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## Journal Pre-proof

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**One-pot electrosynthesis of ultrathin overoxidized poly(3,4-  
ethylenedioxythiophene) films**

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**Abstract**

In an aqueous electrolyte under an anodic polarization, most of the conductive polymers could undergo an overoxidation due to the hydroxyl radicals formed during water oxidation. Regarding poly(3,4-ethylenedioxythiophene) (PEDOT) only a few reports studied its overoxidation. In this paper, we propose a facile and rapid strategy to prepare an ultrathin (15 nm), pinhole-free and non-conductive overoxidized PEDOT film by electropolymerization of EDOT under potentiostatic conditions in the presence of solely weak-acid ions in the monomer solution. The influence of the pH of this solution as well as the applied potential was studied notably by electrochemical impedance spectroscopy. It was pointed out that the PEDOT film is overoxidized when its electrosynthesis is performed in an aqueous monomer solution of pH 10.5, at 1.1 V/SCE, the monomer solution containing only weak-acid ions as anions (phosphates or carbonates). XPS analyses show that some C and S atoms of the film are oxidized leading to a break of the polymer conjugation and therefore to a decrease of its electronic conductivity. Finally, after adding in the monomer phosphate solution of pH 10.5 perchlorate ions that allow to avoid total overoxidation of the film formed at the very beginning of the process, PEDOT nanowires were obtained.

**Keywords**

Poly(3,4-ethylenedioxythiophene); overoxidation; electrosynthesis; EIS; 2D film

## 1. Introduction

Over recent decades, electrically conductive polymers such as polypyrrole (PPy) [1-4], polythiophene (PTh) [5-7], polyaniline (PANI) [8-10] and their derivatives have attracted great attention across academia and industry. Poly(3,4-ethylenedioxythiophene) (PEDOT) has developed into one of the most popular materials among all the conductive polymers due to its high and stable electrical conductivity in oxidized state [11-15]. However, only a few reports studied its overoxidation under anodic polarization in an aqueous medium.

Electropolymerization of EDOT can be carried out in organic and aqueous solutions by cyclic voltammetry or chronoamperometry in a certain range of applied potential. In an aqueous electrolyte, when the applied potential is high, a side reaction that is water oxidation can occur. Therefore, EDOT electropolymerization could be accompanied by the polymer overoxidation which results from the  $\text{OH}^\bullet$  radicals produced during water oxidation. Du and Wang have shown that in an aqueous solution containing 0.01 M EDOT and 0.1 M  $\text{LiClO}_4$ , the anodic current decreased with time under potentiostatic conditions in the range of 1.1 - 1.5 V/SCE, due to the overoxidation of the polymer which becomes non-conductive [16]. Overoxidation is avoided in most studies in order to not disturb the polymerization process. However, overoxidized PEDOT (O-PEDOT) films exhibit some unique properties and can be applied for sensing with determination of dopamine [17], uric acid [18] and lead ion [19]. Besides, a very thin pinhole-free O-PEDOT film could be an essential step of the formation of nanostructured PEDOT films, taking into account the studies performed on polypyrrole [20-22]. PEDOT films with nanostructures have great potential to be used for various applications such as (bio)sensors or energy storage devices.

In general, the most common way to obtain an O-PEDOT film is first preparing a PEDOT film by an electrochemical method and then applying a relatively high potential to overoxidize it in an aqueous solution which does not contain any monomer. During the process of overoxidation, the doping anions are expelled from the film, the conjugation length of the polymer is decreased [23] and the morphology of the film could be changed [24-26]. The influence of the overoxidation conditions, such as applied potential [27, 28] and pH [29], and the electrochemical properties of O-PEDOT have been studied. However, O-PEDOT films prepared by this two-step procedure are still partially conductive. Because the first step leads to a thick PEDOT film and the anions inside the film are hard to be completely expelled. Sometimes some thin cracks or crevices are observed because of the internal stress changes during the second step [24].

In contrast, one-step electrosynthesis can simplify the process and allow one to obtain an ultrathin, pinhole-free, non-conductive film. It has been reported in our previous works [30-32] that the presence of solely weak-acid anions, such as monohydrogenophosphate or carbonate, which confer a relatively high pH to the monomer solution, allows one-step electrogeneration of an ultrathin overoxidized polypyrrole (O-PPy) film under potentiostatic and potentiodynamic conditions. Actually, weak-acid anions capture the protons which are released during monomer oxidation and lead to a situation that no anions are available at the electrode/solution interface. Due to the high applied potential at the electrode, water oxidation takes place and hydroxyl radicals are generated, these radicals react with the polymer film initially electrogenerated resulting in its overoxidation. The resistance of O-PPy film prepared by one-step is about ten times higher than the one prepared by a two-step process [32]. One can notice that these O-PPy films can be applied to develop biosensors implying  $H_2O_2$  detection [33, 34]. Additionally, this is the very first step of the electropolymerization of pyrrole leading to PPy nanowires [20, 22, 35,

36]. Although the O-PPy one-step electrosynthesis mechanism can be considered to other conductive polymers, certain conditions need to be met, such as (i) a high monomer concentration in order to have the oxidation of numerous monomers and therefore a high release of protons (reaction (1)) that are captured by the weak-acid ions leading to a drastic decrease of the anion concentration at the electrode/solution interface and (ii) proper potential of the monomer oxidation in agreement with water oxidation potential to have only formation of a few hydroxyl radicals able to react with the polymer initially formed rather than with themselves forming  $\text{H}_2\text{O}_2$  that is then oxidized into  $\text{O}_2$ . Unfortunately, EDOT has much lower solubility than pyrrole in an aqueous electrolyte and a higher redox potential. In another word, the balance between EDOT polymerization, water oxidation and PEDOT overoxidation is harder to be achieved by controlling the applied potential and the concentration of anions in one-step electrosynthesis. Actually, full overoxidation of PEDOT films by an electrochemical method has never been reported. The high stability of PEDOT due to the dioxane structure makes it difficult to be overoxidized. In the meantime, PEDOT with nanostructures is also difficult to be electrodeposited without the use of a template for the same reasons [37]. PEDOT films usually have a cauliflower-like structure [28, 38]. PEDOT nanowires are commonly obtained by using silicon or metal oxide template [39-43]. Recently, Guittard's group [44-46] successfully obtained various conductive polymers with various structures, including PEDOT derivatives, by soft-template, such as  $\text{O}_2$  or  $\text{H}_2$  bubbles, and surfactant-free electropolymerization. The structures are between nanoscale and microscale because the  $\text{O}_2$  or  $\text{H}_2$  bubbles are generated at the electrode/electrolyte interface instead of the electrode/film interface as for PPy electrosynthesis in monomer solution containing phosphate anions, which leads to bubbles having a lower size because of less merging of the bubbles inside the film than in the electrolyte [20, 22, 35, 36]. To better control the morphology of PEDOT, organic solvents [47], surfactants [48] and emulsions

[49] are commonly used. To the best of our knowledge, the mechanism of nanostructured PEDOT electrogeneration in aqueous solution without any surfactants has not been discussed yet. Herein, we report, for the first time, a one-pot electrosynthesis of ultrathin film of O-PEDOT that was carried out in an aqueous solution containing EDOT monomer and phosphate anions ( $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ) or carbonate anions ( $\text{CO}_3^{2-}$ ). We confirm that the presence of weak-acid anions in the monomer solution can lead to the formation of an overoxidized polymeric film. The influence of pH and applied potential over the electrochemical process has been studied notably by electrochemical impedance spectroscopy (EIS), and a mechanism of PEDOT overoxidation in an aqueous solution has been proposed including the presence of carboxylic groups which have been successfully activated by using N-ethyl-N'(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and N-hydroxysulfosuccinimide (NHS) solution [50-52]. In our future work, glucose oxidase (GOx) will be immobilized to this amine-reactive NHS ester. Indeed O-PEDOT/GOx can be used as a high selective amperometric biosensor [53]. In the end, we prove that, as for PPy, it is possible to electrogenerate a nanostructured PEDOT film by adding perchlorate ions to the phosphate monomer solution. The film has high specific surface area and has the potential to be further used for various applications, such as biosensors [54-56] or supercapacitors [57-59].

## 2. Experimental

EDOT and  $\text{H}_3\text{PO}_4$  solutions,  $\text{K}_2\text{HPO}_4$ ,  $\text{K}_3\text{PO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ , KOH,  $\text{LiClO}_4$ , KCl,  $\text{Ru}(\text{NH}_3)_6\text{Cl}_2$ ,  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ , N-ethyl-N'(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and N-hydroxysulfosuccinimide (NHS) salts were purchased from Aldrich. All the solutions were prepared with bi-distilled water.



The electrochemical experiments were performed with an Autolab PGSTAT100 (Ecochemie) potentiostat in a classical three-electrode electrochemical cell. A platinum wire was used as a counter electrode and a saturated calomel electrode (SCE) as the reference one. During the electrosynthesis, a double junction was used in order to avoid chloride diffusion into the EDOT solution. The working electrode was either Au or Pt ( $S = 0.07 \text{ cm}^2$ ) (similar results were obtained on both) for electrochemical studies or Au/mica substrate for XPS analyses and SEM observations. The temperature of the EDOT solution was fixed at  $30 \text{ }^\circ\text{C}$  by water bath heating to be sure that the EDOT monomers were totally dissolved without any addition of an organic electrolyte. The initial solution was  $0.2 \text{ M K}_2\text{HPO}_4$  with a pH around 9. The pH of the solutions was adjusted in the range of 3.3 - 11.5 by adding  $\text{H}_3\text{PO}_4$  or KOH to the initial solution ( $\text{H}_3\text{PO}_4$  pKa: 2.15, 7.2, 12.3, see repartition diagram in Figure S1). For the best experimental conditions, tests were done with carbonates ( $\text{H}_2\text{CO}_3$  pKa: 6.4, 10.3) instead of phosphates. The solutions were deaerated by argon bubbling. The EDOT polymerization was conducted under either potentiodynamic or potentiostatic conditions. The potential range of cyclic voltammetry (CV) was from 0.2 to 1.3 V/SCE. For potentiostatic conditions, the applied potential was varied from 0.9 to 1.2 V/SCE. The electrochemical impedance spectroscopy (EIS) experiments were performed at the open circuit potential of the electrolyte containing  $10 \text{ mM K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6 + 0.1 \text{ M KCl}$  or  $3 \text{ mM Ru}(\text{NH}_3)_6\text{Cl}_2/\text{Ru}(\text{NH}_3)_6\text{Cl}_3 + 0.1 \text{ M KCl}$ , from 50 mHz to 70 kHz, with a 10 mV (r.m.s.) ac perturbation.

The scanning electron microscopy (SEM) micrographs were obtained from a field emission gun scanning electron microscope (FEG-SEM), Ultra55 Zeiss, operating at 5 kV.

The chemical composition of the polymers was determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed on a VG ESCALAB 250i-XL spectrometer using

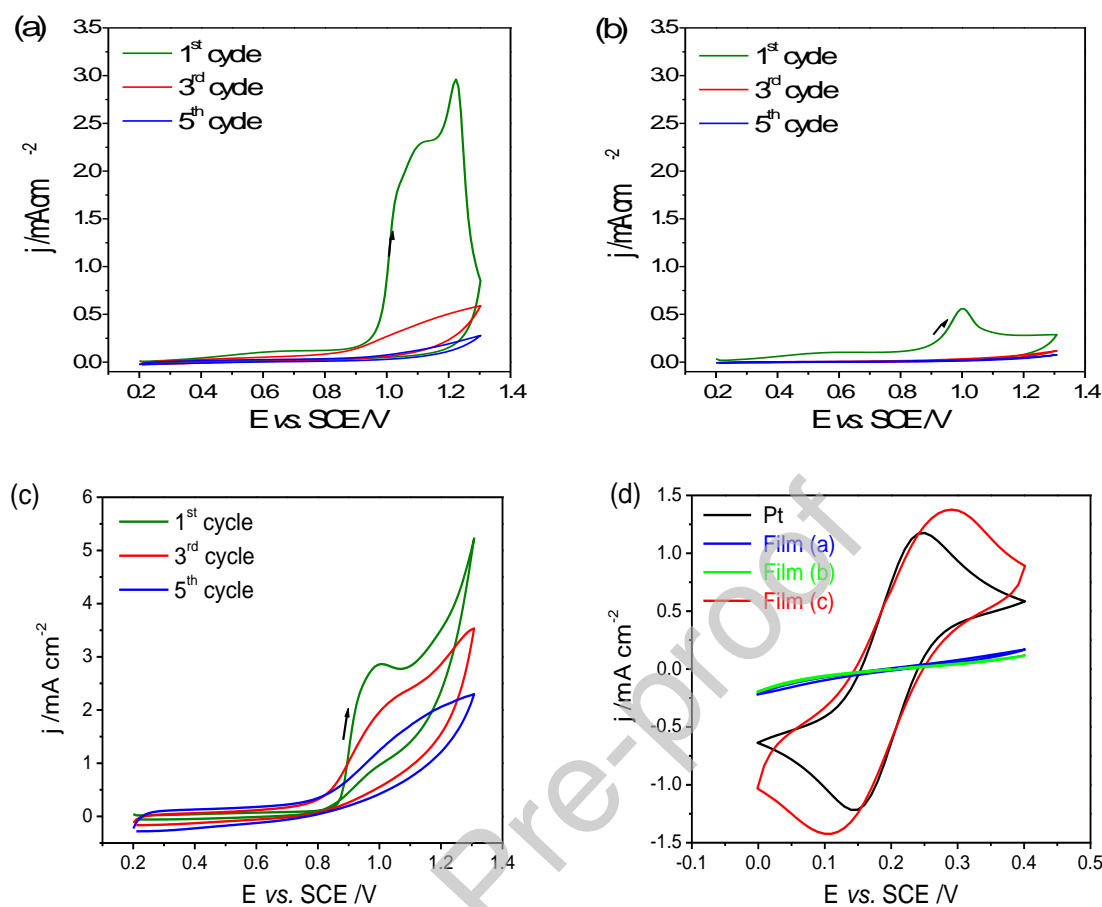
monochromatic Al K $\alpha$  radiation as the X-ray source. Survey and high-resolution spectra were recorded with a pass energy of 100 eV and 20 eV, respectively, in the constant analyzer energy mode. The photoelectron collect angle was 90° with respect to the plane of the sample.

### 3. Results and discussion

#### 3.1 EDOT electropolymerization under potentiodynamic conditions

Firstly, to determine the best potential, EDOT monomers were electrochemically oxidized under potentiodynamic conditions. Figures 1(a) and 1(b) show the CV curves recorded in solution containing 0.011 M EDOT and 0.2 M HPO<sub>4</sub><sup>2-</sup>/PO<sub>4</sub><sup>3-</sup> at pH 9 and 10.5, respectively. From these curves (same scale), it is obvious that the electrolyte pH has an important influence on the process. At pH 10.5, the anodic peak of the first cycle is about six times lower than the one obtained at pH 9. However, in both conditions, the anodic current decreases strongly after the first scan, indicating that the PEDOT film formed is not very conductive. Actually, the anodic current is almost null for the fifth cycle, which implies that non-conductive PEDOT films have been formed, *i.e.* overoxidized films have been deposited onto the metallic electrode. In contrast, in a solution containing 0.011 M EDOT and 0.1 M LiClO<sub>4</sub> whose pH has been adjusted to 10.5, the anodic current keeps increasing with the increase of the applied potential and it is still high after 5 scans (Figure 1(c)). Therefore the high pH of the monomer solution is not responsible for the overoxidation of the PEDOT film during its electrosynthesis. In the absence of weak-acid anions in the monomer solution, EDOT polymerization will be the only reaction regardless of the pH of the solution. These conclusions are well supported by the CV responses of these films in a solution containing Fe(CN)<sub>6</sub><sup>4-/3-</sup> redox probe. Figure 1(d) allows one to compare these responses

to the one obtained at a bare Pt electrode. No anodic and cathodic peaks can be observed in the curves recorded at the electrodes coated with the PEDOT film generated in the presence of phosphate ions (Figures 1(a) and 1(b)). The current recorded at the  $\text{ClO}_4^-$ -doped PEDOT/Pt electrode (Figure 1(c)) is even higher than the one recorded at bare Pt electrode due to the higher surface of the cauliflower structure of PEDOT. The curve obtained for the O-PEDOT film synthesized at pH 10.5 is the flattest. Taking into account this finding and the comparison between Figures 1(a) and 1(b), it is obvious that pH 10.5 is a better condition than pH 9 for preparing an O-PEDOT film. However, during potentiodynamic experiments, polymers are charged and discharged and the growth process is interrupted [60]. Hence, the potentiostatic method was used in the rest of this work, based on Figure 1, the potentials tested were in the range from 0.9 to 1.2 V/SCE.

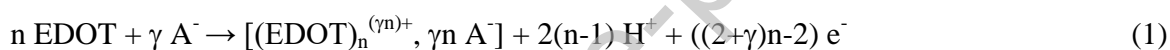


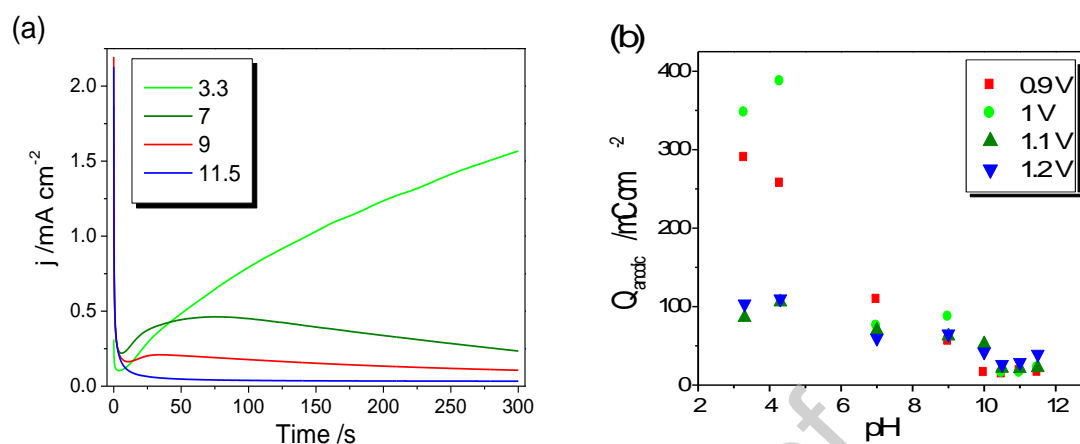
**Figure 1.** Cyclic voltammograms (CV) at a Pt electrode, at  $20 \text{ mV s}^{-1}$ , in solution containing 0.011 M EDOT and (a) 0.2 M  $\text{K}_2\text{HPO}_4/\text{K}_3\text{PO}_4$ , pH 9 ; (b) 0.2 M  $\text{K}_2\text{HPO}_4/\text{K}_3\text{PO}_4$ , pH 10.5 ; (c) 0.1 M  $\text{LiClO}_4$ , pH 10.5. (d) CV responses at a bare Pt electrode and at PEDOT films obtained after synthesis shown in (a), (b) and (c), in 0.01 M  $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6 + 0.1 \text{ M KCl}$  solution.

### 3.2 Influence of the pH of the monomer solution

To study the influence of the pH of the monomer solution, electrosynthesis of PEDOT at different pH were performed under potentiostatic conditions. From Figure 2(a), it is obvious that the anodic current after 300 s of polarization depends on the electrolyte pH. The higher the pH is the lower the final anodic current is. Since the applied potential is fixed, the resistance of the film is higher when the current is lower. In another word, the current value indicates the level of

overoxidation of the PEDOT film. The charges obtained after 300 s of polarization are reported in Figure 2(b). Notice that these charges are due to EDOT oxidation and/or water oxidation. The lowest charges are obtained for pH around 10.5-11, in this pH range whatever the applied potentials tested, the charges are similar. These results are in good agreement with our previous work [35]. The process contains four main reactions. During EDOT electropolymerization (reaction (1))  $H^+$  are released, these ions are captured by the phosphate anions (reaction (2)). When no anions ( $A^-$ ) are available at the electrode/solution interface, reaction (1) can't take place anymore, water oxidation occurs and hydroxyl radicals are generated (reaction (3)) due to the relatively high applied potential and pH of solution, these radicals react with the polymer initially formed leading to its overoxidation (reaction (4)).



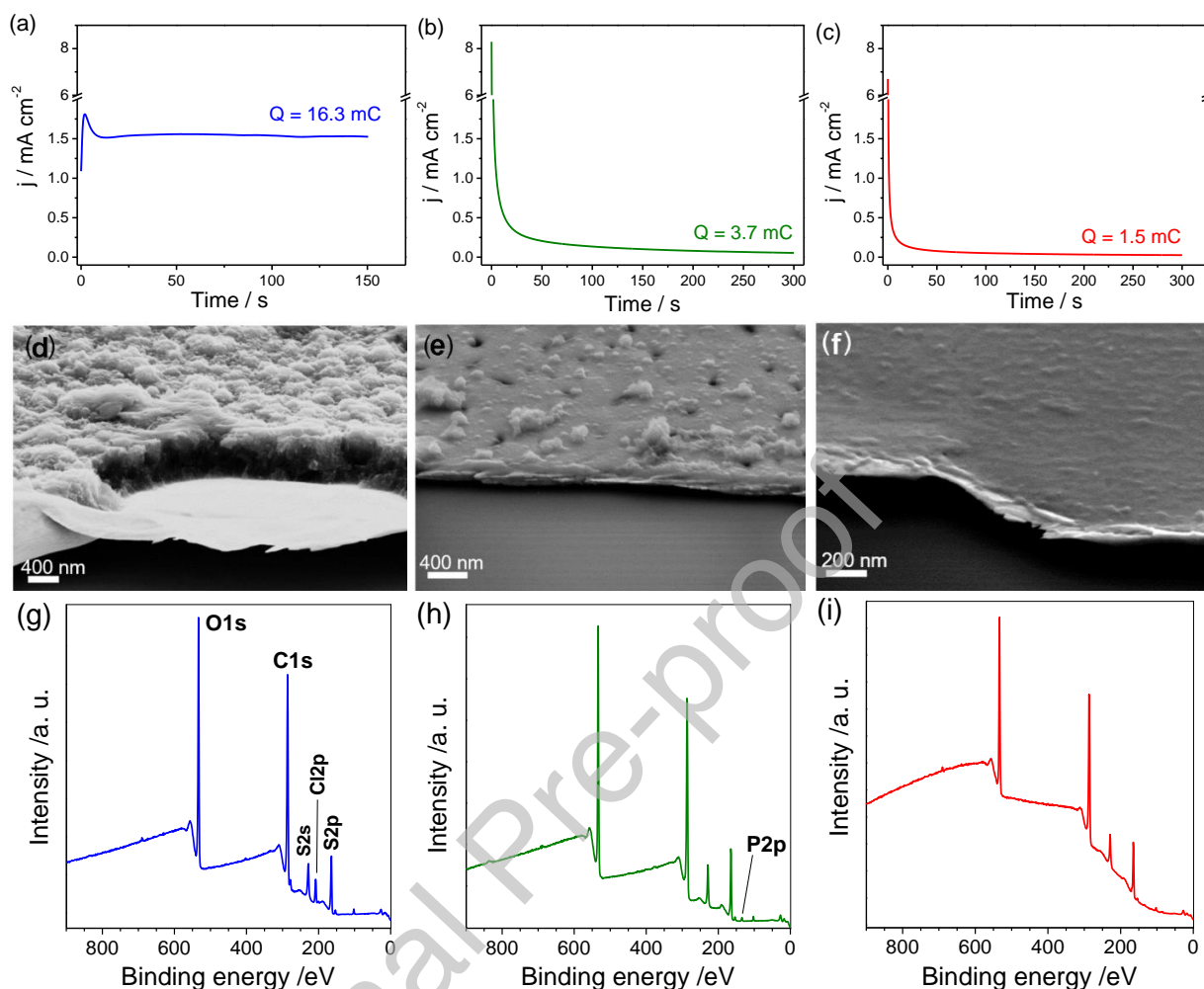


**Figure 2.** (a) Current density vs. time at a Au electrode polarized at 0.9 V/SCE, in electrolyte of pH 3.3, 7, 9 and 11.5. (b) Anodic charge vs. pH after 300 s of polarization of a Au electrode at different potentials in 0.011 M EDOT + 0.2 M  $\text{H}_3\text{PO}_4/\text{KH}_2\text{PO}_4$  or  $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$  or  $\text{K}_2\text{HPO}_4/\text{K}_3\text{PO}_4$  solution.

To confirm the influence of the pH on the morphology and chemical composition of the films, SEM observations and film characterization by XPS were performed. A classical PEDOT film and two overoxidized PEDOT films at pH 9 and pH 10.5 were prepared (Figure 3 (a)-(c)), named PEDOT- $\text{ClO}_4$ , O-PEDOT-9 and O-PEDOT-10.5, respectively. PEDOT- $\text{ClO}_4$  film was electrogenerated at 0.9 V/SCE for 150 s in 0.011 M EDOT + 0.1 M  $\text{LiClO}_4$  aqueous solution. O-PEDOT-9 and O-PEDOT-10.5 films were electrogenerated at 1.1 V/SCE for 300 s in 0.011 M EDOT + 0.2 M  $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$  aqueous solution at pH 9 and pH 10.5, respectively. As shown in Figure 3(a), for the PEDOT- $\text{ClO}_4$  film during its synthesis the anodic current is stable and has a high value (about 1.5  $\text{mA cm}^{-2}$ ) due to the good conductivity of this PEDOT film. In this condition a film having a classical cauliflower-like structure with a thickness around 600 nm is obtained (Figure 3(d)). On the other hand, two thin films were observed for the O-PEDOT films (Figures 3(e) and 3(f)) having a thickness around 75 nm and 15 nm, for films in the solution of

pH 9 and 10.5, respectively. The thickness of these films is in good agreement with the low anodic charge recorded during their synthesis, as shown in Figure 3 (b)(c). However, compared to the smooth surface of the O-PEDOT-10.5 film, some nanoparticles can be observed on the O-PEDOT-9 film surface (Figure 3(e)). The different anodic charges and morphologies of films between PEDOT-ClO<sub>4</sub>, and O-PEDOT-9 and O-PEDOT-10.5 are due to the overoxidation of the PEDOT film formed at the very beginning of the synthesis. The non-conductivity of the O-PEDOT prevents further monomer oxidation and therefore the thickness of the O-PEDOT film remains very low because it does not grow with time. The low current detected is due to water oxidation, at the electrode/film interface, instead of EDOT oxidation.

The XPS survey spectra of these samples are shown in Figures 3(g), 3(h) and 3(i). In all cases, C1s, O1s and S2p photo-peaks are detected. Besides, Cl2p and P2p contributions are visible in the survey spectrum of PEDOT-ClO<sub>4</sub> and O-PEDOT-9, respectively. It means that PEDOT-ClO<sub>4</sub> and O-PEDOT-9 are doped with anions (perchlorate and phosphate, respectively) while O-PEDOT-10.5 doesn't contain any phosphate anymore. C1s and S2p high-resolution spectra of O-PEDOT-9 and O-PEDOT-10.5 are similar (Figure S2). For the C1s photo-peak a new contribution around 288.5 eV is detected, it is ascribed to carbonyl or carboxyl groups. For the S2p spectra, a new contribution at high binding energy, around 168 eV, is also detected, which is ascribed to sulfone groups. These peaks which are not detected for the PEDOT-ClO<sub>4</sub> sample, confirm that the films obtained in phosphate monomer solution are overoxidized, likely the C of the ethylenedioxy functional group are oxidized. What's more, among these three films, only the baseline of the survey spectrum of O-PEDOT-10.5 is very high, which is characteristic of the non-conductive electrical property of the film. Therefore, O-PEDOT-9 is only partially overoxidized and O-PEDOT-10.5 is totally overoxidized. A non-conductive

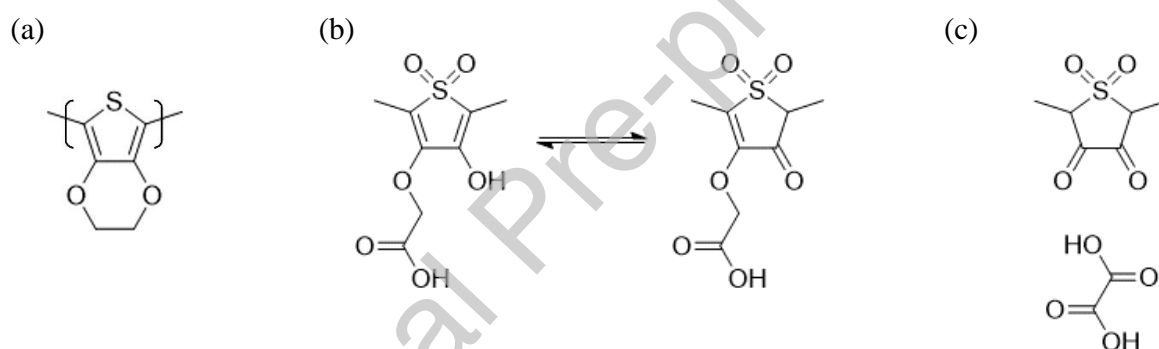


**Figure 3.** Current density vs. polarization time recorded during synthesis, SEM micrographs of the cross section and XPS survey of (a)(d)(g) PEDOT-ClO<sub>4</sub> film electrogenerated at 0.9 V/SCE for 150 s in 0.011 M EDOT + 0.1 M LiClO<sub>4</sub> aqueous solution; (b)(e)(h) O-PEDOT-9 film electrogenerated at 1.1 V/SCE for 300 s in 0.011 M EDOT + 0.2 M HPO<sub>4</sub><sup>2-</sup>/PO<sub>4</sub><sup>3-</sup> aqueous solution at pH 9; (c)(f)(i) O-PEDOT-10.5 film electrogenerated on Au/mica at 1.1 V/SCE for 300 s in 0.011 M EDOT + 0.2 M HPO<sub>4</sub><sup>2-</sup>/PO<sub>4</sub><sup>3-</sup> aqueous solution at pH 10.5. Tilt: 60°. (a)-(c): Au electrode. (d)-(i): Au/mica electrode.

polymer is obtained at pH 10.5, the doping anions are no more present in it, some C and S atoms are oxidized and the double bonds are no more conjugated.



However, it is difficult to discriminate between the presence of carbonyl or carboxyl groups from XPS analysis. It has been reported that ester groups are observed after PEDOT overoxidation [17]. But ester groups are not stable in alkaline solution. Therefore, we believe that the cleavage of ester groups leads to a carboxyl group. In this condition, a hydroxyl group is attached to one end of the alkene double bond which is also not stable. So enol and its isomer ketone both exist (Figure 4(b)). Combining the mechanism of overoxidation of thiophene [61], we propose a possible final product of PEDOT overoxidation, as shown in Figure 4(b), and the loss of carbon (under oxalic acid form) may come from double cleavage (Figure 4(c)), which happens to a small amount of EDOT.



**Figure 4.** Structures of (a) PEDOT; (b) and (c) possible final products after overoxidation.

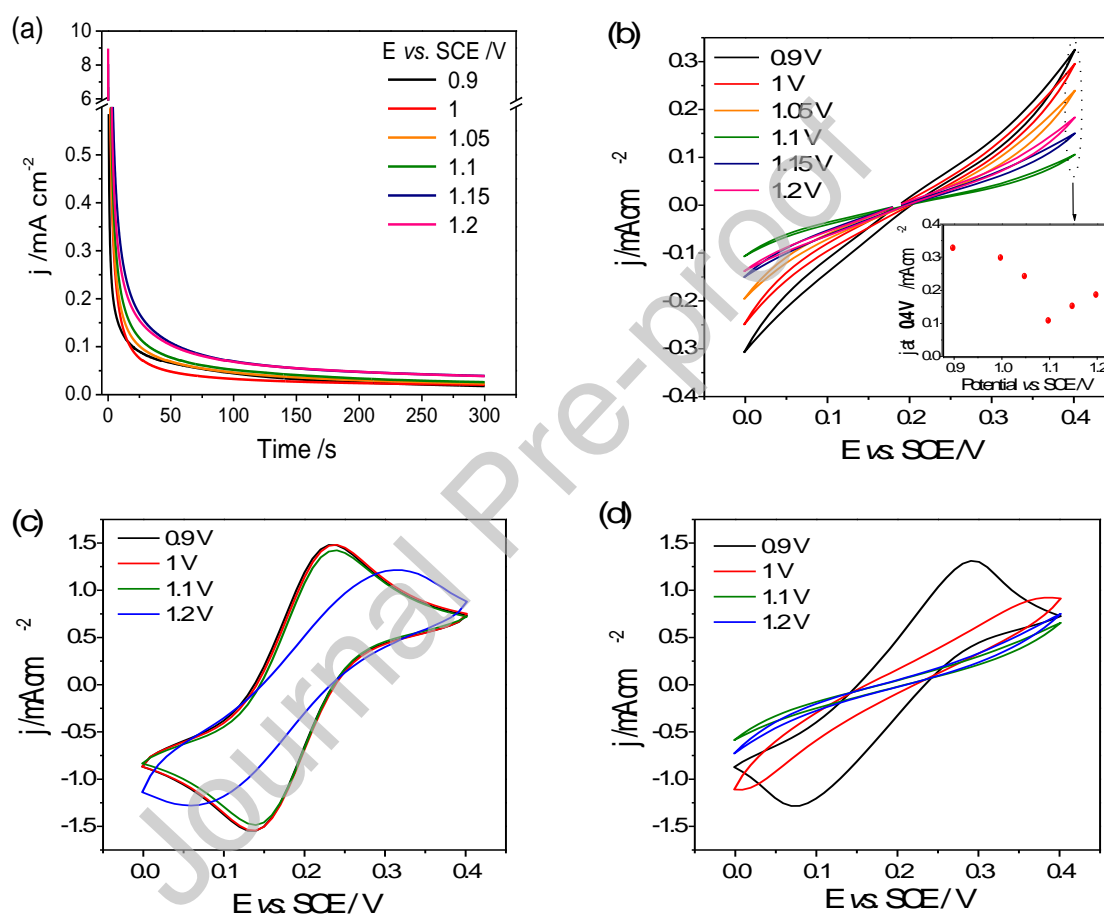
To further confirm the existence of carboxyl groups we used EDC and NHS to activate these groups. O-PEDOT film was prepared at 1.1 V/SCE for 300 s in 0.011 M EDOT + 0.2 M  $K_2HPO_4/K_3PO_4$  solution at pH 10.5. It was then immersed in a phosphate buffer solution (pH 7.4) that contains 30 mM of EDC and 90 mM of NHS for 1 h [50]. Then the O-PEDOT/EDC/NHS film was rinsed by water. XPS was employed to detect if NHS has successfully activated the carboxyl groups. As shown in Figure S3, N1s photo-peak is detected in the survey spectrum which indicates the presence of amine-reactive NHS ester and confirms the presence of some carboxyl groups at the surface of the O-PEDOT film. In the future, glucose oxidase enzymes will

be immobilized onto the O-PEDOT film in order to obtain a high selective amperometric glucose biosensor, via the detection of  $\text{H}_2\text{O}_2$  [34].

### 3.3 Influence of the applied potential

As a further step, the influence of the potential imposed during the polymer synthesis was studied. Experiments were performed under different potentials from 0.9 to 1.2 V/SCE at pH 10.5. As one can notice in Figure 5(a), the shape of  $j(t)$  curves is the same whatever the applied potential. The current densities are high at the very beginning then they decrease rapidly in the first 20 seconds and then remain stable at a very low value. The charges increase slightly with the increase of the applied potential, they are in the range of 14-30  $\text{mC cm}^{-2}$ . Electrochemical characterizations of these films were carried out by CV and EIS in 0.1 M KCl solution containing the  $\text{Fe}(\text{CN})_6^{4-/3-}$  or  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  redox probe. In the presence of  $\text{Fe}(\text{CN})_6^{4-/3-}$ , all the voltammograms depicted in Figure 5(b) are flat. The current densities are lower than  $0.3 \text{ mA cm}^{-2}$  and the oxidation and reduction of the redox probe hardly even occur, indicating on the one hand that the films are non-conductive and on the other hand that they are pinhole-free since the redox species could not cross the film to reach the metal electrode. The lowest current (green line in Figure 5(b)) is obtained for the film synthesized at 1.1 V/SCE (see inset of Figure 5(b)). In contrast, Figures 5(c) and 5(d) show the CV responses of a PEDOT film prepared in  $\text{LiClO}_4$  solution and 0.2 M  $\text{K}_2\text{HPO}_4/\text{K}_3\text{PO}_4$  solution at pH 9, respectively. In Figure 5(c), the response of the film synthesized at 1.2 V is flatter than the other, likely due to partial overoxidation of the film. The curves of the films synthesized at 0.9, 1.0 and 1.1 V/SCE are similar to the response of a bare Au electrode, which means these films are conductive. From Figure 5(d), it is obvious that for a monomer solution of pH 9 the influence of film synthesis potential is high. Although the

lowest response is also obtained at 1.1 V/SCE, the current density is higher than for the films prepared at pH 10.5 (Figure 5(b)). Figure S4 shows the  $j(t)$  curves recorded during the electrosynthesis in these two conditions. All the anodic charges obtained for the three conditions are reported in Table S2. At pH 10.5, the charge slightly increases with the increase of applied potential.



**Figure 5.** (a) Current density vs. time at a Au electrode polarized at different potentials in 0.011 M EDOT + 0.2 M K<sub>2</sub>HPO<sub>4</sub>/K<sub>3</sub>PO<sub>4</sub> solution at pH 10.5. Cyclic voltammograms in 0.01 M Fe(CN)<sub>6</sub><sup>4-/3-</sup> + 0.1 M KCl solution, at 20 mV s<sup>-1</sup>, of PEDOT coated Au electrodes at different potentials in (b) 0.011 M EDOT + 0.2 M K<sub>2</sub>HPO<sub>4</sub>/K<sub>3</sub>PO<sub>4</sub> solution at pH 10.5, (c) 0.011 M EDOT + 0.1 M LiClO<sub>4</sub> solution; (d) 0.011 M EDOT + 0.2 M K<sub>2</sub>HPO<sub>4</sub>/K<sub>3</sub>PO<sub>4</sub> solution at pH 9. Inset: Current density at 0.4 V vs. SCE in function of the applied potential used for the PEDOT film synthesis.

As indicated previously, the total anodic charge is due to monomer oxidation and to water oxidation. To estimate each contribution, we performed the experiments in the same electrolyte without EDOT monomer. Obviously in this case only water oxidation takes place. The anodic charges due to water oxidation after 300 s of electrode polarization at various potentials are shown by curve (a) in Figure S5 while curve (b) shows the charges obtained in the same electrolyte but in the presence of EDOT. The difference between (a) and (b) at 0.9, 1, 1.1 V/SCE are 10.4, 9.1 and 8.7 mC cm<sup>-2</sup>, respectively. At 1.1 V/SCE, in the presence of EDOT, the charge is higher while the part due to water oxidation seems lower, which is in agreement with the fact that the CV of the film synthesized at 1.1 V/SCE is flatter than for the other potentials (Figure 5(b)). As at 1.2 V/SCE, the charge is lower than water oxidation because strong water oxidation leads to much more OH• radicals (reaction (3)) and these radicals react with themselves producing H<sub>2</sub>O<sub>2</sub> (reaction (5)) instead of reacting with the PEDOT film (reaction (4)). The formation of PEDOT film also leads to a decrease of water oxidation. Curve (c) in Figure S5 shows the charges at an O-PEDOT-coated Au electrode in 0.2 M K<sub>2</sub>HPO<sub>4</sub>/K<sub>3</sub>PO<sub>4</sub> solution. In this condition, the anodic charges are due to water oxidation. Water molecules could diffuse through the O-PEDOT film to be oxidized at the Au electrode. Obviously, the anodic charges are lower when the electrode is coated with the O-PEDOT film, confirming that this film is non-conductive, water oxidation is limited by the diffusion of the solvent molecules through the O-PEDOT film.



To confirm these findings, electrochemical impedance spectroscopy experiments were performed at open circuit potential in Fe(CN)<sub>6</sub><sup>4-/3-</sup> solution. Nyquist diagrams (Figure 6(a)) show slightly depressed semicircles, the amplitude of which varying with the potential applied for the film

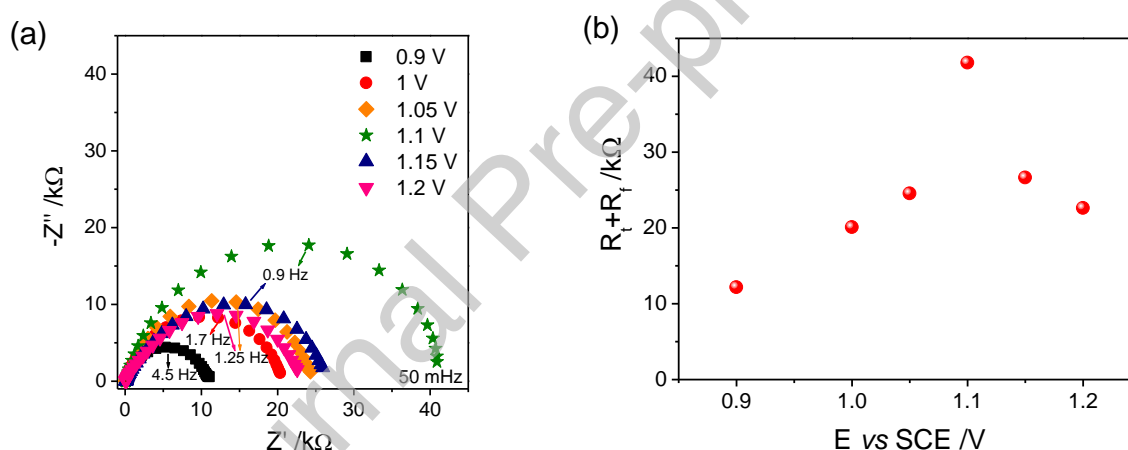
synthesis. The frequency dependence of the phase points out there is a distribution of time constants. They can be expected to arise from the polymeric film and the charge transfer impedance responses. The measured impedance can be numerically represented using the electrical equivalent circuit depicted in Figure S6. The film impedance, approximated by a CPE element ( $Q_f, n$ ), lies in parallel with the charge transfer impedance. The latter is constituted by the charge transfer resistance  $R_t$  in parallel with the double layer capacitance  $C_{dl}$ , this circuit being in series with a resistance  $R_f$  accounting for the ohmic drop across the PEDOT film. These elements are in series with the electrolyte resistance  $R_s$  and a self  $L$  accounting for the phase lag at high frequencies due to the electrical wires. The fitting procedure was performed using the ZsimpWin software demonstrating the validity of the proposed equivalent circuit. The fitting Nyquist diagrams of the films electrogenerated at various potentials are shown in Figure S7 and the fitted parameters are given in Table S3. The main capacitance loop centred around a few Hz arises from the parallel combination of the global resistance,  $R = R_t + R_f$ , and the film impedance represented by the CPE element. The apparent diameter of the Nyquist diagrams is clearly determined by the global resistance, the highest  $R$  value is obtained for the film formed at 1.1 V/SCE (see Figure 6(b)). In this condition,  $R_f$  is about 10 k $\Omega$  (Table S3). Taking  $\delta$  the film thickness ( $\approx 15$  nm, Figure 3(c)) and  $S$  the electrode surface ( $0.07$  cm<sup>2</sup>), the electrical conductivity of the film,  $\sigma = \delta/SR_f$ , is around  $2.1 \cdot 10^{-9}$  S cm<sup>-1</sup> that is a value characteristic of a non-conductive material.

Additional information can be gained from analysing the film impedance. The CPE behaviour has been explained by assuming a gradient of resistivity across the film since the overoxidation is due to  $\text{OH}^\bullet$  radicals produced at the electrode/film interface. According to [62], assuming the dielectric properties to be homogeneous and a power law for the variations of the resistivity

across the film, it is possible to estimate the resistivity domain ( $\rho_\delta$ ,  $\rho_0$ ) covered by the O-PEDOT films between the two interfaces. Taking  $\epsilon$  the dielectric permittivity of the film ( $\approx 8$  [63]),  $\rho_\delta$  and  $\rho_0$  are given by the following expressions:

$$Q = \frac{(\epsilon\epsilon_0)^n S}{g\delta(\rho_\delta)^{1-n}} \text{ and } Z(\omega = 0) \approx R = \frac{g\rho_0^n \rho_\delta^{1-n} \delta}{S}$$

where the quantity  $g$  is given by the expression :  $g = 1 + 2.88(1-n)^{2.375}$  according to reference [62]. The calculated values of  $\rho_\delta$  and  $\rho_0$  are given in Table S3, showing that the highest  $\rho_0$  resistivity value is obtained for the film formed at 1.1 V/SCE.



**Figure 6.** (a) Nyquist plots of PEDOT coated Au electrodes ( $j(E)$  curves are shown in Figure 5(b)) in 0.01 M  $K_4Fe(CN)_6 / K_3Fe(CN)_6 + 0.1$  M KCl solution, (b) Resistance vs. potential imposed during the film synthesis.

To confirm that the O-PEDOT-10.5 film is really pinhole free *i.e.* that in the presence of  $Fe(CN)_6^{4-/3-}$  the absence of current is not due to the rejection of anions, a cationic redox probe was used. Similar results were obtained *i.e.* a flat CV response was obtained in an electrolyte

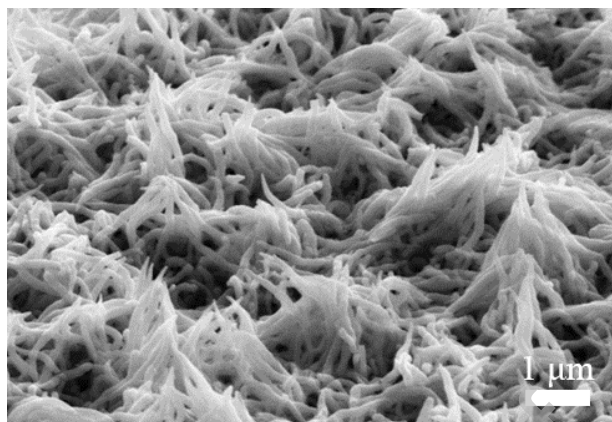
containing  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  and a Nyquist diagram showing a very large semicircle with a diameter, corresponding to  $R=R_t + R_f$ , about  $64 \text{ k}\Omega$  was obtained (see Figure S8).

Moreover, to confirm that the nature of the weak-acid anion does not influence the process, carbonates were used instead of phosphates. The film obtained at pH 10.5, after 300 s of polarization at 1.1 V/SCE, has the same characteristics as the film obtained in the presence of phosphate (see figure S9).

### 3.4 Electrosynthesis of PEDOT nanowires

In the end, to extend the application of O-PEDOT, we successfully obtained PEDOT nanowires by adding 0.75 mM  $\text{LiClO}_4$  to the monomer phosphate solution (Figure 7). The electrosynthesis was performed by applying a single potential. During water oxidation,  $\text{OH}^\bullet$  and  $\text{H}_2\text{O}_2$  are produced. Some  $\text{H}_2\text{O}_2$  molecules are oxidized leading to the formation of  $\text{O}_2$  (reaction (6)) during the EDOT polymerization.



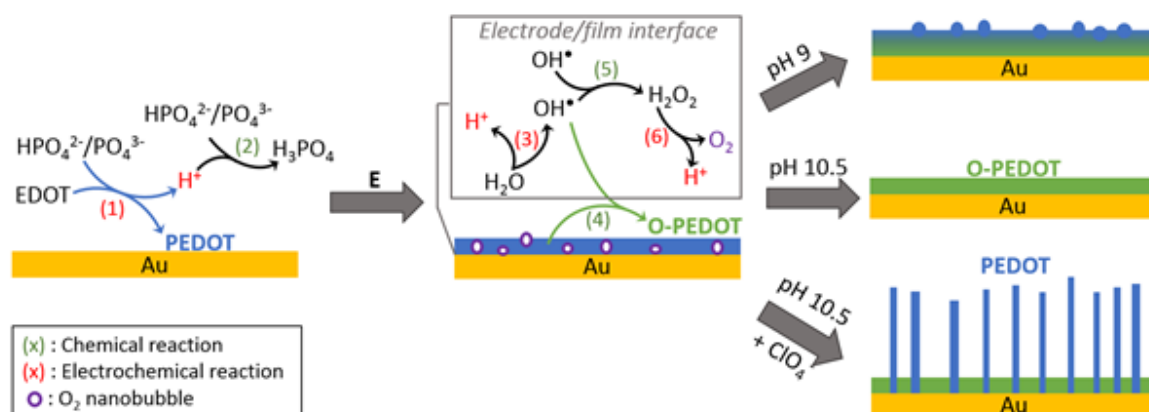


**Figure 7.** SEM micrograph of a PEDOT film electrosynthesized at 1.1 V/SCE for 300 s in 0.011 M EDOT + 0.2 M  $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$  + 0.75 mM  $\text{LiClO}_4$  solution at pH 10.5 solution. Tilt 60°.

Because  $\text{O}_2$  is generated inside the polymeric film, the growth of the bubbles is very limited and therefore their size is at the nanoscale. The  $\text{O}_2$  bubbles protected some parts of the PEDOT film from overoxidation. When anions are again present at the interface due to the diffusion, the monomer oxidation continues at the parts previously protected by the  $\text{O}_2$  bubbles and leads to nanowires. The schematic model of this process and the process of film overoxidation at pH 9 and pH 10.5 are shown in Figure 8. The film with nanowires has a large specific surface area indicating that it can be used for supercapacitors and biosensors after functionalization by enzymes, for example, glucose oxidase.

This nanostructured film is conductive since the anodic current is always high during the synthesis and the electrochemical response of the film in  $\text{Fe}(\text{CN})_6^{3-/4-}$  solution is well observed by CV and EIS (see Figure S10).





**Figure 8.** Schematic model of PEDOT overoxidation and the growth of nanostructure under polarization.

#### 4. Conclusions

Non-conductive and ultrathin O-PEDOT films were prepared by one-pot electrosynthesis in an aqueous solution containing EDOT monomer and only phosphates or carbonates as anions. This method is simple and environmentally friendly. By potentiostatic method, the film overoxidation occurs at pH 10.5, the doping anions are expelled from the polymer electrogenerated at the very beginning of the process. Some C and S atoms are oxidized to carboxyl and sulfone, respectively, leading to disruption of the chain conjugation and therefore to the non-conductive property of the film. The influence of the applied potential has also been studied. At pH 10.5, all the potentials from 0.9 V to 1.2 V/SCE lead to the synthesis of an overoxidized PEDOT film. Indeed in the presence of a redox probe, very low currents are detected by CV and slightly depressed semicircles are obtained in Nyquist diagrams. The film prepared at 1.1 V/SCE shows the lowest redox response and the highest resistance, it means it has the lowest conductivity ( $2.1 \cdot 10^{-9} \text{ S}\cdot\text{cm}^{-1}$ ). Some enzymes such as glucose oxidase could be immobilized onto this film in order to develop a selective amperometric  $\text{H}_2\text{O}_2$  biosensor. In the end, PEDOT films with conductive

nanostructures were obtained by the same method simply by adding perchlorate ions in the monomer solution. This result extends the prospect of the one-pot electrosynthesis method and the nanostructured PEDOT has great potential for various applications such as supercapacitors due to the very high specific surface area of the PEDOT film.

Journal Pre-proof

## **CREDIT AUTHOR STATEMENT**

**Dantong Wang:** Investigation, Visualization, Writing – Original Draft

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**Hubert Cachet:** Formal analysis

**Catherine Debiemme-Chouvy:** Conceptualization, Supervision, Validation, Writing – Review  
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## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Graphical abstract

