

Enhancement of Photochromism and Electrochromism in MoO₃/Au and MoO₃/Pt Thin Films

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Freshly vacuum-evaporated, neat amorphous MoO₃ thin films exhibit only UV photochromism. Visible-light photochromism is induced in these films when they are cathodically polarized for a short duration in a nonaqueous electrolyte. The efficiencies of the UV and visible-light photochromism of the MoO₃ thin films increase at least 2-fold when they are coated with a thin layer (~20-nm thickness) of Au or Pt. The enhancement in photochromism is attributed to the presence of a large Schottky barrier at the metal–semiconductor interface, which facilitates electron capture by Au or Pt. The electron capture by the metal produces a longer electron–hole separation lifetime, thereby enhancing the photochromic process. For the electrochromic process, the coloring and bleaching current densities for the MoO₃/Au thin-film electrode are about 1.5 and 2.0 times larger than the respective current densities for the MoO₃ thin-film electrode. The enhancement in electrochromism is ascribed to the electrocatalytic effect of the gold overlayer. The benefits of surface modifications are (1) inhibition of electron–hole recombination, which enhances photochromism, (2) enhancement of electrochromism, and (3) inhibition of corrosion reaction of surface MoO₃.

I. Introduction

Transition-metal oxides can be deeply colored with band-gap excitation using UV light in a photochromic process or with an applied potential in an electrochromic process.¹ These effects have been a subject of numerous investigations because of their potential technological applications in information display and sensor and high-density memory devices. Consequently, many different kinds of transition-metal oxides have been investigated for such purposes. These include WO₃,^{1–18} MoO₃,^{18–25} V₂O₅,^{7,26} TiO₂,²⁷ Ir(OH)₃,²⁸ Rh₂O₃,²⁹ SrTiO₃,³⁰ NiO,^{31–33} Cr₂O₃,⁴ MnO₂,³⁴ Nb₂O₅,^{35,36} and mixed-oxide systems.^{37–39}

The applications of transition-metal oxides as photochromic materials, however, are handicapped because most of these oxides require UV-light excitation, and most of the commercially available inexpensive light sources are visible lasers. Recently, a breakthrough was reported in which MoO₃ thin films, after cathodically polarized for a short duration in a nonaqueous electrolyte, exhibited visible-light photochromism.²⁵ In view of this result, this investigation was carried out to probe into the enhancement mechanism as well as to study the improvement of the efficiency of the visible-light photochromism and electrochromism through surface modification of MoO₃ with a thin Au or Pt overlayer. Surface modifications of semiconductors with noble metals have been shown to enhance photocatalytic activities of semiconductors for some reactions.^{40,41} Several studies have been made to improve the efficiency as well as the lifetime of the electrochromism of transition-metal oxides. Examples are admixing of Pt onto WO₃,^{10,11} WO₃ doped with Co, Ni, Mo, Zn, and Ru,^{12,14} transition-metal oxide based electrochromic devices with polymeric electrolytes,^{42–44} and WO₃–TiO₂-mixed films.¹³

II. Experimental Section

A. Thin-Film Preparation. The MoO₃ thin films were prepared by vacuum evaporation of high-purity powder (99.99%, KOSO Chemicals, Tokyo) onto conductive SnO₂-coated glass substrates (NESA, 1-mm thickness). The vacuum of the evaporation chamber was maintained at 1×10^{-5} Torr. The thickness of the deposited MoO₃ thin film was about 1000 nm. The MoO₃/metal samples (where metal is Au or Pt) were then fabricated by evaporating the desired metal film of 20-nm thickness onto MoO₃ at 1×10^{-5} Torr. The film-thickness measurements were made with Talystep (Rank Taylor Hobson). The configuration of the MoO₃/Au thin film is shown in Figure 1.

B. Photochromic Experiments. The band-gap excitation of MoO₃ was provided by using the UV output of a 500-W high-pressure mercury lamp. For the visible-light photochromic experiments, a sharp cutoff filter was used to obtain light of wavelength $\lambda \geq 500$ nm. All of the photochromic experiments were performed in air.

C. Electrochromic Experiments. The samples were polarized cathodically at 0.05 mA/cm² for 10 mC in a 0.2 M LiClO₄/propylene carbonate solution that served as a nonaqueous electrolyte. The reference electrode was a Ag/AgCl/KCl (sat'd) electrode, whereas the counter electrode was a Pt electrode. All electrochemical experiments were performed with a potentiostat unit PS-02 (TOHO Technical Research).

D. Absorbance Measurements. The photochromic or electrochromic response of the thin films is accompanied by a change in the absorbance. The larger the response, the larger the absorbance change. Hence, the magnitude of the absorbance change is used as a measure for these two processes. For MoO₃, the maximum absorption is around 900 nm. All absorbance measurements were done on a UV–visible double-beam spectrophotometer (Shimadzu UV-3101 PC).

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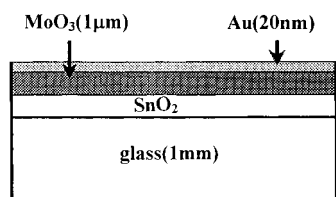


Figure 1. Configuration of the MoO₃/Au thin film.

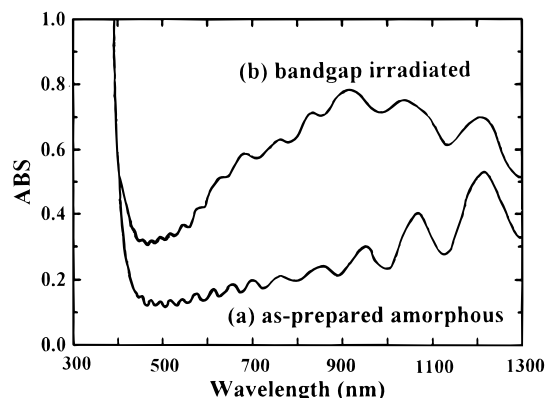


Figure 2. (a) Absorption spectrum of a MoO₃/Au film; (b) spectrum taken after the film (a) was irradiated with UV light for 3 min in air.

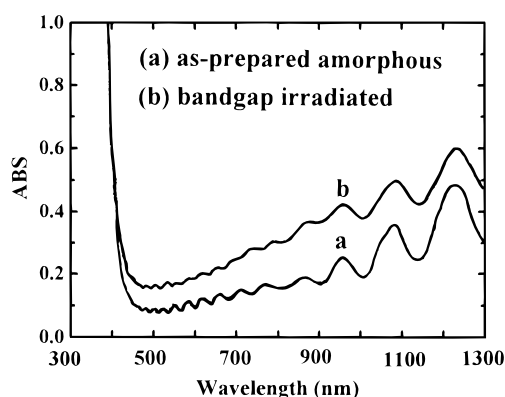


Figure 3. (a) Absorption spectrum of a MoO₃ film; (b) spectrum taken after the film (a) was irradiated with UV light for 3 min in air.

E. Surface-Photovoltage Spectroscopy (SPS) Measurements. The SPS measurements were done on the freshly prepared (untreated) and electrolytically treated MoO₃ samples in Professor T. Li's laboratory at Jilin University (China). Experimental details are given in ref 45.

III. Results

A. UV Photochromism. Both MoO₃ and MoO₃/Au thin films exhibit photochromism. They turn blue when they are irradiated with UV light in air. Figure 2 shows the change in the absorption spectra of a MoO₃/Au thin-film sample before and after UV irradiation. Prior to the irradiation (or coloration), the films are almost transparent at wavelengths longer than 400 nm (curve a). The absorption spectrum of the UV-irradiated sample has a broad peak centered around 900 nm (curve b). The absorbance change (Δ ABS) at 900 nm before and after UV irradiation was 0.56. Figure 3 shows the absorption spectra of a MoO₃ thin film before and after the UV irradiation. The absorbance change (Δ ABS) was 0.21 at 900 nm. Direct comparison of Δ ABS values was possible because the background absorbance due to the glass/SnO₂ substrate was the same in both cases. The same substrate was used for the fabrication of the MoO₃/Au samples;⁴⁶ after the absorbance of the

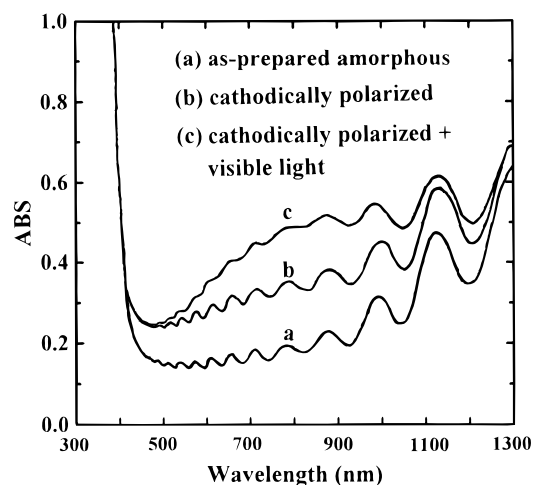


Figure 4. (a) Absorption spectrum of a MoO₃ thin film; (b) spectrum taken after the film (a) was polarized at -0.05 mA/cm^2 for 10 mC in 0.2 M LiClO₄/propylene carbonate solution; (c) spectrum taken after the film (b) was irradiated with visible light ($\lambda \geq 500 \text{ nm}$) for 10 min in air.

MoO₃ film was made, the sample was cut into two. One-half was evaporated with an Au overlayer, and then both halves were subjected to 3-min UV irradiation in air under identical conditions.

The above findings indicate that MoO₃ thin films with gold overlayers exhibited enhanced UV photochromic responses over neat amorphous MoO₃ thin films, with the absorbance change (Δ ABS) 2.7 times that of the latter. Similar results were obtained on several other samples.

B. Visible-Light Photochromism. Molybdenum trioxide is a wide band gap n-type semiconductor ($E_g \approx 3.15 \text{ eV}$).²⁰ Therefore, MoO₃ thin films do not show photochromism with visible-light excitation. However, after they have been polarized cathodically for a short duration, they become sensitive to visible light, and this is known as "visible-light photochromism".²⁵

For more than 10 samples of MoO₃ thickness of $1000 \pm 50 \text{ nm}$ investigated, the MoO₃/Au thin films, in all cases, showed visible-light photochromism at least twice as large as that for the MoO₃ thin films. This visible-light photochromic system was reported recently in ref 25. Figure 4 shows the visible-light photochromic results for a MoO₃ thin-film sample, whereas Figure 5 shows the same for a MoO₃/Au thin-film sample. Table 1 shows Δ ABS1 and Δ ABS2 of MoO₃ and MoO₃/Au thin-film samples. The Δ ABS1 is the difference in absorbance at 900 nm before and after cathodic polarization of the samples for 10 mC in 0.2 M LiClO₄/propylene carbonate solution. The Δ ABS2 is the difference in absorbance at 900 nm before and after visible-light irradiation of the cathodically polarized samples, and thus, it represents the visible-light photochromic response. The MoO₃ and the MoO₃/Au thin-film samples were cathodically polarized such that the Δ ABS1 was about the same. After the cathodic polarization, the samples were then irradiated with visible light ($\lambda \geq 500 \text{ nm}$) for 10 min in air. The irradiated samples turned deep blue. The Δ ABS2 of the MoO₃/Au thin-film sample was 0.30 and was 2.3 times that of the MoO₃ thin-film sample.

Similar results were obtained when a Pt overlayer was used in lieu of the Au overlayer. In fact, a larger enhancement was observed. Figure 6 shows a comparison of the visible-light photochromic responses of MoO₃, MoO₃/Au, and MoO₃/Pt thin-film samples. The samples were fabricated such that they all gave the same values of Δ ABS1. In this way, the values of Δ ABS2 provide a direct comparison of the magnitudes of the

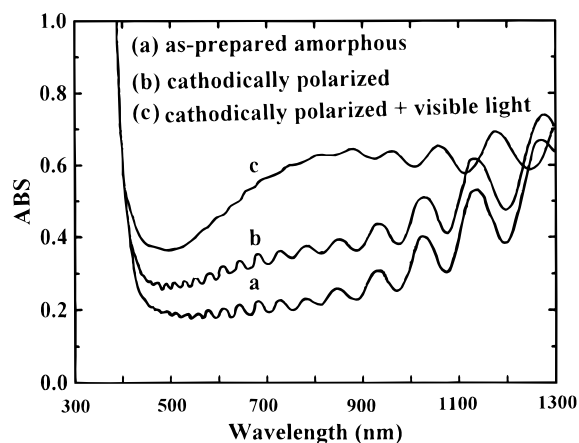


Figure 5. (a) Absorption spectrum of a MoO₃/Au thin film; (b) spectrum taken after the film (a) was polarized at -0.05 mA/cm^2 for 10 mC in 0.2 M LiClO₄/propylene carbonate solution; (c) spectrum taken after the film (b) was irradiated with visible light ($\lambda \geq 500 \text{ nm}$) for 10 min in air.

TABLE 1: Visible-Light Photochromic Responses at 900 nm of the MoO₃ and MoO₃/Au Thin Films

samples	ΔABS1^a	ΔABS2^a
MoO ₃	0.13	0.13
MoO ₃ /Au	0.12	0.30

^a In absorbance units AU.

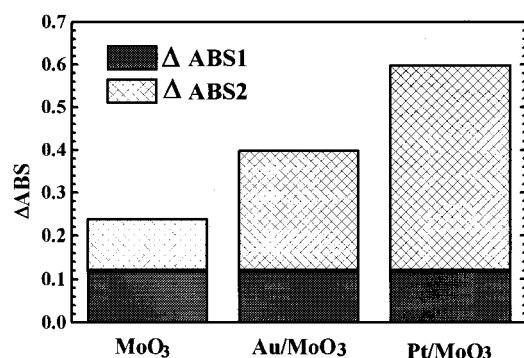


Figure 6. Comparison of visible-light photochromic responses at 900 nm of MoO₃, MoO₃/Au, and MoO₃/Pt thin-film samples.

TABLE 2: Visible-Light Photochromic Responses (at 900 nm) of MoO₃, MoO₃/Au, and MoO₃/Pt Thin-Film Samples and the Work Functions of the Metals

metal overlayer	(MoO ₃)	Au	Pt
work function (in eV)		5.10	5.64
ΔABS2 (in AU)	0.12	0.30	0.49

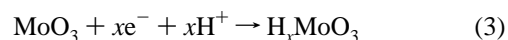
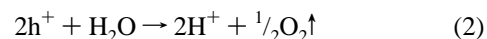
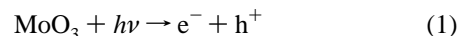
visible-light photochromic responses. Table 2 gives the values of ΔABS2 of these samples together with the work functions of the metals.⁴⁷ The visible-light response of the MoO₃/Pt thin-film sample was 4.1 times that of the MoO₃ thin-film sample and was 1.6 times that of the MoO₃/Au thin-film sample.

C. Electrochromism. The current–potential curves of the MoO₃/Au and MoO₃/Pt thin-film electrodes in 0.2 M LiClO₄ + propylene carbonate solution vs Ag/AgCl/KCl (sat'd) reference electrode is shown in parts A and B of Figure 7, respectively. The shapes of these curves are similar to each other, but the current densities are different. In Figure 7A, the cathodic current, starting at approximately +0.5 V, is associated with the coloring process. This process involves the incorporation of Li⁺ ions into the MoO₃ lattice, resulting in the formation of Li_xMoO₃ ($0 < x$),⁴⁸ which is responsible for the coloring. In

the meantime, some of the Mo⁶⁺ ions in the MoO₃ lattice are reduced to Mo of lower valence states. The blue color of the MoO₃ lattice intensifies with a further increase in the cathodic potential. Hence, the magnitude of the cathodic current, or the coloring current, at a given potential can be used as an indication of the amount of the Li⁺ ions injected into the MoO₃ lattice or as an indication of the degree of coloration. The anodic current, or the bleaching current, which appears when the potential sweep is reversed, is associated with the bleaching process, the process in which the Li⁺ ions are evicted from the MoO₃ lattice. The peak of the bleaching current was observed at about +0.2 V. The coloring-current density for the MoO₃/Au thin-film electrode was observed at 0.57 mA/cm², whereas that for the MoO₃ thin-film electrode was 0.37 mA/cm². Similarly, the bleaching-current density for the MoO₃/Au thin-film electrode was observed at 0.23 mA/cm², whereas that for the MoO₃ thin-film electrode was 0.11 mA/cm². Thus, the coloring- and bleaching-current densities for the MoO₃/Au thin-film electrode are enhanced 1.5 and 2.0 times from the respective current densities for the MoO₃ thin-film electrode because of the surface modification.

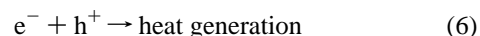
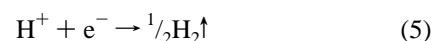
IV. Discussion

A. Enhancements in UV- and Visible-Light Photochromism. The UV photochromic process of the MoO₃ thin films is explained as follows:²²



Electrons and holes are formed when a thin film of MoO₃ is irradiated with UV light [eq 1]. The photogenerated electrons are then injected into the conduction band of MoO₃, and the photogenerated holes react with adsorbed species such as H₂O, forming protons [eq 2], which then diffuse into MoO₃. Subsequently, hydrogen molybdenum bronze (H_xMoO₃) is formed and the film turns blue [eq 3].

The following reactions may compete with reactions 1–3, resulting in the loss of efficiency of the photochromism:



Reaction 4 is the photocorrosion reaction²⁴ of MoO₃, and reaction 5 is the hydrogen-evolution reaction. In our experiments, these reactions were not observed. Reaction 6 is the recombination of the photogenerated charge carriers, which is detrimental to the efficiency of the photochromism of MoO₃.

As mentioned earlier, molybdenum trioxide is an n-type semiconductor with $E_g \approx 3.15 \text{ eV}$,²⁰ and it is only photosensitive to the UV radiation. Therefore, for the untreated freshly evaporated MoO₃ thin films, electrons and holes can only be generated by the band-gap UV excitation. When the MoO₃ thin film is polarized cathodically, Li_xMoO₃ is formed in the MoO₃ lattice.⁴⁸ The Li_xMoO₃ produces trap states with energy levels that lie inside the band-gap region, and they are accessible by the visible light. Excitations to these states give rise to the visible-light photochromism. From our recent experimental

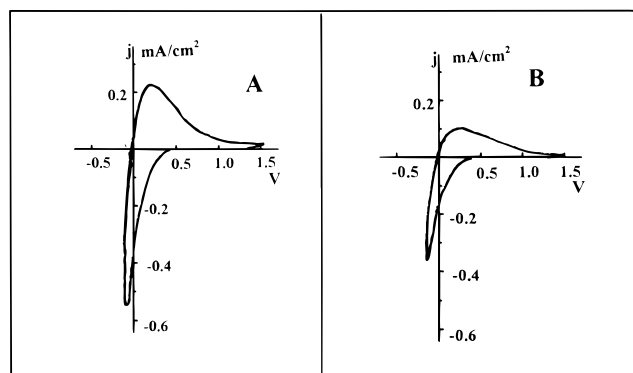


Figure 7. Current–potential curves of the MoO₃/Au and MoO₃ thin-film electrodes in 0.2 M LiClO₄ + propylene carbonate solution with potential sweep rate = 10 mV/s: (A) MoO₃/Au; (B) MoO₃.

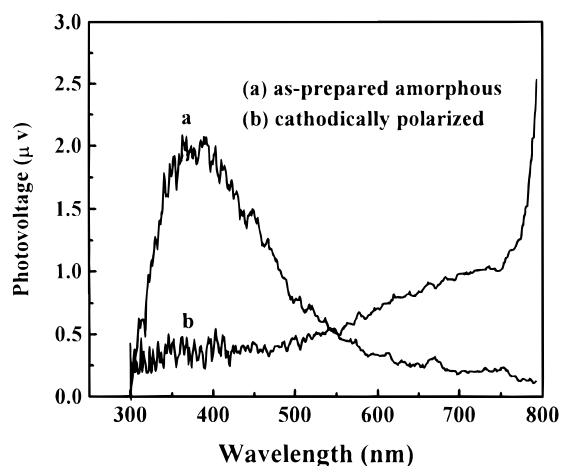


Figure 8. (a) Surface-photovoltage spectrum of a freshly vacuum-evaporated (untreated) MoO₃ thin-film sample; (b) surface-photovoltage spectrum of a MoO₃ thin-film sample after it was cathodically polarized for 10 mC.

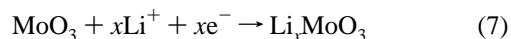
results, these trap states are believed to be stable, in contrast to a previous belief.²⁵ It is observed that the cathodically polarized MoO₃ thin films can be left in air for a prolonged period of time with little deterioration in the quality and coloration of the films.

The presence of energy states inside the band-gap region is supported by the surface-photovoltage spectroscopy (SPS) experimental results. Figure 8 shows the SPS of the as-prepared and untreated (curve a) and electrolytically treated (curve b) MoO₃ thin-film samples. These two samples obviously have very different photovoltage vs wavelength responses. The electrolytically treated sample is photosensitive to light of wavelengths $\lambda \geq 500$ nm, whereas the untreated sample is photosensitive to light of wavelengths around 400 nm or lower.

The enhancement in the visible-light photochromism in the MoO₃/Au and MoO₃/Pt thin-film samples can be explained by the presence of a Schottky barrier at the metal–semiconductor interface. The conduction band energy of MoO₃, $E_c(\text{MoO}_3)$, is calculated, using a method described by Frese,⁴⁹ to be 0.14 V vs NHE. This gives a value of 0.34 V vs NHE for the Fermi energy level of MoO₃, $E_F(\text{MoO}_3)$. The work functions for Au and Pt are 5.10 and 5.64 eV, respectively,⁴⁷ and thus, the differences in the Fermi energy levels between MoO₃ and the metals are $\Delta E_F(\text{MoO}_3\text{–Au}) = -0.27$ V vs NHE and $\Delta E_F(\text{MoO}_3\text{–Pt}) = -0.77$ V vs NHE. Hence, Pt produces a higher Schottky barrier than Au. When the electrolytically treated samples are irradiated, electrons and holes are formed (as in eq

1). The electron capture by Au or Pt results in a longer electron–hole pair separation lifetime and thus enhances the photochromic process. Since Pt has a higher Schottky barrier, the electron capture by Pt thus produces a longer electron–hole pair separation lifetime. This explains the observation that Pt has a larger enhancement than Au. This photochromic enhancement effect is analogous to the photocatalytic enhancement effect when Pt or a noble metal is deposited on semiconductor surfaces.^{40,41}

B. Enhancement in Electrochromism. The electrochromism of MoO₃ is due to the double injection of an electron (e^-) from the electrode and a positive ion (Li^+ in our case) from the electrolyte into the MoO₃ lattice,⁴⁸ forming the molybdenum bronze (Li_xMoO_3). The reaction is given by the following equation:



The MoO₃/Au thin-film electrode shows a higher coloring current and bleaching current than the MoO₃ thin-film electrode. This may be due to the electrocatalytic effect of gold. Tseung and co-workers^{10,11} have shown that admixing of Pt with WO₃ in an electrochromic film decreased the overpotential and increased the rate of hydrogen-atom formation during the coloring process. The hydrogen atoms formed on Pt immediately diffused into the tungsten trioxide lattice, generating hydrogen tungsten bronze.

V. Summary and Conclusions

Metal overlayers on MoO₃ thin films have been studied to determine their effects on the photochromism and electrochromism of MoO₃. The following observations and conclusions are made.

- (1) The efficiencies of the UV and visible-light photochromism increase at least 2 times when MoO₃ is coated with a thin layer (~ 20 -nm thickness) of Au or Pt.
- (2) The coloring- and bleaching-current densities for the MoO₃/Au thin-film electrode are about 1.5 and 2.0 times larger than the respective current densities of the MoO₃ thin-film electrode, which demonstrates enhanced electrochromism in the former case. The enhanced electrochromism will result in lower operating potentials for electrochromic devices. This could lead to a decrease in the power consumption and possibly an increase in the lifetime of the electrochromic system.
- (3) The enhancement in photochromism, both UV- and visible-light, is attributed to the presence of a large Schottky barrier at the metal–semiconductor interface, which facilitates electron capture by Au or Pt.
- (4) The enhancement in electrochromism is attributed to the electrocatalytic effect of the surface Au layer.

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