

Chromatic Color Representation in Silver Deposition Based Electrochromic Cell toward Color Reflective Display

Norihisa Kobayashi

Graduate School of Engineering, Chiba University,
1-33 Yayoicho, Inage-ku, Chiba-shi, Chiba, 263-8522, Japan
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ABSTRACT

We reported Ag deposition-based electrochromic cell (ECD) which showed reversible color change from transparent to chromatic color, black and silver-mirror in a single device. This coloration is based on the absorption by localized surface plasmon resonance (LSPR) enhanced by the silver nano deposit. In this paper, we review a relationship between optical properties, deposition process and morphology of silver nanoparticles toward color reflective display.

1 Introduction

Electrochromism (EC) is defined as reversible color change caused by electrochemical redox reactions. ECD 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 have reported silver (Ag) deposition-based EC device achieving three optical states—transparent, silver mirror and black—in a single device.¹ Its underlying mechanism was based on the electrodeposition of Ag nanoparticles on transparent electrodes, a flat indium thin oxide (ITO) electrode or 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 the electrode causes the electrodeposition of Ag on its surface.

Although progress for multi-chromatic representation in full-color EC displays has been expected,²⁻⁴ control of the multi-chromatic state using inorganic EC devices has been reported but a few. Among our study on metal deposition-based EC device, we recently found multiple coloring phenomena based on electrochemically size-controlled Ag nanoparticles.^{5,6} This mechanism can be explained by a change in optical state based on their localized surface plasmon resonance (LSPR) of the Ag nano deposit. The LSPR band is known to change its absorption wavelength depending on the size and shape of the nanoparticles.^{7,8} Therefore, dramatic changes in color are achieved by manipulating these bands.

In order to obtain 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. 1): 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 .^{9,10} Therefore, growth of the Ag nanoparticles and the resultant color of the device can be controlled by changing t_2 .

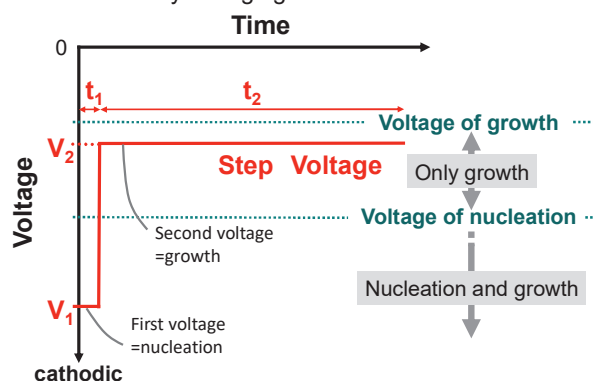


Fig.1 Schematic representation of voltage step method.

In this paper, we review a relationship between optical properties, deposition process condition and morphology of silver nano deposits toward color reflective display.

2 Experiment

2.1 Materials

All chemicals such as AgNO_3 , CuCl_2 , Dimethyl sulfoxide (DMSO), LiBr and Poly(vinyl butyral) (PVB) was used without further purification. The ITO electrode ($10 \Omega/\text{sq.}$) was used after adequate washing.

2.2 ECD Fabrication

The gel electrolyte for the ECD was prepared by dissolving adequate amount of AgNO_3 , LiBr, CuCl_2 and PVP into DMSO. The ECD was fabricated by sandwiching PVB-based gel electrolyte between the flat and rough surface ITO electrodes, maintaining the inter-electrode distance of $500 \mu\text{m}$ with a Teflon spacer. The device area was $1 \text{ cm} \times 1 \text{ cm}$.

3 Results and Discussion

The ECD enabled selective three optical states of

clear transparent, silver-mirror and black color by applying constant voltage. For example, by applying -2.5 V for 20 s to facilitate Ag deposition on the flat ITO electrode, the device represented a mirror state that reflectance between 500–700 nm is ca. 70%. (Fig.1 bottom left). On the other hand, Ag deposition on the rough ITO surface side gave a black state (Fig. 1 bottom right) due to the quenching of the incident light caused by multiple scattering and absorption.

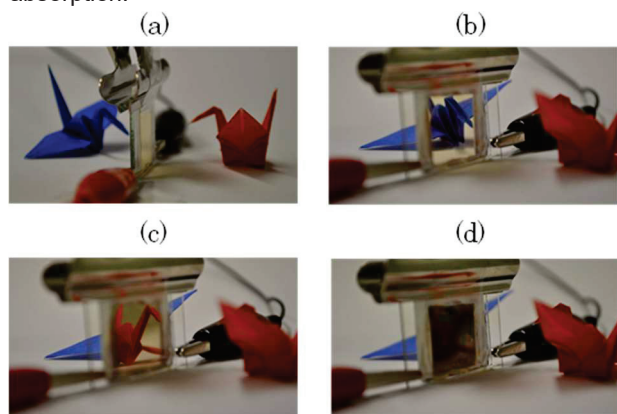


Fig.2 Photographs of Ag deposition-based EC cell from side view (a), transparent (b) silver-mirror state (c) and black state (d).

Next, we applied voltage-step method to realize chromatic color by using only Ag deposition. By optimizing the Ag ion concentration, driving voltage and deposition condition, vivid and bright colors of cyan and magenta (Fig. 3 top). This improvement was due to the generation of fine Ag nanoparticles and the prevention of the connection of Ag particles.

Further, by decreasing V_1 voltage for lower Ag ion concentration device, spherical Ag nano deposits were successfully obtained, and the device showed yellow and green colors (Fig. 3 bottom). By comparing the LSPR behavior of the device with that of Ag nanoparticles dispersed in solution and using FDTD calculations, the

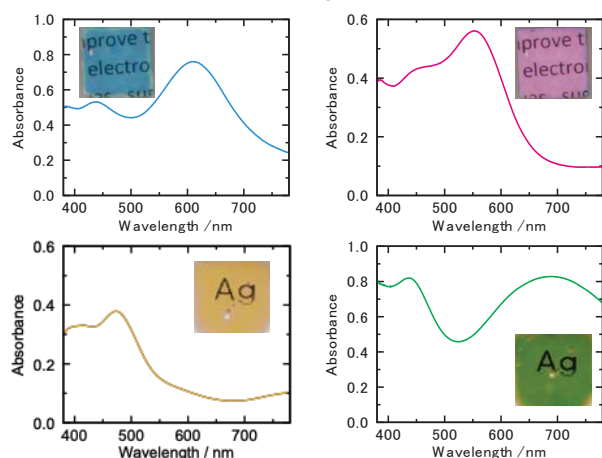


Fig. 3 Absorption spectra and photographs (insets) of cyan, magenta, yellow, and green states of the EC device.

mechanism of the yellow and green colors was investigated in detail. As a result, it was indicated that the yellow coloration with an absorption band in the 400–500 nm region was caused by LSPR absorption of isolated spherical Ag nanoparticles.

4 Conclusions

it was revealed that the coexistence of isolated spherical particles and aggregations of Ag nanoparticles induced two types of LSPR bands, leading to a good green color.

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. 14, pp. 122-126 (2012).
- [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, pp. 136-139 (2008).
- [3] K. Imaizumi, Y. Watanabe, K. Nakamura and N. Kobayashi, "Multicolored electrochromism in 4,4'-biphenyl dicarboxylic acid diethyl ester," *Phys. Chem. Chem. Phys.*, vol.13, 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, pp. 3197-3201 (2013).
- [6] A. Tsuboi, K. Nakamura and N. Kobayashi, "Multicolor EC Showing Three Primary Color States (Cyan–Magenta–Yellow) Based on Size- and Shape-Controlled Silver Nanoparticles," *Chem. Mater.* Vol. 26, pp. 6477-6485 (2014).
- [7] D. D. Evanoff, Jr. and G. Chumanov, "Size-controlled synthesis of nanoparticles. 2. Measurement of extinction, scattering, and absorption cross sections," *J. Phys. Chem. B*, 108, pp. 13957-13962 (2004).
- [8] T. Huang and X-H. Nancy Xu, "Synthesis and characterization of tunable rainbow colored colloidal silver nanoparticles using single-nanoparticle plasmonic microscopy" *J. Mater. Chem.*, 20, pp 9867-9876 (2010).
- [9] G. Sandman, H. Dietz, and W. Plieth, "Preparation of silver nanoparticles on ITO surfaces by a double-pulse method," *J. Electroanal. Chem.*, 491, pp78-86 (2000).
- [10] M. Ueda, H. Dietz, A. Anders, H. Knepp, A. Meixner, and W. Plieth, "Double-pulse technique as an electrochemical tool for controlling the preparation of metallic nanoparticles," *Electrochim. Acta*, Vol. 48, pp. 377-386 (2002)..