Multi-step template-assisted approach

for the formation of conducting polymer nanotubes onto conducting polymer films

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Figure S1. Optical micrographs of PE44 electrospun fibers obtained using a needle tipcollector distance of 15 cm and an applied voltage of 25 kV. The influence of both the polymer concentrations and the flux on the morphology of the fibers was examined by considering PE44 concentrations of 5, 6.5, 10 and 13 w/v-% combined with flow rates of 2.5 and 5 mL/h.

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Figure S2. Visual aspect of PE44 samples after 24 hours of immersion in 1:0, 75:25, 50:50, 25:75 and 0:1 v/v acetonitrile:water mixtures at 25 °C.



Figure S3. Weight loss (WL, in %) of PE44/5/5 and PE44/10/2.5 mats after 24 hours of immersion in acetonitrile at 25 °C.



Figure S4. Topographic (3D and 2D) and amplitude AFM images of PE44/10/2.5 fibers (a) as prepared and (b) after 24 h in acetonitrile at 25 °C. It should be noted that the micrometer-length scale dimensions of PE44/10/2.5 fibers facilitates the detection of possible acetonitrile-induced alterations with respect to PE44/5/5, which are much thinner.



Figure S5. Representative chronoamperograms obtained for the oxidation of a 10 mM EDOT solution in acetonitrile with 0.1 M LiClO₄ on the surface of $1 \times 1 \text{ cm}^2$ steel sheets, previously used to collect PE44/5/5 mats, and applying a constant potential of 1.40 V. Profiles correspond to EP-T= 1, 3 and 5 s. Temperature 25 °C.



Figure S6. 3D topographic (top) and phase (bottom) AFM images of PE44/5/5 nanofibers, which were prepared using ES-T= 12 s, coated with PEDOT that was electropolymerized using EP-T= 5 s (window size = $5 \times 5 \ \mu m^2$).



Figure S7. Representative chronoamperogram obtained for the oxidation of a 10 mM EDOT solution in acetonitrile with 0.1 M LiClO₄ on PE44/5/5 nanofiber mats electrospun (ES-T= 3 s) on the surface of 1×1 cm² steel sheets by applying a constant potential of 1.40 V. The polymerization time is EP-T= 50 s. Temperature 25 °C.



Figure S8. 3D topographic image of PE44/5/5 nanofibers, which were prepared using ES-T= 3 s, coated with PEDOT that was electropolymerized using EP-T 50 s (window size = $5 \times 5 \ \mu m^2$).



Figure S9. 3D topographic and phase images of: (a) the PEDOT film electropolymerized onto steel using EP-T= 180 s; (b) electrospun PE44/5/5 nanofibers (ES-T= 5 s) collected onto the PEDOT surface displayed in (a); and (c) PE44 electrospun fibers coated with PEDOT that was electropolymerized using EP-T= 180 s. Window size = $10 \times 10 \ \mu\text{m}^2$ for (a) and (c), and $5 \times 5 \ \mu\text{m}^2$ for (b).

The roughness of the internal PEDOT layer (Fig.S9a) is significantly higher than that obtained for films produced using EP-T= 50 s (&& and && nm, respectively). This rough topography affects electrospun PE44/5/5 fibers collection. Thus, some segments of electrospun fibers are not directly supported by the internal PEDOT layer but suspended (red circle in Fig.S9b), giving place to the apparition of empty spaces at the PEDOT/PE44 interface. The empty spaces at the interface are rapidly filled by the CP in the second polymerization step, resulting in an incomplete coating of the fibers.



Figure S10. SEM micrographs of hollow PEDOT microtubes prepared using the multistep 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 (a) the wall and (b) the cross sectional breakage have been used to confirm that microfibers transformed into hollow nanotubes.