UNIVERSITI PUTRA MALAYSIA

ELECTROCHEMICAL CHARACTERISATION AND APPLICATION OF SOLID ELECTRODES CHEMICALLY MODIFIED WITH C60-FULLERENE, TETRATHIAFULVALENE AND SILICON POLYOXOTUNGSTATE

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By

GOH JOO KHENG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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Dedicated to my beloved parents, Shawn and Kelvin Choi

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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November 2005

Chairman : Associate Professor Tan Wee Tee, PhD

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The modified glassy carbon electrodes by adhered microcrystals of fullerene (C_{60}), tetrathiafulvalene (TTF) and α-Keggin silicon polyoxotungstate, $[SiW_{12}O_{40}]^{4-}$ has been studied extensively in characterization and application of these modified electrode in mediating some selected compounds such as cysteine, methionine and nitrite ions in the presence of aqueous electrolytes.

The use of a glassy carbon electrode modified by adhered microcrystals of fullerene (C_{60}), mediates the oxidation of cysteine in the presence of aqueous potassium containing electrolytes. Under conditions of cyclic voltammetry, the potential for the oxidation of cysteine was lowered by approximately 100 mV and current was enhanced significantly relative to the situation prevailing when a bare glassy carbon electrode was used. Additional mediation occurs when the potential range covered includes that of C_{60}/C_{60}^{n-} redox couples. The sensitivity under condition of cyclic voltammetry was significantly dependent on pH, temperature and C_{60} dosage. Excellent analytical and recovery data were obtained with vitamin pill, cassamino acid (hydrolyzed casein) and for a range of beverages.

The usefulness of a C_{60}-fullerene modified gold (Au) electrode was extended in mediating the oxidation of methionine in the presence of potassium ions electrolyte. During cyclic voltammetry, an oxidation peak of methionine appearing at +1000 mV vs. Ag/AgCl was observed. The oxidation current of methionine was enhanced by about 2 times using a modified gold electrode. The current enhancement was significantly dependent on pH, temperature and C_{60} dosage. The variation of scan rate study shows that the system undergoes diffusion-controlled process.

Then, diffusion coefficient and rate constant of methionine were determined using hydrodynamic method (rotating disk electrode) with values of 1.11×10^{-5} cm^2 s^{-1} and 0.0026 cm s^{-1} respectively for unmodified electrode while the values of diffusion coefficient and rate constant of methionine using C_{60} modified Au electrode were 5.67×10^{-6} cm^2 s^{-1} and 0.0021 cm s^{-1} respectively. Excellent analytical and recovery data were obtained with root beer beverage.

Tetrathiafulvalene modified glassy carbon electrode has been characterized and been applied in the determination of L-cysteine at the potential of +800 mV vs. Ag/AgCl. It has shown to catalyze the oxidation peak of cysteine in the alkaline buffer solution under cyclic voltammetry conditions. The sensitivity of tetrathiafulvalene modified electrode was found to be dependent on pH and dosages of varying concentration of TTF in acetonitrile. Excellent analytical and recovery rates also has been obtained using vitamin pills and root beer syrup either with known amount of cysteine or added deliberately into the samples.

The voltammetric reduction of α form of Keggin silicon polyoxotungstate anions, α-$[SiW_{12}O_{40}]^{4-}$ has been carried out under acidic conditions. The cyclic voltammograms obtained from the solution voltammetry of the Keggin polyoxotungstate anions, α-$[SiW_{12}O_{40}]^{4-}$ showed cyclic voltammogram of a two reversible, one-electron process and a reversible two-electron process in the potential range of +200 mV to -1000 mV (vs. Ag/AgCl). However, only the first reduction process was undertaken in this study.

The use of Keggin silicon polyoxotungstate anion, α-$[SiW_{12}O_{40}]^{4-}$ was successfully applied to the synthesis of ruthenium bipyridine silicon polyoxotungstate, $[Ru(bipy)_3]_2[\alpha\text{-}SiW_{12}O_{40}]$ via reduction of α-$[TBA]_4[SiW_{12}O_{40}]$ solvent cast onto the glassy electrode in sulphuric acid. The reduction of nitrite has shown to be catalyzed by $[Ru(bipy)_3]_2[\alpha\text{-}SiW_{12}O_{40}]$ modified electrode at lower pH of aqueous sulphuric acid media. Bulk electrolysis technique was employed to

reduce α-$[SiW_{12}O_{40}]^{4-}$ to form a blue solution of α-$[SiW_{12}O_{40}]^{5-}$. The reduction of α-$[SiW_{12}O_{40}]^{4-}$ to α-$[SiW_{12}O_{40}]^{5-}$ was measured spectrophotometrically and there was no stable complex formation between α-$[SiW_{12}O_{40}]^{5-}$ and reduction product of NO_2^- species in the acidic solution. Therefore, the mechanism involving the catalytic effect on α-$[SiW_{12}O_{40}]^{4-}$ in the presence of nitrite suggested that nitrous acid, HNO_2 has been reduced to a product that possibly containing NO. Beta, β form of Keggin $[SiW_{12}O_{40}]^{4-}$ was found to be less active as compared to the α-$[SiW_{12}O_{40}]^{4-}$.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

ELEKTROKIMIA PENCIRIAN DAN APLIKASI ELEKTROD PEPEJAL MODIFIKASI KIMIA DENGAN C_{60}-FULLERENE, TETRATHIAFULVALENE DAN SILIKON POLYOXOTUNGSTAT

Oleh

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November 2005

Pengerusi : Profesor Madya Tan Wee Tee, PhD

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Modifikasi elektrod karbon kaca melalui pelekatan mikrokristal fullerene (C_{60}), tetrathiafulvalene (TTF) dan α-Keggin silikon polyoxotungstat, α-$[SiW_{12}O_{40}]^{4-}$ telah di kaji dengan terperinci dalam pencirian and aplikasi elektrod-elektrod ini sebagai perantaraan sebatian terpilih, contohnya, sistina, metionina dan ion nitrit dalam elektrolit akues.

Penggunaan modifikasi elektrod karbon kaca melalui pelekatan mikrokristal fullerene C_{60} telah meningkatkan pengoksidaan sistina dalam kehadiran elektrolit akues yang mengandungi ion kalium. Dalam keadaan voltametri siklik, potensi bagi pengoksidaan sistina telah direndahkan kira-kira 100 mV dan arus ditingkatkan relatif kepada situasi di mana elektrod karbon kaca tanpa modifikasi digunakan. Pertambahan mediasi telah berlaku apabila skala potensi meliputi proses redoks C_{60}/C_{60}^{n-}. Sensitivi di bawah keadaan siklik voltametri adalah bergantung kepada pH, suhu, dan dosej C_{60}. Data analisis dan perolehan semula yang baik diperolehi menggunakan pil vitamin, asid cassamino (casein yang dihidrolisis) dan juga beberapa jenis minuman.

C_{60}-fullerene terlekat pada elektrod emas juga digunakan bagi mediasi pengoksidaan metionina dengan kehadiran ion kalium dalam elektrolit akues. Puncak oksidasi methionine diperhatikan muncul pada potensi +1000 mV (vs. Ag/AgCl) semasa siklik voltametri. Arus pengoksidaan methionine telah ditingkatkan sebanyak 2 kali dengan penggunaan modifikasi elektrod emas. Peningkatan arus ini adalah bergantung kepada pH, suhu, dan dosej C_{60}. Kadar imbasan yang berbeza menunjukkan sistem ini melalui proses terkawal resapan.

Justeru itu, pemalar penyerapan and pemalar kadar methionine telah diperolehi menggunakan cara hidrodinamik (elektrod cakera putar) dengan nilai masing-masing 1.11×10^{-5} cm^{2} s^{-1} dan 0.0026 cm s^{-1} untuk elektrod tanpa modifikasi. Manakala, pemalar penyerapan and pemalar kadar metionina untuk C_{60} modifikasi elektrod emas adalah masing-masing 5.67×10^{-6} cm^{2} s^{-1} and 0.0021 cm s^{-1}. Data analisis dan perolehan semula yang baik didapati menggunakan minuman root bir.

Modifikasi elektrod dengan tetrathiafulavalene telah dicirikan dan juga diaplikasikan dalam penentuan kehadiran sistina pada potensi +800 mV vs. Ag/AgCl. Ia menunjukkan katalisis puncak pengoksidaan sestina dalam penimbal alkali elektrolit di bawah keadaan siklik voltametri. Sensitiviti tetrathiafulvalene modifit elektrod didapati bergantung kepada pH, dosej TTF/ACN, dan kepekatan TTF/ACN. Data analisis dan perolehan semula yang baik telah dicapai dengan penggunaan pil vitamin and root bir sirup samada dengan kepekatan sistina yang diketahui ataupun yang ditambahkan kepada sampel.

Voltametri bagi penurunan bentuk Keggin silikon polyoxotungstat anion, α-$[SiW_{12}O_{40}]^{4-}$ telah diperolehi di bawah keadaan berasid. Siklik voltamogram yang diperolehi daripada larutan voltametri Keggin polyoxomethalate anion, α-$[SiW_{12}O_{40}]^{4-}$ menunjukkan dua proses berbalik satu elektron dan satu proses berbalik dua elektron pada potensi antara +200 mV to -1000 mV (vs. Ag/AgCl). Walau bagaimanapun, hanya puncak penurunan yang pertama di ambil kira dalam projek ini.

Penggunaan jenis Keggin silikon polyoxotungstat anion, α-$[SiW_{12}O_{40}]^{4-}$ telah berjaya diaplikasikan kepada sintesis $[Ru(bipy)_3]_2[\alpha\text{-}SiW_{12}O_{40}]$ melalui penurunan dalam asid sulfurik α-$[TBA]_4[SiW_{12}O_{40}]$ yang dilekat atas elektrod karbon kaca menggunakan cara pengewapan pelarut. Penurunan nitrit, NO_2^- telah dikatalis oleh penurunan ruthenium bipyridine silikon polyoxotungstat, $[Ru(bipy)_3]_2[\alpha\text{-}SiW_{12}O_{40}]$ modifikasi elektrod pada pH rendah asid sulfuric.

Teknik elektrolisis pukal telah digunakan untuk menurunkan α-$[SiW_{12}O_{40}]^{4-}$ kepada larutan biru, α-$[SiW_{12}O_{40}]^{5-}$. Penurunan α-$[SiW_{12}O_{40}]^{4-}$ to α-$[SiW_{12}O_{40}]^{5}$ telah dianalisis dengan spectrofotormeter dan didapati tiada komplek yang stabil terbentuk antara α-$[SiW_{12}O_{40}]^{5-}$ dan produk penurunan NO_2^- spesis dalam larutan α-$[SiW_{12}O_{40}]^{4-}$. Dengan demikian, mekanisma melibatkan kesan katalisis α-$[SiW_{12}O_{40}]^{4-}$ dalam kehadiran NO_2^- telah dicadangkan bahawa asid nitrous, HNO_2 telah diturunkan ke suatu produk yang mengandungi nitric oxida, NO. Bentuk beta, β Keggin $[SiW_{12}O_{40}]^{4-}$ telah didapati kurang eletrokatalitik aktif dalam kehadiran nitrit berbanding dengan α-$[SiW_{12}O_{40}]^{4-}$.

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I certify that an Examination Committee met on 30 November 2005 to conduct the final examination of Goh Joo Kheng on her Doctor of Philosophy thesis entitled "Electrochemical Characterisation and Application of Solid Electrodes Chemically Modified with C_{60}-Fullerene, Tetrathiafulvalene and Silicon Polyoxotungstate" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

GOH JOO KHENG

Date: 20 FEBRUARY 2006

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