Designed Electrochromic Display Devices with Ru(II)-Based Metallo-Supramolecular Polymer For Experience-Based Exhibits at Ehime Prefectural Science Museum

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Abstract Metallo-supramolecular polymers (MSPs) are a novel type of electrochromic (EC) materials. Ru(II)-based MSP (polyRu) composed of Ru(II) and bis(terpyridyl)benzene showed reversible color changes between orange and pale green. The orange color was caused by the metal-to-ligand charge transfer (MLCT) absorption in polyRu and disappeared by the electrochemical oxidation of Ru(II) to Ru(III). The pale green was returned to the original orange by the electrochemical reduction of Ru(III) to Ru(II). EC devices with polyRu were fabricated by the combination of an electrolyte solution, counter material, and two ITO glasses. The character images were displayed on the EC devices using insulating films. The insulating films prevented the electron transfer between the ITO glass and the polyRu layer and made the image stand out in the device. The fabricated EC display devices were presented at a science museum of Japan as experience-based exhibits.

Keywords: electrochromic, metallo-supramolecular polymer, nonvolatile, experience-based exhibit, museum.

1. Introduction

Electrochromism is electrochemical color changes in material and Tungsten oxide and viologens are the representative ones [1]. The electrochromic (EC) materials are used as smart window or anti-glare mirror in airplanes, vehicles, and office. Recently, metallo-supramolecular polymer (MSP) has been investigated as a novel EC material [2-11]. MSPs have advantages such as the solution-based processability and the wide color variation, compared with the conventional EC materials. MSPs are synthesized by complexation of metal ion and multi-topic organic ligand. The 1:1 complexation of metal ion having six coordination sites (Fe, Co, Ru etc.) and ditopic ligand bearing two tridentate coordination moieties (e.g., bisterpyridines) results in the formation of linear MSPs (Fig. 1a). The polymer structure is controlled by changing the ligand. For example, two-dimensional nanosheets with a honey-comb structure is obtained by the complexation of metal ion having six coordination sites and ditopic ligand bearing two BIDENTATE coordination moieties (e.g., bisbipyridines), because a metal can be complexed with three bidentate moieties (Fig. 1b) [12].

Fig.1 The formation of (a) linear and (b) two-dimensional nanosheet structures of MSPs.
Abundant combinations of metal species and ligands in the polymer synthesis have enabled the development of MSPs and the EC devices with novel properties and functions such as the dimension control of the polymer structure, the extension of EC properties to near IR region or the multi-colorization, the introduction of power storage function.

Ru(II)-based MSP (polyRu) (Fig. 2) is synthesized by 1:1 complexation of Ru(II)Cl₂(DMSO)₄ and bis(terpyridyl)benzene. The color of the polymer is orange because the polymer has a strong absorption around 508 nm in methanol, caused by the metal-to-ligand charge transfer (MLCT) absorption of the metal-complex moieties. A thin film of PolyRu cast on a glassy carbon electrode shows reversible redox waves at 0.95 V vs Ag/Ag+ (E₁/₂) in the cyclic voltammetry. This redox is caused by the redox between Ru(II) and Ru(III). A polymer film on an ITO electrode is prepared by the spray coating of a methanol solution of the polymer. The polymer film shows color changes from orange to pale green by applying oxidative potential higher than the redox potential. In the UV-vis. spectroscopy, the disappearance of the MLCT absorption around 508 nm is observed during the color change. The pale green color of the polymer in the Ru(III) state is returned to the original orange color by electrochemical reduction of Ru(III) to Ru(II). The EC changes occur reversibly by the electrochemical redox between Ru(II) and Ru(III) (Fig. 3). Designed EC devices with polyRu and how to display the devices at a museum as experience-based exhibits are reported in this paper.

2. Display Device Fabrication

An EC device with polyRu displaying a character of Ehime Prefecture "Mican" (Fig. 4) was fabricated with an electrolyte, counter material, an insulating film, and two ITO glasses (Fig. 5). A propylene carbonate solution including 0.1 M LiClO₄ was used as the electrolyte. The electrolyte provides ClO₄⁻ ions to the polyRu film to compensate the charge balance when Ru(II) was oxidized to Ru(III). A thin layer of Ni derivative of Prussian blue (NiHCF) was prepared on an ITO glass as the counter material. In the EC device, the opposite reactions happen at the two electrodes. When Ru(II) is oxidized to Ru(III) in the polyRu layer on the electrode, a reduction is caused on the other electrode in the EC device. Then, when the Ru(III) is reduced to Ru(II), an oxidation occurs on the other electrode. Therefore, a redox-active material is required as the counter material on the other electrode.
NiHCF is colorless in the reduced state (Li$_2$Ni(II)$_3$(Fe(II)CN$_6$)$_2$) and yellow in the oxidized state (Ni(II)$_3$(Fe(III)CN$_6$)$_2$). In the ECD with polyRu, the orange state (reduced state) of polyRu is combined with the yellow state (oxidized state) of NiHCF and the pale green state (oxidized state) of polyRu is paired with the colorless state (reduced state) of NiHCF. Therefore, the orange state of the device includes the yellow of the counter material, though the yellow is very pale.

The interface between Ru(II) and Ru(III) states was maintained in the image. It is considered that the redox hopping occurs at the interface, but the hopping speed will be extremely slow because of the electrically insulating properties of polyRu.

With the same device structure, an EC device showing another character "Komican" was also fabricated (Fig. 6). Movies of Figs. 4 and 6 are provided as Supplementary materials (the applied voltage was 1.8 V).

The operation voltage (1.8 V) was determined as the lowest voltage to work the devices smoothly. The counter material, NiHCF, becomes colorless at −0.2 V vs Ag/Ag$^+$ and yellow at 0.5 V vs Ag/Ag$^+$. The redox potential of polyRu is 0.95 V vs Ag/Ag$^+$ and the oxidation to Ru(III) in the polymer is completed at 1.1 V vs Ag/Ag$^+$.

Therefore, the voltage to oxidize polyRu of the device was calculated by Eq. 1 to be 1.3 V. The operation voltage (1.8 V) is slightly higher than the estimated voltage (1.3 V), but it is reasonable because the devices also have wiring resistance.

$$E_{\text{ox,ECD,estimated}} = E_{\text{ox,WE}} - E_{\text{red,CE}}$$

where $E_{\text{ox,ECD,estimated}}$ is the voltage estimated to oxidize the working electrode (WE) of the ECD and $E_{\text{ox,WE}}$ and $E_{\text{red,CE}}$ are the oxidation potential of the WE and the reduction potential of the counter electrode (CE), respectively.

The detailed fabrication procedure is shown in Fig. 7. First, the designed four PET films were sticked on an ITO glass (Fig. 7a). Among the four films, three films were used as masks and the other one film was utilized as an electrically insulating film of the device. A methanol solution of polyRu was sprayed on the ITO glass partially covered with the PET films and a thin layer of polyRu was prepared (Fig. 7b). Among the four PET films, three films were removed (Fig. 7c). The ITO glass with a polyRu layer was stacked with another ITO glass containing the counter material layer, with the electrolyte solution as the binder of the two electrodes. When the two glasses are stacked, it is important to slightly slide them, so that the un-overlapped parts can be used as the connecting parts to a dry battery (Fig.
Finally, the face image of "Mican" was applied on the outside surface of the device (Fig. 7d).

When 1.8 V was applied to the two electrodes of the device with the electrode having the polyRu layer as (+), the orange polymer layer was changed to pale green, because the Ru(II) of polyRu was electrically oxidized to Ru(III) and the MLCT absorption disappeared. However, the polymer layer on the insulating film did not change the color, because the insulating film prevented the electron transfer from the polyRu layer to the ITO electrode. As the result, the face image of "Mican" appeared on the device by the voltage application.

After the character image appeared, the image maintained for 5 to 10 minutes without applying a voltage. The nonvolatile feature is one of the unique properties of the EC devices, unlike LCDs or OLEDs. The character image was erased by changing the background color of pale green to the original orange. When the opposite voltage was applied to the two electrodes of the EC device, the Ru(III) of polyRu was reduced to Ru(II) and the pale green was returned to the original orange. The change of the images based on the electrochromic behavior occurred repeatedly. The ECDs nicely worked during 44 days of the exhibition.

As to the energy consumption in the ECDs, no electrical power is necessary to show the orange state, because the reduced state of polyRu is stable. The energy is consumed when the color is changed between the orange and the pale green. The required electronic charge to change the color of polyRu was estimated to be 3 to 5 mC/cm², which was calculated from the polymer coating conditions. After the color is changed to pale green, the color is maintained for 5 to 10 minutes without any electric power, but gradually returned to the stable orange state. Therefore, "refresh", occasional short-time power supply, is required to keep the pale green state.

### 3. Experience-Based Exhibits

Experience-based exhibits are one of effective ways to introduce new technologies, because they greatly help the understanding of people. As to the designed EC devices, a box-type of experience-based exhibit was set up as shown in Fig. 8.

The detailed structure of the exhibit is illustrated in Fig. 9. The whole size of the exhibit box is 46 cm (width) × 33 cm (depth) × 13 cm (height). The vertical and horizontal length of the displayed EC devices of "Mican"
“Komican” are 10 cm and 11 cm, respectively. The small EC devices with 5 cm × 5.5 cm, displaying the four marks of playing cards, were also placed in the exhibit, as shown in Fig. 9. As the exhibition room where the EC devices were displayed was not so bright, a backlight was used to light up the devices. In addition, the part except for the devices (blue part of the figure) was shaded to decrease the glitter. In the exhibit, the EC devices were covered with a plastic plate to prevent that the guests could not touch the devices directly.

The EC display devices change the color when a voltage from a DC power supply was applied between the two electrodes (gray parts in the figure). The guests apply a voltage using two stick electrodes, which are connected to the DC power supply. They have the two stick electrodes with both hands and touch the tips of the sticks to the electrodes of the devices, which are exposed from the plastic cover plate. Then, the color of the devices is changed. When the guests change the color to the original color, they touch the opposite electrodes with the sticks. An LED lights and a register are introduced between the sticks and the DC power supply to control the voltage applied to the EC device and to prevent any accidents of the guests by the short-circuit. In addition, the LED lighting up lets the guests know the voltage was applied to the device. After using the sticks, the guests return the sticks to the stick holder.

4. Conclusion

Designed EC display devices were fabricated using polyRu. The character images could be displayed by introducing a designed insulating film between an ITO glass and a polyRu layer, because the insulating film prevented the electron transfer between them. The fabricated EC display devices were presented at Ehime Prefectural Science Museum as experience-based exhibits (Fig. 10).

A thin layer of MSP was prepared by the spray coating of the polymer solution on an ITO glass. Therefore, a
PET film, which was not tough to high temperature, was also available when the MSP was coated. As the result, we succeeded in fabricating the designed EC devices using Ru(II)-base MSP. As described in Introduction, various MSPs have been developed. Many attractive experience-based exhibits will be performed based on this research results in the future.

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Supplementary materials

Movies of the EC devices shown in Figs. 4 and 6 are provided as supplementary materials.

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