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Scanning Tunneling Microscopy with Atomic Resolution in Aqueous Solutions

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A scanning tunneling microscope was constructed for in-situ electrochemical studies. The apparatus could provide atomic resolution of a highly oriented pyrolytic graphite (HOPG) surface in both air and aqueous solutions. The electrodeposition of platinum (Pt) on the surface of HOPG was investigated.

The scanning tunneling microscope (STM) can provide surface topographic imaging and analysis in various environments.[1,2] It has been well demonstrated to image the surface of graphite with atomic resolution in ultra-high vacuum (UHV)[3] and air.[4] However, recent papers describing STM for samples immersed in aqueous solutions[5-9] have suggested that STM will become a powerful tool for in-situ electrode surface characterization. It has been reported that STM could be operated in an electrochemical cell to observe Ag[8] and Au[9] deposits on a graphite substrate. On the other hand, an ex-situ STM in air for the determination of the topography of electrochemically prepared aluminum oxide has been described in our previous paper.[10] Although an ex-situ determination of the electrode nanotopography has recently been reported by Vázquez et al.,[11] it is reasonably expected that in-situ observation will be much useful for electrochemical studies in general.

We describe here an in-situ STM apparatus that has atomic resolution in aqueous solutions. Preliminary results of the electrochemical deposition of

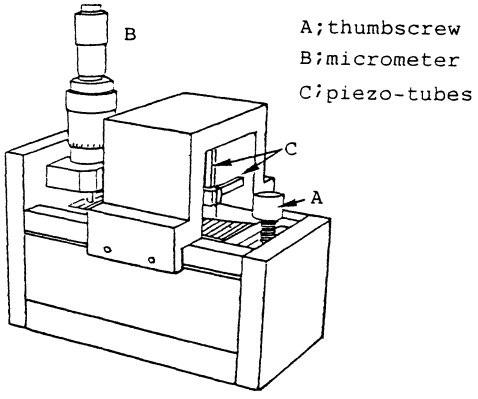

Fig. 1. Illustrative depiction of the STM apparatus.

platinum (Pt) are also presented here.

The microscope illustrated in Fig. 1 uses three orthogonal pairs of piezoelectric tubes (Tokin Co. N-21) in a three-axis micropositioner. The thumbscrew (A in Fig. 1) is the coase adjustment that allows the sample surface to be brought to within 10 μm of the tip under an observation of an optical microscope. A differential micrometer (Mitsutoyo Co.) attached to a spring is used to bring the sample within the tunneling range of the tip. The electrochemical cell, not shown, is a three-electrode type with a HOPG (Union Carbide Co.) working electrode, a Pt quasi-reference electrode, and a Pt counter electrode. The tip was made of pure Pt wire (diameter; 65 μm) and completely covered with a soft glass. Although many sophisticated methods to prepare Pt ultra-microelectrodes have been recently described by Bard et al.[7] and the present author,[12] the electrode used here was simply exposed by turning on a lathe and sonicated in concentrated sulfuric acid for 1 h before use. The background current, which should be less than the tunneling current, was only ca. 0.2 nA in 0.05 M H_2SO_4. A typical tunneling current used in this study was 4 nA, so that the background current was only about 5% in the total set current in the STM measurement.

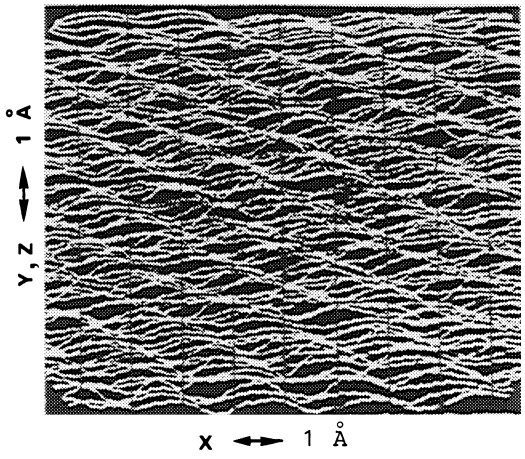

Fig. 2. Image of the graphite surface in water. The current was 4 nA. The tip was +70 mV.

Figure 2 shows a typical example of STM topography of HOPG in deionized water. It can be seen that the individual carbon atoms appear with corrugation height of ca. 1-2 Å. Similar values obtained in water have been reported by Hansma et al.[5,6] We found that atomic resolution images of graphite can be also obtained in a relatively high concentration of sulfuric acid (0.05 M H_2SO_4 or even more). The above results strongly encouraged us to explore its potential application as a powerful tool for in-situ electrochemical studies with an atomic resolution.

The electrodeposition of Pt particles on a glassy carbon (GC) electrode has been described in our previous papers where it was discussed that the Pt deposition on a GC electrode was a typical example of the nucleation and growth

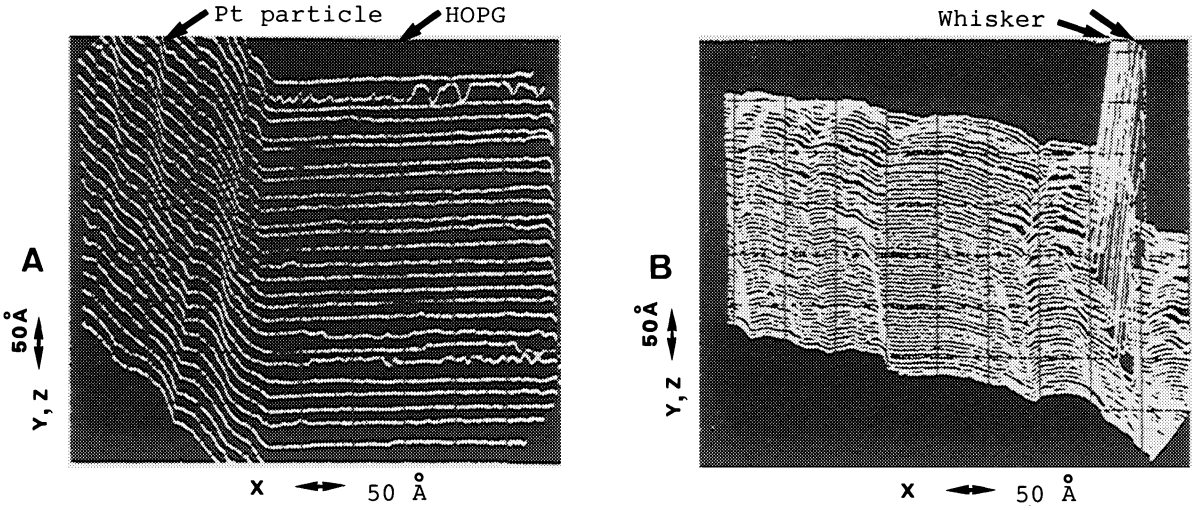

Fig. 3. Images of a Pt particle on HOPG obtained in water with tunneling current of 4 nA. The tip was +100 mV with respect to the graphite.

of the electrodeposition.[13] It is found in this study that almost identical cyclic voltammograms are recorded at a HOPG electrode, although the onset of the nucleation is ca. 0 V vs. SCE (saturated calomel electrode)in 0.05 M H_2SO_4 which is more negative than that (0.2 V vs. SCE in 1 M H_2SO_4)[13] obtained at a GC electrode. The electrodeposition of Pt was carried out by successive potential cycles in a 0.05 M H_2SO_4 solution of 5 mM K_2PtCl_6 in the same method as described previously.[13] The tunneling tip was not used as an electrode during the electrodeposition. After the electrodeposition of Pt particles, the above Pt solution was replaced by deionized water or 0.05 M H_2SO_4 in order to avoid the deposition of Pt on the Pt tunneling tip during the observation of STM.

Figure 3 shows two examples of STM topography obtained in water for a HOPG electrode with a Pt loading level of ca. 20 mC/cm^2. Figure 3-A shows just an edge of a semispherical Pt particle existing on an atomically flat surface of HOPG. When the tip was scanned over the flat region showed in Fig. 3-A, only the atomically flat surface appeared on the storage oscilloscope screen. Under the same magnification as that in Fig. 2, an identical atomic corrugation due to the graphite structure was observed. Figure 3-B was taken on the Pt particle when the position of tip was shifted to the left-hand side of Fig. 3-A. It might be seen in Fig. 3-B that there are two or three whiskers whose sizes were ca. 100-200 Å in height and 10-20 Å in diameter, respectively. It is also easily seen that the shape of the Pt particle is not a completely smooth semisphere. There are many irregular dislocations such as steps and boundaries. The same sample was examined with a conventional scanning electron microscope (SEM) after the observation of

STM. SEM photographs showed semispherical Pt particles on a flat surface of HOPG whose size were in a range of 1000-2000 Å in the diameter. However, the fine structures as shown in Fig. 3 could not be resolved by SEM.

Finally, it is noteworthy that some parts of the apparently flat surface of HOPG showed a very noisy signal in the tunneling current. This behavior might be due to the exsistance of a single Pt ad-atom or clusters. Attempts to image these ultra-micro particles of Pt has not been successful yet on HOPG. However, it is possible to reduce the size of the Pt particle under carefully controlled electrochemical conditions for the electrochemical deposition of Pt. The initial stage of the electrodeposition is now of special interest.

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