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Scanning Tunneling Microscopy Studies of Iodide Adsorption on Au(111): Direct Observation of Adlattice Orientation

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Introduction

We report here ex situ, atomic resolution scanning tunneling microscopy images of iodide adsorbed from aqueous solution on Au(111) films on mica. In addition, we have been able to image an interface between iodide-coated and bare Au(111) substrate. Adsorbed molecules and ions play an important role in many interfacial processes, especially electrochemistry. The high lateral and vertical resolution of scanning tunneling microscopy (STM) has allowed imaging of adlayers on substrates in various environments.1 Sulfur or sulfide monolayers on metals have been atomically resolved with vacuum STM and display a variety of structural habits depending on the metal and adlayer deposition conditions.2 Recent advances in STM applied to electrode surfaces demonstrate that atomic resolution adlayer images can be obtained; Yau et al. have demonstrated the capability of imaging iodine on Pt(111) in air or electrochemical environment with atomic resolution, relying on nonvacuum preparation techniques.3 Such progress has given much hope to investigators applying STM to electrochemical systems.

To further both the variety of substrate and the STM resolution on that substrate, we have begun using epitaxial films of Au(111)

on mica67 in our electrochemical and STM endeavors. Such Au substrates are relatively inexpensive to produce in large numbers and have atomically flat areas of up to 300 × 300 nm. Several investigators have implemented Au(111)/mica in the STM study of electrochemically induced processes, such as roughening and dissolution45 of Au and metal deposition.10 In addition, Widrig et al. have recently reported in air atomic resolution STM images of n-alkanethiols on Au(111)/mica substrates,11 indicating that these substrates are ideal for the STM study of adsorbates.

Experimental Section

Preparation of Adsorbate Layers. Au(111) thin films (150 nm) were prepared by thermal evaporation of Au onto air-cleaved mica.6 High-purity Au (99.99%) was evaporated at 0.2 nm/s in a Plasmatron P-30 thin film system operating at 2 × 10⁻⁴ Torr vacuum. The mica (Asheville-Schoonmaker, Newport News, VA) was heated to 310 °C and held there for 30 min before deposition was carried out at that temperature. Once the substrates had cooled to approximately 100 °C, the chamber was backfilled with N₂ and the Au/mica films were either placed in 10⁻² to 10⁻⁵ M aqueous KI (Johnson-Matthey Grade 1, Alfa, Danvers, MA) or

solvent on top of C₆₀ clusters12 and provide evidence for symmetrical cage structure of C₆₀. Analytical HPLC showed the content of C₆₀ to be 13% in the extract and 9% in the sample sublimated at 400 °C. The results of FTIR and ¹³C NMR provided evidence for symmetrical cage structure of C₆₀. C₆₀ may form fcc or hcp crystalline structures, depending on the sublimation conditions. A new phase with tetragonal symmetry has been found, possibly formed by C₆₀ or even larger fullerenes.

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Registry No. C₆₀, 99685-96-8; C₆₀, 115383-22-7; graphite, 7782-42-5.
Samples were left in the laboratory ambient. High-purity water (Millipore Milli-Q purification system, >18 MΩ cm) was used throughout. Samples were left in the KI solutions for various times and were rinsed with water and dried in N₂ before transfer to the STM for imaging.

Instrumentation. In all cases STM images were obtained with a NanoScope II scanning tunneling microscope (Digital Instruments, Santa Barbara, CA) operated in air. Large-scale scans (350 × 350 nm) were obtained in the topographic (constant current) mode to locate the large, atomically flat crystallites, with subsequent constant-height mode used for atomic resolution images. If necessary, images were lightly filtered using the spectrum filter option of the NanoScope II software.

Typical tunneling current and bias conditions were 1–3 nA and 20–50 mV. Tunneling tips were made by electrochemically etching 0.01-in. tungsten wire at 10 V ac in 1 M KOH solution. Sometimes retouching was necessary in order to obtain noise-free images. Calibration of the piezoelectric was obtained with highly oriented pyrolytic graphite and/or bare Au(111).

Results and Discussion

STM Imaging of Bare Au(111). Shown in Figure 1 is the atomically resolved Au(111) surface imaged in air by STM. The hexagonally shaped arrays in the image are characteristic of Au(111), with a measured periodic spacing of 0.29 ± 0.02 nm. This value is in good agreement with the value of 0.29 nm reported in previous studies. Images such as those in Figure 1 were most often obtained with freshly prepared Au films, as impurities often degrade the imaging process. Atomic resolution of Au(111) surfaces is obtained on a daily basis in our laboratory with both W and 80%/20% Pt/Ir tips and tunneling conditions as described above. Tip quality is of utmost importance for imaging Au(111) and I/Au(111) in air; a good tip usually degrades with time as evidenced by the quality of the STM images, but occasionally the tip will abruptly change.

Imaging of I/Au Surfaces with STM. An STM image of a Au substrate treated with a KI solution is shown in Figure 2. The image is clearly not that of the Au(111) surface (Figure 1). We have imaged many bare Au(111) films and have never observed patterns like those in Figure 2; only Au films exposed purposely to KI solutions exhibit this packing. The nearest-neighbor and next-nearest-neighbor spacings of the periodic structure are 0.50 ± 0.03 and 0.88 ± 0.05 nm, respectively. These spacings were observed over several areas on at least six different samples. This structure is reproducible and can be imaged in areas up to 25 × 25 nm with no apparent defects (see Figure 3). The spacings obtained here are consistent with a (3√3×√3)R30° adlayer structure, which has been previously reported by LEED studies.

Figure 1. Constant-height image of a 3 × 3 nm area of an uncoated Au(111) film. $V_t = 20$ mV; $i_t = 3.0$ nA. The gray scale is 0–0.7 nm.

Figure 2. Constant-height image of a 3 × 3 nm area of an iodide-coated Au(111) substrate prepared by dosing in 10⁻² M KI solution for 30 min. $V_t = 50$ mV; $i_t = 1$ nA. Z range is 0–1 nm. The image is uncorrected for thermal drift.

Figure 3. Constant-height image of a 25 × 25 nm area of an iodide-coated Au(111) substrate prepared by dosing in 10⁻² M KI solution for 30 min. $V_t = 50$ mV; $i_t = 1$ nA. Z range is 0–0.7 nm. The image is uncorrected for thermal drift.

for I/Au. We attribute the adlayer to adsorbed iodide, which has been shown to undergo oxidative adsorption on Au surfaces from aqueous solutions. X-ray photoelectron spectroscopy data of our I/Au surfaces indicate no evidence for counterions ($K^+$), in agreement with previous Auger and X-ray photoelectron spectroscopy data. Thus, the Au/I surface is assumed to be uncharged as a result of H₂(g) evolution in protic solvents.

Variation of the iodide concentration in the dosing solution from 10⁻² to 10⁻³ M had no effect on the spacing of the adlayer as determined by STM, although bare areas could be imaged occasionally at the lower concentrations indicating defects in the layer. LEED data from gas-phase dosing with I₂ and solution dosing with aqueous I⁻ of Au(111) demonstrated several different types of surface coverages of I with respect to Au, depending on dosing conditions. Solution dosing with an iodide concentration of 10⁻³ M at fixed electrode potentials with subsequent LEED and Auger analysis showed an I surface coverage varying from 0.25 to 0.4, giving rise to three assignible LEED patterns. One of the LEED patterns observed at electrode potentials of ~0.4 to ~0.2 V vs Ag/AgCl was assigned to a (3√3×√3)R30° adlayer structure. We did not observe any packing arrangement other than the (3√3×√3)R30° structure using the aqueous dosing

treatment described here. Adsorbate concentrations below $10^{-6}$ M were not explored. LEED work on I/Pt(111) systems employing solution dosing demonstrated a dependence of adlattice unit cell with respect to the uncoated region. Previous electrochemical desorption$^{13,14}$ and quartz crystal microbalance$^{15}$ studies indicate a surface coverage with respect to the Au surface of 0.33 (i.e., 1:3 I: Au), which is consistent with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ adlattice structure.

Crystallographic Site Discrimination in Aluminophosphate Molecular Sieves by Solid-State NMR: Influence of the Field-Dependent Isotropic Second-Order Quadrupolar Shift on High-Resolution $^{27}$Al DOR NMR

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The application of double-rotation (DOR) NMR in relatively low magnetic fields proves to be particularly advantageous to enhance the dispersion of the isotropic second-order shifts of quadrupolar nuclei located in different crystallographic sites. As an illustrative example, the low-field high-resolution $^{27}$Al DOR NMR spectrum of the very large pore aluminophosphate VPI-5 is shown; the data fully support the recently reported crystal structure refinement and demonstrate the importance of the isotropic second-order quadrupolar shift for crystallographic site discrimination.

The NMR technique of magic-angle spinning (MAS) has proven to be a useful approach to resolution enhancement for spin systems of $1/2$ in the solid state by spatially averaging anisotropic interactions such as chemical shifts and by reducing dipole–dipole line broadening.$^1$ In contrast to the case of spin systems $1/2,$...