

Tris(2,2'-bipyridyl) Ruthenium(II) Doped Silica Film Modified Indium Tin Oxide Electrode and Its Electrochemiluminescent Properties

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An approach was reported to synthesize silica hybridized ruthenium bipyridyl complex through amidation reaction by covalent attachment of bis(bipyridyl)-4,4'-dicarboxy-2,2'-bipyridyl-ruthenium to (3-aminopropyl)-triethoxysilane. The hybrid complex then was gelatinized through acid catalytic hydrolysis method and a sol-gel modified indium tin oxide electrode was prepared via spin coating technique. As prepared indium tin oxide electrode possesses good stability therein with excellent electrochemiluminescence behavior.

Keywords electrochemiluminescence, sol-gel, modified electrode

Introduction

Electrochemiluminescence¹ (also called electrogenerated chemiluminescence, ECL) of tris(2,2'-bipyridyl) ruthenium(II) [Ru(bpy)₃²⁺] has received more and more attention by many researchers due to its great scientific and technological importance to, for example, clinical tests and biomolecule detection.^{2,3} Compared with ECL system in solution,⁴ the immobilization of Ru(bpy)₃²⁺ on electrode surfaces has been widely studied because of several advantages, such as reducing the consumption of expensive luminescent reagent, simplifying experimental design and its compatibility with microchip technique.⁵ Quite a lot of different methods have so far been employed to immobilize Ru(bpy)₃²⁺ on a solid surface, such as Langmuir-Blodgett technique,⁶ self-assembly technique,⁷ electrostatic attachment⁸ and sol-gel entrapment.⁹

Owing to their similarity to bulk sol-gel materials, sol-gel silica films have been commonly used as matrices for a great deal of biomacromolecules,¹⁰ molecular assemblies,¹¹ and functional molecules.¹² The sol-gel method presents an useful approach for doping of organic dyes and coordination compounds such as Ru(bpy)₃²⁺ in inorganic oxides.^{9,13} One can easily prepare homogeneous thin film modified electrode surfaces by forming silicate sol-gel films on conductive solid electrode such as gold, platinum, various types of carbon based materials, and indium tin oxide. As for ECL application, active species, Ru(bpy)₃²⁺, was usually entrapped in silica sol-gel non-covalently.⁹

In this paper, we report our approach to synthesize silica hybridized ruthenium bipyridyl complex through amidation reaction by covalent attachment of bis(bipyridyl)-4,4'-dicarboxy-2,2'-bipyridyl-ruthenium to (3-aminopropyl)triethoxysilane (Scheme 1). Then the sol of silica hybridized ruthenium complex was obtained through hydrolysis. And a sol modified indium tin oxide electrode was prepared using spin coating technique and the electrochemical behavior and electrochemiluminescence of the pre-prepared electrode were characterized.

Experimental

Chemicals

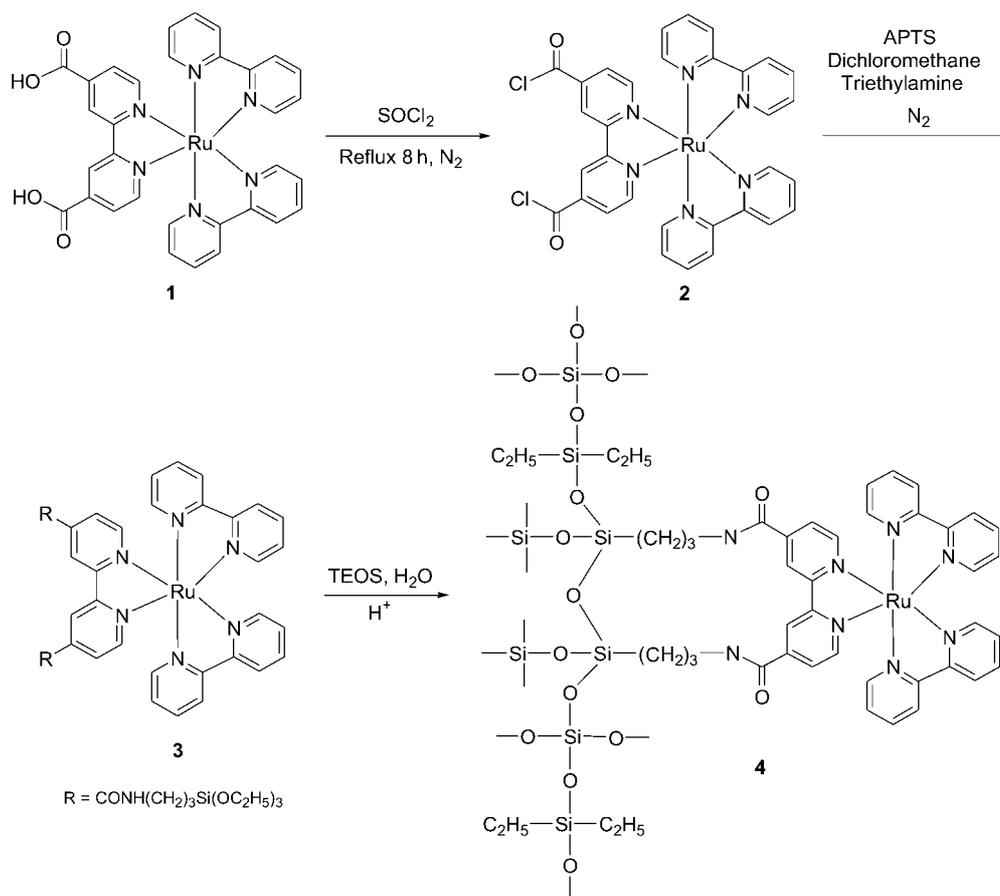
For synthesis, reagent grade solvents and reactants were used as received. For electrochemical and electrochemiluminescence characterization, analytical grade chemicals and reagents were used without further purification. Ruthenium(III) chloride hydrate was obtained from Kunming Institute of Precious Metals (Kunming, Yunan, China). Tripropylamine (TPRA), sodium hexafluoro-phosphate (NaPF₆), tetraethyl orthosilicate (TEOS), and (3-aminopropyl)triethoxysilane (APTS) were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). Thionyl chloride was purchased from Fluka.

All aqueous solutions were prepared with deionized water (18.2 MΩ·cm⁻¹) processed with Milli-Q ultra-high purity water system (Millipore, Bedford, MA, USA).

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Scheme 1 Synthetic procedure for formation of bis(bipyridyl)-4,4'-dicarboxy-2,2'-bipyridyl-ruthenium-silica hybrid materials and their predicted structure

Instrumentation

The electrochemical and electrochemiluminescent measurements were performed with a CHI 800 workstation (CH Instruments, Austin, TX, USA) with an ECL detector using a three-electrode system. The working electrode was modified indium tin oxide (ITO) electrode. A KCl-saturated Ag/AgCl electrode and a platinum wire electrode were used as the reference and the auxiliary electrode respectively. The ECL emission was detected with a Model MCFL-A chemiluminescence analyzer systems (Xi'an Remax Science & Technology Co. Ltd., Xi'an, China). The voltage of photo multiplier tube (PMT) used in Model MCFL-A chemiluminescence analyzer was set at 800 V in the process of detection.

Infrared (IR) spectra were measured within the $4000\text{--}400\text{ cm}^{-1}$ region using a Perkin-Elmer model 580 B infrared spectrophotometer with the KBr pellet technique. Absorption spectra were recorded on a Cary 500 Scan UV-Vis-NIR spectrophotometer at room temperature. Fluorescent emission spectra were recorded on a Perkin Elmer LS55 luminescence spectrometer at room temperature. The SEM images were obtained on an XL30 ESEM FEG scanning electron microscopy operating at 20 kV.

Synthesis and preparation

Bis(bipyridyl)-4,4'-dicarboxy-2,2'-bipyridyl-ruthenium (**1**) was synthesized according to a previous literature procedure.¹⁴

The silica hybrid ruthenium complex (**3**) was synthesized as follows (Scheme 1): 53.1 mg (0.056 mmol) of **1** was dissolved in 20 mL of thionyl chloride. The reaction mixture including **2** was refluxed under N_2 for 8 h. After the reaction, the thionyl chloride was removed by vacuum distillation. The resulting dark red solid was partially dissolved in dichloromethane. 100 μL of APTS were dissolved in 10 mL of dichloromethane (DCM) and then added to the refluxed mixture. 10 mL of triethylamine were added. The solution mixture was then stirred at refluxing temperature under N_2 for 24 h. Finally, the solvent was removed under reduced pressure, and the resulting dark red solid was dried in vacuum at $60\text{ }^\circ\text{C}$ overnight.

Preparation of silica hybrid ruthenium complex sol (4): A total of 9 mg of **3** was dissolved in 4.5 mL of ethanol. The silica hybrid ruthenium complex sol was prepared according to a previously reported method.¹⁵ 1 mL of H_2O , 0.1 mL of 0.1 mol/L HCl and 0.5 mL of TEOS were introduced into 0.5 mL of 2 mg/mL **3** in

ethanol. The mixture was further sonicated for *ca.* 30 min until a clear and homogeneous sol solution formed.

Preparation of sol film modified ITO electrode: ITO electrode (0.35 cm²) was covered with epoxy resin except for the sol film surfaces. 50 μ L of above sol solution (**4**) were dripped onto the ITO electrode and the sol film was produced through a spinning technique at 1000 r/min. The sol film modified ITO electrode aged over night before electrochemical and ECL measurement.

Electrochemical and ECL measurements: Cyclic voltammetry (CV) was performed from 0 to 1.3 V (vs. Ag/AgCl) at 50 mV/s in 100 mmol/L phosphate buffer solution (pH=7.5) with and without 0.1 mmol/L TPrA using a modified ITO electrode and ECL signal was recorded simultaneously.

Safety considerations: Thionyl chloride is harmful and should be handled with caution.

Results and discussion

IR spectra

The formation of bis(bipyridyl)-4,4'-dicarboxy-2,2'-bipyridyl-ruthenium-silica hybrid material was verified by IR spectra. Figure 1 shows the infrared transmittance spectra for 4,4'-dicarboxy-2,2'-bipyridyl, **1** and **3**. It can be seen that the spectrum of **3** was dominated by the $\nu(\text{Si}-\text{OEt})$ and $\nu(\text{Si}-\text{O}-\text{Si})$ absorption bands compared to those of 4,4'-dicarboxy-2,2'-bipyridyl and **1**. And the grafting reaction can be evidenced by the band located at *ca.* 1639 cm⁻¹, corresponding to amide groups. That absorption bands characteristic of the carboxylic acid or carboxylic acid chloride functions of reactants at 1718 and 1737 cm⁻¹ vanished in **3** was a further proof of the hybridization reaction. The broad band at *ca.* 3430 cm⁻¹ was attributed to silica bonds. The bending vibrational mode of the CH₃ group in TEOS as a sharp peak located near 1260 cm⁻¹, while the rocking vibrational modes of the CH₃ as a broad

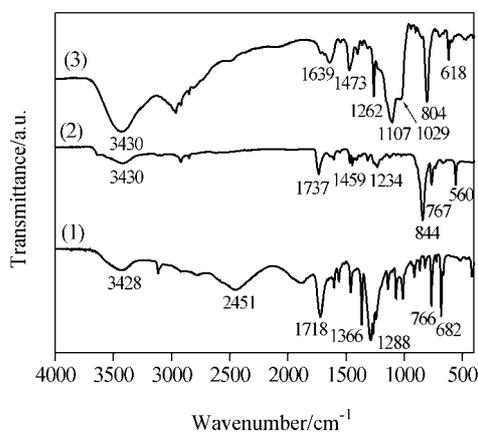


Figure 1 IR spectra of 4,4'-dicarboxy-2,2'-bipyridyl (trace 1), **1** (trace 2) and **3** (trace 3).

band was observed near 1107—1029 cm⁻¹. $\nu(\text{Si}-\text{O}-\text{Si})$ absorption bands at 804 cm⁻¹ indicated the formation of siloxane bonds.

UV-Vis absorption and emission spectra

For the further characterization of bis(bipyridyl)-4,4'-dicarboxy-2,2'-bipyridyl-ruthenium-silica hybrid materials, UV-Vis absorption and emission spectra were recorded in ethanol solution. Figure 2 depicts the electronic adsorption of **3**, and the adsorption spectrum of **1** was also recorded as a comparison. Both of the two complexes present a broad absorption band in the visible region (400—500 nm) due to spin allowed $d\pi(\text{Ru})-\pi(\text{ligand})^*$ metal-to-ligand charge transfer (MLCT) transitions. In the UV region, they exhibit an intense band assigned to intra-ligand $\pi-\pi^*$ transitions.¹⁶ And there are no significant changes in the adsorption properties of the **1** and its silica hybrid counterpart.

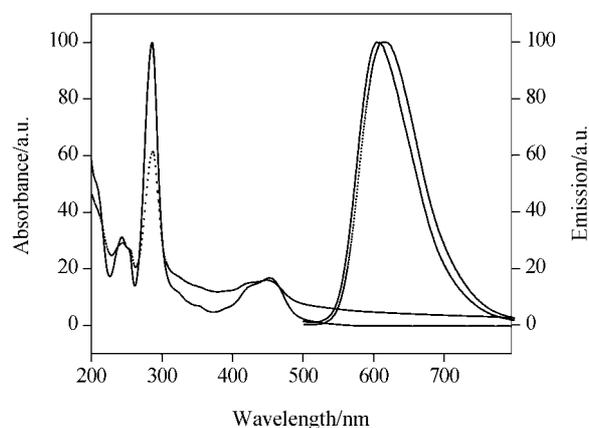


Figure 2 Absorbance (left) and emission (right) spectra of **3** (solid line) and **1** in ethanol solution (dot line). The excitation wavelength is 460 nm in the emission spectra.

The emission spectra of the two complexes in ethanol solution are also depicted in Figure 2. Due to luminescence from the triplet MLCT excited state (³MLCT) to the ground state, there are emission peaks centered at *ca.* 635 nm.¹⁷ Usually when organic dyes such as Ru(bpy)₃²⁺ are encapsulated in sol-gel matrix, the emission spectra exhibit hypsochromic shift according to so-called “rigidochromism effect”.¹⁸ However, unlike the previous reports, Ru(bpy)₃²⁺ entrapped in sol-gel matrix in this study through covalent amidation exhibits no significant blue shift compared to the emission spectrum of its precursor in ethanol solution.

Characterization of modified ITO electrode

The sol-gel thin film fabricated on the ITO electrode was investigated by scanning electron microscopy. Figure 3 shows the SEM image of sol-gel modified ITO electrode, which reveals the formation of homogeneous films on the substrate. This can be assigned to the self-assembly of **4** on the ITO electrode. It can be seen

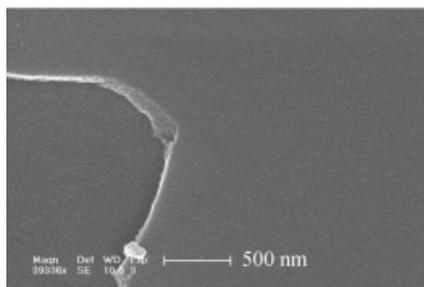


Figure 3 SEM image of bis(bipyridyl)-4,4'-dicarboxy-2,2'-bipyridyl-ruthenium-silica hybrid film formed on the surface of an ITO electrode (10 nm thickness gold coating formed by sputter coating onto the sol-gel silica film).

clearly that a nano-meter thick film was obtained via spin coating technique. For further characterization of the ITO electrode, the UV-Vis absorption spectroscopy was employed and the results are depicted in Figure 4. It exhibits a broad absorption band in the visible region (400–600 nm) due to spin allowed $d\pi(\text{Ru})-\pi(\text{ligand})^*$ metal-to-ligand charge transfer (MLCT) transitions.¹⁶ This may be attributed to our sol-gel preparation method in which enough water and ethanol have been used, so dye molecules in hybrid sol-gel matrix might be surrounded by these solvents resulting in an enough residual freedom of rational motion.

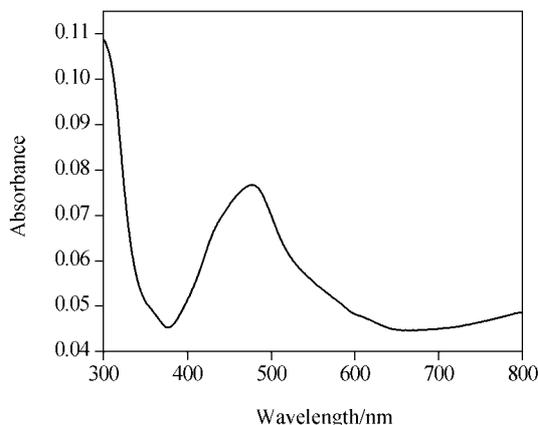


Figure 4 Absorbance spectrum of bis(bipyridyl)-4,4'-dicarboxy-2,2'-bipyridyl-ruthenium-silica hybrid materials modified ITO electrode.

Electrochemical and ECL measurements

To check the electrochemical and ECL properties of $\text{Ru}(\text{bpy})_3^{2+}$ immobilized on the modified ITO electrode, the cyclic voltammograms (CV) were recorded in a detection reservoir with and without 0.1 mmol/L TPrA (in 100 mmol/L phosphate buffer solution, pH=7.5). As shown in Figure 5, the onset of luminescence occurred at *ca.* 1.0 V, at which $\text{Ru}(\text{bpy})_3^{2+}$ was oxidized to $\text{Ru}(\text{bpy})_3^{3+}$. The ECL signal arose quite deeply when 0.1 mmol/L TPrA was added into the reaction buffer. As for electrochemical behavior of the prepared electrode, only irreversible redox waves of electroactive species

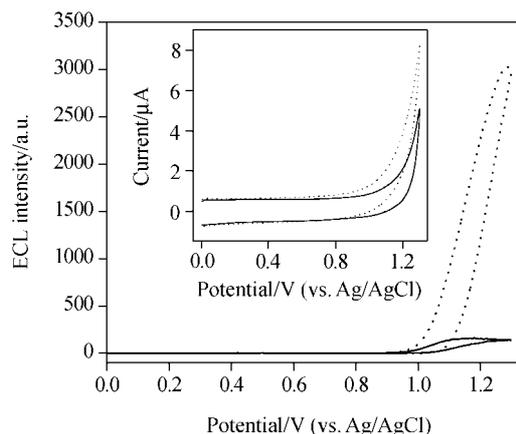


Figure 5 ECL intensity-potential curves for hybrid materials modified ITO electrode in the absence (solid line) and presence (dot line) of 0.1 mmol/L TPrA. Inset: current intensity-potential curves for hybrid materials modified ITO electrode in the absence (solid line, line 1) and presence (dot line, line 2) of 0.1 mmol/L TPrA. Phosphate buffer solution, 100 mmol/L, pH=7.5; scan rate, 50 mV/s; PMT biased at 800 V.

$\text{Ru}(\text{bpy})_3^{2+}$ were observed both with and without co-reactant TPrA (Figure 5, inset). The poor CV response may be due to the silica matrix protection that resulted in the inhibition of effective mass transfer and electron transfer. However, electrochemical response increased when TPrA was added which was in accordance with the “oxidative-reductive” system for the ECL of $\text{Ru}(\text{bpy})_3^{2+}$ and TPrA system (Eqs. 1–4).^{3c} And the onset of catalytic potential was at about 1.0 V, which was consistent with what we observed in ECL behavior.

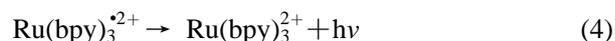
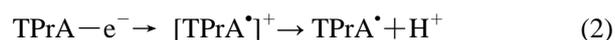
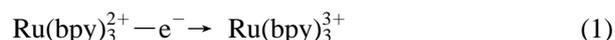


Figure 6 shows the ECL intensity-potential curves of hybrid materials modified ITO electrode in 100 mmol/L phosphate (pH=7.5) buffer solution containing 0.1 mmol/L TPrA under continuous CV for 25 cycles. The relative standard deviation of the peak height was 4.64%, which reflects the good stability of the silica hybrid ruthenium complex modified ITO electrode. The results suggest that the modified ITO electrode should possess excellent ECL behaviors.

Conclusions

Thin-film electrochemiluminescence based on tris(2,2'-bipyridyl) ruthenium(II)-complex-doped silica nanofilms was reported in this paper. We synthesized silica hybridized ruthenium bipyridyl complex through amidation reaction by covalent attachment of bis-

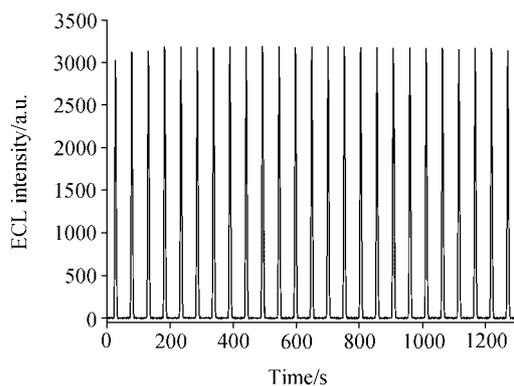


Figure 6 ECL intensity-potential curves of hybrid materials modified ITO electrode in 100 mmol/L phosphate (pH=7.5) buffer solution containing 0.1 mmol/L TPrA under continuous CV for 25 cycles. Scan from 0 to 1.3 V (vs. Ag/AgCl); scan rate, 50 mV/s; PMT biased at 800 V.

(bipyridyl)-4,4'-dicarboxy-2,2'-bipyridyl-ruthenium to (3-aminopropyl) triethoxysilane. The corresponding sol of silica hybridized ruthenium complex was obtained and a sol modified indium tin oxide electrode was prepared. The pre-prepared electrode was characterized thoroughly and exhibited excellent ECL behavior.

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