



HAL
open science

Electrochemical Sensor Based on Thioether Oligomer Poly(N-vinylpyrrolidone)-modified Gold Electrode for Bisphenol A Detection

Fairouz Aberkane, Abdoullatif Barakat, Abdelhamid Elaïssari, Nadia Zine, Tahar Bendaikha, Abdelhamid Errachid

► **To cite this version:**

Fairouz Aberkane, Abdoullatif Barakat, Abdelhamid Elaïssari, Nadia Zine, Tahar Bendaikha, et al.. Electrochemical Sensor Based on Thioether Oligomer Poly(N-vinylpyrrolidone)-modified Gold Electrode for Bisphenol A Detection. *Electroanalysis*, 2019, 31 (11), pp.2112-2119. 10.1002/elan.201900060 . hal-02989981

HAL Id: hal-02989981

<https://hal.science/hal-02989981>

Submitted on 17 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Electrochemical Sensor Based on Thioether Oligomer Poly(N-vinylpyrrolidone)-Gold Electrode for Bisphenol A Detection.

F. Aberkane^{1,2,3}, A. Barakat³, A. Elaissari², N. Zine³, T. bendaikha¹ and A. Errachid³

¹Faculty of matter science, Department of chemistry, University of Batna 1, 05000, Algeria

²University of Lyon, F-69622 Lyon, France, University Lyon 1, Villeurbanne, CNRS, UMR 5007, LAGEP-CPE, 43 Bd. 11 Novembre 1918, Villeurbanne F-69622, France

³Université de Lyon, Institut des Sciences Analytiques, UMR 5280, CNRS, Université Lyon 1, ENS Lyon - 5, rue de la Doua, F-69100 Villeurbanne, France

Abstract :

Presently, Bisphenol A (BPA) has been added to the list of substances of very high concern as endocrine disruptors. According to literature data, exposure to bisphenol A even at low doses may result in adverse health effects. In this study, new electrochemical sensor of Bisphenol A based on oligomer thioether DDT-Poly(N-vinylpyrrolidone) has been developed. The oligomer thioether, which is capable of recognizing BPA, was prepared and used for gold electrode modification. The characterization of the modified gold electrode was carried out by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM). Obtained results indicate that the electrode exhibits excellent electrochemical activity and sensitivity for BPA probably because of the repetition of the amide bond along the chain of the oligomer, which can create interaction with BPA molecules. The proposed sensor showed good performance for BPA determination with a linear range of 4.38 pM – 87.6 pM (1pg/ml-20pg/ml). Several interfering species, such as phenolic compounds were used and their behaviors on the modified gold electrode were investigated.

Keywords :

Electrochemical sensor, bisphenol A, endocrine disrupt, oligomer thioether, modified gold electrode, poly(N-vinylpyrrolidone).

Introduction

Bisphenol A (BPA) is classified as a Xenoestrogen compound; a type of xenohormone that imitates estrogen, which has estrogenic effects on a living organism. It can interfere with natural estrogenic substances produced by the endocrine system and disrupts hormonal levels^{1,2}. BPA has been extensively studied during the 1930s in the search for synthetic estrogens as medication in hormonal disorder, but it has never been used, because of the discovery at the same time of diethylstilbestrol, which has properties deemed more interesting³. However, its use was only started in the 1950s by the plastics industry^{4,5}. It has been used as a monomer in the manufacture of plastics such as polycarbonates and epoxy resins, as well as plasticizer, antioxidant or flame-retardant for other plastics. Plastic is widely used in our daily lives such as food packaging, water bottles, baby bottles, toys, lining canned food and beverages, medical materials and water pipes^{6,7,8}. Unfortunately, it has been demonstrated that free BPA can leach from plastics under normal conditions of use, the rate of leaching accelerate as the temperature increases and in contact with acidic or basic substances⁹. In Consequent, there is extensive human exposure to BPA, the current analytical techniques have detected BPA in over 95% of human blood, serum, tissues, and urine¹⁰.

Food and drinks have been identified as the main source of BPA exposure in humans, due to its migration from the plastic containers to the food products. Research has shown that BPA is absorbed rapidly and efficiently into the gastrointestinal tract, converted to BPA-glucuronide and rapidly eliminated from the blood by urine, nearly 100% of exposed BPA is recoverable in urine within 24 hours¹¹. Unfortunately, unconjugated BPA, its strength is as high as estradiol, which can act at very low doses and results in changes in certain cell functions at concentrations ranging from 1 pM to 1 nM^{10,12}. Studies have reported that BPA can be measured in humans serum, follicular fluid, amniotic fluid, placental tissue and umbilical cord blood^{8,13}; there is considerable evidence that bioaccumulation of BPA can occur during pregnancy¹⁰. Some other studies suggest that the effects of BPA may be more pronounced in the foetus, infants and young children; they are less effective in removing substances from their systems¹. The potential effects of BPA on the brain, behavior and prostate glands of foetuses, infants and young children have been studied. Moreover, Increased risks of cancer, obesity, diabetes, heart problems, reduce immune function and impaired reproduction in adults have been also studied^{1,2,14,15}. Therefore, it is very important to establish a reliable method for determination and monitoring of the trace amounts of BPA and evaluates the potential risks associated with cumulative low-dose exposures of BPA.

Currently, many analytical methods have been used for the determination of BPA such as high performance liquid chromatography (HPLC)^{16,17}, liquid chromatography–mass spectrometry^{18,19}, gas chromatography–mass spectrometry (GC–MS)^{20,21}, fluorescence analysis²², immunoassay-based methods²³, colorimetric methods²⁴, molecular imprinting technics²⁵ and electrochemical methods²⁶. However, electrochemical technics are most important due to their high sensitivity, simplicity, low cost, miniaturization, cheap

instrument and fast response compared to the other methods. The development of electrochemical sensors via a modifying electrode is a common strategy for the electrochemical detection of BPA. Therefore, various types of electrodes have been modified, for this purpose, with the use of enzymes²⁷, antibodies²⁸, chitosan²⁹, graphene³⁰, carbon nanotubes²⁵, gold nanoparticles³¹, quantum dots³² and polymer³³.

In this research, thioether oligomer DDT-Poly(N-vinylpyrrolidone) has been prepared by a simple bulk radical polymerization in presence of a thermal initiator Benzoyl peroxide (POB or BPO??) and transfer agent dodecanethiol (DDT). Resulting oligomer has been used for gold electrode modification for BPA sensing. The characterization of synthesized thioether oligomer DDT-Poly(N-vinylpyrrolidone) and the corresponding modified gold electrode was carried out by FTIR, SEC, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM). The novel thioether oligomer based sensor has been used for BPA sensing in range of 1 pg/ml - 20 pg/ml (4,38 pM – 87.6 pM). In addition, several interfering species, such as phenolic compounds were used and their behavior on the modified gold electrode was investigated.

Experimental

Materials

All chemicals required for experiments were of analytical purity and used as received; N-vinyl pyrrolidone (NVP, +99%) was purchased from Aldrich. Hydroquinone (+99%), Resorcinol (99%) and Phosphate buffer saline were purchased from sigma. Phenol (>99,5%) was obtained from Riedel-DeHaën. Bisphenil A (≥99%), Potassium hexacyanoferrate(II) trihydrate(>98,5%), Potassium hexacyanoferrate(III) (>99%), heaxane (≥99%) and chloroform (≥99%) were purchased from Sigma-Aldrich. 1-dodecanethiol (DDT, >97%) and Benzoyl peroxide (POB, ≥99%) (POB or BPO??) was obtained from Fluka. All the measurements were carried out at room temperature in a 0,01M PBS buffer solution containing ions $[\text{Fe}(\text{CN})_6]^{3-/4}$ at a concentration of 5 mM (PH = 7,4).

Methods

Electrochemical experiments were carried out with a VMP3 multichannel potentiostat (Biologic-EC-Lab, France) with a conventional three-electrode cell. A saturated calomel electrode (SEC) and a platinum electrode were used as reference electrode and auxiliary electrode, respectively. The working electrodes, used for electrochemical experiments, are macro-gold electrodes with 300 nm thick gold layers deposited on Si/SiO₂. A layer of resin is deposited on the gold surface to protect the gold surface during the cutting and storage.

Infrared spectra of monomer and synthesized thioether oligomer were recorded on FTIR spectrometer Nexus 470 (Thermoscientific France) in a total Reflexing attenuated on

Crystal of Diamond in monoreflexion (Smart-orbit, Thermo Scientific). The average weight and Polydispersity of synthesized thioether oligomer was determined by using steric exclusion chromatography (SEC). The analyzes are carried out using an AGILENT 1200 Series isocratic pump equipped with an AGILENT 1200 Series automatic switch and a set of columns. Detection is performed by an AGILENT 1260 Infinity Series refractometer with debit $1.0 \text{ mL}\cdot\text{min}^{-1}$ in 30°C (columns).

The hydrophilicity of the modified gold electrodes was investigated by contact angle measurements using 'Digidrop' from GBX (France). $5 \mu\text{l}$ of deionized water were dropped on the modified electrode surface and the digital camera associated with the instrument purchases the image. The contact angle was obtained for different areas and the volume and the size of the drops were kept constant.

DDT-Poly(N-vinylpyrrolidone) synthesis (DDT-PNVP)

The synthesis of thioether oligomer (DDT-PNVP) was carried out by the free-radical bulk polymerization as following: 2ml of N-vinyl pyrrolidone (NVP, $18,76\text{mmol}$) was heated at high temperature between 100°C and 110°C for 48 h in the presence of thermal initiator, benzoyl peroxide POB (10mg , 0.0413 mmol) and 0.96 ml of dodecanethiol (DDT, 4mmol). The mixture was degassed for 30 min by using ultrasonic apparatus before heating in an oil bath. After cooling, viscous product, yellow to orange in color, was obtained. For removing unreacted monomer and oligomer with very low weight, the final product was dissolved in chloroform and re-precipitated in cold n-hexane several times. Oligomer thus obtained was dried, at ambient temperature then at 50°C to a constant weight. The yield of thioether oligomer DDT–PNVP was 62.68%.

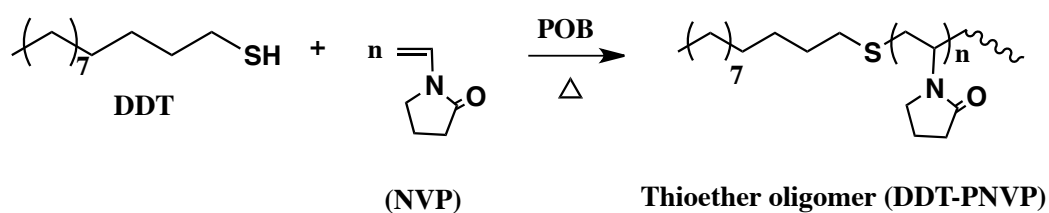
Preparation of modified-gold electrode GE/DDT-PNVP

Gold substrate was washed twice with acetone in an ultrasonic bath for 15 min, followed by incubation in piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$: 3v/1v) for 5 min to remove the inorganic and organic impurities present on the surface, then, the substrate was rinsed thoroughly with absolute ethanol and distilled water and finally dried under a flow of nitrogen. The cleaned gold substrate was incubated in the thioether oligomer solution (0.35 g/ml of DDT-PNVP) in chloroform for 48 hours at 4°C . Prior to ~~any~~ electrochemical measurement, the gold substrate was rinsed with ethanol and distilled water several times for a few minutes to remove the unattached oligomer. Electrochemical measurements of the modified gold substrate were performed in a three-electrode cell; in which the modified gold substrate described above was used as the working electrode (working surface 0.28 cm^2). The measurements were made in PBS buffer containing Ferro/Ferricyanide ions at a concentration of 5 mM ($\text{pH} = 7.4$).

Results and discussion

Synthesis and Characterization of DDT-PNVP

Oligomer thioether DDT-PNVP was synthesized by the facile chain transfer radical polymerization method using N-vinylpyrrolidone as a monomer and DDT as the chain-transfer agent (Scheme 1). The use of DDT is for the purpose of having a chain end containing sulfur. The polymerization reaction is initiated by a thermal initiator, benzoyl peroxide POB at 100-110°C for 48h, in fact DDT also contributes to the initiation of the polymerization; sulfur has a great affinity to radicals and can easily lose its thiol-hydrogen in radical form³⁴. Radical polymerization is carried out in bulk to avoid the chain transfer reactions could possibly take place in the presence of solvent. The molecular weight of the DDT-PNVP oligomer was determined using size exclusion chromatography (SEC). The average molecular weight (Mw) was found to be 1790 g/mol relative to polystyrene standards, with a polydispersity index (PDI) of 1.37. The calibration is carried out with polystyrene standards of increasing molecular weight masses (3600, 7200, 10050, 12900, 21720). The molecular weight of N-vinylpyrrolidone is 111.14 g/mol that corresponding kinetic chain length approximately (polymerization degree, PD= 16) DP=16. However, the low molecular weight of the polymer (<2000 g/mol) and the molecular weight distribution relatively narrow, are due to the radical polymerization technique used.



Scheme 1: The polymerization reaction of NVP in the presence of DDT.(please change POB by BPO)

The Fourier transform infrared spectroscopy (FTIR) was selected to validate the structure of oligomer DDT–PNVP. Spectrum of PNVP is provided in Figure 1, the absorption peaks at 2953.36 and 2892.91 cm^{-1} are associated with the asymmetric and symmetric stretching vibrations of aliphatic methylene ($-\text{CH}_2-$) and methyl ($-\text{CH}_3$) coming from oligomer and from DDT linked at its extremity. The band at 1662.98 cm^{-1} originates from the vibration of the carbonyl bond ($\text{C}=\text{O}$). The large band around 3440 cm^{-1} can be attributed to the O–H stretching vibrations; this is because the carbonyl groups can form hydrogen bonds with traces of water (moisture). The strong band at 1288.94 cm^{-1} is the stretching vibration of C–N bond. In the monomer (NVP) spectrum (Fig. 2), the strong bands at 1629.24 cm^{-1} and 1705.05 cm^{-1} correspond to the absorptions of the double bond ($\text{C}=\text{C}$) and carbonyl bond respectively. The absorption peaks at 3109.03, 981.82 and 930.72 cm^{-1} are attributed to the bond ($=\text{C}-\text{H}$) of the double bond. The stretching vibration of C–N bond in the monomer appeared at 1285.8 cm^{-1} . On the spectrum of polymer, the band characteristics of vinyl group are disappeared, which clearly shows the disappearance of the monomer after the polymerization reaction and the purification step.

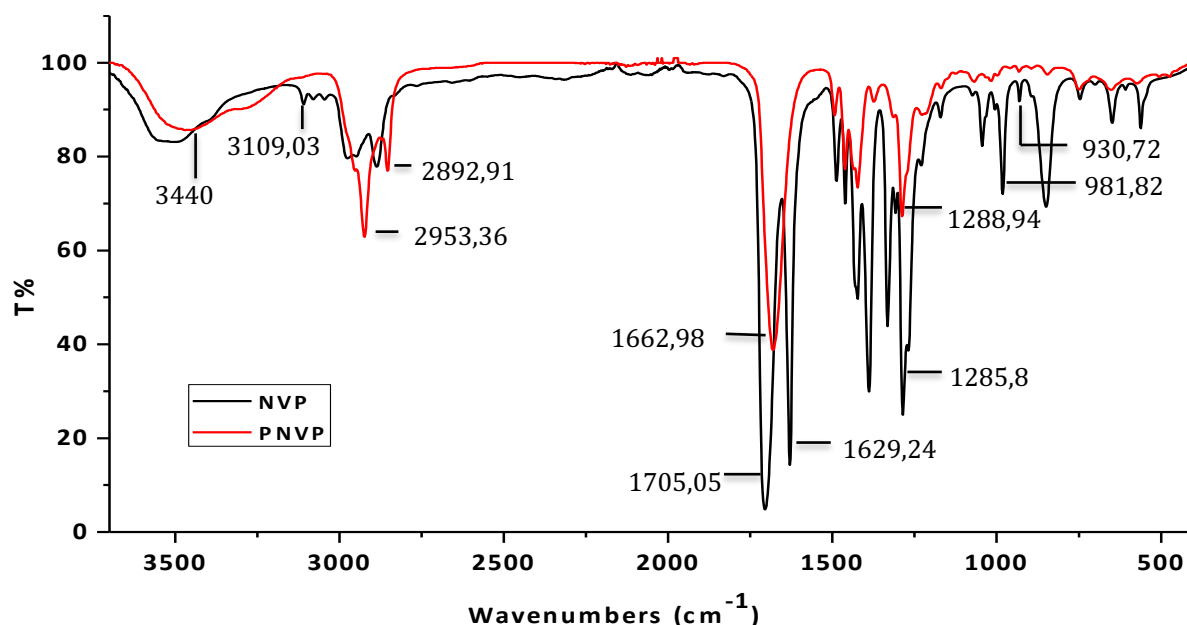


Figure 1. FTIR spectra of the monomer NVP and resulting thioether oligomer DDT-PNVP

Characterization of modified gold electrode GE/DDT-PNVP

The modified gold electrode GE/DDT-PNVP was prepared by a simple incubation of clean gold substrate in thioether oligomer poly(N-vinylpyrrolidone) (DDT-PNVP) solution in chloroform. The presence of the DDT fragments at the end of the oligomer chain, which contain sulfur, helps the oligomer to attach at the surface of gold because sulfur atom is known by its affinity to Gold. However, thioether is weak in comparison with thiol. Thiol can form, according to the literature, a covalent bond with gold (Au-S) with a complete disappearance of the hydrogen atom in S-H bond³⁵. Contrary to this, the thioether retains its structure because the S-C bond is very difficult to break then S-H and the type of thioether interaction with gold is probably electrostatic³⁴. The Fig. 2 shows the proposed morphology of the modified gold electrode GE/DDT-PNVP.

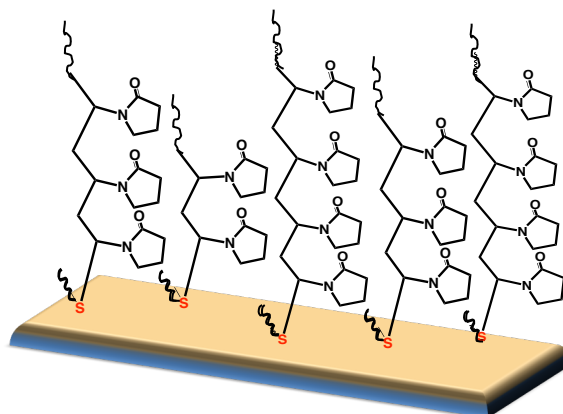


Figure 2. Morphology of gold electrode modified by thioether oligomer poly(N-vinylpyrrolidone) (GE/DDT-PNVP) (this figure 2 is not discussed in the text)

The electrochemical properties of the modified gold electrode were determined by cyclic voltammetry (CV) and by electrochemical impedance spectroscopy (EIS). Figure 3

shows the cyclic voltammograms of the bare gold electrode (A) and modified gold electrode GE/DDT-PNVP (B) recorded by varying the potential of -400 mV to +600 mV with a scan rate of 100 mV/s. At bare gold, a couple of redox peaks of $\text{Fe}(\text{CN})_6^{3-/4}$ (supporting electrolyte) were observed with peak-to-peak separation (ΔI_p) of 1.66 mA and (ΔE_p) of 24,54mV. When the substrate was covered with thioether oligomer DDT-PNVP, a decrease of charge transfer was observed; a couple of redox peaks of $\text{Fe}(\text{CN})_6^{3-/4}$ were obtained with peak-to-peak separation (ΔI_p) of 1.09 mA and (ΔE_p) of 31,26mV. The decrease in current indicates that PNVP could effectively decrease the electron transfer rate between the gold electrode surface and $\text{Fe}(\text{CN})_6^{3-/4}$ solution which could be attributed to the bad conductivity of oligomer thioether DDT-PNVP.

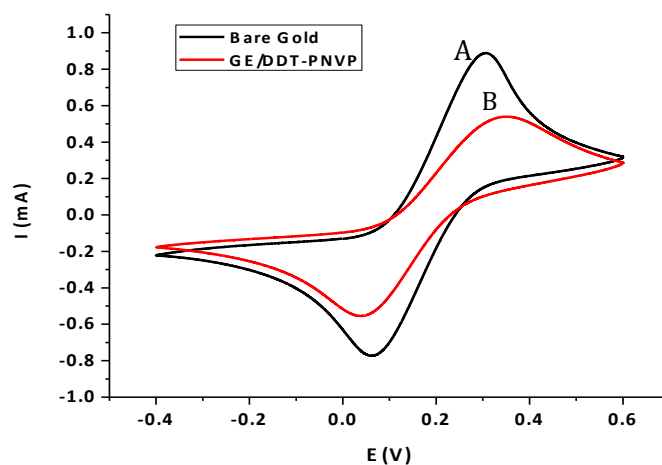


Figure 3. Cyclic voltammograms of gold electrode (A) before and (B) after modification by DDT-PNVP. The measurements were made in the presence of $\text{Fe}(\text{CN})_6^{3-/4}$ as the redox probe with scan rate of 100 mV/s.

Nyquist plots presented in Figure 4 clearly demonstrate the impedance difference between unmodified and modified gold electrode. Firstly, the impedance spectrum of the bare gold electrode indicates the lowest and the fastest transfer of electron on the interface of the bare electrode. After the modification with thioether oligomer DDT-PNVP, the diameter of the semicircle of the impedance spectrum is much larger than that of the bare electrode. This increased impedance is induced by the formation of thioether oligomer layer, on the gold electrode, and implying good blocking behavior and complete control of charge transfer for the transfer process. The Faradaic impedance measurements are in good agreement with CV measurements as the diameter of semicircles for the Nyquist diagrams increase significantly after the modification stage. The recovery rate is found to be $\theta=57,7\%$.

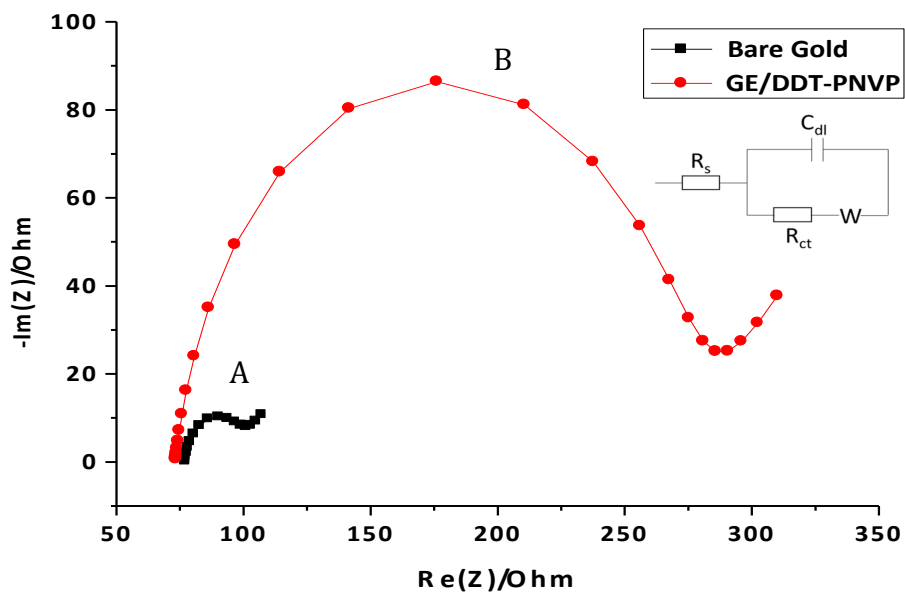


Figure 4. Nyquist plots of bare gold electrode (A) and DDT-PNVP modified gold electrode (B). The EIS were recorded in the presence of $\text{Fe}(\text{CN})_6^{-3/-4}$ at a frequency range between 1 Hz and 200 kHz and at potential of 0.2V. The impedance behavior of the electrolyte can be fitted to a Randles model; that includes the solution resistance (R_s), charge transfer resistance (R_{ct}), constant phase element (C_{dl}) and Warburg impedance element (W).

The hydrophilic/hydrophobic properties of the DDT-PVP modified gold surface have been studied using water contact angle measurements. A camera recorded the image of the drop deposited on the gold electrode surface and the contact angle was calculated from the drop shape by an image-analysis system. The measurements were repeated with four drops of water at different areas of the gold electrode surface. The contact angle value for the bare gold electrode, treated with the piranha solution, was found to be 67.19° , approximately the same value was obtained in further reported in literature³⁶. After the modification with DDT-PNVP, the contact angle of the modified gold substrate revealed a considerable reduction from 67.19° to 45.88° (Fig 5), which confirms that the surface has been modified with success and the sensing film was deposited on the gold surface. The decrease in the angle of contact is explained by the good hydrophilicity of the thioether oligomer DDT-PNVP.

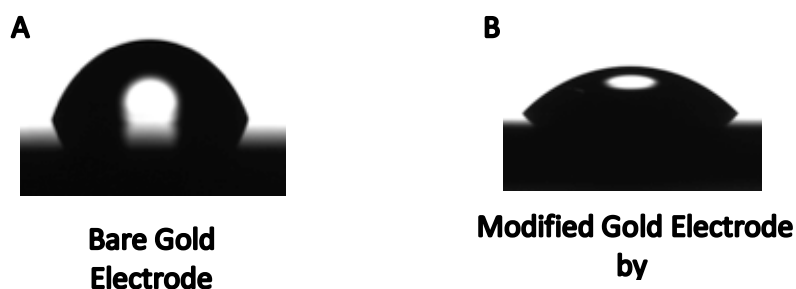


Figure 5. Contact angles of a drop of water on the gold substrate before (A) and after modification by DDT-PNVP (B)

The topography of the modified gold electrode surface was achieved using AFM in contact mode in a range of 50 μm x 50 μm of the substrate. Figure 6 shows the surface morphology and film thickness of the oligomer thioether DDT-PNVP deposited on gold electrode (B) and surface morphology of the unmodified electrode (bare gold) (A). At the micrometric scale, the oligomer layer is in the form of relatively dense and homogeneous globules. The roughness parameter was calculated in order to permit the comparison of the layer density after modification. The bare gold has a roughness factor of 0.43 nm, after modification the oligomer layer has a roughness factor of 3.7 nm. This increase of roughness factor, which is of the order of 3.27 nm, confirms the surface modification of the gold substrate.

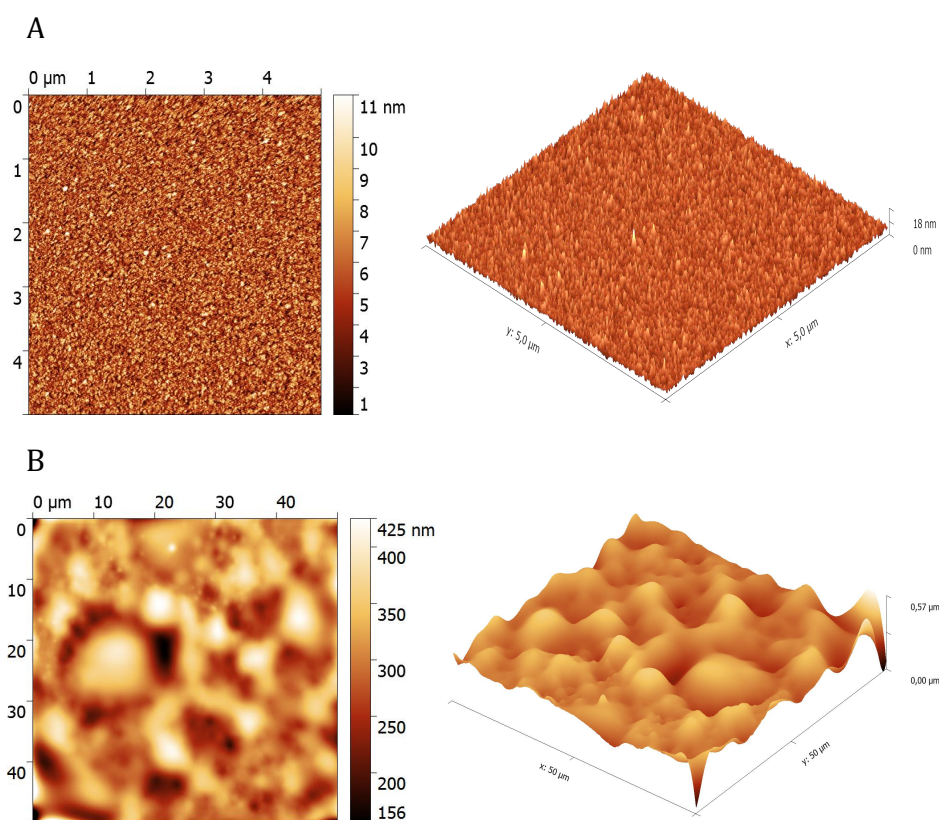


Figure 6. AFM images of gold electrode: (A) bare gold and (B) modified gold electrode by DDT-PNVP

Electrochemical Behavior of Bisphenol A on DDT-PNVP modified-gold electrode

To detect BPA, the prepared GE/DDT-PNVP electrode was immersed into solution containing BPA with different concentrations ranging from 0 pg/ml to 20 pg/ml for 30 min. After incubation, the modified electrode was washed with absolute ethanol and water. Electrochemical measurements were carried out in a 0,01M PBS buffer solution containing $\text{Fe}(\text{CN})_6^{-3/-4}$ at a concentration of 5 mM (PH = 7,4) with a three-electrode cell. The determination of the electrochemical behavior of bisphenol A on the modified gold electrode GE/DDT-PNVP, was carried out by electrochemical impedance spectroscopy EIS,

by following the change in charge transfer on the gold surface after adsorption of bisphenol A. EIS measurements have been recorded in the frequency ranging from 1 Hz to 200 KHz at a potential of 0.2 V. Resulting impedance spectra, obtained in the presence of different concentrations of BPA, were modeled by the equivalent electrical circuit shown in figure 4, and the parameters estimated from electric model were presented in table 1. From the figure 7, a distinct EIS response (Nyquist diagram (A) and Bode plot (B and C)), of the modified electrode GE/DDT-PNVP in BPA sensing was observed. The radiuses of the semicircles, in the Nyquist plots, decrease linearly with increasing of BPA concentration. The efficient trapping of BPA molecules within thioether oligomer caused the increase on the electrochemical current. In the work of Dahlia C. Apodaca et al, they found also, that the total impedance, obtained during the rebinding of the different concentrations of BPA on the imprinted film, decreases with an increase in BPA concentration³⁷. Changes in the impedance obtained during the adsorption of the different concentrations of BPA on the modified gold electrode were used to calculate the amount of BPA using the following equation; equation of the line, $\Delta R/R = -0.0203[\text{BPA}] - 0.4261$ ($R^2 = 0.9792$), as illustrated in Figure 8. BPA molecules are assumed to have activated surface electrode the electrode surface and that the range of such activation is BPA concentration dependent on the concentration of BPA. It is supposed that the BPA molecules were able to penetrate and bind with the chemical functions present within the thioether oligomer layer such as carbonyl and amine by strong hydrogen bond.

Table 1. Parameters estimated from electric model

Potential (mV)	C _{BPA} (pg/ml)	R _s (Ohm)	R _{ct} +R _s (Ohm)	R _{ct} (Ohm)	$\Delta R/R : (R_{ct}-R_{ct_0})/R_{ct_0}$	C ($\mu\text{F}.\text{cm}^2$)	χ^2
200	0	73.29	202.8	129.51	/	2.670	0.8884
	1	71.21	145.8	74.59	-0.4240	2.185	0.9055
	5	71.18	129.1	57.92	-0.5527	2.127	0.9062
	10	67.50	115.7	48.20	-0.6278	2.009	0.9112
	15	69.22	102.4	33.18	-0.7438	1.992	0.9123
	20	66.00	89.55	23.55	-0.8181	1.887	0.9186

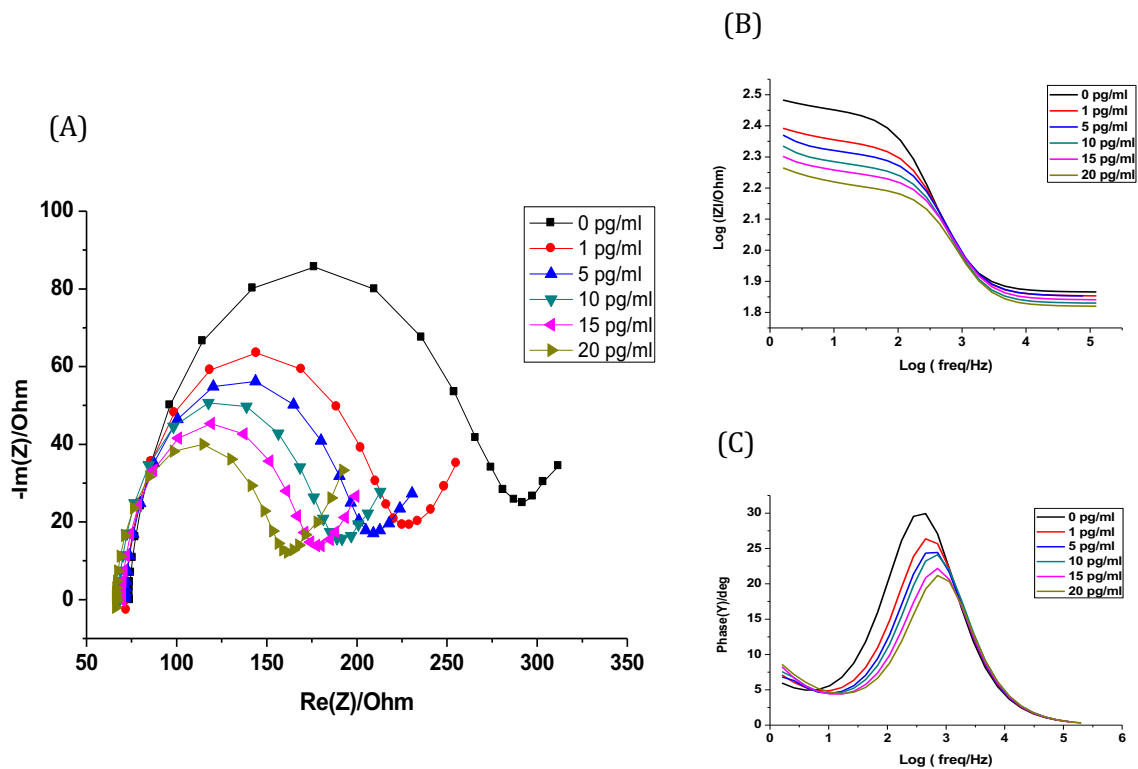


Figure 7. Electrochemical detection of BPA: (A) Nyquist plots and (B),(C) Bode plots of the GE/DDT-PNVP. EIS analysis, in PBS and $\text{Fe}(\text{CN})_6^{-3/-4}$, obtained from the increasing concentration of BPA from 1 to 20 pg/ml

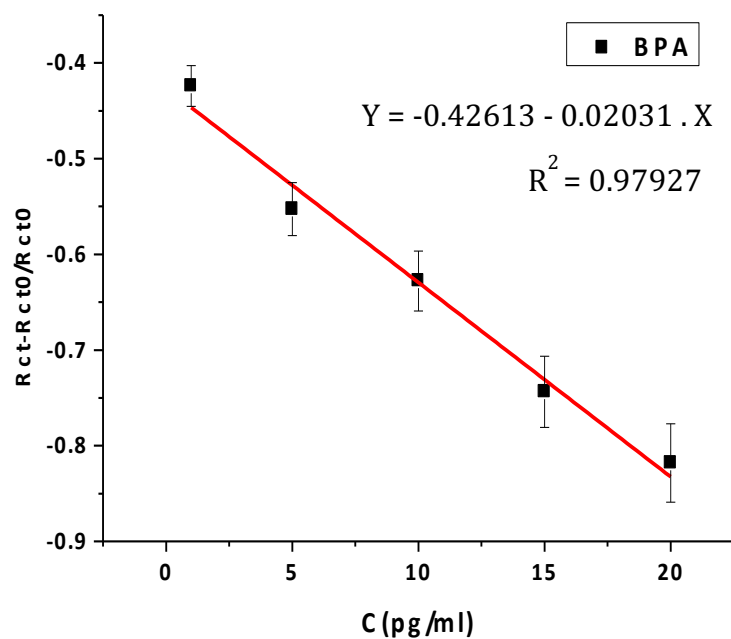


Figure 8. Calibration plot of the BPA modified gold electrode sensor

In Yesim Tugce Yaman and Serdar Abaci work, they used the same polymer Poly(N-vinylpyrrolidone) as sensitive layer in their modified electrode. Interference studies were carried out based on molecules such as 2,4-Dinitrophenol, p-Nitrophenol and o-Nitrophenol, and ions such as Hg^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , and Fe^{3+} . Obtained results show that PNVP (poly(N-vinylpyrrolidone)), used in this study as a recognized layer for BPA, had high selectivity even in the presence of these interfering molecules³⁵. In our work, selective recognition of BPA by the prepared electrode (GE/DDT-PNVP) was investigated ~~tested~~ and proved using the elaborated electrode with another molecules, which possess the same chemical functions as BPA (hydroxyl function). Here, Phenol and hydroquinone, employed usually in plastic manufacture as a monomer, stabilizer or inhibitor, were used to check selectivity of the present sensor. As shown in Fig 9, the calibration curves, obtained after incubation of GE/DDT-PNVP in different concentrations of interfering product between 0 and 20 pg/ml, are not linear. This indicates that the GE/DDT-PNVP electrode has no sensitivity for both phenol and hydroquinone products.

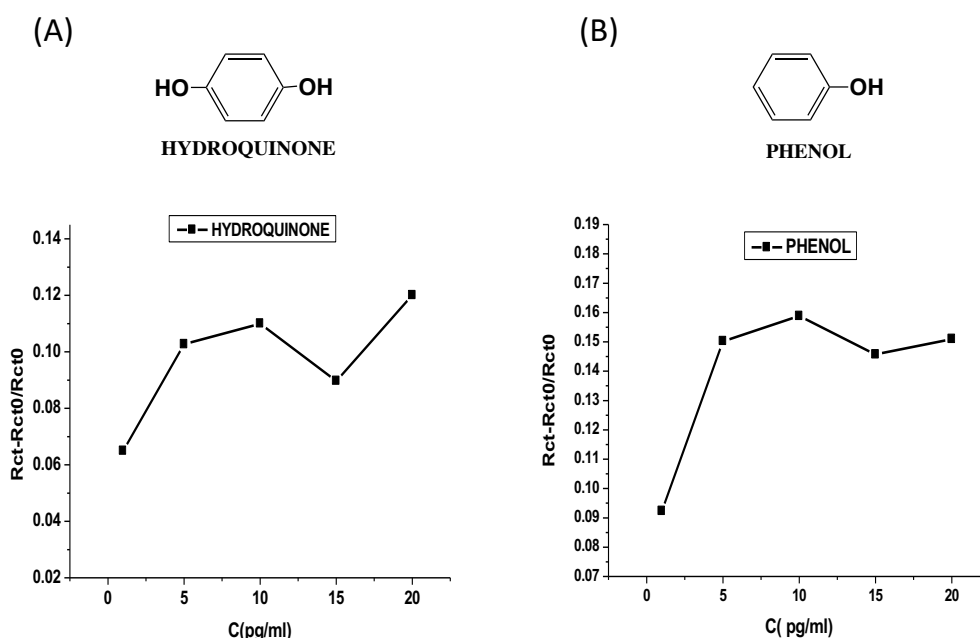


Figure 9. Calibration plots of the modified gold electrode in Hydroquinone (A) and Phenol (B) sensing.

Conclusion

In the present work, a new electrochemical sensor of bisphenol A (BPA) has been developed by a very simple method. A thioether oligomer DDT-poly(N-vinylpyrrolidone) has been synthesized and used to modify the surface of a gold electrode. The oligomer thioether represents the sensitive layer in the chemical sensor. Synthesis of oligomer has been carried out by radical polymerization in the presence of a transfer agent the dodecanethiol, the transfer agent leads to the formation of polymer chains with an extremity that contains sulfur. Sulfur atom has a remarkable affinity for noble metals, it can help the oligomer chains to be attached on a gold surface leading to and form a stable layer

formation. Achieved results demonstrate that the novel oligomer-based sensor has appreciable sensitivity for BPA detection and exhibits excellent performance for BPA determination with a linear range of 1 pg/ml - 20 pg/ml (4.38 pM – 87.6 pM). Several interfering species, such as phenolic compounds (phenol and hydroquinone) were used and their behaviors on the modified gold electrode were investigated. The obtained results demonstrate that the elaborated GE/DDT-PNVP electrode was found to be more sensitive to BPA than Phenol and hydroquinone.

References

1. Stragierowicz, J. BISPHENOL A – APPLICATION , SOURCES OF EXPOSURE AND POTENTIAL RISKS IN INFANTS , CHILDREN AND PREGNANT WOMEN. **28**, 209–241 (2015).
2. Michałowicz, J. Bisphenol A – Sources , toxicity and biotransformation. *Environ. Toxicol. Pharmacol.* **37**, 738–758 (2014).
3. Ribeiro, E., Ladeira, C. & Viegas, S. Occupational Exposure to Bisphenol A (BPA): A Reality That Still Needs to Be Unveiled. *Toxics* **5**, 22 (2017).
4. Eladak, S. *et al.* A new chapter in the bisphenol a story: Bisphenol S and bisphenol F are not safe alternatives to this compound. *Fertil. Steril.* **103**, 11–21 (2015).
5. dodds1936.pdf.
6. Begley, T. H. Determination of Bisphenol-A in Reusable Polycarbonate Food-Contact Plastics and Migration to ... Determination of Bisphenol-A in Reusable Polycarbonate. (2015). doi:10.1021/jf970072i
7. Composites, D. Journal of Dental Research. (2012). doi:10.1177/0022034512458691
8. Vandenberg, L. N., Hauser, R., Marcus, M., Olea, N. & Welshons, W. V. Human exposure to bisphenol A (BPA) &. **24**, 139–177 (2007).
9. Mercea, P. Physicochemical Processes Involved in Migration of Bisphenol A from Polycarbonate. 3–5 (2009). doi:10.1002/app
10. Welshons, W. V, Nagel, S. C. & Saal, F. S. Large Effects from Small Exposures . III . Endocrine Mechanisms Mediating Effects of Bisphenol A at Levels of Human Exposure. **147**, 56–69 (2014).
11. Tsukiokai, T. *et al.* Development Trace of Analytical Amounts Estimation Method for Determining Samples of BPA in Urine of Exposure to BPA. **14**, 57–63 (2004).
12. Wetherill, Y. B. *et al.* In vitro molecular mechanisms of bisphenol A action &. **24**, 178–198 (2007).
13. Ikezuki, Y., Tsutsumi, O., Takai, Y., Kamei, Y. & Taketani, Y. Determination of bisphenol A concentrations in human biological fluids reveals significant early prenatal exposure. **17**, 2839–2841 (2002).
14. Zhou, Y. *et al.* Neurotoxicity of low bisphenol A (BPA) exposure for young male mice : Implications for children exposed to environmental levels of BPA *. *Environ. Pollut.* **229**, 40–48 (2017).
15. Santangeli, S. *et al.* Effects of BPA on female reproductive function: the involvement of epigenetic mechanism. *Gen. Comp. Endocrinol.* (2016). doi:10.1016/j.ygcen.2016.08.010
16. Sun, Y. *et al.* Determination of bisphenol A in human breast milk by HPLC with column-switching and fluorescence detection. **507**, 501–507 (2004).
17. Rezaee, M., Enginee, E., Shariati, S., Branch, R. & Sciences, M. Dispersive Liquid – liquid Microextraction Combined with High-performance Liquid Chromatography-UV Detection as a Very ... (2017). doi:10.1016/j.chroma.2008.12.091
18. Thomaidis, N. S. Determination of bisphenol A in milk by solid phase extraction and liquid chromatography- mass spectrometry Determination of bisphenol A in milk by solid phase extraction and liquid chromatography – mass spectrometry. (2006). doi:10.1016/j.chroma.2006.06.103
19. Science, E., Liao, C., Academy, C. & Kannan, K. Determination of Free and Conjugated Forms of Bisphenol A in Human Urine and Serum by. (2012). doi:10.1021/es300115a
20. Olmo, M., Navas, N. A. & Vilchez, J. L. Determination of bisphenol A (BPA) in water by gas spectrometry. **2670**, (1997).
21. Gatidou, G. & Thomaidis, N. S. Simultaneous determination of the endocrine disrupting compounds nonylphenol , nonylphenol ethoxylates ... (2007). doi:10.1016/j.chroma.2006.10.037
22. Wu, X. *et al.* Sensors and Actuators B : Chemical Molecularly imprinted polymers-coated gold

- nanoclusters for fluorescent detection of bisphenol A.
23. Zhang, J., Zhao, S., Zhang, K. & Zhou, J. Chemosphere Cd-doped ZnO quantum dots-based immunoassay for the quantitative determination of bisphenol A. (2013).
 24. Xu, J., Li, Y., Bie, J., Jiang, W. & Guo, J. Colorimetric method for determination of bisphenol A based on aptamer-mediated aggregation of positively charged gold nanoparticles. (2015). doi:10.1007/s00604-015-1547-z
 25. Huang, J. *et al.* Electrochemical sensor based on imprinted sol e gel and nanomaterials for sensitive determination of bisphenol A. **22**, 786–791 (2011).
 26. Lu, B., Liu, M., Shi, H. & Huang, X. A Novel Photoelectrochemical Sensor for Bisphenol A with High Sensitivity and Selectivity Based on Surface Molecularly Imprinted Polypyrrole Modified TiO₂ Nanotubes. 771–779 (2013). doi:10.1002/elan.201200585
 27. Mita, D. G., Attanasio, A., Arduini, F., Diano, N. & Grano, V. Enzymatic determination of BPA by means of tyrosinase immobilized on different carbon carriers. **23**, 60–65 (2007).
 28. Ishi, K. N., Akai, M. T., Orimune, K. M. & Hkawa, H. O. Molecular and Immunochemical Characteristics of Monoclonal and Recombinant Antibodies Speci[^]c to Bisphenol A.
 29. Yu, C., Gou, L., Zhou, X., Bao, N. & Gu, H. Electrochimica Acta Chitosan – Fe₃O₄ nanocomposite based electrochemical sensors for the determination of bisphenol A. **56**, 9056–9063 (2011).
 30. Zhang, Y. *et al.* Talanta Electrochemical sensor for bisphenol A based on magnetic nanoparticles decorated reduced graphene oxide. **107**, 211–218 (2013).
 31. Chen, L. Molecularly imprinted polymers-coated gold nanoclusters for fluorescent detection of bisphenol A Article in Sensors and Actuators B Chemical · February 2015. *Sensors Actuators B. Chem.* **211**, 507–514 (2015).
 32. Yin, H. *et al.* Sensitivity and selectivity determination of BPA in real water samples using PAMAM dendrimer and CoTe quantum dots modified glassy carbon electrode. **174**, 236–243 (2010).
 33. Wang, J., Su, Y., Wu, B. & Cheng, S. Talanta Reusable electrochemical sensor for bisphenol A based on ionic liquid functionalized conducting polymer platform. *Talanta* **147**, 103–110 (2016).
 34. Huang, X. *et al.* Facile preparation of size-controlled gold nanoparticles using versatile and end-functionalized thioether polymer ligands. *Nanoscale* **3**, 1600–1607 (2011).
 35. Lee, H. J., Jamison, A. C. & Lee, T. R. Boc-protected ω-amino alkanedithiols provide chemically and thermally stable amine-terminated monolayers on gold. *Langmuir* **31**, 2136–2146 (2015).
 36. Houcine Barhoumi, Y. B. Characterization of Urea Biosensor Based on the Immobilization of Bacteria Proteus Mirabilis in Interaction with Iron Oxide Nanoparticles on Gold Electrode. *J. Biosens. Bioelectron.* **6**, 1–9 (2015).
 37. Apodaca, D. C., Pernites, R. B., Ponnampati, R., Del Mundo, F. R. & Advincula, R. C. Electropolymerized molecularly imprinted polymer film: EIS sensing of bisphenol A. *Macromolecules* **44**, 6669–6682 (2011).