
PRAP-CVD: A Novel Technique to Deposit Intrinsically Conductive Polymers

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Abstract

Polymers provide extraordinary opportunities for functionalizing surfaces integrated into flexible devices contributing to a significant advancement in thin-film technologies. Both the advantageous characteristics of conventional polymers (e.g. low weight, flexibility) and the functional physical properties of conventional semiconductors (e.g. absorption and emission of light and a tuneable conductivity) can be found in polymers providing innovative materials. Among polymers with heterocyclic structures, called conjugated polymers, polythiophene remains one of the most intensely researched materials in the field of so called organic electronics owing to the relatively facile and well-established synthetic modifications of the corresponding monomers and its derivatives. In particular, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising owing to its exceptional stability, transparency, and electrical conductivity. Nevertheless it is difficult to process PEDOT into thin-films by traditional solution-based methods. Plasma Radicals Assisted Polymerisation via Chemical Vapour Deposition (PRAP-CVD) is a novel technique able to overcome the challenges caused by the conventional techniques.

Keywords: chemical vapour deposition, conjugate polymers, poly(3,4-ethylenedioxythiophene), conductivity, organic electronics

1. Introduction

Considering the early days of conjugated and conducting polymer synthesis, the first works on polypyrrole as well as polyaniline are often referred to as landmark developments in this field [1, 2]. Despite these polymers resulted completely insoluble and infusible as formed from oxidative polymerisation, they served as basis for inducing electroactivity into polymer

systems. The Nobel Prize winners, Heeger, MacDiarmid and Shirakawa, have the merit of discovering that the treatment of these polymers with controlled amounts of halogens could induce conductive behaviour, demonstrating for the first time conductive properties of an organic polymer [3–5]. They were the pioneers of the investigation of the mechanisms and physical origins underlying the charge transport in this new class of materials, starting by studying polyacetylene [6].

A few years later, in 1980, the discovery of electrical conductivity in oxidised polythiophenes was reported respectively by Yamamoto and Lin [7, 8]. The mechanism responsible of polythiophene conductivity was found to be similar to that one of oxidatively doped polyacetylene, i.e. generation of delocalized radicals by an oxidising dopant, and subsequent stabilisation via ionic interactions between the charged polymer and the spent dopant. Although the first observations recorded low conductivity values (0.001–0.1 S/cm) compared to doped acetylene, thiophene monomers could offer a more diverse opportunity for functionalization than bare acetylene owing to their chemical structure. Since the evolution of conjugated polymers and their use as semiconductors, polythiophene and its derivatives have remained one of the most intensely researched materials in the field of so called organic electronics. Polythiophenes have been vastly explored in a variety of applications such as organic field-effect transistors (OFETs), organic light-emitting diode (OLEDs), organic photovoltaics (OPVs), and sensing devices in medical and biological fields [9–11].

The studies of polythiophene derivatives culminated with the synthesis of Poly(3,4-ethylenedioxythiophene) (PEDOT) by Bayer in 1988 [12]. PEDOT or PEDT, belongs to the moderate amount of conductive polymers, which have not only attracted remarkable scientific interest but also companies since it is currently used as material in different products of modern life. When PEDOT was invented in 1988, a so huge number of its potential applications was not really realised at that time. Since then this has dramatically changed, and nowadays PEDOT is probably the best conducting polymer available in terms of conductivity, processability, and stability. Looking at the number of PEDOT patents and scientific papers published every year, about 1500 documents per year are produced, highlighting an obvious and remarkable interest for PEDOT from the scientific community. Additionally, about 40% of these figures represent patent applications, demonstrating an additional intense industrial interest in this material.

Over the years, many synthetic strategies have been employed in the development of well-defined oligothiophenes, most of them based on fundamental polymer chemistry approaches [13]. Two main relevant mechanisms for polymerisation are commonly accepted: step-growth and chain-growth methods. These methods provide polymers with distinctly different structures in terms of repeat unit functionality, molecular weight, and dispersity. In particular, chain-growth polymerizations to form addition polymers are most often accomplished using monomers with multiple bonds and loss of unsaturation. In particular, in the chain-growth mechanism, a reactive intermediate is first created in an initiation step and subsequently propagates via repeated monomer addition to provide a macromolecule. When the reactive intermediate is ionic, impurity termination or quenching processes can kill the reactive intermediate, while in the case of radical polymerisation, coupling termination can lead to

an overall doubling of the average molecular weight [14]. This approach has been widely used to produce PEDOT. Despite its huge potentialities PEDOT itself does not present high conductivity values; as matter of fact, the conjugated bond structure in PEDOT leads to a rigid conformation, maintaining electron orbital overlap along the backbone of the polymer. Crystallisation is favoured and prevents the material from easily dissolving or melting. As a result, PEDOT has good chemical and thermal stability that makes it difficult to process into thin-film form [15].

Alternatively, a conjugated polymer can be deposited by *in-situ* oxidative polymerisation directly at the surface. On conducting substrates this can be achieved by electrochemical polymerisation, which generally gives coatings of high quality. This method is however rarely suited for large-scale applications and cannot be used to add electronic functionalities to non-conducting surfaces. Furthermore, electropolymerization of EDOT in aqueous media is limited by the low solubility of the monomer. However, it is reported that the addition of surfactants improves its solubility. So it is often required to derivatise the polymer with soluble side chains or to dope the polymer with polyelectrolytes acting as solubilisers in order to be able to process these polymers [16, 17].

According to the latter proposed solution, a particularly conductive form of PEDOT, synthesised with the addition of poly(styrene sulfonic acid) (PSS) and also stabilised by, has been put in place and introduced on the market as an aqueous dispersion under the brand-name Baytron, and most recently changed to Clevios [18]. The additional oxidising the neutral polymer prompts conductivity behaviour. The positive charges of PEDOT backbone induced by oxidation are balanced by anions present on PSS. The appropriate choice of the counter-ion highly contributes to the properties of the conductive complex. Pristine PEDOT:PSS yields a conductivity below 0.1 S/cm, too low to be used as an electrode in an efficient solar cell [19]. Despite the appealing properties of this complex, degradation phenomena of PEDOT:PSS have been detected inducing to irreversible morphological and chemical changes which affect film properties [20–22]. As example, an insulating layer of PSS preferentially segregates to the surface of PEDOT:PSS films as identified by Greczynski et al. [23]. The presence of this phase segregation has been also supported by Jukes et al. using small-angle neutron scattering [24]. Given the vertical phase separation, it is not surprising that PEDOT:PSS films exhibit anisotropic conductivities. Conduction, as expected, is inefficient through the depth of the film and enhanced in the plane of the film (10^{-5} and 10^{-3} S/cm, respectively) [25]. It is well known that addition of solvents, such as ethylene glycol, glycerol, dimethyl sulfoxide, and sorbitol significantly improved the conductivity of PEDOT:PSS by up to 2 or 3 orders of magnitude. On the other hand the fabrication processes that involve solvents are often restricted by the solvent-substrate incompatibility as in the case of printed electronics where high importance is played by the interactions between PEDOT:PSS and flexible substrates, mainly consisted of polymers and papers. The non-evaporated solvent could also prompt swelling or degradation phenomena into the non-sensitive substrate after drying step [26].

The synthesis of PEDOT can be also obtained by chemical vapour deposition (CVD) in order to circumvent most of all the disadvantages of liquid phase chemistry approach. CVD is not a

new process. Its first practical use was developed in the 1880s in the production of incandescent lamps to improve the strength of filaments by coating them with carbon or metal [27]. CVD may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapour phase. CVD has several important advantages over the liquid phase chemistry which make it the preferred process in many cases: absence of solvent, high deposition rate, good surface conformity. CVD equipment does not normally require ultrahigh vacuum and generally can be adapted to many process variations. Its flexibility is such that it allows many changes in composition during deposition and the co-deposition of elements or compounds is readily achieved. In this scenario, several kinds of CVD techniques are currently used to obtain PEDOT films.

The first one is the so called plasma-assisted or plasma-enhanced CVD (PE-CVD), introduced in the fabrication of semiconductor from 1960s and for long time restricted to the synthesis of inorganic compounds, becoming an essential factor in the manufacture of semiconductors and other electronic components. This technique is based on electrical energy rather than thermal energy to initiate homogeneous reactions for the production of chemically active ions and radicals that can participate in heterogeneous reactions, which, in turn, lead to layer formation on the substrate. A major advantage of PE-CVD over thermal CVD processes is that deposition can occur at very low temperatures, even close to ambient, which allows the use of temperature sensitive substrates [28]. Unfortunately, monomers injected into the glow discharge are often irregular and fragmented by the electrons, ions/radicals present into the glow discharge. Furthermore such plasma polymers are often irregular and have rather short chain lengths. Plasma polymerisation leads to a random poly-recombination of radicals and fragments of monomers. A variation could be represented by pulsed-PE-CVD. In this case, the glow discharge is pulsed and when it is switched on (plasma-on), the activate molecules can produce radicals which initiate the polymerisation mechanism. When the glow discharge is switched off (plasma-off), the residual radicals initiate a conventional chemical chain-growth reaction. In this case a more 'conventional' product is obtained but the chain propagation is restricted by the low probability of attaching a new molecule monomer to the radical at the growing chain-end. Moreover the deactivation of chain propagation is expected under the common vacuum conditions (0.1 Torr) owing to the recombination of neighbouring radicals. This leads to a significant loss of the active radical sites during the plasma-off period. Glow discharge is thus re-ignited to reproduce fresh initial radicals. The resulting polymer film has a structure and composition closer to its counterpart produced by liquid phase but it shows repeatable irregularities induced by the plasma-on period [29].

Another known CVD method is the vapour phase polymerisation (VPP), where the solubility of the conjugated monomer is no longer required. VPP directly translates the step-growth mechanism established for the liquid phase synthesis via solvent-less environment [30]. VPP is usually performed by two-step process. The first one consists of the pre-application of the oxidant to the substrate, which is typically carried out by spin coating, while the second step consists of the exposure of the pre-treated substrate to monomer vapours under vacuum reaction chamber. The VPP delivers conducting polymers, like polypyrrole and PEDOT, using iron(III) chloride as oxidant [31, 32]. Spreading the oxidant all over the surface limits the

use of VPP to non-liquid sensitive substrate [33]. Analogous to VPP, another process called oxidative CVD (oCVD) has been developed by Prof. K.K. Gleason at Massachusetts Institute of Technology [34]. The oCVD is a single step process, where both oxidant and monomer, in vapour phase, are delivered to the substrate into the chamber reaction. This is the main difference between the VPP and oCVD methods. Deposition of PEDOT films by oCVD using iron(III) chloride has been described in detail in the literature [35]. With this method smooth PEDOT films with conductivity higher than 1000 S/cm have been obtained [36]. Actually one of main drawback of using iron(III) chloride, as oxidant compound in the polymerisation of EDOT, lies in the use of post processing step carried out with methanol to remove the unreacted iron (III) chloride and by-products as iron(II) chloride as well as any oligomers or short chains formed during the polymerisation process as they become contaminant during device fabrication. Additionally it is also rather difficult to provide sufficient oxidant flux since it is often a powder [37].

Halogens have been widely used as a dopant for making conducting polymers [38, 39]. So in an attempt to make oCVD process completely dry, bromine has been used as the replacement for iron(III) chloride. Use of bromine resulted in a completely dry process with no post processing required. The achieved conductivity was around 380 S/cm but details on surface area covered by PEDOT film as well as resistance over the time were not disclosed. Despite these encouraging results any further papers using bromine as oxidant have been published [40]. In this framework, quite recently a novel CVD technique has been developed by Dr. D. Lenoble and co-workers at Luxembourg Institute of Science and Technology (LIST). The process, named Plasma Radicals Assisted Polymerisation via CVD (PRAP-CVD), has been demonstrated as an efficient alternative to CVD processes in depositing conductive thin films [41]. This method is directed to form conjugated polymer directly on a substrate.

2. Experimental

PEDOT has been investigated as case study to prove the effectiveness of PRAP-CVD.

PRAP-CVD polymerisation results from surface reaction of the monomer and oxidant flows, here 3,4-ethylenedioxythiophene (EDOT) and bromine, respectively [41]. The oxidation of EDOT to form PEDOT shows some similarities to the oxidative polymerisation mechanism of pyrrole suggested by Diaz [42, 43]. The proposed polymerisation mechanism of EDOT to form PEDOT is illustrated in **Figure 1** [41].

A preliminary step takes place in a plasma chamber, where bromine radicals are generated while the glow discharge is switched on. Progressively they reach the reaction chamber where EDOT monomer is parallel injected. Bromination of EDOT molecules occurred in α position by the formation of a radical that shows several resonance forms. A dimer is formed by combination of two of these radicals. Substitution of the EDOT thiophene ring at the 3,4-positions blocks β -coupling, allowing new bonds only at the 2,5-positions. The dimer can be oxidised to form another radical following the steps described above. The alternating single and double bonds of the oligomers are π -conjugated, which delocalizes the electrons

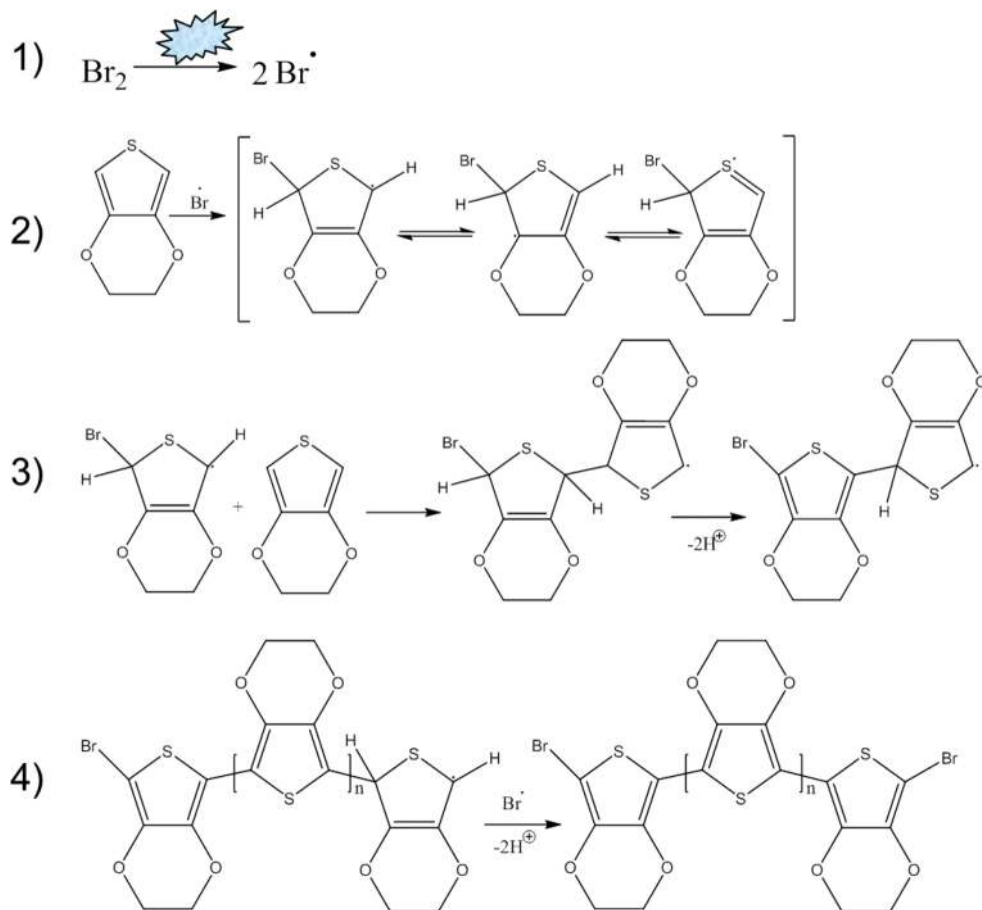


Figure 1. Polymerisation mechanism of EDOT to form PEDOT. (1) Ignition of glow discharge fed with bromine gas allows the production of bromine radicals. (2) Bromination of EDOT molecules occurs in α position. (3) Radical polymerisation propagates. (4) Polymerisation stops when also α' position is brominated [41].

and decreases the oxidation potential [34]. In PRAP-CVD the bromine acts as radical initiator as well as oxidant, and the final electronic arrangement presented in the polymer is depicted in **Figure 2**.

PRAP-CVD PEDOT, which is carried out in PRODOS-200 PVPD™ R&D System (AIXTRON SE, Herzogenrath, Germany), owing to the facilities of the machine and the mild experimental conditions, can be deposited on a wide range of substrates, both in terms of dimension and in terms of composition: from silicon wafer to fabrics and up to $15 \times 15 \text{ cm}^2$, as reported in **Figure 3**.

Raman studies were conducted to determine the vibrational modes of the different regions in the wavenumber range of $250\text{--}1800 \text{ cm}^{-1}$, and to prove the obtained EDOT polymerisation.

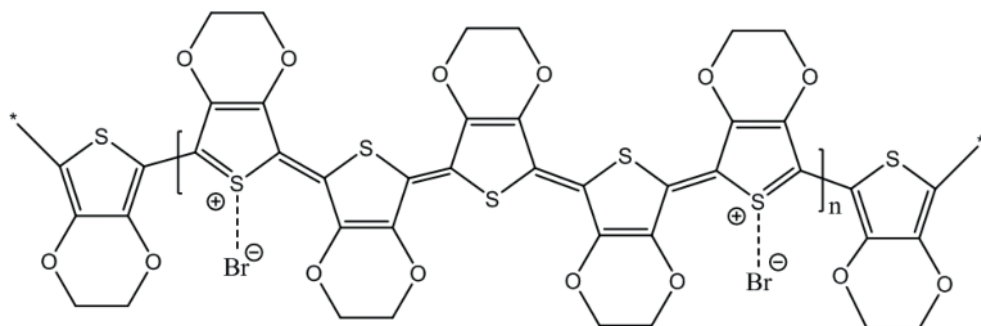


Figure 2. Electronic arrangement of Br-PEDOT films. The bromine acts as radical initiator as well as oxidant [41].



Figure 3. Examples of substrates treated via PRAP-CVD to obtain PEDOT films: (a) silicon wafer (20 cm in dia), (b) glass (15 × 15 cm²), and (c) PET fabric (12 × 12 cm²) [41, 44].

PEDOT was deposited on silicon wafer, prevented covered with a thin layer of SiO₂ (deposited in house by Rapid Thermal-Chemical Vapour Deposition – RT-CVD) to avoid any interferences during the electrical measurements, as reported in **Figure 4**.

The spectrum of monomer was compared with that one of polymer. Six strong Raman bands were detected in the spectrum of EDOT, **Figure 4a**, at 1486, 1423, 1185, 892, 834, and 766 cm⁻¹ [45]. The shape of spectra was completely different and the spectrum of PEDOT showed much more bands related to different vibration modes owing to presence of the polymer chain. In **Table 1** the assignment related to the bands are reported. A good agreement with literature data was found to support the accuracy of the proposed polymerisation mechanism [46, 47].

Furthermore, the confirmation that the polymerisation took place in the right way, i.e. without thiophene opening ring, in favour of correct PEDOT film formation, came also from the absence of the band at 1705 cm⁻¹ [48].

The mild experimental conditions carried out in the PRAP-CVD allow even the treatment of sensible substrates as papers or fabrics without any damages. To prove this advantage of PRAP-CVD compared to the other CVDs, a few temperature sensitive substrates have been treated and a PEDOT thin layer was deposited. SEM micrographies were recorded and shown in **Figure 5** where (a) PET fabric, (b) cotton fabric, (c) linen fabric and (d) paper cellulose fibres are reported.

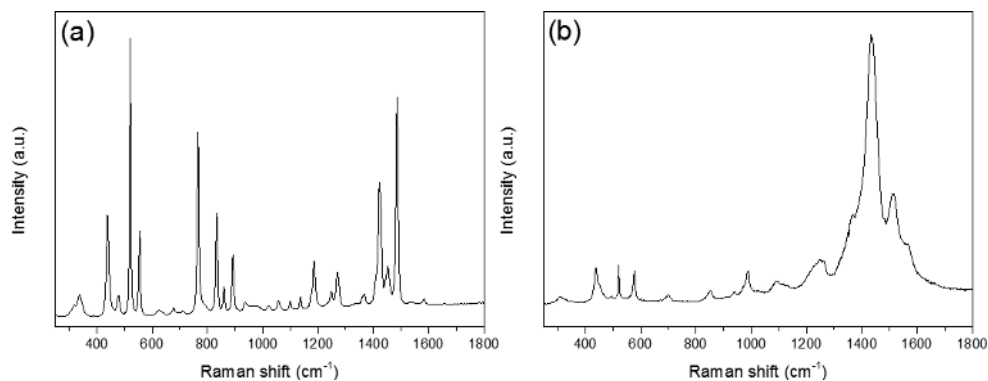


Figure 4. Raman spectrum of (a) EDOT and (b) PRAP-CVD PEDOT films recorded at an excitation wavelength of 633 nm.

Wavenumber (cm ⁻¹)	Assignments
1509	Asymmetric $\nu C\alpha = C\beta$
1432	Symmetric $\nu C\alpha = C\beta$ (-O)
1366	$\nu C\beta-C\beta$
1266	Inter-ring $\nu C\alpha-C\alpha$
1096	$\nu C-O-C$
990, 573	Oxyethylene ring deformation
699	Symmetric $\nu C-S-C$
439	δSO_2

Table 1. Observed frequencies of doped poly(3,4-ethylenedioxythiophene) with assignment of principal bands.

Samples have been investigated after the deposition without any further manipulation. Not only by PRAP-CVD it is possible to treat fibres but PRAP-CVD benefits of a quite unique property in terms of conformal deposition on complex substrates, as of the matter of fact, fibres are, **Figure 6**.

PET fabrics have been chosen as reference substrate for this series of characterizations. Correspondence of the textile morphology between the uncoated and coated sample illustrated the high conformal coverage of the fibres with polymer thin film, **Figure 6a** and **b**. The presence of PEDOT was confirmed by Energy Dispersive X-ray (EDX) spectroscopy investigation reported in **Figure 6c** and **d**, respectively. In the spectrum of PET, peaks of carbon (C) K α at 0.3 keV and oxygen (O) at 0.5 keV were detected while the spectrum of fibres treated via PRAP-CVD highlighted the presence of sulphur (S) at 2.3 keV and bromine (Br) at 11.9 keV. Sulphur as well as carbon and oxygen could be attributed to the chemical composition of EDOT while bromine to the dopant. PEDOT film resulted in defect/pin-hole free, as attested by the high magnification SEM micrographs. In order to deeply prove this

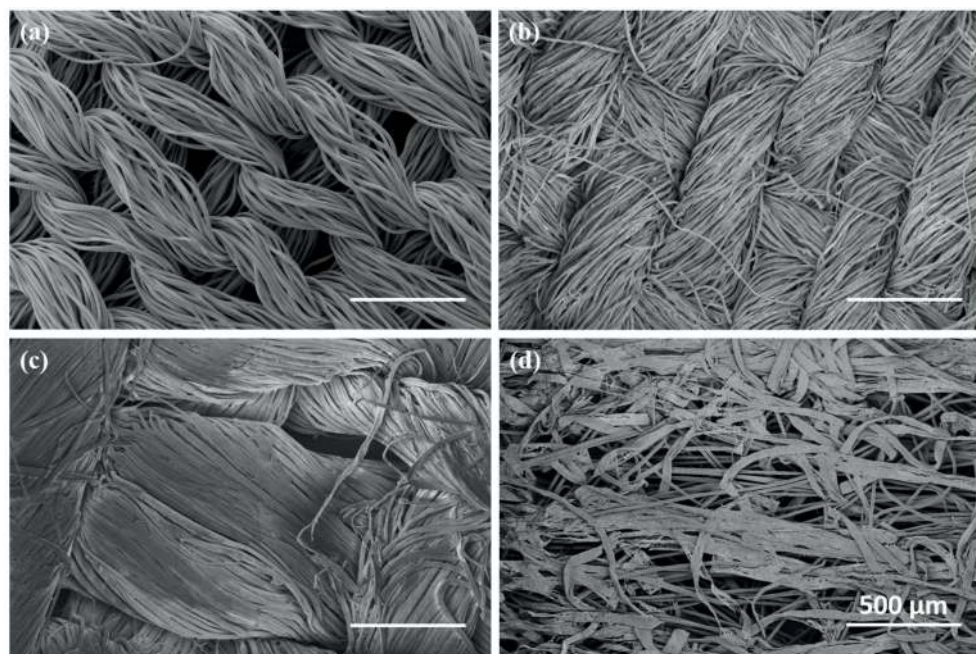


Figure 5. SEM microscopies of PRAP-CVD PEDOT film deposited on (a) PET fabric, (b) cotton fabric, (c) linen fabric and (d) paper cellulose fibres. Samples have been investigated after the deposition without any further manipulation [44].

peculiarity of PRAP-CVD, a stripe of PET fabric covered with PEDOT was cut by means of a scalpel and analysed. In **Figure 7**, micrographs of the same PEDOT/PET area, recorded at different magnifications, are reported (**Figure 7a** and **c**).

The cut induced a physical convergence of fibres. The lighter part of image could be attributed to the PEDOT which responded differently from PET under the irradiation of the electron beam. In the same experimental conditions, PET, as all non-conductive materials, suffers of charging effects, revealing a darker image than PEDOT/PET. The same images were also artificially coloured by Image J software as reported in **Figure 5b** and **d** to easily identify the layer of PEDOT which conformably surrounded each fibre although the convergence of fibres. By SEM it was possible on one side to investigate the conformality of the film and on the other anticipated its electrical conductivity properties too. Following FIB cross-sectioning step, an accurate thickness measurement of film could be determined. A thickness of (215 ± 10) nm allowed to establish a deposition rate of 6 nm/min. This level of coating quality is unequalled to current wet and dry PEDOT synthesis. PRAP-CVD allows to modify only the surface of substrate without impacting on the bulk properties, as demonstrated by XPS spectra in **Figure 8** [41].

Chemical states of carbon (C 1s) in PET and PEDOT/PET C 1s were identified by XPS. In **Figure 8a** three chemical states of C 1s, reflecting the presence of the three peaks, were

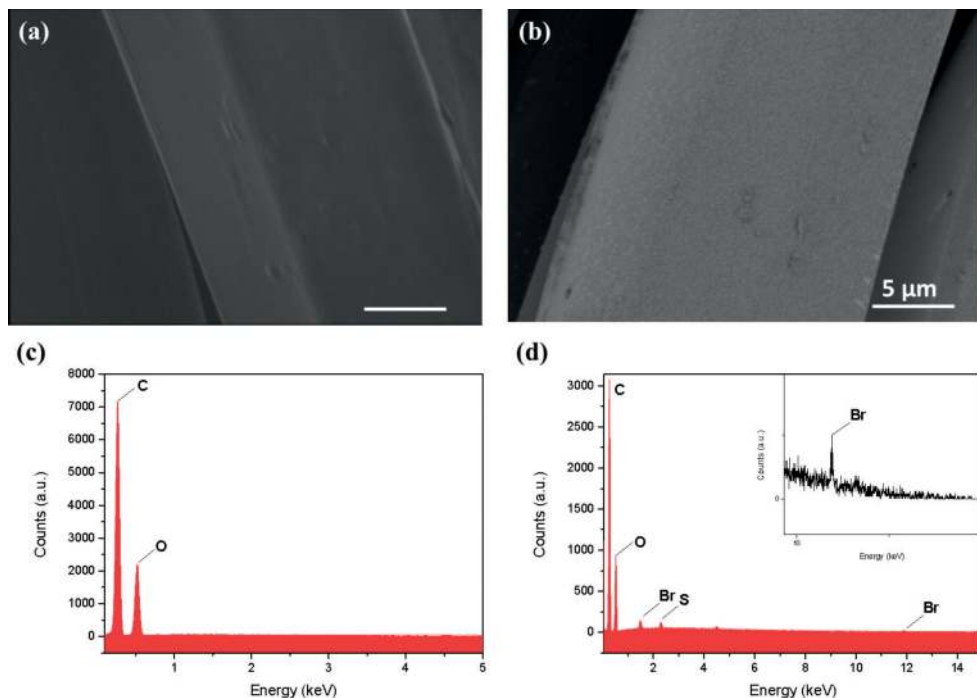


Figure 6. SEM images of textile fibres (a) before and (b) after the PRAP-CVD process. Owing to the induced conductivity of PEDOT, the two images resulted in different colours, darker the raw PET and lighter the PEDOT/PET fibre. Respective EDX spectra identified the presence of (c) carbon and oxygen in raw PET and (d) also sulphur and bromine residues in the PEDOT coated fabric [44].

identified in the PET. They could be attributed to C–C/H bond (aliphatic/aromatic carbon atoms) (C1 – BE: 284.5 eV), C–O bond (methylene carbon atoms singly bonded to oxygen) – (C2 – BE: 286.0 eV), –COO– bond (ester carbon atoms) (C3 – BE: 288.5 eV) and π – π^* shake-up transition associated with the aromatic ring at 291 eV. By performing the best fitting procedure, the following percentage areas: 54.2% C1, 24.6% C2, 14.6% C3, and 6.6% shake-up were obtained [49]. In **Figure 8b**, the distribution of functional groups of PEDOT/PET C 1s showed three different components: C–C/H bonds (C1 – BE: 284.4 eV), C–S bonds (C2 – BE: 285.5 eV) and C–O bonds (C3 – BE: 286.1 eV). Additionally, an asymmetrical peak at about 288 eV was also identified and attributed to the contribution from the π – π^* shake-up transition and positively polarised or charged carbon [50]. Peak areas were calculated as 34.8% for C–C/H, 42.5% for C–S, 17.3% for C–O and 5.4% for the shake-up, respectively [51]. Best-fitting procedure was also applied to S 2p core-level, which corresponded to single sulphur bonding environment in PEDOT with a spin-split doublet, 2 p_{1/2} and 2 p_{3/2} separated by 1.18 eV in binding energy and an area ratio 1:2, as shown in **Figure 9**.

The pick presented an asymmetric tail at higher binding energy, which could be related to the doping process, where the delocalized π -electrons in thiophene ring broaden the binding

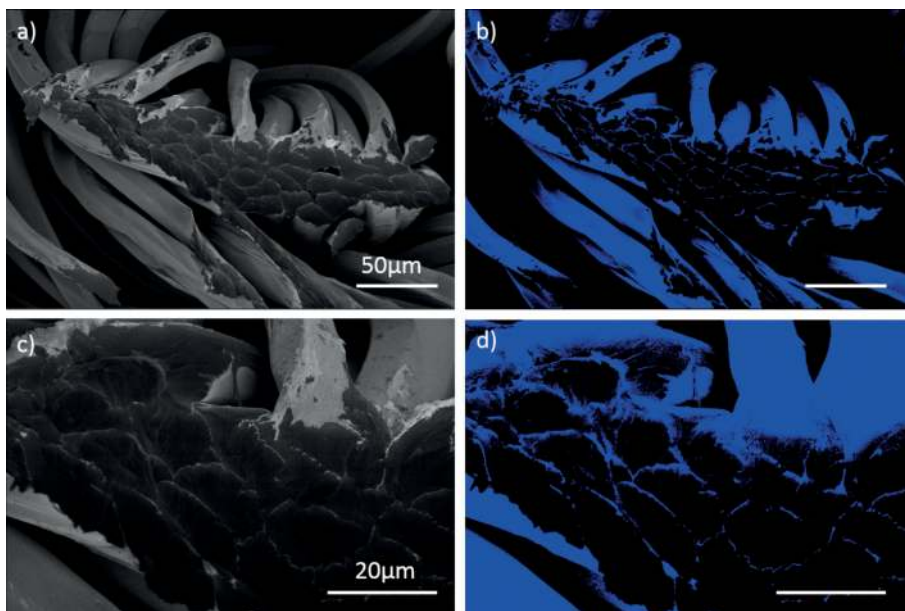


Figure 7. SEM micrographs of PET fibres cross-section with PEDOT film (a, c) at different magnification; (b, d) corresponded coloured picture at same magnification. The darker area corresponded to PET fibres. Conductive PEDOT film responded differently from PET while irradiated by the electron beam [44].

energy spectrum of the sulphur atom [52]. The quantitative analysis of PEDOT film showed the followed atomic percentage of 66% C, 21% O, 9% S, and 4% Br [41].

In the last years the demand of transparent flexible and conductive electrodes increased suddenly, in particular the research of materials to replace indium tin oxide (ITO). The main drawbacks presented by ITO are on one side the cost of indium itself and the remaining amount of this element the earth and on the other the brittleness of ITO based electrodes. PRAP-CVD PEDOT could answer to these requirements because as demonstrated it can be deposited on flexible substrate as plastic and it shows optical transparency properties, as reported in **Figure 3**. More in detail, transmittance and absorbance values of PEDOT deposited on glass in UV range were recorded and presented in **Figure 10**.

In **Figure 10a**, the transmittance of PEDOT thin films decreased while wavelength increased beyond 500 nm, this is owing to the presence of the free carrier tail but PEDOT still showed a value of transmittance over 70%.

In **Figure 10b**, the peculiar absorption feature, which characterises PEDOT film, known in the literature as a 'free carrier tail', is confirmed and can be attributed to the conductivity of the polymer films [53]. The presence of this band has been found and investigated for the first time in the doped polyaniline. It corresponds to the polymer having a longer conjugation length and greater order, which allows for greater mobility of charge carriers [54].

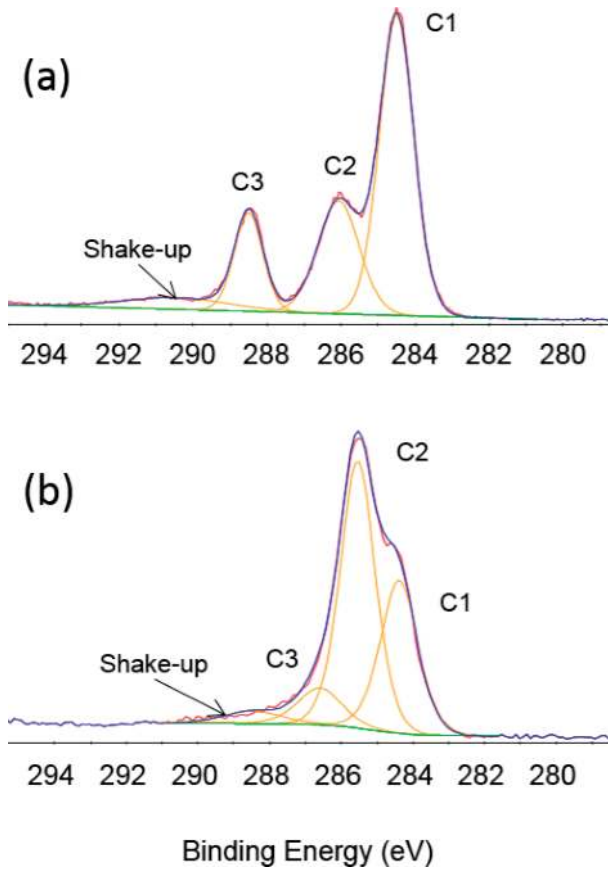


Figure 8. XPS C 1s high resolution spectra of (a) PET and (b) PEDOT/PET and relatively chemical states [44].

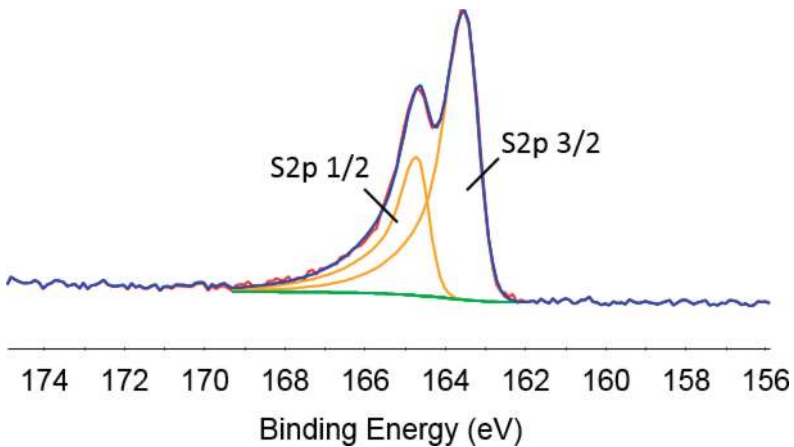


Figure 9. XPS HR high resolution spectra of S 2p.

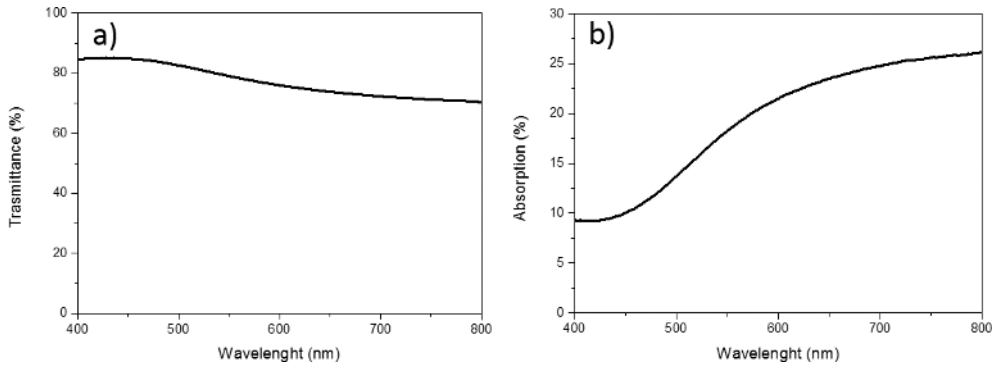


Figure 10. UV-Vis-NIR spectrum of thin PEDOT films as a function of (a) transmittance and (b) absorbance.

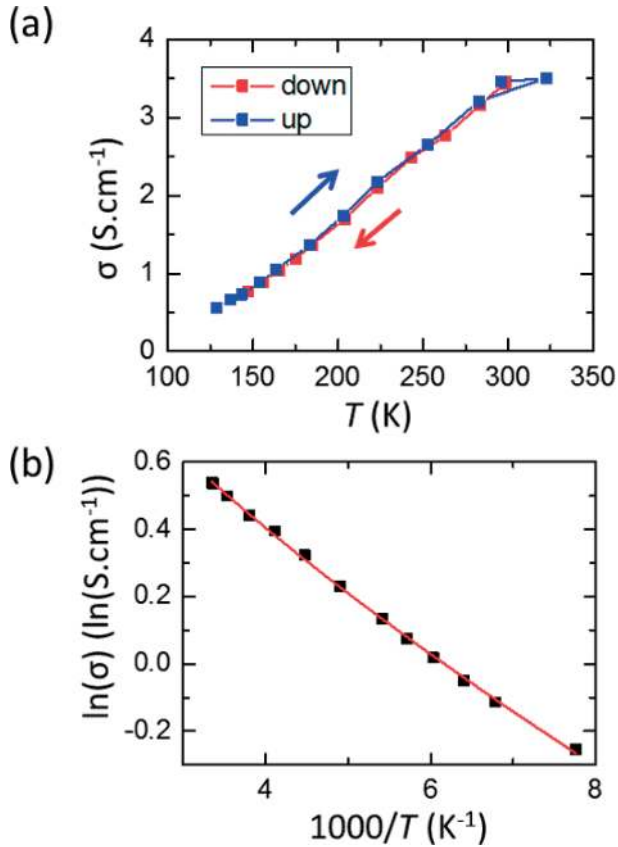


Figure 11. (a) Conductivity of the 50 nm thick PEDOT film deposited on BOROFLOAT® 33 as a function of the sample temperature. The measurements were performed both during cooling-down (red) and warming-up (blue) the sample. (b) Natural logarithm of the conductivity plotted as a function of $1000/T$ (black points) for the data measured during the cooling-down. The red curve is a fit of the data by Eq. (1), with the power $\alpha = 0.63 \pm 0.07$.

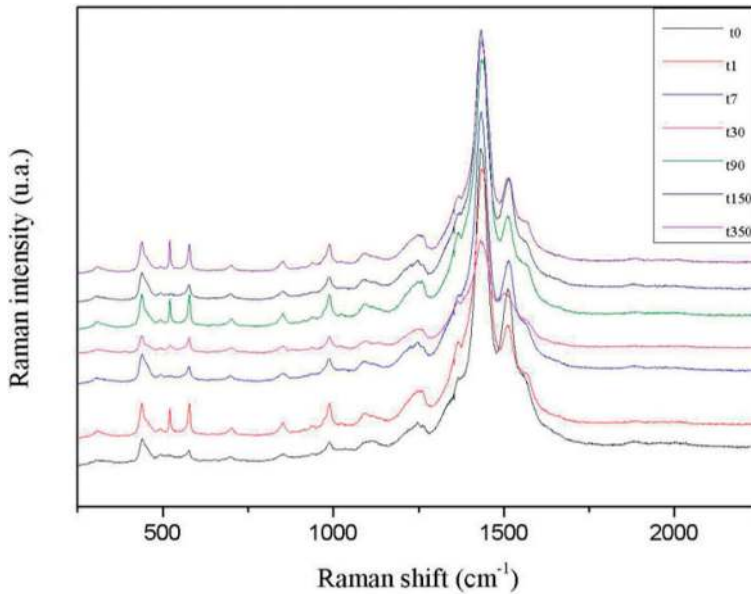


Figure 12. Raman spectra of PEDOT film recorded all along 1 year [41].

Performances of films have been investigated also in terms of conductivity as function of temperature. **Figure 11** shows the conductivity as a function temperature in the range 130–350 K, both when cooling-down and warming-up the sample.

The good reproducibility showed that there was no structural changes in the film, and that the temperature-dependence of the conductivity was owing to the intrinsic carrier transport mechanism in the film. The observed decreasing in conductivity, while the temperature decreases, is typical for an organic conductor, where carrier transport usually occurs by hopping conduction. In order to further investigate the carrier transport mechanism, in **Figure 11b** the natural logarithm of the conductivity as a function of the inverse temperature, $1/T$ have been reported. It was observed a good fit with a power, implying the following dependence for the conductivity as reported in Eq. (1):

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right) \alpha \right] \quad (1)$$

The best fit was obtained with $\alpha = 0.63 \pm 0.07$. This value is far from $1/4$, already reported for 3D variable range hopping (VRH), far from 1, as reported for nearest neighbour hopping, and far from $1/3$, as reported for 2D variable range hopping [25, 55, 56]. The value is closer to $1/2$, already reported for PEDOT:PSS and which corresponds to 1D VRH or hopping in a granular material where, the exponent α for 3D VRH varies from $1/4$ to $1/2$ due to charging energy-limited tunnelling between grains [57, 58].

Another requirement that PEDOT film has to show is the stability of the time. PEDOT films were exposed to ambient conditions over 1 year and its chemical structure was followed by Raman spectroscopy investigation, as reported in **Figure 12**.

Previous studies suggested that exposure to water vapour in the atmosphere could induce an increase in PEDOT, in particular PEDOT:PSS, sheet resistance as the hygroscopic polymer absorbs moisture over time [59, 60]. As shown in **Figure 12**, the main Raman peaks did not suffer of changing during the year. This different behaviour can be explained by the absence of PSS, which reveals all its acid character when exposed to the moisture.

3. Conclusions

PRAP-CVD has been successfully demonstrated to be a novel promising technique to deposit conjugated polymers. In particular, PRAP-CVD of EDOT leading to the formation of uniform conducting doped PEDOT film, by using bromine as oxidant, has been attested. Raman spectroscopy confirmed the chemical composition of PRAP-CVD PEDOT films. The use of bromine, as oxidant, allows to avoid every supplementary rinsing process, making the process completely dry, comparing to the PSS. All issues related to the corrosion, owing to the acidic behaviour of PSS, are bypassed in the PRAP-CVD. The use of bromine and the absence of PSS allow the use of PRAP-CVD on a wide range of substrates which could be damaged by a wet step like papers, plastics, etc. as demonstrated above. 3D samples benefit of a high conformal coverage. PRAP-CVD, developed in a β -side machine version, allows the treatment of quite large samples compared to VPP. This technique can be easily scaled up featuring highly competitive growth rate compared to other vapour phase growth of PEDOT thin films. Finally PRAP-CVD PEDOT film is transparent in the visible range and stable over the year.

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Appendices and nomenclatures

BE	Bonding Energy
CVD	Chemical vapour deposition
EDX	Energy Dispersive X-ray
ITO	Indium tin oxide

LIST	Luxembourg Institute of Science and Technology
OFET	Organic field-effect transistors
OLED	Organic light-emitting diode
OPV	Organic photovoltaics
oCVD	Oxidative chemical vapour deposition
PE-CVD	Plasma enhanced-chemical vapour deposition
PRAP-CVD	Plasma Radicals Assisted Polymerisation via CVD
PEDOT	Poly(3,4-ethylenedioxythiophene)
PSS	Poly(styrene sulfonic acid)
PVPD	Polymer vapour phase deposition
RT-CVD	Rapid Thermal-Chemical Vapour Deposition
VPP	Vapour phase polymerisation

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