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Multicolor Electrochromic Device with LSPR of Silver Electrodeposition toward Color Reflective Display

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Abstract

Novel multicolor electrochromic (EC) device based on electrochemical silver deposition was successfully demonstrated. The EC device exhibited reversible multicolor change of primary colors— transparent, magenta, cyan, yellow, black (CMYK) and silver mirror —in a single cell by using electrochemical method which controlled the morphology of silver deposit. In this paper, we particularly analyzed the coloration mechanism in detail.

Introduction

Electrochromism (EC) is defined as reversible color change caused by electrochemical redox reactions. Electrochromic display has various advantages comparable to conventional displays, such as high visibility under sun light, a memory effect, and color variation. Electrochromic display has been attracting significant interest for strong candidate in information displays such as electronic paper (e-paper).

We had reported silver (Ag) deposition–based EC device achieving three optical states—transparent, silver-mirror, and black—in a single cell [1]. Its underlying mechanism was based on the electrodeposition of Ag nanoparticles on two facing transparent electrodes, a flat indium thin oxide (ITO) electrode and an ITO particle modified electrode. The EC material, gel electrolyte containing Ag^+ ion, was sandwiched by the two electrodes. The device's default state was transparent, whereas, applying a negative voltage to one or the other electrode causes the electrodeposition of Ag on its surface. When Ag was deposited on the flat ITO electrode, the device turns mirror. On the other hand, when Ag was deposited on the rough ITO particle modified electrode, the device turns black (Fig. 1).

Although progress toward multichromatic representation in full-color EC displays has been expected [2-4], control of the multichromatic state using inorganic EC devices has rarely been reported. Among our study on metal deposition–based EC device, we recently found multiple color changing phenomena based on electrochemically size-controlled Ag nanoparticles [5]. In the research, we focused on the Ag nanoparticles exhibiting various optical states based on their localized surface plasmon resonance (LSPR). The LSPR band is known to change its absorption wavelength depending on the size and shape of the nanoparticles [6, 7]. Therefore, dramatic changes in color are achieved by manipulating these bands.

Experimental

Materials

Silver nitrate ($AgNO_3$, Kanto Chemical Co. Inc.) and copper chloride ($CuCl_2$, Kanto Chemical Co. Inc.) were used as received. Dimethyl sulfoxide (DMSO, Sigma Aldrich Japan) was used as received. Lithium Bromide (LiBr, Kanto Chemical Co. Inc.) was used as supporting electrolyte without further purification. Poly (vinyl butyral) (PVB, Sekisui Chemical Co. Ltd.) was used as a host polymer for electrolyte gelation. The ITO electrode (<10 Ω/□) was used after adequate washing. ITO particle dispersed solution (Sigma Aldrich, particle size is less than 100 nm (DLS)) was used for preparation of the ITO particle modified electrode.

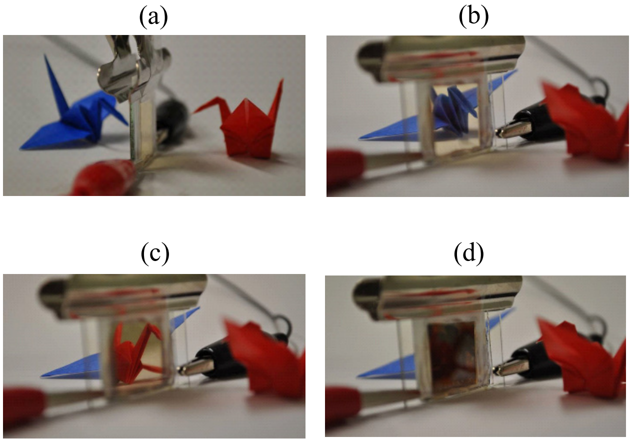

Fig. 1 Photographs of Ag based EC cell from side view (a), before (b) and after application of bias voltage; -2.5 V for mirror state (c) and 2.5 V for black state (d).

Sample preparation

The gel electrolyte for the electrochromic cell was prepared as follows: 50 mM of $AgNO_3$ as electrochromic material, 250 mM of LiBr as supporting electrolyte, and 10 mM of $CuCl_2$ as electrochemical mediator were dissolved in DMSO. Subsequently, 10 wt.% of PVB as host polymer was mixed into the DMSO-based electrolyte solution. The ITO particle modified electrode was prepared by spin coating of ITO particle dispersed solution on a flat ITO electrode (500 rpm 5 s, 1500 rpm 15 s). Subsequently, the modified electrode was baked at 250 ° C for 1 h.

Fabrication of electrochromic cell

The electrochromic cell (flat ITO electrode cell) was constructed by sandwiching the PVB-based gel electrolyte between two flat ITO electrodes, maintaining the inter-electrode distance of 500 μm with a Teflon spacer. The other electrochromic cell (ITO particle modified electrode cell) was constructed by sandwiching the gel electrolyte between the ITO particle modified electrode (as working electrode) and the flat ITO electrode (as counter electrode), also maintaining the inter-electrode distance of 500 μm. The cell areas were both 1 cm × 1 cm.

Apparatus

Chronoamperometric measurement was carried out using a potentiostat/galvanostat (ALS, 660A) equipped with a computer. Absorption spectra were recorded by on a diode array detection system (Ocean Optics, USB2000). The surface morphology analyses of deposited Ag nanoparticles on the electrodes were carried out using a field emission scanning electron microscope system (FE-SEM; JEOL, JSM-6700F).

Results and Discussion

In order to obtain reversible changes among multiple colors by shifting the LSPR band, in the study the "voltage-step method" was applied using an Ag deposition-based EC device. In this method, two different voltages are applied successively (Fig. 2): the first voltage V_1 is applied for a very short time t_1 to initiate the Ag nucleation, and the subsequent second voltage V_2 is applied for a time t_2 to promote growth of the Ag nuclei. Because V_2 is more positive than the nucleation voltage, further nucleation is no longer possible during t_2 [8, 9]. Therefore, growth of the Ag nanoparticles and the resultant color of the device can be controlled by changing t_2.

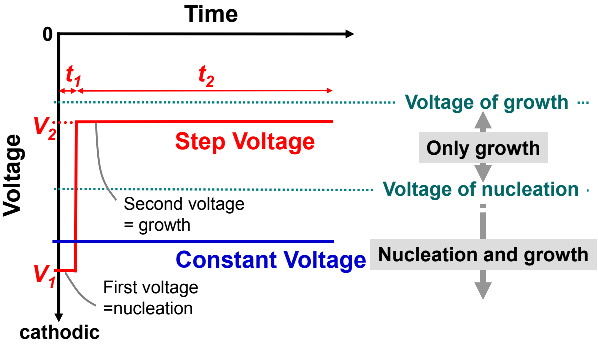

Fig. 2 Schematic representation of the voltage-step method. The first voltage V1 is applied for a brief time t1 to form nucleation sites. The first voltage is immediately followed by the second voltage V2 for a time t2. Because V2 is more positive than the nucleation voltage, no further nucleation is possible.

By applying the voltage-step method, magenta and cyan color states have been successfully observed in the Ag deposition–based EC device in our previous study [5]. However, the ability to show three primary colors (yellow in addition to cyan and magenta) is more desirable for representation in full-color EC displays. It is known that silver nanoparticle exhibits yellow color if its size is very fine (about 5–10 nm) [7]. In this research, therefore, to obtain fine and uniform Ag nanoparticles, we introduce the voltage-step method and vary the electrode surface structure. We measured the optical properties of the EC cell with flat ITO or ITO particle modified electrode during the step voltage application. As a result, we newly enabled Ag deposition–based multicolor EC device to achieve yellow color representation in addition to cyan and magenta states. Additionally in order to discuss the relationship between the morphologies of the electrodeposited Ag nanoparticles and the device color, we carried out field emission scanning electron microscopy (FE-SEM) analysis of silver-deposited electrodes.

The electrochromic cell (flat ITO electrode cell) was constructed by sandwiching the PVB-based gel electrolyte between two flat ITO electrodes, maintaining the inter-electrode distance of 500 µm with a Teflon spacer. The gel electrolyte for the electrochromic cell was prepared as follows: 50 mM of $AgNO_3$ as electrochromic material, 250 mM of LiBr as supporting electrolyte, and 10 mM of $CuCl_2$ as electrochemical mediator were dissolved in DMSO. Subsequently, 10 wt.% of PVB as host polymer was mixed into the DMSO-based electrolyte solution. The other electrochromic cell (ITO particle modified electrode cell) was constructed by sandwiching the gel electrolyte between the ITO particle modified electrode (as working electrode) and the flat ITO electrode (as counter electrode), also maintaining the inter-electrode distance of 500 µm. The cell areas were both 1 cm × 1 cm.

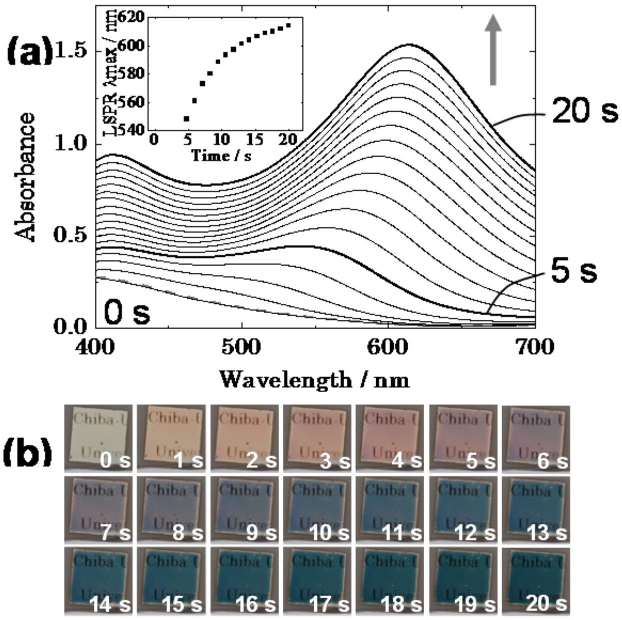

Fig. 3 a) Changes in absorption spectra of the flat ITO electrode cell during the Ag deposition process under an applied step voltage (the first voltage V1 = −4.0 V, t1 = 20 ms; the second voltage V2 = −1.6 V, t2 = 0–20 s). Insert shows plots of the LSPR peak wavelength vs. the application time of the step voltage. b) Photographs of the cell taken on a light box under the same applied step voltage.

Firstly the optical properties of the flat ITO electrode cell or ITO particle modified electrode cell were measured during the step voltage application. Fig. 3a and insert show the absorption spectra changes of the flat ITO electrode cell and plots of the LSPR peak wavelength vs. the application time of the step voltage ($V_1 = –4.0$ V, $t_1 = 20$ ms, $V_2 = –1.6$ V, $t_2 = 0–20$ s), which varied depending on the V_2 application time t_2. In particular, absorbance of the cell below 500 nm increased within the first 5 s, and then the absorption peak of these spectra sifted to the longer wavelength side. Finally, 20 s later, a spectrum with a maximum absorbance at around 620 nm was observed. The LSPR peak wavelength showed large red shifts (approximately 100 nm) during the step voltage application. Fig. 3b shows photographs of the cell taken on a light box under the applied step voltage. As can be seen in the photos, the cell first turned magenta ($t_2 = 4$ s) and then changed to cyan ($t_2 = 20$ s). The colors of the cell observed on a light box corresponded well with their absorption spectra, demonstrating that the voltage-step method for the electrodeposition of Ag on flat ITO electrode enabled the EC cell to selectively display magenta and cyan based on the shift of the LSPR band.

Then, we investigated electrochromic properties of the ITO particle modified electrode cell. Fig. 4a and insert also shows the absorption spectra changes of the ITO particle modified electrode cell and plots of the LSPR peak wavelength vs. the application time of the step voltage ($V_1 = –4.0$ V, $t_1 = 50$ ms, $V_2 = –1.6$ V, $t_2 = 0–20$ s). Absorbance of the cell at 410 nm increased in early times and then the absorption peak wavelength of these spectra sifted linearly to the longer wavelength side with increasing application time. 20 s later, a spectrum with a maximum absorbance at around 430 nm was observed. The LSPR peak wavelength shifted 20 nm during the step voltage application. Interestingly, the degree of the LSPR shift of the Ag nanoparticles deposited on ITO particle modified electrode was much smaller than that on flat ITO electrode (Fig. 3a). Fig. 4b also shows photographs of the cell taken on a light box under the applied step voltage. The cell first showed yellow color ($t_2 = 3$ s) and then changed to orange. The LSPR bands and resultant colors of deposited Ag nanoparticles were obviously different between on the flat ITO and the ITO particle modified electrode. The voltage-step method, therefore, newly enabled the Ag deposition–based EC cell to produce yellow color representation in addition to cyan and magenta color by introducing ITO particle modified electrode.

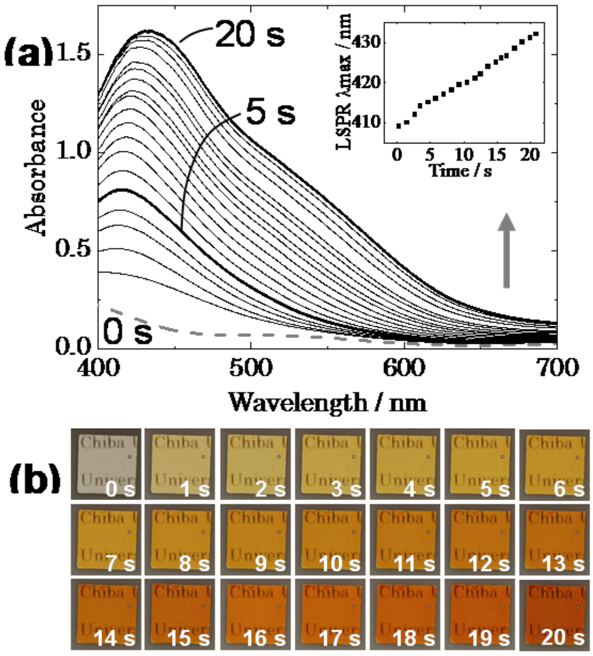

Fig. 4 a) Changes in absorption spectra of the ITO particle modified electrode cell during the Ag deposition process under an applied step voltage (the first voltage V1 = −4.0 V, t1 = 50 ms; the second voltage V2 = −1.6 V, t2 = 0–20 s). Insert shows plots of the LSPR peak wavelength vs. the application time of the step voltage. *b) Photographs of the cell taken on a light box under the same applied step voltage.*

Finally, to demonstrate a capable of displaying three primary colors, black (CMYK), and silver-mirror in this LSPR-based multicolor EC device, we combined this technique with our previously reported Ag deposition–based EC device that shows three optical states (transparent, silver-mirror, and black) [1]. An EC cell shown in Fig. 5a was fabricated and coloration of the EC cell was observed. When a constant voltage was applied, the cell entered a mirror state as Ag was deposited on the flat ITO electrode (−2.5 V for 20 s, Fig. 5b). When Ag was deposited on the rough ITO particle modified electrode (+2.5 V for 20 s), on the other hand, the cell turned black (Fig. 5c). Furthermore, when Ag nanoparticles were electrodeposited uniformly on the flat ITO electrode using the voltage-step method described above, the cell turned magenta or cyan depending on the V$_2$ application time (Fig. 5d, e). In addition, when fine and uniform Ag nanoparticles were electrodeposited on the ITO particle modified electrode using the voltage-step method, the cell turned yellow color (Fig. 5f). These changes in the optical states were all reversible. The optical change between transparent, silver-mirror, and black was stably maintained even after 2500 test cycles [1]. All optical changes in this device are based on the same mechanism of Ag deposition, so the repetition stability of the magenta, cyan, and yellow color changes is expected to be comparable with that of the change between the mirror and black state.

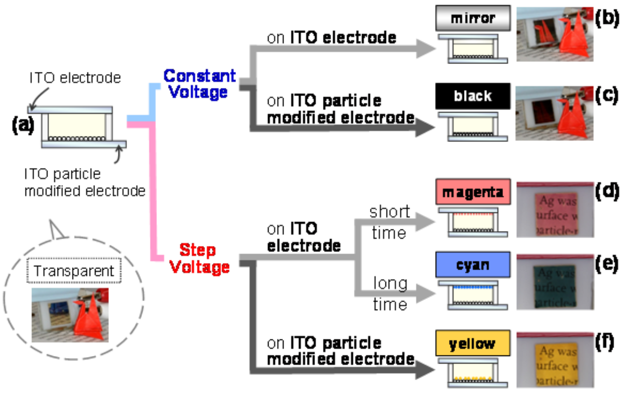

Fig. 5 Scheme and photographs of the two-electrode EC cell: a) transparent state (before voltage application), b) mirror state (constant-voltage application of −2.5 V for 20 s), c) black state (constant-voltage application of +2.5 V for 20 s), d) magenta state (step-voltage application of –3.8 V for 20 ms and −1.4 V for 4 s), e) cyan state (step-voltage application of −3.0 V for 50 ms and −1.4V for 20 s), and f) yellow state (step-voltage application of +4.0 V for 50 ms and +1.6 V for 3 s) .

Conclusion

Three primary colors of magenta, cyan, and yellow have been successfully observed in the Ag deposition–based EC device by introducing the voltage-step method. This color change was based on the control of the LSPR band of the Ag nanoparticles deposited on the flat ITO or ITO particle modified electrode. Then, we applied this technique to our previously reported transparent–silver-mirror–black EC device, as a result, we successfully achieved the LSPR-based EC device with six states of transparent, silver-mirror, black, cyan, magenta, and yellow (mirror + CMYK). The multifunctionality of this LSPR-based multicolour display device could make it suitable for use in information displays and light-modulating devices such as full-color E-paper, digital signage, and smart windows.

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References

[1] S. Araki, K. Nakamura, K. Kobayashi, A. Tsuboi, and N. Kobayashi, “Electrochemical Optical-Modulation Device with Reversible Transformation Between Transparent, Mirror, and Black,” *Adv. Mater.*, vol. 24, no. 23, pp. OP122-OP126, 2012. E. Peli, “Contrast in complex images,” *J. Opt. Soc. Am. A,* vol. 7, no. 10, pp. 2032-2040, 1990.

[2] N. Kobayashi, S. Miura, M. Nishimura, and H. Urano, “Organic electrochromism for a new color electronic paper,” *Sol. Energy Mater. Sol. Cells,* vol. 92, no. 2, pp. 136-139, 2008.
[3] K. Imaizumi, Y. Watanabe, K. Nakamura, T. Omatsu, and N. Kobayashi, “Multicolored electrochromism in 4,4’-biphenyl dicarboxylic acid diethyl ester,” *Phys. Chem. Chem. Phys.*, vol. 13, no. 25, pp. 11838-11840, 2011.

[4] Y. Watanabe, T. Nagashima, K. Nakamura, and N. Kobayashi, “Continuous-tone images obtained using three primary-color electrochromic cells containing gel electrolyte,” *Sol. Energy Mater. Sol. Cells,* vol. 104, pp. 140-145, 2012

[5] A. Tsuboi, K. Nakamura, and N. Kobayashi, "A Localized Surface Plasmon Resonance-Based Multicolor Electrochromic Device with Electrochemically Size-Controlled Silver Nanoparticles," *Adv. Mater.,* vol. 25, no. 23, pp. 3197-3201, 2013.

[6] D. D. Evanoff, and G. Chumanov, "Size-controlled synthesis of nanoparticles. 2. Measurement of extinction, scattering, and absorption cross sections," *J. Phys. Chem. B*, vol. 108, no. 37, pp. 13957-13962, 2004.

[7] T. Huang, and X.-H.N. Xu, "Synthesis and characterization of tunable rainbow colored colloidal silver nanoparticles using single-nanoparticle plasmonic microscopy and spectroscopy," *J. Mater. Chem.,* vol. 20, no. 44, pp. 9867-9876, 2010.

[8] G. Sandman, H. Dietz, and W. Plieth, "Preparation of silver nanoparticles on ITO surfaces by a double-pulse method," *J. Electroanal. Chem.,* vol. 491, no. 1, pp. 78-86, 2000.

[9] M. Ueda, H. Dietz, A. Anders, H. Kneppe, A. Meixner, and W. Plieth, "Double-pulse technique as an electrochemical tool for controlling the preparation of metallic nanoparticles," *Electrochim. Acta.,* vol. 48, no. 4, pp. 377-386,

Author Biography

Nori Kobayashi received his BS (1983) and his Dr. Eng. (1988) in applied chemistry from Waseda University, Japan. Since then he has worked in the Department of Image Science at Chiba University, Japan. His research interest has primarily focused on imaging-related photoelectronic-functional materials including polymer for development of photoconductive materials, materials with high electronic carrier mobility, highly emissive materials, light emitting materials, ionic conductive materials, electroactive materials, chromogenic materials and so on