A novel electrochemiluminescnece sensor based on an Ru(bpy)₃²⁺ - Eu₂O₃ - nafion nanocomposite and its application in the detection of diphenhydramine

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An ultrasensitive solid-state electrochemiluminescence (ECL) sensor based on the efficient and stable enhancement of tris-(bipyridine)ruthenium(II) (Ru(bpy)₃²⁺) by diphenhydramine (DPH) in a carbon paste electrode has been developed. The ECL intensity was found to be correlated to the concentration of DPH. Incorporation of europium oxide (Eu₂O₃) nanoparticles in the carbon paste electrode (CPE) led to the development of the novel ECL sensor. Eu₂O₃ showed attractive sensitizing effects for the Ru(bpy)₃²⁺-DPH electrochemiluminescence system. Under optimized conditions, the linear response of the ECL intensity to DPH concentration was in the range of 1.0×10^{-9} to 1.25×10^{-7} mol/L ($R^2 = 0.998$) with a detection limit (S/N=3) of 3.0×10^{-10} mol/L and a relative standard deviation (RSD) of 4.1%. The evaluations proved the method as being very sensitive, selective and simple. The sensor was also used in the analysis of DPH concentration in serum and urine specimens.

1. INTRODUCTION

After the introduction of the electrochemiluminescence (ECL) of tris(2,2-bipyridyl)ruthenium(II) (Ru(bpy)₃²⁺) [1], Ru(bpy)₃²⁺ ECL has always been regarded and used as a powerful detection method offering excellent detection sensitivity, and high selectivity, the capability

of being miniaturized and requiring no expensive instrumentation [2-4]. Its applications in the detection of pharmaceutical and environmental analyses, image lasing, and optical studies have widely been reported [5-7]. Moreover, as $Ru(bpy)_3^{2+}$ is regenerated during the ECL process, a reagent-free ECL sensors can be constructed by immobilizing $Ru(bpy)_3^{2+}$ on an electrode surface [8]. Contrary to the solution-phase electrochemiluminescnece routines, immobilizing $Ru(bpy)_3^{2+}$ does not require the use of chemical reagents , which greatly simplifies experimental design, and hence various approaches have been used for immobilizing $Ru(bpy)_3^{2+}$ on the surface of solid elements. Some of these approaches include the Langmuir-Blodgett [9], self-assembled [10], and electrostatic attachment techniques [11]. Yet, the resulting films of the immobilized $Ru(bpy)_3^{2+}$ species have proven to be rather unstable due to the high potentials required [12].

In the course of the present research we used carbon paste electrode (CPE), which has the widest potential window in aqueous systems among its other rivals, as the working electrode [13]. CPEs have been widely used in electroanalytical chemistry owing to their low residual currents and simple surface polishing procedures [13].

Nanomaterials including nanoparticles and nanoclusters of metals, semiconductors, carbon or polymeric species, are of considerable interest in the electrochemical fields owing to their unique physical and chemical properties, which has led to novel sensors that have exhibited high sensitivity and stability [5, 6, 14-24].

Eu_2O_3 nano-particles (Eu_2O_3 NPs) are among the most effective materials used in up-conversion materials, low voltage cathodoluminescent devices, biochemical applications, super-capacitors, photo-electrochemical applications, and electro-analytical chemistry [25]. The chemical and electrochemical characteristics of these particles, including their electron mediation and electrocatalytic features [26], stems from their 4f electron configuration [27].

In this work, we used Eu_2O_3 NPs as an electrode modifier acting as an electron mediator between carbon past and the incorporated $Ru(bpy)_3^{2+}$, leading to the increased $Ru(bpy)_3^{2+}$ oxidation currents. This was found to greatly enhance the ECL signals and DPH detection sensitivity.

DPH is a popular H1-receptor and a well-known over the counter antihistaminic and anti-nausea medication, whose sedative and analgesic effects are of clinical importance [28-30]. It is also used to suppress coughs, treat motion sickness, induce sleep, to treat mild forms of Parkinson's disease [31-34]. But DPH overdose can cause acute poisoning, lethargy, heart palpitations, muscle tremors, blurred vision, confusion and even seizures and other reactions [35,36]. So, sensitive and fast detection of DPH, both in the process of drug preparations and in human plasma and urine samples after its application, is of great value. Several methods have been developed and used for the determination of DPH including flow injection spectrophotometry (FISP) [37], capillary electrophoresis (CE) [38], spectrophotometric method (SPM) [39], high-performance liquid chromatography (HPLC) [40], screen-printed electrode (SPE) [41] and electrochemiluminescence(ECL) [42]. Yet, the development of fast, sensitive, simple and low cost methods for the detection of DPH is still desirable.

The results of this work present a new ECL sensor based on a carbon paste composite modified with Eu_2O_3 NPs for determination DPH.

2. MATERIALS AND METHODS

2.1. Chemicals

Analytical grade chemical were used throughout the experiments without any further treatments. Tris (2.2′-bipyridyl) ruthenium (II) $Ru(bpy)_3^{2+}$ chloride hexahydrate was obtained from Sigma Co, and the Nafion perfluorinated ion-exchange (5% solution in 90% alcohol), carbon graphite powder and paraffin oil, were procured from Fluka (Buchs, Switzerland).

2.2 Apparatus

The ECL emission was detected by an LS 50 (Perkin-Elmer) photomultiplier. A three electrode system was chosen as the electrochemical system, in which a platinum wire and an Ag|AgCl|KCl sat'ed electrode were used as the auxiliary and reference electrode. As previously reported[5], The Eu_2O_3 NP -$Ru(bpy)_3^{2}$+-CPE nano-composite was mounted in an equatorial position on a 4mL quartz cell, placed in front of the photomultiplier (see Fig.S1). Cyclic voltammetry (CV) was performed by a PalmSens PC potentiostat–galvanostat (Netherlands). All ELC experiments were performed in a light tight black box.

A KYKY-EM 3200 Digital Scanning Electron Microscope (China) was used for the characterization of the morphology of Eu_2O_3 NP-$Ru(bpy)_3^{2}$+-CPEs, as well as the size of the Eu_2O_3-NPs through scanning electron microscopy (SEM).

2.3. Sensor fabrication

The general routine for preparing the carbon paste electrode started with thermally treating the graphite powder in a furnace, at 750 °C for 2 minutes. The thermally treated powder was subsequently cooled to ambient temperature in a desiccator. In parallel the $Ru(bpy)_3^{2+}$ - nafion solution, was prepared by dispersing 200 µL of a 2.5×10^{-2} M $Ru(bpy)_3^{2+}$ solution in 500 µL of a 5wt% nafion solution. Next 90 mg of the treated graphite powder, various amounts of Eu_2O_3 NPs, and 200 µL of the $Ru(bpy)_3^{2+}$- nafion solution were mixed. This mixture was then homogenized and aged at ambient temperature for half an hour, before 40µL of the paraffin oil was added to the solid substance obtained (i.e modified carbon powder) and the resulting combination was hand-mixed into a uniform paste. In a next step, various quantities of the resulting modified carbon paste were loaded into the end of a pyrex tube (5 mm i.d). A copper wire was into the other end of the tube and extended so that it entered the paste to establish the electrical contact. Eventually, the outer surface of the resulting modified CPE was cleaned with a piece of fine abrasive paper.

2.4. Preparation of Eu_2O_3 nanoparticles

As previously reported in the case of other lanthanide oxide NPs [[5, 6]], first normal europium oxide powder was dissolved in asuitable volume of nitric acid under sonication. The resulting solution

was next diluted with ethanol before being added to a 20/80 wt% mixture of polyvinyl alcohol and water under vigorous stirring. Then 2ml of a 32% NH_4OH solution in water added to the above solution in a dropwise manner, and the resulting solution was heated to 90 °C and kept under stirring for 120 minutes. The condensation of the hydroxyl network under these conditions led to the formation of a dense porous gel, which was dried at 110 °C in an oven and then calcinated at 400 °C to obtain Eu_2O_3 nanopartocles (NPs).

3. RESULT AND DISCUSSION

3.1. Characterization of the Eu_2O_3 NPs

The size and morphology of Eu_2O_3 NPs and the modified CPE were studied by SEM. Fig. 1 shows the SEM images of Eu_2O_3 NPs and modified CPE, which reveals a narrow size distribution for Eu_2O_3 NPs, as well as a uniform surface modification in the case of the modified CPE.
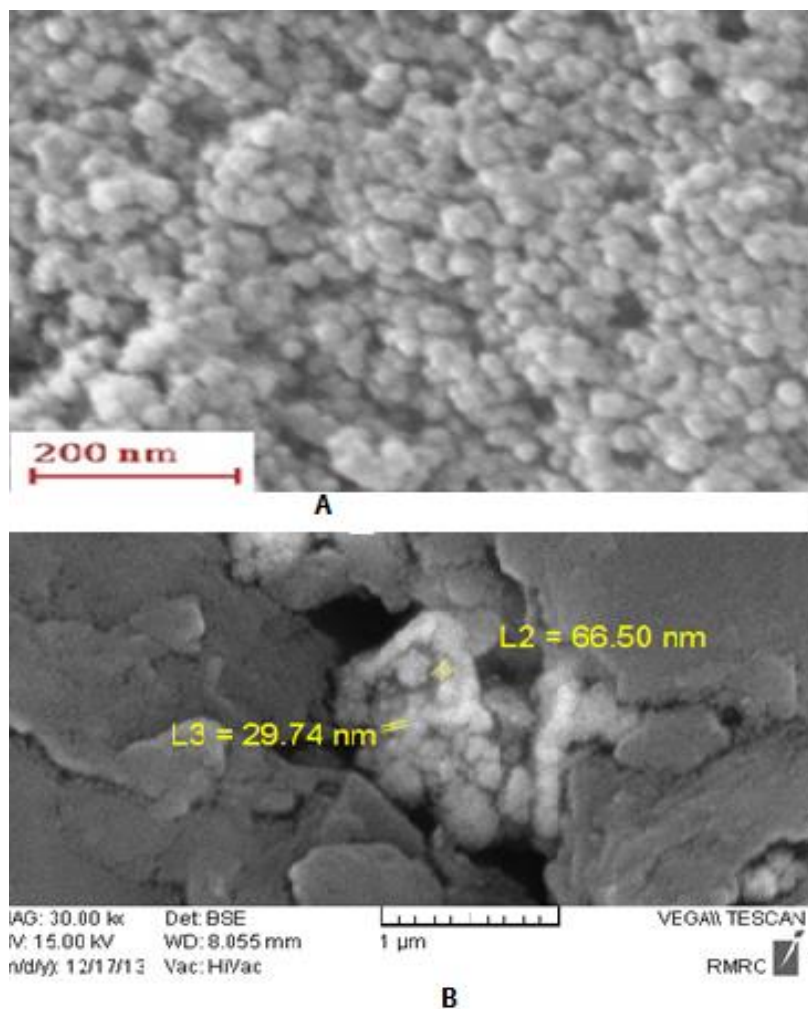
Figure 1. SEM image of Eu_2O_3 NPs (a), incorporation of Eu_2O_3 NPs in CPE(b).

3.2. Electrochemical and ECL behaviors Ru(bpy)$_3^{2+}$– Eu$_2$O$_3$ NPs – CPE

Electron mediation properties of metal and metal oxide NPs such as Ceria NPs, Sm$_2$O$_3$ NPs, and CeO$_2$/TiO$_2$ ECL reaction have been evaluated in previous studies [[5, 6, 43]]. The electro-catalytic and possible ECL activity of the Eu$_2$O$_3$ NPs in the carbon paste composite were studied through performing cyclic voltametric studies (CVs) at a scan rate of 100 mV s^{-1}, in the range of 0.0 and 1.4 V vs. Ag|AgCl|KClsat. The results of the cyclic voltammetry of the CPE, CPE-Ru(bpy)$_3^{2+}$ and Eu$_2$O$_3$ NP-Ru(bpy)$_3^{2+}$ - CPE in a phosphate buffer (pH=8.5) are illustrated in Fig. 2. These results indicate that the Eu$_2$O$_3$ NP -Ru(bpy)$_3^{2+}$- CPE lead to larger charging currents, due to the enhanced surface area of the electrodes and electron mediation properties of Eu$_2$O$_3$ between Ru(bpy)$_3^{2+}$ and the carbon paste. Eu$_2$O$_3$ NP-Ru(bpy)$_3^{2+}$-CPE composite also revealed a couple of redox peaks at +1.153 V under the reaction conditions. Also, the effect of incorporating Eu$_2$O$_3$ NP in the CPE composition revealed to be effective in increasing the ECL annihilation signal (Fig. 3). It seems that Eu$_2$O$_3$ NPs greatly improved the oxidation of Ru(bpy)$_3^{2+}$ and increased electro-generated CL species, which leads to better sensitivity. The effect of the amount of Eu$_2$O$_3$ NPs in the carbon paste was also studied and optimized in Fig. 3 inset and the results revealed that 4 mg of Eu$_2$O$_3$ NPs per 90mg of the carbon paste leads the maximum annihilation ECL intensity.
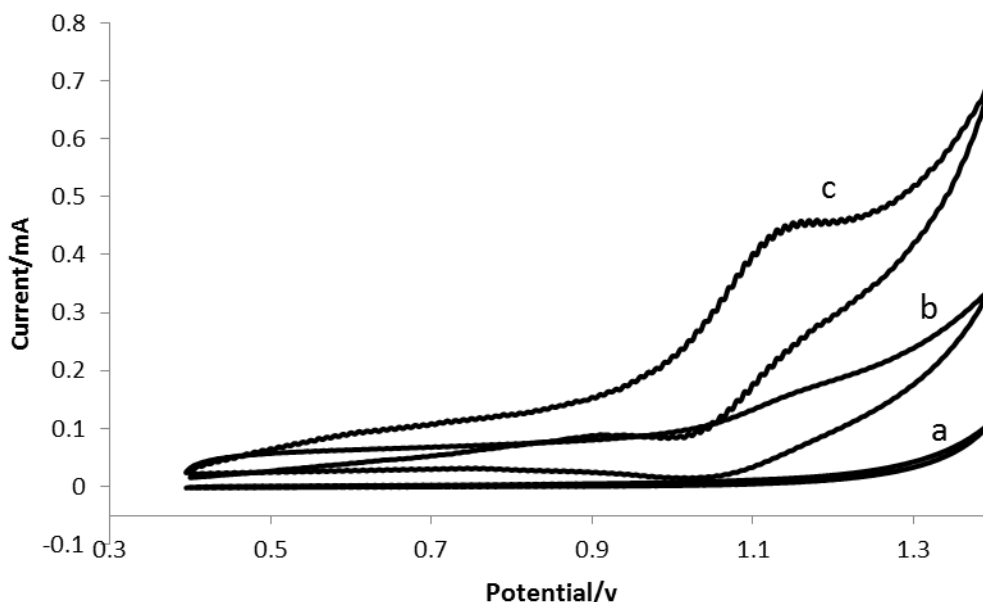
Figure 2. Cyclic voltammograms CPE (a), Ru(bpy)$_3^{2+}$ - CPE (b) Eu$_2$O$_3$ NPs -Ru(bpy)$_3^{2+}$- CPE (c). Supporting electrolyte buffer solution (0.1M and pH 8.5) and 100 nM DPH; potential scan rate, 100 mVs^{-1}.
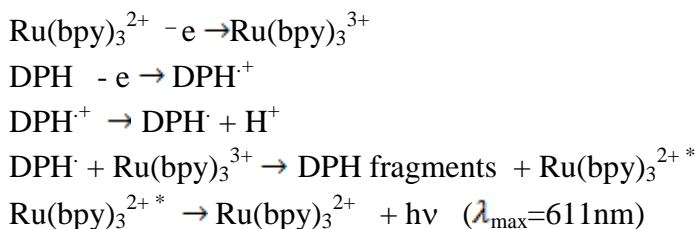
The ECL intensity at various wavelengths led to a maximum intensity at nearly 611nm (Fig. S1), at the Ru(bpy)$_3^{2+}$ emission wavelengths of 610 or 620nm, indicating a similar emission process like that reported in the literature [44]. In order to optimize the performance of the ECL of the proposed Eu$_2$O$_3$ NP -Ru(bpy)$_3^{2+}$-CPE towards DPH the effects of pH, the amount of Eu$_2$O$_3$ NPs the concentration of Ru(bpy)$_3^{2+}$ and the scan rate, on the intensity of ECL signal were investigated.
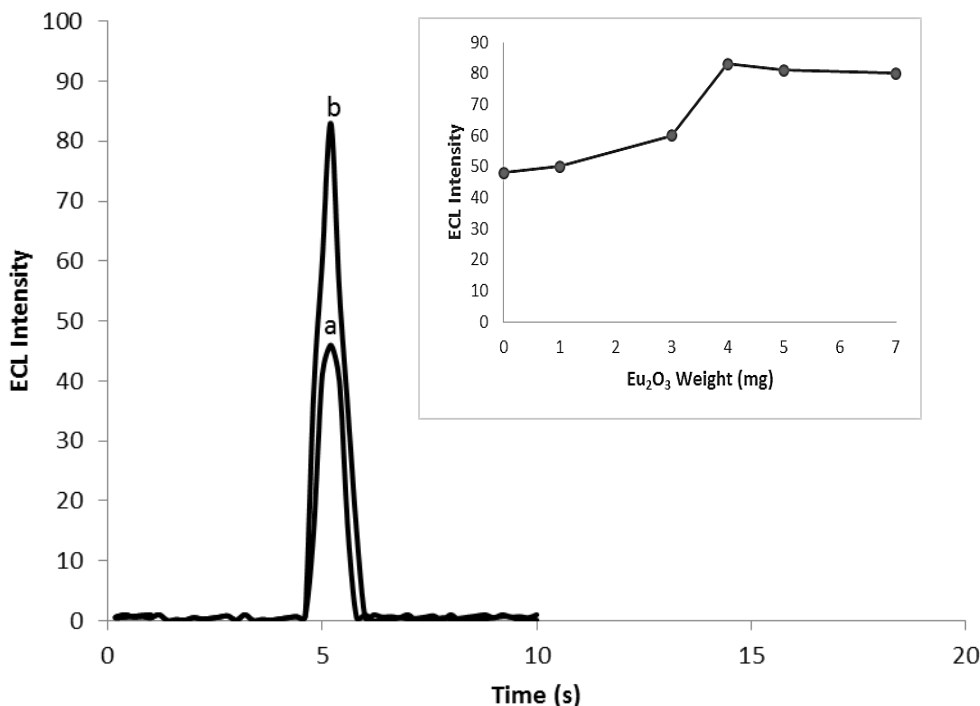
Figure 3. Annihilation ECL responses of Ru(bpy)$_3^{2+}$ - CPE (a) Eu$_2$O$_3$ NPs -Ru(bpy)$_3^{2+}$- CPE (b) in 0.1 M pH 8.5 phosphate buffer; Inset, optimization of Eu$_2$O$_3$ weight in Ru(bpy)$_3^{2+}$ - CPE in 0.1 M pH 8.5 phosphate buffer.

3.3. Mechanism of ECL enhancement

As previously reported [[42]], DPH can act as coreactant in a Ru(bpy)$_3^{2+}$ ECL system. In the absence of DPH in a phosphate buffer, only weak annihilation emission was detected (Fig. S2). The addition of DPH was found to cause a tremendous enhancement in the ECL intensity, which was attributed to the chemiluminescence of the high energy electron transfer between DPH and Ru(bpy)$_3^{3+}$ radicals that re electrochemically generated on electrode surface. The oxidative-reductive ECL mechanism of aliphatic amines as coreactant is shown below. First DPH and Ru(bpy)$_3^{2+}$ are oxidized at the surface of the electrode, and then DPH radicals are quickly deprotonated and react with Ru(bpy)$_3^{3+}$ to produce the excited state of Ru(bpy)$_3^{2+*}$, which is an emitting species [[45]].

$$Ru(bpy)_3^{2+} - e \rightarrow Ru(bpy)_3^{3+}$$
$$DPH - e \rightarrow DPH^{\cdot+}$$
$$DPH^{\cdot+} \rightarrow DPH^{\cdot} + H^{+}$$
$$DPH^{\cdot} + Ru(bpy)_3^{3+} \rightarrow DPH\ fragments + Ru(bpy)_3^{2+\ *}$$
$$Ru(bpy)_3^{2+\ *} \rightarrow Ru(bpy)_3^{2+} + h\nu \quad (\lambda_{max}=611nm)$$

3.4. Effect of pH

Th results of evaluating the effect of pH on the intensity of the electrochemiluminescnece of DPH over the pH range of 6.0 to 10.0, as illustrated in Fig. S3, indicates that the ECL intensity is

significantly enhanced with increasing the pH from 6.0 to 8.5, due to the increase in the concentration of the molecular form of DPH, which leads to a better enhancement in co-reactant mechanism of ECL. On the contrary, when the pH of the buffer solution exceeded 8.5, the ECL intensity of DPH decreased most probably due to the poisoning of the electrode surface. Thus, a phosphate buffer solution (pH=8.5) was chosen for further ECL studies.

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

The concentration of $Ru(bpy)_3^{2+}$ in the modified CPEs, was investigated as one of the important factors. In the presence of 100 nM of DPH the ECL intensity linearly increased with the $Ru(bpy)_3^{2+}$ concentration over the range of 1×10^{-2} mol/L to 2.5×10^{-2} mol/L in the case of the modified CPE composition. No significant signal improvements were obtained at higher $Ru(bpy)_3^{2+}$ concentrations and above 3.5×10^{-2} mol/L, the modified CPE showed signs of leakage of $Ru(bpy)_3^{2+}$ into the buffer solution. So, 2.5×10^{-2} mol/L was chosen as the optimum value and used in further experiments.

3.6. Effect of the scan rate

Cyclic voltammetric studies were performed at different scan rates, to assess the mechanism of the electrochemical process and find the optimal scan rate for obtaining the highest ECL intensity. In presence of 100 nM of DPH, both the oxidation and reduction currents were found to linearly amplify with increasing the scan rate. The oxidation and reduction currents shifted in positive and negative directions and maximum and minimum current separation increased, which are indicative of a quasi-reversible electrode process. As shown in Fig. S4, a scan rate of 100 mV s^{-1}, which led to the best sensitivity, was selected for DPH detection.

3.7. Interference studies

The interferences posed by some commonly occurring species on the DPH signal were evaluated under the optimal conditions. To this end the the tolerable concentration of the foreign species was defined as the levels not leading to relative errors over ±5%, of the signal of the analyte. The studies revealed no interference, when up to 1000 folds of Mg^{2+}, K^+, Cl^- 500 folds of glucose, 300 folds of L-methionine, Citric Acid, uric acid, Dopamine, and 100 folds of ascorbic acid were present in the sample.

3.8. Analytical performance

The response of the electrode toward DPH was found to be linear from 1.0×10^{-9} to 1.25×10^{-7} mol/L (with a regression equation of I=1.5×10^9 C+123.6) and a lower detection limit of 3.0×10^{-10} mol/L (S/N=3) was reached under the optimum conditions. Fig. 4 illustrates the typical calibration

curve for DPH acquired using the ECL sensor. The evaluations showed the relative standard deviation of the analysis to be 4.1% for the determination 1.0×10^{-8} mol/L solutions of DPH (n=7).
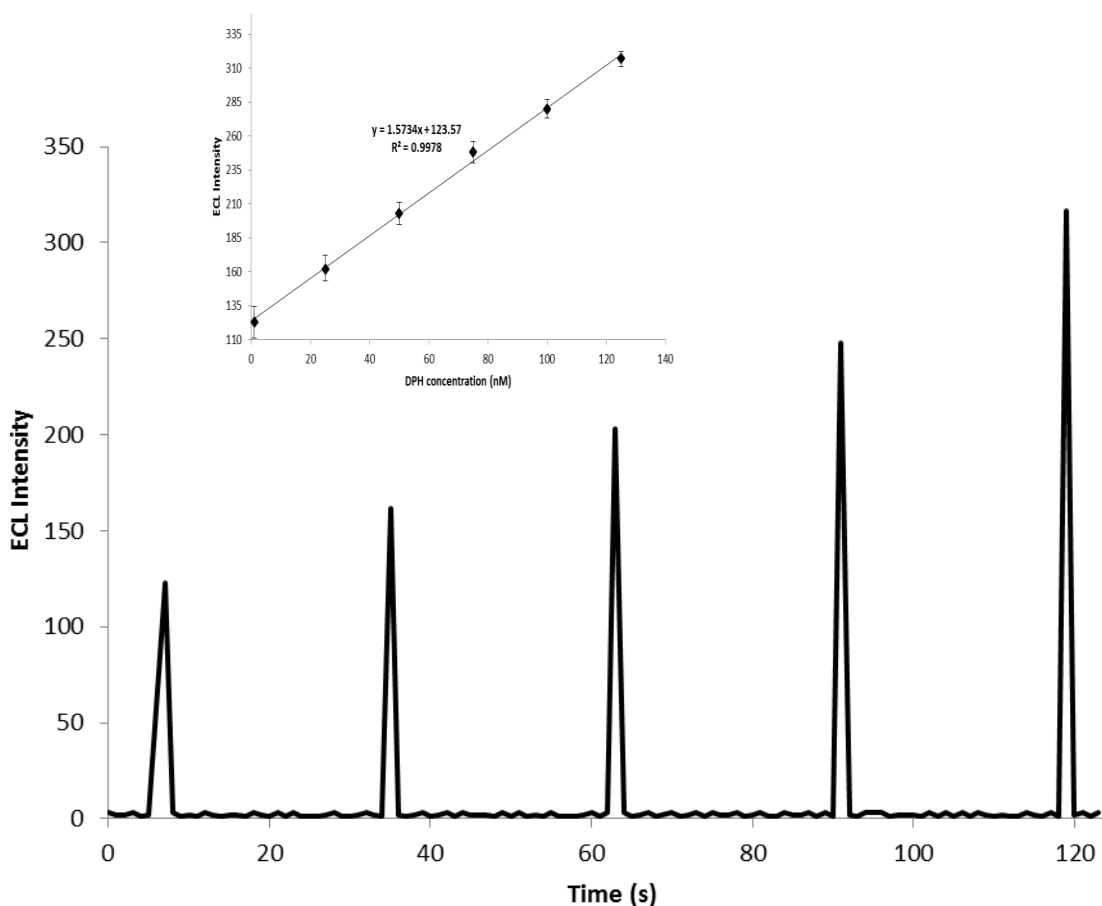

Figure 4. ECL responses of Eu_2O_3 NPs - $Ru(bpy)_3^{2+}$- CPE in the presence of 1.0×10^{-9} M, 2.5×10^{-8} M, 5.0×10^{-8}M, 7.5×10^{-8} M, 1.0×10^{-7} M, and 1.25×10^{-7} M of DPH, Inset shows linear relationship between the ECL intensity and the concentration of DPH.

In a phosphate buffer containing 100 nM of DPH, the ECL intensity of the sensor did not show detectable changes upon ten repeated cyclic potential scans, which proves the device to enjoy good reproducibility (Fig. 5).

Further studies on the stability of the electrode, based on the repetitive measurements of the ECL response over a long period of time, showed that after 60 days, the ECL response did not considerably decrease and the sensor was still capable of producing 92% of its original response intensity.

A comparative evaluation of the results obtained using this and previous devices was performed (Table 1). As can be seen, spectrophotometric method, flow injection spectrophotometry, capillary electrophoresis and high performance liquid chromatography have lower sensitivity, LOD and also difficult operation due to the complex instrumentation of these methods [37-40].
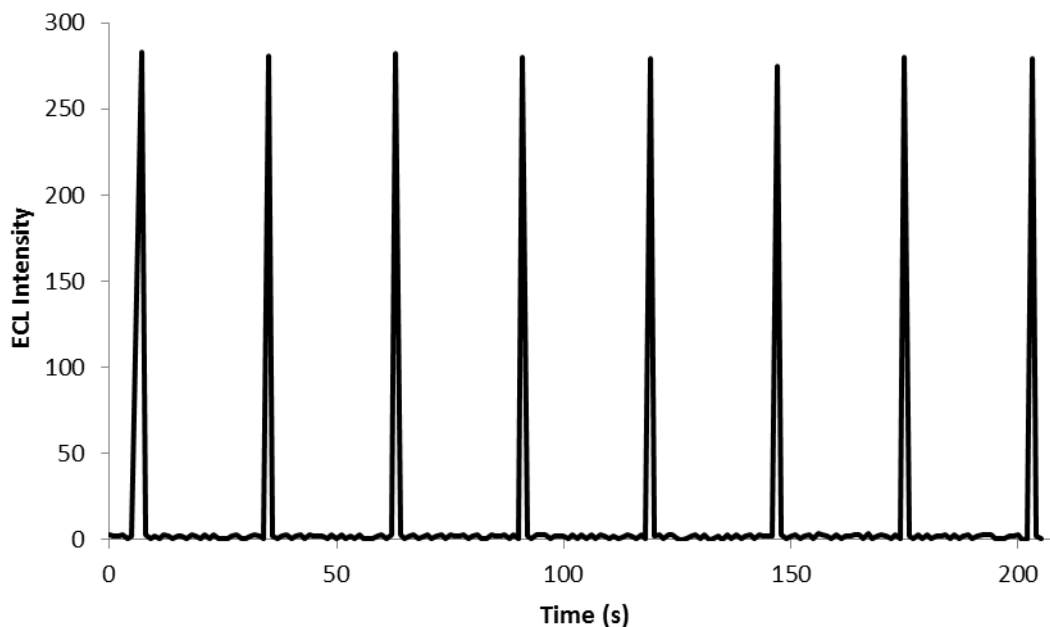
Figure 5. Stability of ECL signal from Eu_2O_3 NPs -$Ru(bpy)_3^{2+}$- CPE in 0.1 M pH 8.5 phosphate buffer solution, containing 100 nM DPH under ten continuous cycles of CV scan.

Electrochemical methods present high sensitivity and low LOD [46, 47], however ECL methods are based on redox performance of chemicals even at low concentration which exhibit undetectable current values but detectable ECL signals. Previously ECL based sensors [42, 48] also illustrated in Table 1, the higher sensitivity and significantly better LOD value (i.e. 6.0×10^{-10} mol/L) of proposed sensor could be explained by supreme performance of Eu_2O_3 NPs -$Ru(bpy)_3^{2+}$- CPE due to the outstanding effect of Eu_2O_3 NPs on sensitivity of generated ECL signal in DPH detection.

Table 1. Comparison of the characteristics of the proposed sensor with those of the previously reported for DPH.

Method	Detection Limit (M)	Dynamic Range (M)	Ref.
FI - spectrophotometry	0.3×10^{-5}	$1.9 \times 10^{-5} – 7.3 \times 10^{-4}$	37
Capillary electrophoresis	2.5×10^{-6}	$2.5 \times 10^{-5} – 1.6 \times 10^{-3}$	38
Spectrophotometric method	8.1×10^{-6}	$4.8 \times 10^{-5} – 5.8 \times 10^{-4}$	39
High performance liquid Chromatography	1.1×10^{-6}	$3.1 \times 10^{-4} – 6.1 \times 10^{-4}$	40
Boron doped diamond	1.8×10^{-7}	$6.0 \times 10^{-7} – 6.0 \times 10^{-5}$	46
CdO/SCNT IL CPE[1]	9×10^{-9}	$5.0 \times 10^{-8} – 7.0 \times 10^{-4}$	47
Electrochemiluminescence	1×10^{-6}	$5.0 \times 10^{-6} – 5.0 \times 10^{-4}$	48
Electrochemiluminescence	6.7×10^{-9}	$2.0 \times 10^{-8} – 7.5 \times 10^{-4}$	42
Electrochemiluminescence	6.0×10^{-10}	$1.0 \times 10^{-9} – 1.25 \times 10^{-7}$	This work

[1] CdO single wall carbon nanotube carbon paste electrode

3.9. The analytical application

Human urine and serum samples were examined using the proposed sensor. The spiking method was applied to the real samples and the concentrations were measured by obtaining a calibration plot. Table 2 shows the results of the real sample analysis, which indicated both the recovery and repeatability of proposed sensor to be very satisfactory. In this light the sensor was judged as having a great potential for the detection of DPH in biological samples.

Table 2. ECL determination results and recoveries of DPH samples using a Eu_2O_3 NPs -$Ru(bpy)_3^{2+}$- CPE   modified

| Sample	Added (molL^{-1})	Found ^{a} (molL^{-1})	Recovery(%)
Human Serum	5.2×10^{-9}	$5.0\,(\pm0.2)\times10^{-9}$	96.36
	6.5×10^{-9}	$6.0(\pm 0.2)\times10^{-9}$	92.32
Urine	5.8×10^{-9}	$5.4\pm(\,0.1)\times10^{-9}$	93.10
	7.0×10^{-9}	$6.7(\pm 0.2)\times10^{-9}$	95.71

4. CONCLUSION

In summary, an ECL sensor for DPH was fabricated using Eu_2O_3 NPs as the electron mediator and signal amplification agent. The incorporation of Eu_2O_3 NPs in carbon paste medium has led to effective oxidation of $Ru(bpy)_3^{2+}$ and high ECL signal amplification. On the other hand, it seems the immobilization of Eu_2O_3 NPs in the sensor also has an electrocatalytic oxidation of DPH and increasing DPH radicals on the surface of the sensor which also caused higher ECL signal enhancement. This sensor showed high sensitivity (detection limit of 3.0×10^{-10} mol/L and a linear range from 1.0×10^{-9} to 1.25×10^{-7}mol/L) and selectivity and could successfully apply in biological matrices.

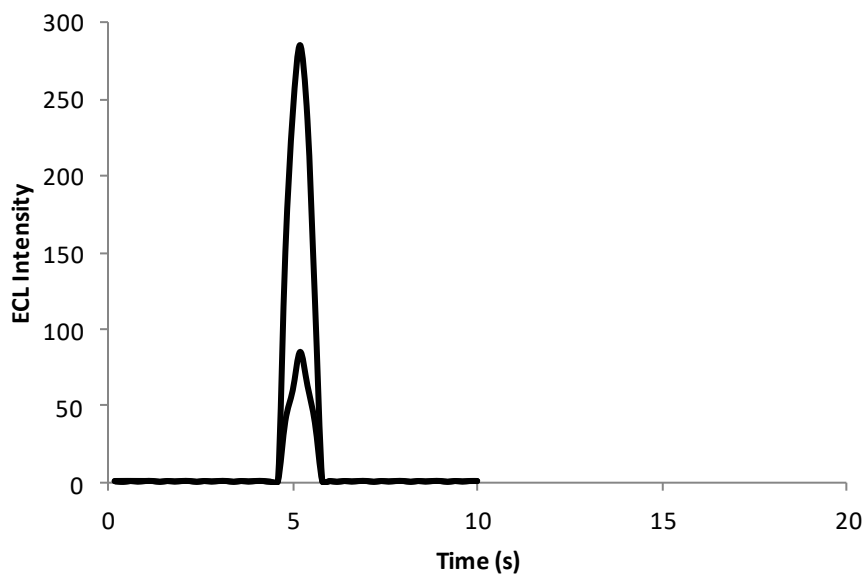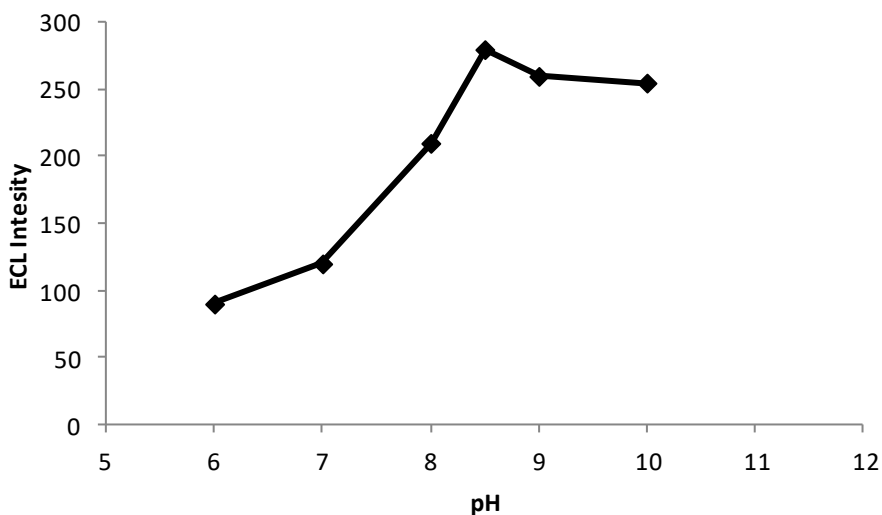*SUPPLEMENTARY DATA*
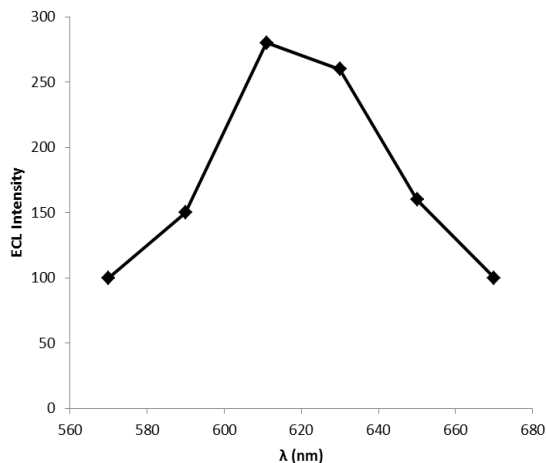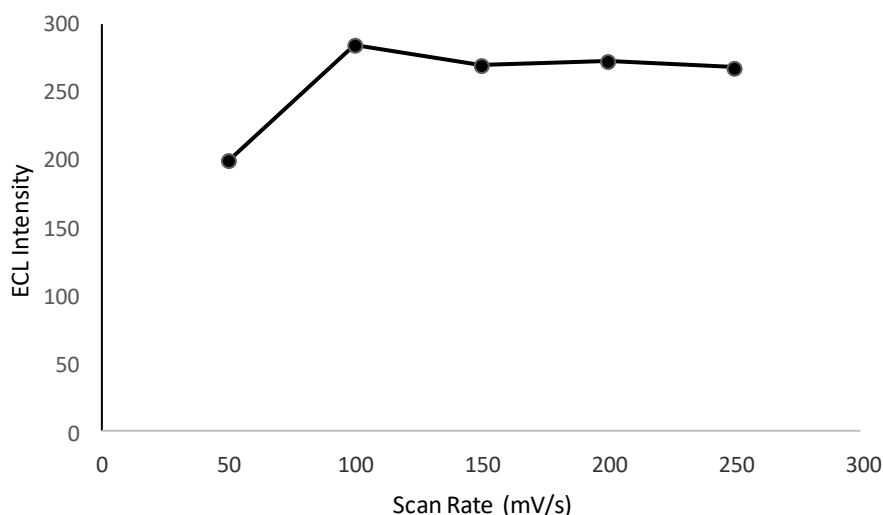
Figure S1. ECL intensity in various wavelengths, Eu_2O_3 NPs -$Ru(bpy)_3^{2+}$- CPE in 0.1 M pH 8.5 phosphate buffer containing 100 nM DPH.

Figure S2. ECL responses of $Ru(bpy)_3^{2+}$ - CPE (a) Eu_2O_3 NPs -$Ru(bpy)_3^{2+}$- CPE (b) in 0.1M pH 8.5 phosphate buffer containing 100 nM DPH.

Figure S3. ECL response in pH values of 6, 7, 8, 8.5, 9 and 10, solution containing 100 nM of DPH.

Figure S4. Effect of CV scan rate on ECL response of Eu_2O_3 NPs -Ru(bpy)$_3^{2+}$- CPE in 0.1 M pH 8.5 phosphate buffer containing 100 nM of DPH at 50, 100, 150, 200, 250 , 300 and 350 mVs^{-1}.

References

1. N. E. Tokel and A. J. Bard, *J. Am. Chem. Soc*., 94 (1972) 2862.
2. M. M. Richter, *Chem. Rev*., 104 (2004) 3003.
3. J. Li and E. Wang, *The Chemical Record*, 12 (2012) 177.
4. H. Wei and E. Wang, *TrAC Trends in Anal. Chem.*, 27 (2008) 447.
5. M. Hosseini, M. R. Moghaddam, F. Faridbod, P. Norouzi, M. R. K. Pur, and M. R. Ganjali, *RSC Adv.*, 5 (2015) 64669.
6. M. Hosseini, M. R. K. Pur, P. Norouzi, M. R. Moghaddam, F. Faridbod, M. R. Ganjali, and J. Shamsi, *Anal. Methods*, 7 (2015) 1936.
7. M. R. K. Pur , M. Hosseini, , F. Faridbod, A. S. Dezfuli, and M. R. Ganjali, *Anal. Bioanal. Chem.*, 408 (2016) 7193.
8. X. B. Yin, S. Dong, and E. Wang, *TrAC Trends in Anal. Chem.*, 23 (2004) 432.
9. X. Zhang and A. J. Bard, *J. Physical Chem.*, 92 (1988) 5566.
10. Z. Guo, Y. Shen, M. Wang, F. Zhao, and S. Dong, *Anal. Chem.*,76 (2004) 184.
11. Y. Zhou, N. Hu, Y. Zeng, and J. F. Rusling, *Langmuir*, 18 (2002) 211.
12. Y. S. Obeng and A. J. Bard, *Langmuir*,7 (1991) 195.
13. I. Svancara, K. Vytras, K. Kalcher, A. Walcarius, and J. Wang, *Electroanalysis*, 21 (2009) 7.
14. H. Karimi-Maleh, M. R. Ganjali, P. Norouzi, and A. Bananezhad, *Mater. Sci. Engin. C* 73 (2017) 472.
15. A. S. Dezfuli, M. R. Ganjali, and H. R. Naderi, *Applied Surf. Sci.*, 402 (2017) 245.
16. M. Hosseini, M. R. K. Pur, P. Norouzi, M. R. Moghaddam, and M. R. Ganjali, *Mater. Sci. Engin. C* 76 (20 17) 483.
17. M. Mehrzad-Samarin, F. Faridbod, A. S. Dezfuli, and M. R. Ganjali, Biosens. Bioelectron. 92 (2017) 618.
18. M. Aghazadeh, I. Karimzadeh, M. R. Ganjali, and M. Mohebi Morad, *Mater. Lett.*, 196 (2017) 392.
19. M. Rahimi-Nasrabadi, S. M. Pourmortazavi, M. Aghazadeh, M. R. Ganjali, M. S. Karimi, and P. Novrouzi, *J. Mater. Sci. Mater. Electron.,* 28 (2017) 3780.

20. M. Rahimi-Nasrabadi, S. M. Pourmortazavi, M. R. Ganjali, P. Novrouzi, F. Faridbod, and M. S. Karimi, *J. Mater. Sci. Mater. Electron.*, 28 (2017) 3325.

21. I. Karimzadeh, M. Aghazadeh, M. R. Ganjali, P. Norouzi, T. Doroudi, and P. H. Kolivand, *Mater. Lett.* 189 (2017) 290.

22. A. S. Dezfuli, M. R. Ganjali, H. Jafari, and F. Faridbod, *J. Mater. Sci. Mater. Electron.*, 28 (2017) 6176.

23. M. Aghazadeh, M. Asadi, M. G. Maragheh, M. R. Ganjali, P. Norouzi, and F. Faridbod, *Applied Surf. Sci.*, 364 (2016) 726.

24. H. R. Naderi, P. Norouzi, and M. R. Ganjali, *Applied Surf. Sci.*, 366 (2016) 552.

25. H. M. Shiri and A. Ehsani, *J. Colloid Interface Sci.*, 473 (2016) 126.

26. A. S. Dezfuli, M. R. Ganjali, P. Norouzi, and F. Faridbod, *J. Mater. Chem. B*, 3 (2015) 2362.

27. A. W. Xu, Y. Gao, and H. Q. Liu, *J. Catal.*, 207 (2002) 151.

28. Y. Humphries, M. Melson, and D. Gore, *J. Burn Care & Res.*,18 (1997) 34.

29. F. Roila, M. Tonato, C. Basurto, M. Picciafuoco, S. Bracarda, D. Donati, P. Malacarne, L. Monici, F. Di Costanzo, and L. Patoia, *J. Clin. Oncol.*, 7 (1989) 1693.

30. S. G. Carruthers, D. W. Shoeman, C. E. Hignite, and D. L. Azarnoff, *Clin. Pharm. Therap.*, 23 (1978) 375.

31. I. M. Paul, K. E. Yoder, K. R. Crowell, M. L. Shaffer, H. S. McMillan, L. C. Carlson, D. A. Dilworth, C. M. Jr. Berlin, *Pediatrics*, 114 (2004) e85.

32. M. Partinen, *Journal of Neurology*, 244 (1997) S3.

33. H. I. Chinn, S. W. Handford, T. E. Cone, and P. K. Smith, *Am. J. Med.*, 12 (1952) 433.

34. D. Radovanovic, P. J. Meier, M. Guirguis, J. P. Lorent, and H. Kupferschmidt, *Hum. Exp. Toxicol*, 19 (2000) 489.

35. R. F. Clark and M. V. Vance, *Annals Emerg. Med.*, 21 (1992) 318.

36. W. Zareba, A. J. Moss, S. Z. Rosero, R. Hajj-Ali, J. Konecki, and M. Andrews, *Am. J. Car.*, 80 (1997) 1168.

37. P. Tipparat, S. Lapanantnoppakhun, J. Jakmunee, and K. Grudpan, *J. Pharm. Biomed. Anal.*, 30 1 (2002) 105.

38. Y. Dong, X. Chen, Y. Chen, X. Chen, and Z. Hu, *J. Pharm. Biom. Anal.*, 39 (2005) 285.

39. S. T. Ulu and F. T. Elmali, *Spectrochim. Acta A*, 77 (2010) 324.

40. Ö. A. Dönmez, B. Aşçı, A. Bozdoğan, and S. Sungur, *Talanta*, 83 (2011) 1601.

41. E. Y. Z. Frag, G. G. Mohamed, and W. G. El-Sayed, *Bioelectrochemistry*, 82 (2011) 79.

42. C. Miao, A. Zhang, Y. Xu, S. Chen, F. Ma, C. Huang, and N. Jia, Sens. Actuat. B, 213 (2015) 5.

43. Y. Zhu, G. Li, S. Zhang, J. Song, C. Mao, H. Niu, B. Jin and Y. Tian, *Electrochim. Acta*, 56 (2011) 7550.

44. D. Ege, W. G. Becker, and A. J. Bard, *Anal. Chem.,* 56 (1984) 2413.

45. J. K. Leland and M. J. Powell, *J. Electrochem. Soc.*, 137 (1990) 3127.

46. J. M. Freitas, T. d. C. Oliveira, D. T. Gimenes, R. A. A. Munoz, and E. M. Richter, *Talanta*, 146 (2016) 670.

47. S. Cheraghi and M. A. Taher, *J. Mol. Liq.*, 219 (2016) 1023.

48. Q. Xiang, X. D. Yang, Y. Gao, L. Y. Tian, J. Tang, and K. Q. Wang, *Advanced Mater. Res.,* 881-883 (2014) 169.