Modification of glassy carbon electrode with NiO nanoparticles prepared using Ocimum sanctum leaf extract as urea sensor

P R Arief, Y Yulizar and T A Ivandini

Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Corresponding author’s e-mail: yokiy@ui.ac.id

Abstract. NiO nanoparticles (NiO NPs) have been prepared with green synthesis method using Ocimum sanctum leaf extract (OSLE), which contains secondary metabolite compounds of alkaloids as a weak base source and capping agent. Characterization using Particle Size Analyser (PSA) showed a particle size of NiO about 52.42 nm. NiO NPs was used as modified on glassy carbon (GC) electrode, and then characterized using cyclic voltammetry (CV) and Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX). GC-NiO NPs was used for preliminary studies of urea sensor. The results showed that GC-NiO NPs can detect urea with limit of detection (LOD) values of 0.12 mM and linearity R of 0.97. In addition, the repeatability of urea sensor studies with GC-NiO NPs electrode shows % RSD of 2.854, while its stability shows % RSD of 7.90 for 3 days.

Keywords: glassy carbon electrode, GC-NiO NPs electrode, Ocimum sanctum, urea

1. Introduction

High urea content can cause various adverse effects to the human body. In spite of the low urea content, this can also causes harmful effects such as neurological disorders and hepatitis. Due to the dangerous effects of urea in the environment, it is important to investigate the level of urea in the environment [1]. The organic Ni-metal framework on double-walled carbon nanotubes has been synthesized to detect the presence of non-enzymatic urea showing that the electrode has a high sensitivity of 685 μA.mM.cm–2, with a low detection limit of 3 μM and a response time of 10 s. In addition, the sensor also exhibits high stability after 30 days of storage [2]. The non-enzymatic urea sensor prepared using nickel oxide deposited on carbon nanotube (CNT) cellulose showed an excellent sensitivity with good response time. The electrode also exhibited high stability in sensitivity after the storage for 2 months [3].

Nanomaterials have revolutionized in the area of sensor development, due to their materials size and shape, as well as various types to design the sensing platforms for different applications [4]. Metal oxides such as NiO, CuO, and ZnO are known to be low costs substances and well-recognized redox properties, have been utilized for direct electro-catalytic oxidation and to determine numbers of biochemical compounds, namely urea, glucose, and ethanol. Among some transition metals, Ni has excellent anodic electrocatalytic properties [3].

There are various methods for synthesis of metal and metal oxides nanoparticles such as precipitation method, sol-gel [5], hydrothermal [6] and green synthesis. Green synthesis of nanoparticles also provides some beneficials such as convenient, single-stage, low cost, environmentally friendly, comparatively reproducible as well as stable materials [7]. Taken into account the comprehensive potential of plants, this research focuses to utilize a biological green method to synthesize the nanoparticle. In this regard, leaf extract of Ocimum sanctum contains secondary metabolites such as alkaloids, flavonoids, saponins, tanins, and terpenoids [8].
In this study, glassy carbon (GC) electrode was modified with NiO NPs (GC-NiO NPs). *Ocimum sanctum* leaf extract (OSLE) was used as a weak base source and capping agent. Although this method is potential for synthesis of nanoparticles, it has never been applied for synthesis of nanoparticle on the surface of carbon electrodes, especially GC. OSLE was used to modify GC surface with NiO NPs. Furthermore, a modified GC electrode with NiO NPs showed promising application as urea sensor.

2. Materials and methods

2.1. Materials

Analytical-grade of nickel nitrate hexahydrate, Ni(NO$_3$)$_2$.6H$_2$O was purchased from Merck. *Ocimum sanctum* leaves as the main raw material were received from conservation unit of biopharmaca (UKBB), center study for tropical biopharmaca, LPPM IPB, Bogor, Indonesia.

2.2. Preparation of OSLE

*Ocimum sanctum* leaves were washed, dried and mashed to form powder. The extraction was done in two steps. The first, 50 g of leaf powder was macerated in 250 mL of methanol for one week by stirring every day. The filtrate was partitioned using n-hexane. The methanol fraction was isolated and concentrated with a rotary vacuum evaporator. The evaporated methanol fraction was dissolved in water to obtain a stock solution of OSLE.

2.3. Synthesis and characterisation of NiO NPs

The synthesis of NiO NPs followed the method as described in our previous report [9]. 0.05M Ni(NO$_3$)$_2$ was reacted with OSLE by stirring at 80 °C for 6 h. The formed colloids were heated at 100 °C for 4 h, and then calcined at 450 °C for 2 h. NiO NPs were characterized using Fourier Transform Infrared (FT-IR), UV-Vis Spectrophotometer, X-Ray Diffraction (XRD) and Particle Size Analyser (PSA).

2.4. Modification of GC electrodes with NiO NPs

The modification of glassy carbon electrodes (GCE) with NiO NPs referred to a method as reported by Susanti et al. [10] with some modifications. GCE was polished with 0.5µM α-alumina and washed by sonication for 5 min in isopropanol and deionized water, respectively. It was then dried. The cleaned GCE was dipped into 0.05M Ni(NO$_3$)$_2$ and OSLE by stirring at 80 °C for 6 h. The results were further heated at 100 °C for 4 h and then calcined at 450 °C for 2 h. GC-NiO NPs were characterized using Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX).

2.5. Preliminary study of sensors urea

GCE-NiO NPs were used for preliminary study of urea sensor. In the electrochemical cell, GC-NiO NPs was applied as the working electrode, while Pt wire and Ag/AgCl as the counter and reference electrodes, respectively and 1M KOH as the supporting electrolyte. Cyclic voltammetry was applied as the determinant for calibration, limit detection, reproducibility and stability.

3. Results and discussion

3.1. Characterisation of NiO NPs

FT-IR characterisation aims to determine the functional groups both NiO and OSLE as shown in figure 1a. OSLE shows the vibration at 3324 cm$^{-1}$, 2936 cm$^{-1}$, 1685 cm$^{-1}$ and 1076 cm$^{-1}$, which corresponds to the vibration of -OH, C-H, C-C, and -CN groups, respectively. The presence of -OH, C-H, C-C and -CN groups assumed that OSLE contains alkaloid compounds, which acts as a weak base source and a capping agent in NiO NPs synthesis. NiO shows no vibration of -OH and C-H groups. However, NiO has strong band at 422 cm$^{-1}$ of which assigned to Ni-O stretching vibration mode [11].

The analysis of both structure and average crystalline size of NiO NPs was characterized by XRD as shown in figure 1b. XRD pattern of NiO NPs shows five diffraction peaks at 37.15º, 42.20º, 62.77º, 75.43º and 79.31º indexed to (111), (200), (220), (311), (222), respectively. These results are in accordance with the COD literature of NiO No. 96-101-0096 [5]. Based on those Miller indices, the crystalline structure of NiO was theoretically known as cubic. The average size of NiO crystals was 28.74 nm calculated using the Debye-Scherrer’s formula. According to the PSA characterisation, the
3rd International Symposium on Current Progress in Functional Materials  
IOP Conf. Series: Materials Science and Engineering 763 (2020) 012039  
doi:10.1088/1757-899X/763/1/012039

Figure 1. (a) FTIR spectra of OSLE and NiO (b) XRD pattern of NiO

Figure 2. PSA result of NiO NPs

The particle size distribution average of NiO NPs was quite homogeneous with a sharp peak at 52.42 nm as shown in Figure 2.

3.2. Modification of GC electrode with NiO NPs

The morphology and elemental composition of both bare GC and GC-NiO NPs electrodes were respectively characterised by SEM (mapping)-EDS as shown in Figure 3. In GC-NiO NPs electrode mapping, NiO NPs exhibited lighter color than bare GC. It demonstrates that NiO has higher conductivity than bare GC. Therefore, NiO has been successfully deposited on the GC surface. This result was also supported by EDS analysis before and after modification with NiO NPs. EDS data indicated that the presence of Ni was around 28.52%. NiO was only a few deposited on the GC surface due to its tendency to form the non-homogeneous aggregates.

Figure 4 shows the electrochemical properties of Ni, bare GC, and GC-NiO NPs electrodes using CV. When GC-NiO NPs electrode was compared to the bare GCE and Ni electrodes, it has the characteristic of two electrodes combination, which the GC-NiO electrode has a wide potential window but it was not wider than the GC bare, the peaks of oxidation and reduction are also like the Ni electrode. Ni(II)/Ni(III) peaks were observed approximately at 0.5V vs Ag/AgCl. The reaction is represented in alkaline medium through a proton diffusion that formed NiOOH compound.
Figure 3. SEM-EDS characterizations of (a) bare GC and (b) GC-NiO NPs electrodes

Figure 4. Cyclic voltammogram of Ni, bare GC, and GCE-NiO NPs electrodes

3.3. Preliminary study of urea sensor
Figure 5 shows that the change process of NiO to NiOOH is contributed to the electrocatalytic oxidation of urea in an alkaline medium. The usage of GC-NiO electrode showed the presence of a redox peak of NiO (Ni⁺) and NiOOH (Ni²⁺). The electrocatalytic mechanism occurred when the cathodic peak of Ni³⁺ to Ni²⁺ decreased as long as the urea concentration increased as follows:

$$\text{NiO} + \text{OH}^- \rightarrow \text{NiOOH} + e^- \quad \text{(1)}$$

$$6\text{NiOOH} + 2\text{CO(NH}_2\text{)}_2 + 2\text{H}_2\text{O} \rightarrow 6\text{Ni(OH)}_2 + 2\text{N}_2 + 3\text{H}_2\text{O} + 2\text{CO}_2 \quad \text{(2)}$$
Table 1. The values of reproducibility and repetition of electrode for urea sensor

| Electrode     | Sensitivity (mA/mM.cm) | Linearity | LOD (mM) | % RSD Repeatability |
|---------------|-------------------------|-----------|----------|---------------------|
| Ni            | 0.0703                  | 0.9884    | 1.13     | 4.74                |
| GCE-NiO NPs  | 0.3001                  | 0.9787    | 0.12     | 2.85                |

Figure 5. Cyclic voltammogram of (a) Ni and (b) GC-NiO NPs electrodes, (c) plot of anodic peak I vs concentration with Ni and (d) GC-NiO NPs electrodes.

Figure 5a and figure 5b show the higher urea concentrations could accelerate the Ni(II)–Ni(III) redox reaction because the Ni(III) species could oxidize the urea. The electron transfer rate could be happened rapidly, which is signed by a higher current at the increase urea concentration. Figure 5c and figure 5d show a linear correlation between concentration and current from urea oxidation. Ni and GC-NiO NPs electrodes were used to determine the limit of detection (LOD). The LOD of Ni electrode was 1.13 mM with the concentration range of 1–10 mM and $R^2=0.9884$, while the LOD of GC-NiO NPs electrode was 0.12 mM with the concentration range of 0.1–1 mM and $R^2=0.9787$. The LOD value of GC-NiO NPs electrode was lower than the Ni electrode. The GC-NiO NPs electrode gave a better result in urea sensor due to its lower background current that could make it more sensitive at a lower concentration.

The reproducibility and repetition of electrode for urea sensor were investigated as shown in figure 6. Ni and GC-NiO NPs electrodes were examined by a relative standard deviation (RSD) using CV in 1 mM urea. The RSD value of Ni and GC-NiO NPs electrodes were 4.74 and 2.85 %, respectively. Table 1 shows the summary of the performance of the prepared sensors. This result concludes that GC-NiO NPs electrode has a better result as an urea sensor than Ni electrode.
4. Conclusions

NiO NPs were synthesized using OSLE, which contains secondary metabolites as weak base sources and capping agents. The modification of GC electrode has been successfully performed with NiO NPs. The LOD of both GC-NiO NPs and Ni electrodes were 0.12 and 1.13 mM, respectively. The precision of both Ni and GC-NiO NPs electrodes showed the RSD of 4.74 and 2.85 % (n = 10), respectively. The stability test of GC-NiO NPs electrode with CV measurement showed a fairly good stability with the RSD of 7.90 % for 3 days.

Acknowledgements

The authors would like to thank Universitas Indonesia for funding this research through PIT-9 Grant Universitas Indonesia and PT DKSH (Malvern) for supporting characterization of Particle Size Analyzer.

References

[1] Arain et al. 2016 RSC Adv. 6 39001–6
[2] Nguyen N S and Yoon H H 2016 Sens. Actuators B 236 304–10
[3] Nguyen N S, Das G and Yoon H H 2016 Biosens. Bioelectron. 77 372–7
[4] Liu C M, Chen C and Tseng Y C 2012 J. Electrochem. Soc. 159 K78–82
[5] Wang X, Yang X, Chen S, Li Q, Wang W, Hou C, Gao X, Wang L and Wang S 2016 Front. Plant Sci. 6 1243
[6] Luwang M N, Ningthoujam R S, Jagannath, Srivastava S K and Vatsa R K 2010 J. Am. Chem. Soc. 132 2759–68
[7] Mittal J, Batra A, Singh A and Sharma M M 2014 Adv. Nat. Sci.: Nanosci. Nanotechnol. 5 043002
[8] Al-Temimi S S M and Al-Mashhedy L A M 2015 Int. J. Pharm. Bio. Sci. 6 999–1007
[9] Sulaiman N and Yulizar Y 2018 Mater. Sci. Forum 917 167–71
[10] Susanti W, Gunlazuardi J and Ivandini T A 2018 AIP Conf. Proc. 2023 020085
[11] Kumary V A, Nancy T E M, Divya J and Sreevalsan K 2013 Int. J. Electrochem. Sci. 8 2220–8

Figure 6. Cyclic voltammogram using (a) Ni and (b) GC-NiO NPs Electrodes