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Hot electron-induced electrochemiluminescence at polyetherimide-carbon black-based electrodes☆

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ABSTRACT

Various luminophores produce strong electrogenerated chemiluminescence during cathodic pulse polarization of the present insulating film-covered carbon paste electrodes in fully aqueous solutions. First electrodes made of a commercial conductive carbon paste were successfully utilized as working electrodes and their surface was characterized by ESCA. Then custom in-laboratory made improved composite electrodes were manufactured from the same insulating polymer and conducting carbon black particles. The relationship between the amount of carbon present on the composite electrode, in the bulk and on the surface, and the intensity of electrogenerated chemiluminescence was studied further. The overall performance of these composite electrodes makes them viable low-cost replacements for metal/insulator type electrodes such as oxide-coated silicon electrodes.

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1. Introduction

Hot electron-induced electrochemiluminescence (HECL) is an analytical method that uses hot electron injection into aqueous electrolyte solutions to initiate chemiluminescent reactions. The excitation of one compound, typically a label or beacon, is caused by a chemical reaction between otherwise nonreactive species that have been reduced by hot/solvated electrons, which are introduced to the electrochemical cell during a pulse polarization step. Utilization of energetic hot and/or solvated electrons as reactants in the excitation pathways allows efficient excitation of various luminophores, some with prolonged luminescence emission. This in conjugation with low background signal allows sensitive detection of luminophores in pico-molar concentrations, with rather simple and low-cost instrumentation in comparison to other spectroscopic methods [1]. HECL has found use in e.g. immunoassays, where luminescent labels are utilized [2–4].

In HECL the working electrode is typically covered by a uniform thin insulating film, common electrode materials include e.g. oxide-coated aluminum, silicon and magnesium electrodes [5–7]. The presence of the insulating layer allows transportation of electrons into solution by field-assisted tunneling, making the electrons transferred considerably more energetic than those transferred from active metal electrodes or typical semiconductor electrodes [8,9]. This is based on the electrodes ability to reach cathodic potentials that are more negative than the conduction band edge of water before the conducting base material of the electrode starts to tunnel emit electrons through the insulator film. Electrons injected to the conduction band of water are first thermalized and subsequently hydrated, forming highly oxidizing radicals when reacting with dissolved oxygen or the added co-reactants (e.g. peroxodisulfate or hydrogen peroxide). This simultaneous presence of both extremely strong oxidants and reductants allows redox reactions, not achievable at normal-sized active metal electrodes (e.g. platinum and gold), to take place.

Recently there have been reports of using carbon based composite materials as the working electrode in HECL [10,11]. Compared to the more traditional metal/insulator-electrodes these type of electrodes offer wider usable pH range, lower background signals and less tedious preparation process. Wu et al. have shown that certain conductive commercial carbon pastes can be used to produce working electrodes for HECL use [11]. Conductive pastes contain chemical(s) that are added to prevent the conducting particles from agglomerating during prolonged storage and binder (s) that help the paste to adhere into substrates and to glue the conducting particles together. The surface passivation caused by these species is unwanted in typical electrochemistry applications,

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often warranting a need for a surface pretreatment. However in HECL this surface passivation is normally a necessity.

The problem of using commercial conducting pastes in HECL is twofold: the composition of the paste is optimized for electrical conductivity and general usability. Secondly, the chemical nature of the insulating matrix is typically not given by the manufacturer which leads to guesswork when it comes to chemical compatibility. For example Wu et al. found out, that in order to achieve the optimal HECL emission intensity, they had to pretreat the carbon paste electrodes by soaking them in sodium hydroxide. This time-consuming part could be avoided, if the chemistry of the insulating material was known and the ink composition was tailored for HECL use.

To solve these problems we studied the surface composition of a commercial conductive carbon paste. According to X-ray photoelectron spectroscopy analysis the insulating layer on electrode surface was likely polyetherimide. By mixing polyetherimide with conductive carbon black particles at various weight-ratios we produced composite electrodes that provided more than thirty-fold increase in HECL-emission intensity with less than one sixth of the standard deviation when compared to the electrodes made from commercial paste.

2. Experimental methods

Flexible, pad printable carbon paste (#119-28) was obtained from Creative Materials Inc. Prior to use the paste was mixed with T-10 homogenizer (IKA) at 13 000 RPM for 10 minutes. Electrodes made from this paste (abbreviated hereafter as CM-electrodes) were made by depositing a 120 μm thick wet layer to brass substrate with ZFR 2040 4-sided applicator and dried in laboratory oven for 15 minutes at 130 degrees Celsius.

Polyetherimide (PEI, obtained from Sigma-Aldrich) was dissolved overnight in analytical grade chloroform at mass concentration of 50 g dm^{-3}. Carbon black VULCAN® XC-72 (CB, product of Cabot), was added in various mass ratios to PEI-chloroform solution. Obtained mixtures were likewise mixed at 13 000 RPM for 10 minutes to ensure homogenous aggregate-free dispersion. Inks were stable in room temperature even ten days after the mixing. This PEI-CB ink was spin coated to brass discs (15 mm in diameter). Prior to deposition the substrates were cleaned in ultrasonic bath (150 W for ten minutes) with acetone and dried overnight at ambient conditions. Spin coating was done at 3500 RPM for 40 seconds, followed by a one second acceleration to 5500 RPM (60 seconds in duration) to dry the electrodes completely. The metal/PEI-CB-electrodes are herein simply abbreviated as PEI-CB-electrodes.

The aluminum electrodes used as reference were cut from nominally 99.9% pure Al (Merck Art. 1057, batch 721 K4164557) and used without pretreatments of any sort.

The electrochemical cell was a PTFE-cylinder (10 mm diameter) with an integrated platinum wire counter electrode (0.9 mm in diameter) positioned close to the edge of the cell. Distance between electrodes was roughly 1 mm. The cathodic excitation of luminophores was done with an in-laboratory-built coulostatic pulse generator, delivering voltage pulses fixed to −35 V with a pulse charge of 39 μC at 20 Hz. For anodic excitation the cell polarity was switched and same settings used. Time-resolved HECL measurements (TR-HECL) were carried out with electrochemiluminometer composed of Nucleus MCS-II multiscaler card, photomultiplier tube module (Perkin Elmer) and Stanford Research SR400 Photon Counter. In TR-HECL the emission was measured 50 μs after the end of each excitation pulse for four milliseconds. Unless otherwise stated the emission light was measured in the presence of an interference filter: 545 nm for Tb(III) chelate and 620 nm for $Ru(bpy)_3{}^{2+}$, both filters had a half-bandwidth of ca. 20 nm. Emission spectrums were measured with Andor Technology DV465C-FI electron multiplying charge-coupled device (EMCCD) detector attached to an Oriel Instruments MS125 (model 77400) spectrograph. Long exposure photographs (15 s) were taken with Canon EOS 7D digital camera equipped with Canon EF 100 mm f/2.8L Macro IS USM lens. Cyclic voltammetry was performed with conventional three-electrode system with a platinum wire as the counter electrode and a saturated calomel electrode as the reference electrode.

Terbium(III) chloride hexahydrate was purchased from Sigma-Aldrich, 2,6-bis[N,N-bis(carboxymethyl)amino-methyl]-4-benzoylphenol chelate was synthesized as presented in detail elsewhere [12]. 7-hydroxy-4-methylcoumarin, $Ru(bpy)_3{}^{2+}$ and fluorescein were obtained from Sigma-Aldrich. All HECL measurements were done in $Na_4B_4O_7$ buffer at pH 9.2 with 0.1 M Na_2SO_4 as the supporting electrolyte.

XPS analyses of deposited conductive carbon paste were performed using AXIS Ultra electron spectrometer with monochromatic irradiation at 100 W (Kratos Analytical, Manchester, UK). Elemental composition was calculated from survey spectra while high resolution carbon C 1s, oxygen O 1s and nitrogen N 1s regions were utilized for more detailed evaluation of surface chemistry. Each sample was measured at three locations with area of 400 × 800 μm. Carbon spectra were peak fitted using Gaussian of equal FWHM, all binding energies were fine-tuned with the C 1s aliphatic component at 285 eV and conditions in ultrahigh vacuum during the experiment were monitored with fresh cellulose *in-situ* reference sample [13,14].

3. Results and discussion

3.1. HECL with the CM-electrodes

Aromatic Tb(III) chelates cannot be cathodically excited in aqueous electrolyte solutions using traditional electrochemistry at active disc electrodes and therefore serve as useful beacons when studying previously untested materials for HECL instrumentation [1]. The long luminescence lifetime, around two milliseconds with certain chelates, makes their emission easy to detect on the basis of time discrimination. The emission spectrum measured with EMCCD detector during the pulse polarization of CM-electrode shows that the Tb(III) chelate was excited with the present experimental setup (Fig. 1).

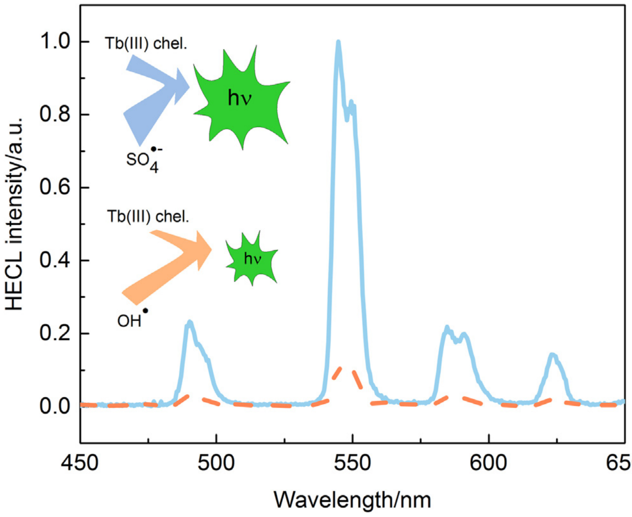

Fig. 1. ECL spectrum of 10^{-5} M Tb(III) chelate at CM-electrodes. Solid lines measured in the presence of 10^{-3} M $K_2S_2O_8$ and dashed lines in the absence of $K_2S_2O_8$.

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