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Self-assembled PMo_{12}^{3-} / DODA^+ composite superlattice thin films with photochromic properties

TIE RUI ZHANG, WEI FENG, RAN LU, CHUN YAN BAO, XIN TONG ZHANG,
TIE JIN LI, YING YING ZHAO

Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China

JIAN NIAN YAO

*Institute of Chemistry and Center for Molecular Science, Chinese Academy of Sciences,
Beijing, 100080, People's Republic of China*

E-mail: luran@mail.jlu.edu.cn

A layered superlattice PMo_{12}^{3-} / DODA^+ self-assembled composite film has been successfully prepared. Infrared (IR) spectra revealed that the Keggin structure characteristic of the $\text{PMo}_{12}\text{O}_{40}^{3-}$ anion was preserved in the composite film. A well-ordered superlattice structure, d spacing of 2.945 nm, was identified by X-ray diffraction (XRD). The superlattice film showed good photochromic properties. On irradiation with UV light, the transparent film changed from light yellow to blue. Then, bleaching occurred when the film was in contact with ambient air or O_2 in the dark. The photochromic mechanism was studied by electron spin resonance (ESR), IR spectra, and UV-Vis spectra.

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1. Introduction

Polyoxometalate (POM) anions constitute a distinctive class of inorganic compounds that have been receiving increasing interest in recent years. Indeed, their chemical, structural, and electronic versatility made them very useful in research fields as diverse as catalysis, medicine, biochemistry, material science, and so on [1–3]. Their structures can be depicted as molecular fragments of close-packed metal oxides with the general formula $[\text{X}_x\text{M}_m\text{O}_y]^{n-}$ (where M represents Mo, W, V, etc.; X: P, Si, As, etc.). They present interesting properties, such as high solubility in many solvents, depending on the counter-ion, quite a small size and a very high electronic density. Their high electronic density and redox properties are ideal for their use as photochromic and electrochromic materials [4, 5]. In the past thirty years, photochromic studies on POM mainly focused on solid and solution, but those materials are difficult to manipulate into practical devices, which limits their applications.

Practical applications of POM in photochromic and electrochromic areas depend on the successful preparation of thin POM-containing films. Self-assembly is a very simple and powerful approach to construct supramolecular thin films on solid surfaces [6, 7]. It has now been extensively explored in chemistry and material science as an effective strategy for fabricating a wide variety of complex ordered structures that are difficult or impossible to generate using traditional approaches. Indeed, this technique has been widely applied to create new materials that can be used as chemical

sensors, modified electrodes, or for molecular electronic devices [8–10]. In this work, we have prepared layered PMo_{12}^{3-} / DODA^+ composite superlattice film with good photochromic properties via self-assembly and studied its structure and photochromic mechanism.

2. Experimental section

2.1. Materials

Phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) was prepared according to the literature method [11]. Dimethyldioctadecylammomium chloride (GR) was obtained from TCI of Japan. All other chemicals were of analytical grade and used as-received. Water was purified by a Milli-Q system (resistivity $> 14 \text{ M}\Omega \text{ cm}$). 0.24 mmol DODA was dispersed in 50 ml of water by sonication, to which was added 10 ml of aqueous $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (conc. = 8 mM, $M = 1 \text{ mol dm}^{-3}$) with stirring. A yellow precipitate was collected by filtration, washed with water and dried. Analysis: calculated for $3\text{DODA}^+ \cdot \text{PMo}_{12}^{3-}$, C, 39.36; H, 6.96; N, 1.21; P, 0.89; Mo, 33.16. Found; C, 39.62; H, 7.08; N, 1.40; P, 0.85; Mo, 33.12. The molar ratio of DODA^+ to PMo_{12}^{3-} was consistent with the value expected from the electric charges of DODA^+ and PMo_{12}^{3-} .

2.2. Fabrication of the self-assembled PMo_{12}^{3-} / DODA^+ film

The ionic complex, PMo_{12}^{3-} / DODA^+ , was soluble in chloroform. Transparent thin films were obtained by

casting 0.1 mM chloroform solution of $3\text{DODA}^+/\text{PMo}_{12}^{3-}$ on thoroughly cleaned hydrophilic borosilicate glass, CaF_2 , and quartz substrates, respectively, for X-ray diffraction (XRD), Fourier transform infrared (FTIR), and UV-Vis measurements.

2.3. Instrumental analysis

C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer; other elemental analyzes were performed on a Perkin-Elmer 1000 ICP spectrometer. A small-angle XRD pattern was measured on borosilicate glass, with the diffraction vector perpendicular to the plane of the films using CuK_α irradiation ($\lambda = 0.15418 \text{ nm}$) by a Rigaku D/max rA X-ray diffractometer. Infrared spectra were recorded on a Nicolet Impact FT-IR spectrometer in the wave number range of $700\text{--}4000 \text{ cm}^{-1}$. All absorption measurements were made on a Shimadzu UV-1601PC UV spectrometer in the range of $190\text{--}1100 \text{ nm}$. The electron spin resonance (ESR) spectra of samples were recorded on a Bruker ER200-D-SRC spectrometer. Photochromic experiments were carried out using a 500-W high-pressure mercury lamp as the light source. Samples were maintained in contact with air during irradiation.

3. Results and discussion

3.1. Infrared spectra

Fig. 1(b) shows the IR spectrum of the $\text{PMo}_{12}^{3-}/\text{DODA}^+$ film. Note that besides the bands at 2922 , 2852 , and 1466 cm^{-1} assigned to the stretching and scissoring modes of CH bonds of DODA^+ alkyl chains, the IR spectrum shows four characteristic peaks of Keggin anion below 1200 cm^{-1} , which are also observed in the spectrum of the pure 12-molybdophosphoric acid crystal. The bands in the composite film associated with the anions are slightly shifted compared to those of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in a KBr pellet (Fig. 1(a)). This demon-

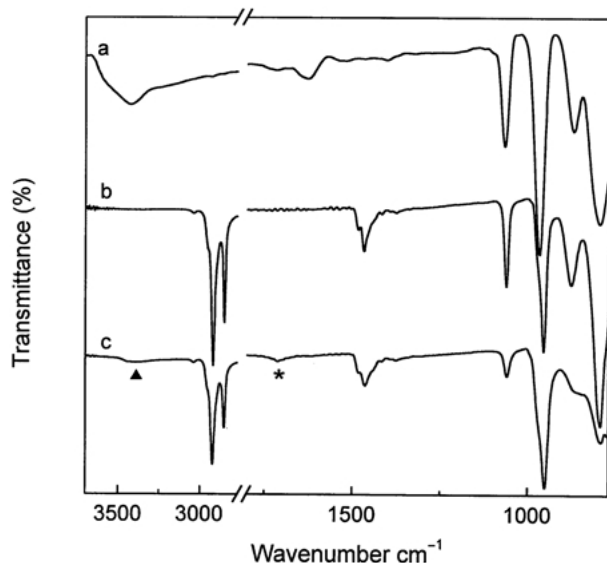


Figure 1 Infrared spectra of (a) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ polyanion in KBr pellet; the $\text{PMo}_{12}^{3-}/\text{DODA}^+$ composite film on CaF_2 substrates; (b) without UV irradiation; (c) with UV irradiation for 40 min. *Assigned to $\nu(\text{C}=\text{O})$; \blacktriangle assigned to $\nu(\text{N}-\text{H})$.

strates that the polyanions are “trapped” in the composite film and their chemical structure is preserved in the films. A more detailed inspection of the vibrational band shifts reveals that the $\text{Mo}-\text{O}_b-\text{Mo}$ and $\text{Mo}-\text{O}_c-\text{Mo}$ bands in the film have blue shifts and the $\text{Mo}-\text{O}_d$ and $\text{P}-\text{O}_a$ bands have red shifts. The shift behaviors are probably related to the organization and especially to the presence of positively charged DODA^+ in the film [12,13]. Generally, the $\text{Mo}-\text{O}_d$ stretching can be considered as pure vibration and is useful for estimating the strength of the anion–anion interaction. The red-shift of $\text{Mo}-\text{O}_d$ asymmetrical stretching frequency of the composite film compared with pure $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ crystal is due to the influence of DODA^+ , which lengthens the anion–anion distances and weakens the anion–anion interactions. But the $\text{Mo}-\text{O}_b-\text{Mo}$ and $\text{Mo}-\text{O}_c-\text{Mo}$ asymmetrical stretching frequencies of the composite film are higher than those of pure $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ because they are different from $\text{Mo}-\text{O}_d$ stretching and present some bend character. This can be assumed from geometrical considerations. As $\text{Mo}-\text{O}_b-\text{Mo}$ and $\text{Mo}-\text{O}_c-\text{Mo}$ vibrations are not pure and cannot be free from bending character, there is a competition of the opposite effects. The strong electrostatic anion–anion interactions lead to an increase in the stretching frequencies and a decrease in the bending vibrations [14]. Moreover, perturbations due to anion–cation interactions result in a decrease in the frequencies of vibrations and weakening the anion–anion interactions efficiently. In the competition of the opposite effects, the decreasing effect is stronger than the increasing one.

3.2. X-ray diffraction

In order to reveal the packing structure of components in self-assembled film, the small-angle XRD pattern of the original $\text{PMo}_{12}^{3-}/\text{DODA}^+$ film on a borosilicate glass substrate is shown in Fig. 2. It can be seen that the composite film has (001), (002), and (003) Bragg peaks at 3.00° , 6.00° , and 9.04° , respectively, corresponding to the d values of 2.945, 1.473, and 0.978 nm. From the d spacing of the composite film, an estimation of the total DODA molecular length (2.6 nm) [15], and the radius of PMo_{12}^{3-} (0.52 nm), we suppose that each inorganic layer consists of one PMo_{12}^{3-} monolayer, and

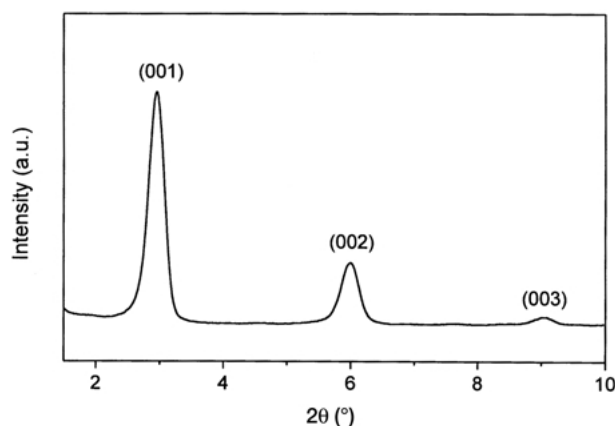


Figure 2 Small-angle XRD pattern of self-assembled $\text{PMo}_{12}^{3-}/\text{DODA}^+$ composite film on borosilicate glass substrate.

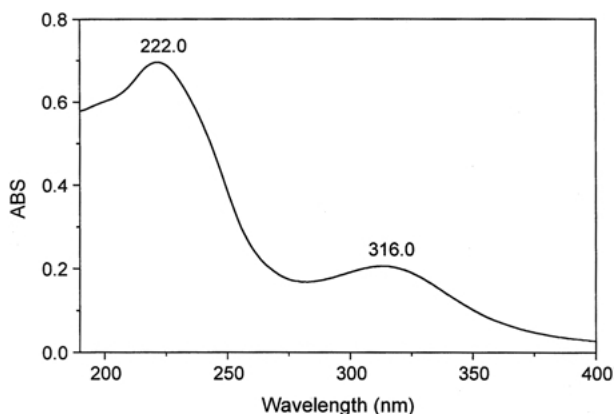


Figure 3 UV spectrum of the $\text{PMo}_{12}^{3-}/\text{DODA}^+$ composite film.

the tilt angle of hydrocarbon chains with respect to the substrate normal was close to 68.51° , as estimated.

3.3. UV spectra

The composite film exhibits two strong characteristic absorption bands at 222 and 316 nm (Fig. 3), which are ascribed to the $\text{O}_d\text{-Mo}$ (O_d : terminal oxygen) and $\text{O}_{b,c}\text{-Mo}$ (O_b or O_c bridge-oxygen) charge-transfer transition, respectively. Both bands have a red shift compared to those of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ aqueous solution at 215 nm and 235 nm. We propose that the red shift may be attributed to compact arrays and identical orientation of organic molecules, which make large π -conjugated bonds of PMo_{12}^{3-} partly overlap. This overlap results in a decrease of intermolecular transition energy, thus the absorption bands have a red shift.

3.4. Photochromic performance

Typical absorption spectra of the $\text{PMo}_{12}^{3-}/\text{DODA}^+$ composite film before and after UV irradiation are shown in Fig. 4. The film shows no significant absorption from 400 to 1100 nm with the exception of an absorption edge at 450 nm before UV irradiation (Fig. 4a). After UV irradiation, two defined bands with maxima around 520 and 770 nm are clearly observed (Fig. 4b); meanwhile, the film became blue. They are characteristic of reduced Keggin molecular species with d-d bands in the visible range and intervalence charge transfer (IVCT, $\text{Mo}^{5+} \rightarrow \text{Mo}^{6+}$) bands in the near IR region [2]. The appearance of IVCT bands shows that electron transfer occurs between the organic substrate and heteropolyanion, converting heteropolyanions to heteropolyblues with simultaneous oxidation of the organic substrate [16].

If the UV-irradiated films were stored in nitrogen, helium, argon, or vacuum conditions, they could retain the blue coloration for a long time. But, on changing the ambient atmosphere back to air or oxygen, the bleaching process happens again. This suggests that oxygen plays an important role during the bleaching process.

3.5. Photochromic mechanism

To explain the photochromic behavior of the composite film, it is necessary to investigate the variation of the

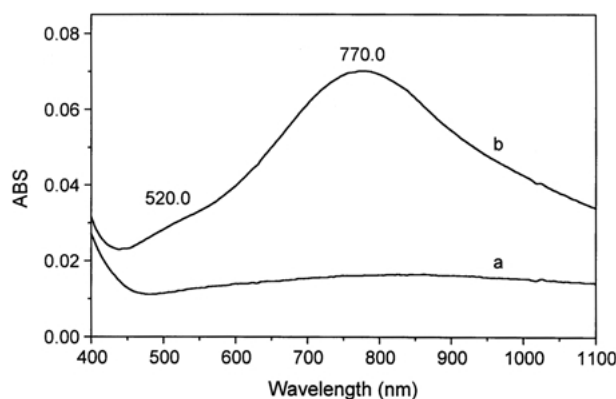


Figure 4 Visible and near IR absorption spectra of the $\text{PMo}_{12}^{3-}/\text{DODA}^+$ composite film: (a) before and (b) after UV irradiation.

electronic structure of the film during the photochromic process so as to make clear the photochromic mechanism of the film. Therefore, we made ESR analysis, which is an efficient and sensitive spectroscopy to characterize polymetalates, on the composite film. The unirradiated sample exhibited no significant ESR signal at 84 K. After UV irradiation, the composite film showed one defined Mo^{5+} signal with $g = 1.937$, which is in agreement with value reported in the literature [17]. Observation of UV-induced ESR signal suggests that the electron transfer takes place in the lattice and PMo_{12}^{3-} acting as an acceptor gains electrons during UV irradiation.

The changes of IR spectra for the composite film after UV irradiation are another powerful proof to identify that DODA^+ was oxidized and PMo_{12}^{3-} was reduced in the photochromic process. As shown in Fig. 1c, after UV irradiation the intensity of the set of bands relative to the PMo_{12}^{3-} is decreasing strongly, meantime, a slight shift and a broadening of these bands are detectable, which results from the formation of heteropolyblue. This indicates that PMo_{12}^{3-} polyanions accept electrons and are reduced [18]. Simultaneously, two new bands around 1710 and 3350 cm^{-1} appear, corresponding to the formation of carbonyl bonds ($\text{C}=\text{O}$) and nitrogen hydrogen bonds (N-H) of secondary amine due to oxidation of DODA^+ (Fig. 1c).

Thus, we suppose that the photochromic mechanism of the composite film is electron transfer from the positively charged $[(\text{CH}_3)_2\text{N}(\text{C}_{18}\text{H}_{37})_2]^+$ to negatively charged $[\text{PM}_{12}\text{O}_{40}]^{3-}$. $[\text{PM}_{12}\text{O}_{40}]^{3-}$ is reduced to $[\text{PM}_{12}\text{O}_{40}]^{4-}$, meanwhile, $[(\text{CH}_3)_2\text{N}(\text{C}_{18}\text{H}_{37})_2]^+$ is oxidized into one or more compounds with carbonyl bonds ($\text{C}=\text{O}$) and nitrogen-hydrogen bonds (N-H).

4. Conclusion

The layered superlattice $\text{PMo}_{12}^{3-}/\text{DODA}^+$ self-assembled composite film has been fabricated. IR spectra showed that PMo_{12}^{3-} anion exists as Keggin type in the composite film. Each inorganic layer consists of one PMo_{12}^{3-} monolayer incorporated in the hydrophilic interlayer with the d spacing of 2.945 nm. When exposed to UV light, the films turned blue due to reduction of PMo_{12}^{3-} and oxidation of DODA^+ . The bleaching could occur when the material is in contact with ambient air or O_2 . The studies on the photochromism of the films

indicate that they can be used as promising materials in the fields of high-density recordings, photoelectric displays, and other high-technology devices.

Acknowledgments

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