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Use of an Electrogenerated Chemiluminescence Sensor Modified with Sm_2O_3 Nanoparticles/Chitosan for the Analysis of Phenylalanine

Sepideh Mohammad Beigi,[1] Chrow Ahmed Khurshid,[2] Fazeleh Mesgari,[1] Tahereh Poursaberi,[3] and Morteza Hosseini[4,*]

[1]Center of Excellence in Electrochemistry, School of Chemistry, College of Science, University of Tehran, Tehran, Iran

[2]College of Pharmacy, University of Kirkuk, Iraq

[3]Analytical Chemistry Research Center, Research Institute of Petroleum Industry, Tehran, Iran

[4]Department of Life Science Engineering, Faculty of New Sciences & Technologies, University of Tehran, Tehran, Iran

*Corresponding Author, Tel.: +982186093196

E-Mail: hosseini_m@ut.ac.ir

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Abstract- After modifying an electrogenerated chemiluminescence sensor with a $Ru(bpy)_3^{2+}/Sm_2O_3$ Nanoparticles(NPs)/chitosan composite, the resulting electrode was used as a sensitive tool for the detection of phenylalanine. The electrochemiluminescence (ECL) signal resulting from the electrochemical interaction between tris(2,2-bipyridyl) ruthenium(II) ($Ru(bpy)_3^{2+}$) and the analyte on the surface of the modified sensor. The presence of the Sm_2O_3NPs was found to enhance the ECL signal. Further the influences of $Ru(bpy)_3^{2+}$ concentration, potential scan rate and solution pH on the intensity of the signal were monitored and optimized. The method showed a linear response in the range of 5.0×10^{-11} to 5.0×10^{-7} M (R^2=0.9824) with a detection limit of 1.4×10^{-11} M. The modified ECL sensor was further used for the analysis of phenylalanine in human serum samples and an RSDs of 4.4% was observed, proving the high sensitivity, selectivity, and good stability of the sensor.

Keywords- Electrochemiluminescence, Phenylalanine, Samarium, Enhance

1. INTRODUCTION

Various amino acids have been evaluated as potential biomarkers and are precursors of different critical bio-chemicals [1-3]. As a non-polar essential amino acid, phenylalanine (Fig. 1) has hydrophobic qualities due to the presence of aromatic groups in its structures. This amino acid also acts as the metabolic precursor of the non-essential tyrosine and its derivatives and is used in preparing bacitracin, gramicidin, tirocidin in pharmaceutical industries, further to its application as the sweetener (aspartame) in food industry [4,5]. Phenylalanine is converted to tyrosine in by an enzyme, i.e. phenylalanine hydroxylase (PAH), mainly in the liver and to a lesser degree in other tissues such as kidneys, pancreas and the brain[1].The product of this enzymatic reaction, i.e. tyrosine, acts as a precursor for monoamine neurotransmitters like dopamine, epinephrine and norepinephrine, that are associated with mood changes, depression and anxiety and hence, phenylalanine is critical in maintaining the balance of these neurotransmitters in the brain. After diffusing to the brain, L-phenylalanine converts to L-tyrosine and then to L-dopa in the presence of PAH, and further to dopamine, epinephrine and norepinephrine. As a next step dopamine is further converted to adrenaline and noradrenaline. Given the various roles of phenylalanine has and its products, in case drugs which hinder the breakdown of the mentioned neurotransmitters lead to enhancing mood, memorizing and concentration, increasing the amount of phenylalanine or tyrosine could have similar effects [4,5].

Various techniques are currently used for the quantification of amino acids. These range from application of electrochemical sensors [6,7], electrochemiluminescence [8], chemiluminescence [9], high-performance liquid chromatography (HPLC) [10,11], liquid chromatography-mass spectrometry [12], and capillary electrophoresis [13], to enzymatic colorimetry [14] and enzymatic electrode methods [15]. Some of these, however, require costly instrumentations and complicated sample treatment steps or have low selectivity and hence anew, accurate, rapid and simple detection techniques for the analysis of is always welcomed. Electrochemiluminescence (ECL) methods that combine chemiluminiscence and electrochemical methods, has attracted a great deal of extensive attentions [16]. In ECL phenomena electrochemically generated compounds react to produce light [17]. The ECL reactants are mainly formed through two mechanisms: co-reactants and annihilation. Each mechanism has its own advantages pathway to form the excited reactants which finally emit light [18]. ECL is a highly sensitive method, since no additional light source is used which allows for avoiding light scattering and luminescence of impurities. The method also has better selectivity since the formation of excited compounds can be controlled by manipulating the electrode potentials [19-21]. $Ru(bpy)_3^{2+}$ system has been used in the analysis of amino acids amino acids [22], drugs [23-26], DNA [27,28] and protein [29,30], given its good stability, high ECL quantum yield and biocompatibility. Immobilizing $Ru(bpy)_3^{2+}$ on the surface of

electrodes can not only reduce the need for using expensive reagents, it also enhances the ECL signal and simplifies experimental design [31].

Reviewing current studies further shows an increased interest in the development and use of new materials, such as graphene, nanoparticles, and carbon nanotubes for modifying surface properties of electrodes [32]. Metal nanoparticles as an instance have been found to enhance mass transport, reduce the dependence of the method on the solution resistance, lower the limit of detection and the signal/noise ratios [33-56].

The considerable mechanical stability and dielectric constants, as well as the large band gap characteristics of rare earth oxides (REOs) have made them the topic of different research studies in areas such as optoelectronic devices, switching mechanisms for logic devices, and memories [57]. REOs have been known for their high surface basicity, the high mobility of oxygen in their structures and good catalytic properties [58].

Samarium(III) oxide (samaria), is an important REO which has been the topic of various and extensive studies given its different valence properties [59-60]. Nanocrystals of Sm_2O_3 have shown promising effects for the bottom-up assembly of novel nanostructures with high potential applications in field such as solar cells [40], nanoelectronics [61], semiconductor gases and in biochemical sensors [62].

The focus of the present work is on developing a novel sensitive solid-state ECL biosensor for phenylalanine using Sm_2O_3 NPs, $Ru(bpy)_3^{2+}$ and chitosan (CHIT) modified glassy carbon electrode (GCE) to obtain larger specific surfaces area, a rapid electron transfer rate and improved ECL intensity.

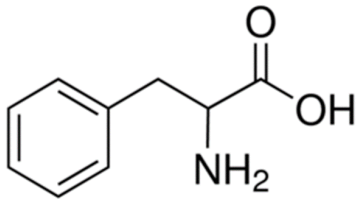


Fig. 1. Chemical structure of phenylalanine

2. EXPERIMENTAL

2.1. Reagents and chemicals

Analytical reagent grade chemicals were obtained and used without any treatments. Tris (2.2′-bipyridyl) ruthenium(II) ($Ru(bpy)_3^{2+}$) chloride hexahydrate was supplied by Sigma Co. Phosphate buffer solutions (PBS, pH=8.5) were prepared through mixing K_2HPO_4, NaH_2PO_4, and KCl.

2.2. Apparatus

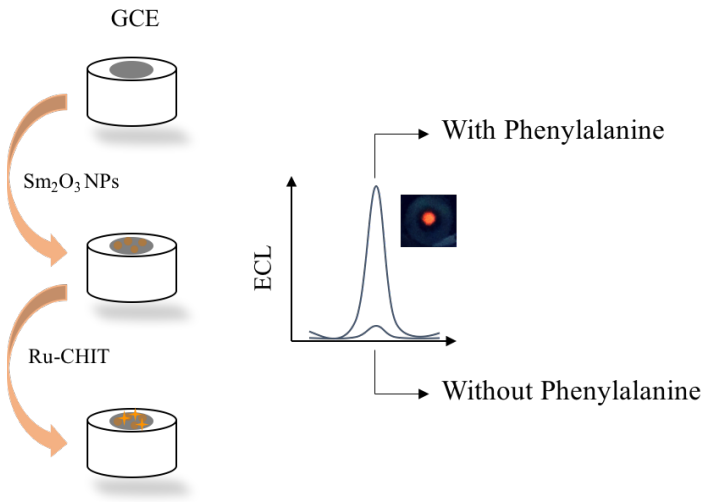
ECL studies were performed using an LS 50 (Perkin-Elmer) photomultiplier. An electrochemical setup including a platinum wire as the auxiliary electrode, an Ag|AgCl|KCl sat'ed reference electrode and the modified Sm_2O_3 NPs -$Ru(bpy)_3^{2+}$-GCE nano-composite electrode as the working electrode was used. Based on previous reports [64], the working electrode equatorially mounted on a 4 mL quartz cell located in front of a photomultiplier detector. Cyclic voltammetry (CV) studies were conducted on a PalmSens PC potentiostat–galvanostat (Netherlands) instrument. All of the ELC experiments were carried out in a light-tight box. To study the morphology of the samples, a KYKY-EM 3200 Digital Scanning Electron Microscope (China) and a scanning electron microscope (SEM) were used.

2.3. Synthesis of Sm_2O_3 NPs

A solution of samarium nitrate in water was prepared through dissolving the samarium oxide powder in nitric acid under sonication, and the solution was diluted using ethanol. Next it was added to a 20 wt% polyvinyl alcohol/water mixture under stirring and the mixture was heated to 90 °C and kept under these conditions for 2 h. Upon condensation of the hydroxyl network (by giving off water) a dense porous gel was formed. This gel was dried in an oven at 110 °C, and calcinated at 400 °C for various periods to form Sm_2O_3 NPs [65,66].

2.4. Preparing the sensor

To prepare the modified electrode a GCE was polished with 1.0, 0.3, and 0.05 μm alumina slurries using a piece of cloth. The GCE was next washed with water, and the subjected to ultrasonic radiation in ethanol and then in distilled water.



Scheme 1. Schematic of the electrode preparation steps

Then, a 100 µl aliquot of a 2.5×10^{-3} M $Ru(bpy)_3^{2+}$ solution in water was added to a 600 µl solution of 0.5 wt% chitosan in 3% acetic acid. The modified ECL electrode eventually prepared through casting 12 µl of a suspension of Sm_2O_3 nanoparticles on the electrode, drying at room temperature and then 8 µl of the $Ru(bpy)_3^{2+}$/CHIT suspension was dropped the assembly and dried at ambient temperature (Scheme 1).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Sm_2O_3 NPs

The morphology and dimensions of the Sm_2O_3 NPs were evaluated by FE-SEM and based on the results (Fig. 2) the tested Sm_2O_3 NPs had a narrow size distribution range, uniform surfaces and were spherical.

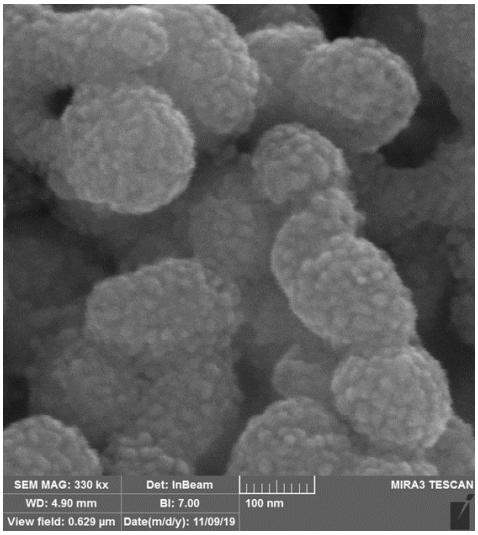


Fig. 2. SEM image of Sm_2O_3 NPs

3.2. Electrochemical and ECL behaviors the modified GCE

Electrochemical impedance spectroscopy (EIS), as one of the most informative electrochemical methods, was used to characterize the surface modification process of the ECL sensor. Fig. 3 shows the Nyquist plots at different modified states. The semicircular portion and the linear portion of the impedance spectra are corresponding to the electron-transfer-limited process and the diffusion process, respectively. And the semicircle diameters correspond to the electron-transfer resistance (R_{et}). Chitosan as a kind of insulating polymer, hindered the electron-transfer at the electrode surface, thus R_{et} was increased because of the modification of chitosan (curve b). After modification of the electrode with Sm_2O_3 NPs, the semicircle diameter was much smaller, indicating a lower R_{et} value for $[Fe(CN)_6]^{3-/4-}$ (curve c). This showed that the Sm_2O_3 NPs could increase the conductivity of the electrode surface.

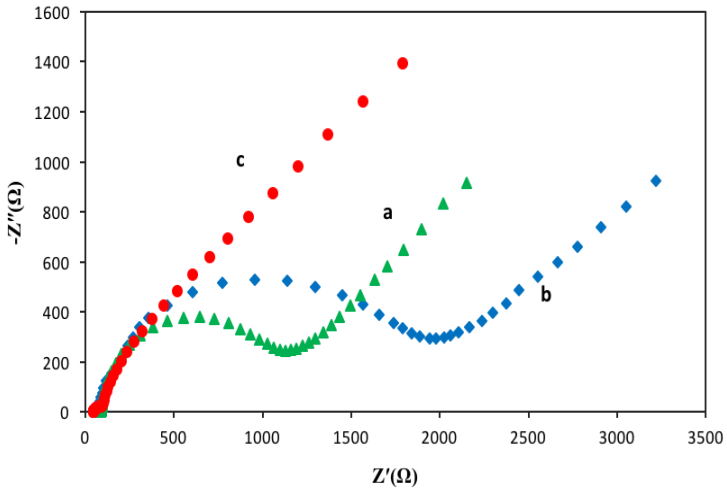
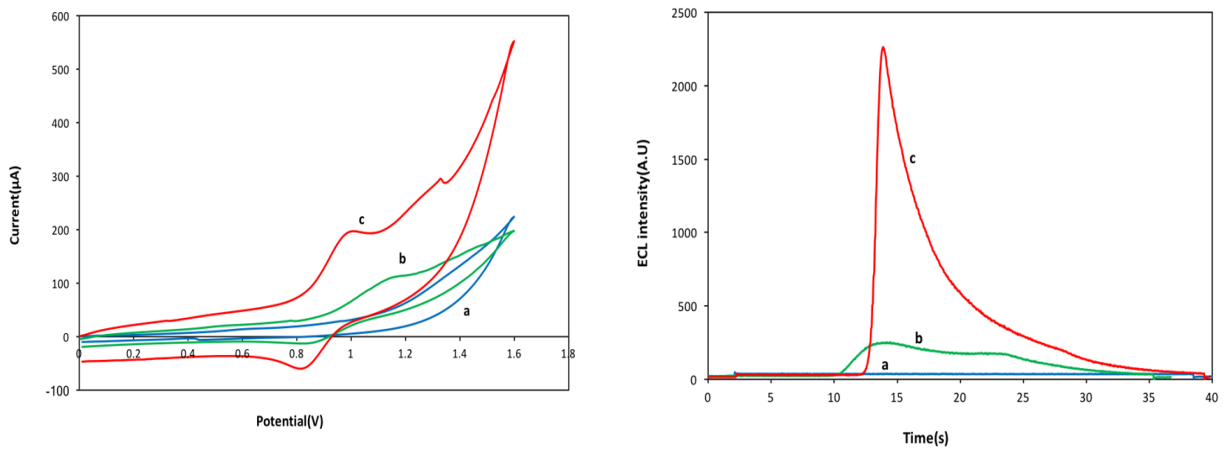


Fig. 3. Nyquist impedance spectra of (a) GCE, (b) $Ru(bpy)_3^{2+}$/chitosan/GCE, (c) Sm_2O_3 /$Ru(bpy)_3^{2+}$/chitosan/GCE, solution containing $[Fe(CN)_6]^{4-/3-}$ 5 mM and KCl 250 mM



(a) **(b)**

Fig. 4. (a) Cyclic voltammograms GCE(a), $Ru(bpy)_3^{2+}$-GCE(b), Sm_2O_3NPs-$Ru(bpy)_3^{2+}$-GCE(c). supporting electrolyte buffer solution (0.1 M and pH 8.5) and 5×10^{-8} M Phenylalanine; potential scan rate, 100 mV s^{-1}; **(b)** ECL responses of GCE(a), $Ru(bpy)_3^{2+}$-GCE(b), Sm_2O_3NPs-$Ru(bpy)_3^{2+}$- GCE(c) in 0.1 M pH 8.5 phosphate buffer containing 5×10^{-8} M Phenylalanine; potential scan rate, 100 mV s^{-1}

Former reports highlighted the catalytic effect of metal and metal oxide NPs including Pt-NPs, Au-NPs, Ag-NPs,Pd- NPs and ZnO-NPs on the chemiluminescence (CL) and ECL behaviors of electrodes. In this light the electro-catalytic and possible ECL activity of the modified GCE were evaluated by CV experiments at 100 mVs^{-1}, from 0.0 to 1.6 V *vs.* Ag|AgCl|KClsat. The CVs were obtained for GCE, GCE-$Ru(bpy)_3^{2+}$ and Sm_2O_3 NPs-

$Ru(bpy)_3^{2+}$-GCE in a PBS (pH=8.5) (Fig. 4a) and revealed that using the Sm_2O_3 NPs-$Ru(bpy)_3^{2+}$- GCE larger charging currents could be achieved This was attributed to the increased surface area of the modified electrodes, as well as the electron mediation quality of the Sm_2O_3 between $Ru(bpy)_3^{2+}$ and the GCE. The modified electrodes further gave rise to a couple of redox peaks at +0.97. Evaluating the effects of the presence of Sm_2O_3 NPs on a GCE also showed enhancements in the ECL signal (Fig. 4b), reflecting that the presence of these nanoparticles greatly enhances the oxidation of $Ru(bpy)_3^{2+}$ and increases the electro-generated CL species, increasing the sensitivity.

To determine the optimal values for the factor affecting the response of the Sm_2O_3 NP - $Ru(bpy)_3^{2+}$-GCE to phenylalanine the effects of pH, $Ru(bpy)_3^{2+}$ concentration and scan rate were studied.

3.3. Effect of pH

The interaction of pH and ECL signal was evaluated in the pH range of 6.5 to 9.5 and according to the result (Fig. 5) the ECL intensity greatly increased by increasing the pH from 6.5 to 8.5. Above this range, however, the ECL intensity decreased. Given these fact 8.5 was chosen and used as the optimal pH and a PBS with this pH was used during the ECL determinations.

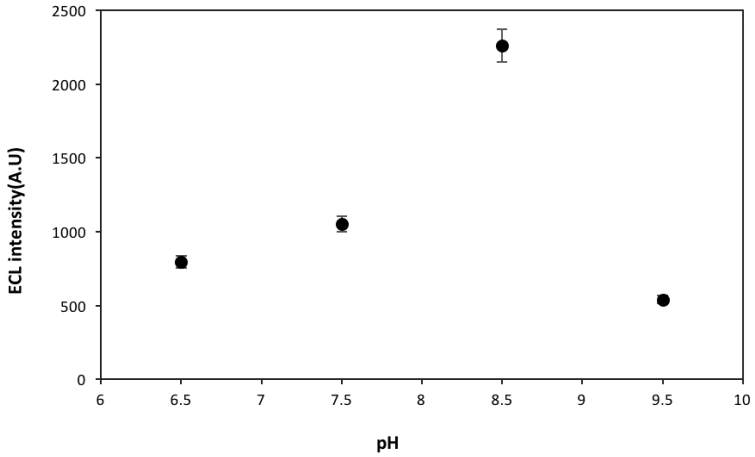


Fig. 5. Effect of pH on the ECL intensity

3.4. Effect of $Ru(bpy)_3^{2+}$ concentration

The effect of the amount of $Ru(bpy)_3^{2+}$ present on the modified GCE on the intensity of the ECL response was studied using a a 5×10^{-8} M phenylalanine solution. Based on the results the ECL signal linearly increased with increasing the $Ru(bpy)_3^{2+}$ concentration from 1.0×10^{-2} M to 2.5×10^{-3} M, but further increases up to 1.0×10^{-2} M did not further enhance the intensity

of signal, while this still enhanced the background ECL signal. Consequently 2.5×10^{-3} M was chosen as the optimal value for $Ru(bpy)_3^{2+}$ concentration.

3.5. Effect of scan rate

The changes in the ECL and the CV signals of the modified electrode were monitored using a 5×10^{-8} M phenylalanine solution, while the scan rate was changed from 50 to 200 mV/s. The results (Fig. 6) indicated that increasing scan rate from 50 to 100 mV/s increased the intensity of the ECL signal of the modified electrode and the highest signals were achieved at 100 mV/s. At lower scan rates, the intermediate is formed very slowly lowering the ECL intensity. Over this range the shorter reaction time available immediately lowered the concentration and reduced transmission of the reaction, led to lower ECL intensities. In this light 00 mV/s was selected as the optimal scan rate.

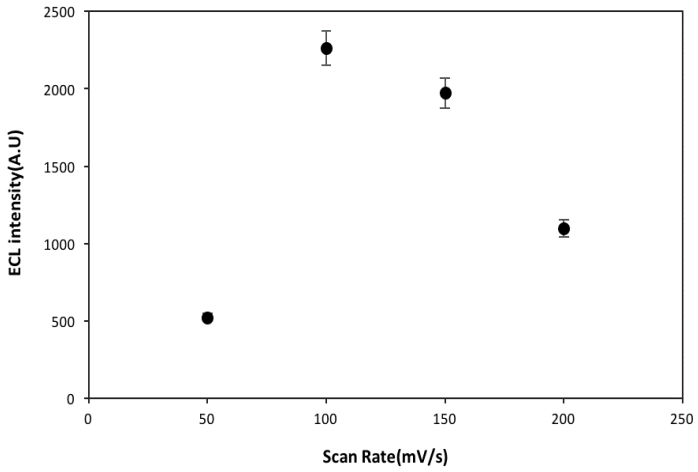


Fig. 6. Effect of scant rate on the ECL responses of Sm_2O_3NPs- $Ru(bpy)_3^{2+}$- GCE in 0.1 M pH 8.5 phosphate buffer at 50, 100, 150, and 200 mVs^{-1}

3.6. Interference effects

To evaluate the selectivity of the ECL sensor, the current responses of the modified electrode to a 1.0×10^{-9} M phenylalanine in the presence of common interfering specie present in pharmaceutical formulations, like starch, talc, magnesium stearate and lactose monohydrate were recorded and the results revealed that the sensor reveals a considerable electrochemilunescence response only for phenylalanine.

3.7. Analytical performance

The ECL sensor was used to analyze different concentrations of phenylalanine under optimal conditions. The ECL intensity increased with increasing the phenylalanine

concentrations and had a linear profile was observed between the signal and the logarithm of phenylalanine concentration from 5.0×10^{-11} to 5.0×10^{-7} M (Fig. 7), with a regression equation and correlation efficient of I=-792.23C+8082.9 and 0.9824 (I and C being the ECL response and the logarithm of phenylalanine concentration (inset)). The detection limit obtained with the method was 1.4×10^{-11} M (S/N=3).

The analytical performance of the sensor was also compared with the results in former reports and the results are given in Table 1 [9,11, 47-49], according to which the proposed sensor has a wider dynamic range with a lower detection limit.

The reproducibility of the signal was evaluated by immersing the electrode in a PBS containing 5×10^{-8} M of phenylalanine. Based on the observations, no changes happened in the ECL intensity upon the repetitive cyclic potential scans. This reflects the good reproducibility of the ECL sensor in the analysis of phenylalanine.

Further, the stability of the response produced by the electrode was evaluated by repetitive ECL measurements over a long period. After 2 months, the ECL response did not show any delectable decreases and the sensor still maintained 92% of its original response, reflecting its good stability.

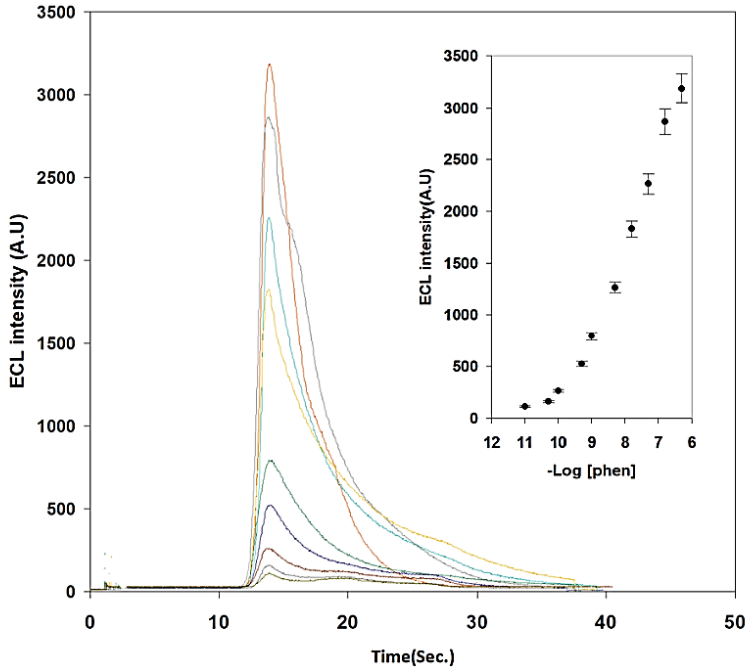


Fig. 7. ECL responses of Sm_2O_3 NPs - $Ru(bpy)_3^{2+}$- GCE in the presence of 1.0×10^{-11} to 5.0×10^{-7} M of phenylalanine, Inset shows linear relationship between the ECL intensity and the concentration of phenylalanine

Table 1. Comparisons of other reported techniques for phenylalanine detection

Analytical Methods	**Linear range (mol L^{-1})**	**LOD (mol L^{-1})**	**Reference**
MIP	1.0×10^{-8}-1.0×10^{-7}	1.0×10^{-9}	[7]
Chemiluminescence	1.0×10^{-6}-2.7×10^{-5}	8.4×10^{-7}	[9]
Aptamer-based biosensor	1.0×10^{-9}-1.0×10^{-8}	1.0×10^{-9}	[68]
Fluorescent	1.0×10^{-7}-8.2×10^{-7}	2×10^{-8}	[69]
MIP	1.3×10^{-5}-1.0×10^{-7}	1.3×10^{-5}	[70]
ECL	1.0×10^{-11}-5.0×10^{-7}	1.4×10^{-11}	This work

3.8. Mechanism of enhancement of ECL by Phenylalanine

The ECL signal of Sm_2O_3 NPs -$Ru(bpy)_3^{2+}$-GCE in phosphate buffer in absence of phenylalanine showed only weak background ECL emission, indicating that the ECL emission of the system presumably arose from the energetic electron-transfer reaction between electrogenerated $Ru(bpy)_3^{3+}$ and the reducing intermediate, the deprotonated form of oxidized Phenylalanine ion free radical, to produce the excited state $Ru(bpy)_3^{2+*}$, which is an emitting species. The electrochemical mechanism for the response was presumably analogous to that of the TPA– $Ru(bpy)_3^{2+}$ system[67].

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

phenylalanine - e → phenylalanine$^{\cdot +}$

phenylalanine$^{\cdot +}$ → phenylalanine$^{\cdot}$ + H^+

phenylalanine$^{\cdot}$ + $Ru(bpy)_3^{3+}$ → phenylalanine fragments + $Ru(bpy)_3^{2+*}$

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

3.9. Analytical applications

The applicability of the proposed sensor to determination of phenylalanine in human serum samples was examined. ECL intensities after spiking a standard aliquot of phenylalanine to the diluted serum were obtained using Sm_2O_3NPs-$Ru(bpy)_3^{2+}$-GCE at optimum conditions as described earlier. The concentrations were measured using the calibration plot, and the results are shown in Table 2. The recoveries indicate that both the accuracy and repeatability of the proposed sensor are very satisfactory. Based on the experimental results, this method has a great potential for the determination of trace amounts of this compound in biological samples.

Table 2. Recovery of phenylalanine studies performed in spiked serum samples for applicability of the developed biosensor (n=4)

Serum samples	Added ($molL^{-1}$)	Found ($molL^{-1}$)	Recovery (%)
1	3.0×10^{-10}	$2.73(\pm0.054)\times10^{-10}$	91.0
2	5.0×10^{-9}	$4.54\ (\pm0.080)\times10^{-9}$	90.8

4. CONCLUSIONS

In this work, an ECL sensor was fabricated for the determination Phenylalanine using glassy carbon modified Sm_2O_3 nanoparticles. The immobilized $Ru(bpy)_3^{2+}$ shows a diffusion electrode process and has an electrocatalytic action to the oxidation of Phenylalanine, which results in the formation of an emitting species which produces the ECL signal. The proposed ECL sensor had a low detection limit of 1.4×10^{-11} M and a linear range from 5.0×10^{-11} to 5.0×10^{-7} M. The applicability of a proposed sensor to the determination of phenylalanine in tablet samples has also been evaluated, and it found to have a good reproducibility and enough sensitivity for the detection of Phenylalanine in serum samples.

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