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A Highly Selective and Sensitive Detection of Ellagic Acid by Using Ethylenediamine Ligand Based Cobalt (II) Complex Modified Glassy Carbon Electrode

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We have successfully prepared simple and sensitive ethylenediamine ligand based cobalt (II) inorganic complex ($[Co(en)_3]^{2+}$) (en = ethylenediamine) modified glassy carbon electrode (GCE) and used for the electro chemical detection of Ellagic acid (EA). The prepared inorganic complex was characterized by the suitable physical and chemical characterization technique. Moreover, the modified electrode performance was monitored by the cyclic voltammetric (CV) and amperometric technique (*it*). Besides, the GCE/ $[Co(en)_3]^{2+}$ electrode has remarkably enhance the electrocatalytic activity towards the detection of EA. Using the optimized condition, the sensor exhibited the linear detection response range (0.1μ M-929 μ M) with the limit detection (0.035 nM) and the sensitivity is ($0.06709 \ \mu A \ \mu M \ cm^{-2}$). Furthermore, the fabricated electrode is an exhibited the acceptable repeatability, reproducibility and stability. On the other hand, the GCE/ $[Co(en)_3]^{2+}$ modified electrodes have been applied for the real sample analysis, which exhibit the acceptable recovery. The practical application of the modified electrode vas successfully applied for the determination of EA from the real samples with good recovery.

Keywords: Ellagic acid, Electrochemical sensor, Cobalt complex, Real sample analysis, Limit of detection.

1. INTRODUCTION

Ellagic acid (EA) (2, 3, 7, 8-tetrahydroxy benzopyrano-5, 4, 3-cdebenzopyran-5, 10-dione) is a derivative of gallic acid, which is found in vegetables and fruits including raspberries, grapes,

strawberries and walnuts [1, 2]. The EA content is used in food preservation, such as juices and jams. Moreover, it is used as food additive causes of antioxidative and antiviral properties. [3] Besides, the EA have more attention for its potential application to protect number of human diseases. It exhibit antioxidant and antimutagenic activity towards vitro and in vivo. Anticancer activities of EA are effective and fighting with various types of cancer such as, lung tumors, breast cancer and pancreatic cancer [4, 5]. Furthermore, this polyphenols react with free radicals via three feasible mechanisms: single-electron transfer-proton transfer, hydrogen atom transfer and sequential proton loss electron transfer. The thermodynamic aspect, the hydrogen atom transfer is the most important mechanism for EA [6] oxidation. Hence, the selective and sensitive detection of EA is more important due to the medical reasoning [7, 8].

Now a day's various analytical methods have been used for the detection of EA such us, chromatography [9], capillary electrophoresis [10], spectrophotometry [11] and high performance liquid chromatographic (HPLC) [12]. These kinds of techniques are poor accuracy, expensive instrumentation and need large amount of sample. Therefore, we need to find other alternative detection methods for the detection of EA. Among the various analytical techniques, electrochemical technique is the best alternative detection method for high selective and sensitive detection [13]. However, unmodified bare electrodes proposed low sensitivity, high overpotential and electrode fouling in EA detection. Therefore, we need to develop the bare electrode for sensitive and selective detection. In recent years, carbon nano materials and metal complex have been widely used in electrochemical sensor application [13-15].

Schiff bases ligand combined with transition metal complexes have an enormous interest in the field of organometallic chemistry. Besides, the Schiff bases an important role in coordination chemistry for the formation of stable complexes with transition metals.[16-18] The Schiff base inorganic complex has alkyl, aryl, amine, aldehyde and ketone functionalities. The cobalt (II) Schiff base complex exhibit better catalytic activity than that of the other transition metal complexes due to its excellent electrochemical properties. Moreover, it has exhibit enormous interest in supercapacitors, lithium ion batteries and electrochemical sensors device preparation [19, 20]. The cobalt (II) Schiff base complexes are potent antiviral, antibacterial, antitumor agents for axial ligand and more stability. Moreover, the $[Co(en)_3]^{2+}$ complexes have outer-sphere electron transfer and well redox properties. Hence, the higher activity complex of $[Co(en)_3]^{2+}$ have been used for electrochemical sensor application. In the present work, we have prepared GCE/ $[Co(en)_3]^{2+}$ modified electrode by electrostatic interaction. This novel electrode used for the highly selective and sensitive electrode for the electrochemical detection of EA.

2. EXPERIMENTAL

2.1 Materials and methods

Ethylenediamine, oxalic acid and cobalt (II) chloride $(CoCl_2 \cdot 6H_2O)$ were purchased from Sigma Aldrich, Taiwan. The buffer solution (PBS) was prepared by using Na₂HPO₄ and NaH₂PO₄, the pH of the solution was adjusted by using H₂SO₄ or NaOH. Analytical grade reagent and chemicals used in this electrochemical work without further purification. In the electrochemical cell, the electrolyte was deoxygenated with purified N_2 for 15 min. All the experimental procedure were carried out at room temperature and all the reaction solutions were prepared by using double distilled water. Electrochemical performance was carried out at the CHI 410 workstation. The electrochemical cell have glassy carbon electrode as a working electrode, Ag/AgCl as a reference electrode and Pt wire as a counter electrode. The electrochemical experimental studies carried out in N_2 purged electrolyte. The scanning electron microscope (SEM) characterization was carried out by Hitachi S-3000H SEM instrumentation. UV-visible spectra were taken on a Perkin Elmer spectro photometer and EIS spectra were carried out by Jasco FT-IR 6600 spectrometer and X-ray diffraction (XRD) studies were performed at XPERT-PRO diffractometer.

2.2 Synthesis of $GCE/[Co(en)_3]^{2+}$ inorganic complex modified electrode

The $[Co(en)_3]^{2+}$ inorganic complex was prepared based on previous report. [21-23] An ethylenediamine (2 ml) was dissolved in ethanol and the solution was added in to the oxalic acid (0.75 g) and cobaltous chloride (CoCl₂. 6 H₂O) (2.5 g) was refluxed for 3 h in the presence of ammonia in to water bath. Then, cooling the reaction solution orange color crystal of $[Co(en)_3]^{2+}$ was obtained. After, the product was filtered, washed with ethanol and dried. The obtained product was stored in desiccators and further used for electrode preparation. Furthermore, the GCE/[Co(en)_3]^{2+} modified electrode was prepared by the following procedure. The prepared $[Co(en)_3]^{2+}$ inorganic complex (10 mg) was dispersed in methanol (1 mL), then the obtained solution was treated in to ultrasonication for 30 min. After, the pretreated GCE electrode was coated on the 6 µL of prepared $[Co(en)_3]^{2+}$ complex. The prepared GCE/[Co(en)_3]^{2+} modified electrode was dried and used for the electrochemical detection of EA (Scheme 1).



Scheme 1. Schematic representation for the preparation of $GCE/[Co(en)_3]^{2+}$ modified electrode for the EA detection

3. RESULTS AND DISCUSSION

3.1 Characterization of Cobalt Complex $[CO(en)_3]^{2+}$



Figure 1. (A&B) SEM images of $[Co(en)_3]^{2+}$ complex (C) IR spectra of $[Co(en)_3]^{2+}$ and (D) XRD spectra of $[Co(en)_3]^{2+}$ complex.

Scanning electron microscope characterization technique is used to investigate the surface morphology of prepared complex. Figure 1 A & B shows the low and higher magnification SEM image of $[Co(en)_3]^{2+}$ complex. The low magnification SEM image depicted crystalline Co particles are in rod and spherical shape. Moreover, the higher magnification SEM image of $[Co(en)_3]^{2+}$ shows individual crystal are randomly aggregated. The FT-IR spectra provide the valuable information about the chemical structure and nature of the prepared nanomaterials. Figure 1C shows the FT-IR spectra of $[Co(en)_3]^{2+}$ inorganic complex. The inorganic complex exhibits the two bands at 3195 and 3074 cm⁻¹ which represent to the NH₂ group in the complex. Moreover, the IR spectra show at 510-600 cm⁻¹ region for CO-N Stretching vibration, which is confirm the formation of $[Co(en)_3]^{2+}$ inorganic complex [24-26]. The XRD pattern of cobalt complex shows well defined peaks were observed. The diffraction peaks shows at 15.52, 17.87, 25.42 and 30.26 which were consistent with the previous literature data of materials characterization. These results confirmed the formation of $[Co(en)_3]^{2+}$ inorganic complex. The electronic absorption spectra (UV-vis) were used to identify the structural information about the

inorganic complex. Figure 2A shows the UV visible spectra of $[Co(en)_3]^{2+}$ inorganic complex. The synthesized $[Co(en)_3]^{2+}$ shows an absorbance peak at 268 nm due to ligand to metal charge transfer (LMCT) which confirms the formation of $[Co(en)_3]^{2+}$ inorganic complex [27-29]. Figure 2B shows the EIS plots of (a) bare GCE, (b) GCE/ $[Co(en)_3]^{2+}$ modified electrode in 5 mM $[Fe(CN)_6]^{-3/4}$ with KCl (0.1 M) as a supporting electrolyte medium.



Figure 2. (A) UV-Visible spectra of $[Co(en)_3]^{2+}$ (B) Electrochemical impedance spectrum of (a) bare GCE, (b) GCE/ $[Co(en)_3]^{2+}$ modified electrode in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$

The Randles equivalent circuit model used to fit the experimental data. The modified electrodes GCE and GCE/[Co(en)₃]²⁺ exhibited different diameters semi circles, which is proposed different R_{ct} value. The R_{ct} value of GCE and GCE/[Co(en)₃]²⁺ modified electrode is 870 Ω and 558 Ω respectively, which is proposed that the resistance of the GCE/[Co(en)₃]²⁺ modified electrode decreased due to the electron transfer behavior between the ligand and metal. Hence, the EIS results proof that the GCE/[Co(en)₃]²⁺ fabricated electrode have higher electron transfer properties with low electron transfer resistance than that of the bare GCE.

3.2 Electrocatalytic ixidation of EA at $GCE/[CO(en)_3]^{2+}$ Electrode

3.2.1 Different film and different concentration

Figure 3A exhibit that the electrocatalytic oxidation of EA at different modified electrode such as (a) bare GCE and (b) $\text{GCE/[Co(en)_3]}^{2+}$ modified electrode in 10 mM EA in purified nitrogen saturated PBS (pH7) at the scan rate 50 mVs⁻¹. The bare GCE shows, there is no peak appeared for the oxidation of EA. After the modification of GCE with $[\text{Co(en)_3}]^{2+}$ complex, interestingly the GCE/[Co(en)_3]²⁺ modified electrode shows the oxidation peak around at 0.53 V and the peak current of 17.34 μ A. This is the higher oxidation peak current and lover oxidized peak potential than that of the bare GCE. Therefore, the $[\text{Co(en)_3}]^{2+}$ complex as a best electrode material for the electrocatalytic oxidation of EA due to the activity (Scheme 2).



Figure 3. Cyclic voltammetric response of (a) bare GCE and (b) $\text{GCE/[Co(en)_3]}^{2+}$ in presence of 200 μ M EA at nitrogen purged PBS (pH7) at the scan rate 50 mVs⁻¹.



Scheme 2. Electro oxidation of ellagic acid (EA)

Moreover, the GCE modified with inorganic complex and the electrode exhibit the higher electrocatalytic activity for oxidation of EA than previously reported modified electrodes. Figure 4A shows, the cyclic voltammogram of GCE/[Co(en)₃]²⁺ modified electrode in 0.1 M PPS (pH7) with increasing the concentration of EA form 50-250 μ L the oxidation peak current increased linearly with increasing the concentration of EA. Which indicate that the prepared electrode act as an suitable electrode material for the electrocatalytic oxidation of EA. Figure 4B exhibit the linear relation between the plot of the peak current Vs EA concentration, which is indicates that the electro catalytic oxidation of EA at the GCE/[Co(en)₃]²⁺ modified electrode as a surface controlled process [30].



Figure 4. (A) Cyclic voltammetry response for the different concentration of EA from 100 μ M to 700 μ M, (B) Calibration plot for the different concentration EA vs oxidation peak current (I_{pa}).

3.2. Effect of different scan rate and pHs



Figure 5. (A) Effect of scan rate at $\text{GCE}/[\text{Co}(\text{en})_3]^{2+}$ modified electrode towards the oxidation of EA (200 μ M) in PBS (pH 7). (B) Calibration plot between the scan rate vs oxidation peak current of EA.

The effect of the scan rate on the oxidation of EA at the GCE/ $[Co(en)_3]^{2+}$ complex modified electrode was investigated in the presence of 0.1 M PBS (pH7). As can be observed in Figure 5, increase the scan rate the anodic peak current (I_p) increasing and shifted to positive side (50-500 mVs⁻¹). Figure 5B shows the linear relation between the oxidation peak current of EA and scan rate, with a correlation coefficient of 0.9847. Which is indicates that the EA oxidation at the GCE/ $[Co(en)_3]^{2+}$

modified electrode as a surface controlled process [31,32]. The effect of pH of the electrolyte nature has been investigated towards the detection of EA. Figure 6A shows, the electrocatalytic oxidation of EA was studied in at different pHs from 5 to 11, at GCE/[Co(en)₃]²⁺ inorganic complex modified GCE electrode. The EA oxidation peak current was not affected by pHs, even though the peak potential (E_p) was shifted from positive to negative side due to increasing the pH.



Figure 6. Cyclic voltammetry response of EA oxidation at different pHs from 5 to 11. Effects of pH on the EA oxidation peak current Vs pH (6A) and Peak Potential Vs pH (6B).

The Figure 6B shows the linear relationship between pHs and E_p . The E_p shifted from positive to negative potential when pH changes from 3 to 11. Moreover, the linear plot observed between pHs and E_p (Figure 6c). The slope value is 59 mV/pH, which indicating that an equal number of protons and electrons transfer in the oxidation of EA. Interestingly, the higher oxidized peak current obtained at pH 7; therefore the modified electrode has the most advantage of working in neutral pH. Hence, we have chosen the neutral pH 7 for the all electrochemical experiments.

3.2.3 Amperometric studies

The amperometric (*i-t*) detection of EA performance of $[Co(en)_3]^{2+}$ modified rotating disc electrode (RDS) was monitored at the rotation speed of 2000 RPM in each addition of EA for every 50 second into continuous stirred PBS applied potential of + 0.75 V (Figure 7A). In every addition of EA, the stable and notable amperometric response was obtained and the amperometric response current was linearly increased upon increasing the concentration of EA (0.1-929 μ M). Moreover, Fig 7B shows the calibration plot of amperometric current versus EA concentration and the linear regression equation

was I_p (A) = 0.0057 [EA] (μ M) + 0.003. Besides, the sensitivity of the modified electrode was calculated to be 0.0670 μ A μ M cm⁻² and the detection limit (LOD) of 0.035 nM. The prepared EA sensor has been accessed as an acceptable sensitivity, low detection limit and wide linear range. The $[Co(en)_3]^{2+}$ modified electrode was compared with previous EA sensor as can be seen from the table 1. However, the detection limit of the EA at the GCE/ $[Co(en)_3]^{2+}$ modified electrode substantially lower than that of the other modified electrodes such us, Paraffin impregnated graphite electrode (LOD=1.135 nM), MWCNTs/carbon paste electrode (LOD=21 nM), graphene modified SPCE (LOD=0.05 ppm), SPCE/(Cu-Au) fabricated electrode obtained the EA detection at low level than other aforementioned sensor. Because, the cobalt complex could be an enhanced electrocatalyst for the oxidation of EA due to the higher electron transfer and well redox properties. Hence, this result demonstrate that the GCE/ $[Co(en)_3]^{2+}$ has been used as an prominent electrode towards detection of EA.



Figure 7. (A) Amperometric response for the oxidation of EA with different concentration in PBS (pH 5). The calibration plot of peak current vs. EA concentration.

3.2.4 Repeatability, reproducibility and stability studies

Repeatability and reproducibility of the $[Co(en)_3]^{2+}$ inorganic complex modified GCE electrode have been carried out by the CV technique in nitrogen saturated PBS containing 0.1 M EA at the scan rate 50 mVs⁻¹. The modified sensor shows an acceptable repeatability with 3.12 % relative standard deviation (RSD) for 10 continuous repetitive measurements carried out by single modified electrode. Furthermore, the sensor exhibit the acceptable reproducibility of 2.98 % for the five independent measurements carried out in five independent modified electrodes.

Electrode	Limit of detection	Linear range	Reference
Paraffin impregnated/GR	0.135 μM	0.5 μΜ - 8 μΜ	1
MWCNTs Paste electrode	21 nM		2
SPE-GPH	0.05 ppm		5
SPCE/(Cu-Au) nano electrode	4.1 $\mu g L^{-1}$	$0.2-200 \text{ mgL}^{-1}$	3
GCE	0.1 µM	0.1 μΜ-1.5 μΜ	30
$\text{GCE/[Co(en)3]}^{2+}$	0.035 nM	0.1µM-929µM	This work



Figure 8. Operational stability studies of $GCE/[Co(en)_3]^{2+}$ inorganic complex modified electrode.

Besides, the storage stability of the $[Co(en)_3]^{2+}$ inorganic complex modified GCE electrode towards detection of EA, it was monitored by every day regularly. During the storage period, the modified electrode exhibited well catalytic response towards detection of EA without any changes. Notably, 96.42% of the initial response current (*Ip*) were retained after the thirty days continuous using, it is the evidence of the good storage stability. Moreover, the operational stability of the $[Co(en)_3]^{2+}$ modified electrode was carried out by amperometric technique (Figure 8). The results exhibit that the well stable amperometric response was obtained only 7 % initial current was loss after continuous rotation. The stability results exhibit that the excellent operational stability of $[Co(en)_3]^{2+}$ inorganic complex modified electrode.

3.2.5 Interference studies

Figure 9 shows, the selectivity studies of the $[Co(en)_3]^{2+}$ inorganic complex modified sensor was analyzed by using the amperometric (i-t) methods. The selectivity of the modified electrode

determination of EA.



E/V. vs. Ag|AgCl

Figure 9. Relative error of the interference studies towards detection of 50 μ M EA (a) in presence of 5 fold higher concentration of other interfering compounds such as dopamine (b), acetaminophen (c), Catechol (d), Hydroquinone (e), Gallic acid (f), Uric acid (g), ascorbic acid (h) and Morin (i).

3.2.6 Real sample analysis

Samples	Added (µM)	Found (µM)	Recovery (%)	RSD ^a (%)	Average Recovery (%)
Raspberry		10.2		3.2	
	10	20	99	3.3	101
Strawberry		10.7		2.9	101
	10	20.1	103	3.1	

Table 2. Analysis of EA from fruit samples using $\text{GCE}/[\text{Co}(\text{en})_3]^{2+}$ modified electrode

^aRelative standard deviation for three repetitive measurements.

Evaluate the practicability of the modified sensor towards determination of EA is more important. Hence, the raspberry and strawberry fruit sample was used for the real sample monitoring. Table 2 shows, the standard addition method was used for the real sample analysis. Hence, the acceptable recoveries are obtained from the various samples which is revealed that the $[Co(en)_3]^{2+}$

inorganic complex modified GCE electrode used for the practical applicability of the determination of EA.

4. CONCLUSION

We have successfully prepared $[Co(en)_3]^{2+}$ inorganic complex by facile chemical method and the prepared complex was confirmed by the SEM, UV, FT-IR and XRD. The electrochemical performance of the complex was characterized by the CV and amperometric methods. The $[Co(en)_3]^{2+}$ complex exhibited superior electrocatalytic activity towards detection of EA. Moreover, the modified electrode exhibited the extraordinary analytical performance, such as a long linear range from 0.1-929 μ M, very low detection limits (LOD) 0.035 nM and high sensitivity for the detection of EA. Moreover, the sensor shows the high selectivity and stability in the presence of other interfering molecules. Moreover, the prepared sensors have well electrocatalytic activity, stability, repeatability and reproducibility. Hence, the GCE/[Co(en)_3]²⁺ inorganic complex modified electrode as an excellent electrode material for the detection of EA.

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