Observation of individual organic molecules at nitronyl nitroxide single crystal surface by using atomic force microscopy

Like Ruan, Chunli Bai, Hailiang Wang, Zhongying Hu, and Meixiang Wan
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, Peoples Republic of China

(Received 24 July 1990; accepted 27 November 1990)

The surface studies of nonconductive single crystal of the organic ferromagnetic material, 2-(4-nitrophenyl)4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy 3-oxide, have been first carried out by the atomic force microscope (AFM) developed in our laboratory. The individual molecules are clearly resolved in the AFM images and the molecular arrangement is in good agreement with the bulk crystal structure.

I. INTRODUCTION

The atomic force microscope (AFM) was invented by G. Binnig *et al.*[1] after the development of the scanning tunneling microscope (STM).[2] It can be used to investigate surfaces of insulators as well as conductors and semiconductors. Inorganic materials are able to be studied by AFM with atomic resolution. Recently, some applications of AFM to organic materials have also been reported. Those samples include DL-leucine crystal,[3] purple membranes,[4] polymers,[5] etc.

Four years ago, ferromagnetic exchange interactions (FMEI) in poly[1,4-bis(2,2,6,6-tetramethyl-4-piperidyl-1-oxyl)-butadiin] (POLY–BIPO), a material without the existence of metallic ions, were first reported.[6] The discovery provides the possibility of applying organic materials to record materials, which have been associated only with inorganic materials formerly. Since organic materials exhibit good flexibility and low density, molecular ferromagnetic materials have arisen an increasing interest.

We have prepared recently 2-(4-nitrophenyl)4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy 3-oxide (NTDIOO), a kind of nitronyl nitroxide. The measured Curie and Weiss constants of this compound are 2.13 θ/K and 0.36 C/emu K mol^{-1}, respectively. Because of poor yield of ferromagnetic fraction and incomplete characterization of their magnetic properties reported, it is necessary to study more in order to understand the structure of the molecular ferromagnetic materials. Awaga *et al.*[7] have investigated the NTDIOO by x-ray crystal diffraction and molecular orbital (MO) calculation. They have revealed the relationship between the crystal structure and the ferromagnetic intermolecular coupling. To get a better understanding of the surface structure of the molecular ferromagnetic material, we have carried out the surface studies of the NTDIOO crystal with AFM.

II. EXPERIMENT

Our AFM closely resembles our previous STM design.[8] There are several modes for operating the force microscope, which depend on the nature of the force involved. The repulsive regime is used in our AFM. The deflection of the cantilever is detected by tunneling to the back of it, while the sample is scanned below its stylus. Two piezoelectric transducer (PZT)-5H tubes are used in our AFM, which are 25.4 and 12.7 mm long, respectively. One of them is used to drive the sample and the other is used to control the movement of the tunneling tip. The tunneling tip we used is a mechanically prepared Pt–Ir wire.

The force sensor is the crucial element in any AFM. Three requirements: a sharp tip, a low spring constant, and a high mechanical resonance frequency must be met. This can be achieved by reducing both size and mass of the cantilever. Generally, there are two methods to construct the force sensing cantilever stylus, cutting thin metal foils,[1] wires[9] or carbon fiber,[10] or fabricating SiO_2 cantilever.[11]

For the work described here the force sensor was made of tungsten. A piece of foil ripped from a W wire 0.5 mm in diameter was electrochemically etched in a solution of NaOH, resulting in a tongue-shaped cantilever with the dimensions of $200 \times 15 \times 4\ \mu$m. A typical cantilever made this way has a spring constant of 2.3 N/m and an eigenfrequency of 6.8 kHz (calculated results).

The NTDIOO was prepared by the reported method[12] and was purified by recrystallizing twice from benzene solution. Then 1.00 g of purified crystals were dissolved in 100 ml benzene solution in a conical flask covered with a piece of filter paper with small holes. The solution was left in the dark at room temperature for two months. After the solvent had been evaporated, about 0.5 g single crystals of NTDIOO were obtained. A piece of single crystal ($\sigma < 10^{-8}\Omega^{-1}\,\mathrm{cm}^{-1}$) with the dimensions of $2 \times 2 \times 1$ mm^3 was chosen as the sample in our AFM experiments.

III. RESULTS AND DISCUSSION

The AFM image of highly oriented pyrolitic graphite (HOPG) with atomic resolution is shown in Fig. 1. The observed in-plane lattice constant is 0.25 nm, which is used for calibrating our AFM. We can get reproducible good images for several days by using the same cantilever.

It is necessary to get understanding of the bulk structure of the NTDIOO crystal. The architecture of the kind of nitronyl nitroxide is akin to a layered structure. The crystal belongs to the monoclinic crystal system [unit cell parameters: $a = 10.960(3)$, $b = 19.350(3)$, $c = 8.257(3)$ Å. $\beta = 131.6$, $V = 1309.2(7)$ Å^3, $Z = 4$].[7] Figure 2 shows the projection of the crystal structure along the b axis. The regular two-dimensional (2D) networks are formed mainly by the Coulomb $N\cdots O$ attraction.

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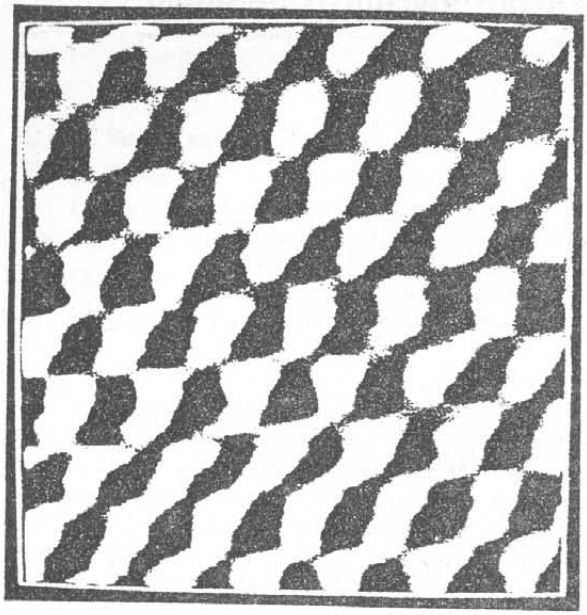
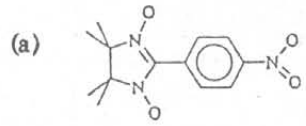


FIG. 1. The atomic resolution AFM image of HOPG, with the scanning area of 15×15 Å^2.

AFM observations for NTDIOO were performed over the a–c plane of the crystal on the basis of supposing the crystal we used has the same structure mentioned above. Figure 3(a) shows an AFM image of the crystal surface with a scanning area of 9×9 nm^2, which was recorded at the bias



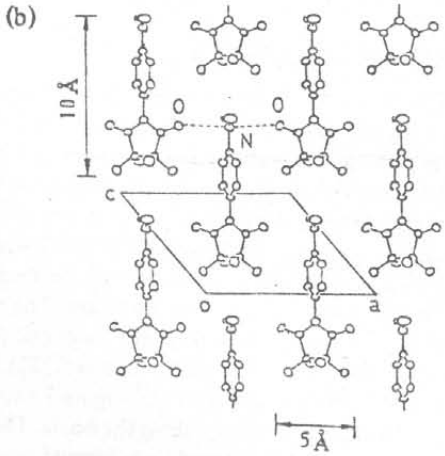


FIG. 2. (a) The molecular structure of NTDIOO. (b) the projection of the crystal onto a–c plane according to Ref. 7

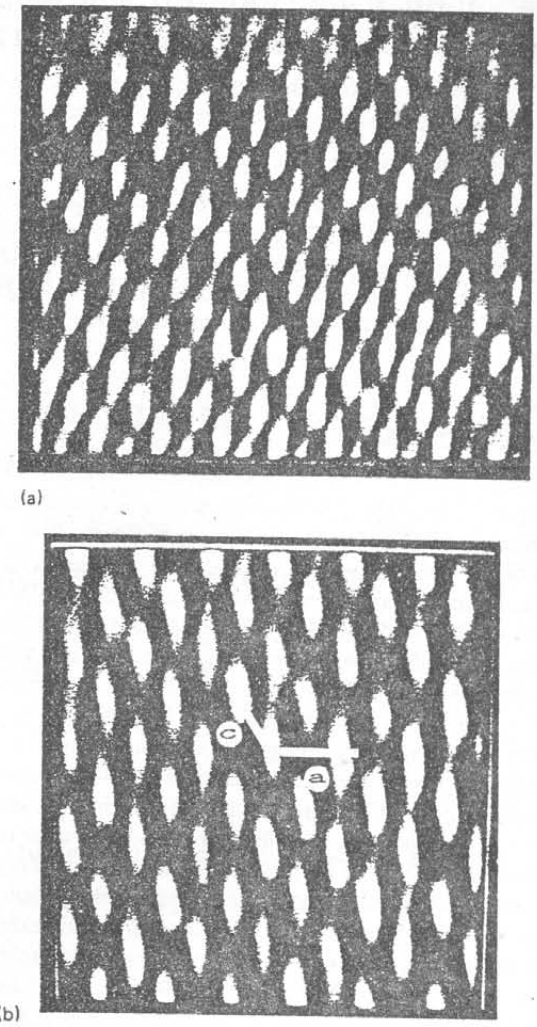


FIG. 3. (a) The AFM image of NTDIOO, with the scanning area of 9×9 nm^2. (b) The image calibrated by a linearly transformation, with the scanning area of 68×68 Å^2. The ordered structure is clearly visible and the bright dots along a and c are separated by 11 and 8 Å, respectively. The units for the crystal axes a and c are the same as that in Fig. 2.

voltage of 18 mV and the tunneling current of 0.7 nA. Since a single piezotube was used as the scanner, as we know, the motion in the X–Y plane would be nonorthogonal unless the tip had been exactly positioned along the axis of the tube and the outer wall of the piezotube had been equally divided. There are several ways to get over the problem of X–Y nonorthogonality. Since the distortion is constant in time, the same transformation can be used for all samples once the scanner is calibrated with a known structure such as graphite. Figure 3(b) shows an image of NTDIOO calibrated by using a linearly transformation computer program after the image was taken. The ordered structure can be observed along the diagonal line in the figure. The a and c lattice spacings may be identified with 11 and 8 Å repeats in Fig. 3(b), which are close to the lengths of a and c axes obtained by x-ray diffraction experiments. This result indicates that the surface observed in our AFM images is the a–c plane. Comparing Fig. 2(b) with Fig. 3(b), it is probably safe to say that

the protrusions (about 3×9 Å in diameter) correspond to the individual molecules at the *a–c* plane of the crystal surface. The molecular arrangement observed by AFM is in well agreement with the bulk structure of the crystal obtained by x-ray diffraction method.

The studies of x-ray diffraction and MO calculation of the titled compound by Awaga *et al.*[7] have indicated that the regular 2D networks are linked by the intramolecular Coulomb attraction between N of the nitrophenyl and O of the imidazolyl. Each of the 2D sheets along *b* axis is connected by hydrogen bonds. They pointed out that the intramolecular exchange interactions (spin polarization effect) result in the ferromagnetic intermolecular coupling. Our AFM results demonstrate that there is no surface reconstructions in this organic material. It is suggested that the ferromagnetic exchange interactions might also exist on the surface of NTDIOO crystal.

In order to fully understand the molecular ferromagnetism, further investigation of microfield of ferromagnetic media of this sample, which can only be achieved with magnetic force microscope, another force microscope, is also needed besides the understanding of the topography provided by AFM.

IV. CONCLUSIONS

The AFM is an important tool for investigating the topography of insulators. The AFM images of NTDIOO clearly shows that within the accuracy of our measurements the surface structure is in well agreement with the bulk structure determined by x-ray diffraction experiment. We suppose that FMEI may also exist on the *a–c* plane of the crystal surface.

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