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Construction of Self-Assembled Ultrathin Polyoxometalate/1,10-Decanediamine Photochromic Films

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A series of polyoxometalates (POM)/1,10-decanediamine ultrathin films were fabricated by self-assembly, and their photochromic properties were investigated. It is found that the films fabricated from molybdenum POMs show better photochromic responses than those from tungsten POMs. The photochromic responses of these hybrid films are related to the reduction potentials of the POMs. The higher the reduction potential of the POM is, the better the photochromic response of the hybrid film. Among these systems, the $\text{PMo}_{12}\text{O}_{40}/$ 1,10-decanediamine ultrathin film with a thickness of 70 nm shows a change as high as 0.168 in UV–visible absorption spectra before and after 10 min of UV irradiation.

Introduction

Photochromic materials, whose optical absorption properties can change reversibly, have potential applications in many high-technology devices, such as high-density optical memory and photooptical switching.^{1–5} Polyoxometalates (POMs) have been considered as an attractive class of photochromic materials due to their structural and electronic versatilities.^{6–8} For device fabrication, it is necessary to deposit the photochromic materials into thin film structures.⁹ However, these POMs are poor film formers¹⁰ and it is difficult to fabricate thin POMs films directly. Self-assembly is an effective and convenient approach to fabricate ultrathin film, and several kinds of inorganic/organic photochromic ultrathin films have been constructed by self-assembly of tungsten oxides and organic diamines.^{11–13} However, those composite films show poor photochromic responses and are not qualified for fabrication of practical devices. Therefore, how to fabricate a system with excellent photochromic properties is still a great challenge and essential for its potential/practical applications.

According to the photochromic mechanism of POMs, the valence electrons, which are mainly comprised of O 2p electrons, will be transferred to the conduction band of POMs under irradiation ($>h\nu$). This will induce reduction of the central metals and result in photochromism.¹⁴ The more efficient the valence-electron transfer is, the greater the amount of reduced central metals and thus the better the photochromic performance will be. It is known that the electron-donating or -withdrawing ability of one molecule depends greatly on its redox potential. To understand the relation between the redox potential of POMs and the photochromic response of the self-assembled ultrathin

films from them, four POMs, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (denoted as PW_{12} , SiW_{12} , PMo_{12} and SiMo_{12} respectively), with different reduction potentials were employed as inorganic components to construct photochromic ultrathin films with an organic diamine (1,10-decanediamine) by self-assembly and their photochromic performances were investigated.

Experimental Section

Materials. PMo_{12} , PW_{12} , and 1,10-decanediamine (denoted as 1,10-DAD) were purchased from Aldrich, SiW_{12} was purchased from Alfa Aesar, and SiMo_{12} was purchased from Strem Chemicals. All the chemicals were of analytical grade and used without further purification.

Fabrication of SAM Film. The POM/1,10-DAD SAM films were fabricated by the method reported in the literature.^{11–13} The APS (3-aminopropyltriethoxysilane) modified substrates (quartz or silicon wafers) were immersed into 0.1 M HCl solution to get an amino cation covered surface, and then immersed into the solution of POM (0.005 M) for about 2 h to obtain saturated absorption of POM ions. Thus the substrates were covered with one layer of inorganic compound and their surface charge was reversed. After the substrates were rinsed with ultrapure water and dried under nitrogen flow, they were transferred into the solution of protonated 1,10-DAD (0.006 M) for 30 min. Repeating the above steps in a cyclic fashion for 30 min each, well-ordered multilayer films of POM alternating with 1,10-DAD were obtained.

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 (SAXRD) was carried out on a D/max-rB type X-ray diffraction instrument with the X-ray

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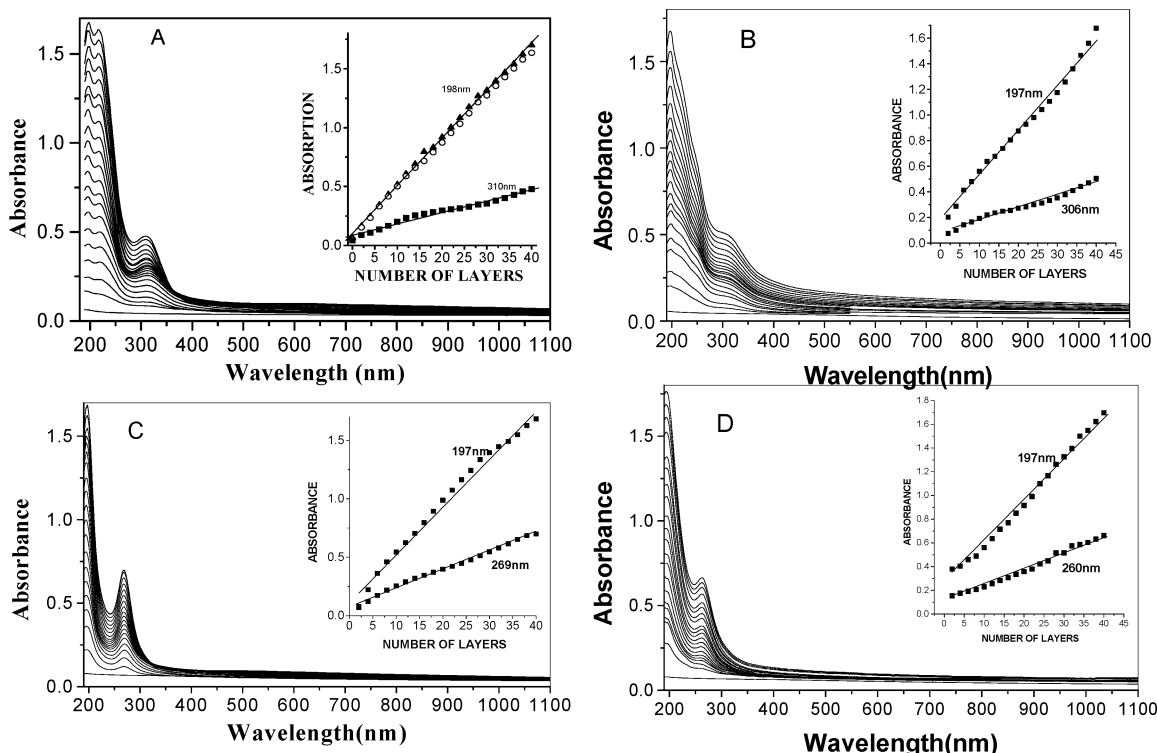


Figure 1. UV-visible spectra of POM/1,10-DAD SAM films with different numbers of layers. The insets are the dependence of optical absorbance of these films on the number of layers at different wavelengths. (A) $\text{PMo}_{12}/\text{DAD}$, (B) $\text{SiMo}_{12}/\text{DAD}$, (C) $\text{PW}_{12}/\text{DAD}$, and (D) $\text{SiW}_{12}/\text{DAD}$.

source of Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm). The X-ray photoelectron spectra (XPS) of the SAM films were recorded on a USWHA150 photoelectron spectroscope using monochromatic Al K (1486.6 eV) radiation. The instrument resolution was about 0.2 eV. The Raman spectra were measured by a Renishaw-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.¹⁵ The photochromic experiments were carried out using a 500 W high-pressure Hg lamp as the light source with a 365 nm filter to filter out visible and infrared light. The light intensity was measured by means of potassium ferrioxalate actinometry.

Results and Discussion

Structure of SAM Films. The growth process of the self-assembled films was followed by UV-visible spectra using quartz slides as substrates. Figure 1 illustrates the UV-visible spectra of four 40-layer POM/1,10-DAD SAM films with the inorganic components as the outermost layers. The insets show an obvious 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. There should be only one layer formed in every deposition process.¹¹ The UV-visible spectra of the investigated POM/DAD systems mainly differ in the positions of the bands (listed in Table 1), which correspond to $\text{O} \rightarrow \text{M}$ ($\text{M} = \text{Mo}$ or W) ligand to metal charge transfer (LMCT) of POMs.¹⁶ It can be seen that the position of this band for the SAM film fabricated by molybdenum POM is around 310 nm, whereas that for the film fabricated by tungsten POM is around 260 nm.

Figure 2 shows the small-angle X-ray diffraction patterns of the self-assembled multilayer (SAM) films prepared from different POMs. Two diffraction peaks are observed at the small-angle region, indicating the layered structure of the SAM films.

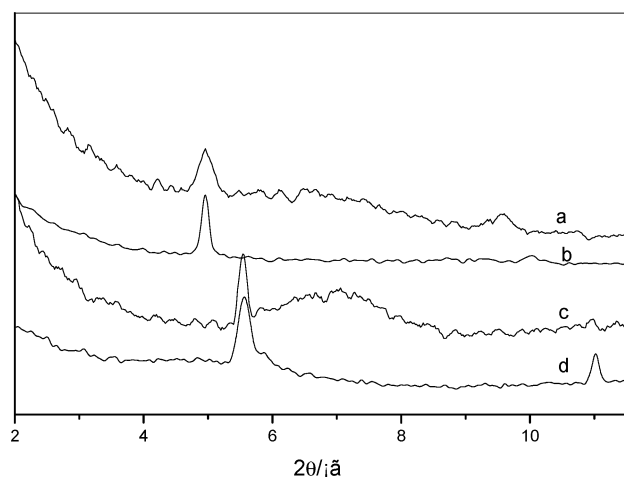


Figure 2. XRD patterns of prepared POM/1,10-DAD SAM films. (a) $\text{PMo}_{12}/\text{DAD}$, (b) $\text{SiMo}_{12}/\text{DAD}$, (c) $\text{PW}_{12}/\text{DAD}$, and (d) $\text{SiW}_{12}/\text{DAD}$.

The d spaces of the films are calculated from the patterns, and the results are listed in Table 1. The thicknesses of the 40-layer films were measured, and the results are given in Table 1. The values for the d spaces of the SAM films calculated from the thickness measurements are consistent with the results from SAXRD (see Table 1).

The $\text{PMo}_{12}/\text{DAD}$ SAM film was selected as the representative to show the layered structure of the prepared POM/DAD SAM films. The diameter of each PMo_{12} molecule with Keggin structure is about 1 nm;¹⁷ therefore, the remnant space available for DAD cation is determined to be about 0.782 nm. In addition, the length of 1,10-DAD molecule is known to be 1.5 nm;⁹ thus the inclination angle for the organic molecules is calculated to be about 31.4° .¹¹ For $\text{SiMo}_{12}/\text{DAD}$ system the tilt angle is determined to be about 31.9° . For the SAM films fabricated by tungsten POMs, the inclination angles for the 1,10-DAD

TABLE 1: Some Key Parameters for the Prepared SAM Films

POM	reduction potential ^a (V)	O → M LMCT ^b (nm)	O 2p electronic binding energy (eV)	Δ ABS ^c	concn of reduced Mo or W (%)	thickness of 40-layer SAM film (nm)	d^d space (nm)	d^e space (nm)
PMo ₁₂	0.27	310	6.45	0.168	32	70	1.782	1.75
SiMo ₁₂	0.23	306	6.50	0.151	28	68	1.779	1.70
PW ₁₂	-0.02	269	7.01	0.030	5	64	1.598	1.60
SiW ₁₂	-0.24	260	7.22	not obvious	not obvious	65	1.602	1.62

^a From refs 20 and 21. ^b Maximum band position in UV–visible spectra. ^c Maximum at visible region after 10 min UV irradiation. ^d Calculated by XRD. ^e Calculated by thickness measurement.

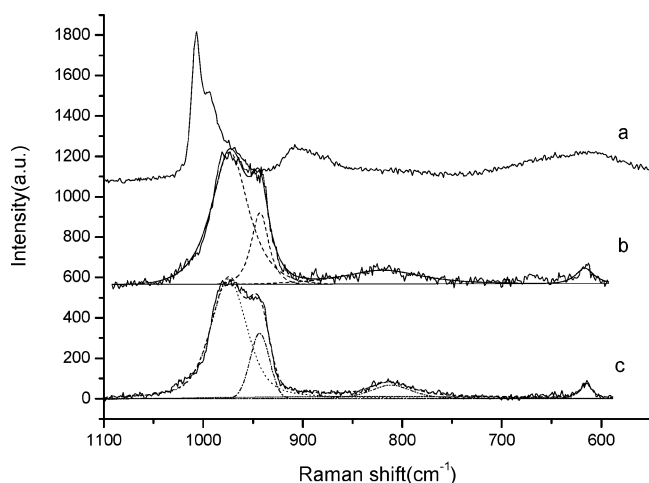


Figure 3. Raman spectra of polycrystalline PMo₁₂ (a) and PMo₁₂/1,10-DAD SAM film on Si(111) before (b) and after 5 min UV irradiation (c). The dashed lines are the deconvoluted spectra, the smooth lines are the fitted spectra, and the wavy lines are the original spectra.

molecules are calculated to be about 23.4° and 23.6° respectively since the diameter of each PW₁₂ is known to be about 1.2 nm.¹⁸

Raman spectra of the PMo₁₂/DAD SAM film as well as the pure polycrystalline PMo₁₂ powder are shown in Figure 3. By comparison, it is clearly seen that there exists a notable difference between the spectrum of PMo₁₂ and that of the SAM

film. The bands at 998 and 978 cm⁻¹ attributed to the symmetric and asymmetric stretching vibration of Mo=O terminal group of PMo₁₂ shift to 976 and 940 cm⁻¹, respectively, in the film. The Mo₂-O corner-sharing and Mo₃-O stretching vibration bands of PMo₁₂ at 894 and 602 cm⁻¹ shift to 819 and 612 cm⁻¹, respectively, after being assembled into the film.¹⁹ These Raman spectral changes indicate that the structure of the PMo₁₂ lattice is distorted after being assembled into the SAM film. The interaction between PMo₁₂ molecules and amino headgroup on the modified substrate can result in the formation of hydrogen bond and lead to such distortion. It is noted that the Mo₂-O vibration band experiences a great red shift of as much as 70 cm⁻¹, suggesting that the Mo₂-O corner-sharing position is the active position involved in the interactions with hydrogen atoms in the amino headgroup of the diamine to form hydrogen bonds.

The schematic representation of the layered structure of the fabricated SAM film is illustrated in Figure 4. The POM layers interact with the tilted 1,10-DAD molecules through hydrogen bonds and electrostatic interactions. The difference for the four POM/DAD systems is the tilt angle of the 1,10-DAD molecules, which may be attributed by the different weights of the POM molecules. The tungsten POM is much heavier than molybdenum POM, resulting in the smaller tilt angle of 1,10-DAD molecules and thus lower *d* spaces of the SAM films.

Photochromism of SAM Film. Figure 5 gives the photochromic responses of the 40-layer PMo₁₂/DAD SAM film around 800 nm with different UV-irradiation times. After UV

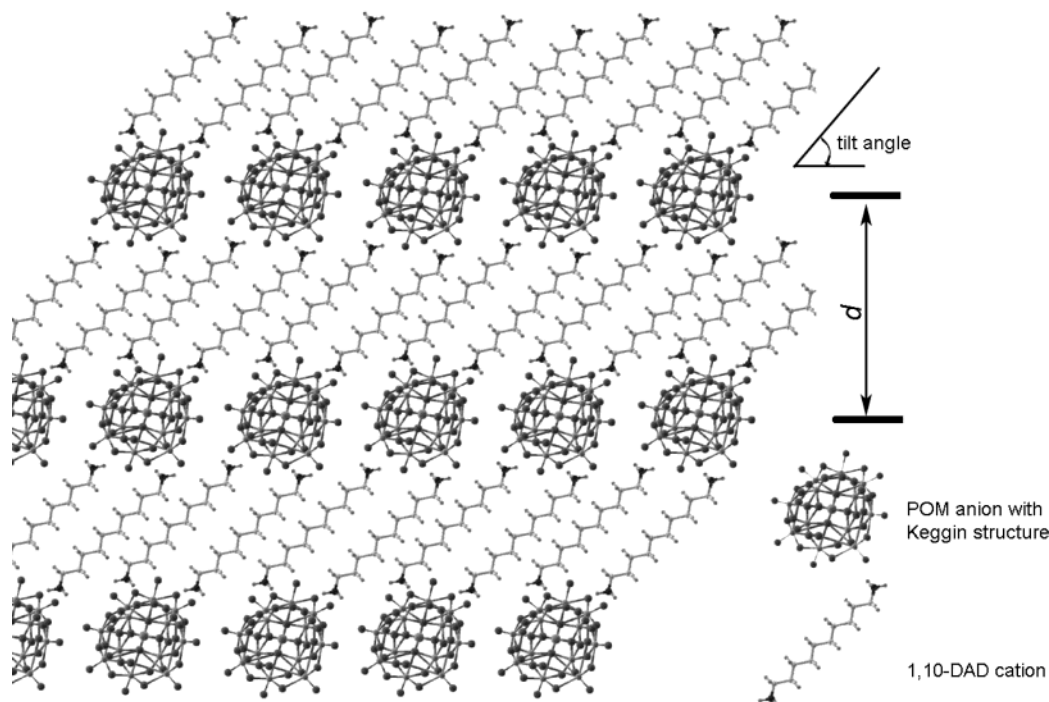


Figure 4. Schematic representation for structure of POM/1,10-DAD SAM films.

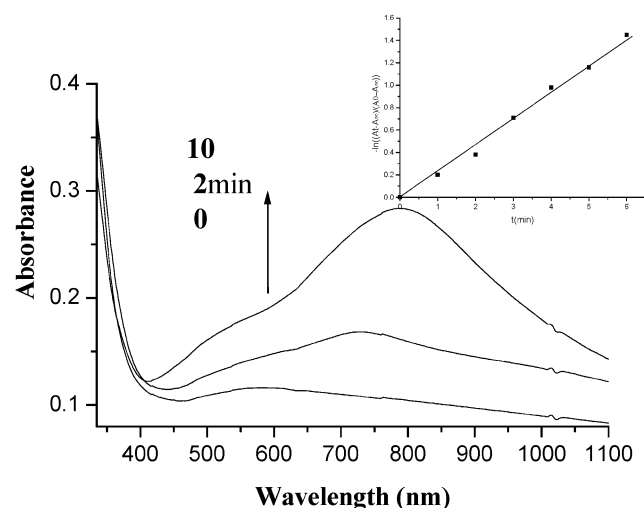


Figure 5. Absorption spectra of 40-layer $\text{PMo}_{12}/1,10\text{-DAD}$ SAM film with different UV irradiation times at near-IR region. The inset is the kinetic plot of the photochromic process of the film.

irradiation, the transparent film turns deep blue in color. As shown in Figure 5, the absorbance change at 780 nm is as much as 0.168 higher after 10 min of UV irradiation. Such a change from the film with a thickness of 70 nm is much greater than for pre-reported photochromic SAM films^{11–13} and good enough for practical device fabrication. The photochromic process is fitted to be first-order, and the kinetic constant k is calculated to be 0.24 min^{-1} from the kinetic plot in the inset of Figure 5. The quantum efficiency of the photochromism is measured to be 0.12. After coloration, the film can keep the blue color for more than 1 year when it is stored in the dark, indicating that the SAM film is stable in air and retains its coloration memory for a rather long time. The deeply colored film can be bleached by heating at 70°C in air or oxygen. When it is subjected to UV irradiation again, the bleached film turns blue, its absorption spectrum is approximate to that of the first colored state, and the recoloration efficiency is similar to that of the original one. The bleaching reaction is fitted to be first order, and the rate constant k is measured to be 0.15 min^{-1} . For practical applications such as long-life memory, it seems acceptable to bleach the film by heating in air or oxygen. In this way, this “write/erase” process can be repeated more than 50 times with little fatigue.

The SiMo_{12} system shows almost the same photochromic properties as PMo_{12} except a little lower photochromic response. The other two tungsten systems have quite different photochromic properties. The maximal absorbance change is only 0.03

for the PW_{12} system, and the photochromic response is not obvious for the SiW_{12} system. The maximum absorbance changes of the four systems in the visible region after coloration are listed in Table 1. The bleaching process for the $\text{PW}_{12}/1,10\text{-DAD}$ system is easier and faster than that for the molybdenum POM systems, and the process can go at room temperature in air.

It was known that the color change of POMs was attributed to the reduction of M^{6+} by photoinduced electrons for such hybrid systems.¹⁴ XPS analyses show that, after coloration, the concentrations of reduced metal ions (Mo^{5+} or W^{5+}) are different for the four POM/1,10-DAD systems. Figure 6 shows the XPS spectra of Mo 3d level of the $\text{PMo}_{12}/\text{DAD}$ SAM film before and after UV irradiation. It can be seen that, after UV irradiation, Mo^{5+} ions are produced in the SAM film and the concentration of the Mo^{5+} is about 32% (calculated by deconvolution of the spectra). The concentrations of reduced M^{5+} in the different system are listed in Table 1. It is seen that the different photochromic responses are related with the concentrations of reduced metal ions in the films. Compared with reduction potentials^{20,21} of the POMs listed in Table 1, it is found that, with the increase of reduction potentials of the POMs, the concentration of reduced M^{5+} and the photochromic response increase.

As shown in Figure 3, after UV irradiation, the $\text{Mo}_2\text{—O}$ band at 819 cm^{-1} shifts to 810 cm^{-1} , whereas the other three bands remain almost unchanged for the film. Such a red shift of the Mo—O vibration band suggests the insertion and attachment of hydrogen with Mo—O bond during photochromism.²² In our system, it is supposed that the hydrogen is most likely to come from the protonated amino headgroup since it is in close contact with the PMo_{12} molecules. That is to say, during the photochromic process, proton from the amino headgroup is transferred to PMo_{12} molecule. For such POM/organic amine hybrid systems, upon irradiation, valance electrons mainly located on the O 2p orbital will be transferred to the conduction band and result in reduction of the central metals; simultaneously, a proton from amino headgroups will be transferred to MO_6 octahedron to form a stable charge-transfer complex at a photoreducible site.¹⁴ The O 2p electronic binding energies of the four POMs determined by XPS are listed in Table 1. The electronic binding energies of O 2p are in the order of $\text{PMo}_{12} < \text{SiMo}_{12} < \text{PW}_{12} < \text{SiW}_{12}$, the same as the blue-shift tendency of $\text{O} \rightarrow \text{M}$ LMCT bands of the POM/1,10-DAD films (Table 1). It is noted that the lower O 2p electronic binding energy of the POM is, the better the photochromic response observed. Theoretical calculations proved that the molybdenum POMs had higher proton affinities than their tungsten counterparts,^{23,24} indicating

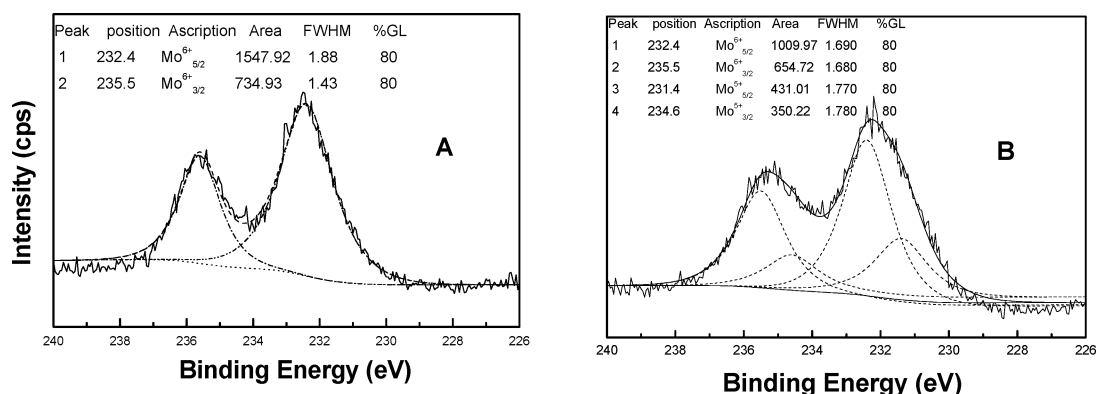


Figure 6. XPS spectra of Mo 3d level of $\text{PMo}_{12}/1,10\text{-DAD}$ SAM film before (A) and after UV irradiation (B). The inset tables are the deconvoluted results of the spectra.

that the proton transfer to molybdenum POM is much easier than that to tungsten POMs. Therefore, it can be expected that the different O 2p electronic binding energies of these POMs may result in the difference in proton-transfer efficiency and thus different amounts of central metal ions reduced and photochromic responses of the POM/1,10-DAD ultrathin films. As a result, the films fabricated by molybdenum POMs with lower reduction potentials show better photochromic response than those by tungsten POMs with higher reduction potentials.

Thus it can be concluded that the photochromic properties (including photochromic responses, photochromic stability, and reversibility) were strongly correlated to the reduction potentials of the inorganic component of the self-assembled films. Also, these photochromic properties would further strongly affect the properties of photochromic devices.

Conclusion

In summary, a series POM/1,10-DAD ultrathin films were fabricated by self-assembly. It is found that the films fabricated by molybdenum POMs show better photochromic response than those by tungsten POMs. The ultrathin PMo₁₂/1,10-DAD film with a thickness of 70 nm shows a change as high as 0.168 in absorption spectra after coloration, which is good enough for practical application. It is identified that the photochromic properties of the films are related to the reduction potentials of the POMs. The improved photochromic responses are attributed to the lower O 2p electronic binding energy and higher proton affinity of the POMs. Such a result will be helpful for designing efficient POM/organic hybrid photochromic ultrathin films for practical application.

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