

# Propylene Glycol and Glycerol Addition in Forming Silver Nanowires (AgNWs) for Flexible and Conductive Electrode

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**Abstract.** Silver nanowires (AgNWs) are promising materials due to their flexibility, high

transmittance, high conductivity, and low sheet resistances to replace ITO (Indium Thin Oxide) based electrodes. In this work, we studied the Propylene Glycol and Glycerol addition in Ethylene Glycol solvent to form AgNWs with polyol method. AgNWs was made thin film by spin coating method (with 1 – 3 layers variation) in PET substrate at 3000 rpm. The best morphology AgNWs formed by EG: PG: Gliserol (7 : 0 : 3) solvent composition with average diameter, length, and thickness are 210.32 nm, 6.68  $\mu\text{m}$ , and 2.1  $\mu\text{m}$  respectively. In optical properties, transmittance of AgNWs thin film was in range of 54.6 – 70.6 %. The sheet resistance of 3 layers AgNWs thin film was 2.8 – 30.2  $\Omega/\text{sq}$ . Sheet resistance of AgNWs thin film was better than ITO-PET (transmittance 60% sheet resistance 45  $\Omega/\text{sq}$ ).

## 1 Introduction

Nowadays, almost all electronic devices use Indium Tin Oxide (ITO, 90%  $\text{In}_2\text{O}_3$  and 10%  $\text{SnO}_2$ ) as a conductive electrode. But these materials suffer from a number of drawbacks, including high cost, brittleness (ceramic properties), rigidity, and harmful composition [1]. Inspired numerous study has been conducted to find alternative material as conductive electrode that are flexible, effective, efficient, and environmentally friendly. As a result, some materials such as graphene, carbon nanotube, conducting polymer, and metal nanowires (AgNWs, CuNWs, dan AuNWs) could be replaced ITO PET [2]. In contrast to carbon material, metal nanowires have higher electrical conductivity and transmittance. Concurrently, conductive polymer materials are easier to synthesize and manufacture, but have lower and unstable conductivity and transmittance than ITO [3]. Due to the shortcomings in carbon materials and conductive polymers, metallic nanowires especially silver (AgNWs) have been considered as prospective and potential candidates in Flexible and Transparent Conductive Electrodes (FTCE), because AgNWs could produce better transmittance, electrical conductivity, and flexibility than ITO [4].

From various methods of AgNWs synthesis, polyol is the most effective method because of low cost, simpler synthesis process, suitable for large-scale production (industrial) and produces AgNWs with high aspect ratio. In general, polyol method uses  $\text{AgNO}_3$  as a precursor, polyvinylpyrrolidone (PVP) as capping agent and stabilizer, and requires solvent polymer as reducing agent.

Polyol method could produce AgNWs with diameter of 20 – 80 nm, length of  $\geq 20 \mu\text{m}$ , transmittance of 80 – 92%, low resistance of 20 – 80  $\Omega/\text{sq}$ , and high electrical conductivity of  $4 \times 10^6 \text{ S/m}$  [5]–[10]. However, there are drawbacks including uniform size and still having byproducts such as nanoparticles/nanorods.

One important component in formation of AgNWs morphology is solvent as reducing agent. Several polymers, including ethylene glycol (EG), propylene glycol (PG), glycerol, N-methyl pyrrolidone (NMP), diethylene glycol, and triethylene glycol, are applied as solvents in AgNWs synthesis. These solvents can be used separately, however, numerous research has looked into the effects of mixing different solvents for synthesizing AgNWs. The following studies on solvent mixing have been conducted: glycerol-EG [11], NMP-glycerol-EG [12], and (diethylene glycol-triethylene glycol-glycerol-EG) [13]. Propylene Glycol was used because of its advantages that can produce small diameter AgNWs ( $\leq 60 \text{ nm}$ ), while Etylen Glycol can produce long AgNWs (up to 100  $\mu\text{m}$ ). Additionally, combining NMP and glycerol can improve the thin film of AgNWs' transmittance while lowering its resistance.

Each solvent has advantages in specific parameters based on research that has been mentioned. As of right now, ethylene glycol continues to be the best solvent for AgNWs synthesis. However, the impact of combining different solvents on the properties of AgNWs has only been examined in a small number of investigations.

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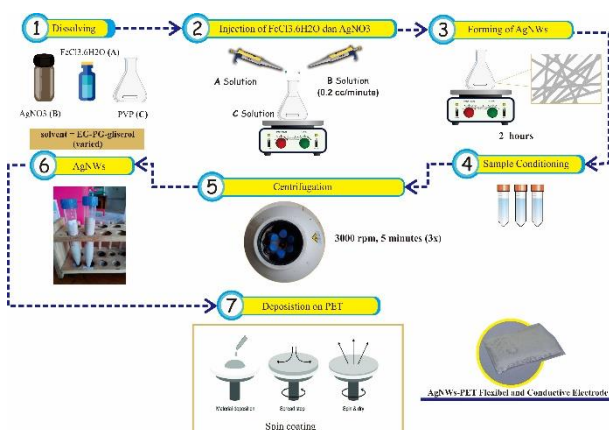
Since no one has ever done it and it has potential to enhance optical and physical properties of the AgNWs thin film, it is therefore required to conduct a solvent mixing process, particularly using EG, PG, and glycerol.

## 2 Methods

The following materials were used in the synthesis: AgNO<sub>3</sub> 99% (Merck, kGaA, Darmstadt, Germany), FeCl<sub>3</sub>.6H<sub>2</sub>O, polyvinylpyrrolidone (PVP, Mw 1300000 by Sigma Aldrich, USA), ethylene glycol (EG, Merck, kGaA, Darmstadt, Germany), propylene glycol (PG), glycerol 85% (Merck, kGaA, Darmstadt, Germany), ethanol, alcohol, deionized water (DI), and Polyethylene terephthalate (PET).

In the synthesis, EG solvents were a fixed variable (7) while the composition of PG and glycerol was an independent variable (EG : PG : G = 7 : x : 3-x). In the beginning step of synthesis, 0.204 grams of FeCl<sub>3</sub>.6H<sub>2</sub>O were dissolved in 10 ml of mixing solvent and stirred until homogenous to obtain FeCl<sub>3</sub>.6H<sub>2</sub>O 0.04 M (**A solution**). Next, 1.53 grams of AgNO<sub>3</sub> were dissolved in 30 ml of mixing solvent, and 10 minutes were spent stirring to obtain 0.3 M AgNO<sub>3</sub> (**B solution**). Third, 1.5 grams of PVP were dissolved in 30 ml of a mixing solvent for 1 hour at a temperature of 130 °C (**C solution**).

The following step involves using a syringe pump to continuously inject 100 µL of A and 24 ml of B to C for two hours. Following that, the mixture was stirred for next two hours to allow AgNWs growth. Additionally, the solution was washed with DI water, ethanol, and acetone after centrifuging three times at 3000 rpm for five minutes. Finally, centrifuged AgNWs are spin coated on a PET substrate as a Flexible and Conductive Transparent Electrode (FTCE). The visualization synthesis is shown in Figure 1

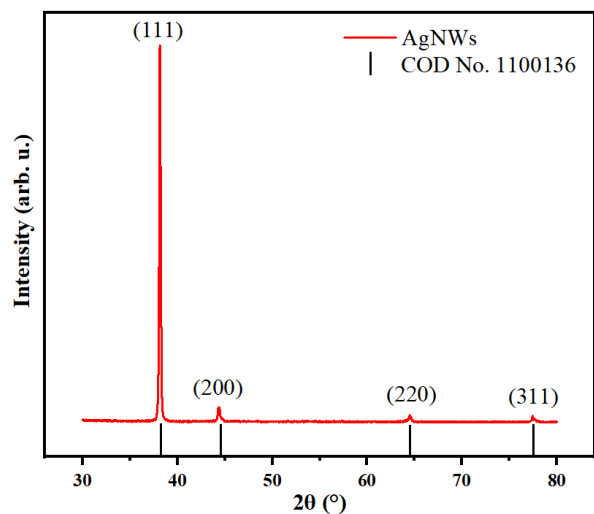


**Fig 1.** Synthesis method of AgNWs

## 3 Results and Discussion

X-ray diffraction pattern peaks at 2θ 38.15°, 44.43°, 64.47°, and 77.41°, which had hkl (111), (200), (220), and (311) planes, respectively, demonstrated the development of AgNWs (**Fig. 2**) [14].

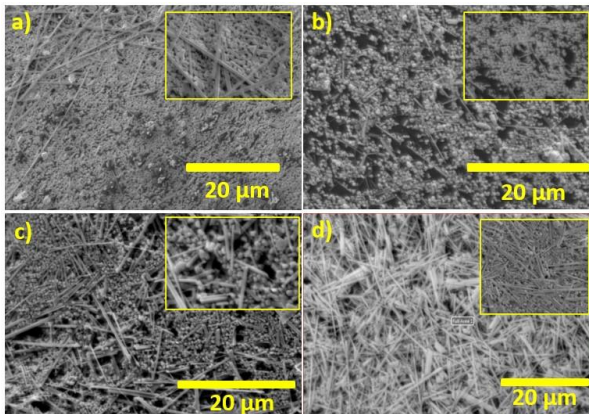
The resulting diffraction peak data is in accordance with the Crystallography Open Database (COD) no. 1100136. Ag atoms typically develop anisotropically to produce AgNWs in plane (111), which has the highest intensity [15], [16]. In this study, AgNW additionally demonstrated a high aspect ratio. This is due to the XRD diffraction signal peak being higher at (111) than at (200) [17].



**Fig 2.** XRD Pattern of AgNWs thin film

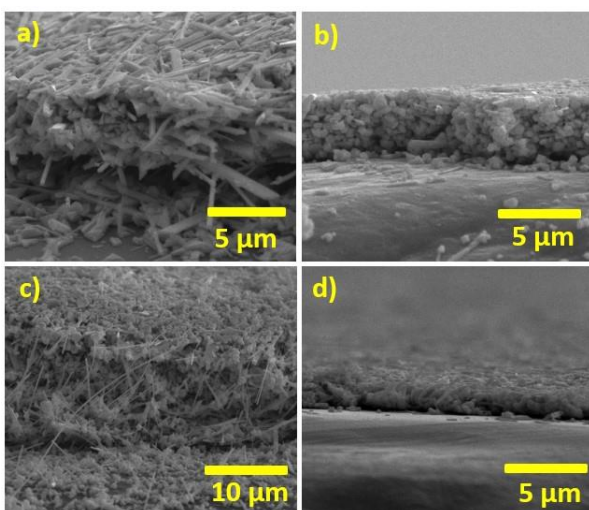
Due to the high aspect ratio (length to diameter ratio) of an AgNWs-based conductive electrode, the nanostructure offers excellent conductivity, low sheet resistance, and transparency [18], [19]. In order to analyze AgNWs' morphological, **Figure 2** showed SEM result. AgNWs synthesis with solvent composition Ethylene Glycol (7) : Propylene Glycol (0) : Glycerol (3) has produce more and more uniform of AgNWs than the other compositions (Figure 2d). This is because EG and glycerol have different reducing capacities and viscosities, which are crucial in regulating nucleation at the beginning of process. High-viscosity glycerol slows the migration rate of Ag<sup>0</sup> and supports the formation of uniform Ag NWs with small diameters, which is assisted by the molecular technique of PVP (as a capping agent) which is selectively adsorbed on the surface of Ag seed [11]. Meanwhile, AgNW is more difficult to form due to negligible viscosity difference between ethylene and propylene glycol, as shown in Figures 2a, 2b, and 2c. Samples E7P3G0, E7P2G1, E7P1G2, and E7P0G3 had average AgNW diameter of 201.94 nm, 278.67 nm, 263.58 nm, and 210.32 nm and lengths 32.97 µm, 9.65 µm, 27.71 µm, and 18.39 µm, respectively (**Fig. 3**).

As in previous research, other forms such nanoparticles, nanospheres, nanorods, and nanotriangles were still detectable [20], [21]

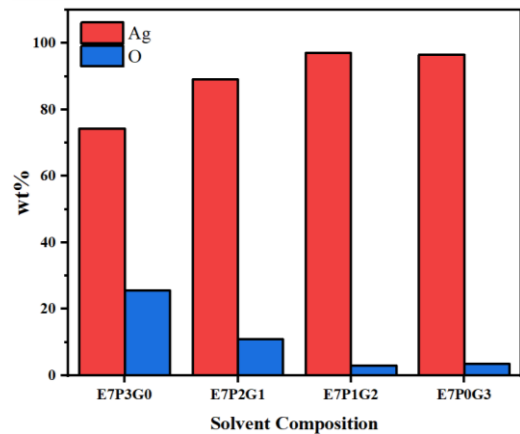


**Fig 3.** AgNWs morphology with 2000x magnification: a) E7:P3:G0, b) E7:P2:G1, c) E7:P1:G2, d) E7:P0:G3

On the other hand, the thickness of each AgNWs sample was measured to determine flexibility of the AgNWs-PET conductive electrode. The thickness of AgNWs is inversely proportional to the flexibility, because ability of AgNWs to flex decreases as increasing layer thickness. According to the results of SEM cross-section, the AgNWs E7P0G3 sample has the lowest thickness, at 1.6 µm (Fig. 4). The wt% of the components contained in the AgNWs-PET thin layer will be revealed by an EDX analysis, which is necessary to establish the formation of AgNWs. On the sample, only Ag and O content was determined. This indicates that the synthesis process is successful because no residues of other synthetic components, such Fe, are left there. The samples E7P3G0, E7P2G1, E7P1G2, and E7P0G3 had respective Ag contents of 74.39%, 89.1%, 97.05%, and 96.53%. (Fig. 5).

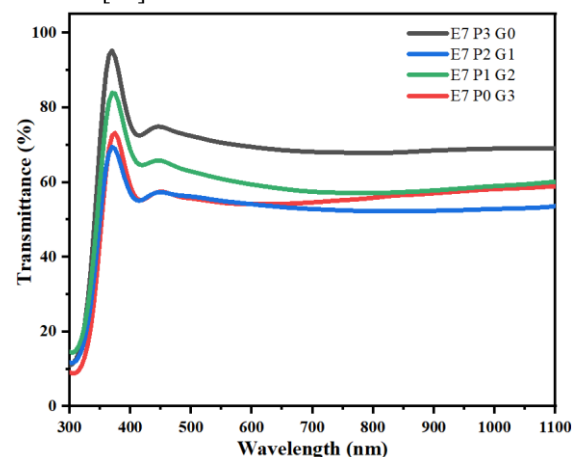


**Fig 4.** AgNWs film thickness on PET substrate, a) E7:P3:G0, b) E7:P2:G1, c) E7:P1:G2, d) E7:P0:G3



**Fig 5.** EDX results of AgNWs-PET

The ratio of light intensity entering to leaving the AgNWs layer is known as transmittance, which is an optical property in transparent and conductive electrode. Since visible light with a wavelength of 550 nm is the one that can be viewed the majority of the time under normal conditions, AgNWs electrodes are always evaluated for their transmittance values at that wavelength [22]. AgNWs with a solvent composition of E7P3G0 had the highest transmittance rating, at 70.6%, whereas other samples ranged from 54 to 60%. (shown in Fig. 6). The low sheet resistance is the most important factor of the AgNWs-PET conductive electrode product (in this study, varied by layer deposition). In 1 layer, the lowest sheet resistance ( $R_s$ ) value was found in sample E7P0G3 which was 30.9  $\Omega$ /sq, while in samples E7P3G0, E7P2G1, E7P1G2 the values were respectively 69.4  $\Omega$ /sq, 136  $\Omega$ /sq, and 126  $\Omega$ /sq. Value of  $R_s$  declines significantly and even drops to 90% of its initial value as 2 and 3 layers AgNWs (Fig. 7). The decreased  $R_s$  when the deposition layer is added caused by addition of AgNWs from each layer so more AgNWs networks are connected to each other on the surface of the PET substrate. Comparing all variations in other samples, E7P0G3 with 3 deposition layers has the lowest sheet resistance at 2.8  $\Omega$ /sq, which is significantly less than commercial ITO-PET ( $\Omega$ /sq) [9]. Additionally, this indicates the low or removal of PVP residue, which can increase sheet resistance[23].



**Fig 6.** Transmittance of AgNWs synthesized with different solvent compositions

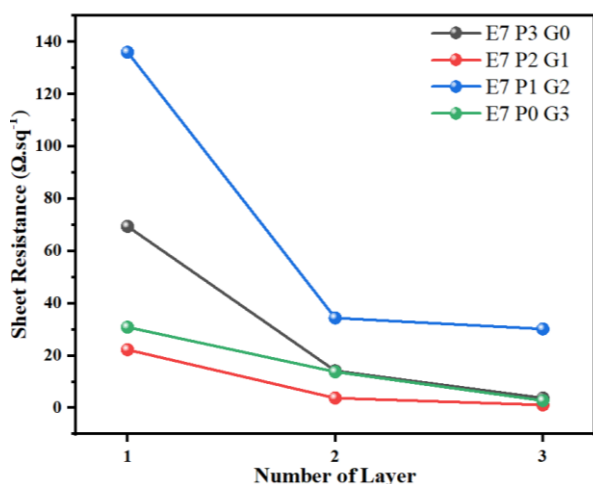


Fig 7. Sheet Resistance ( $R_s$ ) of AgNWs with deposition layer variation

## 4 Conclusion

This research succeeded in making AgNWs-PET conductive electrodes, by mixing solvent (Ethylene Glycol: Propylene Glycol: Glycerol). The sample with the composition EG7:PG0:G3 has the best morphology and the lowest resistivity with an average diameter of 210.32 nm, the longest size is 18.39  $\mu\text{m}$ , film thickness is 1.6  $\mu\text{m}$ , and sheet resistance is 2.8  $\Omega/\text{sq}$ . The results of this study are expected to be a future reference in overcoming dependence on ITO-PET electrodes and for the sake of welcoming flexible electronic electrodes.

The suggestion in further research is applied AgNWs film to simple electronic devices, not limited to the characterization of thin films AgNWs.

## Acknowledgement

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