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Fabrication of Novel Reflective–Emissive Dual-mode Display Cell Based on Electrochemical Reaction

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We successfully demonstrated a novel reflective–emissive dual-mode display (DMD) cell with electrochromic and electrochemiluminescence reactions. This DMD cell has simple structure and allows the selection of reflective or emissive mode by selecting DC or AC driving, respectively.

Present display devices are classified into two categories, reflective and emissive modes. Reflective mode displays such as printed material and electronic papers (EP) have high visibility under daylight conditions but are useless in dark place. Although the other emissive mode displays such as plasma display panel (PDP) and organic light-emitting diodes (OLED) can be seen clearly in a dark room, these are difficult to see under direct sunlight. In addition, reflective displays are driven by lower energy consumption than emissive displays. Therefore, dual-mode display (DMD) is desired to exploit both advantages. The DMD has both reflective and emissive display mechanisms, and we can choose either as the situation demands. However, it is difficult to realize dual-mode display because it must possess two display mechanisms in the same device. In the past, there were only a few reports of dual-mode display using different display mechanisms.[1] However, those reported dual-mode displays had complex structure and driving mechanism.

Electrochromism (EC) is defined as reversible color change by electrochemical redox reaction. Corresponding reflective display devices are called electrochromic displays (ECD) which have many advantages such as high visibility, memory effect, and color variation. Therefore, ECD has been attracting significant interest as a potent candidate in paper-like reflective displays.[2–4] Electrochemiluminescence (ECL) is a well-known light emission phenomenon arising from electrochemical reaction, and emission occurs from an excited state formed by collision of a cation radical and anion radical generated at a cathode and anode, respectively.[5] ECL devices are driven by direct current (DC) and alternate current (AC). The response time of emission using a common DC method is slow (approximately a second).[6] This is because the emission occurs after diffusion of cation and anion radicals generated from opposite electrodes. In AC-driven ECL (AC-ECL), both cation and anion radicals are generated from one electrode due to repeated change of electrode polarity. AC-ECL improves the turn-on response by colliding with cation radical and anion radical at near the one electrode (millisecond time scale).[7,8]

In order to achieve dual-mode operation, we focused on an electrochemical reaction which can lead to both reflective display of EC and emissive display of ECL. Then we invented a novel DMD cell model with reflective and emissive modes by combining both EC and ECL materials in a simple cell as schematically represented in Figure 1. The expected mechanism of the novel DMD is described below. EC material is fixed on one electrode as reflective layer, and ECL material is fixed on the other electrode as emissive layer. This DMD cell is fabricated by sandwiching an electrolyte layer between these electrodes. We can use both the reflective mode of EC and emissive mode of ECL as the situation demands by selecting operation method. Reflective mode is driven by DC voltage (Figure 1a). Under the application of DC voltage, the color change of EC material occurs by oxidative or reductive in the reflective layer. In contrast, emission of ECL material does not occur because only one cation radical or anion radical is generated in emissive layer. Therefore, we can realize the reflective mode by applying DC voltage. On the other hand, emissive mode can be achieved by applying AC voltage (Figure 1b). When applying AC voltage, the emission of ECL material occurs by generation of both cation radical and anion radicals in the emissive layer. Meanwhile in the reflective layer, detectable color change does not occur because of very fast consecutive oxidation and reduction. As a result, we can get only emission by AC voltage application. If this DMD model is correct, we can realize DMD devices with simple structure and current driving circuit. In this letter, we demonstrate behaviors of this DMD cell.

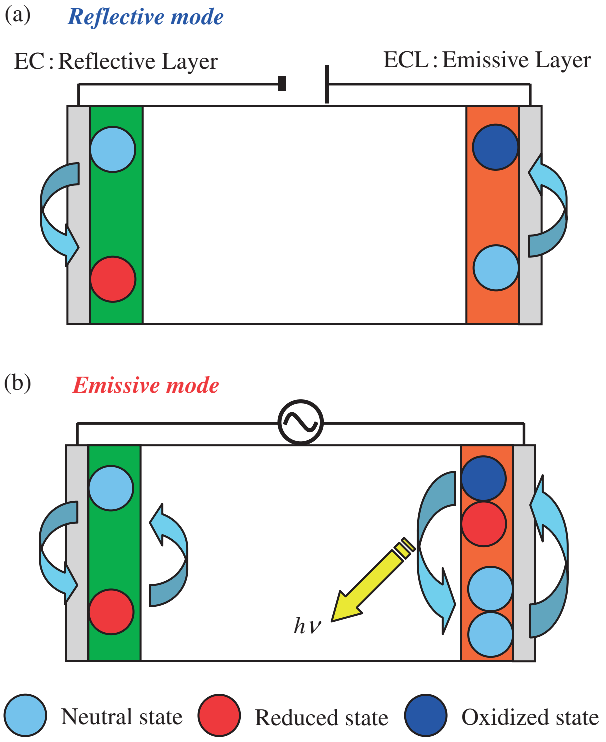
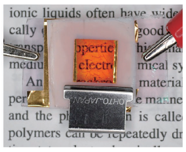


Figure 1. Driving mechanisms of invented novel DMD model at (a) reflective mode and (b) emissive mode.

(a) Initial state



(b) ***Reflective mode*** (c) ***Emissive mode***

Figure 2. Photographs of DMD cell at (a) initial state (this orange color is based on Ru complex), (b) reflective mode under the application of DC voltage, and (c) emissive mode by applying AC voltage.

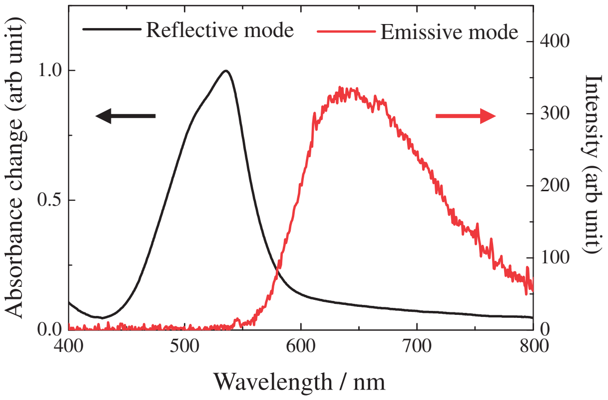


Figure 3. Emission spectrum and difference absorption spectrum of DMD cell at (red line) emissive mode and (black line) reflective mode.

The DMD cell was prepared as follows. Solvent-soluble poly(ethylene terephthalate) (PET) derivative (VYLON200, TOYOBO Co., Ltd.) and $[Ru(bpy)_3]^{2+}$ complex ($[Ru(bpy)_3]Cl_2$, Tokyo Chemical Industry Co., Ltd.) were used as EC and ECL material, respectively. Dimethyl sulfoxide, DMSO (Sigma-Aldrich Co.) and tetrahydrofuran, THF (Kanto Chemical Co., Ltd.) were used as solvent after removing water by molecular sieves. Tetrabutylammonium perchlorate (TBAP) (Kanto Chemical Co., Ltd.) as a supporting electrolyte, poly(vinyl butyral) (PVB) (BX-1, Sekisui Chemical Co., Ltd.) as a host polymer for the gel electrolyte, hexamethylene diisocyanate-based polyisocyanate (DURANATE P-301-75E, Asahi Kasei Chemicals Corporation) as crosslinking agent and ion-exchange membrane (Flemion, Asahi Glass Co., Ltd.) were used as received.

PET and polyisocyanate were dissolved in THF in a ratio of OH:NCO = 1:2. PET film as EC layer was spin-coated with 10 wt % PET solution on an ITO glass electrode and then heated at 100 °C for 1 h to crosslink. A Flemion-coated ITO glass electrode was soaked in 10 mM aqueous $[Ru(bpy)_3]Cl_2$ solution for 12 h to prepare the ECL-material-modified electrode. One gram of the 50 mM TBAP/DMSO solution was mixed with an appropriate amount of PVB, and the resulting mixture was allowed to stand for a week to obtain a PVB-based gel-like electrolyte.[9] A DMD cell was fabricated by sandwiching gel electrolyte with EC- and ECL-material-modified electrodes keeping an interelectrode distance of 300 µm by using Teflon spacer.

We confirmed behaviors of the invented DMD cell (Figure 2a). Figure 3 (black line) shows the differential absorption spectrum of a DMD cell under application of DC −4 V to the EC electrode. In the EC layer, crosslinked PET film was clear and colorless in the neutral state and changed from colorless to magenta (absorption peak: 530 nm) in the reduced state. Also in the ECL layer, the ion-exchange membrane (Flemion film) was clear and colorless, but the Ru complex was orange in the neutral state. Therefore, the EC layer and the ECL layer were clear colorless and orange in the neutral state, respectively. In Figure 2a, the orange color of the initial state of the DMD cell resulted from the absorption of the Ru complex in the ECL layer. After switching, in reflective mode, the color of the EC layer changed from colorless to magenta by electrochemical reduction. However, the color of the ECL layer was not changed by electrochemical oxidation. As a result, the color of the DMD cell varied from bright orange to deep red. A photograph of this reflective-mode DMD cell is shown in Figure 2b. This color change is attributed to subtractive color mixture of magenta and orange. This is indicated by difference absorption spectra of the DMD cell before and after applying DC −4 V in Figure 3. The Ru complex had broad absorption band around 450 nm. Hence, the absorption spectrum of the EC layer in reduced state overlapped with that of Ru complex. If we use the original absorption spectrum, it is difficult to clarify the origin of the color change. Therefore, we measured the differential absorption spectrum of DMD cell with reference to the initial absorption spectrum, in order to clarify that this color change resulted from the EC of the PET film. In addition, ECL was not observed because oxidative reaction of Ru complex occurred in the ECL layer. In this way, we were able to obtain only reflective mode by applying DC voltage.

Next, we tried to demonstrate emissive mode by applying AC voltage. Figure 3 (red line) shows the emission spectrum of a DMD cell under application of AC voltage of 4 V at 50 Hz. The emission spectrum and photograph of the cell (Figure 2c) clearly indicated the generation of AC-ECL from Ru complex. This is because both oxidative and reductive reactions of Ru complex occur alternately by applying AC voltage. Also in the EC layer, both reductive reaction from neutral to anion radical state and oxidative reaction from anion radical to neutral state occur as with the ECL layer. In other words, PET film repeated color change between colorless and magenta quickly. The time of a half cycle at 50 Hz is a mere 0.01 s. Sufficient reduction for detectable color change did not occur within 0.01 s because of the slow response time of EC reaction.[10] Therefore, we could not recognize color change of DMD cell by the naked eye before and after applying AC voltage. Thus we could obtain only emission of ECL by applying AC voltage. As seen from the above results, we demonstrated that the invented DMD cell was effective for dual-mode driving. In this DMD cell, we could achieve the reflective mode and emissive modes at lower voltage. The DMD behaviors of the cell were obtained by applying over 2.8 V. However, in the case of low-voltage application, we could not obtain sufficient color change and emission intensity.

Therefore, we applied AC 4 V for emissive-mode operation according to ref 8. Also, DC 4 V was chosen to emphasize the fact that this DMD can be controlled by only selecting DC or AC driving. The lifetime of our DMD cell was not so long at this stage. The unoptimized lifetime of emissive mode was about 1 h, and long-term switching stability of reflective mode was over 100 cycles. The lifetime would depend on driving voltage and the type of EC and ECL material. Therefore, we are now studying dual-mode behaviors and mechanisms of various DMD cells with other couples of EC and ECL materials in order to improve the performance of the DMD cell. The driving voltages of the DMD cell were varied in accordance with combination of EC and ECL materials. Further study is in progress to improve the performance of the DMD cell (color, emission, and long-term stability).

In conclusion, we successfully demonstrated a novel DMD cell based on EC and ECL. The DMD cell achieved dual-mode behaviors by the application of DC or AC voltage. Furthermore, this model will achieve DMD using combination of other EC and ECL materials. Those DMD cells would develop DMD application such as color variations of reflective and emissive mode, low power consumption, and simplified cell configuration.

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