

Advanced Electrochromic Display Utilizing Electrochemical Control of Silver-deposited Nanoparticle Form

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ABSTRACT

The novel electrochromic system utilizing electrodeposition of silver can express various optical properties such as mirror, black, cyan, magenta, yellow, and green in a single device. It is expected to be used as an advanced reflective electrochromic display.

1 Introduction

Electrochromism is a phenomenon of reversible color change induced by electrochemical redox reactions of electrochromic (EC) materials. It has been applied to practical devices such as e-paper, digital signage, smart windows, and anti-glare mirror. EC devices show a distinct color change by applying a few volts of voltage application, and the colored state can be maintained even without a power supply; thus, EC devices are driven by the low power consumption in general. EC displays have various advantages such as simple structure, large viewing angle, low power consumption, high visibility under sunlight, image retention properties without electric power, and color variation compared to conventional systems such as liquid-crystal displays with backlight or organic light-emitting diodes. Smart windows utilizing the EC technology can maintain a comfortable environment in a room or inside a car in terms of brightness and temperature. In addition, smart windows will become promising candidates for energy-saving devices, contributing to the reduced power consumption of air-conditioners.

There are various organic and inorganic EC materials have been reported so far. Conductive polymers[1], viologen derivatives[2], and phthalate ester derivatives[3] are well known as organic EC materials. Organic EC materials can switch their colors with few amounts of charge injection and release, and it is relatively easy to change the colors by designing the molecular structure. EC Materials showing multiple colors based on multi-step redox states from a single compound have been also reported[4], thus organic EC materials are expected to be applied for multi-color devices or full-color devices. However, the stabilities of these highly oxidized or reduced states are not usually enough. Therefore, it is difficult to maintain a certain color at a high voltage and to satisfy adequate cycling stability. Some inorganic materials such as transition metal oxides[5], prussian blue, and Prussian

blue analogs[6] are also known to exhibit EC and have been used in practical applications such as smart windows. Color changes of these materials are based on the intervalence charge transfer between metal atoms with different valences or two species of metal atoms. Thus, it is difficult to achieve vivid and multi-step coloring like organic materials and is generally considered difficult for multi-coloration devices.

Although there are commonly known organic and inorganic EC materials as mentioned above, our interest is a novel type of EC based on electrochemical deposition and dissolution of Silver. By controlling the form of silver deposit on the electrodes, our Ag deposition-based EC device achieved switching various optical states such as specular mirror, black, in addition to some chromatic colors from the transparent state[7]–[9]. Chromatic colors such as cyan, magenta, yellow, and green are due to absorption by localized surface plasmon resonance (LSPR) enhanced by the deposited silver nanoparticles. The LSPR band is known to change its absorption wavelength depending on the size and shape of nanoparticles. In our device, morphologies of deposited silver were successfully controlled, and it made it possible to manipulate dramatic changes in the color corresponding to LSPR bands. This novel EC system utilizing electrodeposited silver expected to be applied for the device equipping both cycle stability and ability to represent various colors. In this paper, we will review our previous report and discuss strategies to control the various optical states in the single device.

2 Experiment

In this study, the change in optical properties by electrochemical reduction of Ag^+ ions to metal silver were utilized as the EC reaction. The device was fabricated with a pair of ITO electrode sandwiching Dimethyl sulfoxide (DMSO) based gel EC electrolyte. The electrolyte contains silver(I) nitrate (AgNO_3) as EC material, copper(II) chloride (CuCl_2) as electrochemical mediator and counter reaction material, and lithium bromide as the supporting electrolyte. In addition, Polyvinyl butyral (PVB) was mixed as the host polymer.

3 Results and discussion

3.1 Switching between transparent, black and mirror

By applying -2.5 V for 20 s to the transparent device, silver was deposited on the ITO electrode and the device represented a mirror state that reflectance between 500–700 nm is ca. 70%. (Fig.1 left bottom) Furthermore, as shown in the schematic picture (Fig. 1) when one side of electrodes was modified with ITO nanoparticles and formed a rough surface; and silver was deposited on this surface, the device represented a black state (Fig.1 right bottom).

The differences in the optical properties can be explained by forms of the electrodeposited silver. For mirror state, it was revealed by observation with scanning electron microscopy (SEM) that the silver deposit on the flat ITO surface (Fig. 2 top left) forms thin film (Fig. 2 top right) by fusion between silver particles. The flatness of the deposited surface was evaluated by a laser microscope, root mean square roughness (RMS) was 86 nm (Fig. 2 bottom right). The formation of such a smooth deposited silver form makes the device a mirror state that reflects the incident light (Fig. 2 bottom left). On the other hand, when silver was deposited on the rough surface side (Fig. 3 top left), silver was deposited on the hollow between the ITO particles (Fig. 3 top right) and formed an uneven deposition surface (RMS 997 nm, Fig. 3 bottom right). Such a complex and uneven shape of the silver deposit causes quenching of the incident light due to multiple scattering, and the device turned to a black state (Fig. 3 bottom left).

As described here, the reversible control of the optical state of the device between transparent, mirror, and black in the single device are utilizing electrodeposition of silver. Furthermore, this EC device has high stability which is a characteristic of inorganic EC devices; reversible color changing of tens of thousands of times was already demonstrated.

3.2 Representation of chromatic colors

Ag deposition-based EC system is also able to represent chromatic colors such as cyan, magenta, yellow, and green. These 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 nanoparticles. Therefore, dramatic changes in color are achieved by manipulating these bands.

For the representation of vivid colors, silver nanoparticles with uniform particle size and shape are necessary to induce a specific LSPR band. For this purpose, the “voltage-step method”[10] was applied to the Ag deposition-based EC device to obtain multiple colors by shifting the LSPR band.

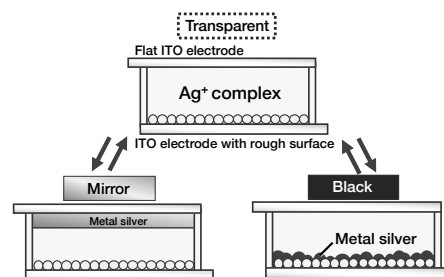


Fig. 1 The schematic picture of the Ag deposition-based EC device. Only one side of the ITO electrode was modified and formed rough surface.

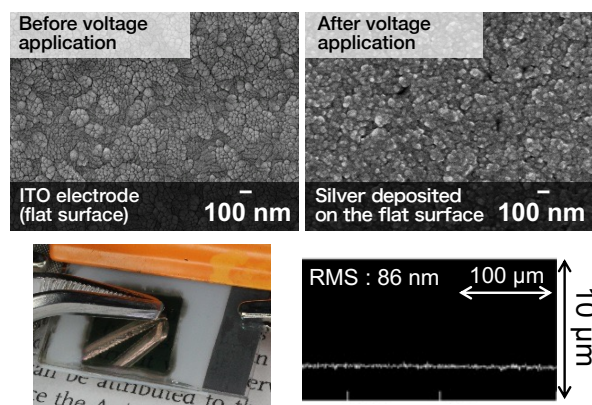


Fig. 2 SEM image of flat ITO electrode surface (top left). SEM image of the silver deposit on the flat ITO electrode (top right). EC device representing mirror state (bottom left). Result of surface measurement of the silver deposited surface by a laser microscope (bottom right).

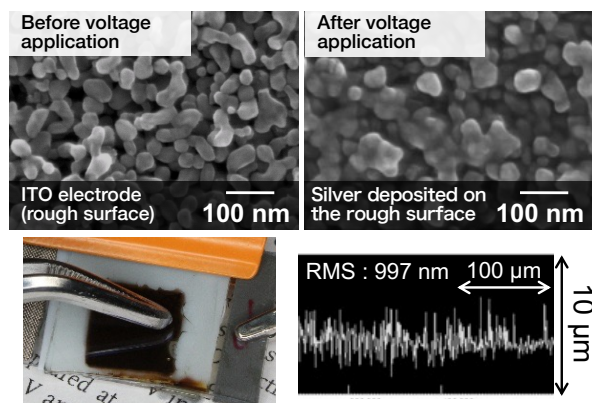


Fig. 3 SEM image of ITO electrode surface with rough surface (top left). SEM image of the silver deposit on ITO electrode with rough surface (top right). EC device representing the black state (bottom left). Result of surface measurement of the silver deposited surface by a laser microscope (bottom right).

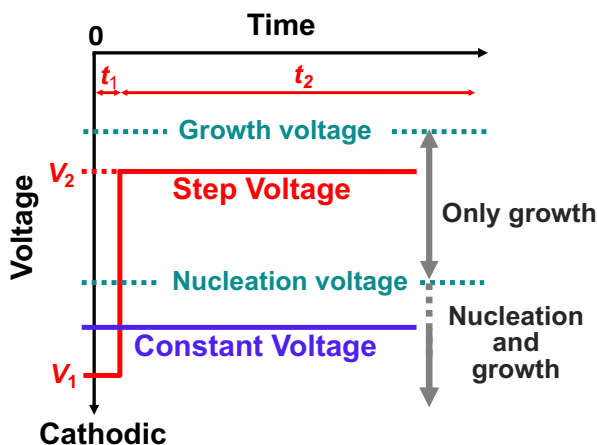


Fig. 4 Schematic representation of the voltage-step method.

In this method, two different voltages are successively applied (Fig. 4): the first voltage V_1 is applied for a very short time t_1 to initiate Ag nucleation, and the second voltage V_2 is applied for t_2 to promote the growth of the Ag particles. As V_2 is more positive than the nucleation voltage, further nucleation is no longer possible during t_2 . In this EC device, by adjusting the parameters (V_1 , t_1 , V_2 , t_2), it is possible to control the number of deposited silver particles (density) and diameter of particles, and the resultant device color.

For example, four colors (cyan, magenta, yellow, and green) shown in Fig.5 appeared in a single device by applying different parameters of step voltages. SEM images on the electrode where each coloration was obtained are also shown in the right figures in Fig. 5.

In the case of cyan, by applying the first voltage ($V_1 = -3.4$ V), then applying voltage for particle growth ($V_2 = -1.6$ V), silver nanoparticles fused each other and the induced LSPR absorption band shifted to longer wavelengths. The forms of silver deposits in this state had high anisotropy due to the fusion of several tens of nanometers of particles. $V_1 = -3.4$ V is 1.2 V larger than nucleation voltage (-2.2 V), which is the minimum voltage required for nucleation, thus, the number of deposited silver nanoparticles (density) was high, and leading to the connection and fusion between particles.

For magenta, the first voltage ($V_1 = -4.4$ V), was applied higher than in the case of cyan. This was because to increase the density of generated nuclei for getting higher vivid colors. The absorption increased faster than in cyan, and magenta shown in Fig. 5 appeared for 20 s of V_2 application. The spherical silver nanoparticles of less than 20 nm in diameter were fused with each other in this state. The anisotropy of the particles was smaller than that of cyan, and the diameter of the sphere composing the particle cluster is also smaller.

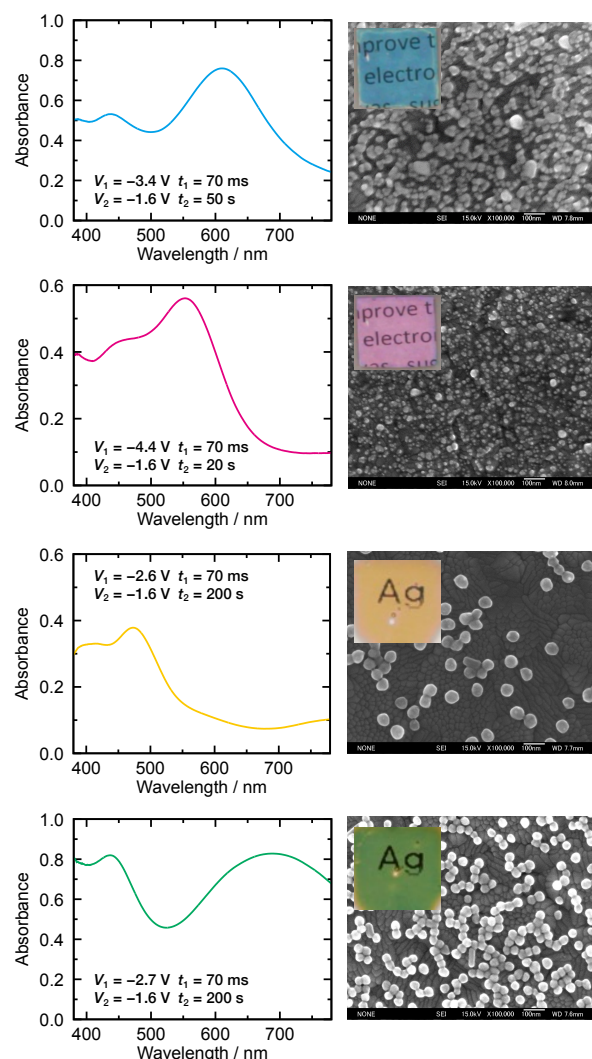


Fig. 5 Absorption spectra (left) and photographs (right) of cyan, magenta, yellow, and green colored device, and SEM images of electrode surfaces(right). Parameters of step voltages are shown within spectra.

The LSPR absorption band induced by spherical silver nanoparticles with small anisotropy is 400–500 nm. Then, the LSPR absorption band shifts to the long-wavelength direction according to the increase of the anisotropy of particles. In other words, magenta and cyan coloration described above by absorption in the longer wavelength region than 500 nm were realized by controlling the anisotropy of the particles by the parameters of voltage application.

On the other hand, for yellow coloration, non-anisotropic and sphere nanoparticles, which enhance the LSPR absorption band at 400–500 nm, are required. For reducing the density of particles, the first voltage ($V_1 = -2.6$ V), which is close to the nucleation voltage (-2.2 V), was applied, subsequently, the second voltage ($V_2 = -1.6$ V) was applied. As a result, particles grew while

maintaining their isolation, finally spherical and non-anisotropic silver nanoparticles were obtained as shown in SEM image in fig.5. As for the color of the device, an LSPR absorption band peaking at 473 nm was induced and the device represented yellow color successfully.

Green coloration is peculiar because it absorbs two regions (400–500 and 600–700 nm) of the incident light, unlike cyan, magenta, and yellow as described above. This absorption at the long-wavelength region (600–700 nm) is due to plasmon coupling. In the case of green, the application of 0.1 V higher than that of yellow as the first voltage, caused high-density nucleation; and finally, sphere particles were obtained higher in dense than in the case of yellow. Consequently, plasmon coupling occurred and absorption of light in the region of 600–700 nm in addition to the region of 400–500 nm. It is well known that when metal nanoparticles are close to each other and plasmon coupling occurs, the LSPR absorption band is dynamically shifted to the long-wavelength region[11]. As shown in the SEM image of the green color state, the spherical silver nanoparticles are in contact with each other. This deposited form leads to plasmon coupling and induces a second LSPR absorption band in the long-wavelength region, which is not possible only by the spherical particles alone. In other words, the green coloration of this device was realized by the combination of two absorptions: at short wavelength region below 500 nm by the silver nanoparticles alone, and at the longer wavelength region than 600 nm, which occurs by plasmon coupling.

4 Conclusions

Ag deposition-based EC device represents mirror, black, various chromatic colors including three primary colors of CMY, from the transparent state in a single device. In this paper, the strategy to control the forms of silver deposits on the electrode affecting the optical properties of the device was discussed. This EC system is based on only reversible electrodeposition of silver to switch the optical state; thus, unlike conventional multicolor EC systems, it does not require a multi-step redox reaction and is expected to have excellent repeat stability. And due to the simplicity of the device structure, it is also expected to be used in industrial applications such as electronic display, e-paper, and smart windows.

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