Voltammetric Determination of Nitrophenol using PEDOT Decorated Graphene Oxide as Composite Film

Nafiu Muhammad[1,3], Jaafar Abdullah[1,2,], Yusran Sulaiman[1,2], Lim Hong Ngee[1,2]*

[1] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor DarulEhsan, Malaysia
[2] Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor D.E., Malaysia.
[3] Department of Pure and Industrial Chemistry, Faculty Natural and Applied Sciences,Umaru Musa University Yar'aduaKatsina, PMB 2218, Katsina state Nigeria
[*]E-mail: jafar@upm.edu.my

A composite film of poly(3,4-ethylenedioxythiophene) (PEDOT) and reduced graphene oxide (ERGO) deposited on screen printed carbon electrode (SPCE) was developed for the sensitive detection of 3-nitrophenol(NP). The electrode was modified with PEDOT/ERGO by using electropolymerization technique on the surface of SPCE. This new hybrid sensing material exhibits high electrocatalytic activity and good selectivity towards the reduction of 3-NP due to its excellent electrical conductivity, strong adsorptive ability and large effective surface area of PEDOT/ERGO composite film. The enhancement factor of the PEDOT/ERGO modified SPCE towards 3-NP was calculated to be 4 times higher compared to bare SPCE. Experimental parameters such as pH of buffer, scan rate, accumulation time and accumulation potential were optimized. Under optimum experimental conditions, the linear calibration curve of the sensor towards concentration of 3-NP was in the range of 0.3 µM to 70 µM with the detection limit of 0.08 µM. Furthermore, the PEDOT/ERGO sensor shows good repeatability and reproducibility with relative standard deviation (RSD) of 3.83 % and 4.85 %, respectively. The sensor also demonstrated potential application for the detection of 3-NP in water samples.

1. INTRODUCTION

Nitrophenols are important phenolic derivatives widely used in production of pesticide, rubber chemicals, pharmaceuticals, dyes, explosives and pigments [1]. Due to their uses, tenth of thousand tons are produced annually in which some escape into ecosystem. Unfortunately with all they uses,

nitrophenols are classified as hazardous waste and priority toxic pollutants by USEPA and other world environmental protection agencies dues they toxicity. Nitrophenols are bioaccumulative as such they can penetrate human body through all routes, they causes fervescence, liver and kidney damage [1,2] and also causes oxygen deficit in the body as result conversion of haemoglobin to methamoglobin due to oxidation of iron(II) to iron(III) [1].

Conventional approaches have been employed for monitoring of NP such as chromatography, capillary electrophoresis, spectrophotometry and immunoassays. Although these methods have good advantages however they are associated with some difficulties, they required complicated sample pre-treatment, they are time consuming and required expensive instrumentation [3,4]. Due to increase in legislation and environmental control over released of pollutant into the environment several analytical techniques for monitoring of NP have been initiated. Recently many researches have focused on electrochemical sensor because of its simplicity, high sensitivity, high accuracy, good reliability and inexpensive instrumentation as compared to the conventional methods.

PEDOT is a thio conductive polymer widely explored in the development of electrochemical sensor due to its properties which offer excellent stability, high conductivity, moderate band gap, optical transparency, easy processing and biocompatibility. However, it structure and chemical properties are still major issues that limited its usage in various practical applications [5,6]. To further improve the application of PEDOT in sensor development, it has been hybridized with different nanoparticle to form nanocomposite which shows large surface area, good conductivity, good electro-activity, high mechanical strength, etc. [3]. The combination of PEDOT with novel carbon nanostructure such as graphene may be another potential solution to the shortcomings.

Graphene is family of carbon in crystalline form which storms the world in 2004.Graphene is a monolayer of aromatic carbon atoms, single-atom thick in two-dimensional arrangement in carbon sp^2 hybridization [7-11]. These structures make it have unique and remarkable mechanical, thermal, optical, and electrical properties [11]. As such these properties has widely been explored for the applications in electronics, catalysis, sensors, energy conversion and storage of energy, optics, optoelectronics, biomedical engineering, tissue engineering, medical implants and medical devices [13-14]. Deng et al. [15] explored the presence of π electrons on graphene sheet in the development of electrochemical sensor for the detection of bisphenol. The result showed that the presence of π electrons on graphene sheet significantly enhanced the sensitivity of the sensor because the graphene can absorb more bisphenol through π-π attraction on the surface of working electrode.

Therefore in this study, we attempt to fabricate SPCE modified PEDOT decorated ERGO based on one-step electro-deposition for the detection 3-nitrophenol (3-NP). The idea is to explore the excellent electrocatalytic activity, strong adsorptive ability, large effective surface area and good selectivity of the PEDOT/ERGO sensing material in the reduction of 3-NP.

2. EXPERIMENTAL

2.1 Chemicals

All chemicals used in this experiment were of analytical grade. Sodium phosphate dibasic, sodium phosphate monobasic, sodium citrate trihydrate, sodium acetate, sodium chloride, potassium

ferrocynide, poly(3,4-ethylenedioxythiophene) (PEDOT), nitrophenols were obtained from Sigma Aldrich and Fluka (Switzerland). Iron(II) sulphate, catechol, pentachlorophenol were acquired from BDH chemicals (United Kingdom). Sodium hydroxide and resorcinol were from Merck (USA). Ethanol, acetic acids, nitric acids, and potassium chloride were obtained from R&M chemicals (United Kingdom), graphene oxide was purchased from Graphenea (Spain). Deionized water was used throughout the experiment. All electrochemical measurements were performed with Autolab potentiostat (Netherlands) controlled by GPES software unless otherwise stated connected to a PC and screen printed carbon electrode (Dropsen, Netherlands).

2.2 Preparation of modified SPCE with PEDOT/ERGO

PEDOT/ERGO was prepared by mixing 0.7 mg/ml graphene oxide (GO) with 0.001 M 3,4-ethylenedioxythiophene (EDOT) in 0.00M LiClO$_4$. The mixture was sonicated for 2 hour to obtain homogenous mixture. The PEDOT/ERGO modified SPCE was prepared by electropolymerization of EDOT/GO mixture on working electrode of SPCE by cyclic voltammetry (CV) in the potential range of -1.5 to 1.1 V and scan rate of 100 mV/s for different cycles depending on the study. The prepared SPCE was denoted as PEDOT/ERGO/SPCE.

Characterization of the SPCE modified with PEDOT/ERGO was carried out using Raman Spectroscopy, Field Emission Scanning Electron Microscopy (FESEM) and EDX, respectively.

2.3 Electrochemical measurements

Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy were performed using Autolab type II (Netherland). Electrochemical experiments were carried out at ambient temperatures.

2.4 Comparison of the developed sensor response

The response of the sensor towards different concentrations of 3-NP was carried out and compared with a standard colorimetric method (American Public Health Association, APHA). The reaction is based on interaction of phenolic compounds with 4-aminoantipyrine at pH 7.9 in the presence of potassium ferricyanide to form a red color antipyrine dye. The measurement was monitored spectrophotometrically at wavelength of 500 nm [15].

3. RESULTS AND DISCUSSION

3.1 Characterization of the modified SPCEs

The surface morphology of modified SPCE was characterized using FESEM at 20K magnification and the image was shown in Figure 1. Figure 1A shows the morphology of SPCE

modified with PEDOT. The image confirmed that the PEDOT was uniformly deposited on the surface of SPCE and shows a high roughness and loose structure with holes typical of PEDOT structure. Figure 1B shows the morphology of PEDOT/ERGO. The image shows that the ERGO is well distributed in the PEDOT film filling the rough and loose structure of PEDOT with crumpled structures typical to ERGO.
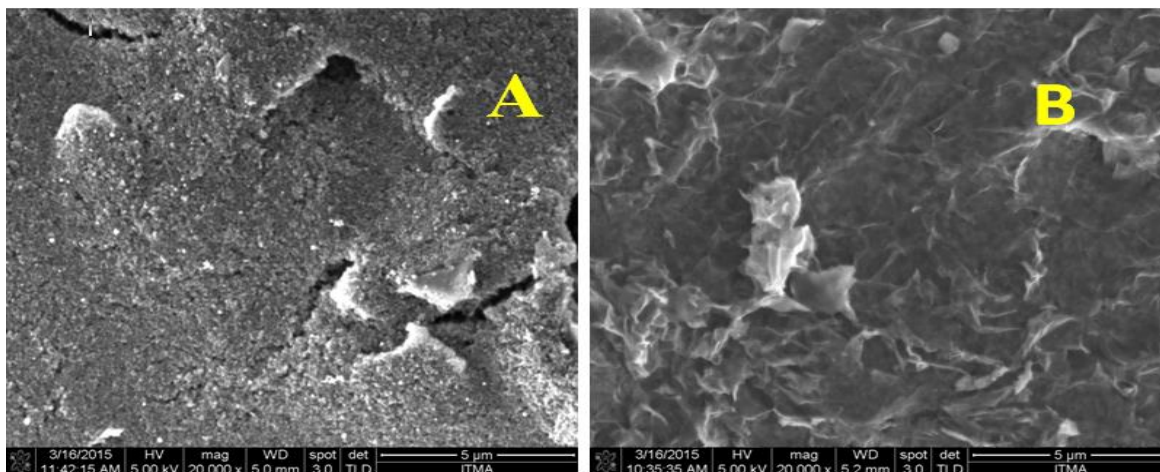

Figure 1. The FESEM images of SPCE modified with A) PEDOT B) PEDOT/ERGO
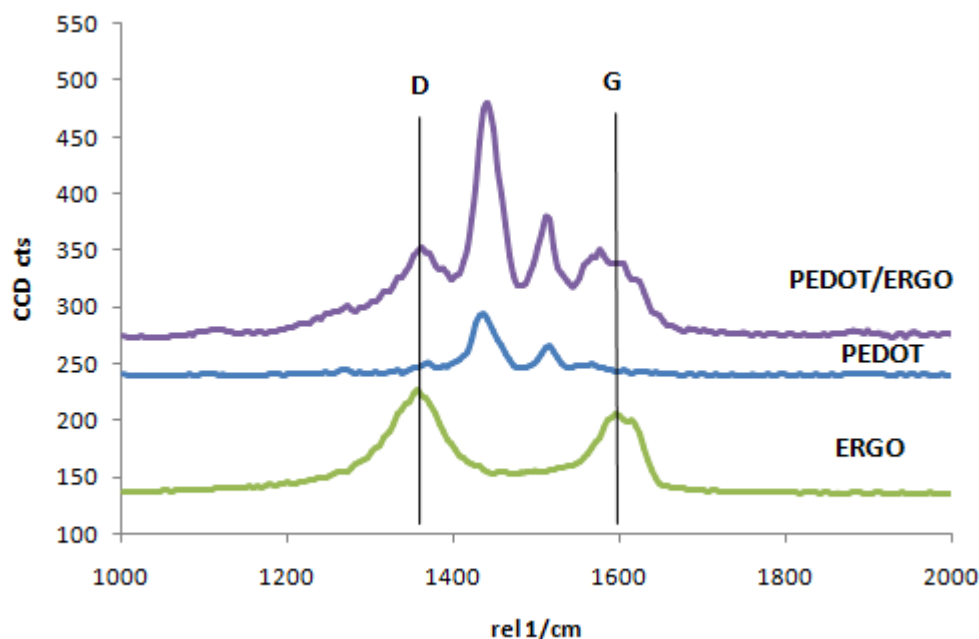

Figure 2. Raman spectrum of SPCE modified with ERGO, PEDOT, and PEDOT/ERGO

Structural composition of the modified SPCEs was characterized using Raman spectroscopy as shown in Figure 2. It can be observed that ERGO showed two visible peaks associated to disorder-induced D band and G band around 1350 cm^{-1} and 1594 cm^{-1}, respectively. Similar findings were also

observed by the previous reported work which illustrated the presence of these peaks confirmed the presence of ERGO on SPCE [16]–[20]. The spectrum of PEDOT demonstrated similar structure as previous reported work [16] while the spectrum of PEDOT/ERGO composite incorporated the common characteristic of both graphene (D and G band) and PEDOT, which indicate the formation of the composite film[16].

3.2 Electrochemical characterization of the modified SPCE

The electrochemical behaviour of the modified SPCEs in terms of current enhancement, active surface area and charge transfer property were investigated using cyclic voltammetry (CV) in 5 mMK$_3$[Fe(CN)$_6$]/0.1 M KCl (Figure 3). As shown in Figure 3a, bare SPCE gave a redox peaks which are attributed to the reduction and oxidation of Fe^{3+}/Fe^{2+} ions in cyclic form. Significant current enhancement can be seen when the SPCEs was modified with ERGO suggesting the conductive material was successfully deposited on the SPCE (Figure 3b). The SPCE modified with PEDOT (Figure 3c) shows higher and broader current compared to ERGO/SPCE. The broadness of the redox peak shows capacitance current which is typical characteristics of conductive polymers [21]. The SPCE modified with PEDOT/ERGO (Figure 3d) shows excellent enhancement current compared to other modified SPCEs which might be related to the presence of more electrochemical activity sites of the combination of ERGO and PEDOT [16]. The peak-to-peak potential separation (E_p) for the curve PEDOT/ERGO shows reversible system with lower value of 149 mV than that for the PEDOT (168 mV), indicating a rapid electron transfer occurs between the modified SPCE surface and the electrolyte [16], [22]. The active surface areas of bare SPCE and SPCE modified with ERGO, PEDOT and PEDOT/ERGO were calculated using Randles-Sevcik equation and were found to beat 0.037 cm^2, 0.093 cm^2 0.141 and 0.225 cm^2, respectively. These results indicated that the presence of PEDOT/ERGO improved the active surface area of the SPCE, which lead to the enhancement of electrochemical response on the modified SPCE.
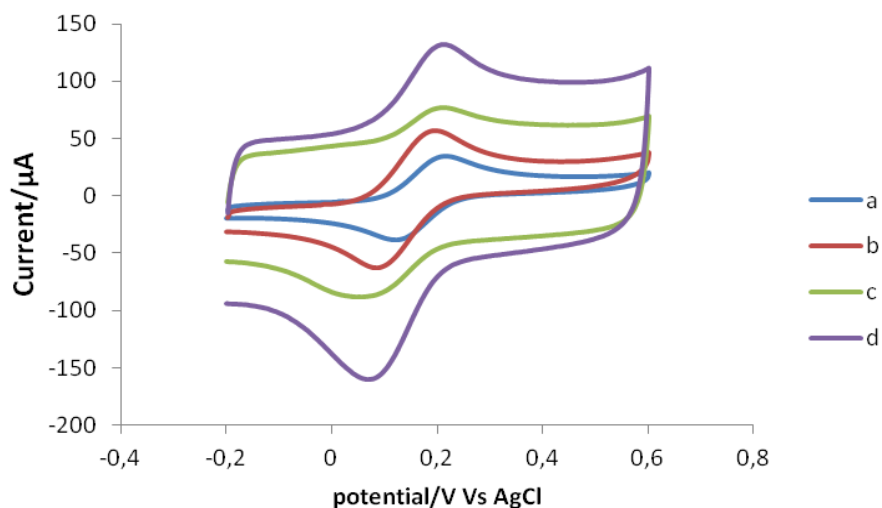

Figure 3. Cyclic voltammogram of the modified SPCE in 0.1 M KCl/5 mM K$_3$Fe(CN)$_6$ with scan rate of 100 mV/s. a) bare-SPCE b) ERGO c) PEDOT d) PEDOT/ERGO

Electrochemical impedance spectroscopy (EIS) was also carried out to investigate the respective resistance SPCE of bare, modified ERGO, PEDOT and PEDOT/ERGO towards $K_3[Fe(CN)_6]$/0.1M KCl. EIS is an efficient method of probing the interface properties of modified electrodes control by electron transfer resistance (R_{et}) of the system [23]. The electron transfer resistance measurement was carried-out using Nyquist graph. In Nyquist plot of EIS, the semicircle diameter at higher frequencies is attributed to the electron transfer limited process, whereas the linear part at lower frequencies indicate a diffusion-control process [24]. The EIS study of the modified SPCEs were recorded in 5 mM $K_3[Fe(CN_6)]$/0.1 M KCl at frequency of 100 KHz to 0.1 Hz and amplitude of 0.01 V. As can be seen in Figure 4, the bare SPCE (curve a) shows a semicircle curve with its diameter indicating that electron transfer process is controlled by diffusion but as the SPCEs were modified the graphs gave entirely different pattern indicating the deposition of the modifiers on the SPCE was successful.
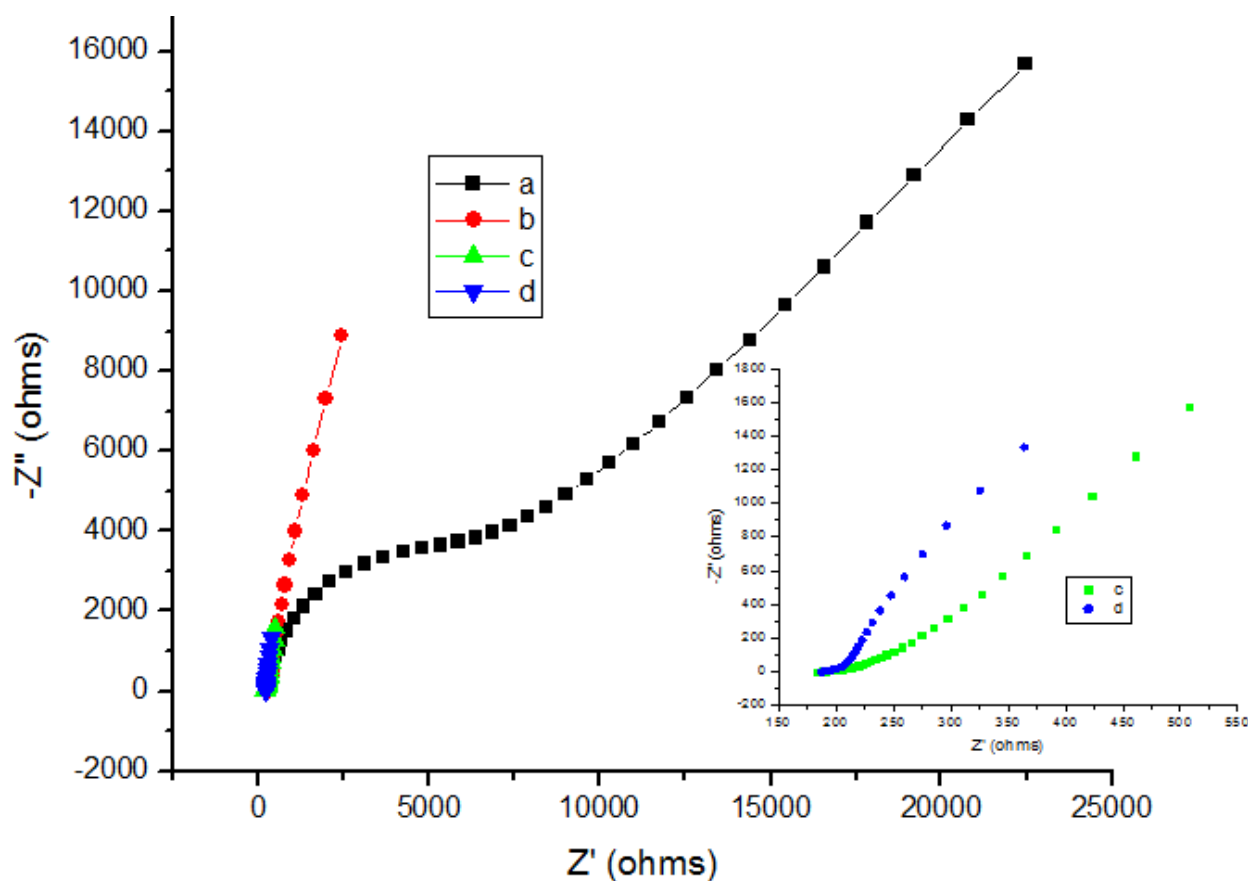

Figure 4. The EIS of a) Bare SPCE, b) ERGO, c) PEDOT and d) PEDOT/ERGO in 5 mM$K_3[Fe(CN_6)]$/0.1 M KCl with frequency 100 KHz to 0.1 Hz and amplitude 0.01 V

ERGO modified SPCEs shows almost straight line graph which indicate low resistance (R_{et} of 150 Ω) and enhancement of conductivity as compared to the bare (1.6 KΩ). Furthermore the SPCE modified with PEDOT and PEDOT/ERGO depict nearly a vertical low-frequency capacitive lines as expected for conductive polymers (CPs) modified electrodes [22]. The result confirmed the successful

deposition of PEDOT and PEDOT/ERGO on the SPCE. By comparing the PEDOT and PEDOT/ERGO curves, it can be seen that PEDOT/ERGO modified SPCE shows lower R_{et} (15.2 Ω) than PEDOT/SPCE (99 Ω). This indicates that the presence of ERGO in the matrix play an important role in increasing surface area of the electrode thereby facilitating good electron transfer between the solution and electrode interface [25].

3.3 Electrochemical characterization of modified SPCEs towards 3-Nitrophenol

Figure 5 shows linear sweep voltammetry (LSV) of bare SPCE and modified SPCEs with ERGO, PEDOT and PEDOT/ERGO in the absence and presence of 3-NP. It can be observed that in the absence of 3-NP both electrodes did not show any response within the selected potential range (Figure 5a-d). After the addition of 3-NP (0.1 mM) in 5 ml PBS an anodic peak current appeared around potential of -0.4 V to -0.7 V suggesting electrochemical reduction of 3-NP to 3-HAP was occurred (Figure 5e-h)[26]–[28].An increase in anodic peak current response compared to bare SPCE can be observed in Figure 5g when the SPCE was modified with PEDOT and this result showed better conductivity of PEDOT/SPCE. As can be seen in Figure 5f, the ERGO/SPCE have better performance compared to PEDOT/SPCE in the determination of 3-NP. This illustrates that ERGO has more electrocatalytic activity towards 3-NP than PEDOT, this is because ERGO can absorbed more 3-NP through π–π stacking[26] than PEDOT. This absorption has great influence on the peak current. Furthermore it can be observed that the PEDOT/ERGO gave a higher current response compared to other SPCEs. The enhancement factor of the PEDOT/ERGO modified SPCE toward 3-NP was found to be 4 times higher compared to bare SPCEs. This observation might be due to excellent conductivity, large surface area and good electrocatalytic activity of PEDOT/ERGO.
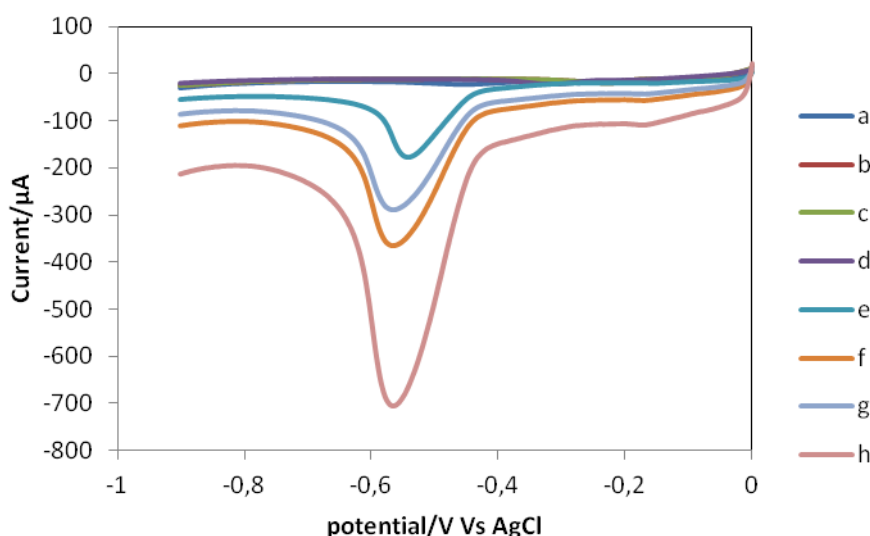

Figure 5. The LSV of bare-SPCE (a and e), ERGO/SPCE (b and f), PEDOT/SPCE (c and g) and PEDOT/ERGO (d and h) in the absence and presence of 3-NP (1mM) in 0.1M PBS (pH 6.0) at scan rate of 100mV/S

3.4 Parameter optimization study

For the preparation of PEDOT/ERGO, number of cycles in CV process influenced the thickness of film formation on the SPCE. Therefore, the effect of thickness of PEDOT/ERGO film formed by varying the number of cycles of CV was investigated. An anodic peak current increased with increase in number of cycles from 3 to 5. It reached maximum response at number of cycles of 5 and further increase in number of cycles resulted to decline in the anodic peak current. This behaviour suggest that as the number of cycles exceed 5, the thickness of the PEDOT/ERGO film formed on the SPCE caused the electron transfer between the SPCE and 3-NP difficult as such resulted in the decrement of reduction peak current[29]. Therefore, considering the electrochemical activity and sensitivity of PEDOT/ERGO to 3-NP, the optimized number of CV cycles for polymerization of PEDOT was fixed at 5 for the composite film preparation.

The effect of pH of PBS on the PEDOT/ERGO/SPCE response was also evaluated by LSV in the pH ranging from 4 to 8. The electrochemical response of PEDOT/ERGO/SPCE increased with increasing pH from 4 to 6.5 and maximum current was obtained at pH 6.5. Further increase in pH, resulted to decrease of the peak current. Therefore, pH 6.5 was selected as optimum pH for subsequent analysis.

Accumulation time is an important parameter affecting the behaviour of electrochemical sensor. Therefore it effect on the system was investigated by varying the time from 0 to 90 s. The result shows that the reduction peak current increased with increase in accumulation time from 0 to 30 s. This phenomenon is probably due to the ability of the composite to absorbed 3-NP through π-π stacking with ERGO in the composite[26]–[28]but sudden decrease in reduction peak current can be observed beyond 30 s. This might be due to the saturation of 3-NP on the surface of modified electrode or constant current achievement in reduction process[27]. For better performance of the sensor the accumulation time of 30 s was chosen.

Accumulation potential was also tested by varying the potential from – 2.0 to 2.0 V. When the accumulation potential increases from - 2.0 to 0.0 V, the reduction peak current was also increased. Above accumulation potential of 0.0 V, the peak current starts to decrease and disappeared at potential of 2.0 V. The disappearance of the peak at 2.0 V may be related to instability of PEDOT/ERGO composite during electrolysis or blockage of electron transfer between the surface of SPCE and 3-NP by PEDOT/ERGO at potential of 2.0 V [30].Thus, accumulation potential of 0.0 V was chosen for further study.

3.5 Analytical performance of SPCE modified PEDOT/EGO

The performance of the sensor for the detection of 3-NP was investigated by conducting LSV under optimum condition for different concentration of 3-NP. The calibration curve of the sensor was obtained by the addition of 3-NP concentration ranging from 0.3 to 70 µM (Figure 6). It can be seen from Figure 6A that the reduction peak current increased proportionally with increase in concentration of 3-NP. The calibration curve (Figure 6B) of the developed sensor shows a linear response with regression equation y = 5.0042x + 45.674, R^2 = 0.9934 with the detection limit of 0.08 µM.
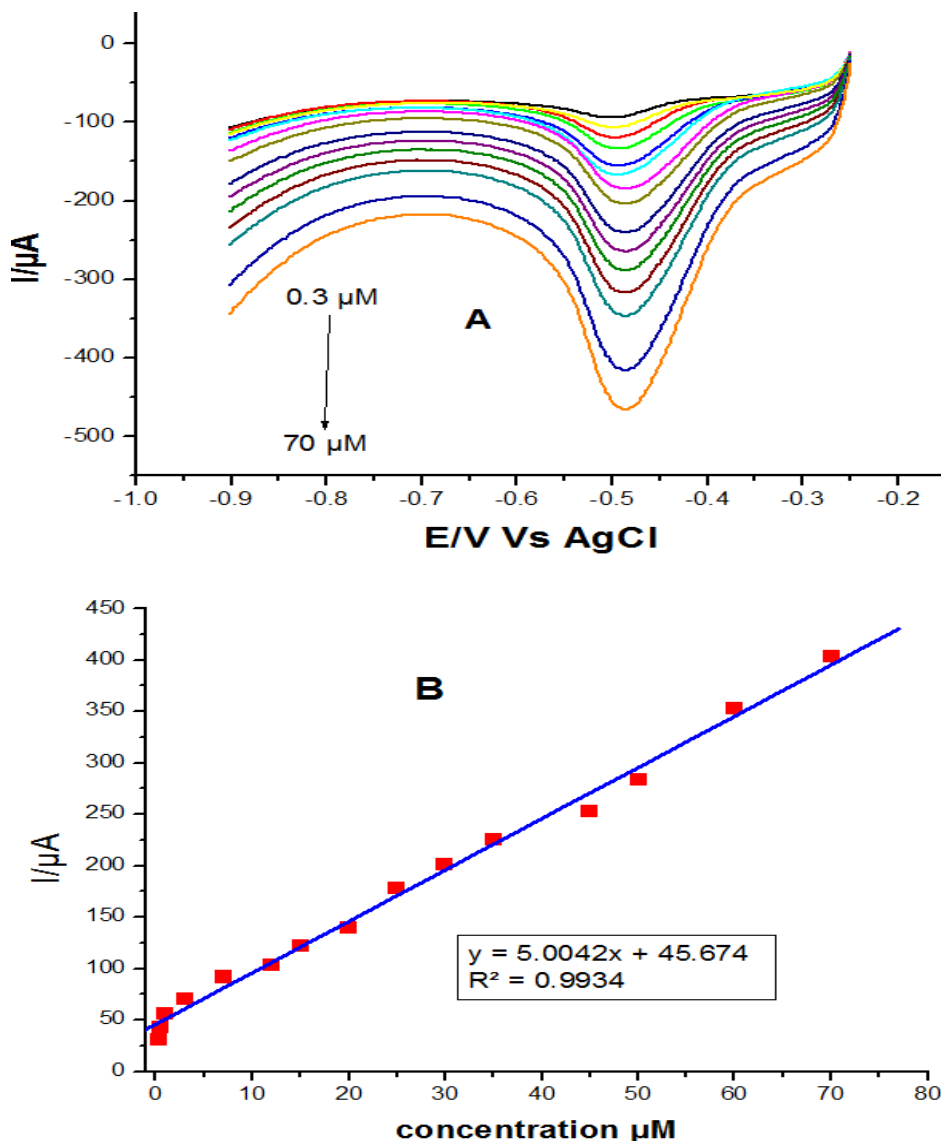
Figure 6. Dynamic response of the sensor towards different concentration of 3-NP in 0.1 M PBS (pH 6.5), accumulation time and potential were fixed at 30 s and 0.0 V, respectively. Inset is linear calibration curve of the sensor

The performance of the proposed sensor was compared with some reported works and summarized in Table 1. The linear range of the proposed method (0.3 – 70 μM) was broader than the reported range obtained from modified electrodes such GCE/CD/RGO (7.0 – 43.0 μM) [31] and CD-SBA/CPE (0.2-1.6 μM) [32]. The limit of detection of the proposed method was estimated to be 0.08 μM which is lower than some modified electrodes such as GCE/CNT (6.0 μM) [33], GCE-AuNps (5 μM) [34], and GCE/CD/RGO [31]. It can be concluded that PEDOT/ERGO is an excellent platform for the detection of 3-NP and good performance of the proposed sensor could be ascribed to the electrocatalytic activity and the adsorption ability of PEDOT/ERGO towards 3-NP.

Table 1. Comparison of several modified electrode for detection 3-NP

Modified electrode	Methods	Linear range (µM)	LOD (µM)	Reference
GCE-CD-RGO	DPV	7.0 – 43.0	0.7	Liu et al., 2012 [31]
GCE-AuNPs	SDV	7.5 – 2000.0	5.0	Zhang et al., 2011 [34]
CNT/GCE	LSV	10 – 1000.0	6.0	Luo et al., 2008 [33]
CD-SBA/CPE	DPV	0.2 – 1.6	0.05	Xu et al., 2011 [32]
PEDOT/ERGO	LSV	0.3 – 70.0	0.08	This work

Note: CD-RGO: β-cyclodextrin functionalized reduced graphene oxide; AuNPs: nano gold, SDV:semi-derivative voltammetric; CD-SBA: β-Cyclodextrin functionalized mesoporous silica; CPE: carbon paste electrode.

3.6 Interference Study

Table 2. Effect of some inorganic and organic foreign species on the sensor response

Interferent	Tolerance limit in fold	Relative error (%)
Phenol	10 fold	- 0.98
catechol	10 fold	1.06
Resorcinol	10 fold	- 4.17
Pentachloro phenol	30 fold	4.84
M-Cresol	20 fold	- 5.00
2-Nitrophenol	Equal fold	6.07
4-Nitrophenol	Equal fold	8.74
Mg^{2+}	150 fold	3.40
Fe^{2+}	2 fold	4.46
Na^+	145 fold	4.67
K^+	125 fold	4.85
SO_4^{2-}	60 fold	- 5.03
Cl^-	150 fold	- 4.97
NO_2^-	150 fold	- 4.32
I^-	145 fold	4.37

To evaluate the selectivity of the sensor, influence of some foreign substances which includes several phenolic derivatives and inorganic species were tested. The effect of every interfering substance was evaluated individually by recording LSV response for 50 µM of 3-NP in the presence of interfering substances. The concentration of the interfering substance was varied from equal fold to 150 fold towards 3-NP. It can be noted from Table 1 the inorganic species show no significant interference given that the RSDs of the responses within ±5 % except for SO_4^{2-} appear to cause interference. For phenolic derivatives no significant interference were observed except for 2-NP and 4-NP which indicated their presence can interfere the sensor response. This might be due to similar functional group (-NO$_2$) to 3-NP. From the result it can be concluded the developed sensor had an

excellent selectivity toward detection of 3-NP even in the presence of some foreign species with exception for SO_4^{2-}, 2-NP and 4-NP.

The reproducibility of the developed sensor was estimated by recording measurements of PEDOT/ERGO/SPCEs (n=6) towards 35 µM of 3-NP under optimum condition. The result gave good reproducibility with relative standard deviation (RSD) of 4.85 %. Repeatability of PEDOT/ERGO/SPCEs was also evaluated by using single electrode and good repeatability with RSD of 3.83 % (n=6) was obtained.

3.6 Comparison of the sensor response and analysis of spiked real samples

The feasibility of the developed PEDOT/ERGO/SPCE sensor in the analysis of real water samples spiked with 3-NP was investigated and compared with those obtained using APHA method. For unspiked water samples, no 3-NP was detected by the developed sensor and the APHA method. The results from both methods were summarized in Table 2. The results demonstrate that the sensor and the APHA method detected approximately 92-99 % and 90-101 % of 3-NP in the spiked water samples. Statistical analysis for comparing the two means of the developed sensor and the APHA was also examined. The calculated values of |t| were found to be less than the tabulated value, thus the difference between the two methods used is insignificant at the 95% confident level and null hypothesis is accepted. The result shows that the two methods used for the determination of 3-NP samples were in good agreement and comparable.

Table 3. Comparison of real sample analysis between the developed sensor and APHA method

Sample	Sensor (n = 4)			APHA method (n = 4)			
	Added (µM)	Found (µM)	Recovery (%)	Added (µM)	Found (µM)	Recovery (%)	Calculated t-Test
1	2.50	2.48	99.47	2.50	2.51	100.41	0.914
	3.50	3.52	97.97	3.50	3.44	98.38	1.675
	5.00	5.04	98.60	5.00	4.91	100.57	2.831
	6.30	6.10	96.83	6.30	6.33	98.32	2.871
2	2.50	2.408	96.32	2.50	2.46	98.38	0.584
	3.50	3.486	99.61	3.50	3.30	96.30	3.061
	5.00	4.795	95.90	5.00	4.59	91.70	2.182
	6.30	5.987	95.04	6.30	5.93	94.15	0.362
3	2.50	2.317	93.49	2.50	2.419	96.76	2.350
	3.50	3.227	92.21	3.50	3.178	90.80	0.898
	5.00	4.692	93.84	5.00	4.534	90.69	1.548
	6.30	5.995	95.15	6.30	6.215	98.64	1.321

$t_3 = 3.182$ at 95% confidence limit

4. CONCLUSION

An effective method for electrochemical determination of 3-nitrophenols with potential applicability on real samples was developed based on ERGO composited with PEDOT on the surface of SPCE. The modified electrode exhibits high electrocatalytic activity and good selectivity toward the reduction of 3-NP due to the excellent electrical conductivity, strong adsorptive ability and large effective surface area of PEDOT/ERGO nanocomposite. The enhancement factor of the PEDOT/ERGO modified SPCE towards 3-NP was calculated to be 4.0 times higher compared to bare SPCE. The developed sensor showed a remarkable reproducibility (RSD of 4.85 %), repeatability (RSD of 3.83 %) and a good sensitivity towards 3-NP. Under optimal conditions the sensor response was linear in the concentration range of 0.3 to 70 µM with the detection limit of 0.08 µM, respectively. Furthermore, the applicability of the developed sensor towards water samples indicate that it can be used for site monitoring of 3-NP.

References

1. T. Zhang, Q. Lang, D. Yang, L. Li, L. Zeng, C. Zheng, T. Li, M. Wei, and A. Liu, *Electrochim. Acta*, 106 (2013) 127.
2. S. Larous and A. Meniai, *Desalin. water Treat.*, 51 (2013) 5014.
3. J. Svitel and S. Miertus, "*Environ. Sci. Technol.*, 32 (1998) 828.
4. C. Kun, Z. Zhang, Y. Liang, and W. Liu, *Sensors*, 13 (2013) 6204.
5. T. G. X. Wu, F. Li, W. Wu, *Vacuum*, 101 (2014) 53.
6. B. Satish, R. Venkateswara, S. Chakra, and T. Thunugunta, *Int. J. Adv. Biotechnol. Res.*, 4 (2013) 142.
7. J. Chen, B. Yao, C. Li, and G. Shi, *Carbon N. Y.*, 64 (2013) 225.
8. J. Liu, J. Tang, and J. Gooding, *J. Mater. Chem.*, 22 (2012) 12435.
9. V. Loryuenyong, K. Totepvimarn, P. Eimburanapravat, W. Boonchompoo, and A. Buasri, *Adv. Mater. Sci. Eng.*, 2013 (2013) 1.
10. H. Yin, Y. Zhou, X. Meng, K. Shang, and S. Ai, *Biosens. Bioelectron.*, 30 (2011) 112.
11. C. K. Chua and M. Pumera, *Chem. Soc. Rev.*, 43 (2014) 291.
12. S. Goenka, V. Sant, and S. Sant, *J. Control. Release*, 173C (2013) 75.
13. M. Song and D. Cai, *Polymer-Graphene Nanocomposites,* 26 (2012) 1.
14. P. Deng, Z. Xu, and Y. Kuang, *J. Electroanal. Chem.*, 707 (2013) 7.
15. APHA, "Standard Methods for the Examination of Water and Wastewater, 15th ed., American Public Health Association, Washington, DC.," 1981.
16. F. Jiang, Z. Yao, R. Yue, Y. Du, and J. Xu, *Int. J. Hydrogen Energy*, 37 (2012) 14085.
17. G. K. Ramesha and S. Sampath, *J. Phys. Chem. C*, 113 (2009) 7985.
18. 1X. Zhang, D. Zhang, Y. Chen, X. Sun, and Y. Ma, *Chinese Sci. Bull.*, 57 (2012) 3045.
19. W. J. Basirun, M. Sookhakian, S. Baradaran, M. R. Mahmoudian, and M. Ebadi, *Nanoscale Res. Lett.*, 8 (2013) 397.
20. D. Wang, W. Yan, S. H. Vijapur, and G. G. Botte, *Electrochim. Acta*, 89 (2013) 732.

21. L. Lu, O. Zhang, J. Xu, Y. Wen, X. Duan, and H. Yu, *Sensors Actuators B. Chem.*, 181 (2013) 567.
22. Z. Feng, Y. Yao, J. Xu, L. Zhang, Z. Wang, and Y. Wen, *Chinese Chem. Lett.*, 25 (2014) 511.
23. P. Raghu, T. M. Reddy, P. Gopal, K. Reddaiah, and N. Y. Sreedhar, *Enzyme Microb. Technol.*, 57 (2014) 8.
24. M. Liu, Y. Wen, D. Li, R. Yue, J. Xu, and H. He, *Sensors Actuators B*, 159 (2011) 277.
25. W. Si, W. Lei, Y. Zhang, M. Xia, F. Wang, and Q. Hao, *Electrochim. Acta*, 85 (2012) 295.
26. X. X. Jiao, H. Q. Luo, and N. B. Li, *J. Electroanal. Chem.*, 691 (2013) 83.
27. J. Li, D. Kuang, Y. Feng, F. Zhang, Z. Xu, and M. Liu, *J. Hazard. Mater.*, 201 (2012) 250.
28. D. Peng, J. Zhang, D. Qin, J. Chen, D. Shan, and X. Lu, *J. Electroanal. Chem.*, 734 (2014) 1.
29. Y. Zhang, L. Wu, W. Lei, X. Xia, M. Xia, and Q. Hao,*Electrochim. Acta*, 146 (2014) 568.
30. A. Muhammad, N. A. Yusof, R. Hajian, and J. Abdullah, *Sensors*, 16 (2016) 1.
31. Z. Liu, X. Ma, H. Zhang, W. Lu, H. Ma, and S. Hou, *Electroanalysis*, 24 (2012) 1178.
32. X. Xu, Z. Liu, X. Zhang, S. Duan, S. Xu, and C. Zhou, *Electrochim. Acta*, 58 (2011) 142.
33. L. Luo, X. Zou, Y. Ding, and Q. Wu, *Sensors Actuators B*, 135 (2008) 61.
34. L. Chu, L. Han, and X. Zhang, *J. Appl. Electrochem.*, 41 (2011) 687.