Multi-Step Template-Assisted Approach
for the Formation of Conducting
Polymer Nanotubes onto Conducting
Polymer Films

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ABSTRACT

After exhibit the important limitations of the template-assisted approach when electropolymerization on simple stainless steel electrodes and electrospun insulating polymeric templates are combined, hollow poly(3,4-ethylenedioxythiophene) (PEDOT) nano- and microtubes have been successfully prepared using an alternative approach. In this procedure, which is based on a two-step electropolymerization process, electrospun fibers are collected onto a relatively flat PEDOT film that plays a crucial role for the complete coating of the template in the second electropolymerization process. Once the insulating fiber templates have been eliminated by solvent etching, the ability to exchange charge reversibly of the resulting hollow tubes is very similar to that observed for films while the amount of electroactive surface is noticeably higher. The diameter and density of hollow tubes can be easily controlled through this multi-step template-assisted approach, allowing prepare such PEDOT structures onto simple steel electrodes. The multi-step strategy overcomes the limitations of the conventional approach, which was restricted to the use of neural electrode sites and restricted to applications related with neural prostheses, opening the door to the use of PEDOT hollow nano- and microtubes in many important applications, as for example the detection of biomolecules and the fabrication of organic and bio-organic batteries.
INTRODUCTION

In the last decade much attention has been paid on the preparation of 1D-nanostructured (e.g. nanotubes, nanofibers, nanowires and nanorods) conducting polymers (CPs) because of the unique properties associated to such low dimensionality (e.g. high surface-to-volume ration and enhanced current ability).\(^1\)\(^-\)\(^4\) Furthermore, a number of promising potential applications exist in the fields of biomedical science and electrical nanodevices.\(^2\)\(^,\)\(^5\)\(^-\)\(^8\)

Among commercially available CPs, poly(3,4-ethylenedioxythiophene) (PEDOT) is the most important due to its high electrical conductivity (up to \(10^3\) S/cm), good transparency, excellent electrochemical and thermal stability, fast doping-dedoping processes and biocompatibility.\(^9\)\(^-\)\(^14\) PEDOT can be synthesized by electrochemical polymerization or by oxidative chemical polymerization to obtain aqueous dispersions stabilized by a water-soluble poly(styrene sulfonate).\(^15\)\(^-\)\(^17\) In last years, PEDOT and its derivatives have been widely applied in many fields, as for example to fabricate the cathode and anode in all-organic batteries,\(^18\)\(^,\)\(^19\) smart conductive substrates for cell growth and stimulation,\(^20\)\(^-\)\(^22\) electrochemical microactuators,\(^23\) electrodes for selective (bio)detection\(^24\)\(^-\)\(^26\) and catalysts for polymer electrolyte fuel cells.\(^27\)\(^,\)\(^28\)

PEDOT nanofibers and nanotubes have been prepared using electrochemical solid template-assisted methods,\(^2\)\(^,\)\(^29\)\(^,\)\(^30\) and chemical methods such as reverse microemulsion polymerization,\(^31\)\(^,\)\(^32\) interfacial polymerization,\(^33\)\(^,\)\(^34\) chemically oxidative polymerization,\(^35\) and metal ion reduction mediated vapor deposition polymerization.\(^36\) CP nanotubes have also prepared using pre-prepared reactive templates, such as MnO\(_2\) nanowires.\(^37\) In this case, the 1D polymerization induced by template and its simultaneous dissolution of the templates promote the hollow tube-like structure. Furthermore, vertically aligned PEDOT nanotubes have been prepared using
electrochemical deposition onto nanoporous anodic aluminum oxide, and ZnO nanowires and titanium nanotubes, and vapor deposition polymerization onto nanoporous templates. A very simple and interesting technique for the fabrication of flexible and bendable PEDOT nanotubes is the polymerization of the latter around electrospun polymeric fibers. This strategy has been successfully applied to coat electrospun fibers made of a wide variety of polymers (e.g. poly(methyl methacrylate), polyacrylonitrile, polyvinylpyrrolidone, and polystyrene) with PEDOT by vapor deposition polymerization. On the other hand, Martin and co-workers prepared controlled release systems for neural prostheses by electropolymerizing PEDOT around electrospun fibers of poly(lactic acid) or poly(lactide-co-glycolide) loaded with dexamethasone. Besides, the same authors fabricated hollow PEDOT nanotubes by polymerizing electrochemically the CP around the surface of poly(L-lactic acid) (PLA) electrospun fibers and, subsequently, removing the template fibers by dissolving them with dichloromethane. In all cases neural electrode sites made of iridium or gold were used, such devices being properly designed to interface the resulting PEDOT nanotubes with the central nervous system for neural recording.

The main advantage of the template-assisted approach used by Martin and co-workers, which is schematically depicted in Figure 1a, resides on the synthesis of the CP since electrochemical polymerization is the simplest method to produce PEDOT. In spite of this, such approach exhibits important drawbacks, as was discussed by the own authors. More specifically, in that method much of PEDOT did not come in contact with the PLA template, which is electrically inert, and thus PEDOT tends to be electrodeposited onto the metallic electrode. In addition, the method was restricted to relatively thin films, since otherwise PLA fibers are fully embedded within the CP matrix, and is unable to produce complete discrete nanotubes.
In this work we show that the preparation of hollow PEDOT nanotubes using the template-assisted approach displayed in Figure 1a is severely limited, becoming almost an impossible task, when conventional and relatively large (1×1 cm²) steel electrodes rather than neural electrode sites, which are restricted to applications related with neural prostheses, are employed. In order to overcome these impediments we propose a new easy approach to obtain relatively dense distributions of hollow PEDOT nanotubes using simple stainless steel electrodes. In this alternative procedure, electrospun fibers are collected onto a relatively flat PEDOT film that plays a crucial role for the complete coating of the template in a second electropolymerization process. After eliminate insulating fiber templates by solvent etching, the resulting hollow nanotubes exhibit electrochemical properties very similar to those observed for films while the amount of electroactive surface is noticeably higher.

**METHODS**

**Materials.** 3,4-Ethylenedioxythiophene (EDOT) monomer, acetonitrile and 2-chloroethanol were purchased from Aldrich and used as received. Chloroform (99.9%), acetone and dry ethanol (99.5%) were purchased from Panreac Química S.A.U. (Spain) and used as received without further purification. Anhydrous LiClO₄, analytical from Aldrich, analytical reagent grade, was stored in an oven at 80 ºC before use in the electrochemical trials.

PE44 was supplied by Showa Denko K.K. as Bionollone® 1001 MD. According to the manufacturer, this PE44 has molecular weight of 175000, a density of 1.26 g/cc, a glass transition temperature (Tₕ) of -32 ºC and a melting point of 114 ºC.
**PE44 Electrospinning.** The templates used in this work were prepared using PE44 rather than PLA since the properties of the fibers prepared using the former polyester can be controlled very easily. PE44 was electrospun from a chloroform : 2-chloroethanol mixture with a 7:3 mass ratio at polymer concentrations ranging from 3 w/v-% to 13 w/v-%. Electrospun fibers were collected on a target, which was placed at a distance of 15 cm from the syringe tip (inside diameter of 0.84 mm). The voltage (25 kV) was applied to the collecting target using a high-voltage supply (Gamma High Voltage Research, ES30-5W). The polymer solutions were delivered via a KDS100 infusion syringe pump from KD Scientific to control the mass-flow rate (2.5 and 5 mL/h). All electrospinning experiments were carried out at room temperature.

**PEDOT polymerization.** CP films were synthesized by chronoamperometry (CA) under a constant potential of 1.40 V, which was reported to be the optimum oxidation potential for the experimental conditions employed in this work, using a PGSTAT302N AUTOLAB potentiostat-galvanostat connected to a PC computer controlled through the NOVA 1.6 software, using a three-electrode two-compartment cell under nitrogen atmosphere at 25 ºC. The anodic compartment was filled with 40 mL of a 10 mM EDOT solution in acetonitrile containing 0.1 M LiClO₄ as supporting electrolyte, while the cathodic compartment was filled with 10 mL of the same electrolyte solution. Steel AISI 316 sheets of 1×1 cm² were employed as working and counter electrodes while the reference electrode was an Ag|AgCl electrode containing a KCl saturated aqueous solution (Eº = 0.222 V at 25 ºC).

**Morphology.** Optical microscopy studies were performed with a Zeiss Axioskop 40 microscope. Micrographs were taken with a Zeiss AxiosCam MRC5 digital camera.
Atomic force microscopy (AFM) images were obtained using either a Dimension 3100 Nanoman AFM or a Multimode, both from Veeco (NanoScope IV controller) under ambient conditions in tapping mode.

Scanning electron microscopy (SEM) micrographs were obtained using a Focus Ion Beam Zeiss Neon 40 instrument (Carl Zeiss, Germany). Samples were visualized at an accelerating voltage of 5 kV. Diameter of electrospun fibers was measured with the SmartTiff software from Carl Zeiss SMT Ltd.

**Gravimetric assays.** PE44 fiber mats were cut into 1×1 cm² pieces. After dry for 2 h in a desiccator, each piece was weighted and introduced in an Eppendorf that was subsequently filled with acetonitrile. The sample remained immersed into the organic solvent at 25 ºC for 24 h. Subsequently, the sample was extracted from the Eppendorf and introduced in a desiccator for 3 h. After this time, the sample was weighed and the loss of weigh determined with respect to the initial weight (i.e. before the immersion into acetonitrile). Each assay was repeated five times.

**RESULTS AND DISCUSSION**

**Electrospun PE44 fibers**

Although the voltage, the solvent and the needle-tip collector distance used to obtain continuous PE44 microfibers were taken from the literature several flows and polymer concentrations were tested to evaluate the influence of these parameters in the thickness of the fibers (optical micrographs displayed in Figure S1). The minimum polymer concentration required to avoid the formation of droplets and electrospun beads is 5 w/v-%. Besides, the amount of beads decreases when the flow rate increases from 2.5 mL/h to 5 mL/h, especially for the lower polymer concentrations. The thickness of the
fibers increases with the PE44 concentration but decreases with increasing flow rate. Further AFM and SEM studies were focused on representative nano- and microfibers, the following conditions being selected for this purpose: (1) nanofibres obtained using a concentration of 5 w/v-% and a flow rate of 5 mL/h (hereafter denoted PE44/5/5); and (2) microfibers obtained using a concentration of 10 w/v-% and a flow of 2.5 mL/h (PE44/10/2.5).

The density of electrospun nano- and microfibers, which were collected onto steel AISI 316 sheets of 1×1 cm², was controlled through the electrospinning time (ES-T). In order to obtain clear AFM images (Figure 2), the density of PE44 fibers was kept low by restricting the ES-T to 3 s only. Cross-sectional profiles of the topography AFM images suggest the flattening of PE44/5/5 and PE44/10/2.5 fibers. This phenomenon is more pronounced for the former than for the latter. Thus, the cross sectional height and width measured for such nanofibers / microfibers are $h_{AFM} \approx 30$ nm / 1 μm and $w_{AFM} \approx 130$ nm / 2 μm ($w_{AFM}/h_{AFM} \approx 4.3$ and 2 for PE44/5/5 and PE44/10/2.5, respectively). Although the attraction exerted by the steel surface towards the PE44 structures is enhanced by the low density of fibers, the pronounced flattening suggested by the high $w_{AFM}/h_{AFM}$ values should be considered with caution. Thus, $w_{AFM}$ values are considerably overestimated due to the limitations of this technique at the fiber/substrate interface (i.e. the internal periphery of pseudo-cylindrical fibers that contacts with the surface is not properly considered by this technique). In spite of this limitation, the deformations undergone by PE44 nano- and microfibers upon deposition onto steel substrates are qualitatively analogous to those derived from the comparison between organic dendrimers⁵¹,⁵² and dendronized polymers (DPs).⁵³ Thus, DPs are less deformable than organic dendrimers of the same generation because of the organization of their outermost branching units, which interact with the backbone through
backfolding effects, and the effective strength of interdendron interactions.\textsuperscript{53} In the case of PE44 fibers, the deformability of PE44/10/2.5 is lower than that of PE44/5/5 because the stiffness increases with the amount of interacting polymer chains.

SEM micrographs of dense fibers mats, which were obtained by increasing the ES-T to 12 s, are included in Figure 2. SEM images reveal a smooth surface texture, beads and broken fibers being infrequent. Furthermore, these micrographs evidence that PE44/5/5 fibers are significantly thinner than PE44/10/2.5 ones. Thus, the diameter ($\phi$) of PE44/5/5 and PE44/10/2.5 fibers (Figure 2) extend from 43 to 109 nm and from 206 to 796 nm, respectively. The average diameter ($\phi_{av}$) for these nano- and microfibers is 58.2±0.2 and 352.6±22.1 nm, respectively. However, in opposition to the $w_{AFM}$ values, which were overestimated because of the already described limitations of the AFM technique, $\phi_{av}$ values are probably underestimated due to a partial melting of polymer fibers caused by the energy of the electron beam. The absorption of such energy increases with the thickness of the fibers and, therefore, such underestimation is expected to be more pronounced for PE44/10/2.5 than for PE44/5/5.

**Influence of the PEDOT polymerization medium in the template**

It should be noted that, in order to avoid structural defects in PEDOT nano- and microtubes, the reaction medium should not affect the template. More specifically, alterations at the surface of the PE44 template through global or local swelling phenomena should be avoided during the PEDOT electropolymerization process.

Apparently PE44 does not swell upon immersion in acetonitrile (Figure S2), which is the reaction medium used in the template-assisted anodic polymerization of PEDOT (next sub-section). However, the possible negative effects of such organic solvent in PE44 fibers have been also examined by both gravimetric methods and AFM. The
weight loss (WL) after 24 h of immersion in acetonitrile of PE44/5/5 and PE44/10/2.5 fibers (Figure S3) is around 7% and 3%, respectively. Although the values are very small, these results indicate that the morphology of polyester template, especially the PE44/5/5 nanofibers, could be affected by the organic solvent. However, comparison of the AFM images obtained for PE44/10/2.5 samples immersed 24 h in acetonitrile and as prepared (Figure S4) indicates that the influence of the organic solvent in topography is virtually none.

**Polymerization of PEDOT around electrospun PE44 fibers: Limitations of the template-assisted approach**

Following the approach discussed in the Introduction section (Figure 1a), PEDOT was electropolymerized by chronoamperometry (CA), using a constant potential of 1.40 V,16 on steel AISI 316 electrodes that were previously used employed to collect PE44/5/5 or PE44/10/2.5 electrospun fibers (ES-T = 3 s in both cases). In order to grow a nanometric PEDOT layer around such PE44 fibers, the electropolymerization time (EP-T) was kept very low (i.e. 1, 3 or 5 s only). The current density decreases with increasing EP-T reaching values comprised between 5.3 and 4.6 mA·cm² (Figure S5), this behavior being independent of the fibers diameter.

Figures 3a and 3b display representative AFM images of the PE44/5/5 nanofibers after coating with PEDOT using EP-T= 1 and 3 s, respectively. In spite of such short EP-Ts, a monolayer of PEDOT aggregates deposited onto the steel substrate is clearly observed in both cases. Besides, small PEDOT clusters are also identified around the PE44 nanofibers. These clusters are homogeneously distributed around the fibers when the polymerization process is restricted to 1 s only, while PEDOT aggregates virtually cover the entire nanofiber surface when EP-T= 3 s. The cross-sectional profiles indicate
that the height of the coated nanofibers is $h^{AFM} \approx 200\text{-}250$ nm for both EP-T= 1 and 3 s. On the other hand, AFM images of the PE44/10/2.5 microfibers coated with PEDOT using EP-T= 5 s are provided in Figure 3c. In this case, the CP grows onto the steel surface coating only specific regions of the microfiber to connect clusters located at the two sides, while the rest of the microfiber remains completely uncoated. The $h^{AFM}$ value derived from the cross-sectional profile, $\sim 0.8 \, \mu m$, is fully consistent with this feature.

Dense mats of PE44/5/5 nanofibers (Figure S6), which were prepared using ES-T= 12 s, were also employed as templates for the preparation of hollow PEDOT nanotubes. Visual inspection of samples obtained using the template-assisted approach displayed in Figure 1a and EP-T= 5 s revealed that the color of the PE44 mats was preserved. In contrast, a deep blue thin film, which corresponds to PEDOT directly electrodeposited onto the steel surface, appeared upon lifting the PE44 nanofibers with tweezers. Consistently, the topographic AFM image displayed in Figure S6 reflects the absence of PEDOT aggregates around the surface of the nanofibers, while the corresponding phase image clearly indicates that PEDOT chains grow from the surface of the steel electrode. These results prove that oxidized EDOT monomers do not interact electrically with PE44. However, such small molecules diffuse across the dense nanofiber distribution and reach the conducting electrode surface, giving place to the growing of PEDOT chains through a radical cation polycondensation mechanism.

In order to surmount the limitations discussed above, additional experiments were carried out increasing the EP-T from 5 to 50 s. Figure S7, which displays the chronoamperogram recorded for the polymerization of EDOT onto steel coated with PE44/5/5 nanofibers prepared using ES-T= 3 s, shows that the current density stabilizes around 2.5 mA/cm$^2$. AFM micrographs (Figure S8) reveal that the whole surface is coated by aggregates typically observed in PEDOT films, whereas no morphology
related with the nanofibers is detected. Thus, PE44 nanofibers are trapped within the PEDOT matrix when the polymerization time is increased.

The overall of these results evidence the difficulties associated with the electrochemical polymerization of CPs around insulating polymeric templates. Thus, electropolymerization of monomers onto insulating electrospun fibers is unsuccessful, a conducting electrode surface being strictly necessary. However, PEDOT clusters adhere to the surface of PE44 fibers when these are in direct contact with electrode (i.e. mats with a low density of fibers), which has been attributed to the favorable interactions between the two polymers. Additionally, fiber templates become totally immersed into the CP matrix when the EP-T is increased to promote their coating. In order to overcome all these limitations, a new approach is proposed in the next section.

**Multi-step template-assisted approach**

In order to overcome the limitations previously discussed, here we report a robust, simple and straightforward method for the fabrication of hollow PEDOT nano- and microtubes. This method, which has been denoted multi-step template-assisted approach, has been inspired in the favorable interactions between PEDOT and PE44 fibers, which were responsible of the formation of CP clusters onto the insulating polymer. In order to take advantage of such interactions, the template-assisted approach has been modified by introducing a new step. Thus, the multi-step template assisted approach is a four-step process (Figure 1b): (i) electropolymerization of PEDOT onto the steel electrode; (ii) electrospinning of PE44 fibers onto the PEDOT film generated in the previous step; (iii) electropolymerization of PEDOT onto PE44 fibers; and (iv) elimination of the PE44 templates by dissolving them with chloroform. The addition of the first step to the conventional template-assisted strategy provokes a drastic change:
Electrospun fibers are collected onto a soft and irregular CP surface rather than onto the steel electrode surface. A SEM micrograph and AFM images displayed in Figure 4a show the porous morphology and heterogeneous topography of PEDOT films obtained using EP-T= 50 s. Thus, the CP surface consists on micro- and submicrometric clusters, which are located at very different heights and are connected through ultra-thin fibers, alternated with relatively deep pores. Electrospun PE44/5/5 nanofibers collected onto the surface of the PEDOT film are displayed in Figure 4b. Nanofibers, which were obtained using an electrospinning time of ES-T= 15 s, are satisfactorily adhered to the CP surface. After this, a second layer of PEDOT has been generated by anodic polymerization using EP-T= 50 s onto the PE44/5/5 nanofibers. Figure 4c, which shows the morphology and topography of the resulting system, evidence the success of the multi-step template-assisted approach. Thus, coated nanofibers can be perfectly identified onto the PEDOT surface. Furthermore, AFM phase images indicate that, although the coverage of the PE44 nanofibers with the second CP layer was not entire yet, such coating process was considerably more complete and better defined than that achieved for nanofibers directly collected onto the steel electrode. Interestingly, the heterogeneous morphology of PEDOT remains after deposition of the second CP layer, even though the porosity decreases considerably with respect to the first layer (Figures 4a and 4c). Overall, these results suggest that a completely coverage of the nanofibers could be obtained by adjusting EP-T and/or ES-T.

Different trials were performed to adjust the EP-T and the ES-T, results for the most representative ones being displayed in Figure S9. Comparison of the results led us to conclude that the polymerization times used to obtain the first and second PEDOT layer (hereafter denoted EP1-T and EP2-T) should be different. Regarding to the internal
PEDOT layer, EP1-T should be low enough to keep the roughness at reasonably low values \((i.e.\) the roughness of PEDOT films is known to increase considerably with the polymerization time \(^{54}\)). Thus, the contact between the internal PEDOT layer and the collected electrospun PE44 fibers greatly depends on the surface topography of the CP deposited onto the steel electrode. If the roughness is too high, the CP topography induces the apparition of empty spaces at the PEDOT(film)···PE44(fiber) interface since relatively long segments of the fiber are suspended rather than supported on the PEDOT surface (Figure S9). Such empty spaces are filled by the CP in the second polymerization step, affecting the coating of the fibers unfavorably. According to these observations, EP1-T was kept at 50 s since the generated PEDOT layer is flat enough to allow a good contact with the electrospun fibers. In contrast, the polymerization time of the second electropolymerization step, EP2-T, depends on the density of PE44 fibers. Thus, EP2-T grows with ES-T, these two parameters are completely independent of EP1-T.

The efficacy of the multi-step template-assisted approach is illustrated in Figure 5, which shows AFM images of the internal PEDOT deposited onto steel (EP1-T= 50 s), the electrospun PE44/5/5 nanofibers obtained using an electrospinning time of 7 s, and the coating PEDOT layer (EP2-T= 180 s). In this case PE44 nanofibers were perfectly covered by the CP, corroborating that the internal CP layer must be electropolymerized using relatively short EP1-T values.

**PEDOT fibers and hollow tubes: Electrochemical response**

In order to transform the coated PE44/5/5 nanofibers into hollow PEDOT nanotubes, samples were immersed into 3 mL of chloroform, which is capable of dissolving the polyester but not the CP. Three different immersion times were tested at this stage: 1 h,
3 h and 24 h. Despite the insolubility of PEDOT, microcrevasses appeared at the surface of films immersed 3 h, while the adhesion of the CP to the steel surface was considerably affected after 24 h of immersion in chloroform. Accordingly, samples immersed during 1 h, which preserved the structure, adherence, color and uniformity, were the only consider for further characterization.

SEM micrographs displayed in Figures 6a-b and S10 correspond to PEDOT microtubes derived from the multi-step template-assisted approach (EP1-T= 50 s, PE44/10/2.5 template from ES-T= 3 s and EP2-T= 50 s) after 1 h of immersion in chloroform. It should be emphasized that such SEM micrographs were focused on structural deficiencies such as small breaks at the walls (Figures 6a and S10a) and, cross-sectional breakages (Figures 6b and S10b). Thus, although these elements were relatively infrequent, they allowed us to corroborate that microfibers transformed into hollow microtubes in the selective solvent etching process. Accordingly, chloroform molecules penetrate through the pores of the PEDOT external layer, dissolving the PE44 microfiber.

Cyclic voltammograms of samples with hollow nano- and microtubes prepared as described in the previous subsection (EP1-T= 50 s, ES-T= 15 s and EP2-T= 180 s for both PE44/5/5 and PE44/10/2.5 templates) in acetonitrile with 0.1 M LiClO$_4$ are shown in Figure 6c. For comparison, the voltammogram recorded for a PEDOT film that was obtained using a two-step electropolymerization process with identical polymerization times but without introducing the PE44 templates, is also displayed. The electroactivity of the bilayered PEDOT film is 12% higher than that of PEDOT nanotubes. This small reduction has been attributed to the aggressive conditions applied during the multi-step template-assisted approach, which promote degradative processes in the CP chains. Among them, the high voltage (25 kV) applied to the collecting target, which is coated
by the first PEDOT layer, during the electrospinning process and the immersion in chloroform for 1 h to eliminate the PE44 template deserve special consideration. For microtubes, the electroactivity decreases 43% with respect to bilayered films, indicating that the micrometric hollow cavities affect negatively the ability to exchange charge reversibly. Thus, such micrometric cavities probably act as structural breakage elements, making more difficult the entrance and escape of dopant ions into the bulk CP matrix during oxidation and reduction processes, respectively.

In order to compare the electrochemical responses of hollow PEDOT tubes with those of PEDOT fibers, cyclic voltammograms were also recorded for samples before the immersion in chloroform (Figure 6d). The ability to exchange charge reversibly of nano- and microfibers is slightly worse than that observed for the corresponding hollow architectures (i.e. the electroactivity is 2% and 7% lower for nano- and microfibers, respectively, than for nano- and microtubes). This slight reduction has been attributed to the interface between the CP and the insulating PE44 templates, which eliminates the effective surface area associated to cavities in nano- and microtubes. Thus, the insulating templates preclude the exchange of dopant ions between the CP and the electrolytic medium during oxidation and reduction processes. However, this negative effect, which as expected is more pronounced for microfibers than for nanofibers, is partially compensated by the fact the CP matrix is not submitted to the degradative effects induced by the chloroform solvent. Consequently, the electrochemical response undergoes a small reduction only.

**CONCLUSIONS**

Once have been established the limitations in the implementation of the conventional template-assisted approach for the preparation of hollow PEDOT nano- and microtubes
onto steel electrodes, a multi-step strategy has been designed and used for such purpose. In such multi-step procedure, the steel electrode is coated by a relatively flat PEDOT layer before to collect the electrospun PE44 fibers. The favorable interactions between the chains of the two polymers facilitate the coating of the PE44 nano- and microfibers by PEDOT in the second electropolymerization step. The elimination of the PE44 templates through solvent etching results in PEDOT bilayers with hollow morphologies onto its surface, enhancing considerably the active surface of the CP. Despite the CP molecules are subjected to drastic conditions during the multi-step template-assisted strategy (e.g. high voltage and immersion into an organic solvent for 1 h), the electrochemical response of PEDOT is maintained, especially in the case of nanotubes.

This straightforward procedure, which enables the use of simple steel electrodes, opens the door to applications other than sophisticated neural prostheses. For example, the high active surface provided by hollow PEDOT nano- and microtubes can be used to enhance the performance of this CP as detector of neurotransmitters\textsuperscript{26} and main component of solid organic super-capacitors.\textsuperscript{55} Regarding to the latter, it should be remarked that electrodes prepared in this work exhibit high aspect ratios, high surface area and high porosity, suggesting that they can be extensively applied in energy-storage devices. On the other hand, it should be remarked that this procedure can be extrapolated to other systems based on the combination of soluble polymers that can be electrospinned (e.g. polylactic acid and nylon) and other polyheterocyclic CPs (e.g. polypyrrole derivatives).
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CAPTIONS TO FIGURES

**Figure 1.** Schematic representation of different steps involved in the (a) conventional template-assisted approach and (b) the multi-step template-assisted approach.

**Figure 2.** AFM and SEM images of electrospun (a) PE44/5/5 and (b) PE44/10/2.5 fibers. The density of fibers into the mats was controlled through ES-T: 3 s and 12 s for AFM and SEM images, respectively. AFM images in (a) and (b) are 1×1 and 10×10 μm², respectively. The cross sectional profiles of the above AFM images have been used to estimate $h_{AFM}$ and $w_{AFM}$ values. The diameter distributions of the electrospun fibers have been derived from SEM images and used to evaluate $\phi_{av}$ values.

**Figure 3.** 3D topographic and height AFM images of: PE44/5/5 electrospun nanofibers coated with PEDOT generated using (a) EP-T= 1 s and (b) EP-T= 3 s (window size = 2×2 μm² in both cases); and (c) PE44/10/2.5 electrospun microfibers coated with PEDOT obtained using EP-T= 5 s (window size = 5×5 μm²). In all cases the conventional template-assisted approach was used, PE44 fiber mats being prepared employing ES-T= 3 s. The cross sectional profiles of the above AFM images have been used to estimate the $h_{AFM}$ values.

**Figure 4.** SEM micrograph (left), 3D topographic (center) and phase (right) AFM images of the systems involved in the multi-step template-assisted approach when the EP-T employed for the internal and external PEDOT layer is the same: (a) PEDOT film electrogenerated onto steel (EP-T= 50 s); (b) electrospun PE44/5/5 nanofibers (ES-T= 15 s) collected onto the PEDOT surface displayed in (a); and (c) PE44 electrospun fibers coated with PEDOT (EP-T= 50 s). Window sizes of AFM images: 10×10 μm² for (a) and 20×20 μm² for (b) and (c).

**Figure 5.** 3D topographic and phase (right) AFM images of the systems involved in the multi-step template-assisted approach when the EP-Ts employed for the internal and
external PEDOT layer is different: (a) PEDOT film electrogenerated onto steel (EP1-T= 50 s); (b) electrospun PE44/5/5 nanofibers (ES-T= 7 s) collected onto the PEDOT surface displayed in (a); and (c) PE44 electrospun fibers coated with PEDOT (EP2-T= 180 s). Window sizes of AFM images: 10×10 μm².

**Figure 6.** (a) and (b) SEM micrographs of hollow PEDOT microtubes prepared using the multi-step template-assisted approach. The parameters for this process were: (i) EP1-T= 50 s for the internal PEDOT layer; (ii) electrospun PE44/10/2.5 microfibers (ES-T= 3 s) as template; (iii) EP2-T = 50 s for the external PEDOT layer; and (iv) immersion in chloroform for 1 h. The small break at the wall in (a) and the cross sectional breakages in (b) have been used to confirm that microfibers transformed into hollow nanotubes. (c) Cyclic voltammograms of hollow PEDOT nano- and microtubes prepared using EP1-T= 50 s, ES-T= 15 s and EP2-T= 180 s in acetonitrile with 0.1 M LiClO₄. (d) Cyclic voltammograms of PEDOT nano- and microfibers in which the PE44/5/5 and PE44/10/2.5 templates have not been eliminated. The times for the different steps is the same that for (c). The cyclic voltammogram recorded for a bilayered film prepared using two consecutive anodic polymerization steps of 50 and 180 s has been included in (c) and (d) for comparison.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6