CHAPTER I

INTRODUCTION

Electrochemical techniques such as amperometric and potentiometric detection are alternative methods that are widely used in the analytical application because they are easy to operate, fast and inexpensive. The heart of these methods is the working electrode. Hence, the searching and synthesis of the new electrode material is necessary. Boron-doped diamond thin films (BDD) have been emerged as a new electrode material in the various fields of electrochemistry, especially in the electroanalysis applications due to its unique properties including wide working potential window in aqueous solution, stable and low background current, slight adsorption of polar molecules and long term stability of the response [1]. However, researchers have tried to modify the diamond surface to extend the analytical capabilities of a diamond electrode. The simplest technique involves the treatment with the oxidizing acid solution such as sulfuric acid or alkaline solution such as potassium hydroxide to convert the hydrogen termination surface to oxygen termination. Diamond electrodes have been found to be more sensitive after an electrochemically oxidizing pretreatment. They were retained the excellent properties of the as-deposited diamond electrode. Anodized diamond electrode can be used to determine uric acid in the presence of ascorbic acid [2] chlorophenol [3], and homocysteine [4]. These anodized electrodes have exhibited a number of attractive properties such as excellent stability and high reproducibility.

BDD was found completely inactive for the catalytic reaction. However, it is found that the dispersion of metallic particles within an organic polymer or an inert surface resulting in drastic increase of the catalytic activity and sensitivity of the electrode. It was found that the dispersed particles behave like microelectrode array. Therefore, metal modification should resolve the problem of the catalytic properties of the bare diamond electrode. A stable, inert electrode with low background current such as BDD film would be the best choice for the deposition of metal catalysts. Preparation of some metal-modified electrodes for electrochemical deposition can be easily carried out by using chemical precipitation and electrodepositon or ion

implantation into a material. The advantages of BDD as the support of the metal catalyst are the following [5]: (i) it does not form a macroscopic oxide layer on the surface when put in contact with an aqueous solution, (ii) it shows a high chemical and electrochemical stability, (iii) BDD gives a very low background current and large electrochemical window, and (iv) the BDD can also be heated in air up to 500^0C without undergoing the surface oxidation. Modification of boron-doped diamond electrode with redox active particle/compounds offers significant advantage in the development of sensors. Several papers deal with the deposition of metallic particle (mercury, lead, silver, ruthenium, platinum and iridium oxide) on the diamond surface. Recently, hydrous iridium oxide film deposited on the diamond electrode exhibited an excellent analytical performance for hydrogen peroxide detection.

Tetracyclines are board spectrum antibiotics for their high activity against nearly all gram-positive and gram-negative bacteria. Tetracycline, chlortetracycline, oxytetracycline and doxycycline are four members of this antibiotics group that are commonly used in food protection animals (including honeybee), because of their board spectrum activity and low production cost. However, the use of these drugs has become a serious problem as regard to infectious diseases, as they are substances that leave residue in milk or meat. Tetracyclines can be directly toxic or else cause allergic reactions in some hypersensitive individuals. Owing to their extensive use in infectious diseases therapy, there are various methods that have been used to determine these compounds in pharmaceutical preparations, biological samples and milk. Official methods are microbiological approaches that are not only time consuming, laborious and expensive, but also poor in term of sensitivity and selectivity. Other developed methods are based on batch procedures with spectrophotometry, chemiluminescene, spectrofluorimetry and electrochemical methods.

Hydrogen peroxide is a clear solution that has strong oxidizing properties and is therefore a powerful bleaching agent that used as a disinfectant, as an oxidizer and in rocketery. It is commonly used to bleach human hair. Hydrogen peroxide is also utilized in several industrial processes due to its high oxidant power, particularly in the food and textile industries and for effluent treatment where it acts as a sterilizing, cleaning and oxidizing agent. The determination of hydrogen peroxide is quite important to process quality and efficiency. It can be carried out by several methods

such as iodometric, spectrophotometric or fluorimetric chemiluminescene and electrochemical approached for both liquid and gas sample. Among the analytical methods, electrochemical methods based on measurement of current derived from hydrogen peroxide oxidation or reduction play a predominant role, especially in the topic of biosensors, as hydrogen peroxide is produced by the action of enzyme upon reaction with bio-substrate. Owing to high overvoltage of hydrogen peroxide and possible interference, a detection scheme for hydrogen peroxide in the presence of easily oxidizable interference does not seem feasible. A catalyst modified electrode could provide an adequate solution to reduce high overvoltage potential problem. Recently, Wang and co-worker utilized series of precious metal, such as Pd and Rh, to reduce the applied potential for the determination of hydrogen peroxide through coupling of a flavin-containing oxidase [6-8]. A mixed-valence cluster is a polynuclear compound with two or more metal centers linked by a bridging ligand. This mixed valence compound is simply prepared by mixing two solutions of an anionic metal ion and a cationic metal ion. In this perspective, various redox compounds and in particular Prussian blue have found a large use.

As mentioned above, the most widely used method for the determination of tetracyclines and hydrogen peroxide are based on spectrophotometric detection. However, these methods have some limitations e.g. derivatization with some chemicals are required. The requirements of the rapid measurement led to the promotion of flow injection system for the analytes determination. Moreover, because of the interference from the non-analyte present in the real sample, the chromatographic systems were also needed to couple with the detection system to achieve the separation and the high accuracy for the determination. The use of anodized diamond and mix-valent chromium (III) hexacyanoferrate (II) as a working electrode in amperometric detector in flowing system for the determination of tetracycline antibiotics and hydrogen peroxide were firstly introduced.

Objectives of the research

This research was separated into two parts:

Main part, the modification of BDD electrode was studied. This works focused on two modification methods (i) anodized BDD electrode for the

determination of tetracycline antibiotics and (ii) chromium (III) hexacyanoferrate (II) modified BDD electrode to determine the hydrogen peroxide.

The other was separately discussed in chapter V, the study of change in conformation of J-aggregate 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin (H_2TPPS) by addition of nonionic surfactant (Triton X-100).