STM을 이용한 Heteropolyoxometalate의 규칙적배열 및 NDR 거동 고찰

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Ordered Array Formation and Negative Differential Resistance Behavior of Heteropolyoxometalate Monolayers Probed by Scanning Tunneling Microscopy

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INTRODUCTION

Scanning Tunneling Microscopy (STM) is a relatively new surface science technique which allows surfaces to be imaged at an atomic level [1]. Although the emphasis of much early STM work was on the study of semiconductor surfaces [2], it has been used to image graphite, metals and superconductor [3]. Many insulating materials such as proteins [4], liquid crystals [5], petroleum asphaltenes [6], and Langmuir-Blodgett films [7] have been imaged successfully using STM by depositing the molecules on a conducting substrate. STM images of some heteropoly and isopoly acids deposited on graphite surface were reported in a previous work [8]. They reported that the heteropoly acids (HPAs) deposited on graphite surface exhibited a distinctive I-V behavior called negative differential resistance (NDR). HPAs as both acid catalysts and oxidation catalysts [9] have been widely investigated and have been used in a commercial process producing methacrylic acid [10]. HPAs are very attractive catalysts because (1) the acidic and redox properties can be controlled in a systematic way and (2) owing to their ability to form a pseudo-liquid phase, catalytic reactions sometimes proceed not only on the surface but also in the bulk [11].

Images and NDR behavior of cation-exchanged Keggin HPAs deposited on a highly oriented pyrolytic graphite (HOPG) surface were successfully probed by STM. We established a correlation between NDR voltage and reduction potential of HPAs. STM images of pyridine-adsorbed HPAs were also reported. 2-Dimensional ordered array and molecular dimension of some polyoxometalates having Dawson, Finke and Preyssler structure were investigated.

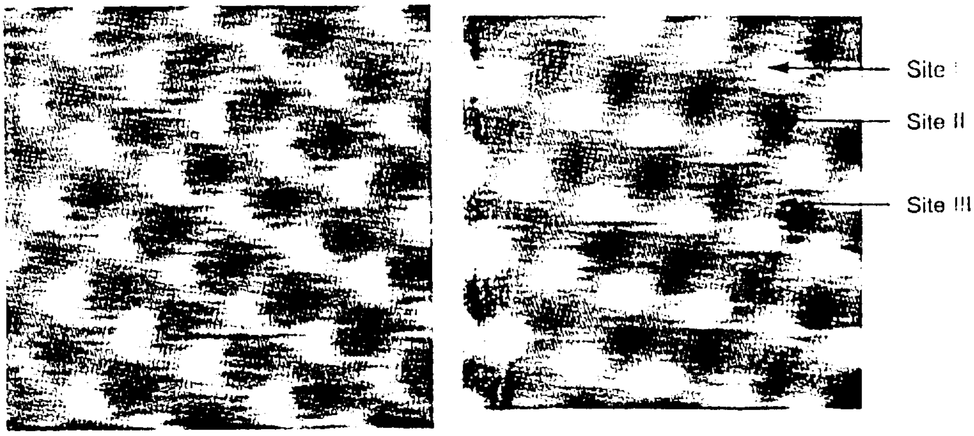
EXPERIMENTAL

$H_3PMo_{12}O_{40}$ was obtained from Aldrich Chemical Co. Cation-exchanged HPAs such as $H_{3-x}Cs_xPMo_{12}O_{40}$ (x=0-3) and $H_{3-x}Cu_xPMo_{12}O_{40}$ (x=0-3) were prepared by ion exchange. $H_7P_2Mo_{17}V_1O_{62}$ (Dawson HPA) was kindly supplied by DuPont Company. $K_{12.5}Na_{1.5}(NaP_5W_{30}O_{110})$ (Preyssler HPA) and $Na_{16}[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]$ (Finke HPA) were prepared. Approximately 0.01 M aqueous solutions of each sample were then prepared. A drop of solution was deposited on HOPG and allowed to dry in air for ca. 1 hr.

STM Images were obtained in air using a Topometrix TMX 2010 instrument. mechanically formed 90/10 Pt/Ir tips were used. Scanning was done in a constant current mode at a positive sample bias of 100 mV and tunneling current of 1-2 nA. Tunneling spectra were measured in air and in a glove box filled with nitogen by both Topometrix TMX 2010 and LK Technologies LK-1000 STM instruments for consistency and reproducibility. The sample bias was ramped from -2 to +2 V with respect to the tip and the tunneling current was monitored. The voltage axis in the tunneling spectrum represents the potential applied to the sample relative to that of the tip.

RESULTS AND DISCUSSION

Fig. 1 shows STM images of $H_3PMo_{12}O_{40}$ and $Cs_3PMo_{12}O_{40}$. The periodicity of $H_3PMo_{12}O_{40}$ is 10.8 A and that of $Cs_3PMo_{12}O_{40}$ is 13.7 A. These values are in good agreement with the molecular dimension of HPAs reported by XRD. The difference in periodicity of two HPAs implies clear evidence for the flexible nature of the secondary structure of HPAs [12]. I-V spectra of $Cs_3PMo_{12}O_{40}$ array on HOPG taken at two different sites, denoted as Site I and Site II in Fig. 1(b), are shown in Fig. 2(a). Site II exhibits the typical I-V spectrum of HOPG and Site I exhibits the characteristic I-V spectrum of $Cs_3PMo_{12}O_{40}$. The latter spectrum shows a NDR at -1.5V as dI/dV is negative in this region as shown in Fig. 2(b). The difference in I-V spectra of the two sites indicates that the array of HPA on HOPG is a monolayer. The striking NDR behavior of HPAs measured by STM may be closely related to the electronic properties of the materials, and may be serve as a fingerprint of their redox properties. NDR behaviors of Cs- and Cu-exchanged $H_3PMo_{12}O_{40}$ are shown in Fig. 3. Replacement of proton by a Cs decreases the reduction potential of HPA and increases the NDR peak voltage. Cu-exchanged HPA shows enhanced redox potential and less negative NDR voltage with the increase of Cu content. The more reducible the HPA, the less negative the NDR peak voltage in tunneling spectrum [13-16].



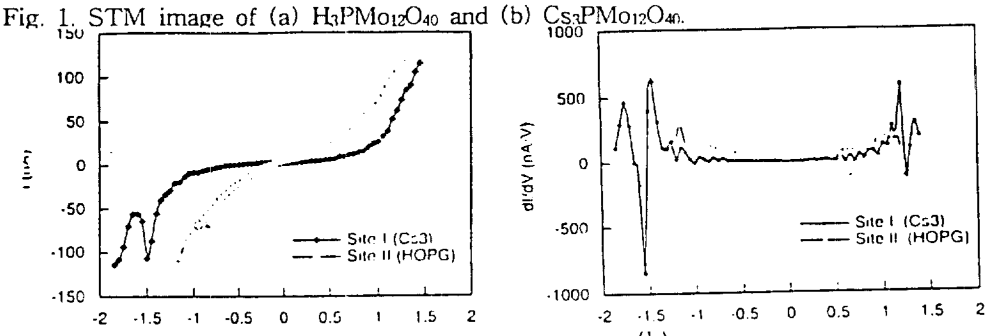
5.07 nm x 5.07 nm

(a)

7.0 nm x 7.0 nm

(b)

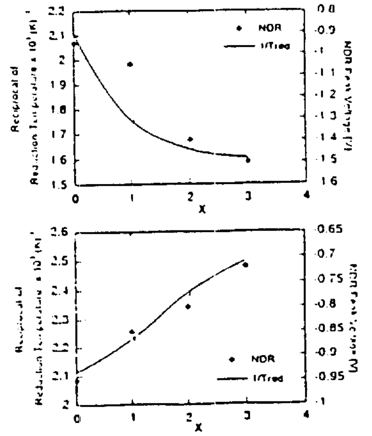
Fig. 1. STM image of (a) $H_3PMo_{12}O_{40}$ and (b) $Cs_3PMo_{12}O_{40}$.



(a)

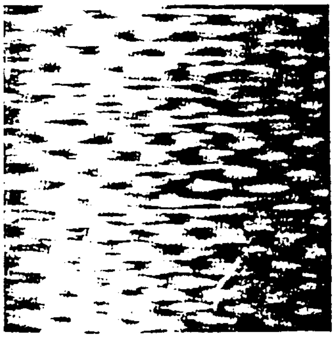
(b)

Fig. 2. Tunneling spectra taken at two sites : (a) I-V and (b) dI/dV.



(a) $H_{3-x}Cs_xPMo_{12}O_{40}$ (b) $H_{3-x}Cu_xPMo_{12}O_{40}$.

Fig. 3. Reduction potential [10] and NDR voltage of cation-exchanged HPAs.



16.9 nm x 16.9 nm

Fig. 4. STM image of pyridine-adsorbed $H_3PMo_{12}O_{40}$.

Fig. 4 shows STM image of pyridine-adsorbed $H_3PMo_{12}O_{40}$ [17]. We observe well-ordered two-dimensional array formation even after pyridine adsorption by the HPA, but it is obvious that, unlike the nearly square array formation seen in Fig. 1(a), the array pattern seen here is hexagonal. The periodicity of the arrays increased from 10.8 A for the fresh sample to 16.5 A upon pyridine adsorption. Based on the molecular dimension of ca. 6A for a pyridinium and ca. 11A for the almost spherical HPA, one would expect that pyridine is adsorbed in the intersticial space between polyanions. This result also gives strong evidence for the flexible nature of HPA arrays.

CONCLUSIONS

Two-dimensional ordered array and NDR behavior of HPAs were successfully probed by STM. The NDR voltages were correlated with the reduction potential of HPAs. Visual evidence for the flexible nature of secondary srtucture of HPA was also demonstrated by imaging pyridine-adsorbed HPAs.

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