ELECTROCHEMICAL CHARACTERIZATION OF FOUR DIFFERENCE SCREEN-PRINTED ELECTRODES AND ITS APPLICATION FOR DETERMINATION OF NITRATE

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Abstract: Four difference designs in sizes and configurations of screen-printed electrode (SPE) printing on a substrate of polyacrylic sheet, were investigated. The working and counter electrodes were printed by carbon ink while the reference electrode, conducting track, and insulator were printed by silver/silver chloride, silver, and insulating inks, respectively. The electrochemical signal of $Fe(CN)_6^{3-/4-}$ was used for selection the best SPE design. The selected SPE was modified by Cu nanoparticle as a catalyst by cyclic voltammetric method on the working electrode for determination of nitrate. The Cu nanoparticles on that working electrode were characterized by scanning electron microscope. Cyclic voltammetric and square wave voltammetric methods were performed to evaluate the performance of nitrate sensor. The nitrate sensor response was linear over the range in three orders from μM to mM, with high sensitivity and low detection limit (0.3 μM).

Introduction

Intensive agricultural activities and especially over fertilization induce an increase of nitrate concentration in groundwater. Nitrate consumed with drinking water can be converted into nitrite in human body and may cause methaemoglobinaemia in newborns, as well as other side effects like hypertension. The U.S. Environmental Protection Agency (EPA) set the Maximum Contaminant Level (MCL) for nitrate at 10 ppm or 0.71 mM.

Many research groups studied electrochemical for nitrate analysis. Wang [1] studied derivatized silver nanoparticles as sensor for ultra-trace nitrate determination based on light scattering phenomenon. Xuejiang [2] used conductometric nitrate biosensor based on methyl viologen/Nafion®/nitrate reductase interdigitated electrodes. Mahajan [3] used Zn(II) complex-based potentiometric sensors for selective determination of nitrate anion, and Aravamudhan [4] developed micro-fluidic nitrate-selective sensor based on doped-polypyrrole nanowires.

In this research, we described the preparation/ fabrication of SPE and applied to be a nitrate sensor based on the $CuSO_4$ solution and CuNPs modified SPE.

Materials and Methods

Potassium nitrate was obtained from Analar (England). Hydrochloric acid 37%, copper(II) sulfate pentahydrate and sodium sulfate were purchased from Merck (Germany). Potassium chloride was from Ajax Sinechem (Australia). Potassium hexacyanoferrate(II) trihydrate and potassium hexacyanoferrate(III) were obtained from Riedel-dehaen (Germany). Sulfuric acid 98% was purchased from Lapscan analytical science (Thailand). Deionized water ($R \geq 18.2$ MΩ cm) was obtained from a Milli-Q-gradient system (Millipore, Sweden). Carbon, silver (Ag) and silver/silver chloride (Ag/AgCl) inks were obtained from Acheson Inc. (Netherlands), while the insulator ink was obtained from Chaiyaboon Co. (Thailand).

Electrochemical measurements were conducted using an Electrochemical Analyzer (Model 1230A, CH Instruments) at room temperature by dropped a solution on SPE, which was used for cyclic voltammetric and square wave voltammetric experiments. A SPE was fabricated in the laboratory [5] and consisted of three electrodes with four difference designs as shown in Figure 1. Homemade screen printed frames were designed in four configurations by four silk screen patterns with CorelDRAW® X3 software. The electrodes were screened in four layers by hand on the polyacrylic sheet. The designated template for each ink was screened with a Ag ink as the conductive wire, a carbon ink as the working and counter electrodes, then a Ag/AgCl ink as the reference electrode, and finally a layer of insulator ink as the insulator and the pattern to define the electrode area. Each layer was subsequently cured for 1 h at 70 ∘C and allowed to cool in desiccators to avoid any reaction with oxygen. The four configuration electrodes were cut into a single electrode before use. The CuNPs modified SPE were characterized by the Scanning Electron Microscope (SEM; LEO, Model 1400VP).

Results and Discussion

Figure 1 depicted the homemade SPE fabricated in four differences designs. The best SPE was selected by comparison the current density response of 5 mM

K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ solution obtained from each electrode. The results in Figure 2 showed that the highest current density was obtained for the design D (Figure 1D) as the cyclic voltammogram shown in Figure 2D. It was used in the next experiments.
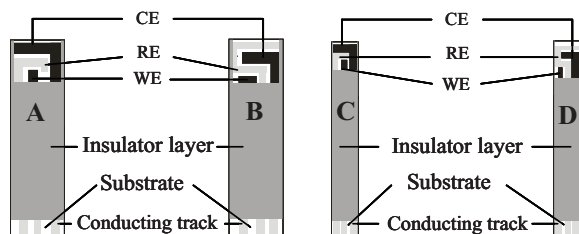

Figure 1. The screen-printed electrode designs on a substrate of polyacrylic sheet with 4 differences in sizes and configurations (WE: working electrode, RE: reference electrode and CE: counter electrode).
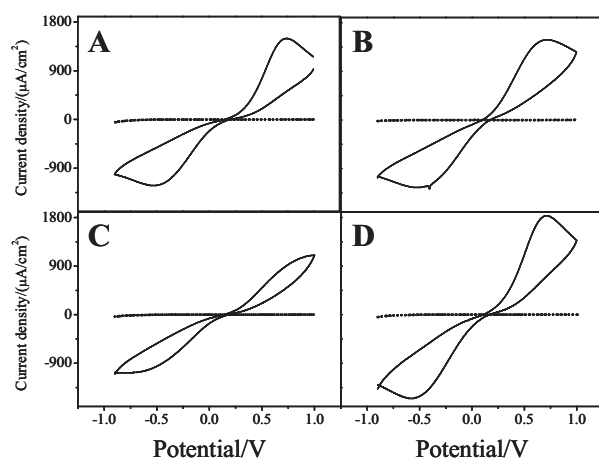

Figure 2. Cyclic voltammograms at four SPEs (from four designs of Figure 1) for 0 and 5 mM K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$.

The CuNPs were characterized by SEM image. This image was shown in Figure 3(A). They were prepared by cycling the potential of cyclic voltammetry (Figure 3(B)) in CuSO$_4$ solution at the potential range between 0.2 to -1.2 V and scan rate 100 mV s^{-1}. The CuNPs were dispersed on SPE surface at the average particle size of 100 nm.

Nitrate electrochemical analysis was studied by square wave voltammetry at the potential -0.4 to -1.2 V, giving the result as shown in Figure 4. The electrochemical behavior of nitrate (KNO$_3$) was investigated at the CuNPs/SPE in 0.1 M NaSO$_4$ solution from pH 2.0 to 5.0 adjust pH with 0.1 M H$_2$SO$_4$ by square wave voltammetric (not shown). It was found that the change in pH affected the reduction peak potential of nitrate. The best response was received at pH 3.0 of Na$_2$SO$_4$ and it was selected for further experiment. Figure 4a, 4b, and 4c showed square wave voltammograms of 0.1 M Na$_2$SO$_4$ pH 3.0 electrolyte, 1.5 mM CuSO$_4$ in 0.1 M Na$_2$SO$_4$ pH 3.0 solution before scan cyclic voltammetric for CuNPs

modified SPE, and 1.0 mM KNO$_3$ with 1.5 mM CuSO$_4$ 0.1 M Na$_2$SO$_4$ pH 3.0 at CuNPs/SPE, respectively. The CuNPs (Figure 4b) are shown reduction peak at 0.94 V, however when comparison with the reduction peak of nitrate shown at 0.91 V, its peak shaper and higher current peak than CuSO$_4$ peak. This result explained to the function of CuNPs as a catalyst for electrochemical reaction of nitrate.
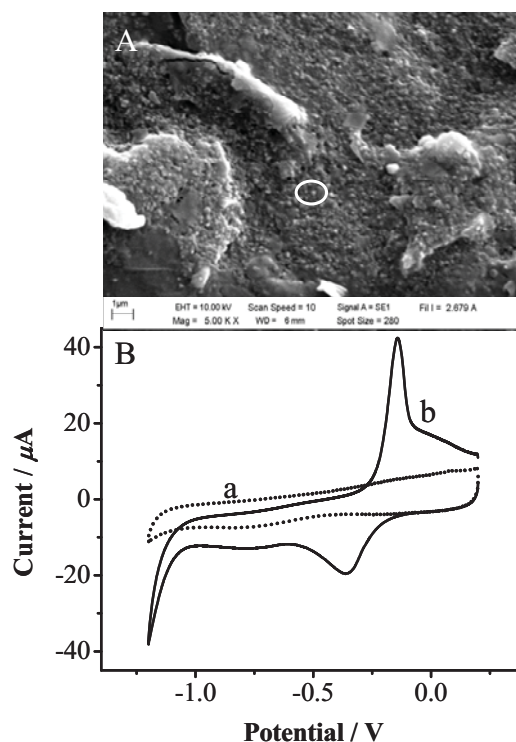

Figure 3. (A) Scanning electron micrographs of CuNPs modified SPE by a cycle of cyclic voltammetric. (B) Cyclic voltammograms of background (a) and CuSO$_4$ (b).
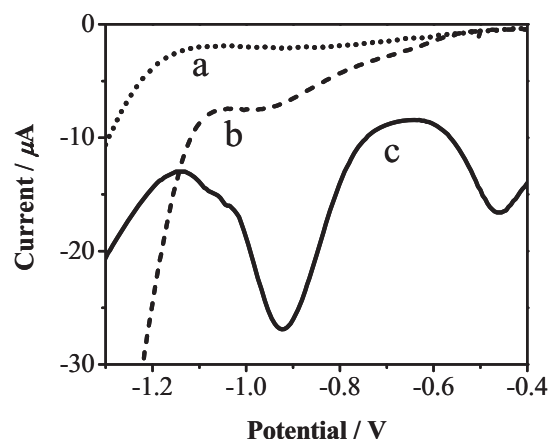

Figure 4. Square wave voltammograms of electrolyte ((a); 0.1 M NaSO$_4$ pH 3.0), added CuSO$_4$ solution (b), and 1 mM KNO$_3$ solution (c) at SPE.

In Figure 5, the linear calibration curve was obtained in range of 10 to 1500 μM and 3.4 μM of

detection limit. The excellent sensitivity was received 27.79 $\mu A/\mu M$ at R^2 = 0.9964. Comparison to Aravamudhan group [4], they prepared micro-fluidic nitrate-selective sensor based on doped-polypyrrole nanowires. Their sensor gave linear range from 10 μM to 1 mM, with a sensitivity of 1.17–1.65 nA/μM and detection limit of 4.5 μM. The detection limit of this work was obtained lower than determined nitrate by in situ electrodeposition of a renewable copper layer onto a copper electrode (11 μM) [6]. The sensitivity was also compared with capillary electrophoresis microsystem coupled with a microchip and a copper-(3-mercaptopropyl) trimethoxysilane complexmodified carbon paste electrode for nitrate analysis as 0.065 ± 0.002 nA/μM [7] lower than this work. The linear range of nitrate determination was obtained 0.1-2.5 mM [6], 0.25-120 μM [7], and 0.617-50 μM [8].
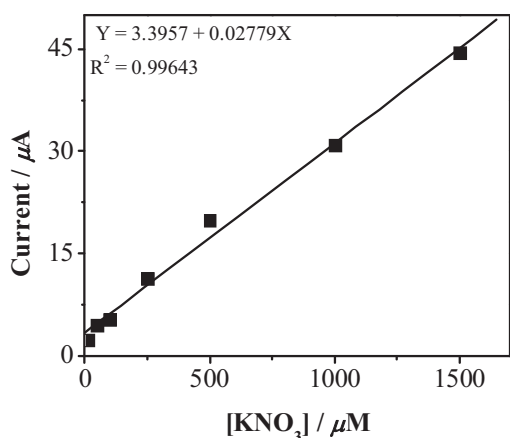

Figure 5. Calibration curve of KNO_3 in 0.1 M $NaSO_4$ pH 3.0 with 1.5 mM $CuSO_4$ solution at CuNPs/SPE. The linear range was between 10 to 1500 μM.

Conclusions

The SPE of different designs was fabricated for a nitrate sensor with $CuSO_4$ solution using CuNPs modified SPE. This nitrate sensor showed the good characters such as low detection limit, high sensitivity, and wide linear range. This proposed method will be applied to determine the contents of nitrate in drinking water.

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