

Application of Dark-Field Microscopy to the Coloration Mechanism Analysis of Ag Deposition-Based Electrochromic Device

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ABSTRACT

We have studied Ag deposition-based electrochromic (EC) device that can represent various optical states. In this study, dark-field microscopy (DFM) was applied to in situ observation of localized surface plasmon resonance (LSPR) of Ag electrodeposits. Light scattering spectra obtained DFM provided detailed information on the LSPR.

1 Introduction

The electrochromic (EC) phenomenon is a reversible color change with the electrochemical reaction of redox active materials. EC technology is expected to be applied for light-modulating devices such as digital signages, e-papers, and smart windows.

For practical applications, an EC device that enables full-color representation is desired. Considering a novel multicolor EC system, we focused on the superior colorability of Ag nanoparticles (AgNPs). In the Ag deposition-based EC system, deposited AgNPs strongly absorb light at a specific wavelength depending on their morphology based on localized surface plasmon resonance (LSPR). In the case of AgNPs, LSPR bands appear in the visible light range, leading to various chromatic colors. Precise electrochemical control of the morphology of AgNPs enables multicolor EC devices with excellent optical properties. Based on this concept, we have reported a multicolor Ag deposition-based EC device, achieving various optical states: transparent, mirror, black, cyan, magenta, and yellow in a single pixel.¹

For further color variation and improvement of color purity of the Ag deposition-based EC device, it is essential to precisely control the morphology of the AgNPs in the device. Therefore, a novel observation method that allows detailed observation of changes in LSPR bands attributed to slight differences in morphology of individual AgNPs during device operation is necessary.

To observe the LSPR from electrodeposited AgNPs during EC device operation, in this paper, we focused on dark-field microscopy (DFM).² DFM was applied to the coloration process in the reversible Ag deposition-based EC device. The generation and growth of AgNPs in the device should be observed as scattered light changes of the LSPR bands. Furthermore, the coloration mechanism of the EC device was analyzed by the results obtained from DFM along with the morphological changes of AgNPs.

2 Experiment

2.1 Materials and preparation of the EC electrolyte

10 mmol/L Silver (I) nitrate (FUJIFILM Wako Pure Chemical Corporation) as the EC material, 10 mmol/L copper (II) chloride (Kanto Chemical Co., Inc.) as the electrochemical mediator and counter reaction material, and 50 mmol/L lithium bromide (Kanto Chemical Co., Inc.) as the supporting electrolyte were dissolved in dimethyl sulfoxide (DMSO, Sigma Aldrich, Japan). Subsequently, 10 wt.% of polyvinyl butyral, as the host polymer, was mixed into the DMSO-based electrolyte solution. ITO electrodes (ALLIANCE Biosystems) were used after washing and ozonation.

2.2 Fabrication of two-electrode EC device

The Ag deposition-based EC device was fabricated by sandwiching the prepared gel electrolyte between ITO electrodes. The effective electrode area was set to 1 cm², and the distance between the electrodes was 450 μ m.

2.3 Apparatus

A potentiostat/galvanostat (ALS/CHI 440A, ALS Co., Ltd.) was used to apply a voltage to the EC device. To observe the light scattering, a transmission optical microscope (BX51, OLYMPUS) was used. Light scattering spectra and absorption spectra were recorded using a photonic multichannel analyzer (PMA-12, Hamamatsu Photonics K.K.). Transmittance without the EC device (i.e., air) was used as a reference.

3 Results and discussions

The step voltage of $V_1 = -2.7$ V, $t_1 = 100$ ms, $V_2 = -1.6$ V, $t_2 = 150$ s was applied to the EC device. By applying such a step voltage, the AgNPs grow to a uniform shape and size and represent vivid chromatic colors by their LSPR.³ Fig. 1 shows the change in absorption spectra during application of the step voltage. At the end of the voltage application ($t_2 = 150$ s, green line), two large absorption bands were observed at 400 - 500 nm and 550 - 700 nm; the EC device exhibited an obvious green coloration (Fig. 1 inset). The absorption band in the shorter wavelength region is attributed to the LSPR of independent AgNPs, while the absorption band in the longer wavelength region is attributed to plasmon coupling.⁴ Each peak red-shifted and increased in absorbance with time of voltage application.

The light scattering spectra measured by DFM method

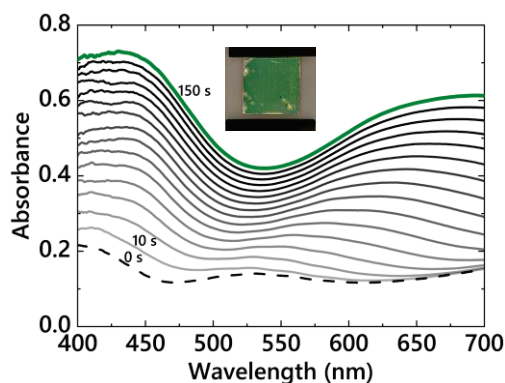


Fig. 1 Change in absorption spectra during step voltage application ($V_1 = -2.7$ V, $t_1 = 100$ ms, $V_2 = -1.6$ V, $t_2 = 150$ s). Inset: Photograph of the EC device in the green coloration.

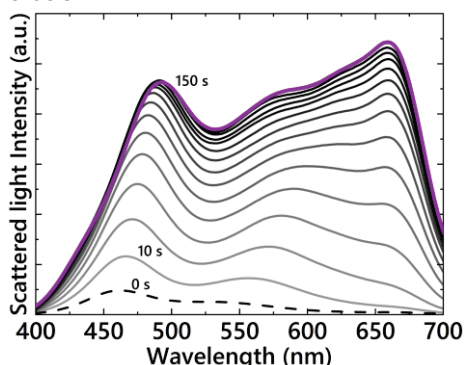


Fig. 2 Change in light scattering spectra during step voltage application ($V_1 = -2.7$ V, $t_1 = 100$ ms, $V_2 = -1.6$ V, $t_2 = 150$ s) obtained from the entire view of DFM.

during application of the step voltage in the same sequence ($V_1 = -2.7$ V, $t_1 = 100$ ms, $V_2 = -1.6$ V, $t_2 = 150$ s) is shown in Fig. 2. At the end of the voltage application ($t_2 = 150$ s, purple line), two light scattering bands were observed in the shorter and longer wavelength regions caused by LSPR, similar to the absorption spectra (Fig. 1). DFM images of the EC device during coloration process under the same voltage application sequence are shown in Fig. 3. Before voltage application, no scattered light was observed because nothing was deposited on the working electrode (Fig. 3a). Upon application of V_2 voltage, deposited AgNPs started to scatter blue light strongly, and the entire view became blue in first 60 s (Fig. 3b). In the continuous application of V_2 , red scattering caused by plasmon coupling was observed in the microscopic view. As a result, a variety of scattered light, such as blue, yellow, and red, was observed after step voltage application for 150 s (Fig. 3c). These results are consistent with the light scattering spectra shown in Fig. 2. For the LSPR band of the plasmon coupling, a single broad peak appeared at longer wavelengths in the absorption spectra. However, two distinct peaks at 580 and 660 nm were observed in the light scattering spectra. These LSPR peaks at 580 nm and 660 nm correspond to different plasmon coupling states, indicating that variety of plasmonic coupling states were

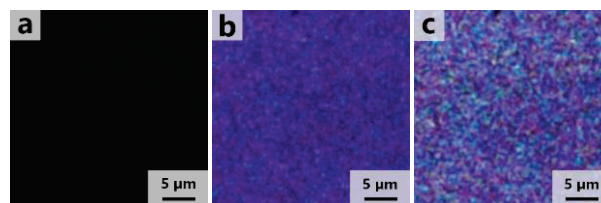


Fig. 3 Dark-field microscopy images during voltage application ($V_1 = -2.7$ V, $t_1 = 100$ ms, $V_2 = -1.6$ V, $t_2 = 150$ s). a: initial, b: 60 s, c: 150 s.

observed even after electrodeposition. The differences between the absorption spectra (Fig. 1) and the light scattering spectra (Fig. 2) can be explained as follows. The measurement area of the absorption spectra was approximately 5 mm in diameter, including variety of aggregation and coalescent structure in AgNPs. By overlapping the LSPR bands of a large number of AgNPs, a broad LSPR band was observed in the absorption spectra. In contrast, the microscopic view of the dark-field microscope is approximately 50 μ m in diameter. Therefore, the obtained light scattering spectra was derived from the LSPR bands of the AgNPs in this narrow measurement area without overlapping.

4 Conclusions

In the Ag deposition-based multicolor EC device, coloration process was particularly analyzed by DFM to clarify the relationship between the coloration and the LSPR properties of AgNPs. Detailed information on LSPR of AgNPs was successfully obtained with DFM for the first time. Change in the light scattering spectra is effective to determine the morphological structure of the AgNPs during the growing process. This novel measurement system using DFM is useful for evaluation optical change in Ag deposition LSPR based EC device.

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