Oxidative Atomized Spray Deposition of Electrically Conductive Poly(3,4-Ethylenedioxythiophene): Electronic Supplementary Information

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1. EXPERIMENTAL

1.1 Oxidative Atomized Spray Deposition of PEDOT Layers

Atomized spray deposition was carried out in an electrodeless, cylindrical, T-shape, glass reactor (volume 820 cm^3, base pressure of 3 x 10^{-3} mbar, and with a leak rate better than 2 x 10^{-9} mol s^{-1}), Figure S1. The atomiser nozzle was mounted perpendicular to the oxidant vapour inlet. The chamber was pumped using a 30 L min^{-1} rotary pump attached to a liquid nitrogen cold trap, and the system pressure was monitored with a Pirani gauge. Prior to each deposition, the reactor was scrubbed with detergent, rinsed in propan-2-ol, and dried in an oven. Substrates used for coating were silicon (100) wafer pieces (Silicon Valley Microelectronics Inc.) and borosilicate glass microscrope slide pieces (Smith Scientific Ltd.), with two evaporated gold surface electrodes. These were placed downstream from the atomizer nozzle (Model No. 8700-120, Sono Tek Corp.). 3,4-Ethylenedioxythiophene (+98%, TCI Europe NV) and triflic anhydride (+99%, Apollo Scientific Ltd.) were loaded into separate sealable glass tubes and degassed using several freeze-pump-thaw cycles. 3,4-Ethylenedioxythiophene precursor was then introduced into the reaction chamber at a flow rate of 0.02 mL s^{-1} by passing through the ultrasonic nozzle operating at 120 kHz, while triflic anhydride vapour was co-fed via a needle valve at a pressure of 6 mbar. Upon completion of deposition, triflic anhydride vapour was allowed to pass through the system for a further 3 min prior to evacuation to base pressure and finally venting to atmosphere.

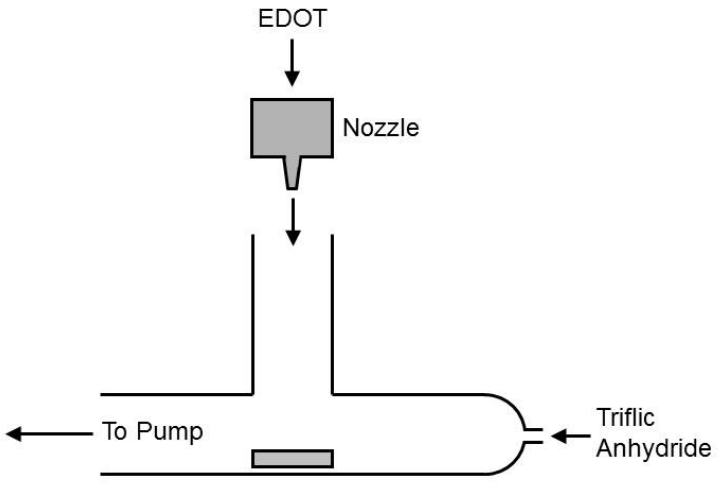

Figure S1. Reactor for oxidative atomized spray deposition of PEDOT layers using EDOT precursor in the presence of triflic anhydride vapour.

1.2 Film Characterization

Surface elemental compositions were determined by X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB II electron spectrometer equipped with a non-monochromated Mg Kα X-ray source (1253.6 eV) and a concentric hemispherical analyser. Photoemitted electrons were collected at a take-off angle of 20° from the substrate normal, with electron detection in the constant analyser energy mode (CAE, pass energy = 20 eV). Experimental instrument sensitivity (multiplication) factors were C(1s): O(1s): S(2p): F(1s) equals 1.00: 0.36: 0.59: 0.24. All binding energies were referenced to the C(1s) hydrocarbon peak at 285.0 eV. A linear background was subtracted from core level spectra and then fitted using Gaussian peak shapes with a constant full-width-half-maximum (fwhm).[1,2]

Infrared spectra were acquired using a FTIR spectrometer (Perkin-Elmer Spectrum One) fitted with a liquid nitrogen cooled MCT detector operating at 4 cm^{-1}

resolution across the 700–4000 cm^{-1} range. Attenuated-total-reflection spectra were obtained using a Golden Gate accessory (Specac Ltd.).

Atomic force microscopy (AFM) images were collected in tapping mode at 20 °C in ambient air (Digital Instruments Nanoscope III, Santa Barbara, CA). The tip had a spring constant of 42–83 Nm^{-1} (Nanoprobe). Root-mean-square (rms) roughness values were calculated over 10 x 10 μm scan areas.

Film thicknesses were measured by freezing coated silicon samples in liquid nitrogen followed by snapping to reveal a cross-section. These were then imaged using an optical microscope (Olympus BX40) fitted with a x20 magnification lens.

Electrical conductivity values were obtained for the films deposited onto glass substrates (which had been precoated with two evaporated gold surface electrodes) by measuring the variation in electrical current across the 0–30 V range (Keithley 2400 SourceMeter), and then calculating the resistance of the films (R_S) from Ohm's law, followed by using the formula $\sigma = l/(R_S A)$ where l = separation of the electrodes, A = the cross-sectional area of the film, and σ = the conductivity of the film. Across-plane rather than film top-to-bottom resistance was measured because the thinness of the latter makes it susceptible to errors from electrode/wire resistances. Given that the deposited films are homogeneous in nature, the across plane and through-thickness resistivity values are expected to be the same.

2. REFERENCES

(1) Friedman, R. M.; Hudis, J.; Perlman, M. L. *Phys. Rev. Lett.* **1972**, *29*, 692.

(2) Evans, J. F.; Gibson, J. H.; Moulder, J. F.; Hammond, J. S.; Goretzki, H. *Fresenius J. Anal. Chem.* **1984**, *841*, 319.