

# Electrochemical Formation of Poly(thionine) Thin Films: The Effect of Amine Group on the Polymeric Film Formation of Phenothiazine Dyes

Ezgi Topçu, Murat Alanyalıoğlu

Atatürk University, Sciences Faculty, Department of Chemistry, 25240 Erzurum, Turkey

Correspondence to: M. Alanyalıoğlu (E-mail: malanya@atauni.edu.tr)

**ABSTRACT:** The electropolymerization of thionine in an aqueous solution has been carried out by using both cycling voltammetry and chronoamperometry experiments. Electropolymerization has been applied at various pHs by using different working electrodes. The characterization of poly(thionine) thin films is performed by using cyclic voltammetry, current–time transients, atomic force microscopy, scanning tunnelling microscopy, ATR-FTIR, and UV–vis absorption spectroscopy techniques. It is deduced from current–time transients and morphological data that poly(thionine) film forms with random adsorption process and exhibits an irregular polymeric film. Poly(thionine) film formation was compared with that of previously published results of phenothiazine derivatives of poly(azure A) and poly(methylene blue). It has been concluded that type of amine functional group of phenothiazine dyes is very effective on the formation of polymeric film structure. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39686.

**KEYWORDS:** electrochemistry; dyes/pigments; surfaces and interfaces; morphology; conducting polymers

Received 19 May 2013; accepted 23 June 2013

DOI: 10.1002/app.39686

## INTRODUCTION

Polymerization of dyes can be achieved by using various techniques, e.g. self-quenching solution polymerization,<sup>1</sup> incorporation into polymeric films or macromolecular deposits,<sup>2</sup> supramolecular chain polymerization,<sup>3</sup> chemical polymerization,<sup>4</sup> AFM tip-induced oxidative polymerization,<sup>5</sup> and electropolymerization.<sup>6–12</sup> Electrochemistry is commonly used to synthesize dye thin films because it is a simple, economic, non-destructive, and environmentally friendly technique. Electrochemistry is also operated at ambient temperature and pressure, and it provides film thickness control by adjusting the electrode potential and electrodeposition time. Nevertheless, the main disadvantage of electrochemical techniques is to require conducting or semi-conducting substrates.

Thionine (TH) is a water-soluble phenothiazine derivative cationic dye and contains two amino groups in the  $\alpha$  positions of phenothiazine ring.<sup>7</sup> Polymeric thin films of TH introduces highly stable, electroactive, and efficient redox centers and these important surface properties allow large electrocatalysis applications. In our best knowledge, electropolymerization of TH have initially been carried out by Ohsaka and co-workers. In their study, they performed electropolymerization from nonaqueous TH monomer solution on pyrolytic graphite electrode and obtained good electrocatalysis of dihydronicotinamide adenine dinucleotide (NADH) for this poly(TH) modified graphite electrode.<sup>6</sup> After this study, McQuillan et al.,<sup>7</sup> Hamnett et al.,<sup>8</sup> Saez

et al.,<sup>9</sup> and Schlereth et al.<sup>11</sup> further investigated the electropolymerization of TH from aqueous TH monomer solutions on graphite, platinum, polycrystalline gold, and gold-coated glass electrodes, respectively. Clavilier et al. also studied electrochemical properties of TH self-assembled monolayers on sulfur-modified gold electrodes.<sup>13</sup> Monomer or polymer TH thin films have been prepared for various biosensing applications of uracil,<sup>10</sup> NADH,<sup>14,15</sup> hydrogen peroxide,<sup>16,17</sup> glucose,<sup>18</sup> deoxyribonucleic acid (DNA),<sup>19</sup> heparin,<sup>20</sup> endocrine,<sup>21</sup> choline,<sup>22</sup> ethanol,<sup>23</sup> nitrite,<sup>24</sup> mercury(II),<sup>25</sup> hydroquinone, and catechol.<sup>26</sup>

These biosensing applications are strongly depend on the surface properties, e.g. crystallinity, conductivity, and porosity of polymer thin film. Surface properties of dye polymer thin films can be analyzed by carrying out nucleation and growth mechanism studies with both morphology and potentiostatic current–time ( $i-t$ ) transient data. We have previously monitored nucleation and growth mechanism of electropolymerization of phenothiazine dyes of methylene blue (MB)<sup>27</sup> and azure A (AA)<sup>28</sup> by using potentiostatic  $i-t$  transient and morphological works.

In this study, we demonstrated film formation mechanism for the electropolymerization of TH. Optimum experimental conditions such as pH of TH monomer solution and applied electrooxidation potential were determined by using various working electrodes for poly(TH) formation. Electropolymerization was performed by using either potentiodynamic (cyclic voltammetry) or potentiostatic (constant potential) techniques.

Morphological investigations were carried out by using STM and AFM. Optical properties of the prepared poly(TH) thin films were studied by ATR-FTIR and UV-vis. absorption spectroscopy. The nucleation and growth mechanism of poly(TH) was also compared with previously published results of poly(MB) and poly(AA) that are analogous structure of TH.

## EXPERIMENTAL

### Materials

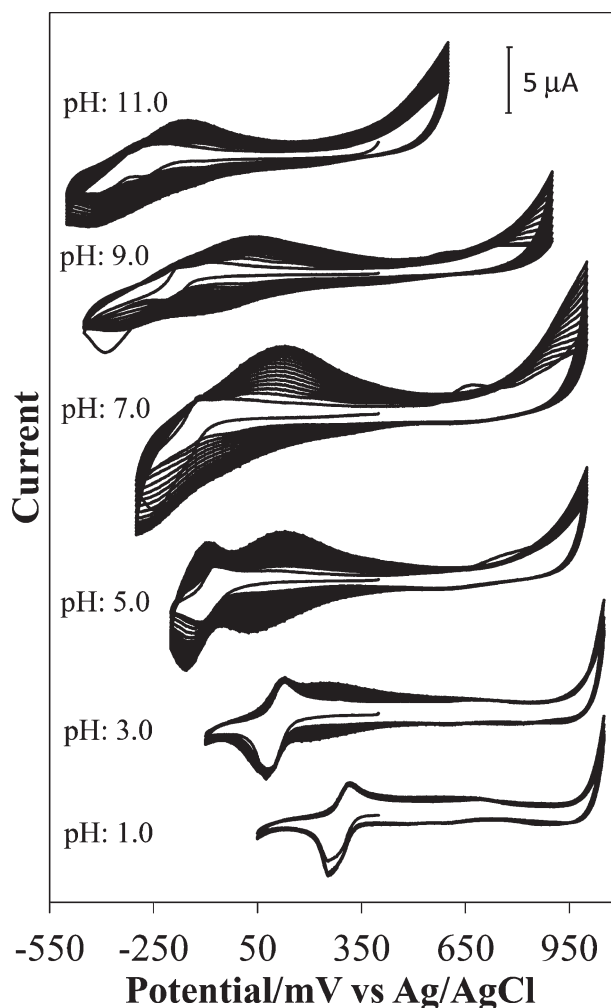
TH was purchased from Sigma Company and used as received. All other chemicals throughout this study were reagent grade and they were purchased from Sigma Company. Experiments were carried out in a Milli-Q ultra pure water (conductivity:  $5.5 \mu\text{S}\cdot\text{m}^{-1}$ ). The buffer solutions used for investigation of electrochemical properties of TH was 0.1M phosphate buffer solution. The solutions were prepared by using  $\text{H}_3\text{PO}_4$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ , HCl, NaOH and the pH of the buffer solutions was adjusted to 1.0, 3.0, 5.0, 7.0, 9.0, and 11.0 by using a Hanna pH-meter. The concentration of TH dissolved in the buffer solutions was 0.1 mM. The temperature of the electrochemical cell was fixed at  $30^\circ\text{C}$  by using a thermostat system to increase the dissolution of TH. The solutions were deoxygenated by passing dry nitrogen through the electrochemical cell for at least 15 min prior to each electrochemical studies.

### Electrochemistry

Electropolymerization of TH was performed by using either potentiodynamic (cyclic voltammetry) or potentiostatic (constant potential) techniques, with an Epsilon (Bioanalytical Systems) potentiostat system connected to a three-electrode cell. Current-time ( $i-t$ ) transients were obtained from potentiostatic application of TH electropolymerization process. Electrochemical studies were carried out by using different working electrodes of single crystal Au(111), polycrystalline Au, Au foil, indium tin oxide coated quartz (ITO), and pencil graphite electrode (PGE).

Single crystal Au(111) electrodes consist an atomically flat surface, which can be used as a reference surface for morphological studies.<sup>29</sup> Single crystal Au(111) substrates were prepared as previously described.<sup>30</sup> Polycrystalline Au electrodes (Alfa Aesar, 99.999% purity) contain a few large (111) facets that are visible by eye. Surface area of these facets is approximately  $1 \text{ mm}^2$ . Prior to each electrochemical experiment, polycrystalline gold electrodes were flame-annealed in  $\text{H}_2$  flame for about 30 s, and after a short time cooling in air, the electrodes were quenched in Milli-Q water. This procedure was repeated at least five times.

Polycrystalline Au and PGE electrodes were used as working electrode to determine the effect of working electrode on electropolymerization kinetics of poly(TH) thin films. PGEs (TOM-BOW 0.7 2B) were cleaned in ethanol by sonication for 5 min and then rinsed with doubly distilled water. The electrochemical activation of the surface of PGEs was carried out by cyclic voltammetry between 0 and 1.6 V in 0.1 M  $\text{H}_2\text{SO}_4$  solution until reproducible electrochemical behavior was observed. Gold foil (Alfa Aesar, 0.1 mm thick) was used as working electrode for attenuated total reflectance-fourier transform infrared (ATR-FTIR) experiments. ITO electrodes (Delta technologies) with

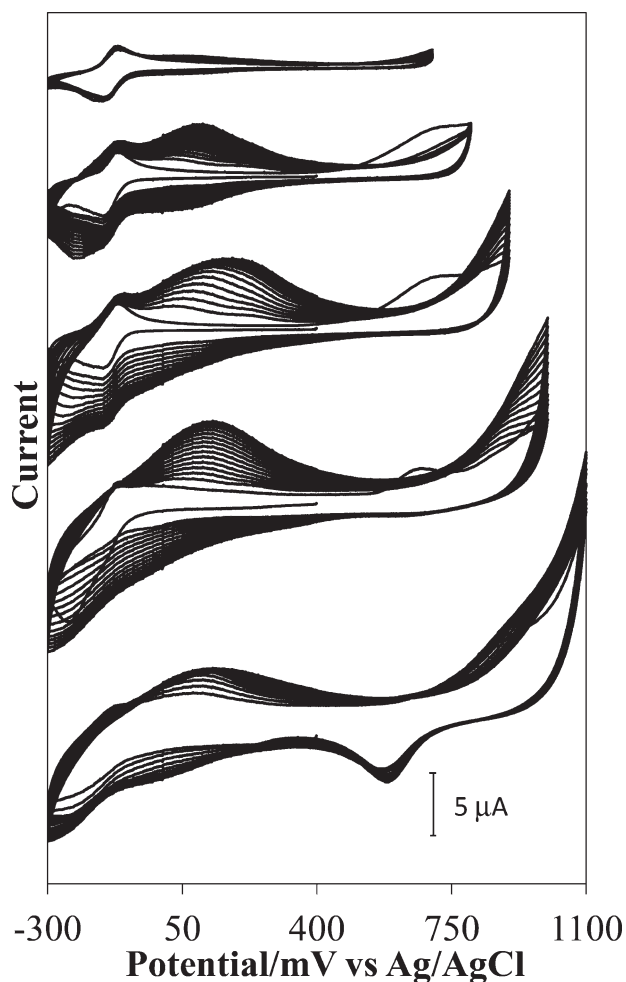


**Figure 1.** Consecutive voltammograms of the electropolymerization of TH on polycrystalline Au electrode in 0.1M phosphate buffer solutions of different pHs containing 0.1 mM TH. Scan rate:  $50 \text{ mV s}^{-1}$ .

sheet resistance of  $10 \Omega\cdot\text{cm}^{-2}$  were used as working electrode for optical characterization of poly(TH). ITO electrodes were cleaned by sonication in detergent solution for 5 min and then rinsed with a large amount of doubly distilled water. Further sonication in ethanol for 5 min was applied before being blown dry with an argon stream. In all cases, an Ag/AgCl (3M NaCl) (Bioanalytical Systems) electrode served as reference electrode and a Pt wire electrode was used as counter electrode.

### Instrumentation

Morphological investigation of poly(TH) thin films was carried out in ambient conditions by using ex-situ scanning tunneling microscopy (STM) and atomic force microscopy (AFM) techniques with a Molecular Imaging model PicoScan instrument. All AFM images were performed in noncontact mode using silicon probes (Pointprobe) having resonance frequency of 190 kHz and force constant of 48 N/m. Pt-Ir (80:20) wire (Alfa Aesar) with a thickness of 0.2 mm was used as tunneling tips for STM imaging. Tips were made by cutting Pt-Ir wire with surgical scissors. FTIR spectra of the polymeric thin films on Au foil were recorded with a Spectrum One model Perkin-Elmer FTIR



**Figure 2.** Consecutive voltammograms of the electropolymerization of TH on polycrystalline Au electrode scanning between  $-300$  mV and different electrooxidation potential limits of 700, 800, 900, 1000, and 1100 mV in 0.1M phosphate buffer (pH 7.0) containing 0.1 mM TH. Scan rate:  $50 \text{ mV s}^{-1}$ .

instrument in ATR with a ZnSe crystal by using a resolution of  $4 \text{ cm}^{-1}$ . The obtained FTIR spectra are averages of 100 scans. UV-vis absorption spectra of poly(TH) thin films on ITO electrodes were collected with a Shimadzu UV-3101PC UV-vis-NIR spectrophotometer.

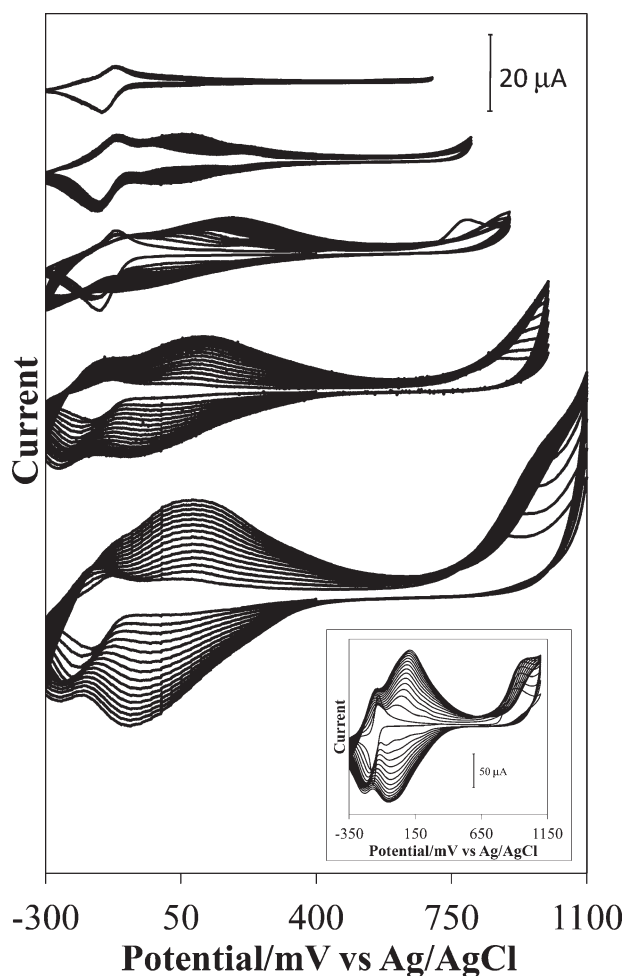
## RESULTS AND DISCUSSION

### Cyclic Voltammetry

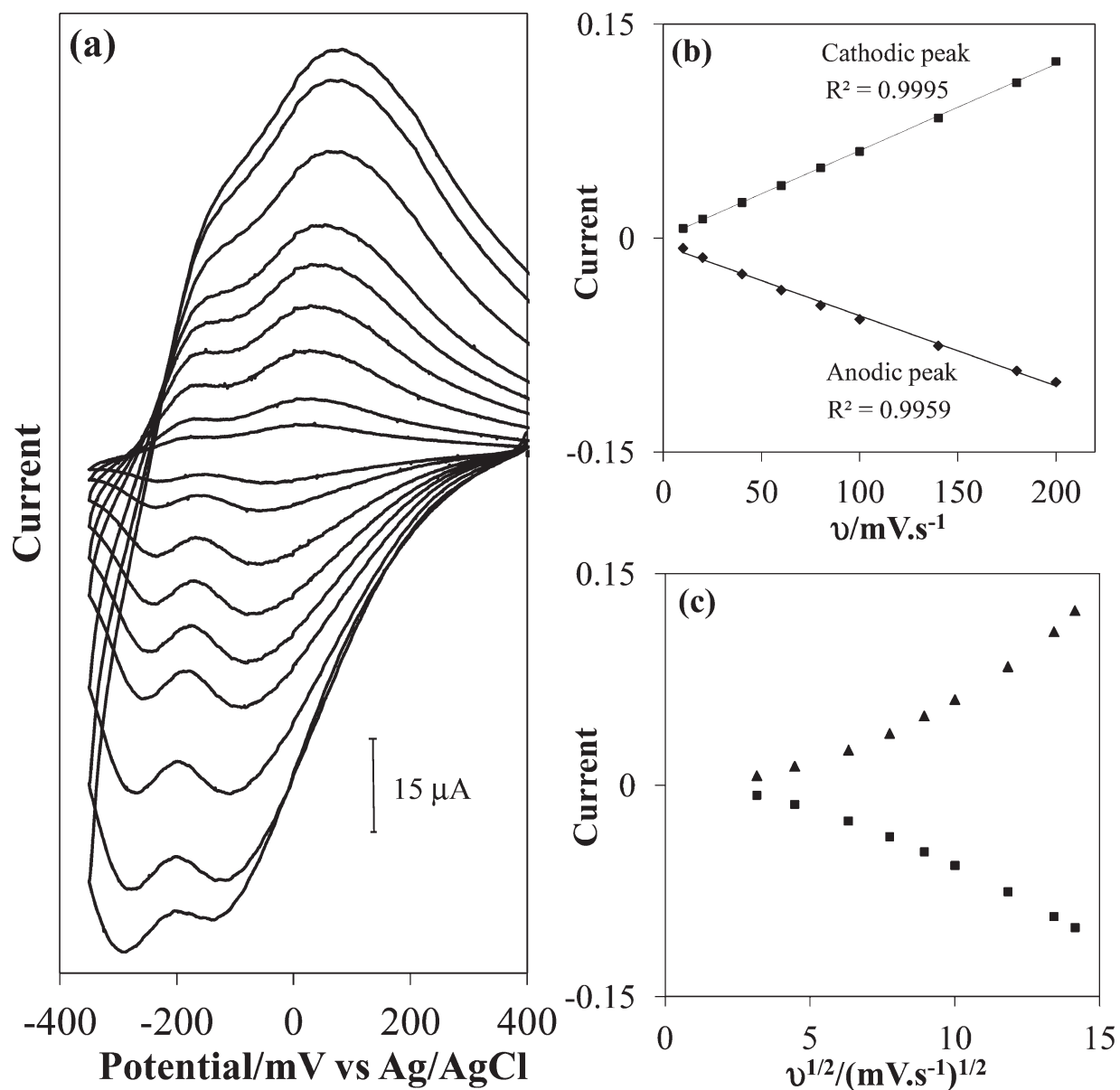
Electropolymerization of TH was carried out by using cyclic voltammetry technique. Figure 1 shows 15 successive voltammetric curves of electropolymerization of TH on polycrystalline Au electrode in the solutions of different pHs of 1.0, 3.0, 5.0, 7.0, 9.0, and 11.0 containing 0.1 mM TH. If potential of the working electrode is scanned from  $+400$  to  $+50$  mV in the solution of pH 1.0, a cathodic peak is observed at about  $+260$  mV. By reversing the potential in anodic direction, an oxidative peak is obtained at  $+300$  mV. This pair of redox peaks corresponds to two-electron reduction and oxidation of TH monomer species in the solution, respectively.<sup>7,31,32</sup> No additional peak is obtained, when potential is scanned to more anodic potential

values. If same potential scan is performed in a solution of pH 3.0, a peak pair at  $75 \text{ mV}/120 \text{ mV}$  is seen corresponding to reduction and oxidation of TH monomer species, respectively. If potential of the working electrode is scanned through more anodic region, current starts to increase after approximately  $+850$  mV and is attributed to oxidation of TH monomer. At the potential values more positive than  $+850$  mV, radical cations of TH monomers are formed and electropolymerization of TH takes place on gold electrode surface.<sup>14</sup> As a result of electropolymerization process and formation of poly(TH) thin film on the electrode, a new anodic peak arises after the first scan at about  $+280$  mV and the current of this new peak gradually increases with increasing number of potential scan.

As can be seen from Figure 1, poly(TH) film formation peak is not observed at pH 1.0 solution and current of this peak gradually increases until pH 7.0. Peak current decreases at pHs of 9.0 and 11.0 indicating that neutral solution is most suitable media for electropolymerization of TH. Potential value of all the peaks



**Figure 3.** Consecutive voltammograms of the electropolymerization of TH on PGE scanning between  $-300$  mV and different electrooxidation potentials of 700, 800, 900, 1000, and 1100 mV in 0.1M phosphate buffer (pH 7.0) containing 0.1 mM TH. Inset: Consecutive voltammogram of the electropolymerization of TH on ITO in 0.1M phosphate buffer (pH 7.0) containing 0.1 mM TH. Scan rate:  $50 \text{ mV s}^{-1}$ .



**Figure 4.** Cyclic voltammograms of poly(TH)/PGE in 0.1M phosphate buffer solution (pH: 7.0) at (a) different scan rates. (b) Plots of peak currents vs.  $v$ , and (c)  $v^{1/2}$ .

shift to negative region by increasing the pH value of TH monomer solution, which means that the redox processes of TH are related to the proton concentration. Same electrochemical behavior was observed in previous studies.<sup>32–34</sup>

The potential scan rate and the upper oxidation potential limit is important factor for preparing poly(TH) modified electrode. In order to determine the effect of the oxidation potential limit on poly(TH) formation, we carried out cyclic voltammetry experiments in pH 7.0 media on polycrystalline Au electrode by cycling from different anodic potential values of 700, 800, 900, 1000, and 1100 mV at a scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$  as shown in Figure 2.

If the potential cycling is applied from 700 mV, poly(TH) formation peak is hardly observed at about 50 mV, which is attrib-

uted to poor oxidation of TH at 700 mV. An anodic irreversible peak at about +650 mV, which is observed at only first scans for all voltammograms arises because of oxidation of  $-\text{NH}_2$  groups of TH molecule.<sup>35</sup> Peak current of poly(TH) formation increases gradually by changing anodic potential limit from 700 to 1000 mV indicating that the electropolymerization rate of TH increases by increasing the upper oxidation potential limit until 1000 mV. Peak current of poly(TH) formation suddenly decreases and a cathodic peak at about +600 mV arises, if potential cycling is applied from 1100 mV. This cathodic peak arises after the potential of the working electrode is reached to a critical oxidation potential of 1100 mV, referring to oxide formation of gold working electrode besides oxidation of TH molecules.<sup>28</sup> Diminishing of poly(TH) formation peak current may

be attributed to both over-oxidation of polymeric TH film and oxide formation on gold working electrode surface at 1100 mV.<sup>27,28</sup>

In order to investigate the latter effect, same cyclic voltammetry experiments were carried out by using different working electrodes. Figure 3 presents 15 successive voltammograms for electropolymerization of TH in pH 7.0 buffer solution on PGE electrode by cycling from different anodic potential limits. Poly(TH) formation peak current at about +90 mV increases gradually by changing anodic potential limit from 700 to 1100 mV because of electropolymerization rate of TH that increases by increasing the oxidation potential limit. Consecutive electropolymerization process of TH on ITO electrode cycling between potentials of -350 and +1100 mV was also presented inset of Figure 3. Almost same electrochemical behavior of TH is observed at all used working electrodes but the reduction peak at +600 mV. This peak is observed on gold electrode (Figure 2) but it is not obtained on both PGE and ITO because these two electrodes provide more positive potential limit than gold electrode. We have previously obtained this reduction peak for poly(azure A) film formation on gold electrodes.<sup>28</sup>

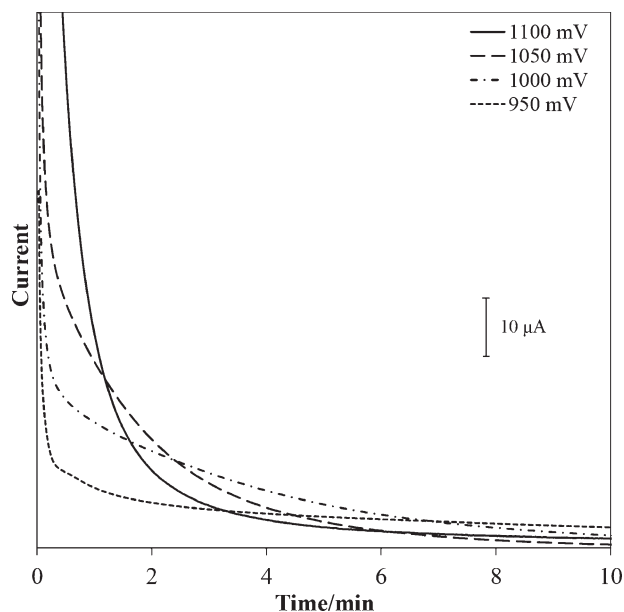
Figure 4(a) shows the cyclic voltammograms of poly(TH)/PGE electrode in 0.1M phosphate buffer solution (pH: 7.0) for different scan rates of 10, 20, 40, 60, 80, 100, 140, 180, and 200 mV s<sup>-1</sup>. As can be seen in this figure, poly(TH)/PGE electrode in background solution shows two redox couples for all scan rates. The negative peak pair (-260/-200 mV) is attributed to a monomer-type redox activity of TH that may be adsorbed between the polymeric layers during the electropolymerization process. The positive peak pair (-80/+40 mV) corresponds to polymer-type redox reaction.<sup>27,28</sup> The dependence of voltammetric responses of both cathodic wave at about -260 mV and anodic wave at about +40 mV on both scan rate and square root of scan rate are exhibited in Figure 4(b,c), respectively. It is obvious that both peak currents show a linear dependency to scan rate but nonlinear dependency to square root of scan rate which can be attributed to adsorption-controlled mechanism of electropolymerization of TH. Same results have been determined in previous studies.<sup>17,20</sup>

### Current–Time Transients

Potentiostatic  $i-t$  transients for electropolymerization process of TH gives a useful information about nucleation and growth mechanism.  $i-t$  transients were obtained by keeping the potential of working electrode constant at various oxidation potential limits of 950, 1000, 1050, and 1100 mV in pH 7.0 monomer solution (Figure 5). An  $i-t$  curve without TH was subtracted from all data. In all  $i-t$  data, current starts from a maximum value and decays exponentially and reaches to zero. This behavior may be attributed to random adsorption for poly(TH) film formation on polycrystalline gold electrode.<sup>27–29</sup> The current for random adsorption term is

$$I_{\text{random}} = I_0 \exp(-kt) \quad (1)$$

where  $I_0$  is initial current,  $k$  is a constant, and  $t$  is time. In the random adsorption process, current density is associated with the empty surface area of the working electrode and TH mole-



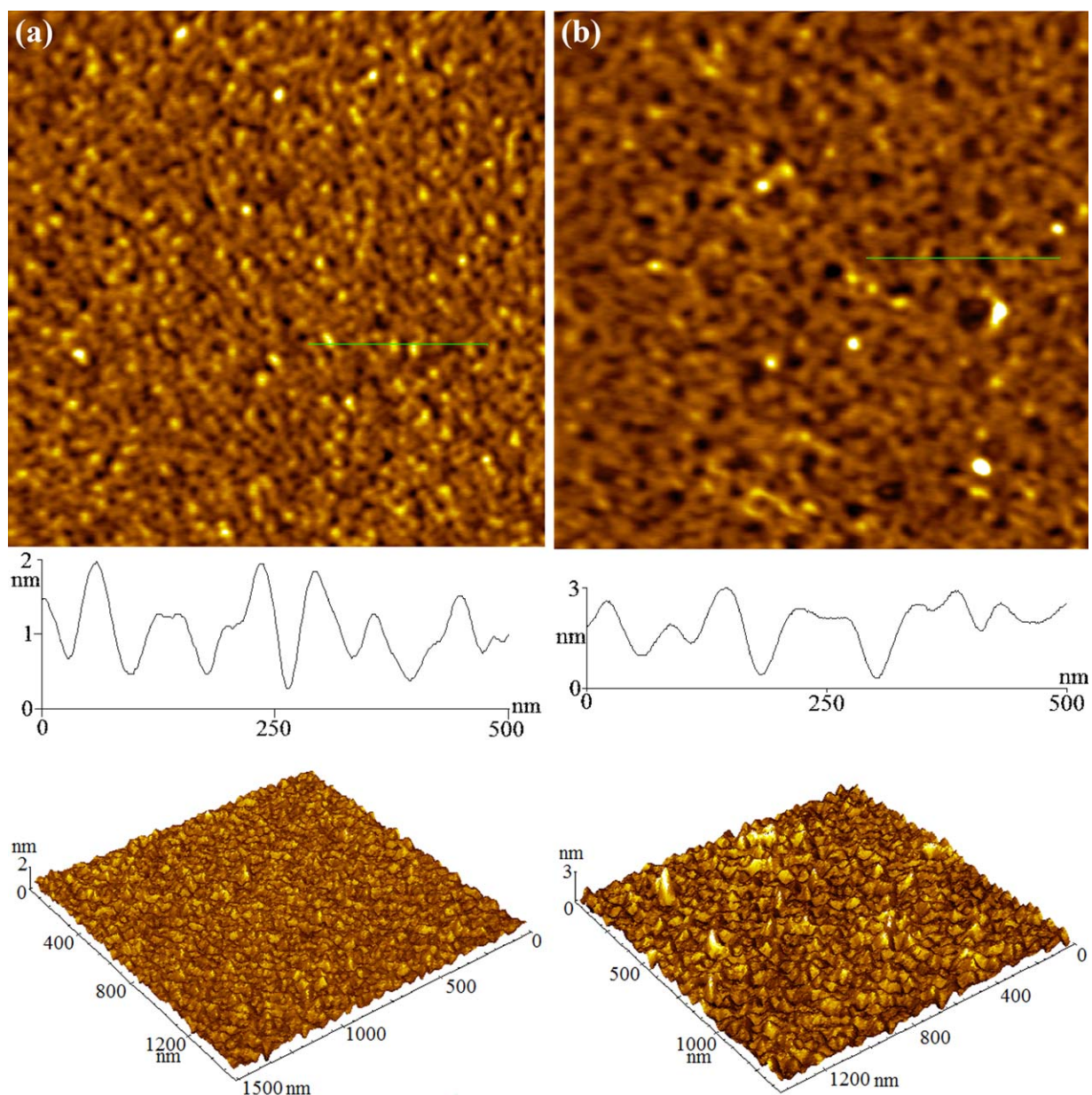
**Figure 5.** Current–time transients for potentiostatic electropolymerization of TH on polycrystalline Au electrode applied at 950, 1000, 1050, and 1100 mV.

cules are randomly adsorbed on gold surface wherever is empty. Therefore, current density starts from a maximum value and decays exponentially to zero. In the case of regular film formation (nucleation and growth mechanism),  $i-t$  curve shows an exponential increase and then declines gradually.<sup>27–29</sup>

We have previously obtained regular film formation for poly(MB)<sup>27</sup> and poly(AA).<sup>29</sup> It is obvious from Figure 5 that  $i-t$  curve is associated with random film formation for poly(TH) and does not follow a nucleation and growth mechanism. As the electrooxidation potential value shifts from 950 to 1100 mV, onset of the curves reaches to zero at shorter times. This situation indicates that poly(TH) films can be synthesized by either at higher potentials for short electropolymerization times or at lower potentials for long electropolymerization times. If compared with other electrooxidation potentials, current starts from very high current value for electrooxidation potential of 1100 mV which may be attributed to oxide formation on gold working electrode surface besides oxidation of TH molecules. As a result of random adsorption for all electrooxidation potential values, it is supposed to be obtained an irregular polymeric films of TH after electropolymerization process on gold surface.

### AFM and STM

Poly(TH) film formation was further verified by using STM and AFM studies. Topographical images of poly(TH) thin films on Au(111) electrode prepared by 10 and 30 successive potentiodynamic scans between -300 and +900 mV in 0.1M phosphate buffer solution (pH 7.0) containing 0.1 mM TH monomer are shown in Figure 6(a,b), respectively. Z-height profiles and 3-D views are also presented under these images. If Figure 6(a) is compared to naked Au(111) surface,<sup>29</sup> it is observed that Au(111) is completely covered with a polymeric film. Most of the poly(TH) particles show irregular distribution on the surface as a result of random deposition. Polymeric film exhibits



**Figure 6.** 2-D and 3-D, (a) STM and (b) AFM images of poly(TH) films on Au (111) substrate prepared by (a) 10 and (b) 30 consecutive potentiodynamic scans in 0.1M phosphate buffer solution (pH:7.0) containing 0.1 mM TH. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

almost uniform roughness and width of around 2 and 40 nm, respectively. Root mean square roughness (RMS) value has been calculated as 1.81 nm for this image. As the number of potentiodynamic scan reaches to 30 [Figure 6(b)], irregular polymeric film formation goes on which means random adsorption is still dominant. It is clear from Figure 6(b) that film structure exhibits polymeric nanoparticles with an average roughness and width of 3 and 60 nm, respectively. RMS value is 2.95 nm for 30 potentiodynamic cycles, which means surface roughness of poly(TH) thin film increases by increasing film thickness. Ferreria et al. morphologically investigated the electropolymerization of TH on platinum electrodes by using tap-

ping mode AFM and they also observed irregular polymeric film formation.<sup>34</sup>

We have previously determined different nucleation and growth mechanisms for electropolymerization of MB<sup>27</sup> and AA<sup>28</sup> by using  $i-t$  transients and morphological studies. Poly(MB) shows progressive layer-by-layer and instantaneous nucleation and growth mechanism besides random adsorption. Poly(AA) formation follows successive two instantaneous nucleation and growth mechanisms besides random adsorption. As can be seen from Figures 5 and 6, poly(TH) formation exhibits random adsorption process with high ratio. TH, AA, and MB are

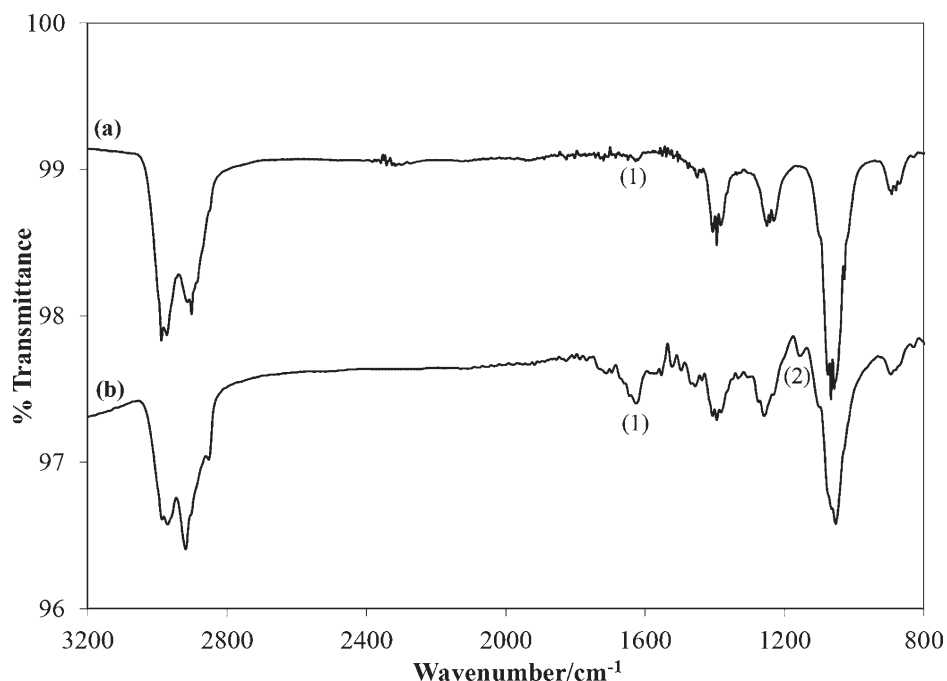


Figure 7. ATR-FTIR spectra of (a) TH monomer film and (b) poly(TH) thin film on Au foil substrate.

phenothiazine derivative dye molecules. A linkage between the nitrogen atom of amine group and carbon atom of phenothiazine ring is the most probable mechanism for the electropolymerization of phenothiazine derivative dyes.<sup>31,36</sup> The discrepancy on polymeric film formation mechanism of these three phenothiazine derivative dyes may be attributed to the possibility of the different C-N linkages in the formation of their polymeric structures. TH has two primary amine ( $-\text{NH}_2$ ) groups that link to phenothiazine ring, whereas AA has a primary and a tertiary amine group and MB has two tertiary amine groups.<sup>12</sup> Chronoamperometric and morphological investigations exhibit that presence of two primary amine groups in the phenothiazine skeleton results with randomly adsorbed irregular polymeric film, whereas the presence of at least one tertiary amine group causes the nucleation and growth besides random deposition.

#### ATR-FTIR Spectroscopy

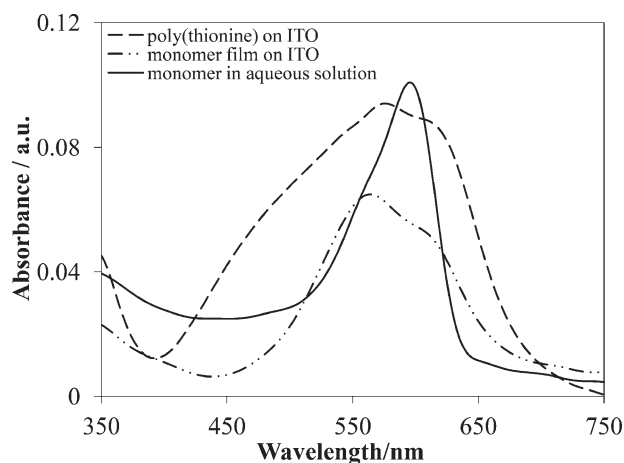
We used IR spectroscopy to characterize poly(TH) structure. The ATR-FTIR spectra of TH monomer film and poly(TH) thin film prepared on Au foil substrate are presented in Figure 7(a,b), respectively. TH monomer thin film was prepared by drop-casting of  $1 \times 10^{-6} \text{ M}$  aqueous TH solution on gold foil, and dried under dry nitrogen stream. Some remarkable differences are observed between these two FTIR spectra: The peaks between 2800 and 3000 are attributed to C-H stretching vibration of aromatic ring hydrogens.<sup>37</sup> Both wavenumber value and shape of these peaks show difference and may be because of a possible coupling of carbon atom of the phenothiazine ring after polymerization. A weak peak is observed at  $1608 \text{ cm}^{-1}$  in the monomer spectrum (peak 1), whereas this peak is observed at  $1616 \text{ cm}^{-1}$  with high intensity in the poly(TH) spectrum. This peak is associated with  $-\text{NH}_2$  in-plane deformation. A pos-

sible coupling from nitrogen atom of primary amine group on the phenothiazine ring may cause a change both in the intensity and wavenumber value of this peak. In many instances, this strong peak which is observed in the polymer spectrum is a characteristic of N atom linked to C atom of aromatic ring.<sup>37</sup>

On the other hand, a peak arises at  $1143 \text{ cm}^{-1}$  in the polymer spectrum (peak 2), whereas this peak is not observed in the monomer spectrum. This peak can be associated with  $\text{PO}_4^{-3}$  ions that interfere into the polymeric structure during the potentiodynamic electropolymerization from the neutral electrolysis solution that contains phosphate buffer.<sup>38</sup> This peak is not seen in the TH monomer film spectrum because phosphate buffer has not been used for the preparation of TH monomer film. These results suggest that a linkage between nitrogen atom of primary amine and carbon atom of phenothiazine ring is a possible dominant mechanism during the electropolymerization of TH. Gao et al. have reported the bonding via amine nitrogen atom in one TH molecule to a carbon atom in another one for the polymerization mechanism of poly(TH) from XPS studies.<sup>14</sup>

#### UV-Visible Absorption Spectroscopy

UV-vis absorption spectra of  $0.1 \text{ M}$  phosphate buffer solution (pH: 7.0) containing  $1 \times 10^{-6} \text{ M}$  TH monomer, TH monomer thin film on ITO, and poly(TH) modified ITO are shown in Figure 8. TH monomer thin film was prepared drop-casting  $1 \times 10^{-6} \text{ M}$  aqueous TH solution on ITO-coated quartz slide, and dried under dry nitrogen stream. Poly(TH) thin films on ITO electrodes were obtained by carrying out cyclic voltammetry conditions of inset of Figure 3. A peak at  $598 \text{ nm}$  with a shoulder at  $559 \text{ nm}$  are observed for TH monomer solution. Yang et al. have reported almost similar UV-vis spectrum for pH 6.5 aqueous TH solution.<sup>17</sup> A main band at  $566 \text{ nm}$  with a shoulder at about



**Figure 8.** UV-vis absorption spectra of TH monomer film and poly(TH) thin film on ITO-coated quartz electrode and TH monomer in solution.

611 nm are observed for TH monomer thin film. These bands are observed at 578 and 618 nm for poly(TH) thin film. If the bands of poly(TH) film is compared with that of TH monomer film, a red-shift at the main bands of polymeric films is clearly observed and this may be associated with a longer conjugation length in the polymeric film. It is clear that the bands of the solid phase of both TH monomer film and poly(TH) film broadens when it is compared to the bands of TH monomer solution. Similar behaviors are observed for the electropolymerization of the other phenothiazine derivatives.<sup>27,28,32,33</sup>

An additional shoulder at about 480 nm arises in the poly(TH) spectrum that is not visible in TH monomer film spectrum. Existence of this additional band may be attributed to the electropolymerization of TH. Liu et al. studied electropolymerization of poly(MB) on Pt-coated quartz electrode and reported that the band at about 245 nm for MB monomer spectrum reveal a blue-shift to 225 nm after electropolymerization.<sup>32</sup> Schlereth et al. also reported that electropolymerization of phenothiazine derivatives causes a blue-shift because of existence of strong interactions among different redox sites on the electrode surface.<sup>39</sup> We also previously observed similar band in UV-vis spectrum of both poly(MB) and poly(AA) thin films on ITO substrates.<sup>27,28,31</sup> Similar results may be attributed to analogous structure of TH, AA, and MB.

## CONCLUSIONS

Electrochemical studies show that neutral monomer solution is a suitable medium for the electropolymerization of TH to prepare polymeric thin films. The cyclic voltammograms obtained by switching from different electrooxidation potential limits for electropolymerization of TH on both gold and PGE electrodes exhibit that the electrooxidation potentials less than 800 mV are not appropriate to form poly(TH) thin films. Oxide formation on gold working electrode takes place besides electropolymerization of TH at higher potentials than 1000 mV in the pH 7.0 monomer solution, whereas this phenomenon does not occur on PGE and ITO electrodes until electropolymerization potential of 1100 mV. Plots of peak current vs. scan rate for poly(TH)/PGE electrodes in background solution present a

linear dependency that means adsorption-controlled process for poly(TH) film formation.

*I-t* transient and morphological investigations for electropolymerization of TH reveal that the formation of polymeric thin films of TH follows random adsorption. UV-vis absorption experiments show a red-shift at the main visible spectrum of poly(TH) thin films when compared to spectrum of the TH monomer film and an additional shoulder at about 480 nm arises in the poly(TH) spectrum, which is not visible in TH monomer film spectrum. These are attributed to the electropolymerization of TH molecules. ATR-FTIR spectra of poly(TH) and TH monomer film exhibit some remarkable differences at C-H stretching vibration of aromatic ring and NH<sub>2</sub> in-plane deformation that may be attributed to a possible linkage between nitrogen atom of amine and carbon atom of phenothiazine ring.

## ACKNOWLEDGEMENT

This work has been supported by Atatürk University (Project: BAP 2011/377).

## REFERENCES

- Rabinowitch, E.; Epstein L. F. *J. Am. Chem. Soc.* **1941**, *63*, 69.
- Morishima, Y.; Isono, M.; Itoh, Y.; Nozakura, S. *Chem. Lett.* **1981**, 1149.
- Hannah, K. C.; Armitage, B. A. *Acc. Chem. Res.* **2004**, *37*, 845.
- Nath, N. C. D.; Sarker, S.; Rahman, M. M.; Lee, H. J.; Kim, Y. J.; Lee, J. *J. Chem. Phys. Lett.* **2013**, 559, 56.
- Chiang, Y. M.; Huang, H. Y.; Wang, C. M. *J. Electroanal. Chem.* **2012**, 677–680, 78.
- Ohsaka, T.; Tanaka, K.; Tokuda, K. *J. Chem. Soc. Chem. Commun.* **1993**, 3, 222.
- McQuillan, A. J.; Reid, M. R. *J. Electroanal. Chem.* **1985**, *194*, 237.
- Hamnett, A.; Hillman, A. R. *J. Electroanal. Chem.* **1987**, 233, 125.
- Saez, E. I.; Corn, R. M. *Electrochim. Acta* **1993**, *38*, 1619.
- Liu, H.; Wang, G.; Hu, J.; Chen, D.; Zhang, W.; Fang, B. *J. Appl. Polym. Sci.* **2008**, *107*, 3173.
- Schlereth, D. D.; Karyakin, A. A. *J. Electroanal. Chem.* **1995**, 395, 221.
- Farias, E. D.; Pfaffen, V.; Ortiz, P. I. *Electrochim. Acta* **2013**, *105*, 622.
- Clavilier, J.; Svetlicic, V.; Zutic, V. *J. Electroanal. Chem.* **1995**, 386, 157.
- Gao, Q.; Cui, X.; Yang, F.; Ma, Y.; Yang, X. *Biosens. Bioelectron.* **2003**, *19*, 277.
- Gao, Q.; Sun, M.; Peng, P.; Qi, H.; Zhang, C. *Microchim. Acta* **2010**, *168*, 299.
- Wang, Q.; Zhang, H.; Wu, Y.; Yu, A. *Microchim. Acta* **2012**, *176*, 279.
- Yang, R.; Ruan, C.; Dai, W.; Deng, J.; Kong, J. *Electrochim. Acta* **1999**, *44*, 1585.



18. Deng, C.; Li, M.; Xie, Q.; Liu, M.; Yang, Q.; Xiang, C.; Yao, S. *Sens. Actuat. B Chem.* **2007**, *122*, 148.
19. Zhang, Y.; Huang, L. *Microchim. Acta* **2012**, 176:463.
20. Huo, H. Y.; Luo, H. Q.; Li, N. B. *Microchim. Acta* **2009**, *167*, 195.
21. Dempsey, E.; Diamond, D.; Collier, A. *Biosens. Bioelectron.* **2004**, *20*, 367.
22. Yang, M.; Yang, Y.; Yang, Y.; Shen, G.; Yu, R. *Anal. Biochem.* **2004**, *334*, 127.
23. Wu, L.; McIntosh, M.; Zhang, X.; Ju, H. *Talanta* **2007**, *74*, 387.
24. Deng, C.; Chen, J.; Nie, Z.; Yang, M.; Si, S. *Thin Solid Films* **2012**, *520*, 7026.
25. Yin, Z.; Wu, J.; Yang, Z. *Microchim. Acta* **2010**, *170*, 307.
26. Ahammad, A. J. S.; Rahman, M. M.; Xu, G. R.; Kim, S.; Lee, J. *J. Electrochim. Acta* **2011**, *56*, 5266.
27. Kaplan, I. H.; Dagci, K.; Alanyalioglu, M. *Electroanalysis* **2010**, *22*, 2694.
28. Kalyoncu, E.; Alanyalioglu, M. *J. Electroanal. Chem.* **2011**, *660*, 133.
29. Alanyalioglu, M.; Arik, M. *J. Appl. Polym. Sci.* **2009**, *111*, 94.
30. Hamelin, A. *J. Electroanal. Chem.* **1996**, *407*, 1.
31. Dagci, K.; Alanyalioglu, M. *Electroanalysis* **2011**, *23*, 777.
32. Liu, J.; Mu, S. *Synt. Met.* **1999**, *107*, 159.
33. Chen, C.; Mu, S. *J. Appl. Polym. Sci.* **2003**, *88*, 1218.
34. Ferreira, V.; Tenreiro, A.; Abrantes, L. M. *Sens. Actuat. B Chem.* **2006**, *119*, 632.
35. Bauldreay, J. M.; Archer, M. D. *Electrochim. Acta* **1983**, *28*, 1515.
36. Kertesz, V.; Berkel, G. J. V. *Electroanalysis* **2001**, *13*, 1425.
37. Vien, D. L.; Colthup, N. L.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, CA, **1991**.
38. Miller, F. A.; Wilkins, C. H. *Anal. Chem.* **1952**, *24*, 1253.
39. Schlereth, D. D.; Schuhmann, W.; Schmidt, H. L. *J. Electroanal. Chem.* **1995**, *381*, 63.