

Fabrication of photochromic phosphomolybdic acid monolayer film

Guangjin Zhang, Tao He, Ying Ma, Zhaohui Chen, Wensheng Yang and Jiannian Yao*

Key Laboratory of Photochemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China.

E-mail: jnyao@iccas.ac.cn; Fax: 86-10-82616517; Tel: 86-10-82616517

Received 13th May 2003, Accepted 29th May 2003

First published as an Advance Article on the web 5th June 2003

A photochromic monolayer film of phosphomolybdic acid (denoted as PMo_{12}) was fabricated by self-assembly approach. UV-visible spectrum and AFM observation show that the monolayer film is composed of aggregated PMo_{12} molecules. The monolayer film shows good photochromic properties, with enough stability and reversibility. The color change of the monolayer after UV-irradiation can be captured by a microscope equipped with a color CCD camera. Photochromic response of the monolayer film can be doubled after being modified by an amine monolayer.

Photochromic materials have received more and more attention for their potential application in many high-tech areas, such as high-density optical memory, optically switches and displays. With the development of ultra-thin and mini-type opto-electronic devices, monolayers of photochromic materials have attracted much interest as building blocks for novel molecular devices.^{1–3} The monolayers of organic photochromic molecules have been well studied, however, the realization of a practical system remains a challenge since organic photochromic compounds have the disadvantage of poor durability.^{4,5} Polyoxometalates (POM), owing to their special structure and interested electronic properties, exhibit significant photochromism which makes them promising building blocks for fabrication of photochromic monolayers.^{6,7} Monolayers of the POMs constructed by LB (Langmuir–Blodgett) and electronic deposition techniques have been reported,^{8,9} whereas, there are only a few reports on the photochromic properties of the POM monolayer, and also the approaches used to fabricate the monolayer are skillful and complicated, which has limited its further application. Here we report on a monolayer of phosphomolybdic acid (denoted as PMo_{12}) that is fabricated by self-assembly technology, and as a key focus of this paper, the photochromic properties and mechanism of the resulting monolayer are investigated.

The monolayer of PMo_{12} was prepared by a simply self-assembly approach as previously.^{10,11} The APS (3-aminopropyltriethoxysilane) modified substrate (quartz or silicon wafers) was immersed into 0.1 M HCl solution to get an amino cation covered surface, then immersed into the solution of PMo_{12} for about 2 h to obtain a saturated absorption of PMo_{12}^{3-} ions.

Fig. 1 shows the UV-visible spectrum of the prepared PMo_{12} monolayer. Two absorption bands of the film were found at 196 and 310 nm respectively, which are characteristic absorption bands of the PMo_{12} anion.¹² The surface coverage, Γ , of PMo_{12} molecules on the substrate surface can be calculated using $\Gamma = [(A_\lambda/2)\epsilon_\lambda^{-1}N_A] \times 10^{-3}$, where A_λ is the absorbance of PMo_{12} in the monolayer at a given wavelength (λ), ϵ_λ is the extinction coefficient of PMo_{12} in solution ($\text{M}^{-1} \text{cm}^{-1}$) at λ , and N_A is Avogadro's number.¹³ Using the absorbance values around 310 nm and the corresponding extinction

coefficients calculated from the solution absorption spectrum of a standard concentration of PMo_{12} , the surface coverage of PMo_{12} in the monolayer was calculated to be about $4.1 \times 10^{-10} \text{ mol cm}^{-2}$. The size of spherical phosphomolybdic acid of the Keggin structure was about 1 nm,⁷ and the theoretical surface density of the PMo_{12} monolayer on a flat surface was $1.7 \times 10^{-10} \text{ mol cm}^{-2}$. Regarding the surface roughness of about 2,¹⁴ the apparent surface density of $4.1 \times 10^{-10} \text{ mol cm}^{-2}$ were corrected to be about $2.05 \times 10^{-10} \text{ mol cm}^{-2}$ which indicates approximately complete monolayer coverage of PMo_{12} on the surface.

An AFM image of the monolayer is shown in Fig. 2. It can be seen that the surface of the substrate is fully covered with clusters of PMo_{12}^{3-} anions. The diameter of the clusters is from several nanometers to about ten nanometers, which is larger than the diameter of the PMo_{12}^{3-} anion.⁷ This may be attributed to the formation of larger clusters of PMo_{12}^{3-} aggregates during the self-assembly process. And also it can be found that all the clusters are connected to each other to form a network structure. Raman spectra of the monolayer as well as the pure polycrystalline PMo_{12} powder are shown in Fig. 3. By comparison, it can be clearly seen that there exists a notable difference between PMo_{12} and the monolayer. The bands at 998 and 978 cm^{-1} , attributed to the symmetry and asymmetry stretching vibration of $\text{Mo}=\text{O}$ terminal group, shift to 976 and 940 cm^{-1} , respectively. The Mo_2O corner-sharing band at 894 cm^{-1} shifted to 819 cm^{-1} , and the Mo_3O stretching vibration bands located at 602 cm^{-1} shift to 612 cm^{-1} .¹⁵ These Raman

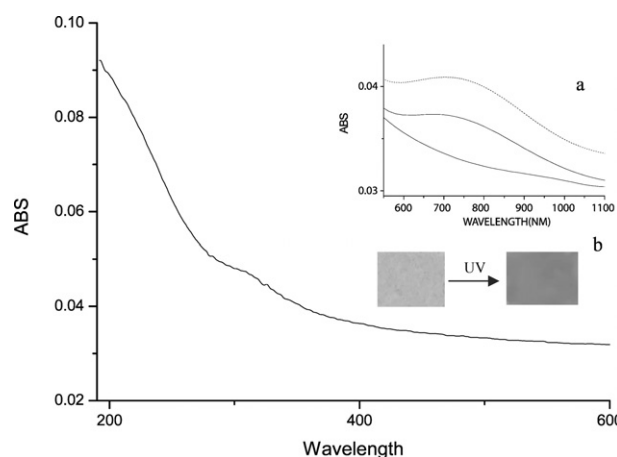


Fig. 1 UV-visible spectrum of the PMo_{12} monolayer. Insert (a) is the UV-visible spectra of the monolayer before and after 5 min UV-irradiation, the dashed line is the photochromic response after the assembly of another organic amine layer on the monolayer film. Insert (b) is the photographs of the monolayer before and after UV-irradiation captured by a microscope equipped with a color CCD camera.

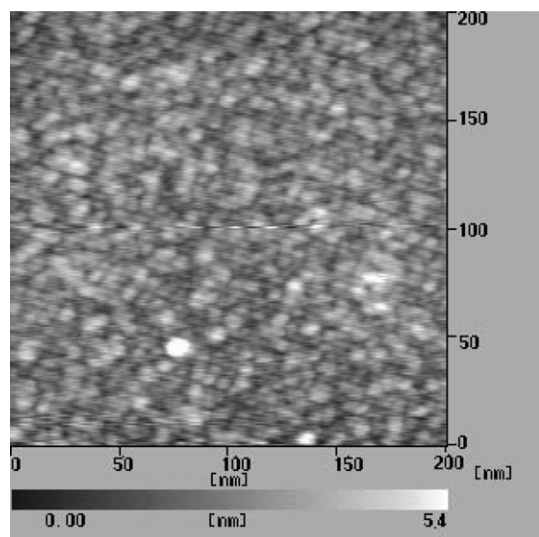


Fig. 2 AFM image of the monolayer on Si(111) substrate.

spectral changes indicate that the structure of the PMo_{12} lattice is distorted after being assembled into the monolayer. The interaction between PMo_{12} molecules and amino-head group on the modified substrate can result in the formation of hydrogen bonds and lead to such distortion. It is noted that the $\text{Mo}_2\text{-O}$ vibration band experiences a red-shift as large as 70 cm^{-1} , suggesting that the $\text{Mo}_2\text{-O}$ corner sharing position is the active position that is involved in the interaction with hydrogen on the amino head group to form the hydrogen bond.

It is interesting that the PMo_{12} monolayer film shows good photochromic properties. The transparent film turned to light blue after UV-irradiation for 5 min (500 W Hg lamp as light source, $\lambda > 200\text{ nm}$). The insert of Fig. 1 shows the absorption spectrum in the near-IR region of the SAM film before and after UV-irradiation, from which we can see that after 5 min UV-irradiation, a new band appears around 780 nm. The shape of the new band is similar to that of UV-colored amorphous MoO_3 films, which is a typical absorption band of $\text{Mo}^{5+} \rightarrow \text{Mo}^{6+}$ intervalence charge transfer (IVCT).¹⁶ This indicates the appearance of photo-reduced Mo^{5+} species in the monolayer after the UV-irradiation, which was confirmed by XPS analysis. A microscope equipped with a color CCD camera can capture the color change of the monolayer. The insert (b) of Fig. 1 shows the pictures of the monolayer before and after UV-irradiation. Under the microscope, it can be

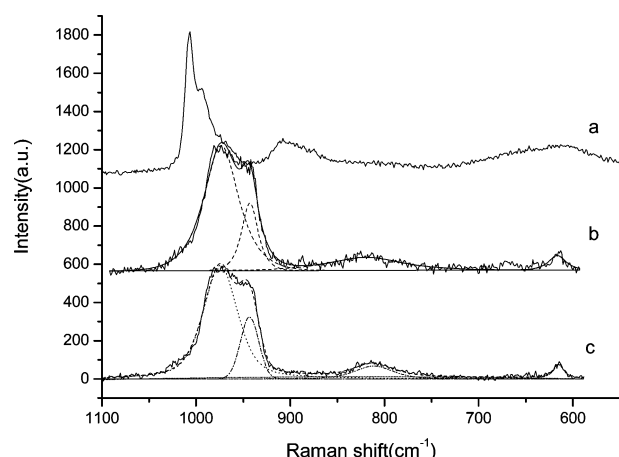


Fig. 3 Raman spectra of polycrystalline PMo_{12} (a), the monolayer film on Si(111) before (b) and after 5 min UV-irradiation (c). The dashed lines are the deconvoluted spectra, the smooth lines are the fitted spectra and the wavy lines are the original spectra.

clearly identified that the color of the monolayer is changed to blue after UV-irradiation. In addition, the monolayer also has good reversibility and stability. After coloration, the film keeps the blue color for more than one year when stored in the dark, indicating that the SAM film is stable in air and retains its coloration memory for a rather long time. However, in the dark, the deep 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 to blue and its absorption spectrum becomes similar to the previous colored state. In this way, this “write/erase” process can be repeated for more than ten times with little fatigue. The experimental results show good foreground application of such monolayers as building blocks for photo-electronic devices.

It is noteworthy that when another organic amine layer is assembled on the monolayer film, with the same experimental conditions, the photochromic response can be enhanced by about two times, as exhibited by the dashed line in the insert of Fig. 1. However, when the pure PMo_{12} molecules are deposited onto an unmodified substrate, no obvious photochromic response is found. These experimental results indicate that the interaction between PMo_{12} molecules and organic amino headgroups plays a key role in the photochromic process of the monolayer. The changes of the Raman spectra of the monolayer can give some information during the photochromic process. As shown in Fig. 3, after the UV-irradiation, the $\text{Mo}_2\text{-O}$ band at 819 cm^{-1} shifted to 810 cm^{-1} , whereas the other three bands remained almost unchanged. According to the previous report,¹⁷ it is known that the red shift of Mo-O vibration band during photochromism is due to the hydrogen insertion and attachment with the Mo-O bond. For our system, because the PMo_{12} molecules closely interacting with the amino headgroup, it is deduced that the hydrogen is most likely to come from the protonated amino headgroup. Thus we can account for the enhancement of photochromic response after the assembly of another amine layer on the monolayer film. For the original PMo_{12} monolayers, only one side of the PMo_{12} clusters comes into contact with the amino group, after the assembly of another organic amine layer, both sides of the PMo_{12} clusters are connected with the amino group. From the photochromic mechanism, only those molybdenum atoms that interact with amino headgroups are photoreducible, therefore after the assembly of another amine layer on the monolayer film, the photoreducible molybdenum atoms are also doubled, thus resulting in the doubled enhancement of the photochromism of the monolayer. XPS analysis confirms that after the assembly of another amino layer on the monolayer film, the concentration of photo-produced Mo^{5+} in the monolayer after the UV-irradiation is also doubled, from 15% to about 28%.

In summary, the photochromic monolayer of PMo_{12} was fabricated by self-assembly. The monolayer is composed of aggregated PMo_{12} molecules. The monolayer shows good photochromic properties, the color change of the monolayer can be captured by a color CCD camera on a microscope. The photochromic response of the monolayer can be doubled after the modification of another amine layer on it.

Acknowledgements

This work is supported by State Key Project for Fundamental Research No.973 (GR19990330), Chinese Academy of Sciences and National Science Foundation of China.

References

- 1 K. Olaf and S. Masatsugu, *J. Am. Chem. Soc.*, 1996, **118**, 9174.
- 2 A. Shigeaki, U. Kingo, Y. Iwao and I. Masahiro, *Langmuir*, 1997, **13**, 5504.

- 3 J. B. Nicholas, E. R. Rachel, K. Sherry and J. L. Graham, *J. Am. Chem. Soc.*, 2001, **123**, 4089.
- 4 A. Sidorenko, C. Houphouet-Boigny, O. Villavicencio, M. Hshemzadeh, D. V. Mcgrath and V. V. Tsukruk, *Langmuir*, 2000, **16**, 10 569.
- 5 K. Shinichi, T. Tetsuo, S. Sohogo, M. Yuko and K. Kenyu, *J. Am. Chem. Soc.*, 1998, **110**, 509.
- 6 M. T. Pope, *Heteropoly and isopoly oxometalates*, Springer-Verlag, New York, 1983.
- 7 S. K. Mahmoud, I. K. Song, D. C. Duncan, C. L. Hill and M. A. Barteau, *Inorg. Chem.*, 1998, **37**, 398.
- 8 J. K. Pawel, C. Malgorzata, M. Krzysztof, L. Adam, A. M. Marcin and K. Alexander, *Electrochem. Commun.*, 2002, **4**, 510.
- 9 L. M. Clemente, B. Agricole, C. Mingotaud, G. C. Gomez, E. Coronado and P. Delhaes, *Langmuir*, 1997, **13**, 2340.
- 10 Z. H. Chen, Y. A. Yang, J. B. Qiu and J. N. Yao, *Langmuir*, 2000, **16**, 722.
- 11 Z. H. Chen, Y. Ma and J. N. Yao, *Thin Solid Films*, 2001, **384**, 160.
- 12 D. Li, B. I. Swanson, J. M. Robinson and M. A. Hoffbauer, *J. Am. Chem. Soc.*, 1993, **115**, 6975.
- 13 J. M. Fruchart, G. Herve, J. P. Launay and R. Massart, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1627.
- 14 The data are supplied by the quartz manufacturer.
- 15 (a) R. Claude, F. Michel, F. Raymonde and T. Rene, *Inorg. Chem.*, 1983, **22**, 207; (b) T. Rene, F. Michel, F. Raymonde and R. Claude, *Inorg. Chem.*, 1984, **23**, 598.
- 16 E. Papaconstantinou, *Chem. Soc. Rev.*, 1989, **18**, 1.
- 17 Y. A. Yang, Y. W. Cao, B. H. Loo and J. N. Yao, *J. Phys. Chem B*, 1998, **102**, 9392.