Int. J. Electrochem. Sci., 6 **(2011)** 1949 - 1967

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Dendritic 7T-Polythiophene Electro-Catalytic Sensor System for the Determination of Polycyclic Aromatic Hydrocarbons

Candice Rassie, Rasaq A. Olowu[*]*, Tesfaye T. Waryo, Lindsay Wilson, Avril Williams,*
Pricilla G. Baker, Emmanuel I. Iwuoha

Sensor Lab, Department of Chemistry, University of the Western Cape, Bellville, 7535, South Africa
[*]E-mail: rolowu@uwc.ac.za

Received: 31 March 2011 / *Accepted:* 15 May 2011 / *Published:* 1 June 2011

Polycyclic aromatic hydrocarbons can be carcinogenic in nature and thereby harmful to the environment. It is thus important that these substances be degraded in a way that is less harmful to the environment and also more cost and time efficient than previous chemical methods. An electrochemical method to degrade these harmful substances was achieved by using a gold electrode that was modified with a synthesized polythiophene dendrimer known as 2,3-di(5,5″-dihexyl-[2,2′;3′,2″] terthiophene5′-yl)thiophene(5) (7T.). The synthesized 7T dendrimer was characterized with Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), UV spectroscopy, energy dispersive X-Ray analysis (EDX), transition electron microscopy (TEM) and electrochemically. The dendrimer modified gold electrode acted as a catalytic electrochemical membrane for degradation of anthracene and phenanthrene. This technique successfully showed an increase in electrochemical activity and appearance of an oxidation peak upon addition of both anthracene and phenanthrene to the modified gold electrode. The number of electrons involved in the oxidation process was estimated by integrating the reduction peak which gives a one electron transfer process. The detection limit of analyte was estimated to be 19 nM, revealing the catalytic behaviour of thiophene dendron modified gold towards the degradation of anthracene and phenanthrene respectively.

Keywords: Electrochemical impedance spectroscopy, degradation, dendrimer, PAHs, Self assembly monolayer (SAM), pollutants

1. INTRODUCTION

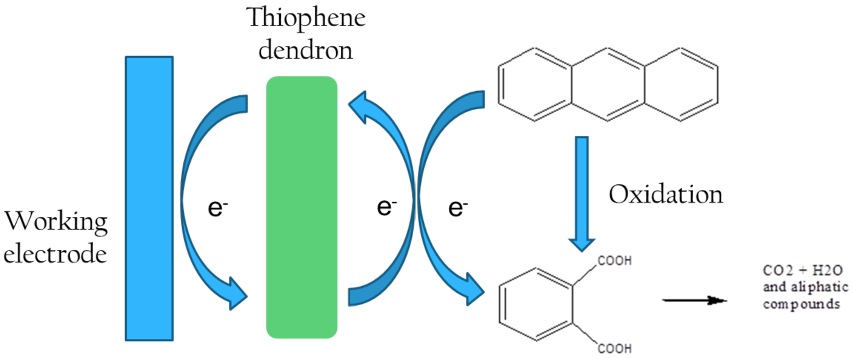
Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat [1]. PAH’s do not contain any substituents or heteroatoms and consist of fused aromatic rings [2]. Examples of polycyclic aromatic hydrocarbons are anthracene, phenanthrene, flouranthene, benz[a]nthracene and benzo[a]pyrene. Pollution due to these substances is on the rise in South Africa since our country still largely depends on fossil fuels for energy generation. These pollutants are mutagenic and carcinogenic in nature [3] and moreover, they have been shown to disrupt sex hormones, affect immune competence of organisms, and pose reproductive and developmental toxicity as well as skin defects in animals [4]. Thus, it is vital to detect and degrade PAHs in an easy and harmless way (i.e. one in which the resulting species are not dangerous). PAHs are most commonly degraded using chemical methods such as Fenton's reagent, where the solvents include hydrogen peroxide and sulfuric acid [5-6]. However, this poses a problem for various reasons including the fact that: various solvents are used in the reaction, some of which are harmful to the environment; the reaction pathway might be long or cumbersome and time consuming and consists of many intermediates or compounds which are labile, volatile and polluting; reagent costs may be high and reaction conditions are strict in order to reach a harmless end product. Numerous methods such as chemical, and bioremediation technologies (i.e. bacteria, algae and fungi) have been employed for the degradation of PAH's [3, 7]. These methods are expensive, and take a very long time for preparation of assay [3]. Bioremediation of PAH's have been widely used by scientists in trying to degrade polycyclic aromatic hydrocarbons. Examples of bioremediation include the use of microbial metabolism, degradation by bacteria, degradation by fungi, degradation by algae and also degradation under anaerobic conditions [3].

A typical PAH, such as anthracene, was successfully degraded in rat liver cytosol in vitro as well as in rat subcutaneous tissue in vivo. The degradation was possible by the oxidation of the metabolitic anthracene [8]. Polycyclic aromatic hydrocarbons such as benz(a)pyrene and benz(a)anthracene are carcinogenic in nature, because the structure of anthracene is found in these carcinogenic substances, it was used as a model PAH [9] and was thus also used as a model in this study. Due to the pollution extent of PAH's in the environment, the need for their continuous monitoring is paramount and this requires the use of simple, low cost, robust and sensitive methods of degradation. The technique that best fit these requirements is an electrochemical sensor. Electrochemical degradation is of particular interest since it provides an environmentally friendly method of getting rid of harmful substances, since electrons are "clean" reagents which cause no damage to the environment as chemicals might do. Electrochemical processes are also energetically feasible; cost efficient; versatile since the same electrochemical reactor can be used for various reactions/purposes; easily automated since the main parameters are current and voltage, user friendly since they do not require extreme temperatures and pressures; and is also selective depending on the reaction conditions [10]. In this study, electrochemical degradation has been attempted using an electrochemical membrane which acts as a catalyst in the degradation of these carcinogenic substances. A related electrochemical method using an Ag-Au alloy nanoparticles/overoxidized-Polypyrrole for the degradation of anthracene has been employed recently by Iwuoha and his group[11]. Alcantara *et al* 2009[1] reported that polycyclic aromatic hydrocarbons are highly hydrophobic in nature and are thus strongly absorbed onto soil and sediments in nature. A study has been done in which surfactants are used in order to remove these PAH's from soil (i.e. using desorption). Alcantara .*et al* 2009 [1] investigated electrochemical degradation of PAHs in order to determine the best surfactant [1]. Another method of PAH degradation using an expanded titanium covered with ruthenium oxide electrode has been reported by Tran L, *et al* 2009 [12]. A good way to enhance the electrochemical degradation of a substrate would be to modify the surface of the working electrode used. Because of the conducting properties of dendrimers, we can assume that they serve as good electrochemical membranes.[10]. It can thus be concluded that electrochemical methods have shown success in degrading harmful organic compounds and thus is a viable method for the degradation of PAH’s [11].

The electrochemical membrane used in this study is a dendritic form of polythiophene [2,3-di(5,5″-dihexyl-[2,2′;3′,2″] terthiophene5′-yl)thiophene(5) (7T.).] which was deposited onto the gold electrode by means of self-assembly based on gold-sulphur chemisorption. Dendrimers are repeatedly branched, roughly spherical large molecules. A dendrimer is typically symmetric around the core, and often adopts a spherical three-dimensional morphology. The spherical and 3-dimensional structure of the dendrimer gives it the conductive characteristics that are better than the linear polymer. Conducting chains within the dendrimer and the stereochemistry of the molecule allow sufficient overlap of π-orbitals.

This causes the dendritic form of the polymer to have a much higher electrical conductivity than its linear counterpart [13]. The polythiophene dendrimer act as an electrochemical membrane by transferring electrons between the gold electrode surface and the substrate to be degraded (i.e. the polycyclic aromatic hydrocarbons) anthracene and phenanthrene. This additional transfer of electrons aids in the degradation of the PAH as a catalyst and is shown in scheme 1. Dendrimers have become important in the field of polymer chemistry because of the unique structure, they are macromolecules with a regular and highly branched three dimensional structure [14]. Thiophene dendrimers were synthesised in a study by Xia C et al 2002 [15] since there was considerate interest in polythiophene derivatives for their optical and electronic properties, also they are shape persistent molecules with nanometre sizes and exhibit interesting aggregation properties. Thiophene dendrimers are also intriguing because of their spatial arrangement and microstructure.

They were synthesised using the convergent method with 2,3-dibromothiophene as a key monomer starting material [15]. Another method of dendrimer synthesis is the electrogenerated poly (dendrimers) which are produced by electropolymerization onto the surface of an electrode and thus acting as a catalyst. In a study by Sebastian *et al* 2000, dendrimers with peripheral bithiophene (BT) groups were successfully synthesised and electroplymerized [16]. A review done by Akinyeye *et al* 2007 in our group further confirmed that nanostructured conducting polymers of polyaniline, polypyrrole and polythiophene as well as their blends/composites have a high stability and serve as a simple, hand held electrochemical sensors as well as excellent catalytic abilities [17]. Dendrimer encapsulated metal nanoparticles were synthesised and its application in catalysis has been studied by Niu *et al* 2003. It was shown that the dendrimer components of the DEMN enhanced the stability of the nanoparticle and increases its catalytic selectivity [18]. Thus dendrimers have been sufficiently studied and proved to be a catalytic enhancer and can therefore be used as a catalytic membrane for PAH degradation.



Scheme 1. Transfer of electrons from the gold electrode surface, through the electrochemical membrane (thiophene dendron) and oxidation of the analyte (PAH)

2. EXPERIMENTAL SECTION

2.1. Chemicals, reagents and instrumentation

2,3-dibromothiophene, butyllitium, 1-bromohexane, NBS/DMF, tributyltin chloride, lithium perchlorate, potassium ferricyanide [$K_3Fe(CN)_6$] and potassium ferricyanide [$K_4Fe(CN)_6$], acetonitrile, anthracene and phenanthrene were obtained from Sigma-Aldrich. The chemicals were of analytical grade and were used as received. Ultra-pure water was used in all aqueous solutions, purified by a milli-Q^{TM} system (Millipore).

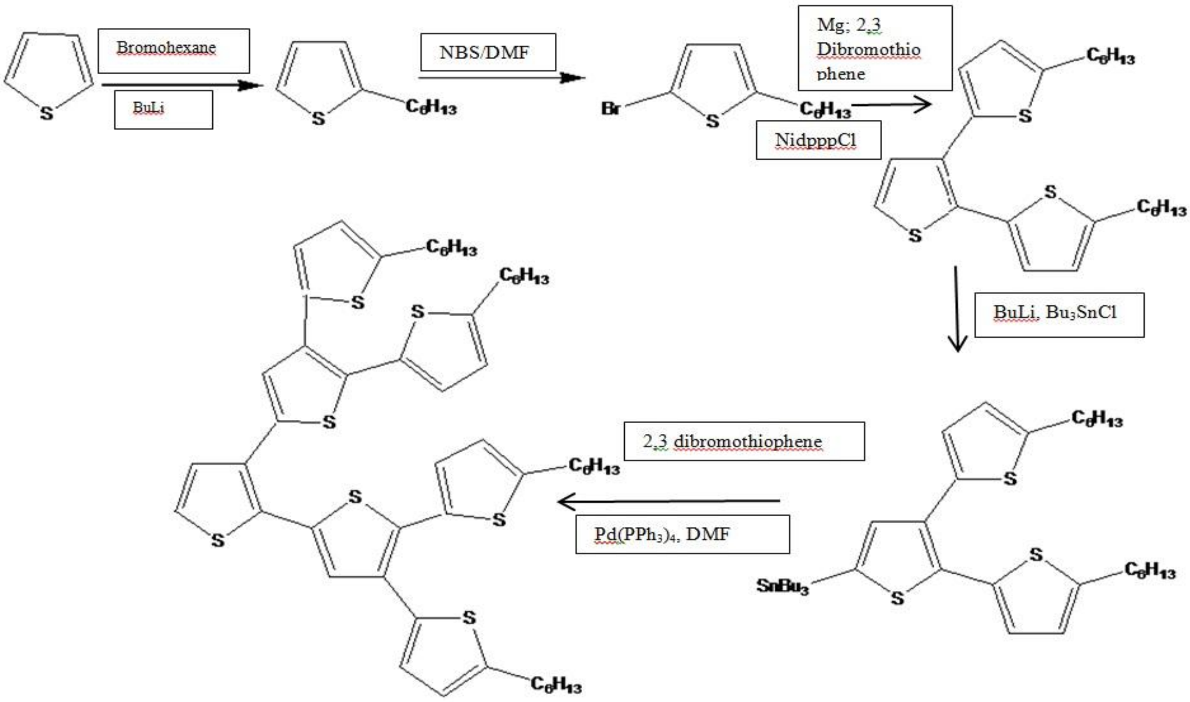
A three electrode system was used for all experiments. The working electrode used was gold with a diameter of 1.6mm, the reference electrode was Ag/AgCl (3M $NaCl^-$) and platinum wire served as the counter electrode. Cyclic voltammetry and Square wave voltammetry at amplitude of 50 mV and a frequency of 25 Hz were applied. Electrochemical impedance were recorded with Zahnner IM6ex Germany at a voltage amplitude of 10 mV and with a frequency range from 100 mHz to 100 KHz. All working solutions were purged with argon for ten minutes before the experiment and the reactions were carried out at room temperature. Infrared spectrum was obtained using PerkinElmer Spectrum 100-FT-IR Spectrometer. UV/Vis spectra were recorded using a Nicolette Evolution 100 spectrometer (Thermo Electron Corporation, UK). ^1H NMR (200) was carried out in $CDCl_3$ using a Varian Gemini XR200 spectrometer. Transmission electron microscope images were obtained from a Tecnai G^2 F$_2$O X-Twin MAT.

2.2. Solutions

0.1 M lithium perchlorate was prepared in acetonitrile and used as supporting electrolyte, saline PBS of pH 7.4 containing 10mM of Na_2HPO_4,KH_2PO_4 and 0.1M KCl was prepared. 5 mM (1:1) solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ was prepared in 100 mL of the PBS at pH 7,4. 5 mM anthracene in 85/15 ratio of acetonitrile and water respectively, phenanthrene was prepared in the same way as anthracene.

2.3. Synthesis of polythiophene dendrimer

The method of synthesis of the dendron was adopted from Xia et al 2002 [15]. A thiophene monomer was treated with bromohexane and butyl lithium, substituting the alpha-hydrogen with a hexyl substituent. The substituted thiophene was then brominated with NBS/DMF resulting in the formation of 1-bromo-5-hexylthiophene. 2,3-dibromothiophene was used as a key starting materials in the convergent synthesis of the thiophene dendrimer. A C-C bond can form through the C-Br group at the 2,3 positions using metal-mediated coupling. The fifth position can undergo other transformations for further coupling reactions, in this case, Stille coupling. Thiophene was treated with butyllithium and 1-bromohexane, and then brominated with NBS/DMF to produce 2-Bromo-5-hexylthiophene. Compound 3T was then treated with butyllithium and tributyltin chloride to give the stannyl compound for the following Stille coupling. An excess of the stannyl compound was used to ensure completion of the coupling reaction to produce the 7T dendrimer. The synthetic pathway is as shown in Scheme 2



Scheme 2. Synthetic pathway of the 7T thiophene dendron

2.4. Preparation of thiophene dendrimer modified electrodes.

The gold electrode was cleaned using the procedure described as follows; the electrode surface was polished using alumina powder of sizes 1.0, 0.3 and 0.05 µm respectively. This was followed by placing the electrode in piranha (ratio 3: 1, H_2SO_4 : H_2O_2) for ten minutes, and then sonicated for 5 min. in ethanol and water respectively. The electrode was also cleaned electrochemically in 1 M sulphuric acid by cycling between the potential of -200 mV to 1500 mV until a reproducible cyclic voltammogram was obtained. The electrode was then rinsed thoroughly with distilled water and dried under a stream of nitrogen gas. A volume of 1 µl of the thiophene dendron was then drop coated onto the surface of the electrode and allowed to dry overnight.

2.5. Electrochemical response of the modified electrode in lithium perchlorate-acetonitrile

A 0.1 M solution of lithium perchlorate in acetonitrile was prepared and used as electrolyte. A volume of 5 ml of this solution was placed into a cell and the bare and modified electrodes were characterised in the solution respectively using cyclic voltammetry. A window potential of 600 mV to 2 V was used for the gold electrode, Square wave voltammetry at an amplitude 20 mV and 25 Hz was used for characterization.

2.6. Electrochemical degradation of PAH

A system containing 0.1M lithium perchlorate and the dendron modified gold electrode was spiked with different concentrations of PAH i.e. 5mM anthracene or phenanthrene. The electrochemical behaviour after each addition of PAH was observed at a window potential of 600mV to 2V. Cyclic voltammetry as well as square wave voltammetry was employed to monitor the degradation process of the PAH (anthracene and phenanthrene).

2.7. Testing of detection limits

To test the detection limits of the modified gold electrode for the PAH's the same procedure was followed as described above. A solution containing 85% acetonitrile and 15% water was used as a "blank" in the absence of analyte i.e. PAH

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

Figure 1 below represents the Fourier transform infrared spectrum of the synthesized thiophene dendron. Bands that are characteristic of the thiophene moiety are at 697cm^{-1} (caused by C-H out-of-plane vibration).and at 594cm^{-1} which attributed to C-S-C stretching [19]. Band at 3067cm^{-1} is due to the C-H stretching of the aromatic proton bands within the thiophene ring. A peak appears at 797cm^{-1} which is characteristic of a C-H out-of-plane vibration within the thiophene ring[14]. The spectra showed an out of plane C-H bending located at the α-position of the thiophene ring observed at 723cm^{-1} . [20] Stretching modes of C=C and C-C in the thiophene ring are seen at 1518, 1463, 1376 and 1340 cm^{-1} respectively[21]. A peak at 2926 cm^{-1} is characteristic of polymeric C-H stretching [22].

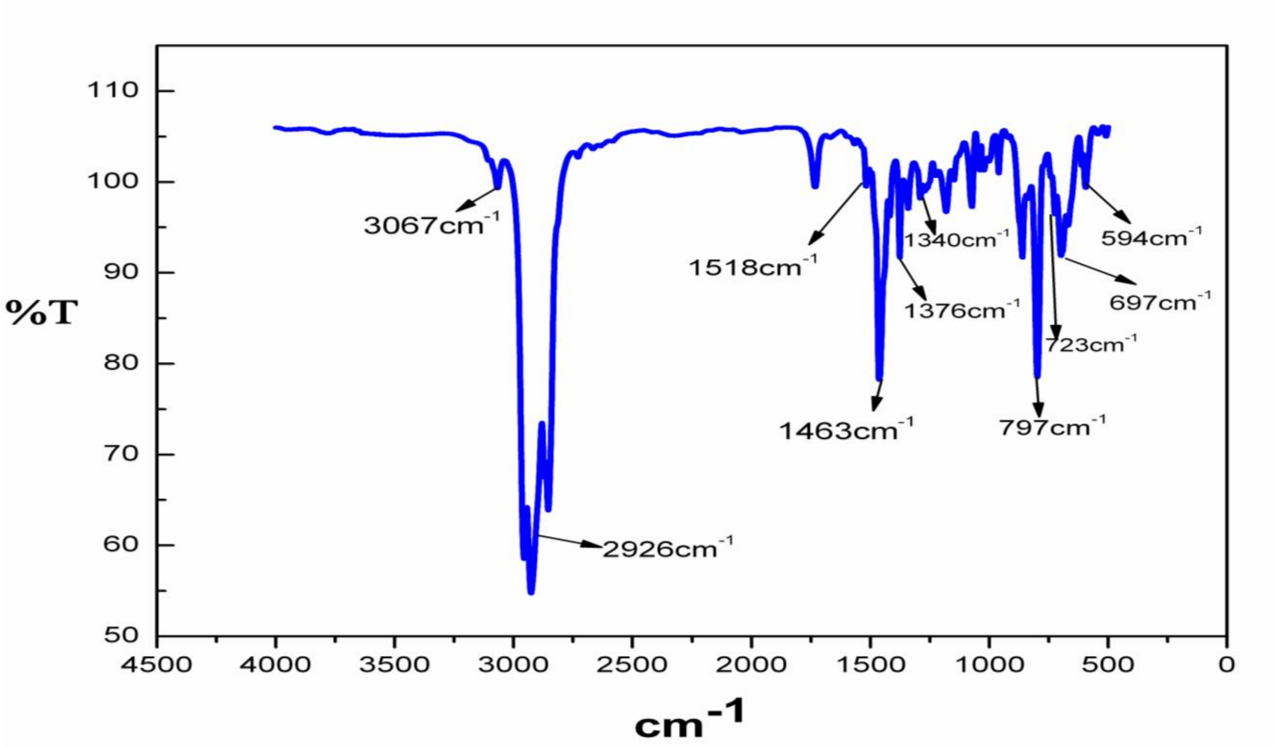


Figure 1. Infrared spectrum of sythensized thiophene dendron

3.2. UV spectroscopy analysis

Further probe into the charcterization of the synthensized thiopehne dendron was carried out with UV spectroscopy and absorbance of the thiophene dendron was determined between 200 and 700 nm. An absorbtion peak was obtained at 303 nm as shown in figure 2 which is characteristic of the thiophene dendron [14].

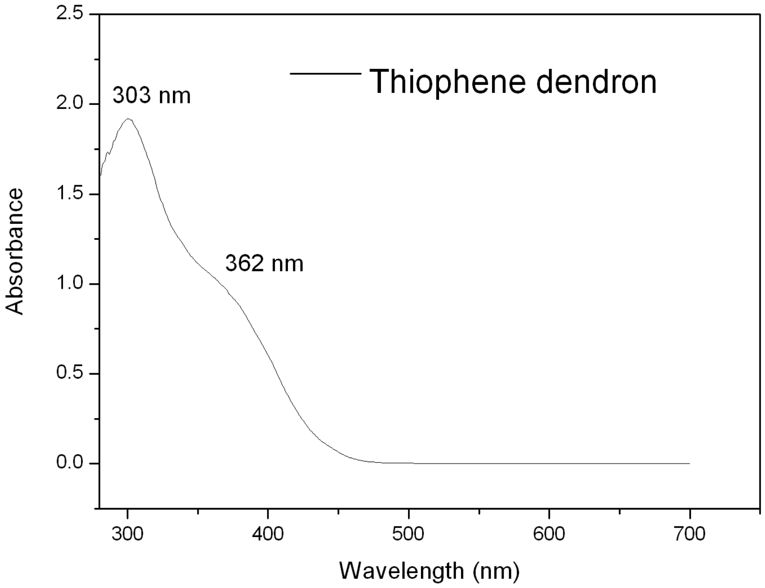


Figure 2. UV absorbance spectra of thiophene dendron

3.3. Nuclear Magnetic resonance analysis

The thiophene Dendron is very soluble in chloroform and thus it was suitable for use as solvent in the NMR determination at room temperature. The NMR spectra showed a new chemical shift at 7.271 ppm which confirmed the synthesis of the dendron since peaks in this area are characteristic of 5 membered thiophene rings (downfield). The doublet at the most downfield point i.e. at 7.271 ppm is attributed to the protons at the focal thiophene which correspond to earlier reports [15]. The multiplets in the upfield region of 0.7-1.6 ppm are due to the 13 protons on the hexyl substituent[22].

3.4. Transmission electron miscroscopy analysis

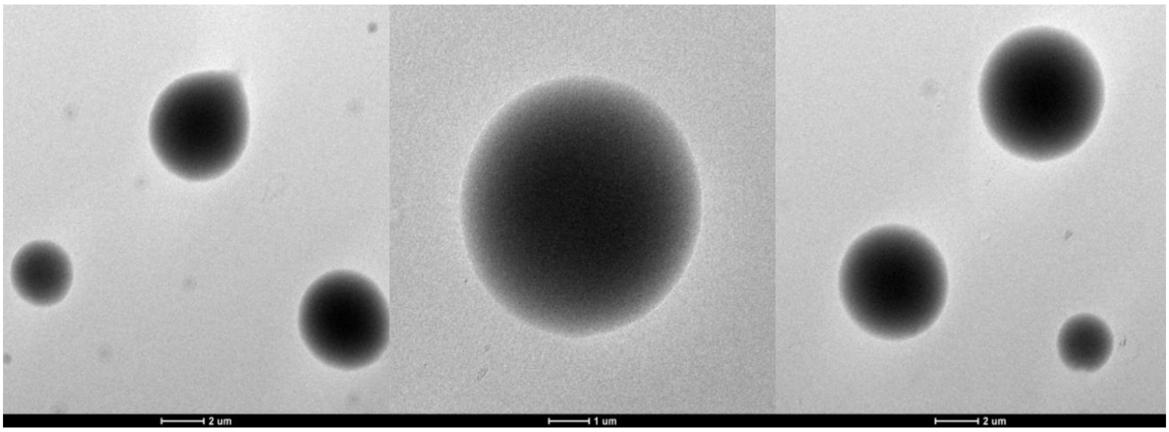


Figure 3. Transmission electron miscroscopy image of the sythesized thiopene dedron.

The TEM images in figure 3 revealed circular agglomerates of the dendron. This confirms the globular structure which is characteristic of a dendron/dendrimer molecule and certifies the synthesis of the thiophene dendron.

3.5. EDX analysis of the thiophene dendron:

Table 2. Quantification results of EDX

Element	***Weight %***	**Atomic %**	**Uncert. %**	**Detector correction**	**k-Factor**
C(K)	85.85	94.49	1.13	0.26	3.940
O(K)	2.82	2.33	0.14	0.49	1.974
S(K)	4.00	1.65	0.12	0.93	1.021
Cu(K)	7.31	1.52	0.17	0.99	1.667

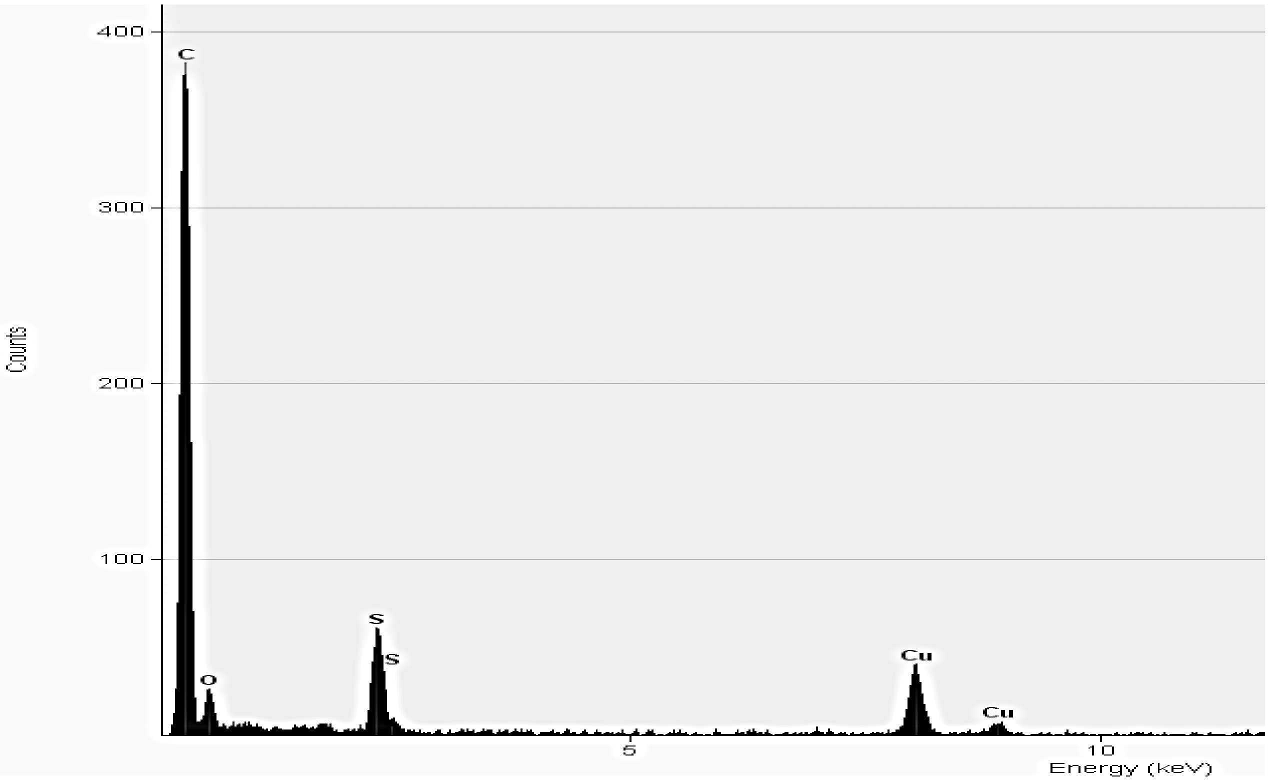


Figure 4. EDX results of thiophene dendron elemental analysis

The EDX analysis revealed that the most abundant element in the sythensized thiopene dendrimer was carbon with a weight percentage of 85%, followed by a weight percentage of 4.00% of sulfur as shown in table 2 as well as figure 4 above. This confirms the formation of the thiophene dendron. The presence of copper and oxygen in the EDX analysis may be attributed to the copper grid used for the analysis.

3.6 Voltammetric response of the thiophene dendrimer modified electrode in 0.1M supporting electrolytes (lithium perchlorate).

The response of the bare and dendrimer modified gold electrode was investigated in 0.1 M lithium perchlorate acting as a supporting electrolyte. Figure 5 below shows the cyclic voltammetric response of the gold electrode compared to the dendron modified electrode. The bare electrode did not exhibit any distinct oxidative peak with low current density. Upon modification of the electrode with thiophene dendron, a catalytic response of the modified electrode was observed with a tremendous increase in current density from 6.352 to 54.83 µA at peak potential of 1515 mV. The catalytic behaviour of the modified electrode may be attributed to the electrostatic interaction that exists between the thiophene dendron back bone and the negatively charged chlorate ion employed as a counter ion for charge balancing. The response of the modified electrode shows that the dendron was successfully immobilized on the electrode surface.

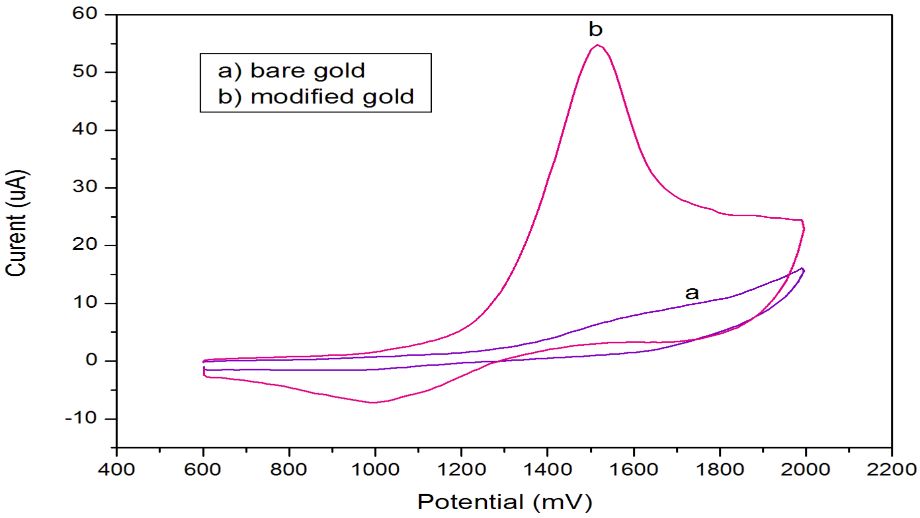


Figure 5. Cyclic Voltammetry response of bare Au and Au|dendron in 0.1M lithium perchlorate

The square wave response as shown in figure 6 below also exhibits similar behaviour as the CV. A shift in peak potential is observed from 1216.1 mV to 1516 mV which may be attributed to the successful modification of the electrode with the thiophene dendrimer. A peak current density increase from 121.5 µA to 211.1 µA was also observed. This further confirms successful modification of the gold electrode and its catalytic behaviour.

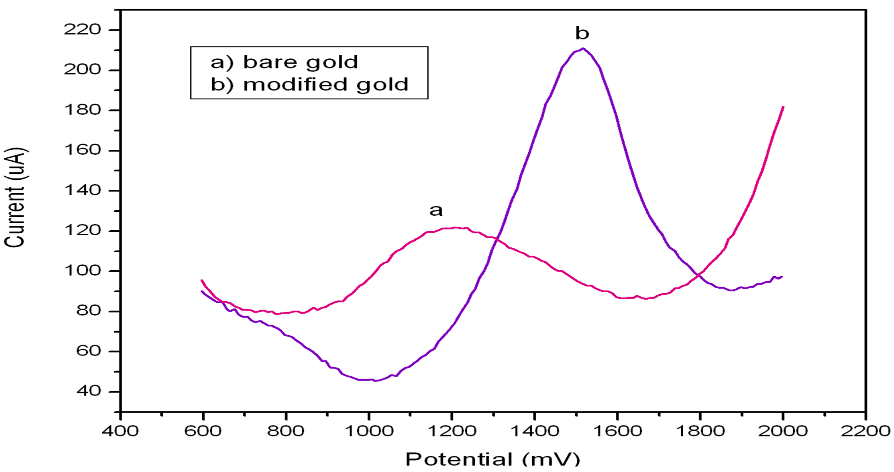


Figure 6. Square wave Voltammetry response of bare Au and Au|dendron in 0.1 M lithium perchlorate.

3.7. Electrochemical kinetic dynamics of Au|Th-Dendron electrode in lithium perchlorate:

The cyclic voltammogram of the dendron modified electrode in 0.1M lithium perchlorate at different scan rates is shown in figure 7 below. The plot of the anodic peak current is directly proportional to the square root of the scan rate giving a linear equation of $ip = 96.71452 + 3.13145x$

and has a correlation coefficient, r^2 = 0.9963. The cyclic voltammetric response of the dendron modified electrode revealed a direct proportionality of the peak current (i_p) to the scan rate which revealed that the dendron is confined on the surface of the electrode and electroactive.

The number of electrons transferred was estimated by employing equation 1c below which was derived from Laviron equation [23-24].

$$i_p = \frac{wn^2F^2A\Gamma\nu}{4RT} \qquad \text{1a}$$

$$Q = nFA\Gamma \qquad \text{1b}$$

$$i_p = \frac{nFQ\nu}{4RT} \qquad \text{1c}$$

Where n=number of electrons, F= Faradays constant (96486 C/mol), A= geometric area of the electrode (0.0201 cm^2), Γ= surface coverage of electrode. The quantity of charge was calculated from the oxidation peak area of the cyclic voltammogram in figure 7. From the slope of anodic peak current vs. scan rate and substituting the value of Q, the number of electrons was estimated to be 1.37, indicating a one electron process of the dendron. The surface coverage of the electrode reaction surface was estimated from equation 1b and found to be 1.154×10^{-10} mol.cm^{-2}.

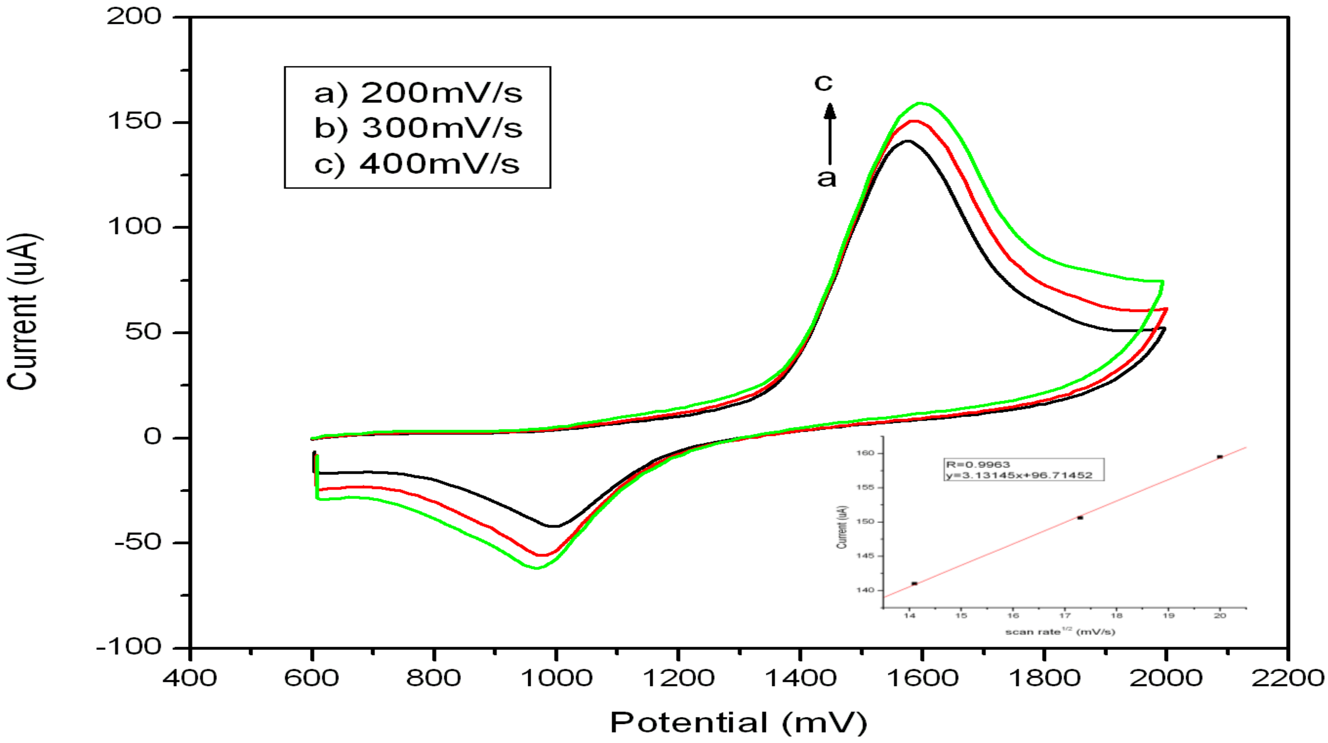


Figure 7. Cyclic voltammetry response of Au|dendron at different scan rates in 0.1 M lithium perchlorate.

3.8. Cyclic voltammetry response of bare Au and Au|dendron in 5 mM $[Fe(CN)_6]^{3-/4-}$ *redox probe*

The bare and modified gold electrodes were also studied using cyclic voltammetry with 5 mM ferrocyanide containing 0.1 M KCl. The cyclic voltammogram response is shown in figure 8. A couple of well-defined redox peaks was observed at bare electrode with distinct cathodic peak (i_{pc}) and the anodic peak current (i_{pa}) values and a peak to peak separation ΔEp of 122 mV. The peak current at Au|dendron increased compared to bare electrode, which may be attributed to large surface area and good conductivity exhibited by the dendron. The dendron film act as a tiny conductive centre which facilitates electron transfer, this allows more of the $[Fe_3(CN)_6]^{-3/-4}$ to be accumulated on the surface of the dendron film modified electrode [18, 9]. Au|dendron exhibited a couple of redox peaks with high peak current and a decrease in peak to peak separation ΔEp of 95 mV shown in Table 3 which is an indication that the modified electrode possesses a larger effective surface area as well as good electrical conductivity [18].

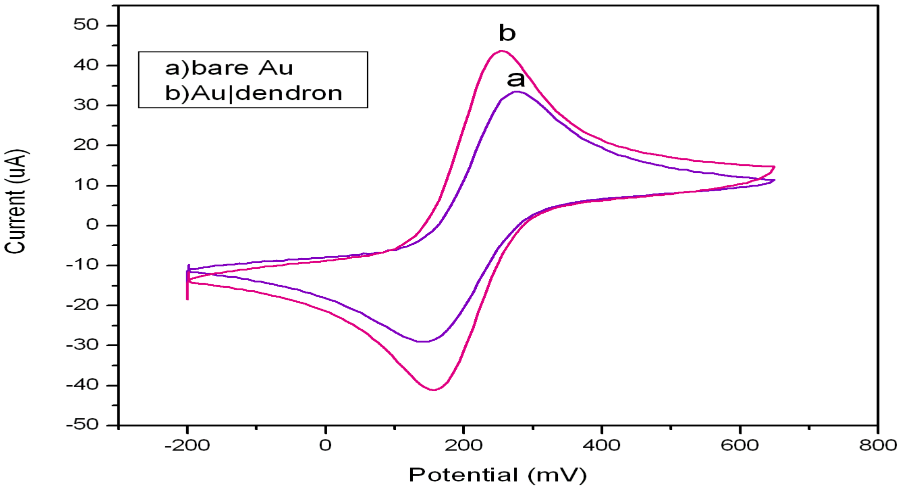


Figure 8. Cyclic voltammograms of 5 mM $[K_4Fe(CN)_6]/[K_3Fe(CN)_6]$ (1:1) containing 0.1 M KCl at (a) bare Au, (b) Au|dendron at a scan rate of 100 mV/s.

Table 3. CV data attained from figure 10

Electrode	E_{pa} (mV)	E_{pc}(mV)	I_{pa} (µA)	I_{pc} (µA)	i_{pc}/i_{pa}	ΔE_p	E^0
Bare gold	272	150	33.51	28.97	0.86	122	211
Au|dendron	253	158	43.8	41.17	0.93	95	205.5

3.9. Electrochemical impedance response of bare Au and Au|dendron modified electrode

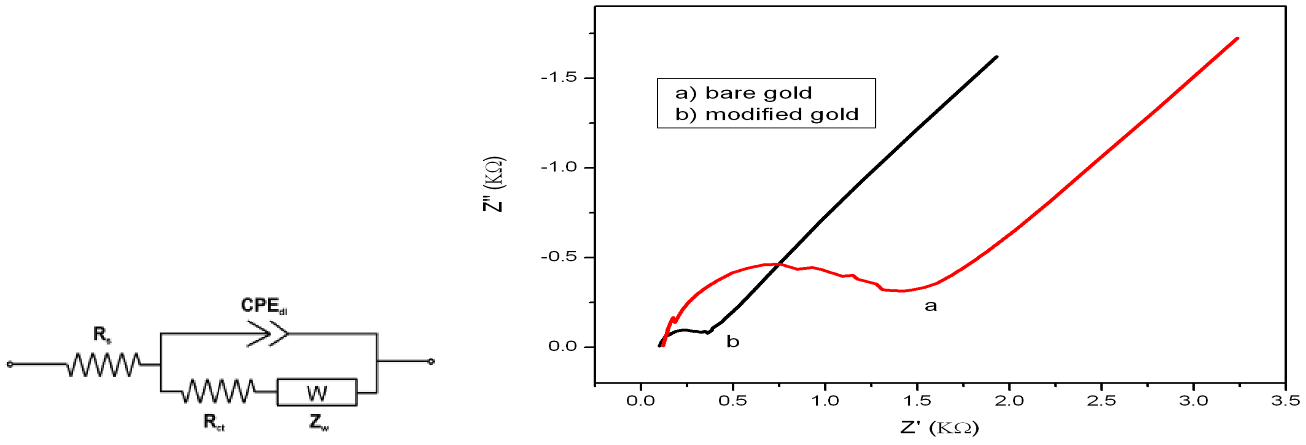
The modification of the gold electrode was also studied using electrochemical impedance spectroscopy (EIS). The results of the impedance experiment were plotted in the form of complex plane diagrams (Nyquist plots). The charge transfer resistance (R_{ct}) value of the bare gold electrode was found to be 1262 Ω (curve a.). Upon modification of the electrode with the thiophene dendron the R_{ct} value decreased to 222.5 Ω (curve b). The decrease in charge transfer resistance (R_{ct}) shows that there is an increase in the transfer of electrons through the electrochemical membrane. This confirms the ability of thiophene dendron as an excellent catalytic membrane. Further investigation into the catalytic behaviour of the dendron modified electrode was carried out by calculating some kinetic parameters such as exchange current ($i_o = \frac{RT}{nFR_{ct}}$), time constant ($\tau = R_{ct} \times C_{dl}$) and heterogeneous rate constant from ($i_o = nFAK_{et}C^*$) [25-26]

(where n= no of electron, F=96486 C ,R=8.314 J/mol/K, T= 298 K ,A =geometric area of the electrode, C* =bulk concentration.)

Table 4. Kinetic parameters obtained from figure 9

Kinetic parameters	Bare Au	Au|dendron
ω_{max} (rad^{-1})	1058.6	3311.35
Exchange current (i_o, A)	$2.03\text{x}10^{-5}$	$1.15\text{x}10^{-4}$
Heterogeneous rate constant (k_{het}, cm.s^{-1})	$4.2\text{x}10^{-5}$	$2.39\text{x}10^{-4}$
Time constant (τ, s.rad^{-1})	$9.44\text{x}10^{-4}$	$3.019\text{x}10^{-4}$
Charge transfer resistance (R_{ct}, Ω)	1262	222.5

The values obtained for the exchange current for the electron transfer process in table 3 were $2.03\text{x}10^{-5}$ and $1.15\text{x}10^{-4}$ A for the bare and dendron modified gold electrodes respectively.



A) B)

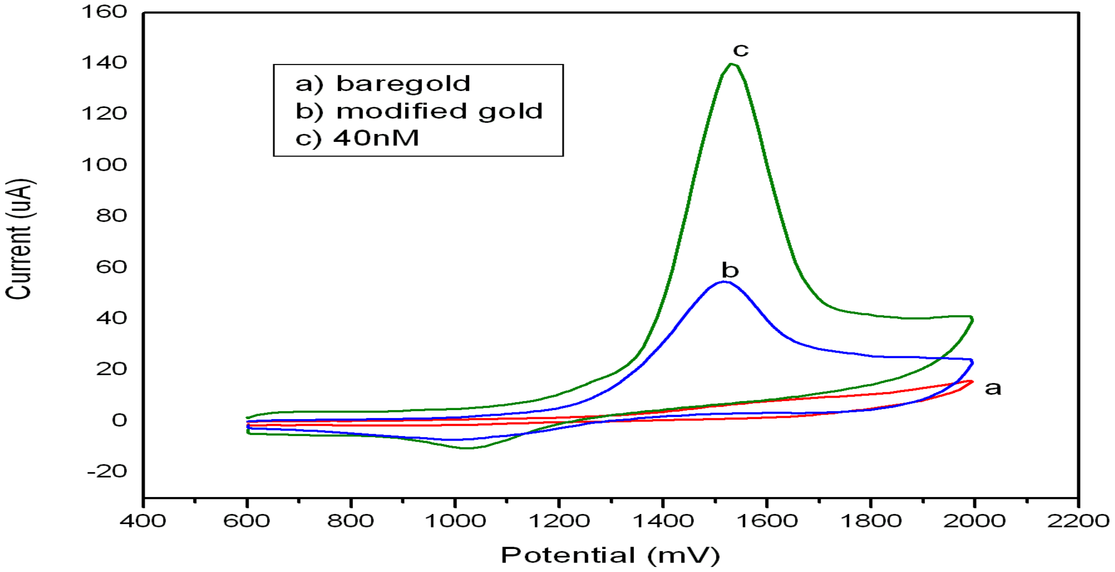
Figure 9. (A) Randles equivalent circuit Nyquist plots obtained for (a) bare gold electrode, (b) modified gold electrode. (B) EIS measurements were carried out in 5 mM $[Fe(CN)6]^{-3/-4}$ containing 0.1 M KCl.

The result revealed a fast electron transfer at the dendron modified electrode compared to the bare gold. The catalytic behaviour of the platform may be attributed to electrostatic interactions that occur between the negatively charged redox probe and the positively charged backbone of the dendron. Heterogeneous rate constant is a measure of the rate of electron transfer. Thus an increase in rate constant from 4.2x10^{-5} to 2.39x10^{-4} cm.s^{-1} at dendron modified electrode also supports the facile flow of electron at the dendron platform. The electrode surface concentration (θ) was estimated using equation [20] and was found to be 82.4%.

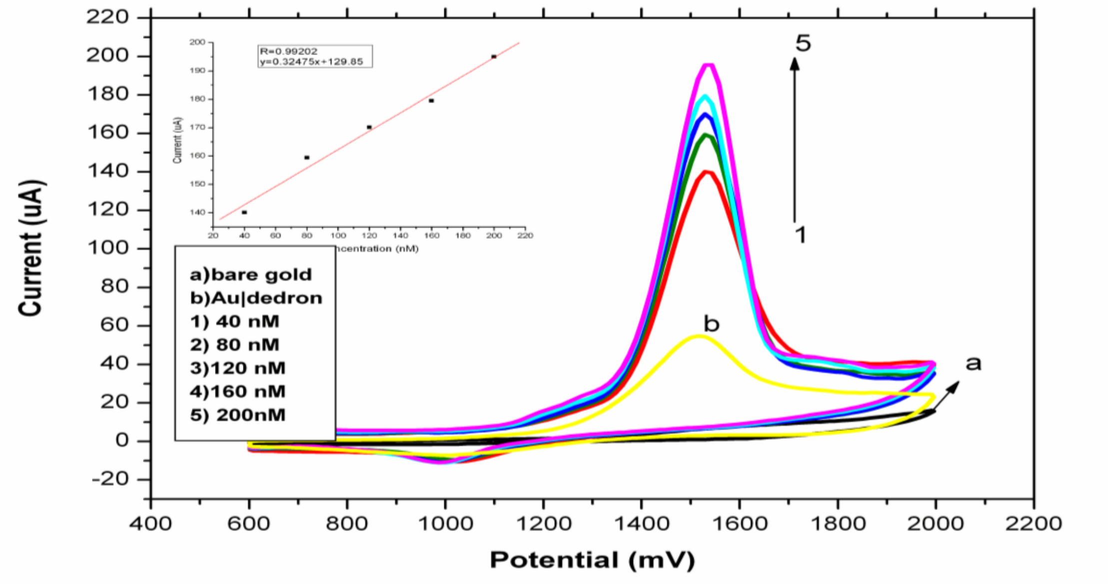
$$\theta = 1 - \frac{Rct^{\text{modified electrode}}}{Rct^{\text{bareelectrode}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

3.10. The electrochemical application of modified gold electrode (Au| dendron) to PAH

Experiments were carried out on the electrochemical behaviour of anthracene with a modified gold electrode in acetonitrile with 0.1 M lithium perchlorate as supporting electrolyte. The electrochemical behaviour revealed the formation of an anodic peak upon modification of the electrode and an increase in this anodic peak upon addition of anthracene and phenanthrene was observed. Figure 10(A) below shows the cyclic voltammetric response upon addition of 40 nM of anthracene. No visible peak is present in the plot of the bare electrode at low current density. A peak appears at 1515 mV upon modification with a current density of 54.83 µA. This peak shifts slightly to a more positive potential of 1539 mV upon spiking with 40 nM PAH with a dramatic increase in peak current of 140.1 µA. The appearance in intensity of this anodic peak indicates that oxidation of anthracene is taking place. An increase in current density upon addition of anthracene to the modified electrode revealed the catalytic behaviour of the thiophene dendrimer. The oxidation of anthracene was increased to a concentration of up to 200 nM as shown in figure 10(B) and the detection limits for the PAH was calculated to be 19 nM. A calibration plot of concentration and current density showed a linear relationship between the two with a correlation coefficient of 0.99202.



A)



B)

Figure 10. Electrochemical behaviour of Au|dendron upon addition of anthracene using cyclic voltammetry (A) bare gold, modified gold and 40nM anthracene (B) addition of increasing concentrations of anthracene to modified gold electrode (inset calibration plot illustrating the relationship between current density and concentration of PAH)

At every addition of anthracene, an increase in peak current occurs which was further confirmed using square wave voltammetry as shown in figure 11 corroborating the oxidation of anthracene by the thiophene modified gold electrode.

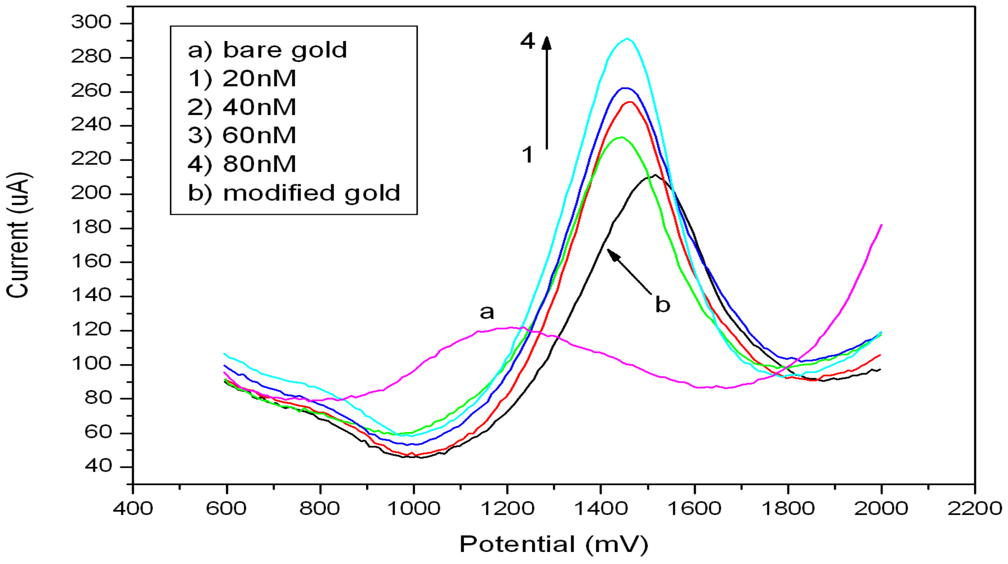
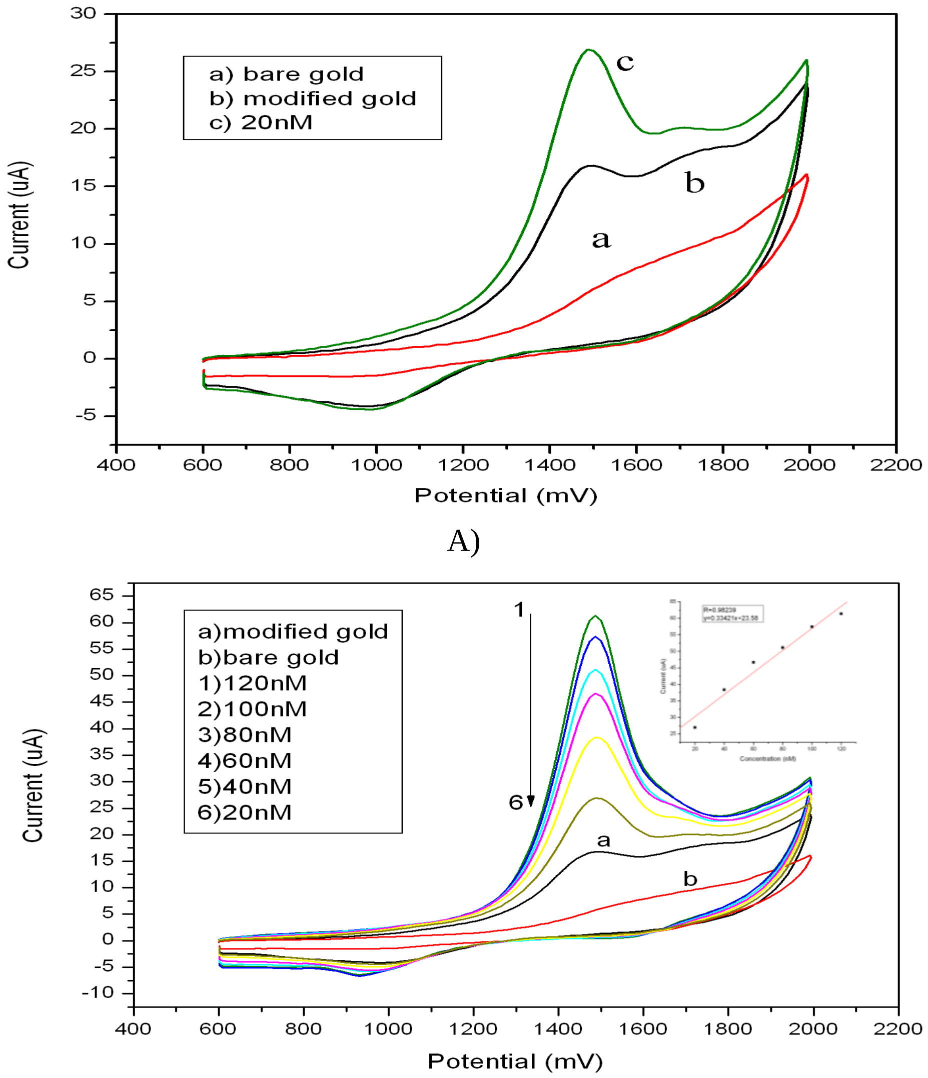


Figure 11: Electrochemical behaviour of Au|dendron upon addition of anthracene using square wave voltammetry:

Additional experiments were also carried out using phenanthrene as analyte. An anodic peak with a current density of 16.81 µA was observed upon modification of the gold electrode with 1 µl of thiophene dendron with no peak at the bare electrode. This anodic peak increased to 26.93 µA upon addition of 20 nM phenanthrene to the modified gold electrode as shown in figure 12(A). The increase in current density of this anodic peak is indicative of oxidation of phenanthrene. Figure 12(B) shows that the concentration of phenanthrene was increased to 120 nM and still showed an increase in the anodic peak which confirmed the catalytic behaviour of the Au|dendron modified electrode.. A plot of concentration vs current showed linearity between the two and has a correlation coefficient of 0.98239. This reavealed the fact that the technique can be used in the degradation of other polycyclic aromatic compounds as well and not only anthracene.



A)

B)

Figure 12. Electrochemical behaviour of Au|dendron upon addition of phenanthrene (A) bare gold, modified gold and 20 nM phenanthrene (B) addition of increasing concentrations of phenanthrene to modified gold electrode

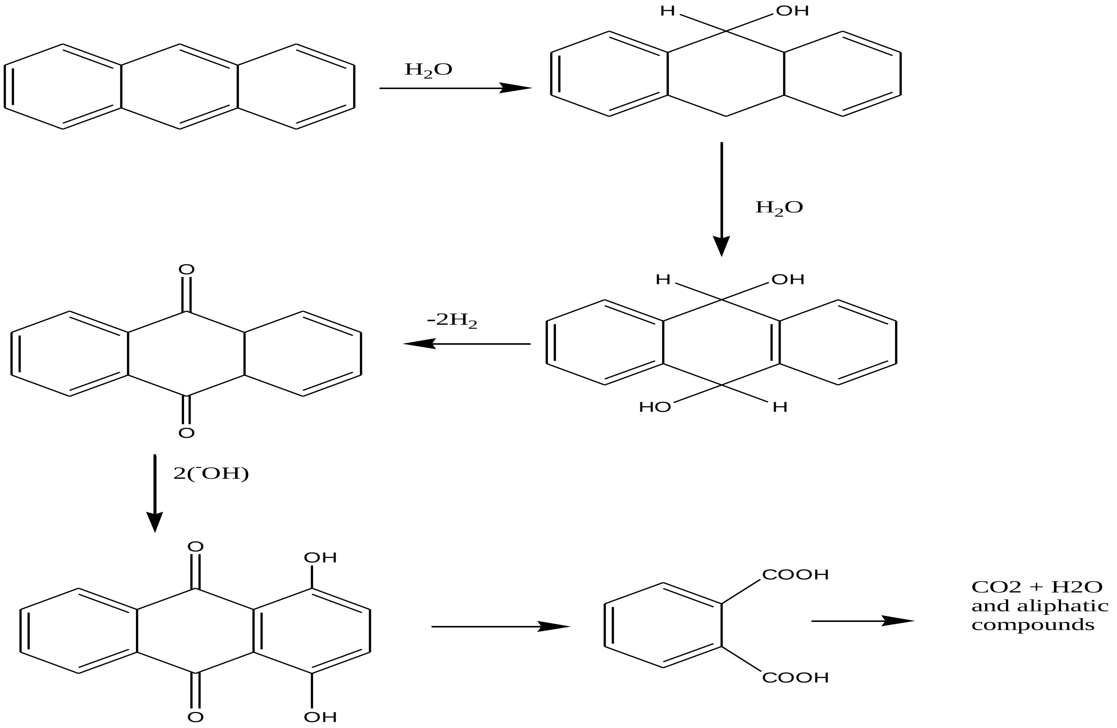
Oxidation of respective PAH was proved by the appearance of an anodic peak and the increase in current density upon addition of PAH to the thiophene modified gold electrode. Below are proposed schematic diagrams of the process occurring at the electrode surface i.e. degradation of respective PAH.

3.11. Proposed degradation mechanism for PAH

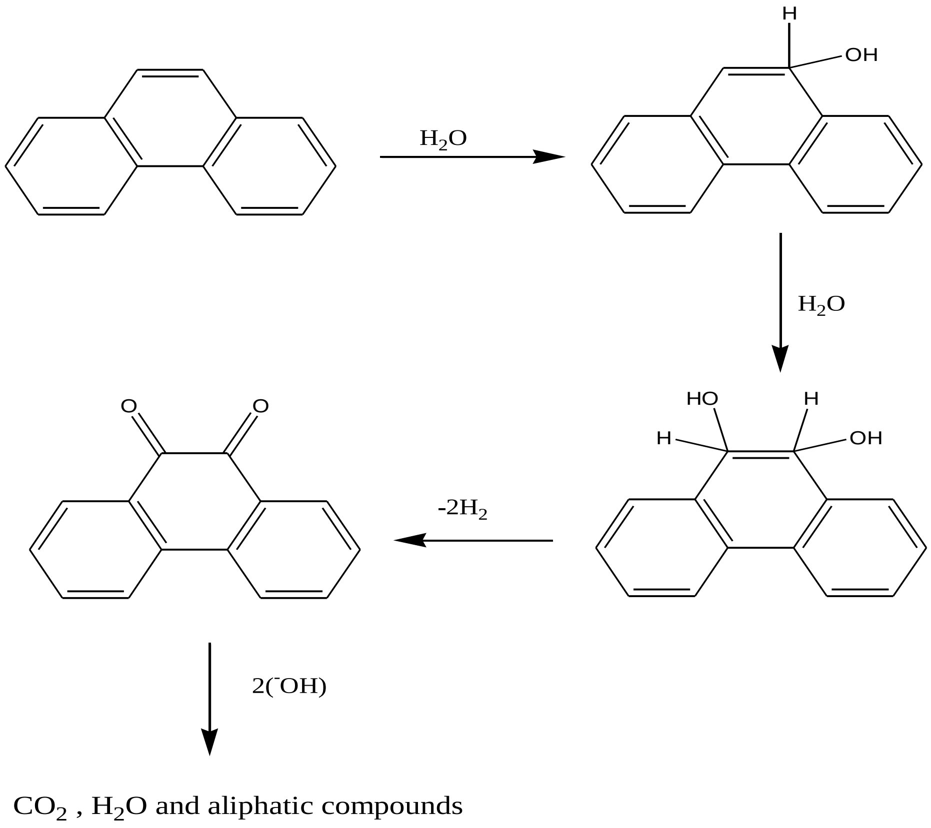
The anthracene and phenanthrene solutions were prepared in 85:15 ratio of acetonitrile and water respectively. Anthracene is insoluble in water but its presence is vital in the degradation of anthracene as shown in figure 13 below, producing CO_2, water and aliphatic compound i.e. harmless substances[27-28].

4. CONCLUSIONS

The thiophene dendron was successfully synthesised and characterised. The dendron was then successfully immobilised on the surface of a gold electrode using self-assembly based on gold sulphur chemisorption. The modified gold electrode showed a great catalytic activity upon the degradation polycyclic aromatic hydrocarbons (PAH's) using lithium perchlorate as a supporting electrolyte. Anthracene and phenanthrene were successfully degraded by the thiophene modified gold electrode via electrocatalysis. This method uses minimal energy, is cost efficient and provides an environmentally friendly method of degrading a harmful substance.



A)



B)

Figure 13. Proposed degradation pathway of (A) Anthracene (B) Phenanthrene

ACKNOWLEDGEMENTS

The research work was funded by the National Research Fund South Africa. We wish to thank the University of the Western Cape for the opportunity given to embark upon this research work

References

1. Alcantara M.T., Gomez J, Pazos M, Sanroman M.A, *J. Hazard. Mater.*166, (2009,) 462.
2. J.C. Fetzer, *Polyaromatic Hydrocarbons*, 27, (2007) 143.
3. Cerniglia C.E, *Current opinion in Biotechnology,*, 4 (1993) 331.
4. F. Lewitzka, *J. Anal. Chem*, 366 (2000,) 408.
5. Retha R. Newbold., P.-B. E., Wendy N. Jefferson., *Endocrinology*, 147 (2006.) S11.
6. Zheng X, Blais J, Mercier G, Bergeron M, Drogui P, *Chemosphere* 9 (2007) 1143.
7. K.L.A. Woodward, *Sci.Total Envir.*, 32 (1984) 103.
8. Myers S.R, Blake J.W, F.J. W, *Biochemical and biophysical research communications*, 151 (1988) 1441.
9. Krivobok S, Miriouchkine E, Seigle-Murandi F, Benoit-Guyo J.L, *Chemosphere*, 37 (1998,) 523.
10. Ndlovu T, Arotiba O.A, Krause R. W, Mamba B.B, *Int. J.Electrochem. Sci.*, 5 (2010) 1179.
11. Mailu S, Waryo T, Ndangili P, Ngece F, Baleg A, Baker P, Iwuoha E, Pages *Sensors*, 10 (2010,) 9449.
12. Tran L, Drogui P, Mercier G, Blais J, *J. Hazard. Mater.*, 164 (2009) 1118.

13. Omotayo A. Arotiba., Priscilla Baker., Bhekie B. Mamba., I. Emmanuel, *Int. J. Electrochem. Sci.*, 6 (2011) 673.
14. S. Deng , J. Locklin , D. Patton, A. Baba, R.C. Advincula, *J Am Chem Soc*, 127 (2005) 1744.
15. C. Xia, X. Fan , J. Locklin , R.C. Advincula, *Org. Lett*, 4 (2002) 2067.
16. Sebastian R, Caminade A, Majoral J, Levillain E, Huchet L, Roncali J, *Chem. Commun*,, (2000) 507.
17. Akinyeye R, Michira I, Botha S, Baker P, Iwuoha E, *Recent advances in analytical electrochemistry*,, (2007) 99.
18. Niu Y, Crooks R.M, *C.R Chimie*, 6 (2003)
19. Sahin E, Carmula P, Toppare L, Mercore V, Ciange I, Y. Y, *J. Electroanal. Chem.*, 579 (2005) 189.
20. A.Olowu R, Arotiba O, Mailu S, Waryo T, Baker P, I. E, *Sensors*, 10 (2010) 9872.
21. Xu J, *J. Mater. Sci.* 40, (2005) 2867.
22. Shiraishi K, Kanbara T, Yamamoto T, G. B, *Polymer*, 42, (2001) 7229.
23. Laviron E, *J. Electroanal. Chem.*, 100 (1979) 263.
24. Greef R, Peat R., Peter L. M., Pletcher D., Robinson J, , , *Elis Horwood, New York*, (1990)
25. O.A. Arotiba, J.H. Owino, P.G. Baker, E.I. Iwuoha, *J. Electroanal. Chem.*, 638 (2010) 287.
26. M.E. Orazem , B. Tribollet, *Electrochemical impedance spectroscopy*, Wiley (reprint 2008) Charpter 13.
27. D.W. Theurich J, Bahnemann D, *Res. Chem. lntermed*, 23 (1996) 247.
28 Beltran F, Ovejero G, Rivas J, *Ind. Eng. Chem. Res.*, 35 (1996) 883