# Oxidative Chemical Vapor Deposition of Electrically Conducting Poly(3,4-ethylenedioxythiophene) Films

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ABSTRACT: An oxidative chemical vapor deposition (CVD) process is presented as an alternative to conventional solution-based processing of poly(3,4-ethylenedioxythiophene) (PEDOT) thin films. This solventless technique yields PEDOT with higher conductivities and conformally coats fibers and other high area morphologies, important for enhancing efficiencies in some organic electronic devices. The CVD method eliminates corrosive poly(styrenesulfonate) that is used to disperse PEDOT in an aqueous suspension for solution-based processing. A mechanistic approach is presented that favors the deposition of the conjugated, conducting form of PEDOT. We achieved conductivities as high as 105 S/cm and demonstrated films about 100 nm thick that do not crack upon bending and are more than 84% transparent to visible light. The compatibility of oxidative CVD deposition of PEDOT is demonstrated on silicon, glass, plastic, and paper substrates.

## Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a conducting polymer widely used in organic electronics, including light-emitting diodes (OLEDs)[1] and photovoltaics,[2] owing to its exceptional stability, transparency, and electrical conductivity.[3,4] As a hole injection layer, PEDOT facilitates charge transfer between the anode and organic optoelectronic materials, extending device lifetimes and improving operating efficiencies.[5] However, the conjugated bond structure in PEDOT leads to a rigid conformation, necessary for maintaining electron orbital overlap along the backbone, that favors crystallization and prevents the material from easily dissolving or melting. As a result, PEDOT has good chemical and thermal stability but is difficult to process into thin-film form.[6] Electropolymerization of EDOT monomer can produce free-standing PEDOT films and coatings on electrode materials. Typical conductivities are around 300 S/cm.[7] Chemical oxidative polymerization of EDOT in a solution containing oxidants like Fe(III)$Cl_3$ or Fe(III) *p*-toluenesulfonate (Fe(III) tosylate) yields PEDOT with similar conductivities. Polymerized films form as solvent evaporates from the reaction mixture cast onto a surface or deposit onto substrates that are immersed in the reaction mixture.[8,9]

Bayer circumvented the insolubility of PEDOT with the use of a water-soluble polyanion, poly(styrenesulfonate) (PSS), to stabilize PEDOT dispersion in water.[10] The aqueous PEDOT:PSS system has a good shelf life and can be spin-coated to form a film, making it the current commercial standard. However, acidic PSS is a likely source of corrosion and device degradation.[11,12] PSS also forms a nonconducting shell around PEDOT aggregates, which affects the electrical properties of the film interfaces[13] and reduces the maximum overall film conductivity to about 10 S/cm. Wet processing techniques also depend on the ability of the solution to wet different materials, and some substrates, like fabric or paper, are incompatible with the required liquid solutions.

We set out to develop a robust vapor-deposition technique for PEDOT films. A solventless method simplifies the coating process on a variety of organic and inorganic materials since it does not depend on evenly wetting the substrate surface. Vapor-phase processing also enables conformal coatings on high-area-surface morphologies, like fibers and pores, important for higher device efficiencies.[14] Past work has shown that plasma CVD of PEDOT fails to maintain sufficient bond conjugation for conductivities higher than about $10^{-3}$ S/cm.[15] Recent experiments have achieved PEDOT films by exposing oxidant-enriched substrates to EDOT vapors that polymerize on the surface.[16−18] The substrates are prepared by coating them with solutions of Fe(III) tosylate and allowing them to dry. Reported conductivities exceed 1000 S/cm. We propose an oxidative CVD technique for the deposition of PEDOT films that, in addition to eliminating the need for PSS, requires no liquid-based pretreatment steps. We used a mechanistic approach that promotes the formation of conducting PEDOT and inhibits unwanted side reactions.

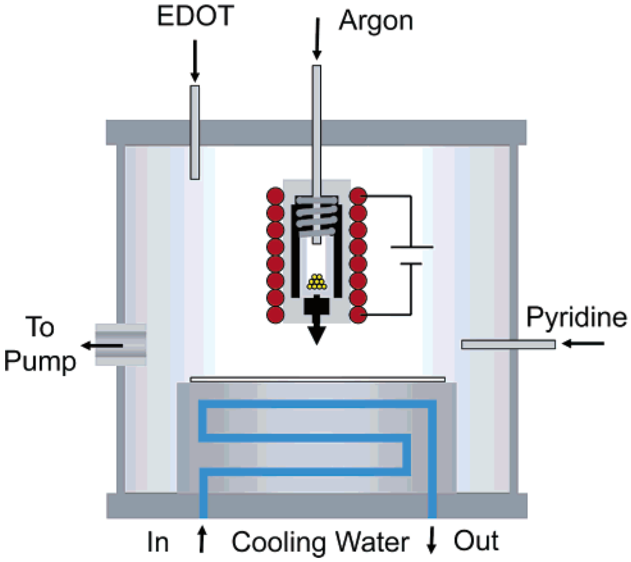

**Figure 1.** Schematic of CVD reactor for depositing electrically conducting PEDOT films. Fe(III)$Cl_3$ is sublimed in a heated crucible above a temperature-controlled stage. The oxidant reacts with adsorbed monomer, introduced as a vapor along with pyridine.

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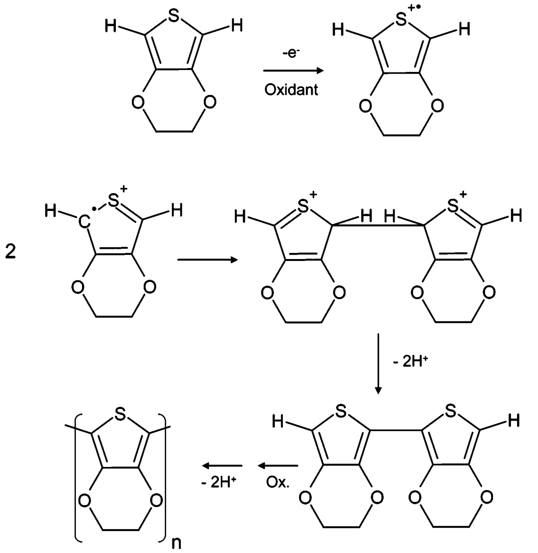

**Figure 2.** The Diaz mechanism is a series of oxidation and deprotonation steps leading to the oxidative polymerization of conjugated PEDOT.

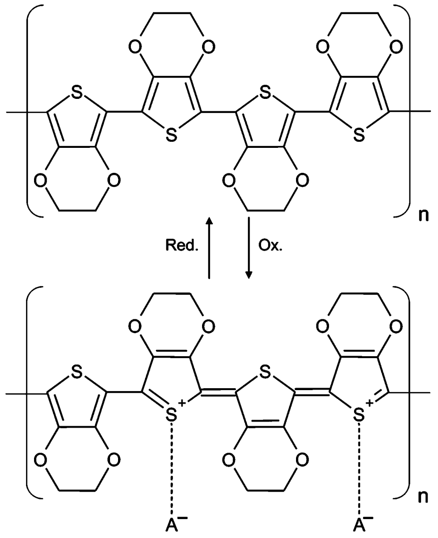

**Figure 3.** Neutral PEDOT is oxidized to form a conducting polycation that is charge balanced with dopant anions (A$^-$).

## Materials and Methods

PEDOT depositions were carried out in a custom-built vacuum chamber that has been described elsewhere[19] and is depicted in Figure 2. Glass slides, silicon wafers, poly(ethylene terephthalate) (PET), and paper were used for substrates. The stage was controlled at 34, 85, or 110 °C, and the chamber pressure was held constant at 300 mTorr. Fe(III)Cl$_3$ (97%, Aldrich) was sublimed at 240 °C in a porous crucible positioned above the stage. Argon was passed through the crucible at 2 sccm as a carrier gas. EDOT (Aldrich) was introduced into the reactor at 10 sccm. A deposition time of 30 min was used for all films. The films were dried in a vacuum oven at a gauge pressure of −15 mmHg heated to 80 °C to remove unreacted monomer. Dried films on glass, silicon, and PET were rinsed in methanol for 5 min to remove additional byproducts including spent oxidant. Films on paper substrates were unrinsed. A reference PEDOT film was made using a Bayer formula for the direct oxidation of BAYTRON M, the EDOT monomer, with BAYTRON CB-40, a 40% mixture of Fe(III) tosylate in butanol. After spin-coating, the film was dried and rinsed using the same conditions as the CVD samples.

A Tencor P-10 profilometer was used to measure film thickness. Conductivity measurements of PEDOT films on glass were done with a four-point probe (model MWP-6, Jandel Engineering, Ltd.). FTIR spectra (Nexus 870, Thermo Electron Corp.) of PEDOT films on silicon were collected for information on chemical composition. A Cary 6000i UV−vis−NIR spectrophotometer was used to characterize the optical transmission of PEDOT coatings on glass and PET.

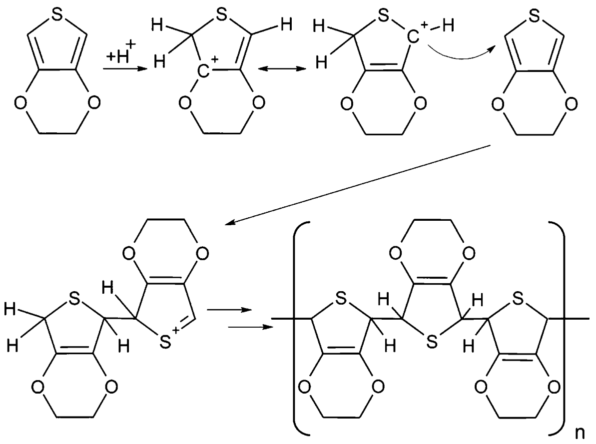

**Figure 4.** Acid-initiated coupling promotes chain growth but yields an unconjugated form of PEDOT that is not conductive without subsequent oxidation.

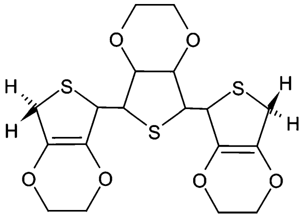

**Figure 5.** A strongly acidic reaction environment forms trimers with broken conjugation.

## Results and Discussion

The oxidation of EDOT to form PEDOT is analogous to the oxidative polymerization of pyrrole, which has been described with a mechanism proposed by Diaz[20,21] and is shown in Figure 2. The first step is the oxidation of the monomer, which generates a radical cation that has several resonance forms. The combination of two of these radicals and subsequent deprotonation form a neutral dimer. Substitution of the EDOT thiophene ring at the 3,4-positions blocks $\beta$-coupling, allowing new bonds only at the 2,5-positions. The dimer can be oxidized to form another positively charged radical that repeats the coupling and deprotonation steps with other monomeric or oligomeric cations. The alternating single and double bonds of the oligomers are $\pi$-conjugated, which delocalizes the electrons and decreases the oxidation potential. Therefore, oligomers are more easily oxidized than the monomer and chains grow faster than new ones are created. The neutral PEDOT polymer is further oxidized to create a positive charge along the backbone every three or four chain segments. A “dopant” anion binds to the polymer and balances the charge. The oxidized form of PEDOT, shown in Figure 3, is the conducting form of the polymer.

The oxidation strength of the oxidant is an important factor to consider when specifying the PEDOT polymerization reaction conditions. It must be high enough to drive the reaction, but low enough to avoid unwanted bond cleavage in the monomer, which leads to imperfections that disrupt conjugation and reduce conductivity.[18] A strong oxidant can be moderated by introducing a base, such as pyridine, into the reaction environment.[17,22] More acidic conditions can support higher polymerization rates

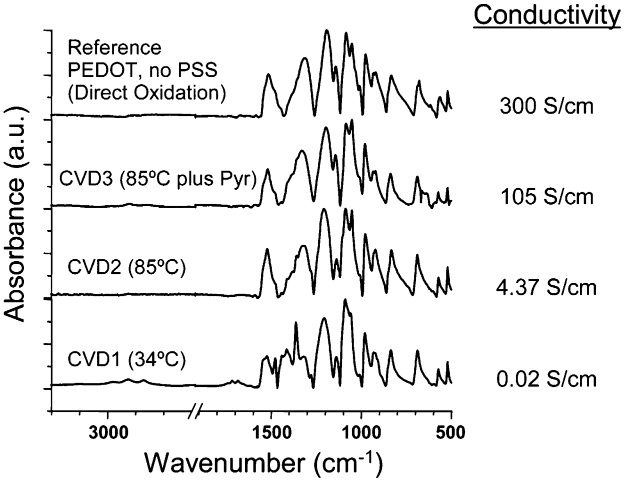

**Figure 6.** FTIR spectrum and conductivity of a solution-based reference PEDOT film (not containing poly(styrenesulfonate)) are compared to CVD PEDOT. The best CVD film was prepared on a heated stage with pyridine as a base inhibitor.

for PEDOT, although partially through an acid-initiated coupling reaction, shown in Figure 4.[20] PEDOT grown in this way is not conjugated without a postprocessing step to oxidize and deprotonate the formed chains. Very high acidity can saturate the 3,4-positions of EDOT radicals, yielding unconjugated trimers, shown in Figure 5.[20,23] Base-inhibited polymerization using pyridine has yielded conjugated PEDOT films with conductivities reported to be higher than 1000 S/cm.[17]

Our experiments combine this learning to optimize the conductivity of PEDOT films deposited with an oxidative CVD process. We selected Fe(III)Cl$_3$ as the oxidant for its relatively high vapor pressure. Fe(III) tosylate was attempted as well, but no conductive films resulted. We suspect that the temperatures necessary for the sublimation of Fe(III) tosylate, exceeding 300 °C, pyrolize the organic ligands of the oxidant. Figure 6 compares conductivity values and FTIR spectra for a succession of CVD PEDOT films. The top spectrum corresponds to a reference film produced by direct oxidation of liquid reagents in the absence of PSS. The CVD PEDOT films had measured conductivity values between $10^{-2}$ and $10^{2}$ S/cm. The CVD1 film (460 nm thick), deposited onto a substrate at 34 °C, exhibits a small carbonyl peak at 1700 cm$^{-1}$, indicating monomer damage resulting from acidic reaction conditions. The CVD2 film (146 nm thick) was deposited at a higher substrate temperature (85 °C) in an effort to reduce acidity by more quickly evaporating HCl as it is generated during deprotonation steps of the PEDOT polymerization reaction in the presence of Cl$^-$ ions from the oxidant. The carbonyl stretch was eliminated, and the film conductivity increased by 2 orders of magnitude. Doping-induced effects in conducting polymers, characterized by broad absorption peaks between 1450 and 700 cm$^{-1}$, indicate better conjugation in the CVD2 film relative to CVD1.[24] Introducing pyridine vapors into the chamber at 2 sccm during the deposition of film CVD3 (86 nm thick), using a stage temperature of 85 °C, resulted in our highest film conductivity of 105 S/cm. We suspect that pyridine neutralizes the HCl as it is generated and blocks the acid-initiated coupling reaction, decreasing the yield of unconjugated PEDOT. Most of the FTIR spectral characteristics of the PEDOT material made by direct oxidation are visible in the CVD3 film. The CVD films have a slightly more distinct shoulder at 1400 cm$^{-1}$. The broad peak overlapping this shoulder is at a higher wavenumber for the CVD films, suggesting a higher prevalence of 3-substituted thiophene moieties.[25] Fewer 2-substituted species may indicate shorter polymer chains.

CVD PEDOT was deposited onto a piece of heavy duty paper towel, using a stage temperature of 85 °C, and poly(ethylene terephthalate) (PET) at 110 °C to demonstrate the method's compatibility with a variety of substrate materials. A multimeter shows the coated paper surface to be conducting, although the conductivity was not quantified because of the difficulty of measuring film thickness and surface area on a fibrous mat. An SEM image of the paper towel fibers (Figure 7) before (a) and after (b) deposition demonstrates the ability of CVD to densely coat PEDOT onto microscale features.

A CVD PEDOT coating on PET (35 nm thick, 25 S/cm) was 84% transmissive to visible light between 400 and 700 nm (Figure 7c). After repeated bending, no visible cracking or decrease in film conductivity was apparent. A separate coating on PET (85°, 130 nm thick) had a conductivity of only 0.15

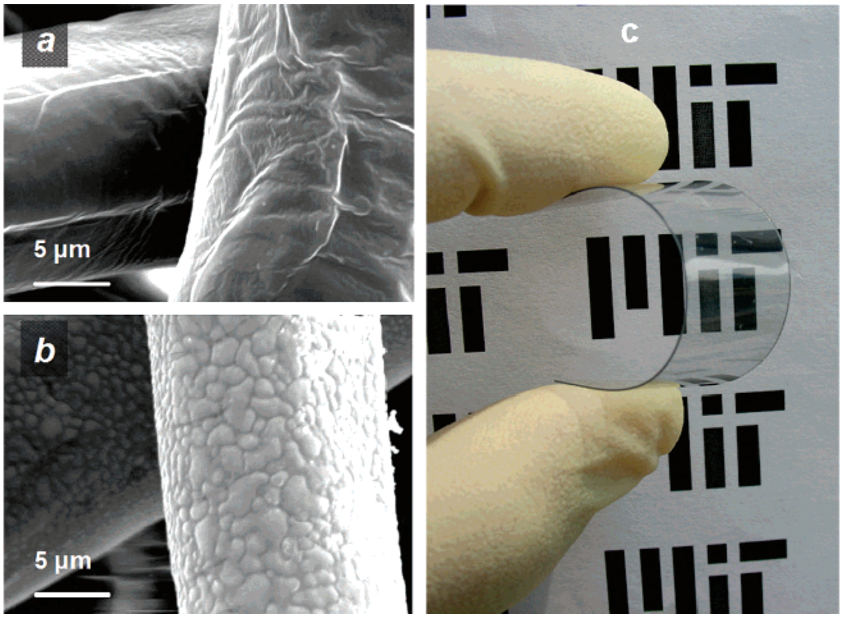

**Figure 7.** (a) SEM image of an uncoated paper towel fiber. (b) SEM image of a paper towel fiber coated with CVD PEDOT. (c) CVD PEDOT coating with 84% optical transmittance on flexible PET.

S/cm, but a transmittance of 89%, approaching the 90% transmittance of indium tin oxide (ITO) optimized for transparent applications.[26] Experiments are underway to optimize the conductivity and transmittance of CVD PEDOT and to quantify the mechanical and electrical integrity of films on flexible substrates after many bending cycles.

## Conclusion

PEDOT hole-injection layers have already advanced the efficiency of organic semiconductor devices, and eliminating the nonconducting and corrosive PSS matrix necessary for solution-based processing should further improve performance and extend device lifetimes. CVD PEDOT films show good optical transmittance, conductivity, and stability. The vapor phase technique maintains high substrate surface areas by conformally coating complex morphologies, like fibers or pores, which we suspect can lead to even higher device operating efficiencies. The solventless process operates at temperatures compatible with paper, plastic, and other flexible substrates. We expect this CVD approach to be extendable to other oxidatively polymerized conducting polymers like polypyrrole and polyaniline because of the similarity of their growth mechanisms. Oxidative CVD expands the toolset available for the low-cost production of organic devices including displays, solid-state lighting, and solar cells.

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