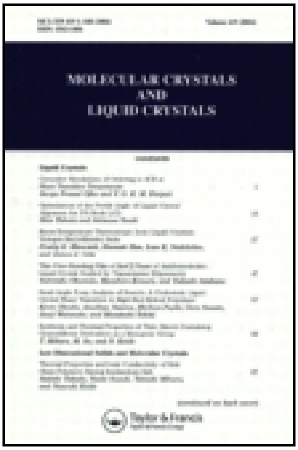

Molecular Crystals and Liquid Crystals

Enhanced Electroactivity and Electrochromism in PEDOT Nanowires

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Enhanced Electroactivity and Electrochromism in PEDOT Nanowires

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Here, we report on an in situ study of the spectroelectrochemical behavior of template prepared poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires by UV-Vis-NIR spectroscopy. A comparative analysis between spectra measured on a PEDOT thin film and on nanowires (diameter: 80 nm, 30 nm) has been made. It gives evidence for – enhanced bipolaronic band in the oxidized state, and – more efficient dedoping in the reduced state, for the 30-nm nanowires. This result, analyzed in terms of higher (de)doping level during the redox process for the smaller diameter, demonstrates improved electroactivity and electrochromism, as required for sensors.

Keywords: electrochromism, nanowire

INTRODUCTION

Extensive research on conjugated polymer nanowires and nanotubes has been undertaken in the past few years. The main interest stems from enhanced physical properties at reduced dimensionality and size.

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To prepare large arrays of nanowires, the “template” synthesis within porous membranes is a good alternative to lithographic techniques. PEDOT nanowires and nanotubes have already been used for nano-LEDs [1], field-emission [2], electrochromic displays [3] and building-blocks for bio- and chemical sensors and drug release [4].

The poly(3,4-ethylenedioxythiophene) (PEDOT) chosen for this study has the major advantage to be very stable in the doped state, with conducting properties that remain almost unaltered under ageing in environmental condition. However, this stability could be a handicap for many applications based on doping and dedoping of the polymer. We show here by an in situ absorption study that for nanowires with a small enough diameter, strongly reduced and oxidized states can be achieved.

In this work, we report on a comparative study of the spectroelectrochemical behavior of PEDOT nanowires and thin film. Both film and nanowires were electropolymerized in the same conditions (aqueous medium, fixed potential). This study indicates that more complete electrochemical doping and dedoping occur for the narrow nanowires than for the larger ones and for the film.

EXPERIMENTAL DETAILS

Confined electropolymerization was carried out by using track-etched nanoporous polycarbonate (PC) templates supported on ITO-glasses especially developed at the Université catholique de Louvain for spectroelectrochemical experiments. Their fabrication has been described in details elsewhere [5].

EDOT electropolymerization was performed in a conventional one-compartment cell, with a Pt counter-electrode and an Ag/AgCl reference electrode. The ITO acted as working electrode. Electrosyntheses were performed at room temperature from an electropolymerization bath developed by Sakmeche *et al.* [6] containing 0.07 M sodium dodecylsulfate (SDS), 0.1 M $LiClO_4$ and 0.05 M EDOT. PEDOT films and nanowires were grown potentiostatically at a fixed potential of 0.8 V using an EG & G Princeton Research Model 273 A potentiostat/galvanostat. All the samples were thoroughly rinsed with deionized water after synthesis. It has to be noticed that PEDOT nanowires prepared under similar conditions were characterized by Raman spectroscopy, electron spin resonance, X.P.S. and electrical measurements [7–9]. But their UV-Vis-NIR spectroelectrochemical behavior has not yet been investigated, because a PC template supported on transparent conducting electrode is required, that has been developed recently.

PEDOT films and nanotubes grown on ITO-coated glass were placed in a quartz cuvette of 1 cm path length, containing a monomer free electrolyte ($SDS + LiClO_4$) aqueous solution. ITO was acting as working electrode. A platinum wire was used as counter-electrode and Ag/AgCl as reference electrode. The PC template was dissolved in CH_2Cl_2 prior to *in-situ* absorption measurements. UV–Vis–NIR absorption spectra of PEDOT films and nanotubes grown on ITO-coated glass were recorded on a Varian Cary 500 Scan UV–Vis–NIR spectrophotometer. A virgin ITO-coated glass was used to record the baseline. The UV–Vis spectra were recorded concomitantly with the application of a potential varying from -800 to $+800$ mV. The presented spectra were recorded 5 min after the potential application, when a constant absorbance was reached.

RESULTS AND DISCUSSION

The UV-Vis-NIR spectroscopy is a powerful technique that gives evidence for electronic transitions between the valence and the conduction bands and for electronic transitions involving intermediate bands (polaronic and bipolaronic bands). Spectroelectrochemical properties of PEDOT films have been investigated [10]. Recently, this technique has already been used to study the electronic structure and the spectroelectrochemical properties of PPy and PANi nanotubes [11].

For conjugated polymers, it is generally admitted that the presence of (bi)polaronic bands is directly related to the doping level and to a certain extent of the disorder. Bipolarons are only expected for heavily doped polymers with a limited disorder extent, while a low doping level results in polarons [12].

Figures 1–3 show absorption spectra recorded at a fixed potential (ranging between -0.80 and $+0.80$ V/Ag/AgCl) for a PEDOT film, 80 nm-diameter nanowires and 30 nm-diameter nanowires respectively. The spectral range was limited to a wavelength of 1350 nm because of absorption by water beyond. It can be noticed that spectra are more noisy for the nanowires than for the film case, due to the small amounts of material. Common features are observed for the three samples. In the reduced state for an applied potential (E_a) of -0.80 V, a wide band is obtained with a maximum at 595 nm. This band is attributed to the π-π^* transition of neutral PEDOT, with an onset at about 770 nm ($\approx$1.6 eV) in good agreement with values reported previously for electropolymerized PEDOT [13]. Upon oxidation, the maximum shifts to higher energy and decreases in intensity. Simultaneously, a new absorption band appears at low

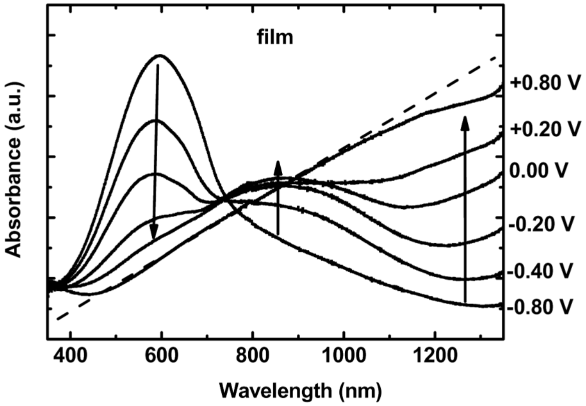

FIGURE 1 Absorption spectra recorded at a fixed potential (ranging between -0.80 and $+0.80\,V/Ag/AgCl$) for a PEDOT thin film.

energy with a maximum at 880 nm. This band, so-called polaronic band, is attributed to transitions involving polarons. For a positive polaron, two electronic levels – bonding and antibonding – are formed within the bandgap and one electron is removed from the polaron bonding level, thus resulting in the observed transitions. The intensity of the polaronic band tends to saturate and slightly decreases for E_a larger than 0.0V/Ag/AgCl. At higher applied potentials, the absorption spectra are clearly dominated by a broad band whose maximum is beyond the maximum wavelength of 1350 nm

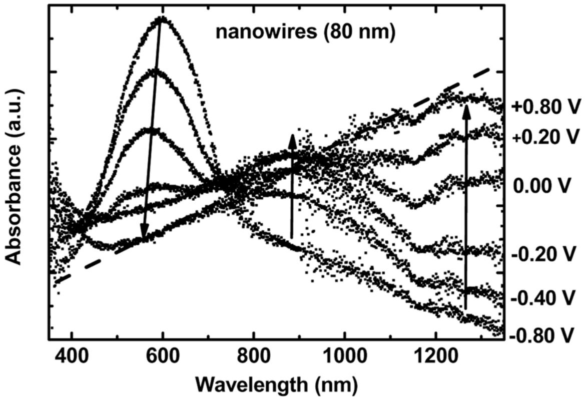

FIGURE 2 Absorption spectra recorded at a fixed potential (ranging between -0.80 and $+0.80\,V/Ag/AgCl$) for 80 nm-diameter nanowires.

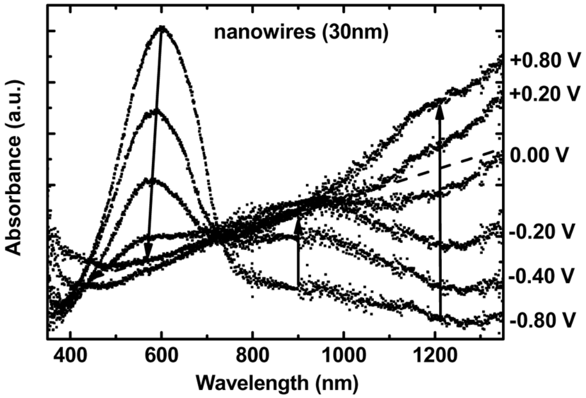

FIGURE 3 Absorption spectra recorded at a fixed potential (ranging between -0.80 and $+0.80\,\mathrm{V/Ag/AgCl}$) for 30 nm-diameter nanowires.

authorized in our experimental conditions. This band can be attributed to the transition between the valence band (VB) and the bonding bipolaronic band expected at high doping level when polarons recombine into spinless bipolarons. This could be also interpreted as the spectroscopic manifestation of the bipolaron bands broadening which in consequence could lead to a metallic state [14].

Significant changes are observed by comparing spectra measured for the PEDOT films and the 80 nm and 30 nm nanowires. For an applied potential of $+0.80\,\mathrm{V}$, the variation of the absorption vs. wavelength appears to be linear in the range 550–1000 nm for the three samples. The corresponding slope is given by the dashed line reported on Figures 1–3. Looking at the respective bipolaronic contributions for wavelengths higher than 1200 nm, the PEDOT film and the 80 nm nanowires present the same tendency, i.e. spectra below the dashed line. On the contrary, the $+0.80\,\mathrm{V}$ spectrum for the 30 nm nanowires present an inflexion point around 1000 nm, and a spectrum above the dashed line. This can be attributed to an enhanced contribution of VB to bonding bipolaron transitions, eventually combined with a reduced contribution from the polaron (as it plays on the linear slope between 550 and 1000 nm). A higher contribution of bipolarons is generally attributed to a higher electrochemical doping level. This enhanced electroactivity for the smaller nanowire diameter is confirmed by the comparison of the absorption spectra in the reduced state ($E_a = -0.80\,\mathrm{V/Ag/AgCl}$) for the film and the 30 nm diameter nanowires, as shown in Figure 4. Indeed, the residual absorption that appears in the range 800–1000 nm for the film, is very strongly

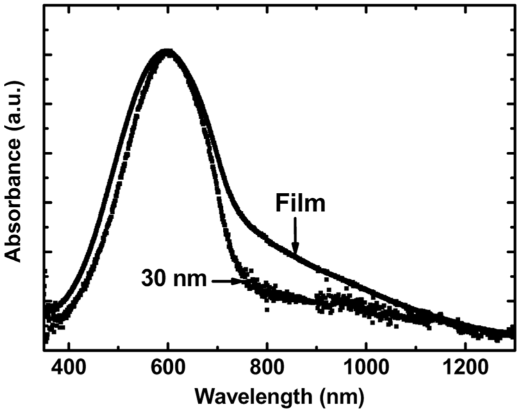

FIGURE 4 Absorption spectra for a PEDOT thin film and for PEDOT nanowires (diameter 30 nm) on ITO in the reduced state (fixed potential = −0.8 V).

reduced for the 30 nm nanowires. This study indicates that both the neutral state and the fully doped state can be reached due to an easier diffusion of the counter-ions when the nanowire diameter is small enough, whereas some counter-ions should remain active in the polymer film and for the 80 nm nanowires in the reduced state. Finally, the π-π^* transition band appears to be significantly narrower for the 30 nm nanowires than for the film (Fig. 4) in the reduced state. This could be explained by a narrower distribution of conjugation lengths, as shown on oligothiophenes [15].

The results reported above are coherent with the results of spectroscopic studies made on PEDOT nanowires prepared under the same conditions, i.e. a fixed potential of +0.80 V in the same electrolyte. From an electron spin resonance study, it has been shown that the polaron density within PEDOT nanowires is reduced by a factor 4 to the benefit of bipolarons when the diameter decreases from 100 nm to 50 nm [8]. And a Raman study gives evidence for larger conjugation length when the nanowire diameter decreases [7]. Such an enhanced molecular and supermolecular structure for template-prepared nanowires and nanotubes are generally attributed to the confined synthesis and to the preferential growth of the polycationic polymer chains induced by anionic sites onto the pore surface [16]. Moreover, our results can be compared with the fast electrochromic response in PEDOT nanotubes (instead of nanowires in this work) evidenced by Seung Il Cho *et al.* [3]. The authors attributed the fast (less than 10 ms) decoloration or oxidation to the very small thickness (20 nm) of the nanotube wall and as a result, to the very small diffusion distance for the counter-ions in the polymer. Such a fast switching rate (smaller than 40 ms for a 24 frames/s) is required for moving-image speeds to be used in paper-like displays (electronic paper). In our study, the speed of the electrochromic response has not been determined, as a fixed potential was applied for several minutes before recording of the absorption spectrum.

CONCLUSION

PEDOT nanowires have been electropolymerized within nanopores of polycarbonate templates. An *in situ* study by UV-Vis-NIR spectroscopy reveals significant changes between the electrochemical behavior for the 30-nm diameter nanowires in comparison to the 80-nm diameter nanowires and to the PEDOT film case. These changes are attributed to the very small nanowire diameter, that facilitates the diffusion of counter-ions from the electrolyte into the polymer during the redox process. These results are of importance for applications based on the electrochemical and electrical behavior of conjugated polymers.

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