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Electrochemical Detection of *o*-Nitrophenol on a Poly(propyleneimine)-gold Nanocomposite Modified Glassy Carbon Electrode

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The electrochemical determination of *o*-nitrophenol by square wave voltammetry using a nanocomposite of generation 2 poly(propyleneimine) dendrimer and gold nanoparticles modified glassy carbon electrode is reported. A characteristic reduction peak at ca -650 mV for *o*-nitrophenol was observed with enhanced current. The nanocomposite electrode was used as a sensor for the detection of this model organic pollutant with very good reproducibility and stability. The reduction peak current was directly proportional to the *o*-nitrophenol concentration in the range between 6.1 x 10^{-7} mol L^{-1} to 6.25 x 10^{-4} mol L^{-1}. A detection limit of 4.5 x 10^{-7} mol L^{-1} was calculated.

Keywords: *o*-Nitrophenol, square wave voltammetry, poly(propyleneimine) dendrimer, gold nanoparticle, nanocomposite, sensor

1. INTRODUCTION

Phenols and substituted phenolic compounds in natural waters have toxic effects on humans, animals and plants and they give an undesirable taste and odour to drinking water, even at low concentrations [1]. For these reasons, many phenolic compounds have been included in environmental legislations thus making their analysis of prime importance [1-2]. Most of these compounds are known to be persistent and thus their recovery or their elimination is required prior to the discharge or the reuse of the waste flow [3].

Nitrophenols (which fall under substituted phenols) are important and versatile organic compounds in industrial, agricultural and defence applications [4]. They are frequently used as intermediates in the manufacture of explosives, pharmaceuticals, pesticides, pigments, dyes, rubber chemicals, lumber preservatives, photographic chemicals, to mention a few [1, 5-7]. They are also produced by microbial hydrolysis of several organo-phosphorus pesticides, for example parathion, or by photodegradation of pesticides that contain the nitrophenol moiety [1, 4-5]. *o*-Nitrophenol (*o*-NP), in particular, poses significant health risks since it is toxic to mammals, microorganisms and anaerobic bacteria. Its toxicity is thought to be due to the nitro group being easily reduced by enzymes to the nitro anion radical, nitroso and hydroxylamine derivatives [4]. These derivatives are responsible for the cytotoxic, mutagenic and carcinogenic properties of nitro compounds. The detection and analysis of nitrophenols in both waste and potable water is thus important.

Nitrophenols are usually detected by chromatographic techniques sometimes associated with mass spectrometry and spectrophotometry [2-3]. Although routinely used, these techniques are relatively expensive, have high analytical cost, lengthy sample preparation and analysis times which are not suitable for in-situ measurement [1, 3]. According to Bebeselea et al, the severe toxicity of nitrophenols requires the development of simple, sensitive and reliable determination methods [3].

Electrochemical methods are low on cost and require short analysis time as compared to some of the known conventional methods [1]. These methods are characterised by high sensitivity, good selectivity, rapid response, and the instruments are relatively simple with the possibility of miniaturization for in-situ measurements [3, 8]. Some researchers have reported the determination of nitrophenols by polarography, cyclic voltammetry, differential pulse voltammetry and square wave voltammetry on Hg, diamond, carbon paste and carbon nanotubes modified electrodes [1, 4].

Electrochemical analysis of nitrophenol on a bare electrode usually has the problem of fouling and low sensitivity. There is need to sought for new materials that can be used as electrode modifiers in the bid to enhance the electrochemical reduction or degradation of phenol and minimisation of electrode fouling. In this work, a nanocomposite of Poly(propyleneimine), PPI dendrimer and gold nanoparticles was used.

Dendrimers are synthetic three-dimensional macromolecules with a well defined, highly branched and globular shaped molecular structure [9]. Modification of a carbon electrode with PPI through electrodeposition has been demonstrated by Arotiba et al [10]. They found that this nanomaterial showed some potential electrochemical properties which can be explored for electrocatalysis of substrates.

Gold nanoparticles, on the other hand, are known for their good conductivity and increasing the electrode surface area [11]. The electro-co-deposition of these two nanomaterials have been carried out and used as a platform for the development of a DNA biosensor [12-13].

The enhancing effect this composite electrode has on the redox chemistry of ferric and ferro cyanide system stimulated us into applying it for a substrate such as *o*-NP. It has also been reported that dendrimers and gold nanoparticle have catalytic properties. We therefore present an electrochemical sensor for *o*-NP based on dendrimer-gold nanocomposite for the electrochemical detection of *o*-NP.

2. EXPERIMENTAL

2.1. Apparatus and reagents

Generation 2 (G2) poly(propyleneimine) (PPI) dendrimer was purchased from SyMO-Chem, Eindhoven, Netherlands while $HAuCl_4$ was obtained from Sigma Aldrich. All other chemicals such as o-nitrophenol, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, KH_2PO_4, K_2HPO_4, HCl, KOH were bought from Merck chemicals. Double distilled water was used for all measurements. Phosphate buffer solution (0.1 M, PBS) of pH 5 and pH 7 was used for *o*-NP solutions and PPI-AuNP modification respectively. A 5 mM solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ (1:1) was prepared in 100 mL of the buffer solution. All electrochemical measurements were done on an Autolab PGSTAT 302N using a three electrode configuration. Working, counter and reference electrode are glassy carbon (3 mm diameter), platinum wire and Ag/AgCl (3M Cl^-) respectively.

2.2. Electrode modification

A glassy carbon electrode (GCE) was modified according to the procedure reported by Arotiba et al [12-13]. Briefly, solutions containing 10 mM Generation 2 (G2) PPI and 5 mM $HAuCl_4$ at pH 7 PBS were prepared. Equal amounts of each of the PPI and $HAuCl_4$ solutions were mixed. Cyclic voltammetry (CV) was performed between potentials -350 mV to 1100 mV for 10 cycles to co-deposit the PPI dendrimer and gold nanoparticles onto the GCE. The modified GCE was rinsed with distilled water and then PBS. It will be referred to as GCE/PPI-AuNP. GCE was also modified with PPI only using the 10 mM PPI solution and scanning between -100 mV and 1000 mV to get an electrode named GCE/PPI. The GCE/PPI-AuNP was electrochemically characterised using cyclic voltammetry (CV) and square wave voltammetry (SWV) in PBS and $[Fe(CN)_6]^{3-/4-}$ electrolytes.

2.3. Detection of o-NP

The GCE, GCE/PPI and GCE/PPI-AuNP electrodes were used to record CV, SWV and differential pulse voltammetry (DPV) of 5 mM *o*-NP. All experiments of *o*-NP were done in PBS at pH 5. Different concentrations (6.1×10^{-7} mol L^{-1} to1.25×10^{-3} mol L^{-1}) of *o*-NP were then prepared and their SWV were used to plot the calibration curve and calculate the detection limit.

3. RESULTS AND DISCUSSION

3.1. The GCE/PPI-AuNP modified electrode

The bare GCE was successfully modified using G2 PPI and Au nanoparticles. The potential window of -350 to 1100 mV chosen enabled a co-deposition of both materials. During the anodic scan at potential between 650 mV and 1000 mV, the free primary amines of the PPI were electro-oxidised onto the GCE surface to form C-N bond. This deposition of PPI onto carbon electrode has been reported. The electro-oxidation peak is best observed on the first cycle while subsequent scans did not show an increase in this peak. This is because the dendrimer forms a monolayer at the surface of the electrode and not polymer. On the other hand, during the cathodic scan, gold nanoparticles were co-deposited with the PPI by reducing Au^{3+} to Au^0 at a potential of ca -200 mV. Figure 1 shows the effect of modification on the oxidation peak of $[Fe(CN)_6]^{3-/4-}$. The GCE/PPI-AuNP shows a marked increase in current as compared to the bare GCE. The effect of the gold nanoparticle can also be seen when compared to only PPI modified GCE - the presence of AuNP increased the conductivity and surface area of the electrode. The presence of Au at the surface of the GCE was also evident by a golden colour of the electrode. The scanning electron microscopic characterisation of this nanocomposite has been reported [12-13].

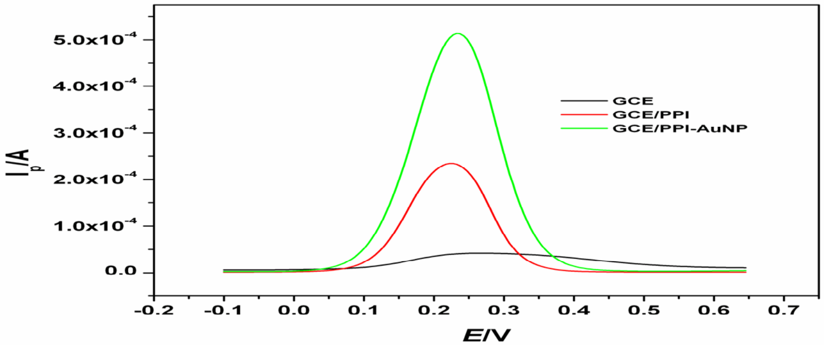


Figure 1. Square wave voltammetry of 5 mM $[Fe(CN)_6]^{3-/4-}$ on GCE, GCE/PPI and GCE/PPI-AuNP

3.2. Electrochemical Detection of o-NP

All *o*-NP measurements were done in PBS at a pH of 5. The optimum pH for the electroreduction of nitrophenols is between 4 and 7 in most electrolytes [14-16]. Figure 2 shows the cyclic voltammetry of 5 mM *o*-NP on the modified GCE/PPI-AuNP electrode.

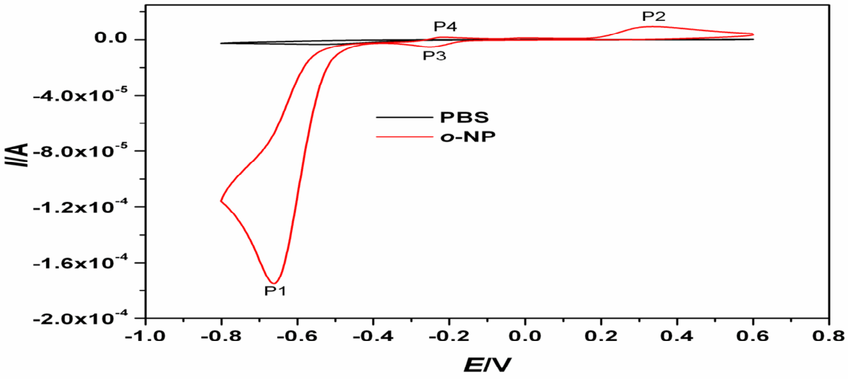


Figure 2. Cyclic voltammogram of 5 mM *o*-NP on GCE/PPI-AuNP in 0.1 mol L^{-1} phosphate buffer at scan rate of 50 mV s^{-1}

Four peaks were observed from the CV of *o*-NP. The reactions occurring at each peak is shown in equation 1 and 2. Peak 1 (P1) was an irreversible cathodic peak at a potential of ca -665 mV. Another irreversible peak was observed on the oxidation sweep (P2) at 362 mV. The observed electrochemical response using CV is consistent with other reports in the literature [15-18]. The appearance of P1 is due to a four-electron irreversible reduction of the nitro group ($-NO_2$) to a hydroxylamine group (-NHOH). P2 is due to the irreversible oxidation of the hydroxyl group [4]. The other two redox couple (P3 at -212 mV and P4 at -195 mV) are due to the reversible two-electron oxidation reduction of the hydroxylamine group (-NHOH) to a nitroso group (-NO). This is illustrated by the following chemical equations:

$$\text{P1:}\quad -NO_2 + 4e^- + 4H^+ \dashrightarrow -NHOH + H_2O \qquad \text{[Eqn 1]}$$

$$\text{P3/P4:}\quad -NHOH \rightleftharpoons -NO + 2H^+ + 2e^- \qquad \text{[Eqn 2]}$$

According to Chen and co-workers the electrochemical reduction of nitro-aromatic compounds has been claimed to be a complex process that depends on the number of nitro groups, their relative positions on the ring, and the nature of the substituent on the aromatic system [17].

Figure 3 presents the square wave voltammogram of *o*-NP on bare GCE, GCE/PPI and GCE/PPI-AuNP. The enhancing and catalytic effects of the nanocomposite on the reduction of *o*-NP is seen by the marked increase in current (94% current increase over bare GCE) as compared to the other two surfaces. It can also be said that the PPI-AuNP - *o*-NP interfacial kinetics (reduction) occurred at a lower energy than that which occurred on bare GCE and GCE/PPI. This statement is drawn from the reduction potential at GCE/PPI-AuNP (E_{red} = -648 mV) which is 65 mV lower than bare GCE. As we know, from transition state theory, Gibbs free energy and Nernst equation, potential is related to energy (activation energy) – hence the catalytic effect. GCE/PPI-AuNP was therefore used for the detection of *o*-NP owing to its better sensitivity.

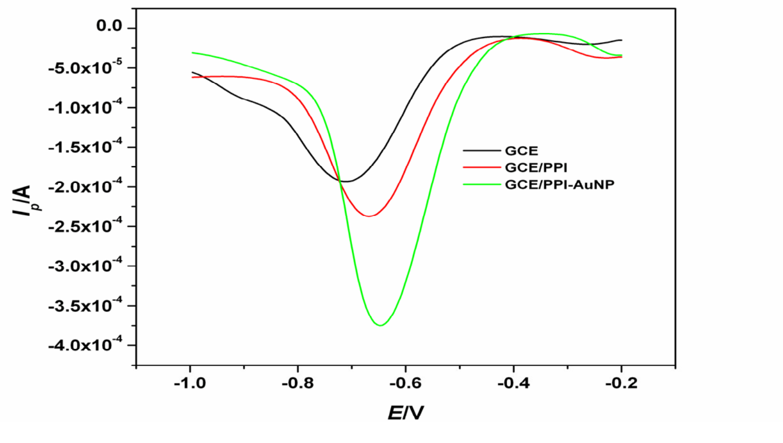
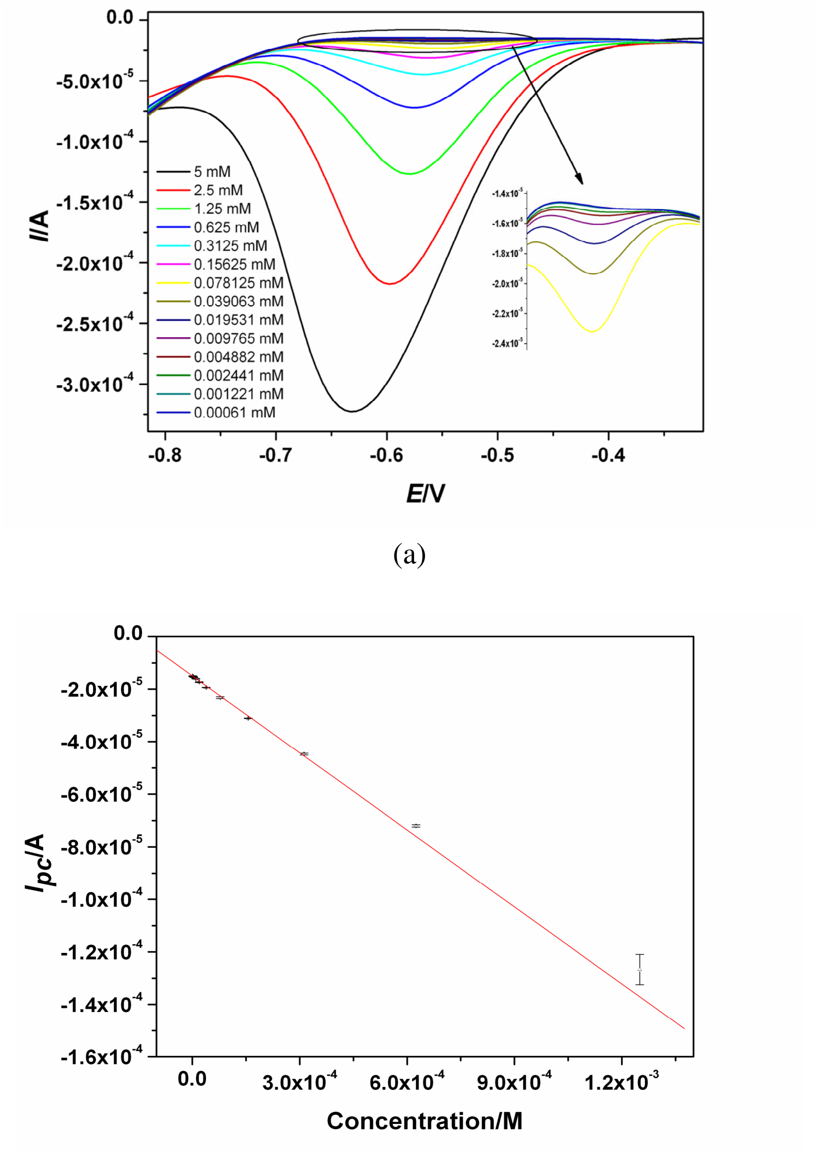


Figure 3. SWV of 5 mM *o*-NP in PBS pH 5 on bare GCE, GCE/PPI and GCE/PPI-AuNP

The reduction potential of the nitro group of *o*-NP and other nitro containing compounds is between -400 mV and -700 mV on other electrodes and electrolytes [2-3, 14].

Fig. 4a and 4b depict the response of different concentrations of *o*-NP in PBS (pH 5) at GCE/PPI-AuNP electrode and the linear calibration plot respectively. The experiment (starting from fresh bare GCE) was repeated three times and the electrode showed good reproducibility as the results of the three experiments were similar. For a concentration of 19.5 µM, the peak current was $-1.28 \times 10^{-5} \pm 1.01 \times 10^{-7}$ A (0.8%). The modified electrode was also left overnight and the same range of concentrations was tested on the electrode still with good reproducibility.



(a)

(b)

Figure 4. a) SWV for different concentration of *o*-NP on GCE/PPI-AuNP in 0.1 mol L^{-1} PBS. b) Calibration plot showing errors bars.

For the same concentration, the peak current observed was -1.27 x 10^{-5} ± 9.27 x 10^{-8} (0.7%). This showed that the electrode was very stable and could be used repeatedly with minimum fouling. From the peak currents obtained, a calibration curve was plotted which showed good linearity between 6.1 x 10^{-7} mol L^{-1} and 6.25 x 10^{-4} mol L^{-1} *o*-NP with a correlation of 0.9994.

The detection limit was calculated using the formular 3σ/slope. σ is the standard deviation of the blank which was taken from five repeats. The detection limit was found to be 4.5 x 10^{-7} mol L^{-1}. This is comparable to other values obtained from other electrodes which also have detection limits in the micrometre scale [14, 16, 19].

4. CONCLUSION

This work adds to the myriads of application of nanomaterials in electrode modification and application towards detection of analyte of importance. A simple and reproducible one step electro-co-deposition of PPI dendrimer and gold nanoparticle on glassy carbon electrode was carried out. The nanocomposite platform enhanced the electrochemical reduction of ortho-nitrophenol hence its detection with good reproducibility. The effect of fouling was also greatly reduced. A detection limit of 4.5 x 10^{-7} mol L^{-1} which is comparable to other electrodes including the dropping mercury electrode was obtained. It also produced linearity over a wide range of concentrations. This nanocomposite electrode is simple to prepare, stable, cheap and can serve as a model platform for the detection of pollutants in water samples.

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