Vol. 16 高等学校化学学报 November
1995 CHEMICAL JOURNAL OF CHINESE UNIVERSITIES 13～16

Preparation of Nanoparticulate $[PMo_{11}Cu(H_2O)O_{39}]^{5-}$-*n*-$C_{18}H_{37}NH_2$ Film Using Langmuir-Blodgett Method*

PENG Xiao-gang**, ZHANG Xin-tong, LI Lin-song, QIN Zhu-jie,
XIAO Liang-zhi, and LI Tie-jin*
(*Department of Chemistry, Jilin University, Changchun*, 130023, *P. R. China*)
Shen Chao
(*Department of Fundamental Science, Jiamusi Institute of Technology Jiamusi*, 154007, *P. R. China*)

Abstract Nanoparticulate $[PMo_{11}Cu(H_2O)O_{39}]^{5-}$ ($PCuMo_{11}$)-*n*-$C_{18}H_{37}NH_2$ composite monolayer can be formed at the air-liquid interface using nanoparticulate $PCuMo_{11}$ as the subphase. The area extrapolated to $\pi=0$ is 0.27 nm^2 per hydrocarbon chain of the monolayer. The collapse pressure is about 3.5×10^{-1} N. The composite monolayer was deposited on the solid substrate using the LB technique. The XPS characterization of the composite monolayer showed that in the film the directional alignment of $PCuMo_{11}$ molecules was in the direction of Cu atoms close to the amino groups of the octadecylamine molecules.

Keywords $PCuMo_{11}$-*n*-$C_{18}H_{37}NH_2$ composite monolayer, XPS, LB technique, Nanoparticle

1 Introduction

There have been a number of papers reporting the preparation and the properties of nanoparticles of metal, semiconductor and insulator for their potential application[1,2]. It is very important for most application to assembling these nanoparticles in an orderly structure and maintaining their isolated particle properties[3-5]. We have reported some work on the orderly assembly of α-Fe_2O_3 nanoparticles[6,7]. However, the further investigation on the properties is limited by the size and the monodispersity of the nanoparticles used. It is well-known that when the size of materials reduces to this scale, the properties of them will change dramatically[1,2]. Since the size of the heteropoly acid (HPA) molecule is in the nanometer scale, the apparent quantum confinement phenomenon should be observed (for example, the size of phosphomolybdlic acid molecule is about 0.8 nm), to orderly assemble the

* Supported by the National Narural Science Foundation of China.

** To whom correspondence should be addressed.

HPA molecules but remain their isolated properties will result in some interesting results, which is expected to have application in the research of molecular device.

The present paper covers the surface mechanical property of the nanoparticulate $PCuMo_{11}$-n-$C_{18}H_{37}NH_2$ composite monolayer investigated. The orderly assembly of $PCuMo_{11}$ was obtained, and the XPS study of this system showed that a special directional alignment occured in it.

2 Experimental Section

The $PCuMo_{11}$-n-$C_{18}H_{37}NH_2$ nanoparticulate film was built up with a RMC-2T multicompartmental round trough from Mayer-Fein Technic Co. (Germany). The solution of $PCuMo_{11}$ in a concentration of 1×10^{-4} mol/L was used as the subphase (pH = 3 — 4). The spreading solution of 1×10^{-3} mol/L was prepared by dissolving octadecylamine in chloroform (A. R. grade). Surface pressure/area isotherms were measured and the LB films were deposited onto a solid substrate (silicon or glass slide) at the constant surface pressure at room temperature. All XPS data were obtained using a VG Escalab Mark I photoelectron spectrometer with an Mg $K\alpha$ X-radiation source.

3 Result and Discussion

3.1 The Surface Mechanical Property of Nanoparticulate $PCuMo_{11}$-n-$C_{18}H_{37}NH_2$ Composite Monolayer

Fig. 1 shows the surface pressure-area isotherm of $PCuMo_{11}$-n-$C_{18}H_{37}NH_2$ composite monolayer on the $PCuMo_{11}$ subphase. The isotherm comprised three regions. Region 1 can be considered to be a gaseous/liquid state; the composite monolayer was observed to be very mobile in this uncompressed state. Region 2 corresponded to the solid phase in which the film was very rigid in this phase. The area extrapolated to $\pi=0$ is 0.27 nm^2 per hydrocarbon chain. It is a bit larger than the value of octadecylamine monolayer which spread on the pure water subphase. Continuation of compression resulted ultimately in collapse at region 3. Further compression resulted in the formation of multilayer solid state film. By comparison with the π-A curve of octadecylamine in the pure water subphase, the surface mechanical property of $PCuMo_{11}$-n-$C_{18}H_{37}NH_2$ composite monolayer varied obviously. We considered that the reason was the smaller size but the excessive charges of the $PCuMo_{11}$ anion. The smaller size resulted in that the amount of octadecylamine molecules combined with the $PCuMo_{11}$ anion was not enough to

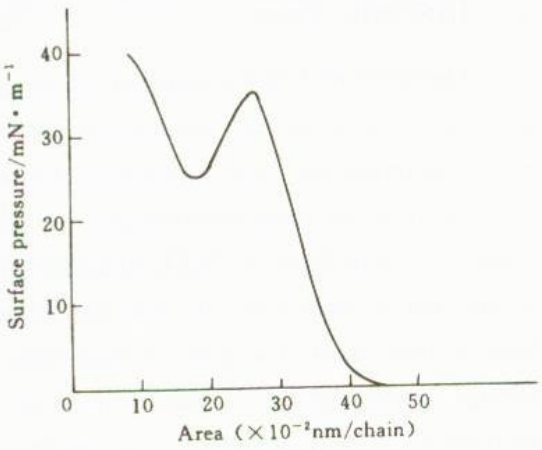

Fig. 1 The π-A isotherm of octadecylamine on the surface of $PCuMo_{11}$ subphase

neutralize the charge of it. The excessive negative charge resulted in the closer linkage of $PCuMo_{11}$ anion with the octadecylamine cation. So, the move of the octadecylamine cation among the $PCuMo_{11}$ anion was difficult to occur, and the manifestation on the π-A curve was the area per hydrocarbon chain and the area was larger than the normal value, the collapse pressure of the π-A curve was smaller too.

3.2 XPS Study of the $PCuMo_{11}$-n-$C_{18}H_{37}NH_2$ Composite Monolayer

Due to the structural characteristics of the composite monolayer discussed above, we can only obtain the composite monolayer which transferred completely. This question should be solved by the replacement of octadecylamine by other amphiphilic molecules, for example, the amphiphilic polymer material which contain amino groups higher in number.

Fig. 2 shows the XPS data of $Cu(2p)_{3/2}$ and $Mo(3d)$ core levels of the $PCuMo_{11}$-n-$C_{18}H_{37}NH_2$ composite monolayer which was transferred on the glass substrate. Because it was a monolayer, the intensity of XPS signal was weaker.

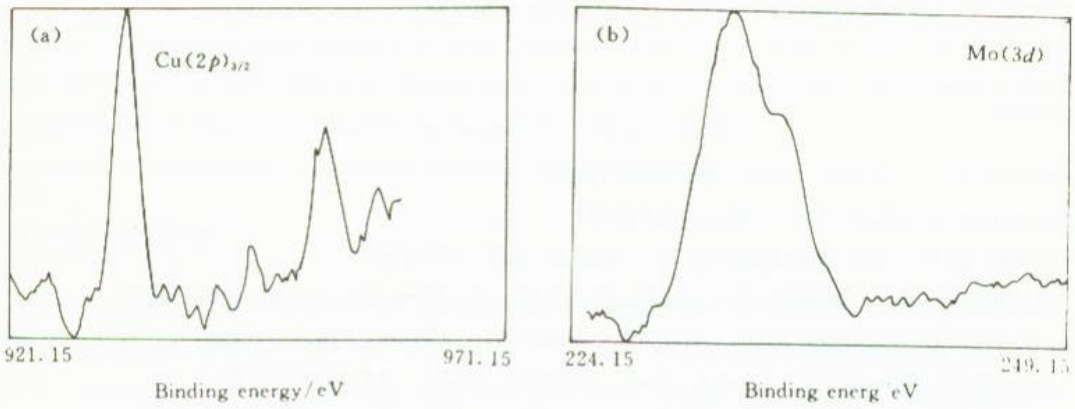

Fig. 2 XPS data of $Cu(2p)_{3/2}$ and $Mo(3d)$ core levels in $PCuMo_{11}$-n-$C_{18}H_{37}NH_2$ composite monolayer deposited on a glass substrate.

(a) XPS data of $Cu(2p)_{3/2}$; (b) XPS data of $Mo(3d)$.

Fig. 3 shows the XPS data of $Cu(2p)_{3/2}$ and $Mo(3d)$ core levels of $Na_5[PMo_{11}Cu(H_2O)O_{39}]$ powder. By comparison with the powder sample, the intensity ratio of $Cu(2p)_{3/2}$ and $Mo(3d)$ increased in LB film system. Because the XPS technique is a kind of method to analyze the surface characteristics, the signal intensity of the XPS technique is a kind of method to analyze the surface characteristics, the signal intensity of the XPS is related to the escape depth of the photoelectron, so this means that in the composite monolayer the directional alignment of $PCuMo_{11}$ anions was in the direction of Cu atoms close to the amino groups of the octadecylamine molecules. This kind of directional alignment is relevant to the electron distribution in $PCuMo_{11}$ anion obviously. The replacement of Mo atom by Cu atom lead to the negative charges in $PCuMo_{11}$ anion distributed asymmetrically, the negative charges would be distributed on the end O atom connected with the Cu atom preferentially. The increase of negative charges distribution around the Cu atom was proved by the XPS spectrum of the $PCuMo_{11}$ powder sample[8]. So, while $PCuMo_{11}$ anions combined with the octadecy-

lamine cations at the air-liquid interface, the end O atoms which linked with Cu atoms combined with the octadecylamine cations priorly, and this resulted in the directional alignment in the composite monolayer.

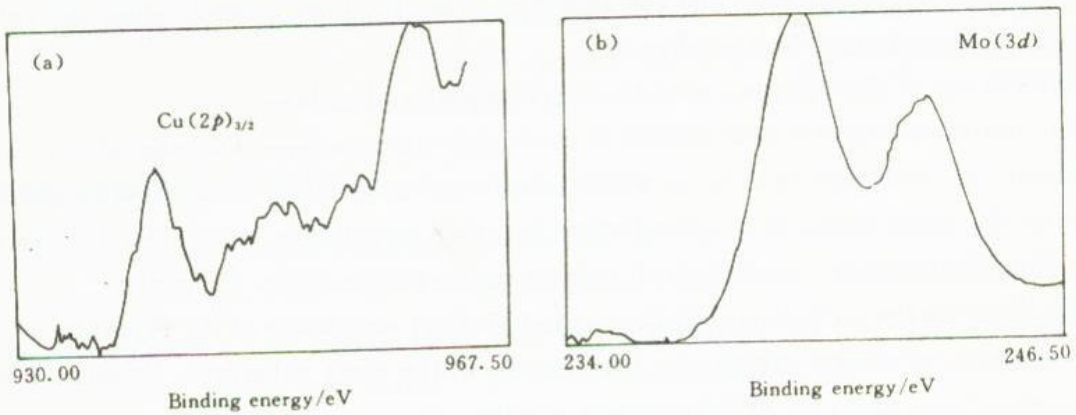

Fig. 3 XPS data of $Cu(2p)_{3/2}$ and Mo(3*d*) core levels in $Na_5[PMo_{11}Cu(H_2O)O_{39}]$ powder
(a) XPS data of $Cu(2p)_{3/2}$, (b) XPS data of Mo(3*d*).

References

[1] Brus L. E., *J. Phys. Chem.* **90**, 2555(1986)
[2] Henglein A, *Chem. Rev.*, **89**, 1861(1989)
[3] Stucky G. D., and MacDougall J. E., *Science*, **247**, 669(1990)
[4] Meldrum F. C., Kotov N. A., and Fendler J. H., *J. Phys. Chem.* **98**, 4506(1994)
[5] Colvin V. L., Schlamp M. C., and Alivisatos A. P., *Nature*, **370**, 354(1994)
[6] Peng X. G., Zhang Y., Yang J. *et al.*, *J. Phys. Chem.*, **96**, 3412(1993)
[7] Peng X. G., Gao M. L., Zhao Y. Y. *et al.*, *Chem. Phys. Lett.*, **209**, 233(1993)
[8] Qin Z. J., Thesis Ph. D., Jilin University, 1993

(Received August 3, 1995)