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COMMUNICATION

Oxidative Atomized Spray Deposition of Electrically Conductive Poly(3,4-Ethylenedioxythiophene)

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Atomized spray deposition of 3,4-ethylenedioxythiophene monomer in the presence of triflic anhydride vapour yields electrically conducting poly(3,4-ethylenedioxythiophene) layers.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is an intrinsically conducting polymer which has found application in dye-sensitized solar cells,^{1,2,3} supercapacitors,⁴ light emitting diodes,⁵ thin film transistors,⁶ oxygen reduction catalysts,⁷ photodetectors,⁸ molecular wires,⁹ memory storage,¹⁰ and antistatic coatings.¹¹ Previous methods for the synthesis of PEDOT coatings have entailed photoelectrochemical deposition,^{1,2} electropolymerization,^{12,13,14} oxidative polymerization,^{15,16} oxidative chemical vapour deposition,^{17,18,19} vapour-phase polymerization,^{7,20} emulsion polymerization,^{21,22} and suspension polymerization.²³ However, these approaches suffer from drawbacks such as the requirement for solvents,¹⁵ removal of byproducts,⁷ conducting substrates,^{1,2} or elevated temperatures.^{18,24}

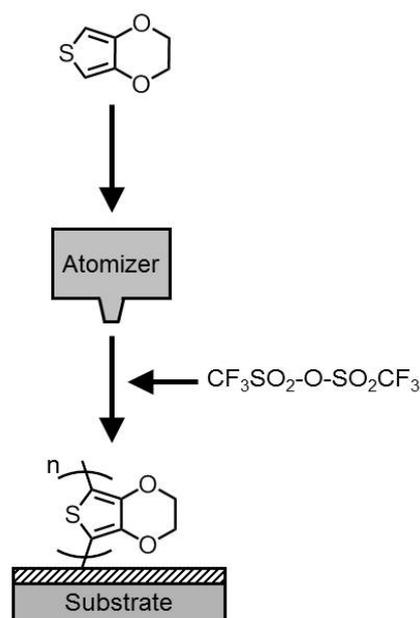
In this article we describe the use of an atomized EDOT precursor spray in the presence of an oxidant vapour (e.g. triflic anhydride) for the high rate deposition of PEDOT layers (oxidative atomized spray deposition), Scheme 1. Oxidation of the EDOT monomer leads to polymerization, whilst triflic anhydride reduction produces triflic and triflinic acid.²⁵

$$2\text{EDOT} + (\text{CF}_3\text{SO}_2)_2\text{O} \rightarrow \text{EDOT-EDOT} + \text{CF}_3\text{SO}_2\text{H} + \text{CF}_3\text{SO}_3\text{H}$$

By carrying out the deposition under sub-atmospheric pressure, the triflic and triflinic acid byproducts are readily pumped away into a cryogenic trap, thereby avoiding acid-induced damage to the growing polymer chains. Akin to other oxidative polymerization mechanisms for EDOT, partial doping happens by remaining oxidant (triflate) anions.^{7,18,24} In contrast to the majority of previously reported vapour-phase deposition processes, which require a separate solvent-based washing step to remove unwanted byproducts,⁷ this method is completely dry. Furthermore, it circumvents the high temperatures necessary for EDOT monomer vaporisation, since the precursor is being introduced as an atomized spray.²⁴

Deposition of PEDOT films entailed using an ultrasonic nozzle to deliver a fine spray of EDOT monomer into an inverted T-shape reactor chamber (base pressure of 3×10^{-3} mbar, ESI: Figure S1). Triflic anhydride vapour was concurrently introduced at a pressure of 6 mbar. After deposition, the reactor was vented to atmosphere. Silicon (100) wafer substrates were used for X-ray

photoelectron spectroscopy (XPS) and FTIR characterization and



Scheme 1 Oxidative atomized spray deposition of PEDOT layers using EDOT precursor in the presence of triflic anhydride vapour.

polypropylene substrates for conductivity measurements.

XPS characterization showed an absence of any Si(2p) signal, thereby confirming pinhole-free coverage of the substrates following the atomized spray deposition of PEDOT in the presence of triflic anhydride vapour, Table 1. The S(2p) spectrum contains two components corresponding to the thiophene ring C-S (163.7 eV)²⁶ and triflate O-SO₂CF₃ (168.3 eV),²⁷ Figure 1. The measured ratio of the respective S(2p) component peaks corresponds to approximately one dopant triflate or triflinate ion to every three EDOT monomer units. This ratio is consistent with the value of 1.0:2.7 calculated by using the F(1s) peak area as a proportion of the elemental XPS concentrations as compared to the theoretical (non-doped) EDOT polymer, Table 1.

The infrared spectrum of the EDOT precursor exhibits the following characteristic absorbances:^{28,29} =C-H ring stretch (3107 cm^{-1}), antisymmetric CH₂ stretch (2919 cm^{-1}), symmetric CH₂ stretch (2869 cm^{-1}), C=C aromatic out of phase stretch (1479 cm^{-1}), C=C aromatic in phase stretch (1444 cm^{-1}), and C-C

deformation (1369 cm^{-1}), Figure 2. Following the atomized spray

Table 1 XPS elemental ratios of oxidative atomized spray deposited PEDOT in the presence of triflic anhydride vapour.

Layer	%C	%O	%S	%F
Theoretical PEDOT	67	22	11	—
Atomized spray deposited PEDOT-triflic anhydride	54±1	24±1	11±1	11±1

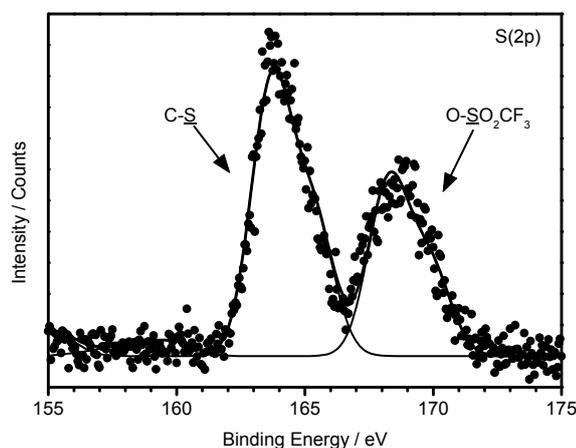


Fig. 1 X-ray photoelectron S(2p) spectrum of oxidative atomized spray deposition of PEDOT layers using EDOT precursor in the presence of triflic anhydride vapour.

deposition of the poly(3,4-ethylenedioxythiophene)-triflic anhydride coating, the =C-H ring stretch is absent (which is consistent with polymerization having taken place via the 2-position on the thiophene ring), whilst the CH_2 stretches confirm retention of the ethylenedioxy substituent. A broadening of the fingerprint region aromatic vibration peaks is consistent with a doped conjugated polymer system.³⁰ Also there are new absorbances attributable to the dopant triflate: SO_3 symmetric stretch (1083 cm^{-1} , denoted A) and CF_3 symmetric stretch (762 cm^{-1} , denoted B).³¹

Deposition rates of $2.9\pm 0.4\text{ }\mu\text{m min}^{-1}$ and film thicknesses between $50\text{ nm} - 10\text{ }\mu\text{m}$ were obtained for the oxidative atomized spray deposition of PEDOT-triflic anhydride films. For film thicknesses of $5.8\pm 0.8\text{ }\mu\text{m}$, atomic force microscopy (AFM) indicated that the films were smooth (RMS roughness = $12\pm 2\text{ nm}$) and black in colour (visible light absorption is high). Electrical measurements yielded a conductivity value of 0.9 S cm^{-1} and an Ohmic response across the $0-30\text{ V}$ range.

Conventional vapour-phase polymerizations of EDOT have required oxidants such as iron(III) chloride or iron(III) tosylate to be placed onto the substrate beforehand, which means an additional washing step is required in order to remove unwanted iron(II) salt byproduct from the deposited PEDOT layer.^{7,18} For cases where bromine vapour is employed as the oxidant (which alleviates the need for a subsequent washing step) there still remains the drawback of heating the EDOT monomer because of its low vapour pressure at room temperature.²⁴ In contrast, the outlined oxidative atomized spray deposition approach circumvents the need for post-deposition washing (since the triflic acid or triflinic acid byproducts are pumped off), and it is

not necessary to heat the EDOT precursor because it is being introduced in the form of a fine mist of droplets into the reactor at ambient temperatures. The electrical conductivity of the deposited PEDOT-triflic anhydride films reaches a value of 0.9 S

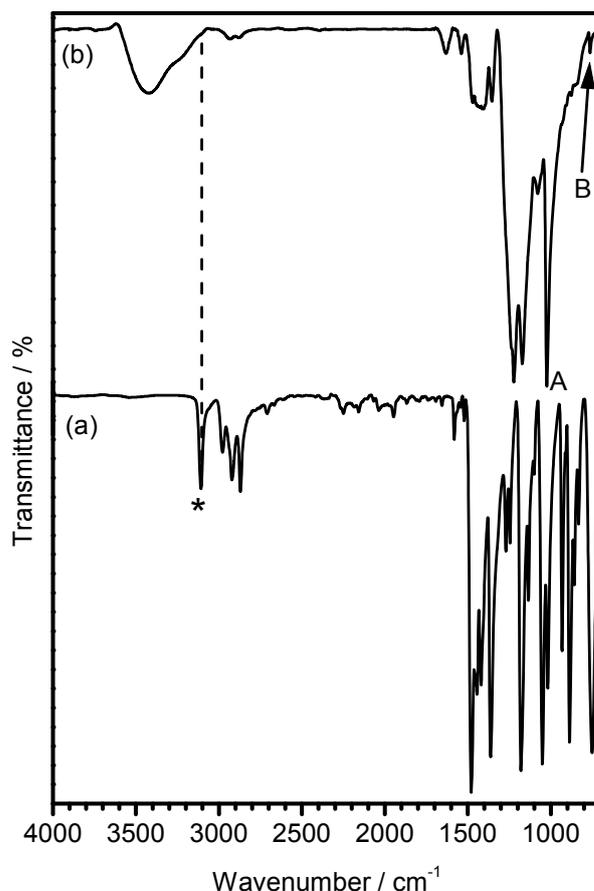


Fig. 2 Infrared spectra of: (a) EDOT monomer; and (b) oxidative atomized spray deposition of PEDOT layers using EDOT precursor in the presence of triflic anhydride vapour. * Denotes =C-H ring stretch; A denotes SO_3 symmetric stretch; and B denotes CF_3 symmetric stretch.

cm^{-1} , which is sufficient for applications such as antistatic coatings,^{32,33} or electrochemical devices (e.g. capacitor electrodes).³⁴ It is envisaged that this oxidative atomized spray deposition approach can be easily miniaturised using inkjet heads or scaled up using roll-to-roll processing to provide high throughput, conformal, electrically conductive coatings. The electrical conductivity measured for the oxidative atomised spray deposition PEDOT layers is comparable to the maximum conductivity of 1 S cm^{-1} reported for the most common industrial version of PEDOT comprising a PEDOT/poly(4-styrenesulfonate) mixture which has the inherent disadvantage of requiring wet chemical processing steps.³⁴

Atomization of 3,4-ethylenedioxythiophene monomer in the presence of triflic anhydride vapour gives rise to the formation of electrically conducting poly(3,4-ethylenedioxythiophene) layers. Key attributes include a single step process, the absence of solvents, ambient temperature, no requirement for conducting substrates, and fast deposition rates.

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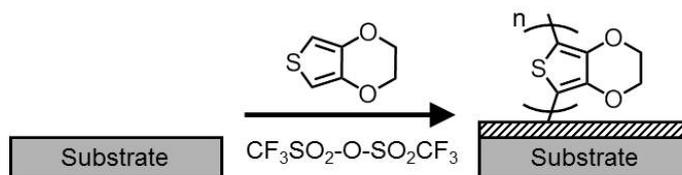
5 Notes and references

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