Enhanced Chemiluminescence of Bis(2,4,6-trichlorophenyl) Oxalate–Hydrogen Peroxide–Dyestuff System in the Presence of Polymer Particles

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Chemiluminescence property of bis(2,4,6-trichlorophenyl) oxalate–hydrogen peroxide–dyestuff system was examined in the presence of polymer particles. The chemiluminescence of the system was enhanced through an interaction between xanthene dyestuffs and polymer particles. For example, when using erythrosine B, the chemiluminescence intensity in the presence of the particles was about 20 times larger than that in the absence of them. It was clarified from preliminary experiments that the enhanced chemiluminescence with the particles was useful for the determination of H_2O_2 and dyestuff-labeled D-glucose.

Chemiluminescence (CL) has been examined in various analytical fields due to its high sensitivity and other advantages. New reaction phases or interfaces to change the CL property were reported for a trace analysis of metal ions, hydrogen peroxide (H_2O_2), dyestuffs, etc. The local microenvironment in ordered surfactant assemblies, such as micelles, reversed micelles, and bilayer membranes, resulted in significant improvements in the analytical performance of CL reaction systems.[1,2] Furthermore, porphyrin complex at a liquid–solid interface was utilized for a CL sensor of chloride ion as well as of adrenaline in a solution.[3,4]

On the other hand, polymer particles having diameters of submicro- or micrometer order have become of interest in development of functional materials. Takagi's group examined the adsorption ability of metal ions to polymer particles.[5,6] The metal-adsorption capability was also improved by introducing an imprinting structure of metal ion on the particles surface.[5,6] The polymer particles as functional materials has been thus found to be promising for progress in analytical and separation science.

In this study, we examined the CL property of peroxyoxalate–H_2O_2–dyestuff system in the presence of polymer particles. The obtained results should provide important information concerning analytical applications of the CL reaction in an emulsion.

All of the reagents used were of commercially available special grade. Ion-exchanged water was distilled for use. Bis(2,4,6-trichlorophenyl) oxalate (TCPO), H_2O_2, and dyestuff (eosin Y, rhodamin B, rose bengal, and erythrosine B) were purchased from Nacalai Tesque, Inc. The xanthene dyestuffs are well known as a common dyestuff to peroxyoxalate–H_2O_2 system. The polymer particles were prepared by seeded emulsion polymerization of divinylbenzene, styrene, butyl acrylate, and methacrylic acid, referring to the methods reported previously.[6] The particles had been named by unimprinted microspheres and their detail preparation procedure and characterization such as elemental analysis, size distribution, SEM, FT-IR, ESR, etc. had been described in the previous paper.[6] By scanning electron microscopy and particle grading analysis, the prepared polymer particles were confirmed to be neatly spherical particles having submicron diameters and a good distribution pattern.

The CL from an emulsion including polymer particles was examined by means of the batch-type detection method as described below. A 20 mL acetonitrile solution containing 1.0×10^{-3} M TCPO, 1.0×10^{-6} M dyestuff, and 37.5 mg dm^{-3} polymer particles was placed in a reaction flask and stirred by a stirrer. A 0.01 wt% H_2O_2 solution (1 mL) was added to the flask by a syringe to induce the CL reaction. The CL was detected by the photomultiplier tube equipped in CL detector (Model EN-21, Kimoto Electric, Inc.).

In order to confirm that there would be no CL of the polymer particles to TCPO–H_2O_2 system, the CL was examined without any dyestuff. No CL was observed in the presence of the polymer particles (37.5 mg dm^{-3}). Thus it was indicated that there would not be any contaminations of the polymer particles to affect the CL measurement.

We examined the CL profiles of TCPO–H_2O_2–dyestuff system in the absence and presence of the polymer particles and compared them each other. The CL intensity increased with increasing of the particles up to 37.5 mg dm^{-3}. However, poor reproducibility of CL intensity was observed above 37.5 mg dm^{-3}, due to aggregation of the particles. Figure 1 shows the CL profiles in both the absence and presence (37.5 mg dm^{-3}) of

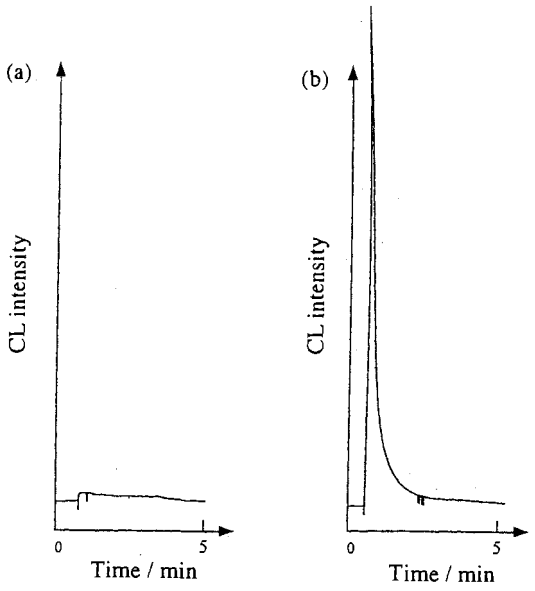

Figure 1. The CL profiles of TCPO–H_2O_2–erythrosine B system in the (a) absence and (b) presence of polymer particles. Conditions: 1.0×10^{-3} M TCPO, 1.0×10^{-2} wt% H_2O_2, 1.0×10^{-6} M erythrosine B, and 37.5 mg dm^{-3} polymer particles.

polymer particles when using erythrosine B. An emulsion containing polymer particles indicated enhanced CL; the ratios of two CL peak heights were about 4, 5, 6, and 20 for eosin Y, rhodamin B, rose bengal, and erythrosine B, respectively. Hydrogen peroxide reacts with the oxalic ester in a nucleophilic process yielding an intermediate. The intermediate interacts with the dyestuff to generate the excited singlet state which then emits in the usual fluorescence process. There would be an influence of the adsorption of the dyestuffs or other chemical species related to CL reaction onto the surface of the polymer particles. The adsorption must provide an effect to enhance the emission in the fluorescence process.

Since an emulsion containing polymer particles is able to be treated almost similarly to a homogeneous solution, it must be useful for a medium in flow-injection analysis (FIA). The CL of peroxyoxalate reagent has been used for the determination of a small amount of H_2O_2 in FIA and HPLC. The present CL system was tentatively applied to the determination of H_2O_2 by use of the present batch-type detector. Calibration curves were examined; an emulsion containing the polymer particles showed larger CL intensities than did a homogeneous solution at all H_2O_2 concentrations. The plots of CL intensity vs H_2O_2 concentration on log–log graph gave a good linearity (correlation coefficient, 0.998–0.999). Hydrogen peroxide in the emulsion and the homogeneous solution was determined over a range of 5×10^{-6}–1×10^{-3} M and 5×10^{-5}–1×10^{-3} M, respectively. The sensitivity for H_2O_2 in the emulsion was about 10 times higher than that in the homogeneous solution. This is interesting as a preliminary experiment for the application of the emulsion to FIA.

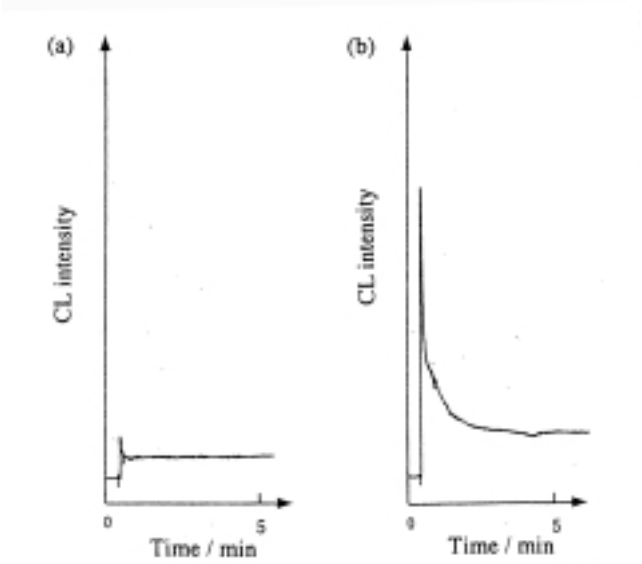

Figure 2. The CL profiles of TCPO–H_2O_2–ANTS-labeled D-glucose system in the (a) absence and (b) presence of polymer particles. Conditions: 1.0×10^{-3} M TCPO, 1.0×10^{-2} wt% H_2O_2, 1.0×10^{-6} M ANTS-labeled D-glucose, and 37.5 mg dm^{-3} polymer particles.

8-Aminonaphtalene-1,3,6-trisulfonic acid (ANTS) is known as a labeling reagent for biological constituents such as saccharides. The compound labeled with ANTS can be also detected with peroxyoxalate reagent. An excess of D-glucose was labeled with 1×10^{-6} M ANTS according to the usual method, giving 1×10^{-6} M ANTS-labeled D-glucose. The enhanced CL of ANTS-labeled D-glucose was observed in the presence of the polymer particles. The CL profiles are shown in Figure 2. The glucose in the absence and presence of the particles were determined over a range of 5×10^{-9}–1×10^{-6} M and 2×10^{-8}–1×10^{-5} M, respectively. The enhanced CL with the polymer particles was found to be useful for sensitive detection of dyestuff-labeled compounds.

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