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Generation of Free Radicals and Electrochemiluminescence at Pulse-polarized Oxide-covered Silicon Electrodes in Aqueous Solutions†

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Cathodic pulse-polarization of thin-oxide-film-covered highly doped silicon electrodes induces tunnel emission of hot electrons into aqueous electrolyte solutions probably resulting in an electrochemical generation of hydrated electrons. Generation of hydrated electrons allows simultaneous production of sulfate radicals from peroxydisulfate ions, and hence, highly reactive radicals are generated in the vicinity of the electrode surface. Generated primary radical species can induce strong redox luminescence from various organic chemiluminophores and luminescent metal chelates, e.g., some lanthanide and transition metal chelates can be detected below nanomolar levels with a linear range of calibration curves of over six orders of magnitude.

Thin-oxide-film-covered silicon electrodes are known to act as cold-cathodes and tunnel-emit hot electrons in solid state devices.[1] This contribution will show that a highly doped silicon/silicon dioxide junction is able to emit hot electrons in aqueous electrolyte solutions as well. These hot electrons can react with compounds that are hard to reduce and, therefore, cathodic reductions generally not possible in aqueous solutions can be produced. During high amplitude cathodic pulse-polarization in dilute aqueous solutions, it is probable that not all of the hot electrons are reacting at the silicon oxide/solution interface with solute species. If the energy of tunnel-emitted electrons is above the conduction band edge of water it is likely that electrons entering the conduction band of water become hydrated electrons after thermalization and solvation via pathways known from photoemission and photoionization studies.[2] Therefore, cathodic reductions can probably be produced simultaneously by heterogeneously transferred hot electrons and hydrated electrons.

Electrochemiluminescence (ECL) of aromatic compounds at active metal electrodes in aqueous solutions is generally impossible for energetic reasons. The simultaneous presence of hydrated electrons ($E^\circ = -2.9$ V)[3] and sulfate radicals ($E^\circ = 3.4$ V)[4] is one of the harshest conditions in aqueous solutions that can exist, capable of generating chemiluminescence from a wide variety of compounds that otherwise are hard to reduce or hard to oxidize.[5] This contribution will show, using several luminophores, that chemiluminescence generation in aqueous media, generally possible only in the simultaneous presence of hydrated electrons and sulfate or hydroxyl radicals or dichlorine radical anions,[5] is produced during cathodic pulse-polarization of thin-oxide-film-covered highly doped silicon electrodes in the presence of peroxydisulfate ions as sulfate radical precursors.

Sulfate radical is an excellent oxidizing radical in aqueous solution because it has a very low reactivity with the solvent [$k(SO_4^{\cdot -} + H_2O) = 6 \times 10^1$ dm^3 mol^{-1} s^{-1}][6] and its reaction with hydroxide ion is not so fast [$k(SO_4^{\cdot -} + OH^-) = 7 \times 10^7$ dm^3 mol^{-1} s^{-1}].[6] In the absence of reactive solutes, sulfate-radical decay is determined mainly by its self-combination rate [$k(SO_4^{\cdot -} + SO_4^{\cdot -}) = 8.1 \times 10^8$ dm^3 mol^{-1} s^{-1}].[6] Sulfate radical is purely a one-electron oxidant that is capable of rapidly oxidizing even benzene, and has only a weak tendency to addition or hydrogen abstraction reactions.[6]

Present luminophores generally show redox luminescence via oxidation-initiated reductive pathways (*ox–red* pathway) involving a one-electron oxidation of the substrate followed by a one-electron reduction of the formed radical cation.[5,7] This is due mainly to the high instability of hydrated electron adducts in aqueous media.[8] For example, in the cases of simple benzene derivatives, anion radicals formed are extremely rapidly protonated to produce cyclohexadienyl-type radicals, which rapidly

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combine and disproportionate, thus being very poor stepping stones for redox luminescence.[8] This is a fact also in the case of sulfate radical acting as an oxidant, although sulfate radical would be capable of providing a lot of free energy for the excitation step of the *red–ox* pathway. In principle, an *ox–red* excitation pathway is possible for a luminophore, if the one-electron oxidized substrate has a sufficiently long lifetime to encounter a strong reductant capable of donating an electron to the LUMO levels rather than to the hole in HOMO levels. Analogously, the *red–ox* pathway (one-electron reduction of the substrate followed by one-electron oxidation of the radical anion formed) is possible if the oxidant of the second step of the pathway is a strong enough oxidant to abstract an electron from HOMO levels rather than the electron at the SOMO of the one-electron reduced substrate. The *ox–red* and *red–ox* pathways can result in an excited luminophore even in its excited singlet state, but generally the excited triplet state is more often formed.[7] If the reductant/oxidant of the second step of *ox–red* or *red–ox* pathways, respectively, is not sufficiently strong, no excitation takes place and only a ground-state reaction product is formed.

Experimental

Antimony-doped n-Si with orientation (111) and resistivity of 0.008–0.015 Ω cm was used as the electrode material. Silicon discs were purchased from Okmetic Oy (Finland) and cut into 60×7.0 mm pieces to fit into 1-cm spectrophotometer cuvettes. The cell consisted of a sample holder made of Teflon and of a Pt-wire counter electrode. The sample holder had a 3.5×31.0 mm window which restricted the working electrode surface area to 0.11 cm^2. Measurements were made in 1.0 mol dm^{-3} sodium sulfate solutions buffered by 0.2 mol dm^{-3} boric acid–borate buffer at pH 9.2 (known to be unreactive with hydrated electrons and hydroxyl radicals).[3] The excitation was performed with a microprocessor-controlled pulse generator made in our laboratory and Pine Instruments RD4 potentiostat. The excitation pulse train consisted of a 5 V anodic square pulse followed by a −10 V cathodic square pulse with pulse widths of 200 μs. The intermittent zero level had a duration of 10.0 ms, and thus the pulse frequency was ca. 100 Hz. The ECL intensity was measured by single photon counting with an apparatus that consisted of a Hamamatsu R 1527 photomultiplier, Stanford Research Systems SR-440 preamplifier, Ortec 928 Octal discriminator and Nucleus MCS-II scaler card attached in a PC computer. The MCS-II scaler card allowed time-resolved measurements and simultaneous measurements of light emitted during anodic, cathodic and intermittent zero voltage.

Only cathodic light emission intensity responded at the concentration of the luminophores and peroxydisulfate ion. An anodic pulse was used for two reasons: first, to oxidize anodically the surface of the electrode prior to cathodic pulses, and secondly, to remove trapped electrons from E-type[9] centers. The electric field required to make SiO_2 ionically conductive for O^{2-} ions is reported to be 2.6×10^7 V cm^{-1} which results in the formation of an anodic oxide film of thickness 0.38 nm V^{-1} if anodization is allowed to occur to equilibrium and the voltage drop in the cell occurs solely across the oxide film.[10] If it is assumed that pulse anodization results in the same anodization ratio as DC-anodization the 5 V anodic pulses make the natural oxide film grow in thickness to ca. 1.9 nm.

ECL spectra were measured with an ordinary Perkin–Elmer LS-5 luminometer (with the excitation shutter closed using the widest possible gate time) and ECL excitation with the above-mentioned excitation electronics. The light emission intensity during anodic pulses was negligibly small during ECL spectra measurements.

Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate and 9-fluorenylmethyl chloroformate (FMOC) were purchased from Aldrich. Sodium tetraborate·10-hydrate, 4-amino-1-naphthalenesulfonic acid and potassium peroxydisulfate were *pro analysi* products from Merck, and disodium sulfate was a *suprapur* reagent from Merck. FMOC was allowed to be hydrolyzed to (9-fluorenyl)methanol (FMOC-OH) prior to use.[11] Tb^{III}-L chelate [Tb^{III} chelated by 2,6-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-4-benzoylphenol] was synthesized as described elsewhere.[12] Quartz-distilled water was used for the preparation of all solutions.

Results and discussion

Luminophores. Various organic and inorganic luminophores and luminescent metal chelates can be cathodically excited at oxide-covered silicon electrodes in the presence of peroxydisulfate ion. Figs. 1 and 2 present structures and emission spectra of a selection of luminophores emitting in a very wide spectral region, from UV to the red end of the visible region.

Electron injection into aqueous electrolyte solution. The oxidation of silicon to silicon dioxide occurs in contact with air resulting in an oxide-film of thickness ca. 1 nm within a couple of weeks.[13] Therefore, silicon is generally always covered with a thin passive oxide film unless hydrogen passivation is used. Silicon dioxide is a good insulator with a band gap (E_g) ca. 9 eV.[14a] However, even highest purity SiO_2 always has intrinsic defect states within the band gap in its amorphous state, and also in all of its crystalline or partially crystalline forms.[9,14a]

Fig. 3 shows an energy diagram of the present insulator electrode at an imaginary step prior to the electrode attaining open circuit potential after immersion in the electrolyte solution. The diagram is constructed on the following basis: (i) −4.4 eV on a vacuum scale corresponds with 0 V vs. SHE,[15] (ii) the conduction band edge (E_c) of SiO_2 is 0.8 eV below the vacuum level on the physical energy scale,[14a] (iii) the barrier height from highly doped n-Si to the E_c of SiO_2 at an n-Si/SiO_2

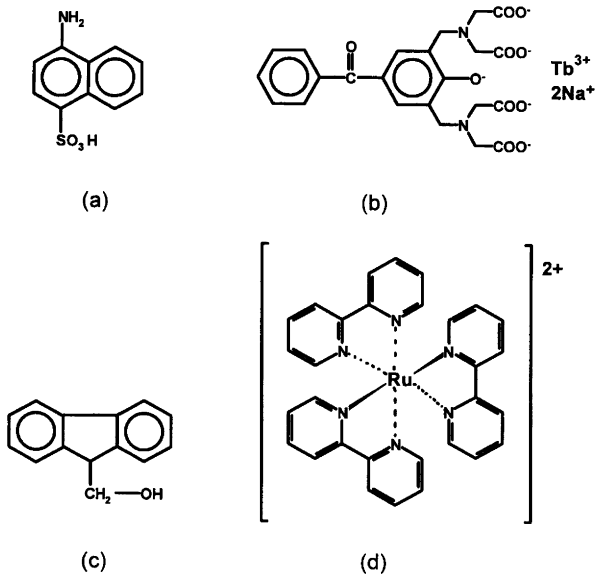

Fig. 1. Structures of luminophores used: (a) 4-amino-1-naphthalenesulfonate (ANS); (b) Tb^{III}-chelated by 2,6-bis[*N,N*-bis(carboxymethyl)aminomethyl]-4-benzoylphenol (Tb^{III}-L); (c) hydrolyzed 9-fluorenylmethyl chloroformate (FMOC-OH); (d) tris(2,2′-bipyridine)ruthenium(II) [$Ru(bpy)_3^{2+}$].

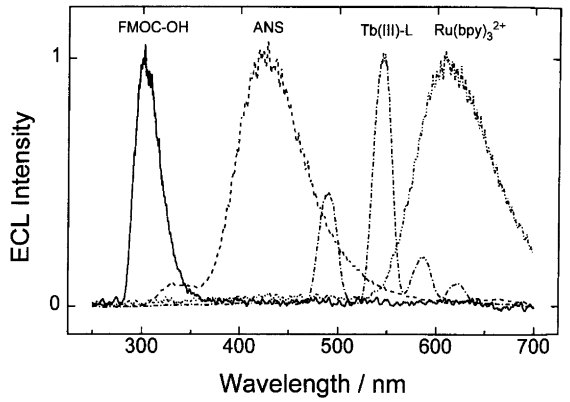

Fig. 2. Uncorrected ECL spectra of several luminophores at an oxide-covered silicon electrode. Spectra are normalized to unit height selecting the peak ECL intensity obtained with the strongest electrochemiluminophore Tb^{III}-L as unity and thus the signal measured from 1×10^{-6} mol dm^{-3} solutions was multiplied by factor 6.0 (FMOC-OH, ——), 1.7 (ANS, – – – –), 1 (Tb^{III}-L, –·–·–) and 4.5 [$Ru(bpy)_3^{2+}$, ·–·–·]. Conditions: 3×10^{-3} mol dm^{-3} $S_2O_8^{2-}$, 0.2 mol dm^{-3} boric acid–borate buffer, pH 9.2, scan speed 240 nm min^{-1}, emission slit 20 nm.

junction is reported to be 3.1 eV,[16] (iv) the present highly doped n-Si is a degenerate semiconductor with a Fermi-level at the level of E_c(Si),[14b] (v) an E_g of 9 eV[14a] results in a valence band edge at −9.8 eV, (vi) the energy level of ground state E_1'-center (an electron trapped in an oxygen vacancy) is 6.2 eV below the $E_c(SiO_2)$ (dashed line in the middle of the anion vacancy and E-type trapped electron center band),[9b] (vii) the conduction band edge of water is at −1.3 eV[17] and the level of the hydrated electron (e_{aq}^-) is ca. 0.2 eV below the

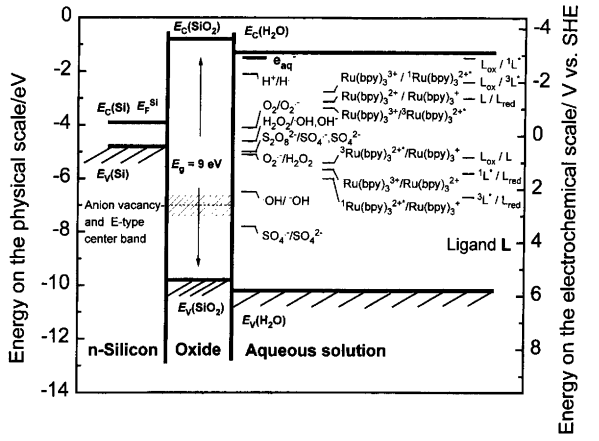

Fig. 3. Energy diagram of a highly doped n-Si/SiO_2 electrode in contact with aqueous electrolyte solution prior to attaining an open circuit potential. The diagram contains the formal redox potentials of the primary radicals and combined redox and luminescence properties of two of the luminophores used. The diagram demonstrates clearly that on a thermodynamic basis, both selected luminophores could be excited even to their singlet excited states in the simultaneous presence of hydrated electrons and sulfate radicals via both *ox–red* and *red–ox* pathways. However, the *ox–red* pathway seems to be predominant in practice in both cases. Aromatic Tb^{III} chelates are excited via chemical excitation of the ligand followed by intramolecular energy-transfer to the central ion which finally emits.[7]

$E_c(H_2O)$,[3] (viii) the valence band edge of water has been reported to lie at −9.0 eV,[18a] but more recent studies suggest that the band gap of water is close to 8.9 eV[18b,c] which results in a valence band edge of about −10.2 eV. Redox potentials of solution additives are placed at appropriate energy levels according to Refs. 3, 4, 5c, 6 and 8(d).

We have shown elsewhere[7] that cathodically pulse-polarized oxide-covered aluminum electrodes produce strong chemiluminescence of aromatic Tb^{III} and $Ru(bpy)_3^{2+}$ chelates, and that the effects of fast hydrated electron scavengers were analogous to those observed during measurements of hydrated electron-induced chemiluminescence of the present chelates generated by other, better known hydrated electron generation methods.[5,7] Oxide-covered aluminum electrodes have closely similar energy diagrams to oxide-covered silicon which allows us to propose the occurrence of similar charge transfer processes known from our studies with oxide-covered aluminum electrodes.[7] According to our results, highly energetic reductions and oxidations can occur at a distance of ca. 100 nm from the oxide-covered aluminum surface during the detection steps of immunometric immunoassays, and the primary reductant and oxidant have closely similar properties to the hydrated electron and hydroxyl radical.[7] In principle, hot electrons with energies above the conduction band edge of water should be able to induce even harder reductions than can the hydrated electron, but the overall cathodic processes at oxide-covered aluminum at the detection step

of labels can be explained only by mediating radical species.

Electrolytically produced primary species. The generation of hydrated electrons can be explained by the insulating film-covered electrodes acting as cold-cathodes, and by hot-electron transfer through the insulating films occurring by field or tunnel emission[19] in case of very thin films, and by Fowler–Nordheim tunneling[14a,19b] in the case of thicker insulator films. Tunnel emission of electrons can occur with thin oxide films (thickness < ca. 5 nm), i.e., electrons do not enter the conduction band of SiO_2 but tunnel directly from an energy level through the barrier to an equal energy level (Fig. 4, hot e^- type I). Fowler–Nordheim tunneling into the conduction band of SiO_2 occurs with thicker oxide films.[16,19] If the SiO_2 film is thicker than 7–8 nm, Fowler–Nordheim tunneling results in a steady state (wide) energy distribution of hot electrons with an average energy ca. 1.1 eV above the bottom of the conduction band of SiO_2 due to the simultaneous effect of the electrons gaining energy in the electric field and losing it in inelastic scattering (Fig. 4, hot e^- type II).[16,19b] However, the high-energy tail of the hot electron energy distribution extends weakly over 9 eV which even allows some band-to-band impact ionizations to occur resulting in solid state electroluminescence and generation of trapped holes in the band gap.[16]

The Fermi-level of n-Si during pulsed excitation in a two-electrode cell can be measured against a separate reference electrode with an oscilloscope with 10 MΩ input impedance having n-Si as a common ground of the excitation and potential measuring circuits.

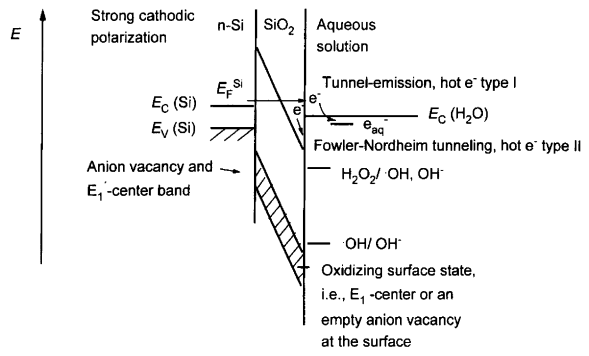

Fig. 4. Schematic representation of the emission of electrons during cathodic high-amplitude pulse-polarization. Tunnel emission injects electrons into the electrolyte solution to an energy level equal to that of the source through very thin oxide films (<4–5 nm), but with thicker films Fowler–Nordheim tunneling produces a hot electron energy distribution extending from the conduction band edge of the oxide up to as much as ca. 9 eV above the conduction band edge of the oxide. However, the average energy of hot electrons is only ca. 1.1 eV above the conduction band edge of the oxide at the oxide–electrolyte interface.[16,19b] In practice, the conduction band edge of SiO_2 at the oxide–electrolyte interface may bend down well below the conduction band edge of water due to the cathodic polarization.[14a]

According to these measurements the Fermi-level of n-Si at the end of applied +5 V (200 μs) anodic, −10 V (200 μs) cathodic pulses, and intermittent 10-ms zero level on the vacuum scale are −10.2 eV (+5.8 V vs. SHE) and +2.0 eV (−6.4 V vs. SHE) and −6.4 eV (+1.4 V vs. SHE), respectively; i.e., n-Si is also anodically polarized during intermittent zero levels between applied voltage pulses. Therefore, under these conditions, direct tunnel emission of electrons results in an injection of electrons into the aqueous electrolyte solution ca. 3 eV above the bottom of the conduction band of water, and no further electron heating in the conduction band of SiO_2 is necessary to explain the observed phenomena.

The generation of hydroxyl radicals can come from four sources: (i) if the electrolyte contains dissolved oxygen, a three-step reduction of molecular oxygen by hydrated electrons is possible,[3] (ii) on a long enough timescale, anodically produced hydrogen peroxide may diffuse from the anode to the cathode and then undergo one-electron reduction,[3] (iii) the electric field in insulating oxide films is generally of the same order of magnitude during hot electron injection in the oxide film as is required to make the film ionically conductive for O^{2-} ions,[7] therefore, cathodic injection of $O^{\cdot -}$ radical ions (a hole self-trapped on an O^{2-} ion) along with O^{2-} ions into the electrolyte solution would naturally result in the generation of hydroxyl radicals from oxide radical ions in neutral and somewhat basic electrolyte solutions,[7] because the pK_a of hydroxyl radical is 11.9,[3] and (iv) either empty anion vacancies or anion vacancies filled only by a single electron (E_1' centers in SiO_2)[9b] at the tunneling distance from the electrode surface may act as oxidants with about equal oxidizing power as the sulfate radical (Figs. 3 and 4); they may oxidize hydroxide ions to hydroxyl radicals, and hence, mediate oxidations at somewhat longer distances from the electrode than the normal tunneling distance from the electrode (ca. 1 nm).[14a] Also, in an undivided cell, the first two routes for hydroxyl radical generation are impossible in a deoxygenated solution during the first few excitation pulses. However in practice, the highly energetic oxidant and reductant-requiring ECL reactions can be observed immediately during the first excitation pulse.[7] Therefore, the above-mentioned solid state routes are regarded as probable and more realistic pathways for the generation of oxidizing radicals at insulating oxide-film-covered metal electrodes, than the three-step reduction of molecular oxygen or one-step reduction of hydrogen peroxide, although hydrated electrons are well-known to reduce oxygen, and successive reduction products, at nearly diffusion-controlled rates.[3] The threshold electric field for ionic conduction in SiO_2 is ca. five times higher than in Al_2O_3,[7,10] and hence, the latter solid state mechanism seems more likely in the case of oxide-covered silicon electrodes.

A corresponding electron center in Al_2O_3 with an E_1' center in SiO_2 (i.e., one electron trapped in an anion

vacancy) is called an F^+ center and lies at a level ca. 0.3 eV lower on the vacuum scale than the E_1' center in SiO_2.[9,20] It is also able to act as a stronger oxidant than hydroxyl radical in the case of pulse-polarized oxide-covered aluminum. In case of SiO_2, the 5 V anodic pulse between each cathodic pulse was able to remove the electrons from the anion vacancy and E_1' center band (Figs. 3 and 4) by a resonance tunneling or hopping conduction mechanism.[21] Thus, in the absence of peroxydisulfate ions, the oxidizing species at the surface of the electrode were produced just before the beginning of each cathodic excitation pulse.

Addition of a suitable concentration of a well-known, fast hydrated electron scavenger, peroxydisulfate ion,[3] generally always induces a strong ECL intensity of any added organic chemiluminophore or ECL-active metal chelate at oxide-covered aluminum or silicon electrodes. Fig. 2 displays the emission spectra of several luminophores generated at an oxide-covered silicon electrode by cathodic pulse-polarization in the presence of peroxydisulfate ions. The spectra demonstrate that the presently used experimental conditions allow the excitation of molecules and chelates with very different redox and luminescence properties, and that the excitation energy of the excitation step can exceed at least 4.4 eV because, e.g., an emission of FMOC-OH can be observed at that energy (280 nm), and some amount of the excitation energy must also have been consumed in non-radiative processes prior to the emission step. Intrinsic cathodic emission of oxide-covered silicon is so weak that the emission spectrum cannot be measured with our apparatus, but in the presence of peroxydisulfate ions a weak, wide band emission having an emission maximum at ca. 420 nm (3.0 eV) could just barely be resolved from the noise. Generally, all of the present luminophores also show ECL in the absence of peroxydisulfate ions, but the intensity can be many orders of magnitude higher in the presence of peroxydisulfate ions. There is a clear explanation for this in the case of aromatic and hetero-aromatic compounds: hydroxyl radicals always react by addition, and this results in an oxidation reaction only if the aromatic substrate has strongly electron-donating substituents which assist the elimination of hydroxide ion or water.[22] Therefore, the production of sulfate radical usually has a beneficial effect on ECL generation although its production consumes reducing equivalents from the primary species. ECL in the absence of peroxydisulfate ions is attributed to the oxidation of luminophores present, either directly by an anion vacancy or an E_1' center or mediated by hydroxyl radical, followed by reduction by hot or hydrated electron (Fig. 3). The *ox–red* pathway is obviously predominant in all other cases of the luminophores studied here, excluding Tb^{III}-L which may also be excited via a *red–ox* pathway due to its high reactivity with hydrated electrons and relatively good stability of the formed anion radical in aqueous media.

Analytical applicability of ECL at oxide-covered silicon. Fig. 5 displays the calibration curves of Tb^{III}-L and $Ru(bpy)_3^{2+}$ chelates which are both suitable labeling compounds in bioaffinity assays.[7,23] The wide range of determination, spanning many orders of magnitude, and the high sensitivity of detection of these labeling compounds makes the use of disposable oxide-covered silicon electrodes extremely attractive as a solid phase for heterogeneous immunoassays. The highly sophisticated silicon technology of the present day leads us to propose other applications not directly in connection with luminescence, because the injection of hot electrons into aqueous solutions easily lends itself to a low-cost method for many kinds of time-resolved studies generally possible only by pulse radiolysis of water.

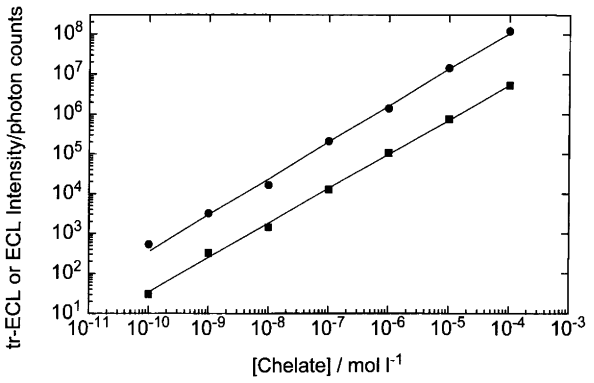

Fig. 5. Calibration curves of Tb^{III}-L and $Ru(bpy)_3^{2+}$ chelates at an oxide-covered silicon electrode: (a) the time-resolved ECL intensity induced by Tb^{III}-L was measured through a 546-nm interference filter with a maximum transmittance of ca. 50% and half-width of the transmission band ca. 10 nm, delay time 50 μs, gate time 8 ms (●); (b) cathodic ECL intensity induced by $Ru(bpy)_3^{2+}$ was measured through a 620-nm interference filter with a maximum transmittance of ca. 30% and half-width of the transmission band ca. 10 nm (■). Conditions: 1.0×10^{-3} mol dm^{-3} $S_2O_8^{2-}$, 1.0 mol dm^{-3} Na_2SO_4, 0.2 mol dm^{-3} boric acid–borate buffer at pH 9.2. The luminescence lifetime of Tb^{III}-L is ca. 2.1 ms, which effectively allows time-resolution from the weak cathodic blank signal with a lifetime ca. 10 μs, but the luminescence lifetime of the ^{3}MLCT state of $Ru(bpy)_3^{2+}$ is too short for time-resolved ECL detection at oxide-covered silicon electrodes with the excitation electronics currently used.

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