

# Influence of Capping Agent on Reflectivity of Silver Electrodeposition based Type Electrochromic Device

Hao Wang<sup>1</sup>, Takanori Sugita<sup>1</sup>, Shunsuke Kimura<sup>1</sup>, Kazuki Nakamura<sup>1</sup>, Norihisa Kobayashi<sup>1</sup>

koban@faculty.chiba-u.jp

<sup>1</sup> Graduate School of Engineering, Chiba University

Keywords: Electrochromism, Silver, Capping agent, Reflective display, Smart window

## ABSTRACT

*The novel Electrochromic (EC) system that utilizing electrodeposition of silver can express various optical properties such as mirror, black, and transparent in a single device. It is expected to be used as an advanced reflective electrochromic display. In this research, the citric acid was added to the electrolyte of the device as an capping agent to simply enhance the reflectance of the EC device.*

## 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, smart windows, and anti-glare mirror. 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. The invention of the device also played an important role in alleviating global warming.

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. 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[4][5][6], prussian blue, and Prussian blue analogs[6] are also known to exhibit EC and have been used in practical applications such as smart windows. The Color changes of these materials are based on the intervalence charge transfer between metal atoms with different valences or two species of metal atoms. However, it is difficult to achieve vivid and multi-step coloring like organic materials and is generally considered difficult for multi-coloration devices[7][8].

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, and transparent [9]. However, despite the novelty of the device, the reflectance of this device is not excellent for application, which is an important reason that limits its large-scale application[10]. In this study, by introducing citric acid as capping agent into the electrolyte of the EC device, the enhancement of reflectance of silver mirror was successfully. After the analyzing of silver film structure, the morphologies of deposited silver were successfully controlled and optimized, the structure of the film tends to be densified and flattened, which is also the reason for the promotion of reflectance. This novel EC system utilizing electrodeposited silver expected to be applied for the device equipping ability to represent optical reflectivity. In this paper, we will review our previous report and discuss strategies to enhance the reflectivity of mirror states in the single EC device.

## 2 Experiment

In this study, the change in optical properties by electrochemical reduction of  $\text{Ag}^+$  ions to metal silver were utilized as the EC reaction. The experiments were carried out in three electrode electrochemical cell. The three electrode electrochemical cell consists of ITO coated glass as the working electrode,  $\text{Ag}/\text{Ag}^+$  reference electrode and platinum wire as counter electrode. The Dimethyl sulfoxide (DMSO) based EC electrolyte is contains 10mM silver(I) nitrate ( $\text{AgNO}_3$ ) as EC material, and 50mM lithium bromide as the supporting electrolyte. The citric acid, a crucial additive in this study will be added to the electrolyte at different concentrations ratio of  $[\text{Ag}^+]:[\text{citric acid}]$  is 1:0, 1:0.5, 1:1, 1:2, respectively.

### 3 Results and discussion

#### 3.1 The electrochemical properties of EC device

By applying the scanning potential of  $-2.5$  V to  $0.5$  V to the transparent EC device (Fig.1). The cyclic voltammetry (CV) curves of the electrolyte containing different concentrations of citric acid are shown in Fig.2.

The Fig.2 shows the results of CV for the electrolytes containing different amounts of citric acid. When the potential starts scanning from the negative direction, it is observed that the reduction current gradually increases from  $-1.5$  V. This is because the Ag ions in the electrolyte are deposited on the ITO electrode. In addition, when the potential is scanned in the positive direction, the oxidation current is occurred from  $-0.8$  V. In addition, in each device, no noticeable differences in current value is observed. From the above cases, the addition of citric acid almost no effect on the redox behaviour of Ag ions. It can be said that the citric acid did not significantly promote or inhibit the rate of silver ion.

For the four type electrolytes above, the chronoamperometry (CA) is performed. By applying constant potential of  $-2.5$  V for  $150$  mC to the each device, silver was deposited on the ITO electrode and the device represented a coloring state that reflectance between the wavelength range from  $400$  to  $700$  nm is measured. (Fig.3). Fig.3 shows the reflection spectral measurements of Ag films prepared in the electrolyte with different amounts of citric acid added. As the concentration of citric acid increases, the reflectivity rises from  $20\%$  to  $60\%$ . It can be seen that, a mirror state with high reflectivity is obtained in the case of high concentration citric acid, while in the case of low citric acid concentration, a film with black state, the low reflectivity is obvious. Furthermore, to illustrate the effect of citric acid on silver precipitation behavior at the microscopic level. The FE-SEM shown in Fig.4 clearly shows the structural changes. As the amount of citric acid added in the electrolyte is increases, the particle size gradually becomes smaller, and the density of the nuclei on the electrode surface becomes larger. At the same time, the roughness of film has obviously decreased. The reason for explain this is the adsorption effect of citric acid on the specific surface of silver nanoparticles.

#### 3.2 XRD analysis of Ag films

The reflectivity has been improved by adding citric acid to the silver electrodeposition based type EC device. The surface of the silver film generated became smoother. As the main cause of this phenomenon, considering the adsorption of citric acid to the specific crystalline surface of silver nanoparticles during silver deposition. Therefore, the crystalline structure of silver that is deposited in the presence of citric acid needs to be evaluated by X-ray diffraction (XRD).

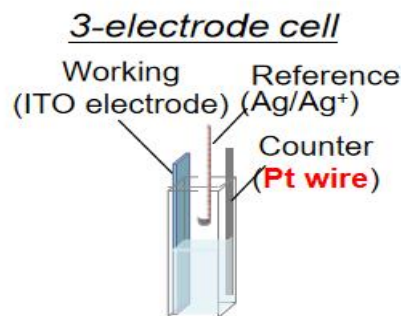


Fig. 1 The schematic picture of the Ag deposition-based 3 -electrode EC device.

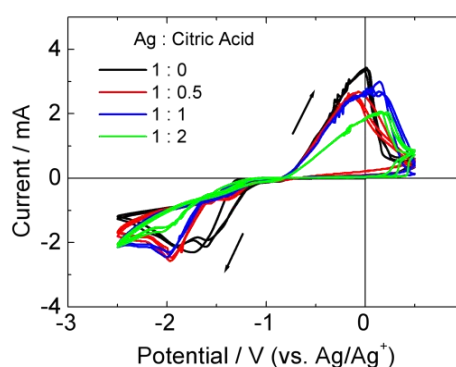


Fig. 2 Cyclic voltammograms of 3-electrode cell at various concentrations of citric acid;  $0$  mM  $\sim$   $20$  mM.

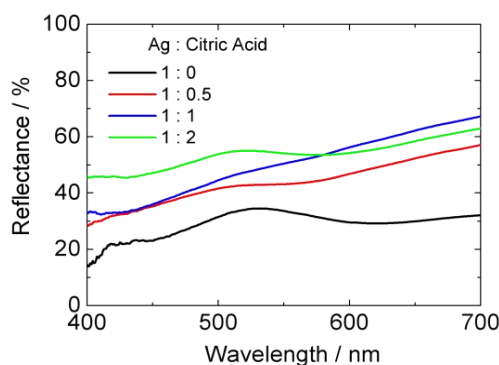
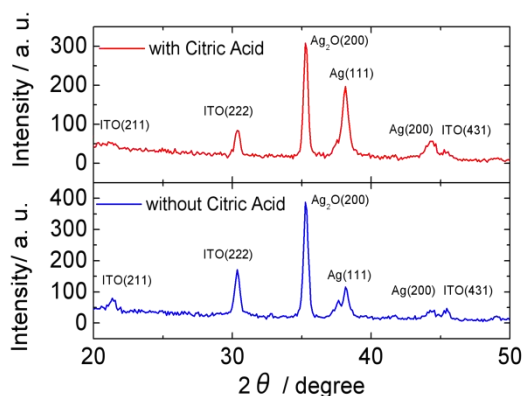


Fig. 3 The reflection spectra of 3-electrode cell after an application of constant potential ( $-2.5$  V,  $150$  mC) at various concentrations of citric acid;  $0$  mM  $\sim$   $20$  mM.

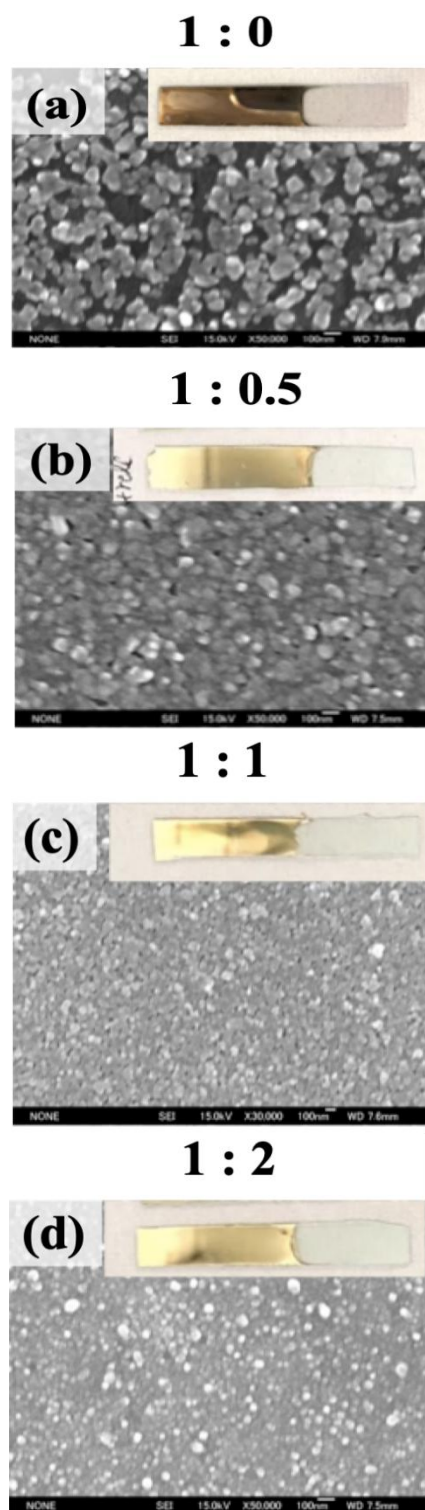


**Fig. 5 XRD graph of deposited silver by the solution with and without citric acid**

Numerous literature shows that adding a certain amount of citric acid to the synthesis of silver nanoparticles can precisely control the shape and size of silver nanoparticles. The citric acid can selectively adsorb to a specific crystal surface of silver to act as a capping agent, the crystal surface covered by citric acid will stop growing in electrodeposition. In this way, the growth of silver nanoparticles will be in anisotropy[11].

Fig. 5 indicates the XRD strength of the silver film precipitated when citric acid is added to the electrolyte and without citric acid. The citric acid is generally adsorbed on the  $\langle 111 \rangle$  crystal surface of silver, which has the effect of inhibiting the deposition of silver on this surface. The results showed that the strength of Ag(111) was greater with the addition of citric acid. This may be due to the adsorption of citric acid on the surface  $\langle 111 \rangle$  of the silver nanoparticles, the growth rate of the silver nanoparticles by protecting the  $\langle 111 \rangle$  plane is mitigated than others, thus a large number of arranged  $\langle 111 \rangle$  plane on the nanoparticles is eventually formed. In summary, the effect of citric acid on silver particles is actually recognized as a protective agent by adding citric acid, so it can be considered that the adsorption of citric acid is the main reason for the enhancement of the reflectivity.

According to the above results, the specific capping agent is useful for controlling the shape of silver. However, it is not known whether citric acid as an capping agent is the optimal strategy. As an EC device, the cycle stability is very important, but in our recent experiments, we found that after adding citric acid, the reflectivity of the device after about 100 cycles cannot be improved.



**Fig. 4 FE-SEM images of of 3-electrode cell after an application of constant potential (-2.5V,150mC) at various concentrations of citric acid;0mM ~ 20mM.**

#### 4 Conclusions

In this study, the citric acid as a capping agent attempts are made to improve the reflectivity of EC devices through specific adsorption on Ag crystal plane. Thus, it was found that the enhancement of reflectivity was actually caused by a adsorption phenomenon by citric acid on the Ag <111> plane in the electrodeposition reaction. Therefore, the citric acid-liked capping agents have been shown to be suitable additives for silver electrodeposition based EC device.

#### References

- [1] G. Sonmez, H. B. Sonmez, C. K. F. Shen, and F. Wudl, "Red, green, and blue colors in polymeric electrochromics," *Adv. Mater.*, Vol. 16, No. 21, pp. 1905–1908 (2004).
- [2] R. J. Mortimer and J. R. Reynolds, "An in situ colorimetric measurement study of electrochromism in the di-n-heptyl viologen system," *Displays*, Vol. 29, No. 5, pp. 424–431 (2008).
- [3] 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).
- [4] 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).
- [5] E. Ozkan, S. H. Lee, P. Liu, C. E. Tracy, F. Z. Tepehan, J. R. Pitts, and S. K. Deb, "Electrochromic and optical properties of mesoporous tungsten oxide films," *Solid State Ionics*, Vol. 149, No. 1–2, pp. 139–146 (2002).
- [6] K. Itaya, I. Uchida, and V. D. Neff, "Electrochemistry of Polynuclear Transition Metal Cyanides: Prussian Blue and Its Analogues," *Acc. Chem. Res.*, Vol. 19, No. 6, pp. 162–168 (1986).
- [7] 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).
- [8] A. Tsuboi, K. Nakamura, and N. Kobayashi, "Multicolor Electrochromism Showing Three Primary Color States (Cyan–Magenta–Yellow) Based on Size- and Shape-Controlled Silver Nanoparticles," *Chem. Mater.*, Vol. 26, No. 22, pp. 6477–6485 (2014).
- [9] S. Kimura, T. Sugita, K. Nakamura, and N. Kobayashi, "An improvement in the coloration properties of Ag deposition-based plasmonic EC devices by precise control of shape and density of deposited Ag nanoparticles," *Nanoscale*, Vol. 12, No. 47, pp. 23975–23983 (2020).
- [10] M. Ueda, H. Dietz, A. Anders, H. Kneppel, 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 (2002).
- [11] T. Jensen, L. Kelly, A. Lazarides, and G. C. Schatz, "Electrodynamics of Noble Metal Nanoparticles and Nanoparticle Clusters," *J. Clust. Sci.*, Vol. 10, No. 2, pp. 295–317 (1999).