



Chloroplatinum(II) complex-modified MWCNTs paste electrode for electrochemical determination of mercury in skin lightening cosmetics



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ABSTRACT

The chemically modified multiwalled carbon nanotubes (MWCNTs) paste electrode with chloroplatinum (II) complex for the determination of mercury is presented. The chloroplatinum(II) complex was characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transforms infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM). The capability of the electron transfer rate on the surface of modified electrode evaluated is by electrochemical impedance spectroscopy (EIS). The square wave stripping voltammetry (SWSV) technique was employed to investigate the performance of chloroplatinum(II) complex-MWCNTs paste electrode for determination of mercury. Several operational parameters such as the composition ratios of the electrode, type of supporting electrolyte, pH of the solution, and the SWSV parameters were thoroughly investigated. Under optimal conditions, the linear range obtained was from 5.0 μM to 0.1 mM with limit detection of 3.7 μM . The interference from other heavy metals such as Ca^{2+} , Mg^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , Ba^{2+} , Mn^{2+} , and Ce^{3+} did not influence the electrochemical response. The chloroplatinum(II) complex-MWCNTs paste electrode was successfully applied to determine mercury in skin lightening cosmetics with a good recovery (98.9%–101.1%).

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1. Introduction

Skin lightening cream is one of the popular cosmetic product among men and women in order to obtain lighter skin tone or as anti-freckle [1,2]. It is known that the application of mercury as an active ingredient in a skin lightening cosmetic has been accepted for centuries [3]. Mercury is known as a neurotoxicant, considered to be one of highly toxic heavy metal ions. According to the Food and Drug Administration (FDA), the maximum concentration of mercury in cosmetics should be less than 1.0 $\mu\text{g g}^{-1}$ [4]. Even the permitted level of mercury concentration in cosmetics is low, continuous exposure to the skin may lead to a serious health problem such as damage to the brain, kidney, intestines, and nervous system [5–7]. Concerned about the toxicity of these

elements at low levels has prompted the development of various selective and sensitive analytical method for its determination.

The most common analytical technique employed for the determination of mercury is spectrometry methods such as cold vapor atomic absorption spectrometry [8–10], inductively coupled plasma mass spectrometry [11–13], and atomic fluorescence spectrometry [14–16]. However, these techniques involve expensive instruments, high operating cost, complicated procedures, and time-consuming. Comparatively, electrochemical methods, particularly stripping voltammetry have been extensively developed recently due to their low cost, simple, high sensitivity, suitable for in situ analysis and an ability to preconcentrate analyte with advanced electrochemical stripping protocols.

Recently, chemically modified electrode by nanomaterials has attracted great attention in the field of electrochemical sensors because of its excellent properties which increase electron transfer rate, catalytic activity and surface area [17–23]. Numerous studies have been done with the determination of mercury by employing different nanomaterials to the electrochemical sensors [24–31]. Previous studies show that the development of chemically

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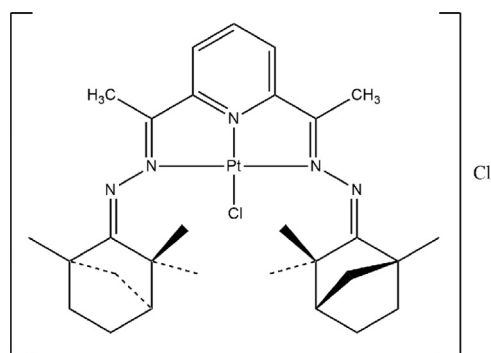


Fig. 1. The structural formulae of chloroplatinum(II) complex.

modified electrode by employing the complexes of Schiff-base ligand 2,6-diacetylpyridine-di-(1R)-(-)-fenchone diazine nano-composite fabricated with MWCNTs have been successfully applied in the determination of trace metals [32,33]. In this work, 2,6-diacetylpyridine-di-(1R)-(-)-fenchone diazine chloroplatinum(II) complex (termed as chloroplatinum(II) complex) uniformly dispersed on the MWCNTs resulting the nanocomposite-modified electrode was successfully applied for the determination of Hg^{2+} by SWSV method.

2. Experimental

2.1. Materials

All chemicals were analytical reagent grade purity. MWCNTs (Timesnano, China) and paraffin oil (Merck, Germany) is for fabrication of paste electrodes. The hydrochloric acid (Merck, Germany) and sodium hydroxide (Sigma-Aldrich, USA) is for adjustment of pH of the solution. All salts such as barium chloride, calcium chloride, zinc chloride, cadmium chloride, cerium(III) chloride, cobalt(II) chloride, manganese(II) chloride, magnesium chloride, mercury(II) chloride, nickel(II) chloride, potassium

chloride, potassium nitrate, sodium chloride, sodium nitrate, sodium acetate, and sodium sulphate (Sigma-Aldrich, USA) for optimization studies were used as received. 1.0 mM of the Hg^{2+} stock solution was freshly prepared by dissolving 0.027 g of mercury(II) chloride with distilled deionized water in 50 mL volumetric flask.

2.2. Instruments

SWASV was performed with a Potentiostat Series-G750 (Gamry, USA). All voltammograms were recorded with a three electrode system consisting of an Ag/AgCl electrode MF-2052 (Bioanalytical system, USA) with a fiber junction as the reference electrode, a platinum wire as the counter electrode and a MWCNTs paste electrode modified with chloroplatinum(II) complex as the working electrode. The pH of a solution was determined using glass electrode 915600 (Orion, USA). The characterization of chloroplatinum(II) complex was done by XRD model APD 2000 (Ital Structure, Italy) at a wavelength of 1.5406 Å, XPS model Axis DLD XPS (Kratos, UK) and EDX model SU 8020 UHR (Hitachi, Japan). The electrochemical impedance spectroscopy (EIS) measurement was carried out on potentiostat/galvanostat Model Ref 3000 (Gamry, USA) and the surface morphology of chloroplatinum(II) complex was characterized by SEM and TEM model SU 8020 UHR (Hitachi, Japan). Metal ion in real samples was analyzed using ICP-OES model 720Axial (Agilent, USA).

2.3. Synthesis of 2,6-diacetylpyridine-di-(1R)-(-)-fenchone diazine chloroplatinum(II) complex

A solution containing 2,6-diacetylpyridine-di-(1R)-(-)-fenchone diazine ligand (316.0 mg) and sodium tetrachloroplatinate(II) (253.0 mg) in methanol (10 cm^3) was boiled for 6 hours and left to stand at 20°C for 1 hour. The solvent was then evaporated to dryness under reduced pressure and solid obtained was collected, washed with water and cold methanol. The product of chloroplatinum(II) complex as dark brown solid was obtained (Fig. 1).

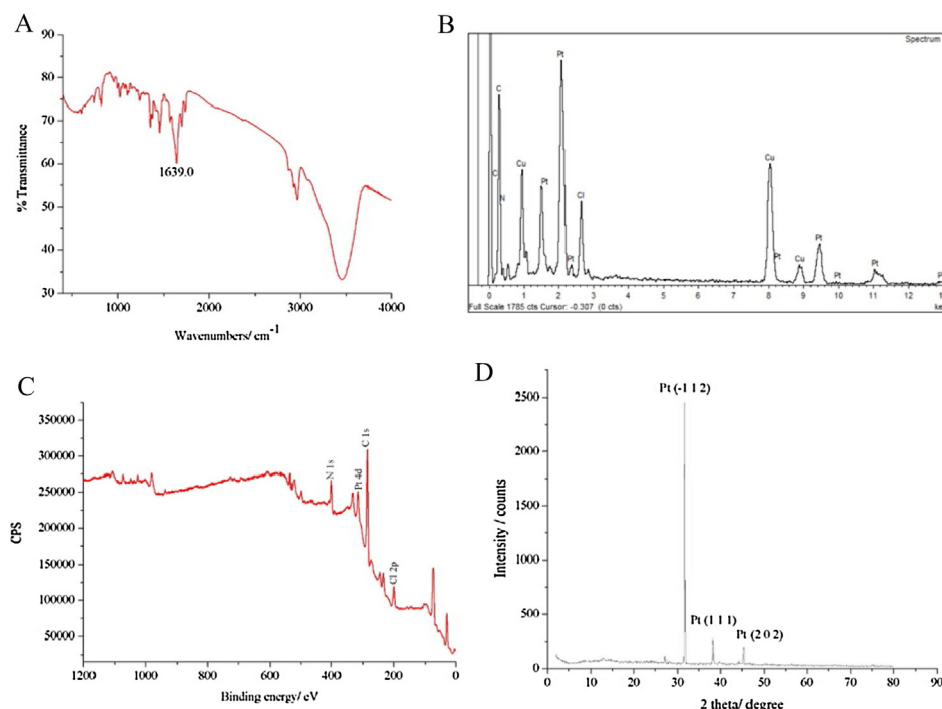


Fig. 2. (A) FTIR spectrum, (B) EDX spectrum, (C) wide scan of XPS analysis, and (D) XRD spectrum of chloroplatinum(II) complex.

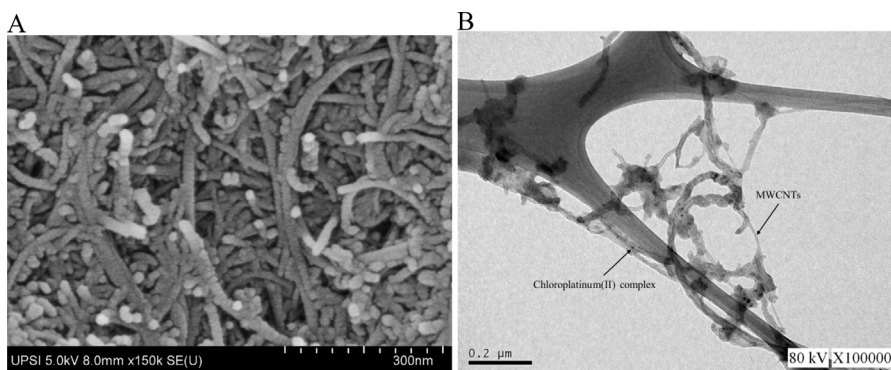


Fig. 3. (A) SEM and (B) TEM image of chloroplatinum(II) complex on MWCNT surface.

2.4. Electrode preparation

Chloroplatinum(II) complex-modified MWCNTs paste electrodes were prepared by mixing 100 mg of MWCNTs with 0, 5, 10 and 15 (% w/w) of chloroplatinum(II) complex and finished with 4 drops of paraffin oil as a binder. The homogenized mixture, then packed firmly into Teflon tubings (i.d. 2.0 mm). One end of the tubing behaved as a disc electrode once smoothed with a soft paper. At the other end, a copper wire was inserted to establish electrical contact. The unmodified MWCNTs paste electrode was prepared in the same way without chloroplatinum(II) complex.

2.5. Analytical procedure

SWSV was applied for the successive determination of Hg^{2+} under the optimized conditions. Hg^{2+} was reduced to Hg^0 at the potential of -0.2 V for 500 s in 0.5 M KCl containing mercury(II) chloride at a desired concentration under stirring conditions. After an equilibration period of 5 seconds, the anodic stripping of electrodeposited Hg^0 was performed at -0.2 V to 0.3 V at a frequency of 50 Hz, step increment of 2 mV and pulse amplitude of 50 mV. The measurements were repeated three times for each experiment. Prior to the next measurement, the electrode surface was mechanically renewed by polishing the electrode on a filter paper. All experiments were conducted at ambient temperature of $25 \pm 2^\circ\text{C}$.

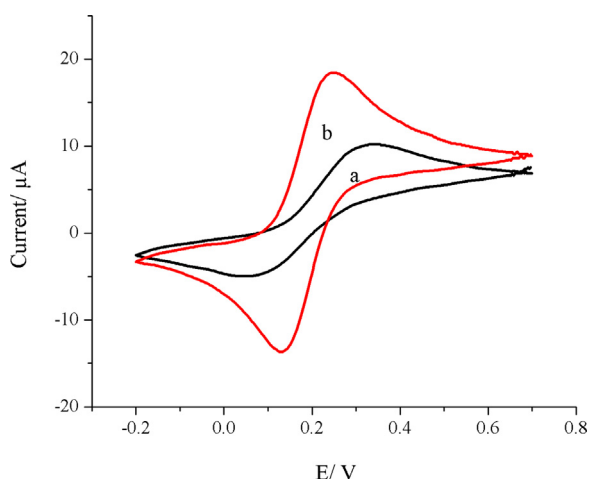


Fig. 4. Cyclic voltammogram of (a) unmodified and (b) modified MWCNTs paste electrode in 4.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution containing 0.1 M KCl. Scan rate of 100 mV s^{-1} .

2.6. Real samples preparation

Three different types of skin lightening cream were purchased from local night markets in Tanjung Malim, Perak, Malaysia. 0.4 grams of each sample placed in a beaker and 15 mL of concentrated nitric acid (69% w/w) was added. The mixture was heated on a hotplate to near dryness. After cooling, 8 mL of distilled deionized water was added to the residue. Then, the solution was filtered using filter paper (Whatman no. 541) and diluted into 50 mL volumetric flask with distilled deionized water. Suitable aliquots of this solution were analyzed by the proposed method for mercury determination.

3. Results and discussion

3.1. Chloroplatinum(II) complex identification

The FTIR spectra of chloroplatinum(II) complex (Fig. 2A) was recorded in the range of $4000\text{--}400\text{ cm}^{-1}$. The FTIR spectra showed the absorption band at $\sim 1639\text{ cm}^{-1}$ attributed to the stretching vibration of C=N and the absorption band at $\sim 3000\text{ cm}^{-1}$ attributed to the stretching vibration of C—H. The ^1H NMR spectrum of chloroplatinum(II) complex showed the resonances for the $\text{CH}_3\text{C}=\text{N}$ proton singlet at 2.31 ppm. The resonances of the methyl protons from the fenchone residue were singlet at 1.22 and 1.27 ppm, respectively. The pyridyl protons gave resonance in the range of 7.75–7.79 and 8.08–8.15 ppm. Additionally, Fig. 2B shows the existence of carbon, nitrogen, chlorine and platinum elements (except copper element of copper grid) of chloroplatinum(II) complex from EDX analysis. This elemental composition was verified by a wide scan of XPS analysis (Fig. 2C) where the electronic spectra of N 1s, Pt 4d, C 1s, and Cl 2p was observed at binding energies of 399.7 eV, 315.7 eV, 285.2 eV, and 199.2 eV, respectively.

Furthermore, Fig. 2D shows the XRD spectrum of chloroplatinum(II) complex where the average particle size calculated by Scherrer equation [34] was 7.2 nm, 7.3 nm and 7.5 nm for relative intensity peak of (-112) , (111) and (202) , respectively. The morphology of chloroplatinum(II) complex on the wall of MWCNTs was observed by SEM and TEM analysis (Fig. 3). It can be seen that the chloroplatinum(II) complex uniformly dispersed on the wall of MWCNTs with the size distribution of $6.5 \pm 1.7\text{ nm}$ where the particle size data were obtained from the counting of more than 200 particles. These average particle size value nearly to the size calculated in XRD analysis which demonstrated the nanostructure of chloroplatinum(II) complex.

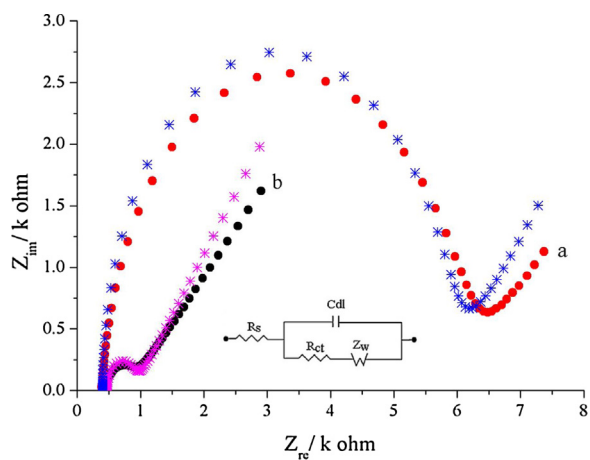


Fig. 5. Nyquist plot of (a) unmodified and (b) modified MWCNTs paste electrode in 4 mM $K_3[Fe(CN)_6]$ solution containing 0.1 M KCl. Frequency range: 1.0 MHz to 1.0 Hz. Inset: Randle's equivalent electrical circuit for the system. The fitting curve of Randle's equivalent electrical circuit shows by symbol of "*".

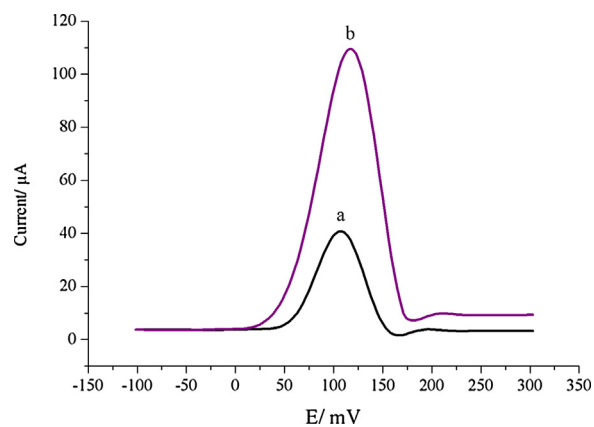
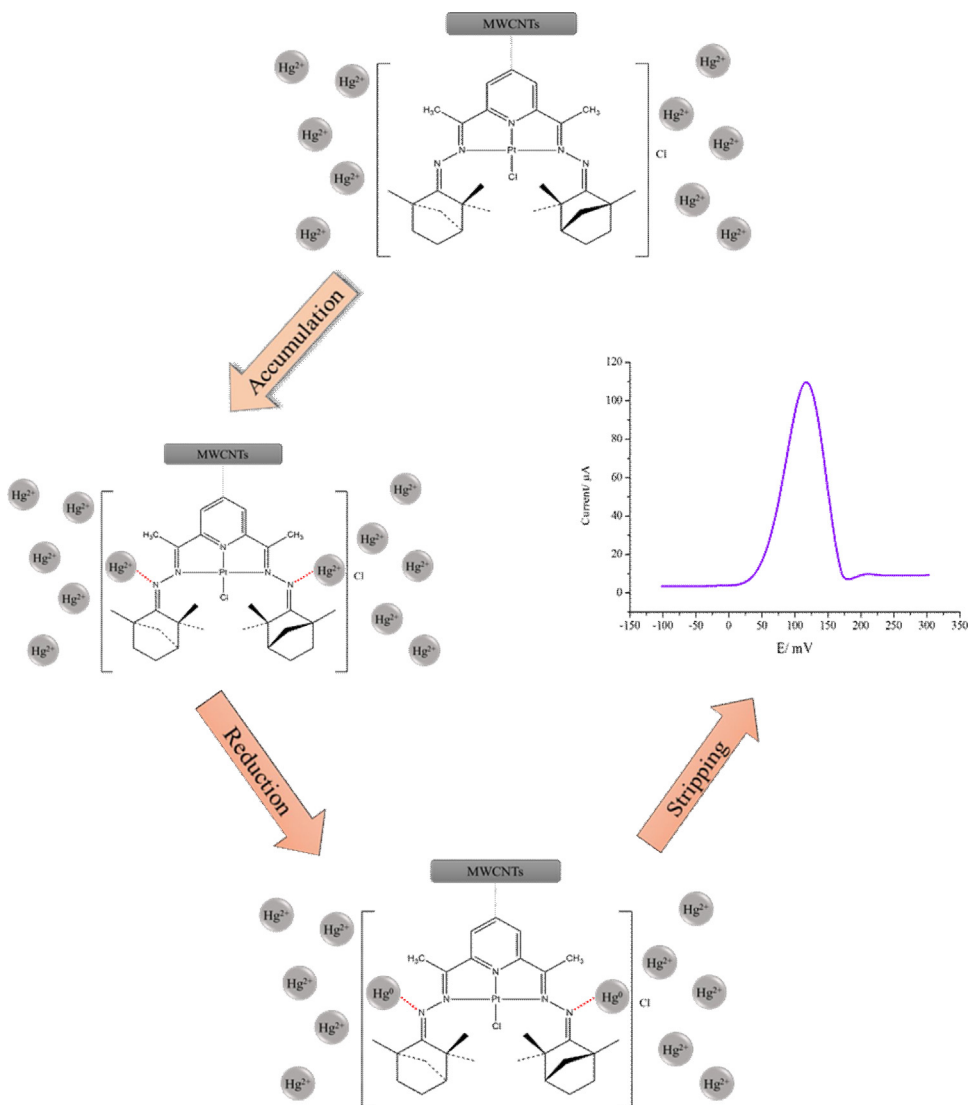


Fig. 6. SWSV voltammogram of (a) unmodified and (b) modified MWCNTs paste electrode in 0.1 mM Hg^{2+} containing 0.5 M KCl (pH 3.0). Deposition time: 500 s; deposition potential: -0.2 V; frequency: 50 Hz; step increment: 2 mV; pulse amplitude: 50 mV; equilibrium time: 5 s.



Scheme 1. Possible reaction mechanism of Hg^{2+} detection at the modified MWCNTs paste electrode.

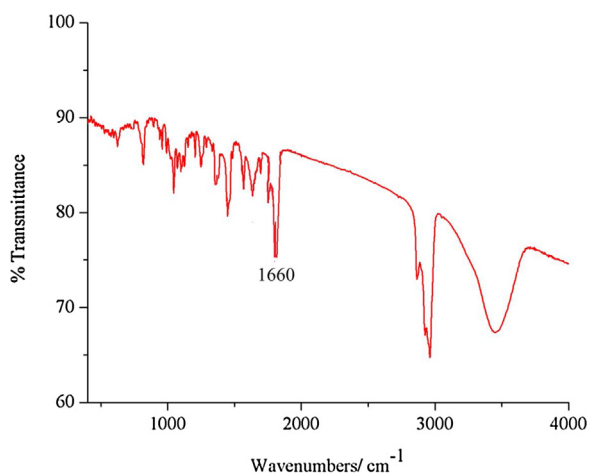


Fig. 7. The FTIR spectra of chloroplatinum(II) complex after the interaction with Hg^{2+} .

3.2. Electrochemical reactivity

The cyclic voltammetry experiment was carried out to investigate the conductivity of the chloroplatinum(II) complex-modified MWCNTs paste electrode and unmodified MWCNTs paste electrode by the use of 4.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution containing 0.1 M KCl as the electrochemical probe. The cyclic voltammogram for both electrode shown in Fig. 4 where the unmodified (curve a) and modified (curve b) MWCNTs paste electrode gave a couple of well-define redox peaks. The unmodified MWCNTs paste electrode exhibited a redox current of $I_{pa} = 8.86 \mu\text{A}$ and $I_{pc} = 5.96 \mu\text{A}$. Meanwhile, the modified MWCNTs paste electrode exhibited a redox current of $I_{pa} = 13.90 \mu\text{A}$ and $I_{pc} = 14.42 \mu\text{A}$. It can be seen that the I_{pa} apparently increased and ΔE_p decreased from 320.9 mV to 120.0 mV indicating that the loading of chloroplatinum(II) complex as a modifier of MWCNTs paste electrode has improved the conductivity and the electron transfer rate of the electrode [35].

The capability of the electron transfer rate on the surface of unmodified and modified MWCNTs paste electrodes was further investigated by performing the EIS measurement of 4.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution containing 0.1 M KCl. The typical result of the EIS was illustrated in Fig. 5 which is often used to interpret simple electrochemical systems. In the Nyquist diagrams, the diameter of the semicircle at higher frequencies presents the interfacial electron transfer resistance, R_{ct} , and the linear portion at lower frequencies corresponds to the diffusion process [36]. Fig. 5 inset showed the Randles equivalent electrical circuits where, the R_s

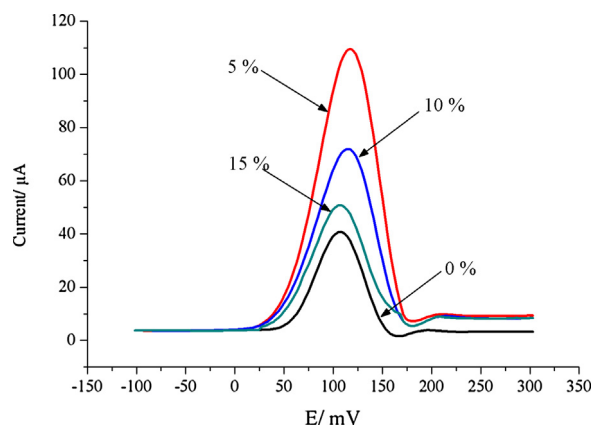


Fig. 8. SWSV voltammogram of modified MWCNTs paste electrode in 0.1 mM Hg^{2+} containing 0.5 M KCl (pH 3.0) at different composition ratios (% w/w) of the modifier. Other conditions are similar as in Fig. 6.

represent the resistance of the electrolyte, C_{dl} , and R_{ct} represent the double layer and charge transfer resistance at the electrode/electrolyte interface, and Z_w is the Warburg impedance related to the diffusion ions in the bulk electrode [37]. It can be seen that the unmodified MWCNTs paste electrode exhibits a large semicircle (curve a) while with the introduction of chloroplatinum(II) complex onto MWCNTs (curve b), the semicircle decreased significantly suggesting the increasing of the electron transfer rate on the surface of the electrode [38]. By fitting Randles equivalent electrical circuits the R_{ct} values of unmodified MWCNTs and chloroplatinum(II) complex-MWCNTs paste electrode were 5.41 k ohms and 0.439 k ohms, respectively. The fitting curve of Randles equivalent circuit also showed in Fig. 5 with the goodness of fit of 0.0029 and 0.0033 for unmodified and modified MWCNTs paste electrode, respectively. Moreover, by applying the electron transfer apparent rate constant, k_{app} :

$$k_{app} = RT/F^2 R_{ct} C \quad (1)$$

Where R , T , and F have their usual meaning. C is the concentration of the $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution. The k_{app} values of the unmodified and modified MWCNTs paste electrodes were $1.23 \times 10^{-8} \text{ cm s}^{-1}$ and $1.52 \times 10^{-7} \text{ cm s}^{-1}$ respectively. The high k_{app} and low R_{ct} values of modified MWCNTs paste electrode indicated of a faster electron transfer process compared to the unmodified MWCNTs. Therefore, it can be concluded that the modification of MWCNTs paste electrode using chloroplatinum(II) complex had contributed to the excellent conductivity of the electrode and in accordance with the cyclic voltammetry studies.

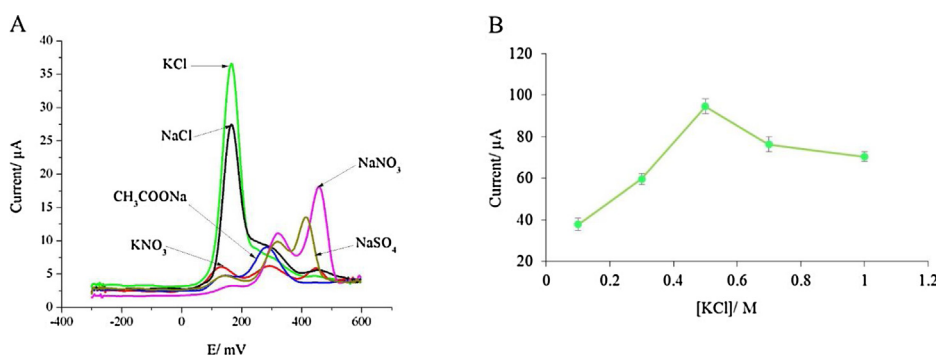


Fig. 9. (A) Effect of various supporting electrolytes at concentration of 0.1 M and (B) Effect of different concentration of KCl on the peak current of 0.1 mM Hg^{2+} . Other conditions are similar as in Fig. 6.

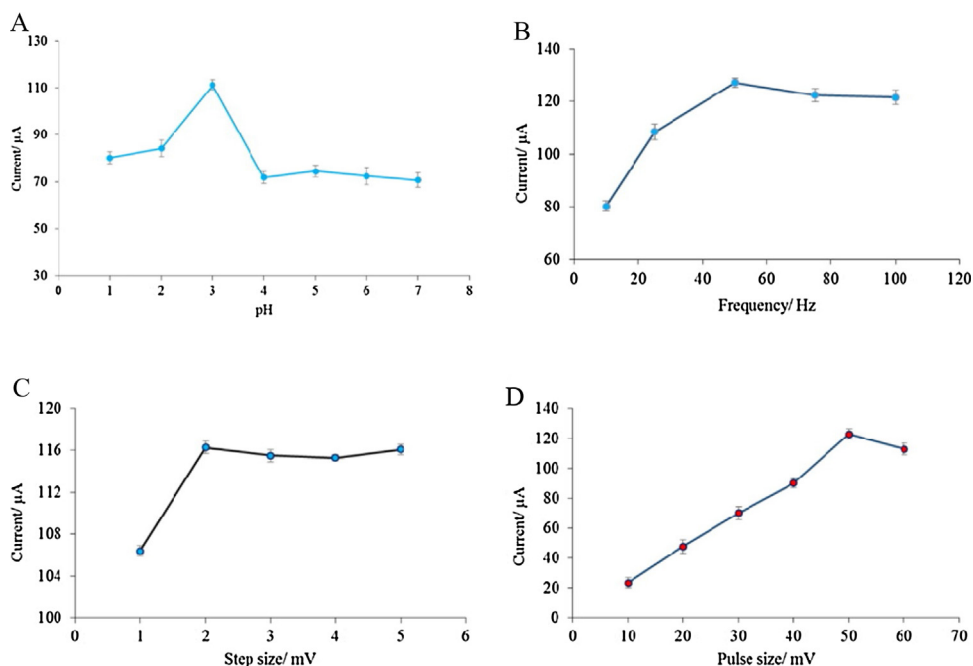


Fig. 10. (A) Effect of the pH of solution, (B) frequency, (C) step size and (D) pulse size on the peak current of 0.1 mM Hg²⁺. Other conditions are similar as in Fig. 6.

3.3. Electrochemical Response of Hg²⁺

The electrochemical response of unmodified and chloroplatinum(II) complex-modified MWCNTs paste electrode were evaluated by observing the SWSV response of 0.1 mM Hg²⁺ containing 0.5 M KCl (pH 3.0). Fig. 6 shows the SWSV voltammogram of unmodified (curve a) and modified (curve b) MWCNTs paste electrodes after 500 seconds of accumulation. It can be observed that both unmodified and modified MWCNTs paste electrode exhibited the sharp I_{pa} response of Hg²⁺ at peak potential of 107.9 mV and 116.9 mV, respectively. However, the I_{pa} of modified was higher than the unmodified MWCNTs paste electrode indicated that the chloroplatinum(II) complex has increased the charge transfer kinetics of MWCNTs paste electrode. The possible reaction mechanism between chloroplatinum(II) complex and Hg²⁺ on the electrode surface was illustrated in Scheme 1. At an accumulation potential of -0.2 V, it is assumed that the Hg²⁺ ions were accumulated on the electrode surface to form a temporary bond with a lone pair from N atom in structural formulae of chloroplatinum(II) complex. The accumulated Hg²⁺ ions were reduced to Hg⁰ forming a thin film on the electrode surface at 500 s of accumulation time. Then, when the stripping potential was applied from -0.2 V to 0.3 V, the Hg⁰ was electrochemically stripped back as Hg²⁺ into solution producing the I_{pa} response. This result was then supported by FTIR analysis in Fig. 7 where the

vibration of C=N was slightly shifted from absorption band of ~1639 cm⁻¹ to ~1660 cm⁻¹.

3.4. Optimization of experimental variables

In order to optimize the performance of chloroplatinum(II) complex-MWCNTs paste electrode for the Hg²⁺ analysis, several experimental variables were optimized such as the composition ratios of the electrode, type of supporting electrolyte, pH of the solution, and the SWSV parameters.

3.4.1. Effect of composition ratios

The modified MWCNTs paste electrode with different composition ratios of chloroplatinum(II) complex (% w/w) was prepared at composition ratio of 0.0, 5.0, 10.0, and 15.0 (% w/w). Fig. 8 shows the modified MWCNTs paste electrode with 5.0% of chloroplatinum(II) complex exhibits the higher I_{pa} response compare to the others. The modification of MWCNTs paste electrode with 5.0% of chloroplatinum(II) complex has increased the conductive area on the electrode surface, then improved the catalytic activity of the electrode [39]. Though, when the percentage of chloroplatinum(II) complex was increased up to 10.0% and 15.0%, the I_{pa} response was decreased perhaps due to the excessive loading of modifier that leads to the alteration of the physical and physiochemical properties on the electrode surface [40]. Therefore, the

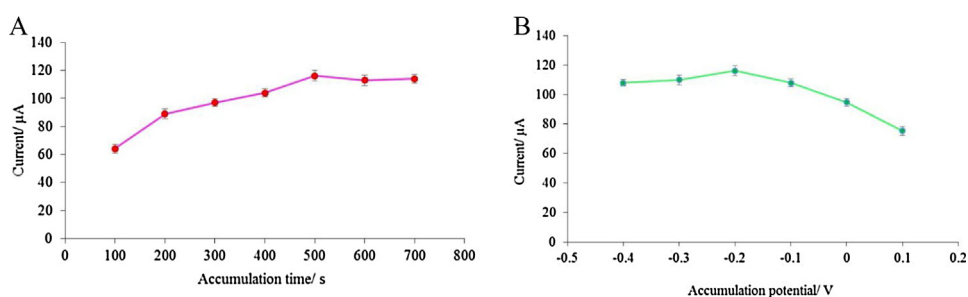


Fig. 11. Effect of (A) accumulation time and (B) accumulation potential on the peak current of 0.1 mM Hg²⁺. Other conditions are similar as in Fig. 6.

modification of MWCNTs paste electrode with 5.0% of chloroplatinum(II) complex was chosen for the subsequent experiments.

3.4.2. Effect of supporting electrolyte and pH

The addition of supporting electrolyte to the electrochemical cell has increased the catalytic current response and decreased the contribution of migration to mass transfer of electroactive species [41,42]. Therefore, the electrochemical response of chloroplatinum (II) complex-modified MWCNTs paste electrode in various inert supporting electrolytes such as NaCl, CH₃COONa, NaNO₃, Na₂SO₄, KCl, and KNO₃ at a concentration of 0.1 M was investigated. According to the previous study, the presence of Cl⁻ in the supporting electrolyte was able to initiate the catalytic effect of Hg²⁺ redox couples [43,44]. Therefore, the SWSV voltammogram shows in Fig. 9A displayed a better peak shape and high I_{pa} response in 0.1 M KCl and 0.1 M NaCl compared to the others. However, the I_{pa} response of Hg²⁺ in KCl was higher than NaCl due to its high ionic strength properties which were capable of improving the adsorption capability for heavy metals ions [45].

Moreover, the effect of different concentration (0.1, 0.3, 0.5, 0.7, 1.0 M) of KCl toward the response of Hg²⁺ was investigated. Fig. 9B shows that the I_{pa} values were increased when the concentration of KCl increased from 0.1 to 0.5 M due to the increasing of the ionic conductivity of an electrolyte which leads to the increased of free moving ions in the system. However, if there are too much free moving ions in the system, the conductivity will become slower due to the stronger attraction of free moving ions among each other. It can be seen, the I_{pa} response was decreased at over 0.7 M KCl. Thus, the highest and the best shape of stripping peak current were used for the subsequent experiment was 0.5 M KCl.

The effect of pH toward the performance of chloroplatinum(II) complex-modified MWCNTs paste electrode was then investigated by varying the pH of 0.1 mM mercury(II) chloride containing 0.5 M KCl between pH 2.0 and 10.0. It can be seen from Fig. 10A, the I_{pa} response was higher at pH 3.0. Then the response started to decrease at pH higher than 3.0 might be due to the hydrolysis of some Hg²⁺ ions in the solution, later prevented the ions to form a temporary bond with chloroplatinum(II) complex on the electrode surface. At pH below 3.0, the lower response was observed perhaps, due to the competition between the hydrogen ions and the Hg²⁺ which might be disadvantages to the deposition of Hg²⁺ at the surface of the electrode. Therefore, pH 3.0 was selected as optimum pH solution for the subsequent experiments.

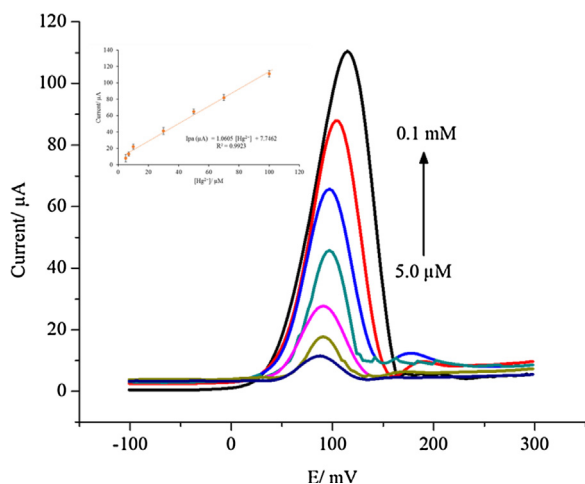


Fig. 12. SWSV voltammogram of modified MWCNTs paste electrode at different concentration of Hg²⁺ in 0.5 M KCl (pH 3.0) at optimum condition. Inset: Calibration plot of Hg²⁺.

3.4.3. Effect of SWSV parameters

In square wave stripping voltammetry, there are a few parameters such as frequency, pulse size and step size that will influence the resolution and sensitivity of voltammogram [46]. Therefore, the optimization SWSV parameters have been studied. The resulting I_{pa} response toward the different values of frequency (10 to 100 Hz) was presented in Fig. 10B. The result showed that the I_{pa} response is increased when the frequency increased from 10 to 50 Hz due to the increase of effective scan rate. However, the I_{pa} response becomes constant and slightly decrease when the frequency increased over the 75 Hz maybe due to the increasing of background current. Meanwhile, the effect of pulse size and step size toward the I_{pa} response of Hg²⁺ were evaluated in the range of 10 to 60 mV and 1 to 5 mV, respectively. It can be seen in Fig. 10C and D, the higher I_{pa} response showed at pulse size of 50 mV and step size of 2 mV, respectively. Over this value, the I_{pa} response was maintained due to peak broadening that causes a poor resolution and sensitivity. Therefore, the frequency of 50 Hz, pulse size of 50 mV and a step size of 2 mV were selected as optimal square wave parameters in this study.

Additionally, the effect of an accumulation time and accumulation potential were investigated in the range of 100 to 700 s and -0.4 to 0.1 V, respectively. As illustrated in Fig. 11A, the I_{pa} response was increased with the increasing of accumulation time up to 500 s. When the accumulation time increased over 600 s, the I_{pa} response showed no significant increase and nearly became constant due to the saturated accumulation of Hg²⁺ on the electrode surface that lead to the decreasing of the electron transfer rate at the electrode/solution interface [47]. Meanwhile, the effect of an accumulation potential was shown in Fig. 11B. The increasing of an accumulation potential toward negative potential has increased the I_{pa} response. However, when the deposition potential is more negative than -0.2 V the peak current slightly decreased ascribed to the hydrogen-evolution effect and increased the possibility of co-deposition of interfering species [48]. Therefore, an optimal accumulation time of 500 s and accumulation potential of -0.2 V was selected for further studies.

3.5. Electrochemical performance for detection of Hg²⁺

Electrochemical performance of chloroplatinum(II) complex-modified MWCNTs paste electrode for detection of Hg²⁺ in 0.5 M KCl (pH 3.0) was investigated by using SWSV method under optimal experimental conditions. It can be seen in Fig. 12, the I_{pa} response increased with the increasing of Hg²⁺ concentration. The calibration curve of I_{pa} versus concentration of Hg²⁺ showed linear response over the range of 5.0 µM to 0.1 mM with correlation coefficients of 0.9923. The linear regression equation was

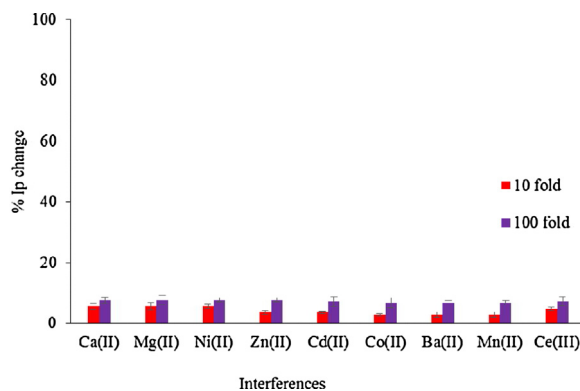


Fig. 13. The effect of interfering ions to 0.1 mM Hg²⁺ at chloroplatinum(II)/MWCNTs paste electrode.

Table 1
Determination of Hg²⁺ in skin lightening creams by SWSV method (n = 3).

Samples no.	Original (μg g ⁻¹)	Added (μg g ⁻¹)	Found (μg g ⁻¹)	Recovery (%)
1	3.3 ^a	15.0	18.5	101.1
2	2.7 ^b	15.0	18.0	101.7
3	2.9 ^c	15.0	17.7	98.9

^a Concentration found by ICP-OES was 3.4 μg g⁻¹.

^b Concentration found by ICP-OES was 2.9 μg g⁻¹.

^c Concentration found by ICP-OES was 3.0 μg g⁻¹.

expressed as $I_{pa} (\mu A) = 1.0605 [Hg^{2+}] + 7.7462$ and the limit of detection ($3\sigma/m$) is 3.7 μM. Moreover, the relative standard deviation of 5 replicated measurement of Hg²⁺ at a concentration of 0.1 mM is 2.9% indicating that the chloroplatinum(II) complex-MWCNTs paste electrode has good reproducibility. Additionally, the response of the electrode decreased 20.3% of its initial value after 6 weeks of continuous used.

3.6. Interference studies

Under optimum conditions, the selectivity of chloroplatinum (II) complex-modified MWCNTs paste electrode was studied by evaluating the effect of interference metal ions in the determination of Hg²⁺. Fig. 13 shows that the relative I_{pa} signal changes of 0.1 mM Hg²⁺ in the existence of 10 fold and 100 fold concentration of Ca²⁺, Mg²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Co²⁺, Ba²⁺, Mn²⁺, and Ce³⁺ are below than 20%. These results indicated that the existence of these metal ions did not affect the ability of chloroplatinum(II) complex-modified MWCNTs paste electrode to detect the Hg²⁺ in the solution.

3.7. Application

The determination of Hg²⁺ in skin lightening creams by using SWSV method was applied in order to access the applicability of the chloroplatinum(II) complex-modified MWCNTs paste electrode for the real sample analysis. The concentration of Hg²⁺ measured by using the SWSV was compared with measured by ICP-OES for validating the method. Table 1 shows that there are no significant differences of Hg²⁺ concentration between the two methods at 95% confidence level. Additionally, the recovery studies were performed to confirm the efficiency and the practicability of the technique. The recovery values were between 98.9% and 101.1% indicated that the chloroplatinum(II) complex-modified MWCNTs paste electrode was capable to work for quantification of Hg²⁺ in the environmental samples.

4. Conclusions

The application of chloroplatinum(II) complex in the development of modified MWCNTs paste electrode for the determination Hg²⁺ in the skin lightening creams analysis has been successfully demonstrated. The TEM and XRD analysis have proved the nanostructure of the chloroplatinum(II) complex with the size distribution of 6.5 ± 1.7 nm. The CV and EIS studies revealed that the modification of MWCNTs paste electrode with chloroplatinum (II) complex has improved the electrochemical reactivity of the modified MWCNTs paste electrode where the low R_{ct} values and higher redox peak current of indicates a faster electron transfer process. Under optimal conditions, the electrode exhibited, working concentration range from 5.0 μM to 0.1 mM with limit detection of 3.7 μM. The performance of the electrode did not interfere with others interfering ions and was successfully employed in the determination of Hg²⁺ in skin lightening creams with recovery between 98.9%–101.1%.

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