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Stability of silver nanowire based electrodes under environmental and electrical stresses†

Céline Mayousse, Caroline Celle,* Alexandra Fraczkiewicz and Jean-Pierre Simonato*

Flexible transparent electrodes fabricated with random networks of silver nanowires (AgNWs) have been widely studied in recent years. This approach appears to be a promising alternative to replace ITO (indium tin oxide) in many optoelectronic applications. Many successful integrations in functional devices have already evidenced the high potential of this technology, but unfortunately only very few studies have been dedicated so far to the stability of this material. We present here a study dealing with the alteration of the electrical properties of AgNW meshes when subjected to different stresses. We demonstrate that AgNW electrodes are very stable when stored under ambient atmosphere up to, at least, two and a half years. Accelerated ageing processes also reveal that concentrated H₂S or exposure to light does not cause any significant sheet resistance modification. However, the combination of high relative humidity and high temperature seems to be more critical. In addition, long lasting contact (two years) with PEDOT:PSS can induce deterioration of the electrical properties. Similarly, AgNW/PEDOT:PSS hybrid materials exhibit weaker stability under electrical stress when compared to pristine AgNW networks.

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Introduction

Various routes have recently emerged for the replacement of ITO (indium tin oxide) to meet the needs of new markets and in particular, new flexible applications. Amongst the main candidates including carbon nanotubes,^{1–3} graphene,^{4–6} PEDOT:PSS,^{7–9} metallic grids,^{10,11} and metallic nanowires.^{12–16} The number of publications relating to the fabrication of functional transparent electrodes based on silver nanowires (AgNWs) has skyrocketed during the last 5 years. Indeed, the fact that silver is the most conductive metal, combined with the rather easily accessible high aspect ratio of wire-shaped nanostructures, allows the realization of highly transparent percolating networks with excellent electrical conductivity. Extensive efforts have been made both at the synthesis step (control of nanowire dimensions and purity) and at the deposition step (random deposition, large area, low-cost, *etc.*) to obtain electrodes with remarkable optoelectronic properties. Thanks to these optimization processes, AgNW-based electrodes with high transmittance (>90%) and high electrical conductivity (<50 Ω sq⁻¹) are now well developed. Moreover, beyond demonstrating optoelectronic performances similar to ITO, AgNW networks can maintain their electrical conductivity

under mechanical stress (bent, crumpled, stretched, compressed *etc.*).^{17,18} The potential of these flexible electrodes has been confirmed throughout their successful integration in many types of devices such as organic solar cells,^{16,19,20} OLEDs (Organic Light-Emitting Diodes),^{21,22} touch sensors (capacitive or resistive)^{23–26} and film heaters.^{27–29} However, these studies are very recent and there is a real lack of feedback concerning the stability of these electrodes. Indeed, for industrial applications it is essential to prove that these electrodes maintain their properties in the long-term and in various environments, depending on specific operating conditions.

Atmospheric corrosion of bulk silver films has been extensively studied; the distinction between outdoor and indoor environments is usually noticeable because the climatic constraints are different (high humidity outside, significant concentration of sulphide compounds inside, *etc.*).^{30,31} Since AgNW networks can be integrated into devices used equally indoors or outdoors, it is essential to study their intrinsic stability. Some studies have reported short stability tests in air atmosphere or in particular environments.^{32–38} However, to the best of our knowledge no studies entirely focused on the stability aspect have been reported so far.

In this paper, we report for the first time sheet resistance monitoring of air-stored AgNW electrodes up to two and a half years. In order to anticipate the critical points that could be encountered by the use of silver nanowires in functional devices, several ageing tests were also carried out. Based on the above considerations the choice of environmental stresses

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was made according to known silver sensibility. In particular, silver nanowire networks were exposed to hydrogen sulphide and light accelerated ageing experiments. Some electrical stresses were also carried out.

Experimental

Silver nanowire synthesis

AgNWs were synthesized according to a previously published procedure.²³ A 160 mL ethylene glycol (EG) solution of NaCl (10 mg) and PVP (3.54 g, $M_w = 40\,000\text{ g mol}^{-1}$) was vigorously stirred at 120 °C and then cooled down to room temperature. This solution was injected slowly using a syringe pump into 80 mL of a magnetically stirred EG solution of AgNO₃ (1.36 g) at 120 °C. The injection rate was set to inject the entire solution in 8 min. At the end of the addition, the reaction mixture was further heated at 160 °C, refluxed for 80 min and cooled down to room temperature in ambient air. To remove the nanoparticles synthesized with the nanowires, a 48 h decantation procedure was used as detailed elsewhere.²³ Finally, the AgNWs were dispersed in methanol.

Electrode fabrication

The fabrication of electrodes was performed on Eagle XG™ glass substrates of alkaline earth boro-aluminosilicate type glass or on 125 μm thick PEN (*i.e.* poly(ethylene 2,6-naphthalate)) substrates obtained from Dupont Teijin (Teonex Q65FA). Deposition was carried out by spin-coating or spray-coating. In the case of spin-coating, electrodes of 2.5 × 2.5 cm² were realized. The air-brush spraying was performed using a vertically mounted commercial airbrush (ExactaCoat Benchtop Ultrasonic Spraying System, from Sono-Tek Corp.). In a typical spray-coating experiment, the substrate was placed on a hot plate at 80 °C. The entire process was performed in air as previously described.²⁷

Stability tests

Controlled exposure to humidity. Samples were stored in two environmental chambers up to 4 months, where the relative humidity and the temperature were 90% and 38 °C and 90% and 60 °C, respectively.

Controlled exposure to light stress. Samples were irradiated using a filtered xenon arc source ($\lambda > 340\text{ nm}$), in a Heraeus Suntest CPS+ (Atlas Inc.) solar simulator, up to 120 h. An additional UV filter was used to simulate outdoor sunlight. Irradiance and temperature were controlled and set respectively at 620 W m⁻² (measured between 290 and 800 nm) and 55 °C.

Controlled exposure to H₂S. Samples were exposed in a home-made test bench to 300 sccm flow of 50 ppm H₂S in air for 20 h.

Stability of the AgNWs-PEDOT:PSS hybrid material. A solution of PEDOT:PSS (Clevios, PH1000) in isopropanol was spin-coated at 1500 rpm for 50 s onto the nanowire network. Samples were stored up to 24 months in the dark and under

ambient atmosphere. Samples were exposed to light only during sheet resistance measurements.

Stability under electrical stress. Several nanowire networks were subjected to a 2 V bias or a current such that the temperature at the center of the sample reaches 60 °C. Current was applied using an ISO TECH IPS 2303 tension and current generator, and bias was applied using a Metrix 3240 generator.

Characterization of the samples

Scanning electron microscopy (SEM) images were obtained using an FEG-LEO XL30 microscope operating at 5 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a NOVA-KRATOS model equipped with an Al K α radiation source (1486.7 eV). Silicon <100> 1–10 Ω cm, 4 in. wafers were used as substrates for XPS analysis. AgNWs were dropped on cleaned silicon surfaces. Experiments were conducted on 1 cm² samples cleaved from the substrate. TEM analysis was performed using a FEI Tecnai Osiris microscope operating at 200 kV. Samples for TEM were prepared by depositing a drop of the original suspension on a carbon coated Cu grid and allowing the solvent to evaporate. Total transmittance values were measured on a Varian Cary 5000 spectrophotometer using an integrating sphere and the substrate as reference. The sheet resistance was measured using a four pin probe with a Loresta EP resistivity meter. To obtain the standard deviation, at least 5 distinct measurements were performed on each sample. For electrical stress experiments, both current and voltage were measured using an Agilent U1251B multimeter connected through a USB to the Agilent Handheld Meter Logger software. Temperature was measured using a K-type thermocouple plugged into the same multimeter.

Results and discussion

Properties of the as-deposited silver nanowire electrodes

Before studying the stability of the AgNW-based electrodes, it is important to know the characteristics of the networks. AgNWs have a mean diameter and length of 65 ± 15 nm and 10 ± 5 μm, respectively. XPS analyses of the samples showed that neither oxide nor sulphide were initially present. A SEM photograph of a small part of the network is shown in the inset of Fig. 1).

At the beginning of our research the electrodes were prepared by spin-coating the AgNW solution onto glass substrates. The anisotropic orientation of nanowires induced by this deposition technique proved to greatly limit the number of possible percolation paths, resulting in the realization of electrodes with low optoelectronic performances. Thus, the spray-coating printing technique allowing an easily scalable and low cost process was preferred. It leads to much better performances through a randomly oriented mesh (see Fig. S1†). Fig. 1 displays the evolution of transmittance of spray-coated AgNW meshes as a function of the sheet resistance. Electrodes demonstrate excellent optoelectronic properties (typically $R_s < 20\ \Omega\ \text{sq}^{-1}$ @ $T_{550\text{ nm}} = 90\%$) without any energy-

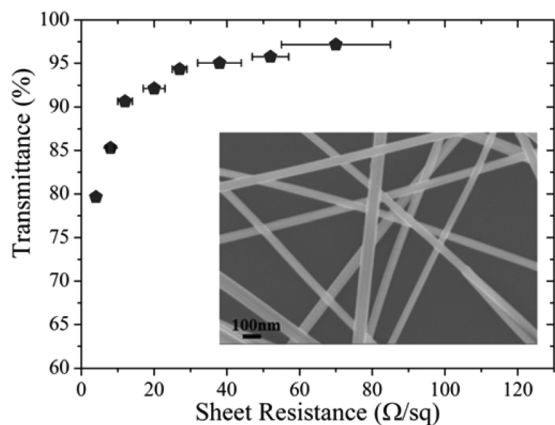


Fig. 1 Transmittance of AgNW spray-coated electrodes as a function of the sheet resistance. Inset: the SEM image of AgNW meshes.

consuming post-treatment (thermal annealing or mechanical compression).

Two and a half years air-storage stability

To investigate the stability of the electrodes, the first step was to simply follow the evolution of the sheet resistance of samples stored under the ambient atmosphere of the laboratory, and protected from light. It can be observed in Fig. 2 that under these conditions the mean electrical conductivity of the first spin-coated electrodes on glass was stable for two and a half years (hatched bars). Similar behaviour was observed for spray-coated electrodes on PEN after 2 years.

Contrary to the Moon *et al.* study which reported an increase of the sheet resistance of their electrodes by a factor of 3 in two months of air-storage,³³ our AgNW meshes were found to be stable during a long-term storage under ambient atmosphere. Though we do not know exactly the nature of their nanowires, the ageing kinetic difference may originate from purification steps or post-treatment (plasma treatment in their case). The long-term stability of our electrodes in

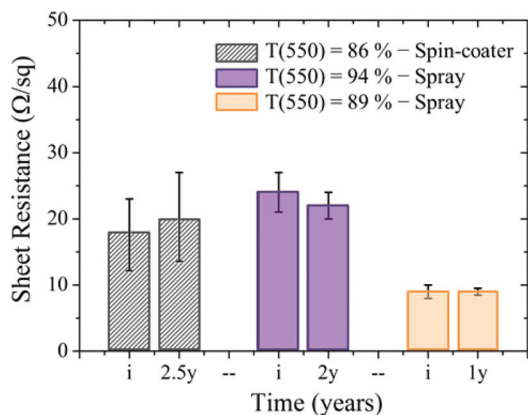


Fig. 2 Sheet resistance of AgNW electrodes with different network densities and printing deposition techniques as a function of air atmosphere and storage duration (i = initial).

ambient air was very encouraging, and it was thus used as a reference for the further stability experiments we performed.

Environmental chamber stability

Two different environmental chambers were used. The relative humidity (RH) was kept the same (90%) but different temperatures were set (38 and 60 °C). Tests were named as follows: 38–90 and 60–90 (*i.e.* T (°C) – HR (%)). We chose to work at high relative humidity (90%) in order to potentially accelerate the ageing phenomena. Fig. 3a shows sheet resistance changes of two AgNW networks with different densities after four months of experiment.

This study revealed that the modification of electrical conduction properties of AgNW meshes clearly depends on climatic conditions. Indeed, the initial sheet resistance of the electrode decreased slightly after four months at 38 °C and 90% RH whereas it increased significantly when the temperature was set at 60 °C. Similar behaviour was observed for the two studied networks. For example, in the case of the electrodes of $T_{550 \text{ nm}} = 90\%$ (red bars in Fig. 3a), the initial sheet resistance ($29 \pm 3 \Omega \text{ sq}^{-1}$) dropped to $23 \pm 7 \Omega \text{ sq}^{-1}$ on average when stored in the 38–90 climate chamber while it rose to $52 \pm 13 \Omega \text{ sq}^{-1}$ on average in the 60–90 chamber. Relative decrease (–20%) and increase (+80%) of the sheet resistance were nearly identical in the case of AgNW electrodes with $T_{550 \text{ nm}} = 93\%$ (blue bars in Fig. 3a).

The morphological observations of these electrodes help to understand the electrical difference as a function of environmental ageing conditions. Indeed, in the SEM image under 60–90 conditions (Fig. 3b), AgNWs show surface roughness. Some nanowire junctions are welded (orange arrows) and many breaks are visible (red arrows). These facts can explain

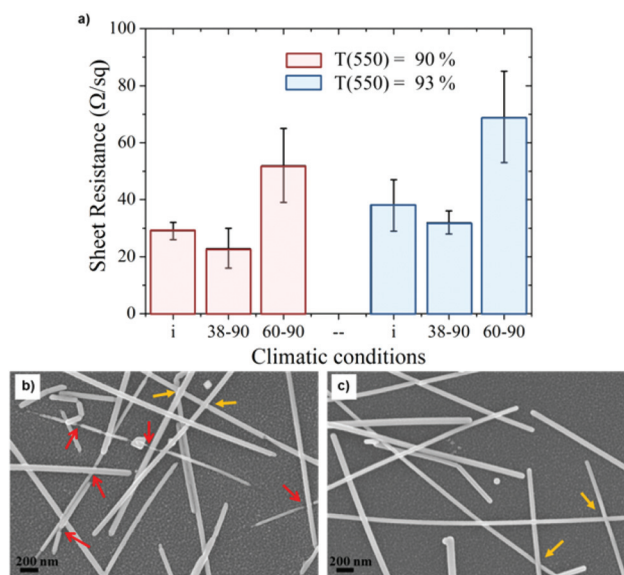


Fig. 3 (a) Sheet resistances of AgNW electrodes of different network densities after 4 months of storage in an environmental chamber (i = initial). SEM images of AgNW networks on PEN ($T_{550 \text{ nm}} = 90\%$) after 4 months at 90% RH and (b) 60 °C and (c) 38 °C.

the degradation and heterogeneity of conducting properties after 4 months of storage in the 60–90 environmental chamber. Observation of many samples (>10) led to the same conclusions, whatever the network density. At constant relative humidity, no nanowire degradation was observed when the temperature was 38 °C. No breaks were detected and some junctions between the two nano-objects were welded (orange arrows Fig. 3c), which can explain the improvement of the electrical conductivity of AgNW electrodes (20% decrease of the sheet resistance value after 4 months).

It appears that after 4 months under high humidity (90% RH) at 38 °C, electrode performances were not degraded. The sheet resistance was even improved. Humidity does not seem to be a critical parameter, which is consistent with studies on thin films of bulk silver showing that the kinetics of silver corrosion are similar regardless of the ambient humidity.³¹ Nevertheless, when high humidity was associated with a temperature of 60 °C, AgNW electrodes remained fully functional and their electrical conductivity degraded after four months of storage. These results are in good agreement with literature reports when different ageing conditions were used, typically lower humidity ($\leq 85\%$) but higher temperature (≥ 70 °C).^{32,34–36} For example, after only 10 days in a chamber at 85 °C and 85% of relative humidity, the sheet resistance of the nanowire network increased by more than 20%.³²

Stability under luminous stress

Amongst the various applications in which AgNW electrodes can be integrated, optoelectronic devices are predominant. It is therefore essential to study the impact of light exposure on the morphology and electrical properties of AgNW electrodes.

AgNW-based electrodes were irradiated up to 120 h under an irradiance of 620 W m^{-2} using a Suntest simulator. This procedure induced ageing, which was calculated to be equivalent to the exposure to sunlight irradiation in central Europe for 48 days (according to Atlas Inc. documentation, see the Experimental section).

As shown in Fig. 4a whatever the density of AgNW networks, the sheet resistance decreased after 120 h exposure. The SEM observations revealed that the nanowire surface was strongly modified after light irradiation (Fig. 4b and c). Surface roughness and the presence of numerous nanoparticles throughout the AgNW surface were observed. However, some contacts between nanowires appeared to be significantly improved (orange arrows – inset Fig. 4b), whereas some nanowires were broken (red arrows). These observations were found to be independent of the nanostructure density.

XPS analyses were performed in order to determine the nature of the extreme surface of the nanowires and provide understanding of ageing mechanisms. Compared to freshly deposited AgNW electrodes, XPS peaks revealed a silver oxide signature after light exposure (see Fig. S2†). Photocorrosion of silver nanoparticles³⁹ or continuous films^{40,41} has already been studied; however, to our knowledge this is the first time that the oxidation of silver nanowires caused by prolonged light exposure has been reported. It is well known that UV

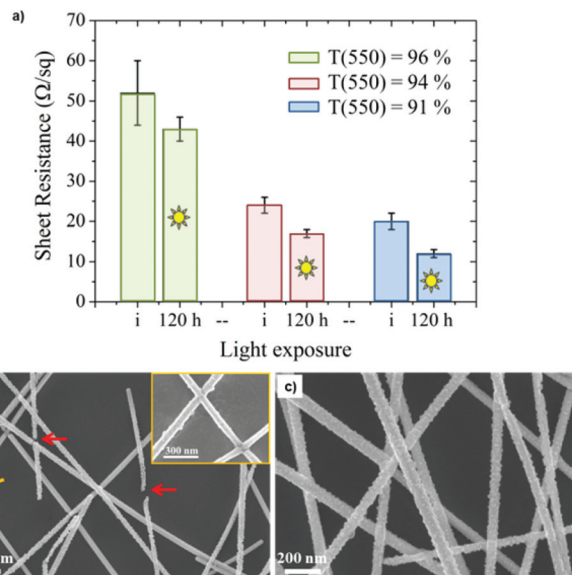


Fig. 4 (a) Sheet resistance of AgNW electrodes with different network densities after 120 h of light irradiation (i = initial). (b) and (c) SEM images at different magnifications of AgNW networks on PEN ($T_{550 \text{ nm}} = 91\%$) after 120 h of light exposure.

light ozone dissociation can be responsible for silver oxide formation; however, considering the poor electrical conductivity of the oxide compared to bulk metal,⁴² the slight decrease of the sheet resistance of AgNW meshes after irradiation remains unclear. It may be ascribed to local sintering (as shown in the inset of Fig. 4b), or possibly to the UV light degradation of organic residues remaining at the nanowire–nanowire contacts.

Sulfidation of silver nanowires

Unlike many other metals, silver does not tend to form surface oxides naturally. However, sulfidation of bulk silver (jewelry tarnishing) is a well-known and widely studied phenomenon.^{30,31,43,44} It has been shown that silver is particularly sensitive to carbonyl sulphide (COS) and hydrogen sulphide (H_2S) whereas it does not react with sulfur dioxide (SO_2). We performed exposure of 2 AgNW networks to a constant flow of 50 ppm H_2S in dry air for 8 h. It must be noted that this concentration is much higher than the usual ambient concentration (*i.e.* 0.1–0.3 ppb). Fig. 5a shows the evolution of the meshes of different densities ($T_{550 \text{ nm}} = 88\%$ and 91%). In the case of $T_{550 \text{ nm}} = 88\%$, the sheet resistance was measured every two hours (blue curve). In both cases, the electrical conductivity of the electrodes was not altered ($R_s = 13 \pm 1 \Omega \text{ sq}^{-1}$ and $20 \pm 1 \Omega \text{ sq}^{-1}$ respectively) by an extended exposure to highly concentrated H_2S flow.

The samples were observed by SEM before and after this exposure to H_2S (Fig. 5b and c). Though the conductivity of the network remained stable, we detected the appearance of tiny particles along the nanowires, probably arising from a reaction between surface silver atoms and hydrogen sulphide. This observation is consistent with the report of Bennett *et al.*

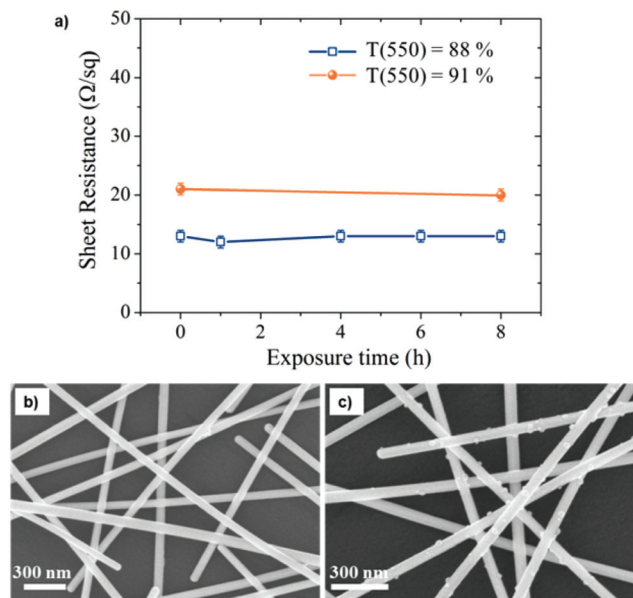


Fig. 5 (a) Plot of sheet resistance of AgNW electrodes with two different network densities vs. time exposure to 50 ppm flow of H_2S . SEM images of AgNW networks (b) before and (c) after exposure to 50 ppm flow of H_2S during 8 h.

showing that when evaporated silver films are corroded, they do not tend to form uniform thin films but a discontinuous series of clumps.⁴⁵ In order to chemically characterize these nanoparticles, TEM and XPS experiments were performed. As illustrated in Fig. 6a, similar nanoparticles were observed after H_2S exposure of AgNWs deposited on a TEM grid during 8 h.

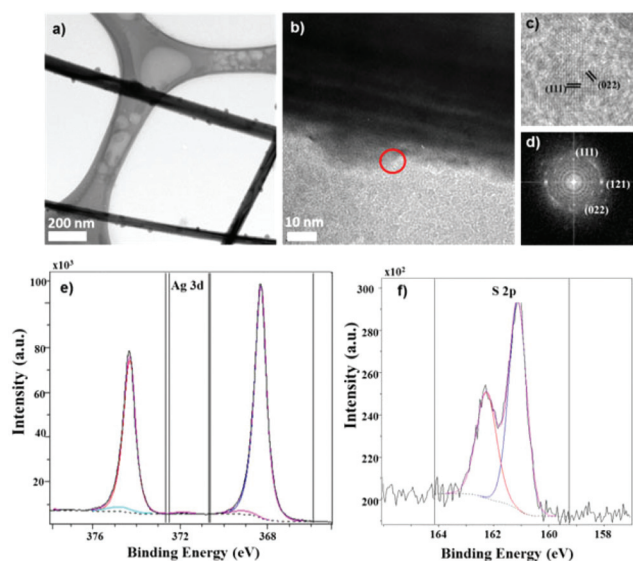


Fig. 6 (a) and (b) TEM images at different magnifications of AgNW exposed under H_2S flow during 8 h (scale bar respectively of 200 nm and 10 nm). (c) High resolution TEM image realized in the red circle area and (d) corresponding FFT image exhibiting (111), (121) and (022) preferential orientations. Curve fitting of (e) Ag 3d and (f) S 2p XPS spectra for AgNW networks exposed to 50 ppm flow of H_2S .

The analysis of the high resolution image (Fig. 6c) of one nanoparticle (illustrated by the red circle in Fig. 6b) and its corresponding fast Fourier transform (FFT) pattern (Fig. 6d) revealed that the inter-planar distances can be indexed as the crystal planes (111), (121) and (022) of the Ag_2S β monoclinic structure.

XPS characterization was also conducted to confirm the TEM analysis.

Analysis of the Ag 3d peaks highlights the presence of a single contribution in the form of a doublet (Ag 3d_{5/2} and Ag 3d_{3/2} with binding energies at 368.3 and 374.3 eV, respectively) corresponding to elemental silver Ag^0 (Fig. 6e). XPS energy resolution of 0.48 eV is not sufficient to discriminate elemental silver Ag^0 and silver sulphide Ag_2S (the binding energies of the metal and the sulphide are very close, $\Delta < 0.48$ eV). However, the sulfur S 2p peak present on the surface of the sample (Fig. 6f) reveals binding energies of 161.1 and 162.3 eV that are characteristic of the metal sulphide Ag_2S , in agreement with the literature.³⁷ Even though the presence of Ag_2S has been confirmed, the fact that it is a poor conductor of electricity compared to bulk silver⁴⁶ has no observable effect on the sheet resistance of AgNW electrodes. This may be ascribed to the localized (nanoparticles) amount of Ag_2S at the very surface of NWs, which does not disturb the overall electrical percolation in the network.

Stability of AgNW/PEDOT:PSS composites

Conductive polymers and in particular PEDOT:PSS are currently present in many optoelectronic devices such as organic solar cells. Several studies have shown that the electrical conductivity of AgNW meshes can be improved by covering them with a thin layer of PEDOT:PSS.^{16,24,47} It is therefore important to monitor the long-term evolution of the sheet resistance of AgNW-PEDOT:PSS composites. Similarly to networks made with pristine nanowires, composites were stored in air and protected from light. The first experiments were performed two years ago, in which AgNWs were spin-coated on glass. As shown in Fig. 7a the electrical resistivity of AgNW meshes covered by a 50 nm layer of PEDOT:PSS increased over time and the evolution was found to be highly dependent on the density of the network. For example, sheet resistance of an electrode at 81% transmittance increased by 150% in two years, while the one with a more transparent electrode ($T_{550 \text{ nm}} = 88\%$), and being therefore less dense, rose by 480%. The measured standard deviation also increased as a function of time, which suggested a non-linear degradation of the network.

This was confirmed with the SEM image (Fig. 7b) where some broken nanowires were observed. Several assumptions can be made to attempt to explain degradation of AgNWs. The first is the acidic nature of the PEDOT:PSS solution. The pH of the PEDOT:PSS (Clevios PH 1000) used in our tests was measured at 2.5. The acidity of the solution of the polymer might explain the rupture of some nanowires over time as observed by SEM. This argument is in agreement with the work reported by Lee's team showing that AgNWs were quickly

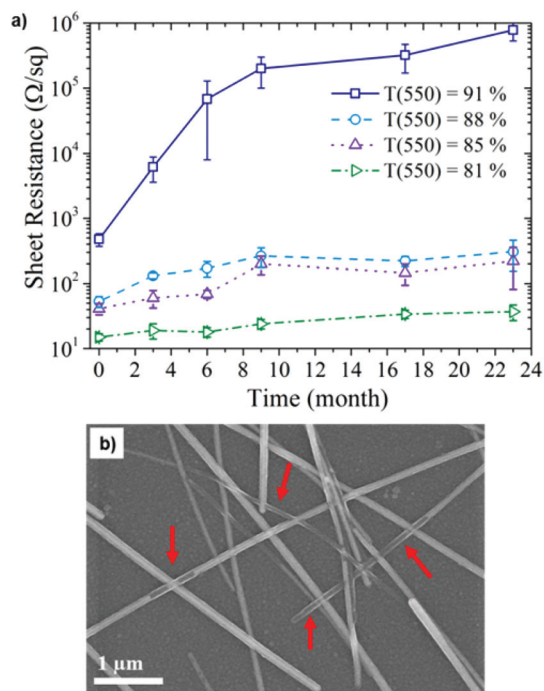


Fig. 7 (a) Sheet resistances of AgNW networks of different densities coated with a 50 nm layer of PEDOT:PSS as a function of time. (b) SEM image of AgNW meshes covered with a 50 nm PEDOT:PSS layer, fabricated 2 years ago.

corroded when immersed in PEDOT:PSS acidic solution.^{35,36} On the other hand, PEDOT:PSS is also known for its tendency to absorb water, which results in a degradation of its own electrical properties.⁴⁷ In our case, the sheet resistance of a 50 nm layer of pure PEDOT:PSS, measured initially at $2 \times 10^5 \Omega \text{ sq}^{-1}$, rose to one order of magnitude higher ($5 \times 10^6 \Omega \text{ sq}^{-1}$) after two years under an air atmosphere and in light-protected storage. This phenomenon may be important, particularly in the case where PEDOT:PSS plays a dramatic role in the conductivity of the electrodes, *i.e.* for low density networks. As demonstrated by Glover *et al.*, nano or macrometric sized silver structures may easily generate very small nanoparticles (only few nanometers) in their vicinity, a phenomenon further exacerbated in the presence of high humidity.⁴⁸ We suggest here that water absorption of PEDOT:PSS could therefore also impact the mechanisms of ageing leading to breakage of nanowires into particles.

Although the electrical properties of AgNW electrodes coated with PEDOT:PSS degraded faster than those of pristine networks,⁴⁹ it must be noted that the sheet resistance usually remained below $300 \Omega \text{ sq}^{-1}$ after 2 years, which can be sufficient for many applications. However, these spin-coated samples did not show a very high transparency. Significant improvements have been realized in the last two years for the purification of nanowires and improvement of electrode properties, thus it would be of interest to perform the same type of monitoring on state-of-the-art electrodes.

Stability under electrical stress

Since the AgNW networks are designed to be used in electronic devices, it seems relevant to study their behaviour under various electrical stresses. To our knowledge, very few studies have been reported on the electrical stability of AgNW networks. A work by Goldthorpe *et al.* showed that their AgNW networks lost conductivity within several hours or days under such a stress.³⁸ To assess the stability of our AgNW based electrodes under an electric stress, we designed two distinct tests. The first, aimed to simulate the conditions appearing in optoelectronic devices such as PV cells or LCD panels, consisted of the application of a continuous voltage (2 V) to samples having an initial resistance of $40 \Omega \text{ sq}^{-1}$. Under these conditions, no significant heating of the electrodes was observed. The second was performed in order to increase the current density, which also simulates the operating conditions of a heating film. We sought to make the electrode temperature induced by Joule heating reach a value of 60 °C, which was achieved by passing a continuous current of 180 mA through a $20 \Omega \text{ sq}^{-1}$ sample.

Fig. 8 shows the evolution as a function of time of the resistances of these samples. It can be observed that there were no significant changes of the resistances compared to the initial values for the samples being subjected to a 2 V bias, or to a current maintaining the temperature at 60 °C. The slight rise of resistance may possibly be ascribed to the irreversible damage of some AgNWs. Low density samples demonstrate a weaker stability because there are fewer nanowires to conduct

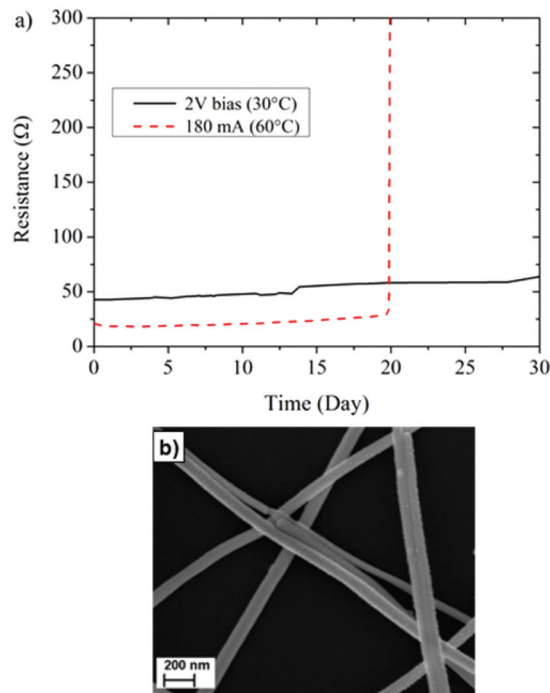


Fig. 8 (a) Evolution of the resistance as a function of time for two different samples. The first one (black solid line) was subjected to a continuous 2 V bias whereas the second one (red dashed line) was subjected to a continuous 180 mA current. (b) SEM picture of AgNWs after 3 weeks of electrically heating at 60 °C.

the current, and damaging one of them is therefore more critical regarding the percolation issue (see Fig. S3†); for a constant current density, each broken percolation path induces an increased current in the other conducting paths, which may accelerate the damaging process. Despite this phenomenon, after more than 4 weeks the 2 V biased electrodes maintained their ability to conduct current without significant changes. The temperature in the center of this electrode was about 30 °C. For a higher temperature set at 60 °C, the electrode was stable for 3 weeks. Then, the PEN substrate melted in its center, irreversibly damaging the electrode. As already reported by Goldthorpe *et al.*, we observed a change of the nanowire morphology, in particular due to the presence of tiny nanoparticles (Fig. 8b).³⁸

We also considered the electrical stability of the AgNW/PEDOT:PSS composites. Fig. 9a shows the evolution of resistance as a function of time for two electrodes containing either nanowires only or AgNWs covered by a thin layer (50 nm) of PEDOT:PSS. Both samples had the same initial sheet resistance ($\sim 25 \Omega \text{ sq}^{-1}$), and the same 2-point resistance ($\sim 25 \Omega$) since samples were square-shaped. It appears obvious that hybrid electrodes are less stable. This was realized on several samples with reproducible results. The much lower stability can be due to the fact that the composite sample contains less

AgNWs at equal sheet resistance. To assess this hypothesis, we subjected two samples containing the same amount of AgNWs to a current in order to reach a temperature of 60 °C. The results are shown in Fig. 9b). Here again, the hybrid electrode is much less stable than the one containing only AgNWs. Therefore, we can conclude that AgNW electrodes are more stable than AgNW/PEDOT:PSS composites. This could also be correlated to the results reported earlier herein, without electrical stress, which mentioned the shorter stability of AgNW electrodes when they were coated with a thin layer of PEDOT:PSS. The SEM observations confirmed the difference in the ageing mechanism. As shown in Fig. 9c, it can be observed after the experiments that some nanowires were cut and new large silver structures appeared. These experiments indicate that adding PEDOT:PSS on the top of AgNW networks decreases stability under long term electrical stress.

Conclusions

In summary, AgNW based electrodes demonstrate good stability under several accelerated ageing processes. After 2 years of storage in the dark and in air, four months of storage at 38 °C and 90% RH, 8 h exposure under a 50 ppm flow of H₂S or 120 h of light exposure (equivalent to 48 days of Central Europe natural sunlight), the sheet resistance of the electrodes was insignificantly degraded, and even improved in some cases. Morphological changes of nanowires due to silver sulphide or silver oxide formation were observed without significant impact on the optoelectronic properties.

Nonetheless, more drastic environmental conditions (60 °C – 90% HR) or prolonged PEDOT:PSS contact caused a degradation of electrical conduction properties.

Also note that AgNW networks demonstrate good stability when low voltage is applied (the experiment was stopped after 30 days). However, stronger electrical stress, raising the network temperature to 60 °C, leads to faster degradation of the transparent electrode (still stable for 20 days in non-stop experiment). In addition, we highlight for the first time that PEDOT:PSS coating can be responsible for early damage of AgNW electrode properties. This fact is important and should be considered for integration of these electrodes since this combination of PEDOT:PSS with AgNW networks is widely used in optoelectronics.

This study brings significant preliminary information on the origins of electrode deterioration. Stability studies are complex because the kinetics and mechanisms of ageing depend on many parameters (nanostructure shape, density of silver nanowire networks, organic residues, temperature/relative humidity, substrate, *etc.*). Further studies are needed to combine several parameters to look deeper into the ageing mechanisms and potential synergistic effects.

An important point is that this study was carried out on pristine nanowires without any encapsulation (except for PEDOT:PSS experiments). Thus it deals with the intrinsic properties of AgNWs and can be considered as a reference point

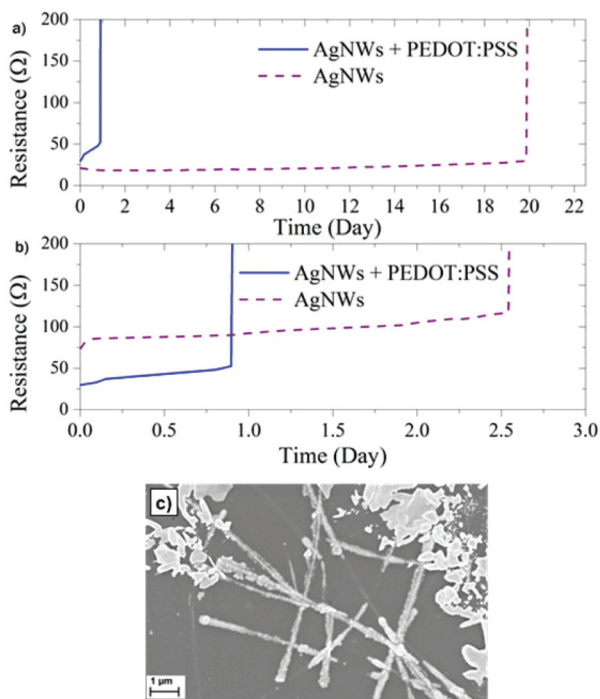


Fig. 9 (a) Evolution as a function of time of the resistance of a pristine AgNW electrode (purple dashed line) and an AgNW electrode covered with 50 nm of PEDOT:PSS (solid blue line) having the same initial resistance, and subjected to 60 °C by Joule heating. (b) Evolution as a function of time of the resistance of a sample of AgNWs (purple dashed line) and a sample of AgNWs with coated PEDOT:PSS (solid blue line) with the same initial density of AgNWs heated to 60 °C by Joule heating. (c) SEM picture of AgNWs in PEDOT:PSS after the loss of conductivity, and grey particles are made of silver (checked by EDX analysis).

for future investigations. Indeed it must be kept in mind that if they are encapsulated by organic or inorganic layers, or integrated in stacked configurations, then many other parameters will have to be taken into consideration and specific studies will be required.

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