Effects of silver halide complexes on optical and electrochemical properties of silver deposition-based electrochromic device

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ABSTRACT

Electrochromic-based optical modulation devices have attracted much interest because of potential application for electric papers and smart windows. We have reported Ag deposition-based optical modulation device which showed reversible changes of optical states between clear transparent and silver-mirror. In the device, formation of silver halide complexes greatly affected the optical states of silver electrodeposit. In this research, the effects of silver halide complexes were investigated by changing halide anion species in terms of the optical properties of the EC devices. The stability of the silver halide complex induced change in reduction voltage to form silver nanoparticles. Diffusion coefficients and electrode reaction rates also have effects on morphology of deposited Ag nanoparticles and resulting optical properties.

1. Introduction

Electrochromism (EC) is reversible optical changes induced by electronic energy and the resulting electrochemical redox reactions of materials. The obtained color changes are based on a change in the electronic state of a material caused by electron transfer between the EC material and an electrode. Tremendous number of reports for the EC materials with organic molecules, conductive polymers and inorganic compounds has been reported previously. These EC materials offer many advantages, including low operation voltages, memory effects, and high visibilities under sunlight. Therefore, EC materials are expected to achieve applications in information displays (i.e., electronic paper and digital signage [1–3]) or in light-modulating devices (i.e., light shutters [4], smart windows [5,6], and variable reflectance mirrors [7]).

Among them, many inorganic EC materials have attracted interests because of their electrochemical stability, and application for practical use. These inorganic EC materials can be classified into three different types. The first and most typical type of inorganic EC materials are transition metal oxides [5,8–10] such as WO_3, NiO, MoO_3 and V_2O_5. In metal oxide systems, the application of the potential to the material in electrolyte solution induces insertions of a cation with a small ionic radius (H^+, Li^+, etc.) into the crystal lattice of the metal oxide owing to charge compensation; the resulting electrochromic color change occurs through inter valence charge transfer. The second type of EC material is based on a switchable mirror phenomenon that occurs in metals (i.e.,

yttrium and lanthanum) and alloys of rare earth–magnesium or nickel–magnesium [11–13]. The reflection states of these metals are controlled by hydrogenation/dehydrogenation reactions. The third type of EC material involves the reversible electrodeposition of metals, such as Ag, Bi, Cu, Ni, and Pb. In this system, the reduction of metal cations dissolved in solution results in deposition of metal particles or films on a transparent electrode to control its color or reflection state [14–16].

Concerning the metal deposition-based EC devices, we have previously reported metal deposition-based EC device which showed reversible changes of optical state between clear transparent and black by Bi deposition [17] and between clear transparent and silver-mirror by electrodeposition of Ag metal [18]. Furthermore, we also reported Ag deposition-based EC device showing three primary colors of cyan, magenta, and yellow in a single device [19,20]. The dramatic changes in color of the deposition-based EC devices were successfully achieved by manipulating the localized surface plasmon resonance (LSPR) bands of deposited Ag nanoparticles. For achievement of such kind of various optical states, uniform and smooth deposition of Ag particles are quite important.

From our previous studies, it has become clear that formation of silver bromide complex ($AgBr_n^{1-n}$) is key factor for creating obvious optical states such as mirror, cyan, magenta and yellow. When bromide ion was absent in the electrolyte solution, the EC device could not create such variety of optical states, resulting in gray or black color. By introducing the formation of $AgBr_n^{1-n}$ in the electrolyte solution, Ag nanoparticles with uniformed size and structure were electrochemically

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deposited. However, mechanism for formation of such uniformed morphology of the Ag nanoparticles is not fully understood at present. Probably, various properties of silver complexes (such as stability, redox potential, electrochemical behavior, and so on) would affect the morphology of the Ag nanoparticles.

In this research, we analyzed effects of silver halide complexes (AgX_n^{1-n}) on the EC properties of the silver deposition-based EC device by changing halide anion species and concentration of halide ions. We first investigated the relationship between the stability and electrochemical reactivity of silver halide complexes. The morphologies of deposited Ag nanoparticles were observed by using field emission scanning electron microscope (FE-SEM); the relationship between the optical property and the morphology of the deposited Ag nanoparticles was evaluated. Then, the mechanism for formation of specific morphology of the Ag deposit was discussed in terms of electrochemical behaviors of rate constants for electrode reaction and diffusion coefficients of AgX_n^{1-n}. Finally, we discussed EC properties of 2-electrode EC devices containing AgX_n^{1-n}.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, Kanto Chemical Co. Inc., Japan), copper chloride ($CuCl_2$, Kanto) and dimethyl sulfoxide (DMSO, Sigma Aldrich, USA) were used as received. Tetrabutylammonium Chloride (TBACl, Sigma Aldrich), tetrabutylammonium bromide (TBABr, Kanto), tetrabutylammonium iodide (TBAI, Kanto) and tetrabutylammonium perchlorate (TBAP, Kanto) were used as source of halide ions and supporting electrolyte. Poly (vinyl butyral) (PVB, Sekisui Chemical Co. Ltd., Japan) was used as a host polymer for electrolyte gelation. The ITO electrode (sheet resistance < 10 Ω/sq., Cyoshin Electronics Co., Ltd., China) was used after adequate washing.

2.2. Potentiometric titration

The electrolyte solutions for potentiometric titration were prepared as follows: $AgNO_3$ (1 mM) and TBAP (50 mM) were dissolved in DMSO for analyte solution. TBACl, TBABr or TBAI (10 mM) were also dissolved in DMSO as titration solution. A silver sulfide wire as indicating electrode and Ag/Ag^+ as reference electrode was placed in the beaker. The potential difference between these electrodes was monitored by using a digital multi tester. 10 ml of DMSO solution containing $AgNO_3$ and TBAP was titrated with DMSO solution containing halide ions by using burette.

2.3. Fabrication of the EC device

The electrolyte solutions for 3-electrode cells were prepared as follows: $AgNO_3$ as electrochromic material, TBACl, TBABr or TBAI as material formation of AgX_n^{1-n} and TBAP as supporting electrolyte were dissolved in DMSO. The detailed concentrations of the reagents for each experiment were mentioned later. The 3-electrode cell was prepared by using ITO electrode (2.0 cm²) as working electrode, platinum wire as counter electrode and Ag/Ag^+ as reference electrode.

The gel electrolytes for 2-electrode EC devices were prepared as follows: $AgNO_3$ (50 mM) as electrochromic material, TBACl, TBABr or TBAI (250 mM) as supporting electrolyte, and $CuCl_2$ (10 mM) were dissolved in DMSO. Subsequently, 10 wt% of PVB as host polymer was mixed into the DMSO-based electrolyte solutions. The 2-electrode EC devices were constructed by sandwiching the PVB-based gel electrolytes between two ITO electrodes, maintaining the inter-electrode distance of 500 μm with a Teflon spacer. In order to measure the electrode potential of the electrolyte solution in the EC devices, we fabricated pseudo 3-electrode cells. The pseudo 3-electrode cell was constructed with two ITO electrodes (inter-electrode distance: 550 μm)

as the working and counter electrodes, and an Ag wire as the reference electrode. The Ag wire was inserted between two ITO electrodes. The cell areas were 1×1 cm².

2.4. Apparatus

Cyclic voltammogram (CV) was measured using a potentiostat/galvanostat (ALS660A, CH Instruments, Inc., USA) equipped with a computer. Absorption spectra were recorded by on a diode array detection system (USB2000, Ocean Optics, USA). The surface morphology analyses of deposited Ag nanoparticles on the electrodes were carried out using a FE-SEM (JSM-6700F, JEOL, Japan). The electrode potential measurements were performed by combining three electrochemical analyzers. ALS660A was used as the voltage source. In addition, potentiostat/galvanostat (ALS440A, CH Instruments, Inc.) and bi-potentiostat (DY2323, CH Instruments, Inc.) were used as the potentiometer.

3. Results and discussion

First, we investigated formation and stability of the AgX_n^{1-n} in the DMSO solutions by potentiometric titration method. Fig. 1 shows the potentiometric titration curves of the $AgNO_3$/DMSO solution titrated by the solution containing halide ion. Measured potentials between indicating electrode and reference electrode were transformed as concentration of free Ag^+ ion by standard curve. The standard curve was obtained by measuring electrode potentials of $AgNO_3$/DMSO solution containing various Ag^+ concentrations. As shown in Fig. 1, concentration of free Ag^+ ion decreased with the titration of halide ion in each solution. When the amount of titrated halide ion reached to equal amount of total Ag^+ ion, i.e. 1 ml of halide ion solution, concentration of the free Ag^+ ion rapidly dropped down and white precipitations were obtained. These behaviors indicated the formation of the silver halide salt (AgX). By adding the halide ions more, the precipitation dissolved again and the free Ag^+ concentration decreased gradually when the halide ions exceeded double amount of total Ag^+ ions (> 2 ml). This indicated formation of AgX_n^{1-n} which was soluble in the organic solvent. By using the concentration of free Ag^+ ion at the point which halide ion became equal to double amount of total Ag^+ ions, we calculated the complex stability of AgX_2^-. Table 1 shows concentration of ion species (Ag^+, AgX_2^-, X^-) and the stability constants of AgX_2^-. As shown in Table 1, concentrations of free Ag^+ were quite low, resulting that most of the Ag^+ formed the AgX_n^{1-n} with halide ions. Among the three complexes, the complex stability of AgI_2^- was the highest, followed in order by that of $AgBr_2^-$ and $AgCl_2^-$. When the titrated halide ions exceeded double amount of total Ag^+ ions (> 2 ml), the concentration of free Ag^+ ion in the iodide-titrated solution maintained the lowest value over the whole region of the titration, suggesting that quite high stability of AgI_n^{1-n} complex followed by
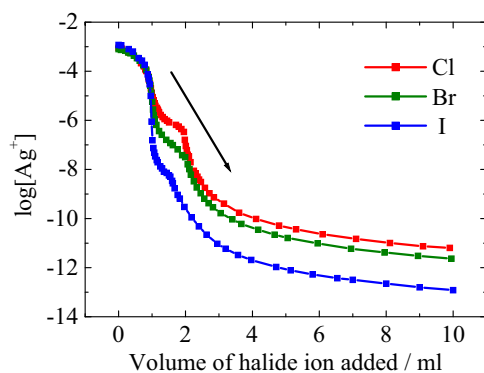

Fig. 1. Potentiometric titration curves of the $AgNO_3$/DMSO solution with the solution containing halide ions.