Letters

Scanning Tunneling Microscopy of Platinum Deposits on the Basal Plane of Highly Oriented Pyrolytic Graphite

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Scanning tunneling microscopy images of Pt vapor deposited on the basal plane of highly oriented pyrolytic graphite, HOPG(bp), under ultrahigh vacuum have been recorded in air at room temperature. Areas of specimens masked during Pt deposition displayed characteristic corrugations associated with bare graphite over 20×20 nm^2 areas, with no indication of surface damage or contamination over much larger sections, 400×400 nm^2. Unmasked areas of samples with coverages in the range between ca. 10% and 40%, as estimated from X-ray photoelectron spectroscopy, contained small features (5-nm average lateral dimension) with internal structures of atomic dimensions. An analysis of variance of the maximum heights for clusters observed on representative areas of 10%, 28%, and 40% Pt/HOPG(bp) specimens provided evidence that the means (ca. 0.38 nm) are not significantly different ($P = 0.80$). Hence, the three distributions appear to have been drawn from the same parent distribution. This strongly suggests that deposition of Pt on HOPG(bp) under the experimental conditions employed in this work gives rise to the preferential formation of essentially two-dimensional Pt structures on the surface.

Introduction

Fine dispersions of platinum on high-area carbon have found wide application in fuel cell technology and other industrial processes, and much effort has been devoted to their morphological, electronic, and electrochemical characterization.[1,2] Despite numerous studies, however, no concensus has been reached regarding the role of particle size effects and metal–support interactions on the electrocatalytic activity, particularly for hydrogen[3] and methanol oxidation[4] and oxygen reduction.[3,5] Work currently in progress in this laboratory has been directed toward the development of model systems to gain insight into these phenomena. The approach involves the vapor deposition of Pt on the basal plane of highly oriented pyrolytic graphite, HOPG(bp), under ultra-high-vacuum, UHV, conditions. After examination with Auger electron spectroscopy, AES, and/or X-ray photoelectron spectroscopy, XPS, the specimens are transferred under UHV to an auxiliary chamber where electrochemical experiments can be performed under extremely clean conditions.

This work will present scanning tunneling microscopy,

STM, images of specimens from which evidence has been obtained that for Pt coverages in the range between 10% and 40%, the deposits display mostly two-dimensional character.

Experimental Section

The HOPG(bp) crystals[21] were cleaved in air with adhesive tape, transferred into the UHV chamber (base pressure 2.7×10^{-8} Pa), and examined immediately with XPS, yielding ca. 3% oxygen and the remainder carbon.[6] A reduction in the amount of oxygen to <1% was observed after heating the specimen to 1300 K.

Low-energy electron diffraction, LEED, patterns obtained from various areas of the sample by using a 1-mm-diameter beam were characterized by a ring with 1–16 bright spots within a 60° arc. This is consistent with the presence of single-crystal regions no larger than 1–0.06 mm^2.

Platinum was vapor deposited onto the HOPG(bp) in the same UHV system by means of a resistively heated source. The evaporation rate was such that about 10–30 s was required to prepare the specimens. Since carbon contamination would be difficult to detect on HOPG(bp), a Pt deposition was made on a clean Ag substrate under similar conditions. No carbon or other impurities were observed by AES in this experiment.

For the STM measurements, the samples were removed from the UHV chamber, left in air for several hours in a closed container, and subsequently transferred without further precautions to the specimen holder of the microscope unit. Although various samples with Pt coverages in the range 1–50% were ex-

(1) For a recent monograph in the area of particle size effects in electrocatalysis, see: Kinoshita, K. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Conway, B. E., White, R. E., Eds.; Plenum Press: New York, 1982; Vol. 14.

(2) Sattler, M.; Ross, P. N. *Ultramicroscopy* **1986,** *20,* 21.

(3) Bagostky, V. S.; Skundin, A. M. *Electrochim. Acta* **1984,** *29,* 757.

(4) (a) Bagotsky, V. S.; Kanevsky, L. S.; Palanker, V. Sh. *Electrochim. Acta* **1973,** *18,* 473. (b) McNicol, B. D. *J. Electroanal. Chem.* **1981,** *118,* 71.

(5) Watanabe, M.; Sei, H.; Stonehart, P. *J. Electroanal. Chem.* **1989,** *261,* 375.

(6) The O percentages were calculated by dividing the area beneath the O 1s peak by the area under the C 1s peak and normalizing with the appropriate values taken from the PHI library of XPS sensitivities (C 1s = 0.296 and O 1s = 0.711).
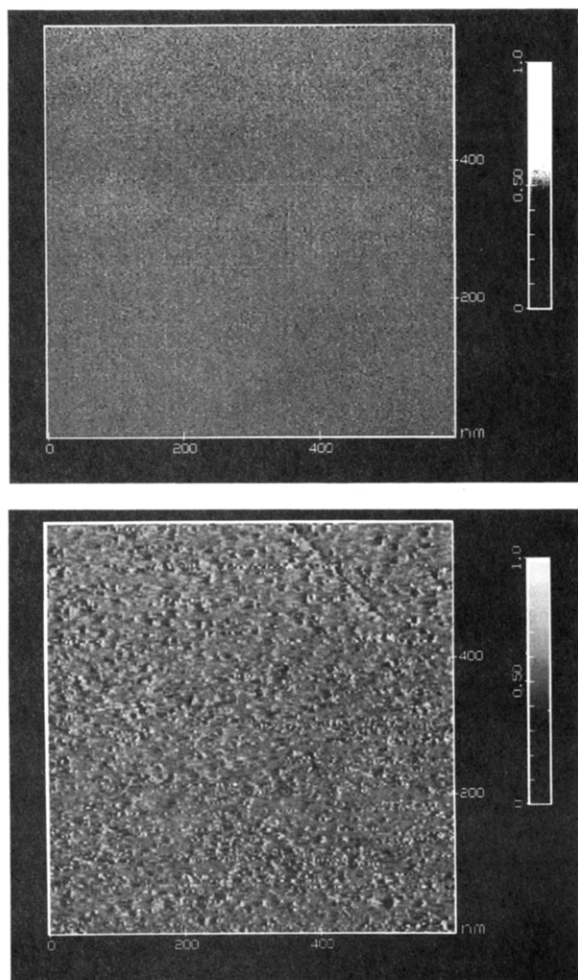
Figure 1. Low-magnification (60 × 60 μm²) images of (A) bare HOPG(bp) and (B) 10% Pt on HOPG(bp). A corresponds to a section of B that was masked while preparing B.

amined, the results presented in this work correspond to Pt/HOPG(bp) specimens with Pt/C XPS signal ratios equivalent to 10%, 28%, and 40% of a monolayer.[7]

All images were collected with a Nanoscope II (Digital Instruments) operating in either the constant-current, CC, or current imaging, CI, mode, with the latter yielding the best atomic resolution. Since the tunneling current varies exponentially with the tip to surface distance, the CI images are displayed as the logarithm of the tunneling current multiplied by a factor which scales the corrugation of clean graphite to that observed in the CC mode. Even though this calibration is rather simplistic, images obtained in the CI mode indicated within a factor of 2 the same corrugation found in the CC mode.

Results and Discussion

Figure 1 shows 0.6 × 0.6 μm² areas of a HOPG(bp) surface before (A) and after (B) deposition of 10% Pt. The image in A was actually obtained from a section of B which was masked during the deposition process. No evidence for the presence of foreign material could be detected from such unexposed sections, which displayed characteristic HOPG(bp) corrugations at sufficiently high magnification.

The 10% Pt specimen, however, was found to exhibit roughly circular features about 3–6 nm in diameter. This
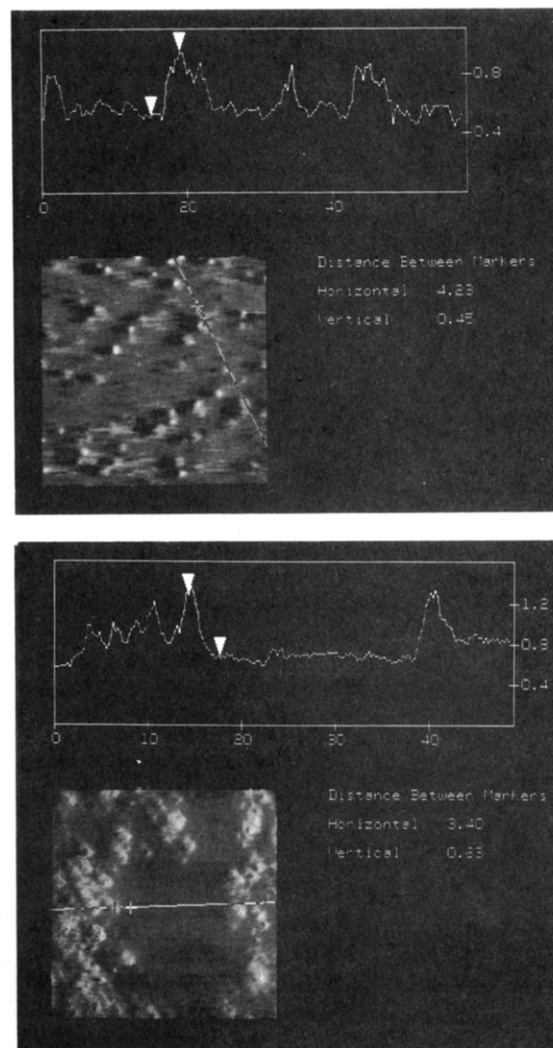
(7) The percent monolayer was determined by using the procedure described in Woodruff, D. P.; Delchar, T. A. *Modern Techniques in Surface Science*; Cambridge University Press: New York, 1989; p 112. The monolayer thickness was taken as the atomic diameter of Pt (0.278 nm). The photoionization cross sections were taken from: Goldberg, S. M.; Fadley, L. S.; Kono, S. *J. Electron Spectrosc. Relat. Phenom.* **1981**, *21*, 285.

Figure 2. Higher magnification (50 × 50 nm²) images of (A) 10% and (B) 40% Pt on HOPG(bp) with a height versus length plot along the indicated straight lines. The crosses in lower figure correspond to the inverted triangles in the upper figure. The horizontal and vertical distances between the markers are 4.33 and 0.45 nm for A and 3.4 and 0.63 nm for B in this figure, respectively.

indicates that the features in Figure 1B are indeed due to Pt deposits on the surface.

Images of 10% and 40% Pt on HOPG(bp) obtained over a 60 × 60 nm² area are shown in A and B, Figure 2, respectively. The open patch shown in Figure 2B was rather unusual. Most of the area was similar to the lower left fourth of the same figure. The depression (or shadowing) adjacent to each of the small clusters in Figure 2A is due to an artifact caused by the STM settings.[22]

The surface morphology,[8] image potential,[9] electronic polarizability,[10] and mechanical compressibility[11] may all contribute to modulating the current recorded by the STM. Thus, topographic conclusions drawn from STM measurements are often complicated. If it is assumed that surface morphology dominates the current modulation profiles, however, a number of interesting observations can be made.

The line scans in A and B of Figure 2 indicate that the maximum heights of these groupings are about 0.4 nm (vide

(8) Binnig, G.; Roher, H. *IBM J. Res. Dev.* **1986**, *30*, 355.
(9) Garcia, N. *IBM J. Res. Dev.* **1986**, *30*, 533.
(10) Spong, J. K.; Mizes, H. A.; LaComb, L. J., Jr.; Dovek, M. M.; Frommer, J. E.; Foster, J. S. *Nature* **1989**, *388*, 137.
(11) Barris, B.; Knipping, U.; Lindsay, S. M.; Nagahara, L.; Thundat, T. *Biopolymers* **1988**, *27*, 1691.
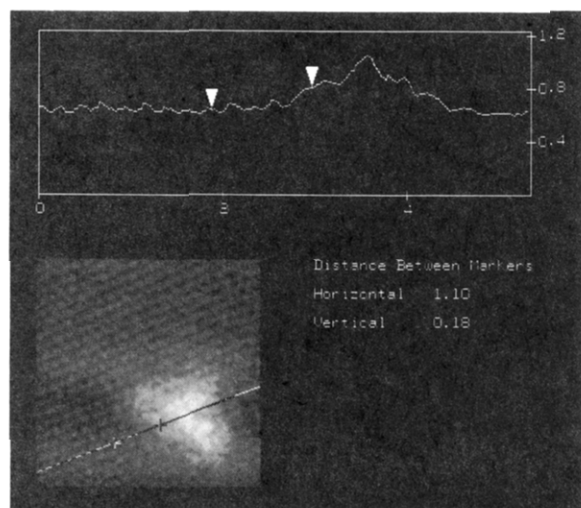
Figure 3. Section of 10% Pt on HOPG(bp) displaying an isolated island about 2.0 nm across. The insert shows a height versus length plot with a distance between markers of 1.10 (horizontal) and 0.18 (vertical) nm. This indicates atomic features on at least two different levels.
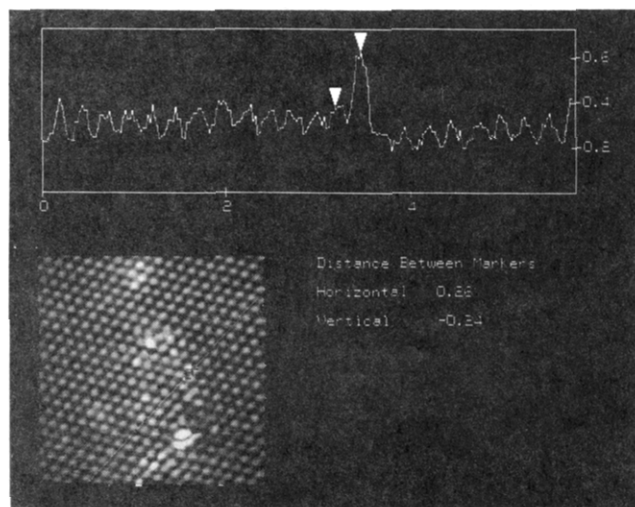

Figure 4. Area of 10% Pt on HOPG(bp) showing a group of loosely associated features composed of a discrete number of units of atomic dimensions. The line scan has been drawn along a row of α-sites.

infra). The features observed at the higher coverage appear to be lateral aggregates of the clusters seen at the lower coverage.

Figure 3 shows at yet higher magnification a group consisting of only a few atoms atop of what appears to be a wider island. This is evidenced by the line scan, in which at least two levels of atoms may be identified. Also found in this specimen were loosely associated features consisting of units of atomic dimensions (see Figure 4). The exact number of atoms observed in these images cannot be determined with certainty because the change in current due to adsorbates is not always a simple step function. This may be attributed to a delocalization of adsorbate charge into the neighboring carbon atoms. Nevertheless, the individual units were reasonably stable (surviving several scans).

A close inspection of these images revealed atomic features both in registry and out of registry with the underlying β-sites.[12] In particular, a prominent feature was observed in the scan along the α-sites (see Figure 4)

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(12) Tomanek, D.; Louie, S. G.; Mamin, H. J.; Abraham, D. W.; Thompson, R. E.; Ganz, E.; Clarke, J. *Phys. Rev. B* **1987**, *35*, 7790.

Table I.   Maximum Heights and Coverages of Pt/ HOPG(bp) Clusters

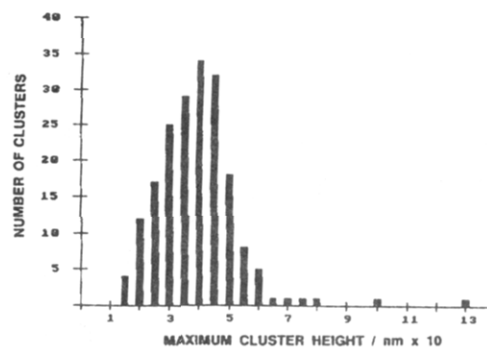| Pt/ HOPG(bp), %	no. of clusters	mean of H_{max}, nm	σ, nm
10	43	0.37	0.24
28	12	0.38	0.17
40	130	0.39	0.10

Figure 5. Histogram of maximum cluster heights for the combined set of 10%, 28%, and 40% Pt/HOPG(bp) surfaces.

with an apparent height measured with respect to the mean graphite corrugation of 0.29 nm. This value is slightly smaller than the average maximum height of the clusters described earlier. In contrast, line scans along with β-sites adjacent to the feature in Figure 4 yielded significantly less pronounced changes in the substrate corrugation. This is consistent with the feature being on a bridged β-site and thus in accordance with observations made by Ganz et al.[13] for other metals deposited on HOPG(bp). The geometric arrangement of these features rules out the possibility of artifacts due to tip effects in which case the "ghost" features would not be expected to be in registry nor have the exact lattice spacing as those observed in these images.

In direct analogy with the results obtained for Ag deposited under UHV and examined in air,[14] the dimensions of the internal structure of the Pt features observed in this work confirm that such adsorbed atoms can indeed be imaged under ambient conditions. These images are also remarkably similar to those reported for similar Ag, Al, Cu, and Au specimens, in which both the deposition and imaging were performed under UHV.[13] It may be noted that recently Shimazu et al.[15] have obtained STM images of Pt microparticles dispersed electrochemically onto glassy carbon. These, however, did not reveal any evidence for atomic size features within the clusters.

Representative areas of 10%, 28%, and 40% Pt/HOPG-(bp) specimens involving a total of almost 200 clusters were carefully examined in order to establish correlations between the maximum heights, H_{max}, of the clusters and the coverage. An analysis of variance[16] for H_{max} of these specimens provided evidence that the means were not significantly different ($P = 0.80$) (see Table I). Hence, the three distributions appear to have been drawn from the same parent distribution.

The total cluster distribution in terms of H_{max}(avg) is displayed in the form of a histogram in Figure 5. Also analyzed were the average widths, W_{avg}, defined as the mean average of the maximum lateral dimension of the

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(13) Ganz, E.; Sattler, K.; Clarke, J. *Surf. Sci.* **1989**, *219*, 33.

(14) Abraham, D. W.; Sattler, K.; Ganz, E.; Mamin, H. J.; Thompson, R. E.; Clarke, J. *Appl. Phys. Lett.* **1986**, *49*, 853.

(15) Shimazu, K.; Uosaki, K.; Kita, H.; Nadasaka, Y. *J. Electroanal. Chem.* **1988**, *256*, 481.

(16) *Biometry*; Sokal, R. R., Rohlf, F. G., Eds.; W. H. Freeman: San Francisco, 1969; p 208.

cluster along and perpendicular to the scan direction. The means in this case ($W_{avg}(10\%)$ = 4.7 nm; $W_{avg}(40\%)$ = 7.9 nm) were found to be significantly different.

On the basis of these results, is may be concluded that within statistical error the clusters appear to be predominantly flat in shape and that their apparent height is independent of the coverage in the range of coverages studies.

Preliminary experiments were conducted on a 1% Pt/HOPG(bp) sample prepared by evaporating Pt at a rate more than 10 times slower than that employed for the higher coverages. H_{max} for this sample was smaller than that observed for the higher coverages (mean of H_{max}-(1%) = 0.24 nm, σ(1%) = 0.085). W_{avg}, however, was found to be about 6.0 nm, in between W_{avg} of the 10% and 40% specimens. Such an apparent discrepancy may be attributed to differences in the evaporation rates rather than to the coverage.[17]

Two of the samples (10% and 28% Pt on HOPG(bp)) were examined by XPS after the STM measurements were completed, yielding a 3-4-fold increase in the amount of oxygen. The best fit to the oxygen signal before and after the STM experiments was obtained by a sum of two Gaussian–Lorentzian curves centered at 532.9 and 531.4 eV, with the latter becoming more prominent after exposure to air. It may be noted that these binding energies are similar to those reported for H_2O (533.2 eV)[18] and PtO_2 (531.4 eV).[19] Unfortunately, it does not appear possible at this time to establish whether all or only part of the Pt oxidizes,

and therefore it is not clear whether the features observed with STM correspond to single atoms or to PtO (or PtO_2). Besides Pt, C, and O, no other elements could be observed in the XPS survey scan after reintroduction of the specimen to the UHV system. Within the level of sensitivity of the XPS instrument, the amount of Pt before and after STM examination was found to be identical.

Experiments are now in progress in this laboratory to extend these studies to depositions involving yet smaller amounts of Pt at lower substrate temperatures to obtain more uniform atomic dispersions on the HOPG(bp) surface. This prospect appears very attractive as it may open the possibility of studying the reactivity of single isolated supported Pt atoms on an inert, well-defined and electronically conducting substrate, as well as various aspects of metal growth on such supports.[20]

(17) *Thin Film Phenomena*; Chopra, K. L., McGraw-Hill: New York, 1969; p 137.

(18) Wagner, C. D.; Zatko, D. A.; Raymond, R. H. *Anal. Chem.* **1980,** *52,* 1445.

(19) Contour, J. P.; Mouvier, G.; Hoogewijs, M.; LeClere, C. *J. Catal.* **1977,** *48,* 217.

(20) Scott, R. R.; White, H. S.; McClure, D. J. *J. Phys. Chem.* **1989,** *93,* 5253.

(21) The HOPG specimens were kindly provided by Dr. Arthur Moore from Union Carbide, Cleveland, OH.

(22) Scans over large areas usually yielded images in which the HOPG-(bp) surface appeared at an angle with respect to the *XY* plane of the tip. Images acquired in the current imaging mode required the use of high enough amplification in the feedback loop controlling the Z-piezo to prevent the tip from crashing into the HOPG(bp) surface. The artifact in A, Figure 2, is dependent on the gain settings of the feedback loop.

Ionic Interactions Play a Major Role in Determining the Electrochemical Behavior of Self-Assembling Viologen Monolayers

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Electrochemical and quartz crystal microbalance (EQCM) methods are used to probe the redox behavior of self-assembled monolayers of viologen derivatives with long alkyl chains and disulfide or thiol groups which provide for attachment to gold electrodes. The EQCM measurements revealed that (1) anions exit and enter the viologen monolayer during reduction and oxidation, respectively, and (2) water molecules also exit and enter the monolayer during reduction and oxidation, respectively, but in amounts which depend on the identity of the anion. The temperature dependence of the full width at half-height of the cyclic voltammetric peaks (E_{fwhh}) for monolayers with different anions was suggestive of normal thermal broadening for the case of Cl$^-$ and NO$_3^-$ and of some type of attractive interaction between the redox groups, which increased in importance as temperature increased for the ClO$_4^-$ case. The E_{fwhh} data for the Cl$^-$ and NO$_3^-$ cases rule out the possibility of hydrophobic interactions between the alkyl chains as the source of these attractions, so the ClO$_4^-$ data are interpreted as being due to strong ionic interactions between the ClO$_4^-$ anions and the viologen dications, probably of the ion-pair type.

The recent interest in self-assembled monolayer systems stems from a recognition of the potential for their use in detailed studies of structure–function relationships at the solid–liquid interface. The monolayers prepared from sulfur-containing species, such as thiols and disulfides, at Au surfaces have been especially well studied because of their tendency toward forming quasi-crystalline monolayers with well-defined structures.[1] This is due, at least