

Synthesis and properties of Polythionine/Co-doped titanate nanotubes hybrid materials



V.C. Ferreira, O.C. Monteiro*

University of Lisbon, Faculty of Sciences, Department of Chemistry and Biochemistry and CQB, Campo Grande, 1749-016 Lisbon, Portugal

ARTICLE INFO

Article history:

Received 7 October 2012

Received in revised form 21 May 2013

Accepted 10 July 2013

Available online 22 July 2013

Keywords:

Cobalt doped titanate nanotubes

Thionine

Electro-polymerization

Conducting hybrid films

ABSTRACT

The synthesis of polythionine (PTN)/cobalt-doped titanate nanotubes (CoTNTs) hybrid conducting films with distinct layouts, using electropolymerization, is reported. The CoTNTs nanocrystalline elongated particles were obtained by a hydrothermal treatment, using an amorphous Co-doped material as precursor. The adsorption ability of the prepared CoTNTs to remove organic dyes from aqueous media was investigated, using thionine (Th). The total amount of Th removed by the nanocrystalline CoTNTs powder was 340.06 mg g^{-1} . During this process, and due to the CoTNTs structural properties, the combination of dye adsorption and intercalation was considered. After dye sensitization, the Th/CoTNTs were characterized and used for Th electropolymerization studies, in order to produce hybrid polythionine (PTN) electroactive films. The electroactivity of the Th molecules after immobilization in the CoTNTs surface is maintained. After electropolymerization, stable and electroactive nanostructured CoTNTs–PTN modified electrodes were obtained. The influence of the experimental parameters in the final electrical and morphological properties of the obtained hybrid films was studied, mainly the presence of the monomer in solution, adsorbed or intercalated in CoTNTs.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Although considering that the titanium oxide (TiO_2) or titania (*anatase* and *rutile*) are the titanium compound most commonly used, the nanostructured titanates have gained considerable research interest [1,2], either protonated or doped with sodium ions, with the general formula $\text{Na}_{2-x}\text{H}_x\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$, with $0 \leq x \leq 2$. The application of nanostructured titanates for photosensitive materials, replacing TiO_2 , has been envisaged. They are very attractive for new photosensitive, adsorbing and catalytic materials platforms development [7,3], essentially due to three reasons: their high specific surface area, in the order of $\text{ca. } 177\text{--}400 \text{ m}^2 \text{ g}^{-1}$ [1,4], when compared with the one typically observed for *titania* ($20\text{--}50 \text{ m}^2 \text{ g}^{-1}$); their band gap energy close to that of TiO_2 *anatase* ($\sim 3.2 \text{ eV}$) [5]; and the possibility of being doped with different cationic ions, e.g. Li^+ , Cs^+ , Na^+ , K^+ and dyes [6–8].

The titanate nanostructures may present distinct shapes, namely nanorods, nanotubes, nanosheets, and nanofibres [1,4]. The titanate nanotubes (TNTs) usually present internal and external diameters of about 2.5 and 5 nm, respectively. The walls of the TNTs have a characteristic multilayered structure consisting of edge- and corner-sharing TiO_6 octahedra, building up zigzag structures with

the sodium ions located between the TiO_6 layers, with an interlayer distance of *ca.* 0.8 nm [9]. The sodium ions can be exchanged and arrangements and adjustments of the interlayer distance are predictable, depending on the inserted cation/molecule dimensions.

The TNTs have been used in the development of electrodes for Dye Sensitized Solar Cells (DSSCs) [1]. Its elongated shape, visible-light absorption efficiency and negatively charged surface (which increases its capability to adsorb cationic dyes) enhances the electron transport and storage in DSSCs.

Small sized Co-doped TNTs (with Na^+ ions in the interlayers) have also shown excellent ability to remove dye molecules, such as methylene blue, from aqueous solutions [10,11]. This feature is very interesting, especially for wastewaters pollutants removal. The existence in the structure of a metal ion, e.g. cobalt, with remarkable electro-catalytic properties make CoTNTs-based materials very attractive and their technological applicability can be extended.

The nanoparticles immobilization on electrode surfaces is an important goal to be achieved, namely if new electrochemical applications are intended for such materials. In order to improve the attachment of active particles to electrode surfaces, several methodologies have been used, e.g. self-assembling, nafion matrices, and conducting polymer films [12–17]. Conducting polymer films have been intensively used for the immobilization of nanotubular materials (e.g. carbon nanotubes) [14,18], noble metal nanoparticles (M-NPs) [15,16] and other inorganic

* Corresponding author. Tel.: +351 217500865; fax: +351 217500088.
E-mail address: ocmonteiro@fc.ul.pt (O.C. Monteiro).

nanoparticles (nanodiamonds, CdS and TiO₂) [17,19,20]. The use of conducting matrices, such as polyaniline (PAni), poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy), have been reported [14–20]. One of the most used approaches, with good control over the amount and distribution of the pre-synthesized particles, is the immobilization through entrapment, during the electro-polymerization process.

Moreover, several cationic dye molecules, frequently related with serious environmental pollution problems, such as thionine (Th), neutral red and methylene blue [21–24], can be electrochemically polymerized from aqueous solutions, resulting in modified electrodes stable in a wide pH range [21,22].

In the present work, CoTNTs nanocrystalline elongated particles were synthesized and their interaction with thionine (Th), used as a model organic molecule, was studied. In order to make this process more sustainable from the environmental and economical points of view, after immobilizing Th over the CoTNTs, the possibility of Th to be electrochemically polymerized was systematically analyzed. Polythionine/CoTNTs modified electrodes, with distinct layouts, were successfully prepared. Then they were evaluated, regarding the effect of the modification approach on the morphology and electrochemical response of the prepared nanostructured conducting films.

2. Experimental

All reagents were of analytical grade (Aldrich and Fluka) and were used as received, without further purification. The solutions were prepared with Millipore Milli-Q ultra-pure water.

2.1. Materials and methods

2.1.1. CoTNTs precursor synthesis

The CoTNTs precursor was prepared using a procedure previously reported [25]. The used titanium source was a titanium trichloride solution (10 wt.% in 20–30 wt.% HCl) diluted in a ratio of 1:2 in standard HCl solution (37%). Then, the required amount to have 5% (molar) of cobalt was added: 0.170 g of metallic cobalt powder was carefully dissolved in ca. 1 mL of concentrated HNO₃. The deep purple solution was heated to evaporate the solvent and ca. 2 mL of HCl (37%) solution was added to evaporate residual nitrates (yellow steam is formed). After no yellowish steam was observed, the solution was diluted with 2 M HCl to 100 mL. This solution was added to 50 mL of the titanium trichloride solution. 4 M ammonia aqueous solution was added dropwise to this solution, under vigorous stirring, until complete precipitation of greenish grey solid (CoTNTs precursor). The resulting suspension was kept overnight at room temperature and then filtered and washed with deionised water.

2.1.2. CoTNTs synthesis

The CoTNTs samples were prepared in an autoclave system using ~6 g of the precursor, in ca. 60 mL of NaOH 10 M aqueous solution [26]. The samples were prepared at 175 °C using an autoclave dwell time of 24 h. After cooling, the suspensions were filtered and the grey solid was washed systematically: the sample was dispersed in ~150 mL of water and magnetically stirred for 1 h. Then, the suspension was filtered and the pH of the filtrate was measured for reference. This procedure was repeated until the filtrate solution has reached pH = 7. Afterwards, the solid (CoTNTs) was dried and stored.

2.1.3. CoTNTs dye sensitization

The thionine (Th) adsorption was performed in suspension; 10 mg of dry CoTNTs were added to 10 mL of the dye solution (500 mg L⁻¹) and allowed to adsorb for 2 h under stirring. After

equilibrium adsorption, the suspensions were centrifuged and the sensitized solids were washed with ultra-pure water, until removing all the un-adsorbed dye. The amount of adsorbed Th was obtained through UV–vis absorption measurements.

2.1.4. Electrochemical polymerization

The electrochemical experiments were carried out with a computer-controlled CHI620A electrochemical workstation in a conventional three-electrode system, using a platinum foil counter electrode and a saturated calomel electrode (SCE) as reference electrode. All potentials are reported with respect to the SCE. The redox potential of the SCE is +0.244 V vs. SHE at 25 °C. The used working electrode was glassy carbon (GC, geometric area $A_{GC} = 0.196 \text{ cm}^2$). When required, the GC electrodes were previously modified with CoTNTs or Th–CoTNTs samples. The immobilization was performed by a drop-cast methodology, typically 5 or 30 μL of a 1 mg mL⁻¹ suspension, overnight.

The Th electrochemical polymerization was performed by cyclic voltammetry, between 0 and 1.05 V (unless otherwise stated) at a scan rate of 50 mV s⁻¹. The used electrolyte was a 0.1 M NaClO₄ aqueous solution. All the solutions were prepared with ultra-pure water and were deoxygenated for ca. 20 min with a nitrogen flow, before use.

For the sake of clarity, the prepared polymeric films were labelled with PTN no. of growth cycles/scan rate (method). For example: the PTN80/50 is the polythionine (PTN) film prepared using 80 cycles and a scan rate of 50 mV s⁻¹ over the GC electrode; the PTN80/50(i) film was prepared using identical conditions (80 cycles and a scan rate of 50 mV s⁻¹) using the method (i) that is described later.

2.2. Characterization

X-ray powder diffraction was performed using a Philips X-ray diffractometer (PW 1730) with automatic data acquisition (APD Philips v3.6B), using Cu K α radiation ($\lambda = 0.15406 \text{ nm}$) and working at 40 kV/30 mA. The diffraction patterns were collected in the range $2\theta = 7 - 60^\circ$ with a 0.02° step size and an acquisition time of 2.0 s/step. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were carried out using a JEOL 200CX microscope operating at 200 kV. Scanning electron microscopy was performed in a field emission gun – scanning electron microscope JEOL-7001F (FEG-SEM), operating at 10–15 kV. Specific surface areas were obtained with the method developed by Brunauer, Emmett, and Teller (B.E.T. method), using nitrogen adsorption data at -196°C , with a volumetric apparatus from Quantachrome mod NOVA 2200e. The samples, weighing between 40 and 60 mg, were previously degassed for 2.5 h at 150 °C at a pressure lower than 0.133 Pa. The amount of adsorbed dye was measured by UV–vis spectroscopy (Jasco V-560).

3. Results and discussion

3.1. Samples identification and morphology

The CoTNTs samples prepared at 175 °C during 24 h were characterized by XRD. The XRD pattern (Fig. 1a) is in agreement with the existence of a Na_xH_{2-x}Ti₃O₇ titanate layered structure. The diffraction peak at $2\theta \sim 10^\circ$ is related with the interlayer distance between the TiO₆ sheets, while the peaks at 24.5° , 28.6° and 48.6° are characteristic of tri-titanate 1D nanomaterials [27].

The CoTNTs morphology was analyzed by transmission electron microscopy and a homogeneous sample was observed (Fig. 1b). The particles were elongated, presenting a narrow

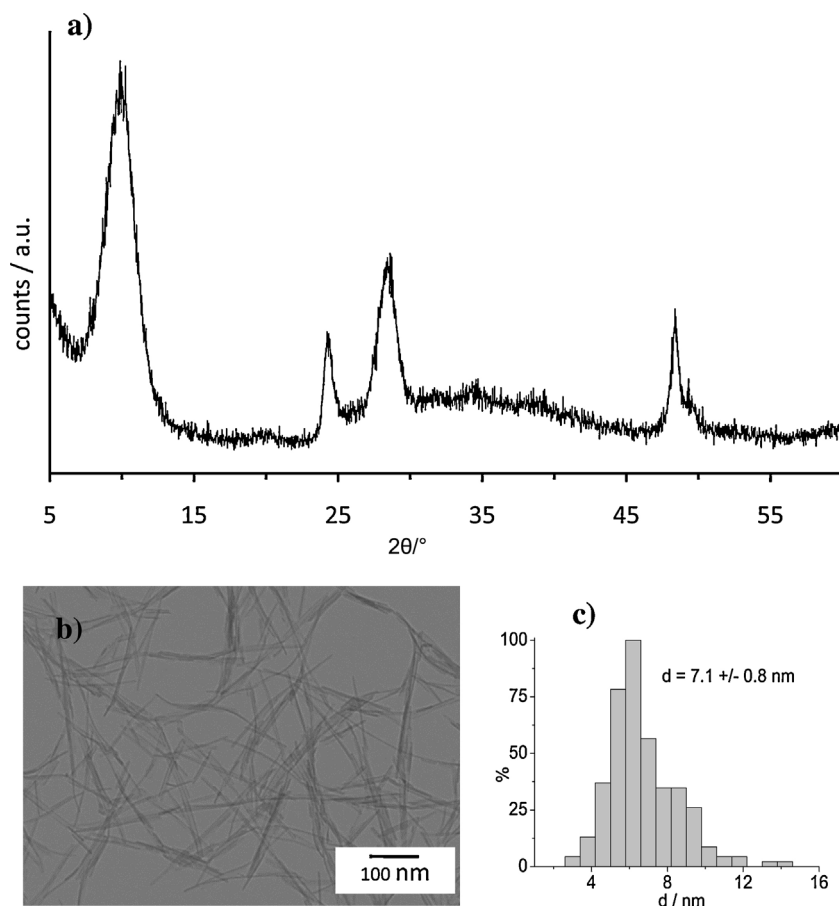


Fig. 1. XRD pattern (a), TEM image (b) and particle size distribution (c) of the CoTNTs sample.

particle size distribution (Fig. 1c). The CoTNTs particle size was calculated and a value of 7.1 ± 0.8 nm was obtained.

3.2. Dye sensitization

The ability of CoTNTs to remove organic pollutants from aqueous solution was studied, using thionine (Th) as a model dye (Fig. 2). Prior to the adsorption experiments, the BET surface area of the CoTNTs sample was measured and the found value was $226.20 \text{ m}^2 \text{ g}^{-1}$. The amount of adsorbed Th, at the equilibrium conditions, was 340.06 mg g^{-1} of CoTNTs.

This result was predictable, since TNTs based materials, when prepared by alkaline hydrothermal synthesis in aqueous media, are negatively charged and are expected to attract cationic species due to the presence of cation binding sites, which have been formed during the synthesis by Na^+ incorporation [27].

Considering the high amount of immobilized Th and the CoTNTs surface area available for the dye adsorption, the occurrence of a dye intercalation process, between the TiO_6 layers, cannot be completely ruled out. On the other hand, the existence of sodium ions in the CoTNTs structure (in the interlayer space) and the reduced dye molecule dimensions can also support this process occurrence.

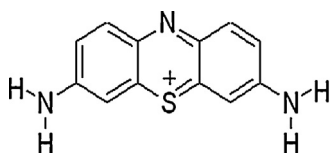


Fig. 2. Schematic representation of the of thionine (Th) chemical structure.

It is reasonable to assume that the cationic dye molecules are adsorbed over the surface through electrostatic interactions and, therefore, oriented with the positive charge towards the nanotubes surface. In this case, the area occupied by each Th molecule will be about 0.12 nm^2 (value estimated using the software ChemSketch). On the other hand, due to the delocalized π system in the aromatic rings of the dye molecule, the flat lying adsorption in the surface is also a possibility, resulting in an area per molecule of *ca.* 0.59 nm^2 . Considering these two limit situations, the area occupied by the total amount of adsorbed dye can vary from 85.52 to $419.06 \text{ m}^2 \text{ g}^{-1}$, respectively. This latter value is superior to the surface area available for adsorption ($226.20 \text{ m}^2 \text{ g}^{-1}$), suggesting that the intercalation of the dye molecules between the TiO_6 layers, together with surface adsorption, should also takes place. In fact, it has been reported that cationic dyes can be intercalated in the interlayer spacing of layered materials such as clays [28] and nanostructured titanates [8].

3.3. Th electropolymerization routes

The combination of cobalt containing titanate nanotubes with conducting polymers to construct new hybrid electrochemical-based architectures is an interesting research subject. Based on this fact and the possibility of producing conducting polymeric hybrid films, through electropolymerization of organic molecules, such as thionine (Th) [21], a systematic study was performed using the prepared Th–CoTNTs particles.

In order to study the influence of the experimental parameters in the final properties of the nanocomposite films, distinct

methodologies were used for the production of polythionine (PTN)–CoTNTs hybrid films:

- (i) Th electropolymerization using the cleaned GC electrode and a freshly prepared suspension containing CoTNTs (2.84 mg mL^{-1}), Th (10 mg L^{-1}) and 0.1 M of NaClO_4 (electrolyte solution);
Film label: CoTNTs–PTN80/50(i)
- (ii) CoTNTs immobilization in the GC electrode surface, by drop-casting, and subsequent electropolymerization in electrolyte solution containing 10 mg L^{-1} of Th;
Film label: CoTNTs–PTN80/50(ii)
- (iii) Drop-cast deposition of CoTNTs into the GC surface and overnight drying; immersion in 250 mg L^{-1} Th solution for 2 h (*in situ* dye adsorption) and posterior electropolymerization in monomer free electrolyte solution;
Film label: CoTNTs–PTN31/50(iii)
- (iv) Drop-cast deposition of the Th–CoTNTs in the GC surface (CoTNTs were previously saturated with Th, *ex situ* adsorption) and electropolymerization in a monomer free electrolyte solution;
Film label: CoTNTs–PTN80/50(iv)
- (v) Drop-cast deposition of Th–CoTNTs in the GC surface (CoTNTs were previously saturated, *ex situ* adsorption) and electropolymerization in an electrolyte solution containing 10 mg L^{-1} of Th;
Film label: CoTNTs–PTN80/50(v)

It is worth to note that the Th concentration in the electrolyte solution was limited by the monomer solubility in the media used.

3.3.1. PTN80/50 film growth and characterization

The cyclic voltammograms obtained during the growth of a polythionine film (PTN80/50), prepared directly in the bare GC electrode, using an anodic limit potential, $E_{\text{al}} = 1.05 \text{ V}$ are shown in Fig. 3. In the first anodic scan, the oxidation peak at about -175 mV corresponds to the reversible Th oxidation in solution, with the corresponding reduction peak at *ca.* -350 mV . The monomer irreversible oxidation occurs at high potential values ($>0.8 \text{ V}$) and the polymer growth is clearly evidenced through a current increase of the oxidation (*ca.* 35 mV) and reduction (*ca.* 10 mV) peaks, with the increase of the potential cycles (at least until the 80th cycle). The increase in the oxidation and reduction currents, related with the monomer, has been previously discussed in the literature [21,29,30]. The redox process, at less positive potential values in the polymerization voltammograms, indicates a strong contribution from the free monomer, since its redox conversion occurs in the same potential range, as observed for the Th monomer response on the GC electrode, observed in Table 1. This was further confirmed by comparing the cyclic voltametric response of the PTN80/50 modified electrode (Fig. 3b) in electrolyte solution with and without monomer.

The redox process at less positive potential values decreases and almost completely disappears upon rinsing the polymer film with a monomer free electrolyte solution (Fig. 3b). Moreover, the difference of the oxidation and reduction charges in the presence and absence of Th in solution is close to that involved in the oxidation (0.043 mC) and the reduction (0.027 mC) obtained in the potential interval corresponding to the Th monomer redox conversion ($E_{\text{al}} = -0.1 \text{ V}$, dashed curve). However the broad reduction peak of the PTN80/50 film, observed after washing it with monomer free solution, indicates the presence of more than one redox process. This has been previously observed in phenothiazine polymer films (e.g. PTN [21,30] and poly(methylene blue) [31]). It has been assigned to the monomer-type redox response and it can be due to monomer units attached to the polymer film through S–S interactions. A lower reversibility of the Th oxidation/reduction process

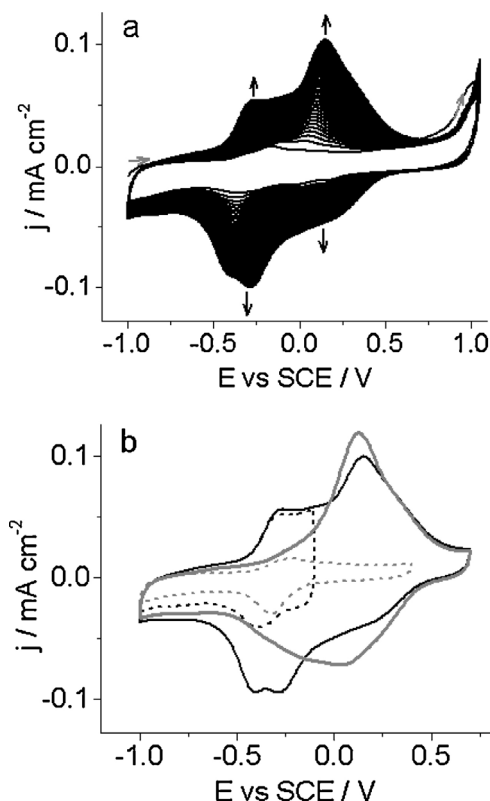


Fig. 3. Cyclic voltammograms of (a) Th electropolymerization on a GC electrode: PTN80/50 film (10 mg L^{-1} of Th in 0.1 M NaClO_4 , $E_{\text{al}} = 1.05 \text{ V}$, 80 cycles) and (b) PTN80/50 film characterization in (— and ---) 10 mg L^{-1} monomer and (——) monomer free solution, and (---) GC electrode in monomer solution.

was observed for the PTN80/50 modified surface ($\Delta E = 132 \text{ mV}$) than the one observed for the GC electrode ($\Delta E = 75 \text{ mV}$), shown in Table 1.

3.3.2. CoTNTs–PTN80/50(i) film growth and characterization

The simultaneous deposition of CoTNTs and PTN film according to method (i), from a suspension containing 2.84 mg mL^{-1} of CoTNTs and 10 mg L^{-1} of Th, was not completed successfully since a poor electroactive film ($Q_{\text{ox}} = 0.01 \text{ mC}$) was obtained (results not shown). This is probably due to the low Th concentration in solution and the increased diffusion of oligomers to the bulk solution (and therefore low polymerization efficiency), which was induced by the stirring process during film deposition. Furthermore, due to the extremely high capability of the CoTNTs to adsorb Th molecules, only 2–5 min were needed, after suspension preparation, to eliminate all the Th molecules from the electrolyte solution. As a direct consequence, the monomer availability in solution, for electropolymerization, drastically decreases.

3.3.3. CoTNTs–PTN80/50(ii) film growth and characterization

The drop-cast approach has proved to be the most effective way for the nanotubes deposition on the GC surface, either using Th-modified or pristine CoTNTs. However, low curing times (e.g. 4 h) has led to a weak interaction of CoTNTs with the GC surface (high detachment to the solution). High amounts of deposited CoTNTs ($30 \mu\text{L}$ of a 1 mg mL^{-1} CoTNTs suspension; overnight) resulted in the hindrance of the monomer access and/or of the electron transfer to the electrode surface (films with poor electroactivity).

Fig. 4 shows the cyclic voltammograms obtained during Th electropolymerization in the GC electrode previously modified with different amounts of CoTNTs, mentioned as film CoTNTs–PTN80/50(ii).

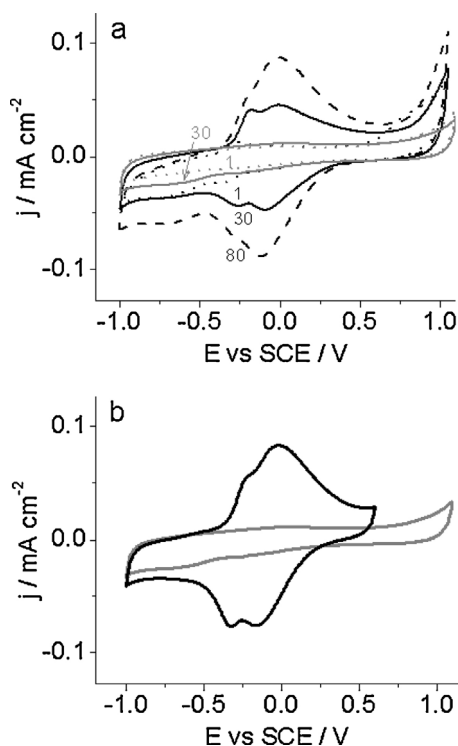


Fig. 4. Cyclic voltammograms of (a) Th electropolymerization on GC electrodes modified with: (■) 30 μL and (■) 5 μL of CoTNTs suspension (1 mg mL⁻¹), cycles (---) 1, (—) 30 and (---) 80 (10 mg L⁻¹ of Th in 0.1 M NaClO₄ aqueous solution, $E_{\text{ai}} = 1.05$ V) and (b) CoTNTs-PTN80/50(ii) film (—) and GC electrode (---) characterization in monomer free electrolyte solution.

The lower amount of deposited CoTNTs (5 μL) enabled the PTN80/50 film growth from a Th solution, according to method (ii); the nanocomposite film CoTNTs-PTN80/50(ii) displays good electroactivity and lower overpotential for the oxidation and reduction, as compared with the PTN80/50 film directly formed on the GC electrode surface, as can be observed in Fig. 4 and Table 1.

A similar electroactivity has been obtained for the CoTNTs-PTN80/50(ii) film and for the pristine polymer prepared directly on the GC surface, 0.117 mC and 0.139 mC, respectively. In addition, enhanced reversibility of the redox conversion has been achieved for the CoTNTs-PTN80/50(ii) modified electrode when

compared with the one obtained over the GC surface (PTN80/50): respectively $\Delta E = 130$ and 68 mV.

It must be stated that under these experimental conditions, the possibility of Th uptake from solution, by the deposited CoTNTs, has not been considered, since the electropolymerization process started immediately after immersion of the CoTNTs-modified electrode in the monomer solution.

3.3.4. CoTNTs-PTN31/50(iii) film growth and characterization

With the *in situ* adsorption method (iii) it is possible to obtain Th-saturated CoTNTs, with monomer molecules available for electropolymerization, as can be seen from the voltammograms in Fig. 5a. The GC electrode, previously modified with 5 μL of a

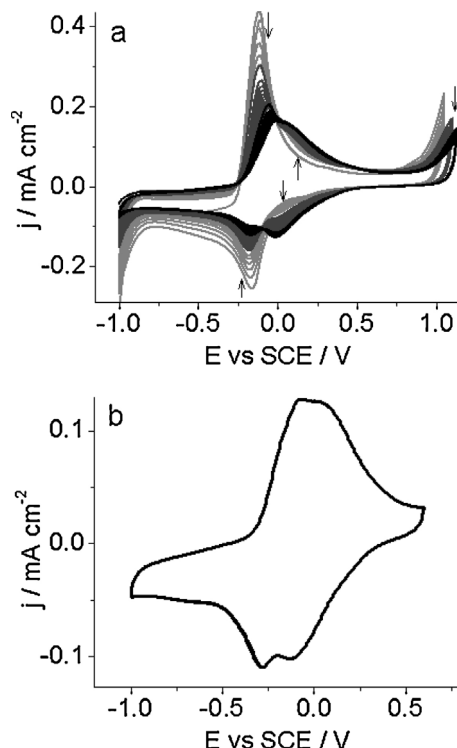


Fig. 5. Cyclic voltammograms of (a) electropolymerization of Th previously adsorbed in 5 μL of CoTNTs deposited on GC electrode, by immersion in a 250 mg L⁻¹ Th solution for 2 h, and (b) CoTNTs-PTN31/50(iii) film characterization in a monomer free electrolyte solution.

Table 1

Oxidation and reduction potential peaks, E , and charge, Q , of the redox conversion of Th in solution and PTN deposited films.

Modified electrode ID	$V_{\text{CoTNTs}}/\mu\text{L}$	E_{ox}/mV	E_{red}/mV	$\Delta E/\text{mV}$	Q_{ox}/mC	Q_{red}/mC
Th 10 mg L ⁻¹	—	—245	—310	75	0.015	0.011
PTN80/50	—	—270	—402	132	0.163	0.143
a	—	—283	—283	—	—	—
	—	147	(68–280)*	64	—	—
b	—	—134	≈ —134	—	0.139	0.128
	—	125	58	68	—	—
CoTNTs-PTN80/50(ii)	5	—7	—137	130	0.117	0.093
CoTNTs-PTN31/50(iii) ^c	5	—78	—278	200	0.210	0.142
	—	34	—123	157	—	—
CoTNTs-PTN80/50(iv) ^d	30	109	44	65	0.055	0.050
	30	100	42	58	0.055	0.051
CoTNTs-PTN31/50(iv) ^c	5	—276	—400	124	0.036	0.023
	—	—83	—158	75	—	—
CoTNTs-PTN80/50(v)	30	≈ —26	—200	174	0.200	0.159
	—	—	≈ —360	—	—	—

Characterization medium: a: Th 10 mg L⁻¹/NaClO₄ 0.1 mol dm⁻³ and b: NaClO₄ 0.1 mol dm⁻³; c: $E_{\text{ai}} = 1.05$ V (6 cycles), 1.10 V (12 cycles) and 1.13 V (13 cycles); d: $E_{\text{ai}} = 1.05$ V.

*Shoulder; peak not well-defined.

1 mg mL⁻¹ CoTNTs suspension, has been immersed in a 250 mg L⁻¹ Th solution for 2 h. After being washed it has been transferred to a blank electrolyte solution for polymer growth, at 50 mV s⁻¹ with different E_{al} : 1.05 V (6 cycles), 1.10 V (12 cycles) and 1.13 V (13 cycles). During polymerization, the anodic limit potential was increased in order to improve polymer grow, since a significant decrease of the irreversible Th oxidation at E_{al} was observed. The electrochemical profiles obtained during the film growth show an increase of the oxidation and reduction currents at about 35 and -13 mV, respectively, which correspond to the polymer formed from the adsorbed Th monomer. A concomitant shift of the peak position towards more positive potential values and the decrease of the monomer oxidation and reduction peaks current, at respectively *ca.* -119 and -161 mV, was observed, since its concentration in the surface decreases with polymer formation. In this case, the signal corresponding to the reversible redox conversion of the monomer is observed at lower potential values than that for the Th in solution, observed in Table 1. Apart from a potential shift of the oxidation process of *ca.* 30 mV, these results agree with the peak potential values obtained for Th molecules adsorbed on CoTNTs; E_{ox} . \approx -150 mV and E_{red} . \approx -267 mV.

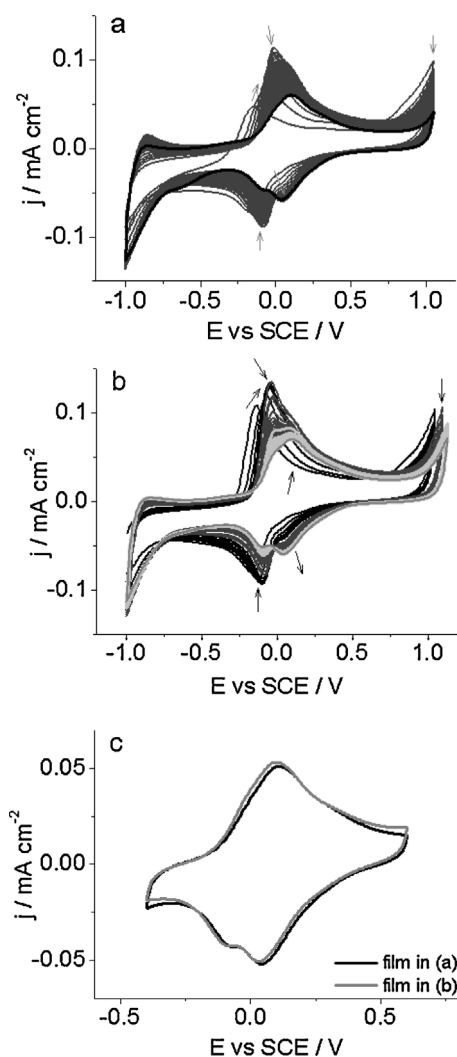


Fig. 6. Cyclic voltammograms of the Th electropolymerization on GC electrodes previously modified with 30 μ L of CoTNTs (suspension with 1 mg mL⁻¹): (a) E_{al} = 1.05 V; 80 cycles, (—) 80th cycle and (b) (—) E_{al} = 1.05 V; 6 cycles, (—) E_{al} = 1.10 V; 12 cycles, (—) E_{al} = 1.13 V; 13 cycles and (—) cycle 31, and (c) CoTNTs-PTN80/50(iv) films characterization in monomer free electrolyte solution.

Fig. 5b displays the cyclic voltammogram obtained for the characterization of the modified electrode after polymerization. This approach enabled the formation of PTN films with 31 potential cycles (CoTNTs-PTN31/50(iii)) with higher electroactivity than those grown with 80 sweep cycles on CoTNTs (5 μ L) modified electrodes from 10 mg L⁻¹ Th solutions (CoTNTs-PTN80/50(ii)), as seen in Table 1.

In spite of the lower reversibility of the redox conversion, when compared with the other modified electrodes, an enhanced electroactivity of this film was observed, when compared with that of PTN80/50 deposited on GC. This suggests that the dye molecules adsorbed *in situ* are more accessible for the electrochemical reaction, most probably due to its lower depth of penetration inside the titanate interlayer. This is probably due to the absence of stirring during the adsorption step.

3.3.5. CoTNTs-PTN80/50(iv) film growth and characterization

The voltammograms of the Th electropolymerization in the modified electrodes, prepared according to method (iv), are represented in Fig. 6(a and b), using 30 μ L of 1 mg mL⁻¹ Th-CoTNTs suspension and with/without constant E_{al} . Under these conditions, the anodic limit potential outline did not influence the electroactivity of the formed polymers, Table 1. On the other hand, using 5 μ L of Th-CoTNTs for the electrode modification (results not shown), a PTN film (CoTNTs-PTN80/50(iv)) with poor electroactivity was obtained (Table 1). This is most probably due to the smaller amount and lower accessibility of the Th, previously adsorbed (*ex situ*) on the CoTNTs surface, for the electrochemical reaction, when compared with the results obtained with higher amounts of Th-CoTNTs.

Furthermore, the monomer oxidation and reduction currents increase and are shifted towards more positive potential values in the initial polymerization cycles, due to the polymer growth; the polymer signal occurs overlapped with that of the monomer.

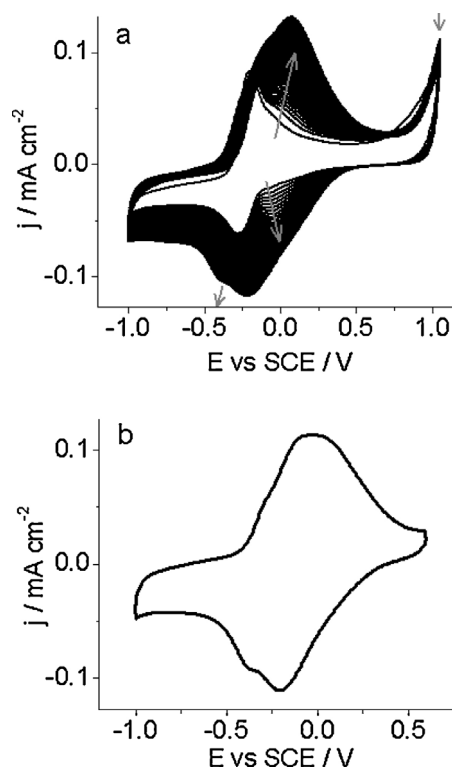


Fig. 7. Cyclic voltammograms of (a) Th electropolymerization (30 μ L of 1 mg mL⁻¹ Th-TNTs suspension (*ex situ* adsorption), in 10 mg L⁻¹ Th solution with 0.1 M of NaClO₄, E_{al} = 1.05 V, 80 cycles, and (b) CoTNTs-PTN80/50(v) film characterization in monomer free electrolyte solution.

This approach did not enable the formation of high electroactive PTN–CoTNTs modified electrodes, because they have a lower electroactivity than those prepared under the method (iii), Table 1. Nevertheless, this methodology has revealed that the adsorbed/intercalated Th molecules can be electrochemically polymerized and that the formed films do not detach from the electrode surface.

3.3.6. CoTNTs–PTN80/50(v) film growth and characterization

The electrodes modified under the method (v) have enabled the formation of films with increasing electroactivity, with potential $E_{al} = 1.05$ V at least until 80 cycles, as illustrated in Fig. 7a.

In spite of the reversibility of the CoTNTs–PTN80/50(v) film redox conversion ($\Delta E = 174$ mV) being lower than that of the polythionine film deposited directly on the GC surface, PTN80/50 ($\Delta E = 68$ mV), the electroactivity of the resulting modified electrode is comparable to the one of CoTNTs–PTN80/50(iii) film.

3.4. CoTNTs–PTN films morphological characterization

The morphology of the modified electrodes was analyzed by FEG-SEM. Fig. 8 shows the morphology of the GC electrode surface after hybrid films preparation; a smooth and compact morphology, related with the polymer existence, can be visualized after PTN80/50 film deposition. The morphology of the CoTNTs–PTN80/50(ii) and CoTNTs–PTN80/50(iii) films is identical: a homogeneous distribution of the elongated CoTNTs particles over the electrode surface is visualized in these two films. No

special morphological features directly related with the PTN presence (when compared with the PTN80/50 film) were observed.

Moreover, CoTNTs–PTN80/50(ii) and CoTNTs–PTN80/50(iii) films are very similar. It is then possible to conclude that there are no significant differences in the morphology of a film prepared using the monomer in solution and the CoTNTs attached to the electrode surface, and a film obtained with the Th adsorbed *in situ* in the CoTNTs after immobilization on the GC electrode.

The morphology of the electrodes surface, after CoTNTs–PTN80/50 modifications, was distinct from those shown in Fig. 8. In this case, on the top of the smooth layer deposited on the surface, heterogeneously sized and shaped bundles of CoTNTs were clearly detected with average sizes of 0.6 ± 0.3 μm and larger aggregates with *ca.* 2.0–4.2 μm spread throughout the surface (image not shown). By increasing the amount of deposited CoTNTs to 30 μL , the average size of the bundles increased to 0.7 ± 0.4 μm and 3.5–6.8 μm . This effect may be related with interactions amongst CoTNTs, due to the presence of adsorbed Th molecules, which induces aggregation in solution. In fact the Th-modified CoTNTs were more hardly dispersed in solution than the corresponding pristine CoTNTs.

4. Conclusions

New nanostructured hybrid thionine–TNTs electroactive materials were successfully synthesized, by using an adsorption and electrochemical polymerization steps combination approach. Materials with different properties were obtained depending on the used sequential procedure. Under the tested experimental conditions, the CoTNTs–PTN films that achieved the best electroactivity were the CoTNTs–PTN80/50(v) and the CoTNTs–PTN31/50(iii). No considerable morphological alterations were visualized for the films prepared using the monomer in solution, CoTNTs–PTN80/50(ii), or adsorbed *in situ* in the CoTNTs surface, CoTNTs–PTN31/50(iii). The nanocomposite film with the highest redox reversibility ($\Delta E = 58$ mV) was CoTNTs–PTN31/50(iv), synthesized by electropolymerization using 30 μL of a 1 mg mL^{−1} suspension of Th–CoTNTs previously immobilized on the GC surface and a monomer free solution.

The main conclusions of this work are the following: (1) the small size cobalt-doped TNTs nanoparticles retain their capability to remove thionine from an aqueous solution, after deposition on electrode surfaces; (2) the Th molecules preserve their electroactivity after adsorption/intercalation on the CoTNTs surface; (3) the adsorbed Th can be electrochemically polymerized, resulting in an electroactive and stable nanostructured CoTNTs–PTN modified electrode; (4) the methodology described can be successfully used for the removal of cationic dyes from aqueous solutions directly to CoTNTs (un)supported in solid surfaces and establishes an adequate and environmental friendly approach for composite modified electrodes development.

Acknowledgments

This work was supported by Fundação para a Ciência e Tecnologia (PTDC/CTM NAN/113021/2009). O.C. Monteiro acknowledges PEst-OE/QUI/UI0612/2011 and Programme Ciência 2007.

References

- [1] D.V. Bavykin, F.C. Walsh, Elongated titanate nanostructures and their applications, *European Journal of Inorganic Chemistry* 2009 (2009) 997.
- [2] S. Zhang, Q. Chen, L.-M. Peng, Structure and formation of $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes in an alkali environment, *Physical Review B* 71 (2005) 014104.
- [3] D.V. Bavykin, J.M. Friedrich, F.C. Walsh, Protonated titanates TiO_2 nanostructured materials: synthesis, properties, and applications, *Advanced Materials* 18 (2006) 2807.

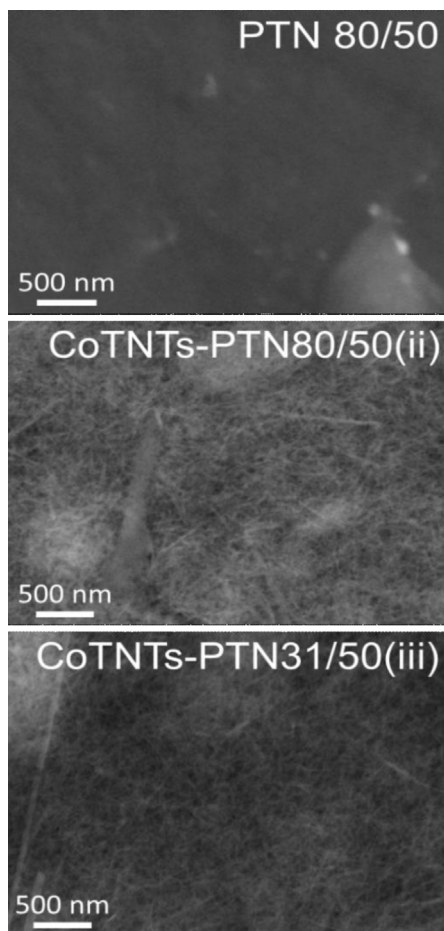


Fig. 8. SEM images of the PTN80/50, CoTNTs–PTN80/50(ii) and CoTNTs–PTN31/50(iii) hybrid films.

- [4] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Formation of titanium oxide nanotube, *Langmuir* 14 (1998) 3160.
- [5] A. Riss, T. Berger, H. Grothe, J. Bernardi, O. Diwald, E. Knozinger, Chemical control of photoexcited states in titanate nanostructures, *Nano Letters* 7 (2007) 433.
- [6] D.V. Bavykin, F.C. Walsh, Kinetics of alkali metal ion exchange into nanotubular and nanofibrous titanates, *Journal of Physical Chemistry C* 111 (2007) 14644.
- [7] M.W. Xiao, L.S. Wang, Y.D. Wu, X.J. Huang, Z. Dang, Electrochemical study of methylene blue/titanate nanotubes nanocomposite and its layer-by-layer assembly multilayer films, *Journal of Solid State Electrochemistry* 12 (2008) 1159.
- [8] N. Miyamoto, K. Kuroda, M. Ogawa, Visible light induced electron transfer and long-lived charge separated state in cyanine dye/layered titanate intercalation compound, *Journal of Physical Chemistry B* 108 (2004) 4268.
- [9] Q. Chen, G.H. Du, S. Zhang, L.-M. Peng, The structure of trititanate nanotubes, *Acta Crystallographica B* 58 (2002) 587.
- [10] L. Xiong, Y. Yang, J. Mai, W. Sun, C. Zhang, D. Wei, Q. Chen, J. Ni, Adsorption behavior of methylene blue onto titanate nanotubes, *Chemical Engineering Journal* 156 (2010) 313.
- [11] K. Hu, X. Xiao, X. Cao, R. Hao, X. Zuo, X. Zhang, J. Nan, Adsorptive separation and photocatalytic degradation of methylene blue dye on titanate nanotube powders prepared by hydrothermal process using metal Ti particles as a precursor, *Journal of Hazardous Materials* 192 (2011) 514.
- [12] H. Dai, H. Xu, X. Wu, Y. Lin, M. Wei, G. Chen, Electrochemical behavior of thionine at titanate nanotubes based modified electrode: a sensing platform for the detection of trichloroacetic acid, *Talanta* 81 (2010) 1461.
- [13] L. Lin, X. Huang, L. Wang, A. Tang, Synthesis, characterization and the electrocatalytic application of prussian blue/titanate nanotubes nanocomposite, *Solid State Sciences* 12 (2010) 1764.
- [14] A.R. Hillman, Q. Dong, M.A. Mohamoud, I. Efimov, Characterization of viscoelastic properties of composite films involving polyaniline and carbon nanotubes, *Electrochimica Acta* 55 (2010) 8142.
- [15] C. Zanardi, F. Terzi, L. Pigani, A. Heras, A. Colina, J. Lopez-Palacios, R. Seeber, Development and characterisation of a novel composite electrode material consisting of poly(3,4-ethylenedioxythiophene) including Au nanoparticles, *Electrochimica Acta* 53 (2008) 3916.
- [16] K. Bouzek, K.-M. Mangold, K. Jüttner, Platinum distribution and electrocatalytic properties of modified polypyrrole films, *Electrochimica Acta* 46 (2000) 661.
- [17] A. Ispas, R. Peipmann, B. Adolph, I. Efimov, A. Bund, Electrodeposition of pristine and composite poly(3,4-ethylenedioxythiophene) layers studied by electro-acoustic impedance measurements, *Electrochimica Acta* 56 (2011) 3500.
- [18] C. Peng, J. Jin, G.Z. Chen, A comparative study on electrochemical co-deposition and capacitance of composite films of conducting polymers and carbon nanotubes, *Electrochimica Acta* 53 (2007) 525.
- [19] A. Madani, B. Nessark, R. Boukherroub, M.M. Chehimi, Preparation and electrochemical behaviour of PPy–CdS composite films, *Journal of Electroanalytical Chemistry* 650 (2011) 176.
- [20] I. Mickova, A. Prusi, T. Grčev, L. Arsov, Electrochemical polymerization of aniline in presence of TiO₂, *Bulletin of the Chemists and Technologists of Macedonia* 25 (2006) 45.
- [21] V. Ferreira, A. Tenreiro, L.M. Abrantes, Electrochemical, microgravimetric and AFM studies of polythionine films: application as new support for the immobilization of nucleotides, *Sensors and Actuators B: Chemical* 119 (2006) 632.
- [22] U. Yogeswaran, S.-M. Chen, Multi-walled carbon nanotubes with poly(methylene blue) composite film for the enhancement and separation of electroanalytical responses of catecholamine and ascorbic acid, *Sensors and Actuators B: Chemical* 130 (2008) 739.
- [23] R. Albuquerque, M.C. Neves, M.H. Mendonca, T. Trindade, O.C. Monteiro, Adsorption and catalytic properties of SiO₂/Bi₂S₃ nanocomposites on the methylene blue photodecolorization process, *Colloid Surface A* 328 (2008) 107.
- [24] R. Pauliukaite, C.M.A. Brett, Poly(neutral red): electrosynthesis, characterization, and application as a redox mediator, *Electroanalysis* 20 (2008) 1275.
- [25] M.R. Nunes, O.C. Monteiro, A.L. Castro, D.A. Vasconcelos, A.J. Silvestre, Magnetic properties of Co-doped TiO₂ anatase nanopowders, *European Journal of Inorganic Chemistry* 28 (2008) 961.
- [26] E.K. Ylhainen, M.R. Nunes, A.J. Silvestre, O.C. Monteiro, Synthesis of titanate nanostructures using amorphous precursor material and their adsorption/photocatalytic properties, *Journal of Materials Science* 47 (2012) 4305.
- [27] V. Bem, M.C. Neves, M.R. Nunes, A.J. Silvestre, O.C. Monteiro, Influence of the sodium/proton replacement on the structural, morphological and photocatalytic properties of titanate nanotubes, *Journal of Photochemistry and Photobiology A* 232 (2012) 50.
- [28] R. Sasai, T. Fujita, N. Iyi, H. Itoh, K. Takagi, Aggregated structures of rhodamine 6G intercalated in a fluor-taeniolite thin film, *Langmuir* 18 (2002) 6578.
- [29] D.D. Schlereth, W. Schuhmann, H.-L. Schmidt, Spectroelectrochemical characterization of ultra-thin films formed by electropolymerization of phenothiazine derivatives on transparent gold electrodes, *Journal of Electroanalytical Chemistry* 381 (1995) 63.
- [30] A.A. Karyakin, A.K. Strakhova, E.E. Karyakina, S.D. Varfolomeyev, A.K. Yatsimirsky, The electrochemical polymerization of methylene blue and bioelectrochemical activity of the resulting film, *Bioelectrochemistry and Bioenergetics* 32 (1993) 35.
- [31] D.D. Schlereth, A.A. Karyakin, Electropolymerization of phenothiazine, phenoxazine and phenazine derivatives: characterization of the polymers by UV-visible difference spectroelectrochemistry and Fourier transform IR spectroscopy, *Journal of Electroanalytical Chemistry* 395 (1995) 221.