

Development of electrochemical sensor based on graphene nanocomposite for determination of β -agonists

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Abstract :

This study reports the development of a reduced graphene oxide/iron oxide nanocomposite modified screen-printed electrode (rGO-Fe₃O₄/MSPE) as a novel system for the preparation of electrochemical sensing for β -agonists determination. To fabricate the sensor, Fe₃O₄ was attached on the rGO surface by covalent linking to obtain rGO-Fe₃O₄ nanocomposite. The nanocomposite was dropped on the surface of SPE to obtain nanocomposite film forming on the electrode. Adsorption of Fe₃O₄ on rGO and structural property were characterized by x-ray absorption near-edge structure (XANES) technique. The electrocatalytic response to β -agonists and the performance of the sensor were investigated by means of differential pulse voltammetry (DPV). The proposed sensor exhibited great electrocatalytic activity and fast response to β -agonists. The linear relation in the range from 1 μ M to 20 μ M with a detection limit of 75 nM based on S/N = 3. The sensor exhibited a sensitivity of 116.4 μ A/mM

Key words: β -agonists, sensor, graphene, nanocomposite, electrochemistry.

Introduction

Graphene possesses many unique features such as large surface area, good electrical, thermal, and mechanical properties that make them has been widely employed for electrochemical analysis [1-2]. In addition, varieties of hybrid materials between graphene and other materials with new functions are promising for utilization in various applications. The integration of iron oxide and graphene oxide may offer a hybrid nanocomposite with synergistic properties improving the catalytic activity and provide more surface area and good biocompatibility.

β -agonists such as ractopamine (RAC) is used illegally as feed additive for growth promotion in farm animals, and such practices can lead to potential risks to human health [3]. Consequently, RAC is an illegal growth promoter for swine and is included in the prohibited list of World Anti-Doping Agency. In this work, the potential applicability of employing rGO-Fe₃O₄ nanocomposite as a potential candidate for the construction of

electrochemical sensor for leanness-enhancing agent was proposed.

Experiment

The Fe₃O₄ NPs was immobilized on GO using EDC and NHS as coupling agents by the formation of an amide link between the amino group of Fe₃O₄ NPs and the carboxyl group of GO. An rGO-Fe₃O₄ based on glucose reduction was prepared. . Finally, the 5 μ l rGO-Fe₃O₄ nanocomposite solution was dropped onto the MSPE surface.

XANES prepared samples were collected at Synchrotron Light Research Institute, Thailand. The Fe K-edge XANES were measured at BL2.2: TRXAS using Si (111) and NMOS detector [4].

All electrochemical experiments were performed with a potentiostat (Metrohm Autolab PGSTAT302N, Ecochemie, Netherlands) in a conventional three-electrode electrochemical cell using a screen-printed electrode (SPE) as a working electrode, a platinum electrode as a

counter electrode and an Ag/AgCl saturated KCl as the reference electrode.

Results and Discussion

The structural property of magnetic material in graphene nanocomposite was investigated through Fe K-edge XANES spectra (Fig. 1). At the energy between 7150-7170 eV, GO- Fe_3O_4 exhibited small pre-edge and a broad white-line peaks. These characteristic features suggested the combination of the iron oxide compounds. Linear combination fitting (LCF) analysis was used to decompose XANES spectrum. The predictors of standard iron-oxide compounds and iron including FeO , Fe_3O_4 , Fe_2O_3 and Fe foil were used. The combination of model spectra displayed the mixed phase between Fe_2O_3 (80.8%) and Fe_3O_4 (16.2%). The existing of Fe_3O_4 phase in GO- Fe_3O_4 nanocomposite confirmed its magnetic character.

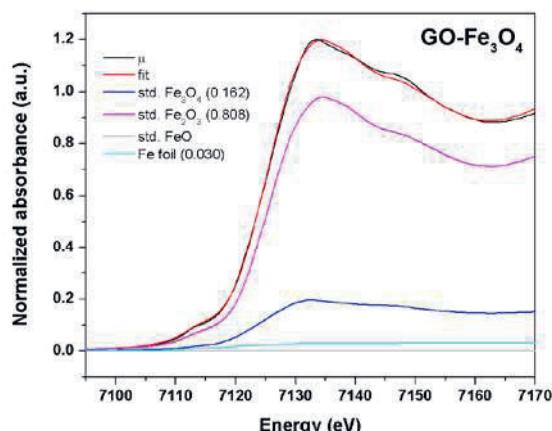


Fig. 1. Linear combination fitting analysis of GO- Fe_3O_4 using FeO , Fe_3O_4 , Fe_2O_3 and Fe foil as the predictors.

The differential pulse voltammetry (DPV) was used for determination of ractopamine with highly sensitive and low detection limit, under the optimum conditions at potential range from 0 to 1.0 V. Fig. 2A shows the typical DPV response for different concentrations of ractopamine from 1 μM to 100 μM . The oxidation peak currents were increases proportional with the increasing of ractopamine concentrations, and the resulting calibration plots are a good linear over the range from 1 μM to 20 μM . The linear regression equations were $I_p(\mu\text{A}) = 0.1164x + 0.3435$ ($R^2 = 0.98$) (Fig. 2B). The detection limit was estimated to be 75 nM at a signal-to-noise ratio (S/N) of 3.

Conclusions

We have successfully employed rGO- Fe_3O_4 nanocomposite modified MSPE as a potential candidate for the construction of RAC sensor. The used of Fe_3O_4 NPs not only increase the

surface area but also have the paramagnetic property which makes them easily manipulated by an external magnetic field to improve stability of the sensor. The nanocomposite shows an excellent electrocatalytic activity, wide range and low detection limit. Moreover, the potential applicability of the nanocomposite modified MSPE as a novel disposable electrochemical sensing platform for β -agonists drugs.

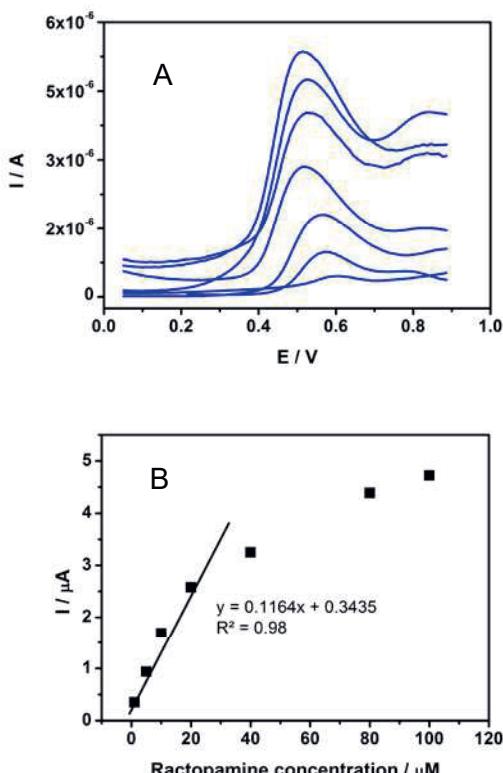


Fig. 2. (A) Differential pulse voltammograms of rGO/ Fe_3O_4 /MSPE at the ractopamine concentration from 1 to 100 μM . (B) The calibration curve between the peak current and ractopamine concentration.

References

- [1] M. J. Allen, V. C. Tung and R. B. Kaner, Honeycomb Carbon: A Review of Graphene, *Chemical Reviews* 110, 132–145 (2010).
- [2] Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay and Y. Lin, Graphene Based Electrochemical Sensors and Biosensors: A Review, *Electroanalysis* 22, 1027–1036 (2010).
- [3] M. X. Xu, X. L. Qian, K. Zhao, A. P. Deng, J. G. Li, Flow injection chemiluminescent competitive immunoassay for the α -adrenergic agonist salbutamol using carboxylic resin beads and enzymatic amplification, *Sensors and Actuator B: Chemical* 215, 323–329 (2015).
- [4] Y. Poo-arporn, P. Chirawatkul, W. Saengsui, S. Chotiwat, S. Kityakarn, S. Klinkhieo, J. Hormes, P. Songsiririthigul, Time-resolved XAS (Bonn-SUT-SLRI) beamline at SLRI, *Journal of Synchrotron Radiation* 19, 937–943 (2012).