Self-Assembly of Silicotungstate Anions on Silver Surfaces

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The past 15 years have seen rapid development of self-assembled organic monolayer chemistry, the chemistry of ordered organic molecular arrays formed spontaneously on solid surfaces upon immersion in a solution of the molecular adsorbate.[1] This chemistry provides a facile and versatile route to functionalized surfaces through incorporation of various organic functional groups into the adsorbate molecules.[2] The self-assembly of inorganic monolayers, while recognized as an important objective due to the potentially superior stability and mechanical properties of inorganic monolayers, has remained an elusive objective.[3]

We report here the self-assembly of α-dodecatungstosilicate anions, α-$SiW_{12}O_{40}^{4-}$, on Ag(111) surfaces from acidic aqueous solution. Figure 1a shows a 28 nm × 28 nm STM image[4] of a Ag(111) surface[5] following about 3 h immersion in an aqueous solution containing 0.1 M $HClO_4$ and 10^{-4} M α-$H_4SiW_{12}O_{40}$. In contrast to the bare metal surface which exhibits the Ag(111) structure, the electrode now displays domains of an approximately square lattice having a nearest-neighbor distance of 10.2 ± 0.5 Å. This spacing matches the diameter of the α-$SiW_{12}O_{40}^{4-}$ ion (see below), and we associate each individual spot in the image with an adsorbed silicotungstate anion.

Figure 1b shows a 110 nm × 110 nm image recorded following about 3 h immersion of Ag(111) in a solution containing 0.1 M H_2SO_4 and 10^{-4} M α-$H_4SiW_{12}O_{40}$. The image shows many small islands of α-$SiW_{12}O_{40}^{4-}$. Some of the islands are isolated, while others are connected to form larger 2D domains. The islands are adsorbed on two flat Ag(111) terraces separated by a step edge, and atomic resolution from the Ag(111) lattice could be obtained. The upper terrace is ca. 2.5 Å above the lower one, which is the correct height for a Ag(111) monatomic step. The measured height of the anion islands is about 5 Å, which is somewhat less than the 10 Å expected height of α-$SiW_{12}O_{40}^{4-}$. This discrepancy could arise from the particular choice of imaging parameters[8] which have been shown to strongly affect the apparent height of adsorbates measured by STM.[9] Nevertheless, the image clearly demonstrates that these STA islands consist of only one layer of the anions. The image shows the initial stages of self-assembly of the adsorbate on the Ag(111) surface. Full monolayer coverage was achieved after about 24 h.

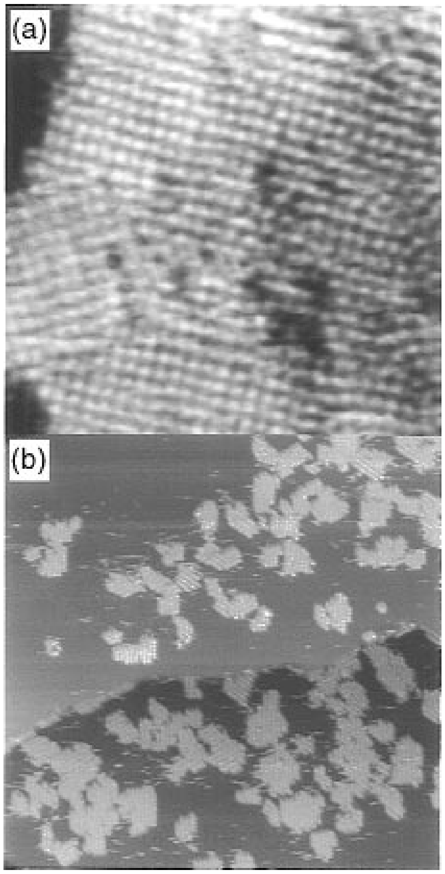

Figure 1. (a) 28 nm × 28 nm STM image of a monolayer α-$SiW_{12}O_{40}^{4-}$ on Ag(111) surface in 0.1 M $HClO_4$. $V_{tip} = 100$ mV; $i_{tip} = 2.7$ nA. (b) 110 nm × 110 nm STM image showing submonolayer coverage of α-$SiW_{12}O_{40}^{4-}$ on the Ag(111) surface in 0.1 M H_2SO_4. $V_{tip} = 135$ mV; $i_{tip} = 2.3$ nA.

Full monolayers of silicotungstate anions on Ag(111) surfaces were observed following immersion into perchloric acid electrolyte with silicotungstic acid concentrations ranging from ~10^{-3} to ~10^{-6} M. These images could be recovered following emersion of the surface, rinsing with water, and reimmersion into pure perchloric acid solution. This indicates that the silicotungstate is strongly bound to the Ag(111) surface.[10] That the adsorption of silicotungstate is slower in sulfate than in perchlorate solution likely derives from the different strength of adsorption of the two anions. On Au[11] and Pt[12] electrode surfaces the perchlorate anion itself is much more weakly

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[4] A NanoScope II electrochemical STM equipped with a fluid cell was used (Digital Instruments, Santa Barbara, CA). The tip was formed from a Pt/Ir wire coated with polyethelyene to minimize the faradaic background.

[5] Two hundred nanometer thick Ag(111) films were obtained by evaporation of Ag onto V2 grade mica in a bell jar evaporator. Atomic resolution *in situ* STM images revealed the expected (111) texture.[6] Solutions were prepared from purified water (Milli-Q UV plus, Millipore Inc., 18.2 MΩ cm) and the following chemicals: $HClO_4$ (E. Merck, Suprapur), H_2SO_4 (J. T. Baker, ULTREX Ultrapure Reagent), and α-$H_4SiW_{12}O_{40}$ (prepared following published procedures).[7] The concentrations of $HClO_4$ and H_2SO_4 were 0.1 M, and the typical α-$H_4SiW_{12}O_{40}$ concentration was 10^{-4} M.

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[10] Auger electron spectroscopy and angle-resolved X-ray photoelectron spectroscopy analysis performed on a Ag(111) single-crystal dip-coated in 0.1 M $HClO_4$ + 10^{-4} M α-$SiW_{12}O_{40}^{4-}$, which was subsequently emersed to air and washed with water, revealed surface concentrations of W and Ag consistent with our STM observations indicating that the silicotungstate monolayer is retained following removal from solution.

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adsorbed than is sulfate, and the same trend is anticipated on Ag surfaces as well. The more strongly bound sulfate is harder to remove, and the slower kinetics of self-assembly in sulfate thus reflect competition between the sulfate and the silicotungstate for the Ag surface.

Electrochemical measurements also support strong binding of the silicotungstate anion to the Ag(111) surface. Cyclic voltammetry obtained from a silicotungstate-modified Ag(111) surface in 0.1 M $HClO_4$ indicates that the electrode is passivated over a wide (up to 2 V) potential range. In contrast, an unmodified Ag(111) surface in the same electrolyte exhibits current peaks due to hydrogen evolution and Ag dissolution separated by only 0.7 V. Interestingly, cyclic voltammograms obtained from silicotungstate solutions at either Hg or Au(111) electrodes show solution waves associated with W-cage redox activity centered at 0 V vs NHE.[13] That the Ag surface-confined system exhibits much more passivation suggests that monolayer formation on the Ag surface has stabilized this system considerably and is an indication of strong interaction between the silicotungstate ion and the Ag surface.

STM[14] and AFM[15] images of bulk deposits of silicotungstate salts and related materials obtained following deposition and evaporation onto highly oriented pyrolytic graphite (HOPG) surfaces all show a hexagonal or quasi-hexagonal structure which is very different from the one observed on Ag(111). Moreover, the spontaneous ordering and persistence observed on Ag surfaces also differ from the behavior observed for bulk deposits of polyanions on HOPG and potential-induced assemblies of sulfate[16] and other anions[17−19] at the solid/liquid interface. Polyoxoanions are strongly adsorbed on HOPG,[17] Hg,[18] and Au(111)[19] surfaces, but ordered arrays are maintained only after imposition of relatively positive potentials. Self-assembly has heretofore not been observed.

We propose that self-assembled α-$SiW_{12}O_{40}{}^{4-}$ monolayers on Ag(111) adopt the square structure shown in Figure 2. Packing the T_d-symmetric α-$SiW_{12}O_{40}{}^{4-}$ anions into this square, D_{2d}-symmetric array with 2.8 Å van der Waals oxygen−oxygen contacts between nearest-neighbor anions yields a 10.4 Å separation between anions, in good agreement with the 10.2 ± 0.5 Å observed experimentally. The ca. 30° misorientation between adlattice domains evident in Figure 1a suggests that anion−substrate interactions affect the packing of the silicotungstate anions on the Ag(111) surface.

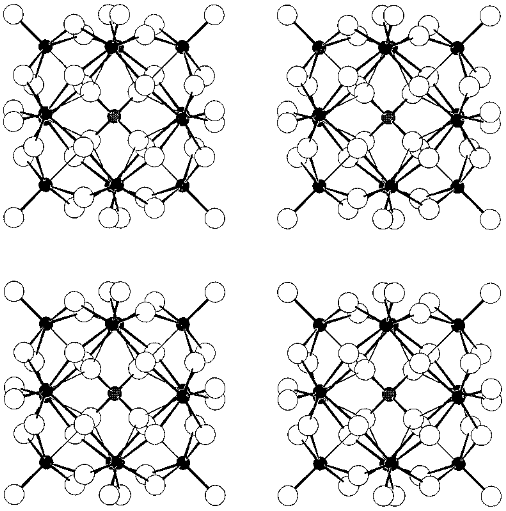

Figure 2. 2 × 2 fragment of the square adlattice structure proposed for α-$SiW_{12}O_{40}{}^{4-}$ ions on Ag(111). Here, the individual silicotungstate ions are viewed down a 2-fold rotational symmetry axis. Oxygen atoms are represented by large open circles, tungsten atoms by small filled circles, and silicon atoms by small shaded circles.

The ability of α-$SiW_{12}O_{40}{}^{4-}$ to form self-assembled monolayers on Ag(111) offers great opportunity for generalization to other functionalized inorganic molecules on other surfaces. We find that the silicotungstate anions will also adhere to Cu surfaces, and we anticipate that they will bind to other oxophilic surfaces (e.g. Al, W, Ni) once the oxide layer is removed. Polyoxometalates function as superacids,[20] ion exchangers, corrosion inhibitors, electron transfer reagents, catalysts, and photochemical oxidants.[21] Since they can accommodate a wide range of organic, organometallic, and inorganic functional groups,[22] we anticipate widespread exploration of these and other classes of inorganic molecules as self-assembled monolayers.

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