

CHAPTER VI

CONCLUSIONS AND SUGGESTION FOR FUTURE WORKS

6.1 Conclusions

In this research, the modified BDD electrodes were used to investigate tetracycline antibiotics and hydrogen peroxide. BDD have been widely used as electrode for many electrochemical applications. The superior electrochemical properties were low background current leads to the enhancement of the S/B ratios, wide working potential window in the aqueous solution and slightly adsorption of polar molecules. However, the BDD surfaces covered with hydrogen make this electrode lack of the catalytic property. The modification of BDD surface to change the functional group on the diamond surface can be extended the catalytic capability and enhanced the sensitivity of the electrode. This work was focused on two modification methods (i) anodized BDD electrode for the determination of tetracycline antibiotics and (ii) mix-valent cluster of chromium (III) hexacyanoferrate (II) modified BDD electrode for the determination of hydrogen peroxide.

The anodized BDD electrode was modified by anodic polarization in the alkaline solution using cyclic voltammetry to make the surface of BDD terminated with oxygen. The obtained anodized BDD electrode was applied to detect tetracycline antibiotics. The electrochemical properties of tetracyclines were investigated using cyclic voltammetry. Comparison results were carried out using glassy carbon and as-deposited BDD electrodes. From the results, all electrodes provided the irreversible cyclic voltammograms. However, the highest current signal was obtained at the anodized BDD electrode. To find the optimum pH for the determination of TCs at anodized BDD electrode, the experiments were carried out in the pH solution 2-9. It was found that the pH 2 gave the maximum current signal because the TCs were formed in the fully positive charge that could be attracted to the negatively charged on the anodized BDD surface. The anodized BDD electrode was used as the amperometric detector in the flow injection system. To find the optimum working potential, hydrodynamic voltammetry of TCs were investigated. The results indicated that the optimum potentials were 1.5 V vs. Ag/AgCl for CTC, and 1.6 V vs.

Ag/AgCl for TCs, OTC, and DC. The analytical performances of anodized BDD electrode in flow system including the linear range and LOD were investigated. The linear ranges were 0.1–50 μM for TC and 0.5–50 μM for OTC, CTC and DC. The LOD was 10 nM for four TCs. The proposed method was applied to determination TCs in the pharmaceutical formulations. The precision of the method based on the intra- and inter-day assay were studied. The results were summarized in the Table 4.5 and 4.6.

The anodized BDD electrode was applied to use as the amperometric detector in the HPLC. To find the optimum condition for the separation, the effect of buffer system (i.e. potassium dihydrogen phosphate (pH 2.5), Britton-Robinson buffer (pH 2.5) and phosphoric acid (pH 2.5)) as well as the composition of mobile phase were also studied. It was found that phosphoric acid (pH 2.5) was the best. The final concentration of acetonitrile chosen for the mobile phase was 19% with the flow rate 1 ml min⁻¹, which allowed the TCs to elute with favorable retention time and adequate resolution. To obtain the optimum working potential, hydrodynamic voltammetry of TCs were investigated. The optimum working potential for the TCs determination was 1.6 V vs. Ag/AgCl for four TCs. The analytical performances of anodized BDD electrode using HPLC including the linear range, limit of detection, and limit of quantitation were investigated. The results were summarized in Table 4.8. The proposed method was applied to the determination of TCs in egg samples. The various extraction methods were used for the sample preparation of TCs. The AOAC method for the sample preparations of TCs in the tissue sample was firstly used. However, this method could not be used for the sample preparation of TCs in egg samples. Because of the deprotenized step was required for the sample preparation of TCs in egg samples. Therefore, three solvents including perchloric acid (aqueous solvent), acetonitrile (moderated polar solvent), and ethyl acetate (non polar solvent) were used. The results were summarized in Table 4.9. The results indicated that the acetonitrile was the best extraction solvent for the extraction of four TCs in egg samples. The recovery results from intra- and inter-day assay using acetonitrile were summarized in Table 4.10 and Table 4.11, respectively.

The deposition of mix-valent cluster of chromium(III) hexacyanoferrate (II) on BDD surface were studied. The hydrogen peroxide was used as a real sample. The optimum conditions for the preparation of chromium (III) hexacyanoferrate (II) modified BDD electrodes were investigated as the followed:

- Electrode pretreatment methods
- Electrodeposition methods
- Molar ratios between chromium nitrate and potassium hexacyanoferrate

The several electrode pretreatment methods were used to pretreat the electrodes prior to the deposition of chromium (III) hexacyanoferrate (II). The results were summarized in Table 4.12. The results indicated that the pretreatment by oxidized the BDD surface with 0.1 M sulfuric acid for 1 hr exhibited the highest current response for the determination of hydrogen peroxide.

The various electrodeposition methods were used for the deposition of chromium (III) hexacyanoferrate (II) on the anodized BDD surface. The results were summarized in Table 4.13. The results indicated that the use of cyclic voltammetry as the deposition method exhibited the highest current response for the determination of hydrogen peroxide.

The various molar ratios between chromium nitrate and potassium hexacyanoferrate were also studied. The results indicated that molar ratio of 4:1 exhibited the highest current response.

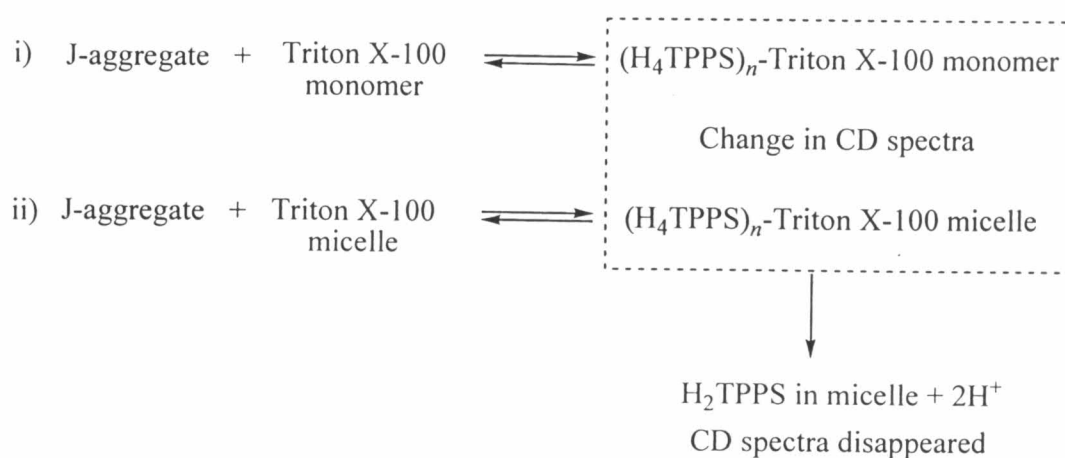
Under the optimum condition, the modified BDD electrode was used to the determination hydrogen peroxide. The optimum condition for the determination of hydrogen peroxide such as the effect of pH and buffer/electrolyte system were studied. The results were summarized in Table 4.14 and 4.15. The results indicated that the potassium chloride (pH 5) exhibited the highest current response for the hydrogen peroxide determination.

The chromium (III) hexacyanoferrate (II) modified BDD electrode was used as the amperometric detector in flow injection system. The optimum potential from hydrodynamic voltammetry at both anodic and cathodic reactions were obtained. The working potential was found to be -0.4 V vs. Ag/AgCl.

The analytical performances of flow injection system coupled with chromium (III) hexacyanoferrate (II) modified electrode were evaluated. The linear range from 0.088 to 440 mM and limit of detection of 44 nM were obtained.

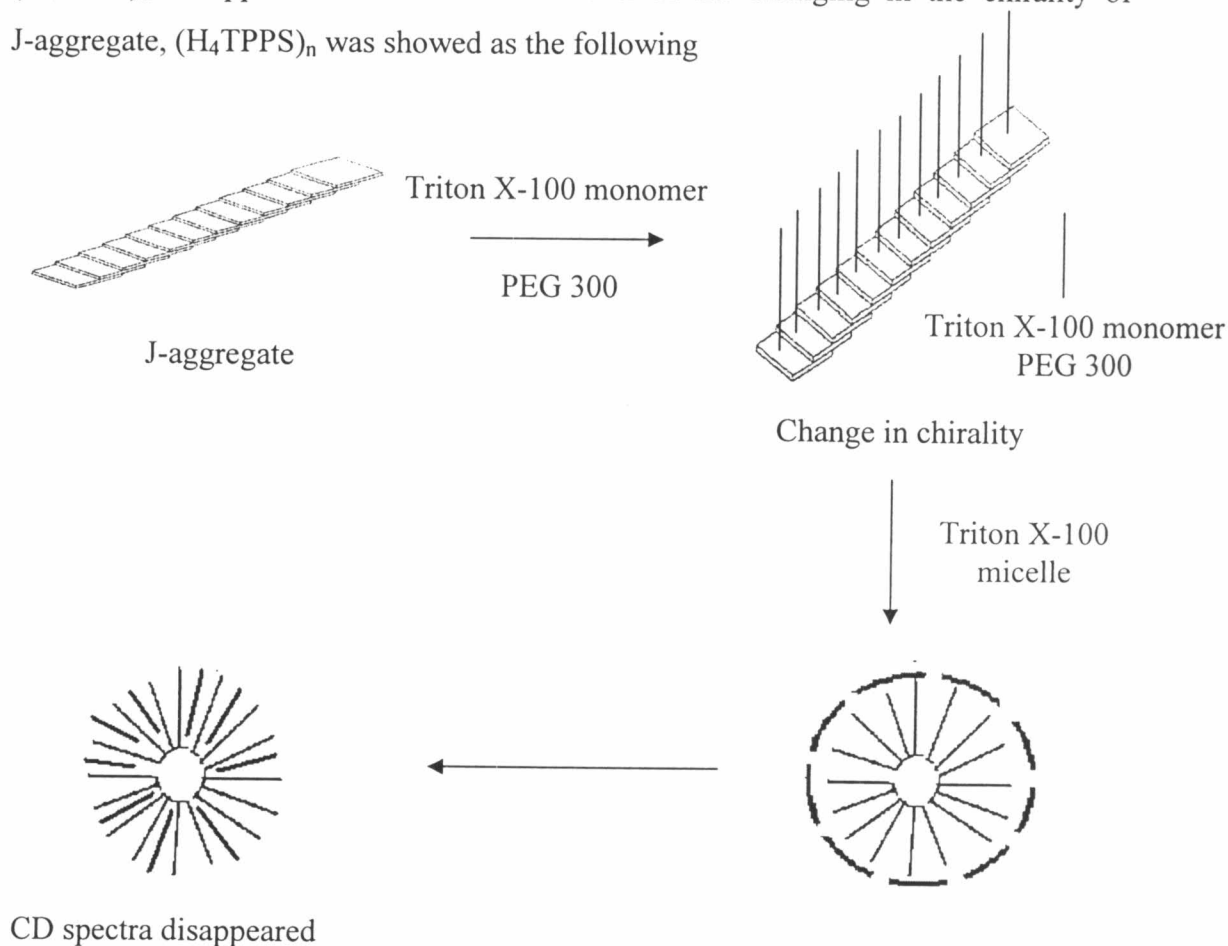
The proposed method was applied to detect the hydrogen peroxide in disinfection solution. Relative errors compared with the claimed amounts were lower than 5%.

The other part was 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). From the change in UV-vis and CD spectra of J-aggregate in the presence of different concentrations of Triton X-100, it was expected that the following two reactions occurred. One was the interaction of J-aggregate, $(H_4TPPS)_n$, with Triton X-100, leading to the change in chirality of $(H_4TPPS)_n$, and the other is the incorporation of the J-aggregate, $(H_4TPPS)_n$ into the micelle of Triton X-100 after releasing proton to form monomer of H_2TPPS . The reaction mechanism was showed as the following:



The interaction between J-aggregate, $(H_4TPPS)_n$ and PEG 300 was also changed the chirality of J-aggregate. The mechanism could be explained by the same mechanism as the mechanism i of Triton X-100 monomer (mechanism i).

The change in chirality of the J-aggregate could be explained by the following possible mechanism. H_4TPPS molecules assemble each other through their induced dipole moments to form helical J-aggregate, and the bound Triton X-100 molecules assemble each other, that may cause the change in chirality of the J-aggregate, $(H_4TPPS)_n$ to opposite direction. The model of the changing in the chirality of J-aggregate, $(H_4TPPS)_n$ was showed as the following



6.2 Suggestions for the future works

The future works should focus on the following:

1. The TCs in egg samples was determined using anodized BDD electrode coupled with HPLC. The standard deviations of obtained recoveries were high especially in the low concentration of spiked standard solution. The future works should to study the effect of the matrix in the egg sample for the determination of TCs
2. The chromium (III) hexacyanoferrate (II) modified electrode could be used to investigate hydrogen peroxide. Future works should be preformed using the other

metals hexacyanoferrate such as cobalt and copper and comparing the results with the chromium hexacyanoferrate.

3. The interactions between the J-aggregate, $(H_4TPPS)_n$ and the nonionic polymer including Triton X-100 and PEG 300 were investigated. The results indicated that the chirality of J-aggregate, $(H_4TPPS)_n$, change drastically in the presence of both nonionic polymer. Further works should be studying the effect of cationic and anionic polymer to the J-aggregate, $(H_4TPPS)_n$ and comparing the phenomena with the nonionic polymer.