Electro-synthesis and Characterization of Polymer Nanostructures from Terthiophene Using Silica Mesoporous Films as Template

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ABSTRACT

Nanostructures of poly(2,2':5',2''-terthiophene) have been synthesized using only electrochemical techniques. To this end, a porous silica film modified platinum disc was used as working electrode (Pt|(SiO₂)_n). The silica coating acts as a template so that the subsequent electro-polymerization occurs in their confined space pores, perpendicular to the electrodic surface. The current response of the obtained polymeric deposit is much greater than that exhibited by the solid massive polymer (generated under identical conditions but without template), accounting for the significant increase of the p-doping/undoping charge. Template removal was accomplished by treating the deposits with HF solutions. It was demonstrated that as the template is removed, the charge of the nanostructured electrodes increases even more. Electro-deposit characterization was supplemented using transmission electron microscopy, TEM, and FT-Raman spectroscopy, which revealed the obtaining of electrodes modified with polymeric nanostructures vertically aligned upon the electrode surface. Thus, a methodology employing solely electrochemical techniques that enables the obtainment of polymeric nanodeposits directly on the electrode surface was proposed. This approach allows foreseeing a significant progress in applications wherein these materials are useful, since this methodology, first tested for polythiophene, is applicable to various starting units capable of being electro-synthesized.

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1. Introduction

Nanostructured conductive polymers exhibit improved performance in technological applications as compared to their respective films, because, by its size, new properties, such as high electrical conductivity or large specific surface area among others,^{1–5} can be obtained. For this reason, a variety of polymeric nanostructures of different dimensions have been reported, e.g. nano-tubes, nano-fibers, nano-networks, nano-sheets, nano-spheres, and nano-micro-containers of many conductive polymers,⁶ among which polypyrrole (PPy),^{3,7} polyaniline (PANI),^{8,9} polythiophene (PTH)¹⁰ or poly-3,4-ethylenedioxythiophene (PEDOT)¹¹ are included, as well as nano-composites where they participate.¹²

Among the mentioned conducting polymers, PTH has received special attention because of its properties, e.g. high environmental stability in both doped and neutral state. Furthermore, the possibility of substitution in one or two β positions of the thiophene ring enables the obtaining of more processable materials and the ability of tuning their electrical and optoelectronic characteristics,^{13,14} in such a way that polythiophene nanostructures and its derivatives have been used in the study of supercapacitors, light emitting diodes, electrochromic and photosensitive devices, antistatic coatings, sensors, batteries, solar cells, transistors, etc., as compiled in the extensive literature available.^{11,15}

Hence, considering the importance that nanomaterials have shown, a great deal of methods has been reported to synthesize them. These methods can be classified into two groups, namely those using a template to guide and organize the material growth

(that can be a “hard-template” with nanoscale preformed molds or “soft-template” typically consisting of a surfactant that guides polymer growth inside or around self-assembled micelles), and those known as “template-free” that uses no template.

As for the synthesis methods employing “hard-template”, the growth of a material occurs within a porous membrane with a well-defined size. It is the simplest method for producing nanostructures, including metals, semiconductors, and conductive polymers. This process is based on filling the porous membrane with a monomer, polymerizing the monomer within the pores and, finally, removing the template, to obtain the free polymer. The diameter of the obtained nanostructure is controlled by the size of the pores or channels in the membrane, whereas the length and thickness are typically regulated by the polymerization time.¹⁶

Difficulties in scaling and necessary conditions to free the polymer are often mentioned as drawbacks of the technique. However, with the unusual asymmetric structures obtained, it has been shown that the use of synthetic methods that employ “hard-template” allows the composition and structure of the materials to be controlled, which is not possible when other methods are used.^{17–19}

To synthesize conductive polymers within a membrane, various methods have been employed.¹ Among these, the one utilizing electrochemical polymerization is the most appropriate, because the polymeric material is deposited upon the electrode surface, which is a requirement for a variety of applications and, in addition, morphology and properties of the deposit can be tailored by controlling electro-polymerization conditions.²⁰

On the other hand, methods employing soft-template, also known as self-assembly methods, are based on the control of non-covalent interactions such as hydrogen bonding, Van der Waals forces, among other, which correspond to the driving force for self-assembly.¹ Among these methods, those using a surfactant as template stand out. Surfactants form thermodynamically stable aggregates that have intrinsically nanoscale dimensions, both in solution and at interface. Thus, utilizing this methodology micro- or nano-scale structures can be obtained with controlled dimensions and the morphology favored by surfactant aggregates that can have different shapes (spherical, cylindrical or planar bilayer), depending on the type of used surfactant.^{21,22}

The disadvantage of these methods, as compared to hard template, is the lack of morphology control and, as is the case with other template methods, it requires a post-synthesis step to selectively remove the surfactant usually required to obtain the polymer with nanoscale dimensions. In any case, it should be noted that preparation of nanostructures using soft template is relatively straightforward and inexpensive.^{23,24}

The so called “free-template” methods are based on the preferential growth of nanostructures of conducting polymers in the presence of an applied driving force using a self-assembly process or structural/molecular ordering. The advantage of this route is that requires no external components, e.g. surfactants, resulting in a much easier synthetic procedure. Furthermore, because the free polymer is obtained at once, no special purification step is needed. However, despite the simplicity of this method, the forming mechanism seems quite complicated and is not well understood. Besides, the morphology of the final structure can hardly be controlled.²⁵

The morphology of nanometric deposits of the polymer is a parameter of the utmost importance, since it has been shown to play a crucial role in the efficiency of various devices wherein they are employed. For instance, in organic solar cells it has been demonstrated that rough surfaces and the presence of cavities may increase the risk of cell short-circuit. This fact has currently led to seek for the obtaining of structures that provide better control over the position of donor and acceptor materials (ordered heterojunctions, OHJ), which entails an improved efficiency in comparison with highly disordered heterojunctions (BHJ), making the choice of the appropriate processing parameters for better structure and morphology control of the films be still necessary.^{26–28}

Considering this background, the purpose of this work is the obtaining, employing oligomeric species as starting units, of polythiophene nanostructures from 2,2':5',2''-terthiophene. This approach enables obtaining more homogeneous polymeric deposits than those polymerized from monomeric species, as verified by studying the effect of the starting unit chain length (thiophene and its oligomers) on the mechanisms of nucleation and growth of the respective electro-synthesized polymer and was then corroborated by scanning electron microscopy (SEM) PTH deposits obtained.²⁰ Furthermore, by electro-polymerizing the starting unit in confined spaces of nanometric size, nanostructure-modified electrodes suitable for use in various types of devices could be directly obtained.²⁹

In the current work, a previously reported technique that combines the outstanding aspects of both hard- and soft-template methods at different times of the synthesis and utilizes thiophene, TH, monomer as starting units,²⁹ was now used to prepare nanostructures from oligomeric units, e.g. terthiophene. This novel approach would ensure a more orderly growth that could improve their properties and, in turn, would allow for testing if the developed technique can be extended to other starting units, i.e., if it can be used for preparing nanostructured polymeric deposits, using just electrochemical methods, directly on the electrodic material wherein will be utilized. The advantage of this “mixed” method is its ability to control the morphology of the obtained deposit by using a silicon

mesoporous film (template) modified electrode,³⁰ whose pores are normal to the working electrode surface, consequently pre-treatment of the surface to be used is not required. In addition, is reproducible, inexpensive, can be used on various electrodic substrates, and so on.

The methodology reported by Badeva et al.³¹ using a one-side polished silicon wafer as electrode substrate, to which an aggressive pre-treatment is made and later etched using a galvanostatic mode, can be compared to the technique used herein, but in this case, the utilized methodology has advantages such as: enables using different electrodic substrates, substrate pre-treatment is unnecessary, no interaction exists between polymeric material and template, thereby facilitating subsequent removal of the latter and, in addition, as previously mentioned, the polymeric nanostructures are normal to the electrode surface.

2. Experimental

All measurements were carried out at room temperature on an Autolab PGSTAT20 potentiostat, using a three-compartment cell. A 0.07 cm² geometric area Pt disc was the working electrode, while the auxiliary electrode was a Pt wire coil of large area, separated from the working electrode by a fine glass sinter. Ag|AgCl electrode dipped into a tetramethylammonium chloride solution, whose concentration is adjusted to match the potential of a saturated calomel electrode at room temperature, was employed as reference electrode throughout this work.³²

Prior to each experiment, the Pt working electrode was polished to a mirror finish, utilizing 0.3 µm alumina slurry on a polishing pad, rinsed with water, acetonitrile and finally dried. In all cases, the glassware was washed with double distilled water, rinsed with acetone and then oven-dried at 60°C for at least 12 hours prior to use.

The solutions were deaerated with high purity argon for minimum 20 minutes and this atmosphere was maintained over the solution during measurements. To prevent the presence of water in the solution, the anhydrous acetonitrile (Aldrich, HPLC grade) was kept under a high purity argon atmosphere over 4 Å molecular sieves previously activated at 200°C. For measurements, the solvent was handled using syringes under argon pressure. 2,2':5',2''-terthiophene (99% (m/m), Aldrich) and tetrabutylammonium hexafluorophosphate, TBAPF₆ (99% (m/m), Aldrich) in acetonitrile were used as starting unit and supporting electrolyte, respectively.

To prepare the porous silica film modified platinum electrode (Pt(SiO₂)_n) the methodology proposed by Walcarius,³⁰ successfully employed by our working group, was utilized.^{29,33} In this case, the working electrode was immersed in the precursor solution and a fixed potential of –0.9 V was applied for a suitable time, depending on the electrode area. Subsequently, the electrode was washed with water and then dried at 130°C for at least 12 hours. Excess surfactant was extracted by shaking the electrode in a H₂O/HCl/CH₃CH₂OH solution for one hour. The permeability of the electrode was evaluated by analyzing the voltammetric response in a 1.24 mmol·L^{–1} ferrocene (98%, Aldrich) and 0.1 mol·L^{–1} TBAPF₆ solution in acetonitrile.^{29,30} Tests to extract the *template*, after polymerization by electro-oxidation of the starting unit, were conducted using HF (extra pure, Aldrich)/H₂O 50/50 (v/v) mixture,³⁴ using Teflon labware. Finally, the device was washed with double distilled water and acetonitrile.

Obtained nano-deposits were assessed by the measurement of stable responses at 10 mV·s^{–1} scan rate in a solution containing just supporting electrolyte. The results are compared with those of deposits obtained without template under similar working conditions.

TEM images were recorded on a LEO Model 142VP scanning electron microscope. In this case, samples were prepared by mechanically removing the deposit from the working electrode.

Figure 1. Voltammetric profiles recorded during the electro-oxidation of $3.42 \text{ mmol}\cdot\text{L}^{-1}$ Trth + $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBAPF₆ in anhydrous CH₃CN on Pt(SiO₂)_n and Pt, using 5 successive potentiodynamic cycles, at $5 \text{ mV}\cdot\text{s}^{-1}$.

Raman spectroscopy experiments were conducted on a Bruker RF S100 (excitation wavelength 1064 nm).

3. Results and Discussion

3.1 Electropolymerization and electrochemical characterization

Optimization of poly(2,2':5',2''-terthiophene), pTrth, deposits electrosynthesis on template modified platinum electrodes (Pt(SiO₂)_n), was accomplished using potentiodynamic electro-oxidation of the starting unit. To this end, studies were conducted concerning the effect of potential scan rate and number of successive voltammetric cycles, on the electrochemical response of the deposit in order to determine the optimal working conditions, namely five potentiodynamic cycles at $5 \text{ mV}\cdot\text{s}^{-1}$. The use of low sweep rates favors adhesion of the polymeric material to the electrode surface, as has already been demonstrated by Zhang et al.³⁵ They pointed out that when working at higher rates removal of the polymeric deposit and its diffusion into the solvent is evident, forming just a thin film upon the electrode, which agrees with what we observed, highlighting the fundamental role the experimental conditions play in the polythiophene electro-obtention.³⁶ This has also been observed when using other oligomeric species as starting unit.^{13,37} Thus, as seen in Fig. 1, a profile showing a current increase after each successive cycle was obtained, consistent with polymer deposit growth on the electrode surface;^{35,38} the deposit growth being greater when Trth is electro-oxidized on the modified electrode, because higher currents are expected as nanostructures exhibit a much larger effective surface area. Another important advantage to be considered for justifying the use of oligothiophene instead of the monomer, is the significant redox potential decreases required for the electropolymerization.³¹

Deposits obtained on Pt(SiO₂)_n and Pt electrodes were initially evaluated by their electrochemical response in solutions containing solely the supporting electrolyte. In this case obtainment of stable and reproducible profiles, as a way to prevent over-oxidation of the polymeric material, was searched for, behavior also observed and reported by other authors.³⁵ A $10 \text{ mV}\cdot\text{s}^{-1}$ scan rate was employed to warrant sufficient time for ion transport within the polymer matrix, either in nanostructured or massive films; in other words that the doping/undoping process occurs in a proper way. Deposit profiles obtained under the same working conditions on template and unmodified electrodes are shown in Fig. 2 wherein a marked current increase for electro-deposition conducted in the presence of template

Figure 2. Voltammetric response of pTrth electro-synthesized from Trth+TBAPF₆ in CH₃CN using 5 potentiodynamic cycles on Pt(SiO₂)_n and Pt, at $10 \text{ mV}\cdot\text{s}^{-1}$, cycle n.

can be seen. This is consistent with a noticeable improvement regarding ion transport and, in turn, with a larger electro-active area of the electrode modified with nano-structured polymeric arrangements.

As Badeva et al. pointed out,³¹ it must be kept in mind that success of pore filling with the polymeric material is an important factor for the efficient obtention of materials. However, no many reports exist that give evidence concerning the level of pore filling, such as parameters for determining how many cycles of polymerization are needed to homogeneously “fill” the pores forming the template; consequently a study comparing the profile of deposit growth performing one to five polymerization cycles was accomplished. All the recorded profiles exhibited higher current density for deposits obtained on Pt(SiO₂)_n electrodes as compared with those obtained on bare Pt electrodes (both experiments conducted under the same working conditions). This may be explained considering that the polymer growth in confined space by the template, makes such growth to occur in one dimension (1D, along the template pore) forming polymeric nanostructures of larger effective area than polymers grown on unmodified platinum. Indeed, comparing the voltammetric response of pTrth deposits it is verified that deposits on the modified electrode exhibited higher current density than on Pt; an indication that nanostructured pTrth was obtained in each case. However, it is important to determine parameters, using criteria other than experimentation (“trial and error”), that enable establishing up to which cycle the polymer should be electro-oxidized to preclude template pore overflow.

Once the preparation of polymeric nanostructures using only electrochemical means was established and seeking to determine whether the presence of the film used as template bears any relevance toward the electrochemical response of the deposits, a methodology was established to assess various strategies to remove the silica mesoporous film from the platinum modified electrode. To this purpose, Pt(SiO₂)_n electrodes with pTrth potentiodynamically electro-deposited during 5 cycles were prepared. The electrochemical response of the electrode was assessed, using $10 \text{ mV}\cdot\text{s}^{-1}$ scan rate, before and after being treated with HF in various ratios and time spans. The effect of such treatment is illustrated in Fig. 3.

The response obtained using the Pt(SiO₂)_n/pTrth electrode (dashed line) shows that concentrate HF solution provokes a current increase, because in this case the electrode is modified only with the pTrth deposit that has grown in the spaces provided by the template, as the latter would have been removed by the HF. To corroborate this, pTrth electro-obtained on a Pt electrode, without template, was

Figure 3. Voltammetric response of electro-synthesized pTrth using 5 potentiodynamic cycles on Pt/(SiO₂)_n (solid line) and Pt (dashed line) in 0.1 mol·L⁻¹ TBAPF₆ in CH₃CN, ν 10 mV·s⁻¹, cycle n, before and after template removal with a) HF for 5 s, b) HF:H₂O for 5 s, and c) HF:H₂O for 10 s.

Figure 4. pTrth voltammetric profile at Pt in 0.1 mol·L⁻¹ TBAPF₆ and CH₃CN at 10 mV·s⁻¹, cycle n, and response after treatment with concentrate HF for 5 s (dashed line).

treated with HF under the same experimental conditions, Fig. 4. It was therefore evidenced that current increase is the result of the nano-structured nature of the polymeric deposit.

Figures 3(b) and 3(c) depict the response of the polymer before and after treatment with a 1:1 (v/v) mixture of HF:H₂O during 10 and 5 s, respectively. Thereby it may be postulated that, usually, after acid treatment, current response experienced a significant increase, even when initially they are less conductive than those that have grown without a template. This outcome may be ascribed to an increase of the effective surface area of the electrode. Furthermore, observing the shape of the voltammetric profile, it is likely that HF has some bearing on the *doping*, as mentioned by Park when studying poly(3-methylthiophene) nanotubes.³⁴

3.2 Morphological characterization

pTrth morphology characterization was accomplished employing TEM. The technique allowed electrodeposited fibers or nanowire formation to be observed, in an array or order much greater than when the polymer is prepared under identical experimental con-

Figure 5. Electro-synthesized pTrth images obtained by TEM in the presence of a mesoporous silica film (SiO₂)_n. 16, 18 and up to 30 nm diameter structures are observed.

ditions, but from the monomer, TH;²⁹ Bearing in mind the declining number of contributions to global nucleation and growth mechanism of the abovementioned polymer²⁰ and as yet no parameters exist to predict how many cycles or polymerization time is required to fill and not exceed the volume of the pores, it is possible that with 5 voltammetric cycles the volume thereof was exceeded and the polymer has grown outside the template. Besides, to obtain TEM images mechanical removal of the polymeric deposit from the electrode surface was necessary. However, despite the above, TEM images still corroborate the formation of nanostructures, even when the polymer has exceeded the template. Moreover, in the first image of Fig. 5 it can be realized a greater organization of the deposit when oligomeric units are employed as starting material and, at the same time, is grown in a confined space.

Images recorded after treatment with HF:H₂O for 10 s revealed more defined nanostructures, evidencing thus the efficiency of the treatment to remove the mesoporous film that composes the template (Fig. 6), although the presence of the template can still be noticed; therefore it is necessary to evaluate if a longer contact time with the HF:H₂O mixture is required.

3.3 FT-Raman spectroscopy characterization

Raman spectra of electro-deposits obtained in the presence and absence of the silicon mesoporous film on fluorine-doped tin oxide electrodes (FTO) were run. In both cases the characteristic signals of α -oligothiophenes,³⁹ with no much difference between them, were observed. Figure 7 shows a signal at 698 cm⁻¹ corresponding to the C-S-C symmetrical deformation of the ring; around 740 cm⁻¹ the signal corresponding to C-H out of plane stretching is seen; at 1048 cm⁻¹ in-plane C-H bendings are located; at about 1220 cm⁻¹ C-C inter-ring vibrations are observed as well as at 1370 cm⁻¹ the C-C symmetric stretching was found, and finally at 1440 and 1505 cm⁻¹, C-C asymmetric stretching signals are seen.

The most remarkable difference between the two spectra corresponds to signals found only for the FTO electrode with template, at around 560 and 1150 cm⁻¹, with intensity of the signals comparable to macroscopic films, these signals being much more intense for nano-poly(2,2':5',2''-terthiophene) deposits, which can be attributed to a better organization of the polymer that, as evidenced, grows forming one-dimension nanostructures, as well

Figure 6. TEM images of pTrth electro-synthesized on a $(\text{SiO}_2)_n$ mesoporous film modified electrode obtained after treatment with $\text{HF}:\text{H}_2\text{O}$ during 10 s. 16, 18 and up to 30 nm diameter structures are observed.

Figure 7. Raman spectra of electro-obtained poly(2,2':5',2''-terthiophene) on $\text{FTO}/(\text{SiO}_2)_n$ and FTO electrodes.

as to a conjugation length increase. The same results have been obtained by Duvail et al. by studying vibrational and transport properties of poly(3,4-ethylenedioxythiophene) nanofibers:⁴⁰ a higher intensity of the main bands as fiber diameter decreases was reported. Furthermore, Akimoto et al.⁴¹ observed similar characteristics in polythiophene. A correlation between conjugation length and the relative intensity of the peaks at 1440 cm^{-1} was found. Improvement of Raman scattering with diameter decrease and morphology dependence have been also evidenced when studying Si nanowires (SiNW),⁴² which agrees with the results obtained in the current study.

4. Conclusions

Polythiophene polymeric nanostructures, starting from an oligomeric unit (2,2':5',2''-terthiophene), was synthesized. Its growth in confined space generated polymeric nanostructures

vertically aligned on platinum electrodes, whose morphologies exhibited an even greater ordering than the ones synthesized from the thiophene monomer, although it is possible that both deposits have exceeded the pore volume. Besides, by employing oligomeric species the oxidation potential considerably dropped and the electro-synthesis conditions are less drastic (absolute anhydrous medium is not required, as with TH).

It has been verified, in turn, that the nanometric architecture improves macroscopic properties of deposits obtained this way, e.g. a significant charge increase in the p-doping/undoping process was observed, precisely thanks to the larger area of the polythiophene nanowires modified Pt electrode.

The use of electrochemical techniques to synthesize the template and the polymer is pioneer in this field, making possible to change both the size of the pores of the template to obtain different diameters and the strategies for the electro-synthesis of the polymer, according to the properties required for its prospective application. In turn, it is noteworthy that this approach enables nanostructured materials to be directly deposited on the electrode surface, which is very important when planning its use in any of the many applications of this kind of materials. However, it remains to establish strategies for the thorough removal of the mesoporous film used as template to optimize nanostructured conformation of the modified electrode. In any case, the obtained results validate the methodology used to obtain polymer nanowires directly on the electrode surface using solely electrochemical techniques.

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