Novel organic multi-color electrochromic device for e-paper application

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Abstract

Electrochromism is reversible color change by electrochemical reaction. In this paper, we designed novel organic electrochromic device based on bispyridinepyrrole derivatives and phenothiazine molecule. The EC properties of the devices were analyzed and discussed for the possibility to multi-color representation

1. Introduction

Electrochromism (EC) is known as reversible color change induced by an electrochemical redox reaction. The EC technologies are applied for optical modulation devices such as smart windows, dimming mirrors, digital signage, and electronic paper.[1-4] In order to develop the information display by using EC technologies, representation of multi-color in single device is extensively desired.

Concerning with multi-color EC devices, conventional way is use of EC materials, which can receive multiple redox reaction related to color change, such as conductive polymers and organic molecules.[5-6] However, higher oxidized or reduced states of these materials are usually unstable; therefore, it is difficult to keep certain color at higher voltages and to have enough cycle stability. Other way for achieving multi-color EC reaction is utilized of local surface plasmon resonances (LSPR) of metal nanoparticles. Depending on the size and shape of electrodeposited metal nanoparticle, the device can show various chromatic colors based on LSPR of the metal nanoparticles.[7-8] Although the metal nanoparticles are stable in comparison with higher oxidized or reduced states of organic compounds, the EC devices requires precise driving techniques.

Among these methods for achieving multi-coloration, we are focusing on the combination of several kinds of small organic EC molecules. The EC molecules, especially those of low molecular weight, can show vivid color changes from clear colorless state to various colors.[9] In the case of the EC devices containing multiple EC molecules, a number of the working electrodes should be stacked in single device for controlling each EC reaction independently.[10-11] Furthermore, the EC molecules must be adsorbed on the working electrodes for preventing color diffusions. For this reason, the structures of the multi-color devices tend to be quite complicated configuration.

In order to simplify the device structures, we aimed to fabricate the multi-color EC device with the simplest configuration, i.e. sandwiching the EC solution between two electrodes. We also employed quite simple EC solution just dissolving two kinds of EC molecules, i.e. combination of cathodic EC molecule and anodic EC molecule, without some kinds of adsorbing treatments.

However, unfortunately, the control and the selection of multi-coloration are quite difficult to achieve by using the simplest sandwiching configuration. When cathodic EC molecule receive electrochemical reduction at certain electrode, electrochemical oxidation of anodic EC molecule MUST occur at opposite electrode in order to compensate the charge consumption in the device. This means that these electrochemical oxidation and reduction always occur in pairs at the same time, and consume the same amount of charge. Therefore, since the EC device show only single color that the two colors are mixed together, we cannot select certain single color from the two EC molecules.

In order to overcome this critical issue, the charge consumption at the working electrode must be compensated by some mechanism without electrochemical redox reaction of the EC molecules. In this research, we employed the ITO particle-modified electrode having porous morphology and large surface area as counter electrode. Because the ITO particle-modified electrode have large capacitance due to formation of electrical double layer, the charge consumption of the EC reaction on working electrode is expected to be compensated by formation of the double layer. If the charge consumption is compensated successfully, we are able to obtain certain color among contained EC molecules selectively.

In this paper, we fabricate novel EC device with the configuration of two facing electrodes; working electrode is flat ITO electrode and counter electrode is ITO particle-modified electrode. As the EC molecules, we employed both cathodic EC molecule of bispyridinepyrrole derivatives (**D-1**) and anodic EC molecule of phenothiazine (**PT**; chemical structures are shown in Fig. 1).

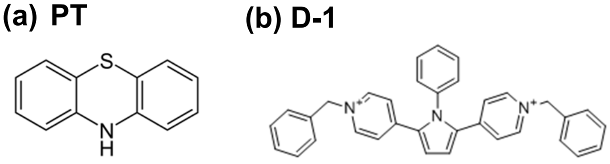


Fig. 1 *Chemical Structures of (a)* ***PT*** *and (b)* ***D-1*** *molecules used in this report.*

2. Experimental

2.1. Materials

Phenothiazine (**PT**), Dimethylsulfoxide (DMSO), tetra-n-buthylammonium perchlorate (TBAP) were purchased from Tokyo Kasei Industries Ltd. ITO nanoparticle dispersion liquid was purchased from Sigma Aldrich. Bispyridinepyrrole derivative (**D-1**) was obtained from RICOH corporation.

2.2. Preparation of modified electrodes

ITO nanoparticle dispersion was dropped onto a planar ITO substrate and spin coated at 500 rpm for 15 s followed by 1500

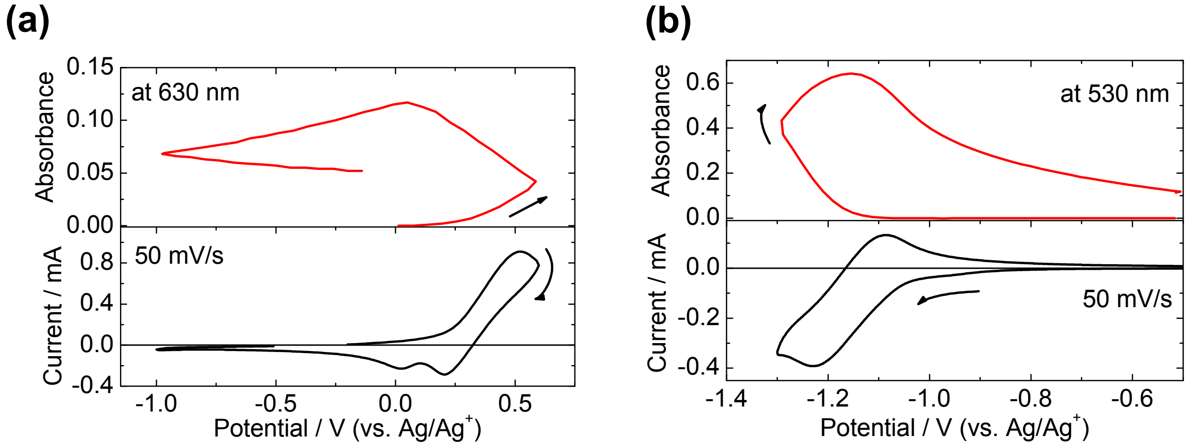


Fig. 2 *Change in absorbance (top) and CV curves (bottom) of (a)* ***PT*** *and (b)* ***D-1*** *molecule (Scan rate = 50 mV/s).*

rpm for 15 s. After spin coating, ITO-nanoparticle film on ITO substrate was heated to 230 ºC for 1 h on hot plate. The ITO-nanoparticle film was measured to be approximately 1.5 µm using a surface profiler (Kosaka Laboratory Ltd., model Surfcorder ET 4000A).

2.3. Preparation of the EC solutions

All the experiment conducted at the ambient laboratory temperature (20–25 °C). The electrolyte solution was prepared by dissolving **PT** (5 mM) and TBAP (100 mM) or **D-1** (5 mM) and TBAP (100 mM) in DMSO. These EC solutions were used for electrochemical measurements of their EC properties in 3-electrode cells. The 3-electrode cell was equipped with ITO electrode as a working electrode and Pt wires as a counter electrode, and an Ag/Ag$^+$ electrode as a reference electrode.

The DMSO solution containing both electrochromic materials of **PT** (10 mM) and **D-1** (10 mM) and TBAP (200 mM) was also prepared for fabrication of two-electrode device. The two-electrode device was fabricated by sandwiching the EC solution between ITO electrode (working) and ITO nanoparticle-modified electrode (counter) keeping inter-electrode distance of 700 µm by spacers. The effective electrode area of the EC device was 1.0 × 1.0 cm^2.

2.4. Electrochemical measurements

Cyclic voltammogram (CV) were measured by ALS model 660A potentiostat/galvanostat equipped with a computer. The scan rate was 50 mV/s. Absorption spectra were recorded in situ by using Ocean Optics USB2000 diode array detection system.

3. Result and discussion

3.1. EC properties of the solutions in 3-electrode cell

First, we measured fundamental EC properties of **PT** and **D-1** molecule in the solution by using 3-electrode cell. Fig. 2 shows CV and Absorbance changes of the **PT** (Fig. 2a), and those of **D-1** molecule (Fig. 2b). In Fig. 2a, as the potential was scanned from –1.0 V in positive direction, anodic current was observed from 0.1 V. This anodic current can be attributed to the current for electrochemical oxidations of **PT**. From 0.1 V, the absorbance at 630 nm increased as a result of the oxidation of **PT** on the ITO electrode and the solution changed to green color. On the other hand, in Fig. 2b, as the potential was scanned in negative direction, cathodic current was observed from –1.1 V. This cathodic current can be attributed to the current for electrochemical reductions of **D-1** molecule. From the potential of –1.1 V, the absorbance at 530 nm increased according to reduction of **D-1** on the ITO electrode, resulting in magenta color.

3.2. EC properties of novel 2-electrode EC device

Then, we investigated EC properties of 2-electrode EC device containing both cathodic EC material of **D-1** and anodic EC material of **PT**. Fig.3 shows CVs and absorbance changes of the EC device having counter electrode of the ITO particle-modified electrode or flat ITO electrode.

In the case of the EC device without ITO particle modified electrode, when the potential was scanned from 0 V to positive direction (Fig. 3a), redox current ascribed to oxidation of PT on the working electrode was observed from 1.2 V. Corresponding to the redox reaction, the absorbance of both **PT** (630 nm) and **D-1** (530 nm) simultaneously increased from 1.2 V, resulting in dark red color. This is because that the electrical charge consumed by oxidation of **PT** molecule was compensated by reduction of **D-1** molecule at the counter electrode. In the case of the EC device having ITO-particle modified electrode, in contrast, only the absorbance of oxidized **PT** molecule (630 nm) increased from 0.7 V as the oxidation current flow. At this time, the EC device showed green color, which corresponded electrochemically oxidized **PT** molecule. This electrochemical response indicated that ITO-nanoparticle modified electrode effectively compensated equivalent amount of charge consumed by oxidation reaction of **PT** on working electrode without electrochemical reaction of cathodic **D-1** molecule. Over 1.2 V, the absorbance at 530 nm, i.e. absorption of reduced **D-1** molecule, began to increase as a result of the reduction of **D-1** on the ITO electrode and showed deep red.

When the potential was scanned from 0 V in negative direction, similar behaviours were observed. In the case of the EC device without ITO particle modified electrode, when the potential was scanned from 0 V to negative direction (Fig. 3b), redox current ascribed to reduction of D-1 was observed from –1.2 V. Corresponding to the redox reaction, the absorbance of both **PT** (630 nm) and **D-1** (530 nm) in the EC device simultaneously increased from –1.2 V, resulting in dark red color. This is because that the electrical charge consumed by reduction of **D-1** molecule was compensated by oxidation of **PT** at the counter electrode. In

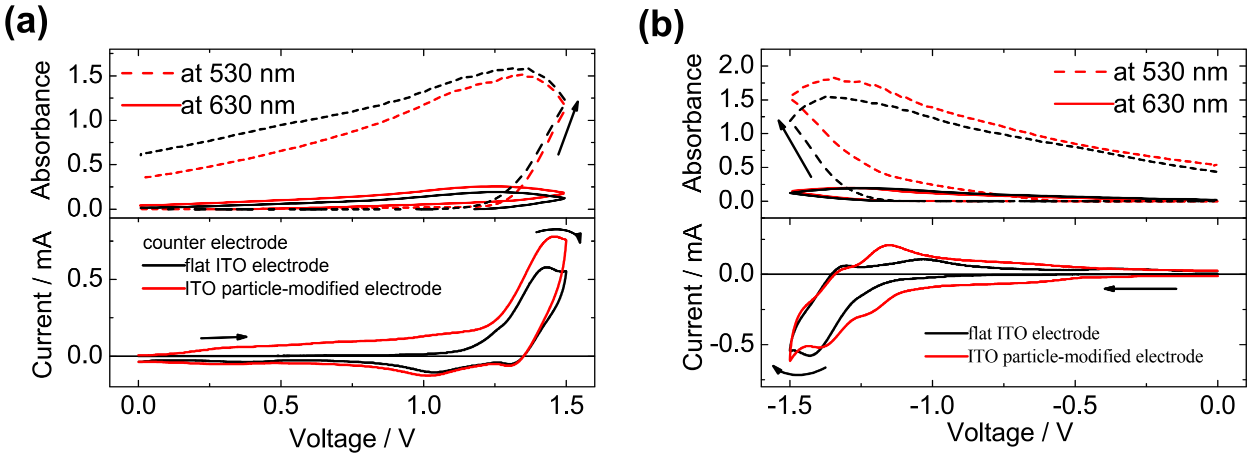


***Fig. 3** Change in absorbance (top) and CV curves (bottom) of devices having flat ITO electrode (as working side) and flat ITO electrode or ITO particle-modified electrode (as counter side) (a) in positive direction (b) in negative direction.*

the novel EC device, the absorbance of only reduced state of **D-1** molecule (530 nm) increased from –0.7 V corresponding to the reductive current flow. In the voltage range from -0.7 V to -1.2 V, the EC device showed magenta color due to the coloration of **D-1** molecule. This phenomenon was the same as the previous positive voltage scanning. Over -1.2 V, the absorbance of oxidized state of **PT** (630 nm) also appeared because oxidation of the **PT** molecule on counter ITO participle-modified electrode had started, resulting in deep red colors.

From these results, the possibility for achieving multi-color EC representation using the novel EC device was indicated.

3.3. Tunable multi-colorations in this EC device

Finally, we measured the optical properties of the EC device having flat ITO electrode and ITO particle-modified electrode in order to confirm multi-color representation. Fig.4 shows the absorption spectra of the EC device with ITO particle-modified electrode under application of certain positive voltages (±1.1 V ~ ±1.3 V). When positive voltage of 1.1 V was applied to the working electrode (flat ITO electrode side), the absorption band of oxidized PT molecule appeared at around 630 nm because only **PT** molecule received electrochemical redox reaction on working electrode. As the result, color of the device changed from light yellow to green (Fig.5a). In this voltage, the electrical charge consumed by oxidation of **PT** molecule was compensated by formation of electrical double layer on the ITO particle-modified electrode having large surface area.

When the applied voltage reached to 1.3 V, absorption band at around 530 nm, i.e. absorption of reduced **D-1** molecule, was being appeared in addition to the absorption band of oxidized **PT** molecule. Because electrical double layer on the ITO particle-modified electrode no longer compensated the charge consumption by oxidative reaction of **PT** on working electrode, electrochemical reduction had started on the ITO particle-modified electrode. In this voltage, the device color was changed to deep red color as the result of subtractive color mixing of green and magenta. On the other hand, the negative voltage was applied to the working electrode, the absorption band of reduced **D-1** appeared from -1.1 V, resulting in magenta coloration (Fig. 5b). When the voltage of –1.3 V was applied, **PT** molecule had started to be oxidized on the ITO particle-modified electrode, and then color of the device changed to deep red (Fig.5b). This deep red color also caused by

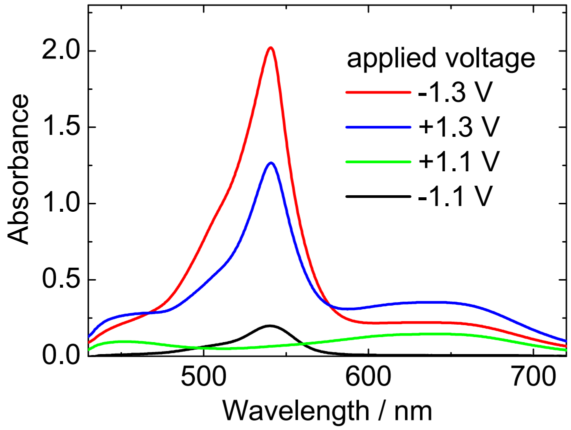
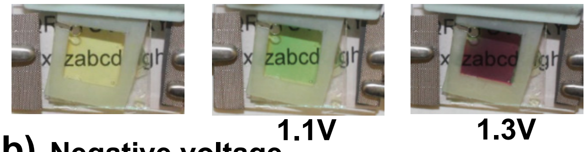


***Fig. 4** Change in absorption spectra of the novel EC device having flat ITO electrode (as working side) and ITO particle-modified electrode (as counter side) under applied voltage of ±1.1~±1.3 V, for 20 s.*

(a) Positive voltage



(b) Negative voltage

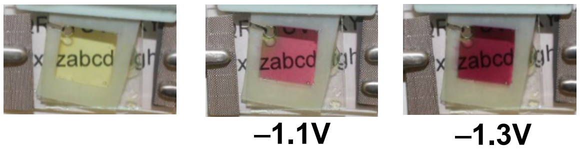


***Fig. 5** Photographs of the novel EC device under the different applied voltages.*

color mixing of magenta (color of reduced **D-1** molecule) and green (color of oxidized **PT** molecule).

From these results, the novel EC device were able to change its color between green, magenta and deep red by controlling the application voltage. The results suggested that charge compensation property of ITO particle-modified electrode was effective for selecting the material, which receive electrochemical redox reaction on working electrode side. Due to the charge compensation by formation of electrical double layer on ITO particle-modified electrode, only one kind of EC reaction on flat ITO electrode can be selected and obtained, achieving multi-color representations.

4. Conclusions

We successfully fabricated novel EC device consisted of flat ITO electrode as working electrode and ITO particle-modified electrode as counter electrode, which can show multi-color representations. The novel EC device was containing two kinds of electrochromic molecules of cathodic EC molecule and anodic EC molecule in the electrolyte solution. The EC device was able to represent three colors of magenta, green, and deep red reversibly by controlling application voltage. This multi-color control was achieved by the selecting the EC molecule receiving electrochemical redox reaction in the device. Charge compensation by formation of electrical double layer on the ITO particle-modified electrode enabled the control of the molecule showing EC reaction on the working electrode. This novel multicolor EC device could make it suitable for use in information displays such as full-color E-paper, digital signage.

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