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Welded Electrochromic Conductive Polymer Nanofibers by Electrostatic Spinning**

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With the availability of electrochromic conjugated polymers^[1] exhibiting transitions of the three primary colors, full-color electrochromic displays could be realized in the near future.^[2] Although many, but not all, of the color transitions have been addressed, there is a need for rapid and wide-area processing methods as well as materials with response times within the millisecond regime in order to obtain an active display. Recently, the electrochromic phenomenon for poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes^[3] prepared using a porous membrane^[4] has been reported to be on the order of 5 ms, rapid enough for active-display applications. Other techniques for producing one-dimensional (1D) nanostructures of conjugated polymers of similar promise include interfacial polymerization,^[5] templated synthesis,^[6] and phase separation of block copolymers.^[7] Apart from electrochromic

conjugated polymer nanostructures could find application as electronic interconnects, optoelectronic device components, chemical and biological sensors, catalysts, membranes, and drug-delivery systems.

Electrostatic spinning (e-spinning) offers a practical means to prepare nanostructured conjugated polymers described above by producing high volumes of conjugated polymer nanofibers continuously, even to lengths of several kilometers. However, the intractability of conjugated polymers has prohibited their processing by e-spinning in pure inherently conductive polymer form. Instead, researchers have reported the blending of conjugated polymers with more readily electrospun polymers such as poly(ethylene oxide) or poly(vinyl pyrrolidone). Most reports of inherently conductive polymer nanofibers formed in this way have utilized polyaniline,^[8] although a report on the e-spinning of poly(phenylene vinylene) and a thiophene-based conjugated polymer has recently appeared.^[9] To our knowledge, there has not been a report of an electrospun conjugated polymer exhibiting electrochromic function.

Herein we describe a technique by which we electrospin a precursor polymer that can later be oxidized either chemically or electrochemically in the solid state^[10] to produce a cross-linked conjugated polymer. Since solvent is used in the conversion process to swell the precursor polymer, the nanofibers naturally weld together during conversion to the crosslinked conjugated polymer, of benefit to multiple properties. In contrast, flash welding of polyaniline (PANI) nanofibers has been reported to give continuous films.^[11] Further, we demonstrate here the capability of a 5 μm thick non-woven mat of this conjugated polymer nanofiber to electrochromically switch between two colored states on the timescale of a few seconds.

The precursor polymer, **1**, used for e-spinning was a 50:50 (mol/mol) random copolymer (Fig. 1) prepared via ring-opening metathesis polymerization (ROMP) of an equimolar monomer feed of two functionalized norbornenes: one bearing a terthiophene group and the other, an acetate group. The structure of **1**, including the ratio of the two different repeat units, was confirmed by ¹H NMR spectroscopy. The molecular weight of **1**, measured using gel-permeation chromatography with poly(methyl methacrylate) standards, was determined to be 46 400 g mol⁻¹.

Nanofibers of **1** were obtained via e-spinning using a 7 wt.-% solution in tetrahydrofuran/dimethylformamide (THF/DMF, 70/30 v/v) while applying 1 kV cm⁻¹ over a gap of 10 cm between the syringe needle and the 20 cm diameter collector. Analysis of the scanning electron microscopy (SEM) image of nanofibers of **1**, Figure 2a, indicates an average diameter of 253 nm (with a standard deviation, sd, of 80 nm). The diameter could be controlled by changing the concentration of the precursor polymer solution. For example, nanofibers obtained from 6 wt.-% solution of **1** in THF/DMF (70:30) upon application of 1 kV cm⁻¹ resulted in an average diameter of 119 nm (sd = 22 nm). Attempts to electrospin **1** at a concentration lower than 4 wt.-% in THF/DMF (70:30) resulted in electro-spraying, i.e., droplet formation.

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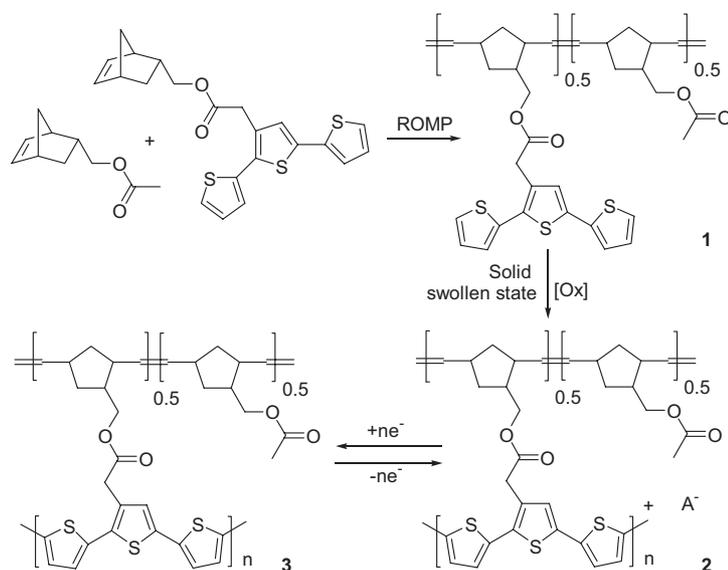


Figure 1. Conversion of insulating precursor polymer, **1**, to conductive polymer, **2**, via solid-state oxidative crosslinking and subsequent redox switching between **2** and **3**.

Solid/swollen-state oxidative crosslinking of the nanofiber mat shown in Figure 2a was performed using a 0.01 M FeCl₃/CH₃CN solution. Upon exposure to the oxidant in solution, the fiber mat changed from colorless and transparent to transparent and deep blue in a few minutes, indicative of conversion of **1** to **2**. Nanofibers of **2**, after the oxidative crosslink-

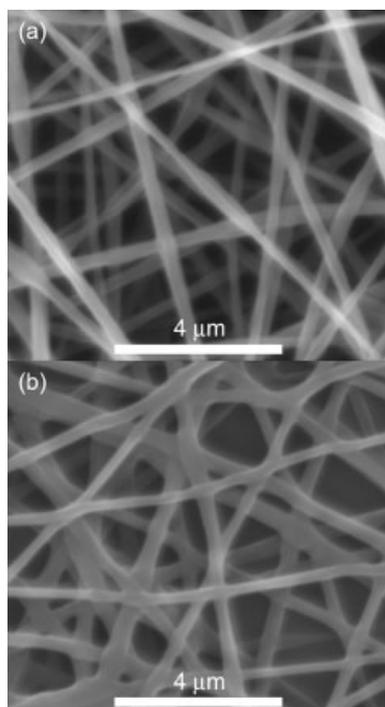


Figure 2. SEM images of a) nanofibers of **1** and b) nanofibers of **2**.

ing process, were then reduced to nanofibers of **3** (Fig. 2b), and these fibers were found to have the same average diameter as that of the nanofibers of **1**. Furthermore, in converting nanofibers of **1** to nanofibers of **2**, the 0.01 M FeCl₃/CH₃CN solution temporarily swelled and softened the fibers, allowing for their “welding”; several of these weld points are shown in Figure 2b.

The electrospun nanofibers of **1** were also converted to conductive polymer, **2**, using electrochemical solid-state oxidative crosslinking. Nanofibers of **1** were collected onto indium-doped tin oxide (ITO)-coated glass, and electrochemical solid-state oxidative crosslinking was performed in 0.1 M tetrabutylammonium perchlorate (TBAP)/CH₃CN via potential scanning between 0 and 1.1 V at 100 mV s⁻¹. The cyclic voltammograms for this electrochemical polymerization process were similar to that reported earlier for thin films.^[10] This electro-oxidative crosslinking of the nanofiber mat followed a similar color transition as that in the chemical process, as evidenced spectrophotometrically in Figure 3. The nanofibers of **1** were found to have a peak wavelength, λ_{max} at 360 nm, attributed to the π-π* transition for terthiophene.

Upon oxidative crosslinking at 1.1 V followed by reduction to nanofibers of **3**, the λ_{max} of was shifted to 480 nm (2.58 eV) as

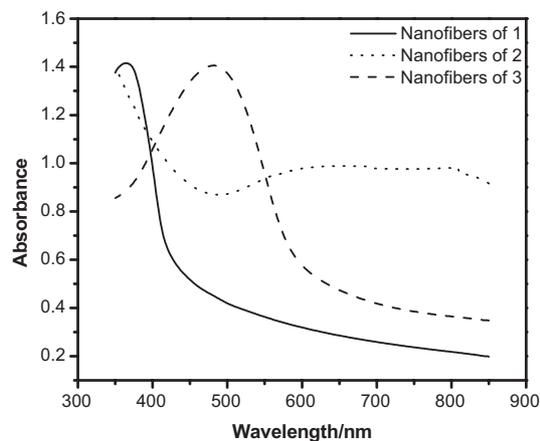


Figure 3. UV-vis spectra of nanofibers of **1**, **2**, and **3**.

a result of the formation of polyterthiophenes. The absorption peak of nanofibers of **3** was red-shifted by 35 nm compared to thin films of **3**, which could be the result of aligning of the pendant thiophene groups in **1** during the e-spinning process; hence, more conjugation in the nanofibers of **3** could have been achieved. Indeed, MacDiarmid and Epstein reported that the absorption spectra of the extended-coil conformation of PANI showed a red-shift compared to the absorption spectra of compact-coil PANI.^[12,13] Visy et al. reported the electrochemical polymerization of terthiophene to yield conjugated materials that have a chain length of approximately eight to

twelve units with a λ_{\max} at 395 nm.^[14] Nanofibers of **3** were approximately 90 nm red-shifted with respect to the λ_{\max} reported by Visy et al., and hence are expected to have a longer conjugation length.

Electrochromism was observed for welded nanofibers of **2**. Figure 4 shows the oxidized and neutral forms of a 5 μm thick nanofiber mat of **2** inside a 0.1 M TBAP/CH₃CN-filled electrochemical cell at 0 and 1.1 V (versus Ag/Ag⁺). Figure 5 shows that the time required to switch the nanofiber mat from

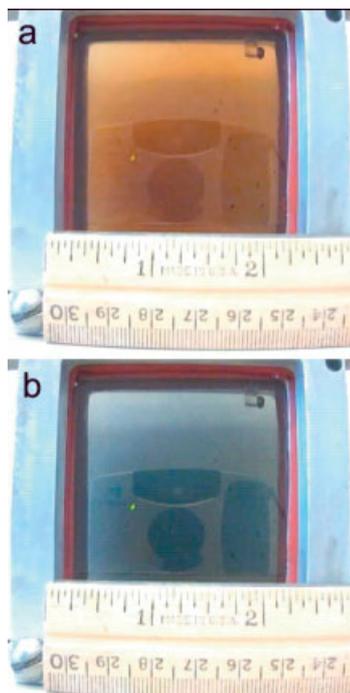


Figure 4. Assembled transparent 31 cm² electrochromic device of cross-linked nanofibers switching between a) **2** at 1.1 V and b) **3** at 0.0 V. (The image of the camera is reflected in the glass of the device.)

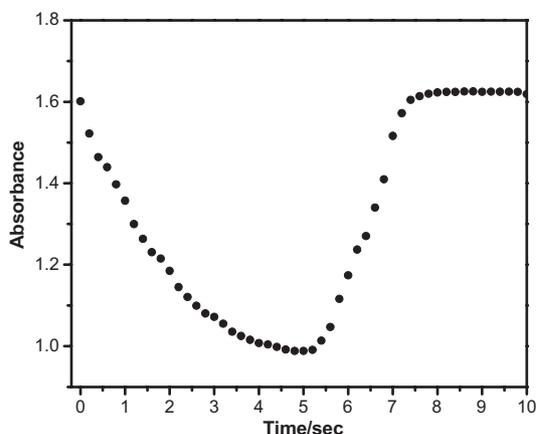


Figure 5. Photometric response of the electrochromic fiber mat of **2** at 480 nm. At time $t=0$ s, the potential is 0.0 V and then switched to 1.1 V. At $t=5$ s, the potential is switched back to 0.0 V.

3 (orange) to **2** (blue), a 100 % change, as measured spectrophotometrically at 480 nm, was ca. 5 s, while the reverse process was complete in 3 s.

In contrast, solid/swollen-state crosslinking of a film with similar thickness did not afford complete switching in the same arrangement and took several minutes even for partial switching. We note that Jirage et al.^[4] and Cho et al.^[3] had shown that nanotubes of polypyrrole and PEDOT exhibited a fast switching response, though with a significantly thinner film.

For comparison, the photometric switching times at 600 nm between the neutral (−1 V) and oxidized state (0.4 V) for a 1 μm thick electrochemically prepared PEDOT film in 0.1 M TBAP/CH₃CN as the electrolyte was found to be ca. 68 s, and ca. 70 s for the reverse process.

In summary, conducting polymer nanofibers with average diameters as low as 119 nm exhibiting electrochromism were prepared via electrospinning of a soluble precursor polymer followed by solid/swollen-state oxidative crosslinking. During the solid/swollen-state oxidative crosslinking, the fibers welded together without significant perturbation of the morphology, thus maintaining the quality and shape of nanofibers, while apparently establishing an interconnected network. The nanofibers were found to exhibit switching times between 2 and 3 s, which was ca. 20-fold faster than 1 μm thick electrochemically prepared films of PEDOT using the same electrochemical conditions. Furthermore, a bathochromic shift in the λ_{\max} value (ca. 35 nm) was found for the nanofibers of **3** compared to thin films of **3**, indicating a possible alignment of the pendant terthiophenes during the electrospinning process, resulting in an increased effective conjugation length.

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All-Solution-Processed n-Type Organic Transistors Using a Spinning Metal Process**

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There has been growing interest in organic thin-film transistors (OTFTs) because of their potential applications in flexible, low-cost integrated circuits, such as smart cards, RF identification tags, and display backplanes, such as liquid crystal displays, electronic paper, and organic electroluminescent displays.^[1,2] In particular, since organic semiconductors based on polymers and oligomers are attractive for their easy solution processing for film formation, recent research on OTFTs has been more focused on flexible electronic devices/display applications. Therefore, the most desired ultimate goal of organic semiconductor devices is to realize flexible electronics and displays that can be processed through *all-solution processes* including deposition of the active organic layers, the gate insulators, and the electrodes. Here we demonstrate all-solution-processed n-type organic transistors for the first time by depositing the source and drain metal by a spinning metal process.

Despite the great interest and progress in organic and polymeric TFTs, most of the high field-effect-mobility OTFTs have been based on p-type channel materials. However, even

if n-channel semiconducting materials are important for making ambipolar transistors^[3,4] and complementary circuits,^[5] they are relatively rare compared with the p-type materials. The reported field-effect mobilities of n-type OTFTs to date also show lower values than those of p-type devices. In addition, it has usually been observed that the solution-processed OTFTs show poorer performance than the vacuum-processed devices: for example, although the vacuum-evaporated pentacene transistor has shown high field-effect hole mobilities exceeding $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^[6] the solution-processed p-type transistor using the pentacene precursor showed low field-effect mobilities below $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[7] Reports about the solution-processed n-type transistors are also relatively rare^[5,8–10] and they usually show low charge-carrier mobilities ($\sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or less)^[5,8,10,11] except that most recently the observation of a field-effect electron mobility as high as $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a solution spin-coated conjugated ladder polymer was reported.^[9] Here we report on solution-processed n-type OTFTs with high field-effect mobilities, based on the soluble derivatives of fullerene (C_{60}) as n-type channel materials. We obtained high field-effect electron mobilities of $0.02\text{--}0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ depending on the work-function of the source and drain metals, demonstrating that the electron injection current is contact-limited because of the Schottky barrier at the contact.

Furthermore, we fabricated n-type OTFTs by an all-solution-deposition process including source and drain metals as well as gate insulators and organic semiconductors. These types of OTFTs are well suited for a wide range of existing and future flexible circuits and display applications that require a simplified production process and low-weight and low-cost products. In order to achieve the solution-processed organic semiconductor film in the OTFTs, we used a thermally curable organic gate insulator. Before spin-coating the organic semiconductor, we deposited highly photosensitive organosilver precursor solutions on top of the organic gate insulator and patterned the films to form reduced silver metal by irradiating with broadband UV light through a photomask.

The organic semiconductor materials used in this work, which are soluble derivatives of C_{60} are shown in Figure 1a: Fulleroid (1-(3-methoxycarbonyl) propyl-1-phenyl)[5,6]C61 (F[5,6]) and methanofullerene 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C61 (M[6,6]). The OTFT structures used are shown in Figure 1b. We fabricated both top-contact (left of Fig. 1b) and bottom-contact (right of Fig. 1b) geometry devices.

The soluble C_{60} derivatives were spin-cast from a chlorobenzene (CB) solution. The cast films were smooth and clear. The root-mean-square (RMS) roughness of the films range from 1.9 to 2.24 nm, depending on the spin speed, and are good enough for device fabrication. The morphology of the M[6,6] film is shown in Figure 2. Interestingly, the surface morphologies are strongly dependent on the spin speed, as shown in Figure 2. When we spun the $\sim 1 \text{ wt. } \% \text{ CB}$ solution at 1000 rpm, we obtained $\sim 100 \text{ nm}$ thick films with a 2.24 RMS roughness. The surface morphology shows a kind of aggregation of the molecules: the morphology of films spin-cast at 1000 rpm

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