Supporting information

New Junction materials by the direct growth of ZnO NWs on Organic Semiconductors

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Raman spectra were obtained using Invia Renishaw Raman spectrometer with an excitation wavelength of 676nm red laser. 2-D PES shows a lot of fluorescence, whereas PEDOT-2D PES gave clear raman peaks for VPP PEDOT as reported in the literature [1]. Bare PES is mostly raman inactive except the C-H stretching frequency around 1020 and 1600 cm⁻¹ with high fluorescence, whereas PEDOT functionalised PES has got various aromatic stretching peaks such as C=C (1422, 1529cm⁻¹), C-C (1254, cm⁻¹), C-H (858 cm⁻¹) and C-S-C (699 cm⁻¹).



Figure S1: Raman spectra of 2-D PES and PEDOT functionalised 2-D PES

PEDOT functionalised 2-D PES and 3-D PES has been further characterised for its morphology using scanning Electron microscopy (SEM) using a JEOL FEG -7001 and NOVA microscope. Uniform thin film of PEDOT has formed on 2-D PES and 3-D PES.





ZnO NWs are grown using a seed mediated growth technique. A seed solution has been prepared by mixing 0.03 M NaOH and 0.01 M Zn(CH₃COO)₂.2 H₂O in methanol at 60° C. Seed solution has spin coated onto PEDOT-2D-PES and dip coated on 3D-PES.Vertically oriented ZnO NWS are obtained on 2-D PES with multiple coating and followed by annealing at 100°C. The NW growth has been conducted in an eqimolar (0.025M) hexamethyltetramine and zinc nitrate hexahydrate at 90°C for 6 hrs. SEM shows highly uniform and oriented nanowires has been obtained on 2D and 3-D PEDOT substrates. EDX has done to confirm ZnO NWs.





Figure S3: Low magnification SEM image for surface coverage and corresponding EDX confirming ZnO

Transition electron microscopy is used to further characterise the ZnO NWs. Technai T-20 microscope with 200KV operating voltage has been used. Wurtzite structured nanowire with (0001) crystal growth direction has found. The d spacing 0.259nm for (0001) plane is observed.



Figure S4: (a) Low resolution TEM image of ZnO NW $\,$ (b) High resolution TEM image d spacing 0.259nm $\,$



Figure S5: (a) Diffraction pattern of ZnO NW

(b) SAED pattern of ZnO NW



Figure S6: SEM images of CuO Nanowalls grown on PEDOT coated (a) 2D-PES (b) 3D-PES

For I-V curves all the electrodes has been realised on glass substrates. PEDOT/Au has been coated, and then ZnO NWs has grown through solution route. And all the measurement has been done inside the faraday cage.



Figure S7: I-V curves for (a) ITO+ZnO-ITO (b) PBTh+ZnO-Au



Figure S8: I-V curves for (a) PBTh+ZnO-PBTh (b) PEDOT+CuO-Au

The resistance measurements were conducted using a Jandal four point probe. The thickness of the film is measured using a profilometer (DEKTAK 150)

VPP PEDOT film sheet resistance 37Ω /square, thickness 381.5nm: Conductivity = 708 S cm⁻¹ AT VPP PEDOT film sheet resistance 8584Ω /square, thickness 318 nm: Conductivity = 3.66 S cm⁻¹

Relation between conductivity and doping level in PEDOT

Introduction

In the doped state, the conjugated polymer poly-3,4-ethylene-dioxythiophene (PEDOT) is an exceptionally stable organic electronic conductor that can attain very high conductivities (>1000 S/cm) when it is properly prepared [1]. This polymer is particularly well suited for use in (polymer) micro fluidic systems, where corrosion resistance, mechanical compliance, and the propensity for patterning under non-vacuum, ambient temperature conditions are important parameters.

A unique property of conjugated polymers is their ability to be switched between a conducting (oxidised) state and a semi-conducting (neutral) state. The electronic conductivity of the polymer may change orders of magnitude during this switching. In application where changes in the redox state of the conjugated polymer may occur either because it is an integral part of the function of these devices (as in electrochromics or in polymer actuators) or because the electrochemical potential of the polymer may be subject to changes (as in certain types of sensors or in electro osmotic pumps), it is essential to be able to predict the changes in conductivity associated with these changes. Especially in situations where reduction is intended to proceed at a voltage below the reduction potential of dissolved oxygen, critical design issues may occur [2].

Here the electronic conductivity of highly conducting PEDOT is determined as function of the oxidation state of the polymer. The PEDOT tested was prepared *in situ* using pyridine as acidity regulating agent – the type of PEDOT known to give very high conductivities. Both as prepared PEDOT and PEDOT that has been subjected to the additional chemical processes involved in lithographical micro patterning was tested.

Experimental

Simultaneous measurement of electronic conductivity and electrochemical control of the composition of PEDOT may be achieved when the investigated material is immersed in a suitable electrolyte – in the present case we have chosen an aqueous solution of NaCl (0.1 M) continuously bubbled with nitrogen. The electrode potential of PEDOT (and thereby its redox state) can then be controlled in a conventional three-electrode configuration. To measure the electronic conductivity, a small sinusoidal ac-voltage perturbation (10 mV pp) is imposed along the length of the PEDOT electrode while monitoring the current. From analysis of the frequency dependent impedance of the sample, the electronic resistance can be determined [3]. If the geometry of the sample is known, the electronic

conductivity can then be determined. In order to perform these measurements, two potentiostats that are able to share a common working electrode are required. In the present work we used a Zahner IM6 potentiostat equipped with an auxiliary EPOT potentiostat.

The PEDOT applied to the electrodes was made by solution casting as described in [4], using Fe(III)tosylate as the oxidant and pyridine as the acidity regulating agent.

Two different electrode configurations were tried: the two-band electrode used previously (see [3] and references herein), and a micro structured electrode with a well-defined narrow conducting channel acting as the dominating resistive element.

At the surface of the *two-band electrode*, two narrow gold bands 0.3 mm wide and spaced approx. 18 µm apart forms two independent contacts to the PEDOT layer formed on top of the electrode. It was not feasible to use spin casting or other application methods that could ensure a precise, even layer thickness. Furthermore, the spacing between the gold bands shows a small variation over the length of the gap. This method can therefore not give absolute values for the conductivity, but requires a calibration for each electrode preparation. In the present case we choose to make a similar PEDOT preparation on a glass slide, and use the experimental conductivity of this sample to calibrate the cell constant of the two-band electrode preparation.

Although requiring calibration, the two-band electrode method has the advantage that a completely even redox level of the PEDOT layer is ensured by all active material being in close proximity to the gold electrodes.

By micro patterning of a spin cast PEDOT film, the structure shown on Figure S9 (a) was made. In this structure a narrow PEDOT strip bridges two large contact pads of gold backed PEDOT. As the dimensions of the bridge are well defined and can be characterised with high accuracy (see Figure S9 (b), an accurate cell constant can be calculated, and using this method the conductivity of PEDOT can be measured without the need for calibration. The disadvantage of this method is that the high aspect ratio may make it difficult to maintain an even redox level throughout the bridge.



Figure S9: (a) Layout of the micro patterned structure used for conductivity measurements (not drawn to scale). The hatched areas are gold backed PEDOT; the other dark areas are PEDOT directly on glass. (b) Topographical image of part of the bridge between the two contact pads obtained with a Fogale Nanosurf optical profilometer.

The following steps were used for micro patterning of the PEDOT coating:

- On a glass slide covered with gold on chromium a 2 mm wide channel was etched through the metal layer across the slide.
- To improve adhesion, the slide was then plasma treated in Ar/H₂, Ar/H₂ + dodecane and Ar + dodecane.
- The mixture of monomer, oxidant and inhibitor [4] was spin cast onto the slide which was then heat treated at 65 °C for PEDOT polymerisation, and subsequently rinsed in ethanol and water and dried. The thickness of the PEDOT layer was measured by profilometry to be 165 nm.
- Photo resist (Microposit S1805) was spun on top of the PEDOT layer and exposed with a shadow mask defining the 1 mm wide channel and the 20 µm bridge between two parts of the slide covered with PEDOT.
- The photo resist was developed in 15% Microposit developer (NaOH solution).
- The exposed PEDOT was removed by reactive ion etching in O_2/Ar .
- After etching, the remaining photo resist were removed by placing the samples a few minutes in ethanol followed by rinsing in water and drying.

The topography of a part of the bridge is shown on Figure S9 (b), showing that the patterned structure has well defined edges and a rather smooth surface.

Results and discussion

Figure S10 shows cyclic voltammograms of a PEDOT layer on the two-band electrode at 1000 and 100 mV/s. To facilitate comparison, the CV current is recalculated as differential capacity by normalisation with sweep-rate. In contrast to the hysteretic behaviour often seen when cycling conducting polymers, the switching of PEDOT apparently occurs at a higher potential when cycled at high sweep rates.



Figure S10: Cyclic voltammograms of the PEDOT covered two-band electrode. The current is normalized as differential capacity by division with sweep rate. Sweep rates are given on the figure.

The impedance measurements on the two band electrode is analysed as was described earlier [3], using the known conductivity of a similar PEDOT preparation as the reference point. The resulting relationship between electronic conductivity and electrode potential is shown on Figure S11 (a) (on a linear scale) and Figure S11 (b) (on logarithmic scale). It is seen that the conductivity decreases as soon as the polymer is reduced below its initial level (corresponding to an electrode potential of approx. 0.4 V vs Ag/AgCl). When the potential is reduced beyond -0.2 V vs Ag/AgCl the conductivity drops off logarithmically with a total decrease upon reduction corresponding to slightly more than 4 orders of magnitude.



Figure S11: (a) Electronic conductivity of PEDOT measured using the two-band electrode. The data are calibrated against a similar preparation of PEDOT coated onto a glass substrate. (b) Electronic conductivity of PEDOT measured using the two-band electrode (circles) and the micro patterned electrode (triangles, different runs, both anodic and cathodic scans).

As mentioned above, the micro patterned electrode does not require calibration as the geometry is well characterised and designed to minimise geometric boundary effects. It is remarkable, that the conductivity of the as prepared polymer has not deteriorated upon exposure to the harsh chemical treatment during the lithographic patterning process. From Figure S11(b) it can be seen that the decrease in conductivity on reduction is smaller than observed with the two-band electrode. There can basically be two different explanations of this phenomenon:

Due to the very high aspect ratio of the PEDOT bridge it is likely, that the middle part of the bridge will not be at the same potential as the contact pads when the potential is decreased below the reduction potential of dissolved oxygen [2]. The parasitic oxygen reaction will cause a partial reoxidation of PEDOT, and the high resistance through the bridge will limit the rate at which charge can be delivered without significant overvoltages.

Alternatively, the chemical treatment during micro patterning leads to change in PEDOT that does not reduce its conductivity, but makes it more difficult to reduce the polymer.

Undoubtedly, both these factors contribute to the difference between the sets of data obtained by the two methods described here. The two-band method is considered to give the results most representative of pristine PEDOT, and on Figure S12 we show how the conductivity of PEDOT varies with the doping level of the polymer. The doping level is calculated from the 10 mV/s voltammogram and the initial doping level of the electrochemically prepared material determined to 0.24 by quartz crystal microbalance.



Figure S12: Electronic conductivity of PEDOT as function of doping level (fractional charge per monomer unit).

We have demonstrated that PEDOT can be lithographically micro patterned without losing its high conductivity. During the time of the measurements (several days), the conductivity did not deteriorate even though the samples were immersed in electrolyte and were subject to a number of redox cycles.

Only on oxidation above 0.8 V vs Ag/AgCl did we observe degradation of electrode performance, probably caused by delamination of the polymer from the glass substrate.

The electronic conductivity is strongly dependent on the redox state of PEDOT, and goes down 4 orders of magnitude when the polymer is reduced below 0.0 V vs Ag/AgCl in a neutral electrolyte. The conductivity of PEDOT is found to depend solely on the electrochemical potential and is independent on its prior history. This is in contrast to polypyrrole dodecyl benzene sulfonate complexes that show marked hysteresis phenomena [3].

These findings demonstrate that PEDOT is well suited as current bearing elements in *e.g.* micro fluidics or other applications where current leads are expected to be in contact with electrolytes. In designing such applications attention must be paid to avoiding the leads to be at reducing potentials if resistance in the leads is a critical issue.

References

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