

Deposition of ZnO Nanoparticles on MWCNTs for Glucose Oxidase Direct Electrochemistry

M. Jafari¹, A.A. Khodadadi¹, Y. Mortazavi², H. Ghorchian³

¹School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran, Mortazav@ut.ac.ir

²Nanoelectronics Centre of Excellence, University of Tehran, Tehran, Iran

³Institute of Biochemistry & Biophysics, University of Tehran, Iran

Abstract

ZnO nanoparticles on multiwall carbon nanotubes (MWCNTs) were prepared by a microwave assisted hydrothermal method, modified by ionic liquid (IL) and used for stabilization of glucose oxidase and its direct electrochemistry. The structure and composition of ZnO/MWCNTs sample was characterized by x-ray diffraction. Cyclic voltammetry was used to evaluate the electrochemical performance of ZnO/MWCNTs nanocomposites modified electrode. IL/ZnO/MWCNTs modified electrode was found to have the best performance for immobilization of glucose oxidase.

Key words: Glucose biosensor, carbon nanotubes, ZnO nanoparticles

Introduction

Numerous efforts have been focused on the development of new materials to design electrochemical biosensors. Among these materials, CNTs have been extensively used in electrochemical biosensor conformation [1]. Recently most of the researches in the field have intended to modify CNTs with other nanomaterials such as metal and metal oxide particles. These modified composite materials possess the properties of ingredients, or even with a synergistic effect. Electrochemical sensors based on metal oxide- modified electrodes have been used to analyze biomolecules. However, they have the disadvantage of poor electrical conductivity that limits their applications. To modify this property the electroactive metal oxides are loaded onto CNTs. CNT can lead to a better dispersion of oxide nanoparticles beside, it can improve transferring of electrons in order to straight conducting pathway [2].

ZnO is a biocompatible with a high isoelectric point (IEP) of about 9.5 which make it suitable for absorption of low IEP proteins such as glucose oxidase (GOx, IEP=4.2). In this work, microwave-assisted aqueous solution method was used to prepare GOx/ZnO/MWCNTs to be used for fabrication of a glucose biosensor.

Experimental

Multi walled carbon nanotubes (MWCNTs) (10-20 nm diameter, 10-30 μ m length with >95% purity) were purchased from Neutrino Co.

KH₂PO₄, K₂HPO₄, NaOH, and Zn(Ac)₂.H₂O were purchased from Merck, while GOx (EC 1.1.3.4, Type X-S from *Aspergillus niger*) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) were purchased from Sigma-Aldrich. All other reagents were of analytical grade. Deionized water was used for preparation of all aqueous solutions. MWCNTs were functionalized by acid treatment, dissolved in deionized water under ultrasonic agitation for 30 min and after adding Zn(Ac)₂.2H₂O and NaOH to adjust pH, the solution was placed in the microwave oven [3]. 3 μ L of ZnO/MWCNTs (2 mg/mL dispersed in DMF) was dropped on the electrode surface. After drying it was immersed in the ionic liquid (IL) and GOx solution (5 mg/mL dissolved in PBS, pH=7, 0.05 M) for 9 and 12 h respectively and kept at 4°C. After each immersion, the electrode was rinsed with water to remove the weakly adsorbed IL and GOx.

Results

XRD pattern of ZnO/MWCNTs is shown in Fig. 1. The peak at 30.06° belongs to graphitic structure of MWCNTs and the peaks at 37.04°, 40.13°, 42.34°, 55.77°, 66.77°, 74.48° and 78.96° belong to the ZnO.

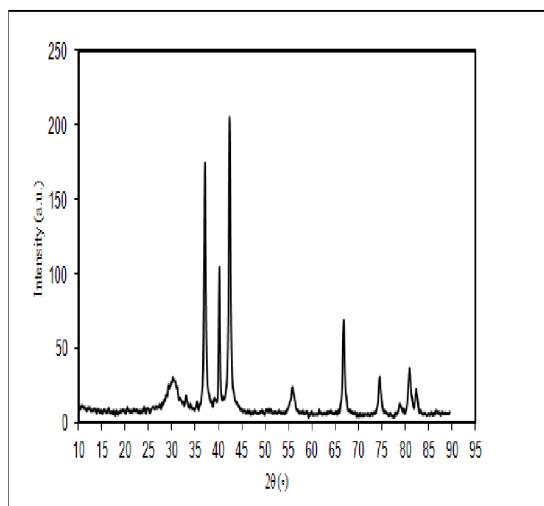


Fig. 1. XRD pattern of ZnO/MWCNTs.

Figure 2 shows cyclic voltametry (CV) of different electrodes in 0.05 M PBS at a scan rate of 50 mV/s. According to this figure electrostatic interaction of ZnO with active center of GOx, generate electrochemical redox peak in potential range from -0.2 to -0.8 V. Addition of IL to the surface of electrode improves this redox peak. The current improvement is due to the high conductivity of the IL. Immobilization of GOx exhibited an increase in current compared to the ZnO/MWCNTs electrode.

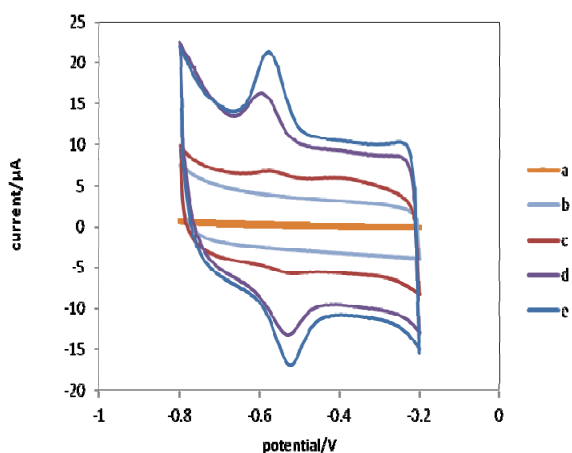


Fig. 2. Cyclic voltammograms of different modified electrodes at 50 mV/s in 0.05 M PBS a: bare b: ZnO/MWCNTs c: GOx/MWCNTs d: GOx/ZnO/MWCNTs e: GOx/IL/ZnO/MWCNTs.

The effect of pH on the potential peak position was investigated and the linear relation was

obtained with correlation of $R^2 = 0.998$ (Fig. 3,4). The slope of linear plot (-0.06 V) shows a good agreement with the theoretical results, i.e. -0.059 V [4]. Figure 3 shows a negative shift in formal potential by increasing the pH. According to Fig. 4 the largest current peak was obtained at pH= 7, thus, it was chosen as the optimum pH.

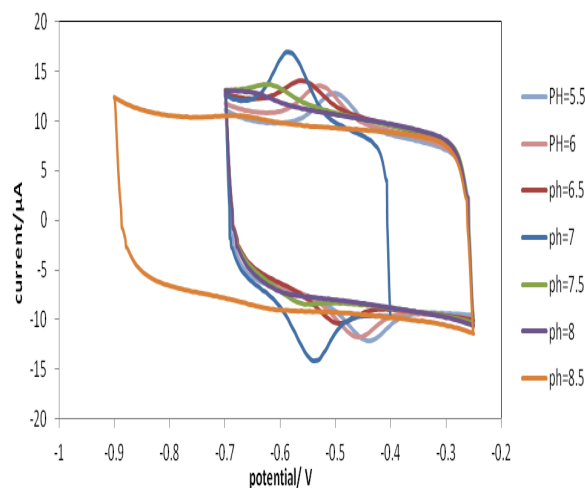


Fig. 3. Cyclic voltammograms of GOx/IL/ZnO/MWCNTs in 0.05 M PBS at pH. 5.5, 6.0, 6.5, 7.0, 7.5, 8.0 and 8.5, from right to left respectively.

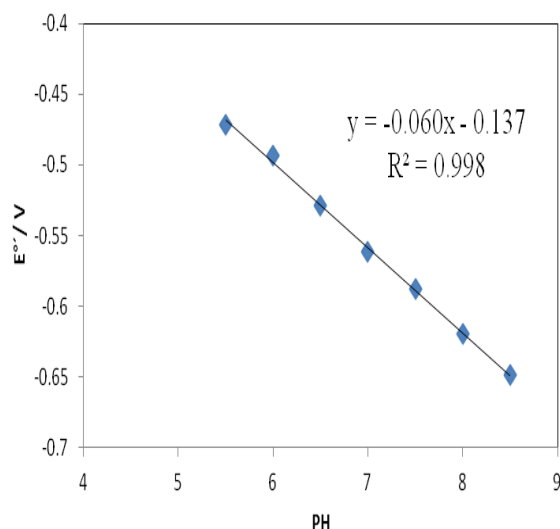


Fig. 4. Plot of E° versus pH.

References

- [1] M.M. Rahman, A. Umarb, K. Sawada, *journal of Sensors and Actuators B* 137, 327–333 (2009); doi: 10.1016/j.snb.2008.10.060
- [2] W. Zhang, B. Xu and L. Jiang, *Journal of Materials Chemistry* 20, 6383–6391(2010); doi: 10.1039/b926341a
- [3] N. Faal Hamedani, A.R. Mahjoub, A. A. Khodadadi, Y. Mortazavi, *journal of Sensors and Actuators B*, 156 737-742 (2011); doi:10.1016/j.snb.2011.02.028
- [4] Nak M. Tasviri, H. A. Rafiee-Pour, H. Ghourchian, M. R. Gholami, *Journal of Molecular Catalysis B: Enzymatic* 68 206–210 (2011); doi:10.1016/j.molcatab.2010.11.005