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Short communication

An electrochemiluminescence sensor based on a Ru(bpy)₃²⁺-silica-chitosan/nanogold composite film

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ABSTRACT

Chitosan, a cationic polysaccharide containing amino and hydroxyl groups, was used to fabricate an electrochemiluminescence (ECL) sensor. In the sensor construction, a glassy carbon electrode (GCE) was first coated by a chitosan film which embedded gold nanoparticles, and then the film was modified by introducing carboxyl groups on the surface, which were used to immobilize tris(2,2'-bipyridyl)ruthenium(II) doped amino-functional silica nanoparticles (NH₂-RuSiNPs) through amido links. The successful modification was confirmed by scanning electronic microscopy and cyclic voltammetry. A binding model between the chitosan/nanogold composite film and NH₂-RuSiNPs was also proposed, in which the amido link was the dominant bonding, accompanied with hydrogen bond interaction. ECL studies revealed that the sensor had very good response to different concentrations of 2-(dibutylamino) ethanol. This sensor was also applied in methamphetamine determination.

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1. Introduction

Electrochemiluminescence (ECL) is a light-emitting phenomenon of excited species which are generated at an electrode surface using electrochemical methods [1]. It is a very popular technique due to its high sensitivity, low back-ground signal and good temporal and spatial control. For decades, studies on this field mainly involve the following aspects: (a) synthesis of novel ECL luminophores at different emission wavelengths, such as quantum dots [2] and metal clusters [3–5]; (b) immobilization of ECL luminophores on an electrode surface to generate stable ECL signals; (c) investigation of ECL mechanisms [6], and (d) improvement of ECL applications [7,8].

The immobilization of ECL luminophores is essential in ECL sensor construction. Generally, there are three main methods for the immobilization of ECL luminophores: (a) ECL luminophores are adsorbed on an electrode surface through hydrophobic–hydrophilic interaction [9] or electrostatic interaction [10]. However, these films are sometimes unstable, easily broken and washed off; (b) ECL luminophores are entrapped in a modified film directly [11] or through nanoparticles carriers [12,13]. This approach is available to immobilize ECL luminophores firmly but restricts the diffusion of reagents through the film;

(c) ECL luminophores are covalently bonded to electrode surfaces [14,15], which provides more stable immobilization. This approach is able to modify an electrode surface layer by layer and better expose ECL luminophores to electrolytes and analytes. Glassy carbon electrodes (GCE) are generally used in ECL. However, since the clean surface of the bare glassy carbon is difficult to link various luminophores, a material as a media layer is necessary to functionalize the electrode surface.

Chitosan is a good film-forming substance which is deacetylated from chitins and rich in amino and hydroxyl groups. It is soluble when the pH is lower than 6.3 because of the protonation of the amino groups, but insoluble in high pH environments. Due to its pH dependent solubility, excellent film-forming ability and chemical modifiable property [16], chitosan has been considered as a promising candidate for fabricating ECL sensors or biosensors [12,13,17–19]. However, in these reports, the amino groups of chitosan limited its application with carboxyl functional ECL luminophores. In this study, chitosan/nanogold composite film was casted on an GCE surface, on which chitosan was derived to contain carboxyl groups and able to immobilize tris(2,2'-bipyridyl)ruthenium(II) (Ru(bpy)₃²⁺) doped amino-functional silica nanoparticles (NH₂-RuSiNPs) on the electrode. The GCE modified with NH₂-RuSiNPs was characterized by scanning electron microscopy (SEM). The modification procedure was monitored by cyclic voltammetry (CV). The binding model between chitosan/nanogold composite film and NH₂-RuSiNPs was also proposed. Using potential step technology, the ECL sensing responses showed good

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relative to different concentrations of 2-(dibutylamino) ethanol (DBAE). Moreover, this sensor was applied in the determination of methamphetamine (METH) samples in drug investigation cases.

2. Experimental

2.1. Chemicals

Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate [Ru(bpy)₃Cl₂·6H₂O], Triton X-100 (TX-100), tetraethyl orthosilicate (TEOS), 3-aminopropyltrimethoxysilane (APTMS), gold(III) chloride trihydrate, 2-(dibutylamino) ethanol (DBAE), chitosan (from crab shells, practical grade), fluorescamine and *N*-hydroxysuccinimide (NHS) were all purchased from Sigma–Aldrich. *N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC) was purchased from Fluka. Succinic anhydride was purchased from Alfa Aesar. Methamphetamine (METH) samples were provided by Institute of Criminal Science and Technology (Xiamen, China). The standard methamphetamine hydrochloride was from the Bio-product Institute of Chinese Medicine (Beijing, China). All chemicals were used as received. The pure water (18.2 M Ω) for the solution preparation was from a Millipore autopure WR600A system (USA), and was used throughout.

2.2. Apparatus

Electrochemical measurements were performed on a CHI 660B Electrochemical Analyzer (CHI Co., Shanghai, China). A standard three-electrode arrangement was employed with a platinum auxiliary electrode and an Ag/AgCl reference electrode. The working electrode was the modified GCE. ECL experiments were carried out with an IFFM-D FIA Luminescence Analyzer (Xi'an Remax Electronic Science Tech. Co. Ltd., Xi'an, China) combined with an Electrochemical Analyzer. SEM images were obtained using a Hitachi S-4800 (Hitachi, Japan). Fluorescence experiments were performed on an F-4500 fluorescence spectrofluorimeter (Hitachi, Japan), and the slit widths at the excitation and emission used in these experiments both were 5.0 nm. UV/Vis spectra were obtained from a UV 2300 spectrophotometer (Techcomp, China). PH values of solutions were measured using a pH510 meter (Eutech, Singapore).

2.3. Synthesis of Ru(bpy)₃²⁺ doped amino functional silica nanoparticles

NH₂-RuSiNPs were synthesized according to the water-in-oil microemulsion method [20]. The reaction in microemulsion was initiated by NH₃·H₂O. After 23 h stirring, 25 μ L APTMS was added to the microemulsion. One hour later, acetone was added sufficiently to precipitate NH₂-RuSiNPs, followed by washing with acetone, ethanol, and water several times.

2.4. Synthesis of gold nanoparticles

Gold nanoparticles (Au-NPs) were synthesized according to previous literature [21]. The product was filtered through a 0.45- μ m membrane and stored in a refrigerator at 4 °C before use. The concentration of Au-NPs was 1.0 nmol L⁻¹, estimated by their UV/vis absorption based on an extinction coefficient of 2.7×10^8 M⁻¹ cm⁻¹ at $\lambda = 520$ nm.

2.5. Modification of electrodes

Chitosan stock solution was prepared by dissolving 50 mg chitosan in a mixed solvent of 10 μ L acetic acid and 5 mL water, stirred

overnight. A GCE (diameter, 5 mm) was polished with 1.0, 0.3 and 0.05 μ m α -Al₂O₃, rinsed and sonicated with water successively after each polishing step, and finally dried in a nitrogen flow. 5 μ L mixtures containing equal volume of Au-NPs and chitosan stock solutions were coated on the polished GCE surface. The electrode was dried overnight in a refrigerator. The electrode was treated with 5% ethylamine phosphate buffer solution (0.05 mol L⁻¹ PBS, pH 7.5) for 0.5 h. Then, it was placed in 0.1 mol L⁻¹ succinic anhydride acetone solution for 1.5 h, washed with acetone and PBS several times, and then immersed into NH₂-RuSiNPs PBS containing 5 mg mL⁻¹ NHS and 5 mg mL⁻¹ EDC for 1.5 h. After washing with PBS, the electrode was blocked by 5% ethylamine. Finally the electrode was sufficiently washed with water, dried, and stored in a refrigerator before use.

2.6. ECL observation

A series concentration of DBAE was dissolved in PBS (0.1 mol L⁻¹, pH 7.4). The electrode was placed in the DBAE solution for 3 min. ECL emissions were recorded under potential steps between 0 and +1.3 V vs. Ag/AgCl.

3. Results and discussion

3.1. Synthesis and characterization of NH₂-RuSiNPs

Ru(bpy)₃²⁺ is one of the ruthenium derivatives and has widely used as an ECL luminophore. It can form the excited state Ru(bpy)₃^{2+*} via high-energy electron-transfer reactions and then emit light. NH₂-RuSiNPs are amino-functional silica nanoparticles and rich in Ru(bpy)₃²⁺. There are no ECL signals could be detected without NH₂-RuSiNPs on the electrode surface. So, it is very important to achieve successful Ru(bpy)₃²⁺ doped silica nanoparticles. There are two steps for one-pot synthesis of NH₂-RuSiNPs. Firstly, TEOS was hydrolyzed by ammonia in microemulsion to produce silica nanoparticles which confined Ru(bpy)₃²⁺ in their lattices. Then, APTMS, which is a silane coupling agent containing amino groups, was added to the microemulsion for its further hydrolysis on RuSiNPs surfaces to form an amino functional shell. The as-prepared NH₂-RuSiNPs were observed uniform and about 60 nm in diameter from SEM (Fig. S1).

Amino groups on NH₂-RuSiNPs surfaces were essential for their further application when grafting to a chitosan composite film. The successful modification of amino groups on NH₂-RuSiNPs could be determined through their reaction with the fluorescamine in ethanol, which resulted in an increase of fluorescence intensity at 498 nm (Fig. S2A) [22]. Moreover, instead of a sharp peak, this fluorescence peak was found to be relatively broad, which was due to the contribution of the broad absorption of Ru(bpy)₃²⁺ at around 480 nm (Fig. S2B).

3.2. ECL sensor fabrication

The fabricating procedure for an ECL sensor is illustrated in Fig. 1. The polished electrode was first coated by a chitosan/nanogold composite film (Fig. 1A). In this composite film, Au-NPs played an important role, which not only bonded with amino groups of chitosan and increased the strength of the chitosan film by cross connecting the linear polymer, but also improved the composite film conductivity. To avoid the unstable ECL signals generated by the adsorption of NH₂-RuSiNPs on Au-NPs, the electrode was pre-treated with ethylamine to block the unbonded sites of Au-NPs. Then, the electrode was immersed in succinic anhydride solution to introduce carboxyl groups on chitosan (Fig. 1B). With the assistance of EDC/NHS catalysts [23], NH₂-RuSiNPs were covalently

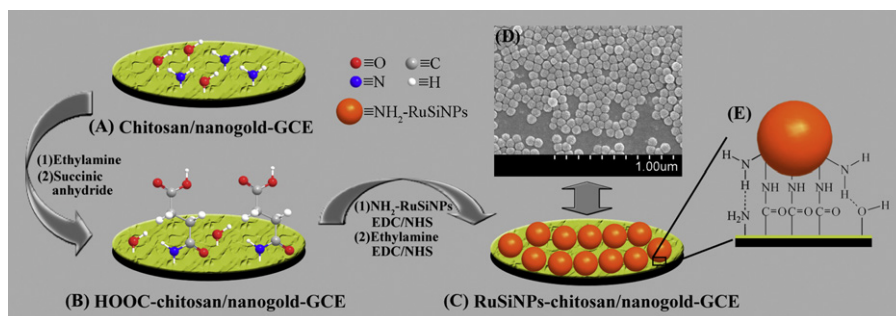


Fig. 1. Schematic diagram of the fabrication of the ECL sensor and the SEM image of NH_2 -RuSiNPs modified electrode.

bonded to the carboxyl groups on chitosan; and then the residual carboxyl groups were blocked by ethylamine (Fig. 1C). The SEM image confirmed that the NH_2 -RuSiNPs were successfully loaded on the chitosan/nanogold composite film (Fig. 1D).

There are three types of interactions between NH_2 -RuSiNPs and chitosan/nanogold composite film: (a) hydrogen bonds between the amino groups of the NH_2 -RuSiNPs and the hydroxyl or amino groups of the composite film; (b) electrostatic interactions between the amino groups of the NH_2 -RuSiNPs and the carboxyl groups of the composite film; (c) amido links formed through a condensation reaction between the amino groups of the NH_2 -RuSiNPs and the carboxyl groups of the composite film in the presence of EDC/NHS catalysts. The amido links fixed NH_2 -RuSiNPs on the composite film more firmly than the other interactions, which was confirmed by the strongest ECL intensity for amido links (Fig. S3). The hydrogen bond and electrostatic interactions were unstable and easily broken at high potential, resulted in lower ECL intensity. In addition, the electrostatic interaction could be minimized by blocking the residual carboxyl groups with ethylamine; while the hydrogen bond interaction could exist due to the steric hindrance and long-distance interaction. In the modification, amido links were the dominant interaction between the NH_2 -RuSiNPs and the chitosan/nanogold composite film, accompanied with hydrogen bond interaction (Fig. 1E).

In the study, CV was used to monitor the modifying procedure according to various electrochemical properties of the electrode surface in each step. On an electrode surface, a positively charged film would attract highly charged redox ferricyanide($3-/4-$) ions, but a negatively charged film would repulse them, which results in the different current intensities. As shown in Fig. 2, the current intensity from the chitosan/nanogold modified GCE was higher than that obtained from a bare GCE. The alkaline amino groups of the chitosan/nanogold composite film were weakly positively charged in tris(hydroxymethyl)aminomethane-HCl (Tris-HCl) buffer solution (50 mmol L^{-1} , pH 7.4); and this positively charged film attracted ferricyanide($3-/4-$) ions with increasing the current intensity. Correspondingly, the current intensity decreased after the introduction of carboxyl groups on the film because ferricyanide($3-/4-$) was repulsed by electronegative carboxyl groups (Fig. 2c). In the presence of EDC/NHS catalysts, carboxyl-chitosan/nanogold film bonded with NH_2 -RuSiNPs [23], which increased the current intensity (Fig. 2d). On one hand, the consumption of carboxyl groups reduced the film electronegativity. On the other hand, NH_2 -RuSiNPs, which were rich in amino groups and positively charged, were helpful for the attraction of ferricyanide($3-/4-$). In the last step, ethylamine was used to block the residual carboxyl groups, and reduce the physical adsorption of NH_2 -RuSiNPs. The loss of carboxyl groups increased the current intensity; however, the reduction of the physical adsorption of NH_2 -RuSiNPs caused

the current decrease. Thus, the final result only showed a slight decrease of the current intensity (Fig. 2e).

3.3. ECL behavior

Potential step, a useful approach in ECL studies, provides higher ECL sensitivity than that obtained by CV [14]. On one hand, ECL signals were generated in a short time after potential stepping, and then decayed due to the depletion of coreactants around the electrode surface. A tenth of one second was sufficient to generate the most intense ECL peak (Fig. S4) and 10 s was enough in quiet time for the next ECL generation. The short time for excitation resulted less consumption of coreactants and faster environment restoration around the electrode surface. On the other hand, the potential step approach resulted higher sensitivity than CV, because the simultaneous oxidation of surface-confined $\text{Ru}(\text{bpy})_3^{2+}$ and coreactants in the solution could maximize the formation of the excited state $\text{Ru}(\text{bpy})_3^{2+*}$ [14].

In the potential step application, the applied potential for ECL generation is an important parameter. Generally, it should be positive enough to oxidize both $\text{Ru}(\text{bpy})_3^{2+}$ ($E_p +1.1 \text{ V vs. Ag/AgCl}$) [6] and DBAE ($E_p +0.8 \text{ V vs. Ag/AgCl}$) [24] without damaging the chitosan/nanogold composite film or producing undesired species. Our experimental results revealed the optimal potential at $+1.3 \text{ V vs. Ag/AgCl}$ (Fig. S5). The 0.2 V more positive potential than the reversible redox potential of $\text{Ru}(\text{bpy})_3^{2+}$ in solution was due to the electronic resistance of the chitosan/nanogold composite film. It was observed that this sensor had lower sensitivity when the

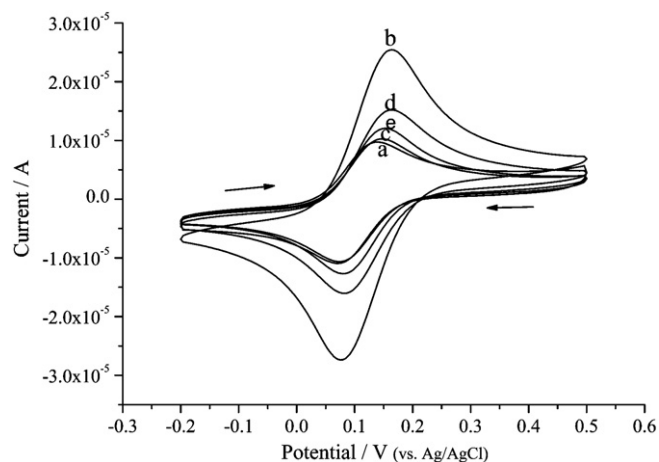


Fig. 2. Voltammetric behavior of 1 mmol L^{-1} ferricyanide($3-/4-$) in 50 mmol L^{-1} Tris-HCl buffer (pH 7.4) at a bare GCE (a), a chitosan/nanogold-GCE (b), a carboxyl-chitosan/nanogold-GCE (c), a RuSiNPs-chitosan/nanogold-GCE without (d) and with (e) ethylamine blocked. Scan rate, 100 mV s^{-1} .

Table 1
ECL determination results and recoveries of METH samples.

Sample ^a	Found (10^{-5} mol L ⁻¹)	Content (%)	RSD (%)	Added (10^{-5} mol L ⁻¹)	Found (10^{-5} mol L ⁻¹)	Recovery (%)
1	5.12 ± 0.20	94.2 ± 3.6	3.9	5.0	10.17 ± 0.39	101.0 ± 7.8
2	5.38 ± 0.25	90.7 ± 4.2	4.6	5.0	10.22 ± 0.43	96.8 ± 8.6
3	5.19 ± 0.23	87.1 ± 3.8	4.4	5.0	10.13 ± 0.46	98.8 ± 9.2

^aSamples were provided by the Institute of Criminal Science and Technology, Xiamen.

applied potential was beyond +1.3 V. This phenomenon could be related to the oxygen generation by oxidizing water at the higher potential, which consumed DBAE intermediate radicals that needed for the generation of the Ru(bpy)₃^{2+*} species [25].

As mentioned above, the amount of Au-NPs in composite film was also an important factor for the performance of an ECL sensor. The results illustrated that the optimal amount of Au-NPs for the best sensitivity of ECL sensor was 0.25 nmol L⁻¹ in chitosan/nanogold mixtures (Fig. S6). Au-NPs played a role as conductor which could enhance the ECL intensity. However, excess Au-NPs would exchange their citrate ligands with amino and hydroxyl groups of chitosan molecules, which may result in less carboxyl groups being introduced to chitosan and less NH₂-RuSiNPs loading.

Under optimal experimental conditions, the calibration curve for ECL intensity responding to the DBAE concentration was plotted using the ECL sensor. A good linearity was presented in the concentration range of DBAE from 2.5×10^{-5} to 2.5×10^{-3} mol L⁻¹ and the correlation coefficient was 0.9930. The detection limit (S/N=3) was 1.2×10^{-7} mol L⁻¹. Under a continuous eight potential steps, the relative standard deviation of ECL intensity responding to 1.0 mmol L⁻¹ DBAE in 0.1 mol L⁻¹ PBS (pH 7.4) was 4.9% (Fig. 3, insert).

This sensor was applied in the determination of METH samples to further verify the extensive applications. A calibration curve for METH was constructed in the range from 2.0×10^{-6} to 2.0×10^{-4} mol L⁻¹. The detection limit was 5.0×10^{-7} mol L⁻¹, which was comparable to previous reports: 2.6×10^{-8} mol L⁻¹ [26], 2.0×10^{-7} mol L⁻¹ [15,27] and 3.3×10^{-8} mol L⁻¹ [28]. METH samples in different cases were tested using this ECL sensor. The results are listed in Table 1. The METH content ranging from 87.1% to 94.2% indicated that the captured METH samples were in high purity. The recoveries of this method, between 96.8% and 101.0%, revealed that

in these samples the ECL determination for METH was not significantly interfered by the coexisting substances, such as precursors and by-products. The good relative standard deviations (RSD) were in the range from 3.9% to 4.6%. This ECL method could be applied in drug investigation cases.

4. Conclusions

In summary, we managed to introduce carboxyl groups to chitosan/nanogold composite film on a GCE for bonding with NH₂-RuSiNPs to fabricate an ECL sensor. Au-NPs were used to improve the inductivity and stability of the composite film. It was proposed that NH₂-RuSiNPs were bonded to the composite film based on the amido link as well as hydrogen bond interaction. The potential step method was applied for ECL generation to detect DBAE and methamphetamine samples. This method extends the bonding ability of chitosan and promises a good way for bonding in many fields.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.talanta.2012.03.046>.

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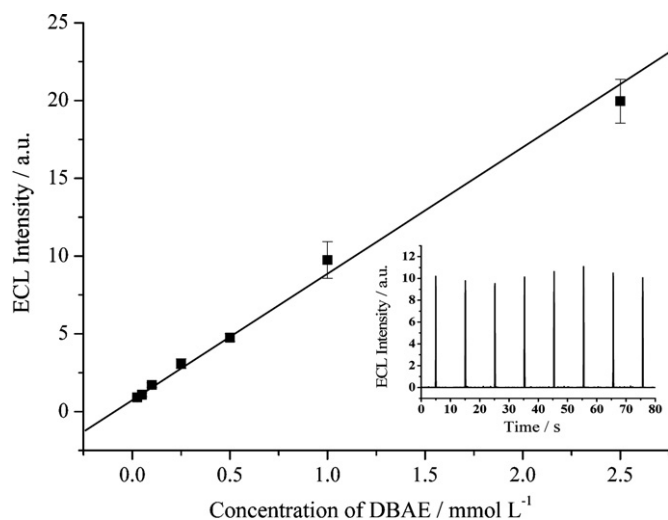


Fig. 3. Calibration curve of ECL intensity and DBAE concentration. The inset shows ECL emission of multi-potential steps for 8 times in 0.1 mol L⁻¹ PBS containing 1.0 mmol L⁻¹ DBAE, pH 7.4.

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