Characterization of Silicotungstate Anion Modified Metal Surfaces

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Methodologies to modify surfaces provides easy and direct ways to impart important properties to those surfaces. These properties include catalytic activity, adhesive and protective effects, and electrochemical modification. In addition to Langmuir-Blodgett techniques developed in the early 1990s, the self-assembly of monolayers provides an easy route to functionalize surfaces by immersion of the surface into the solution containing target adsorbates.[1]

The importance of immobilizing inorganic species such as polyoxometalates onto metal surfaces is several fold. First, the structural and thermal stability of these polyoxometalates is better than most organic molecules. Second, depending on the desired properties, the functionalities of the polyoxometalates can be altered at will. Polyoxometalates can accommodate a variety of functional groups, including organic, organometallic, and inorganic moieties.[2,3] Finally, polyoxometalates provide many rich electrochemical and photochemical properties that make them very applicable as superacids,[4] ion exchangers, corrosion inhibitors, electron transfer reagents, and catalysts.[5]

A majority of the polyoxometalate studies is devoted to the Keggin type of polyoxometalates, including the research currently undertaken in our group.[6-8] The structure of a typical a-Keggin anion consists of a tetrahedrally-coordinated heteroatom, X, which is surrounded by twelve MO_6 octahedra arranged in four trigonal groups as illustrated in Figure 1.
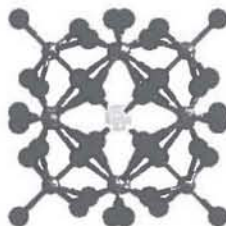
**Figure 1** Side view of a Keggin anion α-$SiW_{12}O_{40}^{4-}$. O atoms are represented by black circles, W by dark gray circles and Si by a light gray circle.

It is shown by STM images that α-$H_4SiW_{12}O_{40}$ spontaneously forms adherent, ordered monolayer arrays on both Ag(100) and Ag(111). Although STM images provide 2-D structural information on how these molecules arrange on Ag surfaces, the interaction between α-$SiW_{12}O_{40}^{4-}$ and Ag surfaces can only be elucidated by means of x-ray reflectivity measurements.

The oscillatory behavior in Figure 2 is associated mainly with constructive and destructive interference of the X-rays by the planes of W atoms from the a-$H_4SiW_{12}O_{40}$

molecule. The Si-Ag layer spacing from the best fit to the S_4 model is $Z = 4.90 \pm 0.02$ Å. Using the Z value of 4.90 Å, the calculated Ag-O bond lengths for a-$H_4SiW_{12}O_{40}$ molecules on atop, bridge, and hollow sites of the Ag(100) lattice were calculated. Only in the configuration where a-$H_4SiW_{12}O_{40}$ is centered in the hollow site with the terminal W-O bonds aligned with the (10) and (01) substrate lattice axes are all the O atoms far enough from the first layer of Ag atoms of the substrate, so that the shortest Ag_O bond length is not smaller than the sum of their covalent radii (2.00 Å).[9] The bond lengths (with Ag-O = 2.06 Å) calculated from the interface structures determined in this study uniquely establish that α-$H_4SiW_{12}O_{40}$ chemisorbs on Ag(100) surface.
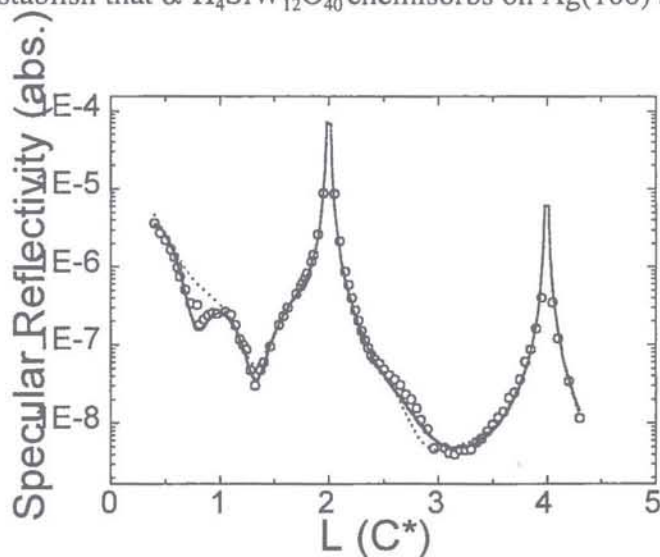
Figure 2 Specular reflectivity (represented in open circles) measured for Ag(100) at +0.10 V in 0.1 M $HClO_4$ containing 0.5 mM a-$H_4SiW_{12}O_{40}$. The solid and dotted lines are the best fits using the models with the S_4 and C_3 symmetry axis perpendicular to the surface, respectively.

Passivation behavior of α-$H_4SiW_{12}O_{40}$ on Ag surfaces are studied electrochemically and compared with the electrochemical responses on Au surfaces. The results show that on Au electrodes, a-$SiW_{12}O_{40}^{4-}$ behaves as a large anion which does not substantially inhibit solution redox response.[10, 11] In contrast, on Ag surfaces with the appropriate potential treatment, a-$SiW_{12}O_{40}^{4-}$ passivates the electrode toward subsequent solution redox chemistry. The appearance of surface-confined peaks of a-$SiW_{12}O_{40}^{4-}$ on Ag(111) surface also suggests the stronger interaction between a-$SiW_{12}O_{40}^{4-}$ and Ag surfaces. Furthermore, IR, Raman, and XPS measurements all indicate the presence of α-$H_4SiW_{12}O_{40}$ on the Ag surfaces.

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