Talanta 85 (2011) 2189–2193

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Fabrication of a highly sensitive electrochemiluminescence lactate biosensor using ZnO nanoparticles decorated multiwalled carbon nanotubes

Behzad Haghighi*, Somayyeh Bozorgzadeh

Department of Chemistry, Institute for Advanced Studies in Basic Sciences, P.O. Box 45195–1159, Gava Zang, Zanjan, Iran

ARTICLE INFO

Article history:
Received 26 April 2011
Received in revised form 19 July 2011
Accepted 20 July 2011
Available online 27 July 2011

Keywords:
Electrochemiluminescence
ZnO nanoparticles
Multiwalled carbon nanotubes
Luminol
Lactate biosensor

ABSTRACT

ZnO nanoparticles (nanoZnO) were decorated on multiwalled carbon nanotubes (MWCNTs) and then the prepared nano-hybrids, nanoZnO-MWCNTs, were immobilized on the surface of a glassy carbon electrode (GCE) to fabricate nanoZnO-MWCNTs modified GCE. The prepared electrode, GCE/nanoZnO-MWCNTs, showed excellent electrocatalytic activity towards luminol electrochemiluminescence (ECL) reaction. The electrode was then further modified with lactate oxidase and Nafion to fabricate a highly sensitive ECL lactate biosensor. Two linear dynamic ranges of 0.01–10 μmol L^{-1} and 10–200 μmol L^{-1} were obtained for lactate with the correlation coefficient better than 0.9996. The detection limit (S/N = 3) was 4 nmol L^{-1} lactate. The relative standard deviation for repetitive measurements (n = 6) of 10 μmol L^{-1} lactate was 1.5%. The fabrication reproducibility for five biosensors prepared and used in different days was 7.4%. The proposed ECL lactate biosensor was used for determination of lactate in human blood plasma samples with satisfactory results.

1. Introduction

Lactate is a key metabolite in the anaerobic glycolytic pathway. Quantification of L-lactate is important not only for the clinical purposes, but also for the food and wine quality assessments [1]. A notable number of spectrophotometric and chromatographic methods have been reported for the determination of lactate [2–5]. But, the most of the proposed methods are relatively expensive, time consuming and involve complicated procedures. Thus, there is an increasing demand for the determination of lactate using inexpensive, rapid and reliable methods. Modern electrochemistry offers a wide range of analytical methods with the ability to provide the desired experimental and analytical features. Electroanalytical methods based on the amperometric technique especially those employing enzyme are particularly suited for the determination of lactate [6–16].

Electrogenerated chemiluminescence so-called electrochemiluminescence (ECL) is a powerful analytical tool which is introduced as a result of link between the traditional fields of analytical electrochemistry and luminescence spectroscopy [17]. ECL has received considerable attention in analytical chemistry due to the advantages of both electrochemical and luminescence techniques such as low background signal, high sensitivity, wide dynamic range and simple and inexpensive instrumental set up [18]. Luminol is one of the most popular ECL luminophor which has been widely used for the fabrication of luminol-based ECL biosensors. In the luminol-based ECL biosensors the reaction between the oxidized luminol and hydrogen peroxide, the product of an enzymatic reaction between the substrate (analyte) and an oxidase enzyme, produces the luminol ECL signal [19–21]. Several luminol based lactate ECL biosensors [20,22–28] have been developed for the determination of lactate in different real samples such as salvia, blood, serum, sweat and whey solutions, but there is still an increasing demand for the simple fabrication of the sensitive lactate ECL biosensor.

The special structure, extraordinary mechanical and unique electronic properties of nano-structured materials such as carbon nanotubes (CNTs), metal nanoparticles (NPs) and metal oxide nanoparticles make them attractive materials for the electroanalytical applications [18] and also for the fabrication of luminol based ECL sensors and biosensors [19,20,29–33]. The attachment of metal or metal oxide NPs to the CNTs which is often referred as a "decoration process" [34] has led to the creation of new class of nano-hybrid materials with the integrated properties of two components [35]. Among the wide variety of nano-structure metal oxides, the nano-structure ZnO shows attractive features of high chemical stability, high electrochemical activity, high biocompatibility and fast electron transfer kinetic. These properties allow using nano-structure ZnO for the fabrication of electrochemical biosensors [36–39]. The sensitization effect of ZnO nano-particles on luminol ECL reaction has been shown previously by Feng et al. [40]. Hence, it was of interest to investigate the enhancement effect of ZnO nanoparticles (nanoZnO) deposited on the surface of multiwalled carbon

* Corresponding author. Tel.: +98 241 4153 126; fax: +98 241 4153 232.
E-mail address: haghighi@iasbs.ac.ir (B. Haghighi).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.07.071

nanotubes (MWCNTs) on the ECL signal intensity of luminol and its possible application for the fabrication of an ECL biosensor.

In the present work, ZnO nanoparticles decorated MWCNTs (nanoZnO-MWCNTs) were prepared using thermal decomposition and then the prepared nano-hybrids (nanoZnO-MWCNTs) were immobilized on the surface of a glassy carbon electrode (GCE). The electrocatalytic activity of nanoZnO-MWCNTs modified glassy carbon electrode (GCE/nanoZnO-MWCNTs) towards luminol ECL reaction allowed to develop a novel ECL lactate biosensor with the improved analytical performance towards lactate detection.

2. Experimental

2.1. Chemicals, apparatus and procedure

All chemicals were of analytical reagent grade and used without further purification. Lactate oxidase (LOx, ≥20 U/mg solid) and L-(+)-lithium lactate (97%) were obtained from Sigma (St. Louis, MO, USA). Nafion perfluorinated ion-exchange (5% solution in 90% light alcohol) was obtained from Fluka (Buchs, Switzerland). Luminol, zinc(II) acetate dihydrate, dimethylformamide (DMF) were obtained from Merck (Darmstadt, Germany). Multiwalled carbon nanotubes (95% purity, OD = 10–30 nm, ID = 5–10 nm and length = 0.5–500 μm) was purchased from Aldrich (Steinheim, Germany).

ZnO nanoparticles decorated MWCNTs containing 10 mol% Zn were prepared according to the method reported previously [34] via manual mixing without modification.

Electrochemical and ECL measurements were carried out in a 4 mL homemade Teflon ECL cell using an Autolab potentiostat–galvanostat model PGSTAT30 (Utrecht, The Netherlands) with a conventional three-electrode set-up and a Hamamatsu photomultiplier module (H7468) (Hamamatsu city, Japan) [29]. The photodetector and ECL cell were enclosed in a light-tight black box. The working potential was applied to the working electrode in the standard way using the potentiostat and the output electrochemical and ECL signals were acquired using Autolab NOVA software and a home-written data acquisition program, respectively. Electrochemical and ECL measurements were carried out in phosphate buffer solution (PBS, 0.1 mol L^{-1}, pH 8.5).

2.2. Preparation of lactate biosensor (GCE/nanoZnO-MWCNTs/LOx/Nafion)

GCE/nanoZnO-MWCNTs was prepared by casting 2 μL suspension of nanoZnO-MWCNTs in DMF (1 mg mL^{-1}) on the polished GCE surface and letting DMF to evaporate at 50 °C in an oven. Then, a 5 μL of phosphate buffer solution (PBS, 0.1 mol L^{-1}, pH 7.4) containing 5 U LOx was pipetted on the surface of GCE/nanoZnO-MWCNTs and allowed to dry in air at room-temperature. Finally, the surface of the prepared electrode, GCE/nanoZnO-MWCNTs/LOx, was coated by 5 μL of 0.5% Nafion solution to fabricate lactate biosensor (GCE/nanoZnO-MWCNTs/LOx/Nafion). For comparison, GCE/Nafion and GCE/MWCNTs/Nafion were prepared through similar procedures.

3. Results and discussion

3.1. Electrocatalytic activity of nanoZnO-MWCNTs towards luminol and luminol–H_2O_2 oxidation reactions

Fig. 1A shows cyclic voltammograms (CVs) of 100 μmol L^{-1} luminol in PBS (0.1 mol L^{-1}, pH 8.5) with the scan rate of 100 mV s^{-1} at a GCE/Nafion (a), GCE/MWCNTs/Nafion (b) and GCE/nanoZnO-MWCNTs/Nafion (c). As shown in Fig. 1A, the anodic peak current intensity of luminol (at about 0.4 V) and also the charging current intensity enhanced by the modification of GCE with MWCNTs and nanoZnO-MWCNTs. It can be clearly seen that the enhancement effect for GCE modified with nanoZnO-MWCNTs was higher than that of with MWCNTs, indicating nanoZnO-MWCNTs in comparison with MWCNTs provided larger surface area and more active sites for luminol oxidation reaction and consequently showed higher electrocatalytic activity and higher current intensity. A similar enhancement effect was also observed in their corresponding ECL signals (Fig. 1B). The ECL signal intensity of luminol at GCE/MWCNTs/Nafion (Fig. 1B(b)) and GCE/nanoZnO-MWCNTs/Nafion (Fig. 1B(c)) enhanced 5-fold and 13-fold, respectively compared to that of at GCE/Nafion (Fig. 1B(a)).

Reactive oxygen species (ROSs) include singlet oxygen ($^1O_2$), superoxide hydrogen ($HO_2^{\bullet}$), superoxide radical ($O_2^{\bullet -}$), hydroxyl radical ($OH^{\bullet}$) and so on, are highly reactive species which can be produced by applying special potential window (range) or constant potential. Superoxide and hydroxyl radicals can be generated at the appropriate potential from the reduction of oxygen and also from the oxidation and reduction of hydrogen peroxide, respectively [41]. Therefore, on the basis of the results obtained in this study for luminol ECL reaction, it is proposed that various reactive oxygen species such as $HO_2^{\bullet}$, $O_2^{\bullet -}$ and $OH^{\bullet}$ as a result of oxygen reduction can be produced at the studied electrodes surface. The production of these electrogenerated reactive species at the electrode surface can be enhanced by the electrocatalytic activity of nanoZnO-MWCNTs towards oxygen reduction. The increase of cathodic current intensity at about 0 V versus $Ag|AgCl|KCl_{sat}$ in Fig. 1A(c) in comparing with that of observed in Fig. 1A(b) is an evidence for the electrocatalytic activity of nanoZnO-MWCNTs towards oxygen reduction. During the course of sweeping potential in positive (oxidation) direction, luminol is oxidized to the luminol radical anion with the maximum peak current intensity at about 0.4 V. The subsequent chemical reaction of luminol radical anions with the electrogenerated reactive oxygen species produces the excited-state 3-aminophthalate anions which emit light. So, the electrocatalytic activity of nanoZnO-MWCNTs towards oxygen reduction and also luminol oxidation significantly enhances the ECL signal by increasing the amount of various electrogenerated reactive oxygen species and also by increasing the amount of luminol oxidation product, luminol radical anions, via accelerating the rate of their redox reactions.

It was also found that the ECL signal intensity of luminol greatly enhanced in the presence of H_2O_2 at the mentioned different electrodes (Fig. 1C). The results showed that the ECL signal intensity of luminol (100 μmol L^{-1}) in the presence of H_2O_2 (1 μmol L^{-1}) increased 6-fold by modification of the GCE with MWCNTs (Fig. 1C(b)), whereas this enhancement was 15-fold by modification of the GCE with nanoZnO-MWCNTs (Fig. 1C(c)).

It has been proposed that ZnO nanoparticles can catalyze the decomposition of H_2O_2 to produce some reactive intermediates such as hydroxyl radical and superoxide anion [42]. It seems, the subsequent chemical reaction of the produced reactive intermediates with luminol radical anions produces the excited-state 3-aminophthalate anions which emit light. Therefore, the observed remarkable enhancement in ECL responses of luminol in the presence of H_2O_2 at GCE/nanoZnO-MWCNTs was attributed to the catalytic activity of nanoZnO-MWCNTs nano-hybrids towards luminol oxidation and also H_2O_2 decomposition via accelerating the rate of their reactions.

3.2. Analytical performance of lactate biosensor

Based on electrocatalytic activity of nanoZnO-MWCNTs on luminol–H_2O_2 ECL reaction, GCE/nanoZnO-MWCNTs/Nafion was

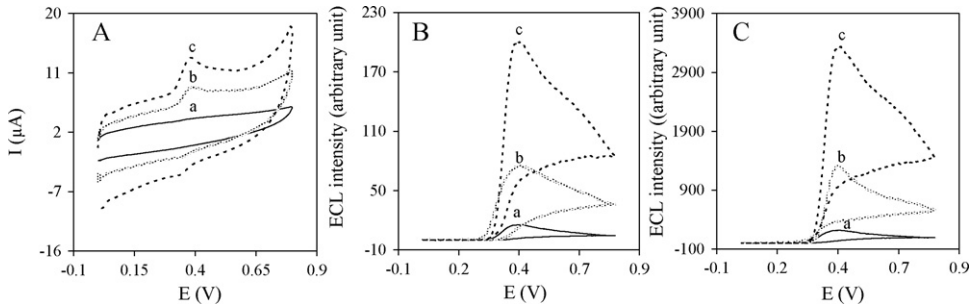

Fig. 1. (A) Cyclic voltammograms and (B) corresponding ECL curves of luminol in the absence and (C) in the presence of 1 μmol L^{-1} H_2O_2 at GCE/Nafion (a), GCE/MWCNTs/Nafion (b) and GCE/nanoZnO-MWCNTs/Nafion (c). Conditions: luminol, 100 μmol L^{-1}; supporting electrolyte, phosphate buffer solution (0.1 mol L^{-1} and pH 8.5); potential scan rate, 100 mV s^{-1}.

further modified with LOx to fabricate an ECL lactate biosensor. The possible ECL reaction mechanism for the proposed ECL lactate biosensor can be simplified using Eqs. (1) and (2). The immobilized LOx at the electrode surface catalyzes the oxidation of lactate to produce hydrogen peroxide (Eq. (1)). The electrochemical oxidation of luminol is catalyzed by nanoZnO-MWCNTs at the electrode surface under sweeping potential in positive direction (oxidation). The produced luminol radical anions are further oxidized by the enzymatically produced hydrogen peroxide to give the excited-state 3-aminophthalate anions that emit light at about 425 nm (Eq. (2)).

$$\text{Lactate} + O_2 \xrightarrow{\text{LOx}} \text{Pyruvate} + H_2O_2 \quad (1)$$

$$\text{Luminol} + H_2O_2 \rightarrow \text{3-aminophetalate} + N_2 + h\nu \quad (425\,\text{nm}) \quad (2)$$

Fixed volumes of nanoZnO-MWCNTs (2 μL), LOx (5 μL) and Nafion (5 μL) solutions with different concentrations were applied during the course of biosensor fabrication and the effect of their loadings on the ECL signal intensity of the biosensor was investigated in the absence and presence of 10 μmol L^{-1} lactate. The results showed the net ECL signal intensity ($\Delta I_{ECL} = I_{ECL\,(\text{in the presence of lactate})} - I_{ECL\,(\text{in the absence of lactate})}$) increased with increasing the concentration of nanoZnO-MWCNTs and then reached a plateau at a concentration about 1 mg mL^{-1} (Fig. 2A). A similar trend was also observed for LOx loading with a plateau at about 5 U LOx (Fig. 2B). But, the ECL signal intensity passed over a maximum at about 0.5% (v/v) of Nafion with increasing the concentration of Nafion (Fig. 2C). Therefore, 2, 5 and 5 μL of nanoZnO-MWCNTs (1 mg mL^{-1}), LOx (1 U μL^{-1}) and Nafion

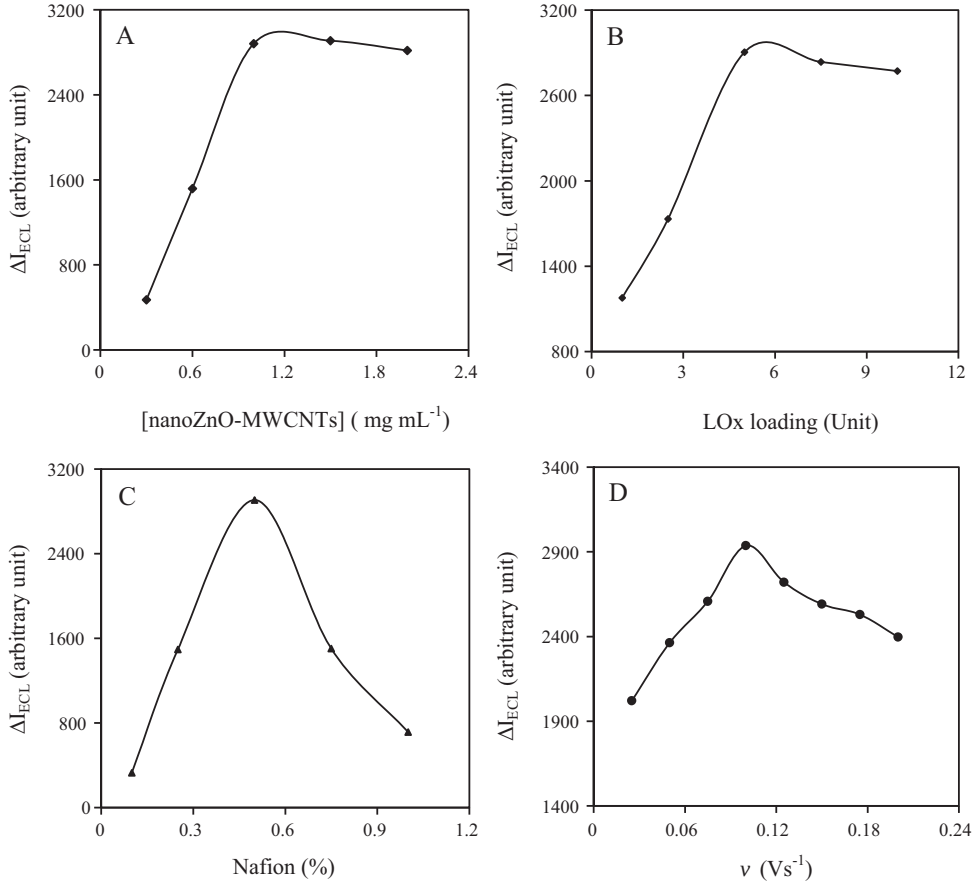

Fig. 2. Effect of (A) nanoZnO-MWCNTs, (B) LOx and (C) Nafion loadings and (D) scan on the net ECL signal intensity ($\Delta I_{ECL} = I_{ECL\,(\text{in the presence of lactate})} - I_{ECL\,(\text{in the absence of lactate})}$) at GCE/nanoZnO-MWCNTs/LOx/Nafion. Conditions: lactate, 10 μmol L^{-1}; luminol, 100 μmol L^{-1}; supporting electrolyte, 0.1 mol L^{-1} phosphate buffer solution (pH of 8.5); potential scan rate (for A, B, and C), 100 mV s^{-1}.

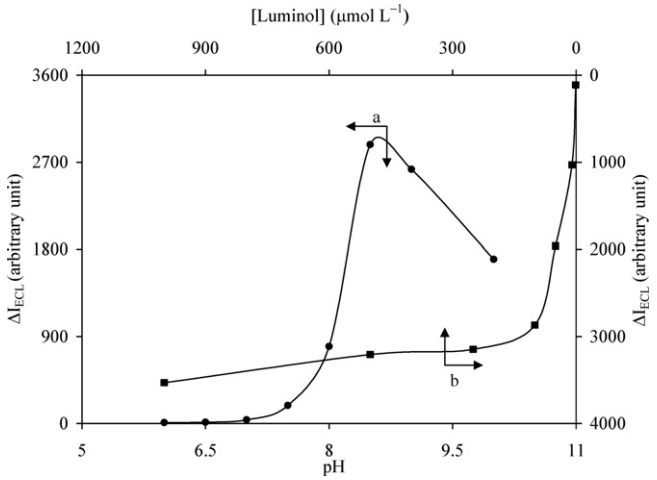

Fig. 3. Effect of pH (a) and luminol concentration (b) on the net ECL signal intensity ($\Delta I_{ECL} = I_{ECL\ (in\ the\ presence\ of\ lactate)} - I_{ECL\ (in\ the\ absence\ of\ lactate)}$) at GCE/nanoZnO-MWCNTs/LOx/Nafion. Conditions: lactate, 10 μmol L^{-1}; luminol, 100 μmol L^{-1} (for a); supporting electrolyte, 0.1 mol L^{-1} phosphate buffer solution (pH of 8.5 (for b)); potential scan rate, 100 mV s^{-1}.

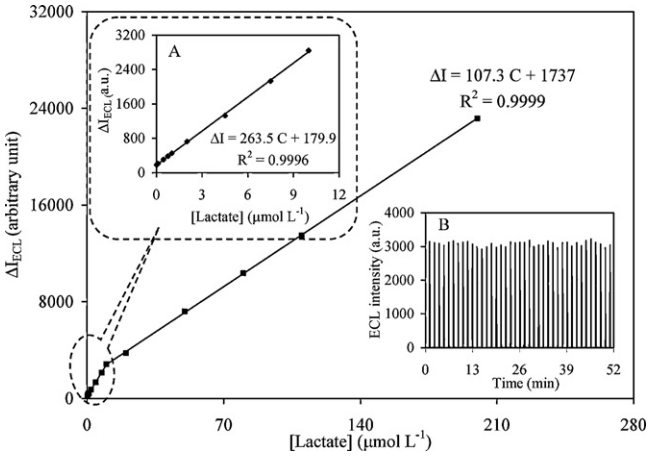

Fig. 4. Typical calibration curve of the net ECL signal intensity (ΔI_{ECL}) versus concentration of lactate (the regression equation is for lactate in the concentration range between 10 and 200 μmol L^{-1}). Inset: (A) calibration curve and regression equation for lactate in the concentration range between 0.01 and 10 μmol L^{-1}. (B) The successively cyclic ECL responses of the biosensor towards 10 μmol L^{-1} lactate. Conditions: luminol, 100 μmol L^{-1}; supporting electrolyte, phosphate buffer solution (0.1 mol L^{-1} and pH 8.5); potential scan rate, 100 mV s^{-1}.

(0.5%) solutions were used for the biosensor fabrication. Also, the effect of potential scan rate (v) on the ΔI_{ECL} showed that the ECL signal intensity passed over a maximum at about 100 mV s^{-1} with increasing v (Fig. 2D). So, a scan rate of 100 mV s^{-1} was selected for further experiments.

Fig. 3 shows the effect of pH and luminol concentration on the net ECL signal intensity of the biosensor in the absence and presence of 10 μmol L^{-1} lactate. As shown in Fig. 3a, ΔI_{ECL} increased with increasing the pH of PBS (0.1 mol L^{-1}) and reached a maximum at a pH about 8.5, then decreased. The decrease of ECL intensity at pH more than 8.5 was attributed to the decrease of LOx activity. Also, it was found that ΔI_{ECL} of the biosensor increased with an increase in the concentration of luminol from 1 to 100 μmol L^{-1}. Further increase in the concentration of luminol (up to 1000 μmol L^{-1}) did not cause more enhancements on the net ECL signal intensity of the biosensor (Fig. 3b). Therefore, PBS (0.1 mol L^{-1}) with the pH of 8.5 and luminol with the concentration of 100 μmol L^{-1} were used for further experiments.

Fig. 4 shows typical calibration plot obtained for lactate using proposed ECL lactate biosensor under optimum experimental conditions. Two linear dynamic ranges of 0.01–10 μmol L^{-1} (Fig. 4, inset A) and 10–200 μmol L^{-1} were obtained for lactate with the correlation coefficient better than 0.9996. The detection limit (S/N = 3) was 4 nmol L^{-1} lactate. The relative standard deviation for the repetitive measurements (n = 6) of 10 μmol L^{-1} lactate was 1.5% (Fig. 4, inset B). The fabrication reproducibility for five biosensors prepared and used in different days was 7.4%. The ECL responses of the biosensor towards 10 μmol L^{-1} lactate were monitored every day over a week to evaluate its operational stability. It was found that the response of the ECL lactate biosensor gradually decreased to almost 80% of its initial value after one week. The biosensor was kept at 4 °C in PBS (0.1 mol L^{-1}, pH 7.4) between experiments. The analytical features of some reported luminol based ECL lactate biosensors using modified electrodes with different modification strategies are summarized in Table 1 and compared with those obtained in this study using GCE/nanoZnO-MWCNTs/LOx/Nafion.

The effects of the presence of potential interfering biological compounds such as glucose, uric acid, ascorbic acid and L-cysteine were investigated on the ECL signal intensity of the biosensor towards 10 μmol L^{-1} lactate. The normal physiological concentrations of ascorbic acid, uric acid and L-cysteine in normal human plasma blood are less than the concentration of lactate. Ascorbic acid [23], uric acid [43] and L-cysteine [44] can interfere by reducing the enzymatically produced H_2O_2 generated from lactate. Additionally, the passivation effects of the species which are produced by electrochemical oxidation on of many electroactive organic substances such as ascorbic acid, uric acid and L-cysteine and adsorbed at the electrode surface can often foul the electrode and reduce the electrode sensitivity [45]. The results showed no interference from uric acid, ascorbic acid and L-cysteine at the concentration about 10 μmol L^{-1}. Also, no interference was observed for glucose at the concentration about 2 mmol L^{-1}. Ascorbic acid, uric acid and L-cysteine at the concentration about 25 μmol L^{-1} decreased the ECL signal intensity of 10 μmol L^{-1} lactate for 13, 18 and 37%, respectively. Glucose at the concentration about 5 mM increased the ECL signal intensity of the biosensor for 8%. The selectivity of the

Table 1
Analytical parameters reported for some luminol based ECL lactate biosensors.

Modified electrodes	LDR (μmol L^{-1})	DL (μmol L^{-1})	pH	Real samples	Detector	Refs.
GCE/polyamide membrane	0.15 to 300[a]	0.15[a]	8.5	Whey and Human serum	PMT	[28]
GCE/DEAE-Sepharose	2 to 200	2	8.5	Human serum	CCD	[26]
GCF/PVA-SbQ	2 to 200	2		Human serum	CCD	[25]
SPGE microarrays/PVA-SbQ	1 to 1000	3	8.5	nr	CCD	[24]
SPGE/BSA-Methocel	8 to 200	2.4	9	nr	PD	[22]
SPGE/BSA-Methocel	10 to 500	5	9	Saliva	PMT	[23]
GCE/nanoZnO-MWCNTs/Nafion	0.01 to 10 10 to 200	0.004	8.5	Human plasma	PMT	This work

LDR, linear dynamic range; DL, detection limit; nr, not reported; BSA, bovine serum albumin; DEAE, diethylaminoethyl; PVA-SbQ, poly(vinyl alcohol) bearing styrylpyridinium groups; GCE, glassy carbon electrode; GCF, glassy carbon foil; SPGE, screen printed graphite electrode; PMT, photomultiplier tube; CCD, charge couple device; PD, photodiode.
[a] nmol.

Table 2
Results of analysis of lactate in human blood plasma samples using proposed ECL lactate biosensor.

Sample	Added (μmol L^{-1})	Found[a] (mmol L^{-1})	Reference value[b] (mmol L^{-1})	Recovery (%)	RSD (n = 3) (%)
Human blood plasma	0	1.10	1.12	98.2	1.92
	10.0	21.1[c]	–	101.2	
	20.0	31.5[c]	–	103.0	
	50.0	61.9[c]	–	102.0	
Human blood plasma	0	1.25	1.23	101.6	2.68
	10.0	22.7[c]	–	103.0	
	20.0	32.6[c]	–	101.0	
	50.0	62.0[c]	–	99.2	
Human blood plasma	0	0.74	0.72	102.8	3.12
Human blood plasma	0	0.59	0.61	96.7	2.28
Human blood plasma	0	0.52	0.51	102.0	1.69
Human blood plasma	0	1.47	1.48	99.3	3.45
Human blood plasma	0	0.61	0.60	101.7	3.68
Human blood plasma	0	0.72	0.73	98.6	2.14
Human blood plasma	0	0.50	0.51	98.0	2.48
Human blood plasma	0	1.50	1.49	100.7	1.87

[a] Calculated value considering dilution factor (101 times).
[b] Determined by hospital; RSD, relative standard deviation.
[c] μmol L^{-1}.

enzymatic reaction justifies the result of lactate determination in the presence of high concentration of glucose (200 times).

The applicability of the proposed ECL biosensor for real sample analysis was assessed by the determination of lactate concentration in human blood plasma samples utilizing the standard addition method. 30 μL of the human blood plasma sample was mixed with 3 mL solution containing PBS (0.1 mol L^{-1} and pH 8.5), luminol (100 μmol L^{-1}) and certain amount of lactate (0, 10, 20 and 50 μmol L^{-1}) and analyzed using the proposed ECL biosensor. The concentrations of lactate in human blood plasma samples were determined and compared with that determined in local hospital. Recovery for the each spiked sample was calculated by comparing the results obtained in the absence and presence of certain amount of lactate. The results are shown in Table 2.

4. Conclusions

Decoration of ZnO nanoparticles on the surface of MWCNTs produced a nano-hybrid material with an efficient electrical network through direct binding of ZnO nanoparticles with the MWCNTs and with more active sites for the catalytic redox reactions of luminol and luminol–H_2O_2. The excellent catalytic activity of nanoZnO-MWCNTs modified GCE towards luminol–H_2O_2 ECL reaction was allowed to develop a novel lactate ECL biosensor with improved analytical performance towards lactate detection.

Acknowledgments

The authors acknowledge the Institute for Advanced Studies in Basic Science (IASBS, grant number G2011IASBS119) for financial support.

References

[1] N. Nikolaus, B. Strehlitz, Microchim. Acta 160 (2008) 15.
[2] M. Wojtczak, A. Antczak, M. Przybyt, Food Addit. Contam. 27 (2010) 817.
[3] G. Cevasco, A.M. Piaogonektek, C. Scapolla, S. Thea, J. Chromatogr. A 1218 (2011) 787.
[4] B.M. Gurupadayya, B.V. Vijaya, Y.N. Manohara, R.D.V. Prasad, S. Hemalatha, Indian Drugs 45 (2008) 193.
[5] D.J. Herrera, K. Morris, C. Johnston, P. Griffiths, Ann. Clin. Biochem. 45 (2008) 177.
[6] C.-L. Lin, C.-L. Shih, L.-K. Chau, Anal. Chem. 79 (2007) 3757.
[7] T.B. Goriushkina, A.P. Soldatkin, S.V. Dzyadevych, J. Agric. Food Chem. 57 (2009) 6528.
[8] R. Zaydan, M. Dion, M. Boujtita, J. Agric. Food Chem. 52 (2003) 8.
[9] K. Kriz, L. Kraft, M. Krook, D. Kriz, J. Agric. Food Chem. 50 (2002) 3419.
[10] E.I. Yashina, A.V. Borisova, E.E. Karyakina, O.I. Shchegolikhina, M.Y. Vagin, D.A. Sakharov, A.G. Tonevitsky, A.A. Karyakin, Anal. Chem. 82 (2010) 1601.
[11] M.R. Romero, F. Ahumada, F. Garay, A.M. Baruzzi, Anal. Chem. 82 (2010) 5568.
[12] V.P. Zanini, B.L. de Mishima, P. Labbe, V. Solis, Electroanalysis 22 (2010) 946.
[13] M. Piano, S. Serban, R. Pittson, G.A. Drago, J.P. Hart, Talanta 82 (2010) 34.
[14] V.P. Zanini, B. Lopez de Mishima, V. Solis, Sens. Actuators B: Chem. 155 (2011) 75.
[15] M.R. Majidi, S. Gholizadeh, M.S. Hejazib, J. Iranian Chem. Soc. 8 (2011) 59.
[16] A.C. Pereira, M.R. Aguiar, A. Kisner, D.V. Macedo, L.T. Kubota, Sens. Actuators B: Chem. 124 (2007) 269.
[17] S.G. Hazelton, X.W. Zheng, J.X. Zhao, D.T. Pierce, Sensors 8 (2008) 5942.
[18] P. Bertoncello, R.J. Forster, Biosens. Bioelectron. 24 (2009) 3191.
[19] H. Dai, Y.W. Chi, X.P. Wu, Y.M. Wang, M.D. Wei, G.N. Chen, Biosens. Bioelectron. 25 (2010) 1414.
[20] X. Cai, J.L. Yan, H.H. Chu, M.S. Wu, Y.F. Tu, Sens. Actuators B: Chem. 143 (2010) 655.
[21] Z.Y. Lin, J.H. Chen, G.N. Chen, Electrochim. Acta 53 (2008) 2396.
[22] A. Martinez-Olmos, J. Ballesta-Claver, A.J. Palma, M.D. Valencia-Miron, L.F. Capitan-Vallvey, Sensors 9 (2009) 7694.
[23] J.B. Claver, M.C.V. Miron, L.F. Capitan-Vallvey, Analyst 134 (2009) 1423.
[24] B.P. Corgier, C.A. Marquette, L.J. Blum, Anal. Chim. Acta 538 (2005) 1.
[25] C.A. Marquette, A. Degiuli, L.J. Blum, Biosens. Bioelectron. 19 (2003) 433.
[26] C.A. Marquette, L.J. Blum, Sens. Actuators B: Chem. 90 (2003) 112.
[27] C.A. Marquette, B.D. Leca, L.J. Blum, Luminescence 16 (2001) 159.
[28] C.A. Marquette, L.J. Blum, Anal. Chim. Acta 381 (1999) 1.
[29] B. Haghighi, S. Bozorgzadeh, L. Gorton, Sens. Actuators B: Chem. 155 (2011) 577.
[30] Z.G. Xiong, J.P. Li, L. Tang, Z.Q. Cheng, Chin. J. Anal. Chem. 38 (2010) 800.
[31] X.M. Chen, Z.M. Cai, Z.J. Lin, T.T. Jia, H.Z. Liu, Y.Q. Jiang, X. Chen, Biosens. Bioelectron. 24 (2009) 3475.
[32] X.Q. Liu, W.X. Niu, H.J. Li, S. Han, L.Z. Hu, G.B. Xu, Electrochem. Commun. 10 (2008) 1250.
[33] Z. Lin, J. Chen, Y. Chi, B. Qui, J. Lin, G. Chen, Electrochim. Acta 53 (2008) 6464.
[34] Y. Lin, K.A. Watson, M.J. Fallbach, S. Ghose, J.G. Smith, D.M. Delozier, W. Cao, R.E. Crooks, J.W. Connell, ACS Nano 3 (2009) 871.
[35] V. Georgakilas, D. Gournis, V. Tzitzios, L. Pasquato, D.M. Guldi, M. Prato, J. Mater. Chem. 17 (2007) 2679.
[36] J.A. Wang, M.Z. Xu, R.R. Zhao, G.N. Chen, Analyst 135 (2010) 1992.
[37] P.R. Solanki, A. Kaushik, A.A. Ansari, B.D. Malhotra, Appl. Phys. Lett. 94 (2009) 143901.
[38] R. Khan, A. Kaushik, P.R. Solanki, A.A. Ansari, M.K. Pandey, B.D. Malhotra, Anal. Chim. Acta 616 (2008) 207.
[39] H.P. Bai, X.X. Lu, G.M. Yang, Y.H. Yang, Chin. Chem. Lett. 19 (2008) 314.
[40] L. Feng, T. Yifeng, J. Instrum. Anal. 25 (z1) (2006) 11.
[41] H.H. Chu, W.Y. Guo, J.W. Di, Y. Wu, Y.F. Tu, Electroanalysis 21 (2009) 1630.
[42] S.-F. Li, X.-M. Zhang, W.-X. Du, Y.-H. Ni, X.-W. Wei, J. Phys. Chem. C 113 (2009) 1046.
[43] J.K. Fleming, R.H.S. Gadsden, I. Kabbani, Clin. Biochem. 21 (1988) 27.
[44] L. Zhang, R. Yuan, Y. Chai, X. Li, Anal. Chim. Acta 596 (2007) 99.
[45] J. Huang, Y. Liu, H. Hou, T. You, Biosens. Bioelectron. 24 (2008) 632.