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Electrosynthesis and Characterization of Poly(3,4-ethylenedioxythiophene) Nanowires

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Using the methodology previously reported for the obtaining of polythiophene by electrochemical methods, on a silica template modified Pt electrode, that tunes the growth into its pores confined space, in the current paper poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires, also obtained directly on the electrode surface, were prepared. The Pt electrode was first modified by potentiostatic deposition of a thin layer of PEDOT. Upon this modified electrode a porous silica film was electrodeposited to serve as template for polymeric nanowires preparation. The modification to the previously reported methodology for polythiophene consists just in the pre-coating of a PEDOT thin film on the bare Pt. Thus, it has been successfully confirmed the validity and usefulness of the proposed methodology, obtaining PEDOT nanowires of diameters between 3 and 7 nm. It was also verified an innovative strategy to establish the time required for the deposit growth takes place only into the template confined space, without exceeding the length of the pore, providing thus a route that allows obtaining polymeric nanowires using solely electrochemical methods, with the advantages that the structures with this type of morphology present and, in addition, deposited directly on the electrode, result that has been achieved so far only with metal deposits.

Keywords: poly(3,4-ethylenedioxythiophene), electropolymerization, template, modified electrodes, electrosynthesis of nanowires, poly(3,4-ethylenedioxythiophene) nanowires.

1. INTRODUCTION

The discovery of conducting polymers (CP) marked the start of the numerous studies this type of materials, due to their unique combination of mechanical, optical and electronic properties [1], have been subject to, which has allowed the CPs to be employed in many applications [2-4]. Among these, polythiophene and its derivatives, such as poly(3,4-ethylenedioxythiophene), PEDOT, have received much attention because, besides the abovementioned properties, they also possess a high chemical stability: thiophene functionalization at positions 3- and 4- removes problems associated with crosslinking, solubility, environmental stability and also reduces monomer oxidation potential [5-7] and, in addition, prevents bonds formation at those positions since, opposite to thiophene, α- and α'-sites on the ring are not free. Thanks to its outstanding properties PEDOT has become commonplace in almost all applications wherein CPs are employed, *e.g.* light emitting diodes, solar cells, electrodes material, electrochemical sensors, etc. [8-13].

The remarkable advances in the synthesis and interdisciplinary research in the field of nanoscience have also reached the CPs, stimulated by the properties of nanostructures, since the quantum confinement of electrons when the size is reduced to the nanoscale, improves the properties or new properties emerge [14, 15]. One-dimensional nanostructures, *e.g.* carbon nanotubes or CP nanotubes/nanowires, among others, have attracted a great deal of attention in the last two decades due to their importance both in the field of fundamental research and for their potential applications in nanoscale devices [16, 17] since, in general, they have shown better performance in applications where they have been used, as compared to the respective films [18, 19].

Thus, many synthesis strategies have been developed, such as self-assembly, electrospinning, template directed, template-free methods [20] and solution techniques, among others, for the fabrication of various kinds of one-dimensional nanostructures, including metals, semiconductors, polymers and composites [15]. Although progress has been made in this field, the methodology employing a template to guide the growth of the electrodeposited material remains very popular [21], because it is a simple approach for polymer nanostructures obtaining. In this case, the material growth occurs within a porous membrane with a defined size. This process was initiated by Martin [22] and is based on filling the porous membrane with a monomer, polymerizing chemically the monomer within the pores of the template and, finally, removing the template with suitable solvents, in order to obtain just the polymer. The diameter of the obtained nanostructure is controlled by the size of the pores or channels of the template, whereas the length and thickness are often regulated by the polymerization time.

Polymeric nanostructures can be synthesized by chemical or electrochemical means. So far the electrochemical approach allows better quality control of the obtained material, by adjusting the electrosynthesis parameters, and also this pathway allows the production, in a single step process, a wide variety of nanostructures [20, 21, 23], *e.g.* nanowires, microcontainers, nanonets, nanosheets, among others, as compiled in the extensive available bibliography [24, 25].

Furthermore, it has been corroborated that a strong relationship between synthesis parameters and morphology of the obtained polymers exists, as the result of changes in the mechanism of nucleation and growth during the electro-polymerization process [26-28].

From this background and based on the gathered experience [29, 30], in the current work obtaining of PEDOT nanowires directly on the electrode surface is proposed. Nevertheless, prior to template deposition, a thin film of the same PEDOT polymer is coated to promote its adhesion onto the electrode surface, while eliminating the influence of the electrode substrate. In other words, the investigation aims to improve the proposed methodology. In addition, determination of the nucleation and growth mechanism, NGM, will be tried to provide a technique that enables, virtually *in situ*, establishing when the template pores are filled, in order to control the electrolysis time and prevent the polymer continues to grow outside the pores confined space.

2. EXPERIMENTAL

Electrochemical techniques were conducted on a CH*Instruments* potentiostat coupled to a computer with the appropriate software to control the experimental conditions and data acquisition. 3,4-ethylenedioxythiophene (EDOT), tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and anhydrous acetonitrile, were purchased from Aldrich and used as received. Anchor type three-compartment electrochemical cells were employed. A 0.03 cm^2 geometric area Pt disks was the working electrode (in the case of direct deposition on Pt, reported current densities are related to this area and to the corrected area when deposited on template, as will be discussed later); a platinum wire coil of large area was the auxiliary electrode. An Ag|AgCl in tetramethylammonium chloride solution, whose concentration is adjusted so that the system matches the potential of the saturated calomel electrode (SCE) at room temperature (20 °C), was used as reference electrode [31]. At least otherwise stated, all potentials quoted in the current work are referred to this electrode.

Previous to each experiment, the Pt working electrode was polished to a mirror-like using a 0.3 μm alumina slurry on a felt pad. Prior to use, the work solutions were thoroughly deareated with high purity argon and then kept under an argon blanket over the rest of the experiment. The first step of Pt electrode modification was potentiostatic deposition of a PEDOT thin layer (1.420 V for 5 s). Upon this modified electrode (Pt|EDOT), a porous silicon oxide film was electrodeposited ($Pt|PEDOT|(SiO_2)_n$), following the methodology proposed by Walcarius [32], at a fixed potential of -1.2 V for 4 s. This layer will serve as template for the subsequent preparation of the polymer nanowires, according to methodology previously reported by us for polythiophene [19, 29]. This methodology is schematically depicted in Fig. 1, where it can be seen that the modification to the previously reported method involves the coating of a CP thin film.

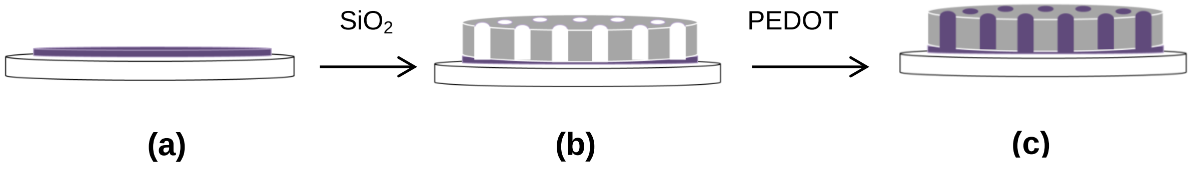

Figure 1. Schematic representation of PEDOT nanowires electrosynthesis: (a) modification of the Pt disc electrode with thin film of PEDOT; (b) SiO_2 template electrodeposit; (c) PEDOT electrosynthesis within template pores confined spaces.

The permeability of the template modified electrodes was assessed by analyzing their voltammetric response in 1.24 $mmol \cdot L^{-1}$ ferrocene solution, using 0.1 $mol \cdot L^{-1}$ tetrabutylammonium hexafluorophosphate as supporting electrolyte, in acetonitrile, within a potential window 0.3-0.8 V at 50 $mV \cdot s^{-1}$, until a stable profile is attained. The results are subsequently compared with the response of the PEDOT modified electrode, under identical working conditions, but template-free. Thus, the ferrocene|ferrocenium redox couple allows the electrode area to be estimated and, therefore, the reported current densities to be calculated. To this purpose, the Randles-Sevcik equation [33] was utilized considering the previously reported diffusion coefficient ($2.3\cdot10^{-5}$ $cm^2\cdot s^{-1}$) [34, 35] whereby 0.038 cm^2 for the Pt disk and 0.012 cm^2 for the template modified electrode were found.

Extra pure HF (Aldrich)-H_2O mixture 50:50 (v/v) was tested (using Teflon labware) for template removal. The array is immersed into the mixture during variable times, after which it was washed with double-distilled water and acetonitrile.

Characterization by transmission electron microscopy, TEM, was performed on a JEOL/JEM 1200 EX II electron microscope at an accelerating voltage of 120 kV. To this end, the polymeric deposits are mechanically removed from the electrode surface and dispersed over copper grids.

3. RESULTS AND DISCUSSION

Optimum working potential for PEDOT nanowires electrosynthesis was previously established by cyclic voltammetry between -1.5 and 1.5 V, by varying initial concentration, number of voltammetric cycles, potential scan rate, etc. It was thus determined that under the described conditions, the response was more stable at low potential sweep rate. Hence, deposition, was accomplished at 10 $mV\cdot s^{-1}$ on both Pt|PEDOT and Pt|PEDOT|$(SiO_2)_n$ electrodes to select, from those voltammetric profiles, the potential to be employed in the potentiostatic approach.

In Fig. 2, the growth profile occurring during the electro-oxidation on these electrodes is shown. It is demonstrated that, for the same number of voltammetric cycles, much higher currents are obtained when working on template modified electrodes; this is in agreement with the formation of nanostructured architectures, adopted by the polymer deposit whose growth takes place into the confined space of the SiO_2 template pores.

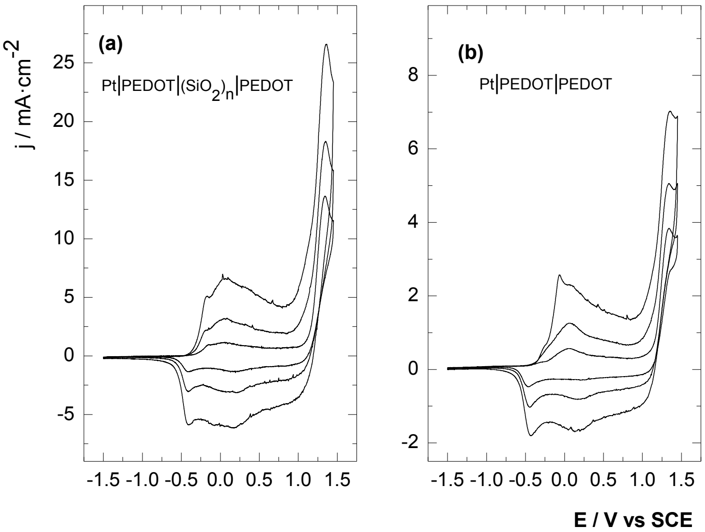

Figure 2. Voltammetric profile of 0.01 $mol\cdot L^{-1}$ EDOT + 0.1 $mol\cdot L^{-1}$ $TBAPF_6$ in anhydrous CH_3CN at $v = 10$ $mV\cdot s^{-1}$ upon: (a) Pt|PEDOT|$(SiO_2)_n$; (b) Pt|PEDOT.

The voltammetric profile shows between -1.5 and 1.2 V the region corresponding to the doping/undoping process and between 1.2 and 1.5 V the region of monomer oxidation, which agrees with previously reported work [36].

The optimum potential for potentiostatic electrosynthesis was found to be 1.42 V, therefore a study was carried out by applying this potential during different times, both on silica template and template-free electrodes. Doing so, the optimal time for nanostructures, without exceeding the space defined by the template, is sought. By way of example, in Fig. 3 transients recorded under identical working conditions for 50 s of electrolysis on both types of modified electrodes (Pt|PEDOT and Pt|PEDOT|$(SiO_2)_n$), are shown. The obtained results are always compared.

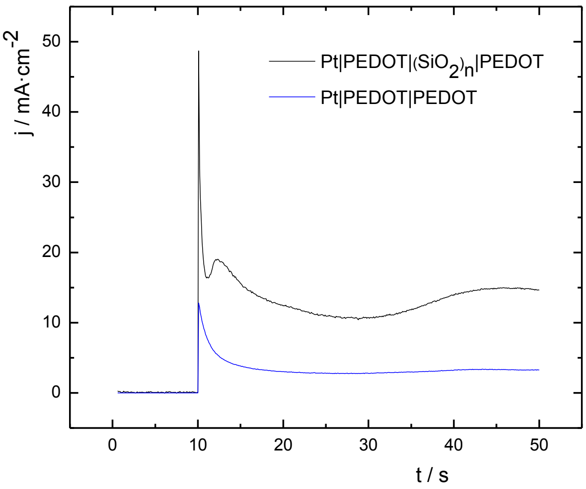

Figure 3. j/t transients recorded during electropolymerization of a 0.01 mol·L^{-1} EDOT + 0.1 mol·L^{-1} $TBAPF_6$ in anhydrous CH_3CN at 1.420 V.

In all cases, the transients show profiles in accordance with CP formation [37] with higher currents recorded on template modified electrodes. Furthermore, clear differences in profile growth, especially in the early seconds of electropolymerization, is evident and has been ascribed to the confined growth within the template pores. As observed in Fig. 3, when PEDOT is electrodeposited on an electrode surface previously modified with a polymer film and SiO_2 template, the exponential current increase occurs after just 1.2 s, which would account for the growth of the polymer within the template pores confined space. This result will be confirmed later through the respective NGM.

Fig. 4 shows the voltammetric response of polymers deposited on modified electrodes, differentiating potential regions within which *p*- and *n*-type doping/undoping processes, characteristic of this polymer, appear. These doping processes involve CP charging due to the corresponding charge-transfer reactions that result in partial oxidation or reduction of the polymer, causing changes in the electronic properties of the material [37, 38]. Clearly, electrochemistry is very useful to conduct and study these processes, being widely used, because allows accomplishing them in a highly controllable and reproducible manner, while the charge transfer can be monitored and regulated. The processes depicted in Fig. 4 indicate that both *p*- and *n*-doping are favored, which would be ascribed to the nanometric structure of the material since the greater charge would be explained by the larger surface area and the quantum confinement this type of structures experience [39-41].

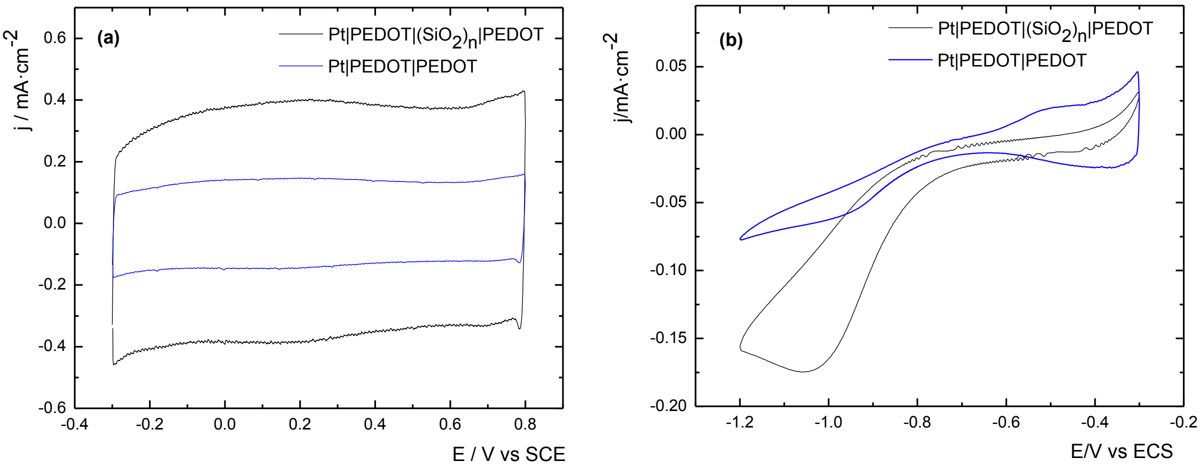

Figure 4. Voltammetric response of PEDOT electrodeposit modified electrodes in 0.1 mol·L^{-1} $TBAPF_6$, CH_3CN at $v = 10$ mV·s^{-1}: (a) *p*-doping/undoping zone; (b) *n*-doping/undoping zone.

The new and improved properties the CP nanostructures present, compared with those of the bulk material, is a field that yet remains under survey, although in this regard Granström *et al*. have explained that the origin of the dependence of conductivity on pore diameter is due to extended conjugation length and a better ordering of the molecules into the nanostructures, which may also translate into higher doping charges [42].

To establish the chemical reversibility of *p*- and *n*-doping/undoping processes, their charges were determined (Table 1). It was found that for both types of modified electrodes (with or without template), the charge of *p*-doping processes is always greater than that of the respective *n*-doping process; this finding is consistent with previously reported studies, and is explained by considering that is easier to oxidize the polymeric matrix, *i.e*. donating electrons, than reduce it by introducing electrons (*p*-doping), to become negatively charged (*n*-doping) [43-46].

Table 1. *p*- and *n*-doping (Q_{pd} and Q_{dn}) and *p*- and *n*-undoping (Q_{pu} and Q_{nu}) charges and their respective ratios, for the electro-obtained polymer on Pt|PEDOT|$(SiO_2)_n$ and Pt|PEDOT.

Electrode	Q_{pd} (mC)	Q_{pu} (mC)	Q_{pd}/Q_{pu}	Q_{nd} (mC)	Q_{nu} (mC)	Q_{nd}/Q_{nu}
Pt|PEDOT|$(SiO_2)_n$	0.568	0.571	0.995	$1.40·10^{-3}$	$3.50·10^{-3}$	0.400
Pt|PEDOT	0.482	0.479	1.006	$2.65·10^{-2}$	$6.74·10^{-2}$	0.393

With respect to the doping/undoping charges ratio, it can be seen that in the case of *p*-doping the value is very close to 1.0 for any of the modified electrodes, *i.e*. the process is always chemically reversible. Instead, in the case of *n*-doping, the process is evidently irreversible (this trend is even greater for the template-modified electrode), since in all cases the *n*-undoping charge is much higher than the *n*-doping one, suggesting a likely deterioration of the polymeric material, as reported elsewhere [36]. It could also be explained bearing in mind the pore size of the deposited material because, growing up by oxidation, this deposit becomes doped with the anion of the supporting electrolyte, which is much smaller than the cation that would be subsequently exchanged in the *n*-doping/undoping process.

From the voltammetric profiles in Fig. 4, it was also verified that the onset oxidation potential (*p*-doping) of PEDOT deposition shifts towards less positive values with respect to those reported for polythiophene [30]. This result was expected taking into account the electron donor nature of the substituents in the 3,4- positions. Furthermore, it has also been reported that alkylenedioxy-substitution geometry modulates oxygen π-donor character and this directly influences the *p*-doping process [1].

Deposits obtained in the presence and absence of the template used to guide the polymer growth were treated with HF or OH solutions at different ratios and time spans in order to remove the template, as well as to analyze the likely effect of these solutions on the polymeric matrix employed. To this end, before and after each treatment the electrochemical response data was collected using cyclic votammetry at 10 $mV\cdot s^{-1}$. It was verified that neither treatment brings about a significant difference, which is consistent with what has been reported when evaluating, in a similar manner, electro-obtained nanostructured polythiophene deposits from thiophene and oligomeric species. A greater response was obtained only after removing the template when longer oligomeric species were used as starting unit. This result is due to the use of longer units that provokes an improvement of the polymeric chain alignment and not to any effect of the aforementioned solutions [47].

The optimum nanowire electrosynthesis time obtained from the deconvolution of the j/t transients recorded during the electrosynthesis will be discussed below. First of all, transient must be analyzed from the time τ, which is defined as j(0,0), since as explained in previous works, it is from this point that nucleation and growth occurs, generating the electro-deposit.

On the other hand, for PEDOT bulk deposition, the NGM has already been studied, finding that, as for other derivatives, the global mechanism is composed of several contributions [48-52]. Hence, a mechanism constituted by instantaneous nucleation with three-dimensional growth under charge transfer control, ($IN3D_{ct}$), has been reported for PEDOT, which is consistent with circular base cone-shaped nuclei of similar size (because the process is instantaneous) and subsequently, the progressive nucleation diffusion controlled three-dimensional growth (PN3Ddif) becomes predominant, yielding semi-spheres of variable sizes, because the process is now progressive. This explains and is consistent with the morphology of PEDOT bulk deposition [36].

Coming again to Fig. 3, it is evident that the shape of the transient obtained on the template is different to that recorded for the growth on PEDOT, which indeed is analogous to that previously reported for the bulk deposit. Clearly, this is explained by a nucleation and subsequent growth by different mechanism(s) that can be best appreciated from the enlargement of these transients in Fig. 5.

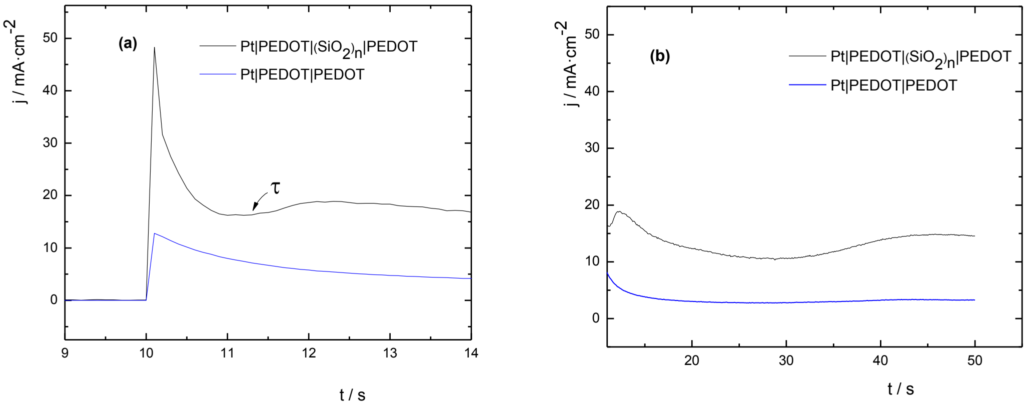

Figure 5. Enlargement of the initial j/t transients region of Fig. 3.

Growth on the template affords a much lower τ value and an exponential growth is observed, after which the curve resumes the same shape as for the massive growth, but with higher charge.

Using equation 1, the referred initial segment can be deconvolved [53], assigning to P1, P2, P3 parameters the values summarized in Table 2.

$$P1[\exp(P2t + P3)] \qquad (1)$$

Table 2. Equation 1 parameters and values obtained from deconvolution.

Parameter	P1	P2	P3
Expression	$nFk4LM \cdot \rho^{-1}$	$4kM \cdot L^{-1}\rho^{-1}$	lnr
Value	$1.53 \cdot 10^{-4}$	4.31	5.989

In these expressions n and F have their usual meaning, M and ρ are the molar mass and density, r the radius at zero time and L the transversal section [48-53]. In Fig. 6 experimental and simulated transient are shown according to these parameters and equation 1.

The excellent correlation between the two curves in Fig. 6 allows stating that, when the Pt|PEDOT|$(SiO_2)_n$ electrode is used, initially the polymer follows an exponential growth, which can be ascribed to a one-dimensional growth of the polymer within the template pores. Thus, during the first second of electro-synthesis, this kind of growth is quickly observed and, once the pores of the template are filled, the same type of growth found for a massive deposition is reached. In this case, time τ is also much lower because, unlike the observed when the deposition is performed directly on the bare electrode, a film of the same polymer has been previously electrodeposited upon the electrode substrate.

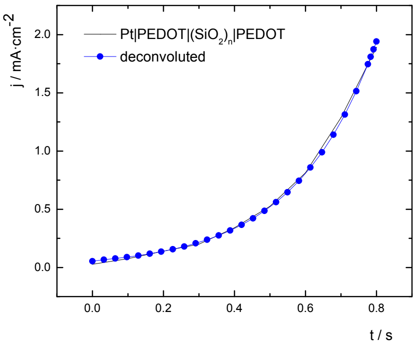

Figure 6. Experimental transient recorded during PEDOT electrosynthesis on Pt|PEDOT|(SiO$_2$)$_n$ at E = 1.420 V and deconvolved utilizing Eq.1.

It is possible to ascertain, therefore, that determination of the duration of the exponential growth time is an excellent tool to determine, practically *in situ*, the suitable electrolysis time to warrant growth inside but not upon the template.

Finally, Fig. 7 exhibits transmission electron microscopy, TEM, images for the morphological characterization of polymer deposits wherein fibers or nanowires are observed, with diameters ranging from 3 to 7 nm (images 7a, b and c), obtained by applying electrosynthesis potentials for up to for 12.5 s, which actually corresponds to 1 s from τ, *i.e*. 1 s of PEDOT nucleation and growth on the template modified electrode. For longer times, *e.g*. image 7d), polymer films, which may have been formed once the PEDOT growth has already exceeded the template pores, are observed. Furthermore, wires with diameters between 10 to 28 nm are perceived.

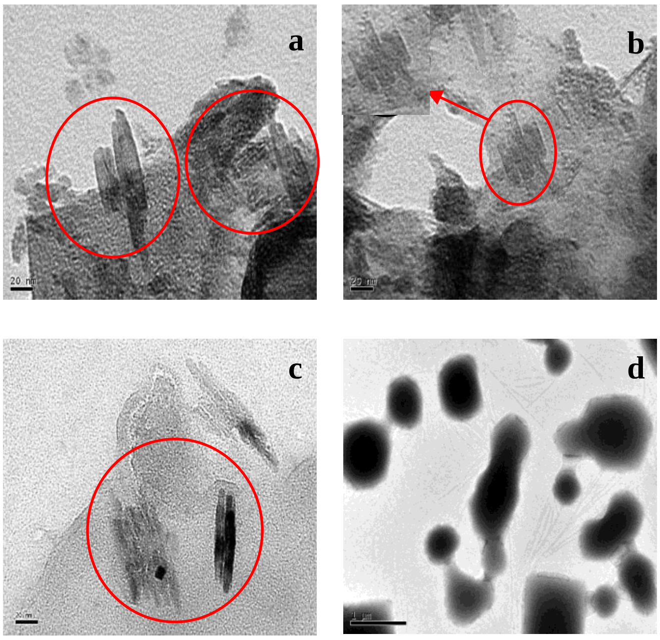

Figure 7. TEM images of PEDOT obtained on Pt|PEDOT|(SiO$_2$)$_n$ electrodes for electrosynthesis total time a); b) and c) 12.5 s (the scale corresponds to 20 nm); d) 40 s (scale 1 nm).

These results are in agreement with what had been able to infer from the detailed analysis by deconvolution of the corresponding j/t transients, since they demonstrated the obtaining of nanowires within the confined space of template pores and, subsequently, when they overflow, the bulk PEDOT growth.

4. CONCLUSIONS

Experimental conditions were optimized for PEDOT electrosynthesis on platinum electrodes previously modified with a film of the same polymer and subsequently with a porous silica film, to guide polymer growth. It was established thus a method for decreasing the influence of the nature of the electrode substrate. Consequently, the nanowires grow upon its same bulk polymer, affording a "brush-like" structure which, besides adherence, offers the advantage of using as supporting electrode cheaper conductive substrates, *e.g.* stainless steel or other material.

Moreover, the validity and usefulness of the proposed methodology using solely electrochemical methods to obtain polymeric nanostructures has been successfully confirmed, with the advantages that structures with this type of morphology present and, further, the deposition of the CP is accomplished directly on the electrode surface, which has only been carried out so far with metal deposits.

Finally, a novel strategy that helps to control parameters for establishing the electrosynthesis time required for the deposit grows only inside the template confined space, without exceeding the length of its pores, is also set forth.

This approach provides a pathway for obtaining a polymeric nanowire directly supported upon the electrodic surface, lacking only to optimize the strategy for total removal of the porous template film following nanowires formation.

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