



## Electrochemistry and electrochemiluminescence for the host–guest system laponite–tris(2,2′-bipyridyl)ruthenium(II)

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### ABSTRACT

The cationic luminescence probe, tris(2,2′-bipyridyl)ruthenium(II) complex ( $[\text{Ru}(\text{bpy})_3]^{2+}$ ), was incorporated into laponite-modified glassy carbon electrode (GCE) via two strategies, namely, the adsorption and intercalation methods. These two incorporation methods resulted in different microenvironment for the immobilized  $[\text{Ru}(\text{bpy})_3]^{2+}$  within laponite as well as the different host–guest and guest–guest interactions. Herein, cyclic voltammetry and electrochemiluminescence (ECL) were innovatively performed to monitor the interactions. Tripropylamine (TPA) was used as coreactant in the electrochemical and ECL system.

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### 1. Introduction

Lamellar clay materials own specific physiochemical properties such as high chemical stability, good adsorption property due to its appreciable surface area, special structural feature, and unusual intercalation property [1]. Therefore, layered clays are intriguing matrix for the fabrication of electrochemical [2–4] and ECL sensors [5].

The incorporation of guest into the host may induce the changes in optical, electronic, and magnetic properties of the guest [6]. To obtain the well-developed electrochemical or ECL sensors and to dominate the properties of the immobilized compounds, host–guest and guest–guest interactions should be precisely controlled. These interactions can be generally characterized by variety of instrumental analysis techniques including, nuclear magnetic resonance (NMR) spectroscopy, electron paramagnetic spectroscopy (EPR), photoluminescence spectroscopy, etc. [6–8]. The main disadvantages of these methods are the complexity and high cost of the equipments needed and the high level of operator's skill required.

Electrochemistry and ECL allow the available and sensitive detection without expensive instruments [9,10]. In this work, we

proposed a simple and sensitive way to monitor the effect of host–guest and guest–guest interactions. The synthetic lamellar clay, laponite and the cationic luminescence probe,  $[\text{Ru}(\text{bpy})_3]^{2+}$ , were selected as model host–guest system in this preliminary study. Laponite ( $\text{Na}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]$ ) is similar to natural hectorite of the smectic group with high cation exchange ability [11].  $[\text{Ru}(\text{bpy})_3]^{2+}$  is used most extensively because of its unique combination of chemical stability, long excited-state lifetime, redox properties, and so on [9,12]. To investigate the electrochemical and ECL behaviors of the immobilized  $[\text{Ru}(\text{bpy})_3]^{2+}$ , TPA was used as representative coreactant, since the  $[\text{Ru}(\text{bpy})_3]^{2+}$ –TPA system has been fully investigated and gives a stronger ECL efficiency [13,14].

### 2. Experimental

#### 2.1. Materials

Tris(2,2′-bipyridyl)dichlororuthenium hexahydrate and TPA were from Aldrich and were used as received. Laponite (monovalent cation exchange capacity:  $\text{CEC} = 0.74 \text{ mmol g}^{-1}$ ) was purchased from Rockwood Specialties Inc.

#### 2.2. Apparatus

Electrochemical measurements were performed on CHI760C electrochemical workstation (CH Instruments, USA) with a

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three-electrode system comprised of a platinum wire as auxiliary electrode, an saturated electrode (SCE) as reference electrode, and the glassy carbon disk electrode (GCE) with a diameter of 3 mm as working electrode. ECL was conducted by a homemade ECL system, including the CHI760C electrochemical working station, an quartz glass electrochemical cell (homemade), a model 1P21 photomultiplier tube (PMT) (Beijing, China), a model GD-1 luminometer (Xi'an, China), and a computer. During measurement, the potential was applied to the working electrode via the electrochemical working station and ECL was generated. ECL intensities were measured through the bottom of the quartz glass electrochemical cell, which was placed in front of the PMT biased at  $-600$  V. The output current of the PMT was amplified by the luminometer and was recorded through  $1\text{-k}\Omega$  resistor to the second WE port of the CHI760C with "scan" choice. Static contact angle measurements were performed at room temperature with a sessile drop method using an OCA 40 system (German). UV-vis measurements were carried out by using UV-2550 spectrophotometer (Simadzu Co., Japan).

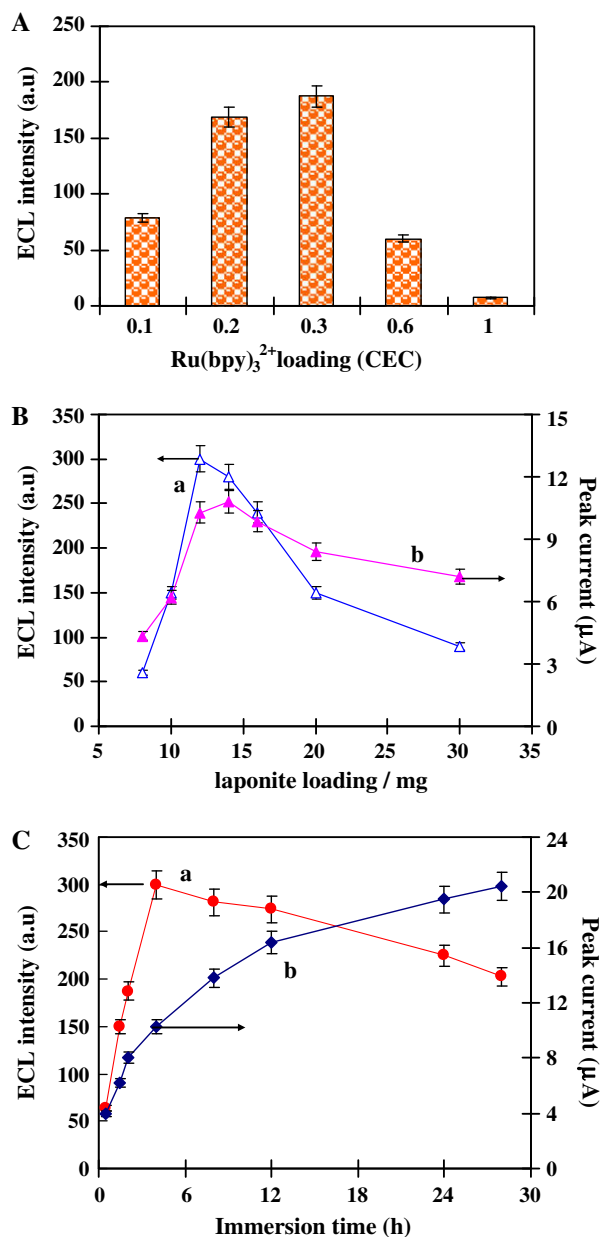
### 2.3. Immobilization of $[\text{Ru}(\text{bpy})_3]^{2+}$ on the surface of GCE

The guest,  $[\text{Ru}(\text{bpy})_3]^{2+}$ , was incorporated into the host laponite-modified GCE by two protocols, namely, adsorption and intercalation methods. The following procedures were performed for the adsorption method: (1) the laponite colloidal suspension ( $2\text{ mg ml}^{-1}$ ) was prepared by dispersing laponite in the deionized water with stirring overnight; (2) a defined amount of laponite colloidal was spread on the surface of GCE and dried in air; (3) the previously prepared laponite-modified GCE was immersed into  $5\text{ mM } [\text{Ru}(\text{bpy})_3]^{2+}$  solution for the controlled time to obtain the desired guest loading. The electrodes as-prepared above were denoted as  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{laponite}/\text{GCE}$ . As for the intercalation method,  $[\text{Ru}(\text{bpy})_3]^{2+}$  should be incorporated into the interlayer space of the laponite nanoparticles initially through facile aqueous exchange. Laponite nanoparticles were dispersed in deionized water containing exact guest quantities. The mixture was stirred for 24 h and the final product was centrifuged and washed several times with deionized water and finally dried in air at room temperature. The obtained  $[\text{Ru}(\text{bpy})_3]^{2+}$ -laponite composite was dispersed into deionized water with the concentration of  $2\text{ mg ml}^{-1}$ . Hybrid suspension ( $6\text{ }\mu\text{l}$ ) was spread on the surface of GCE and dried in air. The electrodes as-prepared above were denoted as  $[\text{Ru}(\text{bpy})_3]^{2+}$ -laponite/GCE.

## 3. Results

### 3.1. Optimization of $[\text{Ru}(\text{bpy})_3]^{2+}$ modified GCE

The content of  $[\text{Ru}(\text{bpy})_3]^{2+}$  intercalated into the interlayer space of the laponite was controlled according to the cation-exchange capability (CEC), from 10% to 100% of CEC. Fig. 1A provides information on the ECL intensity of the  $[\text{Ru}(\text{bpy})_3]^{2+}$ -laponite composite modified GCE with guest loadings. The maximum ECL intensity can be obtained at 30% of the CEC. This optimal guest loading value coincides with that reported by Hagerman et al., for the photoluminescence intensity measurement (28% of the CEC) [7]. However, to obtain the optimal construction of  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{laponite}/\text{GCE}$ , the laponite loading on the surface of GCE and the immersion time of the laponite-modified electrode in the preconcentration step are the two main factors. Thus, in this work, we use electrochemical and ECL measurements to monitor their effects. The results were summarized in Fig. 1B and C. Based on the ECL results, the optimal laponite loading is  $12\text{ }\mu\text{g}$  and the optimal immersion time is 4 h.



**Fig. 1.** (A) Effect of the amount of  $[\text{Ru}(\text{bpy})_3]^{2+}$  incorporated into laponite nanoparticles on ECL intensity. (B) Dependence of ECL intensity (a) and the anodic peak current of the adsorbed  $[\text{Ru}(\text{bpy})_3]^{2+}$  in PBS (b) on the laponite loading; the immersion time in  $5\text{ mM } [\text{Ru}(\text{bpy})_3]^{2+}$  was 4 h. (C) Effect of the immersion time on ECL intensity (a) and the anodic peak current of the adsorbed  $[\text{Ru}(\text{bpy})_3]^{2+}$  in PBS (b) for the laponite-modified GCE into  $5\text{ mM } [\text{Ru}(\text{bpy})_3]^{2+}$ , with  $12\text{ }\mu\text{g}$  laponite loading. ECL intensity was measured for  $1 \times 10^{-5}$  M TPA solution in  $0.1\text{ M}$  PBS at pH 7. The PMT biased at  $600\text{ V}$ .

### 3.2. Electrochemical investigation

The cyclic voltammogram of the  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{laponite}/\text{GCE}$  gave a couple of stable and well-defined redox peaks at scan rate of  $100\text{ mV s}^{-1}$  (curve a in Fig. 2). The anodic peak potential ( $E_{pa}$ ) and cathodic peak potential ( $E_{pc}$ ) are located at  $1.14$  and  $1.05\text{ V}$ , respectively, which is attributed to the redox signal of  $[\text{Ru}(\text{bpy})_3]^{2+/3+}$ . In addition, the CVs of  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{laponite}/\text{GCE}$  display a well-defined peak shape at different scan rates (inset A of Fig. 2). Anodic peak currents vary linearly with the square root of scan rate ( $v^{1/2}$ ) for the scan rates changed from  $10$  to  $500\text{ mV s}^{-1}$  (inset B of Fig. 2), indicating that the redox behavior of the

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