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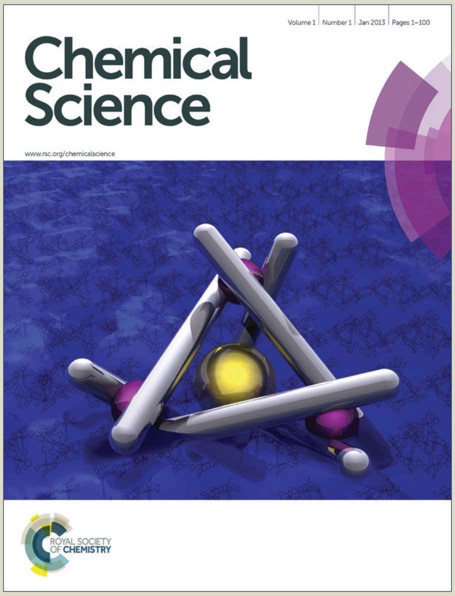

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EDGE ARTICLE

Switchable Silver Mirrors with Long Memory Effect

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Chihyun Park, Seogjae Seo, Haijin Shin, Bhimrao D. Sarwade, Jongbeom Na, and Eunkyoung Kim*

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An electrochemically stable and bistable switchable mirror is achevied for the first time by introducing 1) a thiol-modified ITO electrode for the stabilization of the metallic film and 2) ionic liquids as the anion-blocking layer to achieve long memory effect. The growth of the metallic film was denser and faster at the thiol-modified ITO than at a bare ITO electrode. The electrochemical stability of the metallic film on the thiol-modified ITO was enhanced, maintaining the metallic state without rupture. In the voltage-off state, the metal film maintained bistability for a long period (> 2 h) when ionic liquids were introduced as an electrolyte for the switchable mirror. The electrical double layer in the highly viscous ionic liquid electrolyte seemed to effectively separate the bromide ions outside of the electrocal double layer to protect the metal thin films from the bromide ions when in the voltage-off state.

1. Introduction

An ordinary silver mirror, coated on its back surface with silver, reflects light to produce high quality of images by reflection, owing to the high reflectivity of silver. Recently, tunable mirrors, including liquid-liquid interfacial mirrors started to gather attentions by its high applicability for smart windows, light modulators, and chemical sensors.[1-3] On the other hands, reversible electrochemical mirrors (REMs) are designed to modulate their reflectance, from a highly reflective state enough to mirror a subject to a highly transparent state, according to external stimuli such as electricity, light, or heat[4-6]. A number of REMs have been suggested, including metallic thin films,[7, 8] conducting polymers,[9-11] metal hydrides,[12-14] and colloidal electrochemical devices.[15] None, however, has reached widespread practical application because of critical problems such as the poor stability of the mirror state and lack of bistability in reflectance. Thus, there remain very important challenges to realizing switchable silver mirrors with long memory effect to afford bistable reversible electrochemical mirrors (BREMs). Previous studies have employed electrochemical conversion of a metal (e.g. Cu, Ag, Bi, etc.) onto a transparent conducting substrate to achieve a reflective state.[16-19] The optical properties of these REMs are switched according to the redox state of the metals, as well as their morphologies. Thus, much effort has been directed towards improving the properties of REMs, especially for Ag film-based electrochemical devices,[8, 20] with the addition of Cu ions that stabilize deposited Ag nanoparticles.[17] However, no studies have yet reported on the stabilization of mirror state over a long period, either in the electricity -on or -off state.

In electrochemical metallic mirrors, the reversible reflectance change originates from the electrodeposition of the Ag film, to achieve a mirror state, and the dissolution of Ag as an ion into an electrolyte, to achieve a transparent state. While the transparent state is quite stable, the mirror state is unstable because the deposited Ag film is dissolved into electrolyte solution as anions diffuse into the metallic film at open circuit state. To maintain the mirror state, it is necessary to apply a reduction voltage continuously to avoid the dissolution of Ag film into the electrolyte. However, Ag nanoparticles with aggregated structures and poor adhesion onto a substrate (e.g., ITO) generally yield cracks and wrinkles on the metal films under a prolonged supply of electrical charge. Therefore, it is important to stabilize the metallic film during the mirror formation.[21] The ultimate goal of these studies is to obtain bistability in switchable mirrors—i.e., stability in both the reflective and transparent states—particularly when the electrical power is turned off. This bistable status is critical to hold technological promise for new switchable mirrors of optic devices, memory, as well as energy saving smart windows. The poor bistability of REM originates from the oxidation of metallic silver to soluble $AgBr_n^{(1-n)}$ then to Ag(I), as described well in the literature.[22, 23] The high concentrations of halides increased the rate of Ag dissolution.[24] To protect the metal film from anions, we challenged to introduce the electrical double layer (EDL), which can block the ion diffusion.[25, 26] Highly capacitive ionic liquids (ILs) have been successfully used to stabilize metal nanoparticles[27, 28] or electrochemical devices.[29-31] Herein, we report an electrochemically stable, and bistable reversible electrochemical mirror (BREM), for the first time, by using a reversible silver deposition on a thiol modified ITO electrode in ionic liquids as the electrolyte media.

2. Experimental

2.1 Materials

Dimethyl sulfoxide (DMSO), silver nitrate ($AgNO_3$), copper chloride ($CuCl_2$), (3-mercaptopropyl)trimethoxysilane (MPTMS), 1-methyl imidazole, 1-buthyl imidazole, bromoethane, 1-bromohexane, tetrabutylammonium bromide (TBABr), and Polyvinyl butyral (PVB, Butvar® B-98) were purchased from Aldrich. All chemicals were used as received. 1-Methyl-4-hexylimidazolium bromide (MHImBr), 1-buthyl-4-ethylimidazolium bromide (BEImBr), and 1-butyl-4-hexylimidazolium bromide (BHImBr) were synthesized and purified according to the previous reports.[32-34] Structures of synthesized ILs are listed in Table S3.

2.2 Preparation of surface-modified ITO electrodes (TI)

Surface-modified ITO electrode was prepared by the previously reported procedure.[35] In brief, ITO electrode was cleaned by scrubbing with a soft cloth, sonication in ethanol and acetone for at least 10 min each, and dried under nitrogen. For a sufficient amount of the surface treatment reagent on the ITO electrode, hydroxyl group was formed by treating the bare ITO glass surface the with oxygen plasma. Thus the surface of the cleaned ITO glass was modified by oxygen plasma treatment for 5min with a power of 6.8W (CUTE-MP, Femto Science, USA). Then, the plasma-treated ITO electrode was placed in vacuum chamber with a few drops of MPTMS, and then evacuated for 1h.

2.3 Preparation of electrochemical silver mirrors

The electrochemical mirrors are consisted of an electrolyte filled between the surface-modified ITO glass (TI) and bare ITO (UI) electrode. The TBABr based electrolyte solution (TBAB) was prepared as follows: 0.5mmol of $AgNO_3$, 0.1mmol of $CuCl_2$ and 2.5mmol of TBABr were dissolved in 11g of DMSO with 1.2g of PVB as the host polymer. The ionic liquid based electrolyte solutions (MHIB, BEIB, and BHIB, respectively) were prepared as follows: 0.5mmol of $AgNO_3$ and 0.1mmol of $CuCl_2$ were dissolved in 45mmol of IL with 10wt% of DMSO. The prepared electrolyte was carefully coated on the bare ITO electrode with the polyimide spacer of 500μm thick, window size of 2.0×2.0 cm^2, and then assembled with a surface modified ITO electrode.

2.4 Measurement

Electrochemical measurements for the ionic liquids and prepared REMs were demonstrated using a universal potentiostat [model CHI 624B (CH Instruments, Inc.)]. UV-Vis. spectra were obtained using a PerkinElmer Lambda750 UV/Vis/NIR Spectrophotometer. The figure of merit for reflectance and thickness were calculated by dividing reflectance recorded at 650nm (%) and thickness (nm) by consumed charge density (C/cm^2). SEM images and EDS mapping were obtained using a JEOL-JSM-7001F, and TEM images were obtained using a JEOL-JEM-2100. TEM sample (Figure S1c) of Ag/Cu alloy particle was obtained by collecting alloy particles from sonication of electrodeposited Ag and Cu electrode. The resistance and capacitance of the ILs were determined from an impedance analyzer (Ivium B08016 , Ivium technology) as a function of frequency (from 10 to 10^5 Hz) using a simulation software (Zview 2.8d, Scribner Associates Inc.). A 50um thick IL layer was sandwiched between two ITO electrodes and a laminated top silver contact. For obtaining confocal fluorescence images, the thiol modified-ITO glass was cut into 5cm × 1cm. Then the two ITO glasses were separated 500μm by a polyimide tape spacer and adhered by a hot-melt adhesive. The electrolytes, TBAB and BEIB, containing fluorophore (pyrene 1%) were injected between ITO glasses and then covered with cover glasses. Confocal microscope (Axio Imager Z2, LSM 700, Carl Zeiss) was used for obtaining images of the side view. The laser (wavelength 405nm) was used as the excitation source for pyrene.

3. Result and Discussion

3.1 Electochemical stability of REM device

A highly reflective mirror with smooth surface was obtained from an electrolyte solution containing $AgNO_3$ and $CuCl_2$ (5:1 molar ratio), which was optimized according to the previous study.[20] The other components of the electrolyte were tetrabutylammonium bromide (TBABr) and polyvinyl butyral (PVB) in dimethyl sulfoxide (DMSO) as described in the experimental section. This electrolyte composition is abbreviated as TBAB hereafter. The distribution of metallic nanoparticles, formed upon application of -2.5V on a 2-electrode REM device, was relatively homogeneous and denser in the presence of Cu^{+2} than that without Cu^{+2}. In the SEM images along with EDS mapping, the homogeneous distribution of Ag-Cu bimetallic films was clearly observed (Figure 1e). This improved morphology of the metallic thin film is attributed that Cu induces aggregation of Ag particles. Cu content in the electrodeposited Ag-Cu surface was determined as ~24 % of Ag content from EDS mapping, which was smaller than the feed, possibly due to the charge difference between the two atoms. (Table S1).

A thiol modified electrode (TI) was prepared by anchoring the plasma-treated ITO electrode with (3-mercaptopropyl) trimethoxysilane (MPTMS) (Figure 1a). The metallic film was grown on TI upon application of a reduction potential (-2.5 V), using the solution of TBAB. (Figure S1d-f) It was noteworthy that the deposited metallic film was denser on the surface-modified ITO (TI) than on the bare unmodified ITO (UI), which can be observed in Figure S1d,e and be inferred from the figure of merit for thickness of TITBAB and UITBAB (Figure 1d). The average roughness of Ag film on UI was 66 nm, which was twice larger than that on TI (33 nm) as compared in Figure S2. This effect can be explained by the strong bonds between thiol groups and the metal ions. When TI is prepared with MPTMS, the trimethoxysilane groups are anchored onto the surface hydroxyl group of the ITO electrode while the

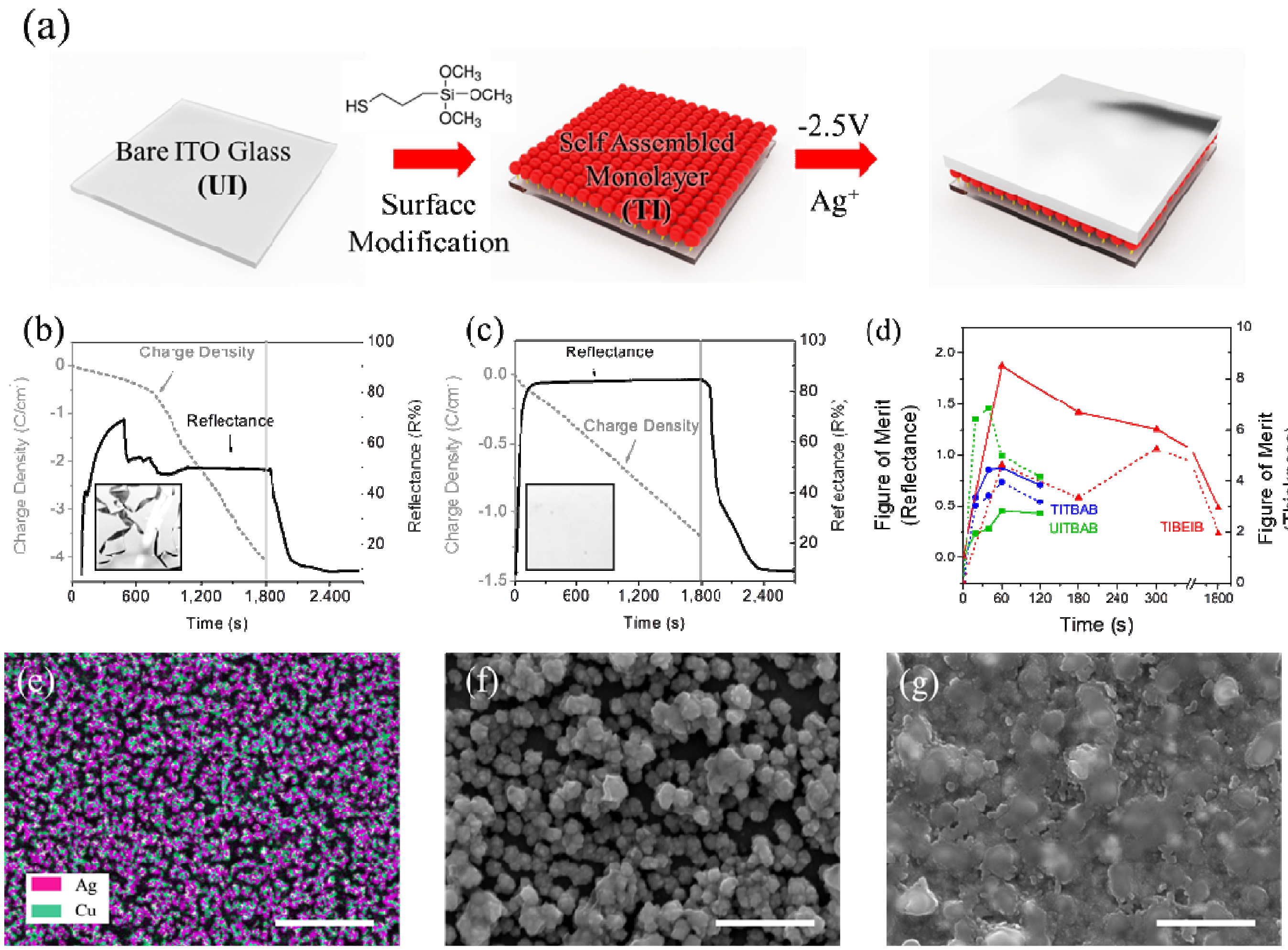

Fig 1. (a) Schematic diagram of the surface modification process and growth of metallic films on a thiol-modified electrode (TI). The reflectance (solid) and charge density (dashed) of the switching device containing (b) UI and (c) TI with TBAB upon application of -2.5 V for 30 min and V-off for 15 min. (Inset ; photographic images of the mirrors after 10 min). (d) Figure of merit for reflectance at 650 nm (solid) and thickness (dashed) for the metallic films of TIBEIB (red), TITBAB (blue), and UITBAB (green). (e) EDS image corresponding to mapping at the Ag and Cu atom for UITBAB. (f) SEM images of the electrodeposited metallic films for UITBAB (f) and TITBAB (g) after 180 s of electro-deposition. Scale bars, 1μm.

terminal thiols are left for metal interaction. These surface thiols could enable to form strong tie with the deposited Ag and Cu metals. Thus, the electrodeposited metal film on TI can be more stable and denser metal film with low roughness than on UI.

The REM with TI as the working electrode, using the TBAB electrolyte (TITBAB) showed a characteristic cathodic current as the potential moved from zero to the negative direction (Figure S3). When the reduction potential was up to -2.5 V, the formation of reflective mirror was observed in the device, as metal ions were reduced. On the other hands, with the applying of positive direction potential, the anodic current was appeared and peaked at +0.2 V. This anodic peak should correspond to the oxidation of the electrodeposited metal particles, because the transmittance of the cell was increased by the dissolution of metallic particles into electrolyte solution. The REM restored its initial transparent state upon application of > 1.0 V for less than 1 min, upon oxidation of Cu^{+1} to Cu^{+2}, which mediates the oxidation of the Ag.[36] The electro-reflectance change of TITBAB was similar to that of the REM using an unmodified ITO (UITBAB), which is the same mirror system reported in the literature,[20] except the electrochemical stability, described below.

Although it was possible to switch between the reflective and transparent states in UITBAB and TITBAB, the mirror state disappeared when the electricity was disconnected, possibly because the deposited Ag film dissolved into the solution immediately. To maintain the mirror state, a continuous reduction potential (-2.5 V) should be applied to the REM. As shown in Figure 1b and c, the Ag-Cu metallic film formed on TI (TITBAB) showed dramatic enhancement in its long-term electrochemical stability. The reflectance increased up to 82% within 3 min, and it was maintained constantly with the prolonged application of -2.5 V for 30 min. The metallic film was also stable, showing a highly reflective state without rupture, as shown in Figure 1c. On the other hand, the metallic film grown on the bare electrode (UITBAB) showed instability after a few minutes at -2.5 V. The metallic films were ruptured, and the reflectance dropped significantly, as shown in Figure 1b, and Movie S1. Also, the charge density recorded with the application of -2.5 V increased abruptly when the metallic film was ruptured in the UITBAB, while the charge density in the TITBAB increased linearly.

Therefore, the ITO surface modification with thiol groups, which is well known to stabilize silver,[21] significantly improved the electrochemical stability of the REM device, resulting in a stable mirror status. The reflectance of the TITBAB was higher than that of UITBAB, as shown in Figure 1b and c, due to the formation of a highly dense metallic film in the TITBAB compared to the UITBAB, as described above. The result indicates that the surface modification afforded a viable method for dramatic enhancement in long-term stability as well as high reflectance. Thus, the surface-treated electrodes were found to be essential for long-term electrochemical stability, and they were used in further experiments. After metal deposition, the mirror state in the UITBAB disappeared immediately after the applied voltage was shut off. The mirror state in the TITBAB was maintained longer than in the UITBAB, possibly due to the denser film, but it lasted only 60 s after the electricity was disconnected. In switchable mirrors, the open circuit memory property—i.e., the ability to maintain the mirror state without further energy consumption—is hard to achieve, although this is commonly observed for at least an hour in other electrochemical color switching systems (e.g., electrochromism).[37-40]

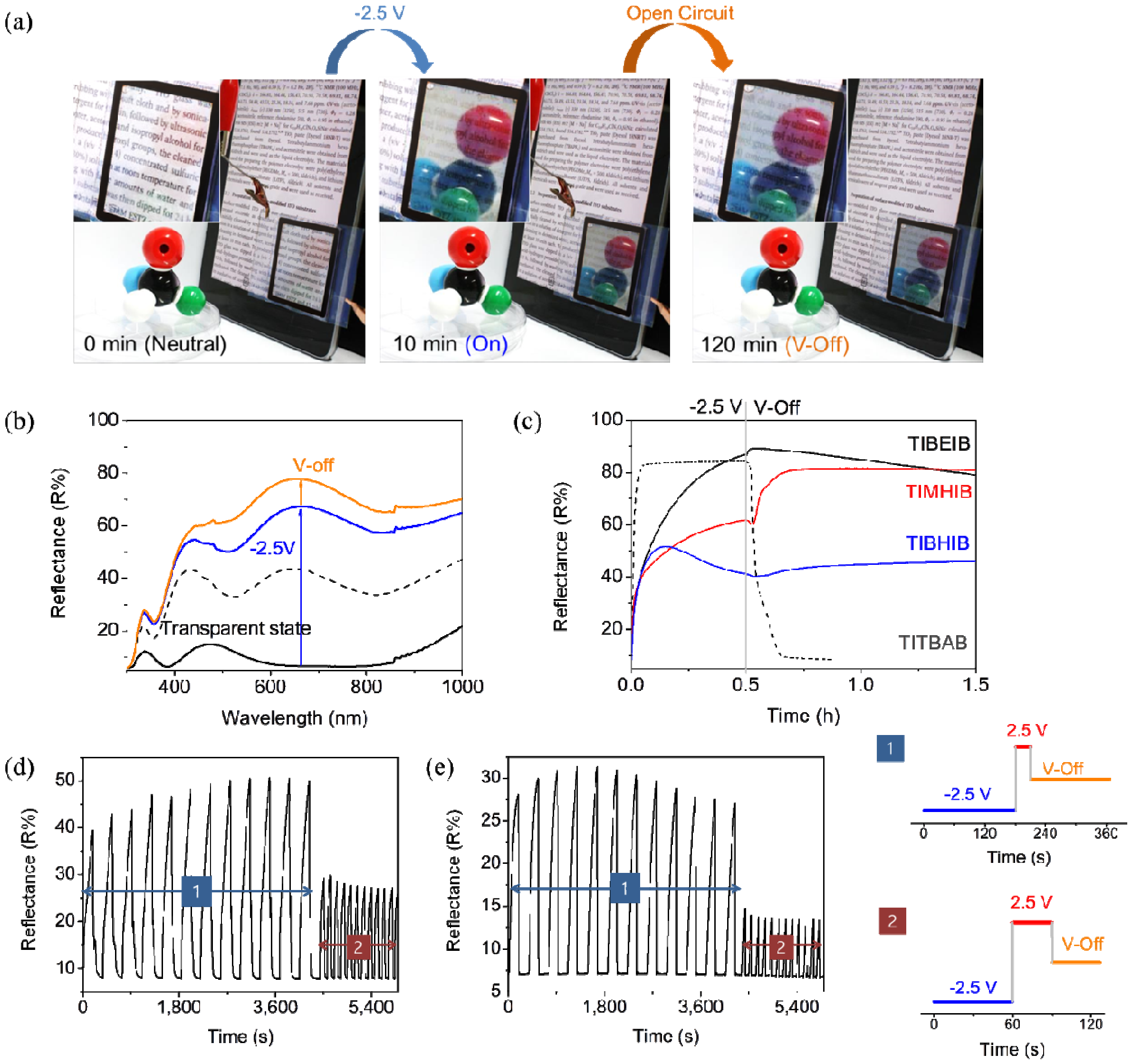

Fig 2. (a) Photographic images of the TIMHIB at transparent state, mirror state under -2.5 V, and mirror state at V-Off. (b) Reflectance spectra of TIBEIB at different states: From initial transparent state (solid black), 5min after application of -2.5V (dashed black) to 10min (blue), V-Off state for 15 min (orange). (c) Reflectance of mirrors monitored at 650 nm, under different ILs (BEIB, MHIB, BHIB, and TBAB). (d~e) Reversible reflectance switching with (d) TITBAB and (e) TIBEIB upon application of repetitive step potentials given in the applied potential cycle.

3.2 Bistable reversible electrochemical mirror

The low open circuit memory in switchable mirrors is inevitable because the electrodeposited metal particles are designed to be dissolved in electrolyte containing excess halide ions, to achieve reversible switching. The mechanism for the Ag dissolution is based on the initial oxidation of metallic silver to form soluble $AgBr_n^{(1-n)}$ then to Ag(I), as described well in the literature.[22, 23] There is a possibility that chemisorbed Br^- ions may catalytically dissolve silver by oxygen dissolved in electrolyte.[41] However, the effect of this oxidative dissolution is negligible due to the low gas solubility in ionic liquids.[42] The soluble anionic complexes (AgX_2^- and AgX_3^{2-}, where X is Cl, Br, or I) have relative stabilities of $I^- > Br^- > Cl^-$ and their formation is accelerated under high concentrations of halides to increase the rate of Ag dissolution.[24] Therefore, the mirror state rapidly disappears in the open circuit, accompanied by dissolution and diffusion of the electrodeposited mirror whenever Br anions are available.

To protect the metal film in the open circuit state, we introduced an electrical double layer (EDL), which can block anion diffusion into the metallic film. A cationic layer was reported to expel anion from the electrode.[25] Therefore, we used an ionic liquid (IL) as an electrolyte for the switching mirrors, taking advantage of the large specific capacitance of ILs. In addition, the nonvolatile, nonflammable, and highly viscous natures of IL confer advantages in REM.[30] The structures of the ILs and their electrochemical properties are summarized in Table 1.

After metal deposition, the mirror state in the TIBEIB disappeared immediately upon application of a positive potential (>2.0 V), rendering an electrochemically switchable mirror similar to the TITBAB. The metallic mirror formation was accompanied by concomitant spectral growth from the UV to the IR region, as shown in Figure 2b for the TIBEIB. Surprisingly, the reflectance of the TIBEIB was maintained after electricity was disconnected (V-Off). The reflectance of the TIBEIB, following application of -2.5V for 30 min, had a slight further increase to 89.3% immediately after V-Off state (Figure 2c, black solid line). The reflectance increase of the TIBEIB, immediately after V-Off state, may be attributed to the additional reduction of Ag-Cu due to the immediate polarization change. Importantly, even after 2 hour at V-Off state, the high reflectance was maintained (Movie S2). Figure 2c shows the memory effect (recorded at 650 nm) of the switching mirrors in different ILs having different alkyl chain lengths. In all of the ILs, the reflectance of the mirrors was maintained for longer than 30 min under V-Off state. The reflectance of the TIMHIB, which used MHImBr as an IL, increased to almost 80% immediately after the electricity was disconnected and the memory effect was longer than 2 h (Figure 2a) without energy consumption or any physical damage.

The mirror switching in an ionic liquid containing BEImBr, abbreviated as TIBEIB, was observed similarly as expected from the similar CV to the TITBAB (Figure S3). Cu content in the electrodeposited Ag-Cu surface from TIBEIB was determined as ~24 % of Ag content, from EDS mapping, which was almost same as that in UITBAB and TITBAB (Table S1), as determined from EDS mapping (Figure S1g). Although the use of IL enabled dramatically increased bistability without the loss in reflectance of the device, the growth of metallic film in ILs was slower than TITBAB, possibly due to highly viscous natures and high capacitance of ILs. (Figure 2c) But interestingly, the figure of merit for thickness of TIBEIB was similar to that of TITBAB. Moreover, the figure of merit for reflectance was two times larger in the REM with ILs than with TBAB (Figure 1d). The mechanism for Ag film deposition can be explained by the reaction of the Ag^+ ion with Br^- ion to form $AgBr_n^{(1-n)}$ (n = 2~4) , which then reduced to give Ag metal on an electrode. It has been reported that immidazolium cations can stabilize $AgBr_n^{(1-n)}$ and metallic granule.[28, 43, 44] This stabilizing interaction could generate a dense film and thus result in a high figure of merit for reflectance in the mirrors using ILs.

Figure 3a shows the schematic diagram for a working mechanism of a bistable reversible electrochemical mirror (BREM) where Br- diffusion into metal film is forbidden due to the electrical double layer (EDL) developed during the switch-on process, allowing the bistability of the switching mirror. The growth of the metallic film, the switching response, and their reflectance increase at V-Off were dependent on the alkyl change length of the ionic liquids; nonetheless, all of the mirrors in the EDL condition showed long bistability. The EDL is immediately removed upon application of the reverse potential (oxidation) so that the reversible reaction toward the transparent state could be achieved repeatedly and reliably. Thus, the mirror state of the TIBEIB was switched to a transparent state only when an oxidation potential was applied

	R_1	R_2	Name	Electrolyte Resistance (R_e) [Ω]	Charge Transport Resistance (Rct) [Ω]	Capacitance (C) [μF]	Constant Phase Element (Q) [μF]	χ2
1	methyl-	n-hexyl-	1-methyl-4-hexylimidazolium bromide (MHImBr)	33.6 (24.1)	14.9 (15.2)	57.0 (69.1)	13.0 (13.1)	0.16 (0.10)
2	n-butyl-	n-ethyl-	1-buthyl-4-ethylimidazolium bromide (BEImBr)	29.2 (18.3)	14.8 (13.6)	78.0 (79.2)	12.0 (11.8)	0.11 (0.10)
3	n-butyl-	n-hexyl-	1-butyl-4-hexylimidazolium bromide (BHImBr)	51.4 (26.4)	17.1 (16.5)	45.0 (62.7)	12.0 (13.2)	0.19 (0.11)
4	Tetrabutylammonium Bromide (TBABr) 0.25M solution in DMSO			23.8 (17.3)	7.15 (18.9)	164.3 (81.7)	11.8 (12.7)	0.05 (0.10)

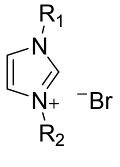

Table 1. Structure of the alkiylimidazolium bromide in ionic liquids (ILs) and resistance and capacitance of electrolytes.[a] of electrolyte containing alkiylimidazolium bromides.

[a] The equivalent circuit was consisted of electrolyte resistance (R_e), charge transport resistance (R_{ct}), capacitance (C), and constant phase element (Q) for measuring the properties of the ionic liquids. (The value in parentheses for electrolytes containing $AgNO_3$, $CuCl_2$ ions.)

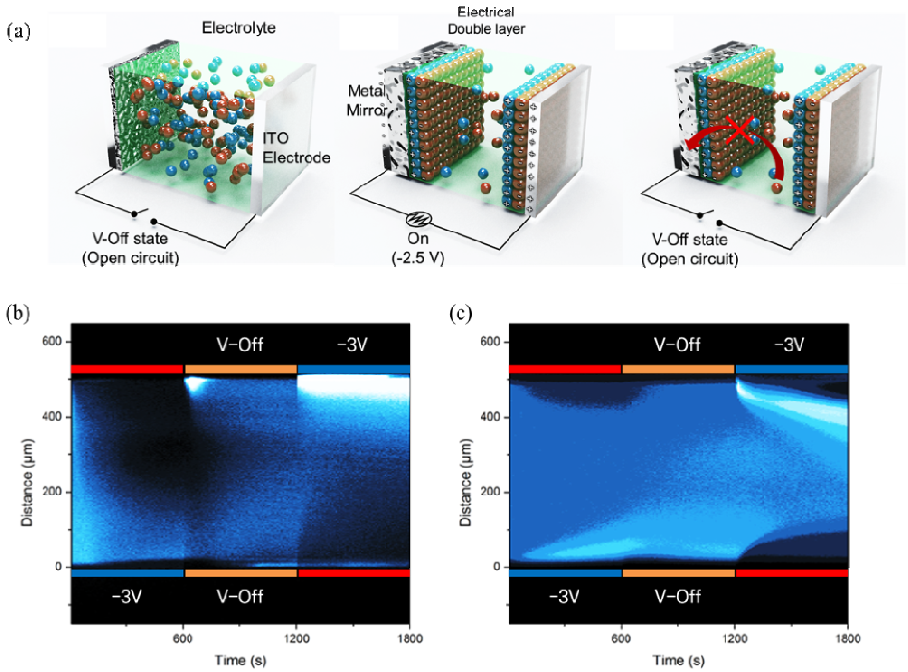

Fig 3. (a) Schematic diagram of the ion distribution at transparent state, reflective state, and V-Off state. In-situ fluorescence intensity between two ITO electrodes visualized by analyzing the confocal microscopic intensity over time, for (b) TITBAB and (c) TIBEIB with pyrene as a fluorophore to trace the ion transport. (λ_{exi} = 405 nm). Light blue region indicates a high concentration of pyrene-Ag^+

(Figure S4, Figure S5). The mirror with ILs was reversibly switched between the mirror and transparent states (Movie S3) by an alternating potential cycle as shown in Figure 2d and e. Table S2 summarizes the electro-reflectance change of the mirrors in this study.

In order to gain further insight on the bistability, we examined the ion transport in TITBAB and TIBEIB from a confocal microscope. (Figure 3b, c and Figure S6) Pyrene was used to elucidate the ion transport, taking advantage of its strong interaction with metal cation [45] and thus would move to the same direction as metal ions do. As shown in Figure S6a, the fluorescence intensity of the TITBAB and TIBEIB was higher near the working electrode, forming a layer of pyrene crowd, when the working electrode was applied with a reduction voltage (-3V). Pyrenes (with metal ions) moved toward working electrode over time and formed a ~ 150 μm fluorescent layer after 10 min at -3V, as clearly shown in Figure 3b, c, and Figure S6a, b. Interestingly, the fluorescent layer was quite stable in the TIBEIB, while it was diffused into entire electrolyte in the TITBAB at V-Off within 10 min. These results verify that there is no ion transfer from the metallic film (coated at working electrode upon reduction) into electrolyte, and vice versa, in TIBEIB at V-Off. On the other hands, the metallic films are dissolved as ions, which return into electrolyte in the TITBAB at V-Off. The localized fluorescent layer in the TIBEIB was diffused only when an oxidation potential (+3V) was applied as seen in Figure 3c. The growth and diffusion of fluorescent layer, and thus ion transfer, were more visible in the Movie S4 and S5.

Conclusions

An electrochemically stable and bistable electrochemical mirror was achieved for the first time by introducing 1) a thiol-modified ITO electrode for the stabilization of the Ag-Cu metallic film and 2) ionic liquids as the anion-blocking layer to achieve bistability in the switching mirror. Although the timescale on which this transition occurs in the BREM is rather slow (several min) at present, there appears to be considerable room for improvement through the choice of ionic liquids and organically modified electrodes. In view of their long memory effect and electrochemical stability, the switchable mirrors could find numerous applications, such as smart windows for energy saving buildings and automobiles, wireless heater, reflective displays, and switchable mirrors for optical systems.

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Notes and references

Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Korea
E-mail: eunkim@yosei.ac.kr
Homepage: http://web.yonsei.ac.kr/eunkim/

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TOC

Switchable Silver Mirrors with Long Memory Effect

Chihyun Park, Seogjae Seo, Haijin Shin, Bhimrao D. Sarwade, Jongbeom Na, and Eunkyoung Kim*

An electrochemically stable and bistable switchable mirror is achieved for the first time by introducing 1) a thiol-modified ITO electrode for the stabilization of the metallic film and 2) ionic liquids as the anion-blocking layer to achieve long memory effect. In view of their bistability and electrochemical stability, the bistable reversible electrochemical mirror could find numerous applications for optical systems.