Compensative Electrochromic Device Utilizing Electro-deposited Plasmonic Silver Nanoparticles and Manganese Oxide to Achieve Retention of Chromatic Color

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Graphical Abstract

Working

| or |

Counter

MnO₂ layer

± e⁻

Ag⁺

± e⁻, Li⁺

Ag nanoparticle

Ox

Red

Transparent

Mirror

Cyan
Title

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Authors

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Abstract

Silver deposition-based electrochromic (EC) device enabled various optical states by using either the electrodeposition of silver thin films or silver nanoparticles on an indium tin oxide electrode. These optical states, including chromatic colors such as cyan, magenta, yellow, and green, are based on absorption by the localized surface plasmon resonance of silver nanoparticles. However, an ideal counter-reaction material that does not affect the color representation by silver nanoparticles and does not dissolve the deposited silver has not been reported. To achieve both color retention and chromatic color representation, MnO$_2$ was utilized as the counter electrode material. The EC properties of the novel device with the MnO$_2$ counter electrode were investigated in terms of charge density and its ability to change color. The novel EC device achieved both representations of chromatic color and retained its color without power supply.
Keywords

Electrochromism, Silver, Manganese oxide, Localized surface plasmon resonance (LSPR)

Main body

1. Introduction

Recently, chromogenic technology has garnered increasing attention because of its potential application in biological sensing, rewritable media, display devices, and smart windows.\(^1\) Electrochromism is a chromogenic technology and is defined as a reversible color change induced by electrochemical redox reactions of functional materials. Electrochromic (EC) technologies are widely utilized as smart windows to control light incidence. It is also expected that EC technologies will be applied to electronic paper and digital signage. This is because EC devices have advantages such as simple structure, large viewing angle, and low power consumption in comparison with conventional systems such as liquid-crystal display systems with backlight or organic light-emitting diodes.\(^2\)–\(^4\)

Various types of EC materials, including inorganic and organic materials, have been investigated. Transition metal oxides\(^5\)–\(^10\), Prussian blue\(^11\)–\(^13\), and Prussian blue analogs\(^14\),\(^15\) are examples of inorganic EC materials. These inorganic EC materials have excellent stability and have already been utilized as smart windows. However, the mechanism of these colorations is based on the intervalence charge transfer; thus, it is generally difficult to express various colors. On the contrary, some organic materials such as conductive polymers\(^16\),\(^17\) and small organic molecules\(^3\),\(^18\),\(^19\) have been observed to achieve multicolor electrochromism. Multicolor can be represented using multiple redox
states of a single material; however, these highly oxidized or reduced states are typically unstable. Therefore, it is difficult for a high-voltage application to maintain a color and to satisfy sufficient cycle stability.

Various organic and inorganic EC materials are widely known. However, materials that are durable, such as inorganic EC materials and have multicolor properties, such as organic EC materials, have not been reported. Therefore, we focused on a novel EC that utilizes the localized surface plasmon resonance (LSPR) of silver nanoparticles. The LSPR of metal nanoparticles causes quenching at a specific wavelength, that is, the LSPR band. The LSPR band depends on the size and shape of the nanoparticles. Therefore, metallic nanoparticles such as silver are known to exhibit various colors depending on their particle size and shape.\(^\text{20, 21}\)

The device (silver deposition-based EC device) is composed of a gel electrolyte containing \(\text{Ag}^+\) and a pair of indium tin oxide (ITO) electrodes sandwiching the electrolyte. In this device, silver nanoparticles or films are deposited on the ITO electrode through application of voltage, and the silver deposits modulate the color and reflection of the devices. The device achieved various optical states such as transparent, silver mirror, black, cyan, magenta, yellow, and green.\(^\text{22-26}\) It also has sufficient durability for thousands of cycles of color change.\(^\text{27}\) Even though our silver deposition-based EC device has excellent ability for various colorations and stability for a cycle of coloring and bleaching, it did not have adequate color retention properties under no electric power supplication, that is, open circuit conditions. For practical applications, color retention properties that contribute to low power
consumption are required. The reason for the inadequate color retention was because of the Cu\(^{2+}\) ions contained in the electrolyte solution. In the device, Cu\(^{2+}\) ions have two functions. The first function is compensation for the redox reaction of silver (Ag\(^0\) ⇌ Ag\(^+\) + e\(^-\)) on the working electrode. The redox reaction (Cu\(^{2+}\) + e\(^-\) ⇌ Cu\(^+\)) on the counter electrode works efficiently as a counter-reaction along with the redox reaction of halogen ions\(^{28,29}\) contained in electrolyte solution as supporting electrolyte (e.g., 3Br\(^-\) ⇌ Br\(_3^-\) + 2e\(^-\)). The second role is to support the oxidative dissolution of deposited silver as an electrochemical mediator. The oxidation potentials of Ag\(^0\) and the reduction potentials of Cu\(^{2+}\) in dimethyl sulfoxide (DMSO) based EC electrolyte solution, which were determined by cyclic voltammetry measurements shown in Fig. S1, are expressed as follows:

\[
\begin{align*}
\text{Ag}^0 & \rightarrow \text{Ag}^+ + e^- : -0.9 \text{ V (vs.Ag/Ag}^+\text{ in DMSO)} \\ 
\text{Cu}^{2+} + e^- & \rightarrow \text{Cu}^+ : -0.25 \text{ V (vs.Ag/Ag}^+\text{ in DMSO)}
\end{align*}
\]

(1) (2)

Therefore, the deposited Ag was dissolved by Cu\(^{2+}\) ions, as expressed in the following equation:

\[
\text{Ag}^0 + \text{Cu}^{2+} \rightarrow \text{Ag}^+ + \text{Cu}^+
\]

(3)

This redox reaction proceeded without the exchange of electrons on the electrode. Therefore, the bleaching process of the EC device proceeded efficiently and was completed. However, Equation (3) demonstrates that color bleaching proceeds automatically owing to the oxidation of deposited Ag\(^0\) by Cu\(^{2+}\) ions even when voltage is not applied. To achieve sufficient color retention characteristics in the silver deposition-based EC device, it was necessary to use an electrolyte that does not contain Cu\(^{2+}\)
ions and introduce another counter reaction to compensate for the reaction charge on the working electrode.

In our previous studies, we fabricated a complementary EC device in which the redox capacity of Prussian blue fixed on the counter electrode was used to compensate for the redox reaction of silver at the working electrode. Prussian blue is one of the most typical EC materials, exhibiting a blue color in the oxidized state and turning transparent in the reduced state. Conversely, in the metal-deposition EC system, the transparent state corresponds to the oxidized state. Therefore, by introducing Prussian blue into the counter electrode of the silver deposition-based EC device, both the working and counter electrodes turned transparent. When voltage is applied, the device represents the ideal mirror state. Moreover, the mirror state was successfully maintained under open-circuit conditions.

However, because the oxidized state of Prussian blue exhibits a dark blue color, it was difficult to obtain an appropriate color based on the LSPR of silver nanoparticles in the EC device. To demonstrate an EC device with a chromatic color retention property based on the LSPR of silver, in this study, we focused on MnO$_2$ that exhibits less coloration than Prussian blue. MnO$_2$ is also known as an EC material that becomes transparent in the reduced state, which is similar to Prussian blue, and it could be used as a counter-reaction material for silver deposition-based EC devices exhibiting a transparent state. MnO$_2$ in its oxidized state exhibits a pale yellow. However, the pale yellow by MnO$_2$ is difficult to perceive; thus, it was expected to work as a counter-reaction material without interfering with the coloration of silver. In this study, a new configuration of a silver deposition-based EC device
utilizing MnO$_2$ as the counter-reaction material was fabricated and electrochemical properties such as the representation of chromatic colors and color retention properties were investigated.
2. Experimental

2.1 Materials

Manganese (II) acetate \((\text{Mn(CH}_3\text{COO)}_2\), Kanto Chemical Co. Inc.) and sodium sulfate \((\text{Na}_2\text{SO}_4\), Wako Pure Chemical Co. Inc.) were used as received to prepare the electrolyte solution for constant-current electrolysis to deposit the \(\text{MnO}_2\) film. Silver nitrate \((\text{AgNO}_3\), Kanto Chemical Co. Inc.), lithium chloride \((\text{LiCl}\), Kanto Chemical Co. Inc.), and dimethyl sulfoxide \((\text{DMSO}\), Sigma Aldrich, Japan) were used to prepare the EC electrolyte without further purification. Polyvinyl butyral \((\text{PVB}, \text{Mw} = 5.0 – 6.0 \times 10^4\), Kuraray Co. Ltd.) was used as the host polymer for electrolyte gelation. An ITO electrode \((<10\ \Omega/\square)\) was used after adequate washing.

2.2 Preparation of \(\text{MnO}_2\) modified electrode and electrolyte solution

\(\text{MnO}_2\) film was obtained on the ITO electrode through constant-current electrolysis \((30\ \mu\text{A cm}^{-2}\) of anodic current for 1000 s) using an aqueous solution containing \(\text{Mn (CH}_3\text{COO)}_2\) \((100\ \text{mmol L}^{-1})\) and \(\text{Na}_2\text{SO}_4\) \((100\ \text{mmol L}^{-1})\). After removing the electrodeposition solution, the electrode was rinsed with pure water and subsequently dried. The gel electrolyte for the EC device was prepared as follows: 10 and 100 mmol L\(^{-1}\) \(\text{AgNO}_3\) as the EC material along with five equivalents of \(\text{LiCl}\) in a molar ratio to \(\text{AgNO}_3\) \((\text{i.e., } 50\ \text{and } 500\ \text{mmol L}^{-1})\) as the supporting electrolyte were dissolved in DMSO. Subsequently, 10 wt% PVB as the host polymer was mixed with the DMSO-based electrolyte solution.
2.3 Fabrication of the two-electrode EC cell

Prior to assembling the EC device, the MnO$_2$-modified electrode was reduced by an applied potential of −1.0 V (vs. Ag/Ag$^+$) in a 500 mmol L$^{-1}$ LiCl DMSO solution. The EC device was fabricated by sandwiching a PVB-based gel electrolyte between an ITO electrode and a reduced MnO$_2$-modified electrode. Using a Teflon spacer hollowed out in 1 cm × 1 cm, an inner area of 1 cm$^2$ and an inter-electrode distance of 500 µm were maintained.

2.4 Apparatus

Electrochemical measurements were obtained using a potentiostat/galvanostat (ALS 660A, CH Instruments Inc., USA) connected to a computer. The MnO$_2$ film was identified through X-ray diffraction (D8 ADVANCE, Bruker, USA). The surface morphologies of the electrodes were examined using FE-SEM (JSM-6510, JEOL, Japan). Absorption spectra were recorded using a diode array detection system (USB2000, Ocean Optics, USA). Reflection spectra were also recorded using a diode array detection system connected to a reflection/backscattering probe (R600-7-UV-125F, Ocean Optics, USA). Ag/Ag$^+$ type reference electrode was used for 3-electrode electrochemical measurements. The inner solution of the reference electrode was an acetonitrile solution containing 10 mmol L$^{-1}$ Ag NO$_3$ and 100 mmol L$^{-1}$ Tetrabutylammonium Perchlorate (TBAP). Ion Permeability Porous Glass (ALS Co., Ltd, USA) was used as liquid junction.
3. Results and discussion

3.1 Electrochemical analysis of MnO$_2$-modified electrode

The MnO$_2$ film was obtained on the ITO electrode through constant-current electrolysis.$^{31}$ MnO$_2$ was formed by oxidation of Mn$^{2+}$ in an aqueous solution$^{32}$ (Equation (4)).

\[ \text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \]  

(4)

The obtained MnO$_2$-modified electrode was transparent and yellowish. The structure of the MnO$_2$-modified electrode was investigated through X-ray diffraction and FE-SEM. The X-ray diffraction pattern and surface morphology observed through FE-SEM are shown in Figs. S2 and S3. The obtained film was identified as a typical MnO$_2$ film by the X-ray diffraction pattern,$^{31, 33}$ and the morphology of the surface was porous, as shown in Fig. S3. The electrochemical characteristics and changes in the transmittance of the MnO$_2$ film were investigated using a 3-electrode electrochemical measurement system. DMSO solution containing 500 mmol L$^{-1}$ LiCl was used as the electrolyte solution, Ag/Ag$^+$ electrode was used as the reference electrode, and Pt wire was used as the counter electrode. The redox reaction of the MnO$_2$-modified electrode (Equation (5)) involves insertion and de-insertion of alkali metal ions such as Li$^+$ and K$^+$ that are essential in the electrolyte solution.

\[ \text{MnO}_2 + x \text{M}^+ + x\text{e}^- \leftrightarrow \text{M}_x\text{MnO}_2 \ (\text{M} = \text{Li}, \text{Na}, \text{K}, \text{etc.}) \]  

(5)

The cyclic voltammogram of the MnO$_2$ layer on the electrode and the change in transmittance at 400 nm during potential scanning are shown in Fig. 1. When the applied potential was scanned in the negative direction, a cathodic current was detected. According to the reduction reaction, the MnO$_2$
layer changed to a transparent state (transmittance at 400 nm reached 70%) from yellowish. An anodic current and a corresponding decrease in transmittance were observed when the potential was reversed in the positive direction from –1.5 V vs. Ag/Ag⁺. The oxidation of MnO₂ caused this anodic reaction and a decrease in the transmittance.

Thereafter, constant potentials for the reduction and oxidation of the MnO₂ film were applied to the working electrode alternately. Changes in the current density and corresponding change in transmittance by applying –1.2 V vs. Ag/Ag⁺ (reduction) and +0.5 V vs. Ag/Ag⁺ (oxidation) are shown in Fig. 2. Cathodic and anodic currents flowed immediately owing to the redox of MnO₂. The transmittance of the membrane was modulated repeatedly from 26% to 73%. Furthermore, the cathodic and anodic reactions and corresponding changes in transmittance were highly reversible. The transmission spectra of the MnO₂ layers in the reduced state after the cathodic reaction and the oxidized states after the anodic reaction are shown in Fig. 3. The range of transmittance in the reduced state was approximately ca. 80%–90% in the visible region. This high transparency contributes to the high transparency of the silver deposition-based EC device when the MnO₂-modified electrode is used as a counter electrode. In the oxidized state, the transmittance at 400 nm was ca. 30%. This value is higher than the transmittance at 700 nm of the Prussian blue modified electrode (12%) which was used as the counter electrode in the previous study.³⁰ It suggests that this novel device is advantageous for color representation by LSPR. The electrochemical capacities of the prepared MnO₂ modified electrodes can be estimated by integrating the current over time. The change in current in the time range of 60–360 s,
shown in Fig. 2, was integrated, and the calculated charge amounts in five redox cycles illustrated in Fig. 4. The reaction charge for all cycles was ca.12 mC cm$^{-2}$, and the charges for the anodic and cathodic reactions were nearly equal in each cycle. This result suggests that the redox reaction of the MnO$_2$ electrode is stable and reversible. An electrochemical capacity of 10 mC cm$^{-2}$ of counter-reaction is necessary for compensation of reduction of Ag$^+$ ion to represent an appropriate mirror state.$^{30}$ In addition, because chromatic coloration of the silver deposition-based EC device is obtained with sparsely deposited nanoparticles, a smaller charge amount than 10 mC is sufficient.$^{23}$ Therefore, a prepared MnO$_2$ modified electrode was observed to be suitable as a counter electrode for the silver deposition-based EC device.

3.2 Electrochemical and optical properties characterization of the two-electrode EC device

The two-electrode EC device was fabricated by sandwiching the gel electrolyte containing 100 mol L$^{-1}$ AgNO$_3$ using an ITO electrode (working electrode) and a reduced MnO$_2$ modified electrode (counter electrode). First, the changes in the optical properties of the device according to the voltage application were investigated. Immediately after fabricating the device, the initial state was transparent. A constant voltage of $-1.8$ V was applied between the working and counter electrodes and the EC device turned to the mirror state. After applying a constant voltage of $+0.3$ V and subsequent sweeping of voltage from $+0.3$ to $+1.0$ V, the device returned to the transparent state. This optical
modulation was reversible and repeated between the transparent and mirror states shown in Fig. 5 using a similar voltage application sequence. The transmission spectra, reflection spectra, and photographs of the device in both the transparent and mirror states, change in transmittance at 550 nm and current according to the voltage applications, are shown in Fig. 5. The voltage application sequence for bleaching is not a simple constant-voltage application because the cathodic reaction of MnO₂ at the counter electrode was relatively slow. When a constant positive voltage was applied, the working electrode potential immediately shifted significantly to a positive value. The reaction that occurs on the working electrode is the dissolution of silver deposited on the electrode. The reaction rate of electrochemical dissolution is a fast process because the reaction is limited by electrode kinetics. However, the reduction reaction of manganese oxide at the counter electrode was excessively slow to follow the reaction on the working electrode. To ensure that the reaction between the working and counter electrodes proceeded simultaneously, the described sequence of applying voltage for bleaching was adopted.

Thereafter, a chromatic color displayed by the EC device fabricated with a MnO₂-modified electrode as the counter electrode was demonstrated. For vivid and high-brightness color display, the silver ion concentration in the electrolyte should be low. Therefore, the two-electrode EC device was fabricated with a gel electrolyte containing 10 mmol L⁻¹ AgNO₃. An ITO electrode was used as the working electrode, and a reduced MnO₂-modified electrode was used as the counter electrode, as described. Chromatic colors are due to absorption by LSPR enhanced by the deposited silver
nanoparticles. The LSPR band is known to change its absorption wavelength depending on the size and shape of the nanoparticles. Therefore, silver nanoparticles of uniform size and shape are required to obtain a vivid color. Thus, the “voltage-step method” should be applied to the silver deposition-based EC device (Fig. 6). In this method, two different voltages are successively applied: the first voltage $V_1$ is applied for a very short time $t_1$ to initiate silver nucleation, and the second voltage $V_2$ is applied for time $t_2$ to promote the growth of the silver nuclei. As $V_2$ is more positive than the nucleation voltage, further nucleation is no longer possible during $t_2$. Therefore, silver nanoparticles with uniform particle size can be obtained on the electrode, and the EC device displays vivid coloration based on LSPR. The following step voltage was applied to the device with MnO$_2$ used as the counter electrode: $V_1 = -3.0$ V, $t_1 = 80$ ms; and $V_2 = -1.4$ V, $t_2 = 60$ s. Consequently, the device changed from an initial transparent state (Fig. 7 (b)) to a cyan state with a peak at 620 nm (Fig. 7 (c)). Because of the yellow color of the oxidized MnO$_2$, the absorption in the 400–500 nm region also increased simultaneously. Because the absorption at wavelengths longer than 550 nm caused by the LSPR of the silver nanoparticles was more significant, the device was able to represent cyan successfully. The FE-SEM image of the silver deposit in the cyan state is shown in Fig. S4. The anisotropic structure of the silver nanoparticles, as shown in Fig. S4, resembled that of the particles of the cyan state in previous studies.

In addition, the color retention property under no-power consumption was investigated. Figure 8 shows the absorption spectra immediately after shifting the open-circuit condition of the
device (0 s), after 500 s, and after 1000 s, respectively. This result indicates that cyan was successfully maintained even after 1000 s. The cyan coloration by the previous device containing CuCl₂ in the electrolyte solution was bleached immediately under an open circuit condition; the color completely returned to the initial state within 60 s. (The change in the absorption spectra during bleaching under open circuit conditions is shown in Fig. S5.) The lack of perfect color retention might be because of the undesirable oxidation species existing in the electrolyte solution. Because the electrochemical reactions of silver and MnO₂ are not completely compensated for, undesirable oxidation species are generated during voltage application. The oxidative species might unfortunately dissolve the silver deposit, leading to the bleaching of cyan. Therefore, for the commercial use of this configuration of silver deposition-based EC devices, further optimization of the driving method and/or improvement of the electrochemical reactivity of the counter layer are necessary.

4. Conclusion

A novel configuration of a silver deposition-based EC device with MnO₂ utilized as the counter redox reaction material was demonstrated. The charge amount of the redox reaction of the MnO₂ layer fixed on the counter electrode was observed to be an adequate charge amount required for the redox reaction of silver on the working electrode. MnO₂ was utterly transparent in the reduced state, and only a slight yellow coloration was observed in the oxidized state. Therefore, this configuration of the EC device could display a chromatic color without being affected by the color of the counter
electrode. Furthermore, unlike previous studies that utilized the redox reaction of copper ions contained in the electrolyte solution, this novel device did not contain any substances that oxidize and dissolve silver in the solution. Therefore, it was also possible to retain the colored state under open-circuit conditions. This new configuration will reduce the power consumption of EC devices, such as smart windows, digital signages, and full-color e-papers.

Supporting Information: The Supporting Information is available on the website at DOI: xxxxxxxxxxxxx.

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6. References
1. C. M. Lampert, *Mater. Today*, 7, 28 (2004).
2. D. R. Rosseinsky and R. J. Mortimer, *Adv. Mater.*, 13, 783 (2001).
3. R. J. Mortimer, *Electrochim. Acta*, 44, 2971 (1999).
4. N. Kobayashi, S. Miura, M. Nishimura, and H. Urano, *Sol. Energy Mater. Sol. Cells*, 92, 136 (2008).
5. X. H. H. Xia, J. P. P. Tu, J. Zhang, X. L. L. Wang, W. K. K. Zhang, and H. Huang, *Sol. Energy Mater. Sol. Cells*, 92, 628 (2008).
6. K. R. Reyes-Gil, Z. D. Stephens, V. Stavila, and D. B. Robinson, *ACS Appl. Mater. Interfaces*, 7, 2202 (2015).
7. S. H. Lee, R. Deshpande, P. A. Parilla, K. M. Jones, B. To, A. H. Mahan, and A. C. Dillon, *Adv. Mater.*, 18, 763 (2006).
8. Y. Ren, T. Fang, Y. Gong, X. Zhou, G. Zhao, Y. Gao, J. Jia, and Z. Duan, *J. Mater. Chem. C*, 7, 6964 (2019).
9. I. Mjejri, A. Rougier, and M. Gaudon, *Inorg. Chem.*, 56, 1734 (2017).
10. Y. Abe, S. Ito, K. H. Kim, M. Kawamura, and T. Kiba, *J. Mater. Sci. Res.*, 6, 44 (2016).
11. Z. Bi, X. Li, Y. Chen, X. He, X. Xu, and X. Gao, *ACS Appl. Mater. Interfaces*, 9, 29872 (2017).
12. M. Ishizaki, H. Ando, N. Yamada, K. Tsumoto, K. Ono, H. Sutoh, T. Nakamura, Y. Nakao, and M. Kurihara, *J. Mater. Chem. A*, 7, 4777 (2019).
13. Y. Yue, H. Li, K. Li, J. Wang, H. Wang, Q. Zhang, Y. Li, and P. Chen, *J. Phys. Chem. Solids*, 110, 284 (2017).
14. T.-C. Liao, W.-H. Chen, H.-Y. Liao, and L.-C. Chen, *Sol. Energy Mater. Sol. Cells*, 145, 26 (2016).
15. K. M. Lee, H. Tanaka, A. Takahashi, K. H. Kim, M. Kawamura, Y. Abe, T. Kawamoto, L. C. Chen, and K. C. Ho, *Electrochim. Acta*, 163, 288 (2015).
16. A. S. Ribeiro, V. C. Nogueira, P. Faria dos Santos Filho, and M. A. De Paoli, *Electrochim. Acta*, 49, 2237 (2004).
17. S. H. Hsiao and Y. Z. Chen, *Eur. Polym. J.*, 99, 422 (2018).
18. H. Urano, S. Sunohara, H. Ohtomo, and N. Kobayashi, *J. Mater. Chem.*, 14, 2366 (2004).
19. Z. Liang, K. Nakamura, and N. Kobayashi, *Sol. Energy Mater. Sol. Cells*, 200, 109914 (2019).
20. D. D. Evanoff and G. Chumanov, *J. Phys. Chem. B*, 108, 13957 (2004).
21. T. Huang and X.-H. N. Xu, *J. Mater. Chem.*, 20, 9867 (2010).
22. A. Tsuboi, K. Nakamura, and N. Kobayashi, *Chem. Mater.*, 26, 6477 (2014).
23. S. Kimura, T. Sugita, K. Nakamura, and N. Kobayashi, *Nanoscale*, 12, 23975 (2020).
24. A. Aoki, A. Ito, and S. Watanabe, *Sol. Energy Mater. Sol. Cells*, 200, 109922 (2019).
25. Z. He, X. Yuan, Q. Wang, L. Yu, C. Zou, C. Li, Y. Zhao, B. He, L. Zhang, H. Zhang, and H. Yang, *Adv. Opt. Mater.*, 4, 106 (2016).
26. V. Rai, N. Tiwari, M. Rajput, S. M. Joshi, A. C. Nguyen, and N. Mathews, *Electrochim. Acta*, 255, 63 (2017).
27. S. Araki, K. Nakamura, K. Kobayashi, A. Tsuboi, and N. Kobayashi, *Adv. Mater.*, 24, OP122 (2012).
28. K. Sheng, B. Xue, J. Zheng, and C. Xu, *Adv. Opt. Mater.*, 9, 2002149 (2021).
29. K. Sheng, F. Xu, K. Shen, J. Zheng, and C. Xu, *Electrochem. commun.*, 111, 106646 (2020).
30. S. Kimura, K. Nakamura, and N. Kobayashi, *Sol. Energy Mater. Sol. Cells*, 205, 110247 (2020).
31. S. Xi, Y. Chen, Z. Bi, S. Jia, X. Guo, X. Gao, and X. Li, *Chem. Eng. J.*, 370, 1459 (2019).
32. T. Okada, H. Abe, A. Murakami, T. Shimizu, K. Fujii, T. Wakabayashi, and M. Nakayama, *Langmuir*, 36, 5227 (2020).
33. S. Devaraj and N. Munichandraiah, *J. Phys. Chem. C*, 112, 4406 (2008).
34. A. Tsuboi, K. Nakamura, and N. Kobayashi, *Sol. Energy Mater. Sol. Cells*, 145, 16 (2016).
35. A. Tsuboi, K. Nakamura, and N. Kobayashi, *Adv. Mater.*, 25, 3197 (2013).
36. M. Ueda, H. Dietz, A. Anders, H. Knepper, A. Meixner, and W. Plieth, *Electrochim. Acta*, 48, 377 (2002).
37. G. Sandmann, H. Dietz, and W. Plieth, *J. Electroanal. Chem.*, **491**, 78 (2000).

**Authors Contribution**

Shunsuke Kimura : Investigation, Writing – original draft

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Kazuki Nakamura : Writing – review & editing

Norihisa Kobayashi : Project administration, Writing – review & editing
Figure Captions

Figure 1.
Changes in the transmittance at 400 nm (top) and cyclic voltammogram (bottom) of the MnO$_2$ layer on the ITO electrode in a 3-electrode electrochemical cell.

Figure 2.
Changes in the transmittance at 400 nm (top) and current density (bottom) of the MnO$_2$ layer on the ITO electrode when applying potentials of $-1.2$ V vs. Ag/Ag$^+$ for 30 s and $+0.5$ V vs.Ag/Ag$^+$ for 30 s alternately.

Figure 3.
Transmission spectra of prepared MnO$_2$ layer on the ITO electrode in its oxidized (yellow line) and reduced (black dash line) states.

Figure 4.
Reaction charge amounts of the MnO$_2$ modified electrode at each redox cycle when applying constant potentials of $-1.2$ V vs. Ag/Ag$^+$ for 30 s and $+0.5$ V vs.Ag/Ag$^+$ for 30 s alternately.
Figure 5.
(a) Transmission and (b) reflection spectra at transparent and mirror states of the EC device. Photographs of the EC device at (c) transparent and (d) mirror states. (e) Change in transmittance at 550 nm of the device (top) and change in current (middle) during voltage application (bottom).

Figure 6.
Schematic representation of the voltage-step method and simple constant voltage application.

Figure 7.
(a) Change in absorption spectra during step-voltage application. Voltage application sequence: $V_1 = -3.0$ V, $t_1 = 80$ ms; and $V_2 = -1.4$ V, $t_2 = 60$ s. The initial state is represented by the black dashed line, and the absorption spectra of the device for every 10 s during $V_2$ application are represented by the solid blue line. (b) Photograph of the device at its initial state. (c) Photograph of the device at its colored state ($t_2 = 60$ s).

Figure 8.
Change in the absorption spectra of the device under the open circuit condition. The initial cyan state (0 s) indicates immediately after finishing step-voltage application, corresponding to the spectrum of $t_2 = 60$ s in Fig. 7.
Figures

Figure 1.

![Figure 1: Graph showing current density vs. potential, with transmittance at 400 nm.](image)

Figure 2.

![Figure 2: Graph showing current density over time, with transmittance at 400 nm.](image)
Figure 3.

![Figure 3](image)

Figure 4.

![Figure 4](image)
Figure 5.
Figure 6.
Figure 7.

![Graph showing absorbance vs. wavelength](image)

Figure 8.

![Graph showing absorbance vs. wavelength](image)