

A DIFFERENTIAL PULSE AMPEROMETRIC NITRITE DETERMINATION ON AuNPs MODIFIED PENCIL CARBON ELECTRODE

Suthasinee Thomporn¹, Sarawut Singse¹, Anurak Chitbuengphrao¹, Tanin Tangkuaram², Anchana Preechaworapun^{1*}

¹ Program of Chemistry, Faculty of Science and Technology, Pibulsongkram Rajabhat University, Phitsanulok, 65000, Thailand

² Program of Chemistry, Faculty of Science, Maejo University, Chiang Mai, 50290, Thailand

* E-mail for Corresponding Author; E-mail: anchanaaph@yahoo.com, Tel. +66 5526 7106, Fax. +66 5526 7054

Abstract: A low cost of pencil carbon electrode was developed for nitrite determination by electrodeposited gold nanoparticles on pencil carbon (AuNPs/PC) electrode. The electrocatalytic activity of gold nanoparticles was investigated with respect to the oxidation of nitrite. The scanning electron microscopy (SEM) and cyclic voltammetry were characterized for confirm the electrodeposition of gold nanoparticles on a pencil carbon electrode. The AuNPs/PC electrode was exhibited the high sensitivity and reproducibility for the electrochemical oxidation of nitrite by differential pulse amperometry. Furthermore, it was provided a long linear dependence on nitrite concentration in the range 0.001 to 3 mM.

1. Introduction

Nitrite (NO_2^-) is a well-known alarming pollutant and a human health-hazard in our daily life because it is an important contamination in environment, beverages, and food products as a preservative. It may combine in the digestive tract with amines and amides to produce highly carcinogenic N-nitrosamine compound. Considering the potential toxicity of nitrite, the sensitive determination of it is very important for environmental protection and public health. Thus, its determination is very important for environmental reason and for public health. In recent year, many methods have been developed for quantitative determination of nitrite, such as spectrophotometry [1,2], ion chromatography [3,4], gas chromatography-mass spectrometry [5], chemiluminescence [6,7], and capillary electrophoresis [8,9]. In compared to other analytical systems, electrochemical methods [10-20] have great advantages such as low cost, portability rapid response, simplicity, high sensitivity and specificity, and low detection limit, so, development of the electrochemical nitrite sensors have been interested.

In this research improved the sensitivity nitrite determination, which can be achieved by 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. Sulfuric acid 98% was purchased Lapsan analytical science Thailand. Deionized water was from a Milli-Q-gradient system (Millipore, $R \geq 18.2 \text{ M}\Omega \text{ cm}$).

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 KCl) and a stainless steel 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. In brief, a mechanical pencil 0.5 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. A total of 10 mm of lead was immersed in solution per measurement. Such length corresponds to an active electrode area of 15.9 mm^2 .

The AuNPs-modified pencil carbon (AuNPs/PC) electrode was prepared by electrodeposition of cycling the potential between -0.6 to 1.2 V for 10 cycles at scan rate 50 mV s^{-1} . The deposition solution contained 10 ppm of HAuCl_4 in 0.1 M HCl/0.1 M KCl. The AuNPs modified PCE in the same condition was characterized by the Scanning Electron Microscope (SEM; LEO, Model 1400VP).

3. Results and Discussion

3.1. Morphological characterization of the electrodes

Figure 1 (A), and (B) illustrates the SEM images of bare PC, and AuNPs/PC electrodes, respectively. Figure 1 (B) reveals the typical highly spotted AuNPs dispersion on the PC surface. The average size of AuNPs is 100 nm.

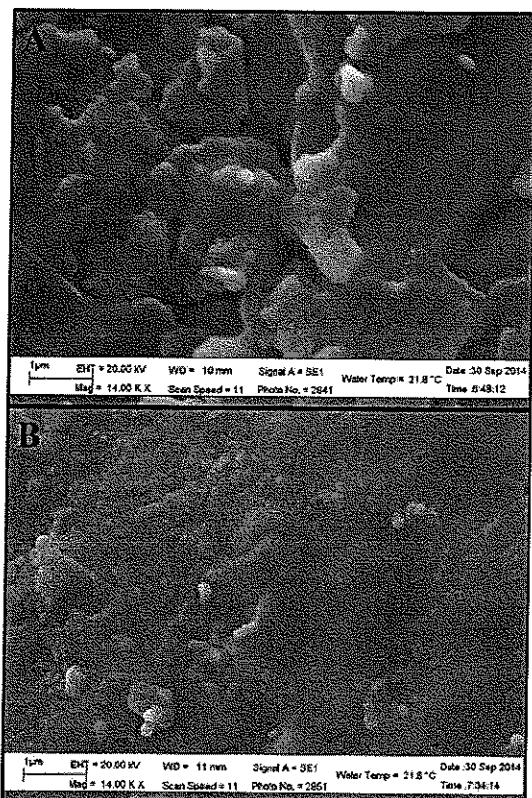


Figure 1. SEM image of (A) bare PCE and (B) PCE after AuNPs electrodeposition by cyclic voltammetry at five cycles.

3.2 Electrochemical oxidation of nitrite on AuNPs/PCE

AuNPs were synthesized by electrodeposited on pencil carbon electrode by cyclic voltammetry. To evaluate the catalytic ability of the Au nanoparticle modified PC electrode, CV experiments were performed in 0.1 M Na_2SO_4 containing various concentrations of nitrite. Figure 2 shows the CVs of a AuNPs/PCE in 0.1 M Na_2SO_4 containing 0–4.1 mM nitrite, at a scan rate of 50 mV s^{-1} . It is reasonable to suggest that the oxidation peak at about 1.0 V is caused by the oxidation of nitrite at the AuNPs/PCE because its peak current increases with increasing the concentration of nitrite. The insert (Figure 2) shows the catalytic current is proportional to concentration. The plot of catalytic current vs. nitrite concentration is linear in the concentration range of 1.4–4.1 mM, which fits the equation $Y = 38.21X - 9$ with a correlation coefficient $R^2 = 0.99994$ using a AuNPs/PCE.

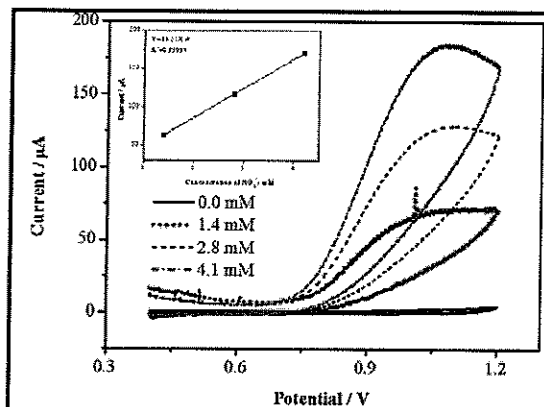


Figure 2. Cyclic voltammograms of 0, 1.4, 2.8, and 4.1 mM nitrite in 0.1 M Na_2SO_4 using a AuNPs/PCE at scan rate 50 mV/s . The inserts, linear plot of 1.4–4.1 mM nitrite of a AuNPs/PCE.

2.3 Optimization of parameters of the sensor

In order to get the optimal conditions for achieving the highest anodic current nitrite determination by the various number of scan for electrodeposition, and pulse potentials (E1 and E2) in differential pulse amperometry were investigated in detail. The effect of the electrodeposition cycles is illustrated in Figure 3. The anodic current peak for nitrite increased with the increasing of electrodeposition until 5 cycles. This is probably because the surface area first increased with the AuNPs dispersion loading, but then decreased with the increase of the sheet agglomeration which blocked the electrical conductivity. Thus, 5-cycles scan was the optimal condition for AuNPs loading. The wave shape of all peak is similar, but the current of peak high at containing nitrite using AuNPs/PC electrode is higher than a bare PC electrode (0 cycles).

The differential pulse amperometry (DPA) was used quantitative nitrite determination. The DPA, a sequential two-step sampling is executed at two different potentials (E1 and E2). Differential current signal of the duplex sampling events is recorded that functions as time domain. Figure 4, effect of potential of pulse E1 and E2 was investigated by fixing pulse E1=1.0 V for finding pulse E2 and fixing pulse E2=0.6 V for finding pulse E1. The optimized pulse E1 and E2 were received 1.3 and 0.6 V, respectively.

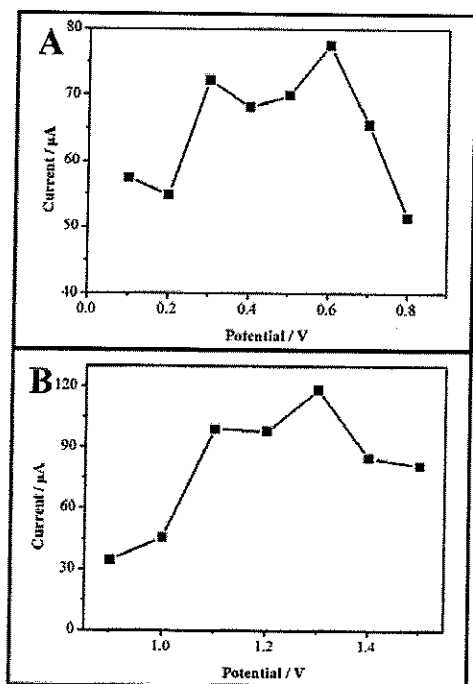


Figure 3. Cyclic voltammograms of 4.1 mM Nitrite in 0.1 M Na_2SO_4 using various cycles of AuNPs cyclic voltametric electrodeposition modified pencil carbon electrodes at 50 mV/s. (B) The relationship between anodic current of 4.1 mM nitrite vs. scan of electrodeposition.

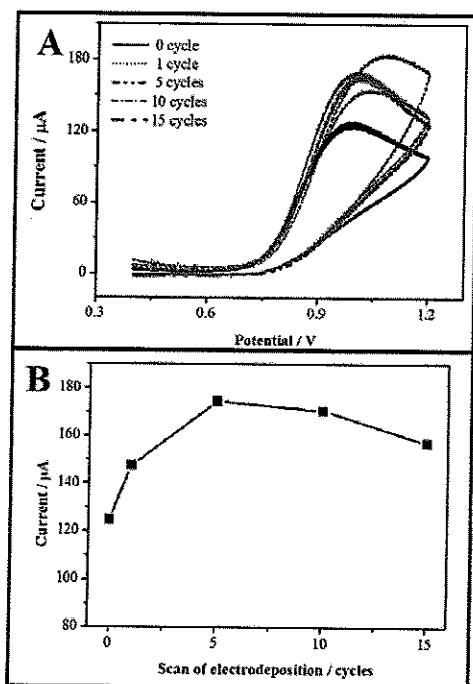


Figure 4. Average anodic current of 0.9 mM ($n=3$) nitrite by DPA at (A) various pulse E2 and (B) various pulse E1 in 0.1 M Na_2SO_4 using AuNPs/PCE.

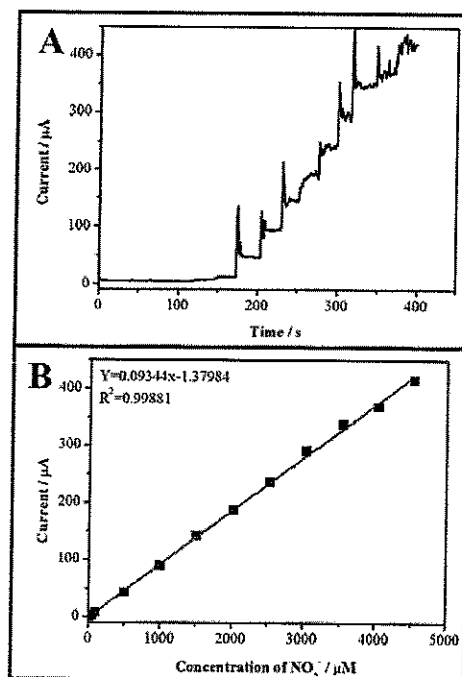


Figure 5. (A) Differential pulse amperogram of nitrite determination at pulse $E_1=1.3$ V and pulse $E_2=0.6$ V using AuNPs/PCE. (B) The linearity of nitrite analysis.

The relationship between the differential pulse amperometric current and the concentration of nitrite was investigated in the range 0.02–4.5 mM (Figure 5). Using the optimized conditions previously reported, a linear response ($y=0.09344x-1.37984$, $R^2=0.999$) was obtained at excellent sensitivity 93.44 $\mu\text{A}/\text{mM}$. The detection limit (3SD) was estimated as 5 μM .

4. Conclusions

In conclusion, we here presented a AuNPs modified PC electrode for electrochemical nitrite determination using DPA. The AuNPs can strongly catalyze the oxidation of nitrite in a 0.1 M Na_2SO_4 . The modified electrode provides a sensitive method for the DPA detection of nitrite. It is expected the AuNPs/PCE will be a promising material in fabricating nitrite sensors.

Acknowledgements

Anchana Preechaworapun acknowledges The Research and Development Institute, Faculty of Science and Technology of Pibulsongkram Rajabhat University.

References

- [1] Pourreza, N., Fa'hi, M.R. and Hatami, A., 2012, *Microchem. J.*, 104, 22.
- [2] Senra-Ferreiro, S., Pena-Pereira, F., Lavilla, I. and Bendicho, C., 2010, *Anal. Chim. Acta*, 668, 195.
- [3] Connolly, D. and Paull, B., *Anal. Chim. Acta*, 441, 53.
- [4] Wang, N., Wang, R.Q. and Zhu, Y., 2012, *J. Hazard M.*, 235–236, 123.

- [5] Tsikas, D., Böger, R.H., Bode-Böger, S.M., Gutzki, F.M. and Frölich, J.C., 1994, *J. Chrom. B Biomed. Sci. Appl.*, 661, 185.
- [6] He, D., Zhang, Z., Huang, Y. and Hu, Y., 2007, *Food Chem.*, 101, 667.
- [7] Zhang, H., Zhang, L., Lu, C., Zhao, L. and Zheng, Z., 2012, *Spectrochim. Acta A.*, 85, 217.
- [8] Della Betta, F., Vitali, L., Fett, R. and Costa, A.C.O., 2014, *Talanta*, 122, 23.
- [9] Öztekin, N., Nutku, M.S. and Erim, F.B., 2002, *Food Chem.*, 76, 103.
- [10] Ait Ramdane-Terbouche, C., Terbouche, A., Djebbar, S. and Hauchard, D., 2014, *Talanta*, 119, 214.
- [11] Azad, U.P., Turlapati, S., Rastogi, P.K. and Ganesan, V., 2014, *Electrochim. Acta*, 127, 193.
- [12] Canbay, E., Şahin, B., Kıran, M. and Akyilmaz, E., 2015, *Bioelectrochemistry*, 101, 126.
- [13] Gholivand, M.-B., Jalalvand, A.R. and Goicoechea, H.C., 2014, *Mater. Sci. Eng. C*, 40, 109.
- [14] Li, Y., Wang, H., Liu, X., Guo, L., Ji, X., Wang, L., Tian, D. and Yang, X., 2014, *J. Electroanal. Chem.*, 719, 35.
- [15] Liu, Y., Zhou, J., Gong, J., Wu, W.-P., Bao, N., Pan, Z.-Q. and Gu, H.-Y., 2013, *Electrochim. Acta*, 111, 876.
- [16] Ojani, R., Raoof, J.-B. and Zamani, S., 2013, *Appl. Surf. Sci.*, 271, 98.
- [17] Palanisamy, S., Karuppiah, C., Chen, S.-M. and Periakaruppan, P., 2014, *J. Electroanal. Chem.*, 727, 34.
- [18] Unnikrishnan, B., Ru, P.-L., Chen, S.-M. and Mani, V., 2013, *Sensor Actuat. B-Chem.*, 177, 887.
- [19] Winther-Jensen, O., Winther-Jensen, B., 2014, *Electrochem. Com.*, 43, 98.
- [20] Zhang, D., Fang, Y., Miao, Z., Ma, M., Du, X., Takahashi, S., Anzai, J.-i. and Chen, Q., 2013, *Electrochim. Acta*, 107, 656.