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Tris(2,2′-bipyridine)ruthenium(II) electrochemiluminescence using rongalite as coreactant and its application in detection of foodstuff adulteration

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ABSTRACT

The persistent reports on the indiscriminate contamination of foodstuffs with inedible chemicals for economic gains and the high cost of the existing analytical methods for their detection make it necessary to develop simple and cheaper methods for the immediate detection of those toxic substances. Here, we report a fast and highly sensitive electrochemiluminescence (ECL) method for the detection of foodstuffs adulteration with an industrial bleaching agent-rongalite for the first time. Under the optimal condition, the ECL intensity of the tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) increases linearly with the concentration of rongalite in the range of 1 μM to 1000 μM with a limit of detection of 0.57 μM (S/N = 3). The developed method has shown excellent selectivity in the presence of co-existing interfering species. The application of the ECL method in this contribution can be extended to other foodstuffs that might be adulterated with rongalite other than the one (tofu) investigated here.

1. Introduction

The adulteration or contamination of food with non-edible chemicals remains a common threat to humanity. The failure to follow established quality control standards during the processing of the food or the deliberate addition of toxic chemicals contributes immensely to the menace of food adulteration.

Adulteration of food makes it unwholesome. Recently, there has been a surge in the food contamination cases; this causes concern about the safety and the quality of the food we consume. Milk, honey, spices and ice creams are among the common foodstuffs that are prone to adulteration [1–5]. Others include oils, wines, sugar, meat, food grains and flour [6–10]. Unfortunately, most of the food adulterants are known carcinogens [11,12], others are neurotoxic [13] or hepatotoxic [14,15].

Rongalite (RGL), also known as sodium formaldehyde sulfoxylate or sodium hydroxymethane sulfinate, is used industrially as a bleaching agent, in redox initiator system as a reducing agent for emulsion polymerization [16,17] or vat dyeing. In the early twentieth century, RGL was used as an antidote for mercury poisoning [18,19] but was stopped following the death of a significant number of the subjects. RGL has a wide range of applications in organic synthesis [20–22]. According to some reports in the literature, RGL is stable in both alkaline and neutral pH [23] and decomposes thermally [24] or in acidic media [25] to form toxic substances such as sulphur dioxide [26], formaldehyde [27], hydrogen sulphide [20] and sodium sulfate [28]. It is increasingly used in cosmetics particularly in hair dye colour removers despite the generation of formaldehyde [27], a well-known carcinogen. The toxicity of RGL and its decomposition products prompted a complete ban on its use in foodstuffs in countries such as China and India. However, it is still found in some foodstuffs such as tofu, corn flour, bean curd, vermicelli and wheat flour [29] as an additive for bleaching purposes and improving tenderness.

Analytical methods such as polarography [30], spectrophotometry [31], electrochemical analysis [32], capillary electrophoresis [33], HPLC [34] and ion-pair chromatography [35] have been used to detect RGL in various substances. Although some of these methods are sensitive, however, most of them require highly expensive instrumentation or derivatization and sometimes determined only the decomposition products [36] instead of RGL directly. Recently, the determination of RGL in a number of different foodstuffs in the presence of sulfite was reported using electrochemical non-enzymatic sensor based

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on cetyltrimethylammonium bromide (CTAB) and chitosan functionalized carbon nanotube modified glassy carbon electrode [32]. This method involved complicated synthesis, tedious electrode modification and low sensitivity. In another recent report, RGL was determined in agrifood *via* a sandwich lateral flow strip using aptamers [37], this method also suffered similar drawbacks. The increase in the adulteration of foodstuffs using RGL and the flaw in most of the existing methods for its detection makes it necessary to develop sensitive and highly selective analytical methods for its immediate detection to forestall a major outbreak of deadly diseases.

Electrogenerated chemiluminescence, also known as electrochemiluminescence (ECL), combines both features of electrochemistry and chemiluminescence. It provides a fast, sensitive and reproducible analytical technique and has been used to detect different analytes in complex matrices [38,39]. ECL has a wide linear range, low limit of detection, excellent sensitivity as well as good selectivity [40].

In this work, we demonstrate for the first time the utility of RGL/tris(2,2′-bipyridine)ruthenium(II) system in the detection of food adulteration. Interestingly, the ECL of $Ru(bpy)_3^{2+}$ increases remarkably with the concentration of RGL. This property is used to detect RGL in tofu, a traditional component of East and Southeast Asian cuisines. The mechanism of the ECL of the developed system is discussed and the selectivity of the method is evaluated in the presence of soluble carbohydrates, amino acids and metal ions.

2. Materials and methods

RGL, sucrose and fructose were supplied by Sinopharma Chemical Reagents Co., Ltd. Glucose, calcium chloride, magnesium chloride and iron(II)sulfate heptahydrate were purchased from Beijing chemical works (Beijing, China). Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate was supplied by Sigma Aldrich. Tofu was purchased from a store near the institute. Britton-Robinson buffer was prepared from 0.04 M acetic acid, 0.04 M phosphoric acid and 0.04 M boric acid, the pH was adjusted using 0.2 M sodium hydroxide. All other reagents were analytical grades and used as received.

A BPCL ultra-weak luminescence analyzer (Institute of Biophysics, Chinese Academy of Sciences Beijing, China) was used to measure the ECL emission. CHI 830B electrochemical workstation (Shanghai, China) was used to perform the electrochemical experiments. A three-electrode cell consisting of a glassy carbon electrode, a spirally coiled platinum wire and Ag/AgCl electrode (3 M KCl) were used as working, auxiliary and reference electrode to perform the electrochemical measurements. The photomultiplier tube (PMT) was maintained at 1000 V throughout the ECL experiments.

Before the first electrochemical measurement, an emery paper was used to polish the surface of the working electrode. Subsequently, the same electrode was further polished using alumina slurry (0.3 and 0.05 μm) to a mirror finish before ultra-sonication in ethanol for 5 min and finally rinsed with doubly distilled water.

2.1. ECL measurement

A three electrode cell having a transparent bottom that allows direct passage of ECL was placed in a dark box perpendicular to a PMT for capturing the ECL. 100 μL aliquot each of $Ru(bpy)_3^{2+}$ and RGL was added to the cell and the volume was completed to 500 μL with BR buffer of appropriate pH. A BPCL software accompanying the ultra-weak luminescence analyzer was used for the acquisition of the ECL data. For spike and recovery experiments, a solution containing tofu was prepared by dispersing 0.5 g of tofu in 5 mL of doubly distilled water and maintained under ultrasonication for 15 min. 3 mL of the homogenized mixture was placed in a test tube and centrifuged for 15 min at 12000 rpm. 1 mL aliquot of supernatant solution was collected and dispersed in another 4 mL of doubly distilled water. Finally, aqueous solutions of RGL having concentration of 15, 30, 45 and 60 μM were added to the as-prepared tofu solution and used for the spike and recovery experiments.

3. Results and discussion

3.1. ECL and electrochemical behaviour of $Ru(bpy)_3^{2+}$ with RGL as a coreactant

Fig. 1A indicates the ECL intensity *versus* potential dependencies of 0.6 mM $Ru(bpy)_3^{2+}$ in the absence and presence of 1 mM RGL on glassy carbon(GC) electrodes. Neither the Britton-Robinson (BR) buffer nor the RGL solutions show ECL signals at pH 7.2. In contrast, the $Ru(bpy)_3^{2+}$ solution in BR buffer (pH 7.2) shows a weak ECL signal due to the reaction between the electrogenerated $Ru(bpy)_3^{3+}$ and the OH^- which occurs usually at a potential about 1.1 V on the GC electrode [41] (*vs* Ag/AgCl). Surprisingly, the introduction of 1 mM RGL to 0.6 mM $Ru(bpy)_3^{2+}$ enhances the ECL signal intensity significantly. The enhancement of the ECL signal of $Ru(bpy)_3^{2+}$ due to the addition of RGL clearly suggests its efficiency as a coreactant of $Ru(bpy)_3^{2+}$.

Fig. 1B indicates the cyclic voltammograms of BR buffer pH 7.2, RGL, $Ru(bpy)_3^{2+}$ as well as the mixture of RGL and $Ru(bpy)_3^{2+}$. RGL shows an irreversible oxidation peak at about 0.71 V (Fig. 1B red curve) indicating that RGL can be oxidized at a bare GC electrode. $Ru(bpy)_3^{2+}$ shows a pair of reversible redox peaks at around 1.1 V and 1.05 V (Fig. 1B blue curve). The addition of RGL to the $Ru(bpy)_3^{2+}$ results in a remarkable increase in the oxidative current of $Ru(bpy)_3^{2+}$ and a substantive decrease in its reductive current (Fig. 1B green curve), suggesting that $Ru(bpy)_3^{2+}$ can catalyze the electrooxidation of RGL.

To further confirm that the ECL emission observed for RGL/$Ru(bpy)_3^{2+}$ system is due to $Ru(bpy)_3^{2+*}$. The ECL emission spectrum for RGL/$Ru(bpy)_3^{2+}$ system was measured using optical filters that selectively transmit light from 400 to 640 nm (Fig. 2). The

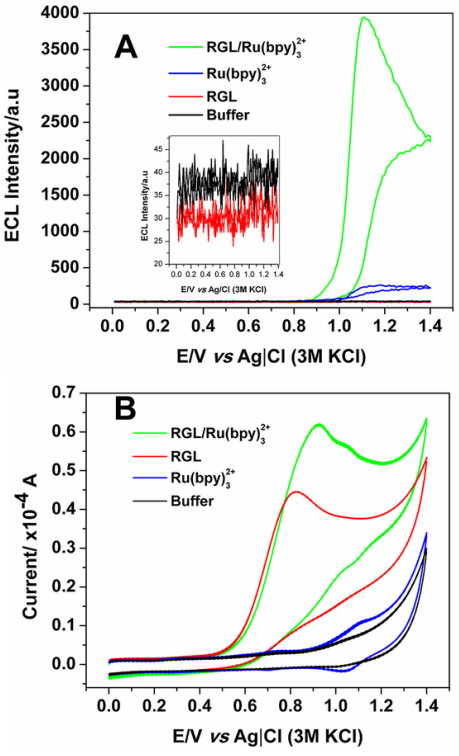

Fig. 1. (A) ECL-intensity potential profile (I_{ECL}-E) (A) and corresponding cyclic voltammograms (B) on glassy carbon electrode in Britton-Robinson buffer (pH 7.2) alone (black), 1 mM RGL (red), 0.6 mM $Ru(bpy)_3^{2+}$ (blue), 0.6 mM $Ru(bpy)_3^{2+}$ and 1 mM RGL (green). Inset: represents enlarged I_{ECL-E} curves for BR buffer and 1 mM RGL. Scan rate: 0.1 V s^{-1}; photomultiplier tube voltage: 1000 V. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

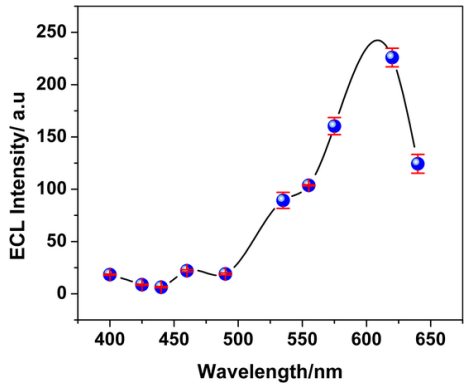

Fig. 2. ECL spectrum of RGL/$Ru(bpy)_3^{2+}$. Conditions: 0.6 mM $Ru(bpy)_3^{2+}$ and 1 mM RGL in BR buffer (pH 7.2) on GC electrode; photomultiplier tube voltage: 1000 V.

maximum ECL of RGL/$Ru(bpy)_3^{2+}$ emission was observed at a wavelength of approximately 610 nm which corresponds to the emission wavelength of $Ru(bpy)_3^{2+*}$ upon relaxation to ground state. This finding is consistent with the previous reports [42,43] in the literature and further confirms that the main ECL emitter is the $Ru(bpy)_3^{2+}$.

3.2. ECL mechanism

It has been reported that RGL can be oxidized to generate formaldehyde and HSO_2^- (Eq. (1)) in neutral medium [30,44]. It has also been reported that water can be oxidized to generate hydroxyl radical (Eq. (2)) and OH• reacts with formaldehyde to produce a strong reducing intermediate •CHO. •CHO can subsequently react with $Ru(bpy)_3^{3+}$ to produce ECL (Eqs. (5), (6)) and react with $Ru(bpy)_3^{2+}$ to generate $Ru(bpy)_3^{+}$ (Eq. (7)) which then reacts with electrogenerated $Ru(bpy)_3^{3+}$ to produce ECL (Eqs. (8), (5)) [45]. Thus, the mechanism of RGL/$Ru(bpy)_3^{2+}$ ECL is proposed as follows:

$$HOCH_2SO_2^- - e \rightarrow HCHO + HSO_2^- \quad (1)$$

$$H_2O - e \rightarrow H^+ + OH^{\cdot} \quad (2)$$

$$HCHO + OH^{\cdot} \rightarrow {}^{\cdot}CHO + H_2O \quad (3)$$

$$Ru(bpy)_3^{2+} - e \rightarrow Ru(bpy)_3^{3+} \quad (4)$$

$$Ru(bpy)_3^{3+} + {}^{\cdot}CHO \rightarrow Ru(bpy)_3^{2+*} + \text{Products} \quad (5)$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu \quad (6)$$

$$Ru(bpy)_3^{2+} + {}^{\cdot}CHO \rightarrow Ru(bpy)_3^{+} + \text{Products} \quad (7)$$

$$Ru(bpy)_3^{+} + Ru(bpy)_3^{3+} \rightarrow Ru(bpy)_3^{2+} + Ru(bpy)_3^{2+*} \quad (8)$$

3.3. Optimization of parameters affecting the ECL signal responses

3.3.1. Effect of pH on the ECL intensity

Previous reports [46–48] in the literature have confirmed that the ECL of $Ru(bpy)_3^{2+}$ is pH dependent, therefore we investigated the influence of pH on the developed electrochemiluminescent method. Fig. 3A shows the dependence of the ECL responses of the RGL/$Ru(bpy)_3^{2+}$

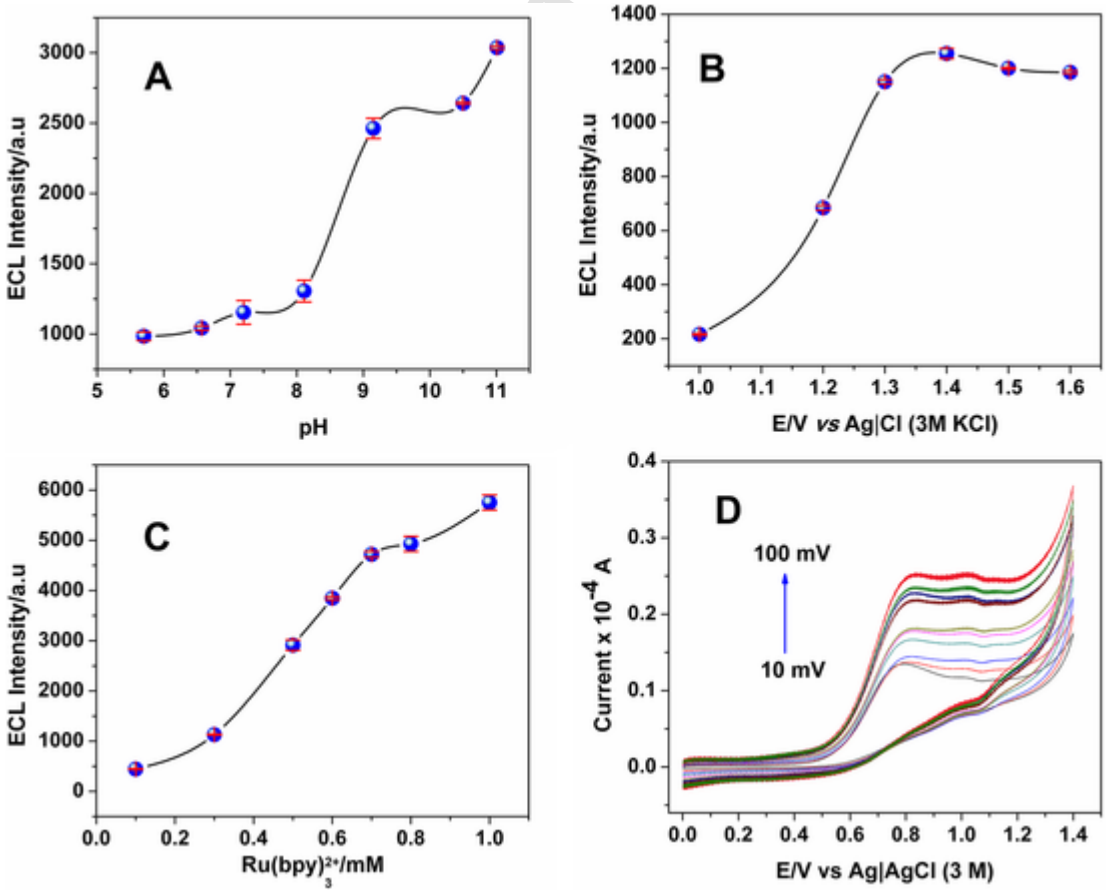

Fig. 3. (A) ECL intensity-pH profile; 1 mM $Ru(bpy)_3^{2+}$ and 1 mM RGL in BR buffer (pH 7.2) on GC electrode; (B) ECL intensity-potential dependencies; conditions as in 2A above. (C) Dependence of ECL intensity on the concentrations of $Ru(bpy)_3^{2+}$; 1 mM RGL in BR buffer (pH 7.2); (D) Scan rate *vs* anodic peak current profile (scr-i_p); 1 mM $Ru(bpy)_3^{2+}$ and 1 mM RGL in BR buffer (pH 7.2) on GC electrode; photomultiplier tube voltage: 1000 V.

system on the pH of the medium. There is a progressive increase in the ECL intensity from pH 5.7 to 8.1. The ECL intensity increases rapidly particularly at pH 9.2 which may be due to the generation of more ECL-active moieties and maintains its former trend until the highest ECL value is attained at pH 11.0. To avoid more side reactions at higher pH values which may possibly interfere with the ECL signal intensity, a neutral pH (7.2) was chosen for further investigation.

3.3.2. Effect of potential on the ECL intensity

Fig. 3B indicates the ECL intensity-potential relationships. The ECL intensity increases remarkably when the potential reaches 1.0 V and continues as such until it reaches its maximum at 1.4 V. The rapid increase in the ECL intensity between the potential range of 1.0 V and 1.4 V is due to the oxidation of $Ru(bpy)_3^{2+}$ and RGL which results in the generation of more ECL-active species. The ECL intensities decrease as the potential increases beyond the optimal value. The decrease in the ECL at higher potential can also be due to the side reactions. The potential value of 1.4 V is being considered as the optimal for the subsequent ECL investigations.

3.3.3. Effect of the concentration of $Ru(bpy)_3^{2+}$ on the ECL intensity

Previous reports on the ECL have shown that the ECL signal intensity is greatly dependent on the concentrations of the luminophore. In this report, the effect of the concentrations of $Ru(bpy)_3^{2+}$ on the ECL responses is also investigated and the results are presented in Fig. 3C. The ECL intensity increases as the concentration of $Ru(bpy)_3^{2+}$ increases from 0.1 to 1 mM. This remarkable increase in the ECL responses due to the increase in the concentration of $Ru(bpy)_3^{2+}$ can be associated with the rate at which the ECL-active species are produced and consumed at the electrode surface.

3.3.4. Effect of the scan rate on the ECL anodic peak current

As noted above, various parameters affect the ECL responses. Meanwhile, the scan rate also affects the ECL anodic peak currents which are directly related to the ECL signal intensities. The variation of the anodic peak currents with scan rate is investigated using cyclic voltammetry and the results are presented in Fig. 3D. As the scan rate changes (10–100 mV s^{-1}), the anodic peak current also increases sharply which correspondingly enhances the ECL intensity to its optimal value. Another deduction from this correlation is that as the scan rate increases, there is a corresponding linear increase in the ECL intensity with the square root of the scan rate. This demonstrates that the ECL reaction of RGL and $Ru(bpy)_3^{2+}$ is diffusion controlled.

3.4. Reproducibility

The reproducibility of the developed ECL method was investigated as shown in Fig. 4 using the coefficient of reproducibility as a measure of precision ($n = 18$). The relative standard deviation is 2.1%. The result shows that the RGL/$Ru(bpy)_3^{2+}$ system is stable and can produce consistent results upon repeated measurements.

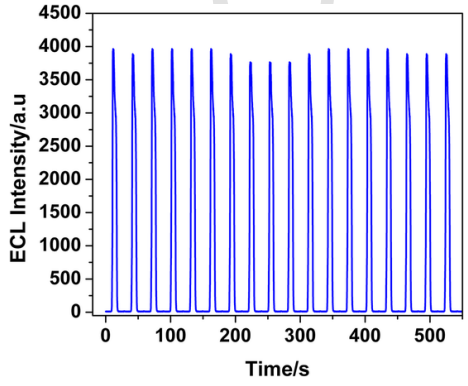

Fig. 4. ECL signal stability *vs* time; 0.6 mM $Ru(bpy)_3^{2+}$ and 1 mM RGL in BR buffer (pH 7.2) on GC electrode; Scan rate: 0.1 V s^{-1}; photomultiplier tube voltage: 1000 V.

3.5. Detection of RGL

RGL detection based on the newly developed system was examined under the optimized conditions. As shown in Fig. 6, the ECL intensity increases linearly as the concentration of RGL increases from 1 μM to 1000 μM. The obtained linear equation is $I_{ECL} = 246.3 + 3701c$ with a correlation coefficient $R^2 = 0.999$. Where I_{ECL} is the ECL signal intensity, c is the concentration of RGL. The relative standard deviation is 2.1% for $n = 18$ using 0.6 mM $Ru(bpy)_3^{2+}$ and 1.0 mM RGL. The limit of detection (LOD) for RGL is 0.57 μM (S/N = 3).

3.6. Selectivity

The application of any developed analytical method depends on its resistance to interference by co-existing species. Soy bean which is the main ingredient for the preparation of tofu consists of about 15% soluble carbohydrates [49], 38% proteins [50–52] and a significant proportion of calcium [53] and iron [54]. Magnesium is also present in the tofu which finds its way from the coagulating agent. In order to test the selectivity of the developed RGL/$Ru(bpy)_3^{2+}$ ECL system, potential interferents were identified based on their presence in the soy bean being the main raw material for the preparation of tofu or in the coagulating agent. 50 μM uniform concentration each of fructose, sucrose, glucose, glutamic acid (Glut. Acid), tyrosine and metal ions including Ca^{2+}, Mg^{2+} and Fe^{2+} were tested. Fig. 5 shows the ECL intensity of the optimized RGL/$Ru(bpy)_3^{2+}$ system and its responses in the presence of the tested interferents. ECL was quenched slightly in the presence of these investigated interferents. It is hypothesised that fructose, sucrose, glucose, glutamic acid, and tyrosine may react with electrogenerated hydroxyl radical, Ca^{2+}, Mg^{2+} and Fe^{2+} may form complexes with RGL, resulting in the quenching of ECL.

3.7. Detection of RGL in real sample

The analytical utility of the proposed method was examined for real tofu sample analysis. Before the spike and recovery experiment, a control sample containing the prepared tofu sample as described in the experimental section was tested. The obtained ECL intensities for the control samples could not be differentiated from the background signal, indicating the absence of RGL in the real samples. Since no RGL is found in the real tofu sample, we used 15, 30, 45 and 60 μM concentrations of RGL and performed spiked and recovery experiments. Analysis of their ECL signal intensities demonstrated quite satisfactory recoveries in the range of 98.7–103.3%. The obtained recoveries and their respective relative standard deviations (RSD) as shown in Table 1

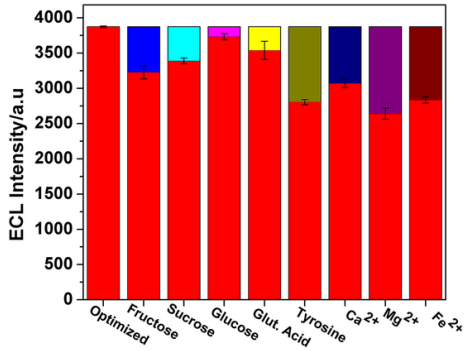

Fig. 5. Relative ECL intensity of the optimized RGL/$Ru(bpy)_3^{2+}$ system in the presence of the co-existing interfering species (IS). Conditions of the measurements: 0.6 mM $Ru(bpy)_3^{2+}$ and 1 mM RGL in BR buffer (pH 7.2) on GC electrode; concentration of the IS: 50 μM; scan rate: 0.1 V s^{-1}; photomultiplier tube voltage: 1000 V.

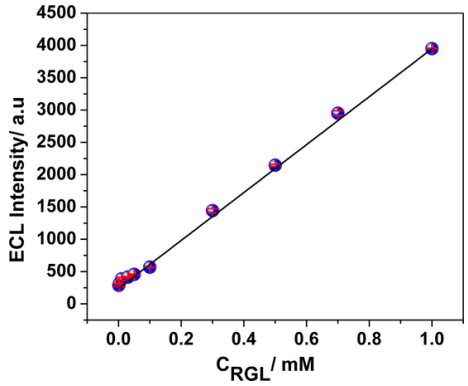

Fig. 6. The linear dependence of the ECL of the $Ru(bpy)_3^{2+}$ on the concentrations of RGL from 0.001 to 1 mM (1–1000 μM). *c* [$Ru(bpy)_3^{2+}$], 0.6 mM; pH, 7.2; PMT, 1000 V.

Table 1
Detection of RGL in real samples (tofu), for triplicate measurement (n = 3).

Sample	RGL spiked (μM)	RGL found (μM)	Recovery (%)	RSD %
1 [a]	0	–	–	2.1
2	15	15.4	102.7	1.4
3	30	31.0	103.3	1.2
4	45	44.4	98.7	3.2
5	60	60.6	101.0	3.9

[a] RGL was not observed in the real sample before the spiking experiments.

demonstrated that RGL can be determined in real tofu samples without significant interference from the components present in the real samples. The obtained results in the proposed methods were comparable with the previously reported techniques for the detection of RGL as shown in Table 2.

4. Conclusion

In the present contribution, we explored the use of RGL as an efficient coreactant for the ECL of $Ru(bpy)_3^{2+}$. Interestingly, the developed ECL system is fast, sensitive and highly selective for the detection of food adulteration using RGL as the food adulterant. The method exhibits wide linear range, low detection limit and excellent selectivity. It was successfully applied to the determination of RGL in tofu. Comparatively, the developed ECL system for the detection of RGL is simple in terms of instrumentation and less expensive compared to the previously reported techniques and can be extended to detection of RGL in other foodstuffs.

Table 2
Comparison of the RGL/$Ru(bpy)_3^{2+}$ ECL system to other analytical methods for the detection of RGL.

Analytical method	Sample	Linear range (μM)	LOD (μM)	Ref.
[a]Ion-pair Chromatography	Air-saturated solutions	90–460	4.23	[35]
[b]ELAA	Food	0.042–0.85	0.0048	[55]
[c]LSFA	Agrifood	–	8.47	[37]
PtCuCo-colourimetry	–	0.3–100	–	[56]
[d]LS-voltammetry	–	30–800	9.60	[32]
ECL	Tofu	1–1000	0.57	This work

[a,b,c,d]To ensure uniformity and ease of comparison in terms of units, the linear range and the LOD were converted to μM.

Author contribution statement

Abubakar Abdussalam: Conceptualization, Methodology, Writing-Original draft preparation, Funding acquisition. **Fan Yuan**: Visualization, Writing-Reviewing and Editing. **Xiangui Ma**: Visualization. **Fangxin Du**: Writing-Reviewing and Editing. **Yuriy T. Zholudov**: Funding acquisition, Writing-Reviewing and Editing. **Muhammad Nadeem Zafar**: Funding acquisition, Writing-Reviewing and Editing. **Guobao Xu**: Supervision, Funding acquisition, Writing-Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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