



Fabrication of self-assembled ultrathin photochromic films containing mixed-addenda polyoxometalates $H_5[PMo_{10}V_2O_{40}]$ and 1,10-decanediamine

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ABSTRACT

A layered phosphovanadomolybdate/1,10-decanediamine (1,10-DAD) self-assembled ultrathin film was fabricated by means of alternating adsorption of mixed-addenda polyoxometalates (POMs) (phosphovanadomolybdate, $H_5[PMo_{10}V_2O_{40}]$) and 1,10-DAD, and its photochromic properties were investigated. It is found that the self-assembled multilayer (SAM) film shows high-photochromic response, excellent photochromic stability and reversibility. The photochromic behavior of the SAM is closely related to the reduction potentials of addenda atoms in mixed-addenda POMs. In the case of photo-reduced mixed-addenda POMs, the electron is localized on the more reducible atom, and the addenda atoms with higher reduction potentials show prior photochromism compared with those with lower reduction potentials. The coloration speed is improved after introduction of V into molybdenum POM. The well-ordered lamellar structure of the film was well maintained during the coloration.

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1. Introduction

Photochromic materials, whose optical absorption properties can change reversibly in response to light, have potential applications in high-density optical memory, optical switching, and chemical sensors [1–5]. For practical application, it is meaningful to deposit the photochromic materials into film structures. Especially, for application in those mini-type optoelectronic devices, it is demanded that the materials should be made into ultrathin films [6]. In recent years, the electrostatic layer-by-layer (LbL) self-assembled technique has proved to be an effective and convenient approach to fabricate ultrathin photochromic films by alternating deposition of inorganic and organic building block, with good control over the layer composition and thickness [7,8]. Polyoxometalates (POMs), as a unique class of inorganic metal-oxide clusters, have proved to be an attractive class of photochromic materials because of their ability to reversibly accept and release a large number of electrons while remaining their structural integrity. In the presence of counter ions with amine, or hydroxyl groups that can donate a proton, the irradiation of POMs by UV light results in a mixed-valency colored, long-lived charge separated state [9–12]. Recently, some complex POM clusters were used on the fabrication of self-assembled multilayer (SAM) films for optical–electronic devices [13–18]. In our previous works, we found that the photochromic

properties of such inorganic/organic SAM films were closely related to the redox potentials of the inorganic clusters and the films fabricated by molybdenum POMs with higher reduction potentials show better photochromic response than those by tungsten POMs with lower reduction potentials [19]. However, the coloration speed of these films constructed by molybdenum POMs is not fast enough for practical application. So it is still necessary to improve the coloration speed of such SAM films. In comparison with Mo^{6+} , V^{5+} shows higher reduction potential in POMs. It is expected that mixed-addenda POMs containing both of vanadium and molybdenum will further improve photochromic properties of hybrid SAM films. Moreover, it will help us not only to design efficient POM/organic hybrid photochromic ultrathin films, but also to further understand POMs' photochromic behavior to investigate the photochromism of mixed-addenda POM/organic SAM films. In this study, mixed-addenda POM, $H_5[PMo_{10}V_2O_{40}]$, was employed as inorganic component to construct photochromic ultrathin film with an organic diamine (1,10-decanediamine). The structure and photochromic properties of SAM films were investigated.

2. Experimental section

2.1. Materials

$H_5[PMo_{10}V_2O_{40}] \cdot 30H_2O$ (PMoV) was synthesized according to a published procedure [20]. 1,10-decanediamine (denoted as

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1,10-DAD) was purchased from Aldrich. 3-aminopropyltriethoxysilane (APS) was purchased from Acros. All the chemicals were of analytical grade and used without further purification. Ultra-pure water with a resistivity of 18.2 M Ω cm was produced using a Mill-Q apparatus (millipore).

2.2. Fabrication of PMoV/1,10-DAD SAM film

The substrates (quartz and silicon wafers) were cleaned by immersion in the “piranha solution”, a 7:3 mixture of concentrated sulfuric acid and 30% hydrogen peroxide, at 80 °C for 40 min and rinsed with copious deionized water. Then, the substrates were immersed in a 1:1:5 mixture of 29% NH₄OH, 30% H₂O₂, and H₂O at 70 °C for 20 min, followed by extensively washing with water. The cleaned substrates were modified with APS in the apparatus from the literature [21]. The APS-modified substrates were immersed into 0.1 M HCl solution to get an amino cation covered surface, and then immersed into the solution of PMoV (10⁻³ M, pH = 1–2) for about 1 h to obtain saturated absorption of PMoV ions. Thus the substrates were covered with one layer of inorganic compound and their surface charge was reversed. After the substrates were rinsed with ultra-pure water and dried under nitrogen flow, they were transferred into the solution of protoned 1,10-DAD (10⁻² M, pH = 1–2) for 30 min. Repeating the above steps in a cyclic fashion for 30 min each, well-ordered SAM films of PMoV alternating with 1,10-DAD were obtained.

2.3. Measurement and instruments

UV-visible spectra were obtained using a Shimadzu UV-1601PC double-beam spectrophotometer. The thicknesses of the films were measured with a surface profile measuring system (Detake 3 Model JGP-560). Small-angle X-ray diffraction (XRD) was carried out on a D/max-rB type XRD instrument with the X-ray source of CuK α radiation ($\lambda = 0.15418$ nm). The X-ray photoelectron spectra (XPS) of the SAM films were recorded on a USWHA150 photoelectron spectroscopy using monochromatic AlK α (1486.6 eV) radiation. The instrument resolution was about 0.2 eV. The Raman spectra were measured by a Ranishaw-2000 microprobe spectrometer (514 nm, Ar⁺ ion laser). Low-laser power (5 mW) was applied to avoid the decomposition of samples due to local heating effect [22]. The photochromic experiments were carried out using a 500 W high-pressure Hg lamp as the light source. The light passed through a circulating water infrared filter and a 365 nm filter.

3. Results and discussion

3.1. Structural characterization of PMoV/1,10-DAD SAM film

The growth process of the SAM film was monitored by UV-visible absorbance with regard to the deposited layer number using quartz slide as substrate. Fig. 1A illustrates the UV-visible spectra of a 40-bilayer PMoV/1,10-DAD SAM film with the inorganic component as the outermost layer. The characteristic bands of PMoV at 220 and 310 nm corresponding to the O \rightarrow M ($M = \text{Mo or V}$) ligand to metal charge transfer (LMCT) transition were observed in the SAM film. This suggests that PMoV had been incorporated into the film. Compared with that of PMoV aqueous solution at ca. 208 and 301 nm (Fig. 1B) [20], the UV-vis absorption bands of the PMoV/1,10-DAD SAM film displayed a red-shift, which is due to the electrostatic and hydrogen-bond interaction effects [23]. This result is also consistent with that of Raman spectra (see below). The inset in Fig. 1A shows an obvious

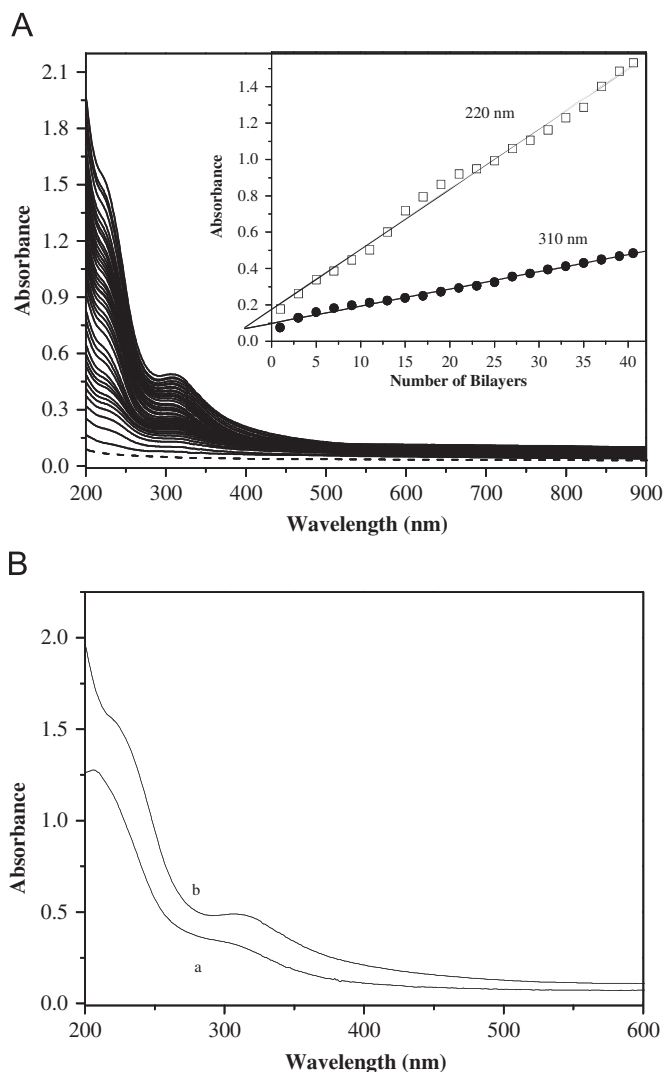


Fig. 1. UV-vis spectra of (A) (PMoV/1,10-DAD)_n SAM films with $n = 1-40$ (solid line) on APS-modified quartz substrate (dash line), in which the inset shows plots of the absorbance values at 220 and 310 nm as a function of the number of deposition cycles (n) and (B, a) PMoV aqueous solution and (B, b) (PMoV/1,10-DAD)₄₀ SAM film.

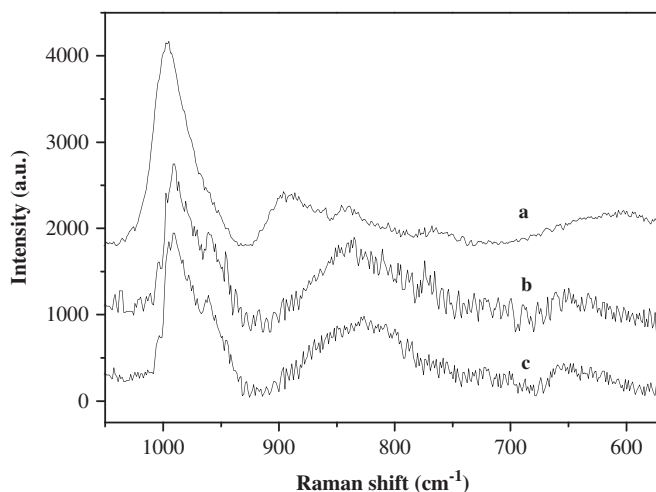


Fig. 2. Raman spectra of polycrystalline PMoV (a) and (PMoV/1,10-DAD)₄₀ SAM film before (b) and after 15 min UV-irradiation (c).

linear relationship between the absorbance of the multilayers vs. the number of layers at different wavelengths, indicating the uniform deposition of the organic/inorganic alternating films with a vertically periodic structure, although a partial loss of PMoV clusters happened after each 1,10-DAD deposition step.

From the Raman spectra shown in Fig. 2, it can be clearly seen that there exists a notable difference between the PMoV solid powder and the PMoV/1,10-DAD SAM film. The bands at 996 and 972 cm^{-1} , attributed to the symmetric and asymmetric stretching vibration of the $\text{M}=\text{O}$ terminal group, shift to 993 and 962 cm^{-1} , respectively, when PMoV is organized into a SAM film. The $\text{M}_2\text{-O}$

Table 1

The assignments of infrared spectra of the PMoV solid and the PMoV/1,10-DAD SAM film.

PMoV (cm^{-1})	PMoV/1,10-DAD (cm^{-1})	Assignments ^a
1059	1059	P-Oa antisym. str.
960	956	M=Od antisym. str.
872	879	M-Ob-M antisym. str.
787	789	M-Oc-M antisym. str.

^a Antisym. str., antisymmetrical stretching; Oa, the oxygen of the central tetrahedral; Ob, the bridged oxygen of two octahedra sharing a corner; Oc, the bridged oxygen sharing an edge; and Od, the terminal oxygen.

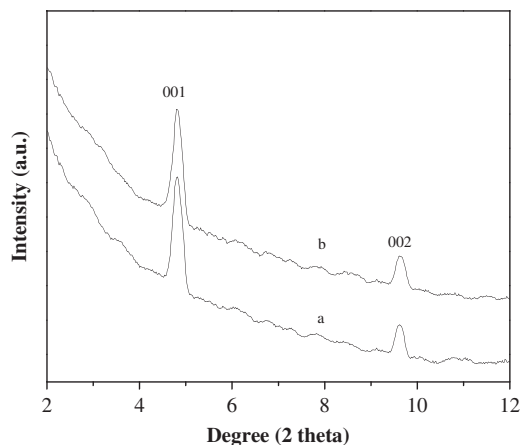


Fig. 3. XRD Pattern of $(\text{PMoV}/1,10\text{-DAD})_{40}$ SAM film (a) before and (b) after 15 min UV-irradiation.

corner-sharing band at 894 cm^{-1} shifts to 835 cm^{-1} , and the $\text{M}_3\text{-O}$ stretching vibration band located at 603 cm^{-1} shifts to 630 cm^{-1} [24,25]. These changes indicate that the vibrations of PMoV is strongly disturbed after assembling into the SAM film by the electrostatic and hydrogen-bond interactions with protonated 1,10-DAD [14,15,19]. FTIR spectra provide further evidence for our point. As presented in Table 1, it is clearly seen that the characteristic bands of PMoV in the SAM film, compared to those of pure PMoV, present a blue- or red-shift, indicating the electrostatic and hydrogen-bond interactions between PMoV and 1,10-DAD disturbed the vibration of PMoV. It is noted that the $\text{M}_2\text{-O}$ corner-sharing band experiences a red-shift as large as 59 cm^{-1} , suggesting that the $\text{M}_2\text{-O}$ corner-sharing position is the active site that is involved in the interaction with hydrogen on the amino head group to form the hydrogen bond.

Fig. 3 shows the small-angle XRD patterns of the PMoV/1,10-DAD SAM film. Two diffraction peaks are observed in the small angle region, indicating the layered structure of the SAM films. The layer distance (d spacing) is calculated as 1.84 nm using Bragg's equation. The measured thickness of the 40-bilayer PMoV/1,10-DAD SAM film was 73 nm and that of each bilayer would therefore be 1.82 nm. It agreed well with the 1.84 nm d spacing determined by XRD. Fig. 4 displays a possible packing model of the layered structure of the prepared SAM film. The diameter of each PMoV molecule with Keggin structure is about 1 nm [10]; therefore, the remnant space available for 1,10-DAD cation is determined to be about 0.84 nm. In addition, the length of 1,10-DAD molecule is known to be 1.5 nm [6]; thus the tilt angle for the organic molecules is calculated to be about 34°.

3.2. Photochromism of PMoV/1,10-DAD SAM film

We wondered how the photochromic behavior of such mixed-addenda POMs would be. To answer this question, we used UV light to irradiate the PMoV/1,10-DAD SAM film. As shown in Fig. 5A, upon UV irradiation, a new broad absorption band with its maximum at ca. 750 nm appears, which is characteristic band of heteropolyblue and assigned to inter-valence charge transfer (IVCT) [9]. With irradiation time increasing, the absorbance of the SAM film gradually reached saturation. Meanwhile, the pale yellow film turns deep blue in color. It should be noted that the colored SAM film showed good stability. After coloration, the film can keep the blue color for more than one year when stored in the dark, indicating that the SAM film is stable in air and retain its

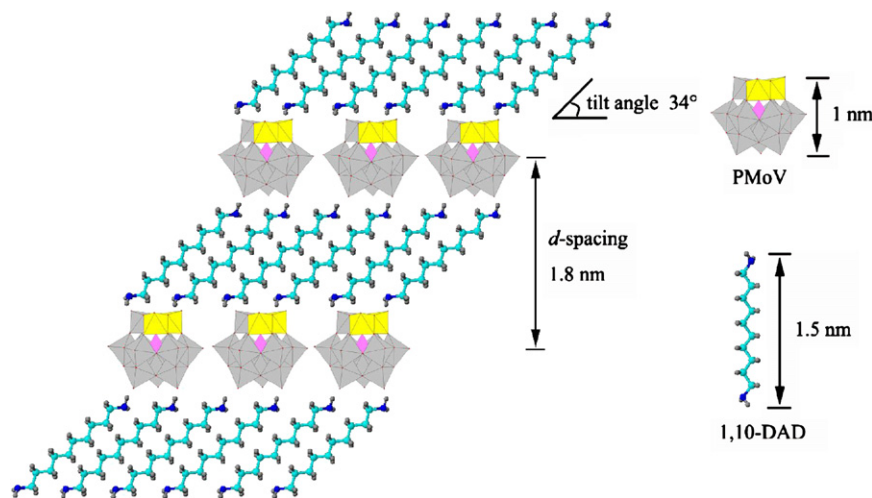


Fig. 4. Schematic illustration of the molecular orientations of the PMoV/1,10-DAD SAM film.

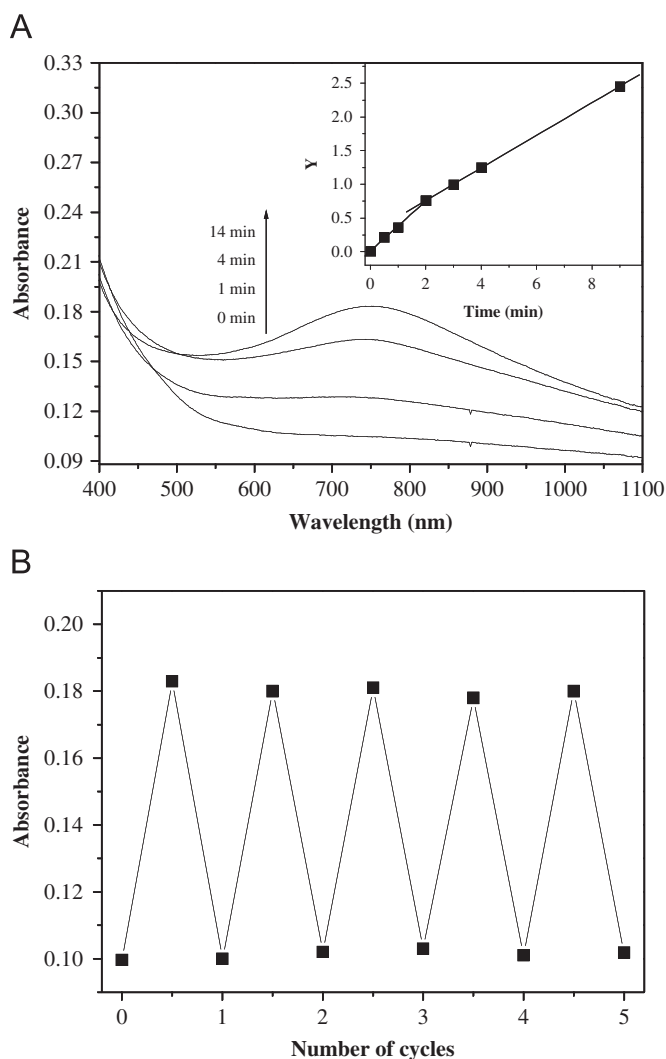


Fig. 5. (A) UV-vis spectra of (PMoV/1,10-DAD)₄₀ SAM film as a function of the UV-irradiation time. The inset is the kinetic plot of the photochromic process of the film. Here “Y” is defined as $-\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ and (B) the plot of reversibility of the composite film in the coloration-decoloration process at 750 nm.

coloration memory for a rather long time. However, the colored film can be bleached by gentle heating at 80 °C in air or oxygen. When exposed to UV-irradiation again, the bleached film turns to blue and its absorption spectrum is approximately that of the original coloration state. In this way, this “write/erase” process can be repeated more than five times with little fatigue, as shown in Fig. 5B. That is to say, the SAM film exhibits excellent photochromic reversibility. It is evident that PMoV/1,10-DAD SAM film presents excellent photochromic performance including high-photochromic response, high-stability, and good reversibility, which is essential for its practical/potential applications in devices and sensors.

An interesting finding is the kinetics of the coloration process, which was investigated by monitoring the absorbance changes at 750 nm as a function of irradiation time. As shown in the inset of Fig. 5A, the overall coloration process does not show exponential relationship with irradiation time. But if we separate the whole process into two parts, both parts can be well fitted to be first-order kinetic equation based on $-\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs. the irradiation time, t . The kinetic constants, k_1 and k_2 , are calculated to be 0.36 and 0.24 min⁻¹, respectively. According to our previous result [19], k_2 (0.24 min⁻¹) may correspond to the reduction of

Mo⁶⁺. Whereas k_1 (0.36 min⁻¹) may be attributed to the reduction of V⁵⁺.

XPS results verify our hypothesis. It is well-known that the color change of POMs can be attributed to the reduction of M ($M = \text{Mo}$ or V) by photo-induced electrons for such SAM film and the efficiency of reduction can be estimated from the change in XPS [26]. Fig. 6 shows the XPS of V ($2p$) and Mo ($3d$) levels of the PMoV/1,10-DAD SAM film before and after UV irradiation. For the as-prepared film, the peak corresponding to the V⁵⁺ ($2p_{3/2}$) orbital is observed at 517.5 eV. After UV irradiation for 14 min, the peak is observed at energy level about 1.3 eV lower than that before UV irradiation (Fig. 6A), thus confirming that all of the vanadium atoms have been reduced to V⁴⁺ [27]. Simultaneously, the two peaks attributed to the Mo⁶⁺ ($3d_{5/2}$ and $3d_{3/2}$) orbitals red-shifted slightly, as shown in Figs. 6B and C. They can be deconvoluted into two sets of peaks with the binding energies of 232.8 and 235.9, and 231.8 and 234.9 eV. The first set is assigned to Mo⁶⁺ ($3d_{5/2}$) and Mo⁶⁺ ($3d_{3/2}$), whereas the second set is assigned to Mo⁵⁺ ($3d_{5/2}$) and Mo⁵⁺ ($3d_{3/2}$). The appearance of the latter indicates that the Mo⁵⁺ ions are produced in the SAM film and the concentration of the Mo⁵⁺ is about 25% (calculated by deconvolution of the spectra) [28]. These above clearly indicate that the reduction rate of V⁵⁺ is larger than that of Mo⁶⁺ in SAM film fabricated by PMoV, and the added electron is accepted firstly by V atom and then by Mo atom. To further verify this point, we monitored the XPS of the SAM film after UV-irradiation for 1 min. It is clearly seen (Fig. 7) that the molybdenum atoms are hardly reduced in the SAM film. This is in agreement with the order of the reduction potential of addenda atom in mixed-addenda POMs: V(V) > Mo(VI) > W(VI) [29]. In a word, in the case of photo-reduced mixed-addenda POMs, the electron is localized on the more reducible atom, and the addenda atoms with higher reduction potentials show prior photochromism compared with those with lower reduction potentials. As a result, the coloration speed of PMoV/1,10-DAD SAM film is larger than that of PMo12/1,10-DAD SAM films [19].

In comparison with that of the SAM film before irradiation, the layer thickness estimated from the XRD pattern (Fig. 3b) after UV irradiation is nearly unchanged, indicating that the layer structure of the SAM film is maintained during photochromism. Therefore, we believe that the reaction of redox during irradiation does not affect the packing structure of the SAM film [30].

Raman spectra provide further evidence for photochromic mechanism of POMs. As shown in Fig. 2c, after UV irradiation, the M₂-O band at 835 cm⁻¹ shifts to 827 cm⁻¹, whereas the other three bands remain almost unchanged for the SAM film. Such a red-shift of the M₂-O vibration band suggests the insertion and attachment of a hydrogen atom into M₂-O bond during photochromism, as previously reported [18,31]. In our system, it is supposed that the hydrogen atom most likely come from the protonated amino headgroup of 1,10-DAD due to its close contact with the PMoV polyanion. Thus, the appearance of the IVCT band reveals electron transfer between 1,10-DAD and PMoV converted into heteropolyblue with simultaneous oxidation of the organic matrix. This process is similar to the photochromic mechanism of alkylammonium polyoxomolybdates solid, proposed by Yamase [27]. Based on the above results, we propose the photochromic mechanism of the SAM film as follows. The photoexcitation of the phosphovanadomolybdate's O → M LMCT band induced reduction of V⁵⁺ and Mo⁶⁺ and the transfer of a proton from the protonated amino headgroup to the bridging oxygen atom of PMoV. Simultaneously, the hole left on the oxygen atom, which was caused by the O → M LMCT transition, interacted with the nonbonding electron on the nitrogen atom, leading to the formation of a charge-transfer complex between the amino headgroup and the oxygen atoms of PMoV. It is this separation

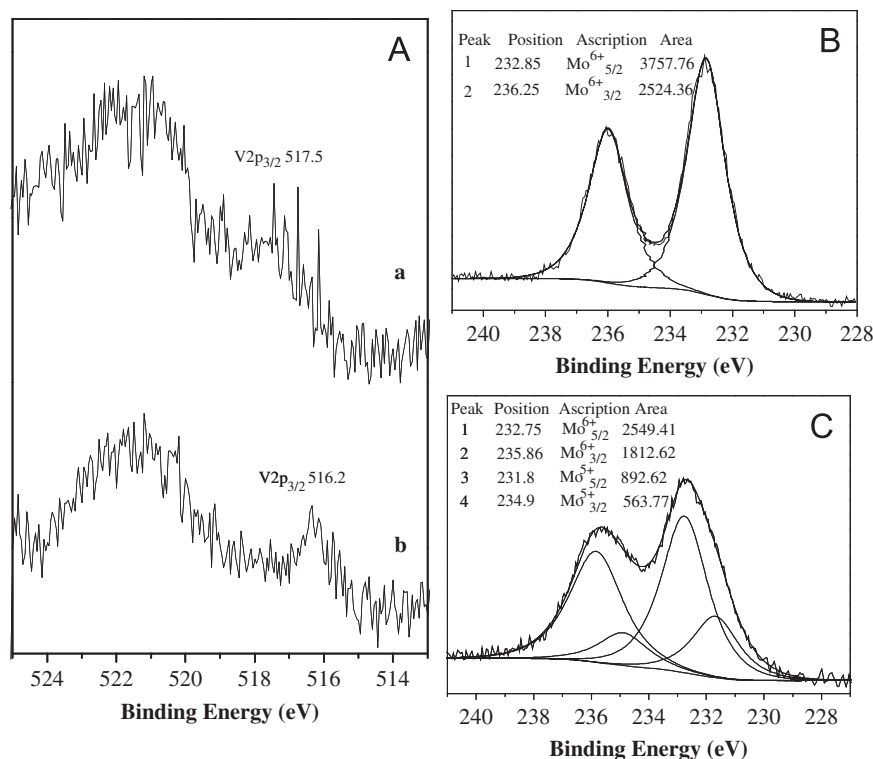


Fig. 6. XPS of V 2*p* energy levels of (PMoV/1,10-DAD)₄₀ SAM film before (A, a) and after UV irradiation for 15 min (A, b), and Mo 3*d* energy levels of (PMoV/1,10-DAD)₄₀ SAM film before (B) and after UV irradiation for 15 min (C).

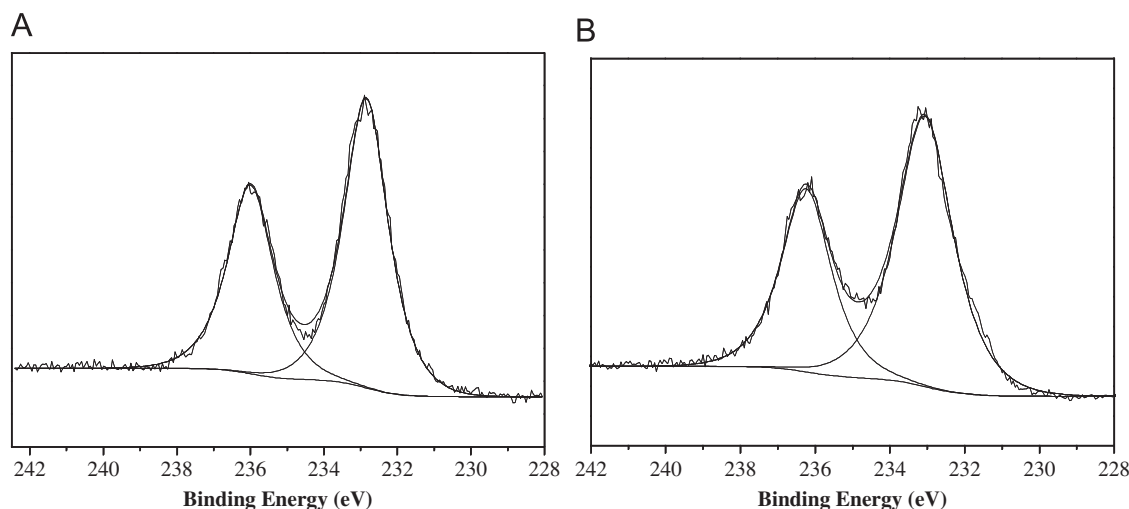


Fig. 7. XPS of Mo 3*d* level of PMoV/1,10-DAD SAM film before (A) and after UV irradiation for 1 min (B).

that keeps the colored state stable. For the reverse process, the bleaching in the presence of oxygen molecules was caused by the back reaction, which was triggered by electron transfer from the M atom to the oxygen molecule, making the reaction reversible.

4. Conclusion

In summary, the layered PMoV/1,10-DAD self-assembled ultrathin film was successfully fabricated by the alternate adsorption method. It is found that the SAM film shows well-ordered lamellar structure and excellent photochromic properties

including high photochromic response, photochromic stability, and good reversibility. It is identified that the photochromic behavior of the SAM is closely related to the reduction potentials of addenda atoms in mixed-addenda POMs. In the case of photo-reduced mixed-addenda POMs, the electron is localized on the more reducible atom, and the addenda atoms with higher reduction potentials show prior photochromism compared with those with lower reduction potentials. As compared with molybdenum POMs only containing one kind of addenda atom (Mo), POM containing the two kinds of addenda atoms (Mo and V) presents higher coloration speed in hybrid SAM film. Such a result will be helpful for designing efficient POM/organic hybrid photochromic ultrathin films for practical application.

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