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Short Communication

Multi-color microfluidic electrochemiluminescence cells

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ABSTRACT

We demonstrated multi-color microfluidic electrochemiluminescence (ECL) cells. 5,6,11,12-Tetraphenylnaphthacene (rubrene), 9,10-diphenylanthracene (DPA), tetraphenyldibenzoperiflanthene (DBP)-doped rubrene, and 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) dissolved in a mixed organic solvent of 1,2-dichlorobenzene and acetonitrile in the ratio of 2:1 (v/v) were used as yellow, blue, red, and green ECL solutions, respectively. Light emissions were confirmed using simple-structured ECL cells consisting of two indium tin oxide (ITO) coated glass substrates with an SU-8 spacer of thickness varying from 0.9 to 6 μm. The SU-8-based microfluidic ECL cells were fabricated using photolithography and heterogeneous bonding techniques through the use of epoxy- and amine-terminated self-assembled monolayers. The emitting layers were formed on-demand by injecting the chosen ECL solutions into the microchannels sandwiched between ITO anode and cathode pairs. Multi-color ECL was successfully obtained at the light-emitting pixels. The microfluidic ECL cells with DBP-doped rubrene solution showed a maximum luminance of 11.6 cd/m^2 and the current efficiency of ca. 0.32 cd/A at 8 V. We expect that the proposed microfluidic device will be a highly promising technology for liquid-based light-emitting applications.

1. Introduction

Organic light-emitting diodes (OLEDs), which consist of solid-state organic semiconductor layers sandwiched between two electrodes, have attracted attention for next-generation full-color flat panel displays and lighting applications because of advantages such as self-emission, wide view-angle, reduced weight, and reduced panel thickness [1]. Several fabrication methods for multi-color OLEDs have been proposed, including vacuum deposition of small molecular organic materials through a shadow mask [2] as well as solution processes such as screen [3,4] and ink-jet printing [5] for electroluminescent polymers. On the other hand, light-emitting devices based on liquid-emitting materials have been reported, such as liquid OLEDs [6,7] and electrochemiluminescence (or electrogenerated chemiluminescence) (ECL) cells [8–15]. Similar to OLEDs that employ solid-state emitters, liquid OLEDs and ECL cells can provide self-emission under appropriate applied voltages. Liquid OLEDs are novel light-emitting devices that employ a liquid organic semiconductor as the emitting layer, as first reported by Xu and Adachi in 2009 [6]. Liquid organic semiconductors have the unique property of being in a liquid phase at room temperature without a solvent. Electroluminescence (EL) is generated by the radiative recombination of electrons and holes injected into the liquid organic semiconductors. Although, liquid organic semiconductors are promising materials for novel organic electronic devices, there are few materials available for use as the emitting material in liquid OLEDs. In contrast, the emitting layer of traditional ECL cells consists of well-established OLED materials dissolved in organic solvents such as acetonitrile [8], 1,2-dichlorobenzene [8,11], benzonitrile [9], and *N*,*N*-dimethylformamide [12]. Several studies on ECL have reported on the use of fluorescent dyes [8,12,14] and phosphorescent dyes [9]. ECL emission was produced by the collision of radical anions and cations generated at the cathode and anode surfaces, respectively. In the current technology, liquid OLEDs and

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ECL cells typically have a simple device structure fabricated by sandwiching a selected liquid emitter between two glass substrates with electrodes. The gap between the electrodes was preserved by approximately a few micrometers to several hundred micrometers using spacer materials such as insulating films [11], wires [12], glass beads [13], and glass rods [14]. The use of liquid emitters as the emitting layer is expected to provide flexible and crack-free light-emitting layers under repeated bending. Although several spacer structures could be easily fabricated and a single-color emission could be obtained from conventional designs of liquid OLEDs and ECL cells under an appropriate voltage, it is difficult to obtain the patterned liquid emitters and multi-color light emission. Therefore, pattering methods for the several liquid emitters on a single device are an important step for developing functional multi-color liquid-based light-emitting devices.

In our previous work, we proposed microfluidic technologies to obtain patterned liquid emitters on a single device [16]. The negative photoresist SU-8-based microfluidic device with a matrix of light-emitting pixels was fabricated using photolithography and heterogeneous bonding technique through the use of amine- and epoxy-terminated self-assembled monolayers (SAMs). In this microfluidic device, the thickness of the microchannels sandwiched between two indium tin oxide (ITO) electrodes was designed to be approximately 6 μm. The fabricated microfluidic device, which we named "microfluidic OLED", successfully exhibited EL of a liquid organic semiconductor injected into the microchannels.

In this study, to obtain multi-color light emission from liquid emitters on a single device, we tested four-color ECL solutions using simple-structured ECL cells and demonstrated single- and multi-color ECL using microfluidic ECL cells. The spacer structure of simple-structured ECL cells was fabricated via photolithography with SU-8. The spacer thickness was controlled to be between 0.9 and 6 μm. For evaluating multi-color emissions, we used the same microfluidic device reported in our previous study [16]. The emitting layers of the microfluidic ECL cells were formed on-demand by simply injecting small amounts of the chosen ECL solutions into the microchannels. The fabricated microfluidic ECL cells with ECL solutions successfully exhibited light emissions under a lower driving voltage when compared with a liquid organic semiconductor [16].

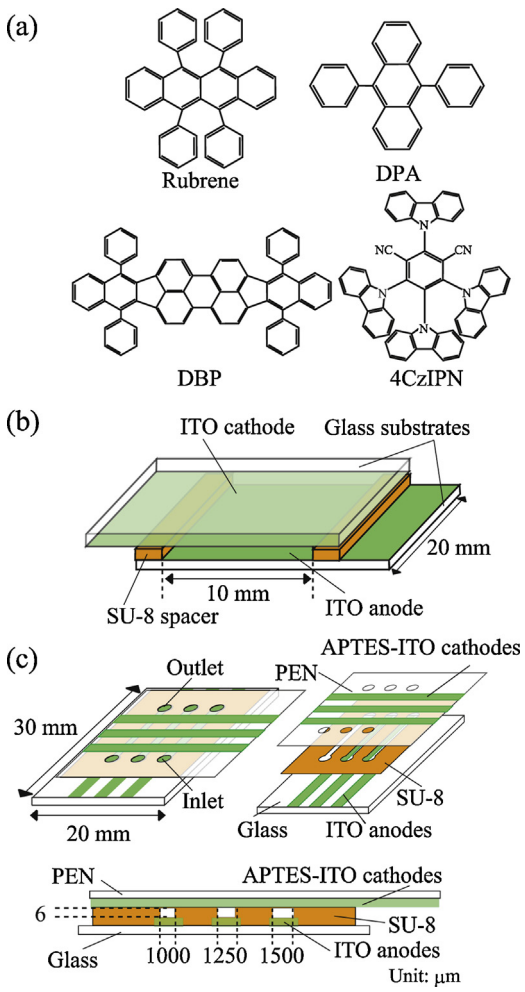

Fig. 1. (a) Chemical structures of the employed emitting materials. (b) Design of the simple-structured ECL cell. The ECL solution was sandwiched between two ITO coated glass substrates with single-micrometer-thick SU-8 spacer. (c) Design of the microfluidic ECL cells. The microfluidic ECL cells have a 3 × 3 matrix of light-emitting pixels in the SU-8 microchannels.

2. Experimental procedure

ECL materials are based on fluorescent emitter, as shown in Fig. 1(a). All the materials were dissolved in a mixed organic solvent of 1,2-dichlorobenzene and acetonitrile in the ratio of 2:1 (v/v), and 1,2-diphenoxyethane was introduced into the solution at a concentration of 180 mM to enhance ECL performance [8]. 10 mM 5,6,11,12-tetraphenylnaphthacene (rubrene) and 50 mM 9,10-diphenylanthracene (DPA) were used as yellow and blue emitters, respectively. Here, we demonstrated 0.3 mM tetraphenyldibenzoperiflanthene (DBP) [17]-doped 10 mM rubrene dissolved in the solvent as red emitter because DBP-doped rubrene has been reported as the solid-state red OLED emitting layer [18–20]. 5 mM 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) was applied as green emitter. In particular, 4CzIPN shows high photoluminescence quantum yield and EL efficiency by thermally activated delayed fluorescent (TADF) system, which reduces the energy gap between the triplet excitons (T_1) and the singlet excitons (S_1), promoting an up-conversion of T_1 into S_1 by thermal activation [21–24]. The ECL solutions were degassed with N_2 gas babbling for 3 min prior to use.

Fig. 1(b) shows the design of the ECL cell which has a simple structure with the ECL solution sandwiched between two ITO coated glass substrates with the SU-8 spacer. The epoxy-based negative photoresist SU-8 has been widely used as a structural material in microelectromechanical systems (MEMS) devices owing to its excellent lithography properties, thermal stability, and good solvent resistance. The light-emitting area was 10 mm × 20 mm. ITO with a 135-nm-thick layer and a sheet resistance of 10 Ω/sq was used as both anode and cathode substrates. The simple-structured ECL cell preparation is as follows. The SU-8 was spin-coated on the anode substrate and exposed through a photomask by 365-nm UV light to obtain a spacer structure. The substrate was developed in the SU-8 developer for removing unexposed parts, followed by hard baking at 180 °C for 30 min. The spacer thickness d was controlled using the SU-8 series. SU-8 2000.5, SU-8 2002, and SU-8 3005 were used for 0.9, 2.6, and 6-μm-thick spacers, respectively. The surfaces of both anode and cathode substrates were cleaned with acetone, followed by isopropyl alcohol, and then dried. The ECL solution was dropped on the light-emitting area of the anode substrate and subsequently covered with a cathode substrate. Finally, the anode and cathode substrates were clipped tightly.

The microfluidic ECL cells have a 3 × 3 matrix of light-emitting pixels in the SU-8 microchannels, as shown in Fig. 1(c). The microchannels were sandwiched between the ITO on a glass substrate (anode substrate) and the polyethylene naphthalate (PEN) film with the amine-terminated SAM-coated ITO (cathode substrate). The widths of the microchannels were 1000, 1250, and