

Synthesis, electrical properties, and nanocomposites of poly(3,4-ethylenedioxythiophene) nanorods

James D. Mendez^{ab} and Christoph Weder^{*ab}

Cellulose nanofibers or "whiskers" derived from tunicates were coated with PEDOT:PSS to produce high-aspect-ratio nanorods with high electrical conductivity. Films made from these PEDOT:PSS whiskers have surface resistivities as low as $97 \Omega/\square$. The nanorods were found to disperse well in polar organic solvents such as dimethylformamide, which allowed the fabrication of nanocomposites with inert host polymers such as poly(methyl methacrylate) and polystyrene. These materials display surface resistivities as low as $760 \Omega/\square$. Due to the high aspect ratio of the PEDOT:PSS-coated whiskers (64) and the formation of well-dispersed whisker networks within the polymer matrices, these materials display a percolation threshold as low as $\sim 2\%$ v/v. Using a sol-gel process, electrically conducting gels and aerogels with a density of 6.4 mg cm^{-3} and a surface resistivity of $\sim 200 \text{ k}\Omega/\square$ were also produced.

Introduction

Nanocomposites involving electrically (semi)conducting conjugated polymers are of interest, because their (opto)electronic properties can, in many cases, be widely manipulated through combination of two or more different types of materials. A plethora of studies have focused on materials in which conjugated polymers are used as the continuous phase into which inorganic nanoparticles,¹⁻³ organic nanocrystals,⁴⁻⁷ carbon nanotubes,⁸⁻¹⁰ and other nanomaterials are integrated (note that a clear distinction is made between nanocomposites and phase-separated blends, whose morphology is often very difficult to control¹¹). Less work has addressed materials in which the nanoparticle used is a conjugated polymer,¹² and even fewer studies have investigated nanocomposites that comprise conjugated polymer particles of high aspect ratio, *i.e.* nanofibers, -rods, or -whiskers.¹³ The one-dimensional nature of such nanofillers imparts several interesting features, including percolation at low concentration^{14,15} (of interest are *e.g.* nanocomposites of conducting polymers with 'inert' matrix polymers for antistatic applications, electromagnetic shielding¹⁶⁻¹⁸), the possibility to create anisotropic materials,¹⁹⁻²¹ and nanocomposites with high internal surface areas (which are useful in sensor applications,^{22,23} rapidly switchable electrochromic devices,²⁴ and heterojunction photovoltaic devices⁴⁻⁷). However, few *broadly applicable* approaches are known, which allow the fabrication of well-individualized and well-defined nanofibers of conjugated polymers by simple processes. Usually, very specific methods are required, which are only applicable to one particular polymer. Examples include templated synthesis²⁵ and the synthesis of polyaniline rods under confining conditions.²⁶⁻²⁸ Direct synthesis often yields ill-defined rod-like shapes, instead of

well-defined wires with high aspect ratio.^{29,30} Other techniques rely on shaping already synthesized conjugated polymers, such as the preparation of nanorods or nanotubes using a porous membrane as a template,³¹⁻³³ phase separation of block copolymers,³⁴ or electrospinning.³⁵⁻³⁸ However, many of these methods are intricate or do not afford well-individualized fibers that can be incorporated as the percolating phase into a matrix polymer by simple mixing.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the technologically most relevant conducting polymers due to its combination of its high electrical conductivity as well as its high transparency in the visible spectrum.^{39,40} Yet, current methods for the preparation of high-aspect ratio PEDOT nanofibers are limited. These current methods can be categorized into three general areas that yield pure PEDOT nanorods,⁴¹ coated fibers (commonly electrospun),⁴²⁻⁴⁴ and coated nanorods (commonly carbon nanotubes).⁴⁵⁻⁴⁷ PEDOT nanorods without any scaffold retain the excellent properties of bulk PEDOT, but most of these nanorods have relatively low aspect ratios.⁴⁸

We here report the synthesis of PEDOT nanofibers by the polymerization of ethylenedioxythiophene (EDOT) in the presence of cellulose nanofibers as a scaffold.⁴⁹ This general approach was introduced by Flandin *et al.* for the preparation of polypyrrole rods.¹² We previously used a modified version of this framework to fabricate polyaniline and poly(*p*-phenylene ethynylene) nanofiber composites.⁵⁰ These materials were prepared by the adsorption of pre-formed polymers onto the cellulose template, rather than *in situ* polymerization. The potential problems of the latter reside in the difficulty of obtaining a smooth and thin layer of the conjugated polymer on the template,¹² the aggregation of the conducting nanofibers during synthesis, the fact that the polymerization also proceeds remote from the template, and the formation of nanoparticles on the nanofibers, as we reported recently for silver, gold, copper, and platinum.⁵¹ However, we show here that, under appropriate reaction conditions, the process allows the formation of high-aspect-ratio nanorods with nm-thin layers of a highly conductive coating, which can readily be processed into conducting films,

^aAdolphe Merkle Institute and Fribourg Center for Nanomaterials, University of Fribourg, Route de l'Ancienne Papeterie CP 209, CH-1723 Marly 1, Switzerland. E-mail: christoph.weder@unifr.ch; Fax: +41 (0)26 300 9624

^bDepartment of Macromolecular Science and Engineering, Case Western Reserve University, 2100 Adelbert Rd., Cleveland, OH, 44106-7202, USA

gels, aerogels, and polymer nanocomposites with low percolation threshold.

Results and discussion

Cellulose nanofibers or “whiskers” can be obtained from a range of renewable bio-sources, including tunicates, wood, cotton, and sisal.⁶³ For this study we employed whiskers isolated from tunicates by hydrolysis with sulfuric acid according to methods reported elsewhere.^{52,53} The whiskers obtained from these sea creatures exhibit high stiffness (tensile modulus ~ 130 GPa) and a very high aspect ratio (average dimensions $26 \text{ nm} \times 2.2 \text{ }\mu\text{m}$, Fig. 1A).⁵⁴ Due to the high density of strongly interacting surface hydroxyl groups, cellulose whiskers have a strong tendency for aggregation. However, if sulfuric acid is used for the hydrolysis, a small number of sulfate groups is introduced, which imparts good dispersibility in water and a range of polar organic solvents, such as dimethylformamide (DMF).^{52,53,55}

PEDOT-coated whiskers were prepared by the oxidative polymerization of EDOT in the presence of the whiskers (Scheme 1). We first attempted the synthesis of *p*-toluenesulfonate-doped PEDOT (PEDOT:TS) with iron(III) *p*-toluenesulfonate as the oxidant (Scheme 1A), since this PEDOT variant exhibits high electrical conductivity.⁵⁶ The synthesis of PEDOT:TS is preferably conducted in aliphatic alcohols, but these solvents do not disperse cellulose whiskers.⁵² On the other hand, DMF is a good dispersant for the whiskers, but not suitable for the polymerization of EDOT. Therefore, our initial protocol used equal amounts of water and methanol along with EDOT and cellulose whiskers in a ratio of 2 : 1 (w/w). Unfortunately, the reaction afforded large aggregates that appeared to be PEDOT, which could not be dispersed by sonicating the isolated reaction product in water (Fig. 2A). The EDOT : whisker ratio was varied between 1 : 1 and 4 : 1 (w/w), but the outcome was similar. We hypothesized that binding of the iron ions to the whiskers might be the cause for aggregation (due to either cross-linking between the whiskers or electrostatic shielding). Support for this was provided in a control experiment where iron(III) *p*-toluenesulfonate was added to a dispersion of neat cellulose whiskers in water; this caused the immediate precipitation of cellulose whiskers. The amount of methanol was therefore reduced to the minimum needed to solubilize the EDOT. These conditions resulted in products, in which the macroscopic PEDOT aggregates were no longer visible and the resistivity of solution cast films was as low as $57 \text{ }\Omega/\square$.

However, closer inspection with transmission electron microscopy (TEM) (Fig. 2B) revealed the formation of nanoscale PEDOT aggregates and the whiskers were inhomogeneously coated.

We next explored poly(styrene sulfonic acid) (PSS) as a counterion (Scheme 1B), since PEDOT:PSS is normally formed and processed as a dispersion in water,³⁹ with sodium persulfate as the main oxidant. Only a catalytic amount of iron is used, *i.e.* far less than required for the toluene sulfonate system described above. Initial experiments were carried out with a 2 : 1 (w/w) EDOT : whisker ratio. Upon termination of the reaction, the product readily formed a homogeneous dispersion in either water or DMF upon sonication for 15 min. TEM images (Fig. 1) reveal individually coated whiskers with an average overall thickness of 30 nm, *i.e.* slightly thicker than the uncoated whiskers (23 nm). The coating appears to be homogeneous and the images are largely free of PEDOT and/or whisker aggregates. The thickness comparison suggests that the PEDOT:PSS-coated whiskers comprise similar volume fractions of electrically conducting coating and cellulose core. Dispersions of such whiskers in both DMF and water ($2\text{--}5 \text{ mg mL}^{-1}$) could readily be cast into thin films. Samples with a thickness of $0.5 \text{ }\mu\text{m}$ produced in this manner had an average surface resistivity of $97 (\pm 27) \text{ }\Omega/\square$ and a bulk conductivity of $7.9 (\pm 2.4) \text{ S cm}^{-1}$. These values are comparable to those of films of neat PEDOT:PSS made in a similar fashion, as well as literature values for PEDOT:PSS ($200 \text{ }\Omega/\square$, 10 S cm^{-1}).^{39,57,58} The choice of solvent (DMF or water) used to redisperse the whiskers and cast the films did not have an appreciable effect on either the film quality or properties.

To further investigate the effect of the reaction conditions on the properties of films or coatings made from PEDOT:PSS-coated whiskers, the EDOT : whisker ratio was systematically varied. The PEDOT:PSS-coated whiskers thus produced were dispersed in DMF and cast into films with a thickness from 0.3 to $1.2 \text{ }\mu\text{m}$. The surface resistivity of these samples varied greatly with the EDOT:whisker ratio. It decreased dramatically from $25 \text{ M}\Omega/\square$ for an EDOT : whisker ratio of 0.5 : 1 (w/w) to $97 \text{ }\Omega/\square$ for an EDOT : whisker ratio of 2 : 1 (w/w) and remained constant at higher EDOT concentrations (Fig. 3). However, at EDOT : whisker ratios of >2 : 1 (w/w), low-aspect-ratio aggregates—presumably PEDOT:PSS—formed, as seen in the TEM images (Fig. 1). Interestingly, the thickness of the PEDOT:PSS coating on the whiskers changed little between the different experimental conditions. Thus, it appears that a thin layer of PEDOT:PSS absorbs readily onto the whiskers, but the growth

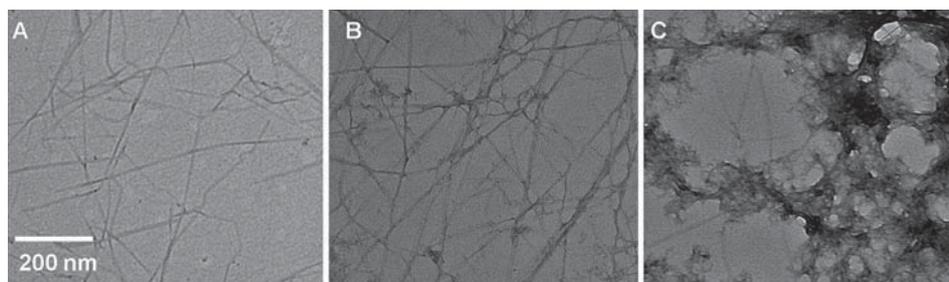
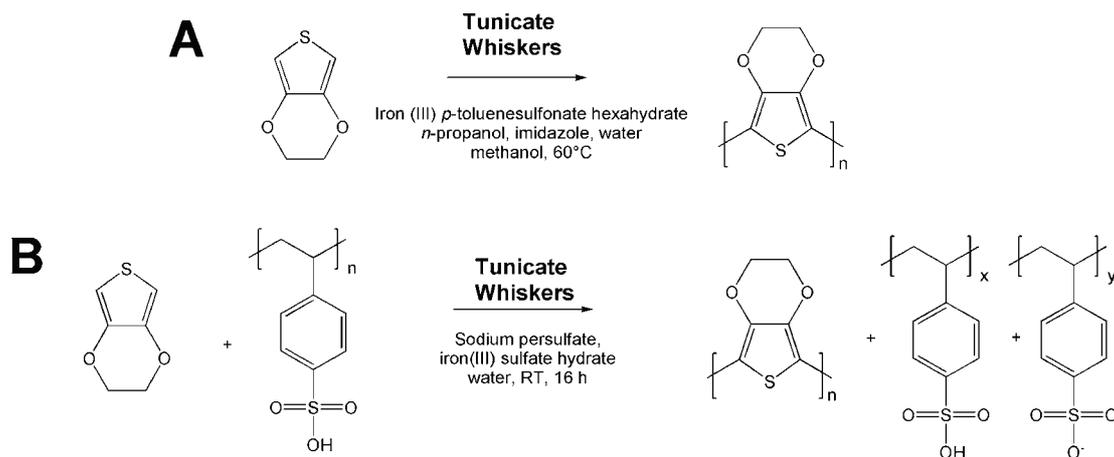


Fig. 1 Transmission electron microscopy (TEM) images of (A) cellulose whiskers isolated from tunicates; (B) cellulose whiskers coated with PEDOT:PSS by synthesis with an EDOT : whisker ratio of 2 : 1 (w/w); and (C) cellulose whiskers coated with PEDOT:PSS by synthesis with an EDOT : whisker ratio of 9 : 1 (w/w).



Scheme 1 Synthesis of PEDOT-coated cellulose whiskers *via* the oxidative polymerization of EDOT with *p*-toluenesulfonate (A) and poly(styrenesulfonate) (B) as the dopant, in the presence of cellulose whiskers isolated from tunicates.

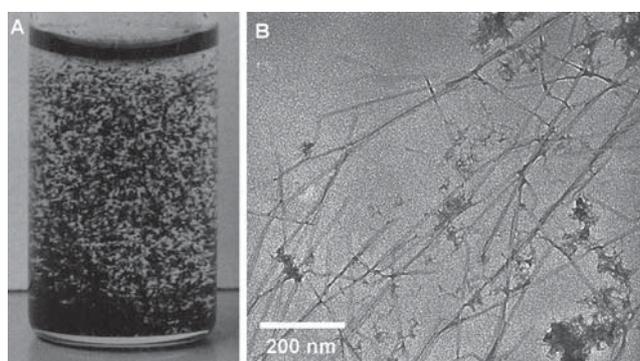


Fig. 2 Photograph of PEDOT:TS-coated cellulose whiskers prepared at high concentration dispersed in water (A) and a transmission electron microscopy (TEM) image of PEDOT:TS-coated whiskers prepared under dilute concentration (B).

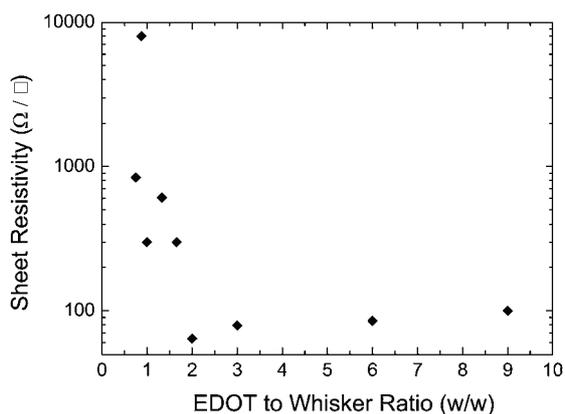


Fig. 3 Surface resistivity of PEDOT:PSS-coated cellulose whisker films as a function of EDOT:whisker ratio in the reaction mixture.

of the coating is not sustained. This might be due to attractive interactions between the iron ions and the whiskers, which might promote that the synthesis occurs predominantly at the whisker surface. After formation of an initial PEDOT:PSS layer, this effect is suppressed, leading (in case of an excess of EDOT) to

conventional polymerization and the formation of PEDOT:PSS aggregates apart from the whiskers. In view of these observations, all subsequent experiments were conducted with whiskers coated with PEDOT:PSS by synthesis with an EDOT : whisker ratio of 2 : 1 (w/w).

The nature of the coatings on the whiskers produced with the above protocol was investigated by infrared spectroscopy (Fig. 4). The characteristically weak PEDOT signals⁵⁹ mostly overlap with those of the cellulose whiskers. However, the C–S stretch (829 cm^{-1}) and the C–O–C stretch (1209 cm^{-1}) are visible upon close inspection, suggesting that the conductive coating is indeed doped PEDOT.

One important feature of PEDOT is its high transparency in the visible region. This makes PEDOT useful for several applications where low absorption is necessary, for example antistatic coatings on lenses and films.⁶⁰ Ultra-violet visible spectroscopy was used to determine the transparency of films of the PEDOT:PSS-coated whiskers (Fig. 5). Significant absorption was not seen on a 250 nm thin film, *i.e.*, one that has a thickness that is above the level where surface resistivity has levelled off (200 nm). A thick film (1200 nm) was also cast and displays distinctive absorption spectrum of PEDOT with a low around 400 nm confirming that the coating is indeed doped PEDOT.

Individually coated whiskers that can be dispersed in organic solvents such as DMF open up many processing options. One

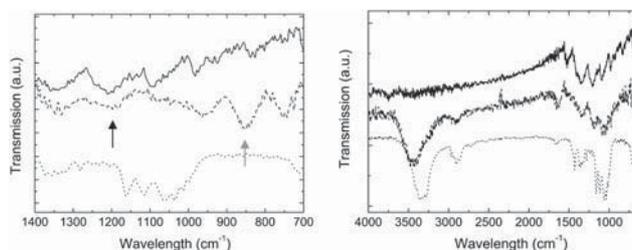


Fig. 4 Infrared spectra of PEDOT:PSS (—), cellulose whiskers (···), and PEDOT:PSS-coated cellulose whiskers (---). The black arrow points to the C–O–C stretch signal around 1207 cm^{-1} while the grey arrow points to the C–S stretch signal around 829 cm^{-1} , which are both present in PEDOT but not cellulose.

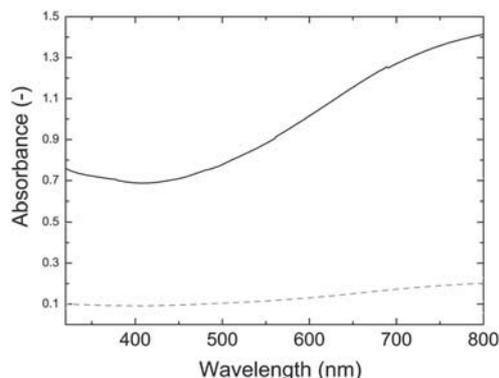


Fig. 5 UV-vis absorption spectra of a thick (1200 nm, solid) and thin (250 nm, dashed) PEDOT:PSS-coated cellulose whisker film (2 : 1 w/w EDOT : whisker ratio).

attractive feature is the high aspect ratio that leads to a very low percolation threshold when incorporating them into an insulating polymer. Theoretically this benefit can be seen in the power law for electrical conductivity:^{61,62}

$$\sigma = \sigma_o[\varphi - \varphi_c(\alpha)]^{t(\alpha)} \quad (1)$$

where σ is the conductivity, σ_o is the conductivity of a film consisting of the coated whiskers only, φ is their volume fraction, $\varphi_c(\alpha)$ is the percolation threshold dependent on aspect ratio, and $t(\alpha)$ is the critical exponent. This equation can be modified to express the conduction in terms of the surface resistivity ρ as follows:⁶³⁻⁶⁵

$$\rho = \rho_o[\varphi - \varphi_c(\alpha)]^{-t(\alpha)} \quad (2)$$

where ρ_o is the surface resistivity of a film consisting of the coated whiskers only (100 Ω/\square).

To probe the usefulness of the present PEDOT:PSS-coated whiskers as the conducting nanofiller in electrically inert matrices, composite films were made by combining varying concentrations of whiskers and two different matrix polymers in

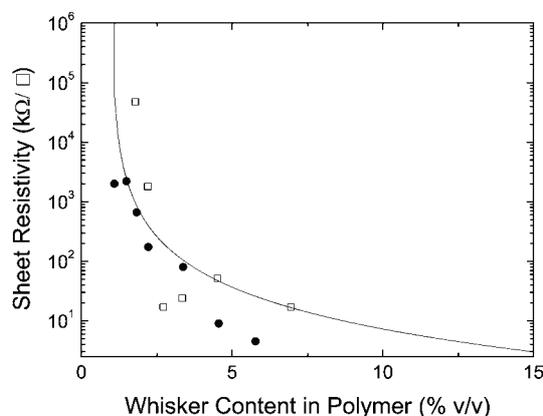


Fig. 6 Surface resistivity of nanocomposites of PEDOT:PSS-coated cellulose whiskers (2 : 1 (w/w) EDOT : whisker ratio) and polystyrene (●) or poly(ethylene oxide) (□). The solid line represents the theoretical conductivity calculated by eqn (2).

a common solvent; water and DMF were combined with solutions of poly(ethylene oxide) (PEO) and polystyrene (PS) respectively. Films were then solution-cast and surface resistivity measurements were made (Fig. 6). The percolation threshold was calculated by dividing the known value for an aspect ratio of 1 (0.6)⁶³ by the aspect ratio for the coated cellulose whiskers (64). A comparison between experimental and theoretical data (Fig. 6) shows an excellent agreement for both systems.

Our group has recently shown that neat cellulose whiskers can be gelled *via* a solvent-exchange method, *e.g.* by substituting water for acetone. Elimination of water as a competitive hydrogen bonding agent switches the strong interactions between the whiskers on, which causes the formation of percolating whisker networks, resulting in stable gels. This approach was here applied to PEDOT:PSS-coated whiskers with much success (Fig. 7). The materials made by gelating an aqueous dispersion by solvent exchange with acetone were dimensionally stable and electrically conductive. In a wet state, *i.e.* swollen with acetone, the gels have a surface resistivity of approximately 200 $k\Omega/\square$ and a bulk conductivity of *ca.* $6.6 \times 10^{-6} \text{ S cm}^{-1}$. After drying the gels into (rather inhomogeneous) films, the surface resistivity was found to be very similar to that of films made by casting PEDOT:whiskers, *i.e.* of the order of 100 Ω/\square (note that due to the irregular dimensions it was not possible to determine this value with high accuracy).

We have shown earlier that cellulose nanofibers can be processed into aerogels (either individually, as hybrids with clay, and optionally with a polymer binder) by lyophilization of aqueous dispersions, and we anticipated that it should be possible to process the present PEDOT:PSS-coated whiskers in a similar manner.⁶⁶ Thus, exploratory experiments were conducted with cellulose whiskers that were coated with PEDOT:PSS by synthesis with an EDOT : whisker ratio of 2 : 1 (w/w). Aqueous dispersions with an initial whisker concentration of 6 mg mL^{-1}

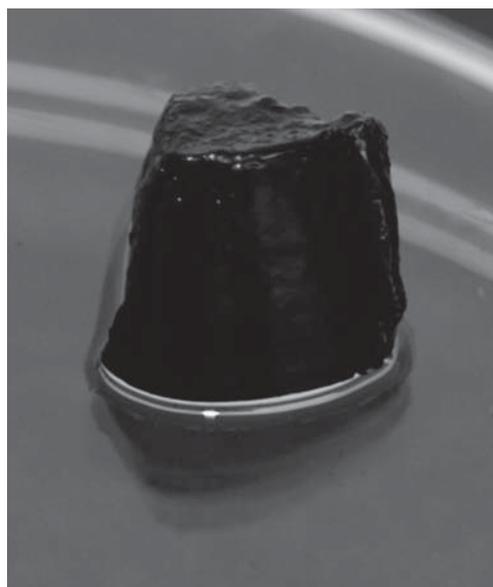


Fig. 7 A picture of a PEDOT:PSS-coated cellulose whisker gel produced from an 8 mg mL^{-1} aqueous dispersion of whiskers (2 : 1 w/w EDOT : whisker ratio) *via* solvent-exchange with acetone.

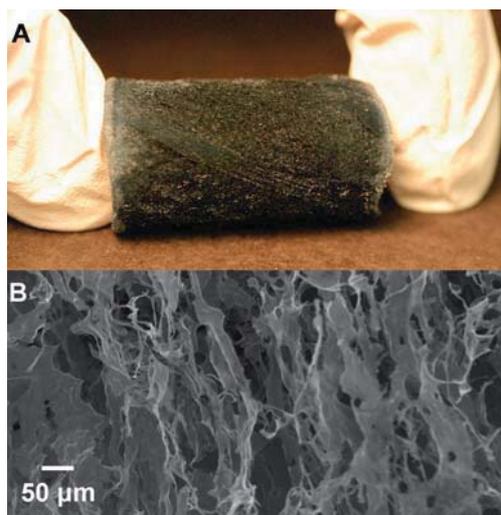


Fig. 8 (A) An image of a PEDOT:PSS-coated cellulose whisker aerogel produced from a 6 mg mL^{-1} aqueous dispersion of whiskers (2 : 1 (w/w) EDOT : whisker ratio). (B) A SEM image of the same material.

were thus freeze-dried as described in the Experimental section, resulting in mechanically stable, self-supporting, foam-like structures with a density of 6.4 mg cm^{-3} . These aerogels (Fig. 8A) have a very similar appearance to aerogels made from the neat (uncoated) cellulose whiskers, except for the dark blue color imparted by the PEDOT:PSS coating. SEM images (Fig. 8B) of these aerogels revealed a layered architecture, in which the whiskers are assembled into thin individual sheets that are separated by large voids. The sheets follow the direction of the ice crystal growth. Overall, the images are very similar to those of aerogels produced from the neat cellulose whiskers.⁶⁶ However, while the latter are electrical insulators, the present materials are electrically conductive. Surface resistivity measurements on the face of the aerogel yielded values of approximately $200 \text{ k}\Omega/\square$. The conductivity of the aerogels investigated here are similar to those of recently reported aerogels based on entangled cellulose nanofibers, which have been rendered conductive by coating with doped polyaniline.⁶⁷

Conclusions

A potentially broadly useful technique for the manufacture of high aspect ratio conductive nanofibers was explored. It was found that by polymerizing EDOT in the presence of cellulose whiskers, individually coated whiskers could be synthesized. In a bulk state, these coated whiskers have a surface resistivity very similar to PEDOT. These coated whiskers can be incorporated into other polymer matrices and demonstrate a very low percolation threshold yielding electrically conductive composites at as low as 2% loading. The coated whiskers can also be made into a variety of gels. Using a sol-gel method, gels can be formed that are electrically conductive. Aerogels can also be made from coated whiskers *via* a freeze-drying method. These aerogels have a low density around 6.4 mg cm^{-3} while maintaining a surface resistivity of approximately $200 \text{ k}\Omega/\square$. These are just a few examples of the many possible uses for coated whiskers. These coated whiskers, made from very abundant and renewable

cellulose, make it possible to achieve the same properties as PEDOT with much less material.

Experimental

Materials and methods

All materials and reagents were of highest available purity and were purchased from Sigma Aldrich. 3,4-Ethylendioxythiophene was further purified by vacuum distillation.

Ultraviolet-visible (UV-vis) absorption spectra were obtained on a Perkin Elmer Lambda 800 spectrometer. Transmission electron micrographs (TEMs) were acquired using a JEOL 1200EX Transmission Electron Microscope. All TEM samples were prepared by deposition of $20 \mu\text{L}$ of the whisker dispersions onto carbon-coated copper grids. Scanning electron micrographs (SEMs) were acquired with a Philips model XL-30 Environmental SEM without any additional coating. Whisker diameter and length were averaged for at least 50 whiskers over 3 images. For ultrasonication of whisker dispersions a Fischer Scientific FS60H ultrasonic bath was employed. For surface resistivity measurements a Keithley 2400 series source measure unit was used in combination with prefabricated copper electrodes, consisting of self-adhesive copper strips fixed onto a microscope slide with spacing of 0.3 cm. For electrical conductivity measurements the samples (film deposited by solution casting onto glass microscopy slides) were pressed against the prefabricated electrode, using a metal clamp. IR spectra were recorded using an ABB Bomen MB series FTIR spectrometer. Freeze-drying was done in a VirTis AdVantage® EL-85 freeze-dryer.

Preparation of PEDOT-coated cellulose whiskers

Isolation of cellulose whiskers. Sulfate-functionalized cellulose whiskers were prepared by sulfuric acid hydrolysis using the general method originally reported by Favier *et al.*^{68–70} and Yuan *et al.*⁷¹ and adapted by us,^{50,52,53} but with minor modifications. After gutting the tunicates of the species *Styela clava* harvested from floating docks at Snug Harbor (Jerusalem, RI), the incrustations on the tunicates' outer walls were removed by heating in aqueous potassium hydroxide (3 L, 5% w/w per 500 g of tunicate walls, $80 \text{ }^\circ\text{C}$, 24 h), followed by mechanical agitation, scrubbing, and two more treatments with aqueous potassium hydroxide (3 L, 5% w/w, $80 \text{ }^\circ\text{C}$, 24 h). After washing with water to pH 7, water (3 L), acetic acid (5 mL), and sodium hypochlorite solution (>4% chlorine, 10 mL) were added, and the temperature was raised to $60 \text{ }^\circ\text{C}$. In 1 h intervals, additional portions of acetic acid (5 mL) and sodium hypochlorite solution (>4% chlorine, 10 mL) were added until the material's color changed from pinkish to pure white. Finally, the bleached de-proteinized walls were washed with deionized water and disintegrated with a blender, yielding a fine cellulose pulp. To a cooled suspension of tunicate cellulose pulp in deionized water (300 mL , $0 \text{ }^\circ\text{C}$, 10 g L^{-1}), sulfuric acid (98%, 300 mL) was slowly added over 30 min while stirring. Subsequently, the dispersion was heated to $60 \text{ }^\circ\text{C}$ and kept at that temperature for 60 min under continued stirring. 500 mL of cold water were then added and the suspension was filtered over a small-pore fritted glass filter. Approximately 2 L of deionized water was passed through until neutrality was reached. Finally, the whiskers were re-dispersed in deionized

water (500 mL) by sonicating for 4 h to produce a whisker dispersion of a concentration of 5 g L^{-1} .

Synthesis of PEDOT:PSS-coated cellulose whiskers. Sodium persulfate (0.400 g, 1.68 mmol), poly(4-styrenesulfonic acid) (0.090 g, 0.45 mmol), 3,4-ethylenedioxythiophene (EDOT, 0.200 g, 1.41 mmol), cellulose whiskers (0.100 g), and water (50.0 mL) were combined and the mixture was stirred at room temperature for 10 min. Iron(III) chloride (1.0 mg, 0.006 mmol) was added to the reaction mixture, which was subsequently stirred at room temperature for another 16 h. The resulting dispersion was centrifuged, the supernatant solution was decanted, the residue was washed with a 1 : 1 water–methanol mixture and the dispersion was again centrifuged. This procedure was repeated twice; in the final step water was employed instead of a water–methanol mixture. The resulting dark blue, wet paste was re-dispersed in either water (20 mL) or DMF (30 mL) by ultrasonication for 2 h. The volume of the DMF dispersion was subsequently reduced to 20 mL under vacuum to remove the remaining water. The concentrations of both aqueous and DMF dispersions (approx. $1\text{--}5 \text{ mg mL}^{-1}$) were determined by solution-casting a known volume of the dispersion, drying and weighing the resulting film.

The above procedure for a EDOT : whisker ratio of 2 : 1 w/w was adapted to EDOT/whisker ratios of between 0.25 : 1 and 1 : 9 w/w by appropriately adjusting the amount of EDOT, sodium persulfate, and iron(III) chloride, while the amounts of cellulose whiskers and water were kept unchanged.

Synthesis of PEDOT:TS-coated cellulose whiskers. Iron(III) *p*-toluenesulfonate hexahydrate (1.20 g, 1.80 mmol), cellulose whiskers (0.060 g), EDOT (0.120 g, 0.79 mmol), methanol (60 mL), and water (60 mL) were combined in one flask. The reaction mixture was then stirred for 16 h at 60°C . The resulting dispersion was centrifuged, the supernatant solution was decanted, the residue was washed with methanol, and the dispersion was again centrifuged. This procedure was repeated twice; in the final step water was employed instead of methanol. The resulting wet paste was re-dispersed in water (20 mL) by ultrasonication for 4 h. The concentration (approx. $1\text{--}5 \text{ mg mL}^{-1}$) of the dispersion was obtained by solution casting a known volume and weighing the resulting film.

The above procedure was adapted to a lower methanol concentration with all the same reactants but at different concentrations with a slightly different protocol. Iron(III) *p*-toluenesulfonate hexahydrate (0.60 g, 0.90 mmol), cellulose whiskers (0.025 g), and water (50.0 mL) were combined in one flask. EDOT (0.050 g, 0.33 mmol) was dissolved in a small amount of methanol ($\sim 1 \text{ mL}$) and the mixture was added to the reaction flask; the reaction mixture was then stirred for 16 h at 60°C . The resulting dispersion was centrifuged, the supernatant solution was decanted, the residue was washed with methanol, and the dispersion was again centrifuged. This procedure was repeated twice; in the final step water was employed instead of methanol. The resulting wet paste was re-dispersed in water (20 mL) by ultrasonication for 4 h. The concentration (approx. $1\text{--}5 \text{ mg mL}^{-1}$) of the dispersion was obtained by solution casting a known volume and weighing the resulting film. The overall concentration of the reaction was also varied by changing the amount of methanol from 10 mL to 100 mL.

Both above procedures for an EDOT/whisker ratio of 2 : 1 w/w were adapted to EDOT/whisker ratios of between 0.5 : 1 and 4 : 1 w/w by appropriately adjusting the amount of EDOT and iron(III) *p*-toluenesulfonate hexahydrate, while the amounts of cellulose whiskers and water were kept unchanged.

Preparation of PEDOT:PSS-coated cellulose whisker gels. These gels were produced by adapting a solvent-exchange procedure described previously.⁵³ Dispersions of PEDOT:PSS-coated cellulose whiskers (EDOT : whisker ratio of 2 : 1 w/w) in DMF (0.6–1.0% w/w) were prepared by diluting stock dispersions and sonicating for an additional 10 min in 20 mL glass vials. Acetone was then carefully added to the vials with care being taken not to disturb the surface of the whisker layer. The top layer of acetone was exchanged twice a day for three days against fresh acetone. After this time the excess solvent was decanted off and the gel that had formed was released from the vial.

Preparation of PEDOT:PSS-coated cellulose whisker aerogels. These aerogels were produced by adapting a freeze drying method described in detail elsewhere.⁷² PEDOT:PSS-coated whiskers (EDOT : whisker ratio of 2 : 1 w/w) dispersed in water (0.6% w/w) were placed into PET or glass vials and the dispersions were frozen in a dry ice/ethanol bath. The samples were then freeze dried using a VirTis AdVantage EL-85 lyophilizer with an initial shelf temperature of -10°C , condenser temperature of -87°C and eventual vacuum of $<10 \mu\text{bar}$. The sample tray was placed on the shelf and the vacuum was turned on and allowed to reach 1 mbar before the shelf began heating to 25°C . Samples were left in the lyophilizer for 4 days to ensure complete drying; they were subsequently stored in a desiccator.

Preparation of PEDOT:PSS-coated cellulose whisker polymer nanocomposites. Nanocomposites with poly(ethylene oxide) were produced by dissolving the polymer in water at a concentration of 20 mg mL^{-1} . Between 0.02 and 0.4 mL of an aqueous dispersion of PEDOT:PSS-coated cellulose whiskers (5 mg mL^{-1} , EDOT/whisker ratio of 2 : 1 w/w) were added to 1 mL of the polymer solution under vigorous mixing. The resulting mixture was then ultrasonicated for 10 min. before being cast onto a glass slide in several 1 mL portions. The films were allowed to dry at ambient temperature for approximately 3 h. After this time, copper strips (with 0.3 cm spacing) were thermally evaporated onto the films (greater than $5 \mu\text{m}$) to serve as contact points for resistivity measurements.

Polystyrene nanocomposites were made in a similar fashion. Polystyrene was dissolved in dimethylformamide (DMF) at a concentration of 20 mg mL^{-1} . Between 0.02 and 0.4 mL of a dispersion of PEDOT:PSS-coated cellulose whiskers (5 mg mL^{-1} , EDOT : whisker ratio of 2 : 1 w/w) were added to 1 mL of the polymer solution under vigorous mixing. The resulting mixture was then ultrasonicated for 10 min. before being cast onto a glass slide in several 1 mL portions. The films were allowed to dry at ambient temperature for approximately 5 h. After this time, copper strips (with 0.3 cm spacing) were thermally evaporated onto the films (greater than $5 \mu\text{m}$) to serve as contact points for resistivity measurements.

The volume fraction of PEDOT-coated whiskers in these nanocomposites was calculated from the weight fraction, the

densities of the neat polymers (poly(ethylene oxide): 1.13 g cm⁻³, polystyrene: 1.05 g cm⁻³), and the density of the PEDOT-coated cellulose whiskers (1.29 g cm⁻³), which was estimated from the density of crystalline cellulose (1.58 g cm⁻³) and PEDOT (1.0 g cm⁻³).

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