Metal nanowire-graphene composite transparent electrodes

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ABSTRACT

Silver nanowires with 40 nm diameter and copper nanowires with 150 nm diameter were synthesized using low-temperature routes, and deposited in combination with ultrathin graphene sheets for use as transparent conductors. A systematic and detailed analysis involving nature of capping agent for the metal nanowires, annealing of deposited films, and pre-treatment of substrates revealed critical conditions necessary for preparing high performance transparent conducting electrodes. The best electrodes show ~90% optical transmissivity and sheet resistance of ~10 Ω/□, already comparable to the best available transparent electrodes. The metal nanowire-graphene composite electrodes are therefore well suited for fabrication of opto-electronic and electronic devices.

Keywords: transparent conductive electrode, silver-nanowire film, copper-nanowire film, graphene platelet, hybrid transparent conductive electrode.

1. INTRODUCTION

As the industry standard, Indium Tin Oxide (ITO) dominates the transparent electrode (TE) market for applications such as Organic Light Emitting Diodes (OLED), touch-screen displays, and Organic Photovoltaic Cells (OPC)[1-5]. This is possible due to the high optical transmittance and low electrical resistivity of the film[6]. There are certain drawbacks to the material, however, which allow for other alternatives to be competitive in the growing TE market. These drawbacks include: high cost and dwindling global supply of indium, and inherent rigidity of the material. Copper, on the other hand, is 1000 times more abundant than indium or silver, and is 100 times less expensive[7]. The market for transparent conducting electrodes is currently $4B (2013) and is projected to grow to $5.1B by 2020[8]. Current market alternatives to ITO in this growing market are: conductive polymers, carbon nanotubes, graphene, silver nanowires, and metal meshes. This non-ITO market is worth $1.6B and is expected to double in growth every year[8]. Our research focuses on the benefits from graphene-oxide films and copper and silver nanowires, particularly their low cost of synthesis and deposition. Due to the possibility of oxidation of silver and copper nanowires, we sought to use graphene materials to provide a passivation layer for the nanowire films, thus preventing oxidation and protecting the nanowire films against other contaminants in addition to improving their electrical conductivity.

2. MATERIALS AND METHODOLOGY

2.1. Materials

2.1.1. Synthesis of Copper Nanowires

Copper nanowires were synthesized in a one-step solution process following the procedure reported by Rathmell *et al*[9,10]. Briefly, in a three-neck flask, 20 mL of NaOH solution (15 M) was heated up to 65 °C. Copper (II) nitrate trihydrate (0.2 M, Sigma Aldrich) was added to the mixture along with 200 μL of ethylenediamine (60.10 MW, Sigma Aldrich) and stirred at 700 rpm for 5 minutes before the addition of 15 μL of hydrazine (35 wt%, Sigma Aldrich). The reaction was continued for 20 minutes. The resulting nanowire aggregates were removed from the solution, and were subsequently dispersed (with vigorous stirring) in a polyvinylpyrrolidone (10,000 MW, Sigma Aldrich) solution. After half an hour, the solution was centrifuged (5000 rpm, 10 minutes) and decanted several times to remove the by-products and excess particulates. The resulting aggregates were then dispersed in methanol for storage and deposition on substrates using the methods discussed below.

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2.1.2. Silver Nanowires

Commercial silver nanowires were purchased from Sigma Aldrich, having lengths ranging from 20 μm to 50 μm, and diameters from 120 nm to 150 nm. In addition, for purposes of cost reduction and characterization comparison, we synthesized our own silver nanowires via a polyol process similar to that reported by Sun *et al*[11]. Our synthesized silver nanowires have average length of 32 μm and diameter of 120 nm.

2.1.3 Graphene materials

Pristine graphene was synthesized through liquid exfoliation[13] to form sheets with areas between 4 μm^2 and 40 μm^2, primarily in the form of monolayers. Additionally, Graphene Oxide was purchased from Graphene Supermarket® in solution form (sheet areas ranging from 1 μm^2 to 20 μm^2).

2.2. Deposition of nanowire and hybrid films

2.2.1. Copper-nanowire film deposition on glass substrate

Spray-coating, and spin-coating were attempted for the preparation of uniform films from the metal nanowires. These methods are chosen for their speed, reproducibility, and scaling capability. Glass substrates were cleaned by sonication in acetone, methanol, and deionized water, before plasma cleaning in low-pressure air (1-5 torr) for 3 minutes. For spray-coating, the wires were dispersed in either methanol or isopropyl alcohol and sprayed using an airbrush (Paasche H) onto a heated substrate at 60 °C. Nanowires were deposited in multiple layers until a percolating film was achieved and then plasma annealed in low pressure air for 1 minute.

For spin-coating, nanowires were centrifuged before use and dispersed in chloroform. Solution was deposited via pipet on the substrate and spin-coated at low speed multiple times until a percolating film was achieved (1-4 layers, depending on the desired electrical conductivity). The film was subsequently plasma cleaned for 1 minute and then characterized.

2.2.2. Silver-nanowire film deposition on glass substrate

Glass substrates were cleaned using piranha solution (3 sulfuric acid: 1 hydrogen peroxide) for 30 minutes followed by sonication in deionized water before being plasma cleaned in low pressure air for 30 seconds. Silver nanowires were then spin coated onto the substrates at 1000 rpm and then plasma cleaned again for 30 seconds. Thermal annealing was also used to fuse the nanowires in a nitrogen-purged vacuum at 170 °C for 1 hour.

2.2.3. Silver nanowire/graphene hybrid films

After silver nanowires were spin coated onto glass substrates and plasma cleaned, pristine graphene platelets were spray-coated over the silver nanowire film using Argon gas (Paasche H airbrush). Alternatively, we used the method of spray-coating to deposit graphene oxide (instead of pristine graphene) platelets on top of silver nanowire films prepared in the aforementioned manner. Unlike pristine graphene, graphene oxide platelets needed to be reduced using the hydrazine vapor reduction process for 24 hours.

2.2.4. Copper nanowire/graphene hybrid films

To combine copper nanowire films with a graphene oxide film, first a percolating nanowire film was deposited on a substrate by successive spin coating (250 rpm, 1-4 times). Graphene oxide (0.2 mg/mL) was then spin-coated onto the copper nanowire film at 2000 rpm and reduced in a hydrazine vapor reduction process for 24 hours.

2.2.5. Copper/silver nanowire hybrid films

Copper nanowire solution (0.4 mg/mL) and silver nanowire solution (1 mg/mL) were mixed at 3:1 ratio, respectively and spin coated at 2000 rpm onto glass substrates.

3. CHARACTERIZATION

Nanowires were initially observed under an optical microscope (Zeiss Observer Z1) to survey lengths. After deposition in thin-film form, nanowires were viewed under high magnification to determine wire network density. Silver and copper nanowires, graphene, and graphene oxide were characterized via SEM (FEI Inspec-S) and

Scanning Probe Microscopy (Digital Instruments Dimension 3100 SPM). Fusion of wire junctions was viewed by cleaving and tilting the films under SEM and AFM. Film conductivity was measured with the four-point probe technique, and optical transmittance was determined via Cary 5000 UV-Vis-NIR Spectrophotometer in the wavelength range from 300 nm to 1100 nm.

4. RESULTS

4.1. Synthesis and deposition of Copper nanowire films

The as-synthesized and purified Cu-NW films were characterized using optical and electron microscopy. The resulting morphological evaluations are shown in Figs. 1(a)-1(c). The Cu-NW suspensions remain well dispersed in chloroform. The histogram obtained by a number of measurements of the microscopic images allowed us to analyze the dimensions of synthesized copper nanowires; see Fig. 2(a). The nanowires were found to be between 30 µm and 50 µm long, with diameters ranging from 120 nm to 500 nm.

Using spray-coating under Argon flow, we were able to achieve percolating films of copper nanowires with optical transmittances between 65−88% (at 550 nm). However, the films do not have any measurable electrical conductivity. After thermal annealing in a reducing atmosphere (5% Hydrogen, 95% Nitrogen) at 180 °C, the measured sheet resistance could be as low as 5 Ω/□. Spin-coated copper nanowire films were created using a number of coating cycles, and the measured transmittances were from 50−82% for sheet resistances of 2.5−700 Ω/□ after plasma annealing in low-pressure air for 1 minute (Fig. 3a). Drop casting copper nanowires in chloroform proved to be an effective method of deposition, achieving percolating layers with resistances of 5−15 Ω/□ after plasma annealing and 50−60% transmittance, but cannot be relied upon for consistent reproducibility. Vacuum filtration and transfer technique was also employed to create percolating films, but was discarded due to the amount of waste generated (Fig. 3b-c).

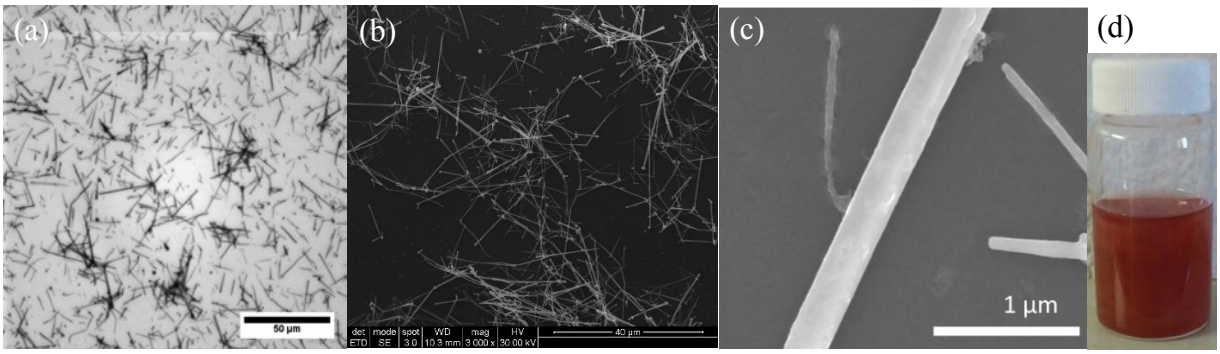

Figure 1. (a) Optical image of the synthesized copper nanowires. (b) SEM image. (c) Close-up SEM image showing wire diameters. (d) Homogeneous suspension of synthesized copper nanowires in a glass vial.

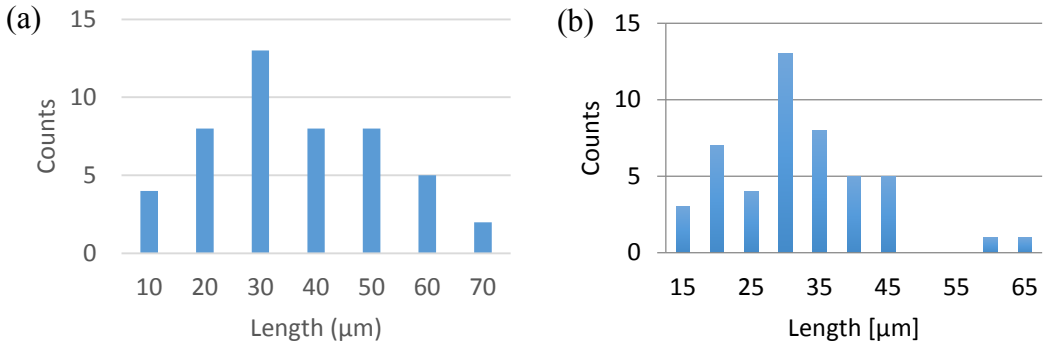

Figure 2. (a) Histogram of synthesized copper nanowire lengths. (b) Histogram of synthesized silver nanowire lengths. Both histograms were obtained from approximately fifty randomly selected nanowires.

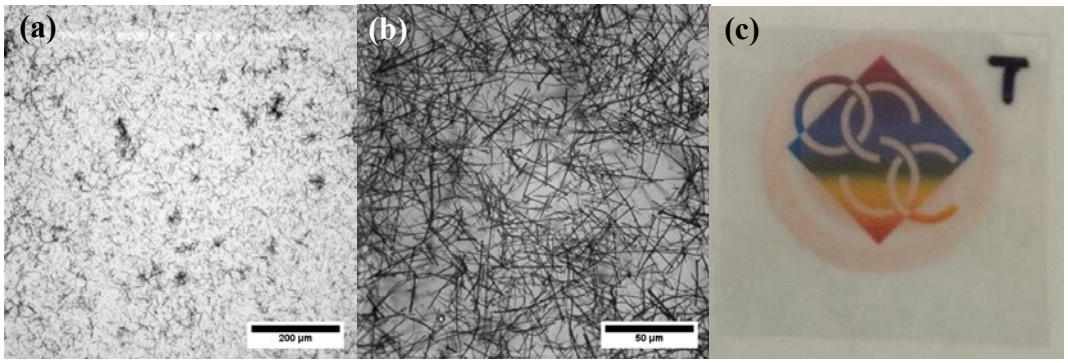

Figure 3. (a) Optical microscope image of spin-coated copper nanowire film. (b) Optical image of copper-nanowire film fabricated by vacuum filtration followed by transfer to a glass substrate. (c) Copper nanowire film fabricated by vacuum filtration followed by transfer to a plastic substrate (optical transmittance ~65%).

4.2. Synthesis and deposition of Silver nanowire films

The as-synthesized nanowires were dispersed in isopropyl alcohol and characterized using optical and electron microscopy. Figures 4(a)-4(c) summarize the morphological evaluations for our synthesized silver nanowires. The histogram obtained by a number of measurements of the microscopic images allowed us to analyze the dimensions of synthesized silver nanowires; see Fig. 2(b). The nanowires were found to be between 30 µm and 45 µm long, with diameters ranging from 90 nm to 150 nm. Prior to plasma cleaning or thermal annealing, the films achieved ~90% transmittance and sheet resistances greater than 2000 Ω/□. With our own synthesized Ag nanowires deposited using the same method as that used for commercially purchased wires, the optical transmittance was measured at 85% while the sheet resistance was found to be ~30 Ω/□ after plasma cleaning. Commercial silver nanowire films made in the same fashion yielded 2.5 Ω/□ for 75% transmittance and 91 Ω/□ for 95% transmittance.

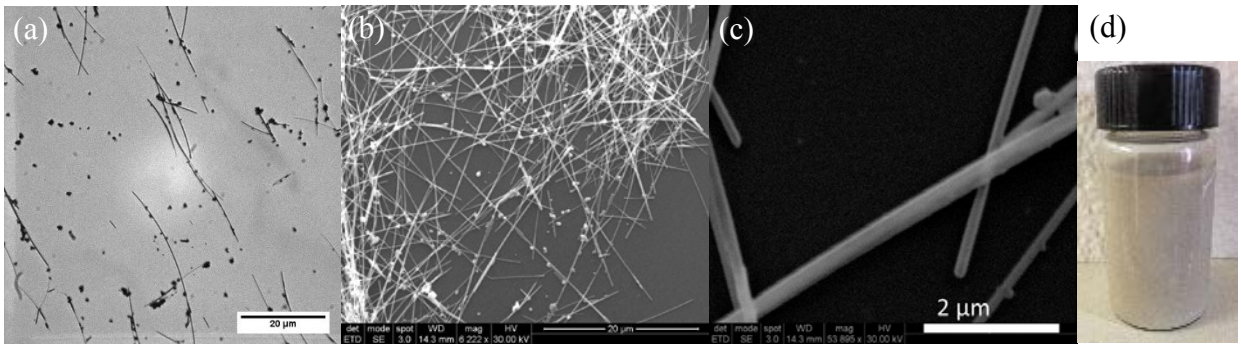

Figure 4. (a) Optical image of the synthesized silver nanowires. (b) SEM image of synthesized silver nanowires. (c) SEM image showing silver nanowire junctions. (d) Homogeneous suspension of synthesized silver nanowires in a vial.

4.3. Graphene material hybrid films

With commercially purchased silver nanowires and our own synthesized pristine graphene sheets [see Figs. 5(a)-5(c)], the sample with the best performance shows optical transmittance of 91% and sheet resistance of 11 Ω/□. We also tested the protective ability of graphene on silver nanowires. An environment of 80 °C and 80% relative humidity was created in a petri dish, and three samples were placed in it: annealed silver nanowires, Ag-NW with reduced Graphene Oxide (r-GO) buffer layer, and Ag-NW with pristine graphene buffer layer. After 48 hours, results show that graphene acts effectively as a buffer layer, helping to maintain the electrical conductivity of the film in this harsh environment; see Fig. 6(a). Long-term testing is still necessary to determine how long this passivation is effective for our nanowire films.

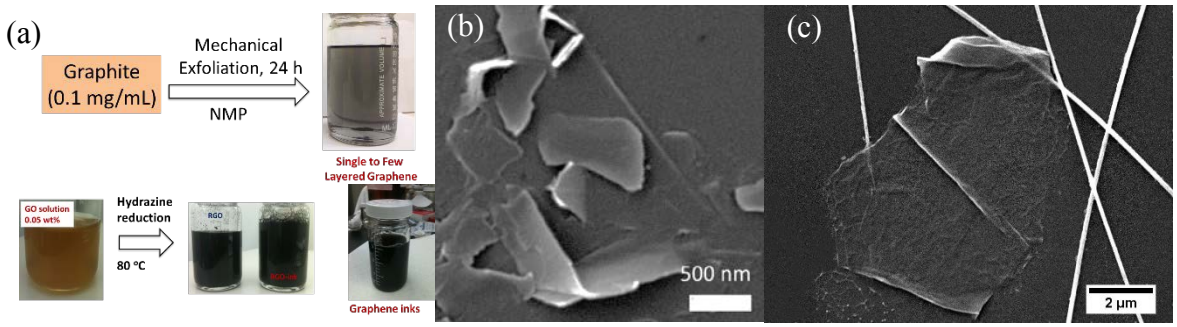

Figure 5. (a) Diagram showing liquid exfoliation for pristine graphene and reduction process for graphene oxide. (b) SEM image of graphene flakes deposited on a glass substrate. (c) SEM image of graphene flake with silver nanowires in a hybrid film.

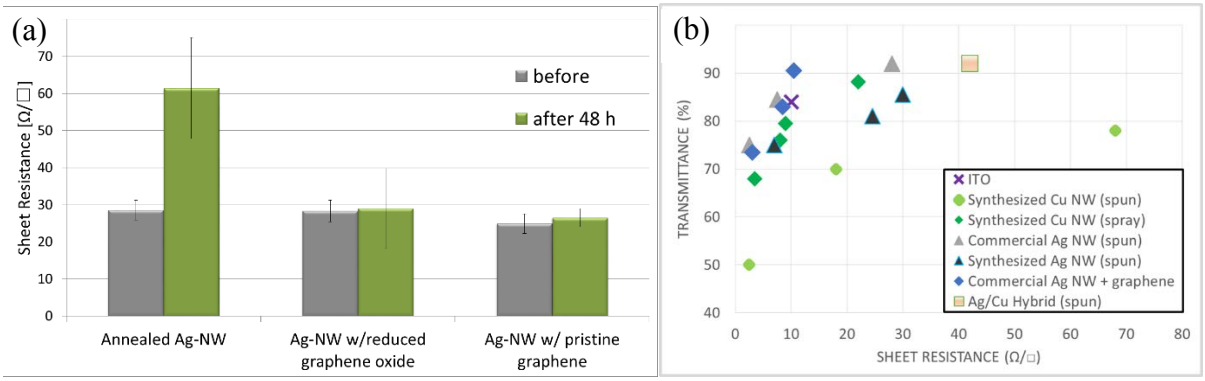

Figure 6. (a) Sheet resistance before and after harsh treatment at 80 °C and 80% relative humidity for silver and silver hybrid films. (b) Transmittance vs. sheet resistance for all reported materials and experimental methods in this work; also shown for comparison are the characteristics of conventional ITO transparent conductive electrode (×).

4.4. Silver/Copper nanowire hybrid films

These films exhibited no electrical conductivity until they were plasma cleaned for 1 minute, after which they yielded sheet resistance of 42 Ω/□ at 92% optical transmittance. This hybrid film, while achieving similar results to bare Ag-NW films and Ag-NW with graphene sheet [Fig. 6(b)], yields percolating films with mostly copper nanowires and only one-quarter of the (more expensive) silver material.

5. CONCLUSIONS

Hybrid metal-nanowire−Graphene films provide a protective layer for nanowires, while improving the electrical conductivity and optical transmittance of the transparent conductive electrode. While silver nanowire films have been used effectively as a transparent conductor, copper nanowires offer a significantly cheaper alternative, which can be spin-coated to produce electrically conducting films as well. Combining this method with spin- or spray-coating of graphene oxide allows for a conducting film and its buffer layer to be deposited quickly and cheaply. Copper nanowire films can be efficiently processed through plasma cleaning in low-pressure air environment, and may be further optimized for improved electrical conductivity by reduction in a forming gas environment. Not only can this process improve the conductivity of the wires and fuse them together, but also it reduces the graphene oxide in the same step. Silver/copper hybrid films provide an excellent alternative to silver nanowire films by providing similar transmittance and electrical conductivity, but with only one quarter the amount of silver needed otherwise.

Further investigation is necessary for these films, particularly long-term viability testing and thermal cycling, before they can be integrated into solar cells and other opto-electronic devices.

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