Scanning Tunneling Microscopy (STM) and Tunneling Spectroscopy (TS) of Heteropolyacid (HPA) Self-Assembled Monolayers (SAMS): Connecting Nano Properties to Bulk Properties

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(Received 19 February 2002 • accepted 3 April 2002)

Abstract—Nanoscale investigation of Keggin-type heteropolyacid (HPA) self-assembled monolayers (SAMs) was performed by scanning tunneling microscopy (STM) and tunneling spectroscopy (TS) in order to relate surface properties of nanostructured HPA monolayers to bulk redox and acid properties of HPAs. Cation-exchanged, polyatom-substituted, and heteroatom-substituted HPAs were examined to see the effect of different substitutions. HPA samples were deposited on HOPG surfaces in order to obtain images and tunneling spectra by STM before and after pyridine adsorption. All HPA samples formed well-ordered monolayer arrays, and exhibited negative differential resistance (NDR) behavior in their tunneling spectra. NDR peaks measured for fresh HPA samples appeared at less negative potentials for higher reduction potentials of the HPAs. These changes could also be correlated with the electronegativities of the substituted atoms. Introduction of pyridine into the HPA arrays increased the lattice constants of the two-dimensional HPA arrays by ca. 6 Å. Exposure to pyridine also shifted NDR peak voltages of HPA samples to less negative values in the tunneling spectroscopy measurements. The NDR shifts of HPAs obtained before and after pyridine adsorption were correlated with the acid strengths of the HPAs. This work demonstrates that tunneling spectra measured by STM can fingerprint acid and redox properties of HPA monolayers on the nanometer scale.

Key words: Scanning Tunneling Microscopy (STM), Negative Differential Resistance (NDR), Heteropolyacids (HPAs), Self-assembled Monolayers, Redox and Acid Properties

INTRODUCTION

Scanning tunneling microscopy (STM) provides a way to observe individual molecules [Carroll et al., 2000] and even chemical reactions on single crystal surfaces [Chiang, 1997]. Examples of molecules imaged include carbon monoxide on Rh(111) [Cernota et al., 2000] and Ag(110) [Lee and Ho, 2000]; oxygen on Pd(111) [Stellenpohl and Mumenthaler, 1999] and Pt(111) [Stipe et al., 1997]; benzoic acid on Cu(110) [Chen et al., 2000]; m-xylene and p-xylene on Rh(111) [Cernota et al., 1998]; and methoxy and formate species on Cu(110) [Silva et al., 1999]. An STM image contains both geometric and electronic information about the sample. Highly resolved STM images can distinguish between different molecules with very similar geometric structures and molecular sizes. For example, metal atoms on an alloy surface have been distinguished by their apparent height difference [Wouda et al., 1996], and metal phthalocyanines on Au(111) have been identified by metal d-orbital occupation-dependent images [Hipps et al., 1996]. Tunneling spectroscopy (TS), which probes only electronic states of surface species, has been utilized as a complementary technique to distinguish between chemically inequivalent sites or adsorbates with nearly identical geometric structures and sizes [Johansson et al., 1996]. The distinction is made based on differences in electronic structures. We have observed that individual molecules of soccer ball-like $\text{H}_3\text{PWO}_{12}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (whose molecular structures and dimensions are nearly identical) in a mixed array can be distinguished by their tunneling spectroscopy responses [Kaka et al., 2002]. In the case of organic molecules, tunneling spectroscopy measured for a single molecule on a metal surface has proven to be a valuable "finger-print" method [Stipe et al., 1998].

Heteropolyacids (HPAs) are early transition metal oxygen anion clusters that exhibit a wide range of molecular sizes, compositions, and architectures [Pope and Müller, 1994]. Among various HPA structural classes, the Keggin-type [Keggin, 1933] HPAs have been widely employed as catalysts in homogeneous and heterogeneous systems for acid-base and oxidation reactions [Lee et al., 1995, 1997; Kozhevenkov, 1995; Hill and Prosser-McCartha, 1995; Choi et al., 2000, Park et al., 2000, Lee and Song, 2000]. One of the great advantages of HPA catalysts is that their catalytic properties can be tuned by changing the identity of charge-compensating counterions, heteroatoms, and framework metal atoms (polyatoms) [Song et al., 1991, 1997; Okuhara et al., 1996]. Recently, members of four HPA structural classes--Keggin-, Wells-Dawson-, Finke-Droege-, and Pope-Jeannin-Preyssler-type HPAs--have been successfully imaged in air using STM by depositing these molecules on graphite surfaces [Kaka et al., 1998]. Previous STM studies of HPAs showed that two-dimensional ordered arrays of these molecules on a graph-
ite surface exhibited a distinctive current-voltage (I-V) behavior referred to as negative differential resistance (NDR) in their tunneling spectra [Watson et al., 1992; Kabu et al., 1996, 1997, 1998, 2000; Song et al., 1996, 1998, 2002; Kinne and Barteau, 2000; Song and Barteau, 2002]. NDR behavior has been explained in terms of resonant tunneling through a double barrier quantum well [Maboudian et al., 1993], and has been observed consistently for the arrays of HPAs. We have shown that NDR peak voltages of HPAs are closely related to electronic properties and, in turn, to the redox potentials of HPAs [Kaba et al., 1996, 1997; Song et al., 1998, 2002; Kinne and Barteau, 2000]. NDR peak voltages can be influenced by the identity of the counter-cations, framework transition-metal atoms, heteroatoms, and adsorbed organic molecules.

In this work, nanoscale characterization of HPA monolayers was performed by scanning tunneling microscopy and tunneling spectroscopy in order to relate surface properties of nanostructured HPA monolayers to bulk redox and acid-base properties of HPAs. Keggin-type HPAs with different counter-cation, polyatom, and heteroatom substitutions were examined for this purpose. HPA samples were deposited on a highly oriented pyrolytic graphite (HOPG) surface in order to obtain images and tunneling spectra by STM before and after pyridine adsorption. The observed NDR peak voltages of HPA monolayers were correlated with the redox properties as well as with the acid properties of HPAs.

**EXPERIMENTAL**

1. **Sample Preparation and Deposition**

A series of the following HPAs were investigated to explore their redox properties: cation-exchanged $\text{RPMo}_{12}\text{O}_{40}$ ($\text{R} = \text{H}^+$, $\text{Cs}^+$, $\text{Ba}^{2+}$, $\text{Zn}^{2+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$, $\text{Bi}^{3+}$), heteroatom-substituted and/or polyatom-substituted $\text{H}_{2}\text{XW}_{12}\text{O}_{40}$ ($X = \text{P}^{5+}$, $\text{Si}^{4+}$, $\text{B}^{3+}$, $\text{Co}^{2+}$) and $\text{H}_{2}\text{XMo}_{12}\text{O}_{40}$ ($X = \text{P}^{5+}$, $\text{Si}^{4+}$) HPAs. Commercially available $\text{H}_{2}\text{PMo}_{12}\text{O}_{40}$, $\text{H}_{2}\text{PW}_{12}\text{O}_{40}$, $\text{H}_{2}\text{SiMo}_{12}\text{O}_{40}$ and $\text{H}_{2}\text{SiW}_{12}\text{O}_{40}$ samples were obtained from Aldrich Chemical Co. $\text{H}_{2}\text{BW}_{12}\text{O}_{40}$ and $\text{H}_{2}\text{CoW}_{12}\text{O}_{40}$ samples were provided by Prof. Craig L. Hill at Emory University. Cation-exchanged HPAs were prepared by replacing all protons of $\text{H}_{2}\text{PMo}_{12}\text{O}_{40}$ with metal atoms, according to published methods [Ai, 1982]. Approximately 0.01 M aqueous solution of each HPA sample was prepared. A drop of solution was deposited on a freshly cleaved HOPG surface and allowed to dry in air for 1 h at room temperature for STM imaging and TS measurements. Heteroatom-substituted $\text{H}_{2}\text{XW}_{12}\text{O}_{40}$ ($X = \text{P}^{5+}$, $\text{Si}^{4+}$, $\text{B}^{3+}$, $\text{Co}^{2+}$) HPAs were also examined to explore their acid properties. For this purpose, pyridine exposure was carried out by placing a drop of liquid pyridine on these previously deposited HPA samples and drying in air for ca. 1 h at room temperature. Reversibly adsorbed pyridine molecules were then removed by evacuating the sample at ca. 25 millitorr for 1 h at room temperature prior to the STM measurements.

2. **STM Imaging and Tunneling Spectroscopy**

STM images were obtained in air by using a Topometrix TMX 2010 instrument. Mechanically formed PtIr (90/10) tips were used as probes. Scanning was done in the constant current mode at a positive sample bias of 100 mV and tunneling current of 1-2 nA. All STM images presented in this work are unfiltered, and the reported periodicities (lattice constants) represent average values determined by performing two-dimensional Fast Fourier Transformation (2D-FFT) analyses on at least three images for each sample which were obtained by using different tips. Tunneling spectra were measured in air. Both Topometrix TMX 2010 and LK Technologies LK-1000 STM instruments were used to confirm consistency and reproducibility of tunneling spectra. To measure a tunneling spectrum, 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. TS measurements were performed at least ten times each by using at least three different tips for each sample to obtain more accurate and reproducible results, and to provide a basis for statistical analyses.

**RESULTS AND DISCUSSION**

1. **Self-assembled HPA Arrays**

Fig. 1(a) shows the molecular structure of the pseudo-spherical (T₄ symmetry) Keggin-type $\text{PMO}_{12}\text{O}_{40}^{5+}$ heteropolyanion constructed from X-ray crystallography data [Strandberg, 1975]. The molecular structure of $\text{PMO}_{12}\text{O}_{40}^{5+}$ consists of a heteroatom, P, at the center of the anion cluster, tetrahedrally coordinated to four oxygen atoms. This tetrahedron is surrounded by twelve MoO₆ octahedra. The van Ader Waals diameter along the 3-fold axis of symmetry is 11.97 Å. Fig. 1(b) shows the three-dimensional array of HPAs comprising heteropolyanions, protons, cations, water, and/or organic molecules, called the secondary structure [Misono, 1987]. The counter-cations are located in the interstitial spaces between heteropolyanions. The primary structure, the Keggin structure [Keggin, 1933], of the heteropolyanion is relatively stable. However, the secondary structure is very labile and may change in different environments by either increasing or decreasing the interstitial space between heteropolyanions [Misono, 1987]. Fig. 1(c) and Fig. 1(d) show the STM image and...