An UV photochromic memory effect in proton-based WO₃ electrochromic devices

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We report an UV photochromic memory effect on a standard proton-based WO₃ electrochromic device. It exhibits two memory states, associated with the colored and bleached states of the device, respectively. Such an effect can be used to enhance device performance (increasing the dynamic range), re-energize commercial electrochromic devices, and develop memory devices. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3029775]

Although the primary application of tungsten oxide (WO₃) has been in electrochromic (EC) devices, this material has emerged as an interesting prospect in areas far beyond this field. Besides the "traditional" applications based on the EC effects, such as "smart" energy-efficient windows, antiglare automobile rear view mirrors, sunroofs, optoelectronic shutters, optical recording, and image storage,[1–4] other applications and phenomena currently being pursued include the photoelectrochemical cell for solar energy conversion, storage, and water splitting to generate hydrogen;[5] chemical and biologic sensors based on the gasochromic effect;[6] photonic crystals;[7] high-temperature superconductivity in WO₃ doped with H, Na, and K, forming organic-inorganic hybrid materials;[8] and ultrahigh-resolution electron beam lithography.[9] In this work, we report an effect related to the unique ability to have bistable optical and electrical states (i.e., both electrochromism and photochromism) in WO₃, an UV photochromic memory (UPM) effect that is observed in proton-based EC devices in both colored and bleached states. This effect on one hand may be used to enhance device performance by improving the contrast because one of the key measurements for the device performance is the transmission contrast between the dark (colored) and transparent (bleached) states; on the other hand, it might be used for manufacturing readable memory devices for optical recording and image storage. In this work, the memory effect will be demonstrated qualitatively with patterns written with an UV laser and quantitatively studied by measuring the change in the transmission.

A number of proton-based EC devices have been used in this study. One Li-based EC device is also used as a reference. The major difference between the two types of devices is that the proton-based EC device employs Ta₂O₅ as a solid-state electrolyte, whereas the Li-based EC device utilizes LiAlF₄ as a solid-state electrolyte.[10] A 325 nm He–Cd laser with 10 mW power is used as the UV source. The photon energy $\hbar\omega = 3.814$ eV is above the band gap of WO₃. A non-focused laser beam (~1 mm size or ~1 W/cm²) is used to write patterns on the device. An expanded laser beam is used to illuminate a large area (approximately a few millimeters) for performing the transmission measurement. The needed illumination time to generate the effect is typically 1–2 min

at a power density of ~1 W/cm² (and longer for a lower power density).

When a proton-based EC device [indium tin oxide (ITO)/WO₃/Ta₂O₅/NiOₓHᵧ/ITO] is illuminated with the UV light, as expected, coloration occurs in the irradiated area due to the normal photochromic effect.[11] Moreover the UV-colored area can be subsequently bleached by an electric field. However, on subsequent coloration under an applied voltage, the area originally colored by the UV light shows enhanced coloration and hence a memory effect. Furthermore, in the bleached mode under a reversed bias, the UV-colored area is found to be more transparent than the background and a reverse image could be observed, which creates a second memory state. These effects are demonstrated with the variation of the contrast of a simple pattern, the letter "E," written by the UV laser, with respect to the nonirradiated background. The result for the colored state can be easily seen on a photograph in Fig. 1. The result for the bleached state is not as easy to see on a photograph but nevertheless, it is quite obvious on the device when viewed with the naked eye. The memory effects can last over periods of months. In other words, an UV-irradiated device can be kept in the bleached state over long periods of time, and the previously irradiated area can be selectively (or preferentially) colored by applying either a positive or negative bias.

FIG. 1. (Color online) A photograph of a proton-based WO₃ EC device in the colored state, showing a letter E written by an UV laser.
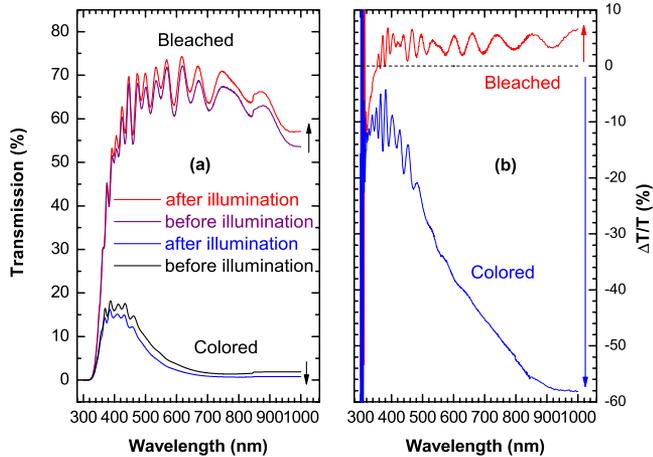
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FIG. 2. (Color online) (a) Transmission spectra of the device shown in Fig. 1 in the colored and bleached states measured before (solid lines) and after (dotted lines) UV illumination; (b) relative changes in the transmission.

This forms the basis for recording an invisible image in a device that can be made visible by applying a voltage, and the process can be repeated as many times as needed during an extended period of time. Such effects are not observed in the Li-based reference device, which reflects a subtle difference in the operating mechanisms of the proton-based versus Li-based EC devices.

To evaluate the memory effect quantitatively, we measured the changes in transmission in both colored and bleached states before and after illumination. The results are shown in Fig. 2. The changes are most apparent starting from 400 nm up to the longest wavelength measured, 1 μm. For the bleached state, the effect is moderate, that is, the transmission is enhanced by ~5% on average; but for the bleached state, the effect is more significant, that is, the transmission is reduced by 20%–50% in the visible spectral region. The dynamic range, which measures the performance of an EC device and is defined as the difference between the transmissions in the bleached and colored states, increases by 4%–16% in the spectral range of 400–1000 nm.

In general, photochromic coloration in tungsten oxide is known to be connected to optically excited electron (e^-) hole (h^+) pairs, which can decompose water incorporated in WO_3.[11] The light-induced decomposition of H_2O can be written as $H_2O + 2h^+ \Leftrightarrow O + 2H^+$, which describes the creation of proton (H^+) and metastable oxygen radicals (O). The protons together with the optically excited electrons lead to the formation of colored tungsten bronze H_xWO_3. Because the oxygen radicals are highly reactive, the instantaneous back-reaction of these O radicals (with resident H^+ ions) to form water (which would hinder the formation of a color center) could occur if these O radicals were not separated immediately. There are two possible ways that the O radicals are separated. The first is the escape of free oxygen out of the film during light exposure. In this case, only O radicals generated near from the interface between electrode and electrolyte can escape. The second is that the O atoms occupy oxygen vacancies and photochromic coloration would occur all across the film thickness. In this case, the decrease in the number of O vacancies would lead to weakened device performance, which has been observed in some cases.[12]

The reversible UPM effect can be explained in terms of a local photochromic phenomenon. A conceptual schematic
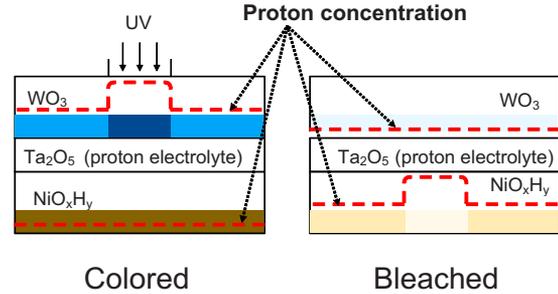

FIG. 3. (Color online) A conceptual schematic of the UPM effect. Dashed (red) lines graphically represent the H^+ proton concentration profiles in the WO_3 and NiO_xH_y layers. UV photochromic irradiation creates a high concentration of H^+ species in the irradiated area, which enhances EC coloration and decoloration.

illustrating this memory effect in EC devices is given in Fig. 3. When a proton-based EC device is irradiated with an UV laser, the WO_3 layer in the EC device can be colored by a photochromic mechanism. This mechanism generates a higher proton concentration in the UV-illuminated area than the surrounding nonilluminated area. When the device is bleached with a reverse bias, protons in the WO_3 layer are intercalated into the complementary-coloring counterelectrode (NiO_xH_y), and another proton concentration profile is created that exactly resembles the original one in the WO_3 layer. As a result, the area illuminated with UV light exhibits a higher bleached state than the surrounding nonilluminated area. This phenomenon is due to the higher local proton concentration induced into the NiO_xH_y counterelectrode. This memory effect eventually diminishes and disappears as the high local proton concentration diminishes with time through lateral diffusion of protons. The diffusion coefficients of the proton in H_xWO_3 are known to be ~10^{-11} cm^2/s, resulting in slow lateral diffusion.[13]

We have observed and explained an UV photochromic memory effect on proton-based WO_3 EC devices. Such an effect is expected to enhance the device performance as well as lead to memory devices. One can envision that commercial EC devices could be "re-energized" periodically with UV irradiation.

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