

Bistable Black Electrochromic Windows Based on the Reversible Metal Electrodeposition of Bi and Cu

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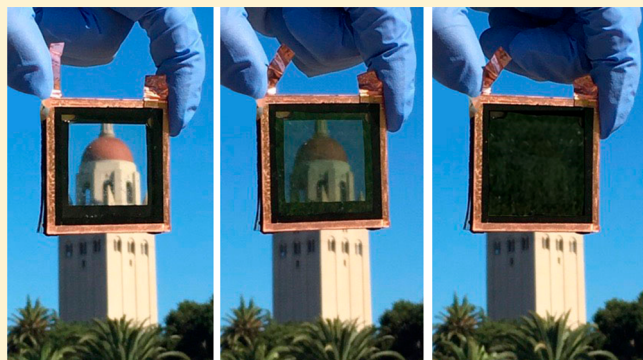
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Supporting Information

ABSTRACT: Optically tunable windows based on reversible metal electrodeposition are an exciting alternative to static lighting control methods such as blinds and shades. In this Letter, we study reversible Bi/Cu electrodeposition on Pt-modified transparent conducting electrodes for electrochromic applications. Spectroelectrochemical measurements combined with scanning electron microscopy images indicate that the electrolytic Bi:Cu ratio drastically affects the electrode switching speed and electrode deposit morphology, which we propose is due to the galvanic displacement of Bi by Cu⁺. These findings allow us to construct 25 cm² black dynamic windows with reversibly tunable transmission at fast switching speeds. This rapid cycling can be maintained over 1000 cycles without degradation in contrast or uniformity. Finally, the Bi–Cu windows consume no power to maintain either their transparency or opacity, making them promising candidates for energy-efficient devices. Their combination of fast switching, color neutrality, durable cycling, and dual-state resting stability make dynamic windows based on Bi–Cu reversible electrodeposition promising and competitive alternatives to traditional electrochromic materials.



Dynamic windows allow users to tune and optimize light flow in and out of buildings and vehicles while maintaining the view through the glass, which is impossible for current technologies that rely on shutters. In addition to aesthetic advantages, implementing dynamic windows in buildings and automobiles can lead to significant energy savings by decreasing heating, ventilation, and air conditioning (HVAC) requirements. For example, the installation of dynamic windows in office buildings leads to an average of 10% energy savings over static low-E windows.¹ Optically tunable sunroofs can also reduce HVAC consumption in cars, which is especially important in electric vehicles.

Over the past 4 decades, the majority of dynamic window research has focused on electrochromic materials such as viologens, polymers, and transition metal oxides, which change color upon application of a voltage.^{2,3} Despite extensive research, however, none of these have simultaneously demonstrated a combination of fast switching speed, color neutrality, adequate durability, and low manufacturing cost.^{2–5}

These problems have limited the commercial implementation of electrochromic windows to niche markets.

We recently demonstrated that a promising alternative strategy to electrochromic materials is to construct dynamic windows based on reversible metal electrodeposition.⁶ Our approach and design of these devices show significant improvement on previous demonstrations of this concept^{7–11} and demonstrate the ability to tint windows, both reversibly and uniformly, at large scale. These windows are comprised of a transparent conducting working electrode, a metal counter electrode, and an electrolyte containing colorless solubilized metal cations. Metal-based dynamic windows change transparency through the electrochemical movement of metal between the two electrodes. To switch these windows from transparent to opaque, metal cations in the electrolyte are electrochemically reduced to metal films on the transparent

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working electrode upon application of a voltage. Metal oxidation on the counter electrode compensates for this reduction reaction. Reversing the polarity of the applied voltage restores the transparency of the window by stripping metal off of the working electrode and replating it on the counter electrode.

Metals make excellent candidates for use in light-modulating devices due to their high optical extinction coefficients. Whereas electrochromic materials are typically 100–1000 nm thick, most metals are completely opaque at thicknesses of 20–30 nm, thus reducing cost through the use of less active material.¹² In addition, WO_3 , the most ubiquitous electrochromic material, is blue in its dark state and is normally deposited using expensive sputtering processes.¹³ In contrast, many metals are color-neutral and can be electrodeposited from aqueous solutions.¹⁴ Additional benefits of most metals include high photostability and chemical inertness, unlike electrochromic polymers that degrade under UV illumination and exposure to moisture.¹⁵

Given that metals possess many promising properties for implementation in dynamic windows, it is surprising at first glance that metal-based technologies have not yet been commercialized. The main challenge associated with the widespread development of dynamic windows based on reversible metal electrodeposition is to uniformly and reversibly electrodeposit metals over a large area. To achieve uniform reversible metal electrodeposition across a large area, the nature of both the electrolyte and transparent electrode must be optimized. Previous metal-based reversible electrodeposition systems have been studied and reported, with reversible Ag electrodeposition being the most widely explored system for dynamic windows. However, until this year, reported devices have only been 1–4 cm^2 in area and suffer from poor durability, which can be attributed to a low Coulombic efficiency.¹⁶ Electrodeposition of Cu is a potentially promising alternative for enabling larger-area metal-based dynamic windows. Decades of optimizing Cu electrodeposition for circuit interconnects have resulted in highly uniform Cu electroplating processes.¹⁷ Unfortunately, Cu alone is not suitable for dynamic windows due to its red color. The electrodeposition of a second color-neutral metal in tandem with Cu is a strategy that exploits the advantageous electrochemical properties of Cu while enabling an aesthetically acceptable black opaque state. Our group recently reported on dynamic windows based on the reversible electrodeposition of bimetallic Pb–Cu and Ag–Cu electrolytic systems.⁶ However, the toxicity of Pb and the large standard reduction potential difference (~ 460 mV) between Ag and Cu are of concern.¹⁸ Bi makes for an excellent complementary metal for incorporation in dynamic windows due to its strongly absorbing black color, nontoxicity, and similar reduction potential (~ 30 mV) to that of Cu.¹⁸ However, Bi is a strong Lewis acid, and its solubility is dependent on acid concentration to prevent the precipitation of insoluble $\text{Bi}(\text{OH})_3$, which limits Bi concentration in aqueous dynamic window electrolytes. Thus, electrolyte composition must be tuned to promote reversible metal deposition while also avoiding potential side reactions such as $\text{H}_2(\text{g})$ evolution from the reduction of H^+ in solution. Systems containing Bi and Cu were previously used to construct pixel-sized (1 cm^2) devices for display applications.^{7–9} In this work, we explore Bi–Cu reversible electrodeposition systems for the construction of robust large-area dynamic windows by tailoring the nanostructure of the

transparent working electrode and the composition of the Bi–Cu electrolyte.

The most appropriate transparent working electrodes for implementation in dynamic windows consist of glass coated with indium tin oxide (ITO) or fluorine-doped tin oxide (FTO) due to their low cost, low sheet resistance, and high transparency. Unfortunately, the nucleation of metal electrodeposits on ITO and FTO substrates is frequently nonuniform due to the heterogeneous surface chemistries of these electrodes,¹⁹ which would lead to poor reversibility and uniformity following extensive electrochemical cycling. To improve the uniformity of metal electrodeposition across large-area (25 cm^2) ITO electrodes, we modified these substrates with a self-assembled monolayer (SAM) of Pt nanoparticles (3 nm) anchored by 3-mercaptopropionic acid (Figure 1A). The

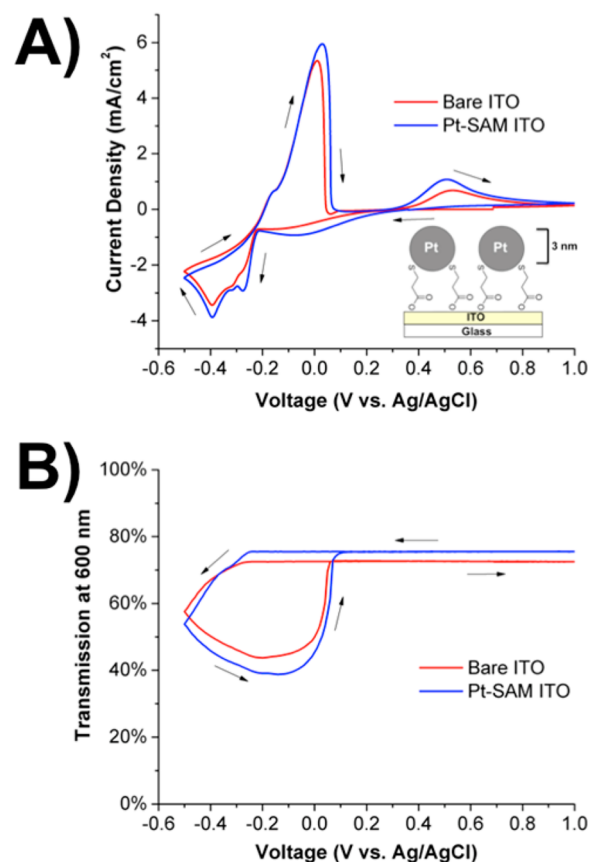


Figure 1. (A) CV of Bi–Cu halide electrolyte using unmodified (red line) and Pt-modified ITO (blue line) (main). Schematic of a SAM of Pt nanoparticles used to modify ITO (inset) and (B) transmission at 600 nm through the spectroelectrochemical cell during the CV in (A).

even distribution of Pt nanoparticles, with a surface coverage of 1500 nanoparticles/ μm^2 , enables uniform metal electrodeposition by facilitating nucleation across the area of the ITO electrode because metal electrodeposition occurs preferentially on the inert Pt seed layer.⁶ The Pt nanoparticles also provide a stable platform for reversible metal electrodeposition over many cycles. These Pt-modified electrodes enable us to construct dynamic windows based on Bi–Cu reversible metal electrodeposition on a 25 cm^2 scale with stable uniformity and contrast following electrochemical cycling.

Finally, we systematically vary the Bi–Cu electrolyte composition and study how these changes affect device performance. Previous studies have shown that adding Cu helps strip Bi electrodeposits from ITO surfaces.^{7–9} In addition to kinetic effects, the presence of Cu also improves electrodeposition uniformity.^{10,11} We further explore these phenomena to gain a mechanistic understanding of reversible Bi–Cu electrodeposition and to optimize the electrolyte composition for use in durable large-scale dynamic windows. On the basis of these findings, we propose that galvanic displacement of Bi by Cu⁺ causes the Bi–Cu electrolyte composition to affect electrodeposition morphology and stripping kinetics. Dynamic windows containing an optimized Bi–Cu electrolyte achieve a 60% contrast ratio twice as fast as the previously reported Pb–Cu electrolyte and also strip three times as fast as the Ag–Cu electrolyte, thus demonstrating superior cycling kinetics to the two previously reported bimetallic systems.⁶

Three-Electrode Cyclic Voltammetry and Transmission Studies of Bi–Cu Electrodeposition. When exploring new combinations of metals for use in dynamic windows, it is helpful to utilize cyclic voltammetry coupled with transmission measurements to study the electrochemical reactions occurring during cycling and then optimize electrolytic formulations that result in high-quality films with desirable optical properties and reversibility. Figure 1A, red line, displays a cyclic voltammogram (CV) of metal electrodeposition and stripping on an unmodified ITO working electrode from an electrolyte containing Bi³⁺ and Cu²⁺ with Cl[−] and Br[−] as the counterions, which has an open-circuit potential of ~500 mV. During the initial negative-going sweep, cathodic current begins to increase at 0.3 V, which is attributed to the electrochemical reduction of Cu²⁺ to Cu⁺. Although under most conditions Cu⁺ rapidly disproportionates, halides are known to stabilize the formation of Cu⁺ in aqueous solutions.²⁰ The unchanged transmission over the voltage range of the Cu²⁺ to Cu⁺ transition (Figure 1B, red line) is consistent with a process that does not involve metal electrodeposition. Following the reduction of Cu²⁺ to Cu⁺, cathodic current begins to increase again at −0.2 V. Transmission through the ITO also begins to decrease following this potential (Figure 1B, red line), thus indicating the onset potential of metal deposition. The deposition current decreases after −0.4 V due to diffusion-limited transport of the metal ions in the electrolyte. An anodic stripping peak centered at 0 V during the subsequent positive-going sweep corresponds to dissolution of the deposited Bi and Cu back to Bi³⁺ and Cu⁺, respectively. Cu⁺ is then further oxidized to Cu²⁺ at potentials more positive than 0.3 V.

The same CV obtained using an ITO working electrode modified with a Pt SAM (Figure 1A, inset and blue line) exhibits similar overall features. However, the peak deposition current density for the Pt-modified electrode is 13% greater than the unmodified ITO case, indicating that the Pt layer gives rise to a greater metal nucleation density. This increase in metal deposition results in a greater change in transmission of the electrode during the CV (Figure 1B, blue line). Furthermore, implementing the Pt-modified electrode increases the Coulombic efficiency by ~6%. Thus, an increase in metal nucleation and reversibility indicates that implementing the Pt layer is important for large-scale dynamic windows with high contrast and durability.

In addition to identifying the electrochemical reactions involving metal oxidation and reduction, it is important to note and avoid potential unwanted side reactions as well. The H₂

evolution reaction (HER) is a common side reaction in aqueous metal electrodeposition systems.¹⁴ HER must be avoided in metal-based aqueous dynamic windows because the formation of H_{2(g)} bubbles on the surface would prevent the plating of metal at that site. Because the formal potential of the HER shifts positively with increasing acid concentration, HER tends to occur more rapidly at low pH. Thus, the electrolyte composition must be tuned such that the diffusion-limited electrodeposition of Bi and Cu precedes the reduction of H⁺ to H_{2(g)}. This requirement, in addition to ensuring adequate Bi solubility, was achieved (Figure S1) by limiting the acid concentration to 10 mM HCl and also adding 1 M LiBr to increase the solubility of Bi³⁺ to form soluble Bi halide complexes such as BiBr₆^{3−}.²¹ The cathodic current in Figure S1 is only due to the adsorption of H⁺ to the surface, which is known to precede the reduction of H⁺ to H_{2(g)}.²²

With a promising Bi–Cu halide electrolyte established, we sought to understand the individual Bi and Cu electrodeposition processes occurring during electrolyte cycling. Figure 2A displays CVs of Bi, Bi–Cu, and Cu halide

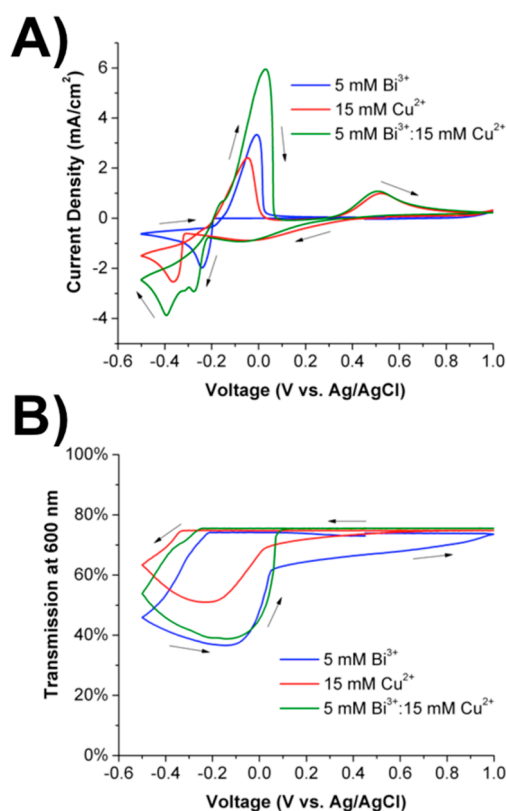


Figure 2. (A) CVs of Bi-only (blue line), Cu-only (red line), and Bi–Cu (green line) halide electrolytes on Pt-modified ITO electrodes and (B) the corresponding transmission at 600 nm through the spectroelectrochemical cell.

electrolytes using Pt-modified ITO working electrodes. The CVs of the Bi-only electrolyte (blue line) and the Cu-only electrolyte (red line) demonstrate that Bi deposition (−0.2 V onset potential) precedes Cu deposition (−0.3 V onset potential), despite the standard reduction potential of Cu being more positive than that of Bi.¹⁸ Bi reduction occurs at a more positive potential than Cu because it proceeds through underpotential deposition (UPD).⁷ Previous studies have shown a correlation between the chemical potential difference

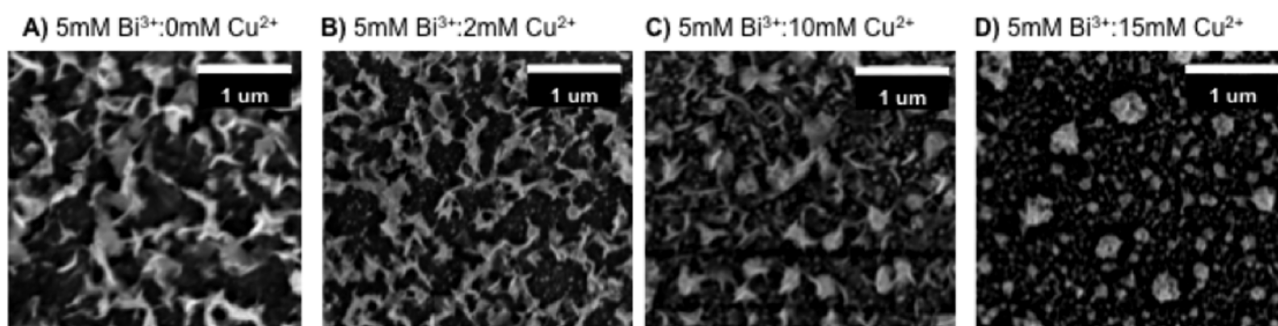


Figure 3. SEM images of electrodeposits on Pt-modified ITO electrodes obtained after applying 30 s at -0.6 V vs Ag/AgCl using electrolytes containing 5 mM Bi^{3+} and (A) 0, (B) 2, (C) 10, and (D) 15 mM Cu^{2+} .

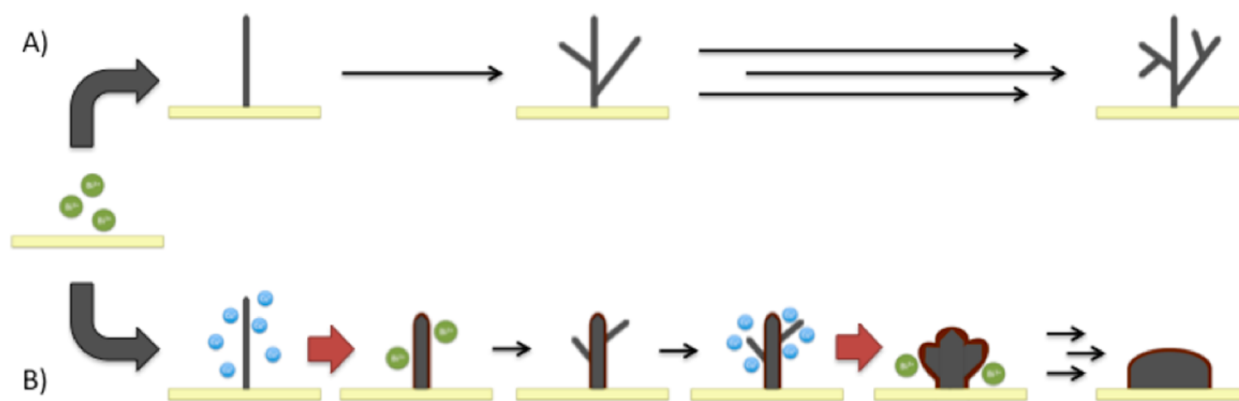


Figure 4. Reaction schematic showing the deposition of Bi in the (A) absence and (B) presence of Cu. Green and blue circles represent Bi^{3+} and Cu^{2+} ions, respectively. The red arrows in pathway B indicate the galvanic displacement reaction.

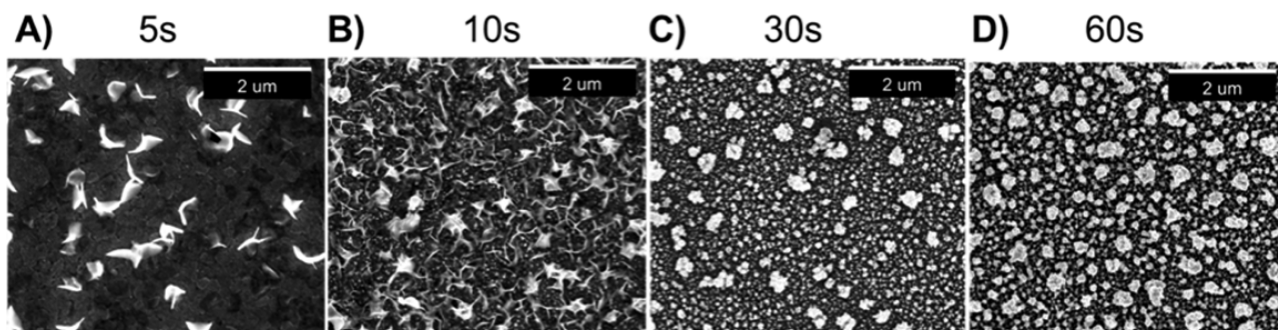


Figure 5. SEM images of electrodeposits on Pt-modified ITO electrodes obtained after applying for (A) 5, (B) 10, (C) 30, and (D) 60 s at -0.6 V vs Ag/AgCl using an electrolyte containing 5 mM Bi^{3+} and 15 mM Cu^{2+} .

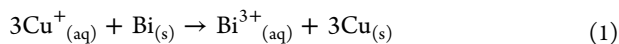
of bulk and surface-adsorbed metal and the work function difference of the metal and substrate.²³ Thus, a greater difference in work function between Bi and Pt/ITO, 1.32 eV/0.49 eV, respectively, compared to that for Cu and Pt/ITO, 0.98 eV/0.15 eV, respectively, correlates to a greater chemical potential difference, which explains why the UPD of Bi occurs more readily than the UPD of Cu on Pt/ITO. The CV of the Bi–Cu halide electrolyte, which possesses features from both monometallic electrolytes, is shown once again in the green line of Figure 2A to aid in comparison.

During the CVs, the transmission at 600 nm of the spectroelectrochemical cell starts at $\sim 75\%$, decreases to varying extents during metal electrodeposition, and returns to its original transmission after metal stripping (Figure 2B). For the Cu-only electrolyte, the transmission during metal electrodeposition decreases to only $\sim 50\%$ due to poor surface

coverage by noncontinuous small-particle growth (red line, Figure S2), and the electrode has the characteristic red color of Cu. Upon the addition of Bi to the electrolyte (green line), the transmission change increases substantially and the electrode appears black. For the Bi-only electrolyte, the transmission during stripping initially rapidly increases to $\sim 62\%$ but then only gradually returns to its original $\sim 75\%$ value (blue line). The slow stripping speed for the Bi-only electrolyte is in stark contrast to the fast stripping kinetics of the Bi–Cu electrolyte (green line), which will be elaborated upon later in this Letter. Thus, the combination of Bi and Cu results in an electrolyte that results in a color-neutral electrodeposit with adequate transmission change and reversibility.

Morphological Effects of Cu Addition to Bi Electrodeposits. To better understand the role that Cu plays in reversible Bi electrodeposition, we analyzed the morphology of electro-

deposits from electrolytes containing varying Bi–Cu concentrations using scanning electron microscopy (SEM, Figures 3, S2, and S3). Figure 3A shows that electrodeposits from the Bi-only electrolyte exhibit dendritic morphology. Increasing the Cu concentration leads to progressively more spherical particle growth (Figure 3B–D).



On the basis of this observation, we propose that a mechanism based on the galvanic displacement of Bi by Cu⁺ induces spherical particle growth (eq 1). This redox reaction is thermodynamically favorable according to the standard reduction half-reactions of Cu⁺/Cu and Bi³⁺/Bi.¹⁸ Electrochemically generated Cu⁺ ions can chemically oxidize dendritic Bi atoms and fill in void spaces with three times more Cu atoms, resulting in a more condensed spherical morphology that suppresses dendritic growth (Figures 4 and 5). The electrochemical reduction of Bi³⁺ and Cu⁺/Cu²⁺ to Bi and Cu, respectively, occurs simultaneously with the aforementioned Bi–Cu galvanic displacement reaction. X-ray photoelectron spectroscopy (XPS) data of an electrodeposit obtained from an electrolyte containing 5 mM Bi³⁺ and 15 mM Cu²⁺ supports this hypothesis, indicating that Bi and Cu continually co-deposit in a ~ 1:3 ratio throughout the depth of the electrodeposit (Figure S4).

Fabrication of a Packaged Window. Having established an understanding of Bi and Cu electrodeposition in a three-electrode spectroelectrochemical cell, we next incorporated this electrolytic system into a practical two-electrode dynamic window. These windows utilize a 25 cm² Pt-modified ITO on a glass working electrode, a Cu foil counter electrode, and the Bi–Cu electrolyte modified with hydroxyethylcellulose to form a viscous polymer solution (Figure 6). A deposition voltage of –0.6 V is applied to the device to induce diffusion-limited co-deposition of Bi and Cu. Under these conditions, the metal film thickness is nearly uniform across the width of the device despite the voltage drop that builds up in the ITO due to series

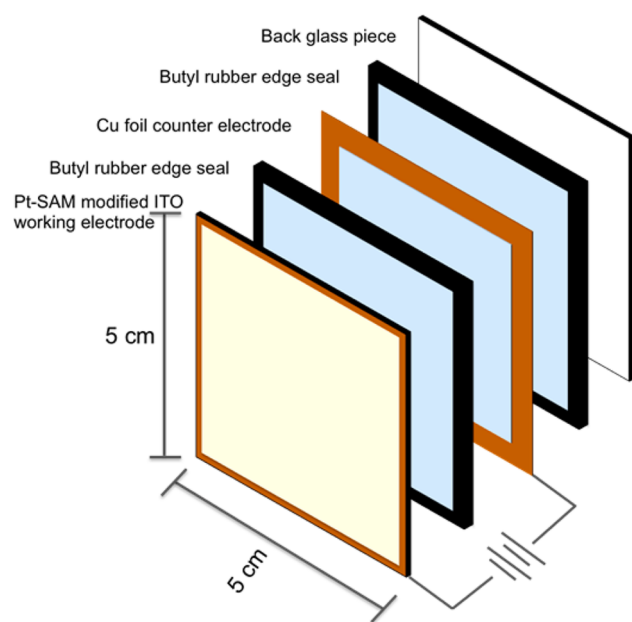


Figure 6. Schematic of the device stack used for constructing 25 cm² dynamic windows.

resistance. This uniform metallic growth causes the initially transparent window to turn progressively more opaque over the course of 60 s (Figures 7A–C and S5). More importantly, the optically uniform electrodeposition of Bi–Cu over the large area of the electrode allows the device to be tuned to any desired intermediate transmission. A significantly less negative voltage applied to the edge disrupts the uniform deposition because the potential becomes insufficient to plate metal in the center. Applying a more negative deposition potential induces hydrogen evolution. Switching the voltage of the device to +0.8 V restores the initial transparency of the window within 10 s (Figures 7D and S5). This stripping voltage ensures the complete reversible oxidation of all Bi and Cu species while avoiding undesirable reactions at higher potentials such as water oxidation and ITO degradation.

Stripping Kinetics in Dynamic Windows as a Function of Bi:Cu Ratio. In a previous section, we demonstrated that the addition of Cu to Bi electrolytes not only affects electrodeposit morphology but also improves the kinetics of metal stripping. We therefore sought to understand this kinetic enhancement and optimize the composition of the Bi–Cu electrolyte in the 25 cm² two-electrode windows. Figure 8A shows the stripping speed of two-electrode devices following 30 s of metal electrodeposition using electrolytes of various Cu²⁺ concentrations with 5 mM Bi³⁺. At concentrations between 0 and 15 mM Cu²⁺, the kinetics of stripping increase progressively with increasing Cu²⁺ concentrations. In contrast, above 15 mM Cu²⁺, the kinetics of stripping decrease with increasing Cu²⁺ concentration. The V-shape of the plot shows that there is an optimal electrolyte composition for fast stripping. An analogous set of experiments in which the contrast ratios of the devices were kept constant instead of the deposition time produced the same trend (Figure S6). These experiments indicate that the trend in stripping speed observed in Figure 8A is not simply due to varying amounts of metal deposited on the electrode during the 30 s voltage step.

The decrease in stripping speed at high concentrations of Cu is caused by the precipitation of insoluble CuBr in the electrolyte during stripping. The formation of CuBr in the electrolyte makes the window temporarily look white and hazy during metal stripping (Figure S7) until Cu⁺ is further oxidized to soluble Cu²⁺. The precipitation of CuBr in devices made with high Cu concentrations leads to two distinct regimes in both the transmission vs time profile and the chronoamperometric curve during the stripping process (Figure 8B, red line and Figure S8, red line). Taken together, these results demonstrate that the stripping speed of the electrolyte is optimal at 15 mM Cu²⁺ with 5 mM Bi³⁺, which is when the concentration of Cu is high enough to promote kinetically fast galvanic displacement of Bi by Cu⁺ but low enough to avoid the formation of insoluble CuBr.

We propose a mechanism that accounts for the various chemical and electrochemical reactions that occur during metal stripping in Bi–Cu halide electrolytes (Figure 9). Prior to the stripping process, a mixture of elemental Bi and Cu exists on the electrode surface. The onset potential of the shoulder in the stripping peak of the Bi–Cu voltammetry (Figure 2A, green line) occurring at the same voltage as the onset potential of the Cu → Cu⁺ stripping peak in the Cu-only voltammetry (Figure 2A, red line) indicates that the first step of metal stripping in the Bi–Cu electrolyte is the oxidation of Cu to Cu⁺ (Figure 9, step 1). The electrochemically generated Cu⁺ can be further oxidized to Cu²⁺ (Figure 9, step 2a). If the ratio of Cu to Bi in

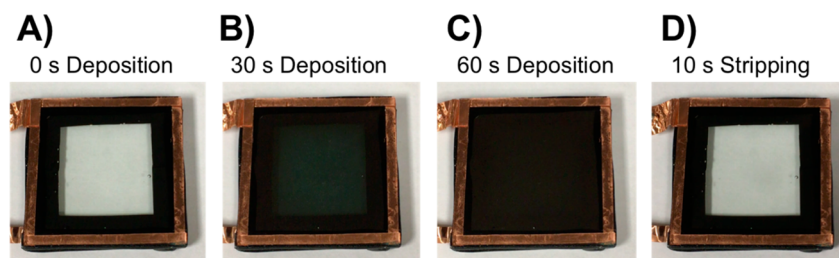


Figure 7. Photographs of 25 cm² dynamic windows using an electrolyte containing 5 mM Bi³⁺ and 15 mM Cu²⁺ taken after (A) 0, (B) 30, and (C) 60 s of metal electrodeposition at −0.6 V and after (D) 10 s of metal stripping at +0.8 V.

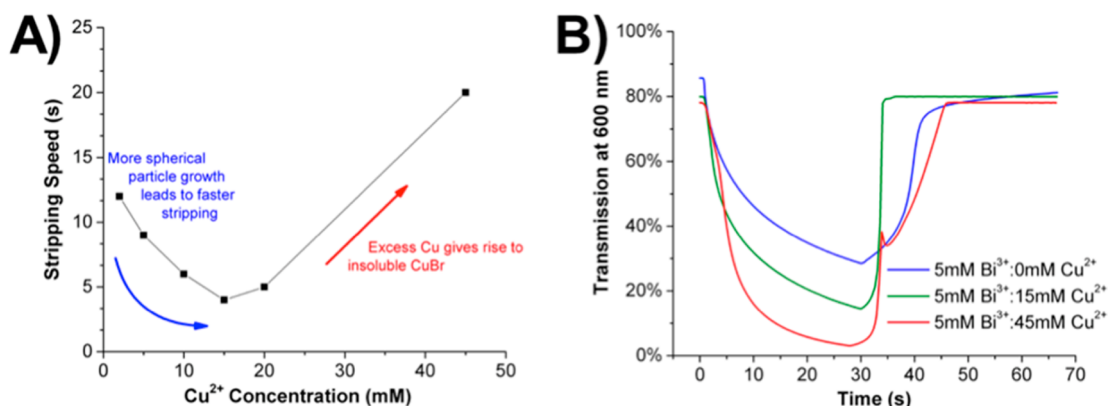


Figure 8. (A) Metal stripping speeds of 25 cm² dynamic windows containing 5 mM Bi³⁺ and varying concentrations of Cu²⁺ at +0.8 V following 30 s of metal electrodeposition at −0.6 V. (B) Transmission at 600 nm versus time of the devices containing 5 mM Bi³⁺ and 0 (blue line), 15 (green line), and 45 mM Cu²⁺ (red line) during 30 s of metal electrodeposition at −0.6 V followed by metal stripping at +0.8 V.

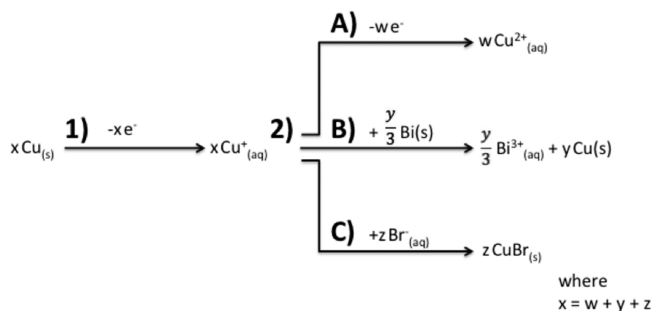


Figure 9. Mechanism of stripping reactions in the Bi–Cu halide electrolyte.

the electrodeposit is relatively low, then the galvanic displacement reaction of Bi by Cu⁺ (Figure 9, step 2b) occurs slowly because there is insufficient Cu⁺ capable of displacing the excess Bi on the surface. As the ratio of Cu to Bi in the electrodeposit increases, the kinetics of the galvanic displacement (Figure 9, step 2b) increase. However, if the Cu to Bi ratio is too high, then the overall kinetics of stripping decrease due to the formation of insoluble CuBr at high Cu⁺ concentrations (Figure 9, step 2c). The competing pathways in this stripping mechanism explain why there is an optimal ratio of Cu to Bi for fast stripping kinetics.

Two-Electrode Device Spectral Performance. We next evaluated the practical performance of 25 cm² dynamic windows containing the optimal 5 mM Bi³⁺ and 15 mM Cu²⁺ electrolyte. Upon application of −0.6 V, the transmission of the window decreases from its original 74–91% across the visible spectrum (Figure 10, lightest blue line) to 11–19% after 30 s of Bi–Cu electrodeposition (Figure 10, black line). The window

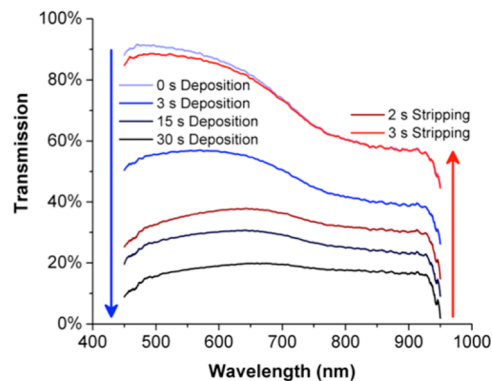


Figure 10. Transmission of a 25 cm² dynamic window with an electrolyte containing 5 mM Bi³⁺ and 15 mM Cu²⁺ as a function of wavelength during 30 s of metal electrodeposition at −0.6 V followed by metal stripping at +0.8 V.

possesses excellent color neutrality, as evidenced by the flat spectral response of the opaque state. Unlike smooth reflective metal films, the window appears black in its opaque state. This black appearance is attributed to the morphology of the electrodeposits, which enhances absorption over reflection (Figure S9). Laser roughening of a smooth metal surface has previously been shown to nearly eliminate reflection.²⁴ The rough features covering a wide size distribution on the nanometer scale promote broadening of plasmon absorption, while similarly rough features on the order of hundreds of nanometers promote light trapping. Both of these effects work together to decrease reflection and increase absorption, yielding the black aesthetic observed in Figure 7. Switching the device to

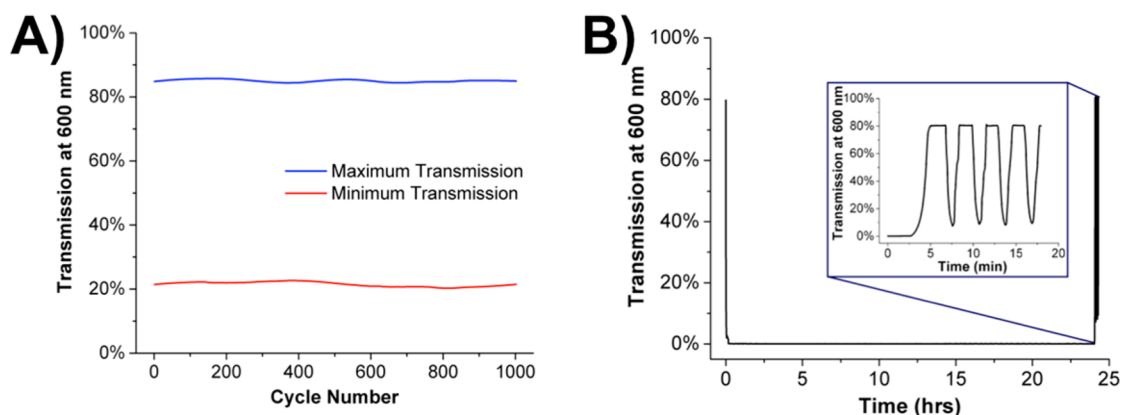


Figure 11. (A) Maximum (blue line) and minimum (red line) transmission values at 600 nm during 1000 cycles of the device. (B) 24 h resting stability test at open circuit following metal electrodeposition at -0.6 V for 180 s in a 25 cm² dynamic window with an electrolyte containing 5 mM Bi^{3+} and 15 mM Cu^{2+} (main). Normal cycling following the 24 h rest (inset).

a positive potential of $+0.8$ V restores the original window transparency within 4 s (Figure 10, light red line).

Cycling Durability and Resting Stability. The dynamic window is capable of cycling 1,000 times without any noticeable degradation in uniformity or contrast ratio (Figure 11A). The device also possesses superb resting stability at open circuit following metal electrodeposition. The transmission of the window does not change significantly at open circuit over the course of 24 h (Figure 11B, main), during which no power is applied to the device. After 24 h in the opaque state, the switching performance of the window does not change (Figure 11B, inset).

In this work, we developed bistable black electrochromic windows based on the reversible electrodeposition of Bi and Cu. To ensure uniform deposition, we implemented a SAM of Pt nanoparticles on the ITO working electrodes, which improved both nucleation and reversibility. Furthermore, by varying the Bi–Cu electrolyte composition, we discovered a trend in stripping speed with increasing Cu concentration and found the kinetically optimal electrolyte composition. From these findings, we propose that the galvanic displacement of Bi by Cu^+ justifies the changes observed in electrodeposition morphology and metal stripping kinetics with varying Bi–Cu electrolyte compositions. After optimizing these components in spectroelectrochemical half-cells, we constructed practical two-electrode 25 cm² dynamic windows with improved kinetic switching speeds compared to previously designed Pb–Cu and Ag–Cu devices. These Bi–Cu devices possess a color-neutral opaque state, subminute switching times with high optical contrast, and dual-state resting stability and do not degrade after 1000 cycles. These excellent metrics suggest that dynamic windows based on reversible metal electrodeposition offer a promising and competitive alternative to traditional electrochromic windows. To enable commercial meter-sized metal-based dynamic windows, future research will focus on implementing a lower sheet resistance working electrode to decrease the potential drop to the center of the window and an optically transparent metal grid counter electrode to decrease ion diffusion lengths.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acseenergylett.7b01072](https://doi.org/10.1021/acseenergylett.7b01072).

Experimental section, XPS characterization of the metal films, and additional electrochemical, optical, and SEM data (PDF)

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Notes

The authors declare no competing financial interest.

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