Potential-dependent Chemiluminescence of Luminol and the Detection of Glucose / Lactate by using Gold Electrode modified with Ferrocenylalkanethiolate Monolayers

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A luminol-peroxide chemiluminescent system has attracted particular interests in the field of bioanalytical chemistry. For generating the light emission, the oxidation of luminol proceeds for the first step. Metal ions and organometallic compounds are known to catalyze the oxidation of luminol with peroxide in strong alkaline solution (pH 10-13) [1, 2]. Enzymes, such as peroxidase and catalase, can catalyze the oxidation even in weak basic media, although their stability is rather poor [3].

In this paper, we propose an electrochemically-controllable chemiluminescence system by using a gold electrode modified with ferrocene-terminated alkanethiol as the catalyst for oxidizing luminol [4]. The surface attached ferrocene moieties were electrochemically oxidized to form ferricinium cation [5, 6], which catalyzed the oxidation of luminol effectively. The modified electrode was stable enough for the repetitive use. This system was adopted for detection of glucose in the presence of glucose oxidase since the light emission was detected even in the neutral and weak acid solution [4, 7].

3-Aminophthalhydrazide (luminol), hydrogen peroxide and 11-ferrocenyl-1-undecanethiol (FcC11SH) were used without further purification. A vacuum deposited gold substrate (thickness: 100 nm, on cleaned slide glass) was used as working electrode. Gold electrode was modified by dip-treatment in ethanol solution of FcC11SH (1 mM) for 1 h. After modification, the electrode was thoroughly washed by pure ethanol and water.

A three electrode electrochemical cell system was constructed in a standard quartz photospectrofluorometry cuvette to perform electrochemical and fluorescence measurements simultaneously. An Ag/AgCl (3 M NaCl) and Pt wire were used as reference and auxiliary electrodes, respectively. Electrochemical and electrochemi-luminescence (ECL) measurements were recorded at room temperature in 0.1 M buffer solution containing 0.1 M $NaClO_4$, luminol (100 µM) and hydrogen peroxide (10 mM) with different pH.

The potential dependence of chemiluminescence and linear sweep voltammogram of the FcC11SH modified gold were measured in the solution containing luminol and hydrogen peroxide. Anodic peaks of oxidation of ferrocenyl group and catalytic oxidation of luminol in solution were observed from +400 mV to +600 mV. The anodic peak current around +400 mV became larger than that measured in solution without luminol. When the potential became more positive than +400 mV, at which the oxidation of attached ferrocene moiety occurred, light emission was observed. The light intensity increased gradually as the electrode potential became positive. The light emission on the unmodified gold electrode was quite small in comparison with the FcC11SH modified gold. These results indicated that ferrocenyl groups of the self-assembled monolayer on gold catalyzed the oxidation of luminol in solution effectively.

We also investigated the effect of pH on light emission. The light intensity became larger as the pH value in solution became higher. The light intensity reached the maximum at around pH 10. It is noteworthy that luminosity was observed even when the weak acid solution was used.

We confirmed that ferricinium moiety participated to generate chemiluminescence reaction as similar to the results using free ferrocene species [8, 9]. In our case, attached ferrocene group participated for catalytic oxidation of luminol anion. When the electrode potential was positive than the redox potential of ferrocene, the oxidized ferrocenyl group catalyzed the oxidation of luminol [4].

In this system, since the light intensity could also be detected in the weak acid solution (~pH 6), the H_2O_2-generation processes can be monitored by using the present modified electrode system in neutral moiety, which is of particular interest in achieving oxidase-coupled assays of the enzyme substrate. We have already succeeded in detecting glucose/L-lactic acid in the presence of glucose oxidase / lactate oxidase by using the ECL reaction on FcC11SH modified electrode system [10]. The present system was also applied to simultaneous determination of glucose and ascorbic acid [11].

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