Novel silver deposit-based electrochromic cell which shows clear transparent, silver-mirror and black color

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ABSTRACT

Novel electrochromic (EC) cell based on electrochemical silver deposition mechanism was successfully demonstrated. The novel EC cell consisting of flat ITO electrode and ITO particle-modified electrode enabled selective three imaging states of clear transparent, silver-mirror and black color in single cell by changing bias polarity.

1. INTRODUCTION

Electrochromism (EC) is defined as reversible color change induced by electrochemical reaction. Electrochromic display (ECD) has some advantages such as reflective display, large viewing angle, memory effect and so on. ECD has been attracting significant interest for strong candidate in paper-like display. The concept of paper-like display is clearly different from current emissive displays including liquid crystal display. Paper-like display requires paper-like looks, feelings and visibility. From this point of view, ECD have more advantages than other displays.

We have studied electrochromic properties of silver (Ag) deposition-based EC cell which showed reversible change between transparent state and mirror state. However, bleaching properties of the cell was unsatisfied due to low electroactivity of deposited Ag metal. It was reported that the bleaching property of metal deposit was improved in the presence of electrochemical mediator.1-4

In this research, we first constructed and studied electrochemical characteristics of novel Ag deposition-based EC cell consisting of flat ITO electrode (working) and ITO particle-modified electrode (counter) which enabled selective three imaging states of clear transparent, silver-mirror and black color by driving procedure. From reflection and transmission spectra measurements, the cell showed mirror state when Ag was deposited on flat ITO electrode. On the other hand, the cell showed black state when Ag was deposited on rough ITO electrode. In order to study the difference of the imaging states of mirror and black color, we carried out scanning electron microscopy (SEM) analyses of silver-deposited electrodes.

2. EXPERIMENTAL

2.1 Materials

Silver nitrate (AgNO3, Kanto Chemical Co., Inc.), copper chloride (CuCl2, Kanto Chemical Co., Inc.) were used as received. Dimethyl sulfoxide (DMSO, Sigma Aldrich Japan) were used as solvent as received. Tetra-n-butylammonium bromide (TBABr, Kanto Chemical Co., Inc.) was used as supporting electrolyte without further purification. Poly (vinyl butyral) (PVB, Sekisui Chemical Co., Ltd.) was used as a host polymer for the gel electrolyte. ITO particle-dispersed solution (Mitsubishi Materials Corporation) was used for ITO particle-modified electrode.

2.2 Fabrication of Ag deposition-based EC Cell

For constructing 3-electrodes EC cell, DMSO-based solution was prepared by dissolving 5 mM of AgNO3 as EC material, 100 mM of TBABr as a supporting electrolyte, 5 mM of CuCl2 as a mediator in DMSO. For PVB-based gel electrolyte, DMSO-based electrolyte solution was prepared by dissolving 50 mM of AgNO3 as EC material, 250 mM of TBABr as a supporting electrolyte, and 10 mM of CuCl2 as a mediator in DMSO. Subsequently 10 wt.% PVB as host polymer was mixed into the DMSO-based electrolyte solution. ITO particle-modified electrode was prepared by spin coating with ITO particle-dispersed solution on ITO electrode (500 rpm 5 s, 1500 rpm 15 s). Subsequently the electrode was annealed at 250 °C for 60 min. 2-electrodes EC cell was constructed by sandwiching PVB-based gel electrolyte between ITO electrode (as working electrode) and ITO particle-modified electrode (as counter electrode) keeping the inter-electrode distance of 500 μm with Teflon spacer.

2.3 Measurements

Chronoamperometric measurement was recorded on ALS model 660A potentiostat/galvanostat equipped with a computer. Transmission spectra and reflection spectra at 700 nm were recorded in situ by using Ocean Optics USB2000 diode array detection system. 3-electrode cell was equipped with platinum wire as counter electrode, and Ag/AgCl electrode as reference electrode. The surface profiles of Ag deposit on ITO electrode and ITO particle-modified electrode were analyzed by scanning electron microscopy (SEM, JEOL, JSM-6510A).

3. RESULTS AND DISCUSSION

Fig. 1 shows 3-electrodes cyclicvoltammograms (CVs) and change in transmittance at 700 nm of the EC solution by using flat ITO electrode (a) and ITO particle-modified electrode (b) as working electrode. In the case of CV using flat ITO electrode, when starting at rest potential to negative direction, cathodic current was observed from -0.7 V, giving reduction peak at -1.2 V. As increase of the reduction current, transmittance of the cell was decreased. The decrease of the transmittance would be due to production of Ag and Cu species on the ITO electrode under negative potential. The cathodic Ag deposition on flat ITO electrode gave specular...
surface. During potential sweep from -2.0 V to positive direction, the anodic current was raised from -0.4 V, giving peak at 0.3 V. This anodic peak was attributed to the oxidation of the electrodeposited Ag species, leading increase of the transmittance by dissolution of Ag particle. However, the transmittance of the cell was not recovered to initial value. This is probably due to less electroactivity of Ag deposit in the electrolyte solution. Whereas, additional oxidation current was found above 0.5 V which was assigned to oxidation of Cu$^{+}$ to Cu$^{2+}$. Since the oxidation potential of Cu$^{+}$ to Cu$^{2+}$ is higher than that of Ag metal to Ag$^{+}$, Cu$^{2+}$ electrically mediated the oxidation of the Ag deposit. The large oxidative current above 0.5 V supports this mediation mechanism. For this mediation, Ag deposit was fully oxidized to Ag$^{+}$, resulting in transmittance increase to initial value. Although the CV shape was broadened compared with flat ITO case, the similar CV and transmittance change were obtained by using ITO particle-modified electrode (Fig. 1 (b)). Those results indicated that the electrochemical reactivity of the EC solution was remained even on ITO particle-modified electrode. Interestingly, the Ag deposit on ITO particle-modified electrode showed non-specular black color.

In order to discuss the difference of optical properties of the Ag deposit on between flat ITO electrode and ITO particle-modified electrode, the transmission and reflection spectra of 2-electrode cell were measured. Fig. 2 (a) shows the transmission spectra of the 2-electrodes EC cell of the transparent state under bias voltage of -2.5 V (20 s) and bias voltage of 2.5 V (40 s). Under the bias voltage of -2.5 V and 2.5 V, the transmittance of the cell were decreased to lower than 20 %. These results indicate that Ag metal was deposited on flat ITO electrode (-2.5 V) and ITO particle-modified electrode (2.5 V) by electrochemical reduction of Ag$^{+}$ ion in the gel electrolyte.

Fig. 2 (b) shows the reflection spectra of the cell measured under bias voltage of -2.5 V and 2.5 V. Under the bias voltage of -2.5 V for deposition of Ag on flat ITO electrode, the reflectance of the cell was particularly increased in the whole region of the visible wavelength, and was reached to 100 % over 500 nm. This result suggests that the cell functioned as mirror device by electrodeposition of Ag particles on flat ITO electrode. The lower reflectance of the cell around 400-500 nm would be due to absorption of surface plasmon band of Ag particle. On the other hand, under bias voltage of 2.5 V for deposition on ITO particle-modified electrode, reflection of the cell decreased to about 10 %. In the
case of 2.5 V application, both transmittance and reflectance were decreased to approximately 10%, resulting that the cell changed the color to black by the application of 2.5 V.

Fig. 3 shows photographs of the EC cell in the transparent state (b), mirror state (c) and black state (d). This EC cell consisting of flat ITO electrode and ITO particle-modified electrode enabled selective three imaging states of clear transparent, silver-mirror and black color in single cell by changing bias polarity.

In order to discuss the mechanism of the appearance of the mirror state and black color state, we carried out SEM analysis of both Ag-deposited electrodes. Fig. 4 shows SEM images of Ag particles deposited on flat ITO electrode and ITO particle-modified electrode. The diameters of Ag particles ware about 90 nm on flat ITO electrode, which was almost uniformed. Furthermore, the Ag particles were connected each other. On the other hand, Ag particles deposited on ITO particle-modified electrode had aggregated structures around ITO particles which were 300-500 nm diameters. The difference of the size and connection of Ag deposits would influences reflectance value.

4. CONCLUSION

We investigated electrochemical characteristics of novel Ag deposition-based EC cell consisting of flat ITO electrode and ITO particle-modified electrode which enabled selective three imaging states of clear transparent, silver-mirror and black color. The EC cell showed reversible color change between transparent state and mirror state by the electrochemical reduction on flat ITO electrode. From reflection and transmission spectra measurements, the cell showed mirror state when Ag was deposited on flat ITO electrode. On the other hand, the cell exhibited black color state when Ag was deposited on rough ITO particle-modified electrode. In order to study the difference of the imaging states of mirror and black color, we carried out SEM analyses of Ag-deposited electrodes. The Ag particles deposited on flat ITO electrode ware smaller than these on ITO particle-modified electrode. The difference of the size and connection of Ag deposits would influences reflectance value. Therefore, we succeeded in constructing novel Ag deposition-based EC cell which shows three imaging states selectively with simple cell structure and drive system. We believed that the results of this research will contribute to the development of novel display devices such as e-papers, digital signages and smart windows.

REFERENCES

