A Trilayer Film Approach to Multicolor Electrochromism

Jun Matsui,*,† Rie Kikuchi,‡ and Tokuji Miyashita‡

†Department of Material and Biological Chemistry, Yamagata University, 1-4-12, Kojirakawamachi, Yamagata 990-8560, Japan
‡Institute for Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, 980-8577, Japan

Ⓢ *Supporting Information*

ABSTRACT: Development of multicolored electrochromic materials is important to realize their applications in electronic devices such as full color electronic paper. One method to increase the number of colors in an electrochromic device is by color mixing. A simple method for color mixing involves two electrochromes deposited at different working electrodes. Selective control of the redox state of each electrochrome allows the generation of both the individual electrochrome colors and a mixture of the two colors. In this paper we report a new strategy that enables color mixing using a single working electrode. A trilayer film composed of an ultrathin layer of a ruthenium complex sandwiched between two layers of Prussian blue (PB) nanoparticles was prepared on an ITO electrode using the Langmuir−Blodgett technique. Cyclic voltammetry and spectroelectrochemistry of the films indicate that the redox state of PB located at the top and bottom layer can be independently controlled using a single working electrode. In this way a mixture of the colors of PB and Prussian yellow could be produced without the necessity for multiple electrodes.

Electrochromism is a process by which the color of a materials is changed through an electrochemical reaction.[1] Several kinds of materials such as transition-metal oxides, mixed valence materials, organic molecules, and conjugated polymers have been reported to show electrochromic properties.[2−6] The ability to reversibly change the absorption of electrochromic materials has aroused interest for application in technologies such as smart windows[4] and electronic papers.[7,8] The use of multiple electrochromic materials or "multicoloring" can allow reproduction of high-quality color in such devices. One method to increase the range of colors available is by mixing two discrete colors.[7,9] This may be achieved by using two electrochromes, with complementary colors deposited onto different working electrodes. The electrochromic reaction of each electrochrome can be selectively controlled using a bipotentiostat. This allows the color of each individual electrochrome and a mixture of the two colors to be generated. Recently, full color electrochromic displays have been reported based on this color mixing concept.[8] However, as color mixing requires as many working electrodes as the number of colors, full color device structures are complicated.

We report a new strategy for color mixing that uses only one working electrode. This strategy is based on bilayer electrodes, which were first reported by Murray et al.[10−13] Bilayer electrodes consist of a conducting electrode coated with a bilayer film, which

is composed of two redox polymers. The interface between the redox polymer films behaves as heterojunction, which shows diode-like behavior. Recently, we applied this bilayer electrode concept to prepare electrochemical charge storage devices using a hybrid ultrathin bilayer film.[14] The hybrid ultrathin bilayer film was composed of a polymer nanosheet, containing a ruthenium complex ($p(DDA/Rubpy_3^{2+})$) as the inner layer and Prussian blue (PB) nanoparticles as the outer layer. In the hybrid ultrathin bilayer film, the ruthenium layers were oxidized at the electrode, whereas the PB layer was catalytically oxidized after the formation of $Rubpy_3^{3+}$. However, reduction of the oxidized PB layer by $Rubpy_3^{2+}$ is thermodynamically unfavorable, which results in the charge trapping at the PB layer by one potential cycle.[14] In the present study, we increased the number of layers and fabricated a trilayer film to demonstrate electrochromic color mixing at a single working electrode. PB is a well-known electrochromic material, with the formula $KFe^{III}[Fe^{II}(CN)_6]$ for "soluble" PB. The color of PB is blue but appears yellow when oxidized; this is named Prussian yellow (PY, $Fe^{III}[Fe^{III}(CN)_6]$). The reduced form of PB is named Prussian white (PW, $K_2Fe^{II}[Fe^{II}(CN)_6]$) and is transparent.[15] Hybrid trilayer films were formed, comprising layers of PB nanoparticles for the first and third layers, sandwiching a ruthenium-containing polymer nanosheet as the second layer. We demonstrate that the redox reaction of PB in the first and third layer can be controlled independently using the charge-trapping phenomenon. The results indicate that PB and PY can exist simultaneously at a single working electrode, allowing the color mixing concept to be applied using simpler device structures.

The copolymer $p(DDA/Rubpy_3^{2+})$ and a cationic polymer $p(DDA/DONH)$ (Figure 1) were synthesized following previously reported methods.[14,16,17] We have reported that $p(DDA/Rubpy_3^{2+})$ forms a stable monolayer at an air−water
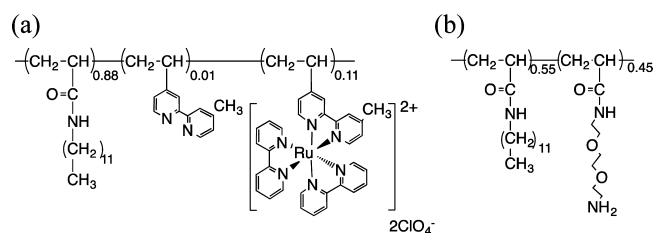

Figure 1. Chemical structures of the polymers (a) $p(DDA/Rubpy_3^{2+})$ and (b) $p(DDA/DONH)$.

interface that can be transferred onto a solid substrate as a Y-type LB film.[14] A PB ultrathin film was prepared using a cationic polymer nanosheet, p(DDA/DONH) as a template.[16] Two numbers of p(DDA/DONH) nanosheet were deposited onto an ITO substrate, and the substrate was immersed into a PB nanoparticle water dispersion. Two numbers of p(DDA/DONH) nanosheet were then deposited onto the PB layer to prevent desorption during electrochemical measurements (Figure 3a). PB nanoparticles were uniformly immobilized on the substrate by the electrostatic interaction between the negatively charged PB and positively charged p(DDA/DONH) (Figure S1). The surface coverage was determined to be about 15% from SEM images. Hereafter the hybrid nanosheet will be described as "PB nanosheet".

Spectroelectrochemistry of the polymer ultrathin films was studied by UV−vis spectra measurements using a homemade cell containing 0.1 M $KClO_4$ electrolyte (Figure S2). The absorption intensities of the films were low and sensitive to movement of the cell because of the ultrathin film. The cell was fixed to the spectrophotometer during the spectroelectrochemical measurement, and the electrochromic behavior of the films was measured as the difference in absorption (ΔA) between that measured at rest potential (vs Ag wire) and that at the target potential. Figure 2 shows a cyclic voltammogram and spectroelectrochemical ΔA
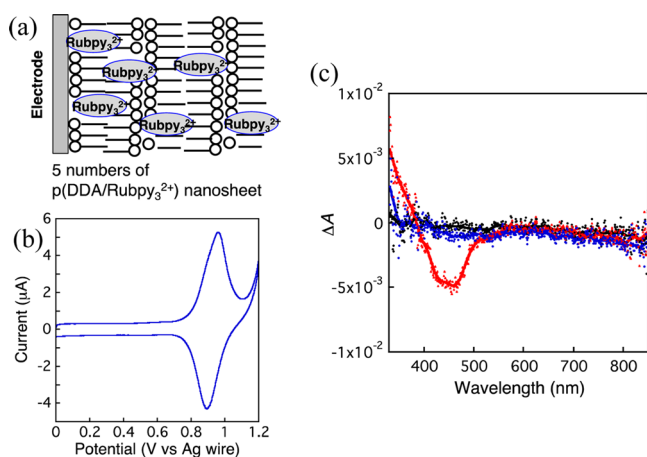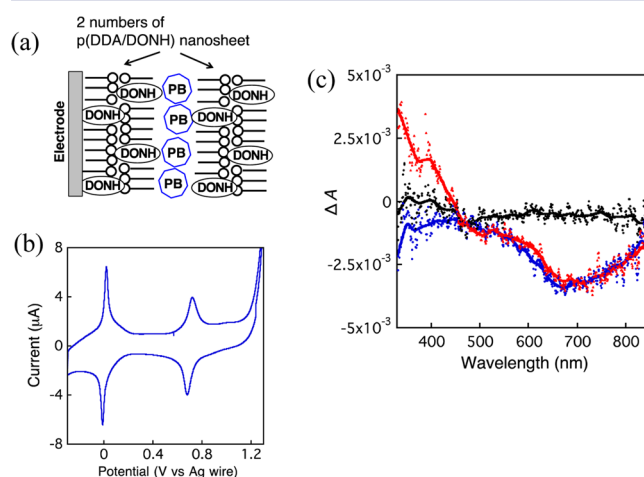

Figure 2. (a) Film structure for the spectroelectrochemistry measurements of the p(DDA/Rubpy$_3^{2+}$) polymer nanosheet. (b) Cyclic voltammogram of the p(DDA/Rubpy$_3^{2+}$) polymer nanosheet. Scan rate: 10 mV sec^{-1}. (c) Spectroelectrochemical ΔA spectra of the p(DDA/Rubpy$_3^{2+}$) polymer nanosheet measured at rest potential (black, used as a baseline spectra), 1.3 V (vs Ag wire) (red), and 0 V (vs Ag wire) after the potential of $0 \rightarrow 1.3 \rightarrow 0$ V (blue). Solid lines are smoothed fits using a locally weighted least-squares method.

spectra for 5 numbers of p(DDA/Rubpy$_3^{2+}$) nanosheet deposited onto a hydrophilic ITO electrode (Figure 2a). The voltammogram showed a well-defined surface wave consisting of symmetric oxidation and reduction peaks of Rubpy$_3^{3+}$ at 0.9 V (vs Ag wire) (Figure 2b). The redox reaction was followed by spectroelectrochemical ΔA measurements (Figure 2c). p(DDA/Rubpy$_3^{2+}$) showed absorption centered at 450 nm, which is attributed to the metal-to-ligand charge transfer (MLCT) absorption (Figure S3a). At 1.3 V (vs Ag wire), most of the Rubpy$_3^{2+}$ was oxidized to Rubpy$_3^{3+}$, which resulted in strong bleaching of the MLCT and a small increase in absorption below 400 nm, which is related to the formation of Rubpy$_3^{3+}$ (Figure 2c

red).[18] The baseline spectrum was recovered by returning the potential to 0 V (vs Ag wire) (Figure 2c blue).

Electrochromic behavior of one number of PB nanosheet was followed by spectroelectrochemical ΔA measurements. The cyclic voltammogram of the PB nanosheet showed clear redox peaks at 0 and 0.7 V (vs Ag wire), which correspond to one-electron redox reactions between PW and PB and between PB and PY, respectively (Figure 3b). PB showed a strong

Figure 3. (a) Film structure for the spectroelectrochemistry measurements of the PB nanosheet. (b) Cyclic voltammogram of the PB nanosheet. Scan rate: 10 mV sec^{-1}. (c) Spectroelectrochemical ΔA spectra of the PB nanosheet measured at rest potential (black, used as a baseline spectra), 1.0 V (vs Ag wire) (red), and −0.3 V (vs Ag wire) (blue). Solid lines are smoothed curve fits using a locally weighted least-squares method.

intervalence charge transfer (IVCT) absorption around 700 nm (Figure S3b). Oxidation of PB to PY resulted in strong bleaching of the IVCT and the appearance of a ferric ferricyanide absorption around 400 nm[15] in the ΔA spectrum (Figure 3c red). Moreover, at a potential of −0.3 V (vs Ag wire), PB was reduced to PW, which resulted in bleaching of the IVCT absorption (Figure 3c blue). The ΔA results of the PB nanosheet show essentially the same electrochromic behavior as PB nanoparticles.[15,19]

We previously reported that a hybrid ultrathin bilayer film composed of 5 numbers of p(DDA/Rubpy$_3^{2+}$) nanosheet (Ru layer) and a number of PB nanosheet (PB layer) (Figure 4a) showed charge trapping because of the diode-like behavior.[14] In the previous report, the charge trapping was confirmed by a large decrease in oxidation current during the second potential scan in cyclic voltammetry as shown in Figure 4b. This charge trapping process was followed by ΔA spectroelectrochemistry. Figure 4c shows the ΔA spectra of the hybrid bilayer film. At 1.3 V, Rubpy$_3^{2+}$ was oxidized to Rubpy$_3^{3+}$ by the electrode and PB was then catalytically oxidized after the formation of Rubpy$_3^{3+}$.[14] The oxidation of Rubpy$_3^{2+}$ and PB resulted in bleaching of the MCLT and IVCT absorption as well as the appearance of absorption of PY and Rubpy$_3^{3+}$ around 400 nm (Figure 4c red). During the reverse scan ($1.3 \rightarrow 0$ V), Rubpy$_3^{3+}$ was reduced to Rubpy$_3^{2+}$, whereas the PB layer remained in the PY state. The ΔA spectrum at 0 V after the potential scan of $0 \rightarrow 1.3 \rightarrow 0$ V shows recovery of the MLCT absorption of Rubpy$_3^{2+}$, which indicates that all of the Rubpy$_3^{3+}$ was reduced to Rubpy$_3^{2+}$. The bleaching of the PB IVCT absorption and the absorption related to ferric ferricyanide were sustained, which suggest that the PB layer was in a PY state
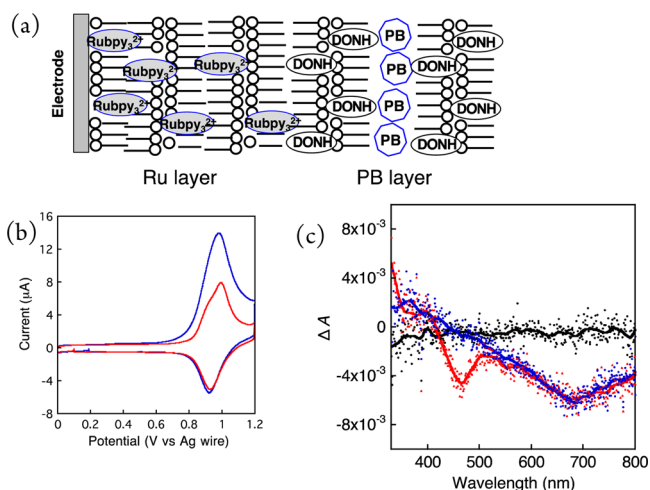
Figure 4. (a) Bilayer film structure. (b) Cyclic voltammogram of the bilayer film at 10 mV sec^{-1}: blue line, first scan and red line, second scan. (c) Spectroelectrochemical ΔA spectra of the bilayer film measured at rest potential (black, used as a baseline spectra), 1.3 V (vs Ag wire) (red), and 0 V (vs Ag wire) after the potential scan of $0 \rightarrow 1.3 \rightarrow 0$ V (blue). Solid lines are smoothed curve fits using locally weighted least-squares method.

even at 0 V (Figure 4c blue). The results indicate that charge trapping can be confirmed by ΔA spectroelectrochemistry.

We demonstrate a new strategy to achieve color mixing from a single working electrode using a hybrid trilayer film. The hybrid trilayer film comprised one number of PB nanosheet for the first and third layers, which sandwiched six numbers of p(DDA/Rubpy$_3^{2+}$) nanosheet that made up the second layer (Figure 5a).[20] The first and third layer of PB nanosheet will be denoted as first- and third-PB, respectively. The CV spectra of the hybrid trilayer film show three redox peaks at 0.1, 0.7, and 1.0 V (vs Ag wire) (Figure 5b). The former two peaks were attributed to the redox reaction of first-PB, and the latter was attributed to that of
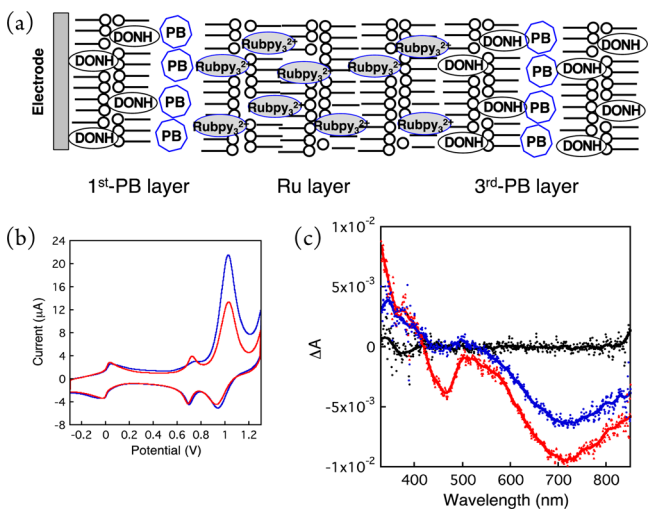
Figure 5. (a) Trilayer film structure. (b) Cyclic voltammogram of the trilayer film. Scan rate: 10 mV sec^{-1}. (c) Spectroelectrochemical absorption difference spectra of the trilayer film measured at rest potential (black, used as a baseline spectra), 1.3 V (vs Ag wire) (red), and 0.4 V (vs Ag wire) after the potential scan of $0 \rightarrow 1.3 \rightarrow 0$ V (blue). Solid lines are smoothed curve fits using locally weighted least-squares method.

the ruthenium complex in the second layer. Similar to the bilayer film, the oxidation current at 1.0 V decreased during the second scan, which indicates that the third-PB layer was catalytically oxidized to PY and remained in the PY state during the reductive scan.[21] The redox state of the first-PB layer can be controlled by the electrode, whereas the third-PB layer was maintained as the PY state irrespective of the electrode potential. To confirm this redox process, the ΔA spectroelectrochemistry of the trilayer film was studied. ΔA spectrum measured at 1.3 V showed considerable bleaching of the MLCT absorption at 450 nm and IVCT absorption at 700 nm as well as an appearance of PY and Rubpy$_3^{3+}$ absorption around 400 nm (Figure 5c red), which is similar to that observed in the bilayer film. The ΔA spectrum and cyclic voltammogram indicates that the redox state of the trilayer film is PY/Rubpy$_3^{3+}$/PY at 1.3 V (vs Ag wire) (Scheme S1b). The redox potential was then reversed to 0 V and swept in the forward direction to 0.4 V (vs Ag wire), which is close to rest potential of the trilayer film. The ΔA spectrum at 0.4 V (vs Ag wire) showed the recovery of the MLCT absorption at 450 nm because Rubpy$_3^{3+}$ was reduced to Rubpy$_3^{2+}$ during the reverse scan. The positive absorption of ferric ferricyanide around 400 nm was slightly decreased and some recovery of the IVCT bleaching at 700 nm was observed (Figure 5c blue). Considering the layer structure, this spectrum change is related to the first-PB layer. During the reverse scan, PY at first-PB was reduced to PB at 0.7 V and to PW at 0 V by the electrode. Finally, PW was reoxidized to PB during the second forward scan (Scheme S1c). The reformation of PB resulted in a certain amount of recovery of the IVCT bleaching at 700 nm. Moreover, the presence of the ferric ferricyanide absorption at 400 nm and bleaching at 700 nm indicates that the third-PB layer remains in the PY form. The redox state of the trilayer film at 0.4 V (vs Ag wire) after a single potential cycle is PB/Rubpy$_3^{2+}$/PY. The spectroelectrochemical ΔA spectra indicate that the PB nanosheet in the trilayer film has a blue color initially with the form PB/Rubpy$_3^{2+}$/PB (Scheme S1a), a yellow color at 1.3 V (PY/Rubpy$_3^{3+}$/PY, Scheme S1b), and a mixture of blue and yellow colors at 0.4 V after one potential cycle (PB/Rubpy$_3^{2+}$/PY, Scheme S1c). It should be noted that the PB nanoparticles are able to present in two different oxidation states (PB and PY) simultaneously at potentials close to the rest potential of the film.

Excitation of the MLCT band of Rubpy$_3^{2+}$ produces Rubpy$_3^{2+}$*, which has a potential 2.1 eV higher than that of Rubpy$_3^{2+}$. In the bilayer film, the charge stored in the outer PB layer was released by a photoinduced electron transfer from Rubpy$_3^{2+}$* to PY.[14] We attempted to photoreduce PY at third-PB using the same process to reproduce the initial PB/Rubpy$_3^{2+}$/PB state. The trilayer film in the PB/Rubpy$_3^{2+}$/PY state was irradiated at 488 nm using an Ar-ion laser. A small cathodic photocurrent was observed upon irradiation (Figure S4). The ΔA spectrum of the trilayer film following light irradiation almost recovered to the initial background spectrum (Figure 6 green), which indicates that most of the PY at third-PB was reduced to PB by the photoinduced electron transfer from the Rubpy$_3^{2+}$*.[22] Therefore the mixed colored state reverted to the initial PB/Rubpy$_3^{2+}$/PB state through the photochemical reaction (Scheme S1d). The spectroelectrochemistry of the trilayer film after the photoirradiation followed a similar trend to that observed in a pristine film of p(DDA/Rubpy$_3^{2+}$). The large bleaching at 700 and 450 nm and the occurrence of absorption at 400 nm were observed at 1.3 V (Figure 6 red). Furthermore, full recovery of the bleaching at 450 nm, a certain amount of recovery of bleaching at 700 nm and the appearance of a new absorption at
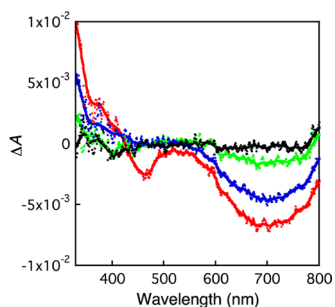
Figure 6. Spectroelectrochemical absorption difference spectra of the trilayer film measured after photoirradiation. Spectra are measured at rest potential (green), at 1.3 V (vs Ag wire) (red), and 0.4 V (vs Ag wire) after the potential cycle of 0 → 1.3 → 0 V (blue). The spectrum of a pristine sample measured at rest potential is shown as a reference (black).

400 nm were observed at 0.4 V after one potential cycle (Figure 6 blue). The changes in the ΔA spectra after the photoirradiation indicate that the electrochromism of the trilayer film is reversible. It should be noted that in principle, the third PY layer can be electrochemically reduced by the $Rubpy_3^{1+}$ state as reported by Murray et al.[23] We performed the multicolor electrochromism reaction, i.e., oxidation to $PY/Rubpy_3^{3+}/PY$, reduction to $PB/Rubpy_3^{2+}/PY$, and photoreduction to $PB/Rubpy_3^{2+}/PB$, four times and observed a good reversibility. Moreover, the previous report of electrochemical charge storage devices prepared by the bilayer film of $p(DDA/Rubpy_3^{2+})$-PB shows reversible charge storage—release cycle more than 10 times. Therefore we believe that the multicolor electrochromism is reversible more than 10 times. The stability of the devices will be increased by chemically cross-linking each layer.[16]

In conclusion, we have reported a new strategy of multicolor electrochromism using the trilayer film structure. Redox reaction of PB located at the first layer and third layer was independently controlled in the trilayer film. Therefore PB in the first and third layer can exist in a different redox state, which results in the presence of a mixture of PB and PY colors at a single working electrode. Accordingly, the trilayer film allows three colors to be displayed related to $PB + Rubpy_3^{2+}$ (blue + orange), $PY + Rubpy_3^{3+}$ (yellow + yellow), and $PB + PY + Rubpy_3^{2+}$ (blue + yellow + orange) using only one working electrode. Our strategy was based upon a bilayer electrode concept and may be applicable to other suitable redox pairs, in which one material has two stable redox couples with potentials that bracket the other electrochrome.[24] Currently, the film thickness of these devices is too thin to allow the color change to be observed by the naked eye. Development of thicker trilayer films that are visible to the naked eye is now in progress. Overcoming the challenges of constructing full color electrochromic devices based on single electrodes is a topic of continuing research.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

jun_m@sci.kj.yamagata-u.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(20) The outer two numbers of p(DDA/DONH) nanosheet in the first-PB was not deposited because the Ru layer prevent desorption of PBs.
(21) A relatively large oxidation current is related to impurities dissolved in the electrolyte. These impurities are hard to diffuse into the trilayer film made from multilayers of a closed packed polymer nanosheet. Therefore, these impurities are also catalytically oxidized by the $Ru(bpy)_3^{3+}$, which result in a relatively large oxidation current. The impurities do not affect the electrochromic behavior of the trilayer film as supported by the reversibility of the electrochromism.
(22) Although, the excited state of ruthenium complex has a potential to reduce PY to PB and PB to PW, the photoproduced PW will be easily oxidized by PY and/or a small amount of oxygen.
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