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A LOW COST OF NITRITE DETERMINATION BY SQUARE WAVE VOLTAMETRIC METHOD USING A GOLD NANOPARTICLE MODIFIED PENCIL CARBON ELECTRODE

Nootjarin Inngam¹, Kulwadee Pinwattana¹, Tanin Tangkuaram², Anchana Preechaworapun^{1,*}

¹ Program of Chemistry, Faculty of Science and Technology, Pibulsongkram Rajabhat University, Phitsanulok, Thailand 65000
² Department of Chemistry, Faculty of Science, Maejo University, Chiang Mai, Thailand 50290

*Author for correspondence ; E-Mail: anchana.ph@yahoo.com, Tel./Fax. +66 55 267106

Abstract: A sensitive and stable nitrite sensor was developed using Au nanoparticles modified a pencil carbon electrode. The scanning electron microscopy (SEM) and electrochemical characterization confirmed the electrodeposited Au nanoparticles on a pencil carbon electrode. The Au nanoparticles modified pencil carbon electrode providing an excellent catalytic ability for NO_2^- determination exhibited the oxidation peak at 0.85 V by square wave voltammetry. The nitrite sensor gave a low detection limit of 30 μM and a long linearity range between 100 μM – 2.5 mM with a high sensitivity of 7.60 $\mu\text{A mM}^{-1}$.

1. Introduction

Voltammetry has been used widely in the investigation of redox reactions and the analysis of organic or inorganic substances using various available electrodes. Among these, the pencil carbon electrode (PCE) provides a lot of advantages such as high electrochemical reactivity, commercial availability, good mechanical rigidity, disposable, low costs, low technology and easy modification. Additionally it was reported that pencil electrodes offer a renewal surface, which is simpler and faster than polishing procedures, the results is reproducible for the individual surfaces. It can also be miniaturized. Therefore PCEs have been increasingly utilized in many different electroanalytical applications recently, such as, application to determine of trace metals[1], DNA[2,3,4,5,6,7], sulfide[8], immunoassay and some drugs in pharmaceutical formulations[9,10,11]. The PCE, when combined with a more highly sensitive and accurate voltammetric technique such as square-wave or differential pulse voltammetry, can lead to an attractive trace analysis technique.

Nitrite is a precursor in the formation of nitrosamines, many of which have been shown as potent carcinogens in human bodies. It is an important contaminant in environment, beverages, and food products as a preservative. Thus, its determination is very important for environmental reason and for public health. In recent year, many methods have been developed such as spectrophotometry [12,13,14], ion chromatography, gas chromatography-mass spectrometry [15], chemiluminescence, and capillary electrophoresis [16,17,18]. The alternative electrochemical devices providing the potential of low cost, portability, rapid

response and simple use are attractive for nitrite determination.

In this research, the higher sensitivity of nitrite determination can be achieved by using AuNPs electrodeposition as electrocatalyst in phosphate buffer solution

2. Materials and Methods

2.1 Reagents

Potassium nitrite was obtained Carlo Erba Reagents, France. Hydrochloric acid 37%, copper(II)sulfate pentahydrate and sodium sulfate were purchased Merck (Germany). Potassium chloride was from Australia. Potassium hexacyanoferrate(II)trihydrate and potassium hexacyanoferrate(III) were obtained Riedel-dehaen. Sulfuric acid 98% was purchased from Lab scan analytical science Thailand. Deionized water was obtained from a Milli-Q-gradient system (Millipore, $R_z \geq 18.2 \text{ M}\Omega \text{ cm}$).

2.2 Apparatus and electrochemical measurements

Electrochemical measurements were conducted using an Electrochemical Analyzer (Model 1230A, CH Instruments) at room temperature. Pencil rods (2B), id. 0.5 mm and length 5 cm, were purchased from STAEDTLER, Germany. A conventional three electrode system consisted of pencil carbon, a Ag/AgCl (3 M) and a platinum wire as working, reference, and auxiliary electrodes, respectively.

2.3 Preparation of the AuNPs on a pencil electrode

The preparation of PCE was carried out as described earlier [11]. In brief, a mechanical pencil 0.5 (Pilot, Japan), was used as a holder for pencil lead. All leads had a total length of 60 mm and a diameter of 0.5 mm. Electrical contact to the lead was achieved by wrapping a metallic wire around the metallic part of the pencil. 10 mm of lead was immersed in solution for the measurement. The length of 10 mm of lead corresponds to an active electrode area of 15.9 mm².

The AuNPs-modified pencil carbon (AuNPs/PC) electrode was prepared by electrodeposition of cycling the potential between -0.6 to 1.2 V for 1 cycle at scan rate of 50 mV s⁻¹. The deposition solution contained 10 ppm of HAuCl₄ in 0.1 M HCl/0.1 M KCl. The AuNPs modified indium-tin oxide (ITO) in the same condition was characterized by the Scanning Electron Microscope (SEM; LEO, Model 1400VP)

3. Results and Discussion

The characterization of AuNPs/ITO surface was shown in Figure 1. Figure 1A shows a typical SEM image of bare ITO surface and the AuNPs/ITO surface in Figure 1B. The surface of bare ITO is clear while the surface of AuNPs/ITO deposited by AuNPs shows the spotted dispersion on the ITO surface. The average size of AuNPs is 100 nm.

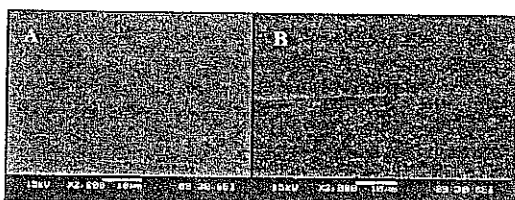


Figure 1. SEM image of (A) Indium-Tin Oxide (ITO) and (B) ITO after AuNPs electrodeposition by cyclic voltammetry.

The electrochemical behavior of nitrite was investigated at the AuNPs/PCE in 0.05 M PBS buffer solution from pH 2.0 to 9.0 by cyclic voltammetry (Figure 2). It was found that increasing pH effected the oxidation peak to higher potential. The best respond was received at pH 4.0 (Figure 2C). Au provides the oxidation peak at 1.25 V. When compared with the oxidation peak of nitrite shown at 0.85 V, it was found that the oxidation peak of nitrite was not overlape with the Au oxidation peak. This result can be explained that AuNPs function as an electrocatalysts for nitrite oxidation. The From these result, pH 4.0 was used for the rest of experiments.

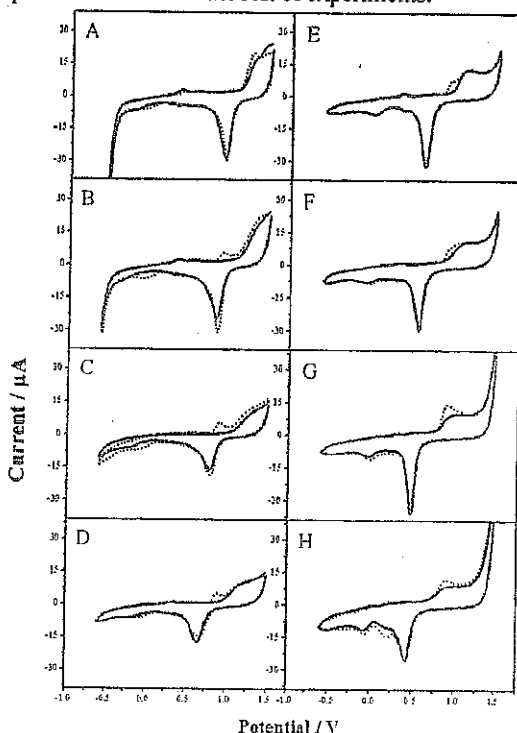


Figure 2. Cyclic voltammograms of 0 mM (solid lines) and 1 mM (dotted lines) Nitrite in pH 2(A), pH 3(B), pH 4(C), pH 5(D), pH 6(E), pH 7(F), pH 8(G), and pH 9(H) 0.05 M PBS buffer using the AuNPs modified pencil carbon electrodes at 50 mV/s

AuNPs were electrodeposited on pencil carbon electroed by cyclic voltammetry at 1 cycle and 10 cycles. The electrodeposited AuNPs voltammograms are shown in Figure 3A. Figure 3B shows the square wave voltammograms of 1.5 mM nitrite in 0.05 M PBS buffer (pH 4.0) at bare PCE and AuNPs electrodeposition on PCE for a cycle and 10 cycles. It was found that both of electrodeposition provide the similar anodic current and higher than 2 times anodic current compare to the bare PCE, so a cycle was selected for nitrite determination.

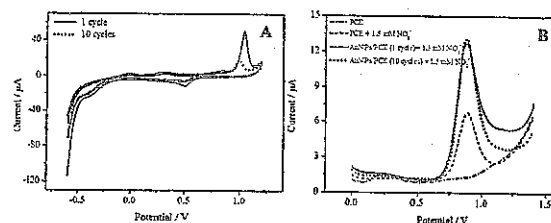


Figure 3 (A) Cyclic voltammograms of 10 ppm Au deposited on pencil carbon electrodes at 1 cycle and 10 cycles using scan rate of 0.05 V/s. (B) Square wave voltammograms of 1.5 mM Nitrite in 0.05 PBS buffer pH 4.0

The electrocatalytic mechanism of AuNPs toward the oxidation of nitrite is;



Figure 4 shows the calibration curve of various nitrite concentrations (0 to 2.5 mM) obtained from square wave voltammetry. The linear range is found to be between 100 μM to 2.5 mM, and the detection limit (S/N=3) is 30 μM. The excellent sensitivity of 7.60 μA/mM was received at $R^2 = 0.99915$. The detection limit and sensitivity are lower and higher than the immobilization of nanometer-sized gold colloid attached to an ethylenediamine monolayer modified electrochemically pretreated glassy carbon electrode, respectively [19].

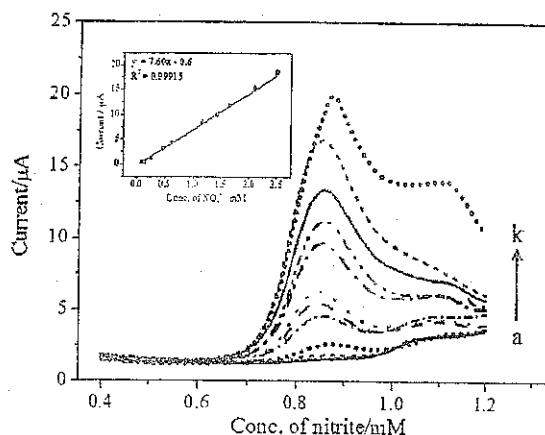


Figure 4. Square wave voltammograms of various nitrite concentrations (0 to 2.5 mM (a to k)). The inset shows a calibration plot of oxidation peak current versus nitrite concentration using square wave voltammetry.

4. Conclusions

AuNPs modified pencil carbon electrode for nitrite determination was investigated in PBS buffer solution. The proposed sensor was used by square wave voltametric method. The linearity between 0.1 – 2.5 mM was received. The sensitivity of 7.60 $\mu\text{A}/\text{mM}$ and the detection limit of 30 μM were obtained by the proposed electrode.

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