COPPER NANOWIRES AND GRAPHENE NANO-COMPOSITE BASED ELECTRODES WITH HIGH TRANSPARENCY AND CONDUCTIVITY

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ABSTRACT
In this paper, we present ITO-free hybrid transparent conducting electrodes that are based on bilayers of reduced Graphene Oxide (rGO) and Copper Nanowires (CuNWs). The unique structural features of these in-house fabricated electrodes allowed for superior performance with an optical transmittance of 84% and sheet resistance of 21.7 Ω/sq obtained, showing their potential of becoming a replacement for ITO based electrodes. The fabricated hybrid electrodes exhibited extreme stability when subjected to various environmental and durability tests. Adoption of such high performance TCEs, will lead to simple, versatile and cost effective solutions for next generation optoelectronics industry.

INTRODUCTION
Transparent conducting electrodes (TCEs) are a part and parcel of many optoelectronic devices including liquid crystals, flat panels, touch panels, organic light emitting diodes (OLEDs) and solar cells [1]. The TCEs are most commonly fabricated using Indium Tin Oxide (ITO) as a conducting medium [1,2]. However ITO has a couple of drawbacks associated with it, mainly ITO’s brittleness and indium’s scarcity [1,3,4]. In addition to that, the production of ITO requires cost-intensive vacuum and high-temperature process, thus making ITO unlikely to be a material of choice for future opto-electronic devices [5]. To address the issues related to ITO, significant amount of research has been devoted, for the development of a low cost, flexible and versatile TCEs that could be integrated into future opto-electronic devices. Promising electrode technologies should have a sheet resistance and visible region transmittance close to 100 Ωm/sq and 90%, respectively, in order to be considered as a promising ITO replacement [6]. Currently, the materials that are being investigated comprise of conducting polymers, carbon nanotubes, Graphene, metal nanowires and grids [2-6].

Our study deals with the fabrication of TCEs that are based on copper nanowires (CuNWs) and reduced Graphene Oxide (rGO). Initially, high aspect ratio CuNWs were synthesized and combined with rGO, using spray coating. Later the samples were annealed in order to produce hybrid electrodes with high optical transmittance and sheet conductance.

The fabricated electrodes were characterized for their morphology using Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM) equipment. The stability of the sample electrodes was characterized, by executing various environmental and flexing tests.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Subscripts</th>
<th>Description</th>
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<tbody>
<tr>
<td>TCEs</td>
<td>Transparent Conducting Electrodes</td>
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<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
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<tr>
<td>CuNWs</td>
<td>Copper Nanowires</td>
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<td>GO</td>
<td>Graphene Oxide</td>
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<tr>
<td>rGO</td>
<td>Reduced Graphene Oxide</td>
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<td>Ni(acac)₂</td>
<td>Nickel(II) acetylacetonate</td>
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<tr>
<td>CuCl₂</td>
<td>Copper Chloride</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl Alcohol</td>
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<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<td>TEM</td>
<td>Transmission Electron Microscope</td>
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<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>Rₙ</td>
<td>Initial Sample Sheet Resistance</td>
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<tr>
<td>R/Rₙ</td>
<td>Normalized Sheet Resistance</td>
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EXPERIMENTAL

(A) Synthesis of Copper Nanowires

The synthesis of copper nanowires was carried out using a single step solution based process reported by Guo et al [7]. Initially, 1.6 mmol Copper Chloride (CuCl₂) and 0.8 mmol Ni(acac)₂ were added to 20ml of Oleylamine solution, in a round bottom 3-neck flask, purged with high purity Argon. The mixture was kept at 80°C for 30 minutes and was stirred continuously. After the full dissolution of materials was achieved, the temperature was increased to 175°C in order to initiate the growth of nanowires, governed by (1).

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\[
\text{CuCl}_2 \xrightarrow{175^\circ \text{C}} \text{Ni(acac)}_2 \xrightarrow{\text{Oleylamine (Solvent)}} \text{CuNWs}
\]

The temperature of the flask containing high purity Argon, was maintained at 175°C for 10 hours in order to achieve a complete synthesis. During this tenure the solution underwent a series of color changes from dark blue to clear brown and finally to opaque red. At the end of the reaction, the solution was allowed to cool down and excess hexane was added to the flask to precipitate the nanowires from the solution. Then, the solution was centrifuged at 6000 rpm for 15 minutes in order to separate the CuNWs from the solvent. The separated CuNWs were transferred into Toluene, in the end.

**B Fabrication of Transparent Conducting Electrodes**

Extremely thin conducting layers of materials were deposited on both glass and PET (flexible) substrates. Initially, the substrates were cleaned via ultra-sonication using acetone, methanol and deionized water. IPA has been proven as an effective solvent in fabricating silver nanowire electrodes via spray coating and showed promising results during the fabrication of CuNWs electrodes, in this study [8]. In order to deposit a percolating layer of copper nanowires on the substrate, the copper nanowires were separated from Toluene and transferred into Isopropyl Alcohol (IPA) solution containing 1wt% of PVP (Polyvinylpyrrolidone). The solution containing nanowires was centrifuged to wash out excess PVP and the resultant nanowires were re-transferred to IPA.

In order to deposit a layer of nanowires, spray coating technique was used, owing to its simplicity and ability to fabricate large scale homogenous coatings and specific patterns [2]. During layer deposition, the substrates were laid on a horizontal hotplate, which was kept at 60°C in order to facilitate the evaporation of solvent and thus to prevent coffee-stain effect that compromises the homogeneous deposition of films.

Hybrid TCEs were created by depositing a layer of Graphene Oxide (GO) onto the substrates. Initially, GO platelets contained in the aqueous solution (commercially-available from Graphene-Supermarket) were separated from the solution and then diluted with IPA to 0.01 mg/ml, which was later sprayed onto the substrate. The density of nanowires and GO was controlled by the concentration and volume of suspension solution sprayed on the substrate.

Lastly, the fabricated electrodes were annealed in a forming gas environment (95% Nitrogen + 5% Hydrogen) at temperatures ranging from 100°C to 300°C. Annealing the samples helped in restoring the conductivity of the samples by burning off the PVP coating on NWs and reducing GO. Furthermore, annealing also improved the structure of rGO by restacking Graphene sheets and thus enhancing conductivity [6, 9]. A schematic representation of the fabricated electrodes is presented in Figure 1.

**RESULTS AND DISCUSSION**

The morphology of the fabricated, hybrid conducting electrodes was studied with the help of various microscopy research facilities. Initially, the samples were characterized using SEM.

**Figure 1.** A schematic representation of hybrid transparent conducting electrode comprising of CuNWs network and rGO buffer layer (a) 3D view (b) top view.

**Figure 2.** SEM characterization (a) Distribution of CuNWs (b) rGO layer on top of NWs network

As it can be seen from Figure 2 (a), the nanowires are homogeneously distributed, forming a connected network that spreads throughout the sample thus guaranteeing superior conductivity. The synthesized nanowires showed a high length to diameter aspect ratio of 72.9 µm/44.5 nm. This has improved the electrode transmittance without compromising conductivity,
by creating large area voids and allowing homogenous distribution. Figure 2 (b) shows the rGO layer on top of CuNWs, which serves as a passivation layer, preventing the bi-directional diffusion of impurities.

The internal structure of nanowires is very important as it has a direct effect on the conductivity and durability of the nanowires. As can be depicted in the TEM image of Figure 3, the nanowires synthesized during our study, have a solid core.

![Figure 3. TEM image showing the internal structure of copper nanowires](image)

The nature of contact between nanowires was characterized using AFM. The fabrication and treatment process resulted in nanowires that are fused (because of annealing), into each other at the point of intersection as seen in Figure 4, demonstrated by the fact that there is no difference in height between the overlapping nanowires. The fusion of nanowires is believed to give mechanical stability to the NWs network and enhance conductivity of the electrode [9].

![Figure 4. AFM image showing the fusion of nanowires at the junction and the height of overlapping nanowires](image)

Apart from the morphological characterization, the stability of the nanowires was also characterized, using various tests. Two different sets of samples, were prepared: ones without and ones with rGO buffer layer, on top of the CuNWs. Both of the sets were exposed to various environmental conditions. Initially, the samples were exposed to harsh environmental conditions (i.e. temperature 80°C and humidity level of 80%), for a time period of 48 hours. At the end of the test, the sheet resistance of the CuNWs/rGO hybrid TCE remained unchanged, whereas the sheet resistance of the CuNWs sample almost doubled reaching a final sheet resistance of 61 Ω/sq, as shown in Figure 5 (a). When exposing the samples to ambient environment, for a time period of 30 days, an increase of 33% and 89% was noted in sheet resistance for CuNWs/rGO and CuNWs electrodes, respectively, Figure 5 (b). This shows the superiority of CuNWs/rGO electrode over the CuNWs TCEs, in terms of environmental stability.

![Figure 5. Environmental stability tests (a) Harsh environment test (b) Ambient environment test](image)

The durability of hybrid CuNWs/rGO electrodes was also tested at high bending strains. The hybrid transparent conducting electrode tend to have no notable difference in the sheet resistance after 1000 folding cycles, as depicted in Figure 6.
The reason behind such remarkable durability results, is that GO layer is acting as a passivation layer and preventing moisture and impurities from getting into the samples and oxidizing the nanowires. Furthermore, it also prevents the nanowires from loosening up and keeps the annealed overlapping, intact.

While establishing a performance comparison (in terms of sheet resistance and transmittance), it can be seen in Figure 7 that the in-house fabricated electrodes exhibited a performance that is quite comparable to ITO and surpasses the performance of similar TCEs, mentioned in the literature [7,10]. It is believed that the high aspect ratio of the copper nanowires is the main reason behind this superior performance. So far, our best performing CuNWs/rGO electrodes have a sheet resistance of 21.7 Ω/sq and a transmittance of 84% at 550 nm wavelength.

It was quite interesting to note that when the conventional CuNWs/rGO TCE configuration was reversed, i.e. with rGO layer underneath the copper nanowires (rGO/CuNWs), the performance of one of the TCEs surpassed that of ITO. This configuration requires further investigation and is deemed useful when considering a multilayer configuration with rGO/CuNWs electrode serving as a base.

CONCLUSION

We fabricated hybrid transparent conducting electrodes, by spray-depositing homogenous layers of CuNWs and rGO on Glass and PET substrates. The hybrid electrodes exhibited a performance that is comparable with ITO, if proper annealing environment is provided. Also, the reduced graphene oxide acted as a passivation layer, protecting the CuNWs from oxidation and diffusion of impurities, when exposed to various environmental conditions. Furthermore, the annealed hybrid electrodes showed no signs of degradation when gone through numerous bending cycles, indicating superior durability. This suggests that the CuNWs/rGO based TCEs may be a potential alternative for ITO for a wide range of optoelectronic applications.

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