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Electrically controlled colour-changing textiles using the resistive heating properties of PEDOT nanofibers†

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Conductive PEDOT nanofiber mats were obtained by the electrospinning of oxidant fibers and subsequent vapour-phase polymerization of the EDOT monomer. The mats presented high conductivities as well as unprecedented resistive heating properties. Electrically controlled colour-changing textiles were produced by coating thermochromic inks on the PEDOT mats and triggering the colour change by applying current to the mat.

Flexible electrochromic systems are being more and more investigated for their promising applications in non-emitting displays[1–5] or other colour-changing surfaces/devices including textile materials.[6,7] The possibility of using electricity as a trigger for the control of the colour change is a significant improvement over relying on less controllable stimuli like temperature or ultraviolet radiation.[8–11] The most important flexible electrochromic materials are the intrinsically conducting polymers (ICPs), which undergo a spectral transition in the visible range when doped/undoped by ions.[12–14] However, electrochromic devices based on ICPs are complicated and difficult to assemble since they require a whole system to be fabricated, incorporating two electrodes (one of which at least having to be transparent), two layers of ICPs and an electrolyte.[12,15,16] The encapsulation of such devices is also a common problem for their use as flexible devices.[17]

On the other hand, some scientists as well as artists have developed much simpler colour-changing systems which take advantage of the resistive heating properties of metal to trigger the colour-change of thermochromic materials.[18–21] When applied to textiles, this approach usually consists of weaving or sewing metallic (or metal-coated) yarns within the fabrics and painting thermochromic inks on top of them. The application of a current through the conductive yarns causes a heat dissipation caused by the resistance to the current flow (named resistive heating effect or Joule effect) and provokes the colour-change of the painted thermochromic materials close to the conductive yarn. Although this strategy has its own drawbacks, such the fact that the colour is changed only at the immediate proximity to the conductive yarn, the simplicity of its design makes it very attractive for the development of flexible electrochromic devices.

In this work we describe the production of non-woven mats of poly-3,4-ethylenedioxythiophene (PEDOT), a widely used ICP, using a two-step procedure combining the electrospinning of an oxidant solution and the subsequent vapour-phase polymerization of the EDOT monomer.[22] These nanofibrous textiles demonstrated high electrical conductivities and efficient resistive heating properties. These latter were used to precisely control the change of colour of thermochromic inks painted on the mats by the use of electricity.

PEDOT nanofiber mats were obtained following a two-step procedure (*cf.* ESI1†). A solution containing an oxidant (iron(III) tosylate) as well as a small quantity of polyvinylpyrrolidone (PVP) and pyridine (used to maintain a basic medium),[23] was first electrospun into nanofibers in a dry environment. After evaporation of the solvent, the nanofibers contained more than 90 wt% of oxidant. The nanofibers were then converted to PEDOT by placing them in a chemical reactor under passive vacuum and containing the monomer (EDOT) vapours. The base-inhibited vapour-phase polymerization proceeded for at least five days, and the PEDOT nanofibers were finally rinsed with methanol and dried under active vacuum overnight. The detailed procedure as well as a structural characterization of the nanofibers has been published elsewhere.[24]

Fig. 1 shows a PEDOT nanofiber non-woven mat. The mat had good mechanical properties and was easy to handle, as can be seen in Fig. 1a. By using a rotating and translating substrate, it was possible to obtain mats with a homogeneous average thickness, which depended on the time of electrospinning (from a few microns for 30 min of electrospinning deposition up to ~100 μm for seven hours of electrospinning).

The nanofibers were semi-transparent and displayed a light blue colour, which is characteristic of doped and conductive PEDOT. The average diameter was 350 ± 60 nm. Due to this very small dimension (smaller than the visible light wavelength range), a significant light scattering effect occurred and caused the nanofiber mats to appear totally opaque and dark blue in color.[25]

The conductivity of the nanofiber mats was measured using a four-point probes technique and showed an average value of 60 ± 10 S cm^{-1}. This is the highest value reported so far for polymer electrospun mats. This is most probably due to the templating effect of the tosylate ion during the vapour-phase polymerization, that leads to the polymerization of highly ordered PEDOT chains,[26] as well as numerous fused connections of the fibers that decreased the fiber-to-fiber charge transfer resistance.[24]

The resistive heating properties of the nanofiber mats were investigated by applying current to nanofibrous self-standing samples, and recording the temperature changes with an infrared camera. The temperature of a point located at the center of the sample was monitored as a function of the applied current.

Fig. 2a shows the temperature/current curve and Fig. 2b the infrared images at several applied currents. The curve shows a two-step behavior. Below 100 mA, the current is efficiently transported through the nanofiber mat, and almost no loss of energy is observed

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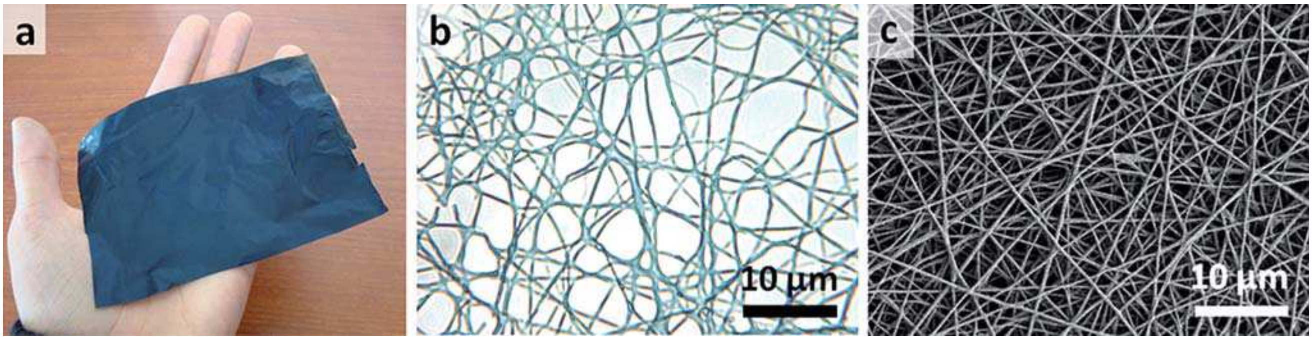

Fig. 1 (a) Picture of a self-standing PEDOT nanofibers mat. (b) Optical microscopy image of a few layers of nanofibers deposited on a glass slide. (c) SEM image of the mat.

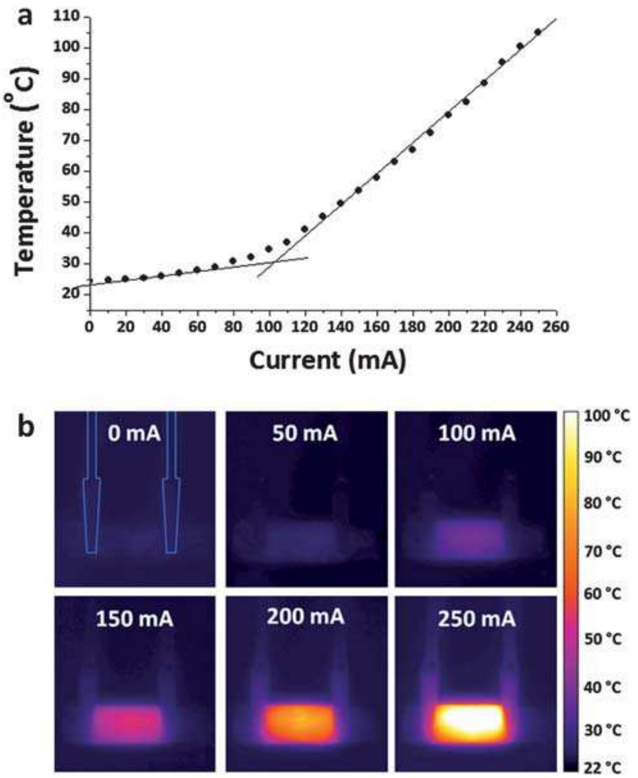

Fig. 2 (a) Current/temperature curve of a mat with dimensions 1.6 cm × 3 cm × 6 µm. (b) Infrared camera images of the mat at different applied currents. For a better clarity of the experimental design, the outline of the electrodes was drawn on the first image.

by heat dissipation. At currents over 100 mA the material becomes less efficient at transporting the electricity, and we can observe a dissipation of the energy through the Joule effect (*i.e.* heating). The more current is applied, the more heat is being generated by the mat, following a linear curve, and reaching a temperature of 105 °C at 250 mA. The images of Fig. 2b show that the heating effect was homogeneously distributed between the two electrodes. At the current value of 250 mA, the voltage was 10.5 V and the power ($P = V \times I$) was then 2.63 W. Taking into account the dimensions of the sample (1.6 cm × 3 cm), the heating power was then 5470 W m^{-2}, a value one order of magnitude higher than the best polypyrrole-coated textiles specifically developed for resistive heating applications.[27–29] Thanks to this high heating power, an impressive temperature of ~100 °C could be reached within a few seconds at low voltage (10 V), whereas PPy-coated fabrics generally do not reach values higher than 50 °C at similar voltages.[30,31]

Fig. 3a shows that the obtained temperature was stable over time when a current was continuously applied to the mat (50 ± 4 °C at 140 mA per 5.9 V in the shown case). The temperature was, however, not steady: variations could be constantly observed (±4 °C), probably due to the fact that the electron flow is subjected to multiple separations/recombinations at fiber junctions, and is then not at equilibrium at each point in the mat. The heat dissipated at one point being directly proportional to the amount of charge that passes through this point, if the electron flow is not constant with time, the

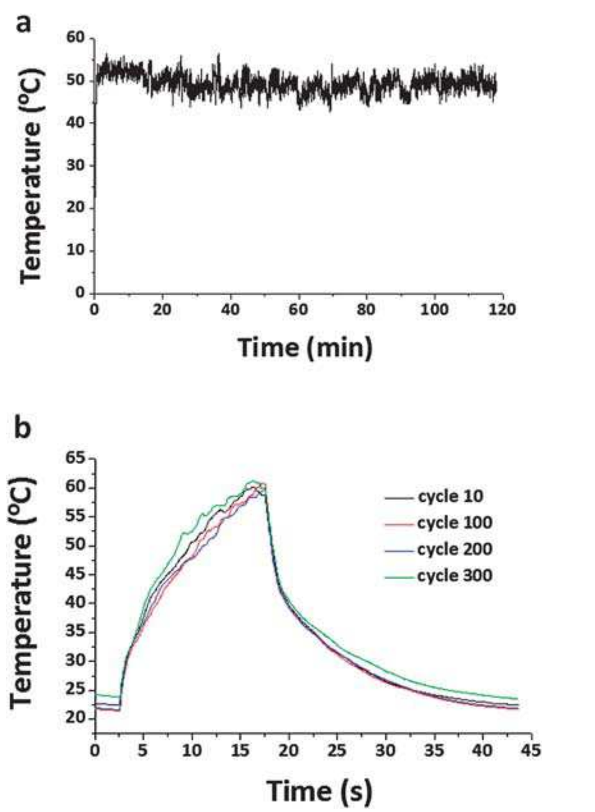

Fig. 3 (a) Temperature stability for 2 h, at a constant current of 140 mA. (b) Temperature cycling stability during 300 repetitive cycles (15 s at 160 mA followed by 25 s at 0 mA).

heat dissipation will change with time accordingly, as observed in Fig 3a. Nevertheless, the total amount of charge applied to the sample being held constant, it is believed that the total heat dissipated by the whole mat is also constant at each time.

The heating/cooling cycling stability was also investigated as can be observed in Fig. 3b. The sample was subjected to successive heating (15 s at 160 mA) and cooling (25 s at 0 mA) steps and showed a perfect stability: no significant changes in heating and cooling rates, nor in the temperature reached (60 ± 1 °C) were observed after 300 cycles. Moreover, the material demonstrated very high rates of temperature change, especially the cooling rate between 60 and 40 °C (less than 1 s). This ultra-fast cooling rate can be explained by the ultraporous nature of the mat (~80% porous) that allows the heat to be very effectively dissipated by the material.

Colour-changing textiles were developed by taking advantage of the resistive heating properties of the PEDOT nanofiber mats. An ink was used to deposit thermochromic microcapsules on the surface of the mat (Fig. 4a). The microcapsules were mainly deposited on top of the mat but also entered within the mat, depending on the pressure applied during the deposition, and quantity of ink. Logos like the Canadian maple leaf emblem (ESI2†) or letters (Fig. 4b and ESI3†) could be drawn on the mat.

The transition temperature of the thermochromic ink was 37 °C. By applying a current above 100 mA, the ink turned from blue to white within seconds (Fig. 4b). The rate of colour-change could be varied by applying more or less current to the mat (*cf.* ESI3†). The homogeneous distribution of the heat within the mat allowed us to paint any kind of colour-changing drawings, and to avoid the main drawback of the incorporated conductive yarns technique, that can only heat up at the proximity of the yarns.

In summary, electrospun non-woven mats of PEDOT have been produced by combining electrospinning and a base-inhibited vapour-phase polymerization procedure. The high structural order of the PEDOT rendered the fibers highly conductive (60 ± 10 S cm^{-1}). Their resistive heating properties were investigated and showed an unprecedented heating power that demonstrated both stability in time and perfect heat–cool cyclability. These nanofiber non-wovens could be used as very effective electro-heating textiles, requiring low voltage and reaching high temperatures at high rate.

By painting letters or logos using thermochromic inks, it was possible to fabricate electrochromic textiles that use the fast resistive heating properties of the non-wovens. Electricity was then used to precisely trigger the colour change of the painted pictures. The rate of the colour transition could also be varied to some extent.

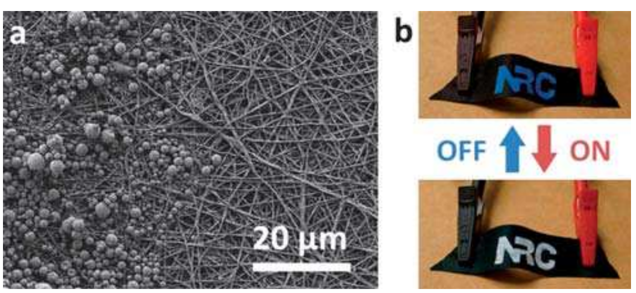

Fig. 4 (a) SEM image of thermochromic microcapsules painted on the PEDOT nanofibers. (b) Illustration of the electrochromic effect by applying 0/120 mA to the electrospun mat.

These nanofiber non-wovens are believed to be of interest for the development of flexible electrically controlled colour-changing devices that could be incorporated into garments and used as active visual camouflage or into interactive textiles.

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