Transparent conducting electrodes based on thin, ultra-long Copper nanowires and graphene nano-composites

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Abstract

High aspect-ratio ultra-long (> 70 μm) and thin (< 50 nm) copper nanowires (Cu-NW) were synthesized in large quantities using a solution-based approach. The nanowires, along with reduced graphene-oxide sheets, were coated onto glass as well as plastic substrates, thus producing transparent conducting electrodes. Our fabricated transparent electrodes achieved high optical transmittance and low sheet resistance, comparable to those of existing Indium Tin Oxide (ITO) electrodes. Furthermore, our electrodes show no notable loss of performance under high temperature and high humidity conditions. Adaptations of such nano-materials into smooth and ultrathin films lead to potential alternatives for the conventional tin-doped indium oxide, with applications in a wide range of solar cells, flexible displays, and other opto-electronic devices.

Keywords: Copper nanowires, graphene, transparent conductive thin film, nano-materials.

1. Introduction

Transparent conductive electrodes (TCEs) are important components of opto-electronic devices, such as display, touch screens, light-emitting diodes, and solar cells [1-5]. Among such applications, transparent conductive metal-oxides (especially Tin-doped Indium Oxide) have been extensively researched and used in devices due to their superior optical transparency and electrical conductivity [6-8]. Due to the scarcity of indium on earth, the price of ITO is soaring; in addition ITO is brittle and therefore not suited for flexible devices. These drawbacks have driven researchers to find replacements for ITO using other materials.

ITO thin films with 10 Ω/sq sheet resistance can transmit ~ 84% of the visible spectrum. For commercial substitutes of ITO, optical transmittance greater than 90% and sheet resistance lower than 100 Ω/sq are usually considered the minimum requirement. To find such substitutes, researchers have focused their attention on nano-materials. Carbon-based materials such as graphene [1-4] have shown excellent carrier mobility and optical transparency. However, high-quality graphene is currently grown via chemical vapor deposition (CVD) and faces the challenges of large-area and inexpensive fabrication [9-10]. Percolating metal nanowire networks also exhibit excellent electrical conductivity and optical transparency. Transparent electrodes based on silver nanowires have already been commercialized and used in devices [11,12]. Recently, copper nanowires have drawn increased attention due to their comparable bulk resistivity to silver and their lower cost [13,14].

In this work we use a catalytic effect to synthesize ultra-long copper nanowires and combine the material with reduced graphene oxide (rGO), turning the combination into smooth thin films with high optical transmittance and good electrical conductivity. These hybrid TCEs fabricated with Cu-NW and rGO exhibit great durability under harsh environments. Moreover, when fabricated on certain plastic substrates, they are flexible and withstand numerous cycles of bending, leading to their potential for applications in high-performance opto-electronic devices.

2. Experiments

2. 1 Chemicals and materials

Oleylamine, technical grade, 70% (Sigma-Aldrich, O7805); Copper(II) Chloride anhydrous ($CuCl_2$), ≥ 99.995% trace metals basis (Sigma-Aldrich, 451665); Nickel(II) Acetylacetonate $Ni(acac)_2$, 95% (Sigma-Aldrich, 283657); Polyvinyl pyrrolidone (PVP) (Sigma-Aldrich, PVP40); Graphene Oxide (GO), single layer > 80% (Graphene-Supermarket, UHC-GO-60).

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2. 2 Synthesis of narrow, ultra-long copper nanowires

Copper nanowires are synthesized using a solution method described by Guo *et al* [15]. Briefly, 20 ml of Oleylamine was pipetted into a 50 ml capacity round-bottom 3-neck flask, in which temperature was precisely controlled by the Glas-Col Digi-II system. Subsequently 1.6 mmol Copper Chloride and 0.8 mmol $Ni(acac)_2$ were added to the flask. The flask was purged with high purity Argon while adding the chemicals. The mixture was vigorously stirred and kept at 80°C for 30 minutes to achieve a full dissolution that had a dark blue color. Then the temperature was ramped up to 175°C to initiate the anisotropic growth of copper nanowires. The flask was kept at this temperature for at least 10 hours to complete the synthesis, during which high-purity Argon was purged into the flask. During the reaction, the solution underwent color changes from dark blue to clear brown to opaque red. After the reaction was completed, the red suspension was allowed to cool down to room temperature. Excess hexane was added to the flask to precipitate the nanowires from the solution. Copper nanowires were then separated from the solvent via centrifugation (6000 rpm, 15 minutes, multiple times). The Cu-NWs were subsequently transferred into Toluene.

2. 3 Fabrication of Cu-NW, Cu-NW/rGO Transparent Conducting Electrodes (TCEs)

Gold Seal Microscope slides ($3'' \times 2''$) were cut into square pieces ($1'' \times 1''$). The substrates were cleaned with acetone, methanol, and deionized water via bath ultra-sonication for 10 minutes. A hot plate was kept at 60°C to facilitate the evaporation of solvent, preventing the so-called "coffee-stain effect" from large droplets while spraying. A solution of Cu-NWs in Toluene was initially used for spraying, and the coffee-stain effect was observed, compromising the homogeneity of our thin films. Isopropyl Alcohol (IPA) has been proven as an effective solvent in fabricating silver nanowire TCEs via spray coating, and so we adopted this method to achieve similar results [12]. To make a homogeneous IPA suspension of synthesized copper nanowires, the nanowires were separated from the original solvent via centrifuging and re-dispersed in an IPA solution containing 1 wt% of poly-vinyl(pyrrolidone) (PVP). The solution was centrifuged again to wash out the excess PVP, and the nanowires were transferred into IPA. The nanowire-density of the TCEs fabricated using spray coating was controlled by the concentration and volume of the suspension sprayed on the substrate. Both rigid glass and flexible plastic substrates were used for spraying.

Graphene Oxide (GO) aqueous solution was purchased from Graphene-Supermarket. The Graphene Oxide platelets were first separated from the original solution via centrifugation, and then diluted with IPA to 0.01 mg/ml before spraying.

2. 4 Annealing of TCEs

Our fabricated thin films were initially non-conductive due to the polymer coating of the nanowires, as well as poor contact between wires at wire junctions, thus requiring an annealing step. Thermal annealing was carried out in a forming gas environment (95% Nitrogen + 5% Hydrogen) at various temperatures (100°C to 300°C).

3. Results

3. 1 Characterization

The as-synthesized Cu-NWs were characterized with an optical microscope (Zeiss Axio Imager Z2), a scanning electron microscope (Hitachi S-4800 Type II), and an atomic force microscope (Digital Instruments Dimension 3100 SPM, tapping mode). Optical transmittances were measured by Cary UV-Vis-NIR spectrophotometer and corrected with blank substrates. Sheet resistances were measured with a four-point probe (SRM-232-2000).

3. 2 Results and Discussion

The synthesized Cu-NWs were examined with SEM (as shown in Fig.1a). Fifty nanowires were randomly selected from the images to determine the distribution of their lengths and diameters. The average wire length was found to be 72.9 μm, and the average wire diameter was 44.5 nm.

No surface functionalization of substrates is necessary prior to deposition of the Cu-NWs or Graphene-Oxide (GO) platelets. The density of Cu-NWs and GO deposited on the substrates can easily be controlled by varying the sprayed volume and/or concentration of materials. Spraying Cu-NWs in Toluene leaves coffee stains on the substrate as shown in Fig.2a. IPA has been proven to be a good solvent for spray-coating silver nanowires [12]. Originally, the as-synthesized Cu-NWs dispersed poorly in IPA. To make a homogeneous suspension, Cu-NWs were first centrifuged and separated from Toluene, and then dispersed in a 1 wt% PVP solution of IPA. Excess PVP was washed away by centrifuging and re-dispersing the nanowires. Spraying with the IPA suspension of Cu-NWs yielded a homogeneously distributed nanowire network on substrates, as shown in Fig.2b.

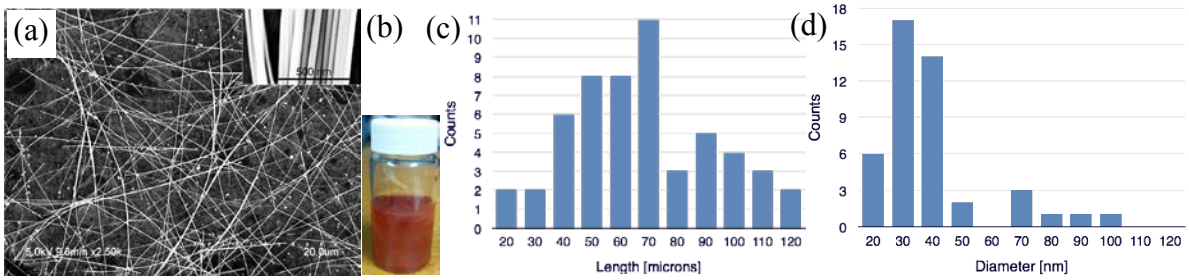

Figure 1. (a) SEM image of synthesized copper nanowires on glass substrate. The inset shows a bundle of nanowires at higher magnification. (b) Photograph of Cu-NW suspension in a glass vial. (c) Histogram of lengths of approximately fifty randomly selected nanowires, averaged at 72.9 μm. (d) Diameter histogram of approximately fifty randomly selected nanowires, averaged at 44.9 nm. The resulting aspect ratio (length/diameter) is ~1600.

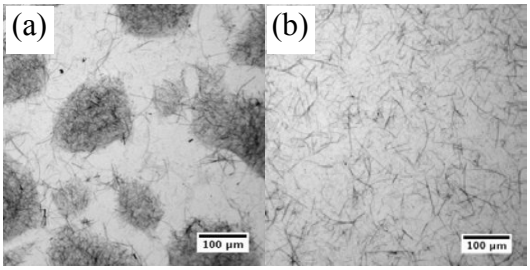

Figure 2. Optical microscope images of spray-coated Cu-NW film on glass substrates. (a) Toluene used as solvent. (b) IPA used as solvent.

GO suspension was sprayed on top or underneath the Cu-NW thin films. Proper dilution of GO suspension is necessary to achieve homogeneously distributed GO platelets on substrates.

Neither the Cu-NW nor the GO films were electrically conductive after deposition. Cu-NWs were prevented from forming good contact with each other due to the PVP coating, while GO platelets needed to be reduced to restore their conductivity. The annealing process was carried out in forming gas environment (95% Nitrogen + 5% Hydrogen). To determine the optimum annealing temperature for the Cu-NWs, five samples with the same density of Cu-NW network were prepared and annealed at different temperatures (ranging from 100°C to 300°C) for an hour. The sample annealed at 100°C had sheet resistance greater than 2000 Ω/sq and therefore did not register on our four-point probe. The results show that annealing is most effective at 200°C, as both the average sheet resistance and standard deviation are better than those obtained at other annealing temperatures. Atomic force microscopy (Fig.3b) of a junction between nanowires reveals the fusion caused by annealing. The thickness of the wire junction is reduced compared to the sum of the thicknesses of individual nanowires, indicating the nanowires are fused at the contact junction, thereby decreasing the electrical resistance of the sample. The composite Cu-NW/GO electrodes were annealed at 200°C and the reduction of GO to rGO was indicated by the darkened color of the annealed thin film.

Cu-NW TCEs and Cu-NW/rGO composite TCEs were fabricated with various optical transmittances by changing the volume of Cu-NW sprayed on the substrates (Fig.4). The optical transmittances were measured with a Cary spectrophotometer and sheet resistances were measured with four-point-probe (different locations were chosen for measurement on each sample). By adding the rGO over-coating layer for passivation, not only were the average sheet resistances of the TCEs reduced, but also the standard deviations decreased significantly, indicating better uniformity of the thin film across the entire electrode (Fig.4b). With increasing density of nanowires on the substrate, both optical transmittance and sheet resistance decrease. Photographs of the fabricated TCEs indicate transparency and homogeneity of our spray-coated thin films. TCEs with an rGO film beneath a CuNW film were also fabricated (Fig.5a). These samples showed lower sheet resistance at the same optical transmittance level (5.9 ± 2.1 Ω/sq @ 83.7%), but the reasons for this behavior remain to be determined. A light pink color can be observed on the TCEs when the optical transmittance is lower than ~85%. The optical transmission spectrum of both Cu-NW and Cu-NW/rGO TCEs are seen to be reasonably flat over the entire visible and NIR spectrum, making them ideal for a wide range of applications.

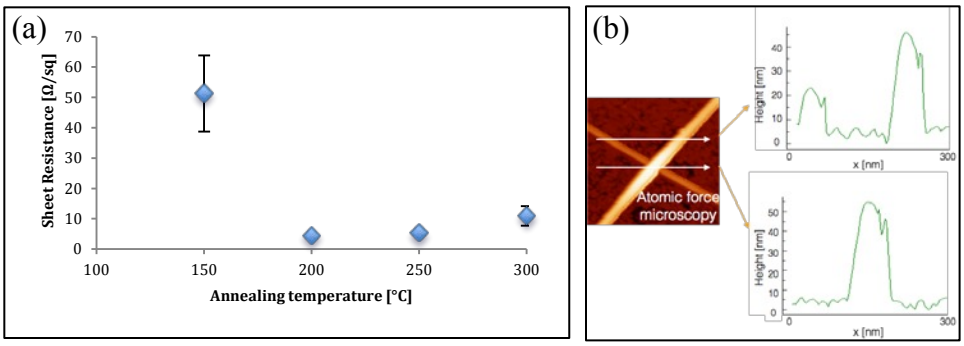

Figure 3. (a) Sheet resistance of Cu-NW TCE annealed at different temperatures, indicating that annealing is most effective at 200°C. (b) AFM image showing fusion at the junction between two overlapping copper nanowires.

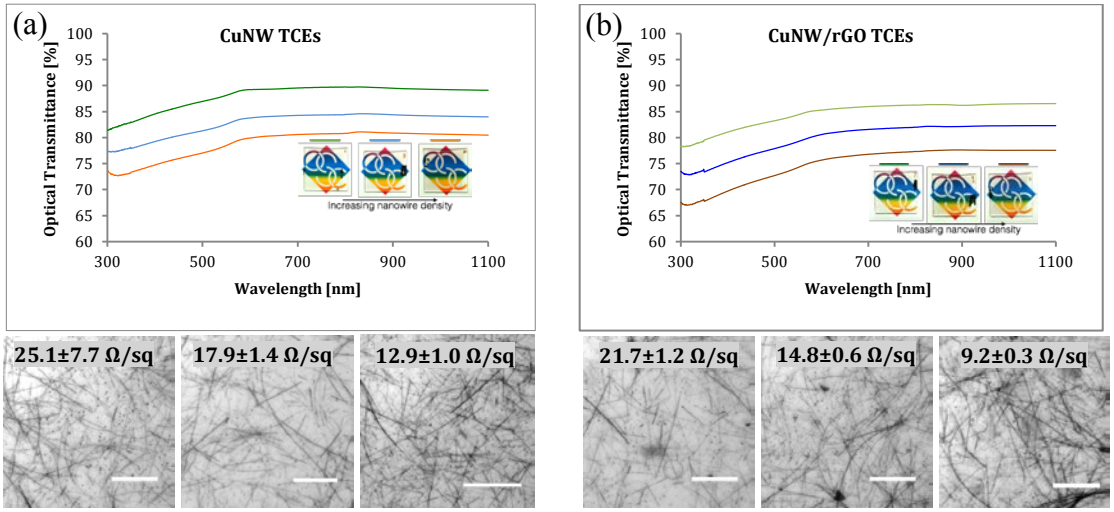

Figure 4. (a) Optical transmittance curves of Cu-NW TCEs; the inset shows a photograph of CuNW-TCEs on *College of Optical Science* logos; below are optical microscope images of corresponding TCEs; scale bar $= 100\ \mu m$. (b) Optical transmittance curves of Cu-NW/rGO TCEs; the inset shows photographs of the samples; below are optical microscope images of corresponding TCEs; scale bar $= 100\ \mu m$.

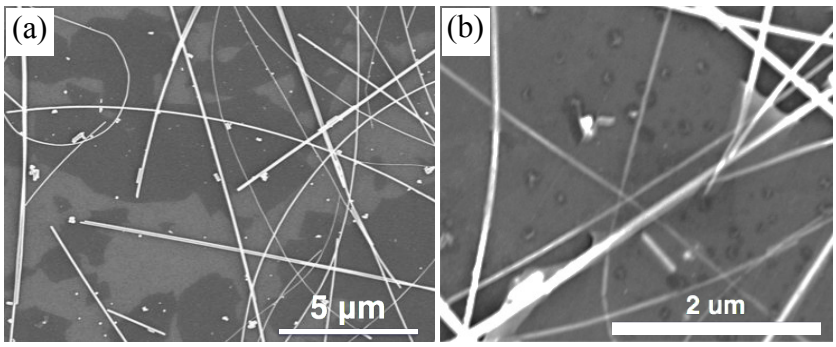

Figure 5. (a) SEM image of Glass/rGO/Cu-NW TCE with 5.9 ± 2.1 Ω/sq @ 83.7%. (b) SEM image of Glass/Cu-NW/rGO TCE with 19.0 ± 3.4 Ω/sq @ 84%. The nanowires are seen to be buried under the rGO thin film.

A plot of optical transmittance versus sheet resistance is shown in Fig.6. It can be seen that the TCEs fabricated in this work have better performance compared to those reported by Guo *et al* [15]. This is believed to be due to the higher aspect ratio of our synthesized wires, which leave larger voids in the deposited nanowire film.

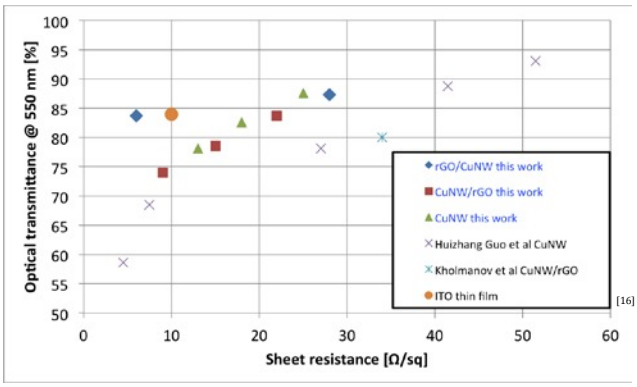

Figure 6. Plot of optical transmittance (at λ =550 nm) vs. sheet resistance.

One of the many concerns for contact electrodes used in solar cells is their long-term durability under harsh environmental conditions. The purpose of adding the rGO passivation layer is to protect the Cu-NW film from oxidation or degradation by impurity diffusion. To test the stability of the fabricated transparent electrodes, we measured the sheet resistance over a period of 48 hours in a harsh environment (80°C and 80% relative humidity, Fig.7a), and 30 days in ambient environment (Fig.7b). Our TCEs with rGO as passivation layer(s) show better stability than those with only Cu-NWs. The composite Cu-NW/rGO electrodes were also fabricated on flexible substrates; no noticeable change of sheet resistance was observed after 1000 bending cycles (Fig.7c).

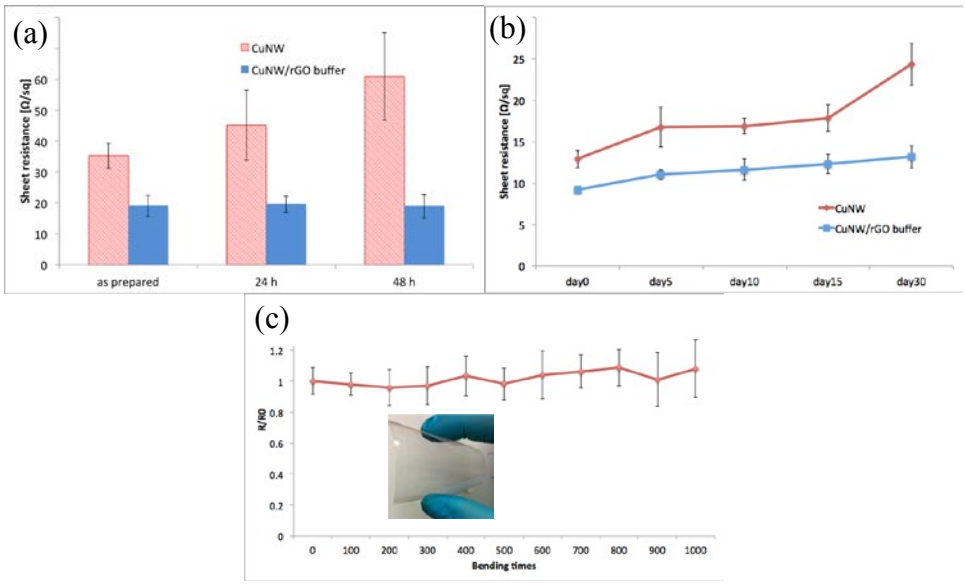

Figure 7. (a) Sheet resistance stability of CuNW TCE with and without rGO passivation under 80°C and 80% relative humidity after 48 hours. (b) Sheet resistance stability of CuNW TCE with and without rGO passivation in ambient environment over 30 days. (c) Normalized sheet resistance versus the number of bendings for a hybrid TCE on a plastic substrate (bending radius ~50 mm).

4. Conclusion

In this work, we synthesized copper nanowires with average length over 70 microns and diameters smaller than 45 nm in a one-step, low-temperature solution approach. These copper nanowires were spray-coated onto rigid glass substrates and also onto flexible substrates, and integrated with reduced graphene-oxide films to fabricate transparent conducting electrodes. After proper annealing, the as-fabricated TCEs exhibit superior optical transmittance and electrical conductivity, comparable to commercially available ITO thin films. In order to increase the durability of such

devices, Graphene Oxide was introduced as a buffer layer. The TCEs fabricated in this work can be utilized in solar cells, touch-screen displays, and other rigid as well as flexible opto-electronic devices.

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