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A Kind of Electrode Enhanced the Electrochemiluminescence

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Abstract: Three kinds of platinum electrodes with different geometry were designed. The relation of the electrochemiluminescence (ECL) intensity with the geometry of these electrodes has been investigated. The optical character of these electrodes was directly studied by observation of ECL image and measurement of the ECL intensity. The results showed that the ECL not only concentrated on the edge of the electrode but also concentrated on the edge of holes, which contain in the electrode. The ECL intensity from $Ru(bpy)_3Cl_2 \cdot 6H_2O$ on round electrode was about half of that on four-hole round disk electrode for a same concentration of $Ru(bpy)_3Cl_2 \cdot 6H_2O$, so the detection limit was improved to 10^{-18} mol/L $Ru(bpy)_3Cl_2 \cdot 6H_2O$ on four-hole round disk electrode, three times higher than that on round disk electrode.

Keywords: Electrochemiluminescence, electrode, geometry.

Electrochemiluminescence (ECL), like other chemiluminescence technique, offers high signal-to-noise ratio. Furthermore, it has the advantage over other chemiluminescence techniques of being initiated by a voltage potential. Thus, it provides a better-controlled luminescence. This technique has been used in measuring many kinds of organic and inorganic matters, and analyzing many kinds of antigen, antibody and hapten, such as carcinoembryonic antigen and alpha-fetoprotein, *etc*[1-6]. The electrode geometry and the detector capability remain problems of ECL assay. Based on the ECL mechanism[1], the electron providing efficiency of the working electrode directly influences the ECL efficiency. So, it is a significant work to study the relation of ECL efficiency to electrodes geometry. In recent technology, working electrodes are usually made of round disk with smooth surface. Yet, according to the “Hem effect” in physics, the distribution of electric charges are not even on the smooth surface of a working electrode. ECL, thus, concentrates on the edge of electrode. Central portion of electrode has nearly no ECL effect. This phenomenon results in a lower ECL efficiency, and limits the concentration detection ability at pmol/L or nmol/L. The research about the electrical and chemical properties of the working electrodes, including round disk, ring, spherical, hemispherical and band electrodes has been reported these years[7-11]. But investigation on the relation of ECL efficiency to the geometry of a working electrode from the ECL image and ECL intensity was not reported yet. This work is to discuss the properties of the working electrodes with various geometries from the ECL

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image and ECL intensity.

Experimental

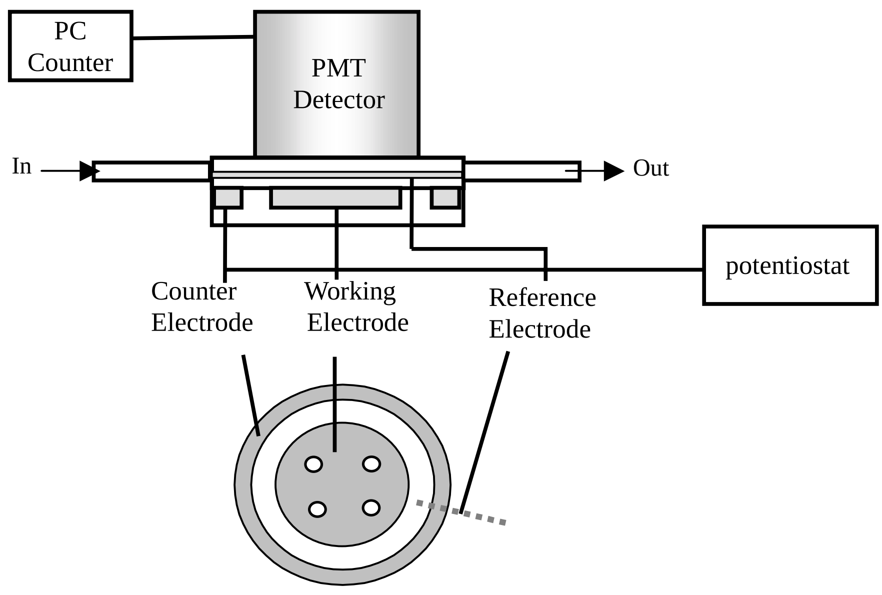
All the reagents were in analytical grade. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ was purchased from Sigma. Tripropylamine (TPA) was purchased from Aldrich.

The imaging system includes a highly sensitive intensified charge-coupled device (ICCD) detector (Princeton Ins., ICCD-576-s/1), which is cooled to -40℃ by a ST-130 controller. The electrochemical reaction cell is placed in a light-tight box. Through a photographic lens (Nikon 50mm,F/1.4) the ECL is imaged on the cathode of the ICCD. The results of ECL measurement are displayed and processed with Winview software.

Assay reaction system was developed in our laboratory. **Figure 1** is a diagram of the essential components of the instruments. The heart of the system is the electrochemical reaction cell, containing the working electrode, counter electrode and reference electrode. The working electrode (disk) and counter electrode (ring) are made from platinum; the reference electrode is an argentine thread above the working electrode. A potentiostat (Fujian Sanming HDV-7C) applies 1.25V to the electrodes. A single photo multiplier tube (PMT, Perkinelmer MP-962) detects the light emitted during the ECL reaction. The signal from the PMT is amplified and discriminated. The output TTL pulses are converted with a multi-function acquisition card (Advantech PCL-836) and analyzed with Labview software. The computer controls the signal collection.

The diameter of the round disk electrode is 1.4 cm. Four 1 mm diameter holes were bored on the round disk electrode. The spiral platinum electrode was made from a platinum thread.

Figure 1 A diagram of the electrochemiluminescence detector



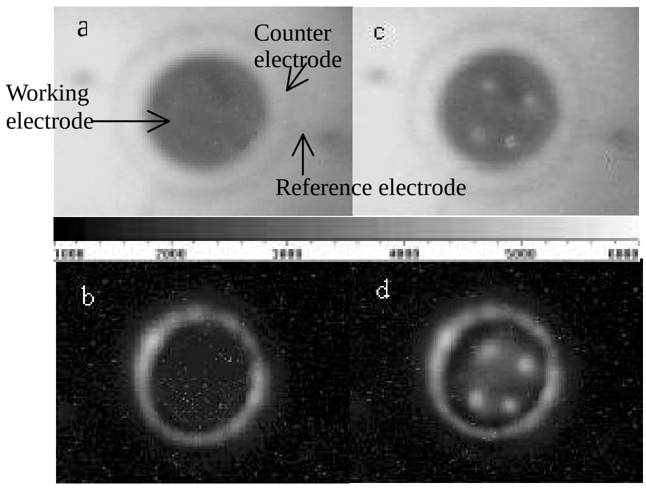
(A cutaway view of electrodes in reaction cell)

$Ru(bpy)_3Cl_2$•$6H_2O$ was dissolved into 1 mmol/L solution in K_2SO_4 (0.1 mol/L) and stored at -20℃. The solution of $Ru(bpy)_3Cl_2$•$6H_2O$ was further diluted to desired concentrations in phosphate-buffered saline (PBS, pH 7.4, 0.01 mol/L, made of tri-distilled water). $Ru(bpy)_3Cl_2$•$6H_2O$ and TPA were added into the electrochemical reaction cell at 2:1 volume ratio. A voltage of 1.25V was applied by potentiostat between working and reference electrodes for detection. ECL images were collected by ICCD and ECL intensity was detected by PMT.

Results and Discussion

The outline and the ECL images of the round disk electrode, four-hole round disk electrode and spiral thread platinum electrode were observed with the ICCD imaging system. Representation results of round disk electrode, four-hole round disk electrode are shown, respectively in **Figure 2**. With the round disk electrode, the light emits from the edge of the electrode. With four-hole round electrode, the light not only emits from the edge of the electrode but also from the holes. The ECL image from spiral platinum electrode shows an identical shape of the electrode geometry (figure not shown). It has been seen that the ECL is concentrated on the edge of the electrode because of "Hem effect". We know from the result that the ECL efficiency is connected with the length of the edge. Given an identical surface area, when the length of the edge is added, the surface area of per gram is increased, the ECL efficiency can be improved.

Figure 2 ICCD images of two kind of electrodes and the ECL on them（100 nmol/L $Ru(bpy)_3Cl_2$•$6H_2O$ and TPA）



a. The shape of round disk electrode b. The ECL on round disk electrode c. The shape of four-hole round disk electrode d. The ECL on four-hole round disk electrode

The ECL intensity from different concentrations of $Ru(bpy)_3Cl_2$•$6H_2O$ and TPA on round disk electrode and four-hole round electrode were detected by PMT. It can be calculated from the results (**Table 1**) that the ECL intensity on round electrode was about half of that on four-hole round disk electrode for a same concentration after the reading of background is subtracted. The detection limit on the round disk electrode was 10^{-15} mol/L $Ru(bpy)_3Cl_2{\bullet}6H_2O$, but on four-hole round disk electrode, the detection limit was 10^{-18} mol/L $Ru(bpy)_3Cl_2{\bullet}6H_2O$, three orders higher than that on round disk electrode.

Table 1 Comparison of ECL intensity on round disk electrode and four-hole round disk electrode

The concentration of $Ru(bpy)_3Cl_2{\bullet}6H_2O$	Round disk electrode Average ECL reading (Counts per second)	S/N[a]	Four-hole round disk electrode Average ECL reading (Counts per second)	S/N
1a mol/L[b]	75 ± 4	1.36	90 ± 5	1.64
1f mol/L	78 ± 6	1.42	130 ± 10	2.36
1p mol/L	105 ± 9	1.91	155 ± 12	2.82
1n mol/L	185 ± 15	3.36	245 ± 23	4.45

[a] Signal-to-noise ratio（S/N）= average ECL reading/average ECL reading of background. Average ECL reading of background =55, n = 15. [b] 1amol/L = 10^{-18} mol/L

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