Catalytic method for modifying the surface of pyrolytic graphite

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A new method for chemically modifying highly oriented pyrolytic graphite based on the catalytic oxidation of the surface with platinum as the catalyst is proposed. The method makes it possible only to modify the outer layer of the crystalline lattice without destroying it. As a result, a great number of "point" defects appear on the outer surface of the crystal, which are uniformly distributed on the surface with high density.

Key words: pyrolytic graphite; scanning tunneling microscopy (STM); modification; catalysis; defects.

Many studies have been devoted to the problem of the modification of pyrolytic graphite.[1—4] High conductivity, atomically-smooth regions of relatively large size on chips, and chemical inertness make it possible to use highly oriented pyrolytic graphite (HOPG) as an electrode in electrochemical reactions[1,2,5,6] or in scanning tunneling microscopy (STM) and atomic-force microscopy (AFM) studies of various objects including biopolymers.[3,4,7] Chemical modification of HOPG is often required for these studies, because its hydrophobicity and inertness often prevent the fixation of biopolymers on its surface. Oxidation of the surface is the first stage in graphite modification. The action of various oxidants or heating in an oxygen-containing atmosphere may result in the appearance of carboxyl or hydroxyl groups on the graphite surface. However, graphite oxidation is usually accompanied by the destruction of the crystal surface. As has been shown earlier,[5,8] the oxidation of HOPG begins at the defects of the crystalline lattice formed by shearing. These defects can be arbitrarily divided into two types: step-like defects and vacancies. The initiation of the reaction at a step that is a boundary of the layer results in the destruction of the atomic layer. When vacancies serve as seeds, "holes", or circular gaps with a depth that is a multiple of the distance between adjacent atomic planes, are formed on the surface of the crystal. Their diameter is proportional to the reaction time and increases as the oxidant concentration increases or as the temperature increases in the case of gasification. The number of "holes" formed remains constant for a significant time and depends only on the initial number of vacancies on the crystal chip. The density of these defects (and, correspondingly, of the "holes" formed) usually lies in the range 0.1—13 μm^{-2} (see Ref. 9) for different samples of HOPG. The anisotropy of the reaction rates[10,11] (the basal plane (001) is less reactive than any of the (*hk*0) planes) makes it impossible to modify the surface layer of the crystalline surface without significantly destroying it. A study of pyrolytic graphite oxidized in air at 600 °C by X-ray photoelectron spectroscopy showed that only 5 % of the sample surface contained carboxyl and hydroxyl groups.[3] From the number of step-like defects formed by crystal shearing and circular gaps ("holes") appearing during oxidation one can estimate the fraction of the surface occupied by the edges of the defects. It turned out that carboxyl and hydroxyl groups are located only at the edges of the defects and the rest of the surface remains unoxidized. This is also indicated by the results of structural studies of the regions of the bottom surface of the "holes" and their edges at atomic resolution, because the bottom of a defect is formed by the undamaged lower-lying atomic layer of the crystalline lattice. Subsequent etching with active substances increases the total area of the boundaries of defects and their number.[3,9]

In the present work a method of catalytic oxidation of HOPG is suggested, which allows one to considerably increase the number of defects per unit area and to achieve their uniform distribution over the sample surface. The method also makes it possible to achieve a high degree of modification without noticeable destruction of the surface layer of the crystalline lattice.

Experimental

The structure of the HOPG surface was studied by a Nanoscope 2 instrument (Digital Instruments, USA). Pt—Ir-probes (Digital Instruments, USA) were used. The images were obtained in a regime of constant height and direct current. The scanning frequency was 4—8 Hz. The voltage between the sample and the probe was 60—100 mV. The tunneling current was 0.6—1 nA.

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A mixture of platinum and carbon (Pt/C) was sprayed with a JEE-4C vacuum setup (JEOL, Japan) by an EK 552 electron gun (Balzers, Lichtenstein). A Pt/C (95 : 5) mixture was sprayed onto freshly sheared HOPG at 10^{-6} Torr. The thickness of the deposition was checked by a QSG 201 D quartz resonance thickness gage (Balzers, Lichtenstein).

A mixture of concentrated H_2O_2 (30 %) and HCl (38 %) in a ratio of 1 : 1 was used for etching; the reaction time varied from 30 min to 24 h. The reaction products were washed with bidistilled water.

Results and Discussion

The basic idea of the suggested method for modifying pyrographite is to use a solid-phase catalyst sprayed on the shearing surface in combination with a comparatively weak oxidative system. It was assumed that in this case oxidation would be initiated not in the initially existing vacancies and defects of the crystalline surface, but at the sites of its contact with the catalyst. The use of a mild oxidative system, which does not oxidize graphite in the absence of the catalyst, would likely allow one to avoid considerable destruction of the crystalline surface. In the extreme case, the reaction would not propagate inside the crystal and only the outer monolayer of the crystalline lattice would undergo modification.

Platinum was chosen as the catalyst because it can be easily sprayed *in vacuo* onto the surface of a fresh chip of pyrographite, for example, by thermal evaporation or by using an electron gun. This deposition allows platinum to be condensed on the surface to form clusters. Further growth of the clusters forms a continuous film whose local thickness and degree of contact with the shearing surface differ at each point.[12,13] The use of a mixture of platinum and carbon (Pt/C) for spraying allows one to decrease the size of the grains[12,14] and thereby to increase the number of possible sites of catalytic oxidation.

It turned out that the Pt/C film made it possible to modify the crystalline surface of pyrographite with the two-component H_2O_2—HCl oxidative system, which is inefficient in the absence of Pt. In Fig. 1, the modified regions are seen as circular nodules; their average height is ~0.7 nm and the diameter is ~2 nm. These defects are not like the ruptures of the crystalline surface obtained by etching with strong oxidants or by gasification[9,15] but resemble very much those formed during the treatment of the HOPG surface by ozone at 100 °C for 10 min.[7] However, their density in our case is ~20 times higher. The defects are uniformly distributed over the crystal surface, and their density is ~ 1000 times higher than that of the vacancies on the chip of pyrographite. In the case of gasification, the density of the vacancies does not usually exceed 60 μm^{-2} and increases up to 130 μm^{-2} after repeated heating.[8,15] The number of modified regions reaches 13000 μm^{-2} for the method suggested.

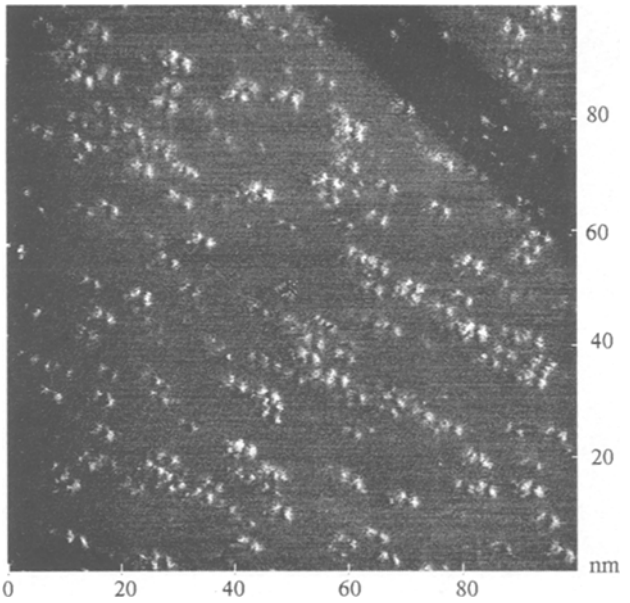

Fig. 1. STM-image of a region of the HOPG surface (area 10000 nm^2) after spraying with 4 nm of Pt/C and treatment with a 1 : 1 H_2O_2 (30 %)—HCl (38 %) mixture for 40 min.

The defects formed are compact and alternate with the unchanged regions of the surface.

The size and number of defects per surface unit depend on the experimental conditions. Three processes occur simultaneously during the reaction: oxidation of graphite, dissolution of the catalyst's film, and decomposition of peroxide. The conditions of each particular experiment determine the contribution of each of them and thereby affect the result obtained. Such parameters of the experiment as the thickness of the deposited Pt/C layer, the reagent concentration, and the time and temperature of the reaction must be optimized to achieve the maximum degree of modification.

When the thickness of the Pt/C film is small (less than 1 nm), modification is poor, apparently, due to the fast dissolution of Pt (the values presented correspond to the integral thickness of the deposited layer measured by a resonance thickness gauge with a detector placed near the pyrographite surface). When the film thickness is more than 40 nm, modification is also poor, possibly because the surface is not easily accessible to the oxidant and because of the premature decomposition of peroxide. The results of the experiments performed show that a the thickness of 2—4.5 nm is optimum for etching with a mixture of concentrated H_2O_2 (30 %) and HCl (38 %) at a 1 : 1 ratio for 30—40 min. Heating to temperatures above the ambient temperature does not noticeably affect the number of defects or their size but causes an increase in the reaction rate. However, the degree of modification decreases at temperatures above 80 °C due to fast decomposition of peroxide.

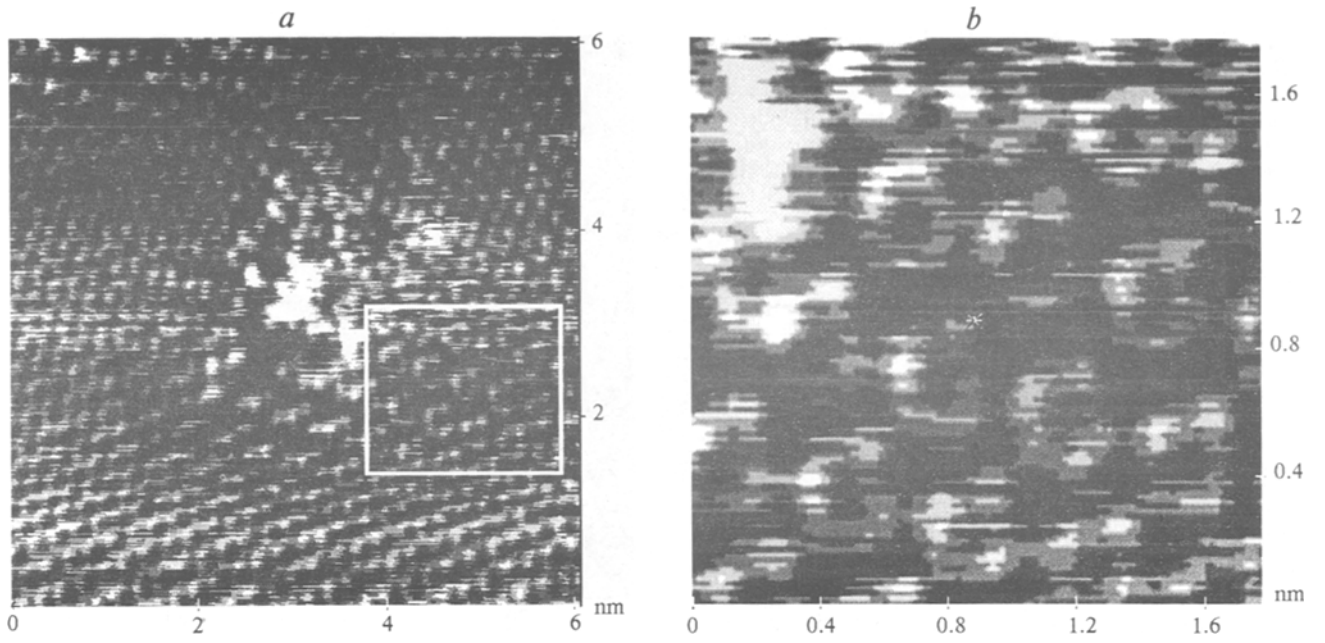

Fig. 2. STM-image of a single defect and its surroundings (the region with benzene-like structures is in the box) (*a*) and enlarged image of the isolated region (*b*).

Several characteristic features can be seen in the structure of the initiated defects by the observation when the modified surface is observed at a resolution close to atomic. Benzene-like formations (Fig. 2) and duplication of the period of the crystalline lattice (Fig. 3) are observed near the defects for almost all of the STM-images. Similar changes in the crystalline surface near the edges of the defects were observed in the study of gasification of graphite.[15] The similarity of the microstructures of the modified regions obtained by catalytic oxidation and the defect edges appearing during the gasification of HOPG[15] leads one to believe that the changes in the chemical composition of the surface for both methods of graphite oxidation are similar. The reason for the appearance of the benzene-like regions has not been established. Probably, a disturbance in the density of the electronic states (this is the effect that is observed in the STM-image) near the defect appears due to the influence of the COOH and CO groups that are formed during oxidation of the surface or due to the shift of the neighboring layers of the lattice.

The anomalous height of some defects (up to 3 nm), compared with that observed in the study of graphite activation[7] and the sharp contrast of their images in the regime of scanning tunneling spectroscopy indicate the elevated density of the electronic states. This leads one to believe that during etching platinum ions can be incorporated in the lattice of the crystal or can add to the COOH and CO groups formed. Platinum fixed at the surface may promote the covalent binding of the adsorbate. However, this problem needs additional study.

Another model that explains the modification of HOPG should be mentioned. The cleavage of C—C bonds (formation of defects) may occur due to the bombardment with Pt ions during the spraying of the film,[16] while the H_2O_2—HCl two-component system only dissolves the film without oxidizing the crystal

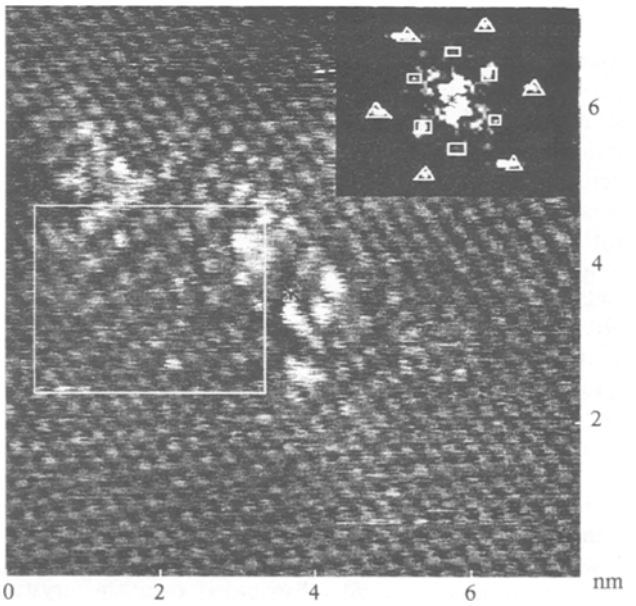

Fig. 3. STM-image of a single defect and its surroundings (the region with the duplicated period of the lattice is in the box). The diffraction of the isolated region is shown at the right corner. The maxima corresponding to the lattice duplication are marked with rectangles, and the lattices of the pyrolytic graphite corresponding to the STM-image are marked with triangles.

surface. However, samples obtained under the same spraying conditions but with different etching regimes differ in the number and size of the defects. For example, platinum goes into the solution during etching by HCl alone, and the HOPG surface remains unmodified. It is also probable that the conjugated oxidation of platinum and the pyrographite surface takes place in our case, however, this does not exclude the catalytic character of the reaction.

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The principle of surface catalysis, in which the catalyst is sprayed onto the surface *in vacuo* and is dissolved during the reaction, was used for the first time for the oxidation of pyrolytic graphite. The method suggested allows one to obtain "point" defects on the outer layer of the crystalline lattice. The graphite surface remains sufficiently smooth for the application of biological macromolecules. The potential binding centers are uniformly distributed over the surface. A more complete characterization of the modified support requires additional studies using other methods, which may provide information about the chemical composition of the surface. The results obtained lead one to expect higher activity of the support and to expect that it might be used as a matrix for further modification.

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