1. Introduction and Motivation

There is a growing demand for flexible and soft electronic devices, therefore, stretchable, wearable strain sensors receive increasing attention. Combined with clothing or directly contacted with skin (electronic skin), they are able to collect physical, chemical, biological and environmental signals in real time. Noble metal materials, especially gold and silver, show distinguishing characteristics in optical, electrical, mechanical, and thermal properties,[1] which can be one of the optimal conductive materials for wearable strain sensors. Because of abundance in the Earth’s crust,[2] copper is about 100 times cheaper than silver and 6,000 times cheaper than gold. In addition, copper resides in the same group 11 elements as gold and silver, therefore possesses similar properties owing to its electronic configuration and face centred cubic (FCC) crystal structure.[3] One-dimensional copper nanowires (CuNWs) exhibit high electrical conductivity, thermal conductivity, malleability and ductility. However, strain sensors based on solid-state materials (including nanoparticles, nanowires and nanotubes) are only applicable for a small-scale strain (less than 100%),[4] which can not afford the multiscale human motion detection.

Therefore, we combined copper nanowires with a liquid-state conductor, PEDOT:PSS. The sensing material is encapsulated in the elastic polymer PDMS due to the flexibility, stretchability, human-friendliness and durability. Because of the excellent mechanical and electrical properties of these materials, the composite strain sensor exhibits large stretchability (120%) and good cycling stability (~1,000 stretching/releasing cycles).

2. Experimental Process

2.1 Synthesis of CuNWs by hydrothermal method

It is reported that we can use several methods to produce abundant shape-controllable, well dispersed CuNWs, such as chemical vapor deposition, electrochemical deposition and template method.[5] Chemical vapor deposition needs preparing CuNWs in vacuum environment, which can effectively prevent the surface oxidation of the nanowires, but it has to pay costly equipment and leads to shapeless nanostructures. Electrochemical deposition is simpler, and the morphology and crystallinity of CuNWs are well controlled, but it brings out poor nanowires, complicated experimental steps and needless template. Liquid-phase reduction method has gradually become the widely used method for preparing CuNWs, due to less restriction on the reaction conditions and suitable for preparing CuNWs.
in large quantities. We prepared CuNWs using a previously reported liquid-phase reduction - hydrothermal method.[6]

Hydrothermal method reduces metal ions to metal atoms with a reductant in a high-pressure closed environment, followed by nucleation, growth and aging, gradually forming nanocrystals.[7] In general, the reduced copper atoms nucleate uniformly in the solution, and the nuclei, as seeds for the growth of nanocrystals, gradually grow into one-dimensional copper nanocrystals under the condition of high temperature and pressure. The nucleating and growing process of copper nanocrystals undergo thermomechanical aging, so that the smaller copper nanoparticles dissolve and form larger nanoparticles with stable nanocrystals. Therefore, the parameters of the reaction process, such as the type of coating agent,[8] the reaction temperature, the reaction time and the ratio of the reactants, play an important role in the morphology of the final product.

The morphology of nanocrystals depends on the growth rate of their different crystal planes.[8] In recent studies, capping agents (adhesion agents) have been widely used to control the surface energy and growth rate of different nanocrystals, so they determine the morphology of nanocrystals. For example, polyvinyl pyrrolidone (PVP) acts as the capping agent for the [100] crystal plane of Ag and Pd in order to control the growth rate.[9, 10] Under the condition, newly synthesized atoms preferentially select the [111] crystal plane, forming nanocubes, double cone and five-fold twin nanowires with [100] crystal plane closed. Besides PVP, bromide can also selectively attach to the [100] crystal plane of Ag, Au, Pd, Pt crystals, inducing the formation of nanocubes, nanoplates or five-twins nanowires.[6]

In the synthesis, 0.42 g CuCl$_2$·2H$_2$O (the precursor), 1.00 g glucose (the reductant), 3.60 g HDA (the capping agent), and 200 mL deionized water were mixed in a beaker at room temperature, and were magnetically stirred at room temperature overnight. Then the solution was transferred to a reaction vessel and heated at 110°C for six hours. As the reaction proceeded, the solution gradually changed its color from blue to darkred (see the photograph in Fig. 1a), implying the formation of Cu$^{0}$ species due to the reduction of Cu$^{2+}$ by glucose. Finally, the solution was stirred with n-hexane and isopropanol to remove the by-products of the reaction and then stored in a glass vial with isopropanol (IPA).

2.2 Strain sensor preparation

Force-sensitive material is the most commonly used material in strain sensors to perceive the mechanical changes of the environment, such as pressure, speed and tensile.[11] Strain sensors convert mechanical signals to electrical signals (resistance, capacitance, or voltage) when subjected to external forces.[12, 13] Conventional force-sensitive materials, such as metal, semiconductor and alloy, are lack of flexibility so that they cannot be applied to flexible sensor, covering the human body. In order to get a flexible wearable sensor, current strain sensors always use composite conductive materials,[14] especially polymer conductive materials.[15] Resistive flexible strain sensors are mainly composed of a conductive sensing film and a stretchable flexible substrate.[16] When subjected to an external force, the change in the microstructure of the sensing film causes corresponding change in resistance. When releasing force, the sensing film is approximately restored to the initial state.

Strain sensors possess a variety of response mechanism, depending on the material, microstructure, as well as the fabrication process.[17] Traditional mechanism emerges from the change in geometry and the piezoelectric resistivity of the material itself. In addition, the response mechanism of flexible strain sensors includes the separation between the sensing components, crack propagation and tunneling effect as well.[17–19]

In the experiment, we use CuNWs, a kind of conductive organic solution, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), and PDMS to form a flexible wearable strain sensor. Fabrication processes of the strain sensor are shown in Fig. 2. Copper nanowires suspension solution is firstly generated by hydrothermal method, and then deposited on the Polyimide (PI) tape attached to a glass substrate to form a conductive network. Liquid PDMS is spin-coated on the glass substrate and cured. The
PDMS film can be peeled off the glass to form micro-channels. Silver wires are connected at both ends of the micro-channels to form connects, and another PDMS slab is used to encapsulate the device. Finally, the PEDOT:PSS solution is injected into the micro-channels with a syringe. A strain sensor based on copper nanowires and elastomers is made, and the device structure is shown in Fig. 2f.

3. Results and Discussion

3.1 Copper nanowires growth mechanism

Figure 3a gives the SEM image of CuNWs, which are smooth and flexible, with an average diameter of 40 nm and length over 50 μm. Figure 3b gives the TEM image of CuNWs, compared with the SEM image, we find that copper nanowires made by hydrothermal method shows high consistency, flexibility but various length. In the process of metal crystallization, a group of crystal nuclei are spontaneously formed in the liquid metal at the same time, and some foreign refractory particles can also act as nuclei to form non-spontaneous nuclei.[9] With time going on, the nuclei continue to grow, while new nucleus are also formed at the same time until the liquid metal disappears and the crystal grow to a whole one. Therefore, the crystallization process is continuous nucleation and growth of the nucleus process.

Figure 3c shows the growing process of this experiment. When glucose reduces Cu$^{2+}$ to Cu$^0$, it appears uniform nucleation in solution. In the late stage of growing process, the grain size of the precipitated phase is different. Since the small particles dissolve while larger particles continue to grow, the average particle size increase continuously. As shown in the Fig. 3c, HDA, as the capping agent, inhibits the growth of [111] and [100] crystal planes of copper crystals during the process. Newly precipitated copper atoms combine only with the [110] plane, leading to the appearance of nanowires.

3.2 Performance of the strain sensor

To examine the advantages of the proposed structure, two types of structures were fabricated with PDMS: (I) a pure PEDOT:PSS solution; (II) a CuNWs thin film combined with the PEDOT:PSS solution. These strain sensors were tested under strains, and the electrical responses were characterized by the variations in the relative resistances, $\Delta R/R_0 = (R - R_0)/R_0$, where $R_0$ and R correspond to the original resistance and the real-time resistance under stretching, respectively. Figure 4a shows the values of $\Delta R/R_0$ with respect to the strain, $\varepsilon = (L - L_0)/L_0$, where $L_0$ and L correspond to the original length and stretching length, respectively. The two type of sensor performed comparably well, even when they were stretched up to 120% of their original lengths. But the combination sensor, the sensor with CuNWs film and PEDOT:PSS (red line), had a much higher sensitivity for large variations in the
relative resistances, $\Delta R/R_0$. The sensitivity is quantified by calculating a figure of merit, i.e. the gauge factor (GF), which is defined as $GF = (dR/R_0)/(dL/L_0)$. Here, $R_0$ and $L_0$ are the original resistance and length of the sensor, and $dR$ and $dL$ are the changes in the resistance and length of the sensor under loading.[20] The sensing principle of the copper nanowires network is closely related to the widening of its microcracks and the disconnection of the nanowires during stretching.[21] When the sensor is under a small strain, the nanowires network is continuous and the current mainly passes through the conductive network. As the strain is increased gradually to 120%, even more slippage and fracture of the network appears in the elastic matrix and leads to a higher resistance. Because of the liquid conductor, percolation paths form through the solid-liquid hybrid, thereby maintaining the integrity of the conductive pathway under large deformation.

Figure 4b shows the durability test of the strain sensor under 60% strain for 1,000 cycles, which led to a gradual increase of $\Delta R/R_0$ in the sensor. It partly resulted from the looseness of electrodes on both ends of conductive thin films. However, an obvious change in resistance with deformation could always be observed after several stretching loops.

In addition to stretchability, sensitivity and durability, strain sensors must have different reactions to various mechanical stimulations, e.g., tension, and pressure. Figure 4c presents the $\Delta R/R_0$ values of the strain sensor when it was stretched to different scales, 20%, 40% and 60%. In this test, the strain sensor responded well to a change in the scale, which indicates the sensor can be used to detect different deformation. The $\Delta R/R_0$ values of the strain sensor were measured under different mechanical actions, as shown in Fig. 4d-e. First, the sensor was subjected to tension bending loops (Fig. 4d). The $\Delta R/R_0$ values increased when the bending degree increased, which was caused by the stretching of the nanowires thin film and a reduction in the cross-section of the PEDOT:PSS solution. Then the sensor was subjected to a pressure test, as shown in Fig. 4e. When subjected to a constant force, the conductive network is prone to deformation and the $\Delta R/R_0$ values increased. The above tests show that the presented strain sensor possesses desirable characteristics of high sensitivity and stretchability, durability, comparable wide sensing range and multiple mechanical reactions, and these strengths are applicable to be a wearable sensor for detecting different human motions.

With the attributes of both the nanowires and conductive organic solution, the sensor should be able to endure and detect the strain of human body during activities. When attached to human body, the real-time sensing range is commonly under 50%. By attaching the sensor to the finger joint (Fig. 5a), we could monitor the resistance change with the bending finger. The resistance variation presented a step-rise growth with the bending angle of the finger increasing. By attaching the sensor to the wrist joint (Fig. 5b), we could monitor the relative resistance variation associated with the repeated bending of the wrist. These
results show that the movement of the human body can be fully monitored by attaching the sensor unit to corresponding human skin.

4. Conclusions

In summary, we proposed and fabricated a highly sensitive wearable strain sensor based on copper nanowires and elastomers. The conductive materials of the device is composed of two parts, the organic solution, PEDOT:PSS, and nanowires network, which are embedded in PDMS. This composite structure allows the device with high sensitivity, stretchability (120%) and flexibility. The sensor can indicate tensile, compression and pressure stimuli, with the relative change in resistance approximately from 0 to 10. Its low working voltage and friendly material enable the sensor to get body motion and gestures. And some dramatic motion can push the relative change of resistance to 40.

Acknowledgment

The authors gratefully acknowledge the financial support of the project from Guangdong Provincial Department of Science and Technology (2015B090924001).

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