

# High-aspect-ratio conducting polymer microtube synthesis by light-activated electropolymerization on microstructured silicon



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## ABSTRACT

Synthesis of conducting polymer (CP) microtubes with characteristic size and period of a few micrometers, height from 5 to 50 micrometers, and aspect-ratio from 1 to 10, is demonstrated by light-activated electropolymerization on microstructured silicon for poly(3,4-ethylenedioxythiophene), poly(3-methylthiophene) and polythiophene. Electrochemical characterization by cyclic voltammetry demonstrates that the entire surface of microstructured CPs is electroactive and can be effectively exploited in electrochemical processes without detaching CP films from the silicon substrate, thus directly and easily taking advantage of the increased polymer surface area. Such a successful merging of CP and silicon microstructuring technologies would break new grounds in different analytical/technological fields connected to microstructured CPs.

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## 1. Introduction

Template-synthesis is a well-established method for “indirect” fabrication of micro/nanostructured materials by replication of the morphology of a suitable template used as a mold. In particular, micro/nanostructuring of conducting polymers (CPs) by template-synthesis has been successfully reported and micro/nanostructured CPs, e.g. nanorods [1], nanosheets [2] and microspheres [3], exhibiting unique features and improved performances with respect to bulk materials, such as enhanced conductivity and higher mass transport rate, have been designed for several applications, ranging from sensing [4] to energy storage [5] and electronics [6]. Despite template-synthesis being in-principle a high-versatile approach for CP micro/nanostructuring, the use of commercial and/or *ad-hoc* templates with limited morphological features, e.g. porous membranes, nanoparticles, surfactants, etc., has somehow reduced the micro/nanostructuring potential of such an approach so far.

In last decades several high-flexibility “direct” micro/nanostructuring methods have been developed for several materials, including silicon [7], silica [8], alumina [9] and titanium [10]. Although silicon is today recognized as the leading material for low-cost and high-flexibility micro/nanostructuring, only a few examples of CP deposition on micro/nanostructured silicon templates have been reported so far [11,12], in which either CP electropolymerization [11] or pre-formed CP deposition by spin-coating [12] on silicon substrates featuring either random [11] or ordered [12] micro/nanopores are carried out. In these works, mainly focused on polypyrrole (PPy)

[11] and poly(3,4-ethylenedioxythiophene) (PEDOT) [12], dissolution of the template after deposition is required for any further applications of CP films, often resulting in the polymer films to be laid down and collapsed, particularly in the case of high aspect-ratio (AR) microstructures, thus limiting the effective exploitation of the microstructured polymers.

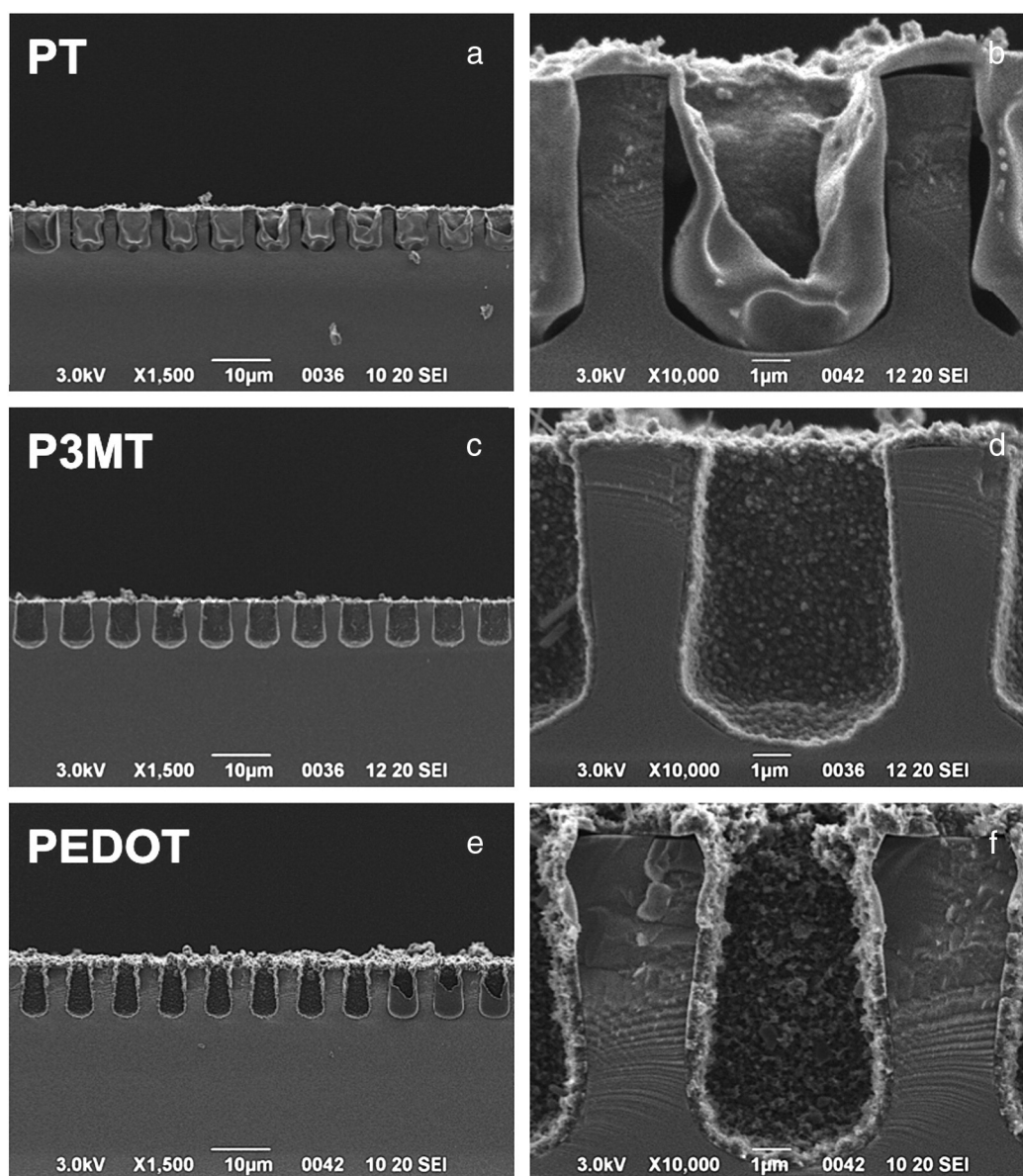
Recently, we demonstrated that high-flexibility in CP microstructuring can be achieved by light-activated electrosynthesis of PPy microtubes on microstructured *n*-type silicon (*n*-Si) templates [13], thus pushing this approach well beyond former works carried out on flat *n*-Si [14,15]. While silicon microstructuring allows fabrication of high-complexity three-dimensional microstructures to be accomplished, electrosynthesis provides an excellent control of the film morphology by easily tuning polymer thickness and electropolymerization rate [16].

In this work, light-activated electropolymerization on microstructured *n*-Si templates is further established as a general and versatile route for CP microstructuring. The proof of concept is given synthesizing PEDOT, poly(3-methylthiophene) (P3MT), and polythiophene (PT) microtubes, with AR ranging from 1 to 10, by replication of the morphological features of microstructured *n*-Si templates with submicrometer accuracy. Cyclic voltammetry (CV) on CP microtubes evidences that the entire surface of microstructured CPs is electroactive and can be effectively exploited in electrochemical redox processes without the need of removing CP films from the silicon substrate.

## 2. Experimental

PEDOT, P3MT, and PT microtube synthesis is carried out by light-activated electropolymerization on micromachined *n*-Si templates

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**Fig. 1.** Typical SEM cross-sections (at two different magnifications) of PT (a, b), P3MT (c, d), and PEDOT (e, f) microtubes obtained by light-activated electrosynthesis on microstructured *n*-Si templates featuring two-dimensional array of pores with AR about 1.

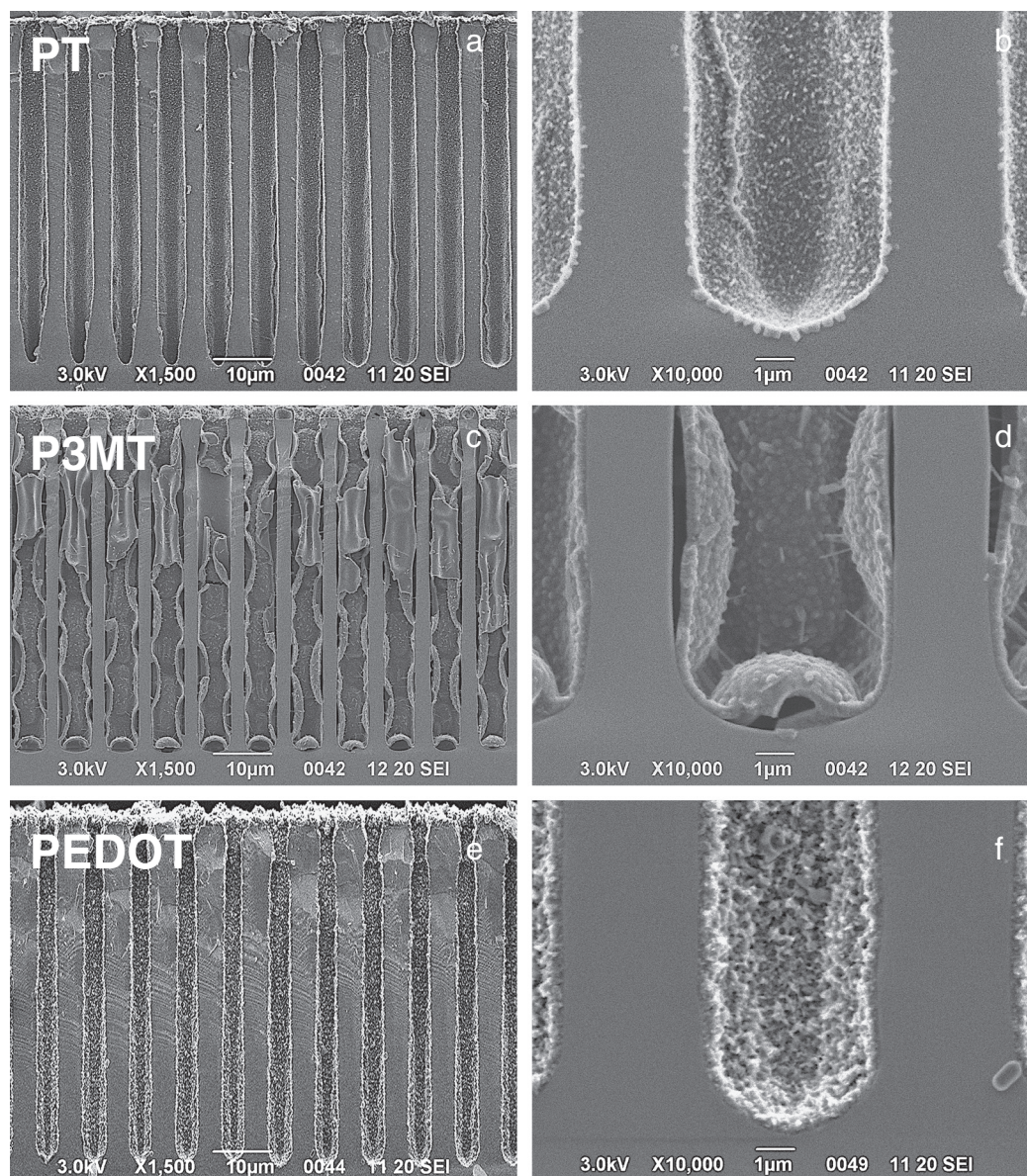
featuring two-dimensional array of pores with size of 5 micrometers, period of 8 micrometer, and AR ranging from 1 to 10. Silicon microstructuring is performed using light-activated electrochemical etching in a HF-based aqueous solution [7,17].

The starting material is an *n*-Si substrate – 3–8 Ωcm resistivity, 550 μm thick, (100) orientation – with a 100-nm-thick silicon dioxide layer on top. The pattern of the microstructure to be fabricated is defined on a photoresist layer by standard lithography, transferred to the silicon dioxide layer by buffered HF etching through the photoresist mask, replicated (seed-point formation) into the silicon surface by potassium hydroxide etching through the silicon dioxide mask, and finally grooved into the bulk material by electrochemical etching of silicon, under back-side illumination and anodic polarization of silicon, using an aqueous electrolyte containing 5 vol% of HF [7,13]. The etching voltage is set to a constant value of 3.0 V for the whole etching process. The etching current is set to an initial value of 16.78 mA, which sets the size of etched structures, and is linearly decreased with time (slope of  $-1.21 \mu\text{A/s}$ ) to ensure constant size of the microstructures over the whole etching depth. The etching time is set to 225, 1000, and 2100 s to obtain 5, 25, and 50 μm deep microstructures, respectively. After electrochemical

etching, the microstructured silicon template is rinsed in ethanol and dried by evaporation at 40 °C. CP deposition is performed by galvanostatic polymerization (applied current: 2 mA, circulated charge density: 105 mC/cm<sup>2</sup>) both on flat silicon and on silicon templates featuring pore arrays with AR values about 1, 5, and 10 (surface area 0.78, 1.5, 6.4, and 12.5 cm<sup>2</sup>, respectively). CP deposition is carried out under back-side illumination and anodic polarization of silicon, in a solution of monomer 0.5 M in acetonitrile (ACN) containing tetrabutylammonium perchlorate 0.2 M. After polymer growth, samples are rinsed in ACN and dried by evaporation at room temperature. For both flat and microstructured silicon substrates for which an electrochemical characterization of the polymer film has to be performed, a 15-nm-thick gold film is deposited on the silicon surface, by thermal evaporation at a residual pressure of  $2 \times 10^{-6}$  mBar, before polymer electrosynthesis, so as to improve electrical contact with the polymer film.

### 3. Results and discussion

Figs. 1 and 2 show typical Scanning Electron Microscope (SEM) cross-sections (at two different magnifications) of PT, P3MT, and PEDOT

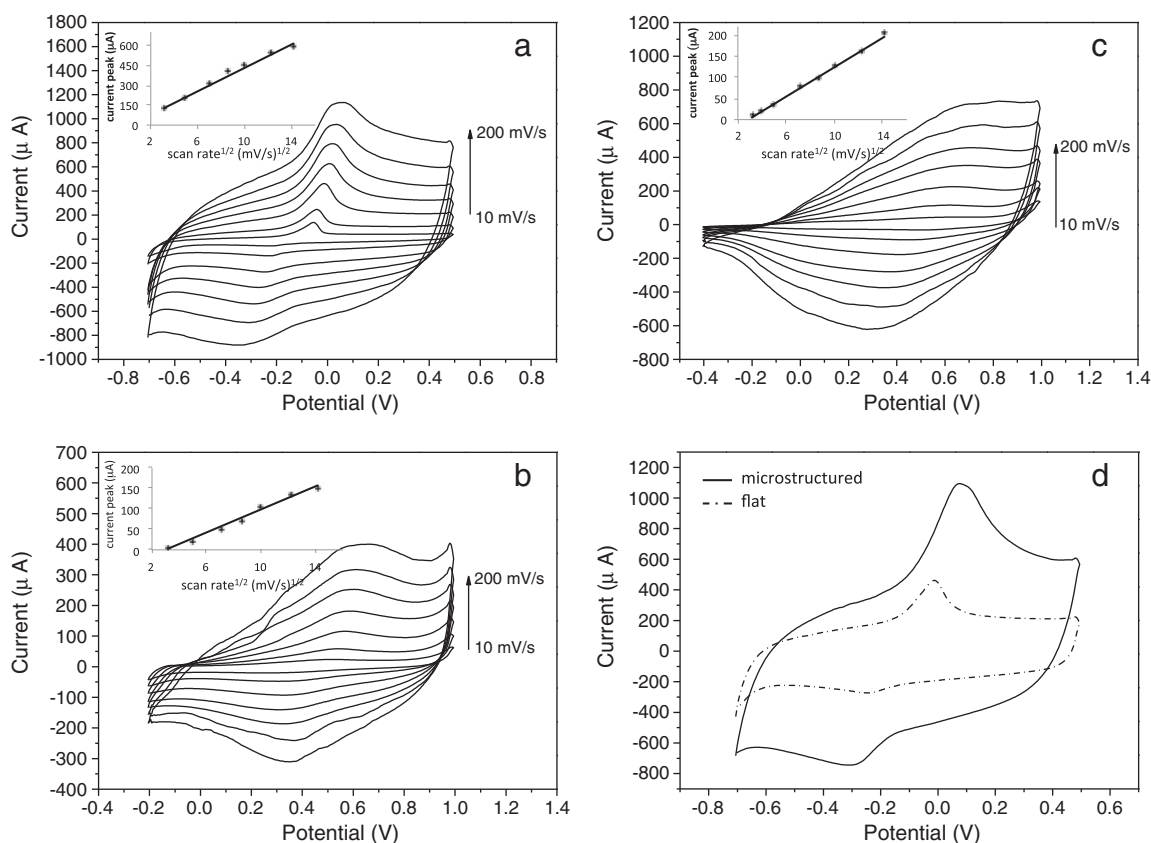


**Fig. 2.** Typical SEM cross-sections (at two different magnifications) of PT (a, b), P3MT (c, d), and PEDOT (e, f) microtubes obtained by light-activated electrosynthesis on microstructured *n*-Si templates featuring two-dimensional array of pores with AR about 10.

films synthesized on microstructured silicon featuring two-dimensional array of pores with AR about 1 (Fig. 1) and 10 (Fig. 2). A highly conformal growth of PT, P3MT, and PEDOT that allows the microstructured surface to be fully covered with the polymer is observed for all tested AR values and geometrical features, in agreement to results obtained for PPy [13]. It can be argued that, on the one hand, back-side illumination produces a homogeneous distribution of charge carriers at the silicon surface in contact with the monomer solution and, in turn, a uniform current flow at the silicon/monomer interface; on the other hand, under the adopted experimental conditions (i.e. monomer concentration, applied current/potential) polymerization reaction is very fast, so that monomer molecules diffusing up to the silicon surface are suddenly consumed to elongate the polymer chain at silicon surface [18]. No differences are observed in the morphology of the polymer films deposited on microstructured silicon electrodes with and without gold layer, thus indicating that electrode-material/monomer interaction is not the main mechanism contributing to the formation of the

observed microstructures. In all cases, film thickness values (about hundreds nanometers) are in agreement with theoretical values calculated on the basis of the circulating charge [19–21]. Macroscopic wrinkle and corrugation of the microstructured CP films (e.g. PT in Fig. 1 and in P3MT in Fig. 2) are due to mechanical cleavage of silicon dies for SEM cross-section analysis.

Conversely to PPy films [13] that feature a pretty smooth surface, PT, P3MT, and PEDOT films show a peculiar nanostructuring of the polymer surface, independently of AR values, which is also observed on flat films (results not shown here). This behavior is in agreement to literature data reported for PT, P3MT, and PEDOT prepared by conventional electropolymerization [22–24]. In particular, PT shows a surface featuring tiny nanosphere-like bumps (Fig. 2b); P3MT shows nanohills on the surface with out-of-plane randomly-distributed nanowires protruding from the surface itself (Fig. 2d); PEDOT shows a cauliflower-nanostructured surface (Fig. 2f). Such an intrinsic nanostructuring produces a further increase of the surface area of the



**Fig. 3.** CVs in  $\text{LiClO}_4$  0.1 M/ACN on films of PEDOT (a), P3MT (b) and PT (c) deposited by light-activated electropolymerization on flat *n*-Si templates at different scan rate: 10, 25, 50, 75, 100, 150, 200 mV/s. Insets: linear variation of the anodic current peak with the square root of scan rate. (d) CVs (scan rate = 50 mV/s) in  $\text{LiClO}_4$  0.1 M/ACN on PEDOT microtubes (solid curve; film deposited on *n*-Si featuring a pore array with AR = 1) and PEDOT flat films (dashed curve).

microstructured polymer, thus significantly enhancing charge-mass transfer processes occurring at the polymer surface. Surface nanostructuring of microstructured polymers can be beneficial in several applications, especially in sensing processes, promoting an easier access to polymer binding sites and, therefore, shorter response time and improved sensitivity, and in fuel-cell applications.

The electrochemical behavior of CP films deposited by light-activated electrosynthesis on both flat and microstructured silicon templates is investigated by CV in a solution of  $\text{LiClO}_4$  0.1 M in ACN, using a conventional three-electrode cell with a Pt wire and an  $\text{Ag}/\text{Ag}^+$  0.1 M in ACN as counter and reference electrodes, respectively. Typical voltammograms for PEDOT, P3MT, and PT films on flat silicon are shown in Fig. 3a–c. CP films exhibit good redox activity, as demonstrated by the presence of well-defined peaks in both direct and inverse scans. In all cases, the separation between anodic and cathodic peak potentials increases with the increase of scan rate from 10 to 200 mV/s. Such a behavior could be ascribed to the electrochemical irreversibility of the redox processes and/or to the contribution of a certain uncompensated resistance due to the polymeric film [25]. The current peak intensity linearly increases with the square root of the scan rate (insets in Fig. 3a–c), as commonly observed on thick polymeric films on electrodes under conditions promoting an electrochemical charge diffusion regime [26]. Good electrochemical stability is also evident, being no significant electroactivity losses observed after 20 redox cycles. Similar voltammograms are obtained on films deposited by conventional electropolymerization on platinum foils with the same configuration cell, thus demonstrating that light-assisted electrosynthesis of polymeric films does not alter electroactivity and conductivity properties.

PEDOT, P3MT, and PT microtubes synthesized by light-activated electropolymerization on silicon templates show redox properties

similar to flat films. As an example, Fig. 3d shows typical voltammograms of PEDOT microtubes synthesized on microstructured silicon (array of pores with AR of 1) and PEDOT films synthesized on flat silicon. Microstructured and flat films exhibit similar redox peak couples, though PEDOT microtubes show a small increase of the peak separation (0.38 V compared to 0.22 V of flat films) probably due to limited diffusion kinetics and/or to a further increase of resistive contribution in microstructured polymers. A significant increase of both anodic and cathodic current peaks is observed for PEDOT microtubes, with respect to flat films, which can be explained in terms of larger surface area exposed to the electrolyte. The ratio between microtubes and flat films anodic (as well as cathodic) current peaks in Fig. 3d is about 2, which is in good agreement with the ratio between surface areas (namely 1.9). These results clearly demonstrate that the entire surface of the microstructured film is electroactive and can be efficiently exploited for further electrochemical applications, without the need of removing the polymer film from the template substrate, thus overcoming one of the most critical drawbacks of conventional template-assisted techniques.

#### 4. Conclusions

This work demonstrates the successful combination of CP electropolymerization and advanced silicon micromachining technologies via light-activated electrochemical processes. Fabrication of several microstructured CPs, namely PEDOT, P3MT, and PT microtubes with AR between 1 and 10 is reported and electroactivity of the whole CP microstructured surface clearly assessed.

Although silicon microstructuring is here performed using light-activated electrochemical etching in a HF-based aqueous solution, any

other silicon micromachining technology, both wet (e.g. potassium hydroxide – KOH, tetramethyl ammonium hydroxide – TMAH, etc.) and dry (e.g. reactive ion etching – RIE, etc.), can be effectively used for the template fabrication. Moreover, although template fabrication is here limited to the case of pores, application of the light-activated electropolymerization technology to other microstructures, with different geometries and AR, can be easily envisaged, thanks to the highly conformal growth of polymer films.

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