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Modification of SPCE by reduction of graphene oxide and electrodeposition of zinc oxide nanoparticles for electrochemical sensor

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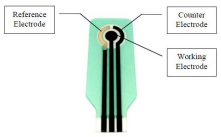
GRAPICAL ABSTRACT



ABSTRACT

Zinc oxide nanoparticles (ZnO-NPs) were prepared for modification of SPCE at simple and less time consuming technique. The electrodeposition method was used to produce zinc oxide nanoparticles on reduced graphene oxide and SPCE (ZnO-NPs/rGO/SPCE) in order to enhance the performing of electrochemical properties of ZnO-NPs in the field of electrochemical sensor. The physical and chemical properties of graphene oxide (GO) before and after reduction along with zinc oxide nanoparticles (ZnO-NPs) were observed by field emission scanning electron microscopy, energy dispersive x-ray and Raman spectroscopy. The C/O ratio in reduced graphene oxide was higher than graphene oxide which indicate the small amount of oxygen containing functional group were still presented in the reduced graphene oxide. The redox reactivity of ZnONPs/rGO/SPCE has been affirmed and compared with rGO/SPCE and bare SPCE by cyclic voltammetry. Besides, the reduced graphene oxide with additional of zinc oxide nanoparticles gave the high electrical conductivity compared to other composites.

Keywords: Graphene oxide, reduced graphene oxide, zinc oxide nanoparticles, electrodeposition, electrochemical sensor

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1. INTRODUCTION

Electrochemical technique is an interesting research in order to develop a fast, high sensitive, user-friendly, low detection limits and specific biosensor for biomolecule detection. Over the past several years, the performance of electrochemical properties being highly recognized by the introduction of screen printed electrodes (SPEs) which accustomed from screen printing technology that originated from microelectronic industry. Therefore, microelectrodes and chemically modified electrode on designing the SPEs give huge advantages upon the most relevant biological compounds in electrochemical detection, hence producing inexpensive and simple analytical methods. Generally, SPEs are disposable devices printed of working electrode (WE), reference electrode (RE) as well as counter electrode (CE) which applying the screen printed methodology [1] as represents in Fig.1. Thus, screen printed carbon electrode was selected as based material for electrochemical applications in this research.

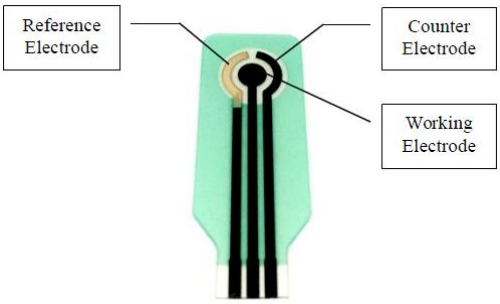

Fig. 1 Screen printed carbon electrode

Owning to this, the modification of SPCE need to be done in order to boost the charge transfer transport processes in working electrode. Furthermore, the electrochemical behaviour of the electrode can change due to the presence of adsorbed species during modification process and exaggerate the peak current response relatively neither increase nor decrease after the modification. Along this line, particle size property has huge advantages to elevate the physical, chemical as well as biological properties of semiconductor nanoparticles. Zinc oxide nanoparticle has been discovered as unique semiconductor with promising materials for broad potentialapplications [2]. A versatile semiconductor material with a large excitation binding energy (60mV) and wide bandgap (3.37 eV) at room temperature can be considered as the valuable properties for zinc oxide. The synthesis of zinc oxide can be done by various way including hydrothermal, chemically and electrodeposition. By previous studies, electrodeposition method demonstrates a good quality as well as effecting the structure and properties of zinc oxide nanoparticles [3]. However, zinc oxide nanoparticles can easily form agglomeration due to van der Waals forces and thus limits its wonderful applications. Due to this lacking properties, graphene oxide was introduced in order to achieve better performance, more stable and dispersed composites [4-5]. Generally, graphene oxide is carbon covalently bonded with functional groups of oxygen and contains sp2 and sp3 hybridized carbon atoms. Good carrier mobility and high surface area of graphene oxide enhance the good impact in connectivity [6]. Anyhow, the conductivity of graphene oxide is relies on the amount of oxidization in the compound together with the synthesis methods and techniques. Thus, it can be enhanced by reducing the graphene oxide to form

reduced graphene oxide. The reduction of graphene oxide increases the capabilities of its sensing properties as well as improving its sensitivity in spite of those of pristine zinc oxide nanoparticles and graphene oxide [7]. The aim for this work was a novel electrodeposition method for synthesis zinc oxide nanoparticles that performed on top of reduced graphene oxide and SPCE as a modification for SPCE. Thus, this work is significant to the evaluation for sensor applications.

2. MATERIALS AND METHODS

2.1 Materials

Graphene oxide, phospahate buffer, zinc nitrate aqueous solution, potassium nitrate.

2.2 Methodology

Graphene oxide was ultrasonicated for 2 hours in phosphate buffer (PB, 9.21) to obtain homogenous suspension. The SPCE was modified by drop casting graphene oxide suspension and then undergo cyclic voltammetry with the scan rate of 50mV/s from range -1.4V to 0 V to obtain reduced graphene oxide (rGO) [8]. Then, SPCE was further modified by deposition of ZnO-NPs through electrodeposition method. 0.1 M zinc nitrate aqueous solution was mixed with 1 M potassium nitrate and fixed at pH 6. Thus, the surface of working electrode was applying potential step of -0.8V for 40s at constant temperature of 65˚C [9-10].

2.2 Characterizations

The morphology of all modified SPCE including GO/SPCE, rGO/SPCE and ZnO-NPs/rGO/SPCE were characterized using a field emission scanning electron microscopy (FESEM) and the composition for each modification were analyzed by energy dispersive x-ray (EDX). In addition, Raman spectra are carried out for all modification of SPCE through Raman spectroscopy. Comparisons of cyclic voltammograms for electrochemical characterization were done using an Autolab system.

3. RESULTS AND DISCUSSION

3.1 Physical Characteristics

Fig. 1 shows the FESEM images of surface morphology of bare SPCE and modified SPCE involving the additional of graphene oxide before and after reduction as well as zinc oxide nanoparticles. Fig. 2(a) obviously observes that bare SPCE had an agglomeration surface morphology compared to after additional of graphene oxide as show in Fig. 2(b). It was formed a wrinkled sheet, crumpled and resembles strongly folded curtain on the top of SPCE. Conjointly, the surface morphology of reduced graphene oxide in Fig. 2(c) show relatively similar to graphene oxide as it was “dressed” on the surface of graphene oxide. Anyhow, the reduced graphene oxide has a smoother surface area than graphene oxide. Per contra, the deposition of zinc oxide nanoparticles shows in Fig. 2(d) resulted on the formation of hexagonal wurtzite shape on the surface of SPCE. Thus, it proved that zinc oxide nanoparticles successfully deposited on the top of graphene oxide.

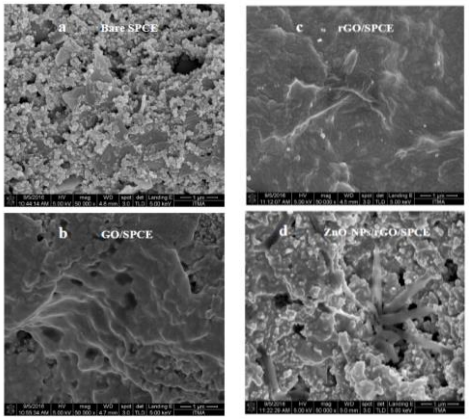

Fig. 2 The surface morphology of (a) bare SPCE (b) GO/SPCE (c) rGO/SPCE (d) ZnO-NPs/rGO/SPCE.

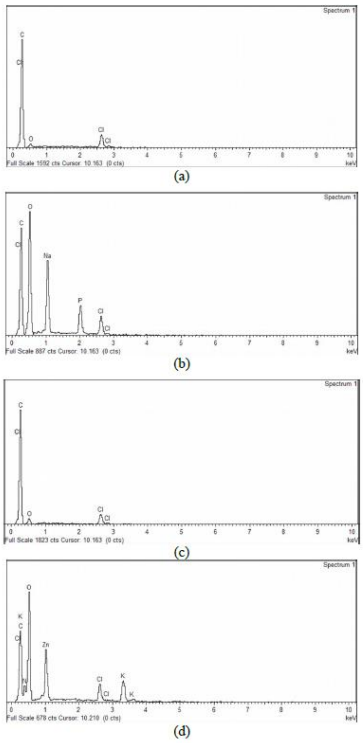

Fig. 3 EDX elemental analysis of (a) bare SPCE (b) GO/SPCE (c) rGO/SPCE (d) ZnO-NPs/rGO/SPCE

3.2 Energy Dispersive X-ray Analyses

The elemental composition analysis was carried out by using EDX for bare SPCE and modified SPCE. The results obtained

were illustrated in Fig.3. and listed in Table 1. Bare SPCE contained the element of carbon (C), oxygen (O) and chlorine (Cl) in spite of carbon only. The present of oxygen and chlorine were due to contamination on bare SPCE. In addition, Table 1 indicates the content of carbon and oxygen elements of reduction graphene oxide and the existence of zinc element after electrodeposition of zinc oxide nanoparticles. The weight composition of carbon in graphene oxide and reduced graphene oxide showed the increment for about 43.97%, while, oxygen weight content decreased by 29.74%. Moreover, the mass ratio of C/O is 13.33 indicates there were some oxygen contents in the reduced graphene oxide. Hence, the additional content of carbon and a dropped of oxygen level before and after reduction of graphene oxide proved that reduced graphene oxide is successfully produced. Soon after, the electrodeposition of zinc oxide occurred and hence gave out the outstanding result of the existence of zinc element. Besides that, the oxygen content showed significant rised from previous oxygen content level. Thus, it proved that zinc oxide nanoparticles were deposited on the SPCE using the electrodeposition method.

Table 1 Elemental analysis of EDX for graphene oxide, reduced graphene oxide and zinc oxide nanoparticles.

Sample	Element			
	Carbon	Oxygen	Zinc	Mass Ratio C/O
	Weight (%)	Weight (%)	Weight (%)	
Graphene Oxide	40.66	36.09	-	1.13
Reduced Graphene Oxide	84.63	6.35	-	13.33
Zinc Oxide Nanoparticles	16.32	40.03	15.03	-

3.3 Raman Spectroscopy Analyses

Generally, Raman spectroscopy can explore the crystal structure, defects and disorder for graphene-based materials. The characterization of Raman spectroscopy nowadays is broadly used for conjugation and double carbon-carbon bonds in order to give high intensities. Two main peaks: D and G bands clarified the changed intensity between graphene oxide and reduced graphene oxide as shown in Fig.4. The reduction of graphene oxide causes by breakdown of translational symmetry or defects is assign as D band (1,330~1,360 cm-1) and first order scattering of the E2g phonon of sp2 carbon atoms allow the formation of G band (1,580~1,600 cm−1) [11]. As a sequel, the intensity ratio, ID/IG increased from 0.99 to 1.02 of the reduction of graphene oxide to form reduced graphene oxide as states in Table 2. It can be investigated that the size of in-plane sp2 domains was reduced and an increment of disorder occurred in the reduced graphene oxide.

3.4 Electrochemical Analyses

The redox reactivity performance of modified SPCE can be seen through cyclic voltammetry analytical studies. The electrochemical properties of modified SPCE investigated by electron-transfer by 0.1 M phosphate buffer saline (PBS) and 0.01 M K3 [Fe(CN)6] as an electrolyte. Fig. 5 illustrates redox reactivity of bare SPCE, modified SPCE of graphene oxide, reduced graphene oxide and after additional zinc oxide nanoparticles onto the working SPCE electrode. The peak current for ZnO-NPs/rGO/SPCE composite showed the highest peak compared to rGO/SPCE, GO/SPCE and bare SPCE. This implies that the additional of ZnO-NPs gave high electrical conductivity compared to other composites. The result clearly described that ZnO-NPs/rGO/SPCE contributed a significant increment for peak current due to extraordinary physical properties such as large specific surface area, high conductivity and a good accumulation efficiency. Hence, the high peak of redox reaction pointed out that the greater edge plane-like defect sites on the surface of ZnO-NPs can be exposed for the electrolyte to give high peak current response.

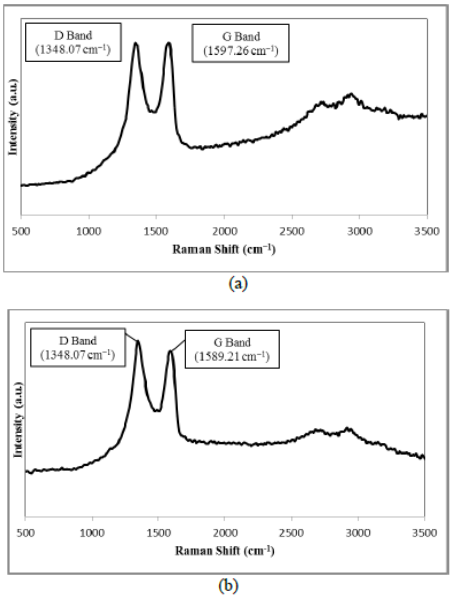

Fig.4. Raman spectrum of (a) graphene oxide and (b) reduced graphene oxide

Table 2 The shift and intensity of reduction of graphene oxide by Raman Spectroscopy

Working electrode of SPCE	D Band		G Band		I_D/I_G
	Shift/cm^{-1}	Intensity /a.u.	Shift/cm^{-1}	Intensity/ a.u.	
Graphene oxide	1348.07	358.20	1597.26	358.33	0.99
Reduced Graphene Oxide	1348.07	336.21	1589.21	328.16	1.02

3.5 Deposition of Zinc Oxide Nanoparticles

The electrodeposition of zinc oxide nanoparticles taken place based on the reaction of OH- ions on the surface of working electrode. The reduction of nitrite ions at the cathode produced hydroxide ions and thusly precipitation of zinc hydroxide occured onto the cathodic electrode. In such a way,

dehydration of zinc oxide was finally generated. The electrodeposition mechanism was supposed as follows [12].

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \quad (1)$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (2)$$

$$Zn2^+ + 2OH^- \rightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

On that account, the reactions can be summed up by Eq. (5).

$$Zn^{2+} + NO_3^- + 2e^- \rightarrow ZnO + NO_2^- \quad (5)$$

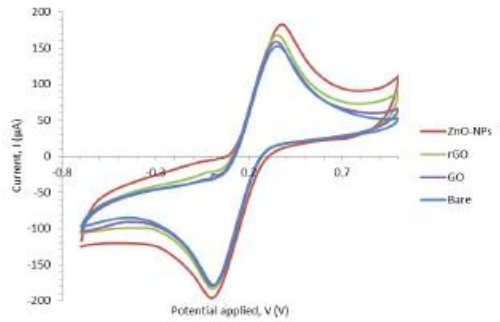

Fig. 5 Cyclic voltammetry of modified SPCE at scan rate 0.1 V/s

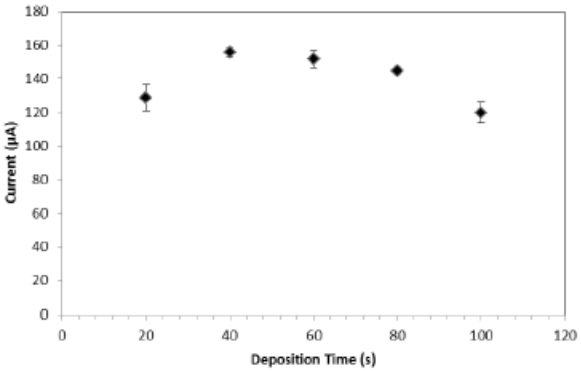

Fig. 6 Peak current response on the effect of deposition time for zinc oxide nanoparticles deposited onto SPCE.

3.6 Effect of Deposition Tme on Zinc Oxide Nanoparticles

The effect of time taken on deposition time of zinc oxide nanoparticles was completely carried out using chronoamperometry technique in a range of 20s to 100s. Roughly, the deposition time for zinc oxide nanoparticles deposited onto the surface of SPCE reached maximum when deposition time was 40s and declined from there on. Wherefore, 40s was picked as the most optimum deposition time.

4. CONCLUSION

In this work, zinc oxide nanoparticles prepared by electrodeposition method from zinc nitrate aqueous solution and potassium nitrate fixed at 65˚C that anchored to the surface of reduced graphene oxide. The characterizations were done by FESEM, EDX, Raman spectroscopy and cyclic voltammetry. FESEM images showed the morphology of rGO/SPCE was smoother than GO/SPCE and the presence of hexagonal wurtzite as a proved on deposition of zinc oxide nanoparticles. In addition, the composition of GO/SPCE, rGO/SPCE and ZnO-NPs/rGO/SPCE were analyzed by EDX and proved that the reduction was occurred along with the success electrodeposition of zinc oxide nanoparticles. Raman spectra showed the presence of D band and G band of both graphene oxide and reduced graphene oxide. Therefore, ID/IG was calculated and showed an increment value of reduction intensity. In term of electrochemical properties of composites were confirmed by comparison of cyclic voltammetry on the individual composite. Along this line, the ZnONPs/ rGO/SPCE gave out the highest peak current among others. Thus, simple-efficient method can be used to modify the SPCE which suitable for electrochemical sensor field.

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