

Recording at the Nanometer Scale on *p*-Nitrobenzonitrile Thin Films by Scanning Tunneling Microscopy**

By Dongxia Shi, Yanlin Song, Daoben Zhu, Haoxu Zhang, Sishen Xie, Shijin Pang, and Hongjun Gao*

Ultrahigh-density data storage has received much attention in recent years because of its technological importance, and substantial progress has been made lately.^[1–6] Haridas and coworkers have suggested three-dimensional high-density data storage based on two photos.^[1] Chou et al. used nano-imprinting lithography for high-density data storage.^[2,3] Scanning probe microscopy (SPM) has a potential application in high-density data storage due to its ability to make local electric fields from the tip on a nanometer scale.^[7–14] Recording at the nanometer scale has been demonstrated by SPM on various materials. Among them, organic molecules have received much attention because of their controllable molecular structures and corresponding properties.^[15–26,28] By changing molecular structure, it is possible to optimize recording on organic materials. Furthermore, the size of the recorded mark can possibly be at a molecular scale. In the past, we have reported molecular recording on a few organic materials up to a data density of about 10^{13} bits/cm².^[5–7,17] To decrease the size of the recorded marks, correspondingly increase their density, and furthermore understand the recording mechanism, we have designed and synthesized different molecules. In this communication, we report molecular recording on an organic *p*-nitrobenzonitrile (PNBN) thin film by STM under ambient conditions, which shows the smallest mark size among all the organic thin films previously studied. A possible recording mechanism is discussed.

Organic *p*-nitrobenzonitrile (PNBN) was used as a data-storage medium. As shown in Figure 1, PNBN is a small organic molecule, in which NO₂ and CN are all strong electron acceptors. This novel structure might help us understand the recording mechanism based on the charge transfer (CT) theory, as we can compare it with other CT complexes on



Fig. 1. Molecular structure of PNBN.

[*] Prof. H.-J. Gao, Dr. D. X. Shi, Dr. H. X. Zhang, Prof. S. S. Xie, Prof. S. J. Pang

Beijing Laboratory of Vacuum Physics
Institute of Physics & Center for Condensed Matter Physics
Chinese Academy of Sciences
PO Box 2724, Beijing 100080 (China)
E-mail: hjgao@aphy.iphy.ac.cn

Prof. Y. L. Song, Prof. D. B. Zhu
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100080 (China)

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which molecular recording has been conducted. Obviously, the origin of this recording can not be attributed to charge transfer in the system.

To understand the data-recording mechanism, we measured *I*–*V* curves of the unrecorded region and the recorded region separately. The results are shown in Figure 2. It can be seen that the electrical resistance of the unrecorded region is much

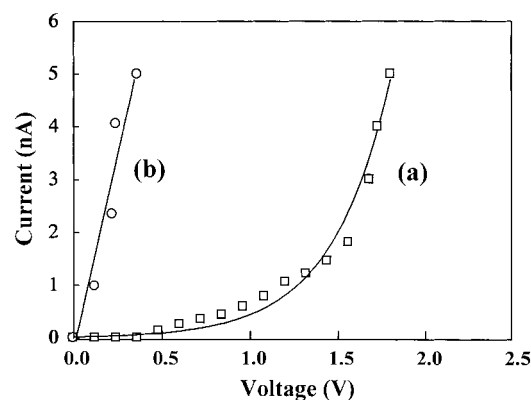


Fig. 2. Typical *I*–*V* curves of the unrecorded and recorded regions in the PNBN film. Curve (a) is from the unrecorded region and curve (b) is from the recorded region, showing the conductance transition after the voltage pulse.

higher than that of the recorded region, which means that a conductance transition occurs after the voltage pulse acting on the film. This *I*–*V* experimental result is consistent with our previous result^[6] that the recording mechanism was due to conductance transition in the recorded regions.

In past studies, the conductance transition or electrical bi-stability was explained to be due to charge transfer from a donor to an acceptor in organic or organic–inorganic complexes,^[7] structural transition from an ordered structure to a disordered structure,^[6] and/or polymerization of organic molecules.^[13] However, in order to decrease the recording size and understand the formation mechanism, we thought it would be helpful to use a single kind of organic material as a storage medium, in which the molecule has two functional radicals: an electron donor and an electron acceptor. Also, from the deposition aspect, the chemical stoichiometry of the deposited film would be easier to control, and the film could be smooth in large areas, which is important for technological applications. However, the organic complex materials may lead to difficulty in preparing thin films needed for this application, in which the recording mechanism is based on the charge transfer theory. In the PNBN system, there is only one molecule and no charge transfer in the molecule. Thus the recording mechanism should not be ascribed to an electron donor radical to an electron acceptor.

As discussed above, the bright dots in the film are created by a change in the conductance of the local region. We have ruled out charge transfer as the recording mechanism. Another possibility is polymerization of the PNBN molecules. Actually, the NO₂ and CN radicals are all strong electron acceptors. From the experimental results, it is clear that there should be free electrons in the recorded region (or molecular

column). From the molecular structure, we can see that there are one σ bond and two π bonds in the CN (cyan) radical. Therefore, it is possible that conductance of the PNB monomer system has a high electrical resistance because the free electrons are localized in the range of a molecule before the voltage pulse applied. However, the π bonds are not strong enough and may be broken when a strong voltage pulse (over a critical value) is applied resulting in the polymerization of the monomer molecules in the local region along the molecular column. The localized electrons of the molecule may freely move around along the molecular column making the local region conductive. Samanta et al.^[27] reported that polymerization of organic molecules can cause a conductance decrease, which is contrary to the present case. Thus the recording mechanism can not be attributed to polymerization. Compared with the results in the NBMN-*p*DA complex,^[6] the recording in the present case may be ascribed to a molecular structural change (i.e., conductance transition from a high-conductance state to a low one due to a change in the molecular structure when a voltage pulse was applied). Detailed information about the direct observation of the structural transition of the thin film after the voltage pulse can be found in another paper.^[28]

Since the thickness of the PNB thin film is less than 100 nm, with the high electrical field from the STM tip it is possible to induce that field evaporation of the film. Then the conductive HOPG substrate may emerge and cause a bright dot. However, unfortunately in the STM experiments, we could not get the HOPG atomic image in the recorded region. In contrast, to obtain the HOPG atomic image, we must clear out the organic molecules in the recorded region. To do so, we must apply a voltage pulse of 5 V for 20 ms to the recorded region and scanned the region at a high tunneling current to get the HOPG substrate. Therefore, the formation of holes in the film is not the mechanism of this recording.

We have found that using an organic PNB molecule of no charge transfer as a recording medium gives the smallest recording mark yet among all the organic molecules employed by us. The size of the recorded marks was 0.6 nm in diameter, corresponding to a possible data-storage density greater than 10^{14} bits/cm². The recorded marks are very stable and have no discernible change during scanning. PNB is competitive with other recording molecules previously used. The recording mechanism can be ascribed to a structural transition at the local region. Our results suggest that the PNB thin film may have a great potential application in ultrahigh-density data-storage devices. However, further experiments and theoretical calculations on this kind of single organic material in ultrahigh-density data storage are needed to understand the recording mechanism.

Experimental

The organic PNB material was deposited on freshly cleaved highly oriented pyrolytic graphite (HOPG) substrates by vacuum evaporation in a system evacuated to about 3×10^{-4} Pa. The organic material was heated to 70 °C in a

crucible in the vacuum chamber. The vacuum during deposition was about 7×10^{-4} Pa. The film thickness was about 50 nm.

STM experiments were performed with a home-made STM (model: CSTM9100) under ambient conditions. The STM tips were Pt/Ir (80/20) wires, snapped with a wire cutter. During the STM operation the tip was in constant-height mode. The recording mark was obtained by applying a voltage pulse of 4.3 V between the STM tip and the HOPG substrate. Current–voltage (*I*–*V*) curves of the unrecorded and recorded region were achieved using the STM, separately. Figure 3 is a typical STM image of a recorded pattern. The scanning area was 24 nm × 24 nm, and the scanning conditions were $V_{\text{bias}} = 0.4$ V and I_{ref}

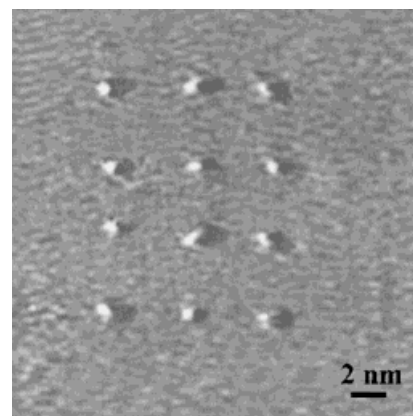


Fig. 3. STM image of a recorded pattern with scanning area 24 nm × 24 nm. The tunneling conditions were: $V_{\text{bias}} = 0.4$ V, $I_{\text{ref}} = 0.24$ nA, scanning rate 0.2 Hz/image, voltage pulse 4.3 V for 10 ms. The size of the marks is 0.6 nm in diameter.

= 0.24 nA. The scanning rate was 0.2 Hz/image. The bright dots (the recorded marks) were obtained when voltage pulses of 4.3 V were applied for 10 ms between the STM tip and the HOPG substrate. From the image the size of the recorded marks was measured to be about 0.6 nm diameter. During the scanning the recorded pattern was very stable and had no discernible change. After 7 days, the recorded marks could still be read by the STM. In addition, the success of the writing on the film was over 90 % in our STM experiments.

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Polygon Building Block Route to sp^2 -Carbon-Based Materials**

By Chi-Young Lee,* Hsin-Tien Chiu,* Chih-Wei Peng, Ming-Yu Yen, Yu-Hsu Chang, and Chao-Shiuan Liu

Elemental carbon exists in two classes, sp^3 -hybridized, such as diamond, and sp^2 -hybridized, such as graphite, carbon nanotubes (buckytubes), carbon onions (buckyonions), and fullerenes.^[1,2] It is well known that diamond usually forms under high temperatures and high pressures. Preparation of the other classes of carbon materials requires high-energy processes too. In many examples, carbon nanotubes (buckytubes), carbon onions (buckyonions), and fullerenes were synthesized by high-temperature arc-discharge between graphite electrodes^[3] or laser ablation of a graphite target.^[4] The processes are simple and are being used to produce most of the new materials for current research activities: they are inefficient and of low yield. Chemical routes have also been attempted; however, suitable precursors are difficult to obtain and the reactions are difficult to control. For example,^[5] it has been shown that strained cycloalkynes with high-energy content can be converted, with limited success, to fullerene-class materials. In another example,^[6] the formation of fullerene in low yield was observed from laser ablation of perchloroacetylene ($C_{12}Cl_8$). Other possible chemical routes, such as flame synthesis^[7] and chemical vapor deposition,^[8] can be utilized to generate carbon nanotubes, but in low quantities. Clearly, a simple high-yield route to these materials is needed if carbon-based technology is to be developed to its full potential.

Many growth mechanisms^[9,10] have been proposed to rationalize how these materials are formed but they do not provide pointers to new synthetic strategies. When we examine the basic constructions of the sp^2 -hybridized carbon materials, we find that graphite and carbon nanotubes are formed from repeating hexagon units of carbon atoms while carbon onions and fullerenes contain, in addition to the hexagons, pentagon units of carbon atoms. According to IPR (the isolated pentagon rule),^[3] twelve (and only twelve) non-adjacent pentagons are essential for the formation of spherically shaped carbon onions and fullerenes. For example, it is well known that the buckyball is composed of twelve non-adjacent pentagons and twenty hexagons. However, as suggested by Kroto and Walton several years ago,^[11] a buckyball could be constructed by using pentagons as the only building block, if their vertices were linked as shown in Figure 1a (linking six pentagons to generate a half-buckyball). No hexagons are needed; they are

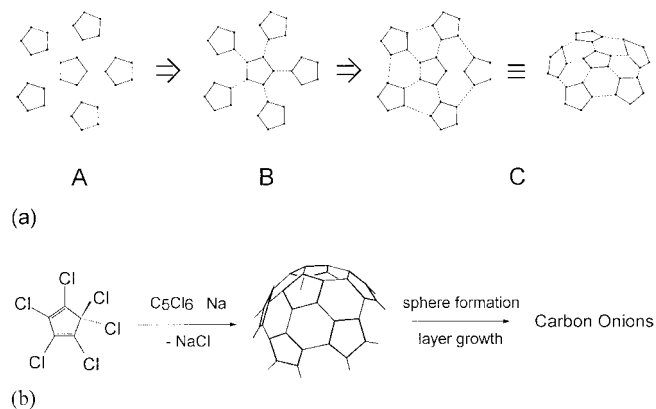


Fig. 1. a) Construction of C_{60} from pentagons only [11]. Two “C” fragments offer a C_{60} molecule. b) Reaction scheme for the formation of carbon onions.

generated as a natural consequence of the linking process. This suggests the possibility of employing pentagonal-shaped organic precursors as the “building blocks” to synthesize fullerene and buckyonions, while hexagonal-shaped precursors are needed to form graphite.

As shown in Figure 1b, letting hexachlorocyclopentadiene, C_5Cl_6 , react with Na through a Wurtz-type reaction at about 100 °C generated black powders containing carbon onions. Based on solid-state ^{13}C NMR (nuclear magnetic resonance) spectroscopy, more than 50 % of the carbon atoms are in an ordered environment.^[12] HRTEM (high-resolution transmission electron microscopy) images of the powder (Fig. 2) show that the sample consists of spherical and elliptical onion structures of various sizes. The number of shells of the onions is in the range 8–50. The smaller onions, such as the one shown in Figure 2a, have about 10 shells. The diameter of the innermost shell of such onions is about 2.5 nm. According to the projection method,^[2] a fullerene with I symmetry has a diameter of 1.985 or 2.779 nm, for C_{500} or C_{980} , respectively. This suggests that the innermost shell may be considered to be a buckyball with the number of carbon atoms in the range 500–1000. Also, this indicates that more C_6 hexagon units have been created than expected. The exact cause is not clear.

[*] Prof. C.-Y. Lee
 Materials Science Center, National Tsing Hua University
 Hsinchu, Taiwan, 30043 (ROC)
 E-mail: cylee@mx.nthu.edu.tw

Prof. H.-T. Chiu, C.-W. Peng, M.-Y. Yen, Y.-H. Chang
 Department of Applied Chemistry, National Chiao Tung University
 Hsinchu, Taiwan, 30050 (ROC)

Prof. C.-S. Liu
 Department of Chemistry, National Tsing Hua University
 Hsinchu, Taiwan, 30043 (ROC)

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