IN THE NAME OF GOD

Razi University
Faculty of Chemistry
Department of Analytical Chemistry

PhD Thesis

Title of the Thesis

Preparation of Nano Quantum Dots, Carbon dots, Protein Nano Fibers, Metal Nano Particles, Carbon Nano Tubes and Organic Compounds Modified Electrodes and their Application to Determination of Pollutants, Medicines and Biological Compounds

Supervisors:

Prof. Mojtaba Shamsipur

Prof. Mohammad Bagher Gholivand

By:

Nader Amini

March 2014

ACKNOWLEDGMENTS

I would like to thank my supervisors Professor Mojtaba Shamsipur and Professor Mohamad Bagher Gholivand for his strong support and encouragement, and for giving me the opportunity to work on very interesting projects. I would like to thank acknowledge the effort of my committee members. I also like to thank Dr Irandoost, Dr Jallali, Professor Farhadi, Professor Fotouhi, Professor Salimi, and Dr Kashaniane for their guidance and cooperation. To all my family I extend my deepest thanks for their constant support. The first of all is my wife for her encouragement, insipiration and love. I am grateful to all my friends, M.Sc and Ph.D students in analytical chemistry research laboratory. Also, I would like to express my special thanks to, Mr Abdollah Khatoni, Dr Nassri, Dr Roushani, Dr Sageghi, Dr. Rajabi, Dr Pashabadi, Dr Mohammadi, Dr Habibi, Dr Barati, Dr Mandomi, Dr Dehdashtian, Dr Hashemi and Dr Hallaj for their friendship and support.

I extend thanks to Miss chamani; finally the author wishes to express his gratitude to department of chemistry of Razi University.

Nader Amini

Dedicate to the most important persons in my life:

My Wife
&
My Son (KAREN Kocholou)

Abstract

Glycation induced bovine serum albumin in which fibrilogenesis (nano fibrils) followed by fluorescence (Thioflavin T) and also by using dynamic light scattering (DLS) and transmission electron microscopy (TEM) to achieve the size and morphology of fibrils, respectively. A novel electrochemical biosensor for the detection of hydrogen peroxide was proposed based on immobilizing poly (alizarin yellow R)/nano-fibris on glassy carbon electrode. Cyclic voltammetry (CV) and amperommetry were used to confirm the successful stepwise assembly procedure of the biosensor. The electrocatalytical behaviors of the sensor were also investigated by cyclic voltammetry and amperommetry. Results showed that poly (alizarin yellow R)/ nano-fibs exhibited a remarkable electrocatalytic activity for the reduction of hydrogen peroxide under optimal conditions. The electrocatalytic response of the sensor was proportional to the hydrogen peroxide concentration in the range of (1µM to 2.2 mM) with a limit of detection and sensitivity of 0.29µM and 0.024 µA/µM, respectively. The modified electrode showed many advantages such as simple preparation, high sensitivity, low detection of limit, excellent catalytic activity at physiological pH values and short response time.

A novel electrochemical sensor for the detection of hydrazine was proposed based on immobilizing ZnS/Mn quantum dots and multi wall carbon nanotube (MWCNT) on glassy carbon (GC) electrode. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), electrochemical impedance spectroscopy (EIS) , cyclic voltammetry (CV) were used to confirm the successful stepwise assembly procedure of the sensor .The electrocatalytic behaviors of the sensor was also investigated by cyclic voltammetry and differential puls voltammetry .Tests showed that hydrazine by (zinc sulfide doped with manganese) Quantum Dots /multi wall carbon nanotube (ZnS/Mn QDs-MWCNT) exhibited a remarkable electrocatalytic activity for the oxidation of hydrazine. Under optimal conditions, the electrocatalytic response of the sensor was proportional to the hydrazine concentration in the range of 0.09 to 1.2µM. With a detection limit and sensitivity of 28nM and $0.0009\mu A\mu M^{-1}$. This electrode shows many advantages such as simple preparation, high sensitivity, excellent catalytic activity at pH 7 and antifouling property toward hydrazine and its oxidation product.

A novel electrochemical sensor for the detection of l-cysteine was proposed based on immobilizing poly (alizarin yellow R)/carbon quantum dots on glassy carbon electrode. Hydrothermal treatment was used to prepare carbon quantum dots (CQDs). Transmission electron microscopy (TEM) and FTIR were used for characterization of carbon quantum

dots. Electrochemical impedance spectroscopy, cyclic voltammetry (CV) and amperommetry were used to confirm the successful stepwise assembly procedure of the sensor. The electrocatalytic behaviors of the sensor were also investigated by cyclic voltammetry and amperommetry. Results showed that poly (alizarin yellow R)/carbon dots exhibited a remarkable electrocatalytic activity for the oxidation of l-cysteine under optimal conditions. The electrocatalytic response of the sensor was proportional to the l-cysteine concentration in the range of (0.3 to 3.6μM) and (3.9 to 7.2 μM) with a limit of detection and sensitivity of 90 nM and 0.482μA/μM, respectively. The modified electrode show many advantages such as simple preparation, high sensitivity, low detection of limit, excellent catalytic activity at physiological pH values, short response time, and remarkable antifouling property toward l-cysteine and its oxidation product.

For the first time, a nonenzymatic electrochemical sensor for the detection of lysine was proposed based on immobilizing Multi wall carbon nanotube (MWCNT) and Titanium oxide nanoparticles (TiO_2NPs) on glassy carbon (GC) electrode. Scaning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) were used to confirm the successful stepwise assembly procedure of the sensor. The electrocatalytical behaviors of the sensor were also investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The results showed that MWCNT- TiO_2NPs exhibited a remarkable electrocatalytic activity for the oxidation of lysine. Under optimal conditions, the DPV response of the sensor was proportional to the lysine concentration in the range of 500 to 5500 nanomolar with a detection limit and sensitivity of 390 nM and 0.1795$\mu A \mu M^{-1}$. This electrode show many advantages such as simple preparation without using any enzyme special electron transfer mediator or specific reagent, excellent catalytic activity at physiological pH values and antifouling property toward lysine and its oxidation product. Furthermore, the selectivity of the proposed sensor was tested in the presence of some amino acids.

A novel electrochemical sensor for the detection of insulin was proposed based on immobilizing silica nanoparticles/Nafion on glassy carbon electrode. Transmission electron microscopy, electrochemical impedance spectroscopy, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to confirm the successful stepwise assembly procedure of the sensor. The electrocatalytical behaviors of the sensor were also investigated by CV and DPV. Results showed that nano-SiO_2 exhibited a remarkable electrocatalytic activity for the oxidation of insulin under optimal conditions. The electrocatalytic response of the sensor was proportional to the insulin concentration in the

range of 10 to 50 nM with a limit of detection and sensitivity of 3.1 nM and 300 $pAnM^{-1}$, respectively. The modified electrode show many advantages such as simple preparation without using any special electron transfer mediator or specific reagent, high sensitivity, excellent catalytic activity at physiological pH values, short response time, and remarkable antifouling property toward insulin and its oxidation product.

The electrochemical behavior of chloropromazine at glassy carbon (GC) electrode modified with silica nanoparticles/ chloropromazine/ Nafion (SNPs/CPZ/Nf) nanocomposite was investigated. The apparent electron transfer rate constant (ks), transfer coefficient (α) and surface concentration (Γc) were found to be 0.56 s^{-1} ,0.49 and 3.49 × 10^{-7} $molcm^{2-}$, respectively. Cyclic voltammetry technique has been used for stabilization of nanocomposite on the surface GC electrode. Transmission electron microscopy (TEM), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and differential pulse voltammetry techniques were used to confirm the successful stepwise assembly procedure of the electrode. The modified electrode showed electrocatalytic activity toward nitrite electro-reduction at 0.12V. The detection limit (signal to noise) and sensitivity are 7µM and 0.0007µA/µM, respectively. The advantages of the nitrite amperometric detector based on the SNPs/CPZ/Nf nanocomposite GCE are a low detection limit, especially a reduction in low potential, high sensitivity and inherent stability at pH 2, catalytic activity for nitrite reduction antifouling property toward nitrite and its reduction product. Furthermore, the proposed electrode was used for determination of nitrite in food samples.
The electrochemical behavior of chloropromazine as a modifier on the surface of electrode was investigated. The electrochemical properties of chloropromazine in to the silica nanoparticles/ chloropromazine/ nafion (SNPs/CPZ/Nf) nanocomposite at pH 2-10 were investigated at a glassy carbon electrode. Well defined reversible redox couples were observed in acidic solutions and irreversible in alkaline solutions. The (SNPs/CPZ/Nf) nanocomposite modified electrodes were characterized with a transmission electron microscopy (TEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The apparent electron transfer rate constant (k_s), transfer coefficient (α) and the surface concentration (Γc) were determined by cyclic voltammetry and they were about 0.025 s^{-1}, 0.50 and 1.26 × 10^{-6} $molcm^{2-}$, respectively. Moreover, electrocatalytic oxidation of sulfide on the surface of modified electrode was investigated with cyclic voltammetry and amperometry methods at pH=7. The detection limit (signal to noise) and sensitivity are 90nM and 0.0021nA/µM, respectively.The prepared modified electrode

showed several advantages, such as a simple preparation method, high sensitivity, very low detection limits and excellent reproducibility. Moreover, the proposed sensor can be used for sulfide analysis in water samples.

Table of contents

Title **Page**

List of Figures

Figures **Page**