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Determination of kojic acid using carbon paste electrode modified by $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex and ionic liquid

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Abstract

A new mononuclear Fe(II) (1) complex with the formula $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ (HL= N-(2-hydroxy-1-naphthylidene)-2-methyl aniline) was synthesized and characterized by Fourier transform infrared spectroscopy (FT-IR), UV-Vis and elemental analysis. The spectroscopy analyses revealed the two Schiff base ligands via oxygen and nitrogen atoms and two chloride atoms create an octahedral geometry. The nano-size of $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ complex (2) was synthesized by the sonochemical process. Characterization of nano-complex (2) was carried out via X-ray powder diffraction (XRD), scanning electron microscopy (SEM), UV-Vis, FT-IR spectroscopy. The nano-complex (2) average size synthesized via the sonochemical method was approximately 52 nm. In this work, a simple sensor based on a carbon paste electrode modified with $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex and the ionic liquid - IL (1-Butyl-3-methylimidazolium hexafluorophosphate) was developed ($[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE) for convenient and fast electrochemical detection of kojic acid. The modified electrode considerably improves voltammetric sensitivity toward kojic acid compared to the bare electrode. Experimental conditions influencing the analytical performance of the modified electrode were optimized. Under optimal conditions, the oxidation peak current was proportional to kojic acid concentration in the range from 0.3 to 237.0 μM with a detection limit of $0.09 \pm 0.001 \mu\text{M}$. The $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE sensor was successfully applied for the highly sensitive determination of kojic acid in real samples with satisfactory results.

Keywords

Electrochemical sensor; voltammetry; real samples, mononuclear Fe (II) complex

Introduction

Kojic acid (5-hydroxy-2-(hydroxymethyl)-4-pyrone, is a metabolic product of several species of the economically valuable genus *Aspergillus*, *Acetobacter*, and *Penicillium* [1,2]. Kojic acid and some of its derivatives are used in cosmetic preparations to achieve a skin-lightening effect by inhibiting melanin formation. In food production, kojic acid has been used as an antioxidant, an additive for

its preservative actions against both chemical and microbial degradation, to preserve food color, and as an inhibitor of nitrosopyrrolidine formation in fried food [3-6]. In addition, kojic acid has also been used as an antibiotic, pesticide, and analytical chemical (in the determination of thorium and rare earth elements) [7]. Although consumption of low levels of kojic acid does not concern safety, studies show that continuous overuse of kojic acid is carcinogenic and tumorigenic [8-10]. Therefore, the development of a convenient, economical, rapid and sensitive method for the determination of trace amounts of kojic acid in different samples is highly desirable.

Various techniques have been developed for the quantitative determination of kojic acid, such as ion-pair liquid chromatography (IPLC) [11], high-performance liquid chromatography (HPLC) [12], fluorescent detection [13], and capillary electrophoresis [14]. Unfortunately, these techniques require expensive instruments and skilled operators and are complicated procedures.

Electrochemical sensors, with their excellent ability for the determination of electroactive substances, have been suggested as powerful analytical tools in recent years [15-20]. Electrochemical sensors are relatively cheap, portable, sensitive, and give rapid response [21-33].

However, the oxidation of kojic acid is kinetically sluggish, and a relatively high overpotential is required at the conventional electrodes [34,35]. In electrochemical analysis, the key component is electrode modification, which requires the selection of suitable material to improve the determination performance [36-43]. Chemically modified electrodes (CMEs) have attracted considerable interest over the past decades as researchers attempted to exert more direct control over the chemical nature of an electrode surface [44-55]. Chemically modified carbon paste electrodes (CPEs) are cheap, easy to make, and have a low background current [56-58].

Ionic liquids and nanostructures have been used to modify CPEs with improved conductivity, high mechanical stability, and fast electron transfer rates [59,60].

In recent years, nanostructured materials received wide attention owing to their unique structure, high specific surface area, high surface-to-volume ratio and excellent electronic conductivity [61-65]. Nanomaterial-modified electrodes exhibit many favorable characteristics for electroanalysis, including fast response, high sensitivity and selectivity [66-70].

Schiff bases are an important class of organic compounds [71]. This kind of ligand has significant importance in chemistry, especially in the development of Schiff base complexes, because Schiff base ligands are capable of forming stable complexes with metal ions [72]. Recently, it has attracted more attention in metal complexes of unsymmetrical Schiff bases ligands with nitrogen and oxygen atoms [73]. Most of these unsymmetrical Schiff bases ligands are obtained by the condensation of different types of primary amines with various ketones and aldehydes by direct syntheses [74]. Schiff base ligands have biological activity and potential applications in many fields, such as oxidation catalysis, and electrochemistry [75]. Facile and inexpensive synthesis, allied with the wide range of structural and electronic features of Schiff bases and their coordination complexes, has increased interest in chemically modifying electrodes with these compounds. Therefore, the resulting electrodes have been used as sensors and/or probes in a variety of fields. All this interest has culminated in the development of low-cost sensors. In particular, the many structural and electronic properties of Schiff bases and their transition metal complexes allow them and the analyte to establish different interactions, which improves sensor selectivity and sensitivity [76-80].

In this work, Schiff base ligand [HL= N-(2-hydroxy-1-naphthylidene)-2-methyl aniline] and its iron(II) complex (1) with (N-(2-hydroxynaphthalen)2-methyl aniline) Schiff base ligand were synthesized. Complex (1) was characterized using spectroscopic techniques such as FT-IR, UV-Vis and elemental analysis. The crystal structures of $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ (1) were determined by X-ray

crystallography. The Schiff base iron nano-complex (**2**) was prepared by the sonochemical method. This synthesis was performed without the use of any surfactants. The nano-sized complex (**2**) was identified using XRD and SEM techniques. Also, we aimed to fabricate a highly sensitive nanostructured sensor based on ionic liquid - IL (1-Butyl-3-methylimidazolium hexafluorophosphate) carbon pastes modified with $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex to investigate the electrooxidation of kojic acid. The electrocatalytic ability of $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE sensor was thoroughly investigated by cyclic voltammetry (CV), chronoamperometry, and differential pulse voltammetry (DPV). The analytical performance of the proposed sensor was assessed by quantitative evaluation of kojic acid in various real samples.

Experimental

Apparatus and chemicals

^1H NMR spectra were accomplished with Bruker AVANCE3 3-300MHz spectrometer using $\text{DMSO-}d_6$ as a solvent and at room temperature (298 K). Fourier-transform infrared spectra were performed on a Perkin-Elmer FT-IR spectrophotometer model spectrum two with KBr discs in the range of 4000 to 400 cm^{-1} . For elemental analyses of new compounds was utilized a Costech ECS 4010 CHNS Elemental Analyzer. UV-Vis spectra were recorded in the range of 200 to 800 nm on Optizen view 2120UVplus Spectrophotometer ver1-2.

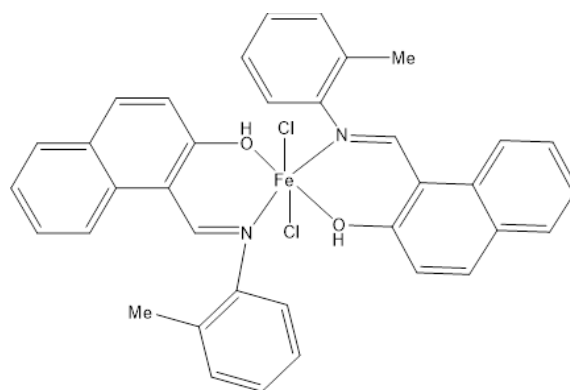
All the electrochemical measurements were carried out on a PGSTAT302N potentiostat/galvanostat Autolab consisting of a traditional three-electrode system: a bare or modified CPE as the working electrode, an Ag/AgCl as the reference electrode and a Pt wire as a counter electrode. Solution pH values were determined using a 713 pH meter combined with a glass electrode (Metrohm, Switzerland). Phosphate buffer solution (PBS) was prepared with phosphoric acid and adjusted by NaOH to the desired pH value. Kojic acid and other chemicals used were analytical grade and were purchased from Sigma Aldrich and Merck.

Synthesis of Schiff base ligand [HL]

The ligand (HL: N-(2-hydroxy-1-naphthylidene)-2-methyl aniline) was synthesized by adding a solution of 2-hydroxy-1-naphthaldehyde (0.17 g, 1 mmol) in 10 mL of ethanol to a solution of 2-methyl aniline (0.11 ml, 1mmol) in 10 mL of ethanol. Then, the mixture was refluxed for 6 h. The resulting yellow solution was placed at room temperature. After 24 h, yellow crystals of HL were formed. The Schiff base ligand was characterized by $^1\text{H-NMR}$, FT-IR, elemental analysis and single-crystal X-ray diffraction [81]. MP: $154\text{ }^\circ\text{C}$; (yield: 88 %); (MW: 261.31); Anal. Calc. for $[\text{C}_{18}\text{H}_{15}\text{NO}]$: C82.73; H6.12; N 5.79; Found: C82.70; H6.09; N5.76. FT-IR (KBr, cm^{-1}), 3421 ν (N-H), 1620 ν (C=N), 1161 ν (C-O), 1479 ν (C=C); $^1\text{H-NMR}$ (300 MHz, $\text{DMSO } d_6$, ppm) 9.61 (1H, s, CH=N), 16.05 (1H, OH), 2.40(3H,CH₃).

Synthesis of complex (1)

The Schiff base ligand (HL: N-(2-hydroxy-1-naphthylidene)-2-methyl aniline) (0.26 g, 1 mmol) was dissolved in 10 ml of methanol and to this yellow solution was added a solution of $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$ (0.10 g, 0.5 mmol) in 10 ml of methanol dropwise. The reaction mixture was refluxed for 6 h. The complex was precipitated, the precipitate was filtered and dried at room temperature. The complex was characterized by UV-Vis, FT- IR, elemental analysis, and single-crystal X-ray diffraction Scheme 1. MP: $220\text{ }^\circ\text{C}$; (yield: 85 %); (MW: 648.103); Anal. Calc. for $[\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{FeN}_2\text{O}_2]$:C66.58; H4.66; N4.31; found: C 66.60; H 4.74; N 4.28. FT-IR (KBr, cm^{-1}), 3418 ν (O-H); 1596 ν (C=N); 1159 ν (C-O), 546 ν (Fe-O); 443 ν (Fe -N).



Scheme 1. Complex (1)

Synthesis of nano-complex (2)

A solution of $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$ (0.10 g, 0.5 mmol) in methanol (10 mL) was positioned in a high-density ultrasonic probe for 10 min. Then to this solution, 10 ml of methanolic solution of Schiff base ligand (0.26 g, 1 mmol) was added dropwise. The resultant solution was then irradiated for 60 min at 60 °C with a power of 100 W. The obtained brown precipitate was filtered and dried in air. MP: 230 °C; (yield: 87 %); (MW: 648.103); Anal. Calc. for $[\text{C}_{36}\text{H}_{30}\text{FeCl}_2 \text{N}_2\text{O}_2]$: C 66.58; H 4.66; N 4.31; found: C 66.62; H 4.70; N 4.30. FT-IR (KBr, cm^{-1}): 3458 ν (O-H); 1596 ν (C=N); 1159 ν (C-O), 543 ν (Fe-O); 444 ν (Fe-N).

Preparation of $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE

$[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE was prepared by mixing of a certain level of ionic liquid and liquid paraffin, 0.1 g of $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex, and 0.9 g of graphite powder. Then the mixture was mixed well for 60 min until a uniformly wetted paste was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess paste out of the tube and polishing it on a weighing paper.

Results and discussion

FT-IR spectra

The FT-IR spectra of complex (1) and nano-complex (2) are shown in Figure 1.

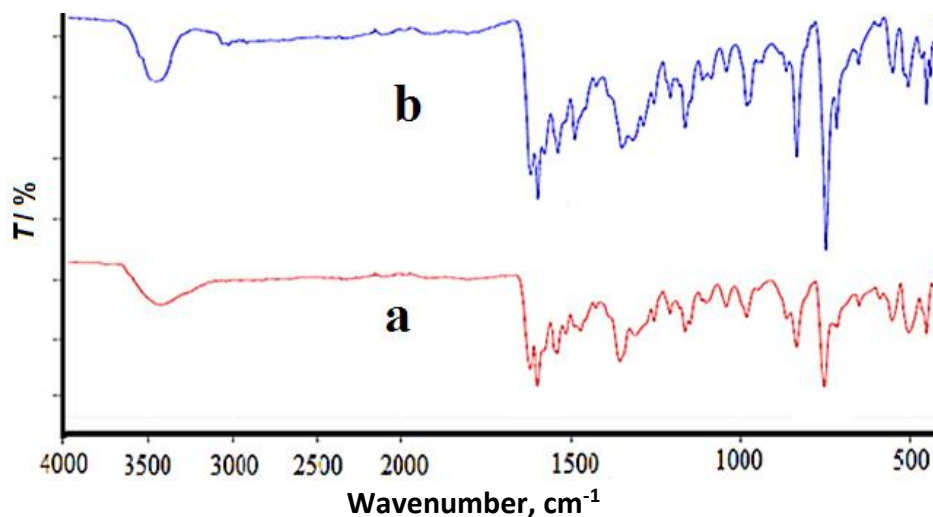


Figure 1. The FT-IR spectra of a: complex (1) b: nano-complex (2)

The FT-IR spectrum of the free Schiff base ligand [HL] exhibits a band in 1620 cm^{-1} due to $\nu(\text{C}=\text{N})$ azomethine and a band at the 1161 cm^{-1} is assigned to the $\nu(\text{C}-\text{O})$ phenolic group [81]. These bands have been shifted to lower frequencies for both complex (1) and nano-complex (2), at 1596 cm^{-1} and in the region of 1146 to 1147 cm^{-1} respectively, which indicates that both compounds are formed by the coordination of the nitrogen and oxygen atoms of [HL] to the metal ion. FT-IR spectra of both complex (1) and nano-complex (2) show weak bands at 546 and 543 cm^{-1} assigned to $\nu(\text{Fe}-\text{O})$ and show weak bands at 443 and 444 cm^{-1} attributed to $\nu(\text{Fe}-\text{N})$. Both complexes (1) and nano-complex (2) display bands at 3418 and 3458 cm^{-1} due to $\nu(\text{O}-\text{H})$ of the phenolic group of [HL] [82].

UV-Vis spectra

UV-Vis spectra of (1) and (2) in methanol solution contain different peaks related to the transition bands are shown in Figure 2. The Schiff base ligand display two bands in 315 and 360 nm attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively [35]. In the electronic spectra of both (1), (2), intra-ligand transitions ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) were shifted to another wavelength in 230 - 250 and 295 - 310 nm , respectively. The electronic spectra of complex (1) and nano-complex (2) showed a d-d transition band in the region of 470 to 480 nm assigned to the transition ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ [82].

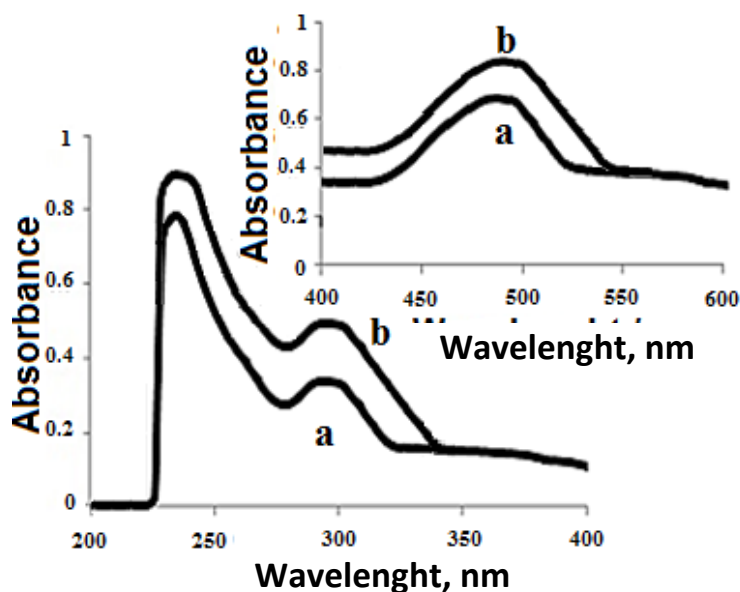


Figure 2. UV-Vis spectra of a: complex (1) b: nano-complex (2) in methanol solution.

XRD and SEM

The XRD patterns of nano-sized Fe(II) complex (2) and standard powder Fe(II) complex (1) were obtained from single-crystal X-ray diffraction and are exhibited in Figure 3. The XRD pattern shows the crystalline phase and the nature of the complex. By investigating the location and intensity of the peaks of both patterns, it can be deduced that the diffraction angle in both complexes obtained by different methods is the same [83]. This indicates that the nano-sized complex (2) has a single crystalline phase that this phase is similar to that obtained by single-crystal X-ray diffraction [84]. The width of the diffraction peaks shows the nanocrystal complex particles (2) are of nanometer scales [85]. The particle size of the nanocrystal complex (2) was calculated using the Debye-Scherrer equation. SEM images of the nanocrystal complex (2) are shown in Figure 4. The SEM photos show the shape of the nano-particles and the surface morphology of the nanocrystal complex as well. The average size diameter obtained from the Debye-Scherrer equation of nanocrystal complex (2) was approximately 52 nm .

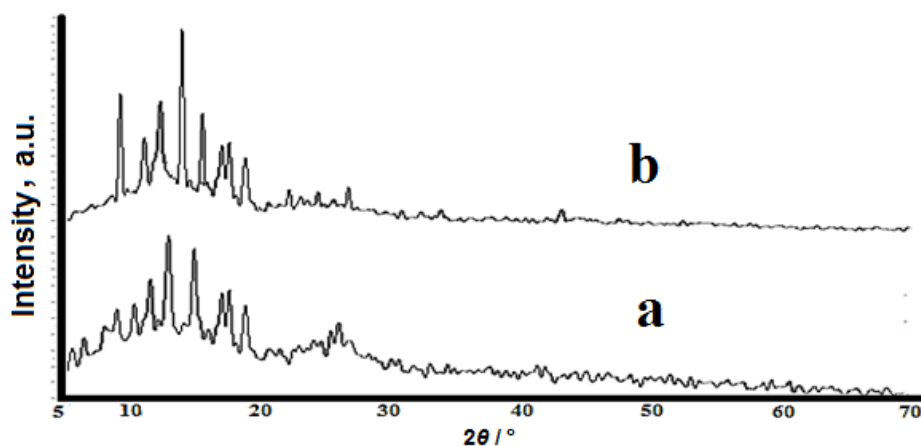


Figure 3. The XRD patterns of a: standard powder Fe(II) complex (1) b: nano-sized Fe(II) complex (2)

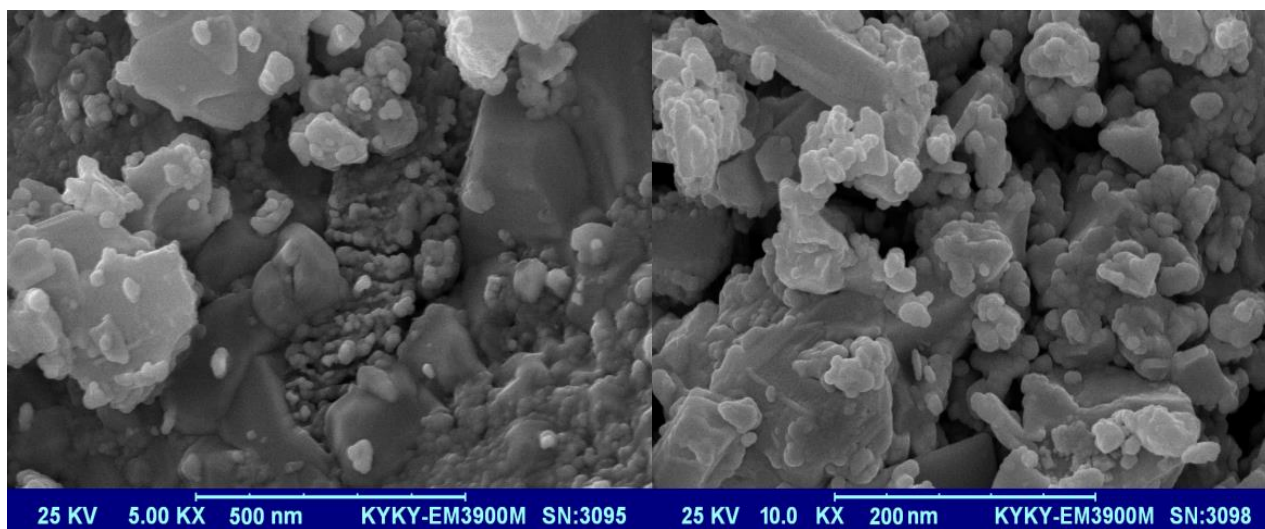
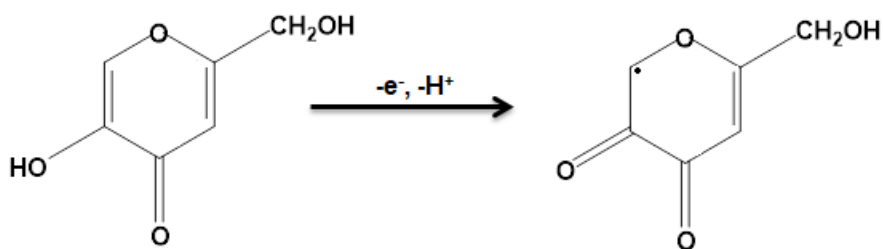


Figure 4. SEM images of the nanocrystal complex (2)

Electrochemical behavior of kojic acid at the surface of various electrodes

To study the electrochemical behaviour of kojic acid, which is pH-dependent, it is necessary to obtain the optimized pH value to achieve accurate results. By performing the experiments using modified electrodes at various pH values ranging from 2.0 to 9.0, it was revealed that the best results for the electrooxidation of kojic acid occur at pH 7.0. Scheme 2 demonstrates the electrooxidation process of kojic acid.



Scheme 2. Electro-oxidation reaction of kojic acid

The electrochemical behavior of kojic acid was investigated by linear sweep voltammetry (LSV). The linear sweep voltammograms obtained using the bare CPE and [Fe(HL)₂Cl₂] nano-complex-IL/CPE in 0.1 M PBS (pH 7.0) in the presence of 100.0 μM kojic acid are shown in Figure 5.

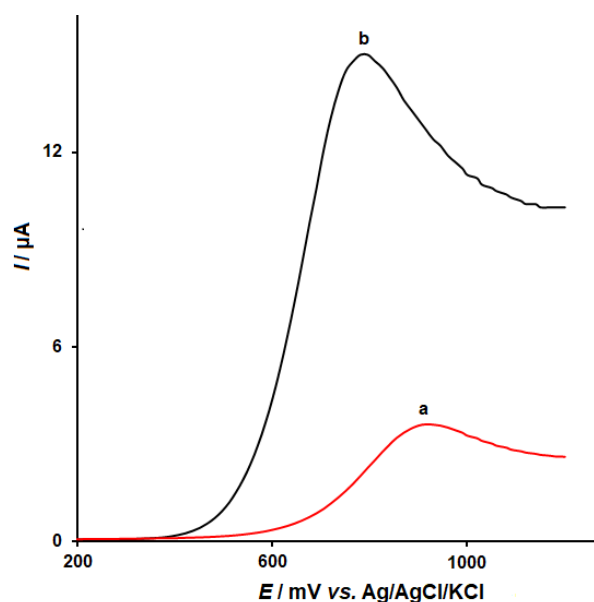


Figure 5. Linear sweep voltammograms of (a) bare CPE and (b) $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE in 0.1 M PBS (pH 7.0) in the presence of 100.0 μM kojic acid at the scan rate 50 mV s^{-1}

At the bare CPE, a weak oxidation peak current ($I_{\text{pa}} = 3.6 \mu\text{A}$) could be seen at 0.93 V. In contrast, $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE exhibited an enhanced sharp anodic peak current ($I_{\text{pa}} = 15 \mu\text{A}$) at much lower overpotential $E_p = 0.8 \text{ V}$. These results confirmed that the $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex and IL improved the sensitivity of the modified electrode by enhancing peak current and decreasing the overpotential of the oxidation of kojic acid.

Effect of scan rate on the determination of kojic acid at $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE

The influence of the scan rate (ν) on the peak currents (I_{pa}) of kojic acid at $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE was investigated by LSV. Figure 6 shows the voltammetric response of 100.0 μM kojic acid at $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE at different scan rates in the range of 10 to 400 mV/s. The oxidation peak current of kojic acid increases linearly with increasing scan rate. Linear regression equation was obtained from the plot I_{pa} and vs. $\nu^{1/2}$ (square root of scan rate) for the oxidation process, which indicates that the reaction of kojic acid at $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE is diffusion controlled.

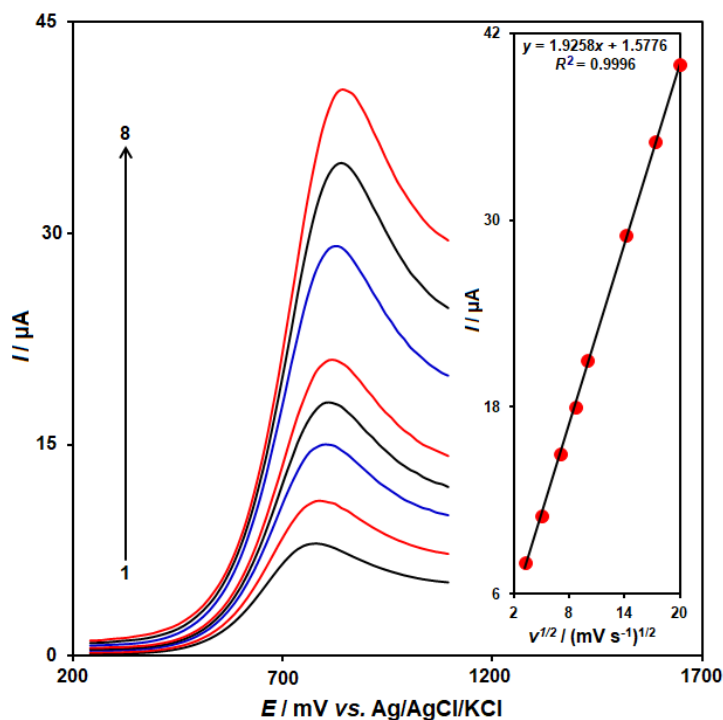


Figure 6. Linear sweep voltammograms of $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE in 0.1 M PBS (pH 7.0) containing 100.0 μM kojic acid at various scan rates; 1-8 correspond to 10, 25, 50, 75, 100, 200, 300, and 400 mV s^{-1} , respectively. Inset: variation of anodic peak current vs. $\nu^{1/2}$

To obtain some information on the rate-determining step, we drew a Tafel plot (Figure 7) using the data from the rising part of the current-voltage curve recorded at a low scan rate of 10 mV s^{-1} for $100.0 \mu\text{M}$ kojic acid. The linearity of the E versus $\log I$ plot implies the intervention of the kinetics of the electrode process. The slope of this plot can be used to estimate the number of electrons transferred in the rate-determining step. According to Figure 7 inset, the Tafel slope for the linear part of the plot was estimated to be equal to 0.208 V . The value of the Tafel slope indicates that the one-electron transfer process is the rate-limiting step, assuming a transfer coefficient (α) of about 0.72 .

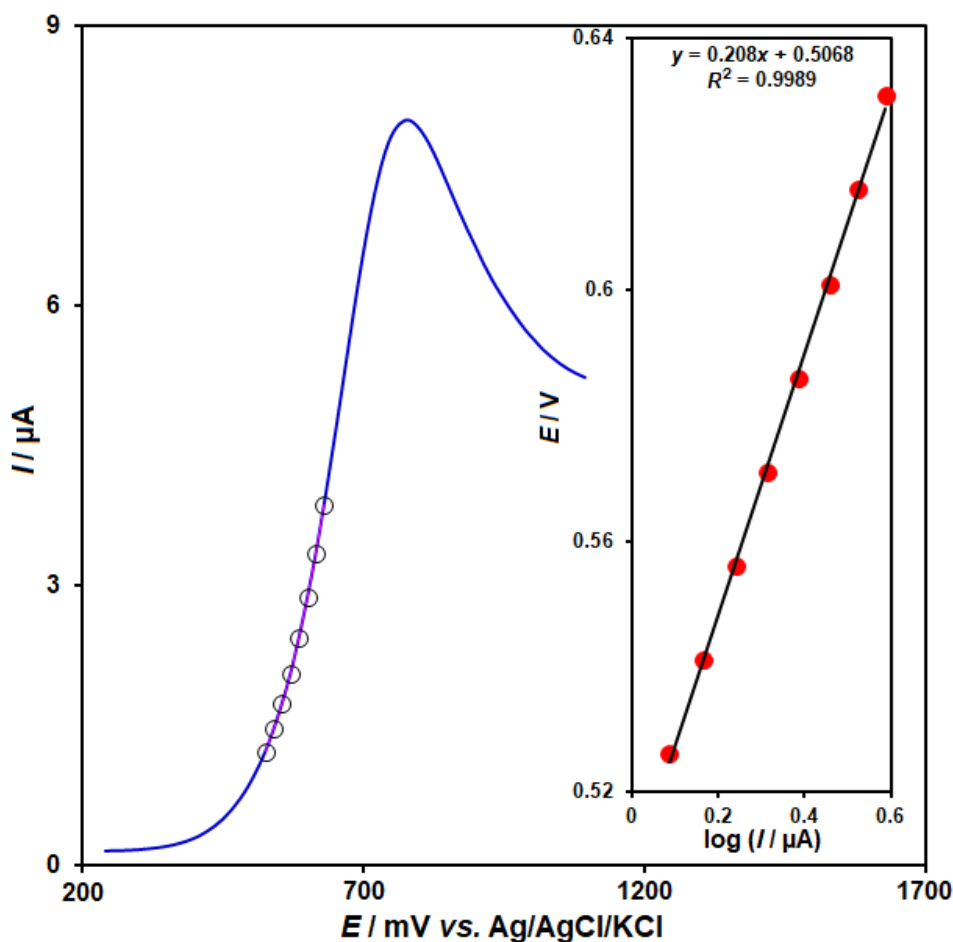


Figure 7. Linear sweep voltammograms for $100.0 \mu\text{M}$ kojic acid with 10 mV s^{-1} scan rate. Inset: The Tafel plot derived from the rising part of the corresponding voltammogram

Chronoamperometric analysis

The analysis of chronoamperometry for kojic acid samples was performed by use of $[\text{Fe}(\text{HL})_2\text{Cl}_2]$ nano-complex-IL/CPE vs. Ag/AgCl/KCl (3.0 M) at 0.85 V . The chronoamperometric results of different concentrations of kojic acid in PBS ($\text{pH } 7.0$) are demonstrated in Figure 8. The Cottrell equation for the chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as presented in Eq. (1).

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (1)$$

where D represents the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), and C_b is the applied bulk concentration (mol cm^{-3}). Experimental results of I vs. $t^{-1/2}$ were plotted in Figure 8A, with the best fits for different concentrations of kojic acid. The resulting slopes corresponding to straight lines in Figure 8A were then plotted against the concentration of kojic acid (Figure 8B). The mean value of D was determined to be $7.8 \times 10^{-6} \text{ cm}^2/\text{s}$ according to the resulting slope and Cottrell equation.

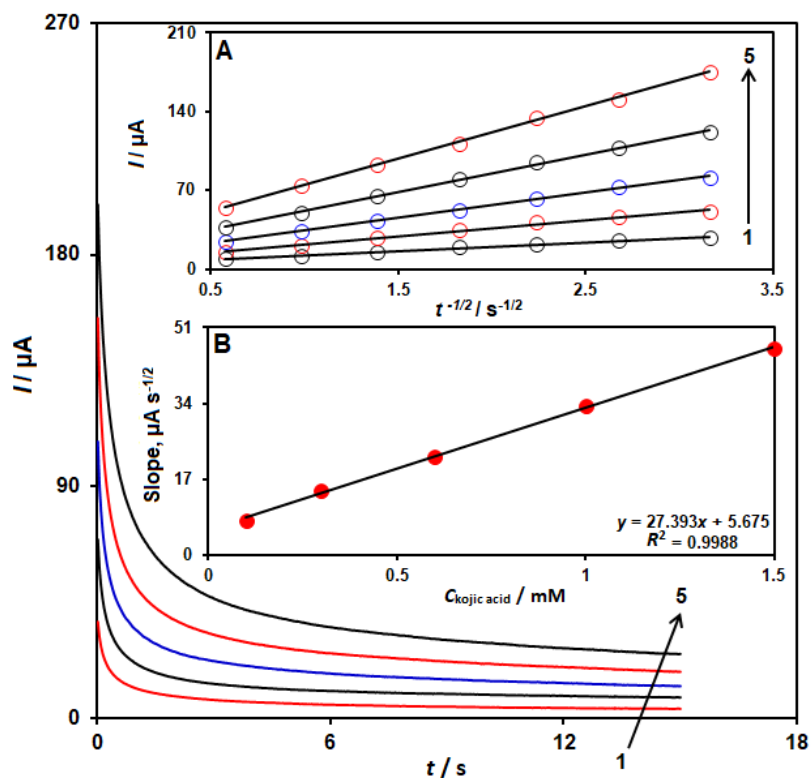


Figure 8. Chronoamperograms obtained at $[Fe(HL)_2Cl_2]$ nano-complex-IL/CPE in 0.1 M PBS (pH 7.0) for different concentrations of kojic acid; Numbers 1-5 correspond to 0.1, 0.3, 0.6, 1.0, and 1.5 mM of kojic acid. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1-5. (B) Plot of the slope of the straight lines against kojic acid concentration

Calibration curve

Because DPV commonly has a higher sensitivity than the CV technology, the DPV technique was applied for the quantitative detection of kojic acid. Figure 9 shows the differential pulse voltammograms of kojic acid at various concentrations using $[Fe(HL)_2Cl_2]$ nano-complex-IL/CPE (potential step = 0.01 V and pulse amplitude = 0.025 V). As seen, the oxidation peak currents of kojic acid enhance gradually by increasing its concentration. The oxidation peak currents (I_{pa}) show a good linear relationship with the concentrations of kojic acid ranging from 0.3 M to 237.0 μ M (Figure 9 (inset)). Also, the limit of detection (LOD) was estimated to be $0.09 \pm 0.001 \mu$ M. In addition, Table 1 shows that the $[Fe(HL)_2Cl_2]$ nano-complex-IL/CPE can compete with other sensors for the determination of kojic acid.

Table 1. Linear range and LOD obtained at the $[Fe(HL)_2Cl_2]$ nano-complex-IL/CPE for the determination of kojic acid compared with other sensors.

Electrochemical sensor	Method	Linear range, μ M	LOD, μ M	Ref.
Poly(glutamic acid)-modified glassy carbon electrode	Cyclic voltammetry	8.0 – 660	0.8	[5]
Polyvinylpyrrolidone (cross-linked) modified acetylene black paste electrode	Linear sweep voltammetry	1.0 - 100	0.5	[8]
Multi-walled carbon nanotubes modified screen-printed electrode	Differential pulse voltammetry	20.0 – 5000.0	16.0	[1]
Ni-Fe layered double hydroxide modified glassy carbon electrode	Amperometric	1.0 - 4500.0	0.73	[10]
$[Fe(HL)_2Cl_2]$ nano-complex-IL/CPE	Differential pulse voltammetry	0.3-237.0	0.09	This work

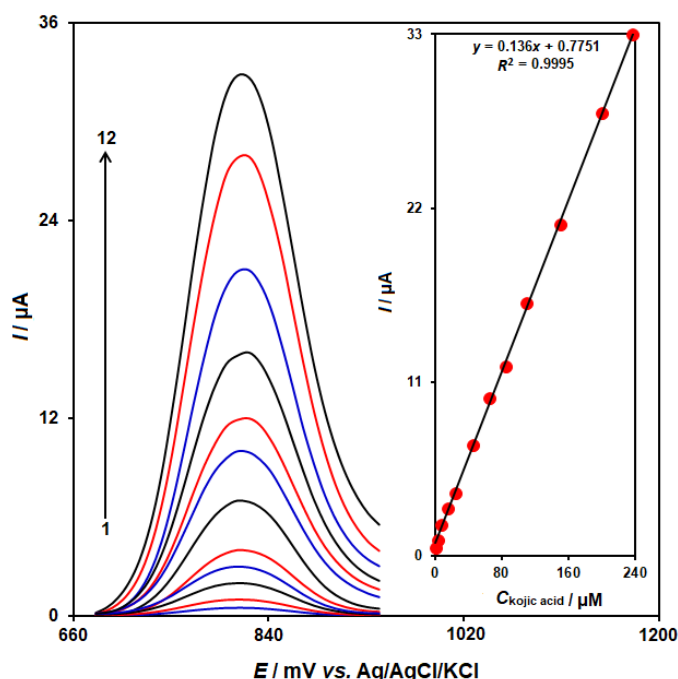


Figure 9. DPVs of [Fe(HL)₂Cl₂] nano-complex-IL/CPE in 0.1 M (pH 7.0) containing different concentrations of kojic acid. Numbers 1–12 correspond to 0.3, 3.0, 7.0, 15.0, 25.0, 45.0, 65.0, 85.0, 110.0, 150.0, 200.0, and 237.0 μM of kojic acid. Inset: plot of the electrocatalytic peak current as a function of kojic acid concentration in the range of 0.3-237.0 μM

Analysis of real samples

The real samples for the analysis were prepared and quantified by the DPV method. The developed sensor was applied to detect kojic acid in real samples. The results are summarized in Table 2. Each measurement was repeated five times. The recovery and relative standard deviation (RSD) values confirmed that the [Fe(HL)₂Cl₂] nano-complex-IL/CPE sensor has great potential for analytical application.

Table 2. The application of [Fe(HL)₂Cl₂] nano-complex-IL/CPE for determination of kojic acid in real samples (n=5)

Sample	C / μM		Recovery, %	RSD, %
	Spiked	Found		
Edible oil	0	2.7	-	3.3
	2.0	4.6	97.9	1.7
	3.0	5.7	101.7	2.4
Chilli sauce	0	4.5	-	1.9
	1.0	5.7	103.6	3.6
	2.0	6.3	97.0	2.1

Conclusions

We have reported the synthesis of a Schiff base ligand and a new Fe(II) Schiff base complex (1). The single crystal X-ray diffraction analysis of the complex showed that metal ions reacted with the ligand in a 1:2 molar ratio. In the formation of the complex, oxygen atoms of two ligands are coordinated to a metal ion, and with two chloride ions attached to the metal ion, octahedral geometry is formed around the metal ion. The XRD patterns indicated both (1) and (2) compounds prepared by different synthesis methods have the same crystal structure. We established a sensitive and fast electrochemical method to detect the kojic acid based on Fe(HL)₂Cl₂] nano-complex (2) and

ionic liquid-modified carbon paste electrode. The voltammetric investigation demonstrates that electrooxidation of kojic acid at the surface of [Fe(HL)₂Cl₂] nano-complex-IL/CPE showed very distinct characteristics due to the presence of nanoparticles of [Fe(HL)₂Cl₂] complex and ionic liquid on the surface of the electrode. Quantitative analysis performed by DPV showed a good linear relation in the concentration range of 0.3–237.0 μM of kojic acid, and the detection limit was 0.09±0.001 μM. Finally, the proposed method was successfully applied in the determination of kojic acid in real samples with satisfactory results.

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