

# Electrochemical Devices Made from Conducting Nanowire Networks Self-Assembled from Amyloid Fibrils and Alkoxysulfonate PEDOT

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## ABSTRACT

Proteins offer an almost infinite number of functions and geometries for building nanostructures. Here we have focused on amyloid fibrillar proteins as a nanowire template and shown that these fibrils can be coated with the highly conducting polymer alkoxysulfonate PEDOT through molecular self-assembly in water. Transmission electron microscopy and atomic force microscopy show that the coated fibers have a diameter around 15 nm and a length/thickness aspect ratio  $>1:1000$ . We have further shown that networks of the conducting nanowires are electrically and electrochemically active by constructing fully functional electrochemical transistors with nanowire networks, operating at low voltages between 0 and 0.5 V.

The construction of functional nanoscopic materials and components through molecular self-assembly has the potential to deliver totally new concepts in fields as widespread as electronics and tissue engineering.<sup>1,2</sup> The route of self-assembled functional materials may eventually allow cheap mass production of complex three-dimensional electronic nanomaterials and nanodevices.

Such bottom-up construction approaches depend on molecular materials with the desired functionality and also on molecular template materials with inherent molecular recognition properties for self-assembly from liquids.

Biomolecules are interesting templates for self-assembly of nanostructures, especially due to excellent molecular recognition properties.<sup>3</sup> The combination of active conjugated polymers (CPs) with biomolecules allows for the addition of general electro-optical properties to biomolecular nanotemplates, which then can be exploited in a variety of functional components.

Nanowires of CPs have been constructed using a number of different techniques such as electropolymerization of PEDOT and polypyrrole within ion track etched channels<sup>4,5</sup> between metal electrodes.<sup>6,7</sup> Transistor devices are one of the types of functional units that have been demonstrated with nanowires with CPs; for example, nanowire networks

of conducting polymers are switched using an electrolyte gate.<sup>8,9</sup>

In previous works, DNA biomolecules have been used as nanotemplates together with conducting CPs. Polypyrrole has been chemically polymerized on DNA to form self-assembled nanowires,<sup>10</sup> polypyrrole and poly(3,4-ethylenedioxythiophene) have been electrochemically polymerized on DNA to form chiral CP structures,<sup>11</sup> and polyaniline nanowires have been formed on immobilized DNA on surfaces using chemical polymerization routes.<sup>12,13</sup>

There are however problems with the method of polymerizing CP onto biomolecules. In many cases the chemical conditions of polymerization are harsh for the biomolecules resulting in degradation or loss of biochemical functionality. Furthermore polymerization of a layer of CP onto biomolecules reduces access to unique biochemical functional groups and thereby limits the number of possibilities for self-assembly into more complex structures. A more interesting route to the construction of self-assembled functional nanostructures involves using water soluble CPs with biomolecules. Some previous work includes using CPs to form bioactive aqueous gel matrices formed by peptide amphiphiles,<sup>14</sup> and the powerful capabilities of combining the functionality of both biomolecules and CPs have been demonstrated in schemes based on combining the molecular recognition capabilities of DNA together with the optical properties of CPs to create supramolecular systems with optical properties that mimic logic operations.<sup>15,16</sup> Our group

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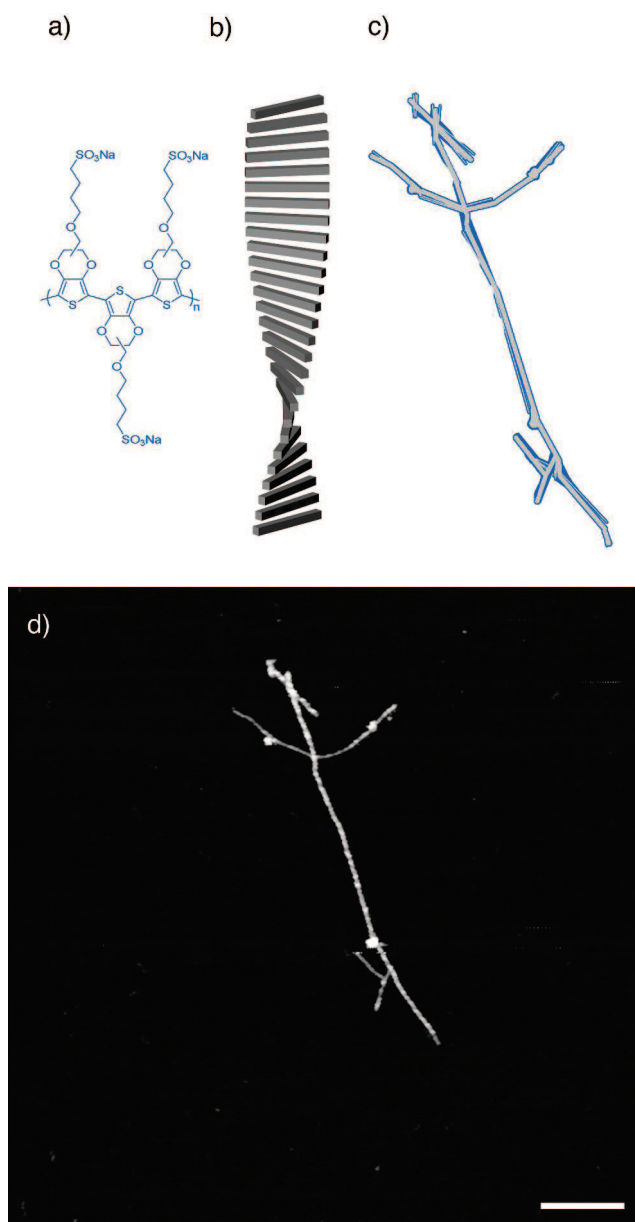
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has previously demonstrated that luminescent conjugated polyelectrolytes can be self-assembled onto amyloid-like protein fibrils,<sup>17,18</sup> and also onto DNA<sup>19</sup> to form self-assembled and aligned optically functional nanowires. Importantly, we have shown that single-stranded DNA complexed with conjugated polyelectrolytes in solution can hybridize specifically.<sup>20</sup> Compared to the relatively simple geometry and recognition possibilities of DNA, proteins offer an almost infinite number of functions and geometries, considering that they serve as well as structural scaffolds and highly complex functional units in biological systems.<sup>21</sup>

Here we have focused on the amyloid fibril as a nanowire template. Amyloid fibrils can be formed from natural proteins and peptides, but also from specifically designed peptides; by exposing them to conditions that destabilize the native state, the formation of stiff, highly stable, and high aspect ratio nanowires is initiated. Normally amyloid fibrils have a width of 7–10 nm and lengths over several micrometers. In this work we have used amyloid fibrils formed from insulin, which is produced in mass scale for diabetes therapeutics, and we show self-assembly of conducting CPs onto these amyloid fibrils.

The conducting poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) is a water soluble material and therefore theoretically compatible with biomolecular systems (amphiphilic). PEDOT/PSS however lacks ionic side chains on the conducting PEDOT backbone, which is probably a necessity for biomolecular interaction. Furthermore, the presence of the large and nonconducting macromolecule PSS prevents smaller biomolecules to be used as nanotemplates. We could therefore not show any sign of self-assembly of PEDOT:PSS with biomolecular amyloid nanowires and to our knowledge no previous work has successfully demonstrated use of PEDOT/PSS together with biomolecules for self-assembly of nanostructures. Therefore we have instead used alkoxysulfonate PEDOT (PEDOT-S)<sup>22</sup> in a new fully water soluble form based on recent synthesis routes.<sup>23</sup> This polymer has anionic sulfonate groups on the side chains and is self-doped in pristine state with conductivities above 1 S/cm. "Particle analysis of PEDOT-S in water has shown very small particles (in average 2 nm) suggesting that PEDOT-S exists as single chains or aggregates of only a few polymer chains in water solution. The small particle size in water indicates that the polymer has a low molecular weight; however, the shortest oligomers were removed through a dialysis step (cut-off 1000 g/mol) in the synthesis of PEDOT-S. These properties combined make PEDOT-S an ideal material of choice for self-assembly of conducting nanowires with biomolecular systems.

Insulin amyloid fibrils were formed by heat incubation (65 °C) of the native protein at low pH. Figure 2c shows a TEM graph of these insulin fibrils in pure form (see Figure S1 for more pictures of amyloids). The unbranched structure and high aspect ratio with widths ~10 nm and over micrometer length is clearly demonstrated in these graphs. PEDOT-S and amyloid fibrils were mixed in water to a final concentration of 0.3 mg/mL and 25  $\mu$ M, respectively, and the solution was kept at room temperature for 10 min. The formation of

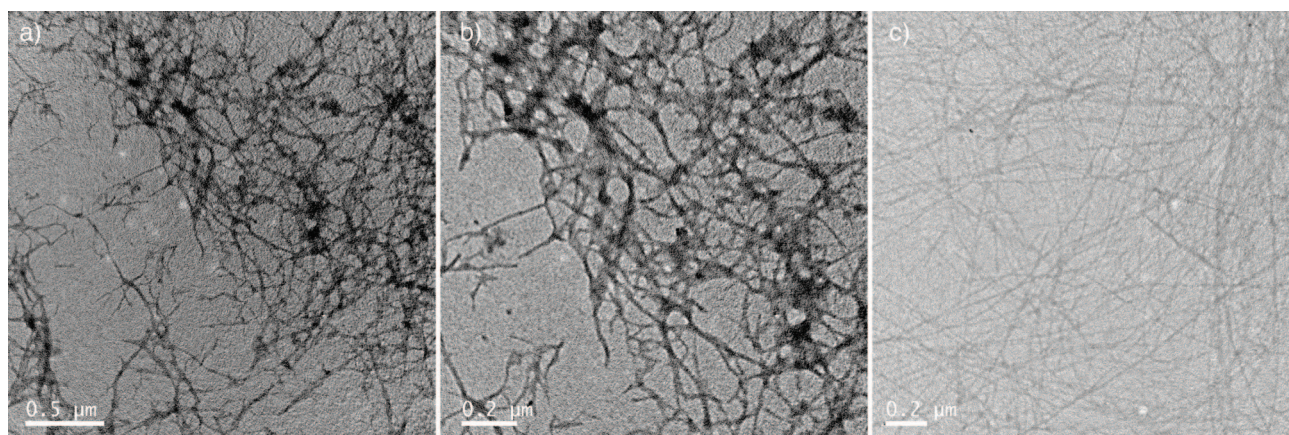


**Figure 1.** (a) Chemical picture of PEDOT-S. (b) Schematic picture of one amyloid chain. (c) Schematic picture of PEDOT-S coated amyloid fibrils forming a nanostructure on mica surface, as shown in Figure 1d. (d) AFM graph from PEDOT-S-stained amyloid fibrils on mica. The scale bar is 1  $\mu$ m.

a complex between PEDOT-S and amyloid fibrils was apparent due to the visible formation of a bluish gel and a less colored supernatant. The solution was filtered through a frit with a pore size of 20–85  $\mu$ m. The frit was rinsed with more than four times the sample volume, ensuring that the filtrate never dried out completely and remaining decorated fibrils that did not pass through the frit were kept for experiments. This filtering procedure was performed in order to remove any excess PEDOT-S that was not attached to amyloid fibrils, any remaining salts, and furthermore to only keep larger self-assembled networks. The extensive rinsing also demonstrates the stability of the complex and the high affinity between the two species.

The remaining water solution, containing decorated fibrils, was further studied by centrifuging the solution and measur-





**Figure 2.** (a, b) Transmission electron microscope pictures of PEDOT-S coated fibrillar networks at different zoom levels. (c) Transmission electron microscope picture of pure and unstained amyloid fibrillar networks.

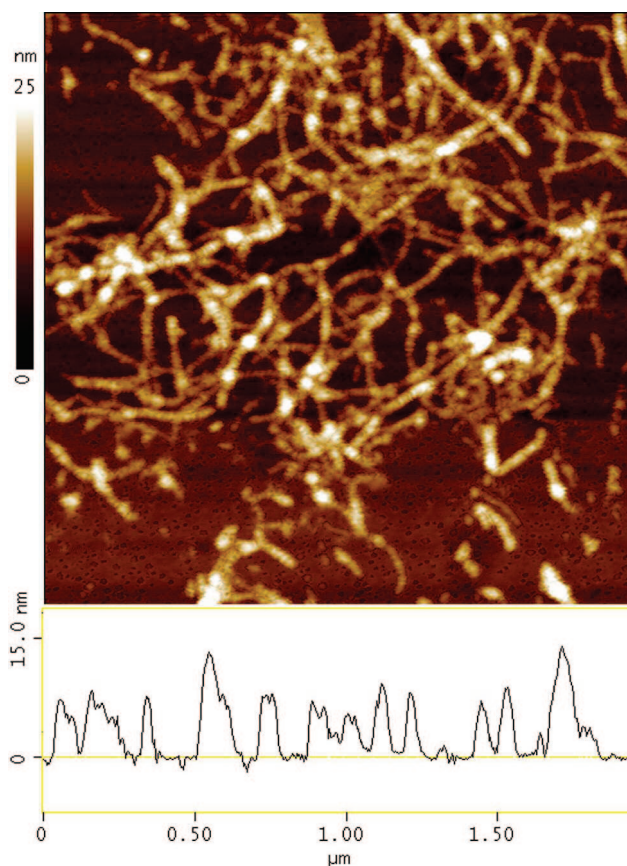
ing conductivity on the supernatant. We could not measure any conductivity on the films from the supernatant showing that all PEDOT-S in this solution were attached to the amyloid fibrils.

The nanowire network solution was placed on freshly cleaved mica, and the solvent was blown away with a nitrogen flow. Amyloid networks do not attach well to the hydrophilic surface of mica resulting in a flat surface sparsely covered with separated nanowires. Figure 1d displays an AFM graph of an individual nanowire structure. This structure probably corresponds to single amyloid fibrils nanowires that are at least partly decorated with PEDOT-S polymers. A schematic of this structure is shown in Figure 1c, together with the chemical structure of PEDOT-S and schematic of single amyloid fibrils in Figure 1a,b, suggesting that the nanowires consist of a core of amyloid fibers with a shell of PEDOT-S.

In order to further study the attributes of the functional nanowire networks, we performed transmission electron microscopy (TEM) and atomic force microscopy (AFM) studies on the nanowire networks, by depositing the networks on carbon-coated Formvar TEM-grids (Ted Pella). The hydrophobic character of the grid allowed for the formation of denser nanowire networks similar to what was formed on glass.

Panels a and b of Figure 2 show TEM graphs at different zoom levels of PEDOT-S coated nanowires on TEM grid, and Figure 2c displays a TEM grid with uncoated, unstained amyloid fibrils.

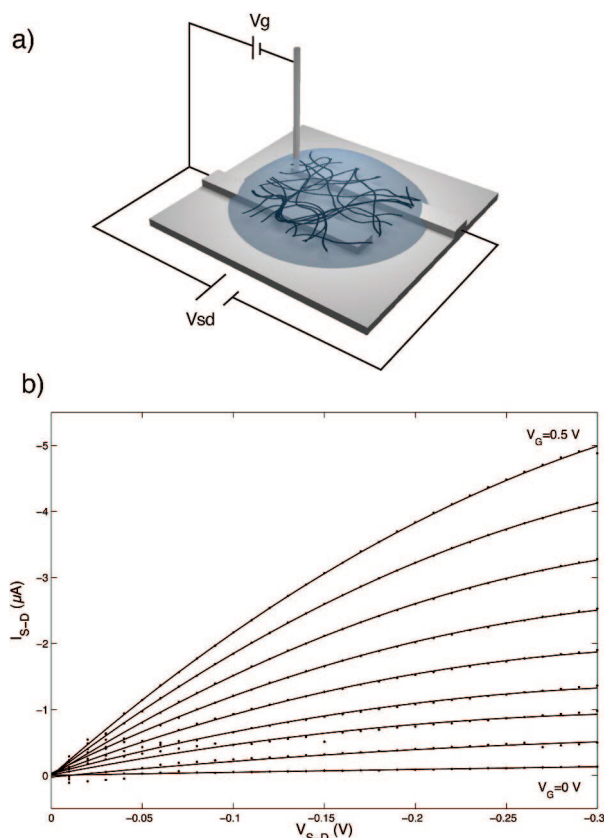
Statistical measurements from these TEM pictures show that the PEDOT-S coated nanowires are wider than the pure amyloid fibrils with an average width of ca. 15 nm and that they also have higher deviation in width; there is also visible geometrical difference between panels a and c of Figure 2 and panel d of Figure 2. Furthermore the coated amyloid fibril networks clearly show higher contrast as compared to pure fibrils in TEM, and the higher contrast is visible on a major part of the entire nanowire network providing additional proof of the presence of a PEDOT-S coating, which has higher electron scattering properties compared to pure amyloid fibrils. In fact the contrast of the PEDOT-S



**Figure 3.** Atomic force microscopy graph taken from the same grid as seen in the TEM graphs of panels a and b of Figure 2.

decorated nanowire is not far from that of the amyloid fibrils negatively stained with uranyl acetate (see Figure S1).

As a complement to the TEM pictures, atomic force microscopy measurements were performed on the very same TEM grids carrying PEDOT-S nanowire networks. These measurements provided additional height profile information as seen in Figure 3, with an average height of ca. 17 nm. The average height of unstained amyloid fibrils was also measured to ca. 9 nm, using AFM measurements with the pure fibrils on similar TEM grids (see Figure S2).



**Figure 4.** (a) Schematic picture of the experimental setup of the electrolyte gated transistor. (b) Electrical characteristics of the electrolyte-gated transistor operating in depletion mode: dots, measured; lines, curve fit. The measurements are done in 0.1 M LiClO<sub>4</sub> acetonitrile electrolyte. The gate voltage is swept from 0 to 0.5 V.

The height difference suggests that we have an average coverage of around 8 nm PEDOT-S around the amyloid fibrils. The displayed section analysis graph also shows a flat surface between the nanowires, demonstrating the absence of any residual conducting film apart from the networks.

The electrical character of the nanowire network was analyzed with an electrolyte gated transistor device. This device was constructed using a platinum interdigitated microgrid (5 μm electrode gap, and a total length of 2 cm) with the nanonetworks deposited on top. A reference was made by spin casting PEDOT-S on an identical interdigitated electrode. The resistance and height of the reference were used together with the resistance and the measured (PEDOT-S) thickness in the networks in order to estimate the coverage of the PEDOT-S networks to around 1/50 of the total area of the interdigitated grid (see Supporting Information for more details.)

The nanowire-decorated grid was immersed in an acetonitrile (0.1 M LiClO<sub>4</sub>) electrolyte and probed with a Pt gate electrode also immersed, as shown schematically in Figure 4a. The choice of Pt and electrolyte material guaranteed very small electrochemical currents from the Pt in the chosen potential window, resulting in a source–drain current that could be almost totally ascribed to the nanowires. The transistor *I*–*V* curves seen in Figure 4b show high source–drain currents reaching –5 μA at on state, as a result

of the high conductivity of PEDOT-S, which has a film conductivity of ~1 S/cm.<sup>23</sup>

The transistor showed repeatable and reversible switching characteristics with an on/off ratio of >40 when sweeping the gate between 0 and 0.5 V. This clearly shows that PEDOT-S has not lost any electrical or electrochemical properties after self-assembly to amyloid fibrils and behaves similar to PEDOT-S in thin films. The nanowire networks further show ohmic connection to the metal, and no detachment during the electrochemical reactions under these conditions could be observed. The retained electrochemical activity of the PEDOT-S in nanostructures suggests that it should be possible to scale the size of the previously demonstrated single microfiber electrochemical transistors<sup>24</sup> with more than 3 orders of magnitude down to single nano/molecular fiber electrochemical transistors.

In conclusion, we have demonstrated self-assembly of highly conducting polymers to biomolecular polymers in a pure water solution and shown that networks of these nanowires can be used in the construction of electronic devices with advanced functions, demonstrated in an electrochemical transistor device.

This constitutes an important step toward the fabrication of advanced self-assembled nanoscopic devices. The mixtures of previously demonstrated self-assembled semiconducting nanowires with the conducting nanowires presented in this work could allow for the construction of principally any advanced electronic device including diodes, photovoltaics, and transistors. These devices could ultimately be assembled with individual components assembled at the nano/molecular scale by using functionalization together with biomolecular recognition schemes.

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**Supporting Information Available:** Description of experimental procedures and figures showing TEM picture of pure amyloid fibrils and AFM height studies of amyloid fibrillar networks and PEDOT decorated amyloid fibrillar networks. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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