In Situ Scanning Tunneling Microscopy of the Anodic Oxidation of Highly Oriented Pyrolytic Graphite Surfaces

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The scanning tunneling microscope (STM) was used to follow the in situ anodic oxidation of highly oriented pyrolytic graphite (HOPG) in 0.1 M H₂SO₄. Prior to electrochemical cycling, the HOPG sample appeared atomically flat and atomic structure was observed with the surface under potential control. Cycling between 0.0 and 1.8 V vs AgQRE (silver wire quasi-reference electrode) resulted in the formation of an amorphous graphite oxide overlayer structure exhibiting reduced barrier heights to tunneling, which grew isotropically into the basal graphite plane. With continued cycling this structure completely covered the surface, forming a rough amorphous film. These images suggest that the graphite oxide overlayer formation occurs according to a nucleation and growth mechanism.

Experimental Section

The STM used in this study represents an evolution of the designs first developed by Kaiser and Jaklevic and Hansma and coworkers and is shown in Figure 1. The sample was bolted to a glass plate with bolts and clips made from Kel-F and Teflon, respectively. The plate was pressed against three stainless steel threaded rods with Viton O-rings. The threads were protected from the solution by small glass cups glued to the sample holder. The XYZ translator was fabricated from a piezoceramic tube, while the tip was placed in a small holder, which was glued to a Macor standoff fixed to the tube and fastened with a set screw. The tube and holder were wrapped with Parafilm, and the tip–holder junction was sealed with silicon stopcock grease to isolate them from the solution. A piezoceramic block under the tube, actuated with a 30-s time constant, provided active compensation for thermal drift. Coarse approach of the tip to the sample was first accomplished by rotating two of the threaded rods until the sample was within 1 mm of the tip. The third threaded rod was then withdrawn slowly by a stepping motor driven by a reduction gear until tunneling current was sensed. The STM was placed on a 30-kg plate suspended from the ceiling with rubber cords. Because the sample and sample holder are immersed into the solution, this design allows the use of substantially larger electrolyte volumes (ca. 40 mL) than those previously used in other high-resolution instruments (ca. 0.2 mL). Large volumes are useful because this minimizes changes in electrolyte concentration over the duration of the experiment, allows one to use larger, more readily replaceable reference and auxiliary electrodes, and makes it easier to seal the cell and das the solution.

The STM electronics used were standard, with the exception that a potentiostat was used to hold the sample at virtual ground. Bias was applied through the tip, and the tunneling current was measured here as well by using a subtraction circuit to remove the contribution from the applied voltage. Potential measurements were made relative to a silver wire quasi-reference electrode (AgQRE), with the voltage sweep provided by a PAR Model 175

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universal programmer. The auxiliary electrode was a 1.5-cm² Pt flag. Barrier height measurements were made by modulating the tip-sample distance by 0.5 Å at 15 kHz, locking in on the tunneling current by using a PAR 5206 lock-in amplifier equipped with a Model 5048 Lin/Log Ratiometer and recording d(log i)/ds, where i is the tunneling current and s the tip-to-sample distance. Data acquisition was with an IBM PC-AT computer equipped with a Keithly Series 500 interface. The barrier height, \( \phi \), was then obtained via the Fowler–Nordheim relationship where \( \phi = \frac{1}{2} \frac{d \log i}{ds} \frac{1}{1.0251} \).

The STM tip was made by electrochemically etching a 125-μm Pt–Ir rod to a point and coating with insulating varnish (Epoxyline 6001, Epoxyline Corp., Irvine, CA). This insulation minimizes the faradaic contribution to the tip current and leaves an estimated bare metal area of ca. 10000 Å².

Highly oriented pyrolytic graphite was obtained from Dr. Arthur Moore of Union Carbide Corp., Parma, OH. Electrical connection to the sample was made by attaching a copper wire to the material with silver paint and then covering the entire wire and contact with Torr-Seal epoxy cement (Varian, Lexington, MA). The edges of the sample were sealed with silicone rubber adhesive sealant (GC Electronics, Rockford, IL), leaving an exposed sample area of about 0.2 cm². H₂SO₄ was reagent grade (21) (a) Gewirth, A. A.; Craston, D. H.; Bard, A. J., to be published. (b) Wightman, R. M. In Electroanalytical Chemistry; Bard, A. J., Ed.; Marcel Dekker: New York, 1988; Vol. 15.


Results and Discussion

Constant-height images of the atomic surface structure of graphite in air and in 0.1 M H₂SO₄ at 0.05 V vs AgQRE are shown in Figure 2. In these images the tunneling current was 5 nA (with 0.02-nA background in solution) and the tip bias was −50 mV, yielding a tunneling resistance of 10⁷ ohms. While the resolution of the image observed in air is somewhat better than that in solution, our ability to obtain these images demonstrates that atomic resolution images in solution are achievable with reasonable tunneling resistances and with the sample under potential control. The reduction in image quality in aqueous solution when coated tips are used may be a result of some residual insulation remaining on the tip. Of particular note in the image obtained in air is a disordered region where the lattice appears through a kink; as discussed below, these kink sites appear to be important in the way the surface oxidizes during anodization.

A 600-Å constant-current STM image of the HOPG surface in 0.1 M H₂SO₄ at 0.05 V vs AgQRE is shown in Figure 3A. Consistent with a previous report in a different electrolyte, this surface is atomically flat over large areas. An additional measure of the smoothness and lack of contamination of these surfaces, even in electrolyte solution, is the featureless barrier height (d(log i)/ds) (Figure 3B) during the scan to record the topographic image. The barrier height to tunneling was 0.9 eV, consistent with that found previously in a vacuum. These images were stable for several hours at 0.05 V vs AgQRE, and atomic resolution could be obtained at any time with the potential held

\( \text{Figure 1. Design of the STM used in this study: (a) steel support plate; (b) piezoceramic tube scanner; (c) Viton O-ring bands; (d) piezo for thermal drift compensation; (e) glass sample plate; (g) 4-80 stainless steel threaded rod; (h) brass holders; (i) glass cups; (k) tip; (m) Kel-F and Teflon sample holders; (n) tip holder. Scale is indicated.} \)

\( \text{Figure 2. Constant-height STM images of highly oriented pyrolytic graphite in (A) air and (B) 0.1 M H₂SO₄ with the sample held at 0.05 V vs AgQRE. } V_{\text{top}} = -50 \text{ mV, } I_{\text{tip}} = 5 \text{ nA. Scan speed was } 780 \text{ Å/s and the corrugation amplitude was } 1.2 \text{ nA.} \)
Figure 3. Constant-current STM images (A, C, E) and d(log i)/ds scans of the same areas (B, D, F) of the anodic oxidation of highly oriented pyrolytic graphite in 0.1 M H$_2$SO$_4$ at 0.05 V vs AgQRE. $V_{tip} = -50$ mV, $I_{set} = 7$ nA. Scan speed was 260 Å/s. (A) HOPG topograph before oxidation and (B) corresponding barrier height measurement (barrier height, 0.9 eV). (C) HOPG topograph after 20 potential cycles and (D) corresponding barrier height. (Barrier height decreases in the upward directions.) (E) HOPG topograph after further oxidation of the surface and (F) corresponding barrier height.

Cycling the potential of the HOPG electrode between 0.0 and 1.8 V vs AgQRE at 200 mV/s yielded cyclic voltammograms showing the characteristic oxidation wave at 1.8 V and a slightly diminished reduction peak at 1.5 V. The oxidation wave has been attributed to a combination of graphite oxidation and the intercalation of HSO$_4^-$ into the graphite lattice. The oxidation of graphite is chemically (but not thermodynamically) reversible, and the reduction wave is attributed to reduction of graphitic oxide and to deintercalation of HSO$_4^-$. In dilute acid solutions, such as that used here, the redox process is less reversible; during the oxidation process the graphite structure is thought to be disturbed, with bonds on the surface broken (possibly due to hydrolysis) and a residual, partially insulating, oxide overlayer, which is stable at 0.05 V vs AgQRE, formed.

At this value. This implies the HOPG surface is quite inert and does not absorb or intercalate material from the solution at this potential.

After 10 cycles STM images at this potential showed widely scattered irregular protrusions between 20 and 30 Å high and about 100 Å in area growing out of the flat HOPG background. Atomic resolution was still obtainable in the flat areas, indicating that no adsorption or surface modification had taken place there. In contrast, the protruded regions showed greatly diminished barrier heights (less than 0.25 eV) and no resolved atoms. A similar effect was observed by Sonnenfeld and Schardt in their study of Ag deposition on graphite.

After another 10 potential cycles, the islands of surface corrugation grew together anisotropically giving STM topographic images such as that shown in Figure 3C. Flat areas of unoxidized graphite, with barrier heights (Figure 3D) of ca. 0.9 eV, were interleaved with channels of rough, oxidized areas. These channels showed reduced barrier heights consistent with the formation of a more insulating layer (less charge on the surface and more charge tightly held) growing into the bulk. As before, atomic resolution of the characteristic graphite structure is possible in the flat regions, indicating that no overlayer was formed on the smooth graphite.

Finally, another 10 potential sweeps gave rise to very rough topographs, as shown in Figure 3E, which, however, showed...
Electrogenerated Chemiluminescent Emission from an Organized (L–B) Monolayer of a Ru(bpy)$_3^{2+}$-Based Surfactant on Semiconductor and Metal Electrodes

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Electrogenerated chemiluminescence (ECL) from an organized monomolecular layer of a surfactant derivative of Ru(bpy)$_3^{2+}$ consisting of a single stearamidomethylene chain linked to one bipyridine unit at the 4-position and abbreviated Ru(bpy)$_3(bpy-C_{19})^{2+}$ has been observed at the surfaces of In-doped tin oxide, Pt, and Au electrodes. The surfactant monolayer was coated on the substrate electrodes by the Langmuir–Blodgett method. ECL was generated in an electrochemical cell containing an aqueous oxalate solution by applying a positive potential to the electrode modified by the monolayer of Ru(bpy)$_3(bpy-C_{19})^{2+}$. The ECL of the emitter monolayer deposited on an In-doped SnO$_2$ electrode was quite intense with Ru(bpy)$_3(bpy-C_{19})^{2+}$, but still easily detectable.

We report here the first observation of the electrogenerated chemiluminescence (ECL) from a monomolecular layer of emitter molecules confined to the surface of a solid electrode. The emitter employed was a surfactant derivative of tri(bipyridine)ruthenium complex, which was deposited on smooth metal or semiconductor electrodes as an organized assembly by the Langmuir–Blodgett (L–B) method.

Ru(bpy)$_3^{2+}$ → Ru(bpy)$_3^{2+}$ + e

(1)

Ru(bpy)$_3^{2+}$ + CO$_2$ → Ru(bpy)$_3^{2+}$ + C$_2$O$_4^{2-}$

(2)

C$_2$O$_4^{2-}$ → CO$_2$ + CO$_2^-$

(3)

Ru(bpy)$_3^{2+}$ + CO$_2$ → Ru(bpy)$_3^{2+}$ + CO$_2$

(4)

Ru(bpy)$_3^{2+}$ + Ru(bpy)$_3^{2+}$ → Ru(bpy)$_3^{2+}$ + Ru(bpy)$_3^{2+}$

(5)

Ru(bpy)$_3^{2+}$ + CO$_2^-$ → Ru(bpy)$_3^{2+}$ + CO$_2$

(6)

This ECL system was found useful in the determinations of both Ru(bpy)$_3^{2+}$ and oxalate at low concentration levels. There have also been studies of the synthesis of surfactant derivatives of Ru(bpy)$_3^{2+}$ and their photochemical properties in solution and as organized monolayer assemblies. The reported luminescent emission of such surfactant monolayers, however,

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