Enhanced electrochemiluminescence sensor from tris(2,2′-bipyridyl)ruthenium(II) incorporated into MCM-41 and an ionic liquid-based carbon paste electrode†

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Received 6th February 2007, Accepted 30th May 2007
First published as an Advance Article on the web 8th June 2007
DOI: 10.1039/b701842h

The electrochemiluminescence (ECL) of tris(2,2′-bipyridyl)ruthenium(II) [$Ru(bpy)_3^{2+}$] ion-exchanged in the sulfonic-functionalized MCM-41 silicas was developed with tripropylamine (TPrA) as a co-reactant in a carbon paste electrode (CPE) using a room temperature ionic liquid (IL) as a binder. The sulfonic-functionalized silicas MCM-41 were used for preparing an ECL sensor by the electrostatic interactions between $Ru(bpy)_3^{2+}$ cations and sulfonic acid groups. We used the IL as a binder to construct the CPE (IL-CPE) to replace the traditional binder of the CPE (T-CPE) – silicone oil. The results indicated that the MCM-41-modified IL-CPE had more open structures to allow faster diffusion of $Ru(bpy)_3^{2+}$ and that the ionic liquid also acted as a conducting bridge to connect TPrA with $Ru(bpy)_3^{2+}$ sites immobilized in the electrode, resulting in a higher ECL intensity compared with the MCM-41-modified T-CPE. Herein, the detection limit for TPrA of the MCM-41-modified IL-CPE was 7.2 nM, which was two orders of magnitude lower than that observed at the T-CPE. When this new sensor was used in flow injection analysis (FIA), the MCM-41-modified IL-CPE ECL sensor also showed good reproducibility. Furthermore, the sensor could also be renewed easily by mechanical polishing whenever needed.

Introduction

Electrochemiluminescence (ECL) is the emission of light from excited states *via* an electrochemical redox reaction.[1] Among various ECL systems, tris(2,2′-bipyridyl)ruthenium(II) [$Ru(bpy)_3^{2+}$]-based ECL has been commonly used and studied due to its superior properties under moderate conditions in aqueous solution.[2] The oxidation–reduction reaction mechanism for $Ru(bpy)_3^{2+}$ ECL postulated by Rubinstein and Bard elucidates that $Ru(bpy)_3^{2+}$ can be regenerated *in situ* at the electrode surface during the ECL process.[3] Therefore, $Ru(bpy)_3^{2+}$-immobilization approaches have been extensively investigated aiming at developing a cost-effective, regenerable chemical sensor. For example, $Ru(bpy)_3^{2+}$ has been immobilized in polymer,[4,5] sol–gel,[6] sol–gel/polymer composite,[7,8] carbon paste,[9,10] ceramic carbon,[11] carbon nanotube/Nafion composite,[12] Nafion-stabilized magnetic nanoparticles,[13] and metal nanoparticle films.[14] Although some of the above methods could attain good sensitivity and stability, one inherent limitation that lies in these methods is the limited amount of $Ru(bpy)_3^{2+}$ immobilized in the composite film. However, if more $Ru(bpy)_3^{2+}$ is needed to be immobilized on the electrode, then the film must become thicker, which may block the transfer of the electron and analyte.

Since the Mobil research group discovered micelle-templated silica,[15,16] the rapidly developing field of this mesoporous material has inspired chemists' interests to study the structures of porous solids on a nanometer scale in a controlled way.[17,18] Ogawa *et al.*[19] elucidated the advantageous effect of electrostatic interactions between sulfonic acid groups and $Ru(bpy)_3^{2+}$ cations to promote the accumulation of these positively charged species in mesoporous silicas, in comparison to the lower maximum amounts of adsorbed $Ru(bpy)_3^{2+}$ in unmodified silicas or corresponding aluminosilicates. However, these materials are insulators or semiconductors and cannot provide direct electron transfer to the immobilized electroactive sites.[20]

Recently, the rapidly developing field of room temperature ionic liquids (ILs) has attracted much attention due to their special characters such as thermal stability, negligible vapor pressure, good ionic conductivity, low melting temperature and wide electrochemical windows, *etc.*[21,22] ILs, as promising binders[23,24] to fabricate carbon paste electrodes (CPEs), have been used to replace the traditionally non-conducting pasting liquids (T-CPE) due to their high viscosity, which depends on big composite ions (containing strong H–F interactions).[25]

In the present work, two chief aspects of work have been highlighted. Firstly, a new ionic liquid-type carbon paste electrode (IL-CPE) ECL sensor composed of graphite powder and 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$), to displace the T-CPE binder silicone oil, was investigated. Then, the sulfonic-functionalized MCM-41silicas were used to immobilize $Ru(bpy)_3^{2+}$ onto the insides of the pores of MCM-41 by electrostatic interactions between $Ru(bpy)_3^{2+}$ cations and sulfonic acid groups. To our surprise,

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† Electronic supplementary information (ESI) available: sample synthesis and characterization details. See DOI: 10.1039/b701842h

the displacement of silicone oil with $BMIMPF_6$ has greatly enhanced the ECL intensity (Fig. 1) and showed good reproducibility, sensitivity and long-term stability. Moreover, the new ECL sensor could also be renewed easily by mechanical polishing whenever needed. These results indicated that the combination of functionalized MCM-41 silicas with ILs provides a promising matrix in ECL sensing applications.

Experimental

Chemical and reagents

$Ru(bpy)_3Cl_2\cdot 6H_2O$, (98%), tripropylamine (TPrA) (98%), tetraethoxysilane (TEOS), (mercaptopropyl)trimethoxysilane (MPTMS) and graphite powder were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Silicone oil, sulfuric acid, ethanol (95%), cetyltrimethylammoniun bromide (CTAB), ammonia (28%) and hydrogen peroxide (30%) obtained from Beijing Chemicals Inc. (Beijing, China). The $BMIMPF_6$ used in this work was synthesized following the procedure described elsewhere.[26] All other chemicals were of analytical reagent grade and were used as received without further purification. Solutions were prepared with deionized water processed with a Milli-Q ultra-high purity water system (Millipore, Bedford, MA, USA).

Sample synthesis

Preparation of thiol-functionalized silicas. Thiol-functionalized silicas (for details see ESI†) were prepared according a previously published procedure.[27] Here, the molar ratio of MPTMS and TEOS was 1 : 4. The sample prepared is referred to as SH–MCM-41.

Preparation of sulfonic-functionalized silicas. The SH–MCM-41 was oxidized as described using H_2O_2 in a methanol–water mixture.[27] These oxidized materials are referred hereafter as SO_3H–MCM-41.

Characterization of samples

The samples prepared were characterized by Fourier transfer infrared (FTIR) spectra, small-angle X-ray diffraction (XRD) and solid-state Nitrogen (N_2) adsorption/desorption isotherms (see ESI†). The SO_3H–MCM-41 incorporating $Ru(bpy)_3^{2+}$ was confirmed by fluorescence data.

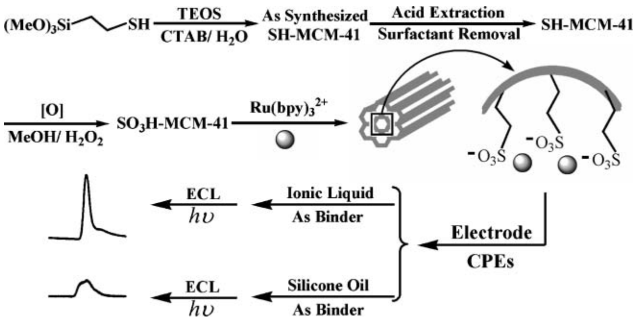

Fig. 1 Schematic illustration of sample preparation and enhanced ECL intensity.

Ion exchage

The SO_3H–MCM-41 incorporating $Ru(bpy)_3^{2+}$ samples were prepared by stirring a suspension of 232 mg SO_3H–MCM-41 in 10 mL of solution containing 25 mM $Ru(bpy)_3^{2+}$ for 24 h. Then the solid particles were filtered, washed extensively with water, and dried in a vacuum for 24 h. The concentration of $Ru(bpy)_3^{2+}$ incorporated into sulfonic-functionalized MCM-41 silicas was (6–8) × 10^{-6} mol g^{-1}, which was larger than the amount of the $Ru(bpy)_3^{2+}$ incorporated into Zeolite Y in previous work[10] by comparing UV-visible spectra of aqueous solutions before and after the exchange.

Sensor preparation

The T-CPE was prepared by hand-mixing silicone oil and graphite powder. Briefly, 200 mg graphite particles and 100 mg particles incorporating $Ru(bpy)_3^{2+}$ were mixed in an agate mortar. 70 mg of the mixture and 20 μL silicone oil were then mulled together. The portion of homogeneous paste was packed into a cavity (3 mm diameter) at the end of a Teflon tube. The electrical contact was provided by a copper handle connected to the paste in the inner hole of the tube. The preparation process of the IL-CPE was similar to that of the T-CPE except for the replacement of silicone oil with $BMIMPF_6$. Prior to use, the surface of the well-prepared CPE was smoothed on a weighing paper to obtain a flat surface.

Apparatus

The FTIR spectra were recorded with a Perkin-Elmer model 580B IR spectrophotometer (USA) with the KBr pellet technique. Solid-state nitrogen (N_2) adsorption/desorption isotherms were measured using a Nova l000 analyzer (USA) with nitrogen. The samples were outgassed for 4 h at 120 °C before the measurements. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and pore sizes by the Barrett–Joyner–Halenda (BJH) method. The XRD was recorded using a Rigaku-Dmax 2500 diffractometer (Japan) using Cu Kα radiation (40 kV and 200 mA) at a step width of 0.02°. The fluorescence excitation and emission spectra were obtained with a HITACHI F-4500 spectrophotometer (Japan) equipped with a 150 W xenon lamp as the excitation source. Absorption spectra were recorded on a Cary 500 Scan UV-Visible-NIR Spectrophotometer (USA) at room temperature. Cyclic voltammetric experiments were performed with a CH Instruments 832 voltammetric analyzer (Shanghai, China). All experiments were carried out with a conventional three-electrode system: a well-prepared CPE, a Pt disk and a Ag/AgCl electrode (saturated KCl) were used as working, counter and reference electrodes, respectively. All of the potentials were measured and reported according to this reference electrode. The ECL signal produced in the electrolytic cell was detected by a model MPI-A capillary electrophoresis electrochemiluminescence system (Xi'an Remax Electronics Inc., Xi'an, China, and Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China). ECL intensities were measured through the bottom of the cell with a photomultiplier tube (PMT) window, and all of them were enclosed in a light-tight box. The PMT was operated in current mode, unless noted, and the PMT was biased at 800 V. Flow injection analysis (FIA) was carried out with an IFI-C flow injection analyzer (Xi'an Remax Electronics Inc.).

Results and disussion

Fluorescence spectra of samples

The fluorescence spectra of SO_3H–MCM-41 and SO_3H–MCM-41 incorporating $Ru(bpy)_3^{2+}$ were recorded in Fig. 2. The fluorescence spectrum of SO_3H–MCM-41 did not show any response, while SO_3H–MCM-41 incorporating $Ru(bpy)_3^{2+}$ exhibited an emission band centered at 600 nm and thus demonstrating that the $Ru(bpy)_3^{2+}$ had been immobilized in the SO_3H–MCM-41 through ion exchange.

ECL response of immobilized $Ru(bpy)_3^{2+}$

The ECL behavior of the $Ru(bpy)_3^{2+}$ immobilized in different CPEs has been investigated with TPrA. The $Ru(bpy)_3^{2+}$–TPrA system was chosen because it has been well studied and gave higher ECL compared with other commonly used reductants such as oxalate.[28] Fig. 3 shows the ECL responses of a T-CPE and an IL-CPE in 0.1 M PBS (pH 7.5) in the presence of TPrA (10 μM) at a scan rate of 50 mV s^{-1}, respectively. As shown in Fig. 3, when the IL-CPE was used as an ECL sensor, the ECL intensity produced at the IL-CPE was *ca.* 30 times larger than that at the T-CPE. Two factors may be ascribed to the ECL enhancement. On the one hand, $BMIMPF_6$, with a high conductivity of 0.14 S m^{-1},[29] activated the immobilized electroactive sites. On the other hand, compared with silicone oil, the IL had larger quantities of caves within its molecular structure, which was facile to hold more charges[30,31] to make the small molecular TPrA permeate into the silica nanoparticles through the pores of the silica to react with the oxidized $Ru(bpy)_3^{2+}$ more easily.[32]

The corresponding ECL–potential profiles recorded at the IL-CPE during cyclic voltammetry at a scan rate of 50 mV s^{-1} are shown in Fig. 4. The onset of luminescence occurred near 1.0 V and the ECL peak intensity occurred near 1.18 V. The ECL intensity was high – up to *ca.* 6000 a.u. – in the presence of TPrA, and ECL responses at the IL-CPEs were very fast due to the structure of the composite film containing $BMIMPF_6$. This phenomenon indicated that $BMIMPF_6$ was a better catalyst for the oxidation of TPrA. The corresponding ECL emissions of IL-CPEs are shown in the inset to Fig. 4.

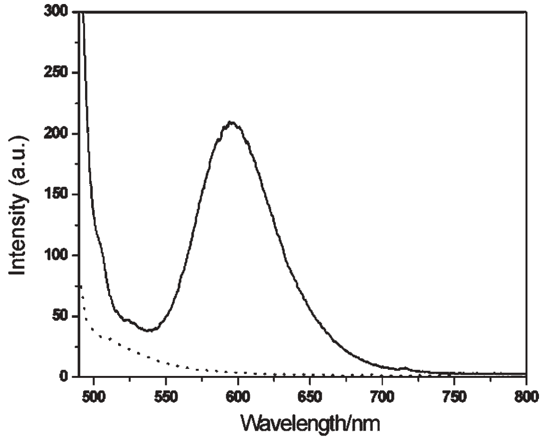

Fig. 2 Fluorescence spectra of sample SO_3H–MCM-41 (dotted line) and sample SO_3H–MCM-41 incorporating $Ru(bpy)_3^{2+}$ (solid line); (λ_{ex} = 475 nm).

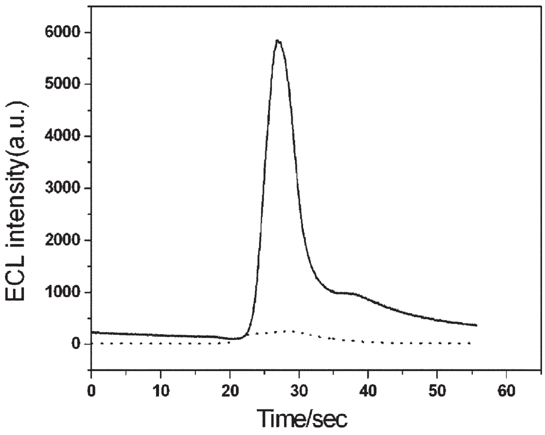

Fig. 3 ECL intensity of $Ru(bpy)_3^{2+}$ immobilized in T-CPE (dotted line) and IL-CPE (solid line) containing 10 μM TPrA in 0.1 M PBS (pH 7.5) at a scan rate of 50 mV s^{-1}.

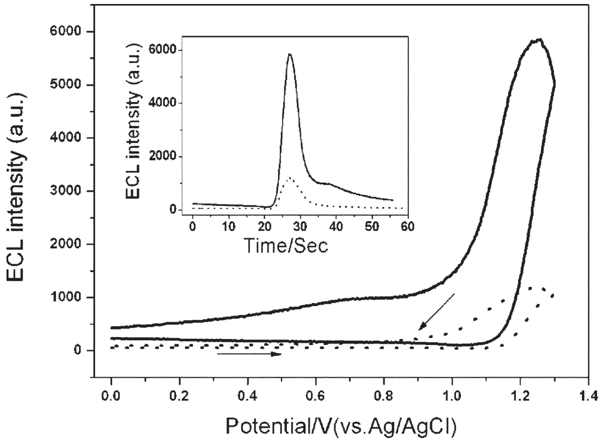

Fig. 4 ECL–potential curves of $Ru(bpy)_3^{2+}$ immobilized in IL-CPE in PBS (pH 7.5) containing 10 μM TPrA (solid line) and without TPrA (dotted line); and (inset) the corresponding ECL intensity of $Ru(bpy)_3^{2+}$ immobilized in IL-CPEs in 0.1 M PBS (pH 7.5) containing 10 μM TPrA (solid line) and without TPrA (dotted line) at a scan rate of 50 mV s^{-1}.

Stability of immobilized $Ru(bpy)_3^{2+}$

When the sensor was immersed in 0.1 M PBS (pH 7.5) containing 10 μM TPrA, there was no detectable change for the ECL intensity under ten repetitive cyclic potential scans, suggesting good reproducibility of the ECL determination of TPrA (Fig. 5). The long-term storage stability was also studied by monitoring its ECL response to 5 μM TPrA in PBS (pH 7.5). After three months, no evident decrease in the ECL response was observed and the sensor could still maintain 85% of the original response. Good stability of the ECL sensor may

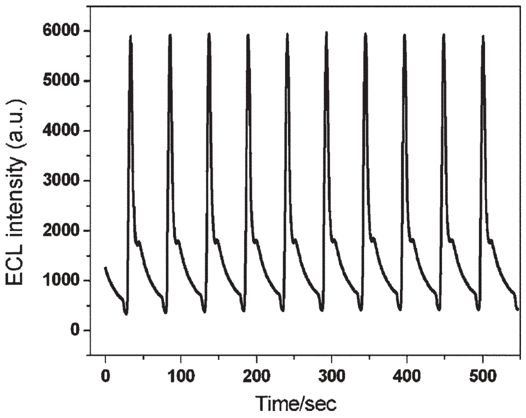

Fig. 5 ECL intensity of $Ru(bpy)_3^{2+}$ immobilized in IL-CPE containing 10 μM TPrA under continuous CV scans for ten cycles at a scan rate of 50 mV s^{-1}.

be attributed to three different kinds of factors: the strong electrostatic interaction between the positively charged $Ru(bpy)_3^{2+}$ and the negatively charged sulfonic acid groups; the pore size (1.38 nm), calculated by BJH method (see the ESI†), being almost alike in size to that of $Ru(bpy)_3^{2+}$ at *ca.* 1.3 nm;[33] and the electrocatalytic activity of the $BMIMPF_6$ due to its good conductivity. In addition, the ECL response of the renewed surface to 5 μM TPrA gave a relative standard deviation of 11–12% (total ECL intensity *ca.* 4000 a.u.) for eight successive renewals. The present sensor showed good linearity with the TPrA concentration and the linear range extended from 2.2×10^{-8} to 1×10^{-5} M. For sensitivity studies, the detection limit for TPrA was 7.2 nM (S/N = 3).

Sensor application

This new sensor was also used in flow injection analysis (FIA), with 0.1 M PBS (pH 7.5) as the carrier stream. Samples containing TPrA (1 mM) were injected, and the ECL peak intensity showed good reproducibility (Fig. 6).

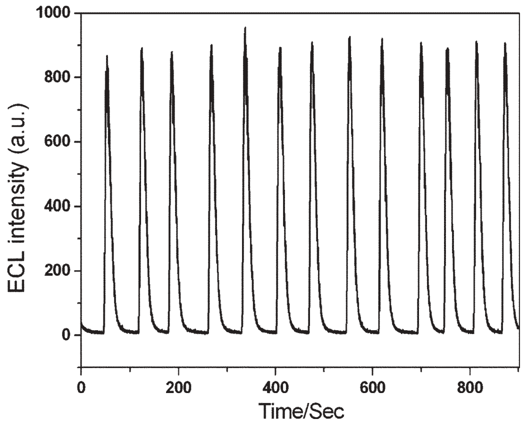

Fig. 6 ECL emission from $Ru(bpy)_3^{2+}$ immobilized in IL-CPE in FIA for 13 consecutive injections of TPrA (1 mM) with a carrier stream of 0.1 mM PBS (pH 7.5), at a potential of 1.2 V (*vs.* Ag/AgCl).

Conclusions

In summary, the coupling of SO_3H–MCM-41 with $BMIMPF_6$ provides an effective approach for the preparation of an enhanced ECL sensor. SO_3H–MCM-41 was used as the exchanger for $Ru(bpy)_3^{2+}$ and $BMIMPF_6$ used as a binder of the CPE due to its similar viscosity compared with silicone oil. When the silicone oil was displaced by $BMIMPF_6$ to fabricate the ECL sensor, the MCM-41-modified IL-CPE sensor greatly enhanced the ECL intensity of $Ru(bpy)_3^{2+}$ immobilized in the CPE. For sensitivity studies, the detection limit for TPrA was at least two orders of magnitude lower than that observed for a T-CPE sensor. Compared with the effective $Ru(bpy)_3^{2+}$ pre-concentration medium Nafion, the detection limit of the IL-CPE ECL sensor is about three orders of magnitude lower. Furthermore, the present sensor has been used in FIA and also showed good stability. Since it is quite easy to fabricate, it is expected to be used as a simple detection method for capillary electrophoresis and high performance liquid chromatography.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 20427003, 200575063 and 20505016) and the China Academy of Sciences KJCX2.YW.H09.

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