu NWs.** Cu NWs were synthesized by the method we proposed in previous studies.<sup>33,34</sup> Hexadecylamine and cetyl-

trimethylammonium bromide were mixed and heated to form a liquid-crystalline medium as tubular structure to guide the growth of Cu NWs. Then the precursor, copper acetylacetonate  $[\text{Cu}(\text{acac})_2]$ , was added into the medium and the reaction system was incubated for a certain period of time. Thereafter, a certain amount of Pt nanoparticles with diameter of 5 nm formed by reducing  $\text{PtCl}_2$  with ethylene glycol were introduced to catalyze the reduction of  $\text{Cu}^{2+}$ . After 12 h of reaction at  $180^\circ\text{C}$ , Cu NWs were synthesized. After being rinsed with toluene several times, the nanowires were kept in toluene with a concentration of  $0.28\text{ mg/mL}$ .

**Preparation of Cu NWs/PDMS Composite Films.** Cu NWs suspensions of  $5\text{ mL}$  were filtrated to form films on polytetrafluoroethylene (PTFE) filter membranes. Then the Cu NWs/PTFE films were heat-treated at various temperatures ( $190, 210, 230, 250$ , and  $290^\circ\text{C}$ ) in a quartz tube furnace for 30 min under a constant flow of

hydrogen to remove organic components and oxides over Cu NWs to gain conductive networks, and the effect of annealing temperature on conductivity of Cu NWs films was investigated. Liquid PDMS (Sylgard 184, Dow Corning) was cast onto glass slides by mixing the “base” and the “curing agent” with a ratio of 10:1, followed by curing at 80 °C for different times (3, 5, 10, 15, 20, and 30 min) until slightly sticky PDMS substrates were obtained. The effect of prepolymerization time was also studied. The annealed Cu NWs/PTFE films were placed carefully onto the PDMS substrates with Cu NWs face down, and then they were put into a vacuum oven for 2 h to polymerize completely. Cu NWs/PDMS composite films were gained after peeling off PTFE and they were cut into strips with the width of 10 mm for electrical and mechanical properties tests.

**Fabrication of Capacitive Strain Sensor.** A Cu NWs/PDMS film with the Cu NWs surface facing down was placed on a glass slide. The PDMS liquid was spread over the surface of the Cu NWs/PDMS film. Before curing, another Cu NWs/PDMS with the Cu NWs surface facing up was laminated onto the wet PDMS and oriented to make sure that both patterns are fully aligned. Then the whole piece was degassed and cured thermally in a vacuum oven at 80 °C for 2 h. The Cu NWs/PDMS substrate was cut into strips to produce capacitive sensors for testing.

**Structural, Electrical, and Mechanical Characterization.** The micromorphology and EDX analysis of Cu NWs were conducted with a field-emission scanning electron microscope (Hitachi S-4800). The sheet resistance of samples was measured with Mitsubishi Chemical Laiesta-EP MCP-T360. The volume resistance was measured using a two-probe method with a FLUKE-15B digital multimeter. The resistance versus strain of Cu NWs/PDMS was analyzed with the combination of Princeton Applied Research Parastat 2273 and a high-precision electronic universal testing machine (CMT6103, MTS Systems (China) Co., Ltd.). The bendability of the Cu NWs/PDMS was measured by a movable stage (ZXT\_050-300\_MA06 (China), Shanghai Zhengxin Opto-electrical Technology Co. Ltd.). Fourier transform infrared (FTIR) spectroscopy data were collected with a FTIR spectrometer (Bruker Tensor 27), which was equipped with an attenuated total reflectance accessory and settled in a glovebox filled with Ar atmosphere. Raman measurements were carried out to study the oxidation state of Cu NWs films by using a 532 nm laser under ambient conditions with a Raman microscope (Thermo Scientific Raman DXR), and the laser spot and power size were  $\sim 0.7\ \mu\text{m}$  and 8 mW. Thermogravimetry analysis was carried out with NETZSCH STA 449C in the temperature range of 40–500 °C at a heating rate of 10 °C/min in nitrogen. The capacitance of capacitive strain sensor was characterized with YD2616D capacitance testing apparatus (Yangzi Electronic Co. Ltd. (China)) at 1 kHz frequency with a 0.1 V ac signal.

### 3. RESULTS AND DISCUSSION

Figure 1a displays the top-view SEM image of pristine Cu NWs on a silicon substrate, where a dense network of long Cu NWs is formed. From the inset we can find that, unlike other bundled Cu NWs reported,<sup>35</sup> homogeneous stable nanowire dispersion without any visible aggregates can be easily obtained via mild sonication. Through calculation of randomly selected 50 nanowires from SEM image (Figure 1b), the average diameter of the Cu NWs is  $\sim 60\ \text{nm}$ . The lengths of the nanowires vary from 10s to 100s of micrometers. Figure 1c illustrates the schematic fabrication process of Cu NWs/PDMS stretchable conductors. Initially, Cu NWs were collected on PTFE filters through vacuum filtration. After annealing treatment, liquid PDMS was cast onto glass slides, following by curing at 80 °C for a period of time until slightly sticky PDMS substrates were obtained. Then the Cu NWs/PTFE films were carefully transferred onto the substrates and they were fully postpolymerized at 80 °C for 2 h in a vacuum oven. Finally, being peeled off from the filters, the Cu NWs/PDMS composite films were obtained. The rough surface of Cu NWs

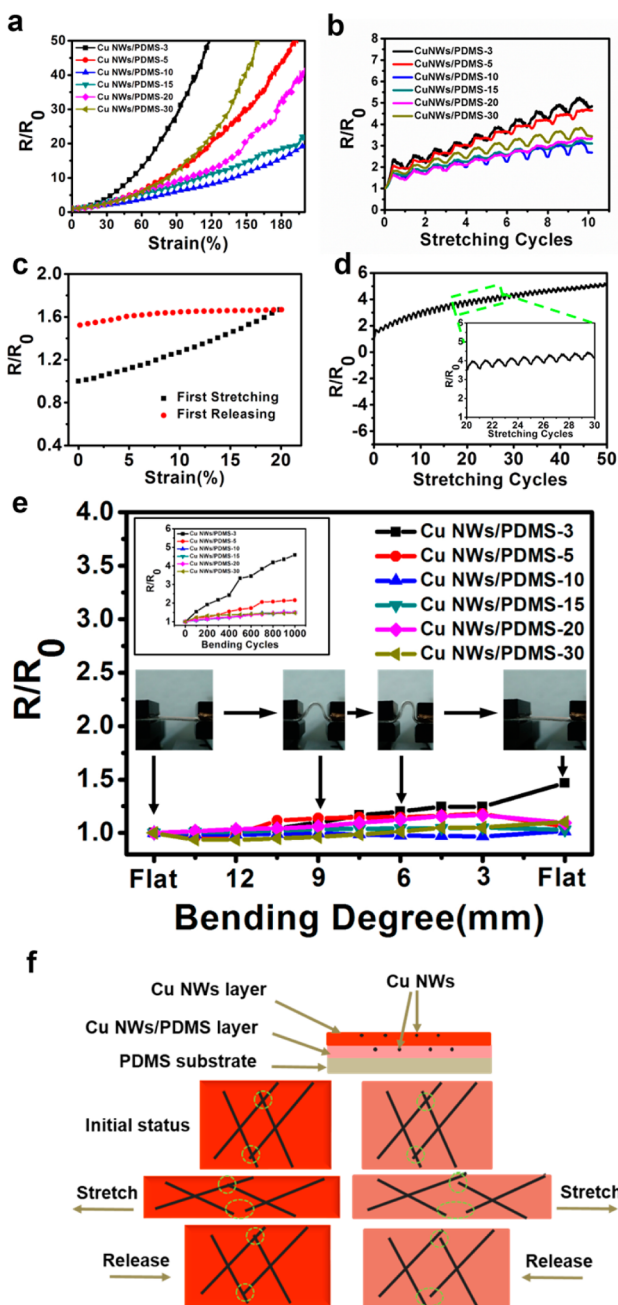
shown from the magnified SEM image (Figure 1d, inset) implicated the existence of organic residues and oxides, which was further confirmed by FTIR, energy-dispersive X-ray spectroscopy, and Raman analysis (Figure S1, Supporting Information). The organic residues will increase the contact resistance between nanowires greatly and need to be removed. Therefore, Cu NWs/PTFE films were annealed at a certain temperature (190–290 °C) in a quartz tube furnace for 30 min under a constant flow of hydrogen. Figure 1e shows the digital photograph and SEM images of Cu NW film annealed at 230 °C. The surfaces of Cu NWs became much cleaner after annealing. Moreover, the peaks ascribed to  $-\text{NH}_2$  ( $3391\ \text{cm}^{-1}$ ),  $-\text{CH}_2$  ( $2917$ ,  $1467$ , and  $719\ \text{cm}^{-1}$ ), and  $-\text{CH}_3$  ( $2847\ \text{cm}^{-1}$ ) disappeared in the FTIR spectrum after annealing, verifying the removal of organic residues. In addition, the oxide layer was also removed by annealing, as confirmed by Raman analysis.

Since the annealing temperature has an effect on the integrity and conductivity of the nanowire films, it was investigated in detail. As disclosed in Figure S2, Cu NWs film annealed at 230 °C possesses the best conductive performance, which is attributed to the effective removal of organic residues and oxide layers, as well as the welding of nanowires. Higher annealing temperatures will lead to breakage of nanowires, which will decrease the conductance of the film. Therefore, Cu NWs films were annealed at 230 °C in the following discussion if not otherwise stated.

During the quasi in situ polymerization process, prepolymerization time is a crucial factor since it determines the stickiness and hardness of the PDMS substrates, which will affect the transfer of Cu NWs greatly. Therefore, composite films fabricated with different prepolymerization times were collected, tested, and characterized by SEM. As shown in Figure 2a, the sheet resistance of the composite films decreases continuously with the prolonging of prepolymerization time and levels off after 10 min. The reason lies in the different embedding depths of Cu NWs into the PDMS substrates, as disclosed in Figure 2b–g. As the prepolymerization time is prolonged from 3 to 30 min, the embedding depth decreases. Prepolymerization time of 3 and 5 min leads to stickier and softer surfaces of PDMS substrate, which will bring in deeper embedding of Cu NW networks during the transfer process, and vice versa. When the prepolymerization time is prolonged to 30 min, Cu NWs are scarcely buried, and most of them cover on top of the PDMS substrate (Figure 2g). Deeper embedding of the nanowire network results in larger sheet resistance of the composite films since wrapping by polymer would increase the contact resistance of the unwelded junctions, which explains the variation trend of the sheet resistance. Moreover, the embedding status of Cu NWs influences their attachment to PDMS substrates pronouncedly. As seen from Figure 2h, Cu NWs/PDMS samples prepolymerized for 3, 5, and 10 min (marked as Cu NWs/PDMS-3, Cu NWs/PDMS-5, and Cu NWs/PDMS-10, respectively) exhibits strong adhesion to the substrates, and no nanowires can be peeled off the substrates by 3 M scotch tapes. In contrast, for Cu NWs/PDMS-15, Cu NWs/PDMS-20, and Cu NWs/PDMS-30, the Cu NWs will be partly removed by scotch tape and the integrity of Cu NWs networks will be broken.

The stretch ability of Cu NWs/PDMS composite conductors were characterized by a tensile system at the speed of 10%/min.  $R/R_0$  was defined as a ratio of the instantaneous resistance at a specific tensile strain to the initial resistance at zero strain. Figure 3a demonstrates the change of  $R/R_0$  as a function of





**Figure 3.** (a)  $R/R_0$  versus tensile strain up to 200% of Cu NWs/PDMS with different prepolymerization times. (b)  $R/R_0$  change of Cu NWs/PDMS-3, Cu NWs/PDMS-5, Cu NWs/PDMS-10, Cu NWs/PDMS-15, Cu NWs/PDMS-20, and Cu NWs/PDMS-30 with tensile strain up to 20% in the first ten cycles. (c)  $R/R_0$  variation of Cu NWs/PDMS-10 with tensile strain up to 20% in the first cycle. (d) Stretching and releasing property of Cu NWs/PDMS-10 in 50 cycles (the inset was a 10 cycles curve of the composite after cycling 20 times). (e)  $R/R_0$  of Cu NWs/PDMS versus the bending degree from flat to 3 mm, and back to flat. The photographs are the composite films bent at various bending degrees, from flat to 9 mm, 6 mm, and back to flat. The insert was the cyclic bending test of Cu NWs/PDMS at a bending degree of 6 mm. (f) Scheme of the structure change of Cu NWs/PDMS composite films with stretching and release.

strain of Cu NWs/PDMS films with different prepolymerization times. The resistances of the composite films rise slowly and then rapidly with stretch, which is similar to the tendency of resistance change as reported before.<sup>36</sup> Cu NWs/PDMS-10

reveals the best tensile strain tolerance, and the resistance increases by 4 times at the tensile strain of 80%, which outperforms many nanomaterial-based stretchable conductors with the nonstructurally engineered elastomeric substrates to date. Stretchable conductors based on Ag NWs/polyacrylate and Cu NWs/polyurethane showed increase on the resistance by 10 and 15 times at the strain of 80%, respectively.<sup>36,37</sup>

The first ten cycles of the six samples with strain up to 20% were investigated and shown in Figure 3b. As expected, Cu NWs/PDMS-10 shows the best performance compared with the other samples and the curves of the change of  $R/R_0$  as a function of stretching cycles reveals fixed periodicity. However, instead of recovering the initial value after releasing, the resistance ascends gradually with cycling. This phenomenon is mainly attributed to the slide between Cu NWs when stretched, which, unfortunately, can only slide back by a certain degree after releasing due to the friction force between Cu NWs and PDMS matrix. The slide of Cu NWs may lead to a smaller overall contact area, thus resulting in the increase of resistance shown in Figure 3c.<sup>32</sup> Except for the reason mentioned above, there is residual strain in Cu NWs/PDMS layer upon unloading as well, due to the rearrangement of Cu NWs during the first stretching, which is similar to networks of CNTs compressed by outside load.<sup>38</sup> Figure 3d discloses that the variation curve of  $R/R_0$  turns flat with cycling, which originates from the formation of a buckled wavy shape of Cu NWs/PDMS layer.<sup>32</sup> Such wavy, sinusoidal shape is beneficial to the stretch-release performance and durability of stretchable conductors, which has been confirmed in many previous reports.<sup>39,40</sup>

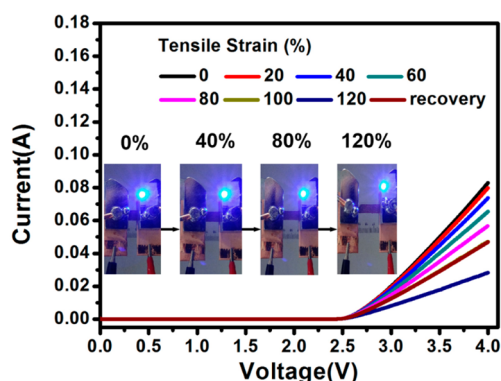
The bendable properties of the Cu NWs/PDMS composite films were also investigated (shown in Figure 3e). For convenience, the distance between the two ends of the bended film was taken as the assessment of the degree of bending. Films 15 mm long were bent from flat to a bending degree of 3 mm gradually and then returned to flat. The variation curves of  $R/R_0$  reveal that these six composite films maintain the conductive stability in the first cycle, especially Cu NWs/PDMS-10, Cu NWs/PDMS-15, and Cu NWs/PDMS-30. Furthermore, a cyclic bending test at a bending degree of 6 mm indicates that the conductivity of Cu NWs/PDMS-10, Cu NWs/PDMS-15, Cu NWs/PDMS-20, and Cu NWs/PDMS-30 remains perfectly stable, even after cycling for 1000 times without conspicuous degradation. The resistance of Cu NWs/PDMS-3, however, increases apparently with cycling.

A scheme of the structure change of Cu NWs/PDMS composite films with stretching and release was proposed to illustrate the reason why Cu NWs/PDMS-10 has the best stretching and bending performance. As shown in Figure 3f, the composite film is mainly composed of three layers, including the bottom PDMS layer, Cu NW-PDMS composite layer, and the unembedded Cu NW layer. The thickness of each layer is dependent on the prepolymerization time as shown in Figure 2. When being stretched, nanowires in the composite layer will slide along the stretching direction due to the friction force between them and the PDMS substrate. This will lead to the damage of some conducting paths, therefore resulting in the increase of the sheet resistance. In contrast, the combining between PDMS with Cu NWs, which are not wrapped by polymers in the unembedded layer, is rather weak. When being stretched, sliding will occur among the nanowires as well as between the nanowire and the PDMS substrate. Therefore, the unembedded Cu NW network deforms less compared with Cu NW-PDMS composite layer, and stays more conductive after

stretching. This can explain the poor stretching performance of deeply embedded samples including Cu NWs/PDMS-3 and Cu NWs/PDMS-5. However, if the polymerization time is prolonged to over 20 min, the nanowire networks are barely embedded, and their attachment to the substrate becomes very weak as well, which results in easier detachment of Cu NWs from PDMS substrates during the stretching process. On the basis of the reasons mentioned above, the Cu NWs/PDMS-10 shows the best stretchable performance. When being released, nanowires could not slide back to the initial state, and many conducting paths were destroyed due to the hindering of the surrounding polymer molecules in the composite layers, which explains the inferior recovery performance of Cu NWs/PDMS-3 and Cu NWs/PDMS-5.

Except for these properties, the antioxidation ability was also investigated. As shown in Figure S3, the change of  $R/R_0$  is less than 1.4 after the films were stored in air for 50 days, testifying to the excellent antioxidant property of the composite films.

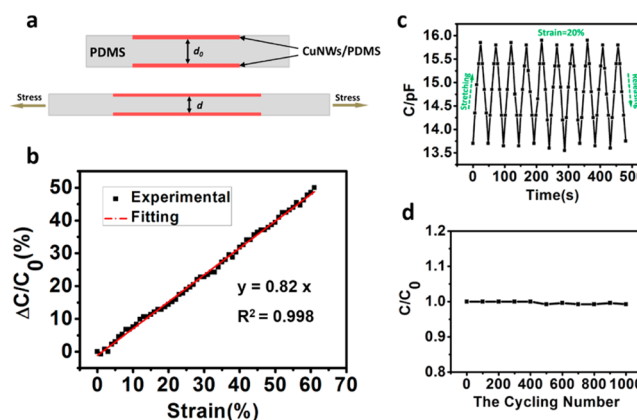
To demonstrate the feasibility of Cu NWs/PDMS conductors, a piece of Cu NWs/PDMS-10 with the length of 2 cm and initial resistance of  $2\ \Omega$  was used as stretchable electric wiring to illuminate a light-emitting diode (LED) lamp. The LED lamp was operated at a voltage of 4 V when it was stretched from 0% to 120% as shown in Figure 4. As seen from



**Figure 4.** Current–voltage measurement of LED integrated by Cu NWs/PDMS-10 at various tensile strains over 120%. Insets show the digital images of the integrated LED circuits operated at 0%, 40%, 80%, and 120% strain. (Note: The curve for 100% tensile strain coincides with the one of recovery.)

insets, no conspicuous degradation of brightness is observed during stretching from 0% to 120%. Although the current decreased as the electric circuit was stretched to a larger strain, owing to the partial damage of the integrity of the Cu NWs network, the LED can still maintain its normal working. The current voltage characteristics were partly recovered when the strain was released. These testing results successfully display the possible applications of the Cu NWs/PDMS films in stretchable electronics.

Because of its high conductivity, stretch ability, and bendability, Cu NW conductor has potential as electrodes in strain sensor application. Herein, a capacitive sensor was fabricated by laminating two Cu NWs/PDMS-10 electrodes with the conducting surface facing outward, which is similar to a parallel plate capacitor (Figure 5a). The initial capacitance of the sensor is given by  $C_0 = \epsilon_0 \epsilon_r \frac{A_0}{d_0}$ , where  $\epsilon_0$  is the electric constant,  $\epsilon_r$  is the dielectric constant, and  $A_0$  and  $d_0$  are the area overlap and separation between the two electrodes (the space



**Figure 5.** (a) Schematically showing a capacitive strain sensor with Cu NWs/PDMS-10 as the electrodes (top) before and (bottom) after being stretched. (b) Change of capacitance  $\Delta C/C_0$  versus strain. (c) Change in capacitance versus time over ten stretching/releasing cycles with 20% stretching strain (stretching/releasing speed is 50%/min). (d) Durability test of Cu NWs/PDMS strain sensor over 1000 times stretching and releasing up to tensile strain of 20%.

between two electrodes is about 1 mm), respectively. When it was uniaxially stretched, the change in capacitance  $\Delta C$  with the applied strain  $\epsilon$  is given by  $\Delta C = a\epsilon C_0$ , where  $a$  is the gauge factor.<sup>32,41</sup> Figure 5b plots the change of capacitance as a function of strain, which shows great linearity with standard deviation  $R^2$  of 0.998 under a large strain range (up to 60%).  $(\Delta C/C_0)/\epsilon$ , is defined as a capacitive gauge factor which is the slope of the linear fit as shown in Figure 5b and is taken as a performance index.<sup>42</sup> The gauge factor of our strain sensor is 0.82 and the minimum detectable strain is about 1%. The performance outperforms many strain sensors with the same work theory and parallel-plate structure. For example, Lipomi et al. reported strain sensor based on CNT film with the gauge factor of 0.41,<sup>43</sup> while Hu et al. and Yao and Zhu fabricated Ag NW strain sensors with the gauge factor of 0.5 and 0.7, respectively.<sup>41,44</sup> Figure 5c records the variation of capacitance versus time over ten stretching and releasing cycles with the 20% stretching strain. In each stretching cycle, the capacitance increases quickly to 1.16 times of the original value and can reverse back to the initial value after releasing, exhibiting a stable response. Furthermore, the durability of the sensor was tested over 1000 cycles of stretching and releasing. As seen from Figure 5d, the capacitance keeps constant during cycling, manifesting the excellent durability of the Cu NWs/PDMS capacitive sensor.

## 4. CONCLUSIONS

In summary, we have proposed a quasi in situ polymerization method to fabricate Cu NWs/PDMS stretchable conductors. Via regulating the prepolymerization time, partial embedment of Cu NWs in PDMS substrates were realized, which endowed the conductors with strong adhesion, excellent conductivity and stability ( $R/R_0 < 1.4$  for 50 days in air), enhanced stretch ability (80% strain,  $R/R_0 \sim 5$ ), and bendability of Cu NWs/PDMS conductors. The composite conductor has been used as the stretchable electric wiring to illuminate an LED, which did not show obvious degradation of brightness during stretching from 0% to 120%. Stretchable capacitive sensor with detection limit as low as 1% strain, and sensitivity as high as 0.82 has also been constructed with Cu NWs/PDMS conductors as electrodes. It is believed that the quasi in situ polymerization method can be

extended to other materials system and find novel applications in many flexible and stretchable devices.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b11143.

The FTIR spectra of Cu NWs on silicon wafer before and after heat treatment, SEM and EDX of Cu NW network without heat treatment, Raman spectra for Cu NWs on PTFE before and after heat treatment, the effect of different heat treatment temperatures on Cu NWs/PTFE films, and long-term stability of Cu NWs/PDMS under air atmosphere (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*Telephone: +86-21-52412717. Fax: +86-21-52413122. E-mail: wangranran@mail.sic.ac.cn.

\*E-mail: jingsun@mail.sic.ac.cn.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was financially supported by the National Basic Research Program of China (2012CB932303), the National Natural Science Foundation of China (Grant No. 61301036), Shanghai Municipal Natural Science Foundation (Grant No. 13ZR1463600), and The Innovation Project of Shanghai Institute of Ceramics.

## ■ REFERENCES

- (1) Lee, P.; Lee, J.; Lee, H.; Yeo, J.; Hong, S.; Nam, K. H.; Lee, D.; Lee, S. S.; Ko, S. H. Highly Stretchable and Highly Conductive Metal Electrode by Very Long Metal Nanowire Percolation Network. *Adv. Mater.* **2012**, *24*, 3326–3332.
- (2) Cheng, Y.; Wang, R.; Sun, J.; Gao, L. Highly Conductive and Ultrastretchable Electric Circuits from Covered Yarns and Silver Nanowires. *ACS Nano* **2015**, *9*, 3887–3895.
- (3) Rogers, J. A.; Someya, T.; Huang, Y. Materials and Mechanics for Stretchable Electronics. *Science* **2010**, *327*, 1603–1607.
- (4) Sekitani, T.; Nakajima, H.; Maeda, H.; Fukushima, T.; Aida, T.; Hata, K.; Someya, T. Stretchable Active-matrix Organic Light-emitting Diode Display Using Printable Elastic Conductors. *Nat. Mater.* **2009**, *8*, 494–499.
- (5) Bae, J.; Lee, J.; Kim, S.; Ha, J.; Lee, B. S.; Park, Y.; Choong, C.; Kim, J. B.; Wang, Z. L.; Kim, H. Y.; Park, J. J.; Chung, U. I. Flutter-driven Triboelectrification for Harvesting Wind Energy. *Nat. Commun.* **2014**, *5*, 4929.
- (6) Hu, L.; Pasta, M.; Mantia, F. L.; Cui, L.; Jeong, S.; Deshazer, H. D.; Choi, J. W.; Han, S. M.; Cui, Y. Stretchable, Porous, and Conductive Energy Textiles. *Nano Lett.* **2010**, *10*, 708–714.
- (7) Ko, H. C.; Stoykovich, M. P.; Song, J.; Malyarchuk, V.; Choi, W. M.; Yu, C. J.; Geddes, J. B., III; Xiao, J.; Wang, S.; Huang, Y.; Rogers, J. A. A Hemispherical Electronic Eye Camera Based on Compressible Silicon Optoelectronics. *Nature* **2008**, *454*, 748–753.
- (8) Takei, K.; Takahashi, T.; Ho, J. C.; Ko, H.; Gillies, A. G.; Leu, P. W.; Fearing, R. S.; Javey, A. Nanowire Active-matrix Circuitry for Low-voltage Macroscale Artificial Skin. *Nat. Mater.* **2010**, *9*, 821–826.
- (9) Lu, L.; Chen, W. Biocompatible Composite Actuator: A Supramolecular Structure Consisting of The Biopolymer Chitosan, Carbon Nanotubes, and an Ionic Liquid. *Adv. Mater.* **2010**, *22*, 3745–3748.
- (10) Wu, J.; Zang, J.; Rathmell, A. R.; Zhao, X.; Wiley, B. J. Reversible Sliding in Networks of Nanowires. *Nano Lett.* **2013**, *13*, 2381–2386.
- (11) Jeong, G. S.; Baek, D. H.; Jung, H. C.; Song, J. H.; Moon, J. H.; Hong, S. W.; Kim, I. Y.; Lee, S. H. Solderable and Electroplatable Flexible Electronic Circuit on a Porous Stretchable Elastomer. *Nat. Commun.* **2012**, *3*, 977.
- (12) Yamada, T.; Hayamizu, Y.; Yamamoto, Y.; Yomogida, Y.; Izadi-Najafabadi, A.; Futaba, D. N.; Hata, K. A Stretchable Carbon Nanotube Strain Sensor for Human-motion Detection. *Nat. Nanotechnol.* **2011**, *6*, 296–301.
- (13) Wang, X.; Gu, Y.; Xiong, Z.; Cui, Z.; Zhang, T. Silk-molded Flexible, Ultrasensitive, and Highly Stable Electronic Skin for Monitoring Human Physiological Signals. *Adv. Mater.* **2014**, *26*, 1336–1342.
- (14) Kim, D.-H.; Rogers, J. A. Stretchable Electronics: Materials Strategies and Devices. *Adv. Mater.* **2008**, *20*, 4887–4892.
- (15) Chen, M.; Zhang, L.; Duan, S.; Jing, S.; Jiang, H.; Li, C. Highly Stretchable Conductors Integrated with a Conductive Carbon Nanotube/Graphene Network and 3D Porous Poly-(dimethylsiloxane). *Adv. Funct. Mater.* **2014**, *24*, 7548–7556.
- (16) Yao, S.; Zhu, Y. Nanomaterial-Enabled Stretchable Conductors: Strategies, Materials and Devices. *Adv. Mater.* **2015**, *27*, 1480–1511.
- (17) Won, Y.; Kim, A.; Yang, W.; Jeong, S.; Moon, J. A Highly Stretchable, Helical Copper Nanowire Conductor Exhibiting a Stretchability of 700%. *NPG Asia Mater.* **2014**, *6*, e132.
- (18) Argun, A. A.; Cirpan, A.; Reynolds, J. R. The First Truly All-Polymer Electrochromic Devices. *Adv. Mater.* **2003**, *15*, 1338–1341.
- (19) Hansen, T. S.; West, K.; Hassager, O.; Larsen, N. B. Highly Stretchable and Conductive Polymer Material Made from Poly(3,4-ethylenedioxythiophene) and Polyurethane Elastomers. *Adv. Funct. Mater.* **2007**, *17*, 3069–3073.
- (20) Chun, K.-Y.; Oh, Y.; Rho, J.; Ahn, J.-H.; Kim, Y.-J.; Choi, H. R.; Baik, S. Highly Conductive, Printable and Stretchable Composite Films of Carbon Nanotubes and Silver. *Nat. Nanotechnol.* **2010**, *5*, 853–857.
- (21) Kujawski, M.; Pearse, J. D.; Smela, E. Elastomers Filled with Exfoliated Graphite as Compliant Electrodes. *Carbon* **2010**, *48*, 2409–2417.
- (22) Park, M.; Im, J.; Shin, M.; Min, Y.; Park, J.; Cho, H.; Park, S.; Shim, M.-B.; Jeon, S.; Chung, D.-Y.; Bae, J.; Park, J.; Jeong, U.; Kim, K. Highly Stretchable Electric Circuits from a Composite Material of Silver Nanoparticles and Elastomeric Fibres. *Nat. Nanotechnol.* **2012**, *7*, 803–809.
- (23) Ge, J.; Yao, H.-B.; Wang, X.; Ye, Y.-D.; Wang, J.-L.; Wu, Z.-Y.; Liu, J.-W.; Fan, F.-J.; Gao, H.-L.; Zhang, C.-L.; Yu, S.-H. Stretchable Conductors Based on Silver Nanowires: Improved Performance through a Binary Network Design. *Angew. Chem., Int. Ed.* **2013**, *52*, 1654–1659.
- (24) Han, S.; Hong, S.; Ham, J.; Yeo, J.; Lee, J.; Kang, B.; Lee, P.; Kwon, J.; Lee, S. S.; Yang, M. Y.; Ko, S. H. Fast Plasmonic Laser Nanowelding for a Cu-nanowire Percolation Network for Flexible Transparent Conductors and Stretchable Electronics. *Adv. Mater.* **2014**, *26*, S808–S814.
- (25) Hu, L.; W, H.; Cui, Y. Metal Nanogrids, Nanowires, and Nanofibers for Transparent Electrodes. *MRS Bull.* **2011**, *36*, 760–765.
- (26) Mata, A.; Fleischman, A. J.; Roy, S. Characterization of Polydimethylsiloxane (PDMS) Properties for Biomedical Micro/Nanosystems. *Biomed. Microdevices* **2005**, *7*, 281–293.
- (27) McDonald, J. C.; Whitesides, G. M. Poly(dimethylsiloxane) as a Material for Fabricating Microfluidic Devices. *Acc. Chem. Res.* **2002**, *35*, 491–499.
- (28) Ng, H. T.; Foo, M. L.; Fang, A.; Li, J.; Xu, G.; Jaenicke, S.; Chan, L.; Li, S. F. Y. Soft-Lithography-Mediated Chemical Vapor Deposition of Architected Carbon Nanotube Networks on Elastomeric Polymer. *Langmuir* **2002**, *18*, 1–5.
- (29) Tan, S. H.; Nguyen, N.-T.; Chua, Y. C.; Kang, T. G. Oxygen Plasma Treatment for Reducing Hydrophobicity of a Sealed Polydimethylsiloxane Microchannel. *Biomicrofluidics* **2010**, *4*, 032204.
- (30) Lee, H.; Lee, K.; Park, J. T.; Kim, W. C.; Lee, H. Well-Ordered and High Density Coordination-Type Bonding to Strengthen Contact



of Silver Nanowires on Highly Stretchable Polydimethylsiloxane. *Adv. Funct. Mater.* **2014**, *24*, 3276–3283.

(31) Akter, T.; Kim, W. S. Reversibly Stretchable Transparent Conductive Coatings of Spray-deposited Silver Nanowires. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1855–1859.

(32) Xu, F.; Zhu, Y. Highly Conductive and Stretchable Silver Nanowire Conductors. *Adv. Mater.* **2012**, *24*, 5117–5122.

(33) Zhang, D.; Wang, R.; Wen, M.; Weng, D.; Cui, X.; Sun, J.; Li, H.; Lu, Y. Synthesis of Ultralong Copper Nanowires for High-performance Transparent Electrodes. *J. Am. Chem. Soc.* **2012**, *134*, 14283–14286.

(34) Cheng, Y.; Wang, S.; Wang, R.; Sun, J.; Gao, L. Copper Nanowire Based Transparent Conductive Films with High Stability and Superior Stretchability. *J. Mater. Chem. C* **2014**, *2*, 5309–5316.

(35) Rathmell, A. R.; Bergin, S. M.; Hua, Y.-L.; Li, Z.-Y.; Wiley, B. J. The Growth Mechanism of Copper Nanowires and Their Properties in Flexible, Transparent Conducting Films. *Adv. Mater.* **2010**, *22*, 3558–3563.

(36) Hu, W.; Wang, R.; Lu, Y.; Pei, Q. An Elastomeric Transparent Composite Electrode Based on Copper Nanowires and Polyurethane. *J. Mater. Chem. C* **2014**, *2*, 1298–1305.

(37) Hu, W.; Niu, X.; Li, L.; Yun, S.; Yu, Z.; Pei, Q. Intrinsically Stretchable Transparent Electrodes Based on Silver-nanowire–cross-linked-polyacrylate Composites. *Nanotechnology* **2012**, *23*, 344002.

(38) Slobodian, P.; Riha, P.; Lengalova, A.; Saha, P. Compressive Stress-electrical Conductivity Characteristics of Multiwall Carbon Nanotube Networks. *J. Mater. Sci.* **2011**, *46*, 3186–3190.

(39) Shin, M. K.; Oh, J.; Lima, M.; Kozlov, M. E.; Kim, S. J.; Baughman, R. H. Elastomeric Conductive Composites Based on Carbon Nanotube Forests. *Adv. Mater.* **2010**, *22*, 2663–2667.

(40) Kim, D.-H.; Xiao, J.; Song, J.; Huang, Y.; Rogers, J. A. Stretchable, Curvilinear Electronics Based on Inorganic Materials. *Adv. Mater.* **2010**, *22*, 2108–2124.

(41) Hu, W.; Niu, X.; Zhao, R.; Pei, Q. Elastomeric Transparent Capacitive Sensors Based on an Interpenetrating Composite of Silver Nanowires and Polyurethane. *Appl. Phys. Lett.* **2013**, *102*, 083303.

(42) Cao, Q.; Rogers, J. A. Ultrathin Films of Single-Walled Carbon Nanotubes for Electronics and Sensors: A Review of Fundamental and Applied Aspects. *Adv. Mater.* **2009**, *21*, 29–53.

(43) Lipomi, D. J.; Vosgueritchian, M.; Tee, B. C. K.; Hellstrom, S. L.; Lee, J. A.; Fox, C. H.; Bao, Z. Skin-like Pressure and Strain Sensors Based on Transparent Elastic Films of Carbon Nanotubes. *Nat. Nanotechnol.* **2011**, *6*, 788–792.

(44) Yao, S.; Zhu, Y. Wearable Multifunctional Sensors Using Printed Stretchable Conductors Made of Silver Nanowires. *Nanoscale* **2014**, *6*, 2345–2352.