

***JN 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**

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**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-fibrils on glassy carbon electrode. Cyclic voltammetry (CV) and amperometry were used to confirm the successful stepwise assembly procedure of the biosensor. The electrocatalytic behaviors of the sensor were also investigated by cyclic voltammetry and amperometry. Results showed that poly (alizarin yellow R)/ nano-fibrils 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 (1  $\mu$ M to 2.2 mM) with a limit of detection and sensitivity of 0.29  $\mu$ M and 0.024  $\mu$ A/ $\mu$ M, 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 pulsed 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 1.2  $\mu$ M. With a detection limit and sensitivity of 28 nM and 0.0009  $\mu$ A/ $\mu$ M<sup>-1</sup> . 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 amperometry 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 amperometry. 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 3.6 $\mu$ M) and (3.9 to 7.2  $\mu$ M) with a limit of detection and sensitivity of 90 nM and 0.482 $\mu$ A/ $\mu$ M, 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<sub>2</sub>NPs) on glassy carbon (GC) electrode. Scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) were used to confirm the successful stepwise assembly procedure of the sensor. The electrocatalytic behaviors of the sensor were also investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The results showed that MWCNT- TiO<sub>2</sub>NPs 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<sup>-1</sup>. 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 electrocatalytic behaviors of the sensor were also investigated by CV and DPV. Results showed that nano-SiO<sub>2</sub> 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<sup>-1</sup>, 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 chlorpromazine at glassy carbon (GC) electrode modified with silica nanoparticles/ chlorpromazine/ Nafion (SNPs/CPZ/Nf) nanocomposite was investigated. The apparent electron transfer rate constant ( $k_s$ ), transfer coefficient ( $\alpha$ ) and surface concentration ( $\Gamma_c$ ) were found to be 0.56 s<sup>-1</sup>, 0.49 and  $3.49 \times 10^{-7}$  molcm<sup>-2</sup>, 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 7 $\mu$ M and 0.0007 $\mu$ A/ $\mu$ M, 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 chlorpromazine as a modifier on the surface of electrode was investigated. The electrochemical properties of chlorpromazine in to the silica nanoparticles/ chlorpromazine/ 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 ( $\alpha$ ) and the surface concentration ( $\Gamma_c$ ) were determined by cyclic voltammetry and they were about 0.025 s<sup>-1</sup>, 0.50 and  $1.26 \times 10^{-6}$  molcm<sup>-2</sup>, 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/ $\mu$ M, 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.



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