RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

A Novel Solid-State Electrochemiluminescence Sensor based on $Ru(bpy)_3^{2+}$ / Nano Sm_2O_3 Modified Carbon Paste Electrode for determination of for L-proline

MortezaHosseini,[a*] Mohammad Reza Moghaddam,[b] Farnoush Faridbod,[b,c] Parviz Norouzi,[b,c] Mohammad Reza Karimipur,[b] Mohammad Reza Ganjali[b,c]

A novel solid-state electrochemiluminescence (ECL) sensor was successfully developed for the determination of L-proline. The ECL signal was generated by a sensitive reaction between $Ru(bpy)_3^{2+}$ and L-proline on a carbon paste electrode (CPE) modified samarium oxide nanoparticles. Presence of Sm_2O_3 nanoparticles (NPs) in the carbon paste was found to enhance the electrochemiluminescence signal. Under optimized conditions, a linear relation between the ECL intensity and the concentration of L-proline was observed in the linear range of 1.00×10^{-9} to 1.65×10^{-7} mol/L (R^2=0.996) with a detection limit of 6.0×10^{-10} mol/L (S/N=3) and relative standard deviation of 3.3%. The method was sensitive, selective and simple and successfully applied to the analysis of L-proline in human serum and urine samples.

[a]*Department of Life Science Engineering, Faculty of New Sciences & Technologies, University of Tehran, Tehran, Iran, * E-mail address:smhosseini@khayam.ut.ac.ir*

[b]*Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran*

[c]*Biosensor Research Center, Endocrinology & Metabolism Molecular-Cellular Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran*

1. Introduction

Since the introduction of electrochemiluminescence (ECL) technique based on tris(2,2′-bipyridyl) ruthenium(II) ($Ru(bpy)_3^{2+}$) by Tokel and Bard,[1]($Ru(bpy)_3^{2+}$), it has received considerable attention as a sensitive detection method for the chemical analysis of various analytes. The method has an excellent stability and high efficiency in aqueous media.[2-9] Solution phase and solid-state methods are two different trends in generating ECL signal. $Ru(bpy)_3^{2+}$ is one of the important ECL probe which is due to the regeneration properties during the ECL process, it can be possible to immobilize it on the electrode surface.[10-13] Compared to the solution-phase ECL procedure, the immobilization of the ($Ru(bpy)_3^{2+}$) reduces the consumption of the costly reagent further to simplifying the experimental design. So far, several different methods have been used to immobilize ($Ru(bpy)_3^{2+}$) on a solid surface, including the Langmuir-Blodgett,[14] self-assembled,[15] and electrostatic attachment techniques.[16] However, the films produced through these techniques have proven to be unstable due to the need for the application of high potentials.[17]

Carbon paste electrodes (CPEs) have been widely used in determination of drugs, biomolecule, as well as other organic species owing to their easy preparation routes and wider potential window of −1.4 to +1.3 V (versus SCE). The residual currents associated with CPE are also 10 times lower than those of glassy carbon or noble metal electrodes. The advantages of modified carbon paste electrodes (MCPEs) in the electroanalytical chemistry has been well established. Hence development of CPE based devices for the analytical applications is still of great interest.[18]

Currently there is further interest in the development and application of new materials, like graphene, nanoparticles, and carbon nanotubes, capable of improving the surface properties of

the electrode.[19] The application of metal nanoparticles, among all, gives rise to distinct advantages such as higher mass transport, less dependence on the solution resistance, low detection limit, and better signal-to-noise ratios.[20,21]

Considering their high mechanical stability, high dielectric constants, and large band gap characteristics, rare earth oxides have recently been extensively investigated for applications, including, optoelectronic devices, switching mechanism for logic devices, and memories.[22] Rare earth oxides are well known to display a high surface basicity, a fast oxygen ion mobility and interesting catalytic properties.[23]

Samarium(III) oxide (Sm_2O_3, also known as samaria), is one of the important rare earth oxide materials and has been extensively studied due to its variable valence properties.[24-25] Sm_2O_3 nanocystals are promising building blocks for the bottom-up assembly of novel nanostructures with high potential applications in various fields such as in solar cells,[26] nanoelectronics, [27] semiconductor gases and biochemical sensors. [28],

Recently, the analysis of L-proline has attracted considerable attention because of its important physical functions, broad distribution in nature and wide application in human life. Various analytical methods such as spectrophotometric,[29] HPLC-amperometric,[30] capillary electrophoresis- electrochemiluminescence [31] and fluorescence [32] methods have been used in the determination of amino acids for food stuff security and health purposes. Some of these methods are complex, time consuming and require tedious sample pretreatments or lack of sufficient sensitivity which limits their applications in many cases. Thus, developing new analytical methods for sensitive and rapid detection of L-proline is still an attractive area of research. In this work, development and application of a new ECL carbon paste composite sensor modified Sm_2O_3 nanoparticles for the determination of L-proline was investigated.

2. Experimental

2.1 Reagents and chemicals

All chemicals were of analytical reagent grade and used without further purification. Tris (2.2′-bipyridyl) ruthenium(II) ($Ru(bpy)_3^{2+}$) chloride hexahydrate was obtained from Sigma Co., and used without further treatment. Nafion perfluorinated ion-exchange (5% solution in 90% light alcohol), carbon graphite powder and paraffin oil were obtained from Fluka (Buchs, Switzerland).

2.2 Apparatus and Procedure

A Perkin-Elmer LS50 luminescence spectrometer with turn-off xenon lamp combined with a PalmSens PC potentiostat–galvanostat (Netherlands) and three- electrode system was used for the ECL spectrum measurement. Cyclic voltammetric (CV) studies were performed using a potentiostat–galvanostat with a conventional three-electrode set-up, in which theSm_2O_3 NPs - $Ru(bpy)_3^2$+-CPE, an Ag|AgCl|KClsat'ed electrode, and a platinum wire served as the working, reference and auxiliary electrodes, respectively. Electrochemical and ECL measurements were carried out in a 4 mL quartz cell, in which the working electrode was placed on an equatorial position in a quartz cell, while its surface precisely faced the window of Fl-win lab photomultiplier LS 50(Perkin-Elmer) and was fixed on holder (see Fig.S1). The detector and ECL cell were enclosed in a light tight black box. Spectral recording and cyclic voltammetry were conducted simultaneously with spectral scan rate at 500 nm min^{-1} and potential scan rate at 100 mV s^{-1} from 0 to 1.5 V.

The size and morphology of the nanoparticles were measured by scanning electron microscopy (SEM) using a KYKY-EM 3200 Digital Scanning Electron Microscope (China).

2.3 Synthesis of samarium oxide nanoparticles

Aqueous samarium nitrate solution was prepared by dissolving samarium oxide powder in an appropriate amount of nitric acid by ultrasound. This solution was next diluted by ethanol and added to a 20 wt% polyvinyl alcohol water solutions under vigorous stirring in a glass beaker and the resulting mixture was heated up to 90°C and stirred for 2h. Upon condensation of the hydroxyl network (by giving off water) a gelation reaction was achieved leading to the formation of a dense porous gel, which was dried in a drying oven at 110°C. The dried gel was then calcinated at 400°C for different periods of time to obtain samarium oxide NPs.[33,34]

2.4 Sensor preparation

The general procedure for the preparation of the CPE was as follows: prior to use, the graphite powder was treated at 800°C for 60s in a furnace and then cooled to room temperature in a desiccator in the presence of activated silica gel. 200µL of 2.5×10^{-2} mol/l $Ru(bpy)_3^{2+}$ was dispersed in a 500µL 5wt% nafion solution to obtain $Ru(bpy)_3^{2+}$-nafion solution. Graphite powder (90 mg) and the appropriate amounts of the Sm_2O_3 nanoparticles were homogenized and thoroughly mixed with a 200µL $Ru(bpy)_3^{2+}$ - nafion solution. This solution was dried at room temperature for 30 min. The modified carbon powder and 50µL paraffin oil were then mixed together by hand-mixing in order to obtain uniformly wetted paste. A portion of the modified carbon paste was placed into the end of Pyrex tube (5mm i.d), and the electrical contact to the paste was established by inserting a copper wire down each tube and into the back of the mixture. Finally the modified CPE was smoothed using a fine piece of paper (see Fig.S2).

3. Result and discussion

3.1 Characterization of the Sm_2O_3NPs

The morphology of the Sm_2O_3 nanoparticles and incorporation of Sm_2O_3 nanoparticles in the carbon paste samples was studied by SEM. The results shown in Fig. S3 (A,B) indicate that the produced nanoparticles are spherical in shape and have uniform surfaces with narrow size distribution.

To obtain further information on the composite, energy-dispersive X-ray (EDX) analyses were performed on the samples without any treatments (Fig.S3. C). The EDX spectra proved the presence of samarium, oxygen, ruthenium and carbon as the main components of the nanocomposites. These data are summarizes in inset Fig.S3. C.

3.2 Electrochemical and ECL behaviors $Ru(bpy)_3^{2+}$–Sm_2O_3NPs–CPE

The catalytic effect of metal and metal oxide NPs such as Pt-NPs,[35] Au-NPs,[36] Ag-NPs[37], ,Pd-NPs [38] and ZnO-NPs [39]on the chemiluminescence (CL) and ECL behavior have been shown in previous studies. In order to investigate the effect of the carbon paste modified Sm_2O_3NPs on $Ru(bpy)_3^{2+}$ oxidation and possible ECL reactions, a CV was applied in the potential range between 0.0 and 1.5 V *vs.* Ag|AgCl|KClsat at a scan rate of 100 mV s^{-1}. Fig. 1A shows the cyclic voltammograms of CPE, $Ru(bpy)_3^{2+}$–Sm_2O_3NPs - CPE in pH 8.5 phosphate buffer at 100 mVs^{-1}. The larger charging currents at the Sm_2O_3NPs -$Ru(bpy)_3^{2+}$- CPE observed in Fig. 1A (c), is attributed to the increase of electrode surface area due to the presence of Sm_2O_3 NPs. Sm_2O_3NPs -$Ru(bpy)_3^{2+}$- CPE exhibited a couple of redox peaks at +1.153 V.

Fig. 1.

Also, the immobilized $Ru(bpy)_3^{2+}$ revealed to be electroactive in the oxidation of L-proline. The result of the electrocatalytic process is a CL emitting species, which generates an ECL signal (Fig. 2).

In order to optimize the performance of the ECL sensor, Sm_2O_3NPs-$Ru(bpy)_3^{2+}$- CPE towards L-proline detection, effects of pH, Sm_2O_3NPsloaded on the electrode surface, concentration of $Ru(bpy)_3^{2+}$ and scan rate on the intensity of ECL signal were investigated.

Fig. 2.

3.4 Effect of pH

The effect of pH on the ECL intensity of L-proline was studied over a pH range from 6.0 to 10.0. Fig. 3 shows the ECL intensity increased considerably with the rising of pH from 6.0 to 8.5. It was observed that at pH values more than 8.5, the ECL intensity of L-proline decreased and hence 8.5 was chosen as the optimum pH value and a phosphate buffer solution with this pH was used for the ECL determinations.

Fig. 3.

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

The effect of the concentration of $Ru(bpy)_3^{2+}$ in the carbon paste electrode on the intensity of the ECL signal was also investigated, and the intensity of the ECL signal in the presence of 100nM proline was found to linearly increase with increasing the concentration of $Ru(bpy)_3^{2+}$ from 1×10^{-2}mol/L to 2.5×10^{-2}mol/L. Although further increase in the concentration of $Ru(bpy)_3^{2+}$ (up

to 2.5×10^{-2}mol/L)did not cause further enhancement in the intensity of the ECL of the sensor, the background ECL signal of $Ru(bpy)_3^{2+}$steadily increased with increasing the concentration of $Ru(bpy)_3^{2+}$ from 1.0×10^{-2}mol/L to 2.5×10^{-2} mol/L. Therefore, 2.5×10^{-2}mol/L was selected as the optimum concentration of $Ru(bpy)_3^{2+}$ in the Sm_2O_3NPs-$Ru(bpy)_3^{2+}$- CPE used for the determining L-proline.

3.6 Effect of Sm_2O_3 concentration

The effect of the loading of Sm_2O_3 on the intensity of the ECL signal was studied by casting different amounts of Sm_2O_3 nanoparticles in the carbon past electrode. It is obvious from Fig.S4, that the amount of Sm_2O_3 in the CPE is a crucial factor influencing the oxidation of $Ru(bpy)_3^{2+}$ and finally the ECL response.

Fig.S4 illustrates the effect of the amount of Sm_2O_3on the intensity of the ECL signal of $Ru(bpy)_3^{2+}$in the presence of 100 nM L-proline. The ECL signal increased upon increasing the amount of $Sm_2O_3$and reached a plateau at 5mg of Sm_2O_3in 90mg of graphite. So, this ratio was used in the preparation of the carbon paste electrodes.

3.7 Effect of scan rate

The effect of the scan rate (v) on the ECL and the CV signals of $Ru(bpy)_3^{2+}$ was investigated in the presence of 100 nM L-proline. The results (Fig.4, a.b) indicated that with increasing v the intensity of the ECL signal reached a maximum at about $100mVs^{-1}$. At the same time, with increasing the scan rate from 50 to 350 mVs^{-1}, both the oxidation and reduction currents increased linearly, while their peak potentials shifted in positive and negative directions and hence the peak to peak separation increased. This indicates a surface controlled quasi-reversible

electrode process. A scan rate of 100mVs^{-1} was selected for further experiments, since the maximum ECL sensitivity was observed at this value.

Fig. 4.

3.8 Interference studies

The influence of some common foreign species on the determination of L-proline was studied under the optimum experimental conditions stated above. The tolerable limit of a foreign species was taken as the concentration causing relative errors not greater than ±5% in the ECL signal of L-proline. No interference were found in the presence of up to 1000-fold (Mg^{2+}, K^{+}, Cl^{-} and Na^{+}), 500-fold L-tryptophan, L -serine, 300-fold (L-methionine, L-valine, L-lysine, L-asparagine), 200-fold uric acid, 100-fold L- histidine, L -isoleucine, L -Lucien.

3.9 Analytical performance

Under the optimum conditions given above, the response to L-proline was linear in the range of 1.0×10^{-9} to 1.65×10^{-7} mol/L, with a regression equation of $I=5.0\times10^{9}$ c+284, as well as a detection limit of 6.0×10^{-10} mol/L (S/N=3). Fig. 5A shows typical calibration traces recorded for L-proline using the proposed ECL sensor. The relative standard deviation was 3.3% for the determination of 1.0×10^{-8}mol/L L-proline (n=7).

Fig. 5.

The reproducibility of the signal of the modified electrode was also studied. Immersing the sensor in a phosphate buffer containing 100nM L-proline, led to no detectable change in the ECL intensity under then repetitive cyclic potential scans, suggesting good reproducibility of the ECL determination of L-proline (Fig. 6).

Also, the stability of the modified electrode was tested through the repetitive measurement of the ECL response. After two months, no evident decrease in the ECL response was observed and the sensor still maintained 92% of the original response. The results suggested that the modified electrode has a good stability.

Fig. 6.

A comparison between the results of this work and some other previously reported methods for the determination of L-proline determination is summarized in Table 1. In comparison with the previous works, the proposed sensor has a wider linear range. The detection limit of the proposed sensors is 6.0×10^{-10} mol/L which is lower than spectrophotometric and fluorescence methods. In term of the linear range and detection limit, it can be seen that the proposed sensor displays even more sensitivity than most of the reported methods.[25-28]

Table 1

3.10 Mechanism of enhancement of ECL by L-proline

The ECL signal of Sm_2O_3 NPs -$Ru(bpy)_3^{2+}$-CPE in phosphate buffer in absence of L-proline 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 L-proline 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.[40]

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

L-proline $- e \rightarrow$ L-proline$^{\cdot+}$

L-proline$^{\cdot+} \rightarrow$ L-proline$^{\cdot} + H^{+}$

L-proline$^{\cdot} + Ru(bpy)_3^{3+} \rightarrow$ L-proline fragments $+ Ru(bpy)_3^{2+*}$

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

3.11 Analytical applications

The applicability of the proposed sensor to determination of L-proline in human serum and urine samples was examined. ECL intensities after spiking a standard aliquot of L-proline to the diluted serum and urine solutions were obtained using Sm_2O_3NPs-$Ru(bpy)_3^{2+}$- CPE 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

4. Conclusions

In this work, an ECL sensor was fabricated for the determination L-proline using carbon paste 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 L-proline, which results in the formation of an emitting species which produces the ECL signal. The proposed ECL sensor had a low detection limit of 6.0×10^{-10} mol/L and a linear range from 1.00×10^{-9} to 1.65×10^{-7} mol/L. The applicability of a proposed sensor to the determination of L-proline in human samples has also been evaluated, and it found to have a good reproducibility and enough sensitivity for the detection of L-proline in different samples.

Acknowledgment

The authors thank the research Council of University of Tehran for financial support of this work.

References

1 N. E. Tokel, A. J. Bard, *J. Am. Chem. Soc.,* 1972,**94**, 2862.

2 M. M. Richter, *Chem. Rev.,* 2004, **104**, 3003.

3 J. Li, E. Wang, *Chem. Rec.,* 2012,**1**, 177.

4 Y. Su, R.Y. Lv, *Soc. Chem. Adv.,*2014, **55**, 29324.

5 Y. Xu, J. Liu, C. Gao, E. Wang, *Electrochem. Commun.,*2014, **48**, 151.

6 O. Kargbo, S. N. Ding, L. Q. Li, *Curr.Anal. Chem.,* 2014, **10**, 622.

7 S. Deng, H.Ju, *Analyst*2013,**138** , 43.

8 M. Hosseini, N. Mirzanasiri, M. Rezapour, M. H. Sheikhha, F. Faridbod, P. Norouzi, M. R. Ganjali, *Luminescecne*in press 2014.

9 M. Hosseini, M. R. Karimipur, P. Norouzi, M. R. Moghaddam, F. Faridbod, M. R. Ganjali, J. Shamsi, *Anal. Method.* in press 2014.

10 X. B. Yin, S. Dong, E. Wang, *Trends Anal. Chem*.,2004, **23**, 432.

11 L. Ge, J. Yan, X. Song, M. Yan, S. Ge, J. Yu, *Biomaterials*2012*,* **33**, 1024.

12 Z. Chen, Y. Liu, Y. Wang, X. Zhao, J. Li, *Anal. Chem.,*2013*,* **85**, 4431.

13 G. A. Crespo, G. Mistlberger, E. Bakker. *J. Am. Chem. Soc*.,*2012*,**134**, 205

14 Z. Zhang, A. J. Bard, *J. Phys. Chem*.,1988, **92**, 5566.

15 Z. Guo, Y. Shen, M. Wang, F. Zhao, S. Dong, *Anal. Chem.,* 2004,**76**, 184.

16 Y. L. Zhou, Z. Li, N. F. Hu, Y. H. Zeng, J. T. Rusling, *Langmuir*2002, **18**, 8537.

17 Y. S. Obeng, A. J. Bard, *Langmuir*1991, **7**, 195.

18 I. Svancara, K. Vytras, K. Kalcher, A. Walcarius, J. Wang, *Electroanalysis*2009, **21**, 7.

19 M. H. Parvin, *Electrochem. Commun*.,2011, **13**, 366.

20 R. M. Penner, C. R. Martin, *Anal. Chem*.,1987, **59**, 2625.

21 M. H. Parvin, M. B. Golivand, M. Najafi, S. M. Shariaty, *J. Electroanal. Chem.,* 2012, **683**31.

22 C. Constantinescu, V. Ion, A. C. Galca, M. Dinescu, *Thin Solid Films.,* 2012, **520**, 6393

23 L. Eyring, K.A Gschneider Jr, The Handbook on the Physics and chemistry of Rare Earths, North Holland Amesterdam, 1979

24 T. D. Nguyen, D. Mrabet, T. O. Do, *J. Phys. Chem*, 2008, **112**, 15226

25 A. Rosengren, B. Johansson, *Phys. Rev. B*., 1982,**26**, 3068

26 K. Kendall, *Nature* 2000, **404**, 233.

27 M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith, C. M. *Nature*, 2002, **415**, 617

28 P. W. Barone, S. Baik, D. A. Heller, M. S. Strano, *Nat. Mater*, 2005, **4**, 86

29 C. Truzzi, A. Annibaldi, S. Illuminati, C. Finale, G. Scarponi, *Food Chem.,* 2014,**150***,* 477.

30 H. J. Sim, E. Moon, S. Y. Kim, S. P. J. Hong. *Chromatog. B,* 2013, **930**, 70.

31 X. Jing, et al., *Chinese J. Anal. Chem.,*2005, **33**, 785.

32 F. Robert-Peillard, J. L. Boudenne, B. Coulomb, *Food Chem.,* 2014, 274.

33 M. R. Ganjali, H. Ganjali, M. Hosseini, P. Norouzi, *Int. J. Electrochem.,*2010,**5**, 967.

34 F. Faridbod, M. R. Ganjali, M. Hosseini, P. Norouzi, *Int. J. Electrochem.,*2012, **7**, 1927.

35 X. M. Chen, Z. J. Lin, Z. M. Cai, X. Chen, M. Oyama, X. R. Wang, *J. Nanosci. Nanotechnol.,*2009,**9**, 2413.

36 B. Haghighi, S. Bozorgzadeh, L. Gorton, *Sens. Actuator B,* 2011,**155**, 577.

37 B. Haghighi, S. Bozorgzadeh, *Microchem. J.,* 2010,**95**, 192.

38 B. Haghighi, S. Bozorgzadeh, *Anal. Chim. Acta,* 2011,**697**, 90.

39 B. Haghighi, S. Bozorgzadeh, *Talanta*2011, **85***,* 2189.

40 J. K. Leland, M. J. Powell, *J. Electrochem. Soc.,* 1990, **137**, 3127.

Figures Legend:

Fig.1. Cyclic voltammograms CPE(a), $Ru(bpy)_3^{2+}$ - CPE (b) SmO_2NPs-$Ru(bpy)_3^{2+}$-CPE(c).supporting electrolyte buffer solution (0.1M and pH 8.5) and 100 nM L-proline; potential scan rate, 100 mVs^{-1}.

Fig. 2.ECL responses of (a) $Ru(bpy)_3^{2+}$ - CPE (b) Sm_2O_3NPs-$Ru(bpy)_3^{2+}$- CPEin 0.1M pH 8.5 phosphate buffer containing 100 nM L-proline; Inset, the picture of ECL of (A)$Ru(bpy)_3^{2+}$- CPE, (B)Sm_2O_3NPs-$Ru(bpy)_3^{2+}$- CPEin 0.1M pH 8.5 phosphate buffer containing 100 nM L-proline. potential scan rate , 100 mV/S.

Fig.3. Effect of pH on the ECL intensity.

Fig.4.(a)Effect of scant rate on the ECL responses, (b)Cyclic voltammograms of Sm_2O_3NPs-$Ru(bpy)_3^{2+}$- CPE in 0.1 M pH 8.5 phosphate buffer at 50, 100, 150, 200, 250 , 300 and 350 mVs^{-1}. Inset: plots of peak currents *vs*. scan rate.

Fig.5. (A) ECL responses of Sm_2O_3NPs -$Ru(bpy)_3^{2+}$- CPE at in the presence of 1.0×10^{-9}M, 4.5×10^{-8}M, 7.5×10^{-8}M, 1.0×10^{-7}M, 1.35×10^{-7}M, and 1.65×10^{-7}M of L-proline, Inset shows linear relationship between the ECL intensity and the concentration of L-proline, potential scan rate , 100 mV/S.

Fig.6. Stability of ECL signal from modified carbon paste electrode in 0.1 M pH 8.5 phosphate buffer solution, containing 100 nM L- proline under ten continuous cycles of CV scan, potential scan rate , 100 mV/S.

Table 1

Comparison of the characteristics of the proposed sensor with those of the previously reported for L-proline.

Method	**Detection Limit (M)**	**Dynamic Range (M)**	**Ref.**
Sepectrophotometry	8.68×10^{-5}	1.5×10^{-3}-2.5×10^{-4}	29
HPLC-amperometric detector	5.0×10^{-8}	1.0×10^{-4}-1.0×10^{-6}	30
CapillaryElectrophoresis-Electrochemiluminescence	2.0×10^{-6}	2.0×10^{-3}-8.0×10^{-6}	31
Fluorescence	6.5×10^{-5}	2.5×10^{-3}-1.7×10^{-4}	32
Electrochemiluminescence	6.0×10^{-10}	1.0×10^{-9}-1.65×10^{-7}	This work

Table 2.

ECL determination results and recoveries of L-proline samples using a Sm_2O_3NPs-$Ru(bpy)_3^{2+}$-carbon paste modified electrode.

Sample	Added ($molL^{-1}$)	Found [a] ($molL^{-1}$)	Recovery(%)
	0	1.9×10^{-9}	-
Human Serum	5.7×10^{-9}	$7.5\ (\pm0.2)\times10^{-9}$	98.7
	6.0×10^{-9}	$8.0(\pm\ 0.2)\times10^{-9}$	101.3
	0	0.9×10^{-9}	-
Urine	4.5×10^{-9}	$5.6\pm(\ 0.1)\times10^{-9}$	103.7
	5.5×10^{-9}	$6.3(\pm\ 0.2)\times10^{-9}$	98.4

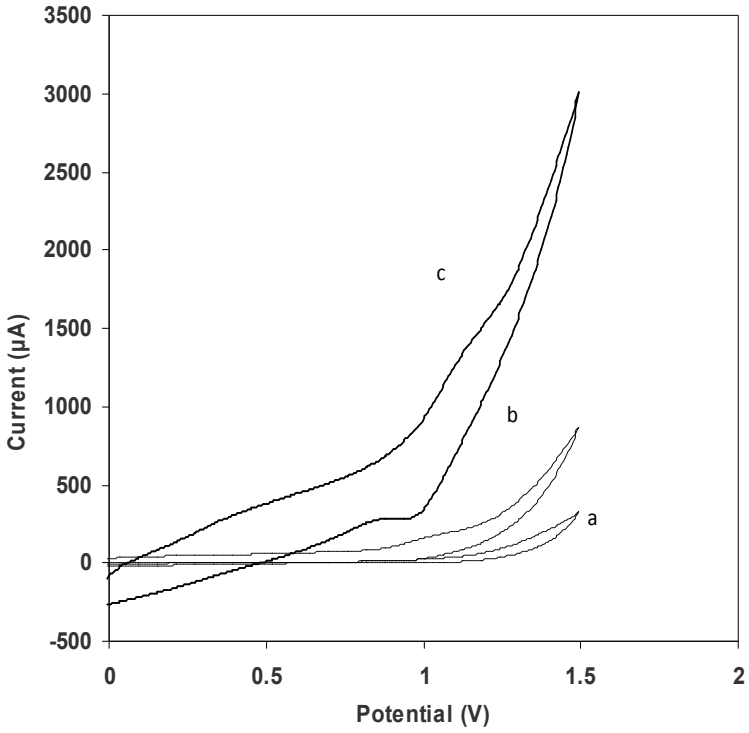


Fig. 1.

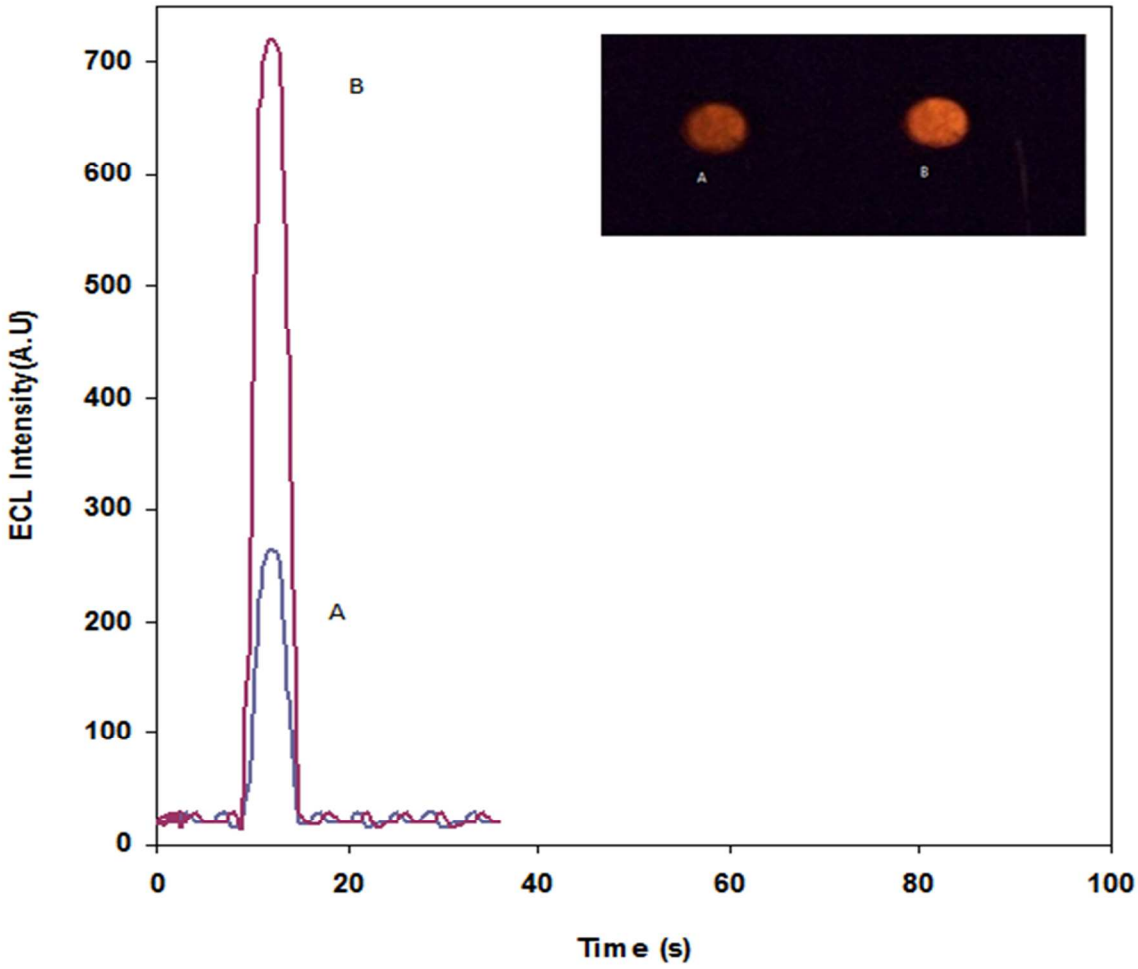


Fig. 2.

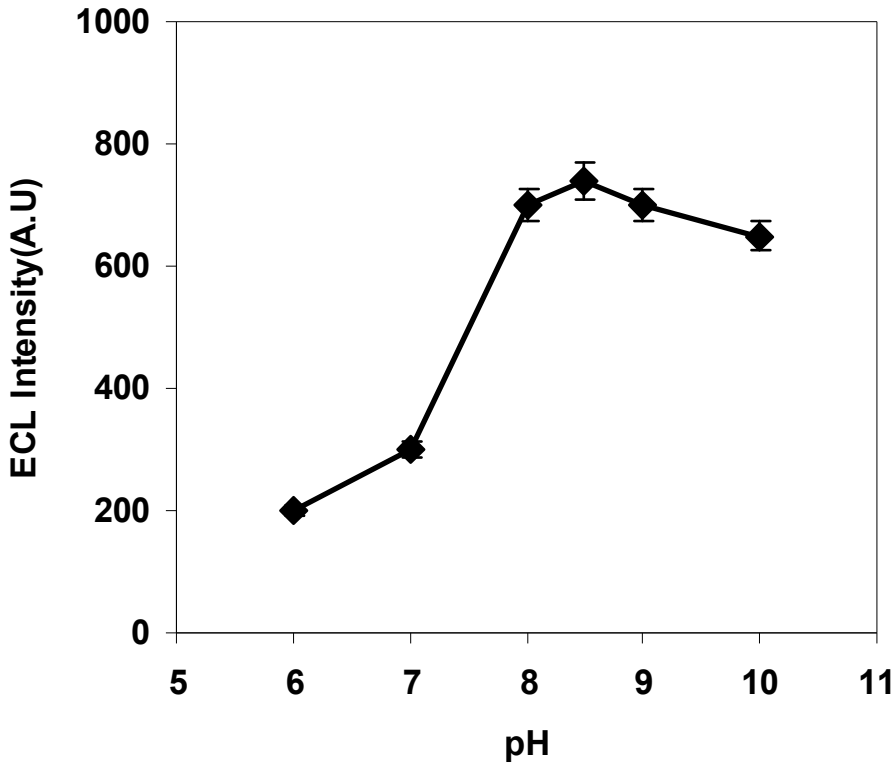
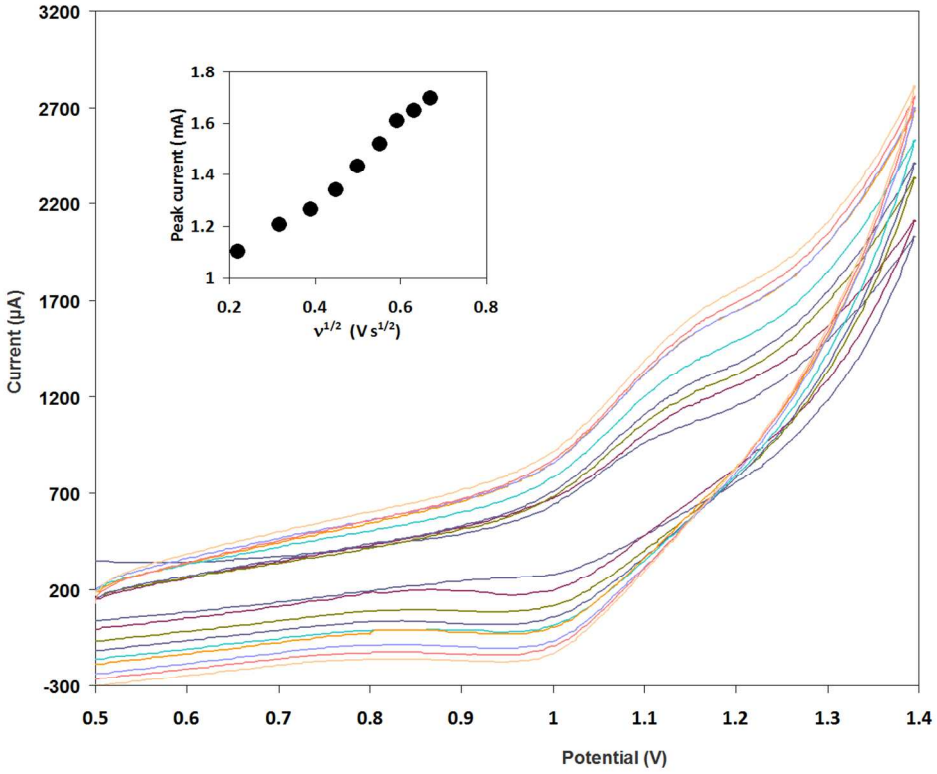
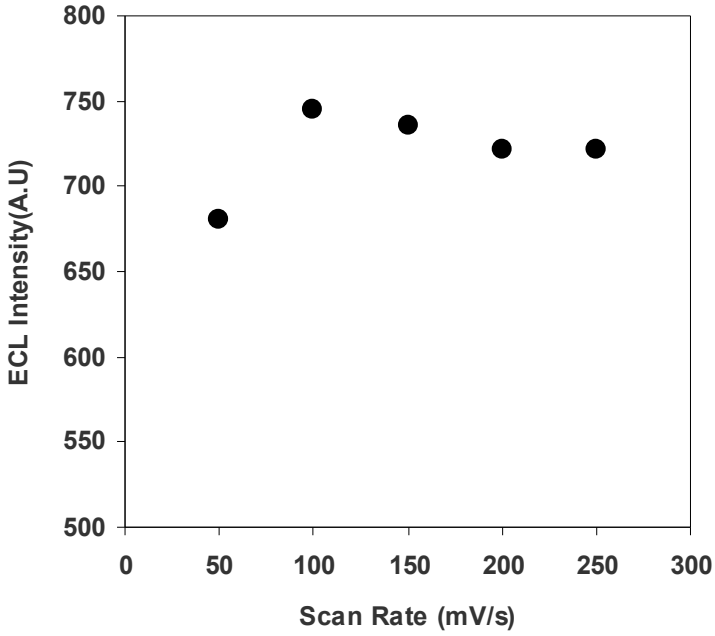


Fig. 3.



b



a

Fig. 4.

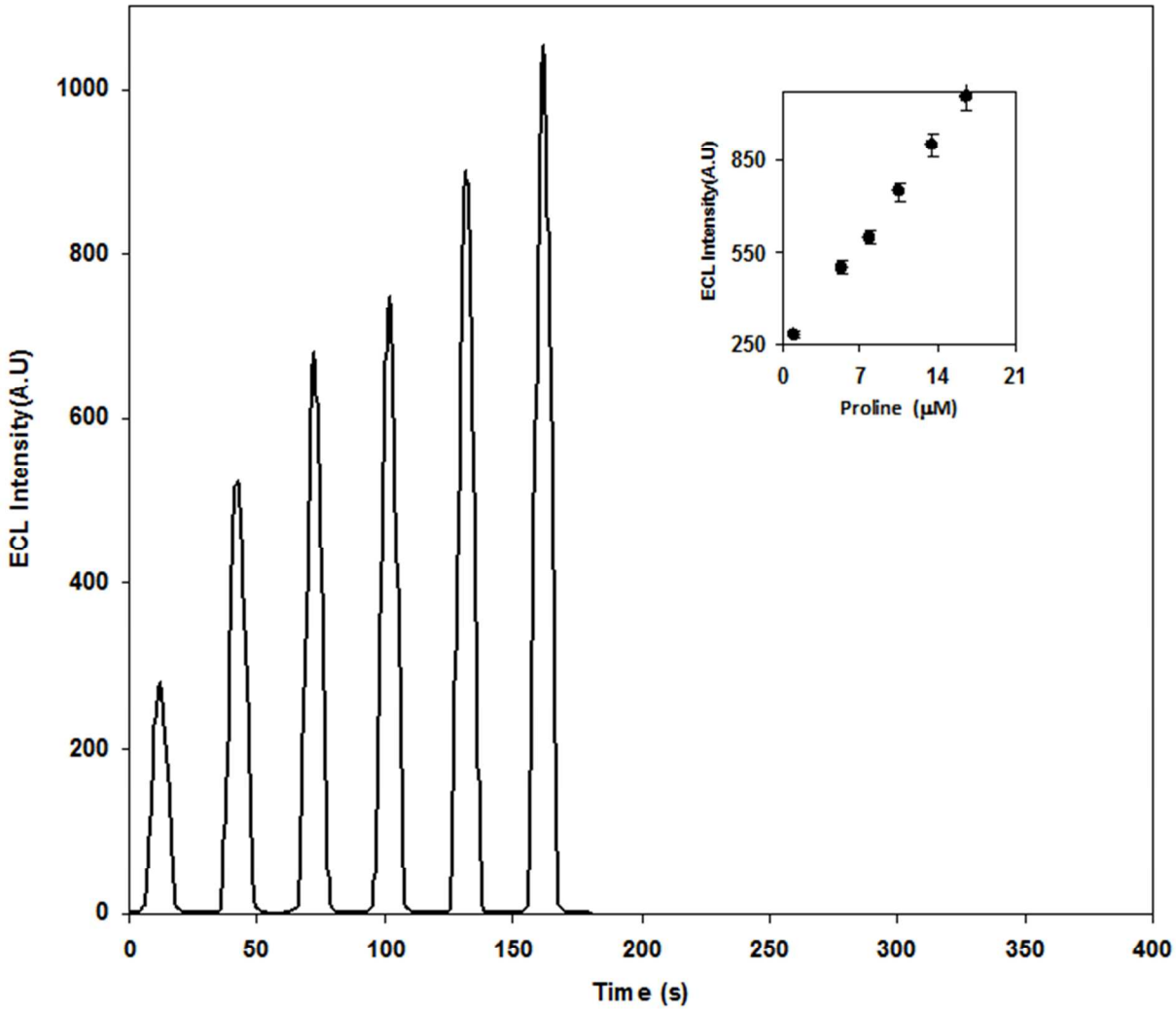


Fig. 5

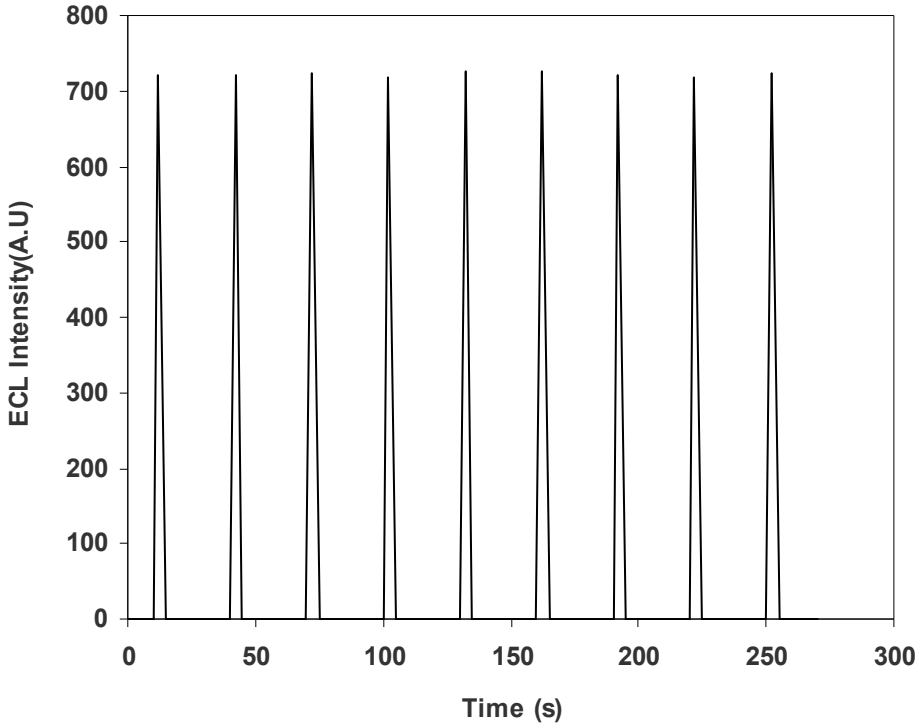


Fig.6