

Woven Electrochemical Transistors on Silk Fibers

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Fiber-based opto-electronic components such as light-emitting diodes (LEDs),^[1,2] solar cells,^[3–5] electrochromic pixels^[6] and transistors^[7–12] attract increasing attention for their alternative, non-planar device architectures, which readily permit integration into ‘smart’ fabrics. Furthermore, devices such as transistors facilitate advanced patterning schemes of electronic circuitry through judicious weaving.^[9–12] In particular conjugated polymers are suited as the (semi)conductor since they either inherently possess the required mechanical toughness or can be processed together with suitable structural polymers—including both, natural and synthetic macromolecules^[13,14]—and thus permit the manufacture of flexible artifacts such as tapes and fibers. Without doubt, one of the most alluring textile materials is silk from the silkworm *Bombyx mori* with its delicate texture and brilliant luster. Besides, once thoroughly degummed *Bombyx mori* silk offers a high degree of biocompatibility,^[15] which is an indispensable characteristic in particular for electronic devices that are intended to operate in a biological environment. As a result, the design of optical,^[16,17] electrical^[18,19] and electronic^[20] components on silk-based templates has been the subject of much recent research. However, all examples have—so far—been limited to devices that comprised inorganic metal/semiconductor thin-film structures on ‘silk films’ that were produced from dissolved silk proteins. Clearly, although attractive due to their biodegradability (cf. Ref. 19 and 20) such architectures fail to benefit from the extraordinary mechanical properties of pristine silk fibers^[21,22] and cannot be woven into fabrics. In a previous report, we have demonstrated that conjugated polyelectrolytes—compounds that are uniquely suited to functionalize polypeptide structures^[23–26]—permit facile staining of recombinant spider silk as well as natural *Bombyx mori* silk.^[13] Depending on the choice of conjugated polyelectrolyte this approach enabled us to produce

electrically conductive or photoluminescent fibers. Here, we explore by which means such conducting silk fibers can be incorporated as the structural as well as active component into electrochemical transistors (ECTs) that employ an electrolyte mixture composed of imidazolium-based ionic liquids as the electrochemical medium. ECTs offer unique possibilities for the realization of fiber-based electronic circuits because of their relative insensitivity to the precise device geometry.^[11] Ultimately, we anticipate that such components will permit fully integrated woven logic based on silk fibers.

We elected to work with silk fibers from the silkworm *Bombyx mori* because of their availability and widespread use in textile manufacturing. Discrete degummed silk fibers and threads thereof were obtained from Aurora Silk (Portland, Oregon, USA) and were used as received. As the conjugated polyelectrolyte we chose the water-soluble poly(4-(2,3-dihydrothieno[3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butananesulfonic acid) (PEDOT-S) (Figure 1a), which was prepared according to previously published procedures.^[13,27] Efficient staining with PEDOT-S was achieved by submerging fibers for one hour in aqueous PEDOT-S solution (10 g L⁻¹) with conditions in accordance with our report on dyeing of recombinant silk fibers (pH 2 and 90 °C; cf. Ref. 13). Then, excess PEDOT-S was removed with ethanol, subsequent to which fibers were tried under tension. Such prepared fibers with a typical diameter D of 50–100 μm and length L of up to 20 cm displayed a bulk electrical conductivity $c_{\text{silk}} = (4.4 \pm 1.5) \cdot 10^{-2} \text{ S cm}^{-1}$; corrected for the fiber length and cross section according to $c_{\text{silk}} = R^{-1} \cdot L \cdot 4\pi^{-1}D^{-2}$, where R is the resistance of a fiber section of length L and diameter D . For comparison, for a 10 cm long fiber this translates to $R \sim 3\text{--}12 \text{ M}\Omega$, which ultimately will have to be reduced significantly in order to minimize resistive losses in larger arrays of woven devices. Unfortunately, c_{silk} unfavorably compared to the conductivity $c_{\text{PEDOT-S}}$ of spin-coated 60–80 nm thin PEDOT-S films, which we measured to be $c_{\text{PEDOT-S}} = 18 \pm 4 \text{ S cm}^{-1}$. This discrepancy can be accounted for at least to some extent by considering that a large fraction of our fibers is composed of insulating protein material. In addition, it is important to note that the PEDOT-S used in this study is of rather low molecular weight,^[27] the increase of which can be expected to improve the formation of percolation pathways along the fiber as well as the conductivity of the conjugated polyelectrolyte in absolute terms. A parallel strategy would be to increase the volume fraction of the bound dye. Certainly, the here utilized method to produce conducting silk fibers is readily compatible with traditional silk dyeing routines, which frequently involve acidic aqueous dye solutions and elevated temperatures.^[22] As we have reported, PEDOT-S interacts with silk through favorable electrostatic interactions and durably dyes the fibers throughout their bulk.^[13] This is in contrast to previous attempts to produce conducting textile fibers, which often championed more laborious and less robust coating of for instance polyamide,

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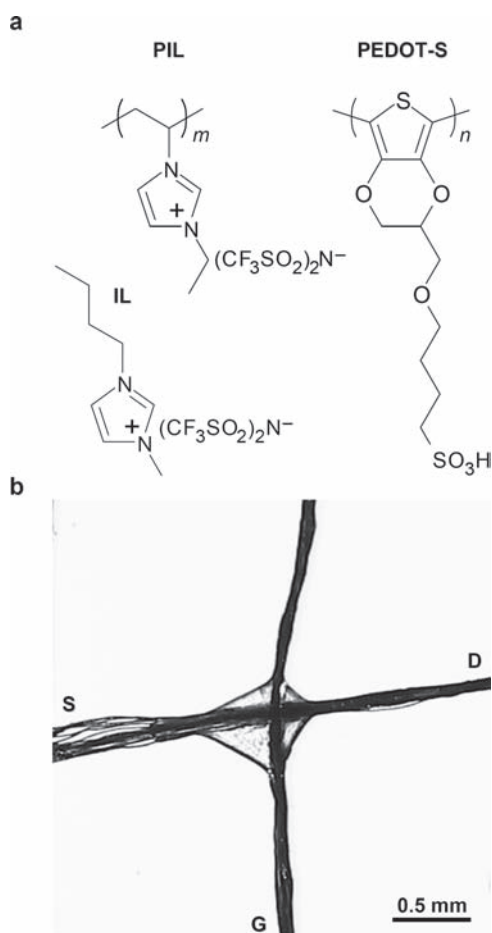


Figure 1. a) The chemical structure of the imidazolium-based ionic liquid:polymer ionic liquid (IL:PIL) electrolyte mixture [bmim][Tf₂N]:poly[ViEtIm][Tf₂N] and the conjugated polyelectrolyte dye PEDOT-S. b) Microscopy image of a silk fiber-based ECT device with source (S), drain (D), and gate (G) as indicated. A drop of IL:PIL bridges the gap between the two fibers at the cross-junction. Note that the source-drain fiber has split into monofilaments close to S.

polyamide as well as silk fibers with conducting polymers from solution^[6,11,28,29] or by means of in situ polymerization.^[30–32]

Electrochemical transistors (ECTs) were fabricated by arranging PEDOT-S stained fibers, which consisted of a number of monofilaments (Figure 1b), in a simple cross-junction configuration. The gap between the two fibers was bridged with a drop of a 1:1 electrolyte mixture by weight of the ionic liquid (IL) 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonimide) ([bmim][Tf₂N]) and the corresponding polymer ionic liquid (PIL) poly(1-vinyl-3-methylimidazolium) bis(trifluoromethanesulfonimide) (poly[ViEtIm][Tf₂N]) (Figure 1a).^[33] The two ends of one of the two fibers represented the ECT source and drain terminals, whereas the orthogonal fiber served as the gate electrode. The transistor channel was defined by the contact area of the IL:PIL electrolyte mixture with the source-drain fiber. An optical micrograph of a complete silk fiber ECT is displayed in Figure 1b. It should be noted that the function of the two fibers as well as of the source and drain terminals is readily interchangeable, which adds to the versatility of our woven ECTs.

Operation of an ECT is facilitated by a reversible redox process that alters the conductivity of the transistor channel in contact with a common electrolyte. The device characteristics of individual fiber ECTs were measured under ambient conditions using a Keithley 4200 parameter-analyzer. Electrodes could be addressed with crocodile clamps or fixated with silver paste (Agar Scientific) to provide for a more permanent connection. A typical set of output, transfer and transient curves is displayed in Figure 2. Upon application of a sufficiently positive gate voltage V_g , PEDOT-S in the transistor channel is dedoped, which results in a significant reduction of the channel conductivity and thus a much decreased drain-source current I_{ds} . The output characteristics of the device presented in Figure 2a show saturation of I_{ds} with increasing drain-source voltage V_{ds} . The transfer characteristics reveal an ON/OFF ratio of approximately 2 orders of magnitude, *i.e.* the ratio of I_{ds} in the ON state at $V_g = 0$ V and in the OFF state at $V_g > 1.2$ V (Figure 2b). Other devices that we had fabricated displayed an ON/OFF ratio of up to 2.5 orders of magnitude, which is an adequate value for ECTs,^[11,34] although changes in conductivity of up to 5 orders of magnitude can be achieved.^[35] Furthermore, we found that the turn-off voltage V_{OFF} , here defined as the gate voltage at which the absolute gate current $|I_g|$ rises above $|I_{ds}|$, varied between 1 and 1.5 V ($V_{OFF} = 1.2$ V for the device characteristics displayed in Figure 2). This highlights the sensitivity of ECT operation to the precise contact area between the IL:PIL electrolyte mixture and the gate as well as channel, which were prone to variation if the fibers were permitted to move relative to each other, whereas the exact distance between the source-drain and gate fiber as well as the amount of IL:PIL electrolyte mixture are less important. Thus, eventually the operation voltage of circuits based on these devices should be selected to be sufficiently high, *e.g.*, 1.5 V, in order to allow for variance in V_{OFF} . Nevertheless, our silk fiber-based ECTs displayed good current modulation and gratifyingly low operation voltages, a crucial requirement if such devices are to be integrated into wearable textiles. The relatively high I_g is intrinsic to ECTs and ultimately limits the packing density of devices along a fiber, which need to be spaced a distance $2 \cdot D$ apart in order to avoid cross-talk (*cf.* Ref. 11).

Unfortunately, the switching speed of our transistors was relatively low as evidenced by the I_{ds} transient displayed in Figure 2c, which indicates that one full ON-OFF period took about one minute. This is little surprising since the electrochemical response time upon a variation in V_g is related to the volume of channel material that requires dedoping/doping and its contact area with the IL:PIL electrolyte mixture. Our silk fibers were stained with PEDOT-S throughout the bulk (*cf.* Ref. 13), which unfavorably compares with for instance 400-nm thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) films laterally gated with a poly(sodium 4-styrenesulfonate)-based electrolyte that have been demonstrated to allow an approximately 6 times faster switching speed (*cf.* Ref. 36 and 37). However, we believe that, in principle, the switching speed of silk fiber-based ECTs can be increased substantially by allowing the IL:PIL electrolyte mixture to more efficiently penetrate the free volume between monofilaments, which can have a fineness of down to 1 dtex only, *i.e.*, $D \sim 10$ μm (*cf.* Figure 1b and Ref. 22). The resulting increase in the effective contact area between PEDOT-S and the IL:PIL electrolyte mixture would permit considerably faster dedoping

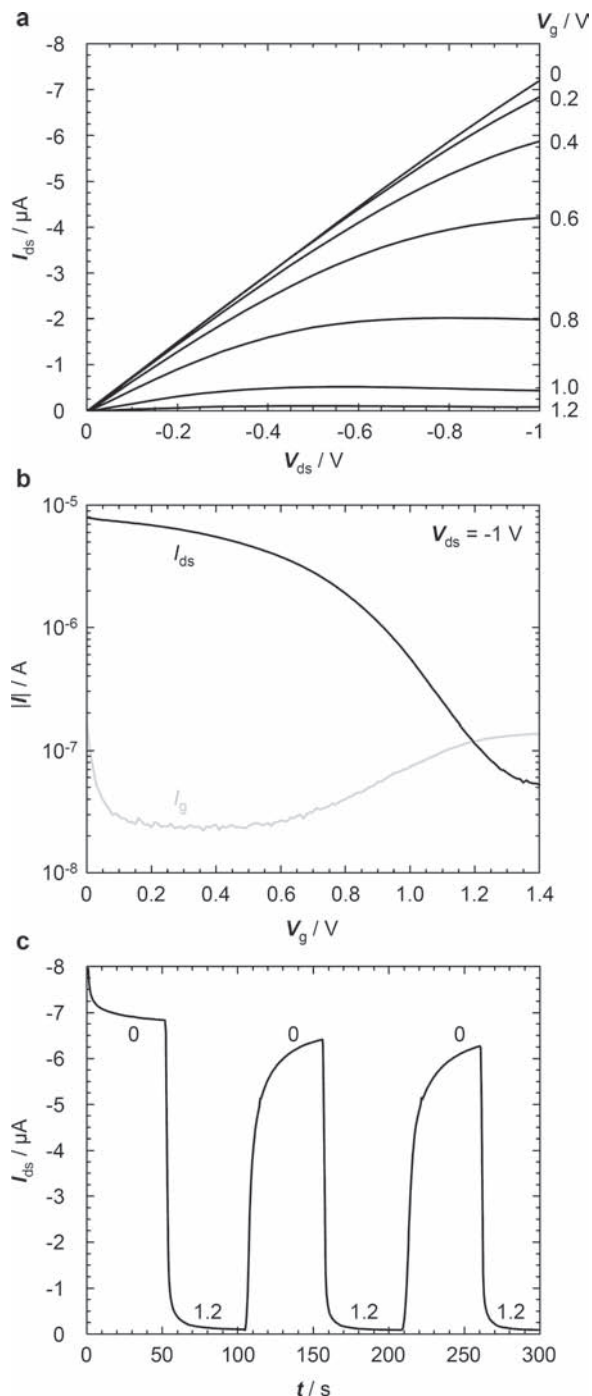


Figure 2. a) Output characteristics of a silk fiber-based ECT showing the drain-source current I_{ds} with respect to the drain-source voltage V_{ds} . The gate voltage V_g was varied from 0 to 1.2 V. b) Corresponding transfer characteristics showing I_{ds} with respect to the applied V_g . The gate current I_g is also shown. $V_{ds} = -1$ V. c) Corresponding transient characteristics showing I_{ds} as a function of time t during repeated switching of V_g between 0 and 1.2 V.

of the transistor channel. In fact, we noted that using a IL:PIL mixture with a higher PIL content, e.g., 75 wt%, and thus increased viscosity less conformally coated the surface of our PEDOT-S stained silk fibers, which resulted in much reduced switching speeds than reported here.

Most interestingly, our silk fiber-based ECTs could be rinsed with distilled water without any noticeable deterioration of device performance, which confirms not only the strong binding between PEDOT-S and silk proteins but also demonstrates the good environmental stability of our devices.

Besides an appreciable level of electrical conductivity, the realization of silk-based electronic textiles also demands excellent mechanical toughness of all fibers that are to be woven into fabrics. Principally, this is because the process of weaving can exert significant stress on the fiber material and, in addition, the use of strong fibers will guarantee robust woven articles. Thus, in a further set of experiments we investigated the mechanical properties of our PEDOT-S stained silk fibers. To this end fibers with $D \sim 50\text{--}100$ μm and a gauge length of 8 mm were tensile drawn at ambient temperature with a TA Instruments DMA Q800 V7.4 analyzer using a ramp force of 0.2 N min^{-1} . Representative stress-elongation curves are displayed in Figure 3a. We find that whereas pristine fibers featured a Young's modulus $E = 9.5 \pm 1.2$ GPa, elongation at break $\epsilon_{\text{max}} = 14\% \pm 3\%$ and true stress at break $\sigma_{\text{true}} = \sigma_{\text{max}} (1 + \epsilon_{\text{max}}/100) = 502 \pm 42$ MPa (here, σ_{max} is the nominal maximum stress at break), staining with PEDOT-S appeared

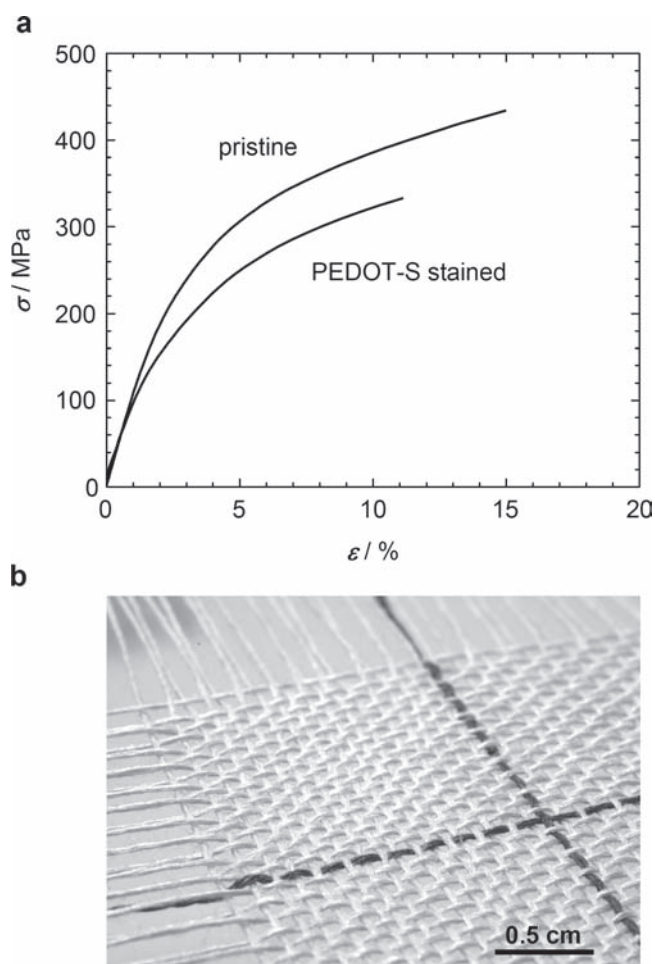


Figure 3. a) Stress-elongation σ - ϵ curves of a representative pristine *Bombyx mori* silk fiber as well as a fiber stained with PEDOT-S. b) Photograph of a basket-weave fabric manually woven with pristine as well as PEDOT-S stained *Bombyx mori* silk threads.

to have weakened the silk fibers, which displayed a similar $E = 8.2 \pm 1.6$ GPa and $\epsilon_{\max} = 11\% \pm 4\%$ but much reduced $\sigma_{\text{true}} = 380 \pm 69$ MPa. Nevertheless, our conducting silk fibers could be subjected to manual weaving as illustrated by a photograph of a basket-weave fabric produced with pristine as well as PEDOT-S stained *Bombyx mori* silk threads (Figure 3b). Furthermore, it is interesting to note that the PEDOT-S stained silk fibers were unaffected by such rough handling, i.e., threading of a conventional sewing needle followed by stitching, as they still displayed the same degree of electrical conductivity that we had measured directly after dyeing. More careful experiments revealed that c_{silk} didn't suffer as long as fibers were not elongated by more than $\epsilon \sim 2\%$, i.e., as long as deformation was ensured to be mostly elastic (cf. Figure 3a). Instead, when fibers were elongated further, c_{silk} decreased irreversibly.

In conclusion, this first demonstration of silk fiber-based ECTs is a significant step towards the realization of electronic textiles and flexible organic electronics in general through the combination of a traditional textile material and carefully chosen polyelectrolyte chemistry. Our approach is readily applicable to established silk processing schemes and the good mechanical as well as environmental stability of our devices add to their unique potential. Furthermore, the use of fibers that consist of a multitude of monofilaments is unlike previously demonstrated synthetic monofilament cross-junction ECTs^[11] and offers the possibility to design three-dimensional electrochemical devices. A higher area to volume ratio as compared to thin-film devices would not only allow to increase the switching speed of the here discussed ECTs but may also be of relevance for other applications such as textile-based sensors or batteries. Finally, the use of biologically relevant electrochemical media may permit to interrogate novel device paradigms that facilitate direct interaction with living systems.

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