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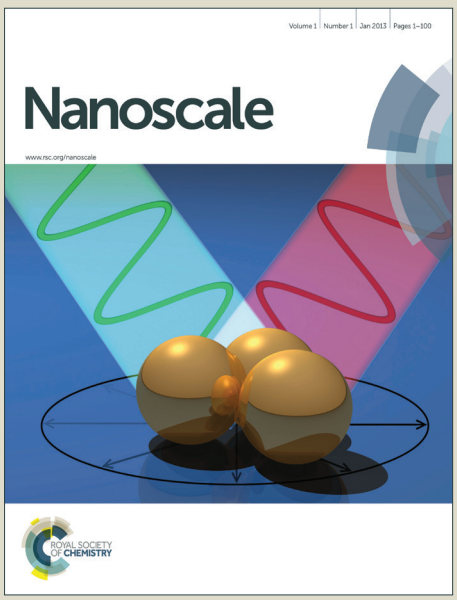

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Stability of silver nanowire based electrodes under environmental and electrical stresses

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Flexible transparent electrodes fabricated with random networks of silver nanowires (AgNWs) have been widely studied in recent years. This approach appears as 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 work 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 in ambient atmosphere up, at least, to two and a half years. Accelerated ageing processes also reveal that concentrated H2S or light exposure do not cause 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.

Introduction

Various routes have recently emerged for ITO (indium tin oxide) replacement 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] metallic nanowires[12–16], the number of publications relating 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) are now well developed. Moreover, beyond demonstrating optoelectronic performances similar to ITO, AgNW networks can maintain their electrical conductivity during mechanical stress (bent, crumpled, stretched, compressed...).[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] or films 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 studied extensively; the distinction between outdoor and indoor environments is usually pointed out because the climate constraints are different (high humidity outside, significant concentration of sulphide compound inside, etc.).[30,31] Since AgNW networks can be integrated in devices used equally indoor or outdoor, it is indispensable 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 work dedicated to this 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 critical points that could be encountered by the use of silver nanowires into functional devices, several ageing tests were also carried out. Based on the above considerations the choice of environmental stresses 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 previous published procedure.[23] A 160 mL ethylene glycol (EG) solution of NaCl (10 mg) and PVP (3.54 g, Mw = 40,000 g/mol) 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 $AgNO_3$ (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 synthetized 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 realized on Eagle XGTM glass substrates of alkaline earth boro-aluminosilicate type glass or 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 2.5x2.5 cm² were realized. The air-brush spraying, using a vertically mounted commercial airbrush (ExactaCoat Benchtop ultrasonic spraying system, from Sono-Tek corp.) ~~allowed fabrication of electrodes up to 30x30 cm².~~ In a typical spray-coating experiment, substrate was placed on a hot plate at 80 °C. The entire process was realized 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 % RH – 38 °C and 90 % RH – 60 °C.

Controlled exposure to light stress. Samples were irradiated using filtered xenon arc source (λ > 340 nm), in a Heraeus Suntest CPS+ (Atlas Inc.) solar simulator, up to 120 h. An additional UV filter was present to simulate outdoor sunlight. Irradiance and temperature were controlled and set respectively at 620 W/m² (measured between 290-800 nm) and 55 °C.

Controlled exposure to H_2S. Samples were exposed in a home-made test bench to a 300 sccm flow of 50 ppm of H_2S in air for 20 h.

Stability of AgNWs-PEDOT:PSS hybrid material. A solution of PEDOT:PSS (Clevios, PH1000) in isopropanol was spin-coated at 1,500 rpm for 50 s onto the nanowire network. Samples were stored up to 24 months in the dark and ambient atmosphere. Samples were exposed to light only during sheet resistance measurements.

Stability under electrical stress. Several nanowire networks were submitted to a 2 V bias or a current such as the temperature in the center of the sample reaches 60 °C. Currents were applied using a ISO TECH IPS 2303 tension and current generator, and bias were applied using a Metrix 3240 generator.

Characterization of the samples – *S*canning electron microscopy (SEM) images were obtained on a FEG-LEO XL30 microscope operating at 5 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a NOVA-KRATOS model equipped with an Al Kα radiation source (1,486.7 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 in 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 standard deviation at least 5 distinct measurements were performed on each sample. For electrical stress experiments, both current and voltage were measured using Agilent U1251B multimeters connected through USB to the Agilent Handheld Meter Logger software. Temperature was measured using a K-type thermocouple plugged in the same multimeters.

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 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 made by spin-coating of 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 Rs< 20 Ω/sq @ T_{550nm} = 90 %) without any energy-consuming post-treatment (thermal annealing or mechanical compression).

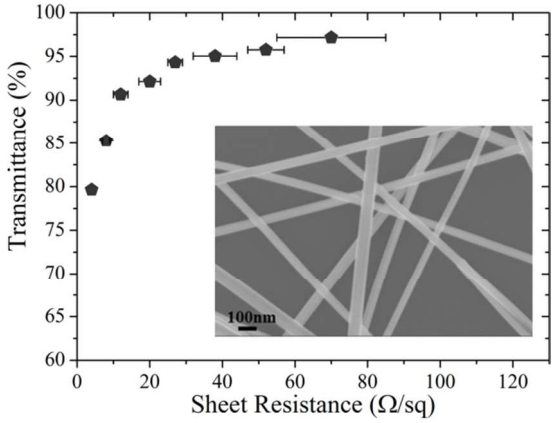

Fig. 1 Transmittance of AgNW spray-coated electrodes as a function of the sheet resistance. Inset: SEM image of AgNW mesh.

Two and a half years air-storage stability

To investigate the stability of the electrodes, the first action was to simply follow the evolution of the sheet resistance of samples stored in the laboratory atmosphere and protected from light. It can be observed on 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.

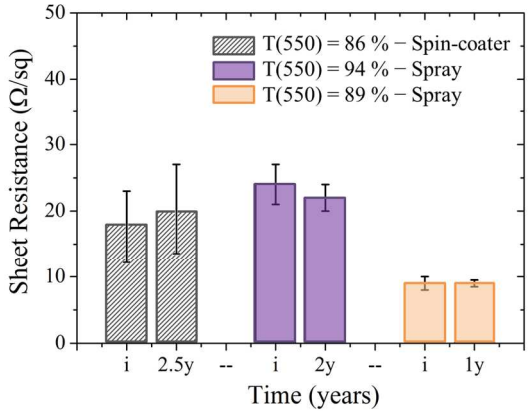

Fig. 2 Sheet resistance of AgNW electrodes with different network densities and printing deposition techniques as a function of air atmosphere and storage duration (i=initial).

Contrary to 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 in 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 ambient air was very encouraging, 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 the same (90%) and 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.

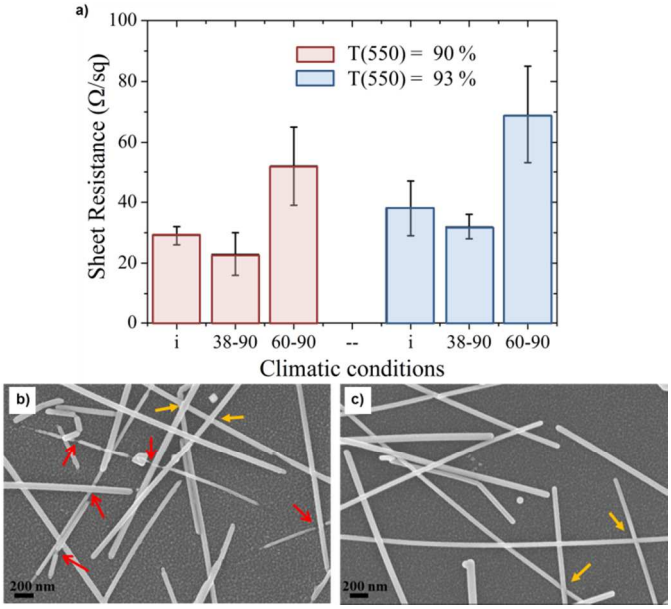

Fig. 3 (a) Sheet resistances of AgNW electrodes with different network densities after 4 months of storage in an environmental chamber (i=initial). SEM images of AgNW networks on PEN (T_{550nm} = 90%) after 4 months at 90% RH and (b) 60 °C (c) 38 °C.

This study revealed that 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_{550nm} = 90 % (red bars in Fig 3a), the initial sheet resistance (29 ± 3 Ω/sq) dropped to 23 ± 7 Ω/sq in average when stored into the 38-90 climate chamber while it rose to 52 ± 13 Ω/sq in average in the 60-90 one. Relative decrease (-20 %) and increase (+80 %) of the sheet resistance were nearly identical in the case of AgNW electrodes with T_{550nm} = 93 % (blue bars in Fig 3a).
Morphological observations of these electrodes help to understand the electrical difference as a function of the environmental ageing conditions. Indeed, on the SEM image for 60-90 conditions (Fig. 3b), AgNWs present surface roughness. Some nanowire junctions are welded (orange arrows) and many breaks are visible (red arrows). These facts can explain 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 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, although AgNW electrodes remained fully functional their electrical conductivity was degraded after four months of storage. These results are in good agreement with literature reports when different ageing conditions were used, typically lower humidity (≤ 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 nanowire network increased by more than 20 %.[32]

Stability under luminous stress

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

AgNW-based electrodes were irradiated up to 120 h under an irradiance of 620 W/m² in a suntest simulator. This procedure induced ageing calculated to be equivalent to exposure to sunlight irradiation in central Europe for 48 days (according to Atlas Inc. documentation, see experimental part).

As shown in Fig. 4a whatever the density of AgNW networks, the sheet resistance was 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.

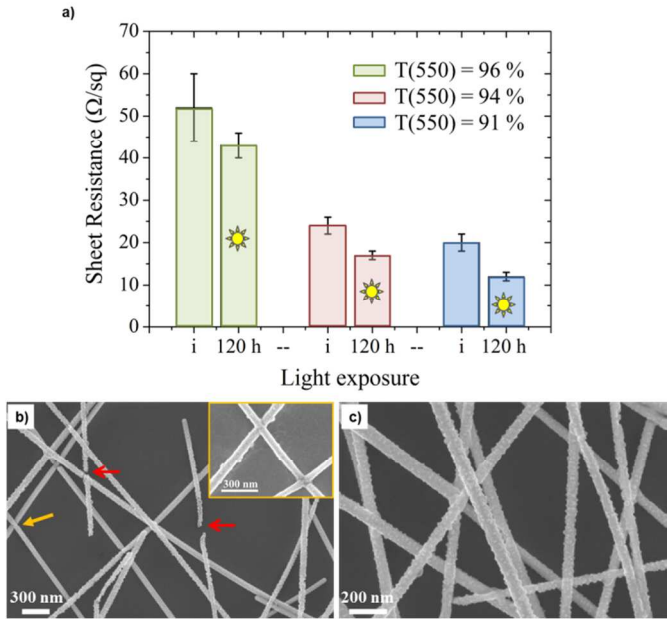

Fig. 4 (a) Sheet resistance of AgNW electrodes with different network densities after 120 h of light irradiation (i=initial). (b) and (c) SEM images at different magnification of AgNW network on PEN (T_{550nm} = 91 %) after 120 h of light exposure.

XPS analyses were performed in order to determine the nature of the extreme surface of the nanowires and provide comprehension about ageing mechanisms. Compared to fresh deposited AgNW electrodes, XPS peaks revealed silver oxide signature after light exposure (see Fig. S2†). Photocorrosion of silver nanoparticles[39] or continuous films[40,41] have already been studied, however to our knowledge it is the first time that oxidation of silver nanowires caused by prolonged light exposure is reported. It is well known that UV light ozone dissociation can be responsible of silver oxide formation, however considering the poor electrical conductivity of 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 in Fig. 4b), or possibly to the UV light degradation of organics residues remaining at the nanowire-nanowire contacts.

Sulfidation of silver nanowires

Unlike many other metals, silver does not tend to form naturally surface oxides. 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_{550nm} = 88 % and 91 %). In the case of T_{550nm} = 88 %, the sheet resistance was measured every two hours (blue curve). In both cases, the electrical

conductivity of the electrodes was not altered (Rs= 13 ± 1 Ω/sq and 20 ± 1 Ω/sq respectively) by an extended exposure to highly concentrated H_2S flow.

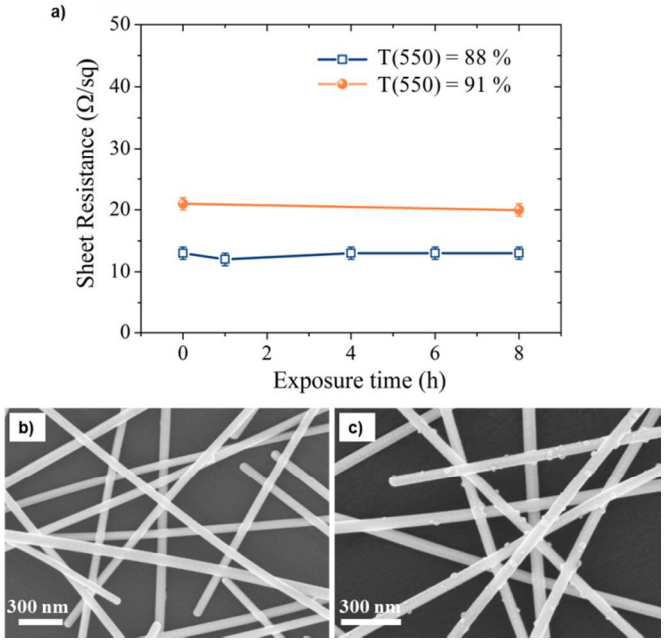

Fig. 5 (a) Plot of sheet resistance of AgNW electrodes with two different network densities vs. time exposure to 50 ppm flow of H_2S. SEM images of AgNW network c) before and d) after exposure to 50 ppm flow of H_2S during 8 h.

The samples were observed by SEM before and after this exposure to H_2S (Fig. 5b and c). Tough 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.* showing that when evaporated silver film 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. 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 characterizations were also conducted to confirm the TEM analysis.

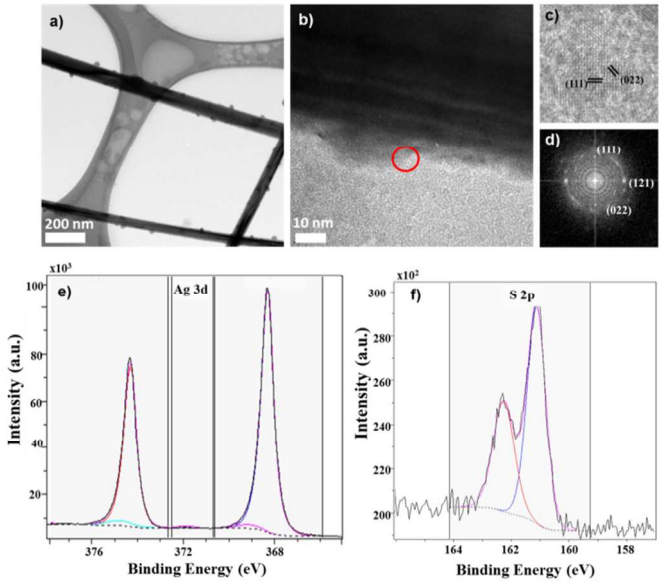

Fig. 6 (a) and (b) TEM images at different magnification of AgNW exposed under H2S flow during 8 h (scale bar respectively of 200nm and 10nm). (c) High resolution TEM image realized in the red circle area and (d) corresponding FFT image exhibiting (111), (121) and (022) preferential orientations.

Analysis of the Ag3d peaks highlights the presence of a single contribution in the form of a doublet (Ag3d5/2 and Ag3d3/2 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 to silver sulphide Ag_2S (the binding energies of the metal and the sulphide are very close, Δ <0.48 eV). However, the sulfur S2p peak presented 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 is confirmed, the fact that it is a poor conductor of electricity compared to bulk silver[46] 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 composite

Conductive polymers and in particular PEDOT:PSS are currently present in many optoelectronic devices such as organic solar cells. Several studies have shown that electrical conductivity of AgNW meshes can be improved through covering with a thin layer of PEDOT:PSS.[16,24,47] It is therefore important to monitor 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, 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 of a more transparent electrode (T_{550nm} = 88 %), and 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.

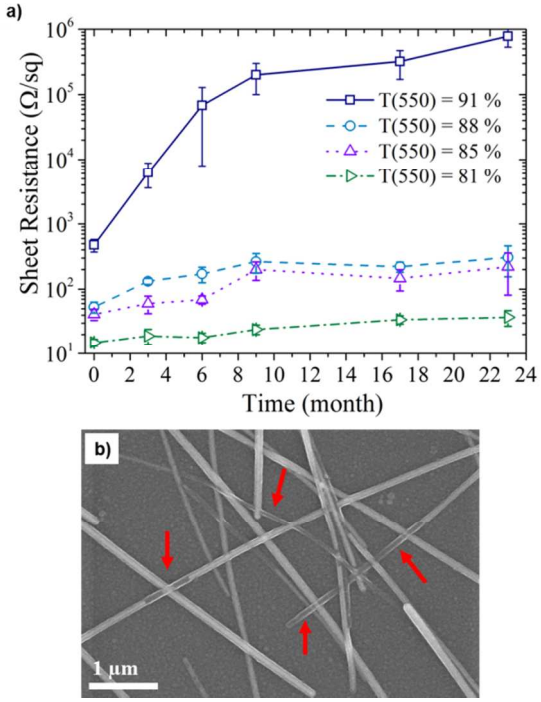

Fig. 7 (a) Sheet resistances of AgNW networks of different densities coated with a 50 nm layer of PEDOT:PSS as a function of time. (b) SEM image of AgNW mesh covered with 50 nm PEDOT:PSS layer, fabricated 2 years ago.

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 one 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 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 corroded when immerged in PEDOT:PSS acidic solution.[35,36] In another 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 2.10^5 Ω/sq, rose to one order of magnitude higher (5.10^6 Ω/sq) after two years in air atmosphere and light-protected storage. This phenomenon may be important particularly in the case where PEDOT:PSS plays a dramatic role in conductivity of the electrodes, *i.e.* for low density networks. As demonstrated by Glover *et al.*, nano or macrometric size silver structures may easily generate very small nanoparticles (only few nanometers) in their vicinity, 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 were degraded faster than those of pristine networks,[49] it must be noted that the sheet resistance usually remained below 300 Ω/sq 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 was realized by Goldthorpe and al. who 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 one, aiming to simulate the conditions appearing in optoelectronic devices such as PV cells or LCD panels, consisted in the application of a continuous voltage (2 V) to samples having an initial resistance of 40 Ω/sq. Under these conditions, no significant heating of the electrodes was observed. The second one was performed in order to increase the current density, which also simulate the operating conditions of a heating film. We sought that electrode temperature induced by Joule heating reached a value of 60 °C, which was obtained by passing a continuous current of 180 mA through a 20 Ω/sq sample.

Fig. 8 shows the evolution as a function of time of the resistances of these samples. It can be observed that no significant changes of the resistances compared to the initial values were observed for the samples being submitted to a 2 V bias, or to a current preserving the temperature at 60 °C. The slight rise of resistance may possibly be ascribed to irreversible damages of some AgNWs. Low density samples demonstrate a weaker stability because there are less nanowires to conduct 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 accelerates the damaging process. Despite this phenomenon, after more than 4 weeks the 2 V biased electrodes kept their ability to conduct the 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, damaging irreversibly the electrode. As already reported by Goldthorpe et

al., we observed a change of the nanowire morphology, in particular due the presence of tiny nanoparticles (Fig. 8b).[38]

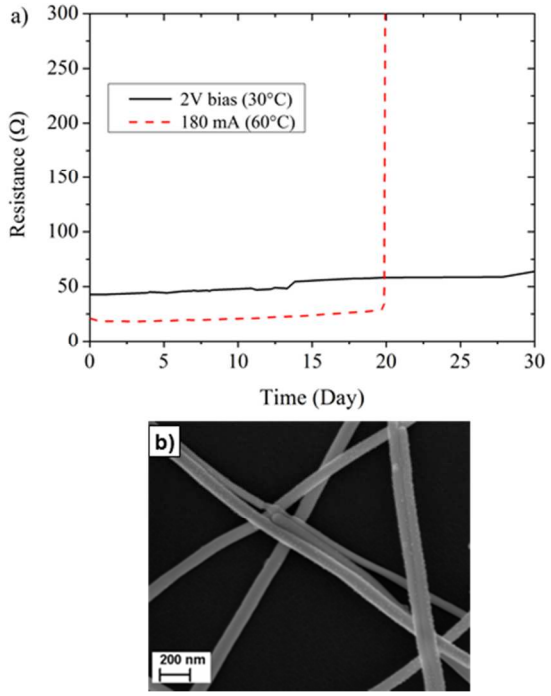

Fig. 8 a) Evolution of the resistance as a function of time for two different samples. The first one (black solid line) was submitted to a continuous 2 V bias whereas the second one (red dashed line) was submitted to a continuous 180 mA current. b) SEM picture of AgNWs after 3 weeks of electrically heating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

We also considered the electrical stability of the AgNW/PEDOT:PSS composites. Fig.9a shows the evolution of the 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 (~25 Ω/sq), and the same 2 point resistance (~25 Ω) since samples were square-shaped. It appears obviously 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 submitted two samples containing the same amount of AgNWs to a current in order to get a temperature of 60 °C. The results are shown in Fig.9 b). Here again, the hybrid electrode is way less stable than the one containing only AgNWs. Therefore, we can conclude that AgNW electrodes are more stable than AgNW/PEDOT:PSS composite. This could be also correlated to the results reported hereinbefore, without electrical stress, which mentioned shorter stability of AgNW electrodes when they were coated with a thin layer of PEDOT:PSS. The SEM observations confirmed the difference of 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 point out that adding PEDOT:PSS on top of AgNW networks decreases the stability under a long term electrical stress.

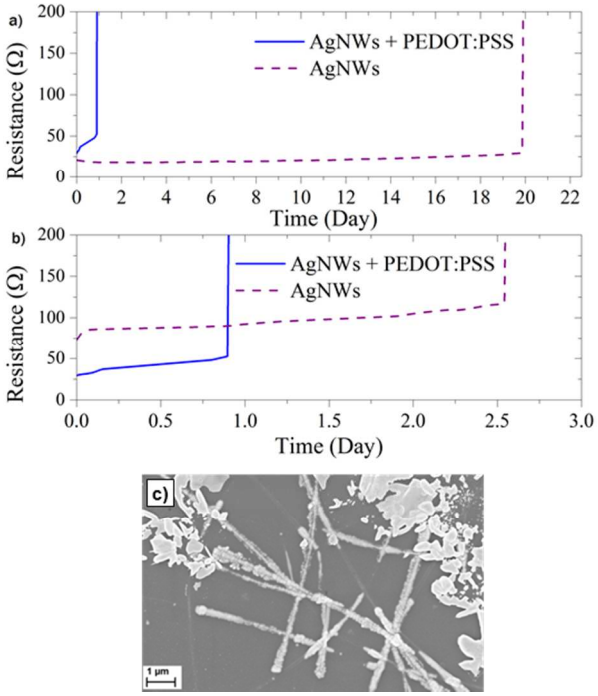

Fig. 9 a) Evolution as a function of time of the resistance of a pristine AgNW electrode (purple dashed line) and an AgNW electrode covered with 50 nm of PEDOT:PSS (solid blue line) having the same initial resistance, and submitted to 60°C by Joule heating. b) Evolution as a function of time of the resistance 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, grey particles are made of silver (checked by EDX analysis).

Conclusions

In summary, AgNW based electrodes demonstrate good stability under several accelerated ageing processes. After 2 years of air and dark storage, four months of storage at 38 °C and 90% HR, 8 h exposure under a 50 ppm flow of H_2S or 120 h of light exposure (equivalent to 48 days of Central Europe natural sunlight), the sheet resistance of the electrodes was almost not 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.

We also point out that AgNW networks demonstrate nice stability when low voltage is applied (experiment was stopped after 30 days). However, stronger electrical stress, arising 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 of early damages 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 work 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 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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Notes and references

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