Cathodic electrochemiluminescence in aqueous solutions at bismuth electrodes

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The high hydrogen evolution overpotential of a bismuth electrode makes it a powerful electrode for cathodic electrochemiluminescence studies in aqueous solutions.

For many years mercury has been the electrode material of choice for stripping analysis applications owing to their high sensitivity, reproducibility, renewability, and large applicable negative potential window. However, there are growing concerns regarding the toxicity, handling, volatility, and disposal of mercury. Recently Wang's group has introduced bismuth electrodes as an extremely attractive alternative to common toxic mercury electrodes. Such electrodes display a well-defined, undistorted and highly reproducible response, favorable resolution of neighboring peaks, high hydrogen evolution, with good signal-to-background characteristics comparable to those of common mercury electrodes. As a result, various bismuth-based electrodes were developed for electrochemical stripping analysis.[1–15] For example, bismuth films have been deposited on carbon substrates, particularly on glassy carbon,[1] carbon fibre,[6] screen-printed electrodes,[7] carbon paste electrodes,[13,14] electrically heated carbon paste electrodes,[15] pencil-lead,[2,3] carbon film resistor electrodes,[8,9] edge plane pyrolytic graphite electrodes,[10] and boron-doped diamond electrodes,[11,12] showing excellent advantages with respect to mercury films. Bismuth bulk electrodes have also been studied.[2,3] The most common application of the bismuth film electrode has been in the determination of trace metals and some organic compounds, in particular by anodic, cathodic, adsorptive stripping voltammetry, potentiometric stripping analysis and chronopotentiometry as well as in sonoelectroanalysis.[2,3] The application of bismuth-based electrodes for electrochemiluminescence (ECL) studies has not been reported so far.

ECL, also called electrogenerated chemiluminescence, involves the generation of species at electrode surfaces that then undergo electron-transfer reactions to form excited states that emit light.[16–23] ECL in many systems is produced by applying a very negative potential,[24–33] such as the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system,[24,29] the $Ru(bpy)_3^{2+}/H_2O_2$ system,[30] and semiconductor nanocrystal systems.[16,25–27] As a result, it is quite difficult to observe stable ECL in these systems in aqueous solutions because of serious hydrogen evolution upon applying very negative potentials. To overcome the problem of serious hydrogen evolution upon applying very negative potentials, Bard's group has reported the use of oxide-covered tantalum electrodes to perform ECL reactions that were only possible on a high hydrogen overpotential metal like mercury.[28] Our group has used carbon paste electrodes to achieve cathodic ECL in aqueous solution.[29] And most cathodic ECL studies of semiconductor nanocrystal systems in aqueous solutions were carried out at carbon paste electrodes so far.[31–33] However, significant hydrogen evolution at the carbon paste electrode makes the carbon paste electrode surface rough and affects cathodic ECL studies upon applying very negative potentials.[29]

Based on the well-known high hydrogen evolution overpotential of bismuth electrodes, we report cathodic electrochemiluminescence in aqueous solutions at bismuth electrodes for the first time, using the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system as a model system. Electrochemical measurements were performed in a conventional three-electrode cell (volume 0.5 mL) with a CH Instrument model 800 B (CHI Inc.). The working electrode, the counter electrode, and the reference electrode are a home-made bismuth bulk electrode, a platinum electrode, and an Ag/AgCl (saturated KCl) electrode, respectively. The bismuth bulk electrode was prepared by encapsulating a bismuth rod in a Teflon sleeve and using a stainless steel screw to make the electric contact. Prior to each electrochemical experiment, the bismuth electrode was polished with 0.05 mm alumina, and ultrasonically cleaned in deionized water. ECL intensities were monitored through the bottom of the three-electrode cell with a BPCL Ultra-Weak luminescence analyzer. Unless noted otherwise, the PMT was biased at 700 V.

Fig. 1a and 1b show the voltammograms of a 0.1 M phosphate buffer solution without and with 10 mM $(NH_4)_2S_2O_8$ on bismuth electrodes. The comparison of Fig. 1a with Fig. 1b indicates that the reduction of $S_2O_8^{2-}$ occurred at a negative potential of about −0.4 V. Fig. 1c shows the voltammogram of a 0.1 M phosphate buffer solution containing 5 mM $Ru(bpy)_3^{2+}$ on bismuth electrodes. The current increases strongly at a potential of −1.37 V and a reduction wave is observed just before hydrogen evolution. The reduction wave can be attributed to the reduction of $Ru(bpy)_3^{2+}$ since the intensity of the wave increased with increasing amounts of $Ru(bpy)_3^{2+}$ added to the solution, and the wave occurs at potentials corresponding to the reduction of $Ru(bpy)_3^{2+}$ to the $Ru(bpy)_3^{+}$ and $Ru(bpy)_3^{0}$ species in pure MeCN. On the reverse scan, after the scan on the reduction wave, an unusual, sharp peak was observed in the voltammogram. This sharp peak can probably be attributed to precipitation or strong adsorption of the uncharged complex on the bismuth electrode.[28]

ECL studies were carried out in 0.1 mol l^{-1} phosphate buffer solution containing either 1 mmol l^{-1} $Ru(bpy)_3^{2+}$, or 1 mmol l^{-1}

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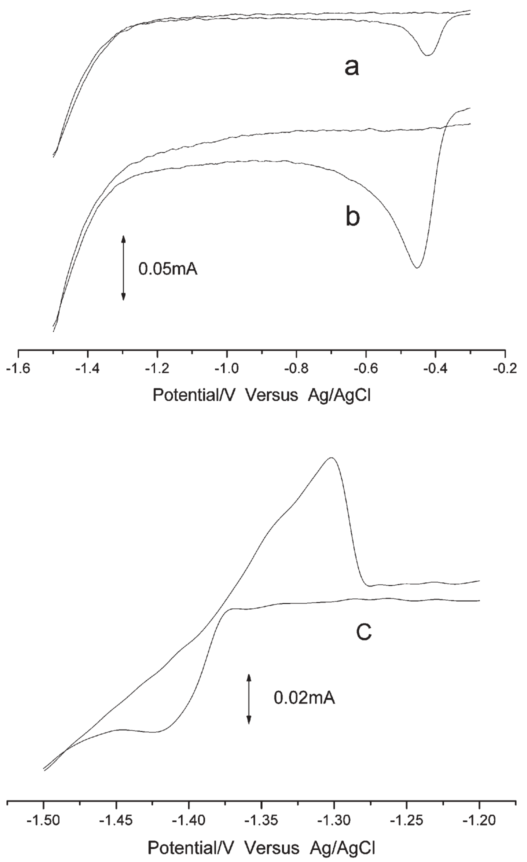

Fig. 1 Cyclic voltammograms at a bismuth electrode in aqueous solution containing (a) supporting electrolyte, (b) 10 mmol l^{-1} $(NH_4)_2S_2O_8$, (c) 5 mmol l^{-1} $Ru(bpy)_3^{2+}$. The supporting electrolyte is 0.1 mol l^{-1} pH 6.85 phosphate buffer.

$(NH_4)_2S_2O_8$, or 1 mmol l^{-1} $Ru(bpy)_3^{2+}$ and 1 mmol l^{-1} $(NH_4)_2S_2O_8$. No ECL was observed in the solution containing 1 mmol l^{-1} $S_2O_8^{2-}$, and very weak ECL was observed in the solution containing 1 mmol l^{-1} $Ru(bpy)_3^{2+}$. Fig. 2 shows an ECL intensity–potential (*I*–*E*) curve in 0.1 mol l^{-1} phosphate buffer solution containing 1 mmol l^{-1} $Ru(bpy)_3^{2+}$ and 1 mmol l^{-1} $(NH_4)_2S_2O_8$. On the forward scan, no ECL was observed at potentials up to about −1.35 V, where $Ru(bpy)_3^{2+}$ is directly reduced at the working electrode. When the potential was biased negative of the onset of the $Ru(bpy)_3^{2+/1+}$ reduction wave (around −1.35 V), an intense ECL peak was observed. It indicates that the electrogeneration of $Ru(bpy)_3^{+}$ is necessary to produce ECL in the presence of 1 mmol l^{-1} $(NH_4)_2S_2O_8$. Therefore, the intense luminescence from the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system may be generated from the excited species, $Ru(bpy)_3^{2+*}$, produced from the following ECL reactions (eqn (1–4)).[24]

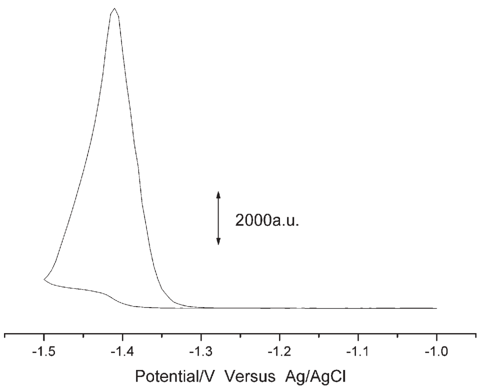

Fig. 2 ECL intensity–potential (I_{ECL}–*E*) curves in 0.1 mol l^{-1} pH 6.85 phosphate buffer solution containing 1 mmol l^{-1} $Ru(bpy)_3^{2+}$ and 1 mmol l^{-1} $(NH_4)_2S_2O_8$. Scan rate: 50 mV s^{-1}.

$$Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+} \quad (1)$$

$$Ru(bpy)_3^{+} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{2+} + SO_4^{2-} + SO_4^{\bullet -} \quad (2)$$

$$Ru(bpy)_3^{+} + SO_4^{\bullet -} \rightarrow SO_4^{2-} + Ru(bpy)_3^{2+*} \quad (3)$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu \quad (4)$$

For further study, ECL was obtained by stepping the potential from −1.0 V to −1.45 V, and the ECL peak intensity obtained was employed. Fig. 3 shows the effect of pH on the ECL intensities of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system. The plot of log of the ECL intensity *vs.* solution pH exhibits a convex curve. The maximum ECL intensity occurs at pH 6.85. The decrease in the ECL intensity observed in acidic solutions may be explained by the consumption of $Ru(bpy)_3^{+}$ (eqn (5)). On the other hand, the decrease in ECL intensity in basic solution was likely ascribed to the consumption of $SO_4^{\bullet -}$ by the scavenging reaction with OH^-.[29]

$$Ru(bpy)_3^{+} + H_3O^{+} \rightarrow Ru(bpy)_3^{2+} + H_2O + \tfrac{1}{2}H_2 \quad (5)$$

As is shown in Fig. 4, the ECL intensity increases with $S_2O_8^{2-}$ concentrations up to 3 mM, and then drops off at higher $S_2O_8^{2-}$ concentrations. The log of the ECL intensity increases linearly with the log of $S_2O_8^{2-}$ concentration over the concentration range of 10^{-3}–10^{-6} mol l^{-1}. The detection limit is 7.8×10^{-7} mol l^{-1}. The RSD for six consecutive determinations of 3×10^{-6} mol l^{-1} $S_2O_8^{2-}$ is 1.6%. This result is comparable to that of the $Ru(bpz)_3^{2+}$ ECL method and the $Ru(bpy)_3^{2+}$ ECL method at a carbon paste

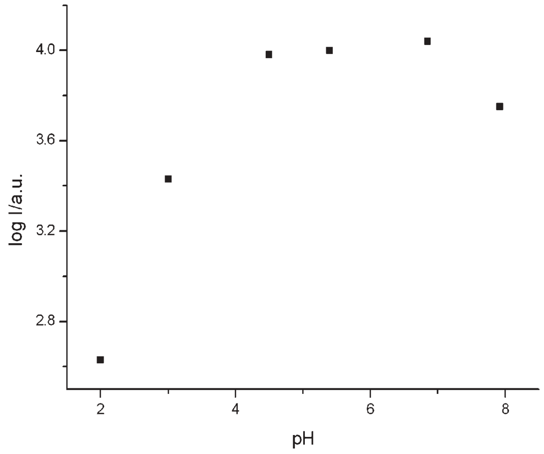

Fig. 3 pH dependence of the ECL intensities in 0.1 mol l^{-1} phosphate buffer solution containing 1 mmol l^{-1} $Ru(bpy)_3^{2+}$ and 1 mmol l^{-1} $(NH_4)_2S_2O_8$.

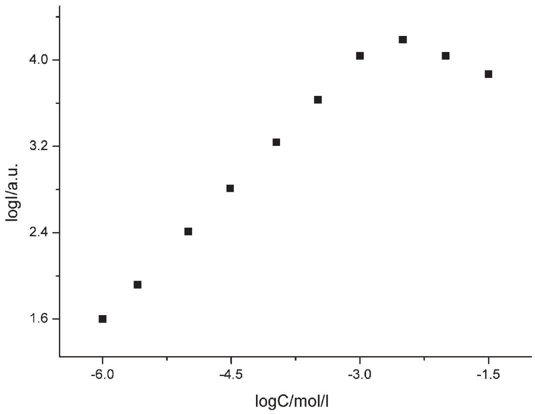

Fig. 4 Dependence of the ECL intensities on $(NH_4)_2S_2O_8$ concentrations in 0.1 mol l^{-1} pH 6.85 phosphate buffer containing 1 mmol l^{-1} $Ru(bpy)_3^{2+}$.

electrode.[29] The decrease in ECL intensity at high concentrations of $S_2O_8^{2-}$ may be ascribed to the quenching reaction of the excited state of $Ru(bpy)_3^{2+}$ by $S_2O_8^{2-}$, which has been reported to be an effective quencher of the excited state of $Ru(bpy)_3^{2+}$. The quenching reaction of the excited state of $Ru(bpy)_3^{2+}$ by $S_2O_8^{2-}$ (eqn (6)) is interesting in that the two strong oxidants generated in the reaction, $Ru(bpy)_3^{3+}$ and $SO_4^{\bullet -}$, can be recycled to produce another excited state $Ru(bpy)_3^{2+}$. Such a recycling reaction is probably partly responsible for the strong emission observed in a solution containing such an effective quencher.[24,29]

$$Ru(bpy)_3^{2+*} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{3+} + SO_4^{\bullet -} + SO_4^{2-} \quad (6)$$

In conclusion, cathodic ECL of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system in a purely aqueous solution was successfully achieved by using bismuth electrodes. Owing to its high hydrogen overpotential, bismuth electrodes, such as bismuth bulk electrodes and bismuth paste electrodes, are expected to be powerful electrodes for cathodic ECL studies in aqueous solutions.[1–3,25–33]

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