Oxidation of copper nanowire based transparent electrodes in ambient conditions and their stabilization by encapsulation: application to transparent film heaters

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Oxidation of Copper Nanowires based Transparent Electrodes in Ambient Conditions and their Stabilization by Encapsulation. Application to Transparent Film Heaters.

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Abstract

Whereas the integration of silver nanowires in functional devices has reached a fair level of maturity, the integration of copper nanowires still remains difficult, mainly due to the intrinsic instability of copper nanowires in ambient conditions. In this paper, copper nanowire based transparent electrodes with good performances (33 ohm.sq^{-1} associated with 88 % transparency) were obtained, and their degradation in different conditions was monitored, in particular by electrical measurements, Transmission Electron Microscopy, X-ray photoelectron spectrometry and Auger electron spectroscopy. Several routes to stabilize the random networks of copper nanowires were evaluated. Encapsulation through laminated barrier film with Optical Clear Adhesive (b-OCA) and Atmospheric Pressure Spatial Atomic Layer Deposition (AP-SALD) were found to be efficient and were used for the fabrication of transparent film heaters.

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Flexible transparent electrodes have attracted strong attention in many technological fields in the last years. In particular, polymer thin films and nanostructured materials have been thoroughly investigated, and appear as promising alternatives to transparent conductive oxides, and notably ITO (indium tin oxide).[1–17] The development of conductive nanosized materials based mainly on carbon and metals has opened new perspectives. In particular, metallic nanowires proved very efficient when used in the form of random networks. In this case, an appropriate density has to be determined in order to reach the percolation threshold, and at the same time, the amount of deposited materials must remain sufficiently low to ensure good transparency.[18,19] The use of solution-processable nanowires appears as a promising approach since it affords low-temperature deposition process, over large areas and at low cost. Silver has been so far the most explored metal for the fabrication of metallic nanowires. This is due notably because the synthesis of silver nanowires is straightforward and because this metal is not prone to fast oxidation.[20–22] However, substitution of silver by copper would be of great interest mainly for economic reasons. Indeed, copper is approximately 100 times cheaper than silver and 1000 more abundant, with a similar electrical conductivity (59.6 10^6 $S.m^{-1}$ vs 63.0 10^6 $S.m^{-1}$). Significant efforts have been devoted to the synthesis of copper nanowires (CuNWs) and their integration into functional devices.[23] Several reports have already pointed out the great potential of CuNW based transparent electrodes.[24–29] However, it is well known that copper is highly sensitive to its environment, and vulnerable to oxygen and water even at room temperature. This results in fast electrical performance decay, preventing any industrial use. Considerable research has been devoted to solve this issue, and efficient routes to stabilize CuNWs either by metallic core-shell architectures[30–33], or by deposition of graphene / graphene oxide onto the active material[34–38] have been recently described. These routes are relevant, however they still need further improvements to become economically competitive.

We report herein the synthesis and characterization of CuNWs and their use as building blocks for the fabrication of transparent electrodes with good performances (33 $ohm.sq^{-1}$ at 88 % transparency). Their degradation in different conditions was monitored and copper oxide appearance was characterized. Several routes to stabilize the random networks of CuNWs were evaluated, in particular, encapsulation through barrier film with Optical Clear Adhesive (b-OCA) and Atmospheric Pressure Spatial Atomic Layer Deposition (AP-SALD). The latter technique has been recently attracting much attention as a fast, vacuum-free, low-temperature and low-cost deposition technique [39],[40]. AP-SALD allows fast and thickness controlled deposition of conformal compact oxide layers, but with orders of magnitude faster deposition rates than conventional ALD thanks to the spatial separation of precursors. In this work, encapsulation through b-OCA and AP-SALD were found to be efficient and were used for the fabrication of transparent film heaters.

Experimental

Synthesis of Copper Nanowires

CuNWs were synthetized by a hydrothermal process. Into 80 mL of deionized water, 139.4 mg of copper (II) chloride (>99.995%, Sigma Aldrich), 1121 mg of octadecylamine (ODA, Sigma Aldrich) and 187.2 mg of dextrose (Sigma Aldrich) were added under stirring. After 45 min of ultrasonic agitation, the emulsion was placed into a 125 mL Teflon™ lined autoclave. The reactor was heated at 160 °C for 48 h under autogeneous pressure, and quickly cooled in cold water. CuNWs were extracted and washed by multiple centrifugations at 2500 rpm during 15 min. In order to remove remaining nanoparticles, a 24 h decantation process was carried out, and the supernatant was discarded. The CuNWs were then transferred into 100 mL of isopropyl alcohol (IPA, Sigma Aldrich) before use.

Fabrication of Electrodes by Ultrasonic Spray Coating

CuNWs were dispersed in isopropyl alcohol at a desired concentration, typically from 50 to 300 mg.L^{-1} for deposition experiments. The fabrication of electrodes was realized on Eagle XG glass substrates of alkaline earth boro-aluminosilicate type glass by titanium/gold (20/80 nm) deposition by vacuum evaporation through shadow mask, or by silver paste (Ferro L200) deposition on 125 µm thick PEN (i.e. poly (ethylene 2, 6-naphthalate)) substrates obtained from Dupont Teijin (Teonex Q65FA). Deposition was carried out by air-brush spraying, using a system from Aztek. In a typical spray-coating experiment, the substrate was placed on a hot plate at 80 °C. The solution was spray-coated with the airbrush at a distance of 20 cm from the substrate at 2 bar air pressure, and after deposition the substrates covered with CuNWs were cooled down to room temperature in air. The barrier film based on an optical grade of polyester film with optically clear adhesive b-OCA was purchased from 3M.

The sheet resistance was set as the mean value of at least 5 measurements by using a four pin probe with a Loresta EP resistivity meter, and the transmittance was measured on a Cary 5000

Varian spectrophotometer using the substrate as reference. The CuNW deposited on the substrate was characterized by scanning electron microscopy (SEM) using a FEG (field emission gun) microscope ZEISS-LEO1530 operating at 5kV. For transmission electron microscopy (TEM) characterization, a drop of the CuNWs dispersed in isopropyl alcohol is deposited on lacey carbon-coated TEM copper grid. The observations were performed using a FEI Themis microscope operating at 200 keV and equipped with a probe spherical aberration corrector and with a Super-X system (4 Silicon Drift Detectors) for X-ray energy dispersive spectroscopy (X-EDS) analyses.

The XPS (VersaProbe-II, ULVAC-Phi equipped with hemi-spherical analyzer), known to be a nondestructive extreme surface analysis, was performed using focused monochromatized Al Kα radiation (1486.6 eV). The spectrometer was calibrated using photoemission lines of gold (Au 4f7/2 = 83.9 eV, with reference to the Fermi level). The core level peaks were recorded with constant pass energy of 23.3 eV with energy resolution of 0.5 eV. The XPS spectra were treated using Multipak V9.1 software. The Auger transitions were recorded by XPS using 23.3 eV pass energy in order to identify the oxidation state of copper.

Al_2O_3 coating layer by AP-SALD

The Al_2O_3 coatings were deposited using a home-made AP-SALD system, as reported previously [41]. The depositions were carried out in vacuum-free, low temperature (100 °C – 200 °C) conditions. Trimethylaluminum ($(CH_3)_3Al$; TMA, Sigma Aldrich) and water vapor (H_2O) were used as precursors for aluminum and oxygen, respectively. The CuNWs samples were placed at a distance of 200 µm under the injection head, oscillating at 10 cm/s. The deposition rate was around 0.6 nm/s.

Results and Discussion

The synthesis of CuNWs was carried out via hydrothermal synthesis. After purification through decantation, the proportion of nanoparticles or other by-products was very low. High aspect ratio nanowires with mean length of 33 ± 15 µm and mean diameter of 100 ± 15 nm were obtained, a typical SEM image is shown in Figure 1a.

The CuNWs were deposited on plane surfaces by spray-coating to ensure a random orientation of nanowires. The density of nanowires could be tailored thanks to the concentration of the solution and the quantity of CuNW suspension sprayed onto the substrate. The electrodes have a reddish aspect (Figure 1b) which is typical for copper based metallic nanowires. Once the percolation threshold is reached, a sheet resistance can be measured. Different electrodes with various densities above the percolation threshold were fabricated. The resulting plot of the total transmittance versus sheet resistance is given in Figure 1c. These performances are among the highest performances reported so far for CuNW based electrodes (*e.g.* 33 ohm.sq^{-1} at 88 % transparency).[1,14,23,25,42]

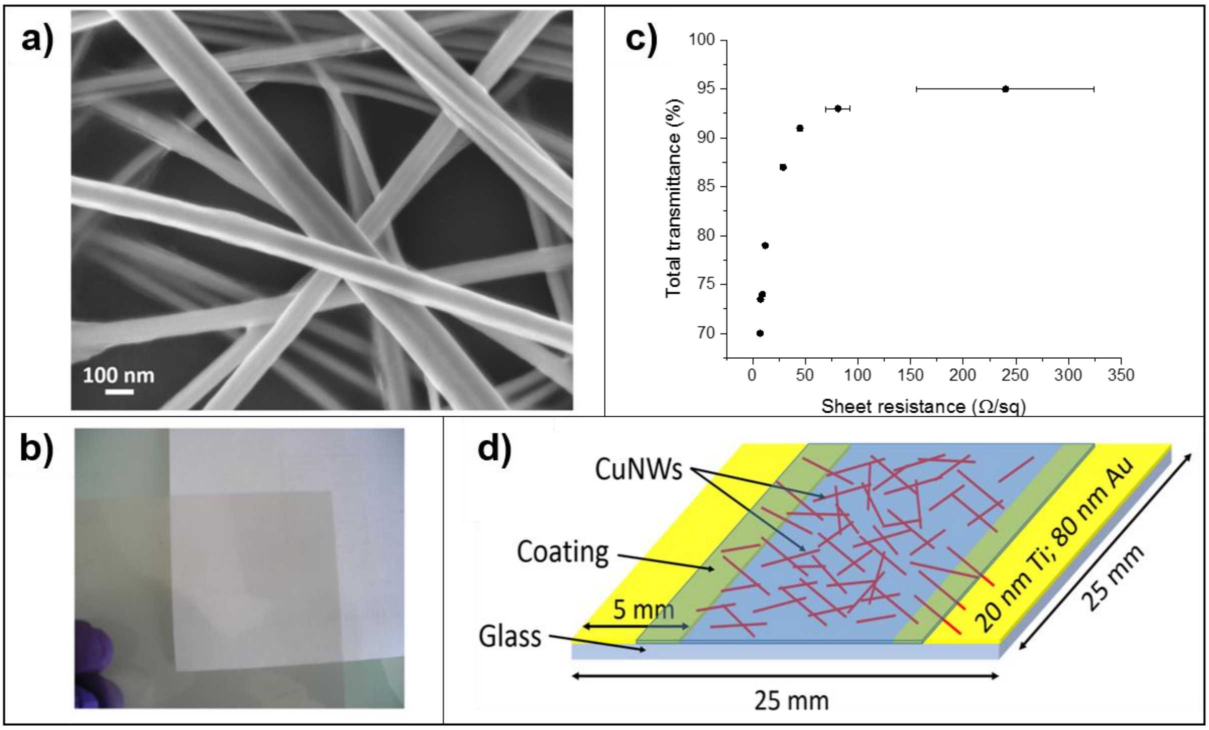

Figure 1. a) SEM image of CuNWs b) Picture of a CuNW transparent thin film (25x25mm²) c) Total Transmittance at 550 nm versus sheet resistance d) Scheme of a CuNWs transparent electrode

It is well known that CuNWs undergo spontaneous oxidation in air. However, we observed a significant difference of stability in dry air between CuNW based electrodes, depending on their initial resistivities, which are related to the initial densities of the networks. This is demonstrated in Figure 2a where the sheet resistances of three networks having initial sheet resistances of 14, 66 and 260 Ω/□ show different evolutions as a function of time. Whereas the denser films (14 Ω/□) still present acceptable sheet resistance after 2 months (58 Ω/□), the other electrodes show much higher sheet resistances. It clearly appears that the density of nanowires plays a critical role in thin films ageing. While sparse networks are very unstable as assessed by the measurement of their sheet resistances, dense networks with CuNWs content far above percolation threshold show lower degradation rate. It can reasonably be assumed that this is related to the percolative nature of the system. Indeed, the breakage of one nanowire or one connection will not lead to a significant loss of conductivity when many other possible pathways co-exist. On the contrary, for low density networks, the percolation threshold is barely exceeded, and the breakage of one nanowire or one connection can lead to a dramatic decrease on the overall conductivity.

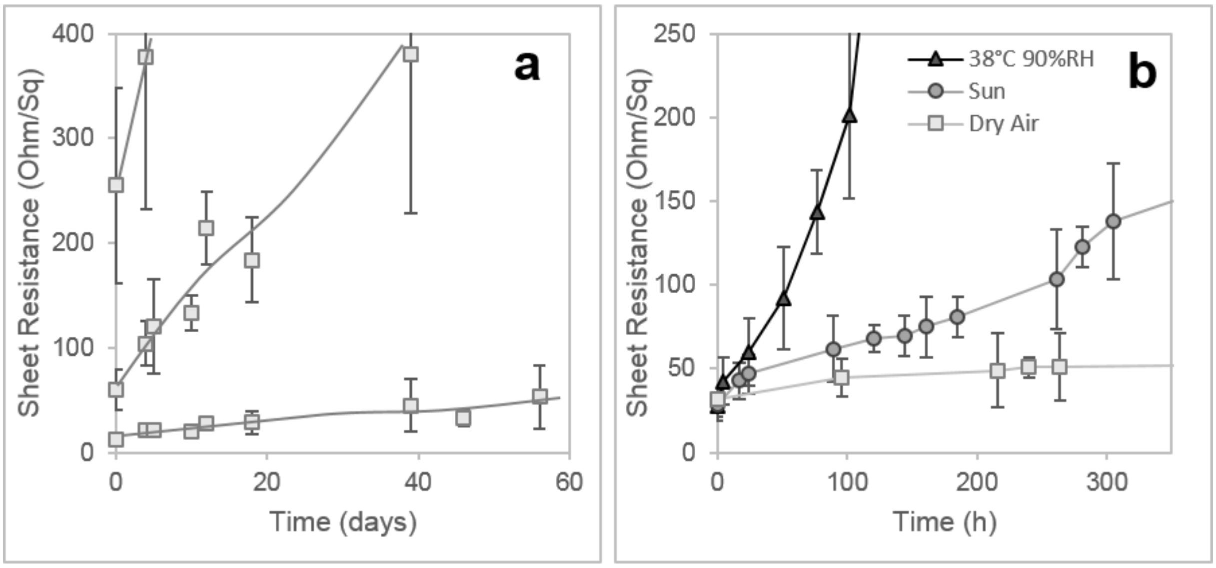

Figure 2. Sheet resistance as a function of time for CuNW electrodes a) in dry air and darkness, for networks with various densities and initial resistances b) under different stresses: high humidity, dry air and darkness, sunlight exposure. Lines are guidelines for the eye.

In order to get more insight into the degradation effect of the environment on CuNWs electrodes, freshly made electrodes with similar properties (28-30 Ω/☐) were stored in three different environments, which are 1) dry air in the dark at ambient temperature, 2) sunlight exposure (1 sun) at 20 % relative humidity (RH) and room temperature, and 3) 90 % RH in the dark at 38 °C. The results are presented in Figure 2b. As previously described, the stability in dry air appears mostly acceptable, with a small increase of the sheet resistance after 2 weeks. In the case of sunlight exposure, resistance is at least doubled after one week. The electrodes keep on loosing conductivity over time until they become not conductive at all. Finally, the presence of a high level of humidity is a crucial point since the electrodes suffer dramatically, showing an intense decrease of the conductivity only within a few hours. This is consistent with the known tendency of copper to oxidize quickly in such environment.

Freshly made CuNWs, as well as some others exposed to sunlight, humidity and dry air for one week were then characterized by XPS, Auger spectroscopy and TEM. High angle annular dark field (HAADF) / Scanning TEM (STEM) images of freshly made CuNWs are presented in Figure S1, showing that the CuNWs have grown along a <110> direction of the Cu face centered cubic crystallographic structure. Most of the CuNWs present a twin boundary parallel to the growing direction. For the same nanowires, high resolution XPS analysis (Figure 3) confirms the exclusive presence of copper with zero valence: the Cu $2p_{3/2}$-$2p_{1/2}$ core level region shows two characteristic peaks at 933.0 eV and 952.7 eV. A weak Cu 2p photoemission satellite was observed at binding energy about 13 eV higher than the main Cu $2p_{3/2}$ peak, in agreement with the quasi closed $3d^{10}$ electronic ground state. It is confirmed by the well-defined Auger transition Cu $L_3M_{45}M_{45}$ peaks of copper around 567 eV and 564 eV.[43] After one week in dry air, core level region peaks have mostly the same binding energy than pure copper nanowires in XPS. However, we observe a slight intensity enhancement of satellite peak, indicating a partial oxidation of Copper toward Cu^{+1}. This result is corroborated by an enhancement of Auger related transition peak at ~569 eV and a decrease of the metal related Auger transition (Figure 3b). This appears consistent with the presence of copper oxide on the surface of the nanowires. Since Auger Electron Spectroscopy has a lower depth of analysis than XPS, the thickness of the oxide layer can probably be considered very thin, on the extreme surface. In the case of humidity treatment which induces faster and deeper oxidation, the XPS spectrum of the core level region shows a flat peak at 944 eV, and a large shoulder at 934eV, both revealing the presence of CuO.[29,43] This result is in accordance with Auger transition peak change, disappearance of metal related transition at lower binding energies.

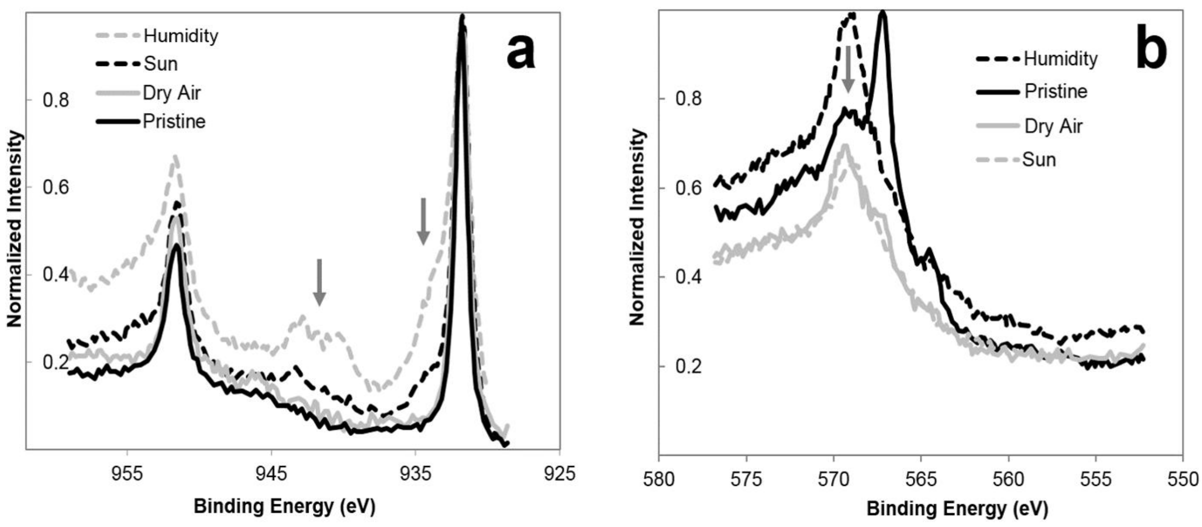

Figure 3. a) High resolution XPS spectra on core-level of copper and b) Auger transition of pristine CuNWs and after ageing under dry air and darkness, sun and high humidity.

Complementary analyses were performed by TEM, using the same set of nanowires aged under the different environments (Figure 4). For the full set of CuNWs, a rather low contrast was observed along the NW surface, which was ascribed to the presence of adsorbed organic materials (*e.g.* the capping agent ODA) on their surface.

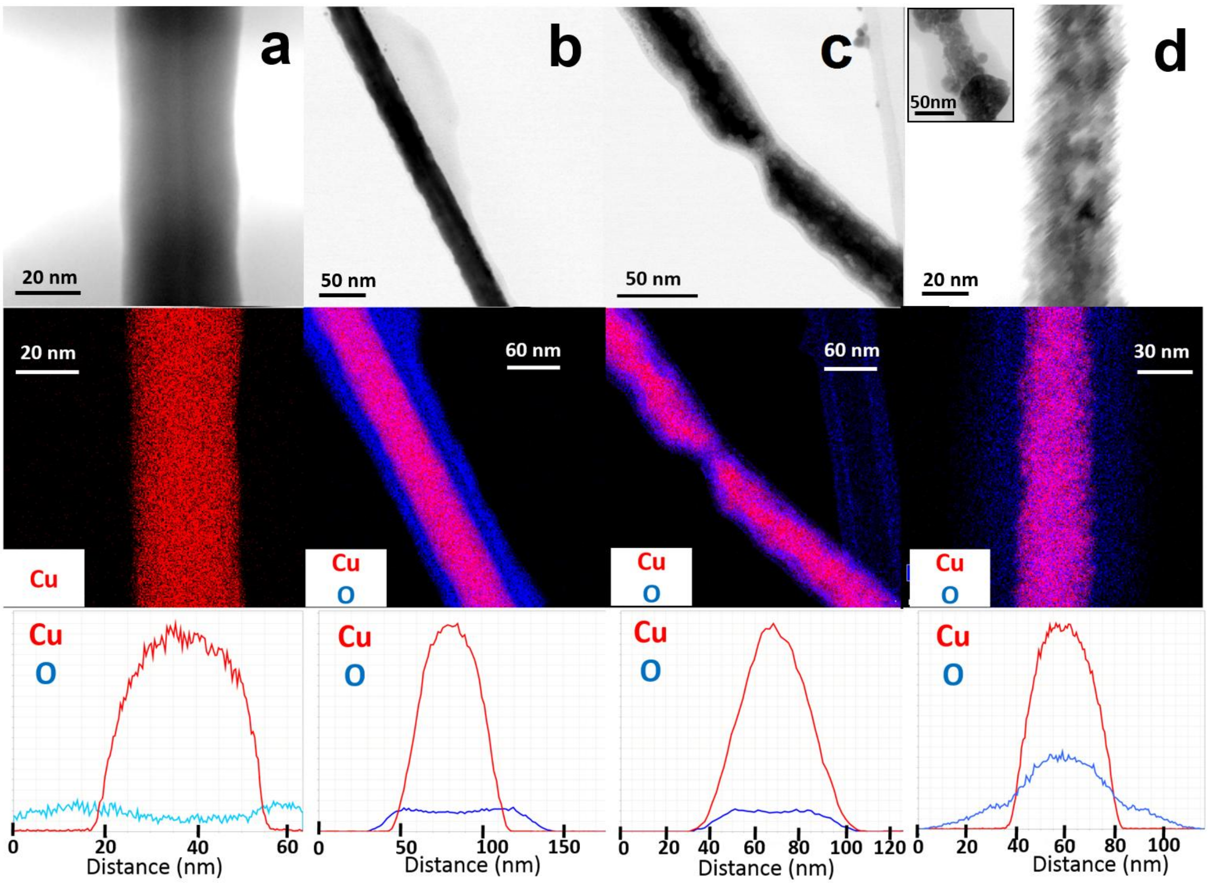

Figure 4. Bright field (BF)/STEM pictures, XEDS Cu and O elemental map and linescan of (a) a pristine CuNW and aged nanowires in (b) dry air and darkness, (c) under sun exposure and (d) at high relative humidity content.

The STEM images and the X-EDS Cu and O elemental maps clearly show that after the different ageing conditions, the structures of the nanowires are undoubtedly modified. A clear core-shell structure is observed for CuNWs after the different ageing conditions with the presence of oxygen enrichment at the surface. This is consistent with XPS and Auger analyses, showing the presence of copper oxide around the nanowires. CuNWs under sun exposure, and even more intensively under high RH content exposure, are strongly modified. Severe degradation leads to high surface roughness and breakdowns of the nanowires. The oxidation of the nanowire core appears to be the highest for high RH conditions, which is consistent with results presented in Figure 2b. Degradation of the CuNWs based electrodes certainly results from nanowire breakages within the resulting surface oxidized nanowires as shown in Figure 4c, and also from loss of contacts between nanowires due to the appearance of low conductivity copper oxides around the nanowires, and thus at the junctions between different nanowires. It is thus clear that such electrodes need to be encapsulated prior to being integrated in devices. When multilayer stacked systems are targeted, then the system stability should be monitored globally since many other parameters have to be considered (*e.g.* interfaces, acidity content, permeation to water and oxygen through several layers, etc.) and specific studies will be required. If the random networks of CuNWs are used alone or as the ultimate layer of a stack, for applications such as capacitive sensors or thin film heaters, then a specific encapsulation system should be developed to prevent fast degradation.

The encapsulation strategy developed in this paper focused on the deposition of continuous capping layers deposited on top of the nanowire network by physical or chemical processes on top of the nanowire network. Indeed, several transparent coatings were performed on CuNWs electrodes with similar optoelectrical properties in order to evaluate potential stability improvement. Optical spectra and thicknesses of the coating layers are presented in Figure S2. The coating was realized as described in Figure 1d, allowing only two-probe resistivity measurements as a function of time under various stresses. The relative increases of the resistance after 15 days in dry air and darkness, after 7 days under artificial sun in ambient air, and after 3 days in 90% RH at 38°C are presented in Figure S3. Under dry air, the mean amplitude of the resistance alterations is very low after 2 weeks, and resistances are mostly stable after one month. Resistance values are even somewhat lowered at first, probably because the coating presses the CuNWs against the substrate, thereby improving the contacts between the nanowires. More significant experiments were carried out under sun exposure and high RH. After 7 days under 1 sun in ambient air, the increase of resistance is observable for all the electrodes, except for AP-SALD coating which demonstrates high stability. The less stable system was the one using polyurethane (PU) coating, possibly due to the reaction of polyurethane with illumination to form radicals and hydroxyl groups which speed up CuNWs ageing. After 3 days of exposure in high humidity conditions, bare CuNW based thin film resistance was multiplied by 10, and it was too high to be measured after 2 weeks. The sol-gel titanium dioxide coating is porous and hydrophilic, the absorption of water within this layer certainly increases the oxidation rate of copper. The polymer coatings show similar effect and lead to a complete degradation of the NW networks after 3 days. Water vapor transmission rate (WVTR) of PU, PSi, TiO_2 and b-OCA are respectively around 500, 80, 23 and less than 1 $mg.m^{-2}.day^{-1}$ respectively. The lifetimes of CuNWs are strongly correlated to this parameter. The barrier film with optical clear adhesive appears as a good coating candidate since it decreases notably the degradation rate of the thin film. Transparent touch sensors using this encapsulating system where found to be efficient for months in ambient conditions.[29] The b-OCA acts as an effective barrier for water molecules that cannot access the nanowires through the coating. However, progressively the red color on the sides of the thin films vanishes, indicating that water can laterally penetrate beneath the OCA and the glass substrate on the sides of the system, which is probably responsible for the low increase of the resistance. Finally, AP-SALD appears as a relevant technology to stabilize the network of CuNWs. Conventional ALD has indeed been used to deposit protective layers, in particular using Al_2O_3, for many different applications.[44–47] In our case, in addition to the good performance obtained, the high throughput and the absence of vacuum offered by AP-SALD makes it a highly suitable method to contribute to the low cost and easy fabrication of devices based on CuNWs. The conditions for encapsulation consisted in 25 cycles of deposition at 100 °C followed by 25 other cycles at 150 °C. It allowed the deposition of a conformal thin alumina shell, with a mean thickness of 50.4 ± 8.7 nm (Figure S4).

The last two processes were found to be the most suitable for the encapsulation of CuNWs, hence they were chosen for the fabrication of transparent thin film heaters. Such heating systems based on random networks of metallic nanowire networks have been widely reported, [19,48,49] the pioneering report dating from 2012.[50] The use of CuNWs as a main building block to fabricate transparent film heaters has been reported scarcely, the first communication being the work published by Sun *et al.* in 2016.[51]

The goal here was not to perform a full study on CuNW based transparent film heaters, but rather to demonstrate that by an adequate encapsulation process these devices can show satisfying stability. Three similar devices were fabricated on glass substrates according to the experimental procedures described hereinbefore (Figure 1d and Figure 5a). One sample was used without encapsulation and two similar devices were covered by b-OCA and by the AP-SALD technique. For the first one, initial resistance between opposite electrodes was 40 Ω. Heating cycles were applied, for each cycle an electrical potential was applied for 10 min in order to reach and stabilize a temperature of 50°C. After ten cycles, the resistance increased slightly to 46 Ω, and after 2 weeks of ageing of storage in dark and ambient air, another increase of resistance was measured, up to 81 Ω. Then in several days, a very high resistance (> 10^6 Ω) indicated that the network was no longer efficient.

Initial two-probe resistances of the b-OCA-coated and the Al_2O_3-coated samples were both 24 Ω, demonstrating a positive effect of the encapsulation process on the network electrical performance. Indeed it is worth noticing that the coating methods used in the present study are performed after the network formation and therefore once the junctions between nanowires have already been created. This is a clear advantage of such coating methods. After 10 cycles of voltage cycles associated to a temperature of 50°C, both values decreased to 22 Ω. Very low variations of resistances after two weeks in air and daylight were observed, the resistances remaining at a value of 22 Ω. After another series of cycles at 50°C and two more weeks of storage, electrodes retained identical performances (see Fig 5b for Al_2O_3-coated sample and Figure S5 for the b-OCA-coated film heater). The stability of the sample in operation was also investigated, a 19 Ω AP-SALD-encapsulated sample was subjected to a 3 V potential for 2.5 h, without significant alteration (Figure 5c). The as-made transparent film heaters were found to be still effective after 6 months, which demonstrates that efficient protective layers can actually prevent oxidation and maintain CuNW based percolative networks efficient in the long term.

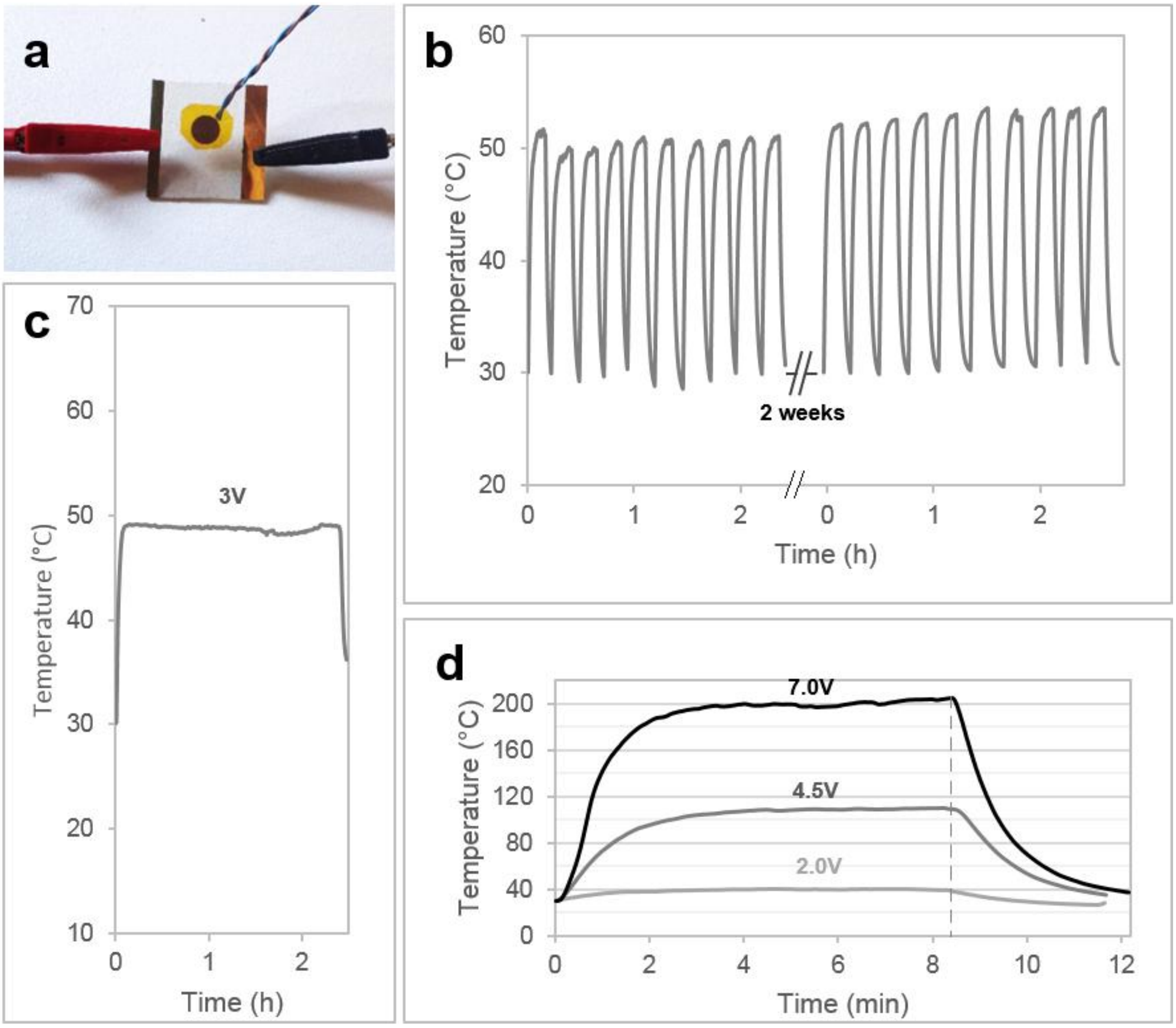

Figure 5. CuNW based thin film heater encapsulated through AP-SALD. a) Picture of the device. The potential is set between the two electrodes. The temperature is measured by a thermal probe glued on the back of the substrate b) Temperature as a function of time for consecutive heating cycles before and after a 2 week storage in dark and ambient air c) Temperature as a function of time under 3V bias (R=19 Ohm) for a 2.5 h dwell time (small variations are due to environmental conditions during the experiment) d) Temperature as a function of time under different voltages (R=19 Ohm), dashed line indicates the end of bias application.

Conclusion

High performance transparent electrodes (*e.g.* 33 ohm.sq^{-1} associated with 88 % transparency) based on random networks of copper nanowires were fabricated through a solution process. Unlike similar systems using silver nanowires, a fast degradation of the electrical properties was observed in ambient conditions, which is ascribed to the fast oxidation of copper. This was demonstrated by different nano-characterization experiments and analyses. It pointed out the absolute need to stabilize the system by an efficient encapsulation layer in order to prevent oxidation of the nanowires and consequently failure of the electrical conductive network. Several protecting coatings were performed, and the best results were obtained thanks to the use of b-OCA adhesives, or very thin alumina coating realized by AP-SALD. Transparent film heaters made of CuNWs protected by these materials were fabricated. Very good performances were measured and the stability of the devices was greatly improved, with a lifetime exceeding 6 months.

Acknowledgements

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Supplementary Material

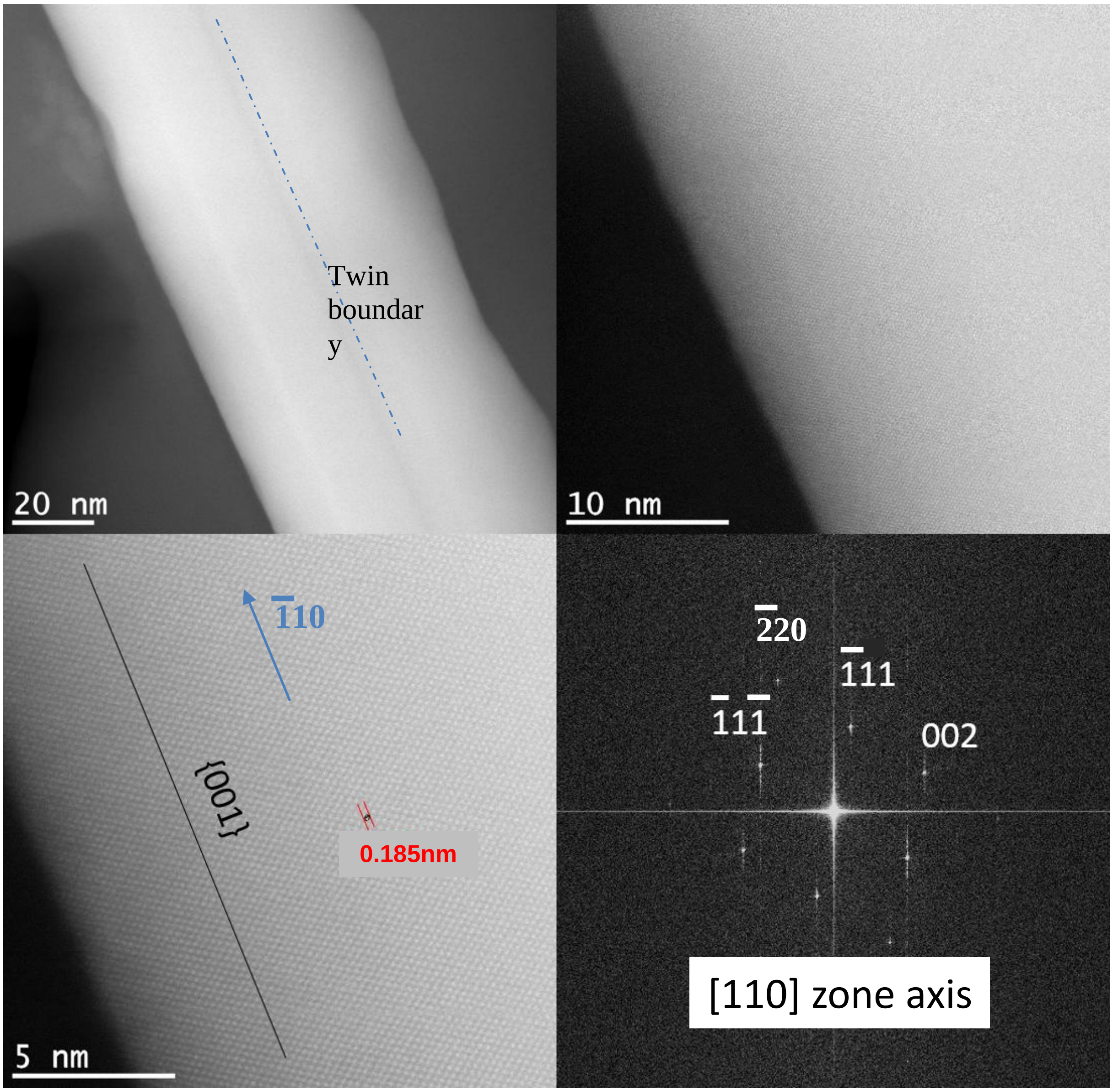

Figure S1. HAADF/STEM images of a pristine CuNW observed along a <011> direction at different magnifications and FFT of the last image.

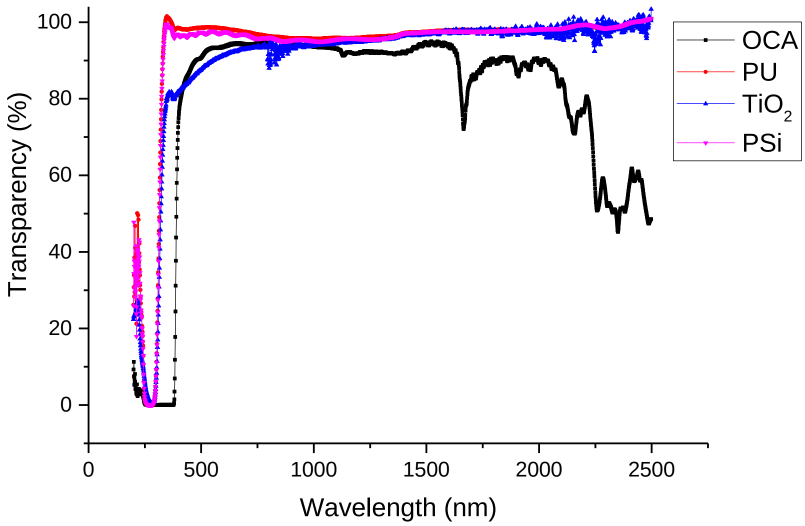

Figure S2. Transmission spectra of different coatings of CuNWs

Thickness of polyurethane (PU) and polysiloxane (PSi) layers were measured by a profilometer and thickness of the titanium oxide (sol-gelTiO_2) thin film was measured by AFM. The thicknesses of PSi, PU and TiO_2 layers are respectively 1.5 µm, 1.0 µm and 0.2 µm.

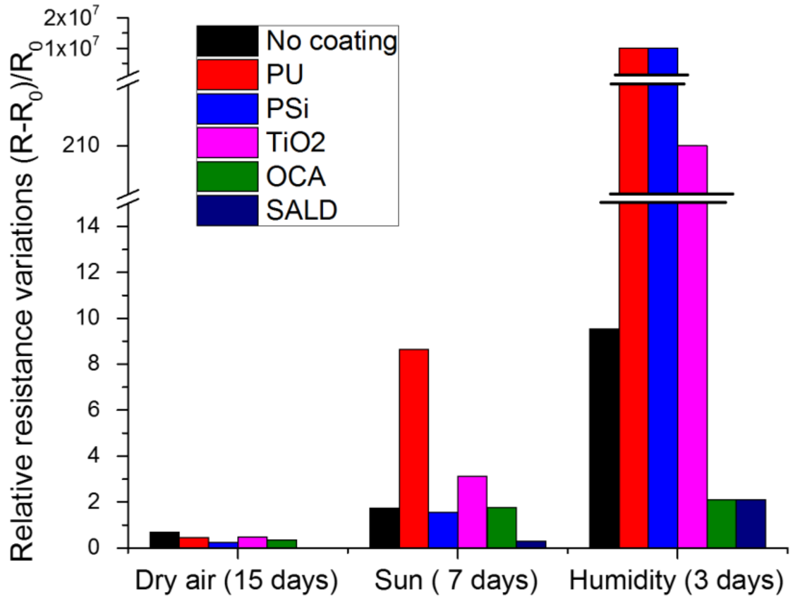

Figure S3. Bar chart representing the resistance evolution of CuNW based electrodes coated with PU (polyurethane), PSi (polysiloxane), TiO_2 (by sol-gel technique), barrier films with Optical Clear Adhesive (b-OCA) from 3M, or AP-SALD under different stresses.

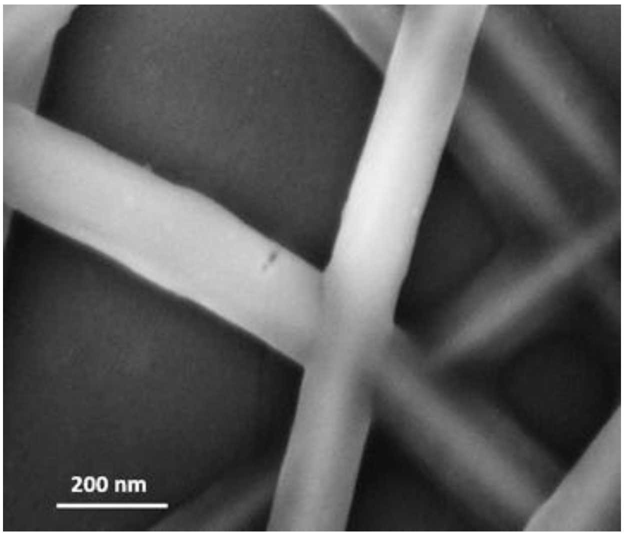

Figure S4. SEM picture of CuNWs protected by a thin alumina layer through AP-SALD (Al_2O_3 shell thickness 50±8 nm)

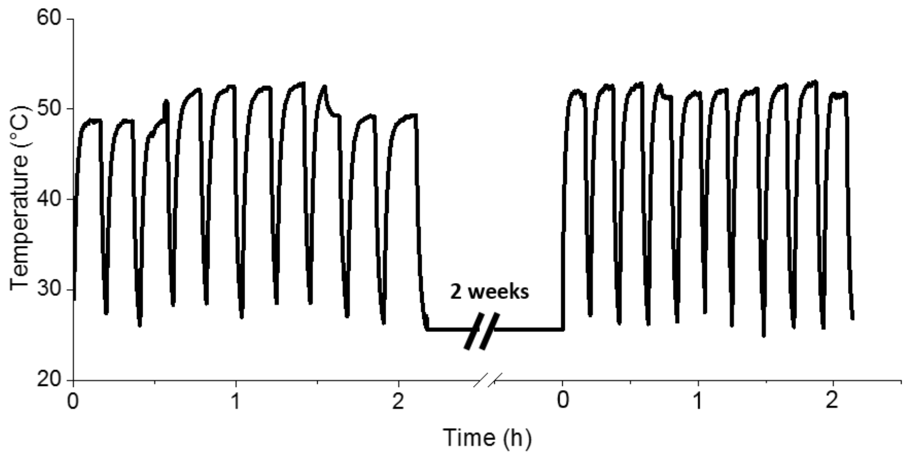

Figure S5. Temperature as a function of time for consecutive heating cycles before and after a 2 week of storage in dark and ambient air for a b-OCA encapsulated transparent film heater.