Dynamically Switchable Multicolor Electrochromic Films

Na Li,* Pingping Wei, Linan Yu, Juny Ji, Jiupeng Zhao, Chuanbo Gao, Yao Li,* and Yadong Yin*

The dynamic optical switch of plasmonic nanostructures is highly desirable due to its promising applications in many smart optical devices. To address the challenges in the reversibility and transmittance contrast of the plasmonic electrochemical devices, here, a strategy is reported to fabricate color switchable electrochromic films through electro-responsive dissolution and deposition of Ag on predefined hollow shells of Au/Ag alloy. Using the hollow Au/Ag alloy nanostructures as stable seeds for site-specific deposition of Ag, elimination of the random self-nucleation events is enabled and optimal reversibility in color switching is allowed. The hollow structure further enables excellent transmittance contrast between the bleached and colored states. With its additional advantages such as the convenience for preparation, high sensitivity, and field-tunable optical property, it is believed that this new electrochromic film represents a unique platform for designing novel smart optical devices.

1. Introduction

The unique localized surface plasmon resonance (LSPR) of noble metal nanostructures offers exciting opportunities in various applications including optical devices,[1] color filters,[2] sensing,[3] and electro-optical switching.[4] The LSPR properties of these nanoparticles can be generally modulated by altering their size, morphology, and composition.[5] The dynamic response to external stimuli in a reversible manner has been regarded as the next revolution in plasmonic materials,[6] which envisions excellent opportunities in creating novel optical devices.[7]

To date, many efforts have been devoted to achieving this goal. One strategy is to take advantage of plasmonic coupling between adjacent noble metal nanoparticles via controlling their assembly and disassembly, leading to LSPR properties that can be conveniently regulated by various stimuli such as stress,[8] magnetic field,[9] pH,[10] and temperature.[11] Another way is to take advantage of the electro-redox chemistry to modify the morphology, chemical composition, and fundamental coupling mechanism of plasmonic nanoparticles in a reversible manner.[12] Kobayashi and co-workers reported an electrochromic device fabricated with Ag nanoparticles, which showed reversible color changes between the transparent and vivid colored states in response to an electric voltage.[13] Depending on the direction of the electric field, two processes could be conveniently controlled, including the oxidation of the Ag nanoparticles (dissolution) and the reduction of the Ag (I) salt (deposition), corresponding to the bleaching and coloring process, respectively. By varying the potential, the size of the Ag nanoparticles could be maneuvered, which allows dynamic modulation of the optical signals within seconds. Compared with the assembly/disassembly strategy, electrochemical switching is more suitable for practical applications because electrically driven actuation can respond to an electric voltage in an accurate, dynamic, and instantaneous way.

In a conventional electrochemical process, Ag can self-nucleate on the film in addition to supporting the growth of existing Ag nanoparticles that were not completely dissolved in the bleaching process. The self-nucleation events occur randomly and often lead to the uncontrollable nanoparticle morphologies and the formation of large agglomerates after repetitive deposition/dissolution cycles, and therefore a dramatic decrease in the reversibility and stability of the electrochromic film. Many efforts have been made to address this issue by preparing the electrochromic devices with the assistance of, for example, anodized aluminum oxide (AAO) and SiO2 templates.[14] Although these templates worked well in isolating the nanoparticles from each other and therefore contributed to the improved reversibility, they involved complex procedures, increased the production cost significantly, and...
limited the sample to small size, making it a major challenge to extend to practical large-scale applications.

An ideal electrochromic film should be prepared conveniently and show good stability, reversibility, and high switching performance. To this end, here we present a new strategy to prepare electrochromic film through electro-responsive dissolution and deposition of Ag on hollow shells of Au/Ag alloy. Using the hollow shells of Au/Ag alloy as stable anchoring sites, we eliminate the random self-nucleation events during the Ag deposition to achieve optimal reversibility in color switching. Further, as the plasmonic resonance of the hollow alloy nanoparticles is in the near-infrared region while the additive deposition of Ag moves the resonance band back to the visible region, the electrochromic film displays a high transmittance contrast between the bleaching and colored states in the visible region. This strategy takes advantage of the pre-formed hollow nanoparticles as the “seeds” to avoid the need for templates and enables instant color switching by utilizing the electrochemical process to drive the fast overgrowth and dissolution of silver atoms surrounding the seeds. Considering its high reversibility and excellent transmittance contrast, we believe this unique strategy holds great promises for the fabrication of many novel smart optical devices.

2. Results and Discussion

Scheme 1 illustrates the strategy for the preparation of hollow shells of Au/Ag alloy on conductive indium tin oxide (ITO) substrates and the operating mechanism of electrochromic switching. A film of uniformly distributed Ag nanoparticles was first deposited on ITO by an electrodeposition process and then immersed in a solution of HAuCl₄, which converted the Ag nanoparticles into hollow shells of Au/Ag alloy via the galvanic replacement reaction. Then the electrochemical process was realized by immersing the film of the hollow alloy shells in an AgNO₃ solution followed by the application of an electric field with varying polarity and strength. When a negative potential was applied, the Ag⁺ in the electrolyte could be reduced, which led to the deposition of Ag atoms on the hollow shells of Au/Ag alloy and thus switched “on” the color of the film. In a similar manner, when a positive potential was applied, the Ag atoms from Au/Ag nanoparticles were oxidized to form Ag²⁺, leaving only the hollow shells of Au/Ag alloy to display a bleached “off” state. By this means, the electrochromic switching of the film could be achieved reversibly.

2.1. Preparation of the Electrochromic Film with Hollow Shells of Au/Ag Alloy

As discussed above, the key challenge to enhance the reversibility is to suppress the self-nucleation in the coloration process so that the formation of large Ag agglomerates could be avoided. For this purpose, we take advantage of the galvanic replacement reaction to convert the pre-deposited Ag nanoparticles into hollow Au/Ag shells, which can serve as the stable deposition sites to prevent Ag atoms from self-nucleating on the ITO substrate in a random manner. Here we employ the strategy of seed-mediated growth to ensure Ag atoms only deposit onto the surface of Au/Ag alloy shells, as the growth on pre-existing nanoparticles is energetically more favorable than homogeneous self-nucleation.[15] The hollow shells of Au/Ag alloy are designed to have multiple functions: 1) They have enhanced chemical stability against oxidation than Ag so that the seeds could remain and retain their positions under positive potential. 2) They serve as seeds to allow site-specific deposition of Ag atoms. 3) Their plasmonic band is in the near-infrared region so that the film becomes almost transparent in the visible region at the “bleached state,” producing a high contrast to the colored state after deposition.

For creating hollow shells of Au/Ag alloy, the film of Ag nanoparticles was firstly prepared via electrochemical deposition method according to our previous work[16] and then the reaction proceeds according to the following pathway[17]

$$3\text{Ag}(s) + \text{AuCl}_4^-(aq) \rightarrow \text{Au}(s) + 3\text{Ag}^+(aq) + 4\text{Cl}^-(aq)$$  

(1)

Because the standard reduction potential of the AuCl₄⁻/Au (0.93 V) is higher than that of the Ag⁺/Ag⁰ (0.80 V), immediately after the film of Ag nanoparticles was immersed into a solution of HAuCl₄ (0.3 × 10⁻⁴ M), the galvanic replacement reaction occurred spontaneously, accompanied by a color change of the film from grayish yellow to blue (Figure 1a, inset). The UV–vis spectroscopy shows a red-shift of the LSPR band from 480 to 510 nm, which is expected for a galvanic replacement reaction (Figure 1a).[18] Meanwhile, a significant decrease in the intensity of the LSPR band was observed, which ensures excellent transparency of the resulting hollow Au/Ag
nanoshells and thus promises a broad range of optical modulation. The hollow structure can be further evidenced by the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 1b), which reveals a bright outline which suggests a hollow structure. The Au and Ag elements are distributed across the entire particle, as revealed by the energy-dispersive X-ray spectroscopy (EDS) mapping (Figure 1b). Partial Ag-rich or Au-rich segments can also be observed, suggesting that Au and Ag are not homogeneously alloyed at the atomic level, consistent with previous observations.[19] scanning electron microscopy (SEM) images confirm that the Ag nanoparticles and the hollow shells of Au/Ag alloy are uniformly distributed on the ITO substrates (Figure 1c,d). The Ag nanoparticles obtained from an electrodeposition process are nearly spherical and uniform in size with an average diameter of 86 nm. The morphology of the nanoparticles has been well retained after the galvanic replacement. It is worth noting that the remaining Ag of the hollow shells of Au/Ag alloy could be leached first from the shells of Au/Ag alloy by oxidation at +0.3 V for 30 s for better transparency of the film, as shown in Figure S1 in the Supporting Information.

2.2. Electrochromic Response

By taking advantage of the deposition/dissolution process of the hollow shells of Au/Ag alloy, we further demonstrate the dynamic modulation of the electrochromic property of the films. In a typical investigation, the Au/Ag film was cycled 100 times, with each cycle containing an applied potential of +0.3 V for 30 s and −0.3 V for another 30 s. Figure 2a shows the typical LSPR extinction spectrum of the electrochromic film in response to an applied potential. When a potential of −0.3 V was applied, two LSPR bands appeared at 580 and 430 nm, respectively, displaying a violet color, indicating the successful reduction of Ag⁺ in the electrolyte and its deposition on the hollow shells of Au/Ag alloy. The LSPR bands at the lower (≈580 nm) and higher (≈430 nm) energy levels could be attributed to the dipole and quadrupole modes resonance of the Au/Ag alloy nanoparticles, respectively. When a potential of +0.3 V was applied, the LSPR band of the electrochromic film disappeared, accompanied by an obvious color change from violet to almost colorless due to the oxidative dissolution of Ag from the Au/Ag alloy nanoparticles. During the potential cycling, the recorded LSPR extinction spectra essentially overlapped at each applied potential (Figure 2a), which reveals excellent reversibility of the electrochromic film, essential for its applications. Figure 2b shows the change of the transmittance of the film at the maximum absorption (580 nm) during the alternative coloration and bleaching cycles. Here we define the switching time as the time required for a system to reach 90% of its full modulation. The coloration and bleaching processes were found to be accomplished within ≈23 and 3 s, respectively. The transmittance contrast (ΔT) between the colored (−0.3 V) and bleached (+0.3 V) states was ≈42%, which was maintained during 100 cycles of the potential switching. The sizes of Au/Ag alloy nanoparticles were measured to be ≈92 and ≈53 nm at the respective states (Figure 3c,d). Thanks to the presence of the
Au/Ag hollow shells as the anchoring sites during the Ag deposition, no agglomerates of the nanoparticles can be observed.

To investigate the dynamic process of the coloration/bleaching of the film, the change in the LSPR property of the electrochromic film was monitored in a deposition/dissolution cycle (Figure 3). The corresponding UV–vis spectrum was recorded real-time (Movie S1, Supporting Information). Upon the application of a negative potential, the originally very lightly colored film became strongly colored, implying the reduction of Ag$^{+}$ to metallic Ag and the subsequent deposition of Ag atoms on the hollow shells of Au/Ag alloy. As the deposition process continued, the transparent film turned to light-blue, purple and eventually reddish in 30 s, suggesting the continuous growth of the Au/Ag alloy nanoparticles (Figure 3a). The change in the color of the film was recorded real-time by a UV–vis spectrometer, as plotted in Figure 3b. With the deposition of Ag atoms, the intensity of the dipole-mode LSPR band of the film gradually increased, and the position continuously shifted from near-infrared to a shorter wavelength. It might be attributed to the increased wall thickness of the Au/Ag alloy nanoshells.[20] Finally, the LSPR band shifted to $\approx$590 nm with a shoulder at $\approx$420 nm at 30 s. We have also measured the near-infrared spectra of the films, however, only a very small shoulder could be observed (Figure S3, Supporting Information) because each film is composed only a monolayer of shells and the resonant intensity of the shells was considerably low when a significant amount of Ag was depleted. When a positive potential (i.e., +0.3 V) was applied to the same film, its color changed quickly from red to almost transparent (Figure 3a). The LSPR band of the nanoparticles disappeared completely in $\approx$3 s, which was ten times faster than the coloration process (Figure 3c). We believe that diffusion of Ag$^{+}$ from the surrounding to the surface of the hollow Au/Ag seeds is relatively slow in driving the coloration of the films, while the color fades immediately.

Figure 2. a) UV–vis spectra of the electrochromic film at the colored state and the bleached state. b) In situ optical response of the electrochromic film, whereby each step the transmittance was measured at 580 nm of the wavelength. c,d) SEM images of the hollow shells of Au/Ag alloy at the colored and bleached state, respectively, after 100 cycles of the potential switching.

Figure 3. a) Digital images of the film during the coloration (5–30 s) and bleaching process (1–3 s). The scale bar is 1 mm. UV–vis spectra of the hollow shell of Au/Ag alloy nanoparticles on the ITO substrate obtained during the b) coloration and c) bleaching processes. The intervals for the recorded spectra were b) 2 s and c) 1 s.
as no long distance diffusion is needed during the oxidation of Ag. The reaction rate and diffusion coefficient were estimated as shown in Figure S6 in the Supporting Information. As expected, the apparent diffusion coefficient of the coloration process is smaller than that of the bleaching process.

The formation of stable Au/Ag alloy seeds was found to be very important to the reversibility of the electrochromic film. The concentration of HAuCl₄ is an important parameter for optimizing the reversibility of electrochromic film. If it was fabricated without the galvanic replacement reaction, the Ag nanoparticles grew into large ones after a few deposition/dissolution cycles (Figure 3a,b). It is obvious that the pristine Ag nanoparticles (as shown in Figure 1d) evolved into irregular shapes after ten cycles, which continued to grow uncontrollably with further application of the pulse potentials. We attribute this phenomenon to the self-nucleation of Ag atoms and their coalescence to form large agglomerates. In this case, only part of Ag could be dissolved at a positive potential of +0.3 V. As a result, after applying the pulse potentials, large Ag nanoparticles covered the ITO surface, leading to a dramatically decreased transmittance of the film (Figure 4e). In clear contrast, if the electrochromic film was fabricated with hollow shells of Au/Ag alloy obtained by the galvanic replacement of 0.3 × 10⁻³ M HAuCl₄, Ag atoms were preferentially deposited on the alloy shells via the heterogeneous nucleation. As expected, no noticeable agglomerates can be observed at both the colored and bleached states even after 100 cycles (Figure 2c,d). A transmittance contrast of the film has been well maintained at ≈42% during the cycling process (Figure 4e). We noticed that when the concentration of HAuCl₄ was further increased to 3.0 × 10⁻³ M for the galvanic replacement, the transmittance contrast of the film decreased from 27% to 10% after 100 cycles. The nanoparticles were still well separated at the colored and bleached states as shown in Figure 4c.d. It is most likely because, with a high concentration of HAuCl₄, the galvanic replacement reaction makes the nanostructure prone to collapse especially after a number of deposition/dissolution cycles, which leads to the lower stability of the electrochromic performance. Although these collapsed nanoparticles can still serve as the anchoring sites for the deposition of Ag, their plasmonic band lies in the visible region, leading to reduced transparency in the bleached state and therefore a low transmittance contrast. These control experiments emphasize the importance of stable hollow shells of Au/Ag alloy in retaining the reversibility and transmittance contrast of electrochromic films.

2.3. Modulation of the Plasmonic Properties

It is known that a dramatic change in the LSPR property can be induced by a minor change in the morphology of the plasmonic noble metal nanostructures. In this system, controlling the strength and time of the external electric field provides a feasible strategy to achieve multicolor and transmittance tuning of the film with a dynamic mode, because the growth of hollow shells of Au/Ag alloy nanoparticles can be conveniently controlled by the electrodeposition process. Figure 5a shows the LSPR extinction spectra of the film recorded at different electrochemical potentials ranging from −0.05 to −0.4 V at a step of 0.05 V during eight switching cycles. With increasing the potentials, more Ag atoms were deposited onto the hollow shells Au/Ag alloy, which results in a shift in the LSPR band with enhanced intensity due to the increased particle size and the compositional transformation. The electrochromic film fabricated with the hollow shells of Au/Ag alloy possesses a reversible plasmon band shift of ≈150 nm, which shows superior electrochemical switching performance. For quantitative characterization of these coloration properties, spectroscopy data were transformed into color coordinates, known as the CIE 1931 diagram, as shown in Figure S4 in the Supporting Information. The color changed from yellowish (L* = 0.05 V) to red and finally to blue (L* = 0.4 V). According to the CIELAB(L*a*b*) chromaticity coordinates (Table S1, Supporting Information), with an increase of the voltage from −0.05 to −0.4 V, the L* value decreased, suggesting a gradual reduction in the brightness of the films. In addition, the transmittance contrast of the electrochromic film could be controlled by tuning the coloration/bleaching time (Figure 5b). The transmittance contrast can be tuned from 24% to 55% at the wavelength of 580 nm when the coloration/bleaching time was elongated from 10 to 90 s. When the switching time was
increased to 130 s, the transmittance contrast could not be further increased, which could be attributed to a depletion of the Ag source in the electrolyte. In addition, the LSPR property of the initial hollow Au/Ag alloy nanostructures was determined by the degree of galvanic replacement of the Ag nanoparticles by different concentrations of HAuCl4, which could be utilized to tune the optical property of the electrochromic film.18b Starting with the Ag films with the LSPR band at 480 nm, we prepared five films by galvanic replacement with different concentrations of HAuCl4 (0.2 × 10⁻¹⁵ to 1.0 × 10⁻¹⁵ m). The colored states of the films changed to deep yellow, red, purple, blue, and cyan, with an increasing concentration of HAuCl4 (Figure 5c). However, not all the films show high stability (Figure S2, Supporting Information), because the stability is related to the concentration of HAuCl4 as we discussed above.

The color change of the films depends on the oxidation/reduction of Ag atoms. When no electric voltage was applied, there were no chemical reactions and the film color remained unchanged over a long term. We have carried out UV–vis measurements of a colored film at open circuit, as shown in Figure S5 in the Supporting Information, which showed no spectroscopic change in a period of 5 h. In addition, no visual change of the color film could be observed for over six months, suggesting good long-term stability. This memory effect, or bistability, helps to reduce power consumption and therefore is important for applications such as displays and smart windows.

3. Conclusion

In summary, we have demonstrated a unique process to the fabrication of an electrochromic film that allows reversible switched between the colored and bleached states effectively by maneuvering the electro-responsive reduction/oxidation of Ag⁺/Ag. The key strategy here is the pre-formation of hollow shells of Au/Ag alloy, which act as anchoring seeds for selective deposition of Ag and thus minimize the random self-nucleation of Ag nanoparticles on the conductive substrates. Such a design accounts for the significantly enhanced stability and reversibility of the resulting electrochromic film. In addition, the alloy nanoshells display minimal plasmonic resonance in the visible spectrum and therefore enable high transmittance at the bleached state, significantly increasing the transmittance contrast between the colored and bleached states. The electrochromic film shows excellent reversibility, sensitivity, and tunability of the optical property, which may find broad uses in many applications such as low-power displays, multicolor smart windows, and optoelectronic devices.

4. Experimental Section

Materials: Silver nitrate (AgNO₃ ≥99%, A.R.), potassium nitrate (KNO₃ ≥99%, A.R.), polyvinylpyrrolidone (Mw ≥45 000), hydrogen peroxide (H₂O₂, 30 wt%), and citric acid were purchased from Aladdin Reagent. All chemicals were used as received without any further purification.

Preparation of the Electrolyte: The electrolyte was prepared by mixing AgNO₃ (1.5 × 10⁻¹⁵ m, 2 mL), KNO₃ (1.5 m, 150 µL), citric acid (0.75 m, 80 µL), PVP (Mw = 45 000, 0.18 m, 80 µL), and aqueous H₂O₂ (30 wt%, 20 µL) in 2 mL of distilled water.

Preparation of the Film of Ag Nanoparticles: The films of the Ag nanoparticles with an LSPR extinction band at 480 nm were prepared by the electrochemical deposition method. ITO substrates (17 Ω cm⁻², 1 cm × 4 cm) were ultrasonically cleaned in acetone, methanol, and distilled water for 15 min and dried under a stream of nitrogen. The electrochemical deposition was performed in a three-electrode system with Pt and Ag wire as the counter and reference electrodes, respectively. The deposition process was conducted on a CHI660E workstation. The deposition potential was −4 V for 0.005 s and then at −0.3 V for 30 s. After deposition, the ITO film of the Ag nanoparticles was washed with distilled water three times and then dried in air before use.

Preparation of the Film of Au/Ag Alloy Hollow Nanoparticles: The Ag nanoparticles on the ITO substrate were immersed in the desired concentration of HAuCl₄ for 5 s. The film was then washed with distilled water and dried in air.

Electrochromic Process: The electrochemical measurements were conducted on a CHI660E electrochemical workstation with a standard three-electrode setup using the as-prepared hollow shells of Au/Ag alloy film as the working electrode, Pt wire as the counter electrode and Ag wire and the reference electrode in the as-prepared electrolyte. The electrochemical reduction/oxidation processes were carried out by applying −0.3 V for 30 s and +0.3 V for 30 s.
Characterizations: The surface morphologies of the films were characterized by SEM (Helios Nanolab 600i, FEI). The transmission electron microscopy (TEM, Talos F200, FEI) with a super X-EDS system was adopted to further characterize and identify the elemental composition of the nanoparticles. The TEM specimen with a thickness of 100–200 nm was prepared by focused ion beam (FIB) technique with Helios Nanolab 600i. Film illumination was carried out from a light source (DT-min-2-GS, Ocean Optics) through an optical fiber; an optical spectrometer (MAIA 2000-pro, Ocean Optics) was used to record the spectra.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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