Highly Ordered Arrays of Silver Nanowires for Transparent Conducting PET Film

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Abstract

Silver nanowires (AgNWs) with ultra-high purity and high yield are successfully synthesized by employing a modified facile polyol method using PVP as capping and stabilizing agent. The reaction is carried out at a moderate temperature of 140 °C and mild stirring rate for about 3 hours. The prepared AgNWs are characterized by UV-Vis spectroscopy, scanning electron microscopy (SEM), X-rays diffraction (XRD) and PL spectroscopy. The luminescent AgNWs exhibit red emission which is accredited to the deep holes. The SEM results confirm the formation of AgNWs of length ranging from 35 to 40 µm and an average diameter of about 86 nm, thus their aspect ratios exceed 400. The AgNWs and hydroxyethyl cellulose (HEC) based ink is transferred to polyethylene terephthalate (PET) film by simple mechanical pressing. The PET film has retained its transparency and flexibility after AgNWs ink coating. The % transmittance of as-
prepared PET film is estimated to be about 92.5% with a lower sheet resistance value ~ 20 Ω, which can make it a potential substitute to commonly used expensive indium tin oxide (ITO) films in the field of optoelectronics.

**Keywords:** Silver nanowires; highly-ordered arrays; visible luminescence; PET film; transmittance; sheet resistance.

1. **Introduction**

Several optoelectronic devices such as solar cells, touch screen, LCD display, organic EL panel, light emitting diodes (LEDs), Organic light emitting diodes (OLEDs) use transparent conductors made of indium tin oxide (ITO) sputtered films [1-3]. These films are widely used because of their high transmittance, low sheet resistance and high electrical conductivity but still have some major drawbacks like expensiveness, intrinsic brittleness due to ceramic nature [4], toxic composition, sputtering process is time consuming and sputtering make the films brittle which limits its application in flexible applications [5].

Numerous materials are under consideration to overcome these challenges. In past few years certain materials such as graphene, carbon nanotubes (CNT), conductive polymers and metallic nanowires are tested commercially as alternative to ITO films [6-8]. Amongst them, graphene and carbo-made materials particularly CNTs display low optical transparency and high sheet resistance owing to their greater tube-tube resistance and lower inherent carrier concentration [9]. Now a days, noble metal nanomaterials viz; gold, silver and copper are extensively employed owing to their superior conductive properties [10]. Among them only silver nanowires (AgNWs)
films outperform ITO films in term of transmittance and electrical conductivity [11]. The AgNWs are important as there is a possibility of overcoming the phenomenal light-matter interaction in visible region. Their optical properties are induced by localized surface plasmon resonance that depends upon the material’s shape, size and environmental [12]. So, AgNWs have gained much attention in replacing ITO because of their low-cost solution-based fabrication, flexibility and high optical transparency [3, 13]. Silver nanowires having ordered structure and high aspect ratio are greatly emphasized because of better plasmonic and optical properties [14]. Therefore, an effective synthetic method is still needed for the preparation of ordered structures of AgNWs.

In order to synthesis silver nanowires several methods have been successfully developed including ultra-violet irradiation, salt-free solution-based, salt-mediated solution-based, photo reduction, hydrothermal, wet-chemical, template reduction (hard and soft templates) and ultrasonic reduction methods [15-20]. Lithographic and hard template methods are used to prepare silver nanowires with well-defined dimensions but, both these methods produce polycrystalline silver nanowires with rough surfaces triggering significant scattering and reducing length propagation, thus affecting the optical properties [21].

Polyol method is promptly considered as most promising and adaptable method [22] in respect of yield, cost, simplicity and reaction time [23] for the preparation of AgNWs of higher aspect ratios. This method simply involves the reduction of metallic salts in the presence of a polyol [24]. This synthetic method was first proposed by Xia and co-workers for the synthesis of uniform silver nanowires. They employed ethylene glycol as polyol to reduce the salt in the presence of polyvinylpyrrolidone using a nucleating agent [25, 26]. Silver nanowires with an
average diameter of 20 nm and length up to 20 µm were synthesized by using high pressure polyol method. The transparent film fabricated by these nanowires would have transmittance of 88% and sheet resistance of 40 Ω/sq. and performance below ITO films. Hence, there is a need to modify this polyol method to produce extra-large and highly ordered silver nanowires to outperform ITO films. Nevertheless, preparation of AgNWs with higher aspect ratio is not enough, as polyol synthesis is extremely sensitive to impurities of nanoparticles. These nanoparticles formed as a by-product of the reaction drastically effect the electrical conductivity and transparency of the silver nanowires network, thus limiting the optoelectronic applications [26, 27].

Herein, a rapid one-pot modified polyol protocol [28] was employed to obtain ultra-pure silver nanowires. In this facile synthesis, ethylene glycol was used as a reducing agent in the presence of PVP, which played an important role of capping agent. Silver nitrate and CuCl₂ were used as sources of silver and metallic salt, respectively. The resultant nanowires grow 35-40 µm in length and 75-97 nm in diameter. Silver nanowires ink was then transferred to PET film whose transmittance was calculated to be 92.5%.

2. Experimental

2.1. Materials

All required chemical reagents were purchased from Sigma Aldrich that included silver nitrate (AgNO₃), ethyl glycol, polyvinylpyrrolidone (PVP), copper chloride (CuCl₂), hydroxyethyl cellulose (HEC), polyethylene terephthalate (PET) Film, acetone and ethanol. All of them were
analytical research grades chemicals that were used as purchased without any purification. Deionized water (DI-H$_2$O) was used as a solvent.

2.2. Preparation of Silver Nanowires

For synthesizing silver nanowires (AgNWs) having high aspect ratios and controlled diameters, ethylene glycol (EG) was used as a solvent and also acted as a reducer. Silver nitrate (AgNO$_3$) was used as a source of silver. The stabilizer used in the reaction was PVP which also acted as a capping agent. In addition to stabilizing and capping agent, PVP also prevented the agglomeration of silver nanowires. The CuCl$_2$ was used as a salt precursor that provided chloride ions. These chloride ions played vital role in regulating the growth of AgNWs.

To prepare self-arranged silver nanowires, first, 150 mL of EG was stirred and heated at 140 °C for 1 hour in order to remove any extra water form EG. The temperature was controlled by using an oil bath. After 1 hour, a trace amount (0.225 mg) of CuCl$_2$ was added into the reaction solution. Then, 1.936 g of PVP dissolved in 5 mL of EG was added dropwise in the reaction mixture after 15-20 minutes. The addition of PVP lasted for almost half an hour. Eventually, 0.48 g of AgNO$_3$ also dissolved in 5 mL of EG was added dropwise in the solution over a period of 1 hour. Initially, the addition rate of AgNO$_3$ in the solution was slow but at the end the injection rate was increased. The stirring rate significantly affected the synthesis of AgNWs. Whole reaction was carried out at mild stirring.

The reaction solution undergoes series of color changes after the addition of AgNO$_3$. Just after the addition of few drops of AgNO$_3$ the solution color changed from transparent to milky gray, then turned to brick red. At the end, the solution color was yellowish white. The yellow color
indicated the presence of silver nanoparticles in the solution. The ratio between AgNO$_3$ and PVP used in the reaction greatly affect the synthesis of silver nanowires [28]. In the present reaction, the ratio of AgNO$_3$ and PVP was 4:1. The solution was then cooled to room temperature by the addition of 30 mL DI-H$_2$O. The cooled mixture was washed and centrifuged twice at 4000 rpm for 10 minutes. The supernatant was removed and the residual bottom solution showed silvery shine which indicated the presence of AgNWs.

The as-prepared AgNWs were then used for various characterizations. The prepared solution was diluted and used for UV-vis spectroscopy and PL spectroscopy. The prepared solution was dried and crushed into fine powder used for SEM.
2.3. **Formulation of AgNWs Ink and Fabrication of Transparent Conducting Film**

A facile method was chosen for synthesizing AgNWs ink which involved the mixing of aqueous solutions of adhesive agent HEC and AgNWs [9]. First, 1.0 wt% solution of HEC was prepared in 100 mL of DI water while stirring at room temperature. Then, 15 mL of HEC solution was mixed with 20 mL of AgNWs solution in ethanol in a separate glass vial under constant stirring. This reaction mixture followed mixing of another 15 mL of HEC solution and stirred at room temperature for 2-3 hours until AgNWs solution was completely mixed with HEC.

As-prepared AgNWs ink was then transferred to 5x5 cm piece of PET film by mechanical pressing. A thin layer of ink was coated onto the surface of the substrate PET film. The ink-coated film was then placed in a preheated oven for 3 min for curing. Curing temperature was 130 °C. A high curing temperature may disrupt the PET film structure and bent the film. The experimental results revealed that after ink coating, the substrate PET film retained its flexibility and transparency, as shown in Figure 2.
2.4. Characterization

The UV-Vis absorption spectra of liquid AgNWs samples are recorded via Cecil 7500 double beam UV-Vis spectrophotometer in 400-800 nm wavelength range. A Bruker-D8 advance X-ray diffractometer, operating at 35 mA and 40 keV, is used to scan the sample from 20° to 85° at room temperature for its structural study. To examine surface morphology of as-synthesized powder sample, a scanning electron microscope (Nova NanoSEM 450 operated at an accelerating voltage of 20 KV) is utilized. Luminescence measurements are taken by the Cary Eclipse MY1806003 photoluminescence spectrometer in the wavelength range 400-700 nm while exciting at 300 nm wavelength. The transmissivity of PET film is measured using the UV-Vis spectrophotometer in visible light wavelength range. A digital multimeter is used to measure sheet
resistance of AgNWs loaded PET film. To test the uniformity and electrical conductivity of as-prepared PET film, a close loop circuit connected to a white LED is utilized in the dark.

3. Results and Discussion

In order to determine the morphology of as-prepared silver nanostructure, they were first characterized by UV-Vis absorption spectroscopic technique. The absorption spectra of silver nanowires depends upon the dielectric material, chemicals used and the particle size [29]. The absorption spectra of two samples was examined. First sample was taken readily after the addition of AgNO$_3$ in the solution and second sample was obtained after washing of the final product.
Figure 3. (a) The UV-Vis absorption spectrum in the middle (red line representing the formation of AgNPs) and at the end of the reaction (black line representing the formation of silver AgNWs) with two insets showing their actual solution colors. (b) XRD pattern of as-synthesized AgNWs sample. (c) PL emission spectrum of AgNWs falling in the range 600-800 nm with red emission. The de-convolution into Lorentzian peaks appears at 607 nm, 657 nm and 718 nm. The red dotted curve is the fit sum of all three Lorentzian peaks. (d) Transmittance vs wavelength plot of AgNWs coated PET film, and the inset shows transmittance vs sheet resistance plot of the PET film.

Figure 3(a) shows one sharp peak at 401 nm which confirms the formation of AgNPs in the solution while the two SPR peaks above 350 nm are the distinguished feature of AgNWs [30], so the formation of AgNWs is confirmed. The SPR peak at 365 nm may be attributed to the plasmon response along transverse axis of AgNWs which is identical to the bulk silver. The second peak at 373 nm is attributed to the longitudinal plasmon resonance of AgNWs. It is also noted that no other peak is observed which shows that the final product is free from contamination of any other nanostructure, such as silver nanoparticles or nanocubes. The SEM results also confirms the purity of the product.

The crystalline purity and structure of as-synthesized AgNWs was studied by X-rays diffraction and the resultant diffraction pattern was analyzed. The different peaks were matched with the JCPDS card numbers 04-0783 and 99-0094 used for AgNWs. The results obtained by the diffraction clearly indicate that the prepared AgNWs have face-centered cubic silver crystal structure having lattice constants (a=b=c= 4.086 Å). The diffraction pattern in Figure 3(b) depicts four distinct peaks. The 2θ values at which these peaks appeared were 38.1°, 44.30°, 64.51° and 77.43° corresponding to the Bragg reflection of (111), (200), (220) and (311). It is also depicted from the XRD pattern that no other peaks except these four peaks were appeared. It is a clear
indication that the final product of the reaction is free from impurities and no oxidation of silver is appeared. It shows that silver nanowires have perfect crystal structure with almost no crystal defects. The crystallite size was measured using Debye-Scherrer equation. The crystal size was found to be 27 nm which is smaller than the diameter of the silver nanowires as calculated by the SEM results.

Table 1. The available literature showing a comparison of various parameters of AgNWs synthesized for transparent conducting PET film.

<table>
<thead>
<tr>
<th>Synthetic method</th>
<th>Aspect ratio</th>
<th>Transmittance (%)</th>
<th>Sheet Resistance (Ω)</th>
<th>Arrangement of AgNWs</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>One step synthesis</td>
<td>2500</td>
<td>88.20</td>
<td>3.5</td>
<td>Disordered</td>
<td>[9]</td>
</tr>
<tr>
<td>Gram-scale Polyol Synthesis</td>
<td>Not defined</td>
<td>&lt;90.0</td>
<td>10.0</td>
<td>Disordered</td>
<td>[31]</td>
</tr>
<tr>
<td>Wet chemical synthesis</td>
<td>Not defined</td>
<td>85</td>
<td>13</td>
<td>Disordered</td>
<td>[32]</td>
</tr>
<tr>
<td>PVP-mediated polyol process</td>
<td>30-1000</td>
<td>91.5</td>
<td>11.4</td>
<td>Disordered</td>
<td>[33]</td>
</tr>
<tr>
<td>One-pot polyol process</td>
<td>~4000</td>
<td>97.70</td>
<td>155.0</td>
<td>Disordered</td>
<td>[34]</td>
</tr>
<tr>
<td>Laser ablation</td>
<td>Not defined</td>
<td>90</td>
<td>Not defined</td>
<td>Disordered</td>
<td>[13]</td>
</tr>
<tr>
<td>Solvo-thermal method</td>
<td>250-400</td>
<td>89.9</td>
<td>58.0</td>
<td>Disordered</td>
<td>[35]</td>
</tr>
<tr>
<td>Method</td>
<td>Temperature</td>
<td>Yield (°C)</td>
<td>PL Intensity</td>
<td>Crystallinity</td>
<td>Ref.</td>
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<tr>
<td>Polyol synthesis</td>
<td>2000</td>
<td>99.1</td>
<td>130.0</td>
<td>Disordered</td>
<td>[1]</td>
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<tr>
<td>One-pot polyol synthesis</td>
<td>1009.2</td>
<td>81.6</td>
<td>11.36</td>
<td>Disordered</td>
<td>[28]</td>
</tr>
<tr>
<td>Polyol method</td>
<td>900</td>
<td>96.4</td>
<td>24.1</td>
<td>Disordered</td>
<td>[36]</td>
</tr>
<tr>
<td>Sonication induced scission</td>
<td>~620</td>
<td>93.42</td>
<td>24.1</td>
<td>Disordered</td>
<td>[37]</td>
</tr>
<tr>
<td>Dynamic heating method using</td>
<td>Not</td>
<td>95.0</td>
<td>35.0</td>
<td>Disordered</td>
<td>[38]</td>
</tr>
<tr>
<td>IR-light</td>
<td></td>
<td>defined</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyol process</td>
<td>625</td>
<td>84.0</td>
<td>15.2</td>
<td>Disordered</td>
<td>[39]</td>
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<td>Etching liquid-phase synthesis</td>
<td>~500</td>
<td>93.0</td>
<td>10.0</td>
<td>Disordered</td>
<td>[40]</td>
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<tr>
<td>Polyol process</td>
<td>Not</td>
<td>86.0</td>
<td>90.0</td>
<td>Disordered</td>
<td>[41]</td>
</tr>
<tr>
<td>Coating method</td>
<td>~833</td>
<td>86.0</td>
<td>38.0</td>
<td>Disordered</td>
<td>[42]</td>
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<tr>
<td>Transfer printing and pressing</td>
<td>~375</td>
<td>93.4</td>
<td>11.5</td>
<td>Disordered</td>
<td>[43]</td>
</tr>
<tr>
<td>Polyol process</td>
<td>~166-583</td>
<td>81.0</td>
<td>130</td>
<td>Disordered</td>
<td>[44]</td>
</tr>
<tr>
<td>Bar coating</td>
<td>444-500</td>
<td>90.3</td>
<td>0.745</td>
<td>Disordered</td>
<td>[45]</td>
</tr>
<tr>
<td>Meyer rod method</td>
<td>1000-1250</td>
<td>91.8-93.9</td>
<td>14.4-17.6</td>
<td>Disordered</td>
<td>[46]</td>
</tr>
<tr>
<td>PVP-mediated polyol method</td>
<td>&gt;400</td>
<td>92.5</td>
<td>~20.0</td>
<td>Highly ordered and side by side placed</td>
<td>[Present]</td>
</tr>
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</table>

The photoluminescence spectrum of silver nanostructures greatly depends upon the size and shape of the nanostructures, and here is used to study emission properties of AgNWs. The PL spectrum in the visible region is associated with the deep holes. These deep holes cause the green red and yellow emissions. While the shallow holes produce blue and violet emissions. Already AgNPs have shown green emission at about 540 nm [47]. The PL spectrum of as-synthesized
AgNWs was excited at 300 nm and the spectrum was observed from 600 to 800 nm wavelength range. In Figure 3(c), the PL spectrum of AgNWs show a broader PL region with high intensity peaks at 657 and 718 nm. These peaks depict transition at different energy levels within the band gap. So, the AgNWs prepared in this experiment give red emission which is attributed to the deep holes.

Figure 3(d) shows the transmittance spectrum of AgNWs loaded PET film. In the present experiment, the PET film has shown a transmittance of 92.5% in the visible region and a sheet resistance of 19.8 Ω in contrast to traditional ITO film provided with lower electrical conductivity and higher transmittance values. The SEM analysis of as-synthesized AgNWs shows that these nanowires exhibit substantial noodles like parallel alignment to each other throughout the region. Usually, special attempts are taken to purify the nanowires [34], but in our case no extra attempts are required to purify as-synthesized AgNWs and the SEM images show a high yield of self-arranged, impurity-free arrays of AgNWs with 100% product yield. Much literature has shown fabrication of conducting PET film while using disordered AgNWs, and thus there is a need of fused intersections of nanowires in order to improve the conductivity and transmittance of PET film [48]. Herein, the end to end arranged nanowires with high yield do not require any additional pressing treatments to achieve nanowires interactions and this ordered assembly not only appears with reduced PET film roughness and resistance but with improved transmissivity.
Figure 4. (a & b) SEM images of as-prepared AgNWs in high yield. (c) A histogram showing the distribution of AgNWs length in prepared sample. (d) An electric circuit showing conductivity through AgNWs loaded PET film (with sandwiched logo print of the of *The Islamia University of Bahawalpur*) while a white LED is lit. The circuit is placed on a glass table. A print of the logo depicted in figure 4(d) was used with the permission form the *The Islamia University of Bahawalpur*.

Thus, AgNWs having length and diameter of about 35-40 µm and 75-97 nm, respectively, are frequently formed in the reaction. The histogram in Figure 4 shows that some nanowires grow up to 4.7 µm in length. The aspect ratio calculated turns out to be more than 400. The length of
silver nanowires may vary predominantly by changing the PVP/AgNO₃ ratio, as reported earlier [28]. The ordered-arrangement of silver nanowires may improve the conductivity and flexibility of PET film when AgNWs ink is coated on it. This flexible and transparent film is bended to demonstrate its curved surface and flexibility (Figure 2). To test electrical conductivity of the film, a white LED is used connected to a pair of batteries and PET film in series to form a closed loop. Thus the study gives a simple, cheap, eco-friendly and non-toxic method to prepare thin, flexible transparent conducting films that could prove very beneficial for flexible transparent optoelectronic devices and could be used in the place of usual ITO films.

**Conclusion**

In summary, a high yield of 100% pure and ordered arrays of silver nanowires were obtained by using a convenient template free polyol method. We prepared AgNWs with an average length of about 35-40 µm and a mean diameter of approximately 86 nm. The XRD analysis conformed the crystallinity of the AgNWs structures. The AgNWs aqueous solution exhibited a broad PL emission band in the red region. The SEM images confirmed that the final product was free from impurities *i.e.* silver nanoparticle, thus eliminating the presence of other nanostructures that could affect the optical and conduction properties, and hence roughness of the film. Silver nanowires ink formulated by adding HEC in aqueous solution of silver nanowires, was then loaded onto the surface of PET film by simple mechanical pressing. The transmittance of AgNWs coated PET film was calculated to be 92.5% at about 20 Ω sheet resistance that can make it possible substitute to traditional ITO films in optoelectronics technology.
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