Short Communication:
Improving the Performance of Transparent Conducting Electrodes Based on Cu Nanowires

Dedi Mardiansyah1*, Sri Rahayu Alfitri Usna1, Suratun Nafisah2, Harsojo Harsojo3, and Rindi Genesa Hatika4

1Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Andalas, Limau Manis, Padang 25163, Indonesia
2Department of Electrical Engineering, Institut Teknologi Sumatera, Jl. Terusan Ryacudu, Jati Agung, Lampung 35365, Indonesia
3Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara BLS 21, Yogyakarta 55281, Indonesia
4Department of Physics Education, Universitas Pasir Pengaraian, Jl. Tuanku Tambusai, Riau 28558, Indonesia

* Corresponding author: email: dedimardiansyah@sci.unand.ac.id
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Abstract: The fabrication of transparent conducting electrodes (TCEs) is dominated by indium tin oxide (ITO). Some efforts are being made to find alternative materials as a substitute for ITO. Cu nanowire (CuNWs) is an equivalent candidate as a replacement for ITO but has a weakness that is easily oxidized. In this contribution, we report an increase in the performance of CuNWs, which can reduce the effect of oxidation. In this study, we provide a coating of CuNWs using PVP, PVA, and silver nanoparticles (AgNPs). The morphology, formation structure, and conductivity of CuNWs have been investigated by scanning electron microscope (SEM), X-ray diffraction (XRD), and IV meter. The average length and diameter of the CuNWs were 5.5 μm and 120 nm, respectively. The transparent conducting has a stable conductivity after coating with PVP, PVA and AgNPs. The application of transparent conducting electrodes are sensors, electronic devices, solar cells, and organic light-emitting diodes (OLEDs).

Keywords: Cu nanowires; oxidation; coating; transparent conducting electrodes

INTRODUCTION

The efforts to produce reliable transparent conducting electrodes (TCEs) in replacing indium tin oxide (ITO)-glass have grown pronouncedly fast [1-7]. TCEs based on silver nanowires (AgNWs) have been proposed as the best candidate to replace ITO due to their simple and fast fabrication [8-12]. Unfortunately, AgNWs are not abundant in nature. So, researchers have still searched for other options. Copper (Cu) is one of the best candidates to replace silver because CuNWs have conductivity and transmittance equivalent to silver. However, CuNWs have an oxidation problem as the main weakness. CuNWs are metallic and can change to Cu2O or CuO which are semiconductive [13-18].

Some methods have been investigated to overcome these intrinsic problems, either in synthesizing CuNWs using coating materials [19-24] or fabricating the TCEs [25-27]. Tong et al. [28], suggest enhancing the stability of CuNWs through the application of an in situ carbon protective layer coating. Lin et al. [29], devised a straightforward method for producing stable TCEs by employing the dip-coating technique with reduced graphene oxide (rGO). However, more coating methods and materials are still required, especially in comparing some materials as coating in fabricating the TCEs. In this study, we provide the study of fabricating the TCEs based on CuNWs coating by PVP, PVA, and silver nanoparticles (AgNPs).
**EXPERIMENTAL SECTION**

**Materials**

The materials utilized in the study include copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99% Merck, Germany), ethylenediamine (EDA, Merck, Germany) sodium hydroxide (NaOH, 99% Merck, Germany), hydrazine (N₂H₄, Merck, Germany) polyvinyl pyrrolidone (PVP, Sigma-Aldrich), polyvinyl alcohol (PVA, Sigma-Aldrich) and silver nitrate (AgNO₃, Sigma-Aldrich).

**Instrumentation**

Scanning electron microscopy (SEM, JEOL JSM-6510) was used to identify the size and morphology of CuNWs. The crystalline structure of CuNWs was analyzed using an X-ray diffraction (XRD, Shimadzu XRD-6000). UV-vis spectroscopy (Shimadzu, UV-11700) was analyzed for the optical properties. The electrical properties of the TECs were measured using current voltage (IV) meters (SMU-2400).

**Procedure**

**Synthesis CuNWs**

CuNWs were produced using an aqueous solution approach (Fig. 1). In a 150 mL reaction flask, 20 mL of 0.1 M Cu(NO₃)₂ was combined with 100 mL of 15 M NaOH. The resulting solution exhibited a deep blue color, indicating the formation of [Cu(OH)₄]²⁻. To this solution, 0.5 mL of EDA and 0.25 mL of N₂H₄ (35 wt.%) were added. Within 2 min of adding EDA, [Cu(EDA)₂]²⁻ was formed. The significant presence of NaOH 15 M promoted the creation of [Cu(OH)₄]²⁻.

Upon adding N₂H₄, the color transitioned to a light blue hue. CuNWs began to form 15 min after the introduction of N₂H₄. After 60 min, the CuNWs were observed to float on the surface of the solution. During the procedure, the blends were agitated at a speed of 60 rpm for a duration of 60 min until uniformity was attained.

**Synthesis CuNWs coating PVP**

A mixture was prepared in a 150 mL reaction flask by combining 20.0 mL of Cu(NO₃)₂ 0.1 M (Fig. 2(a)) with 100 mL of NaOH 15 M (Fig. 2(b)). The difference in this synthesis is PVP as a coating agent. PVP was added after adding EDA to the solution (Fig. 2(c)). The addition of PVP aims to prevent oxidation on the CuNWs. Then, N₂H₄ was added in a soluble form to the solution, after which it was stirred for 60 min. Finally, CuNWs will form above the solution.

**Synthesis CuNWs coating PVA**

The synthesis process of CuNWs coating PVA is almost close to coating PVP. In a 150 mL reaction flask, a solution of Cu(NO₃)₂ 0.1 M (20.0 mL) (Fig. 3(a)) was blended with NaOH 15 M (100.0 mL) (Fig. 3(b)). The difference in this synthesis is PVA as a coating agent. PVA was added after adding EDA to the solution (Fig. 3(c)). The addition of PVA aims to prevent oxidation on the CuNWs. The N₂H₄ was added to the solution as a soluble solution and then stirred for 60 min. Finally, CuNWs will form above the solution.

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**Fig 1.** The synthesis of CuNWs: (a) Cu(NO₃)₂·3H₂O dissolved in water, (b) Cu(NO₃)₂·3H₂O dissolved in water + NaOH, (c) Cu(NO₃)₂·3H₂O dissolved in water + NaOH + EDA + N₂H₄, (d) CuNWs in water

**Fig 2.** The synthesis of CuNWs: (a) Cu(NO₃)₂·3H₂O dissolved in water, (b) Cu(NO₃)₂·3H₂O dissolved in water + NaOH, (c) Cu(NO₃)₂·3H₂O dissolved in water + NaOH + EDA + PVP + N₂H₄, (d) CuNWs in water

**Fig 3.** The synthesis of CuNWs: (a) Cu(NO₃)₂·3H₂O dissolved in water, (b) Cu(NO₃)₂·3H₂O dissolved in water + NaOH, (c) Cu(NO₃)₂·3H₂O dissolved in water + NaOH + EDA + PVA + N₂H₄, (d) CuNWs in water
Synthesis CuNWs coating AgNPs

CuNWs were produced through an aqueous solution method employing Cu(NO₃)₂·3H₂O as the primary material (Fig. 4(a)), EDA as the stabilizing agent, and N₂H₄ as the reducing agent (Fig. 4(b)). Initially, Cu(NO₃)₂ 0.1 M (20.0 mL) was combined with NaOH 15 M (100.0 mL) in a 150 mL reaction flask, resulting in a deep blue solution indicative of the formation of [Cu(OH)₄]²⁻. Subsequently, 0.50 mL of EDA and 0.25 mL of h N₂H₄ (35 wt.%) were added to the solution after 2 min, leading to the formation of [Cu(EDA)₂]²⁻ (Fig. 4(c)). The high NaOH concentration (15 M) facilitated the formation of [Cu(EDA)₂]²⁻.

Upon the addition of N₂H₄, the solution color shifted to a clear blue, with CuNWs initiating formation 15 min thereafter, ultimately floating on the solution’s surface. Throughout the process, stirring was maintained at 60 rpm for 60 min. The CuNWs were subsequently subjected to centrifugation at a speed of 10,000 rpm for a duration of 10 min in order to remove the solvent.

Moreover, the AgNO₃ solution was introduced into CuNWs to initiate the galvanic reaction (Fig. 4(d)). The original red of CuNWs transitioned to a deeper crimson shade after being agitated for 5 min (Fig. 4(e)). Subsequently, the solution underwent centrifugation at 10,000 rpm for 5 min to eliminate the NO₃⁻ (Fig. 4(f)).

RESULTS AND DISCUSSION

In the synthesis process, CuNWs are coated by PVA, PVP, and AgNPs. The result of XRD characterization (Fig. 5) compares CuNWs coated with various materials. Fig. 5(a) shows the pure CuNWs pattern. It shows a CuNWs pattern with crystalline peaks. The peaks are positioned at 43.30°, 50.48°, and 74.13° and match the (111), (200), and (220) planes. Fig. 5(b) shows the peaks on CuNWs with coating PVP. Fig. 5(b) indicates a change in chemical structure due to the coating by PVP. Fig. 5(c) is a chemical structure pattern of CuNWs coating PVA and indicates a change in chemical structure. Peaks appear only at the (200), (113), and (220) planes. Fig. 5(d), Ag nanocrystals shielded CuNWs from oxidation. Ag nanocrystal coating was observed on the CuNWs, covering planes (110), (200), (111), (112), (113), and (220).

Fig. 6 shows the morphology of CuNWs coated with various materials. Fig. 6(a), are CuNWs without the coating process. The CuNWs are randomly scattered and connected from one CuNW to another, then it will affect the conductivity. CuNWs have an average diameter of 120.0 nm and an average length of 5.5 μm. Fig. 6(b) represents the PVP-coated CuNWs and shows that the diameter of the CuNWs has increased, although

Fig 4. The synthesis of CuNWs: (a) Cu(NO₃)₂·3H₂O in water, (b) Cu(NO₃)₂·3H₂O in water + NaOH, (c) Cu(NO₃)₂·3H₂O in water + NaOH + EDA + PVP + N₂H₄, (d) CuNWs in water, (e) AgNO₃ + Cu(NO₃)₂·3H₂O, (f) AgNO₃ + Cu(NO₃)₂·3H₂O centrifugated

Fig 5. XRD patterns of (a) CuNWs, (b) CuNWs-PVP, (c) CuNWs-PVA, and (d) CuNWs-AgNPs
Fig 6. SEM images of (a) CuNWs, (b) CuNWs coating PVA, (c) CuNWs coating PVP, and (d) CuNWs coating AgNPs

the length is still the same. Fig. 6(c) is the morphology of PVA-coated CuNWs. PVA is a polymer that can prevent oxidation. However, the use of PVA and PVP will also hinder connectivity between CuNWs. This will result in reduced conductivity. Fig. 6(d) shows the morphology of CuNWs coated with Ag nanocrystals. This Ag nanocrystal coating process uses the galvanic method. This method is considered capable of coating AgNPs on the surface of CuNWs [3].

TCEs-CuNWs-based electrodes were fabricated using the Mayer Rod coating technique. Mayer rod coating presents a scalable approach for producing transparent conductors utilizing metal nanowires. Compared to spray coating, this method offers greater scalability by facilitating the rapid deposition of nanowires onto the film. In the study, we utilized a 2 mL ethanol solution containing CuNWs for film deposition. Moreover, the Mayer rod allows for precise control over the distribution of CuNWs on the film.

The pristine CuNWs were susceptible to oxygen exposure and environmental contamination. We applied CuNWs with coated PVA, PVP, and AgNPs to TCEs. We investigated the sheet resistance and measured each hour over 7 h. Fig. 7 shows the sheet resistance values of CuNWs coated with various materials. The oxidation has already occurred, and sheet resistance has increased for CuNWs. During the identical timeframe, CuNWs coated with PVA, PVP, and AgNPs exhibit consistent and nearly unchanging resistance, maintaining their resistance to oxidation and minimal increase in resistance for approximately 7 h.

Fig 7. The variation of sheet resistance over a period of time for CuNWs, CuNWs coated with PVA, CuNWs coated with PVP, and CuNWs coated with AgNPs
The CuNWs coated with PVA and PVP experienced an increase in sheet resistance in the first hour. The increase was due to the PVA and PVP layers preventing direct contact among the CuNWs, but steady resistance at times. Whereas CuNWs coated with AgNPs became almost constantly resistant from start to finish. These findings suggest that the main obstacle faced by CuNWs electrodes is their susceptibility to oxidation-induced instability [18,30]. This issue could potentially be addressed through the application of a protective coating on the CuNWs.

**CONCLUSION**

The synthesis and fabrication of TCEs CuNWs have been successfully investigated. CuNWs were synthesized by employing an aqueous solution comprising EDA as a capping agent and N$_2$H$_4$ as a reducing agent. To decrease the effects of oxidation and prevention of CuNWs, we coated the CuNWs with PVP, PVA, and AgNPs. After that, the Mayer rod method was utilized to prepare TCEs of CuNWs. The results of the conductivity were compared based on the time for 7 h. The uncoating CuNWs occur oxidation faster thus decreasing their conductivity. CuNWs coating with PVP and PVA has stability in oxidation. CuNWs coating AgNPs also has stability on the oxidation and more conductivity than PVP and PVA coating.

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**CONFLICT OF INTEREST**

The authors declare no competing interests.

**AUTHOR CONTRIBUTIONS**

Dedi Mardiansyah initiated the research, writing, and editing manuscript. Harsojo conceptualized and reviewed the manuscript. Sri Rahayu Alfitri Usna conducted the experiment. Suratun Nafisah and Rindi Genesa Hatika did material characterizations. All authors agreed to the final version of this manuscript.

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