Title

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Journal

ACS Nano, 10(2)

ISSN

1936-0851

Authors

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et al.

Publication Date

2016-02-23

DOI

10.1021/acsnano.5b07651

Peer reviewed

Solution-Processed Copper/Reduced-Graphene-Oxide Core/Shell Nanowire Transparent Conductors

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Abstract

Copper nanowire (Cu NW) based transparent conductors are promising candidates to replace ITO (indium-tin-oxide) owing to the high electrical conductivity and low-cost of copper. However, the relatively low performance and poor stability of Cu NWs under ambient conditions limit the practical application of these devices. Here, we report a solution-based approach to wrap graphene oxide (GO) nanosheets on the surface of ultrathin copper nanowires. By mild thermal annealing, GO can be reduced and high quality Cu r-GO core-shell NWs can be obtained. High performance transparent conducting films were fabricated with these ultrathin core-shell nanowires and excellent optical and electric performance was achieved. The core-shell NW structure enables the production of highly stable conducting films (over 200 days stored in air), which have comparable performance to ITO and silver NW thin films (sheet resistance ~ 28 Ohms/sq, haze ~ 2% at transmittance of ~90%).

Keywords: Cu nanowires, graphene oxide wrapping, transparent conductors, solution-process, high stability, low haze

Transparent conducting electrodes play an essential role in many optoelectronic devices, such as displays (LCD & LED), photovoltaic devices, touch panels, and electrochromic windows.[1-3] Although indium-tin-oxide (ITO) has been the industrial standard for a long time, several issues remain.[4-7] ITO is relatively expensive, brittle (incompatible with flexible substrates), and shows strong absorption in the near-IR region, which is not ideal for photovoltaic and photodetector applications. Intense research efforts have been devoted to the development ITO replacements for next generation electronics.[8-11] Among these candidate replacements, metal nanowire (NW) films hold great promise for low-cost transparent electrode applications because of their excellent electrical and optical properties, as well as their solution-processibility.[12-16]

Recently, silver nanowires with an average diameter of 50 ~ 100 nm and an average length of ~100 μm have been successfully synthesized.[15,16] Highly transparent and conductive Ag NW based thin films have been fabricated and a low sheet resistance of <20 Ohms/sq with a transmittance of ~ 90% (at 550 nm) were achieved, which is similar to the performance of commercial ITO substrates.[16] However, two problems remain. First, silver is a rare metal and the material cost is high. Second, the diameter of the Ag NWs is large (~100 nm) resulting in strong light scattering.[17] This light scattering by the thick wires leads to large haze values, meaning that pixels in a display behind the transparent conductor become blurred. Copper nanowires are an attractive alternative to Ag. Copper has an intrinsic electrical conductivity similar to that of silver; it is 20 times cheaper than silver; and could potentially exhibit lower light scattering as the synthesis of ultrathin Cu NWs with an average diameter below 20 nm has been demonstrated.[18-22] Good optical and electrical performance was also obtained for Cu NW based transparent films by a number of groups.[18-22]

However, thin Cu NWs are intrinsically unstable under ambient conditions. Rapid surface oxidation of the Cu NWs reduces the conductivity dramatically, preventing the practical application of such transparent electrodes. To improve the stability of the Cu NWs films, several approaches have been examined. For example, over-growth of a layer of Ni on Cu NWs,[23] or coating the Cu NWs with a very thin layer of Al_2O_3 by atomic layer

deposition,[24] *etc*. Although the stability indeed improved, either the total transparency or the overall conductivity of the films decreased significantly. Another approach is to construct hybrid films consist of large graphene/graphene oxide sheets and metal NWs.[25-28] Ideally, to maintain high optical transparency and good electrical conductivity, coating or wrapping a very thin conformal layer of conductive and chemically stable material on the surface of the Cu NWs is desired. Recently, wrapping graphene on Cu NWs has been proposed to address this issue. By studying individual core-shell nanowires, it was found that the graphene coating could improve not only the stability, but also the electric and thermal conductivity of the Cu NWs.[29] To synthesize these structures, plasma enhanced chemical vapor deposition method (at 500 ~ 700 °C) was used to grow the thin layer of graphene on the metal NWs.[30-32] This procedure however is not compatible with the low-cost high-throughput production required for practical applications.

Here, we demonstrate a solution-based method to produce high quality ultrathin copper reduced-graphene-oxide core-shell nanowires. By controlling the surface chemistry, graphene oxide (GO) nanosheets are wrapped onto the Cu NWs surface to form a uniform coating with thickness of around 1 ~ 5 nm. The core-shell nanowires are highly stable in a variety of polar solvents while stored in air. We fabricated transparent conducting films using the core-shell nanowire colloidal suspensions that show excellent conductivity and significantly improved resistance toward oxidation. Moreover, the core-shell nanowire based films show reduced haze values compared to the undecorated Cu NW based films, making them particularly useful for information display panels.

RESULTS AND DISCUSSION

Figure 1 shows an illustration of the overall strategy of GO wrapping and film fabrication. The Cu NWs with an average diameter of ~ 17 nm were synthesized using our recently developed silane based chemistry.[22] To achieve uniform surface wrapping, GO nanosheets with an average diameter of ~ 10 nm were synthesized (see supporting information, Figure S1).[33] The as-synthesized Cu NWs are covered by oleylamine as the surface ligands and can be dispersed in non-polar solvent such as toluene. However, GO

is not soluble in toluene and a mixture of Cu NWs and GO nanosheets can only be achieved in a solvent with intermediate polarity. We found that the mixing and wrapping processes occur effectively in methanol with mild ultra-sonication and the resulting Cu GO core-shell NWs can be well dispersed in polar solvents such as methanol, ethanol, and isopropanol (IPA). The thin native oxide layer (1~3 nm) on the Cu surface (see ref 22 for the TEM images of the crystalline oxide layer) would have strong interactions with the hydroxyl and carboxyl groups. Since GO is highly oxidized, it serves as a multi-dentate ligand and interacts much stronger with the oxide surface than the monodentate amine based ligands. This provides large driving force for the ligand replacement.

Figure 2 shows the structural characterization of the Cu GO core-shell nanowires by a variety of techniques. Interestingly, after wrapping, the core-shell NWs form a very stable colloidal suspension in IPA for several days, whereas the as-synthesized Cu NWs aggregate after a few minutes in either toluene or IPA (Figure 2a-2c). These results provide evidence for successful GO wrapping. The well-dispersed NWs are important to film fabrication because strong aggregation can lead to larger effective wire diameter and stronger light scattering, and thereby reduce the performance. Figure 2d shows a typical transmission electron microscopy (TEM) image of a single GO wrapped Cu NW. It can be seen that a thin layer of GO with thickness of 1 ~ 5 nm has been coated uniformly along the Cu NW. A higher resolution image (Figure 2e) shows a clear interface between the crystalline Cu and amorphous GO nanosheets. Additional TEM images of the Cu NWs before GO wrapping and with different GO loading amount can be found in the supporting information, Figure S2. Figure 2f shows the Fourier transform infrared (FTIR) spectroscopy of the Cu NWs before and after GO wrapping. The signature of oleylamine at 2800 ~ 3000 cm^{-1} becomes negligible, while features corresponding to hydroxyl groups (3000 ~ 3500 cm^{-1}) and carbon-carbon double bonds of GO (~ 1600 cm^{-1}) appear for the GO wrapped Cu NWs. Furthermore, the energy-dispersive X-ray spectroscopy mapping on a single wire confirms the proposed core-shell architecture. As shown in Figure 2g-2k, Cu exists only in the core of the wire, while carbon and oxygen form a uniform thicker shell around the Cu wire. Together, these results indicate that the GO

nanosheets can be effectively wrapped onto the surface of the ultrathin Cu NWs, without changing the morphology of the Cu NWs.

Having demonstrated the ability to form the core-shell nanowire structures, we fabricated nanowire conducting films on glass using a filtration method. A dilute suspension of nanowires in IPA was vacuum filtered onto a filter membrane, after which the resulting film was transferred to a glass substrate by pressing against the open side of the membrane. The films were then annealed under argon with 10% hydrogen to reduce GO and any residual native copper oxides, and create an intimate contact junction between overlapping wires. A schematic of the process can be found in Figure S3.

Figure 3a shows the optical images of the core-shell nanowire transparent films with different loading amounts and the corresponding transmittance spectra from UV to near-IR. The films show high transparency from the UV-Visible range all the way to the infrared, which makes them suitable materials for not only display but also for multijunction photovoltaic cell or thermal applications. Figure 3b summarizes the transmittance *versus* the sheet resistance of different type of films. The black and blue curves indicate the performance of the Cu NW films and Cu GO core-shell NW films annealed at 200 °C, respectively. The core-shell NW films show significantly lower performance, probably because GO cannot be thermally reduced at 200 °C and this insulating layer prevents efficient charge transfer between individual Cu wires. It is known that GO can be effectively reduced under heating at over 250 °C and the reduced GO (r-GO) shows good electric conductivity. To improve the performance of our Cu GO core-shell NW transparent conductors by thermally reducing the GO layer, we annealed the films at higher temperature (up to 350 °C). As shown in Figure S4, the sheet resistance of the core-shell NW film decreases as the annealing temperature was raised to around 260 °C, while at even higher temperature the sheet resistance increases dramatically due to damage of the Cu NWs. Figure S5 shows the scanning electron microscopy of the films annealed at different temperature. The nanowire morphology is well preserved at 200 to 260 °C. At 300 °C, some very thin wires start to melt, and thick bundles of wires (~100 nm) form. At 350 °C, all of the nanowires melt and lose their

morphology. Note that the Cu NWs without GO coating begin to melt at lower temperature (~230 °C), indicating that the GO wrapped wires have higher melting points and better thermal stability. The optimal condition for annealing the Cu GO core-shell NW films was found to be 260 °C, which is higher than that of the Cu NWs without GO coating. Under this condition, the GO nanosheets can be thermally reduced to form r-GO, as indicated by the color of the power, the FTIR spectra, X-ray diffraction, and X-ray photoelectron spectroscopy studies (see Figure S6 for more details). The morphology of the core-shell NW was checked with high resolution TEM. As shown in Figure S7, the core-shell structure was well preserved after the thermal annealing. The pink curve in Figure 3b shows the performance of the high temperature annealed films. Interestingly, they show greatly enhanced performance compared to the 200 °C annealed core-shell NW films, and even better performance than the undecorated Cu NW films. For example, sheet resistances of 14.8 Ohms/sq at transparence of 86.5% (wavelength = 550 nm), 28.2 Ohms/sq at transparence of 89.3%, and 75.0 Ohms/sq at transparence of 93.9% were achieved, which are close to those of commercial ITO or silver NW transparent electrodes (red and green circles in Figure 3b).

The improvement can be attributed to the following. First, higher temperature annealing can effectively reduce GO and improve the connection and charge transfer between wires. We measured the thickness of individual nanowires and the thickness of the wire-to-wire junctions of the annealed films using atomic force microscopy (AFM) and the results are shown in Figure S8. The junction thickness was found to be very close to the sum of the thickness of individual wires. These results indicate that the core-shell nanowires likely do not melt together under the optimized annealing condition. Additionally, the r-GO layer facilitates electric conduction from wire to wire, because the thickness of the r-GO layer is very small and the work functions of r-GO and Cu are similar, resulting in an Ohmic contact.[34] Second, the core-shell NWs form a better colloidal suspension, indicating less wire – wire interaction and aggregation. Therefore, during the filtration process, fewer large bundles form compared to the Cu NWs without GO coating. Third, similar to the case for graphene wrapped Cu NWs, the r-GO coating may also improve the electric and thermal conductivity of the individual Cu NW itself.[29]

The stability of the transparent films in air was studied to demonstrate the advantages of the GO wrapping approach. Three types of conducting film were recorded: Cu NWs (200 °C annealed), Cu GO core-shell NWs (200 °C annealed), and Cu r-GO core-shell NWs (260 °C annealed). The sheet resistance of 5 films for each type at 80 °C (humidity = 40 ± 5 %) were recorded and the average values are summarized in Figure 4. The Cu NW films show poor stability and their performance degraded in a few hours at 80 °C. When wrapped with GO and annealed at 200 °C, the stability improved significantly. The sheet resistance of the Cu GO core-shell NW films doubled after 2 days at 80 °C. The Cu r-GO core-shell NW films show even better stability and no obvious degradation was observed, indicating the r-GO wrapping can effectively prevent Cu NW oxidation. We also examined the stability in high humidity and high temperature environment (temperature = 80 °C, humidity = 80 ± 5 %) and the results are shown in Figure S9. The Cu r-GO core-shell NW films show no obvious degradation after 48 hours, while the Cu NW films degraded in 2 hours. The slight improvement with higher-temperature thermal reduction is probably due to the enhanced packing of r-GO nanosheets, which limits the diffusion of oxygen molecules through the protecting layer. Figure 4b shows the absolute sheet resistance of the Cu r-GO core-shell NW films over 200 days storage in air. All the films show great stability and no obvious degradation was observed, while most of the Cu NW films became insulating after 1-2 months in air (Figure S10).

Haze is another important parameter that defines the quality of a transparent electrode. It is defined as the percentage of transmitted light that is scattered through a larger angle than a specified reference angle (*e.g.* 2.5°) with respect to the direction of the incident beam. It is particularly important for display applications, in which light scattering will greatly reduce the sharpness of the image and result in a blurred image. The haze of the nanowire mesh conducting film highly depends on the diameter of the nanowire and a previous study showed that our ultrathin Cu NWs can be used to produce conducting thin films with very small haze.[22] Here we find that the Cu r-GO core-shell NW films show even lower haze values compared to the Cu NW films. Figure 5a shows the haze values of Cu and Cu r-GO NW films at different total transmittance at a wavelength of 550 nm.

Clearly, the haze values of the core-shell NW films are 0.5 ~ 1% lower than the Cu NW films in a large range of total transmittance, indicating the Cu r-GO core-shell NWs have less light scattering effects. This improvement may be the result of two different phenomena. First, wire-wire aggregation in the well-dispersed GO coated nanowires during the filtration process is largely reduced. Figure 5b shows that the average size of the wire bundles reduced from 29.7 to 23.0 nm in diameter (from SEM images of the annealed samples with similar total transmittance, wires are coated with ~3 nm gold). The thinner wire bundles should reduce the light scattering effect. Second, the r-GO coating introduces a gradual change in refractive index from copper to air, leading to a smaller light scattering cross section for the ultrathin NWs. Figure 5c shows the optical simulation results of a 17 nm thick Cu nanowire coated with a thin graphene layer which indicate that the light scattering cross section in the visible region is reduced. This is because the carbon has an intermediate refractive index (r = 2.3 at 550 nm) between air (r = 1.0 at 550 nm) and copper (r = 3.3 at 550 nm) and such refractive index gradient decreases the portion of scattered light at higher angles (see Figure S11 for the simulations on the angle-dependent light scattering of the NWs).

We further developed a method to model the transmission, haze, and sheet resistance of the core-shell nanowire meshes using Mie theory.[35-37] The calculated haze *versus* transmission for Cu and Cu r-GO nanowires with different thicknesses of r-GO is shown in Figure 5d. This calculation shows that graphene coating decreases haze of the conducting films relative to Cu. The reduction in haze is consistent with the experimental data. The results imply that the average thickness of r-GO around Cu NW is probably less than 1 nm. We also simulate the transmittance spectra (Figure S12) and transmission *versus* sheet resistance (Figure S13) for the core-shell nanowire films, which are also in excellent agreements with the experimental results. The details about the simulation can be found in supporting information or reference 35. The model for Cu r-GO core-shell nanowires presented here can predict the experimental results well, and it can also be extended to other core shell nanowire systems. The simulation results also indicate the r-GO wrapping approach is a feasible way to improve the stability and conductivity of Cu NWs.

CONCLUSION

In summary, we have demonstrated a new solution-based approach to wrap GO nanosheets on the surface of ultrathin copper nanowires. By mild thermal annealing, GO can be reduced and high quality Cu r-GO core-shell NWs can be obtained. High performance transparent conducting films were fabricated with these ultrathin core-shell nanowires; excellent optical and electric performance was achieved. The core-shell NW enables highly stable conducting films, which have comparable performance to ITO and silver NW thin films. This work demonstrates a new approach to improve and stabilize ultrathin metal nanowires, and takes one step further towards the commercialization of copper nanowires as a low cost transparent conductor for optoelectronic devices.

METHODS

Materials: Ultrathin copper nanowires were synthesized using our recently developed methods. Graphene oxide nanosheets with a diameter of ~10 nm were synthesized using a reported method. All the chemicals used in this work were purchased from Sigma-Aldrich and used as received.

Cu GO core-shell nanowire preparation: Graphene oxides nanosheets aqueous solution (1 mg/mL, 0.5 mL) was diluted in 20 mL methanol. To this diluted GO solution, Cu NW toluene suspension (2 mg/mL, 2.5 mL) was added with stir. The mixture was ultrasonicated for 3 min to form the Cu GO core-shell NWs. The NWs was separated by centrifugation at 10000 rmp for 10 mins. Then, the nanowires were washed twice with isopropanol by going through centrifugation-redispersion cycles to remove excess GO and impurities. The product was dispersed in 3 mL isopropanol for storage. The ratio of Cu NW and GO can be modified to tune the coverage and shell thickness of the resulting core-shell NWs.

Conducting film fabrication: To make a conductive thin film, Cu nanowires were diluted using isopropanol by 100 times and ultrasonicated for 5 min to form a homogenous suspension. The thin film was constructed by filtering down the nanowires from the

dispersion onto a polytetrafluoroethylene porous membrane (Sartorius Stedim Biotech, pore size 450 nm) *via* vacuum filtration. The nanowire network was transferred on to a piece of glass by applying pressure to the backside of the membrane and forcing an intimate contact with the substrate. Then, the copper nanowire thin film was annealed under forming gas at different temperature for 30 min to improve junction contact.

Characterizations: The structural properties of the core-shell nanowires were examined using energy dispersive spectroscopy (FEI TitanX 60-300), high-resolution transmission electron microscopy (FEI Tecnai G20), fourier transform infrared spectroscopy, and scanning electron microscope (SEM, JOEL JSM - 6340F). Sheet resistance of nanowire thin film was measured using four-point probe method (CDE-RESMAP-270). The transmittance and haze measurement was carried out on a Shimadzu UV-2550 ultraviolet-visible near-infrared spectrophotometer with an integrating sphere.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Optical simulations details, additional TEM, AFM, SEM images, XPS, XRD, and FTIR results.

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Author Contributions

‡L.D. and F. C. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work was financially supported by BASF Corporation (Award number 53093). S.W.E. would like to acknowledge the Camille and Henry Dreyfus Foundation for financial support, award number EP-14-151. We thank Y. Zhao and J. Baba for the help on the FTIR measurement and simulation, respectively.

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Figures:

Figure 1. Schematic illustration of the graphene oxide wrapping, film deposition, and reduction process to fabricate the transparent nanowire conducting films.

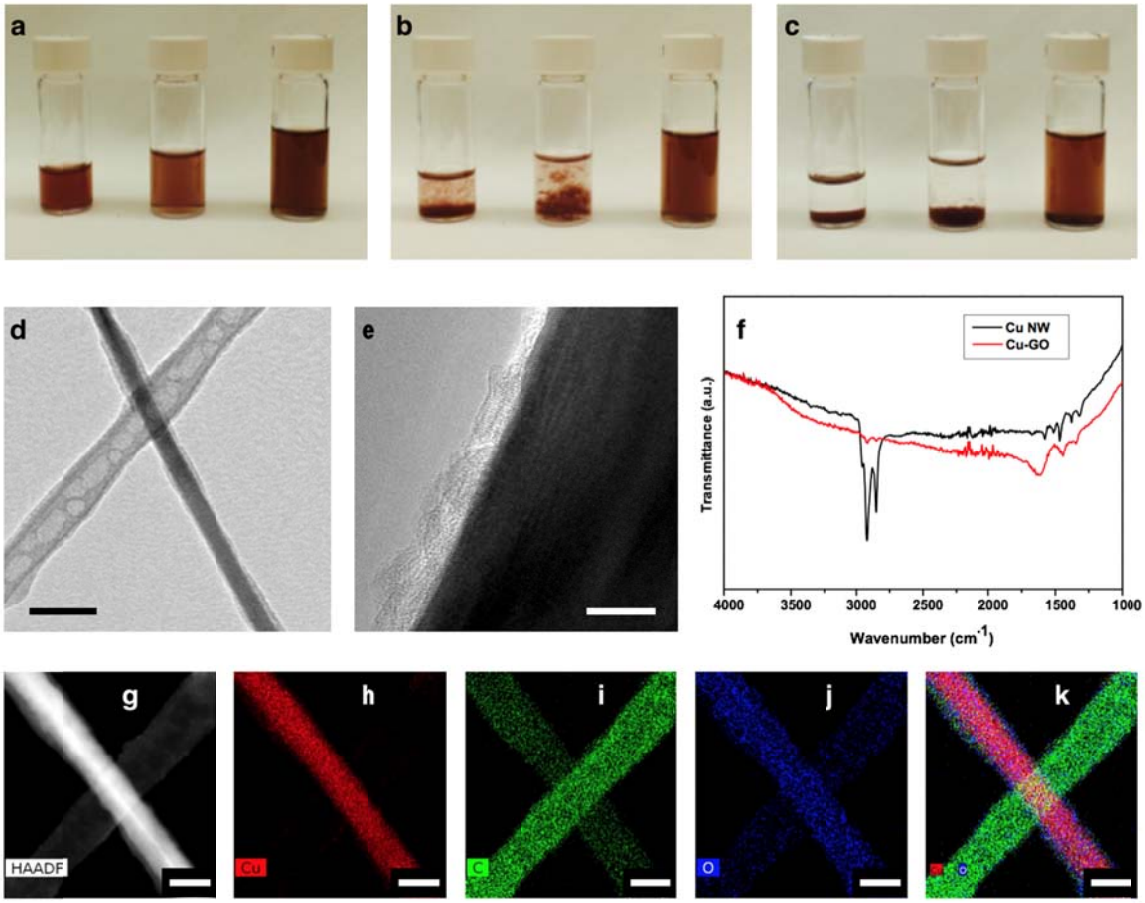

Figure 2. Structural characterization of the copper graphene-oxide core-shell nanowires. (a) Images showing the nanowire suspension stability. Left: Cu NWs in toluene; Middle: Cu NWs in IPA; Right: Cu GO core-shell NWs in IPA. (b) After 20 min. (c) After 24 hours. (d) A TEM image the Cu GO core-shell nanowire. The stripe under the Cu NW is the lacy carbon grid. Scale bar: 50 nm. (e) A high-resolution TEM image the Cu GO core-

shell nanowire. Scale bar: 5 nm. (f) FTIR spectra of the Cu nanowires before and after GO wrapping. (g)-(k) EDS analysis of a core-shell nanowire showing the elemental distribution of copper, carbon, oxygen, and the combination of the three elements. The stripes with strong carbon signals in (i) and (k) are from TEM grid. Scale bars: 40 nm.

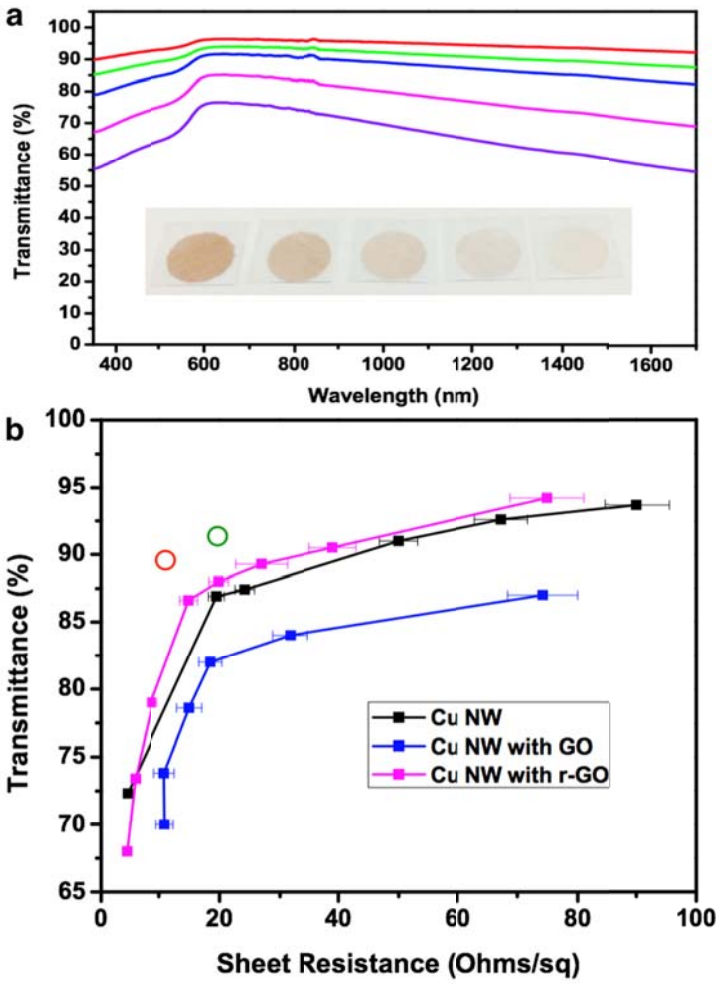

Figure 3. Optical and electrical performance of the nanowire-based transparent conducting films. (a) Transmittance spectra of the films from UV to near-IR and corresponding optical images (inset) after annealing. (b) Transmittance (at 550 nm) *versus* the sheet resistance of different type of films (Cu NW and Cu NW with GO films were annealed at 200 °C, Cu NW with r-GO films were annealed at 260 °C). The red and green circles indicate the commercial ITO and Ag nanowire transparent conductors, respectively.

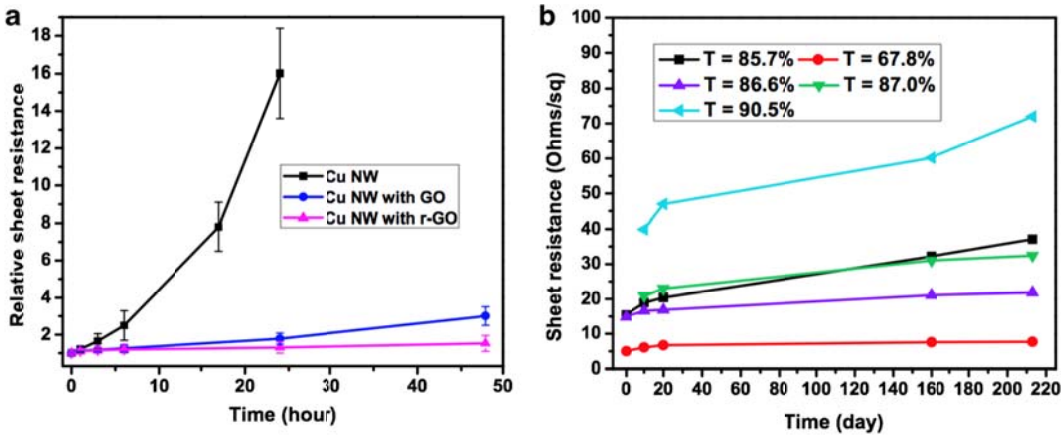

Figure 4. Stability of the nanowire-based transparent conducting films. (a) Different types of films tracked at 80 °C in air. (b) Five individual Cu r-GO films with different transmittance showing long term stability in air after storage for over 200 days.

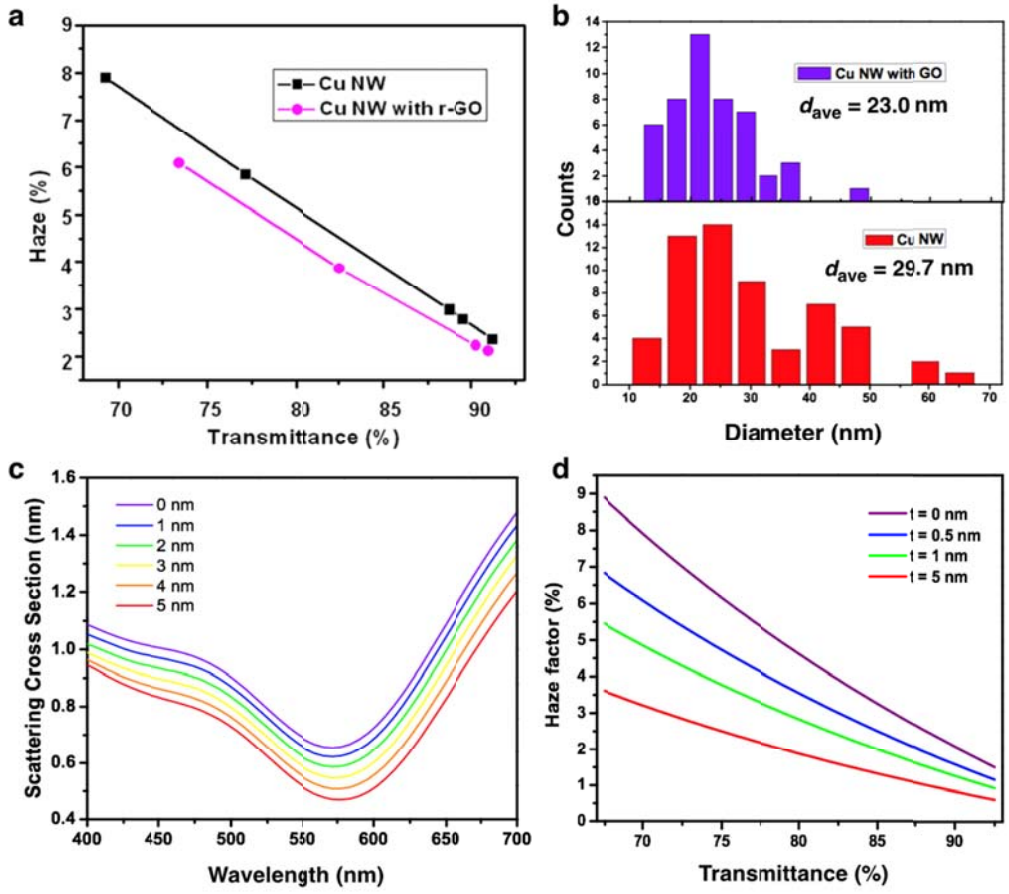

Figure 5. Haze of the nanowire-based transparent conducting films at 550 nm. (a) experimental data of the haze values of Cu NW films with and without r-GO coating. (b)

Nanowire bundle diameter distribution of the conducting films after annealing at the optimized conditions (counted from SEM images with 3 nm Au coated). (c) Simulation of light scattering cross section of a Cu NW coated with a thin graphene layer over variable thickness. (d) Simulation of haze (at 550 nm) *versus* transmittance for the nanowire films using Cu NW coated with a thin graphene layer over variable thickness.

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