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Flexible Conductive Film Based on Copper Nanowires and Its Sensing Applications

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Abstract
Copper nanowires have attracted widespread attention due to the abundant availability of raw materials in nature and their high conductivity. Compared with traditional materials such as metals and semiconductors used in sensors, copper nanowire materials possess characteristics such as high thermal conductivity, low heat capacity, resistance to bending, low cost, and better ductility. Copper nanowires were synthesized through the hydrothermal method and uniformly dispersed on the surface of acrylate polymer to form a flexible conductive film, which has excellent flexibility, conductivity, and light transmittance. This film was further used for temperature sensing, and its performance was tested. The flexible conductive film was combined with thermochromic materials to prepare an electrophoretic color-changing device. By adjusting the applied voltage and current, the temperature changes, thereby causing the color change of the thermochromic material.

Keywords: Copper nanowires, Temperature sensor, Electrochromic device, Flexible film.

1. Introduction

Metal nanowires possess excellent photoelectric properties, high flexibility, and ease of fabrication, making them highly attractive in the field of flexible electronic displays [1-4]. Among various metal nanowires, such as silver nanowires, gold nanowires, and copper nanowires, when it comes to the fabrication of flexible electrodes, their comprehensive performances are comparable. However, copper has a significantly abundant natural reserve (the reserve of copper is 1000 times that of silver) [5], and copper nanowires have a very obvious advantage in production cost, having significant economic research value [6]. They have become the focus of attention in both academic and industrial circles. By combining copper nanowires with polymer materials to prepare flexible conductive films, these films have excellent electrical conductivity, flexibility, and light transmittance, as well as being lightweight, low-cost, and having simple processes. They are a highly promising transparent electrode material.

The rapid development of flexible electronic technology has placed higher demands on the next-generation temperature sensors, which need to possess features such as high sensitivity, mechanical tolerance, and biocompatibility. Traditional rigid temperature sensors are difficult to adapt to complex curved surface scenarios of wearable devices and electronic skins. In recent years, researchers have significantly improved the temperature sensing performance of copper nanowire films through material composites and structural design, laying a material foundation for the development of highly reliable flexible temperature sensors [7-8].

This paper presents a novel copper nanowire/acrylate polymer composite, which is used for temperature sensing and electrochromic devices, and relevant tests are conducted. This film exhibits excellent temperature sensing and electro-heating performance, providing new ideas for the material selection and structural optimization of flexible temperature sensors and flexible electrochromic devices. It is expected to promote its practical application in intelligent medical monitoring and human-computer interaction systems.

2. Preparation of copper Nanowire Films

2.1 Preparation of the copper nanowire dispersion

The preparation of copper nanowires mainly adopts the solution-based synthesis method, including the reduction method [9-10] and the template-assisted method [11-12]. In this paper, a simple and low-cost reduction method is used for hydrothermal synthesis. 0.272 g of copper chloride, 0.64 g of glucose, and 2.304 g of hexadecylamine were weighed and added successively to 80 ml of deionized water. The mixture was stirred for more than 12 hours. The resulting solution turns dark blue. The above solution is poured into the reaction vessel and then placed in an oven. It was then heated at 120 ℃ for 1080 minutes. After it was fully cooled down, it was taken out. Then, 200 ml of n-hexane and 100 ml of isopropanol were added to a centrifuge tube and centrifuged at 5000 rpm for 10 minutes.

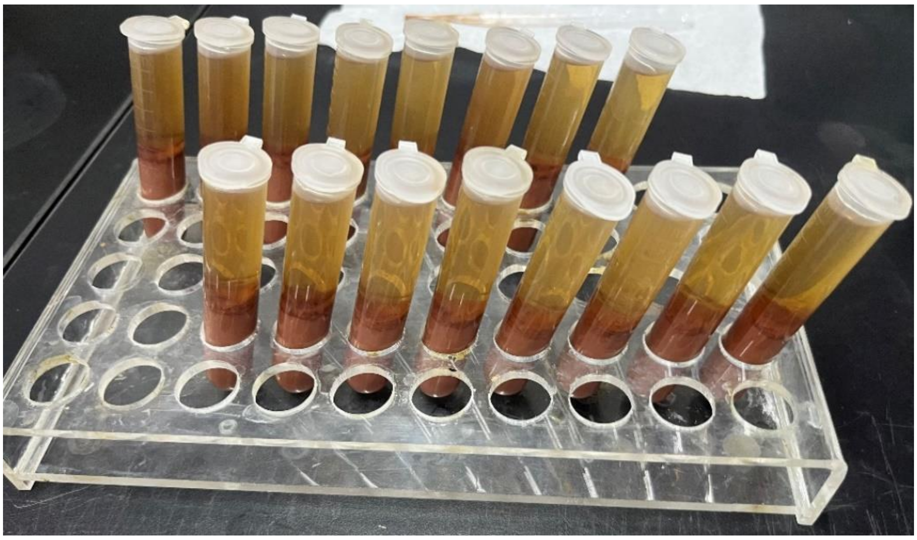


Figure 1 The solution after the first centrifugation

After the centrifugation was completed, the centrifuge tube was taken out and the upper liquid was then removed with a dropper, and then the centrifuge tube was refilled with solvent. After the first centrifugation, precipitate will appear at the bottom of the centrifuge tube. Be sure to break up the sediment at the bottom to facilitate better centrifugation in subsequent steps. The solution after the first centrifugation is shown in Figure 1.

Repeat the above operation until the liquid at the bottom of the centrifuge tube becomes clear. After the centrifugation was completed, add 1 ml of acetic acid to each centrifuge tube to complete the first cleaning. Then, use a dropper to remove the acetic acid and add deionized water for the second cleaning. Finally, use a dropper to take out the deionized water and add anhydrous ethanol for the third cleaning to obtain the copper nanowire dispersion solution.

3. Preparation and Characterization of Conductive Films Based on Copper Nanowires

3.1 Preparation of Conductive Films Based on Copper Nanowires

Copper nanowires can be coated onto the substrate through spin coating, spraying or printing processes to obtain films with the desired thickness, transparency and conductivity. In this paper, the spraying method was used to prepare a uniform copper nanowire layer on a glass substrate. The glass substrate was subjected to multiple ultrasonic cleaning and drying. 500 microliters of copper nanowire dispersion solution was added to an air spray gun and evenly sprayed onto the glass substrate. After spraying, wait for 2 minutes until the solvent on the surface evaporates. Then repeat the spraying process for more than 30 times until the copper nanowires on the glass substrate can conduct electricity. After the copper spraying was completed, first place it in 36% acetic acid to reduce the copper oxide on the surface, and then dry it in an oven for 20 minutes.

The acrylic monomer and initiator mixture was coated on the surface of the above copper nanowire layer, and irradiated under a UV lamp for 60 seconds. The monomer polymerized into an acrylic polymer film. After the acrylic polymer cured, slowly cut the film with a knife, and test the sheet resistance of the film using a square resistance tester. The sheet resistance of the film was approximately 5 Ω/sq, indicating that the copper nanowire film exhibits good electrical conductivity.

3.2 Characterization of Copper Nanowire Films

The surface of the conductive film based on copper nanowires was observed using an optical microscope. The result is shown in Figure 2. It can be seen that the copper nanowires are uniformly and smoothly covering the surface of the polymer layer, and the film has good light transmittance. Moreover, the presence of impurities is minimal, resulting in negligible impact on electrical conductivity.

Figure 2 Copper nanowire film under an optical microscope

4. Application of Temperature Sensors

Fix two electrodes onto the copper nanowire film to construct a simple temperature sensor, then laminate a layer of adhesive tape tightly over the surface to secure the electrical contacts and prevent oxidation of the nanowires. The two wires serve as the two electrodes of the copper nanowire film. Connect the two electrodes with an ammeter, set the constant voltage to 0.5 V, place the copper nanowire film on a heating platform for heating treatment, and measure the changes in the device resistance at different temperatures. The results are shown in Table 1 and Figure 3.

Table 1 Resistance Variation with Temperature Change

Temperature/℃	30	35	40	45	50	55
Resistance/Ω	5.4	5.9	6.1	6.3	7.9	9.7
Temperatur/℃	60	65	70	75	80	85
Resistance /Ω	12.1	14.3	14.6	15.6	17.9	19.4

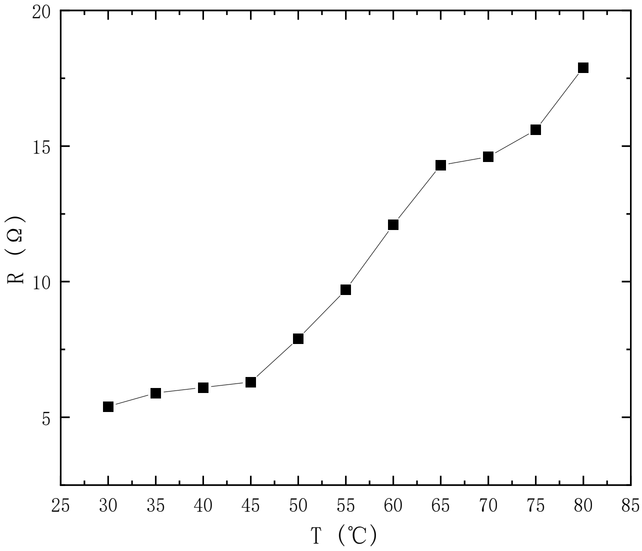


Figure 3 Curve of resistance variation with temperature

As shown in Table 1 and Figure 3, when the temperature increased from 30 ℃ to 85 ℃, the resistance of the conductive film based on copper nanowires rose from 5.4 Ω to 19.4 Ω, showing a basically good linear change. The resistance variation curve with temperature was divided into several stages. In the range of 30 ℃ to 45 ℃, the slope of the curve was 0.06 Ω/℃, that is, for every 1 ℃ increase in temperature, the resistance increased by 0.06 Ω; in the temperature range of 45 ℃ to 65 ℃, the heating rate was 0.4 Ω/℃, and the rate of resistance change with temperature increased, and the linearity of the curve was the most obvious during this period; in the temperature range of 70 ℃ to 85 ℃, the heating rate was 0.24 Ω/℃, and the rate of resistance change with temperature decreased. At this time, due to the sensitivity of the contact resistance between the nanowires to temperature, the resistance temperature coefficient of the conductive film based on copper nanowires was much higher than that of bulk copper materials, demonstrating excellent temperature response characteristics. The copper nanowire-based conductive film demonstrates significant temperature-dependent electrical behavior. Owing to the high thermal sensitivity of inter-nanowire contact resistance, this film exhibits a significantly higher temperature coefficient of resistance (TCR) compared to bulk copper, highlighting its excellent thermoresponsive characteristics.

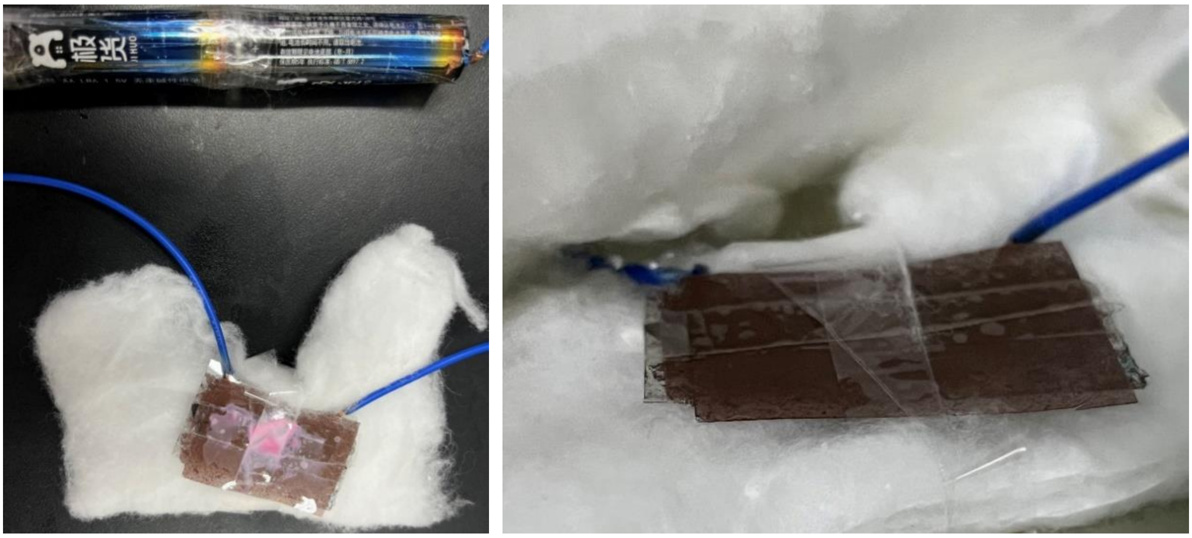
5 Research on Fabrication and Performance of Electrochromic Devices

5.1 Device Fabrication

Electrochromic devices are devices that can change their color or optical properties by the action of an external electric field or current. We combined copper nanowire conductive films with thermochromic materials to assemble flexible electrochromic devices. We chose a red thermochromic material, which changes from red to white when the temperature is above 28°C, and reverts to red from white when the temperature is below 28°C, with a very distinct color contrast. The prepared copper nanowire film was subjected to resistance measurement and conductivity testing. Regions with appropriate resistance and good conductivity were identified and cut out. These sections were then combined with thermochromic materials, and top and bottom electrodes were added respectively. The device was powered using dry batteries connected in series to form a power supply. Wires were used to connect the positive and negative terminals of the battery to opposite ends of the conductive CuNW film. The connections were secured to ensure the battery could provide a stable and continuous current to the CuNW film. By adjusting the strength and direction of the electric field or current, the color or optical state of the device could be effectively modulated.

5.2 Device performance characterization

When the prepared flexible electrochromic device is applied with an external voltage, the copper nanowire conductive film will generate heat. It can be wrapped with cotton to prevent the heat from dissipating easily, thereby achieving the effect of insulation, as shown in Figure 4. Initially, the chromatic part of the flexible electrochromic device appears red (Figure 4a); after the device is powered on for a period of time, when the temperature exceeds 28°C, the thermochromic material undergoes color change and turns white (Figure 4b); when the voltage is removed, when the device temperature cools down to below 28°C, the device returns to red. The copper nanowire-based conductive film effectively fulfilled its intended electrothermal function in the flexible electrochromic device, enabling excellent reversible electrochromic performance.



a b

Figure 4 Flexible color-changing device: (a) before and（b）after applying voltage.

6. Summary

In this paper, copper nanowires were prepared and sprayed onto an acrylic polymer film to obtain a flexible conductive film. This film exhibited excellent temperature sensing performance. At the same time, a flexible electrochromic device was fabricated by combining the copper nanowire conductive film with a thermochromic material. The temperature of the copper nanowires would rise, thereby causing the device to change color. This indicates that the prepared copper nanowires have a good current-thermal effect. This work not only validates the high temperature sensitivity and efficient electrothermal conversion capability of our designed copper nanowire-based flexible conductive films, but also provides new insights for the development of novel intelligent flexible devices.

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