

Hot electron-induced cathodic electrochemiluminescence of rhodamine B at disposable oxide-coated aluminum electrodes

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Abstract

Rhodamine B (RhB) exhibits strong cathodic electrogenerated chemiluminescence (ECL) in aqueous solutions during high-amplitude pulse polarization at thin oxide film-coated aluminum electrodes. This method allows the detection of RhB below nanomolar concentration level and provides linear calibration plots spanning over several orders of magnitude of concentration. In addition, a relatively long ECL lifetime of RhB provides a basis for time-resolved detection. Thus, widely used RhB-based labels can also be suggested to be usable as electrochemiluminescent labels in fully aqueous solutions in bioaffinity assays such as in immunoassays and DNA-probing assays. Support was obtained for the chemiluminescence generation mechanism to be essentially the same as that of radiochemiluminescence in aqueous solution.

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1. Introduction

Rhodamine compounds are a group of xanthene dyes that have been widely used in analytical chemistry e.g. as an active medium of dye lasers [1,2] and in bioanalytical chemistry [3,4]. The photophysical properties of rhodamines in solution have been extensively studied [5] and amongst these compounds, rhodamine B (RhB) dye is excited in the visible part of the spectrum (at about 560 nm), has a large molar extinction coefficient ($88,000 \text{ cm}^{-1} \text{ M}^{-1}$), and a photoluminescence (PL) quantum yield close to unity. In addition, it is quite photostable (e.g., as compared to fluorescein) [6].

In some applications, these rhodamine compounds have been used as chemiluminescent reagents although in many cases (e.g. RhB) they were only considered as a sensitizer for application in other chemiluminescent systems [7–9].

The chemiluminescence characteristics based on oxidation of some xanthene dyes have been studied in aqueous solutions [10–12], however, electrochemiluminescence (ECL) of RhB in an aqueous solution has not yet been studied.

It has earlier been suggested that oxide-coated aluminum electrodes [13–18] and silicon electrodes [19,20] can be used to inject hot electrons into an aqueous solution and induce chemiluminescence not attainable by the means of the traditional electrochemistry at active metal electrodes [13–20].

We have also previously demonstrated that the best known electrochemiluminescent labels, such as, luminol, *N*-(6-aminohexyl)-*N*-ethyl isoluminol (AHEI), *N*-(6-aminobutyl)-*N*-ethyl isoluminol (ABEI) and $\text{Ru}(\text{bpy})_3^{2+}$ -based labels, normally in use in the better established anodic ECL applications can also be efficiently excited with our cathodic pulse method [21,22]. However, the best labels for our method seem to be Tb(III) chelates which allow very low detection limits by time-resolved ECL detection [18,23]. When luminophores exhibit relatively long-lived luminescence,

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time-resolved luminescence detection makes it possible to separate the label specific emission from the short-lived solid-state electroluminescence background signal originated from the oxide film by measuring the luminescence after a certain time has elapsed from the end of excitation pulse. This offers an overall increase in detection ability by considerably improving the S/N ratio. So far, in addition to aromatic Tb(III) chelates Pt(II) porphyrins have been known to be usable as electrochemiluminescent labels for time-resolved measurements using our techniques [24].

Typically, the most important ECL excitation routes of the above-mentioned luminophores have been observed to be reduction-initiated oxidative excitation (red–ox) or oxidation-initiated reductive excitation (ox–red) pathways in which the luminophores are excited in successive one-electron steps by the species cathodically generated at the tunnel emission electrodes [15,17–23].

Radiochemiluminescence (RCL) is still one of the least studied forms of luminescence [25–28] but RhB was already quite a long time ago observed to produce RCL under steady X-ray irradiation in an aqueous solution [29,30]. RCL of RhB was later studied using pulse radiolysis with 2- μ s, 4-MeV electron pulses [31]. During and also after the electron pulse, Pruetz and Sommermeyer [32] observed the existence of both one-electron reduced and oxidized radical forms of RhB ($\text{RhB}_{\text{red}}^{\bullet}$ and $\text{RhB}_{\text{ox}}^{\bullet}$), which were produced by the primary species of the radiolysis of water, i.e. hydrated electrons and hydroxyl radicals, respectively. The oxidation of $\text{RhB}_{\text{red}}^{\bullet}$ by hydroxyl radical and reduction of $\text{RhB}_{\text{ox}}^{\bullet}$ by hydrated electron were assumed to be the sources of the excited RhB^* . The excitation by electron pulses appeared to be approximately 1000 times more efficient than the RCL induced by 8.5 and 24 keV [31] X-rays with the same concentration of dye. The RCL lifetime after the electron pulse was very short but could be made somewhat longer by addition of some hydroxyl radical scavengers from halide series. At pH 10 the absolute quantum yield for reaction



was determined to be 0.018 [32].

We have previously proposed that hot electrons are injected into the conduction band of water during a high-amplitude pulse polarization of thin insulating film-coated cathodes, which probably also results in the generation of hydrated electrons from these presolvated hot electrons by thermalization and solvation. Subsequently, hydrated electrons or presolvated hot electrons can generate highly oxidizing species from suitable precursors, such as peroxodisulfate ions, hydrogen peroxide or molecular oxygen [13–18,21,22]. Thus, simultaneously highly reducing and highly oxidizing conditions can be created in the vicinity of the electrode surface. The hot electrons have been suggested to tunnel through a thin insulator film in direct field-assisted regime (around 3–5 nm thick oxide films) into the conduction band of water. After thermalization and solva-

tion processes [15,17,18], the energetic electrons result in hydrated electrons ($E^\circ = -2.9$ V versus SHE) [33] capable of inducing chemiluminescence from various luminophores and coreactants. Typical for hydrated electron is that it does not follow Marcus electron transfer theory but reduces extremely fast not only in reactions having a moderately negative Gibbs free energy change but also in reactions with an extremely negative free energy change [33]. Thus, simultaneous and parallel reductions of species having very different redox properties can be carried out by hydrated electrons.

In our preliminary tests, we have observed that many fluorescent labels not mentioned above and originally designed for photoluminescence purposes can be electrically excited in our cells, but however, some of the fluorescent luminophores do not give any detectable ECL emission. Thus, RhB should be an excellent probe to shed more light on the mechanisms of our cathodic pulse method: (i) if no ECL of RhB would be generated, we surely would not have both the hydrated electrons and hydroxyl radicals as reducing and oxidizing mediators in our cells and (ii) if the cathodic ECL would exist, the scavenging of hydroxyl radicals and/or hydrated electrons should have a strong quenching effect on the CL and (iii) the ECL should be observable also a short time after the cathodic pulse [32], if hydrated electrons and hydroxyl radicals would exist as redox mediators in the cell.

The purpose of the present work was to study the possibly existing cathodic ECL of RhB at oxide-covered aluminum electrode and the detectability of RhB on this basis.

2. Experimental

The ECL measurement were carried out by using single photon counting with an instrument consisting of a Hamamatsu R 1527 photomultiplier, Stanford Research Systems SR-440 preamplifier, SR-400 gated photon counter and Nucleus MCS-II multiscaler card. Similar measurement system have been described in detail elsewhere [14,34,35]. The difference from previous instrumentation was that SR-400 gated photon counter and nucleus MCS-II multiscaler card were attached to two computers, respectively. This configuration of apparatus allowed time-resolved measurements and simultaneous measurements of light emitted during cathodic and intermittent zero voltage during one measurement. The cell used here is a two-electrode system, consisting of a sample holder made of Teflon, a fine Pt-wire counter electrode and a disposable aluminum working electrode. Aluminum electrodes from usually 99.9% pure aluminum band, 0.3 mm thick (Merk Art. 1057, batch 720 K22720857) were covered by a 2–3 nm thick natural oxide film, and were cut into 15 mm \times 15 mm pieces. The effective area of the electrode in this cell was 63.6 mm². A laboratory-made coulostatic pulse generator [36] was applied to generate cathodic pulses and the pulse generator was adjusted to yield cathodic pulses with 120 μ C of charge, –45 V of voltage at a frequency of 20 Hz.

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