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Facile Fabrication of Transparent Conductor of Cu Nanowire-PEDOT:PSS

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ABSTRACT

We have successfully demonstrated the synthesis of Cu nanowires (CuNWs) by aqueous solution at low temperatures. We have also studied the fabrication of a transparent conductor using Mayer rod coating. In the present study, the problem with the fabrication of CuNW transparent conductor is low oxidation resistance. Based on this purpose, we developed a facile method for coating poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) on CuNW transparent conductor. The PEDOT:PSS can protect CuNW transparent conductors from oxidation. The morphology and crystal structure of the CuNWs transparent conductor were investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD). The SEM images show an increase in connectivity of CuNWs after PEDOT:PSS coating and X-ray diffraction shows peaks at 42.52°, 49.68°, 60.94° and 73.43°. The performance of the transparent conductor was investigated by IV-meter analysis and spectroscopy (UV-Vis). The results indicated that the coated transparent conductor with PEDOT:PSS/CuNWs has a much better performance compared to the uncoated one. The CuNW-coated transparent conductor has a resistance of 220 ohm sq^{-1}, while the uncoated one is 1200 ohm sq^{-1}. The newly designed transparent conductor with PEDOT: PSS/CuNWs could serve as new materials for a wide range of high-performance transparent conductors for future practice.

Keywords: *Oxidation, Electrical properties, Cu nanowires*

1. INTRODUCTION

The transparent conductor is an essential component in fabricating touchscreens, transparent electrodes, organic solar cells, and organic light-emitting diodes (OLEDs) [1-8]. Currently, Indium Tin Oxide (ITO) is most widely used as a transparent conductor due to its low resistance, about 150 Ωsq^{-1}, and high transmittance, about 90%. However, the abundance of indium on the earth is limited therefore producing high materials cost. This limitation drives the need to search for other alternative materials to replace ITO. Among the materials, silver and copper nanowires were the prospective candidates to replace ITO as essential materials in the transparent conductor. Silver nanowires have demonstrated a superior level of performance compared to ITO [9-14]. However, silver has similar disadvantages as ITO in its abundance on earth. In short, transparent conductors made of ITO and silver have a high cost. Another material that may perform a similar function in transparent conductors as ITO and silver is copper. Although copper is only 6% less conductive than silver, it is 1000 times more abundant, but it is 100 times cheaper than silver or indium.

Several research groups have demonstrated the scalable synthesis of CuNWs with different methods [15]. The aims of the methods in synthesizing CuNWs to be used in a transparent conductor are having a high aspect length to diameter ratio using a short time and simple process. Unfortunately, CuNWs have a drawback due to their instability in the environment, especially their reactivity to oxygen [16-18]. Oxidation can decrease the conductivity of CuNWs. Some efforts have been made to overcome this problem such as using a conductive polymer, a coating, as well as using another metal coating such as nickel and silver [19-24]. However, limited studies were done on fabricating transparent conductor of CuNWs and their oxygen protection. This information would be beneficial for researchers in developing various applications based on CuNWs. In this article, we study the fabrication of a transparent conductor based on CuNWs which can still preserve its conductance property using poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS) as a coating agent. By comparing the uncoated and coated transparent conductor based on CuNWs, we found that the coated transparent conductor was superior compared to the uncoated one.

2. EXPERIMENTAL SECTION

2.1. Materials

In the experiment, we used (Cu $(NO_3)_2.3H_2O$) copper (II) nitrate trihydrate (99%, Merck) as precursor material, (NaOH, 99% Merck) sodium hydroxide as maintaining coprecipitation material, (EDA, 99% Merck) ethylenediamine as capping agent, (N_2H_4, Merck) hydrazine as reduction and (PEDOT:PSS, Heraeus PH 1000) poly (3,4-

ethylenedioxythiophene) polystyrene sulfonate as protective oxidation.

2.2. Procedure

2.2.1. Synthesis and Characterization of CuNWs

Synthesis of CuNWs was done following the development by Chang et al., [25] with a bit of modification. In short, to synthesize the Cu nanowire, we mixed (100 mL, 15 M) of NaOH with (20 mL, 0.025 M) of Cu $(NO_3)_2.3H_2O$ added with 150 mL aqua dest?? in the reaction flask. We stirred and maintained the temperature at 60 ºC. About 2 minutes later, we added 0.5 mL EDA (99%) and 0.15 mL of hydrazine (35 wt %). During the process, the solution mixture was stirred at 60 rpm for 60 minutes. The color of the solution will change from light blue to reddish brown. These color changes indicate that CuNWs have been formed. Finally, CuNWs floated on the surface of the solution. The result of CuNWs was filtered and centrifuged in the environment of alcohol at 10000 rpm and repeated five times. Finally, the result of CuNWs was stored in alcohol in a sealed bottle for the next process.

2.2.2. CuNWs for a Transparent Conductor

CuNWs in alcohol were several times coated on the cleaned glass substrate using a roll-to-roll Meyer rod. We checked the resistance during the process to indicate the success of the coating. Finally, PEDOT:PSS solution was coated on top of the CuNW film to ensure the protection of the film from direct environmental exposure. We tested the conductance and transparency of the film using an current-voltage (IV) meter and ultraviolet-visible (UV-vis) spectrometer, respectively.

3. RESULTS AND DISCUSSION

Figure 1a shows the X-ray diffraction (XRD) pattern of the CuNWs. The XRD pattern shows diffraction peaks at the 2θ angles of 42.52°, 49.68°, 60.94° and 73.43°. The values of the diffraction angles were following the CuNWs crystal Miller index of (111), (200), (220), and (311) as the crystalline planes of the Face Center Cubic (FCC) Cu (JCPDS 04-0836) [26-30]. The appearing (110) plane may occur due to the reactions of CuNWs with oxygen in ambient air. CuNWs are estimated to be oxidized following to these reactions,

$$4Cu + O_2 \rightarrow 2Cu_2O, \quad (1)$$
$$2Cu_2O + O_2 \rightarrow 4CuO. \quad (2)$$

This happened because the CuNWs were uncoated. Figure 1b, shows the scanning electron microscope (SEM) images of pure CuNWs with an average length of 25±3 µm and a diameter of 109±4 nm. Figure 2a shows the morphology of the transparent conductor of CuNWs, and Fig. 2b shows the CuNWs without PEDOT:PSS coating. The diameter of CuNWs with PEDOT:PSS coating has increased. This difference will produce different optical transparency, although the film's resistance may be similar. This color difference of the transparent conductor is due to the effect of the coating. Without PEDOT: PSS coating the color of the transparent conductor is reddish due to the color of the nanowire.

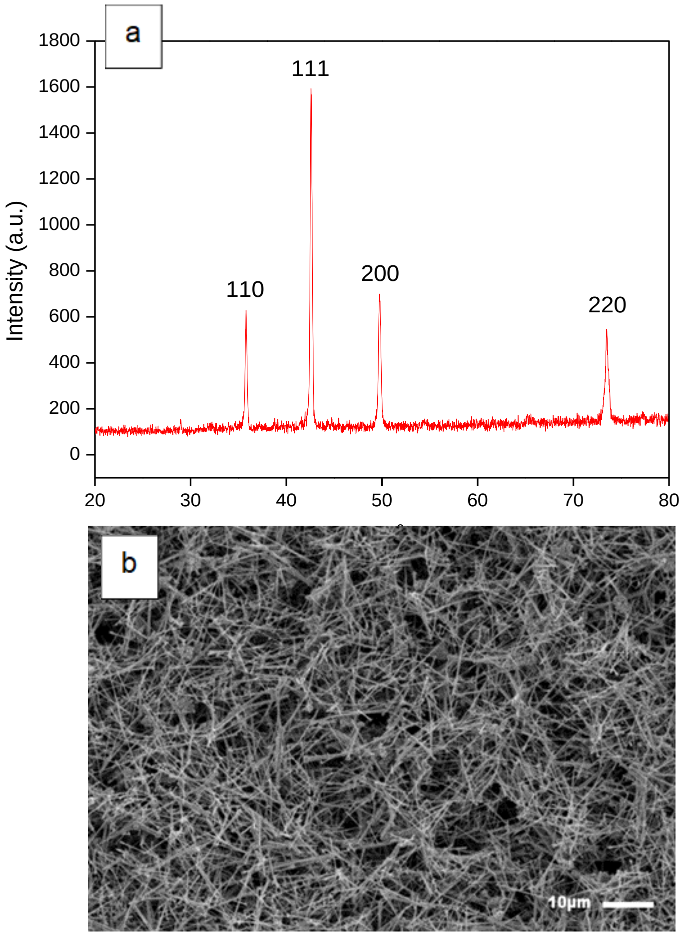

Figure 1. a. XRD pattern of CuNWs. b. SEM image of CuNWs.

While the one coated with PEDOT:PSS, the color is greenish due to the color of the PEDOT:PSS on the CuNWs substrate. The PEDOT:PSS coating can also improve the connectivity among CuNWs for high electron mobility. The high electron mobility of the transparent conductor results in a high conductivity in charge electron transport [19].

Transparent conductors of CuNWs were prepared by the Mayer rod method (Figure 3). Using this method, we deposited a solution of CuNWs on the glass then we controlled using a Mayer rod. The electrical properties of transparent conductors were evaluated using an IV-meter. The optical transmittance of CuNWs was identified using a UV-Vis spectrophotometer. The transmittance graph of CuNWs transparent conductor with variation layer is shown in Figure 4.

Figure 4a shows the layer of CuNW transparent conductor decreasing to the number of layers. The transmittance of the CuNWs film is 75.73% for a single layer, 59.53% for double the layer, and 50.79% for triple the layer. A similar pattern occurred on the CuNWs-PEDOT:PSS with transmittance of CuNWs (1x)-PEDOT:PSS is 70.8%, transmittance of CuNWs (2x)-PEDOT:PSS is 55.67%, and transmittance of CuNWs

(3x)-PEDOT:PSS is 45.17% as shown in Figure 4b. The addition number of layers on transparent conductor decreased the transmittance by approximately 5% when it used the PEDOT:PSS. The decrease of transmittance is presented in Figure 5a.

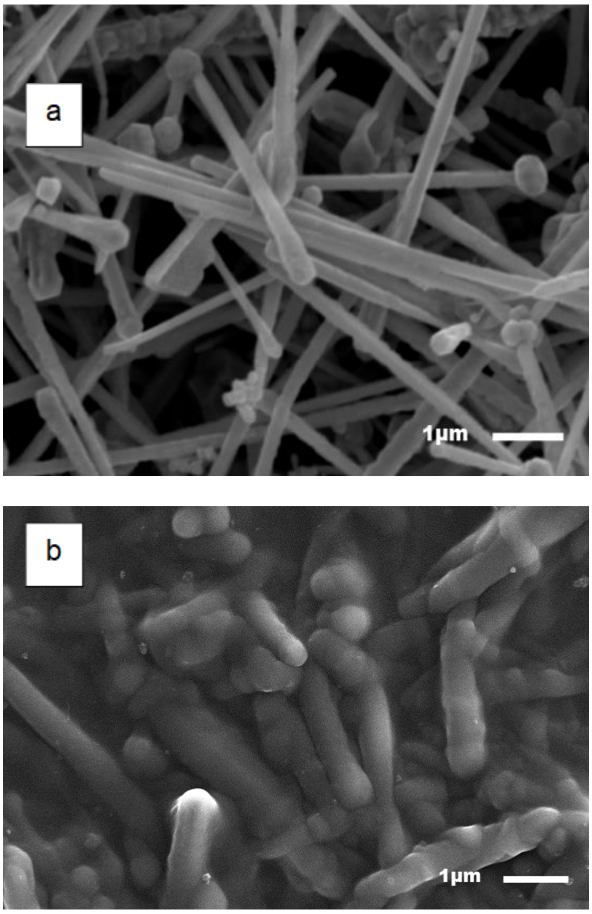

Figure 2. a. SEM image of CuNWs without PEDOT:PSS, b. SEM image of CuNWs with PEDOT:PSS.

The greater the number of layers, the smaller the transmittance. However, the additional PEDOT:PSS on the CuNWs transparent conductor decreases the transmittance [31].

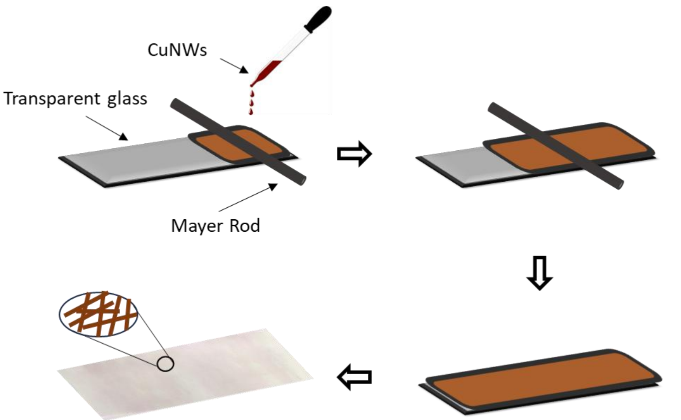

Figure 3. Process of transparent conductor fabrication using the Mayer rod method.

The decrement of transmittance has not influenced its electrical resistance. The CuNWs transparent conductor without PEDOT:PSS has higher transmittance, but the resistance increased with the usage times.

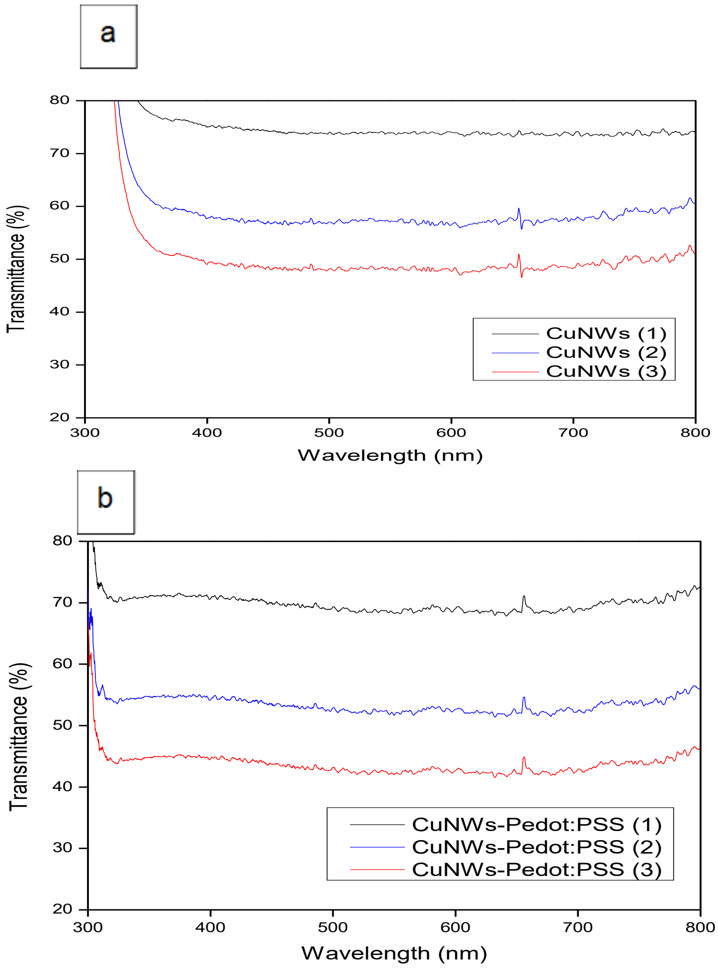

Figure 4. a. Transmittance of CuNWs without PEDOT:PSS. b. Transmittance of CuNWs with PEDOT:PSS.

The number of layers of CuNW transparent conductor can also influence its transmittance and sheet resistance of the transparent conductor. The additional layer makes its transmittance and sheet resistance decrease. The sheet resistance of the CuNWs film is 1035.3 ohm/sq for one layer, it became 592.7 ohm/sq for two layers, and it is 62.3 ohm/sq for three layers. In comparison, the sheet resistance of CuNWs with PEDOT-PSS is 975.9 ohm/sq, 554.6 ohm/sq, and 57.9 ohm/sq, for one, two and three layers, respectively.

The number of layers of transparent conductors can increase the electrical conductivity, but it decreases its transmittance. Figure 5c shows that changing the transmittance can affect the resistance of transparent conductor CuNWs. The decrease in the transmittance affects the decrease in the sheet resistance of transparent conductor of CuNWs. The decrease in the sheet resistance was accompanied by an increase in the conductivity of the transparent conductor of CuNWs.

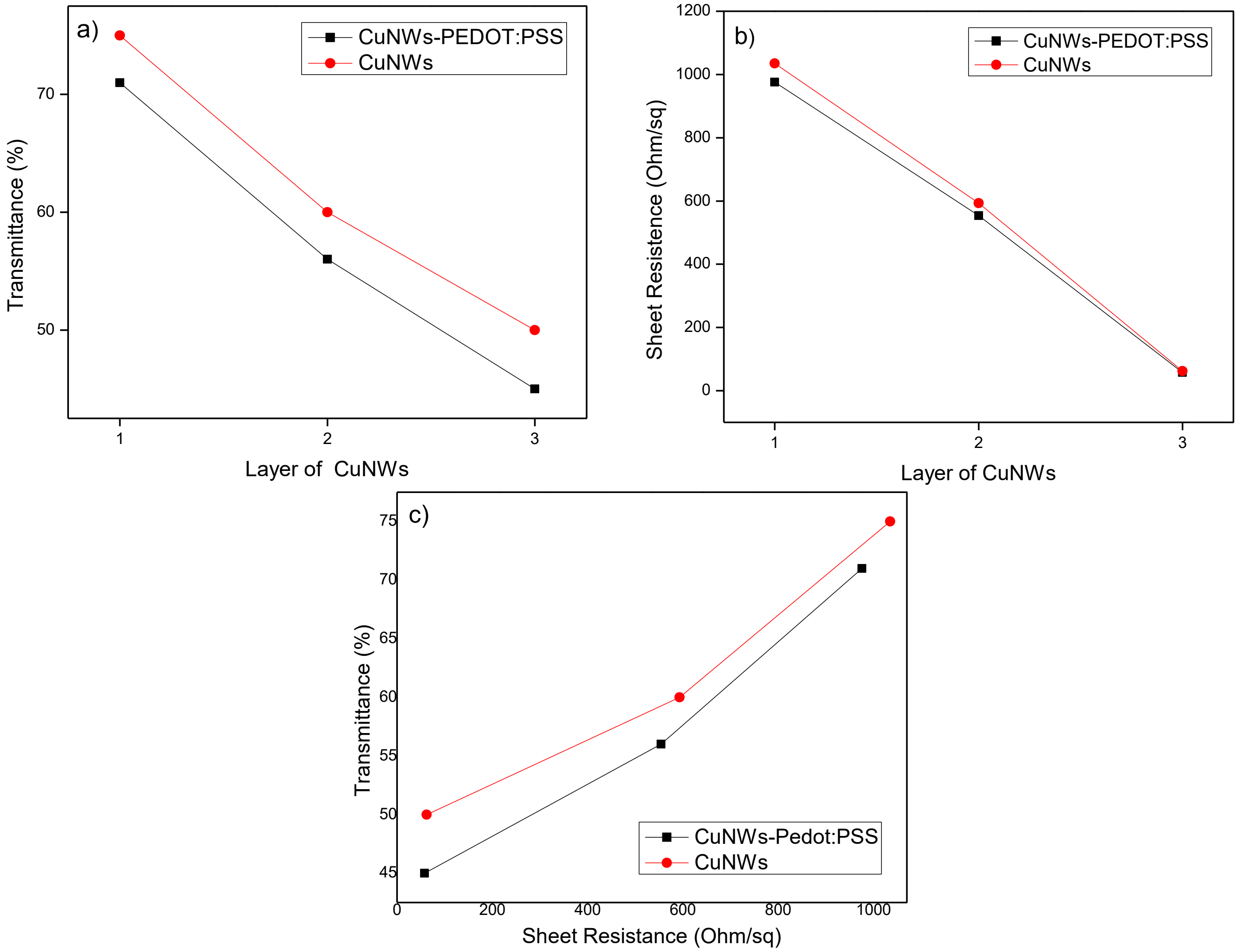

Figure 5. a. Curve of transmittance versus the CuNWs layer. b. The curve of sheet resistance versus the CuNWs layer. c. The curve of the transmittance versus the sheet resistance.

The characteristic of CuNW film was sensitive to oxygen and environmental effects [32]. Figure 6 shows the resistance of both transparent conductors. The sheet resistance of CuNWs is determined every half hour over a period of 7 hours. . The first curve was a transparent conductor of CuNWs. The sheet resistance increases with time due to the environmental oxidation process. From the graph it shows an increase in the CuNWs curve without PEDOT: PSS coating. The second curve was the film of CuNWs-PEDOT:PSS, which was more stable to environmental oxidation. The data indicates that the challenges in using CUNWs are oxidation and instability.

The data also indicates the main problem of CuNW transparent conductors is when facing the ambient environment. The effect of PEDOT:PSS coated on CuNWs-film becomes flexible and has better conductivity without diminishing its optical transmittance.

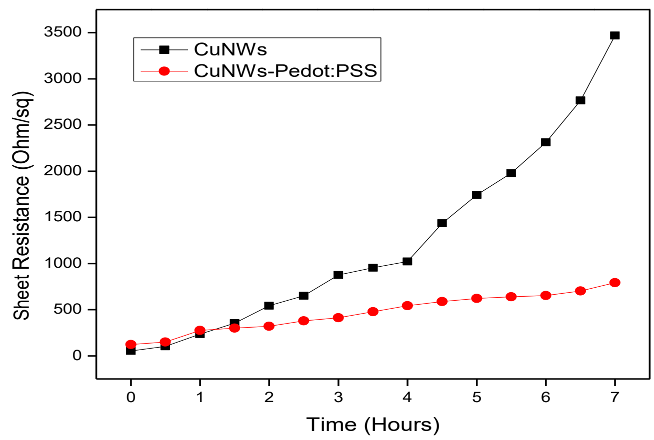

Figure 6. The sheet resistance of transparent conductors

This shows that the coating of PEDOT:PSS qualifies the CuNWs transparent conductor as an alternative conductive film for ITO in future applications.

CONCLUSION

The CuNWs transparent conductors have been successfully fabricated by the Meyer rod coating method. The additional PEDOT-PSS layers to a CuNW transparent conductor can decrease its transmittance and sheet resistance. The coating of PEDOT:PSS on CuNW transparent conductor can effectively protect CuNW transparent conductor from oxidation without decreasing its electrical conductivity. The transparent conductor of PEDOT:PSS/CuNWs fabricated in this study is a very promising alternative to transparent conductors for future applications.

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