Scanning tunneling microscopy of the tetraphenylporphyrin thin films on a graphite single-crystal substrate

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Abstract. Features of the surface topography of a tetraphenylporphyrin film on a graphite single crystal (HOPG) substrate and the local current-voltage characteristics were studied using a scanning tunneling microscope under ambient conditions. STM images of surface were acquired on a scale from a few nanometers to 4 micrometers. Local tunnelling current-voltage characteristics in different ranges of bias voltage and in different directions of voltage scanning can have hysteresis due to the hopping electron conductivity in porphyrin.

1. Introduction
Tetraphenylporphyrin H2TPP (hereinafter porphyrin) is a potential candidate for implementation in molecular electronics and photovoltaic devices as well as in reaction catalysis and medical therapies. They are, in fact, very versatile materials capable of assimilating metals into their own molecular structure and even forming composite materials on molecular scale [1-4]. Recent investigations show that porphyrin macrocycles can grow concentrically and with periodical molecular distribution to form groups of nanowires that can transfer electrons [5]. In order to understand the possible roles of this material in the development of new electronic technologies, it is necessary to set up different working conditions under which we can study its properties. Scanning tunneling microscopy (STM) used in the present work to study the structure of surface and local electron properties of a porphyrin sample under ambient conditions.

2. Experimental setup
The thin film of porphyrin on a graphite single-crystal substrate was prepared by thermal vacuum evaporation using a quasi-closed volume technique with an evaporator temperature of 350°C and a substrate temperature of 200°C. The scanning electronic microscopy (SEM) image of the sample surface (figure 1) showed that porphyrin did not completely cover the surface of the sample, but formed elongated islands all over the substrate surface.

We have used a home-build scanning tunneling microscope with an electromagnetic coarse approach system. All STM measurements were performed at air atmosphere, at room temperature with a bias voltage applied to the sample and the STM tip at zero potential. The constant tunneling current mode with feedback enabled was used to acquire STM images of large surface areas with a current of 0.2 nA at a bias voltage of -0.5 V applied to the sample. The image of the surface topography consists of an array of 128×128 points in the surface plane. The feedback of the control electronics requires about 50 ms for each point. The constant height of the tip mode at a starting current of 1-3 nA and a
bias voltage of -0.5 V was used to get images with atomic resolution. This kind of STM image could be obtained in 3–6 seconds since the feedback was disabled. The STM tips were prepared from tungsten wire by electrochemical etching. Local tunneling spectra of porphyrin islands were measured in different ranges of bias voltage, different directions of voltage scanning and with different signs of the initial bias voltage.

**Figure 1.** SEM image of the porphyrin islands on the surface of a graphite single-crystal substrate.

3. Results and discussion

The porphyrin islands are located on the flat surface of the substrate. The question arises: What is the nature of this flat surface: is it a thin wetting layer of the porphyrin or an open surface of a graphite crystal? Our STM images of this sample area at different space resolutions (figure 2(a) and 2(b)) showed that this is the graphite surface only. There is no wetting layer on the sample surface. The STM image of a large area in figure 2(a) contains step-shaped defects of a graphite single crystal. Small islands of porphyrin can be seen at the top of this image. The STM image with atomic resolution (figure 2(b)) showed a relatively clear well-known hexagonal crystal structure of HOPG with a distance between white spots close to 0.246 nm. This kind of image used commonly for STM calibration [6]. The noise in the image may be due to some adsorbed molecules on the surface under ambient condition.

**Figure 2.** STM images of the area between porphyrin islands: – a large area with steps on the surface (a) and a small area with atomic resolution (b).
The STM image of a fragment of the porphyrin island close to its edge is shown in figure 3(a). The surface of the island is rather smooth without any sharp features. This is a tightly packed surface. The STM image with higher resolution (figure 3(b)) demonstrates a surface with a periodic anisotropic structure of porphyrin molecules. A similar structure of the porphyrins surface can be seen more clearly in STM images obtained under ultrahigh vacuum conditions [7]. The distance between the rows of the molecules is about 2 nm. The origin of the surface anisotropy is not clear yet. This anisotropy can explain the elongated form of the porphyrin islands (figure 1).

![STM image of a fragment of the porphyrin island close to its edge](image)

**Figure 3.** STM images of the surface of porphyrin island: large area close to the island edge (a) and a small area with high resolution (b).

The local tunneling spectra for the porphyrin are presented in figures 4(a-f). Each spectrum consists of two parts – two curves. We can change the sign and value of the initial bias voltage (point A on all spectra). The first curve corresponds to the bias voltage scanning from point A to point B, and the second curve corresponds to the scanning of the bias voltage immediately in the opposite direction from point B to point C. The arrows close to the curves in figure 4 show the scanning directions. Each curve requires about 4 ms to acquire data.

The local tunneling current-voltage characteristics for the bias voltage range between -0.5 V and +0.5V are presented in figures 4(a) and 4(b). All curves are similar to each other, nonlinear and almost symmetrical with respect to zero bias voltage. The current at a negative bias voltage has a slightly higher absolute value than at a positive bias voltage. If these curves represent the energy dependence of the electron density of states in porphyrin in the region around the STM tip, it shows that there is a minimum density of states around the Fermi level.

A new feature in the local tunneling spectra appears for bias voltage between -1.0 V and +1.0 V. The current-voltage characteristics demonstrate hysteresis at different directions of the bias voltage scanning (figures 4(c) and (d)). It means that some dynamic electronic phenomena in the porphyrin around the STM tip. The fact is that the porphyrin has an unusual semiconducting energy spectrum and a hopping mechanism of electron conductivity[8, 9]. The change in the charging of electron states in the porphyrin can occur rather slowly for hopping conductivity. The electrons are tunneling from the sample to the tungsten tip at initial voltage of -1.0 V. It is important that STM image always obtained at the initial voltage for the tunneling spectra to exclude any transients at the beginning of the spectrum measurements. The feedback of the control...
Figure 4. Local current-voltage characteristics between the STM tip and the porphyrin island measured in various experimental settings (see explanations in the text).
electronics uses about 50 ms to place the STM tip in correct position relative to the sample surface. The tunneling electrons with energies in the range 0 – 1.0 eV occupy empty electron levels in the porphyrin near the STM tip and create a dynamic negative space charge due to inertia of the hopping conductivity. As a result, the electric potential difference between the tip and the surface decreases, and the control electronics moves the STM tip closer to the surface to set the initial reference tunneling current. The feedback of the control electronics is turned off and the local tunneling spectrum is measured at a fixed space position of the STM tip. The dynamic negative space charge decreases during this measurement due to a decrease in the tunneling current from the tip and even a change in its sign through electron tunneling from the sample to the tip at the opposite sign of the bias voltage. When the bias voltage applied to the sample returns to negative values the electric potential difference between the tip and the surface is getting higher. As a result, the tunneling current is higher than at the initial bias voltage. The new high negative space charge cannot be created in a few milliseconds. This effect leads to higher hysteresis at the initial voltage -2.0 V (figure 4(e)). Conversely, the initial bias voltage -0.5 V does not create any noticeable space charge and the tunneling current voltage characteristics do not have any hysteresis (figures 4(a) and 4(b)). The explanation of the hysteresis in the tunneling spectra at positive initial bias voltages (figures 4(d) and 4(f)) is similar. The hysteresis is not as high as in the first case. It means that the dynamic positive space charge is not as high as the dynamic negative space charge.

4. Conclusions
Scanning tunneling microscopy of a porphyrin film on a graphite substrate prepared by thermal evaporation in a quasi-closed volume showed that the film has an island structure on the open graphite surface. The islands have an anisotropic periodic structure of porphyrin molecules. The local current-voltage characteristics have nonlinear behaviour at a low bias voltage and have hysteresis at a high bias voltage due to the hopping conductivity of the porphyrin.

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