

**Scanning tunneling microscopy studies of iodide adsorption
on gold (111): direct observation of adlattice orientation**

Robin L. McCarley, and Allen J. Bard

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limited on the substrate and form their own unique ordered array. This speculation will require further TEM study. Recent STM studies indicated the presence of C_{70} on top of C_{60} clusters¹² and a new type of ordering of fullerenes and islands.¹³ The combination of XRD, ED, and STM may provide concrete information of the internal structures of individual fullerenes and the new type of structure.

Conclusions

Buckminsterfullerenes were synthesized in gram quantities by the Krätschmer-Huffman technique. The toluene extract from

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soot mainly consisted of C_{60} and C_{70} . Analytical HPLC showed the content of C_{70} 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 C_{60} . C_{60} may form fcc or hcp crystalline structures, depending on the sublimation conditions. A new phase with tetragonal symmetry has been found, possibly formed by C_{70} or even larger fullerenes.

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Registry No. C_{60} , 99685-96-8; C_{70} , 115383-22-7; graphite, 7782-42-5.

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

Robin L. McCarley and Allen J. Bard*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712
(Received: July 25, 1991; In Final Form: September 23, 1991)

Scanning tunneling microscopy is used in air to image iodide adlayers on Au(111) with atomic resolution over areas as large as 625 nm². Dosing of the Au surfaces with aqueous KI results in only one observable adsorbate structure over the iodide concentration range of 10⁻²–10⁻⁵ M. The I/Au layer has a nearest- and next-nearest-neighbor spacing of 0.50 ± 0.03 and 0.88 ± 0.05 nm, respectively, consistent with a ($\sqrt{3} \times \sqrt{3}$)R30° adlattice structure on Au(111). Direct evidence for the adlayer structure is obtained from atomic resolution images of an interface between iodide-coated and bare Au(111) regions.

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 uncoated regions, allowing direct observation of the adlattice orientation with respect to the underlying 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.^{2,3} 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.^{4,5} 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 mica^{6,7} 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 dissolution^{8,9} 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 × 10⁻⁶ 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 back-filled with N₂ and the Au/mica films were either placed in 10⁻²–10⁻⁵ M aqueous KI (Johnson-Matthey Grade 1, Alfa, Danvers, MA) or

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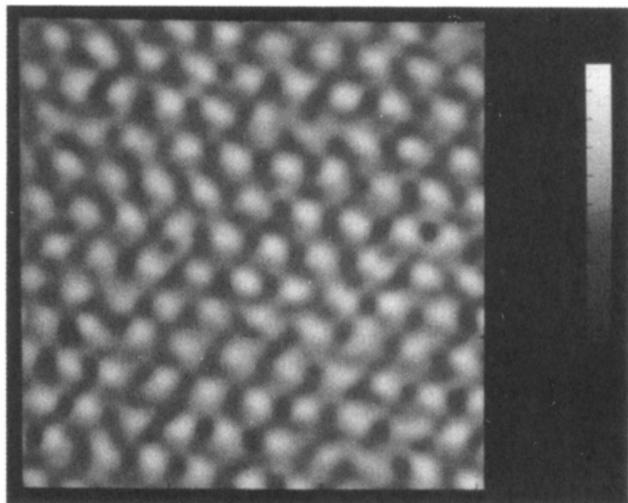


Figure 1. Constant-height image of a 3×3 nm area of an uncoated Au(111) film. $V_t = 20$ mV; $i_t = 3.0$ nA. The gray scale is 0–0.7 nm.

stored in the laboratory ambient. High-purity water (Millipore Milli-Q purification system, >18 M Ω cm) was used throughout. Samples were left in the KI solutions for various times and were rinsed with water and dried in N_2 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 reetching 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.^{7,11} 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 $(\sqrt{3} \times \sqrt{3})R30^\circ$ adlayer structure, which has been previously reported by LEED studies^{12,13}

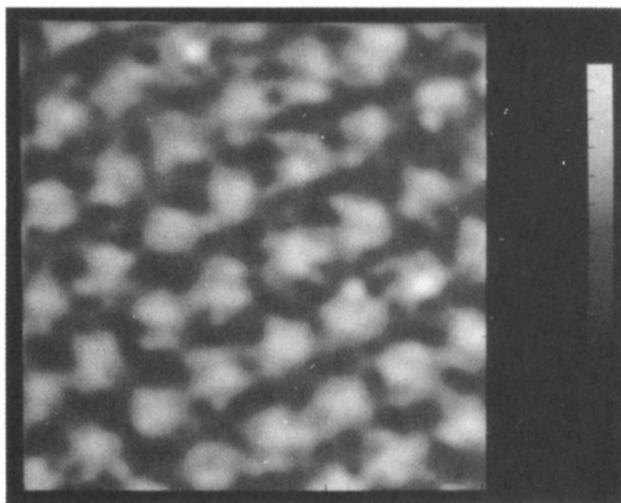


Figure 2. Constant-height image of a 3×3 nm area of an iodide-coated Au(111) substrate prepared by dosing in 10^{-2} M KI solution for 30 min. $V_t = 50$ mV; $i_t = 1$ nA. Z range is 0–1 nm. The image is uncorrected for thermal drift.

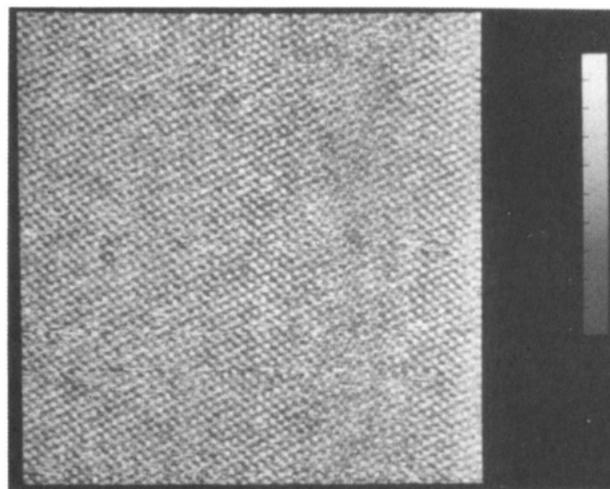


Figure 3. Constant-height image of a 25×25 nm area of an iodide-coated Au(111) substrate prepared by dosing in 10^{-2} M KI solution for 30 min. $V_t = 50$ mV; $i_t = 1$ nA. Z range is 0–0.7 nm. The image is uncorrected for thermal drift.

for I/Au. We attribute the adlayer to adsorbed iodide, which has been shown to undergo oxidative adsorption on Au surfaces from aqueous solutions.^{13,14} 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.^{12,13} Thus, the Au/I surface is assumed to be unchanged as a result of $H_2(g)$ evolution in protic solvents.¹³

Variation of the iodide concentration in the dosing solution from 10^{-2} to 10^{-5} 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 dosing¹² with I_2 and solution dosing¹³ 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 assignable LEED patterns.¹³ One of the LEED patterns observed at electrode potentials of -0.4 to -0.2 V vs Ag/AgCl was assigned to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ adlayer structure. We did not observe any packing arrangement other than the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure using the aqueous dosing

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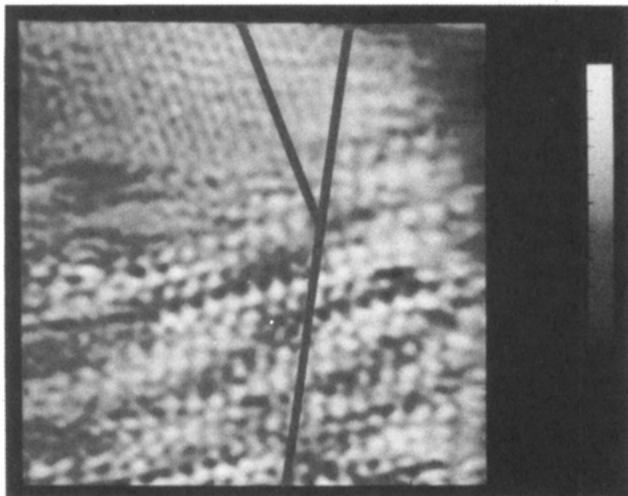


Figure 4. Constant-height image of a 9.5×9.5 nm area near an adlattice defect on a Au(111) substrate. $V_1 = 20$ mV; $i_1 = 3$ nA. Z range is 0–1 nm. Lines show direction of adlattice unit cell with respect to the underlying Au(111).

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 structure on solution dosant concentration;¹⁵ (3×3) and ($\sqrt{7} \times \sqrt{7}$) $R19.1^\circ$ structures were observed with iodide concentrations of $\geq 10^{-4}$ and $< 10^{-4}$ M, respectively. This does not appear to be the case with the I/Au(111) study here. Previous electrochemical desorption^{13,14} and quartz crystal microbalance¹⁶ 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.

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Attempts at determining the registry of adsorbates with respect to the underlying substrate using STM have been limited to studies where the substrate orientation is predetermined^{4,5} or to those where the tunneling current is increased so as to pierce through the adsorbate layer.¹⁷ There has been only one STM report of imaging the adsorbate registry, and that was performed in ultra-high vacuum.¹⁸ Figure 4 is a constant-height STM image of an I/Au–Au domain boundary (a defect region) obtained with a substrate dosed at 10^{-5} M for 30 min. Although the image is noisy near the domain boundary, the rotation and spacing of the adsorbate unit cell with respect to the underlying Au(111) are clearly delineated; the rotation is $30 \pm 2^\circ$ with respect to the Au(111). This agrees well with all the other data presented and provides direct evidence for assignment of the I adlattice structure. We know of no other *in air* STM study where a substrate/adlayer interface has been atomically resolved so as to provide orientational information. Such well-resolved images of interfaces on Au/I are not routinely obtained. Most of the time the I adlattice can be imaged, but the “bare” Au adjacent to it is not atomically resolved. This may indicate organic impurities adsorbed in these regions, but it is difficult to ascertain with the techniques we have used so far. The interfaces at these uncoated regions are not highly mobile; for example, the image in Figure 4 was observed for approximately 20 min.

Conclusion

We have reported here the first atomically resolved STM images taken in air of iodide adsorbed on Au(111) as well as the image of the I adlayer/Au interface. The I adlattice adopts a ($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ structure, consistent with previous LEED studies. The adlayer structure was independent of I^- concentration in the dosing solution and exposure time, but defects in the adsorbed layer are more readily observed at the lower dosing levels. Well-defined, defect-free regions as large as 625 nm^2 have been imaged at I^- concentrations of $\geq 10^{-4}$ M. These studies hold much promise for the real space imaging of adsorbates and their changes on Au(111) as studied by STM.

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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

P. J. Grobet,*† A. Samoson,† H. Geerts,† J. A. Martens,† and P. A. Jacobs†

Centrum voor Oppervlaktechemie en Katalyse, K.U. Leuven, Kardinaal Mercierlaan 92, B-3001 Heverlee, Belgium, and Bruker Analytische Messtechnik, Rheinstetten 4, Germany, and Institute of Chemical Physics and Biophysics, Tallinn, Estonia (Received: August 9, 1991)

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.

Introduction

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 $1/2$,

*Centrum voor Oppervlaktechemie en Katalyse.

†Bruker Analytische Messtechnik.

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