Preparation of copper nanowires conductive films by using cuprous oxide nanowire as template

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Abstract. Polypyrrole-coated cuprous oxide nanowires with a large aspect ratio were prepared via the hydrothermal reduction of copper acetate with pyrrole. Initially, the nanowires were transferred onto a glass substrate by suction filtration and embossing. A copper nanowire conductive film can then be obtained after high temperature annealing reduction and transferred onto a flexible substrate via hot press transfer. The product was analyzed via X-ray powder diffractometry, scanning electron microscopy, and transmission electron microscopy. The visible light transmittance and the surface resistance of the sample were measured by employing an ultraviolet-visible spectrophotometer and a four-probe surface resistance meter, respectively. The effects of the annealing temperature, of the time, the dispersion of the square resistance, and the transmittance of the conductive film were investigated. The results show that the conductive film exhibits a high visible light transmittance (82\%) and a low sheet resistance (62 Ω/sq) upon annealing at 700 °C for 300 seconds.

1. Introduction
Transparent conductive films are widely used in a wide variety of fields, such as transparent electrodes, flat panel displays, touch screens, and thin film photovoltaic cells [1-5]. The most commonly used transparent conductive films consist of indium tin oxide (ITO). This material exhibits a high electrical conductivity (sheet resistance 10 Ω/sq) and an excellent light transmittance (visible light transmittance 90\%). Due to these characteristics, it is commonly used in the manufacturing of mobile phone capacitive touchscreens. However, the texture of ITO is highly brittle and this material cannot easily be bent, limiting its use in the production of flexible displays. In addition, the preparation process of ITO is complex and its production efficiency are extremely low [6-9]. Furthermore, indium reserves are rare, and this material is expensive. Although gold and silver nanowires [10-13] exhibit similar properties to ITO, they are not equally expensive. When compared to silver nanowires, copper nanowires (Cu NWs) have a similar structure, electrical conductivity, thermal conductivity, and ductility. Moreover, copper is inexpensive and abundant in nature. However, due to the low aspect ratio and poor dispersibility of the currently synthesized copper nanowires (Cu NWs), the conductive films prepared via direct hydrothermal synthesis must undergo an annealing treatment. However, their performance remains not
ideal [14-17]. Therefore, in this paper, a liquid phase method, which employs pyrrole as the reducing agent and a structure-directing agent to hydrothermally reduce copper acetate to prepare polypyrrole-coated cuprous oxide (Cu$_2$O-PPy) nanowires with large aspect ratio, uniform diameter, and good dispersibility is investigated [18]. After this process, the cuprous oxide nanowires were transferred onto a glass substrate via suction filtration and imprinting. High-temperature annealing and reduction were performed to obtain the copper nanowire conductive films. The samples were then characterized.

2. Experimental section

2.1. Materials
Cupric acetate monohydrate was purchased from Suzhou Greet Pharmaceutical Technology Co., Ltd. Polyvinylpyrrolidone (PVP, Mw = 24000) was purchased from Shanghai Aladdin Reagent Co., Ltd. Pyrrole and glacial acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. The chemical reagents were of analytical grade and were used without further purification.

2.2. Synthesis of the Cu$_2$O-PPy nanowires
A quantity of 0.2 g of cupric acetate monohydrate was dissolved into 40 mL of deionized water and an aqueous pyrrole solution (0.10 mol/L, 10 mL) was then added into it. The compound was transferred into a Teflon-lined stainless-steel autoclave, which was kept at a temperature of 120 °C for 16 h. The solution was left cool down to room temperature, and the precipitates were easily isolated by removing the supernatant black layer. The products were washed with deionized water and ethanol several times. A yellow-green powder was obtained and dried at 40 °C for 6 h in a vacuum oven.

2.3. Preparation of Cu NWs transparent conductive films
The Cu$_2$O-PPy nanowires were inserted into an ethanol solution to achieve a dispersion of 0.02 mg/ml. PVP was added into the sample with a mass fraction of 2%. Specimens of 4 ml, 5 ml, and 6 ml of the Cu$_2$O-PPy nanowires dispersion were vacuum filtered by using a 0.42 µm microporous filter paper. Then, the Cu$_2$O-PPy nanowires film, which had deposited onto the filter, was imprinted onto a glass substrate to obtain three Cu$_2$O-PPy nanowire films (F-04, F-05, and F-06). The glass substrate was then placed into a rapid annealing furnace, which was evacuated and heated up to 700 °C for 300 s. Finally, the samples were cooled down to room temperature and analyzed.

2.4. Characterization
The morphology of the samples was characterized via scanning electron microscopy (SEM, Sigma 300, Carl Zeiss, Oberkochen, Germany) at 3 kV. The crystal structure of the product was analyzed by using a Cu-Kα radiation diffractometer (XRD, Bruker, Germany) of λ= 1.5418 Å. The visible light transmission of the samples was measured by employing a Specord / 210 plus spectrometer (Analytikjena, Germany) with a test range of 380–780 nm. The surface resistance of the specimens was tested with an RTS-5 dual-electric four-probe tester from Guangzhou Four-Probe Technology Co., Ltd.

3. Results and discussion
In the present study, pyrrole was used as the reducing agent to foster the anisotropic growth of Cu (i) into a nanowire structure [18-20]. Figure 1a illustrates the SEM images of the typical morphology of the Cu$_2$O-PPy nanowires: the nanowires are elongated and their surface is smooth. The length of the Cu$_2$O-PPy nanowires ranges from tens of micrometers to hundreds of micrometers. Moreover, they exhibit a diameter of 150 nm. Figure 1b shows the SEM image of the Cu nanowires, which were produced upon annealing the material at 700 °C. During this process the polypyrrole (PPy) is carbonized due to the high temperature and the cuprous oxide nanowires are reduced into copper nanowires. The Cu nanowires still exhibit a relatively uniform diameter in the 90–100 nm range, but a shorter length (several tens of micrometers). This phenomenon may be induced by the breakage of the copper nanowires at high temperatures.
Figure 1. (a) SEM image of the Cu$_2$O-PPy nanowires; (b) SEM image of the Cu nanowires.

Figure 2 shows the XRD patterns of the pure Cu$_2$O-PPy nanowires and the copper nanowire crystal structures. The diffraction angles of the peaks of Cu$_2$O (JCPDS 05-0667) are 29.5°, 36.4°, 42.2°, 61.4°, 73.5°, and 77.3°, whereas the diffraction angles of Cu (JCPDS 04-0836) are 43.3°, 50.4°, and 74.1°. This shows that pure phase Cu$_2$O-PPy and the Cu nanowires were successfully synthesized. The 20°-broad peak, which is visible in the spectrum, is the signature of the SiO$_2$ substrate.

Figure 2. X-ray diffraction pattern of the (a) Cu$_2$O-PPy nanowires and (b) Cu nanowires.

The results of the conductivity test in the 380–800 nm range of the films are presented in Figure 3. The average visible light transmittance of the F-04, F-05, and F-06 films are 82%, 80.9%, and 79.4%, respectively. The sheet resistance of the films measures 62 Ω/sq, 45.3 Ω/sq, and 14.9 Ω/sq, respectively. This implies that upon the increase in the number of the nanowires, both the sheet resistance and the visible light transmittance decrease, despite a rather high transmittance of 77% can be maintained.

Figure 3. Transmittance of the Cu nanowires films at different wavelengths.
The results reported in Table 1 show that the transparent conductive films prepared in this experiment have a relatively poor electrical conductivity, despite their transmittance has been greatly improved. The authors aim to further increase the transmittance and the conductivity of the conductive film in their next works.

Table 1. Properties of the four transparent conducting films obtained in this work.

| Films       | Transmittance | Square Resistance |
|-------------|---------------|-------------------|
| ITO [6-9]   | 90%           | 10 Ω/sq           |
| Ag NWs [10-13] | 80%         | 20 Ω/sq           |
| Cu NWs [14-17] | 80%         | 80 Ω/sq           |
| The Article | 82%           | 62 Ω/sq           |

4. Conclusion
Cu$_2$O-PPy nanowires with a length ranging between several tens of micrometers to several hundred of micrometers and a diameter of about 150 µm were prepared by reducing copper acetate with pyrrole. The samples exhibit a high aspect ratio and a satisfactory dispersibility. A copper nanowire conductive film was also prepared via vacuum suction filtration and this procedure was followed by high temperature annealing. For a Cu$_2$O-PPy nanowires concentration of 0.02 mg/ml in a 0.4 ml solution, the transmittance of the visible light (380–800 nm) of the conductive film measures 82% and its sheet resistance is 62 Ω/sq. These results suggest that this conductive film has excellent optical and electrical properties.

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