ChemComm

In situ STM observation with atomic resolution on platinum film electrodes formed by a sputtering method

Shueh-Lin Yau,[a] Takahiro Moriyama,[b] Hiroyuki Uchida[b] and Masahiro Watanabe*[b]

[a] *Department of Chemistry, National Central University, Chungli, Taiwan, ROC. E-mail: sly@rs250.ncu.edu.tw*
[b] *Laboratory of Electrochemical Energy Conversion, Faculty of Engineering, Yamanashi University, Takeda 4-3, Kofu, 400-8511, Japan. E-mail: mwatanab@ab11.yamanashi.ac.jp*

Received (in Cambridge, UK) 6th September 2000, Accepted 10th October 2000
First published as an Advance Article on the web

The first high-quality *in situ* STM atomic images of sputtering-deposited platinum film electrodes potentiostated at 0.15 V (*vs.* RHE) in 0.1 M $HClO_4$ are reported showing that potential-induced hydrogen adsorption effectively cleaned the Pt surfaces with predominantly (111)-oriented facets.

The invention of the scanning tunneling microscope (STM) in the early 1980s has revolutionized the study of interfacial structures.[1] It is now extensively used to examine single crystals as well as thin-film materials.[2,3] The strength of STM techniques lies at its sub-nanometer resolution to reveal atomic structures, so far mostly for well ordered interfaces. It is much more difficult to achieve atomic resolution on microscopically rough thin films. Gold films thermally evaporated onto glass or mica have been the only exceptions.[4] Meanwhile, platinum, a widely used electrocatalyst, has been examined by STM but so far only on single crystal electrodes.[2] The more practical polycrystalline or filmy Pt materials have been overlooked. As a new methodology for developing alloyed catalysts, Watanabe and Motoo studied electrocatalysts by mixing a variety of d-transition metals with Pt and discovered the unique electrocatalytic activity of Pt/Ru alloys, accounted for by a bifunctional mechanism.[5] Watanabe and coworkers also recently demonstrated that sputtering is a simple but extremely useful method for the development of new electrocatalysts. The less noble metals such as Fe are found to leach out in acidic solutions, resulting in a thin Pt skin layer with modified electronic structure, which exhibits high CO-tolerance towards H_2 oxidation[6] or high O_2 reduction.[7] The present STM study of Pt film electrodes marks the beginning of our onward effort to explore the interaction between electrodes and adsorbates in Pt-based electrocatalysts at an atomic level.

We prepared platinum thin films of 90 nm thickness by argon-sputtering onto glass at room temperature in the same manner as described previously[6,7] using an rf-magnetron sputtering device (Anelva SPF-332H) and a Pt target with a purity of 99.9% (Tanaka Kikinzoku, Kogyo, Japan). The sputtering chamber was evacuated to $< 5 \times 10^{-4}$ Pa and the argon gas pressure for sputtering was 0.5 Pa. Because Pt films do not adhere tightly to glass substrates, we usually deposited interlayers of titanium and gold prior to that of Pt, these being deposited at room temperature and 300 °C, respectively. The cleaning procedure involved sonication in acetone and alcohol and rinsing with copious amount of triple-distilled water (Bransted Co., New Jersey). The rates of deposition for all the films were estimated to be *ca.* 7 nm s^{-1}. The scanning tunneling microscope (STM) was a Nanoscope E (Digital Instruments, Santa Barbara) equipped with an A-type head for high resolution. All experimental details have been previously described.[2] Several different areas of the samples were examined to ensure that the STM showed general surface features of the Pt film.

Fig. 1 shows typical STM images obtained on a Pt film electrode grown by the procedure described above. The potential of Pt was held at 0.15 V (*vs.* RHE) and the electrolyte was 0.1 M $HClO_4$. Typical STM parameters at this magnification are 100–200 mV bias voltage and 1–3 nA feedback current. Repeated potential cycling between 0 and 1 V, which activated the Pt electrode, preceded the STM imaging. Holding the potential at 0.15 V resulted in a nearly saturated amount of hydrogen atoms at the surface. The 200 × 200 nm image in Fig. 1(a) reveals two morphologically different regions separated by a sharp domain boundary. The upper region is reminiscent of rolling hills, whereas the lower half exhibits clear steps and facets, as shown by the image in Fig. 1(b).

While high-quality STM imaging was difficult for the upper domain, STM could discern the atomic structures of the lower domain. We inspected the appearance of the facets and zoomed into a flat region. Optimization of resolution is necessary through adjusting the bias voltage and feedback current. We found a 50 mV bias voltage (tip positive) and 10 nA feedback current led to clear atomic resolution, as shown in Fig. 1(c). Note that this is an original image without any data processing. The interatomic spacing of 0.27 nm for this hexagonal array is in accord with that of Pt(111). Each protrusion gives rise to a corrugation height of 0.025 nm, as found on a Pt(111) single crystal electrode.[8] Typically, the atomic array spans an area of 10 nm^2. To our knowledge, this is the first observation of atomic features for filmy Pt electrodes.

Fig. 1(d) reveals an atomic image with three extraordinarily bright stripes (indicated by arrows). Close inspection of the image discloses mis-alignment of the atomic rows on the two sides of these pointed features, as outlined by the dotted line. The atomic spacing at these strain regions differs from the ideal value of Pt. While unseen for Pt single crystal electrodes, these dislocation defects may result from how the film is grown, *i.e.* the nucleation-and-growth mechanism. In addition, STM expectedly revealed a high density of steps and kinks but no ordered (100) and (110) domains have ever been observed at a potential of 0.15 V. The reason for the prominence of the (111) hexagonal arrangement could be its superior thermodynamic stability, which guides the deposition of the films. However, the hydrogen atoms adsorbed at 0.15 V could serve to reconstruct the atomic arrangement of the surface from a roughened one to well ordered (111). This view is supported by the cyclic voltammetry (CV) (solid line in Fig. 2). This CV was recorded after the potential was held at 0.22 V for 20 min, resulting in a current spike at 0.76 V in the following anodic scan. This feature, tentatively assigned as the ‘butterfly’ feature,[9] is striking because it is known to be a characteristic of well-ordered Pt(111) electrodes.[10] It is intriguing that unlike the normal CV for Pt(111), there is no corresponding feature in the following cathodic scan. This result may indicate that the (111) structure on the Pt films was unstable upon potential excursion to 1 V. This result bears some resemblance to the potential-induced roughening of a Pt(111) electrode, although this occurs at a somewhat higher potential.[9] Continuous potential sweeps between 0.05 and 1.4 V result in a steady-state CV profile shown by the broken line in Fig. 2. No ‘butterfly’ feature emerges without prolonged potential holding within the hydrogen region in the pure electrolyte.

DOI: 10.1039/b007222m

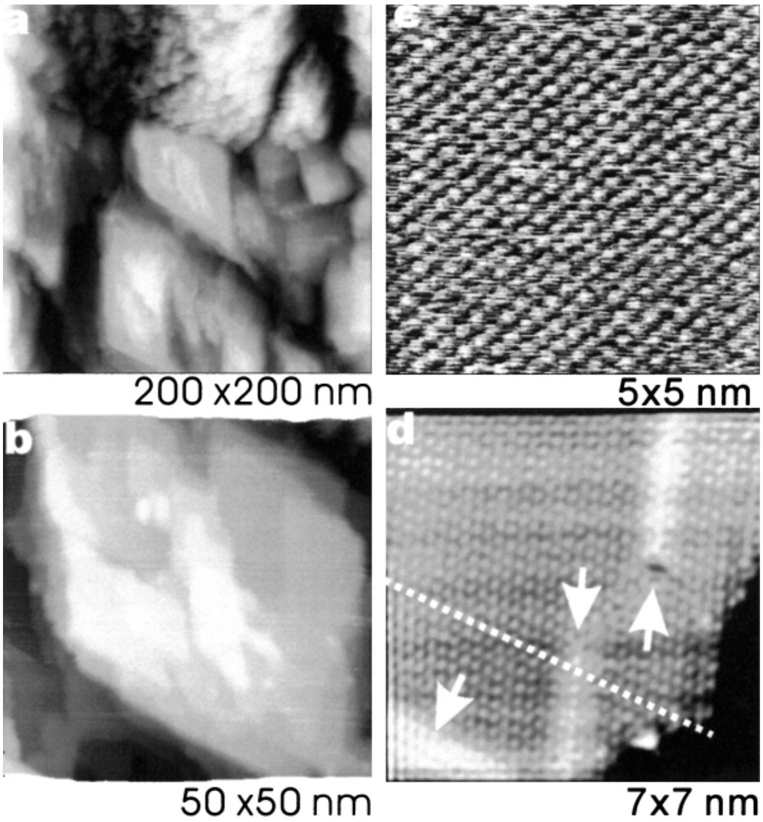

Fig. 1 *In situ* STM topography images, showing two morphologically different domains (a) and the crystalline domain (b), atomic resolution (c), and dislocation defects (d) found at a platinum film. The potential of the Pt film was set at 0.15 V and the imaging conditions in bias potential and feedback current are 100 mV and 3 nA for (a) and (b), and 50 mV, 10 nA for (c) and (d), respectively.

The dotted trace resembles that of a polycrystalline Pt electrode, including typical features of hydrogen adsorption–desorption between 0.05 and 0.35 V, with oxide formation and reduction between 0.5 and 1.4 V.[11] The former features have been examined and they are shown to correlate with the adsorption of hydrogen at (100) and (110) types of sites. Despite presenting only ordered (111) structures, the Pt surfaces also contain intrinsic surface features of steps, kinks and dislocations. We are interested in the roles of these surface structures and defects in guiding interfacial electrochemical events, such as the oxidation of carbon monoxide. More *in situ* STM studies along this vein are currently being investigated.

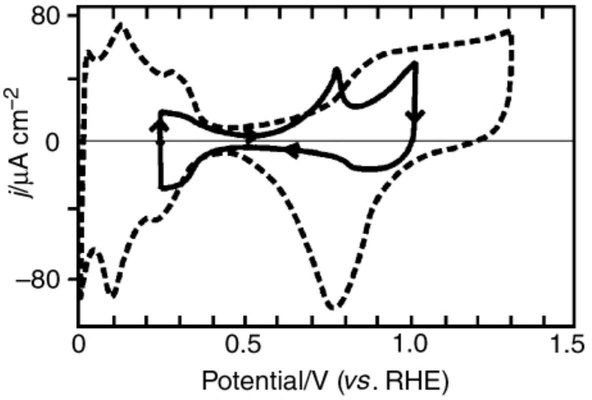

Fig. 2 Cyclic voltammograms of a Pt film electrode in 0.1 M $HClO_4$ at a scan rate of 50 mV s^{-1}. The solid trace represents the first scan after potential holding for 20 min at 0.22 V. The arrows indicate the scan direction. The dashed line represents the steady-state CV of the Pt film electrode.

Financial support from CREST of The Japan Science and Technology (JST) Corporation are gratefully acknowledged.

Notes and references

1 G. Binning, H. Rohrer, Ch. Gerber and E. Weibel, *Phys. Rev. Lett.*, 1982, **49**, 57.
2 For a review, see: K. Itaya, *Prog. Surf. Sci.*, 1998, **58**, 121.
3 N. G. Semaltianos and E. G. Wilson, *Thin Solid Films*, 2000, **366**, 111.
4 S.-G. Gun, W.-B. Cai, L.-J. Wan and M. Osawa, *J. Phys. Chem.*, 1999, **103**, 2460.
5 For an example, M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, 1975, **60**, 267.
6 M. Watanabe, H. Igarashi and T. Fujino, *Electrochemistry*, 1999, **67**, 1194.
7 T. Toda, H. Igarashi, H. Uchida and M. Watanabe, *J. Electrochem. Soc.*, 1999, **146**, 3750.
8 S.-L. Yau, Y.-G. Kim and K. Itaya, *J. Am. Chem. Soc.*, 1997, **101**, 3547.
9 J. Clavilier, A. Rodes, K. El. Achi and M. A. Zamakhchari, *J. Chim. Phys.*, 1991, **88**, 1291.
10 F. T. Wagner and P. N. Ross, *J. Electroanal. Chem.*, 1988, **250**, 301.
11 T. Frelink, W. Visscher and J. A. R. Van Veen, *Electrochim. Acta.*, 1995, **40**, 545 and references therein.