



Reversible Electrochemical Silver Deposition over Large Areas for Smart Windows and Information Display



Varun Rai^a, Naveen Tiwari^a, Mayank Rajput^{b,c}, Salil M. Joshi^b, Anh Chien Nguyen^a, Nripan Mathews^{a,b,*}

^a School of Materials Science and Engineering, Nanyang Technological University, 637553, Singapore

^b Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, 637553, Singapore

^c School of Electrical & Electronic Engineering, Nanyang Technological University, 639798, Singapore

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ABSTRACT

Silver based reversible electrochromic (EC) devices which can be used for smart windows and information display are analysed to examine the factors that determine switching time, color, and scale-up. These devices demonstrate multiple colors: silver, black, magenta, yellow and dark cyan blue with switching time as low as 5 seconds. The usage of redox mediators, applied bias, in enhancing the kinetics of the color transformation while being constrained by the electrochemical window of the DMSO solvent was examined. By a judicious combination of these factors, fabrication of large-area electrochromic devices up to 77 cm² operating at -3.0 V for formation of mirror-like reflective state ($\sim 100\%$ reflectance) in less than 15 seconds; and reverse switching to transparency at 0.5 V in less than 30 seconds have been realised. Devices capable of transforming into different patterns are also demonstrated with similar switching performance.

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1. Introduction

Electrochromic systems have attracted significant research interest for application in information display devices [1–3], digital signage light-modulating devices [4], variable reflectance mirrors [5] and smart window screen [6,7] because of its unique electrical and optical properties. Electrochromic (EC) materials can be categorized into inorganic, organic, inorganic organic hybrid materials [3,8]. Recently, inorganic transition metal oxides, such as WO₃, NiO, MoO₃, and V₂O₅ have been reported as electrochromic materials [7,9–11,12]. In these systems, smaller cations (H⁺, Li⁺, etc.) enter the crystal lattice of metal oxide and results in color changes through inter valence charge transfer upon application of electrical potential. These inorganic EC materials have many advantages as such low operating voltages with efficient electrical energy consumption and high visibility in sunlight. However realizing multiple colors with oxide based EC materials is challenging due to their relatively large band gap.

Organic electrochromic materials [13–15] such as bipyridinium derivatives (viologens), poly aniline, poly pyrrole (conducting polymers) and metallo-polymers, polythiophenes [8] show distinct UV–vis absorption spectra corresponding to their redox state [16]. While metallo-polymers show colors utilizing charge transitions between metal and ligand, multiple colors have not been realized in these materials due to limited redox states. Moreover organic electrochromic materials usually require multi-step procedures and toxic solvents for their synthesis and purification.

Another category of electrochromic systems utilize reversible electrodeposition of metals such as Ag, Bi, Cu, Ni, Mg alloys from their salts [5]. Recently, these systems have been extended to multiple colors under low electrical power, due to presence of various size-dependent optical states and localized surface plasmon resonance (LSPR) [17,18,30]. In general, such electrochromic devices involve transparent electrodes and electrochromic materials dissolved in liquid electrolyte or gel medium [19]. The electrochromic materials undergo reversible optical changes in color under application of electrical potential due to the resulting electrochemical redox reaction [20–23]. Recently, Araki et al reported EC devices based on silver electrodeposition that showed three reversible optical changes: transparent, silver-

* Corresponding author at: School of Materials Science and Engineering, Nanyang Technological University, 637553, Singapore. Tel.: +65 6790 4595.

E-mail address: Nripan@ntu.edu.sg (N. Mathews).

mirror, and black in a single cell ($1 \times 1 \text{ cm}^2$) [24]. Multiple colors such as magenta, cyan blue and yellow colors can also be realized in similar devices by applying pulsed voltage to trigger silver nanoparticle deposition of different sizes and shapes for the corresponding colors [25]. However it is challenging to achieve stable formation of fixed-size nanoparticles over a long period due to the aggregation tendency of nano-sized particles and changes in electrochemistry of electrolyte. A challenge not yet addressed in these systems, is the scaling up of the device area to sizes practical for use. The sheet resistivity of the transparent electrode materials such as indium tin oxide (ITO) would affect both the deposition and dissolution of metallic nanoparticles. Increasing the applied voltage to compensate for higher electrode sheet resistance does not solve this obstacle, but can unfortunately lead to the breakdown of the electrolyte solvent. These factors hence limit the development of metallic nanoparticle based electrochromic devices [26,27]. Color stabilization in silver based EC device entirely rely on fine control of the silver nanoparticles' size and shape [25]. Therefore in order to implement these technologies practically, the effects of scaling on stability and switching time need to be examined carefully.

Herein we have focused on the scaling up of such Ag based reversible electrodeposited system for smart window applications. The challenges behind scaling up and the role of the redox mediator in improving switching time and transparency are elucidated. Electrochromic systems which rely on pulsed deposition of plasmonic nanostructures for coloration could be scaled up to only 6 cm^2 and suffered from instabilities associated with electrolyte degradation under high voltages. By introducing Cu(II) Cl_2 in the electrolyte medium, the electrodeposited silver dissolves faster due to the oxidizing property of Cu(II) which oxidizes Ag(0) into Ag(I). Cu(II) acts as an electrochemical redox mediator which drives dissolution of electrodeposited silver over the electrode surface. Through very simple patterning strategies, information display and decorative patterns are demonstrated. Based on the advances presented here, we have scaled up electrochromic devices which switch between transparent and mirror finish, up to 76.5 cm^2 (active area) with an optical contrast of 85%.

2. Experimental

2.1. Reagents

Indium tin oxide (ITO) dispersion <100 nm particle size, 30 wt. % in isopropanol, silver nitrate (AgNO_3), tetra methyl ammonium bromide, lithium bromide (LiBr), anhydrous cupric chloride (CuCl_2), cupric nitrate $\text{Cu}(\text{NO}_3)_2$, NiCl_2 , PdCl_2 , poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate), dimethyl sulfoxide (DMSO) were obtained from Sigma-Aldrich. ITO coated glass 7 ohm/sq (surface roughness $\sim 2\text{--}3 \text{ nm rms}$) and flexible ITO coated PET sheet 6 ohm/sq (surface roughness $\sim 50 \text{ nm rms}$) were purchased from Xin Yan Technology LTD Hong Kong.

2.2. Sample preparation

The electrolyte solution was prepared by dissolving 42.5 mg AgNO_3 as electrochromic material, 53.5 mg LiBr as supporting electrolyte, 5.1 mg CuCl_2 as electrochemical mediator in 5.0 mL DMSO. DMSO was chosen because of its high polarity (dielectric constant 47) and relatively wide electrochemical windows up to 3.0 V in comparison to aqueous media for electrodeposition [28]. The resulting solution was kept at 120°C for 5–10 mins to achieve complete dissolution. Another electrolyte solution including 5.0 mg polyvinyl butyral -co- vinyl acetate as host polymer in same amount AgNO_3 , LiBr and CuCl_2 was also prepared in 5.0 mL DMSO to understand the role of host polymer. It was found that

gelating polymer helps to stabilize the deposition of plasmonic silver nanoparticles, hence uniform color formation, yet has some adverse effects on switching time between transparent and colored states. A reference electrolyte solution without electrochemical mediator was also prepared keeping same composition of remaining constituents e.g. silver nitrate, lithium bromide. The ITO nanoparticle-modified electrode was prepared by spin-coating the ITO dispersion (additionally diluted by 25% by volume) onto a flat ITO electrode at 1500 rpm for 60 s followed by 3000 rpm for 60 s. After spin coating the modified ITO glass was subjected to annealing at 250°C for 1 h.

2.3. Fabrication of the two-electrode electrochromic device cell

Cleaned ITO glass substrate and modified glass substrate were sandwiched using thermosetting ethylene vinyl acetate (EVA) polymer thickness ($50 \mu\text{m}$) as spacer. Electrolyte solution was filled between the flat ITO glass and modified ITO glass electrode. Care should be taken to fully fill up the space without the formation of air bubbles. Similar process was applied for devices with increasing active areas of 16 cm^2 , 30.25 cm^2 and 76.5 cm^2 . For display of information and decorative pattern, physical masks were used for deposition of ITO nanoparticles over selective areas followed by annealing at 250°C for 1 h. The initial state of EC device remains transparent and silver is electrodeposited selectively on either the flat ITO or modified ITO by applying continuous negative voltage resulting in the appearance of a silver mirror finish or black respectively. In the case of flexible electrochromic devices, ITO PET and ITO nanoparticles modified ITO-PET sheet were sandwiched using thermosetting polymer EVA with the ITO nanoparticles modified ITO-PET annealed at 120°C for improved adhesion.

2.4. Operating procedures for large area devices

Electrochromic devices were subjected to a potential of -3.0 V for 15 s, then allowed to become transparent by applying $+0.5 \text{ V}$ for 30 s. Subsequently -3 V was applied for longer durations of 20 s, 25 s and 30 s with transparency inducing reverse potentials applied in between. This "priming" procedure increased the area covered by the electrodeposited silver. Subsequent applications of -3.0 V resulted in complete silver deposition at short deposition times (15 s) (Supporting information Fig. S1(A) for large area devices). Fig. S1(B) shows the current vs time graph for the same device (76.5 cm^2) before and after priming. As can be seen in Fig. S1 (B), the initial state current passing through the ITO electrode surface at -3.0 V is higher (-0.41 A) after the priming procedure than before.

2.5. Apparatus

Continuous electrical potential and pulsed potential were applied to all electrochromic devices using Autolab PGSTAT302N. Shimadzu UV-3600 spectrophotometer was used to record simultaneous transmittance spectra across EC devices. Surface morphology was examined by JOEL JSM-7600F Scanning Electron Microscope (SEM).

3. Results and discussion

3.1. Electrodeposition of Silver over ITO nanoparticle modified ITO glass and flat ITO

Fig. 1(A) shows the schematic of the electrochromic device cell set up and 1(B) shows images of devices (size of 6 cm^2) in black – silver – transparent and multiple colors. When a potential of -2.5 V was applied to modified ITO electrode, the device turns yellow in

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