Silver Electrodeposition Based Multicolor Electrochromic Device Showing CMY Three Primary Color States

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Abstract

Novel multicolor electrochromic (EC) device with on electrochemical silver deposition mechanism was successfully demonstrated. The novel EC device enabled reversible color change between transparent, red and blue color in a single cell by using voltage step method which controlled the size of deposited Ag nanoparticles.

Introduction

Electrochromism (EC) is defined as reversible color change caused by electrochemical redox reactions. Electrochromic display (ECD) has various advantages comparable to conventional displays, such as high visibility, a memory effect, and color variation. ECD has been attracting significant interest for strong candidate in information displays [1, 2]

Recently, we have reported silver (Ag) deposition-based electrochromic device achieving three optical states—transparent, silver mirror and black—in a single cell [3]. Its underlying mechanism was based on the electrodeposition of Ag particles on two facing transparent electrodes, a flat indium thin oxide (ITO) electrode and an ITO particle-modified electrode; the electrodes sandwiched gel electrolyte containing Ag^+ ion. The cell'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 cell turns mirror. On the other hand, when Ag was deposited on the rough ITO particle-modified electrode, the cell turns black. This Ag deposition-based EC device showed color change to only monochromatic color states; the multichromatic color states have not been achieved. The achievement of multichromatic color representation has considerable promise as full-color EC displays [4-7]. However, control of the multichromatic color was hardly reported by using inorganic EC devices.

In this research, we successfully demonstrated Ag deposition-based multicolor EC cell which showed red and blue states by introducing voltage step method [8, 9]. This method employs the successive application of two different voltages (Fig.1); the first voltage V_1 is applied for very short time t_1 to initiate the Ag nucleation, and the subsequent second voltage V_2 for a time t_2 promotes growth of the Ag nuclei. As V_2 is more positive than the voltage of nucleation, no further nucleation is possible during time t_2. Corresponding to growth of the Ag particles, transmission spectra of the device varied depending on V_2 application time. The device first turned to red color, and then the color was change to blue. In order to discuss the relationship between the morphologies of the Ag particles and the device color, we carried out scanning electron microscopy (SEM) analysis of silver-deposited electrodes.

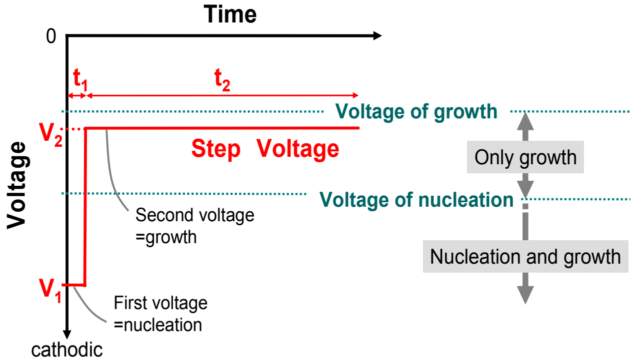

Fig.1 Schematic representation of voltage step method. First voltage V_1 is applied for a brief time t_1 to form nucleation sites. The first voltage is immediately followed by second voltage V_2 for a time t_2. As V_2 is more positive than voltage of nucleation, no further nucleation is possible.

Experimental

Materials and reagents

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 solvent 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 (Matema, 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.

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 with ITO-particle dispersion solution on a flat ITO electrode (500 rpm 5 s, 1500 rpm 15 s). Subsequently, the electrode was baked at 250 ° C for 1 h.

Fabrication of electrochromic cell

The electrochromic cell was constructed by sandwiching PVB-based gel electrolyte between the flat ITO electrodes, maintaining the inter-electrode distance of 500 µm with a Teflon spacer. The other electrochromic cell was constructed by sandwiching the gel electrolyte between the flat ITO electrode (as working electrode) and the ITO particle-modified 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 an ALS model 660A potentiostat/galvanostat equipped with a computer. Transmittances at 700 nm and transmission spectra were recorded on an Ocean Optics USB2000 diode array detection system. The surface morphologies and elemental analyses of Ag deposition on the electrodes were carried out using a scanning electron microscope system (JEOL, JSM-6510).

Results and discussion

Fig.2 shows cyclic voltammogram (CV) and transmittance changes at 700 nm of the cell using two flat ITO electrodes. As the voltage was scanned from 0 V in negative direction, cathodic current was observed from –2.1 V. This cathodic current can be attributed to the current for electrochemical reductions of Ag^+ dissolved in the gel electrolyte. Beyond –2.1 V, the transmittance of the cell decreased as a result of the electrodeposition of Ag on the ITO electrode (under a negative voltage). From these results, the voltage of –2.1 V could be considered as the critical nucleation voltage; the Ag nucleation required application of more negative voltage than –2.1 V. When the voltage was swept from –2.5 V in a positive direction, cathodic current disappeared at –1.3 V. The cathodic current observed between –2.1 V and –1.3 V would be due to the growth of the Ag nuclei. The critical growth voltage of Ag particle, therefore, was defined –1.3 V. When voltage between –2.1 V and –1.3 V was applied, no further nucleation would be induced and only growth of the Ag nuclei proceed, because applied voltage was more positive than critical nucleation voltage of –2.1 V. On the other hand, as the voltage was swept more positive direction, anodic current appears from –0.5 V. This anodic current reflects the oxidation of the electrodeposited Ag, leading to an increase in the cell's transmittance as they dissolve.

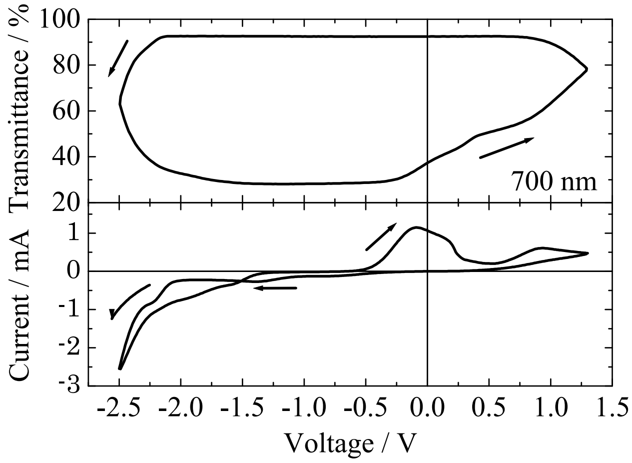

Fig. 2 Fig. Change in transmittance at 700 nm (top) and cyclic voltammogram (bottom) of EC cell.

Based on the result of preliminary experiments, the parameters of step-voltage were chosen as follows:

First voltage (nucleation): $V_1 = –4.0$ V, $t_1 = 20$ ms
Second voltage (growth): $V_2 = –1.6$ V

The voltage for nucleation (V_1) should be more negative than the critical nucleation voltage of –2.1 V, and the application time of the V_1 should be very short time in order to form many nuclei immediately. The growth voltage (V_2) should be more negative than the critical growth voltage of –1.3 V, but be more positive than critical nucleation voltage of –2.1 V, in order to proceed uniformed growth of the Ag particles without further nucleation. Under such condition, almost all Ag nuclei formed by the first voltage would grow uniformly to give similarly-nanosized particles. Nano-size Ag particles interact with visible light by particles effect their optical properties [10]. Therefore, application of the two different distinguished voltages enabling formation of uniformly-sized Ag nanoparticles would be effective for achieving vivid colors using our EC devices. Then, optical properties of the cell were measured by applying voltage step method mentioned above. Fig.3 (a) shows transmission spectrum changes (t_2 = 0 s~20 s) of the cell during the

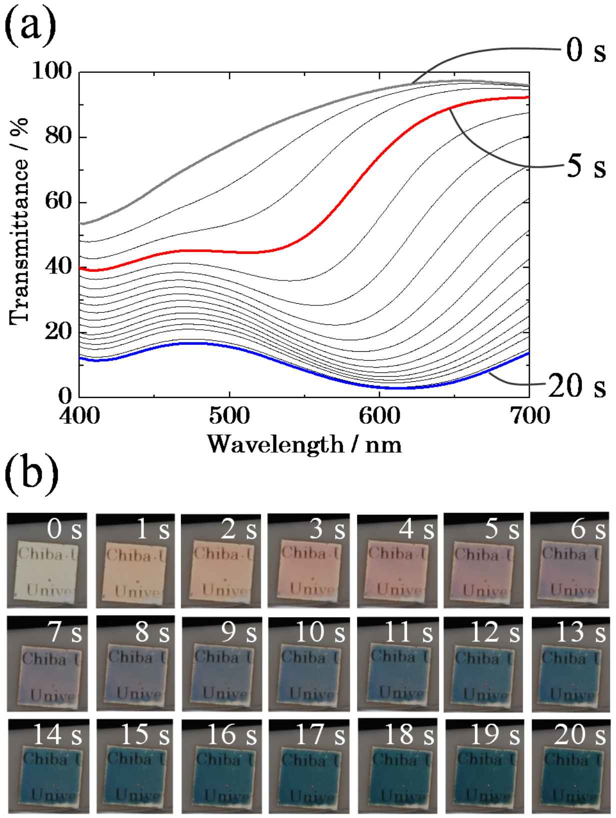

Fig.3 (a) Transmission spectral changes of cell during Ag deposition process under application of step voltage (the first voltage $V_1 = –4.0$ V, $t_1 = 20$ ms, the second voltage$V_2 = –1.6$ V, $t_2 = 0$~20 s). (b) Photographs of cell taken on a light box applied the same step voltage.

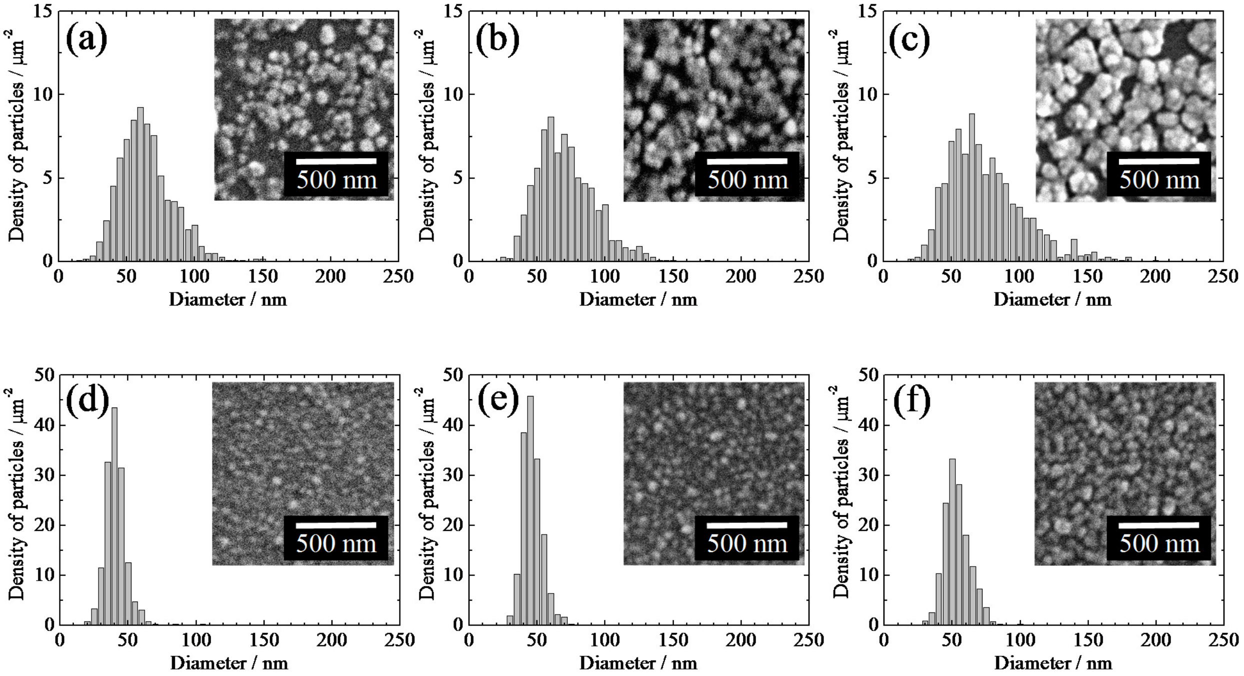

Fig.4 Size histograms of deposited Ag particles on ITO electrode applied constant voltage (–2.5 V/ (a) 5 s, (b) 10 s, or (c) 20 s) or step voltage (–4.0 V/ 20 ms and –1.6 V/ (d) 5 s, (e) 10 s, (f) 20 s). SEM images, from which the histograms are derived by extended particles, are also shown.

application of the step-voltage. The transmission spectra varied depending on V_2 application time t_2. Transmittance of the cell around 500~540 nm decreased at first 5 s, and then the minimum transmittance area in these spectra sifted to longer wavelength. 20 s later, finally, the spectrum with minimum transmittance at around 620 nm was observed. Fig.3 (b) shows photographs of the cell taken on a light box during the application of the same step-voltage. As can be seen in photos, the cell first turned to red color ($t_2 = 4$ s), and then the color was change to blue ($t_2 = 20$ s). Colors of the cell observed on a light box well corresponded to their transmission spectra. Hence, the voltage step method for the electrodepostion of Ag enabled the EC cell to achieve selective multicolor representation of red and blue.

In order to discuss the mechanism of the appearance of the red and blue color, we carried out SEM analysis of Ag deposited electrodes. Size histograms of Ag particles deposited on the ITO electrodes were obtained by SEM images to evaluate the influence of the applied time of the V_2. Fig.4 shows the changes of SEM image and size histogram of Ag particles deposited on ITO electrodes after the aoolication of constant or step-voltage for 5~20 s. Ag particles deposited by conventional constant voltage (–2.5 V) with mean diameter of 67 nm were observed in early time (5 s), and then they grew up to average 78 nm (20 s). The standard deviation of the particles' diameter increaced with application time of constant voltage, and finally, particles size varied widely (about 20~180 nm) for 20 s. This would be due to continues nucleation of the Ag particles during application of more negative voltage than critical nucleation voltage. Otherwise, the particle size distributions with voltage step method were narrower than those with constant voltage application. Uniformly-sized Ag nanoparticles with a diameter of 43 nm were obtained for 5 s, and the nanoparticles grew uniformly depending on V_2 application time, finally Ag nanoparticles with a diameter of 56 nm were observed after 20 s. This uniform growth would be caused by suppression of further nucleation during application the second voltage V_2. Almost all of nuclei formed by V_1 application grew up during the same period of V_2 application (t_2). Corresponding to particle size of uniformed-growth Ag nanoparticles, the absorption band based on localized surface plasmon resonance would shift to longer wavelength [10-12], resulting in the clear color change from transparent to red (particle size would be less than 40 nm), consequently blue (particle size is about 50 nm). The difference of the size of Ag nanoparticles would influence the optical state of the cell.

We showed that the voltage step method allow the control of Ag nanoparticles' diameter and successfully demonstrated Ag deposition-based EC cell which enabled red and blue color states. Based on our recent results [3], the EC cell with same configuration can show mirror state by application of constant voltage (–2.5 V). In addition, when ITO particle-modified electrode is used as the counter electrode of the cell, it turns black due to Ag deposition on the rough surface by applying constant voltage inversely (+2.5 V). Finally, we successfully demonstrated an Ag deposition-based multicolor EC cell that can switch from transparent state to four color state—black, mirror, red, and blue—in a single cell by combining flat ITO electrode and ITO particle-modified electrode (Fig.5). [13]

Conclusion

We investigated electrochemical properies of Ag deposition-based EC cell by introducing voltage step method. The EC cell enabled multicolor representation with electrochemically size-controlled Ag nanoparticles. The EC cell showed reversible color change, and its optical state varied depending on application time of the voltage for particle-growth V_2. The EC cell first turned to red color (4 s), and the the color was change to blue (20 s). From the SEM analyses, uniformly-sized Ag nanoparticles with a diameter of 43 nm were observed for 5 s, and the particles grew uniformly depending on V_2 application time, finally Ag nanoparticles' diameter increased 56 nm after 20 s. Due to uniform growth of Ag nanoparticles, the absorption based on localized surface Plasmon resonance would shift to longer wavelength, resulting in the clear color change from transparent to red, consequently blue. In addition, by using ITO particle-modified electrode for counter of cell, we successfully demonstrated an Ag deposition-based multicolor EC cell that can switch from transparent state to four color state—black, mirror, red, and blue—in a single cell. The multi functionality of this novel device could make it suitable for use in information displays such as electronic paper and digital signage.

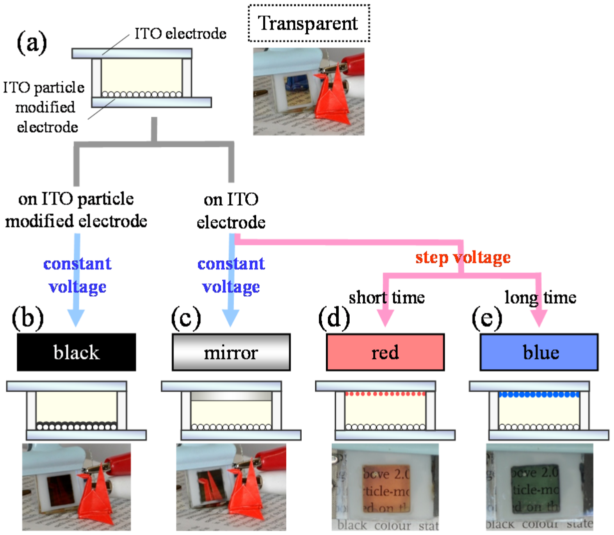

Fig.5 Scheme and photographs of the 2-electrode EC cell. (a) transparent state (before voltage application), (b) black state (constant voltage application: +2.5 V/ 20 s), (c) mirror state (constant voltage application: –2.5 V/ 20 s), (d) red state (step voltage application: –4.0 V/ 20 ms and –1.6 V/ 1 s), (e) blue state step voltage application: –4.0 V/ 20 ms and –1.6 V/ 3 s) [13]

Acknowledgments

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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.