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Highly Flexible Transparent Film Heaters Based on Random Networks of Silver Nanowires

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ABSTRACT

We demonstrate a new concept for the fabrication of flexible transparent thin film heaters based on silver nanowires. Thanks to the intrinsic properties of random networks of metallic nanowires, it is possible to combine bendability, transparency and high heating performances at low voltage, typically below 12 V which is of interest for many applications. This is currently not possible with transparent conductive oxide technologies, and it compares well with similar devices fabricated with carbon nanotubes or graphene. We present experiments on glass and poly(ethylene naphthalate) (PEN) substrates (with thicknesses of 125 μm and extremely thin 1.3 μm) with excellent heating performances. We point out that the amount of silver necessary to realize the transparent heaters is very low and we also present preliminary results showing that this material can be efficiently used to fabricate photochromic displays. To our knowledge, this is the first report of metallic nanowire-based transparent thin film heaters. We think these results could be a useful approach for the engineering of highly flexible and transparent heaters which are not attainable by existing processes.

KEYWORDS

Thin film heater, silver nanowires, transparent, electrode, flexible, thermochromic display

1. Introduction

Transparent heaters are widely used in technologies such as avionics, temperature-controlled liquid crystal display (LCD) displays, window defrosters, and medical equipment. The fabrication of transparent heaters is currently realized with thin films of transparent conductive oxides (TCOs), and in particular indium tin oxide (ITO). The as-made ITO transparent thin film heaters (TTFHs) suffer from limitations like a costly fabrication process, moderate thermal response and brittleness. The use of solution-processable nanomaterials appears to be a promising alternative since it affords a large area and low-cost deposition method, with high performance. Recently some significant work has been carried out using carbon nanotubes [1–6] or graphene [7, 8] for fabricating TTFHs with good performances. Carbon-based TTFHs demonstrate interesting performances, however due to the moderate sheet resistances of these electrodes, either high voltage or/and low transparency are mandatory to achieve good heating performances.

In the past few years, extensive efforts have been made to develop transparent electrodes based on

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metallic nanowires, and in particular silver nanowires (Ag-NWs) [9–23]. These one-dimensional nanomaterials can be synthesized in solution and assembled in random networks with excellent performances that compare favourably with ITO. Typically, sheet resistances lower than a few tens of Ω/sq. can be obtained at 90% transparency in the visible spectrum, which is suitable for transparent film heater fabrication. Among metals, silver has the highest thermal conductivity and the lowest electrical resistance, thus it is *a priori* a good candidate for fabrication of TTFHs [24].

We report herein on the fabrication of random networks of Ag-NWs, made by spin coating or spray coating, and their use as TTFHs. Excellent heating performances were obtained on glass and plastic substrates. We also demonstrate that the amount of deposited silver is very low and fabricate thermochromic displays. This TTFH fabrication appears as a relevant alternative to ITO since it is low temperature, high performance, cost efficient, and well suited for even highly flexible substrates. To our knowledge, there has been no previous report of any TTFH based on networks of metallic nanowires.

2. Experimental

Ag-NWs were prepared according to a published procedure [25]. Then the solution of Ag-NWs in water was centrifuged at 2000 rpm for 15 min and the supernatant was removed. The final product was dispersed in MeOH and used as an ink for deposition processes. The diameters of the nanowires were in the range 40–80 nm, and the lengths between 2 and 25 μm. The solution was found to be stable for several weeks. Deposition was realized by spin coating, or airbrush spraying, using a vertically mounted commercial airbrush (Optima ATM Ⅳ from Bersch & Fratscher GmbH), similarly to a recently reported method [9]. In a typical spray coating experiment, substrates were placed on a hot plate at 80 °C. Eagle XG™ glass substrates are made of alkaline earth boro-aluminosilicate type and 1.1 mm thick. They were purchased from Corning. Poly(ethylene naphthalate) (PEN) substrates were obtained from Dupont Teijin (Teonex, 125 μm thickness) and Goodfellow (ES361010, 1.3 μm thickness). The entire process was realized in air. The solution was sprayed with the airbrush at a distance of 20 cm from the substrate at 2 bar air pressure, and after deposition the substrates covered with Ag-NWs were cooled down to room temperature in air. Eventually, two silver paste electrodes were deposited on the edges of the device. We used the paste Ag L200 from Ferro, and let it dry at room temperature for 30 min. Transmittance was measured on a Cary 5000 Varian spectrophotometer using the substrate (glass or PEN) as reference, and sheet resistance by using a four pin probe with a Loresta EP resistivity meter. Sheet resistances of few tens Ω/sq. were obtained for 90% transmittance at 550 nm which is comparable to ITO (see Fig. S-1 in the Electronic Supplementary Material (ESM)). SEM images presented in Fig. 1 show random networks of Ag-NWs with uniform deposition at various magnifications.

3. Results and discussion

The first TTFHs were realized on Eagle XG™ glass substrates. Temperature was recorded with a PT100 RTD probe on the side of Ag-NWs network. A schematic illustration of the experimental setup is presented in Fig. S-2 in the ESM. The temperature plot as a function of time for a TTFH with a sheet resistance of 33 Ω/sq. is shown in Fig. 2. The film was sequentially submitted to input DC voltages of 3, 5 and 7 V.

Regardless of the applied voltage, the increase in temperature was very fast and nearly steady state temperatures were reached in less than 200 s. As shown in the insert of Fig. 2, the heating/cooling rate calculated from the derivative of the temperature with respect to time is slightly above 1.5 °C/s at an applied voltage of only 5 V. The power dissipated in a resistive conductor can be described by Joule's first law equation: $P = V^2/R$, where V is the applied voltage and R the total resistance.

It can be understood that at lower resistance, higher heat dissipation can be obtained for a fixed bias. In fact, this is an advantage of metallic nanowire networks in that they can afford very low sheet resistances at high transparency. This allows high heating power to be delivered at low bias. After 200 s, the thin film temperature reached a plateau at ~40 °C at 5 V bias and the steady state was maintained for few min.

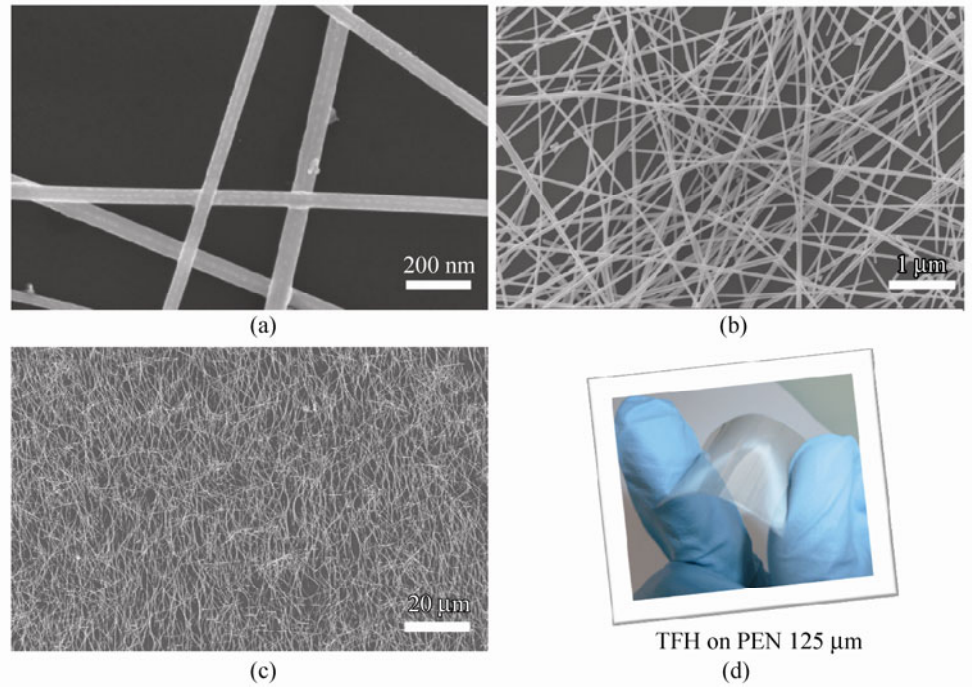

Figure 1 (a), (b) and (c) SEM images of a random network of silver nanowires at various resolutions, (d) image after deposition onto 125 μm thick PEN substrate

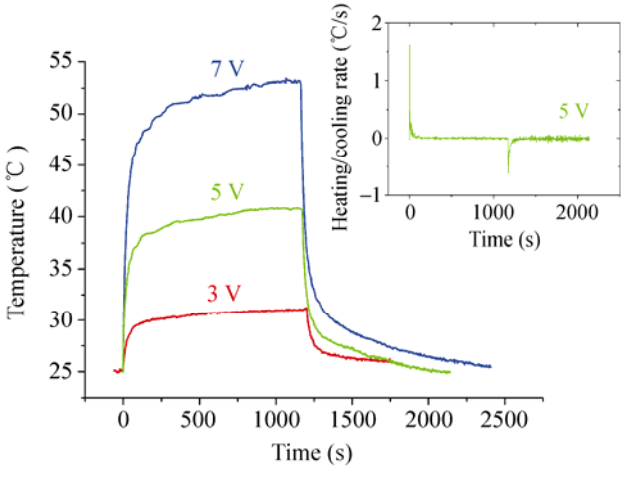

Figure 2 Heating experiments showing temperature as a function of time for a 33 Ω/sq. TTFH on glass at different applied voltages (20 min duration). Insert: derivative of the temperature vs. time at 5 V applied bias

A stable temperature occurs when the heating power compensates for the heat loss at the interfaces, i.e. air and glass support. In order to check the stability of these electrodes under stress and over time, we performed some stability and life-time tests. Operational stability was checked by applying 6 V consistently for nearly 30 hours (Fig. S-3 in the ESM). No variation in temperature, nor performance decrease were observed, indicating that the TTFH is stable in ambient atmosphere for at least tens of hours. Even after long storage without taking precautions, TTFHs could be operated with same performance. A TTFH was also subjected to alternating heating and cooling cycles. As shown in Fig. 3, no significant deviation was observed.

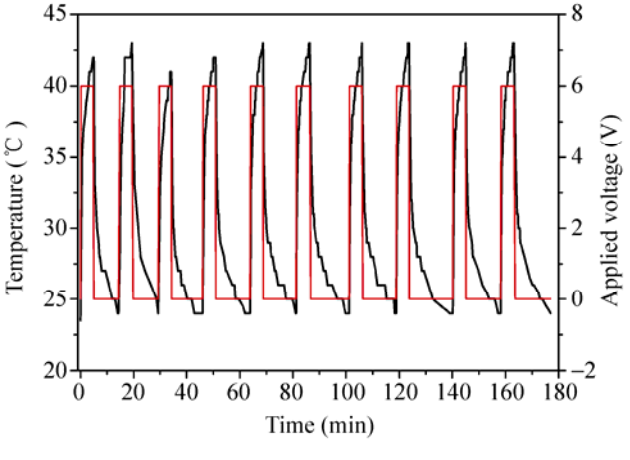

Figure 3 Heating and cooling cycles of an Ag-NW based TTFH on a glass substrate (81.8% T550 nm–28 Ω/sq.)

A major advantage of using metallic nanowires for the fabrication of transparent electrodes comes from the fact that high bendability can be achieved, which is clearly not the case with TCO-based electrodes. This is obviously also true for TTFHs. We prepared flexible TTFHs by spreading nanowires onto PEN substrates. First experiments were carried out with 125 μm thick PEN foils (Fig. 4).

For TTFHs with comparable electrical resistances, the steady state temperatures obtained on PEN were slightly higher than those obtained on glass at similar applied voltages.

Moreover the heating rate was somewhat higher, more than 2 ˚C/s, at 5 V applied voltage (Fig. 4(a), inset). We can also see in Fig. 4(b) that less power is needed to reach a given temperature on PEN as compared with the glass substrate. This may be due to the difference in thermal diffusivity of the substrate materials. Heat disperses more rapidly when a material has a high thermal diffusivity value. At 50 ˚C, the thermal diffusivity of PEN is ~1.5 × 10^{-7} m^2/s [26], whereas the Eagle XG™ glass has a significantly higher thermal diffusivity value (~5.9 × 10^{-7} m^2/s). These values indicate that heat transfer is lower with the PEN substrate and thus heating rate and steady state temperature are slightly higher when compared with the glass substrate.

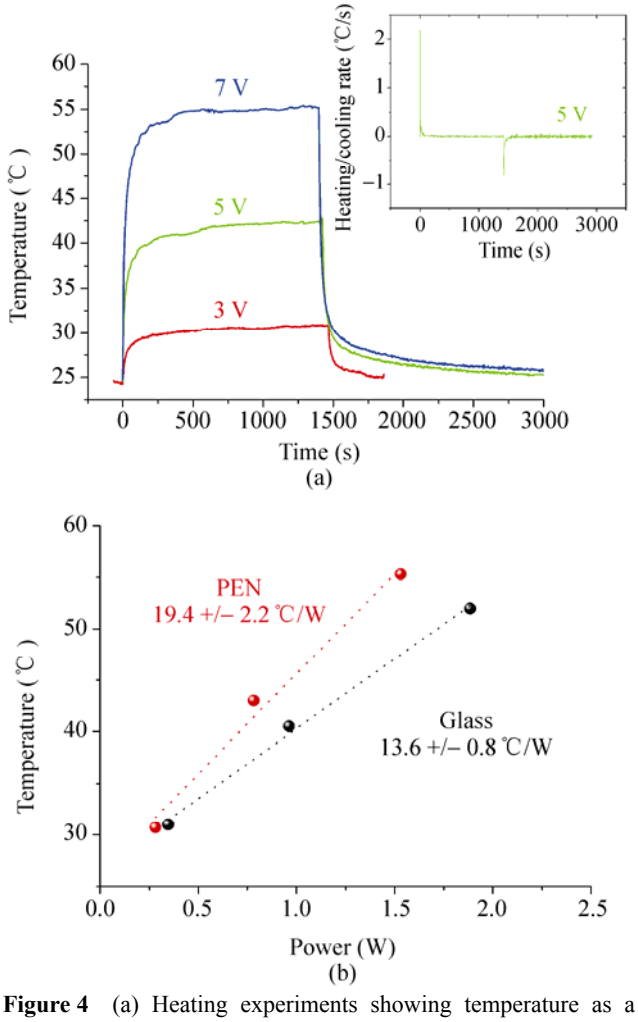

Figure 4 (a) Heating experiments showing temperature as a function of time for a 35 Ω/sq. TTFH on a 125 μm PEN substrate at different applied voltages. Insert: derivative of the temperature vs. time at 5 V applied bias. (b) Input power as a function of the steady state temperature on PEN and glass substrates

During bending experiments, we did not observe any change in the sheet resistance value of TTFHs for radii of curvature down to 5 mm. Hundreds of bendings against the 5 mm radius cylinder were performed using both sides of the flexible electrode alternately, and no alteration in the performance was observed (Fig. S-4 in the ESM). Then we carried out experiments with PEN substrates having thickness of only 1.3 μm. These plastic sheets are very thin, extremely flexible and prone to crumpling. In this case also, the sheet resistance was maintained whatever bending constraints were applied to the TTFH (see Movie S-1 in the ESM). Unfortunately, we were not able to realize any efficient measurement of temperature because the film tore when the thermocouple was put on it.

At high voltage a strong decrease (>20%) in the sheet resistance was observed after the first run. We compared SEM images of random networks of nanowires that had been submitted either to the already known thermal annealing technique [19, 20, 27], or to an applied voltage of 18 V. The images presented in Fig. S-5 in the ESM show that similar melting behavior can be observed. It seems reasonable to assume that local melting of silver at intersections of some nanowires certainly improves the electrical conductance of the network by minimizing local contact resistances. This is supported by a previous report on electrical sintering of silver nanoparticle arrays [28]. Interestingly, even at 18 V the temperature did not exceed 100 ˚C, which is still enough to fuse some NWs. This electrical technique might be considered as a new route to optimize the contacts between Ag-NWs, in addition to thermal annealing, and the recently reported

pressing technique [20]. In fairness, it must be noted that such thermal or 18 V electrical annealings did not always lead to improvements. In some cases (~10%–20% of experiments), the percolation was not present anymore (infinite resistance), indicating that the network had been destroyed.

Since this technology is intended to replace current TCOs, we carried out measurements to estimate the amount of silver necessary to realize TTFHs. We built a calibration curve by dissolving silver nitrate in nitric acid and water. The silver content was quantified by inductively coupled plasma–optical emission spectroscopy (ICP–OES) (Agilent 700 Series). The response was linear over a wide range, with a very good correlation coefficient (>0.9995). Then, electrodes fabricated onto 2.5 cm × 2.5 cm glass substrates with various transmittances were dipped in 65% nitric acid solutions for 30 min to dissolve entirely the Ag NWs and solutions were transferred into volumetric flasks. Figure S-6 in the ESM shows the measured content of silver as a function of the transmittance. The amount of silver as a function of the transmittance follows a linear trend. At 90.5% transmittance, we measured 22.13 μg/6.25 cm^2, that is to say 0.035 g/m^2. Of course this value does not take into account losses of silver during precursor synthesis, nanowire synthesis, the purification process or the deposition step. However it shows that the quantities required are very low. At an average market silver price of 40 $/oz, the cost of silver needed to cover the substrate is less than 0.05 $/$m^2$. This is not a cost estimate of the process, but is simply to point out that nanomaterials, even made of noble metals, can be serious candidates for large area thin film coatings for this kind of application.

Finally we used TTFHs for the fabrication of thermochromic displays. We first prepared TTFHs as described above. Then we sprayed Coloured Chameleon® Reversible thermochromic inks through shadow masks. By applying low voltage to the TTFHs we obtained an increase in temperature which induced a colour change as shown in Fig. 5 and Movie S-2 in the ESM.

The thermochromic displays had a switching temperature of 45 °C. We carried out cycling tests with these displays and did not observe any deterioration even after dozens of cycles. Although these first tests are rather simple, they open the way to realize more complex thermochromic devices with various colours and different switching temperatures. Fig. 5 illustrates that they can also be used simply to show that a transparent defroster (i.e. TTFH) is in operation.

4. Conclusions

We have demonstrated a new method to fabricate high performance TTFHs based on Ag-NWs. Thanks to the intrinsic properties of random networks of Ag-NWs, it is possible to combine flexibility, transparency and high heating performance at low voltage, typically below 12 V which is of interest for many applications. Experiments carried out on 1.3 μm thick PEN substrates demonstrate that TTFHs may be extremely thin and conformable to many substrates. We also point out that the amount of silver necessary to realize the TTFHs is

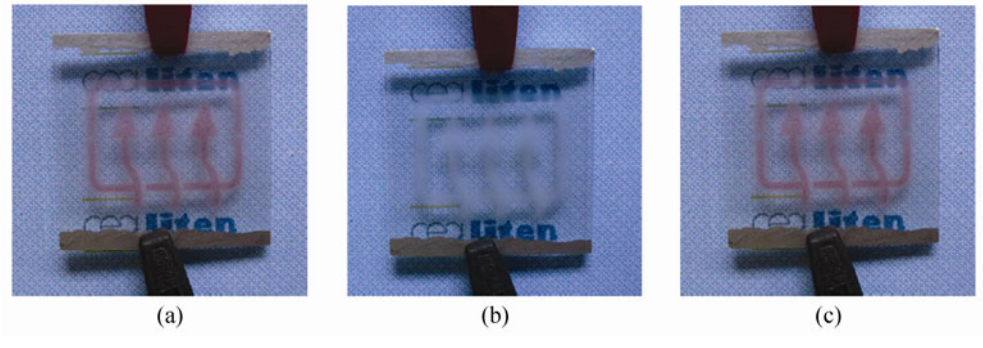

Figure 5 Thermochromic display made with Ag-NW based TTFH (89% T550 nm–82 Ω/sq.); (a) at room temperature; (b) after applying 12 V; (c) after returning to room temperature

very low, about a few tens of mg/m^2. Furthermore, we present preliminary results showing that this material can be efficiently used to fabricate photochromic displays. To our knowledge, this is the first report of a metallic nanowire-based TTFH. We think these results could be a useful approach for the engineering of highly flexible transparent heaters which are not obtainable by current TCO technologies.

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Electronic Supplementary Material: Supplementary material (graph of sheet resistance vs. transmittance, experimental setup, graph of time stability in operation, graphs of bending experiments, SEM images of Ag-NW random networks after annealing, ICP–OES measurements of Ag contents in TTFHs and two movies showing crumpling of TTFHs and thermochromic displays) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-012-0225-2.

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