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# Chromatic control of multicolor electrochromic device with localized surface plasmon resonance of silver nanoparticles by voltage-step method

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## ABSTRACT

Inorganic electrochromic (EC) materials are of interest because of their many possible applications, including use in information displays. The multifunctional EC materials that enable control of multiple colors and color depth have considerable promise as candidates for full color EC display devices. In this research, we focused on Ag nanoparticles that exhibit various colors on the basis of their localized surface plasmon resonance (LSPR). Because the LSPR band depends on the size and shape of the nanoparticles, control of the morphology of Ag nanoparticles can lead to dramatic changes in color. In order to apply this color variation for display devices, we utilized here the electrochemical formation of size-controlled Ag nanoparticles using a voltage-step method that consists of an application of two successive different voltages. In order to improve the variation of colors of the EC cell, the effect of application voltages and their times on morphology of deposited silver were investigated. The relationship between the morphology of the deposited Ag nanoparticles and color of the EC cell was discussed, and then we successfully represented multiple coloration of the EC cell with various color depth.

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## 1. Introduction

Today we obtain much of our information from color images in books, on TV, or on the internet. Therefore, display devices that facilitate our visual communication are indispensable for life. Electrochromism (EC), a phenomenon of reversible color change caused by electrochemical redox reactions of material, is one of the prime candidates for full color display devices because of its various advantages, such as multicolor representation, low operation voltages, memory effects, and high visibility under sunlight [1–5].

For full color representation in EC devices, realization of three primary colors, cyan, magenta, and yellow (CMY), has been expected [6–8]. Multicolor EC systems, displaying more than two different colors in a single cell, have attracted attention because they have the potential to improve the resolution and color quality in full color EC displays [9–17]. However, most of the inorganic EC materials (e.g.,  $\text{WO}_3$ ) exhibit only a single color change, and in most case, inorganic EC materials exhibit darkened and cold colors [3,18–21]. A system that enables control of multichromatic states using only one type of EC material has rarely been reported.

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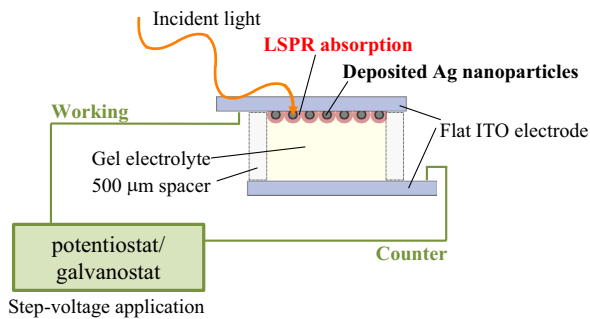
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To address this issue, we recently demonstrated a novel multicolor EC device showing CMY three primary colors on the basis of an electrochemical Ag deposition mechanism (Scheme 1) [22–24]. The devices for reversible electrodeposition systems are basically composed of a pair of transparent electrodes with a gel electrolyte containing  $\text{Ag}^+$  ion between them. The application of a negative voltage to either one of the electrodes causes the Ag metal deposition on the electrode substrate to construct metal nanoparticles or thin film that alters the optical properties of the surface. The color of the devices can also be bleached by applying voltage for oxidation of the Ag deposition, leading to the initial state of transparent condition. The improvements of the highly reversible optical changes between transparent state and colored state will open-up new applications in information displays, light shutters, and variable reflectance mirrors.

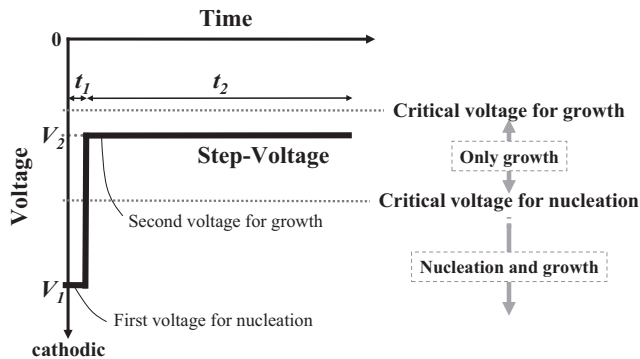
The Ag nanoparticles electrochemically deposited on an electrode exhibit various optical states based on their localized surface plasmon resonance (LSPR) [25–31]. As LSPR bands depend on the size and shape of the nanoparticles, morphological control of the Ag nanoparticles can lead to dramatic changes in color. In order to apply this color variation for display devices, we formed electrochemically size- and shape-controlled Ag nanoparticles by varying the surface morphology of the electrode and by using a voltage-step method, which consisted of the application of two successive

different voltages (Fig. 1). In this method, the first voltage  $V_1$  is applied for a very short time  $t_1$  to initiate Ag nucleation. The second voltage  $V_2$  is subsequently 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 not induced during  $t_2$ . Therefore, growth of the Ag nanoparticles and the resultant color of the device is controlled by changing the time for particle growth,  $t_2$  [32–34]. In our previous study, magenta and cyan color states were successfully observed when Ag was deposited on flat ITO electrode by using this voltage-step method and controlling the particle growth time of  $t_2$  [22–24].

Although the representation of multiple colors with various color densities is expected for practical realization of EC display devices, the method to control the color depth of Ag deposition-based EC cells using step-voltage has rarely been reported. The



**Scheme 1.** Schematic illustration of the LSPR-based EC device with Ag deposition.



**Fig. 1.** Schematic representation of the voltage-step method. The first voltage  $V_1$  is applied for a brief time  $t_1$  to form nucleation sites. Application of  $V_1$  is immediately followed by the application of a second voltage  $V_2$  for a time  $t_2$ .  $V_2$  is more positive than the nucleation voltage and promotes particle growth without further nucleation.

aim of this paper is to improve the variation in the colors of the EC cell by controlling the application conditions of step-voltages. The effect of the step-voltage parameters (i.e.,  $V_1$ ,  $t_1$ , and  $V_2$ ) on coloration of the Ag deposition-based EC device was investigated in detail. The optical property of the EC cell with flat ITO electrodes were measured during the application of step-voltage with various voltages and application times. In addition, the relationship between the morphology of the deposited Ag nanoparticles and the color of the EC cell are investigated by field emission scanning electron microscopy (FE-SEM) analysis.

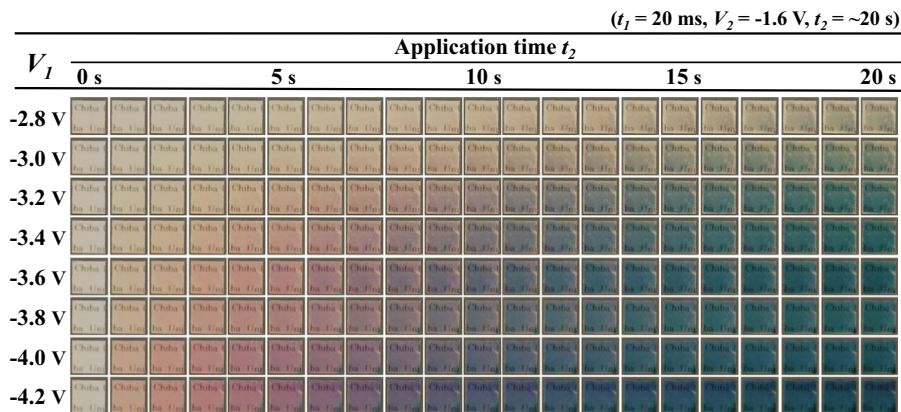
## 2. Experimental

### 2.1. Materials

Silver nitrate ( $\text{AgNO}_3$ ), copper chloride ( $\text{CuCl}_2$ ), and lithium bromide ( $\text{LiBr}$ ) were obtained from Kanto Chemical Co. Inc. Dimethyl sulfoxide (DMSO) was obtained from Sigma Aldrich Japan. Poly(vinyl butyral) (PVB,  $\text{MW} = 10.0 \times 10^4$ ) was obtained from Sekisui Chemical Co. Ltd. These reagents were used as received. An indium tin oxide (ITO) electrode (Wuhu Token Sciences Co. Ltd.,  $< 10 \Omega/\square$ ) was used after adequate washing with pure water and acetone.

### 2.2. Sample preparation and fabrication of electrochromic cells

The gel electrolyte for the electrochromic cell was prepared as follows: 50 mM of  $\text{AgNO}_3$  as the electrochromic material, 10 mM of  $\text{CuCl}_2$  as the electrochemical mediator [35–37], and 250 mM of  $\text{LiBr}$  as the supporting electrolyte and were dissolved in 10 mL DMSO. The  $\text{Cu}^{2+}$  ion in the gel electrolyte works as electrochemical mediator for the oxidation of the Ag deposition, accelerating bleaching speed of the device. The redox process of  $\text{Cu}^{2+}/\text{Cu}^{1+}$  or  $\text{Br}^{3-}/\text{Br}^-$  also work as the auxiliary electrochemical reaction, which prevent degradation of the EC properties of the device, against Ag deposition and dissolutions. Subsequently, 10 wt% of PVB as the host polymer was mixed into this DMSO-based electrolyte solution. The electrolyte thickening by adding PVB would suppress diffusion of the oxidized species generated on the counter electrode, improving coloration properties and bleaching responses of the devices. The electrochromic cell was constructed by sandwiching the PVB-based gel electrolyte between two flat ITO electrodes, maintaining an inter-electrode distance of 500  $\mu\text{m}$  with a Teflon spacer. The relatively wide inter-electrode distance of 500  $\mu\text{m}$  also improve coloration properties of the device by preventing the arrival of the oxidized species to electrodeposited Ag particles. The area of the cell was  $1 \times 1 \text{ cm}^2$ .



**Fig. 2.** Photographs of the EC cell during the Ag deposition process under an applied step-voltage with various parameters of  $V_1$ .  $V_1 = -2.8$  to  $-4.2 \text{ V}$ ,  $t_1 = 20 \text{ ms}$ .  $V_2 = -1.6 \text{ V}$ ,  $t_2 = 0$ –20 s. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

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