Nucleic acid base molecules on Pd(110) surfaces

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Scanning tunneling microscopy (STM) images have been obtained for the nucleic acid bases adenine and thymine, deposited on the surface of Pd(110) single crystal substrates for the study of the electronic structure of and interaction between the DNA bases. The adenine and thymine molecular images are different from each other, revealing distinct shapes and lateral dimensions that reflect the contours of the calculated molecular orbitals. Thus, adenine appears as triangular protrusions with lateral dimensions of ~0.8 nm and thymine as round protrusions of ~0.45 nm diameter. Adenine shows a strong tendency for dimer formation whereas thymine forms islands even at low coverages.

Scanning tunneling microscopy (STM) has been used to obtain images of individual DNA bases, adenine, guanine, thymine and cytosine.[1] It is expected that STM observation of the DNA bases will be a major step towards elucidation of the primary structure of DNA. STM observation of the interactions between the bases is also important for the understanding of secondary structures such as the double helix. In spite of efforts thus far, STM has been used to visualize only macro strings of DNA and closely packed monolayer films of the bases but not isolated base molecules.[2-5] In the present study, we observed isolated DNA bases adsorbed on a well-defined clean Pd(110) surface. The lateral distribution of the molecular electronic states and the interactions between bases and substrate that determine the cluster formation of the bases have been observed for the first time.

Adenine and thymine are planar molecules with lateral dimensions of 0.45 nm and 0.25 nm, respectively, as shown in Fig. 1(a). These bases were deposited onto a clean Pd(110)(1 × 1) surface under ultrahigh vacuum (UHV) conditions. Figure 1(b) shows an STM image of a Pd(110) surface obtained after adenine deposition [~0.1 monolayer (ML), 1 ML = 1.07×10^{15} molecules cm^{-2}]. The temperature of the Pd(110) substrate was kept at room temperature, during both the deposition and the STM imaging. In higher resolution images, isolated adenine molecules are observed as characteristic triangular protrusions with typical lateral dimensions of ~0.8 nm, as shown in Fig. 2(a). The contours of the constant

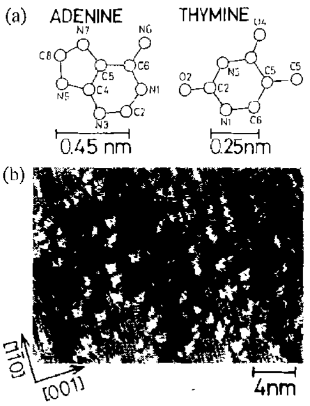

Fig. 1. (a) Molecular structure of adenine and thymine. (b) A typical large-scale image (25 × 18 nm^2) of a Pd(110)(1 × 1) surface observed after the deposition of adenine (~0.1 monolayer (ML)). Tip bias $E_t = -0.01$ V, *tunneling current* $I_t = 1$ nA. The image was obtained using a differential data acquisition mode.

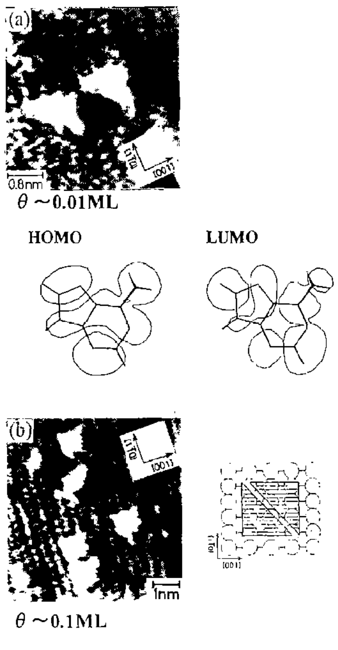

Fig. 2. (a) An expanded image of the isolated adenine molecules (4.1 × 4.1 nm^2). The substrate temperature was room temperature during the deposition and STM imaging. $E_t = -0.2$ V. $I_t = 1$ nA. The contours of constant charge density ($\phi = 0.001$) of the HOMO and LUMO at 0.1 nm above the molecular ring system of a single adenine molecule are also shown. (b) This image (6.4 × 6.4 nm^2) shows paired adenine molecules adsorbed on the Pd(110) (1 × 1) surface obtained at an adenine coverage of ~0.1 ML. The substrate temperature was room temperature during deposition and STM imaging. $E_t = -0.01$ V, $I_t = 1$ nA. All the images were obtained in a differential data acquisition mode.

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charge density (ϕ = 0.001) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied one (LUMO) at 0.1 nm above the molecular ring system of the adenine molecule are also shown in Fig. 2(a). MO calculations were performed by the semiempirical PM3 method using the program MOPAC ver.7.01. It should be mentioned that ab-initio MO calculations[6] for the adsorbed molecules and the underlying substrate is under investigation. The charge density of the HOMO and LUMO is located around the N1, C2, N3, C6, N6, N7 and C8 sites. This distribution can be roughly outlined as a triangle with a lateral dimension of ~0.6 nm. Although the resolution of the observed molecular image is not high enough for the HOMO and the LUMO distinguished, the observed molecular images appear to be in agreement with the calculated contours of the HOMO or LUMO. These results imply that the deposited adenine molecules did not decompose on the Pd(110)(1 × 1) surface at room temperature. Therefore we consider that the electronic structure of isolated adenine molecules has been successfully imaged by STM for the first time.

Fig. 2(b) shows an STM image of a Pd(110)(1×1) surface with an adenine coverage of ~0.1 ML. As before, the substrate temperature was kept at room temperature during the deposition and STM imaging. In addition to isolated adenine molecules, many dimer-like configurations of adenine molecules are observed which appear to consist of a pair of triangles of ~0.8 nm (each corresponding to a single adenine molecule). The pairs are aligned along the [001] direction and not in the $[1\bar{1}0]$ direction, indicating strong substrate-dependent anisotropy of the pairing mechanism.

The interaction energies for various DNA base pairs have been calculated by Hobza and Sandorfy[7] using *ab initio* self-consistent field method. They have reported that three possible adenine pairs have binding energies of −66.2, −61.7 and −38.8 kJ/mol. Although we cannot distinguish which of the pairing structures correspond to the observed structures, the mere fact that dimers are observed provides evidence of attractive interaction.

Qualitatively different behavior was observed for the nucleic acid base thymine. The temperature of the Pd substrate was ~100 K during the deposition and ~270 K during recording of the STM images. As shown in Fig. 3(a), thymine molecules appear as round protrusions with lateral dimensions of ~0.45 nm. The contours of the HOMO and LUMO orbitals of a dienol-type thymine molecule calculated by the semiempirical PM3 method using the program MOPAC ver.7.01 are shown in Fig. 3(c). Considering that adenine molecules have been observed as triangular protrusions with lateral dimensions of ~0.8 nm, it follows that these dimensions and shapes are distinctly different from each other, indicating the possibility of discrimination between these bases by STM. Closer inspection of Fig. 3(a) reveals that most of the distances between nearest-neighbor thymine molecules are about ~0.5 nm, and that there are relatively many open spaces. These results indicate that thymine molecules have a tendency to form islands. This tendency becomes more marked at higher coverages. Fig. 3(b) shows an STM image of thymine coverage of ~0.2 ML. The temperature of the substrate was ~100 K during the deposition and ~265 K during recording of the image. No isolated thymine molecule was found, and only thymine islands are were observed. This tendency towards island formation even at low coverages indicates a markedly attractive interaction between thymine molecules in both the $[1\bar{1}0]$ and the [001] direction. On the other hand, adenine molecules tend to form dimers and are uniformly spread over the Pd(110) surface. Theoretical calculation results indicate that the interactions of adenine pairs lead to a larger stabilization energy than in the case of thymine keto-form pairs (−52.0 ~ −53.2 kJ/mol).[7] A possible explanation for the observed strong interaction between thymine molecules is as follows. Thymine molecules can be converted to enol or dienol forms, both of which contain hydrogen bonding.[8] The hydrogen bonding in the enol form may be stronger than the interaction between adenine molecules. Our results suggest that enol tautomerization plays an important role in the interactions between thymine molecules.

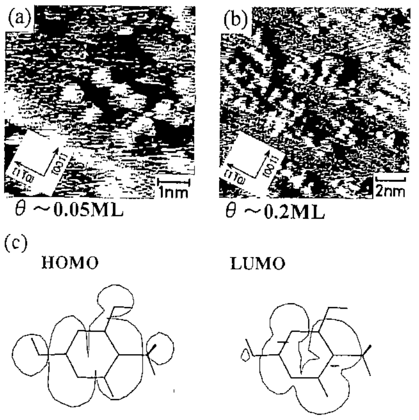

Fig. 3. A series of STM images of thymine islands on a Pd(110)(1 × 1) surface with different coverages. The coverages of thymine are approximately (a) ~0.05 and (b) ~0.2 ML, respectively. The substrate temperature during deposition was ~100 K, and during image recording about 265–270 K for both (a) and (b). The STM imaging parameters were as follows: (a) 6.8 × 6.8 nm^2, E_t = +0.01 V, I_t = 1 nA and (b) 13 × 13 nm^2, E_t = +0.05 V, I_t = 0.2 nA. All the images were obtained in a differential data acquisition mode. (c) The contours of constant charge density (ϕ = 0.001) of the calculated HOMO and LUMO orbitals for a dienol-type thymine molecule at 0.1 nm above the molecular ring system of a single thymine molecule are also shown.

The detail of this work has been published elsewhere.[9]

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