

Development of an optical detection system
assembled with an organic light emitting diode
and an organic thin film based photodiode and
its application to flow analysis

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論 文 名 : Development of an optical detection system assembled with an organic light emitting diode and an organic thin film based photodiode and its application to flow analysis
(有機発光ダイオードと有機薄膜フォトダイオードからなる光学検出システムの開発とその流れ系分析への応用)

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論 文 内 容 の 要 旨

In recent years, many needs for low-cost and disposable devices for use in environmental and clinical analyses have stimulated for the development of compact portable detection systems. Developments of a miniaturized total analysis system (μ -TAS) or a lab-on-a chip (LOC) system, where analytical procedures, such as separation, reaction and detection are integrated onto a single microchip, have been a hot subject and attractive to researchers in interdisciplinary fields. Such analytical systems have many advantages such as rapid analysis, easy portability, reduction of separation time, and negligible consumption of reagents due to their micrometer size flow channels and have been applied to numerous fields in chemistry and life science. Functional integration of light sources and photo-detectors within monolithic substrates is expected to be a key issue for the development of micro-fluidic analytical systems with an optical detector. In the past a decade there have been reports on developments of optical systems fabricated by using an inorganic light emitting diode (LED) as the light source and a silicon photodiode as the detector. Nowadays, a new optical system fabricated for μ -TAS or LOC systems has been assembled with an organic light emitting diode (OLED) as the light source and an organic photodiode (OPD) as the photo detector. In this case, since the emission wavelength of the most used OLED is relatively wide, even when a band-pass filter was used for cutting off the longer wavelength light overlapped with fluorescence of analyte, background light still interfered in fluorescence detection. If the emission light can be narrowed spectrally, the background of fluorescence detection would be reduced and the sensitivity is expected to be remarkably enhanced. Therefore, we try to develop an integrated optical detection system for a micro-fluidic device by using an OLED based on rare earth complexes as a light source to make emit light band narrow and an OPD as a photo detector with high sensitivity to the light at a desired wavelength region for analytes.

In Chapter 1, in order to describe the aim of this research, recent developments in optical detection methods for microfluidic systems are introduced as the background of the present research. In this chapter, the examples of absorbance, fluoresce, chemiluminescence detection are included. Further more, the advantages and disadvantages of the microfluidic analytical system are introduced.

In Chapter 2, the protocol of fabricating the OLED and the OPD is described, and the fundamental performances of the prepared devices are evaluated. In addition, application of the prepared devices for the photometric and fluorometric determination of phosphate and alkylphenol polyethoxylates (APE) is

described.

In Chapter 3, a compact photometric detection system for phosphates was developed by assembling an OLED based on a europium complex ($\text{Eu}(\text{DBM})_3\text{bath}$) as a light source and an OPD based on a double layers of $\text{CuPc}/\text{C}_{60}$ as a photo-detector onto a microchip. For the determination of phosphate, an ion-association reaction between malachite green (MG) and a molybdenum-phosphate complex was utilized because the ion-association complex has absorption band between from 600 nm to 700 nm, which fit very well with the emission peak wavelength of the fabricated OLED. Then, the optical system assembled onto the microchip was applied for the flow injection determination of phosphate by using the reagent solution containing MG and an ammonium molybdate in sulfuric acid, the detection limit ($S/N=3$) of 20 ppb was obtained. Finally, the present optical system was successfully applied to the determination of phosphate in river water samples. This suggests that the assembled optical system with the OLED as a light source and the OPD as a detector can be an economical and compact analytical system for the determination of phosphate in environmental water.

In Chapter 4, a compact fluorescence detection system for APE was constructed from an OLED based on a terbium complex, ($\text{Tb}(\text{acac})_3\text{bath}$) as a light source and an OPD fabricated from a bulk hetero-junction of two layers of $\text{TPTPA}/\text{C}_{70}$ as a photo-detector on a microchip. This combination of the OLED and the OPD is suitable for fluorometric detection of resorufin, which is an enzymatic product of Amplex Red for a reaction with a conventional labeling enzyme, horse radish peroxides (HRP). Then, the resulting fluorometric detection system was applied to a competitive enzyme-linked immunosorbent assay for APE, where an anti-APE antibody was immobilized on the surface of the magnetic microbeads or on the surface of the channel of the microchip. Finally, the present fluorometric detection system was successfully applied to the determination of APE in river water samples. The detection limit ($S/N=3$) of 2 ppb was obtained. This detection limits satisfy Japanese regulation for the determination of APE in tap water samples.

In Chapter 5, the rare earth metal ions and the $\text{YVO}_4:\text{Eu}$ fluorescence phosphor were applied to chemiluminescence detection and the determination of MG. Namely, the chemiluminescence (CL) kinetic characteristic of the reaction and possible of CL reaction mechanism by using rare earth metal ions as the sensitizer in flow injection system were demonstrated. Then, the $\text{YVO}_4:\text{Eu}$ fluorescence phosphor in the determination of MG have been studied.

In Chapter 6, results of the present research are summarized and concluded.

In conclusion, the compact microfluidic analytical system developed in this research has successfully applied to the photometric and fluorometric analysis. The result obtained in the research will be a valuable and useful contribution to the development of new microfluidic analytical system.