

International Journal of Nanoelectronics and Materials

IJNeaM

ISSN 198-5761 | E-ISSN 2232-1535



In Press, Accepted Manuscript - Note to user

Facile Fabrication of Transparent Conductor Cu Nanowire-Pedot:PSS

Dedi Mardiansyah 1*, Dahyunir Dahlan 1, Tio Putra Wendari 2, Ramacos Fardela 1, and M. Fajmi Zukaham 1

¹ Department of Physics, Universitas Andalas, Padang, 25163, Indonesia

² Department of Chemistry, Universitas Andalas, Padang, 25163, Indonesia

* Corresponding author: dedimardiansyah@sci.unand.ac.id

Received 15 May 2023, Revised 12 August 2023, Accepted 11 September 2023

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 CuNWs transparent conductor is low oxidation resistance. Based on this purpose, we developed a facile method for coating PEDOT:PSS on CuNWs transparent conductor. PEDOT:PSS can protect CuNWs 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). SEM images show an increase in connectivity of CuNWs after PEDOT:PSS coating and X-ray diffraction show 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 CuNWs-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

<u>NOTE</u>

Please read these instructions carefully. Authors are to follow the template otherwise the submitted material will not be accepted for publication.

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 Ω sq⁻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 scaleable 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 CuNWs and their oxygen protection. This information would be beneficial for researchers 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 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, (N₂H₄, Merck) hydrazine as reduction and (PEDOT:PSS, Heraeus PH 1000) poly (3,4-ethylene dioxythiophene) 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)₂.3H₂O added with 150 mL aqua dest in the reaction flask. We stirred and maintained the temperature at 60 °C. About 2 minutes later, we added EDA (99%) 0.5 mL 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 5 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 check the resistance during the process to indicate the success of the coating. Finally, PEDOT:PSS solution was coated on top of the CuNWs film to ensure the protection of the film from direct environmental exposure. We tested the conductance and transparency of the film using an IV meter and 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 2 θ 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,

$4Cu + O_2 \rightarrow 2Cu_2 O,$	(1)
$2Cu_2 \ 0+O_2 \rightarrow 4CuO.$	(2)

This happened because the CuNWs were uncoated. Figure 1b, shows the 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 CuNWs and Fig. 2b shows 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. 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 CuNWs film once the layer is 75.73%,

twice the layer is 59.53%, and 3 times the layer is 50.79%. A similar pattern occurred on the CuNWs-PEDOT:PSS with transmittance CuNWs (1x)-PEDOT:PSS is 70.8%, CuNWs (2x)-PEDOT:PSS is 55.67%, and CuNWs (3x)-PEDOT:PSS is 45.17% as shown in Figure 4b. The addition number of layer on transparent conductor decreased the transmittance by approximately 5% when it used the PEDOT:PSS. The decrease of transmittance is presented in Figure 5a.

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 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.



Wavelength (nm). **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 (1x), 554.6 ohm/sq (2x), and 57.9 ohm/sq (3x), respectively.

The number of layers of transparent conductors can increase the electrical conductivity, but it decreases its transmittance. Figure 5c shows that changing the

3

Note: Accepted manuscripts are articles that have been peer-reviewed and accepted for publication by the Editorial Board. These articles have not yet been copyedited and/or formatted in the journal house style

transmittance can affect the resistance of transparent conductor CuNWs. The decrease in the transmittance affects the decrease in the sheet resistance of transparent conductor CuNWs. The decrease in the sheet resistance was accompanied by an increase in the conductivity of the transparent conductor 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. Every 0.5 hours, the sheet resistance of CuNWs is calculated for 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 picture 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 indicate that the challenges in using CUNWs are oxidation and instability.

The data also indicate the main problem of CuNW transparent conductors 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.

ACKNOWLEDGMENTS

This work was supported by the research grant of "Penelitian Dasar FMIPA Universitas Andalas, Tahun anggaran 2022. Contract No.: 19/UN.16.03.D/PP/FMIPA/2022".

REFERENCES

- Harsojo, Puspita, A. L., Mardiansyah, D., Roto, Triyana, K,. (2017) "The Roles of Hydrazine and Ethylenediamine in Wet Synthesis of Cu Nanowire,". Indonesia Journal Chemistry, 17, 1, 43-48.
- [2] Ye, S., Rathmell, A. R., Stewart, I. E., Ha, Y.-C., Wilson, A. R., Chen, Z., and Wiley, B. J., (2014), "A rapid synthesis of high aspect ratio copper nanowires for high-performance transparent conducting films", Chem. Commun., vol. 50, no. 20, 2562–2564.
- [3] M. Mohl, P. Pusztai, A. Kukovecz, Z. Konya, J. Kukkola, K. Kordas, R. Vajtai, and P. M. Ajayan, (2010), "Low-

temperature large-scale synthesis and electrical testing of ultralong copper nanowires", Langmuir, vol. 26, no. 4, pp. 16496–16502.

- [4] Ahn, Y., Jeong, Y., Lee, D., Y. Lee, (2015), Copper nanowire-graphene core-shell nanostructure for highly stable transparent conducting electrodes, ACS Nano 9, 3, 3125–3133.
- [5] Hong, I., Roh, Y., Koh, J.-S., Na, S., Kim, T., Lee, E., An, H., Kwon, J., Yeo, J., Hong, S., Lee, K.-T., Kang, D., Ko, S.H., Han, S., (2019), Semipermanent copper nanowire network with an oxidation-proof encapsulation layer, Adv. Mater. Technol. 4, 4, 1-7.
- [6] Akiyama, Y., Sugiyama, T., Kawasaki, H., (2017), Contribution of ligand oxidation products to high durability of copper films prepared from lowsintering-temperature copper ink on polymer substrates, Adv. Eng. Mater. 19, 1700259, pp. 1-8.
- [7] Ye, S., Rathmell, A. R., Chen, Z., Stewart, I. E., and Wiley, B. J., (2014), "Metal Nanowire Networks: The Next Generation of Transparent Conductors," Adv. Mater., vol. 26, pp. 6670–6687.
- [8] Mardiansyah, D., Triyana, K., Sosiati, H., Harsojo, (2016), "Synthesis of Copper Nanorods by Aqueous Solution Method without Heating External," AIP Conference Proceedings, vol. 150019, no. 1755, pp. 1– 5.
- [9] Jiu, J., Nogi, M., Sugahara, T., Tokuno, T., Araki, T., Komoda, N., Suganuma, K., Uchida, H., Shinozaki, K., J. (2012), Strongly adhesive and flexible transparent silver nanowire conductive films fabricated with a high-intensity pulsed light. Mater. Chem., 22 pp. 23561-23567
- [10] Junaidi, J., Saputra, M.W., Marjunus, R., Sembiring, S., Hadi, S., (2021), The Quenching and Sonication Effect on the Mechanical Strength of Silver Nanowires Synthesized Using the Polyol Method. Molecules 26, 2167 pp. 1-10.
- [11] Jiang, D.-H., Tsai, P.-C., Kuo, C.C., Jhuang, F.-C., Guo, H.-C., Chen, S.-P., Liao, Y.-C., Satoh, T., Tung, S.-H., (2019), Facile preparation of Cu/Ag core/shell electrospun nanofibers as highly stable and flexible transparent conductive electrodes for optoelectronic devices, ACS Appl. Mater. Interfaces 11, pp.10118–10127.
- [12] Zhang, B., Li, W., Jiu, J., Yang, Y., Jing, J., Suganuma, K., Li, C.-F., (2019), Large-scale and galvanic replacement free synthesis of Cu@Ag core-shell nanowires for flexible electronics, Inorg. Chem. 58, pp. 3374–3381,
- [13] Ke, S.-H.; Xue, Q.-W.; Pang, C.-Y.; Guo, P.-W.; Yao, W.-J.; Zhu, H.-P.; Wu, W. (2019), Printing the Ultra-Long Ag Nanowires Inks onto the Flexible Textile Substrate for Stretchable Electronics. Nanomaterials, 9, 686, pp.1-10.
- [14] Mao, Y., Zhu, M., Wang, W., Yu, D., (2018), Welldefined silver conductive pattern fabricated on polyester fabric by screen printing a dopamine surface modifier followed by electroless plating, Soft Matter, 14, pp. 1260–1269,
- [15] Rathmell, A. R., Bergin, S. M., Hua, Y., Li, Z., and Wiley, B. J., (2010), The Growth Mechanism of Copper

Note: Accepted manuscripts are articles that have been peer-reviewed and accepted for publication by the Editorial Board. These articles have not yet been copyedited and/or formatted in the journal house style

Nanowires and Their Properties in Flexible, Adv.Mater., vol. 100190, pp. 3558–3563,

- [16] Mardiansyah, D., Triyana, K., Harsojo, (2016), "Effect of Precursor Molar Ratio on the Yield of Cu Nanowires Synthesized using Aqueous Solution Method," International Journal on Advanced Science Engineering Information Technology, vol. 6, no. 4, pp. 447–450.
- [17] Mardiansyah, D., Badloe, T., Triyana, K., Mehmood, M.Q., Raeis-Hosseini, N., Lee, Y., Sabarman, H., Kim, K., Rho, J., (2018), Effect of temperature on the oxidation of Cu nanowires and development of an easy to produce, oxidation-resistant transparent conducting electrode using a PEDOT:PSS coating, Scientific Report. 8, 10639, pp. 1-9.
- [18] J. Li, J. Mayer, E. Colgan, (1991), Oxidation and protection in copper and copper alloy thin films, Journal of Applied Physics 70, pp. 2820–2827.
- [19] Chen, J., Zhou, W., Chen, J., Fan, Y., Zhang, Z., Huang, Z., Feng, X., Mi, B., Ma, Y., and Huang, W., (2014), "Solution-processed copper nanowire flexible transparent electrodes with PEDOT:PSS as binder, protector and oxide-layer scavenger for polymer solar cells," Nano Research, vol. 8, pp. 1017–1025.
- [20] Chauhan R. P., and Rana, P., (2015), "Nickel ion induced modification in the electrical conductivity of Cu nanowires," Radiation Measurements, vol. 83, pp. 43–46.
- [21] Li, W., Li, L., Li, C., Jiu, J., Suganuma, K., (2018), Enhanced high temperature stability of printed Cu wirings based on large Cu particle ink, Ag element addition, and intense pulsed light sintering, ICEPT, 18162248, pp. 1112–1115.
- [22] Kim, N.R., Shin, K., Jung, I., Shim, M., Lee, H.M., (2014), Ag-Cu bimetallic nanoparticles with enhanced resistance to oxidation: a combined experimental and theoretical study, Journal of Physical Chemistry C, 118, 45, pp. 26324–26331.
- [23] Niu, Z., Cui, F., Yu, Y., Becknell, N., Sun, Y., Khanarian, G., Kim, D., Dou, L., Dehestani, A., Schierle-Arndt, K., Yang, P., (2017), Ultrathin epitaxial Cu@Au core-shell nanowires for stable transparent conductors, Journal of the American Chemical Society,139, 21, pp. 7348– 7354.
- [24] Mardiansyah, D., Khasanah, D., U., Triyana, K., and Harsojo. (2019), Fabrication of Copper Nanowire Coated by Silver Nanocrystal for Protection of Oxidation Transparent Conductive Electrode, Materials Science Forum, 948, pp 243-248.
- [25] Y. Chang, M. L. Lye, and H. C. Zeng, (2005), Large-scale synthesis of high-quality ultralong copper nanowires, Langmuir, 21, 9, 3746–3748.
- [26] Zhang, F.-T., Xu, L., Chen, J.-H., Xie, J.-Q., Fu, X.-Z., Chen, Q., Sun, R., Wong, C.-P., (2018), Adhesion-enhanced flexible conductive metal patterns on polyimide substrate through direct writing catalysts with novel surface-modification electroless deposition, Chemistry Select 3, 26, pp. 7612–7618.
- [27] X. Wang, W. Guo, Y. Zhu, X. Liang, F. Wang, P. Peng, Electrical and mechanical properties of ink printed

composite electrodes on plastic substrates, Applied Sciences 8, 11, 2101, (2018), pp. 1-10.

- [28] Bhat, K.S., Nakate, U.T., Yoo, J.-Y., Wang, Y., Mahmoudi, T., Hahn, Y.-B., (2019), Cost-effective silver ink for printable and flexible electronics with robust mechanical performance, Chemical Engineering Journal, 373, pp. 355–364.
- [29] E.-B. Jeon, S.-J. Joo, H. Ahn, H.-S. Kim, (2016), Twostep flash light sintering process for enhanced adhesion between copper complex ion/silane ink and a flexible substrate, Thin Solid Films, 603, pp. 382– 390.
- [30] Ma, W.-Y., Cheng, Y.-Y., Chen, J.-K., Chan, K.-H., Lin, Z.-J., Chou, W.-H., Chang, W.-C., (2018), Synthesis of antioxidative conductive copper inks with superior adhesion, Journal of Nanoscience and Nanotechnology, 18, 318–322.
- [31] Han, J., W., Jung, B., Kim, W., D., Lim, K., L., Jeong, S., T., Yong Hyun Kim, Y., H., (2019), Transparent conductive hybrid thin-films based on coppermesh/conductive polymer for ITO-Free organic lightemitting diodes, Organic Electronics, 73, 13-17.
- [32] Q. Xiang, R. Navik, H. Tan, Y. Zhao, (2022), Synthesis of oxidation-resistance copper nanowires-formate for high-performance transparent conductive electrodes. Journal of Alloys and Compounds, Journal of Alloys and Compounds, 914, 165265, 1-7.