

Poly(propylene imine) Dendrimer and Gold Nanoparticles as Anti-passivating Electrode Modifiers in Phenol Sensing – a Case Study of 4-Chlorophenol

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The electro-oxidation of phenols usually causes electrode passivation which results in drastic reduction of peak currents in subsequent scans. Electrode modifiers may help improve the peak current of phenolic compounds without the need to polish the electrode surface. The effect of electrode modification was therefore investigated on a fabricated exfoliated graphite (EG) electrode using different nano-materials such as poly(propylene imine) dendrimer, gold, cobalt oxide and bismuth nanoparticles. 4-Chlorophenol (a model phenolic compound) passivated the bare EG electrode such that the phenolic peak (at about 0.670 V) was 88.8% lower for the second scan compared to the first scan. The modified electrodes showed some anti-passivating properties with minimum reduction of peak current on the second and subsequent scans. Poly(propylene imine) dendrimer and gold nanoparticle modified EG electrodes exhibited the best anti-passivating properties.

Keywords: chlorophenol, exfoliated graphite, gold nanoparticles, phenols, poly(propylene imine) dendrimer, passivation

1. INTRODUCTION

The development of electro-analytic sensors is an active research area in analytical chemistry [1]. Electrochemical sensors, in particular, are an important part of chemical sensors where an electrode is used as the transduction element. These sensors have also found a wide range of important application in the fields of clinical, industrial, agricultural and environmental analysis [1]. Therefore,

affordable and readily available electrode materials with good electrochemical properties are continually sought after.

Electrochemical sensors have found wide applications in the detection organic pollutants such as phenols in water. Phenols, which include chlorophenols, are a major class of organic pollutants. Chlorophenols are environmental pollutants that are classified as Persistent Organic Pollutants (POPs) as well as Endocrine Disrupting Compounds (EDCs). They are of environmental concern because of their toxicity and widespread applications. These organic compounds are released into the environment during their production, transportation and application. Some of these chlorophenols such as 2-Chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol are listed as priority pollutants in the United States of America [2].

Chlorophenols are usually measured and monitored using chromatographic techniques such as gas chromatography (GC) and high performance liquid chromatography (HPLC) [2]. These techniques provide high separation efficiency as well as good sensitivity especially when coupled with mass spectrometer (MS) or other detectors [2]. Nevertheless, these methods are time-consuming, require laborious sample preparation and costly (equipment-wise). Furthermore, they are difficult to use for in situ and on site applications [3]. For quick and cost-effective sample screening and monitoring, electrochemical sensors are considered [2,4,5]. However, phenol sensing presents the challenge of electrode passivation or fouling during electro-analysis. The loss of the electrode activity during phenol oxidation as a result of insulating surface film is well documented [6,7]. Although the passivation of electrode due to phenol oxidation has been in literature for a long while; the quest for methods of inhibiting this film formation is still actively ongoing. In order to mitigate electrode passivation, electrode modification has been proposed [8].

Peeters *et al* [5] investigated the oxidation of 4-chlorophenol (4-CP) on a bare Au electrode and its detection on electrodes modified with either cobalt (II) tetrasulphonatedphthalocyanine or 3,4',4'',4'''-copper(II) tetrasulphonatedphthalocyanine where the results suggested that the behaviour of 4-CP depends on the molecular structure of the phthalocyanine thin film layers on the gold surface [5]. In another study, a cobalt (II) phthalocyanine-modified GCE was used for the detection of 2-CP and 4-CP, where the modified electrode was characterised by an increase in the oxidation currents and improved electrode stability [9]. Electrode modification has been proposed to minimise electrode passivation and provide significant improvement in the monitoring of phenols and chlorinated phenolic compounds [8, 10]. A myriad of materials such as polymers and other substances in the nanoscale are being utilised as electrode modifiers.

Nanomaterials have recently found a wide range of applications in the construction of electrochemical sensors owing to their unique chemical, physical and electronic properties. Nanomaterials generally have excellent conductivity; catalytic properties; large surface-to-volume ratio and high dispersivity [11, 12]. Nanomaterials provide a large surface area for adsorption and thus the enrichment of analytes which results in improved sensitivity and selectivity [12]. In some cases they also possess the ability to resist electrode passivation. In this study, exfoliated graphite electrodes were fabricated and modified with four nanomaterials: poly(propylene imine (PPI), gold nanoparticles (AuNPs), cobalt oxide nanoparticles (CoO) and a bismuth film (Bi). The effects of electrode modification on phenolic electrode passivation were investigated by using 4-CP.

2. EXPERIMENTAL

2.1. Reagents and Instruments

Generation 2 Poly(propylene imine) dendrimer (SyMO-Chem, Netherlands); HAuCl_4 and natural graphite (Sigma Aldrich) and others chemicals such as 4-chlorophenol (4-CP), $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, KH_2PO_4 , K_2HPO_4 , HCl , KOH purchased from Merck Chemicals were used as received. Double distilled water was used for all aqueous preparations. A supporting electrolyte of 0.1 M phosphate buffer solutions pH 5 and pH 7 were used for 4-CP and PPI-AuNPs solutions, respectively. Electrochemical readings with a three electrode cell configuration (fabricated exfoliated graphite (working electrode), platinum wire (auxiliary electrode) and Ag/AgCl (3M Cl⁻) (reference electrode)) were obtained from Autolab PGSTAT 302N. Degassing was carried out with ultra pure argon prior to all electrochemical measurements.

2.2. Electrode Modification

The EG electrode was prepared as reported in our previous work [13]. Five nanomaterials namely: poly(propylene imine) dendrimer (PPI), gold nanoparticles (AuNPs), cobalt oxide nanoparticles (CoO), silver nanoparticles (AgNP) and bismuth oxide nanoparticles (Bi) were selected as electrode modifiers.

The electrodeposition of PPI onto the EG electrode surface was accomplished from a 10 mM solution of generation 2 PPI in 0.1 M phosphate buffer solution (pH 7) by cycling the potential from -400 mV to 1100 mV for 10 cycles at a scan rate 50 mV s^{-1} . The PPI modified EG electrode was referred to as EG-PPI. This modified procedure has been reported by Arotiba *et al.* [14, 15]. A similar methodology was used for the preparation AuNPs modified EG electrode (EG-AuNP). However, a 5 mM solution of HAuCl_4 (without PPI) was used as the electrolyte. A nanocomposite of PPI and AuNP was electro-co-deposited onto the electrode surface using equal amounts of the PPI and HAuCl_4 solutions and the resultant electrode was referred to as EG-PPI-AuNP.

For the modification of the EG electrode with cobalt oxide, cobalt oxihydroxide film was electro-deposited onto the electrode surface by scanning between 1200 mV and -1100 mV for 10 cycles in 1 mM CoCl_2 pH7 phosphate buffer solution at a scan rate of 50 mVs^{-1} [16][17]. This electrode was referred to as EG-CoO.

The electro-deposition of bismuth film (EG-Bi) was done using a previously reported method with minor modifications [18, 19]. Briefly, bismuth oxide was electro-deposited by holding the potential at -600 mV for 300 seconds in 0.1 M HNO_3 supporting electrolyte solution containing 5mM Bi_2O_3 . The prepared electrodes were characterised with cyclic voltammetry (CV) and square wave voltammetry (SWV) in $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox probe.

2.3. 4-CP passivating effects on modified EG electrodes

The bare EG electrode was initially used to record the CV and SWV of $40.0 \mu\text{M}$ 4-CP in PBS with a pH of 10 at room temperature. The effect of electrode modification on the passivation caused by

the phenolic group was explored using EG, EG-PPI, EG-AuNP, EG-PPI-AuNP, EG-CoO and EG-Bi. The modified EG electrodes were used to record the SWVs of 40 μM 4-CP five times without electrode renewal. The percentage of peak current reduction was monitored for all the electrodes. The electrode that gave the highest peak current response on the first scan (EG-AuNP) was used to record the SWV for different 4-CP concentrations (1 μM to 50 μM) to obtain a linear relationship which was used to calculate the detection limit of that electrode. All CV experiments were recorded at a scan rate of 50 mVs^{-1} while SWV experiments were acquired at 50 mV and 25 Hz amplitude and frequency respectively. The electrode surface was polished using emery paper with a fine grid of 1600 followed by polishing on a weighting paper to obtain a smooth surface. The electrode was then rinsed in deionised water before use.

3. RESULTS AND DISCUSSION

3.1. Electrode characterization

The bare and modified EG electrodes were electrochemically characterised using CV and SWV in $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox probe as shown in Fig 1. Electrode modification resulted in current enhancement which was more pronounced on the square wave voltammograms in Fig 1b. The increase in peak current in all cases can be attributed to enhanced surface area induced by the nanomaterials.

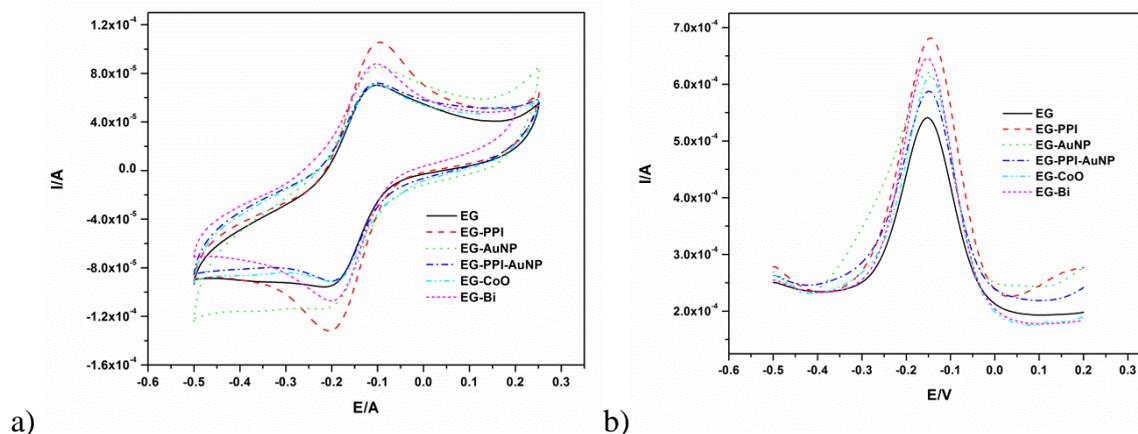


Figure 1. a) CVs (50 mV/s) and b) SWVs of all the modified electrodes in 1 mM $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$.

The slope of peak current versus square root of the scan rate from Randles-Sevcik equation: $i_p = 2.69 \times 10^5 n^{3/2} \nu^{1/2} D^{1/2} AC$ (where n is the number of electrons, ν is the scan rate, D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), A is the area of the electrode and C is the concentration in mol L^{-1}), can be used to estimate the electroactive surface area (A) of an electrode. The electroactive area obtained (from $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$) by this method is related to the amount of electroactive sites for each electrode [22].

The estimated electroactive surface area for the bare and modified electrodes are summarised in Table 1.

Table 1. Surface area (A), peak separation (ΔE) in $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ for bare and modified EG electrode.

Electrode	A (cm^2)	ΔE (mV)
EG	0.046	106
EG-PPI	0.061	111
EG-AuNP	0.051	100
EG-PPI-AuNP	0.048	90
EG-CoO	0.046	88
EG-Bi	0.054	97

The estimated electroactive surface area for all the modified electrodes was higher than the bare EG electrode. This is in agreement with the peak currents observed for all the modified electrodes. The highest electroactive surface area was observed on the EG-PPI electrode which justifies the highest peak current observed on this electrode. The differences in peak current are better observed when using square wave voltammetry (SWV) as shown in Fig. 1b owing to better sensitivity when compared to CV. The values of ΔE can be an estimate of the kinetics of the reaction in which the lower the ΔE the closer to reversibility and hence a more facile electron transfer. The lower ΔE values on EG-AuNP, EG-PPI-AuNP, EG-CoO and EG-Bi compared to the bare EG electrode thus suggest that electron transfer are faster at the interface of the modified electrodes. This is because the kinetic and reversibility properties of electrochemical processes are dependent on electrode's surface [20]. For a reversible one electron system, ΔE is equal to 59 mV, while for quasi-reversible processes, ΔE is larger than 59 mV. All the EG electrodes showed quasi-reversibility. However, EG-PPI electrode had the highest ΔE value which may be due to the electrostatic repulsion between the positively charged PPI and redox probe; and the non-metallic nature of the dendrimer.

3.2. Electrochemical behaviour of 4-CP

The source of the electroanalytical signal for chlorophenols originates from the phenolic group which tends to passivate electrode surfaces. Electrode modification has been proposed to reduce passivation due to the polymerisation of phenolic compounds. The electrochemical behavior of 4-CP was first investigated by using CV on the bare EG electrode as shown in Fig 2.

There was a drastic decrease in the oxidation peak for 4-CP which was seen at about 674 mV. This behaviour is common in most electrochemical studies (using conventional electrodes) of phenol containing groups such as phenol [8, 21], bisphenol A [12, 22] and chlorophenols [2, 5]. There was also no reduction peak on the reversal sweep which shows that the electrochemical oxidation of 4-chlorophenol is an irreversible process as observed in other phenolic compounds [23].

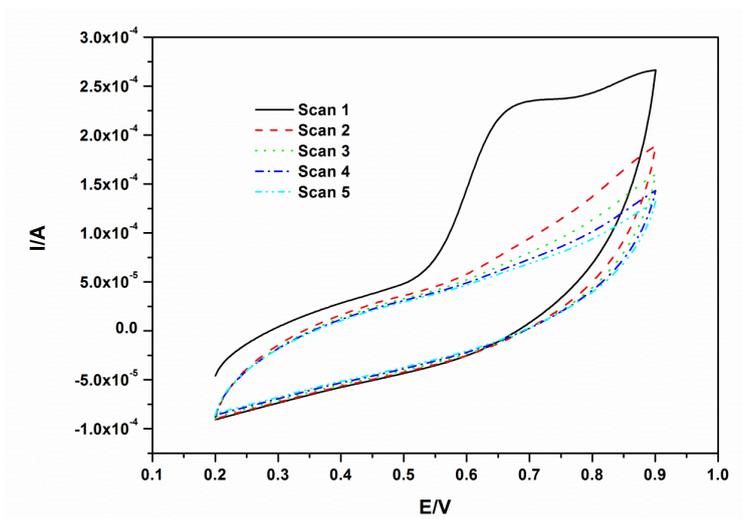


Figure 2. CVs of 40 μM 4-CP in 0.1 M phosphate buffer solution at 50 mVs^{-1} and five scans.

3.3. 4-CP passivating effects on modified EG electrodes

The passivation of the electrode surfaces due to 4-CP polymerisation was also investigated on the bare EG electrode using SWV. The results are shown in Fig. 3, where the first scan gave a sharp oxidation peak at 670 mV. The second and third scans on the same electrode surface (without polishing) resulted in voltammograms that had 11.6% and 9.2% of the peak current observed in the first scan, respectively.

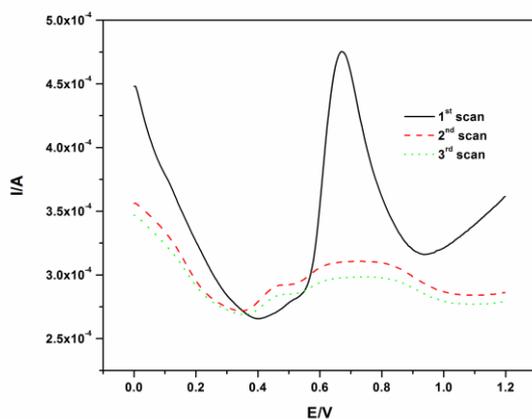


Figure 3. SWVs showing the effect of passivation on the EG electrode by 40 μM 4-CP

The same experiment was repeated on the modified EG electrodes and the results are summarised in Table 2. Modifying EG with the different nanoparticles resulted in increases in the peak currents of the first scan of 4-CP as justified by the observed increase in surface areas (Table 1).

Table 2. Passivation effects of 4-CP (40 μ M) on bare and modified EG electrodes as illustrated by the percentage of the peak current of the second to the fifth scans in relation to the first scan in 4-CP.

Electrode	Percentage peak current of 1 st scan				
	1 st scan (A)	2 nd scan	3 rd scan	4 th scan	5 th scan
EG	1.814 x 10 ⁻⁴	11.6	9.2	-	-
EG-PPI	2.080 x 10 ⁻⁴	82.7	47.4	42.9	40.8
EG-AuNP	2.188 x 10 ⁻⁴	65	47.6	44.2	41.1
EG-PPI-AuNP	1.955 x 10 ⁻⁴	60.0	40.7	30.1	23.0
EG-CoO	1.856 x 10 ⁻⁴	55.3	35.2	27.0	19.3
EG-Bi	1.671 x 10 ⁻⁴	38.6	24.6	18.3	15.1

EG-PPI dendrimer resulted in peak current enhancement of about 20.2% for 4-CP compared to the bare EG. The reasons for this performance of PPI among the other modified electrodes can be as a result of i) the nanometer scale of PPI which increases the electrodes active surface area; ii) the encapsulating ability of PPI owing to its nano cavities; iii) the organic nature of PPI which may encourage π - π interaction with the organic 4-CP or favourable functional group interactions resulting in higher concentration of 4-CP per unit area. On the second scan, I_p was 82.7% of the initial current observed (Table 2). This showed a huge improvement from the bare electrode which recorded a second scan with 11.2% peak current of the first scan. The behaviour observed suggest good anti-passivating properties for the first two scans as the peak current retention is above 80%. The fifth scan still had a phenolic peak which was 40% of the I_p of the first one, much larger than on a bare EG electrode where there is no observed peak on the fifth scan.

The actual voltammograms are shown in Fig 4. It should be noted that the first scan only had the peak due to the oxidation of 4-CP and it was the highest of all the five. The subsequent scans had three additional oxidation peaks at about 150 mV, 308 mV and 507 mV while the magnitude of the peak of interest (*ca* 730 mV for EG-PPI) was decreasing. The decrease of the oxidation peak at 730 mV indicates electrode passivation which results from the polymerisation of the phenolic groups on the electrode surface hence a reduced amount of free electroactive sites and thus a decrease of the corresponding oxidation peak [7].

Based on previous studies, the main oxidation peak (at 730 mV on EG-PPI) can be assigned to the oxidation of the phenolic group, resulting in phenoxy radicals which are resonance stabilised. Chlorophenol oxidation has also been reported to follow the polymerisation pathway.

In this process, the layers of immobile unreactive material formed on the electrode's surface inhibit electrochemical sensitivity of the electrode [5]. The passivation films from the phenoxy radical reactions may consists of quinone-like structures which are soluble in water [5]. Agboola and Nyokong [24] proposed that the oxidation of phenols follows the mechanism shown in Scheme 1.

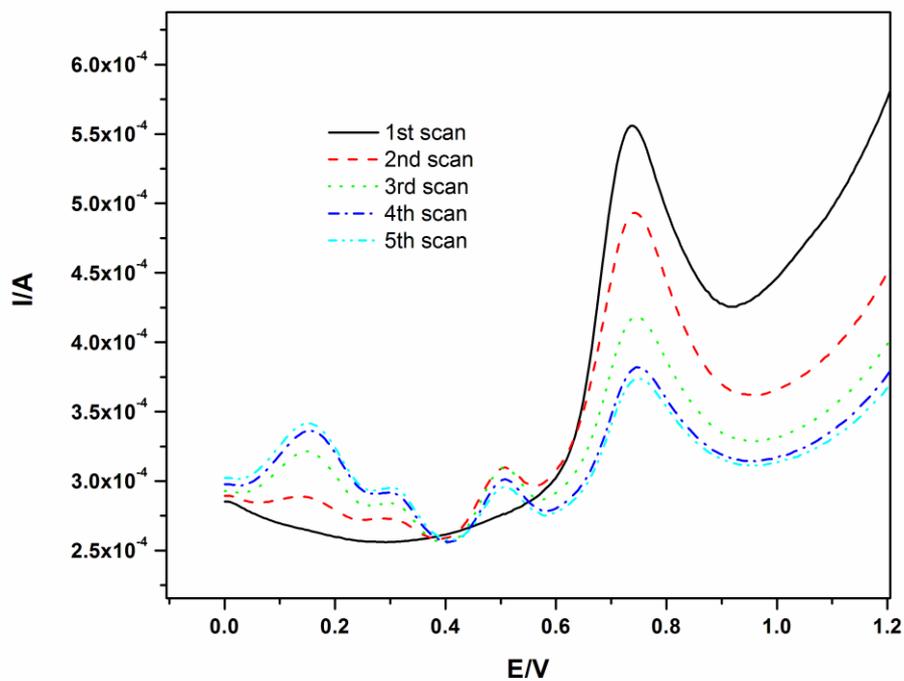
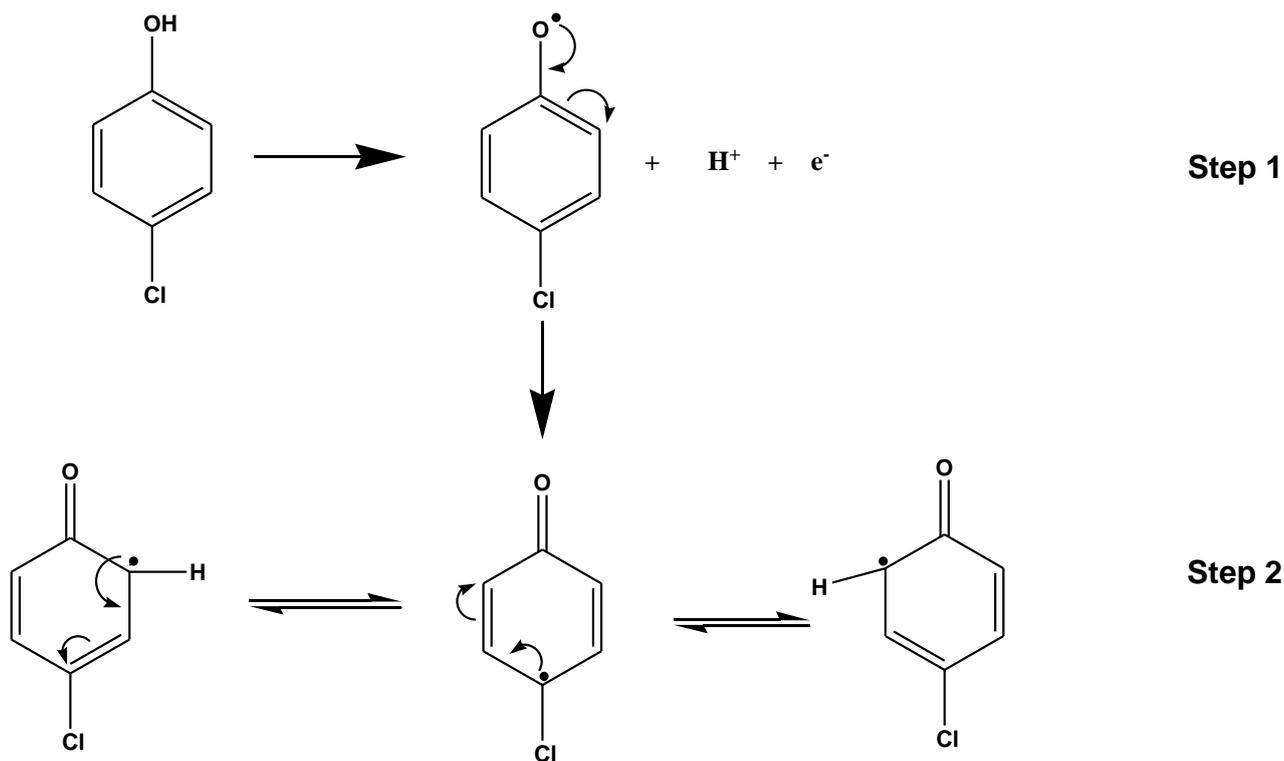
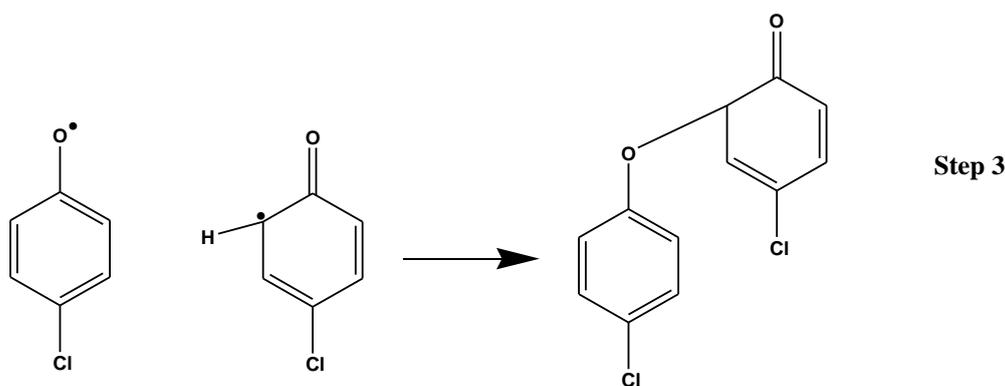


Figure 4. SWVs illustrating the effect of passivation on the EG-PPI electrode by 0.04 mM 4-CP





Scheme 1. Proposed reaction mechanism for electrooxidation processes of 4-CP

They proposed that the electro-oxidation of chlorophenol results in dimerisation with the possibility of the formation of a polymer. Step 1 is the formation of 4-chlorophenoxy radical, which is resonance stabilised (step 2). The final step is the head to head coupling reaction via oxygen atoms as illustrated in step 3 [25]. This mechanism has also been proposed for other phenolic compounds such as bisphenol A [25].

The other peaks that appeared in potentials different from ca 730 mV after the first scan (Fig. 4), were attributed to the reaction of the deposited coating or polymer. The electro-deposited products of phenolic compounds were reported to contain several oxidising centres which are known to contain *o*-quinone or *p*-quinone via a four electron and four-proton process [26, 27] hence more oxidation peaks are observed on subsequent scans.

EG-AuNP showed a 4-CP oxidation peak at 750 mV with a I_p 20.4% higher than the bare EG electrode. The electrocatalytic nature and electroactive surface area enhancement capabilities of AuNP are well known [25, 28]. The voltammograms from all the electrodes (of the first scan) for the oxidation of 4-CP are shown in Fig 5. The second I_p for EG-AuNP was 35% lower than the initial current while the fifth scan gave 41.1% of first scan. The current decrease was higher on the EG-AuNP electrode when compared to the EG-PPI while the I_p values were almost identical on the fifth scan. EG-PPI-AuNP gave I_p values of 7.7% higher than that of the bare EG for the first scan with the second and fifth scan peak currents being 60.0% and 23.0% of the first scan. Though the lowered currents after multiple scans is not the most ideal, the modifier still resisted passivation and thus useful for phenol detection as seen in section 3.4. For unmodified electrodes, passivation is so strong that the second scan (and subsequent scans) cannot give any meaningful phenol detection. This means that the electrode has to be polished after every scan making the detection process tedious.

The sharpest peak current decrease was observed on EG-Bi electrode followed by EG-CoO with a 61.4% and 45.7% I_p which decreased respectively. Even though these were easily passivated, they still performed much better than the bare electrode. The SWV from EG-Bi was characterised by a peak which was not well defined (Fig. 5) which also resulted in the lowest I_p .

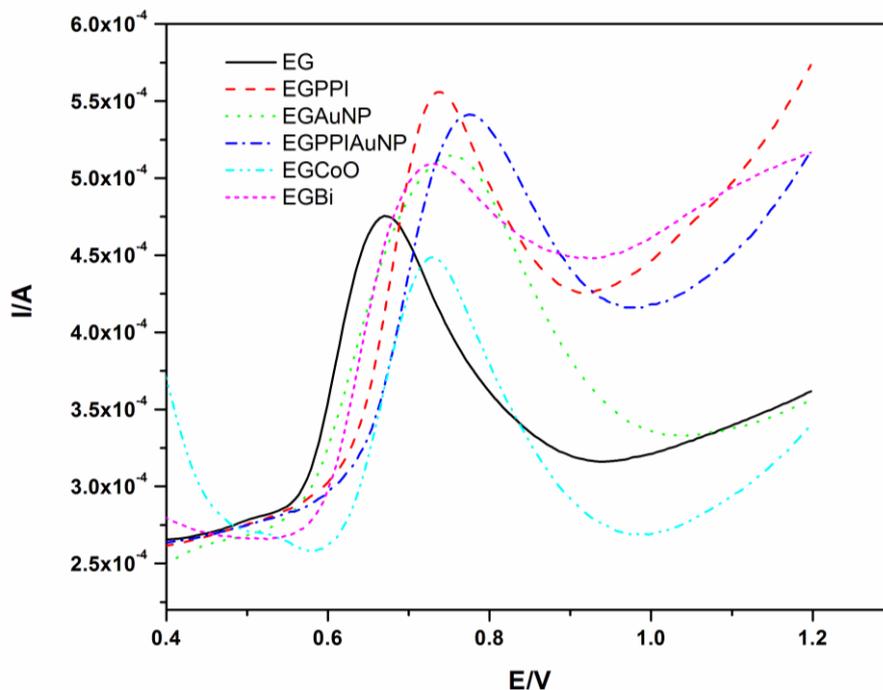


Figure 5. SWVs of the bare and modified electrodes in 0.04 mM 4-CP.

The highest I_p was obtained from EG-AuNP and hence it was used to record SWVs of different concentration of 4-CP and subsequently used to calculate the detection limit.

3.4. Detection of 4-CP on EG-AuNP

The first square wave voltammogram from the EG-AuNP electrode gave the highest peak current (Table 2) hence it was used for the detection of 4-CP. The SWVs of different concentrations of 4-CP were recorded and their peak currents used to plot the calibration curve. This was accomplished by polishing the electrode after every measurement, followed by the electro-deposition of AuNPs onto the electrode surface.

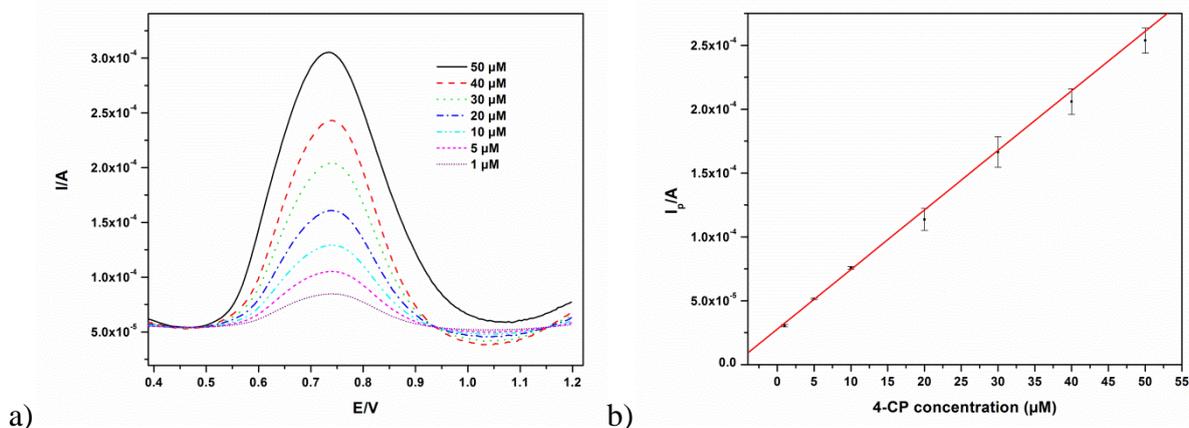


Figure 6. a) SWVs of different concentrations of 4-CP and b) linear variation of peak currents with 4-CP concentration.

A linear relationship between I_p and concentration was observed in the concentration range of 1 μM – 50 μM with $R = 0.991$ as shown in Fig 6. The linear regression equation for this relationship was: $y = 4.66 \times 10^{-3} x + 2.794 \times 10^{-5}$.

The detection limit was calculated to be 0.087 μM when using the EG-AuNP electrode which is in the same range as other electrodes as illustrated in Table 3. These results support the possible application of the modified EG electrode for the electrochemical detection of 4-CP. The experiment was repeated five times with a good reproducibility as denoted by a RSD of 4.8%. The EG-AuNP electrode has the added advantage of resisting passivation which makes it applicable for the detection of phenolic compounds (without polishing and re-modification) with a good response to the analyte.

Table 3. Response characteristics of different electrodes for detection of chlorophenols

Type of composite electrode	Used technique	Correlation coefficient	Detection limit (μM)	Linear range (μM)
Ag-PTA/CTS/ITO [29]	DPV	0.999	0.34	0.001-0.4
β -cyclodextrin functionalized graphene modified carbon paste electrode [30]	DPV	0.996	0.2	1-40
GCE modified by a composition of MWCNTs and nano nickel hydroxide [31]	DPV	0.999	0.5	1.0–750
polystyrene microspheres-arranged GCE [32]	DPV	0.997	0.017	0.05-0.3
Chitosan modified carbon paste electrode [23]	LSV	0.996	0.04	0.1-5.0
EG-AuNP (This study)	SWV	0.991	0.087	1-50

4. CONCLUSION

Electrode modification helps to reduce the effect of electrode passivation caused by the anodic oxidation of phenolic compounds. The peak current of the second scan can be reduced by more than 88% without modification while peak reduction can be as low as 17% on modified electrodes. These anti-passivating properties suggest that there is potential for the use of the modifiers (especially PPI dendrimer and AuNPs) reported in this work for the detection of phenols. The analysis is simple, fast and effective when using these fabricated electrodes.

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