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Lattice Matching of α-Cyclodextrin Commensurate with Molybdenum Disulfide Studied by Scanning Tunneling Microscopy

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Lattice matching between α-cyclodextrin (α-CyD) and molybdenum disulfide (MoS_2) was investigated by scanning tunneling microscopy (STM) using the CyD molecular necklace and molecular tube as specimens. Stable sites for α-CyD on the MoS_2 substrate observed by STM were in good agreement with the model we proposed.

KEYWORDS: cyclodextrin, inclusion complexes, lattice commensurate, molecular necklace, molecular tube, MoS_2, STM

1. Introduction

Cyclodextrins (CyDs), consisting of 6–8 glucose units linked in a cyclic form (Fig. 1), have attracted considerable attention because of their high potential as artificial enzymes.[1,2] Recently, following the creation of the molecular necklace (CyDs threaded on a polymer chain of polyethylene glycol (PEG) (Fig. 2(a))),[3] a tubular structure was synthesized by cross-linking adjacent α-CyD units in a polyrotaxane (Fig. 2(b)).[4] The diameter of α-CyD is ~0.45 nm, and the length of the tube can be controlled by adjusting the chain length in the range of the α-CyD cavity depth, ~0.7 nm. Therefore, the size of the CyD tube is extremely small compared to, for example, carbon nanotubes ranging from about 1 to 30 nm in diameter and a micrometer or so in length. The structure of the CyD molecular tube was examined by scanning tunneling microscopy (STM)[5,6] and was found to be in good agreement with the structural model proposed from the results of other measurements. Since CyDs have selectivity for both catalysis and inclusion of molecules, excellent potential is expected for the application of the CyD molecular tubes.

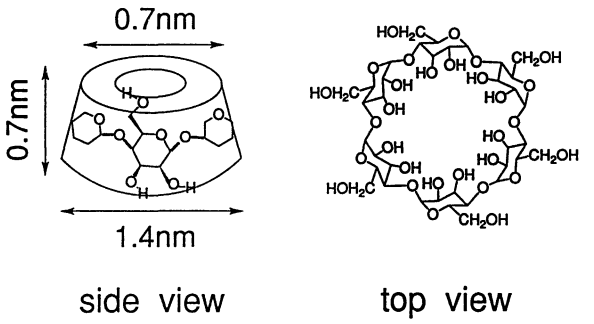

Fig. 1. Structure of cyclodextrin.

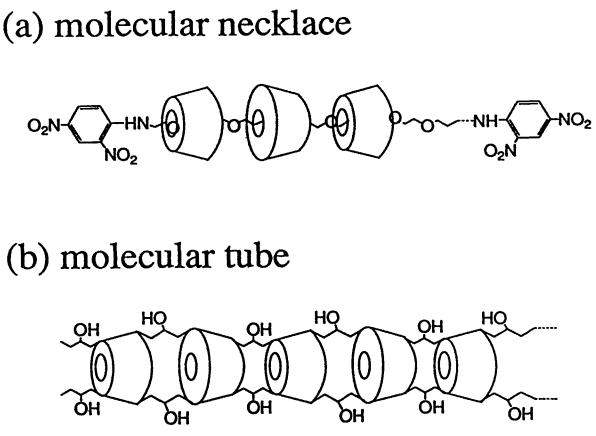

Fig. 2. Structures of molecular necklace (a) and molecular tube (b).

In order to study and fabricate such molecular structures, understanding of the interaction between CyDs and the substrate material is very important. As previously reported, CyD-CyD interaction is dominant compared to the interaction of CyD with the substrate on graphite.[7] When CyDs are dense enough to form a monolayer, new two-dimensional structures are obtained. However, when CyD-CyD interaction is suppressed, the ordered structure cannot be formed. On the other hand, individual α-CyDs have been stabilized on molybdenum disulfide (MoS_2), and three-dimensional clusters were formed, contrary to the two-dimensionally ordered structure observed on highly oriented pyrolytic graphite (HOPG).[5–8] The molecular necklace and molecular tube were also stabilized on a MoS_2 substrate.[5,6]

In this paper, the stability of α-CyDs on MoS_2 will be discussed in consideration of lattice matching between α-CyDs and MoS_2.

2. Lattice-Matching Structures

Figure 3(a) shows an atomic structure of MoS_2[9] with α-CyDs, where open and closed circles indicate S and Mo atoms, respectively. When α-CyDs are placed on MoS_2 as shown in the figure, α-CyDs can be stabilized on the substrate along the rows of S atoms in the first layer. Interaction between negative charges of the S atoms and those of hydroxyls in the α-CyDs is a possible mechanism for the stabilization. Since the atomic structure of the MoS_2 surface has a threefold symmetry, such symmetrically stable sites as shown in Fig. 3(a) are possible for α-CyDs.

Taking into consideration the structure and size of α-CyD, the space which appears between two CyDs on

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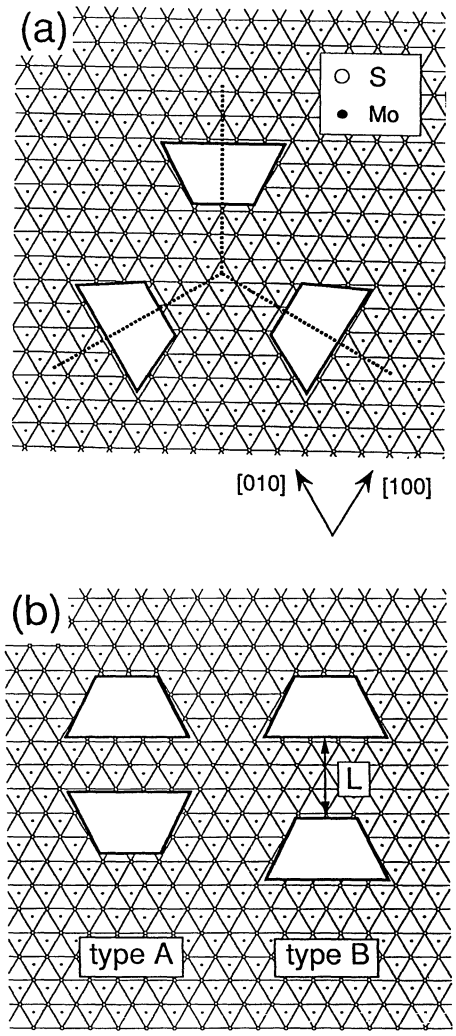

Fig. 3. (a) Lattice matching model between CyD and MoS_2. (b) Two conformations of CyDs on MoS_2.

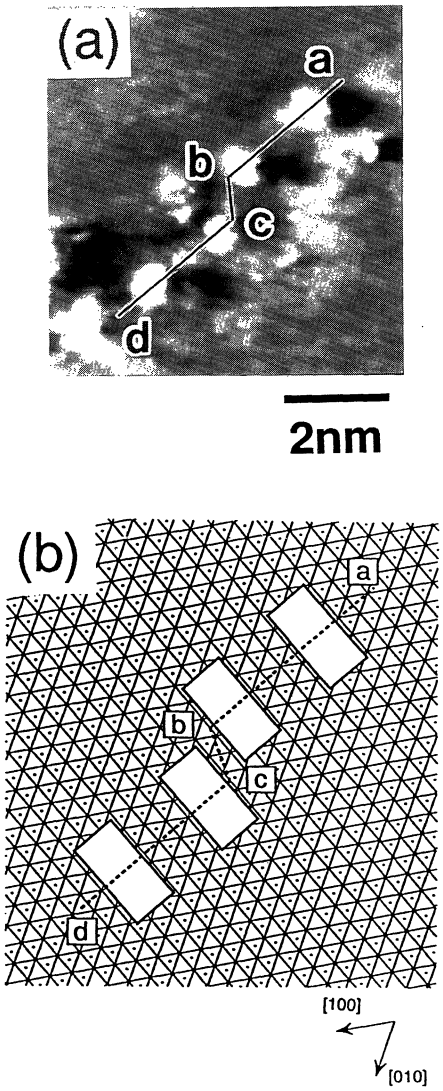

Fig. 4. STM image of molecular necklace on MoS_2 (a) and its schematic structure (b).

the same axis depends on the conformation of the two adjacent CyDs. Thus there exist two types of spacing, as shown in Fig. 3(b). The width of the space "L" between two adjacent CyDs can be represented by the distance "d" between sulfur rows in the [110] direction (~0.27 nm) as $L = n \cdot d$, where the integer "n" is even for type A and odd for type B in Fig. 3(b).

3. Experiment and Results

Since electronic structure depends on the distortion of CyDs, it is difficult to characterize positional relationships between CyD and MoS_2 by observing individual CyDs. Therefore, the molecular necklace[3] and molecular tube,[4] which are chains of CyDs, were used as specimens, in which the orientation of CyDs can be defined more easily by observing the ordering of CyDs.

Specimens were prepared by deposition of aqueous solutions of these materials onto fleshly cleaved MoS_2 surfaces, and STM was performed in air at room temperature. Concentration of materials were weakened enough so that an isolated chain of CyDs can be identified.

Figure 4(a) shows a current image of a molecular necklace (Vt=240 mV, Is=0.9 nA) which is about half-filled with CyDs; ~20 CyD units were threaded on PEG of 77 EG units. PEG is not imaged, but a chain of CyDs is ordered linearly in the directions represented by a-b and c-d in figure. The distance between the a-b and c-d axes is ~0.8 nm, which corresponds to two and a half times the periodicity in the $[1\bar{1}0]$ direction. CyDs in Fig. 4(a) are shown schematically in Fig. 4(b) with the atomic structure of MoS_2. Here, orientations of CyDs are presented based on the ordering of CyDs in Fig. 4(a), i.e., axes a-b and c-d in Fig. 4(a) are oriented in the [110] direction. Agreement between the STM image and the lattice-matching model is quite good. Since details of a CyD structure represented by a trapezoidal shape (Fig. 3) could not be determined based on the STM image, CyDs are represented by rectangles and are placed by fitting the axes a-b and c-d in the figure onto the substrate here. Therefore, the absolute orientation of the CyDs is still uncertain, however, their relative orientations can be determined by analyzing the positional relationships between adjacent CyDs. As shown in Fig. 4(b), two CyDs on a-b and c-d axes are separated by ~0.8 nm ($L = 3 \cdot d$), which corresponds to

the orientation of type B in Fig. 3(b). According to our model for lattice matching, CyDs on a-b and c-d axes have the same orientation. With regard to the relationship between the two type B CyDs, the distance between the two inner CyDs is ~0.3 nm (L=1·d), and its orientation seems to be type B. However, as their axes are shifted two and a half times the periodicity in the $[1\bar{1}0]$ direction, the one-half period shift in the $[1\bar{1}0]$ direction changes the orientation from type A to type B, and vice versa. Therefore, ordering of the CyDs in Fig. 4 becomes B-A-B.

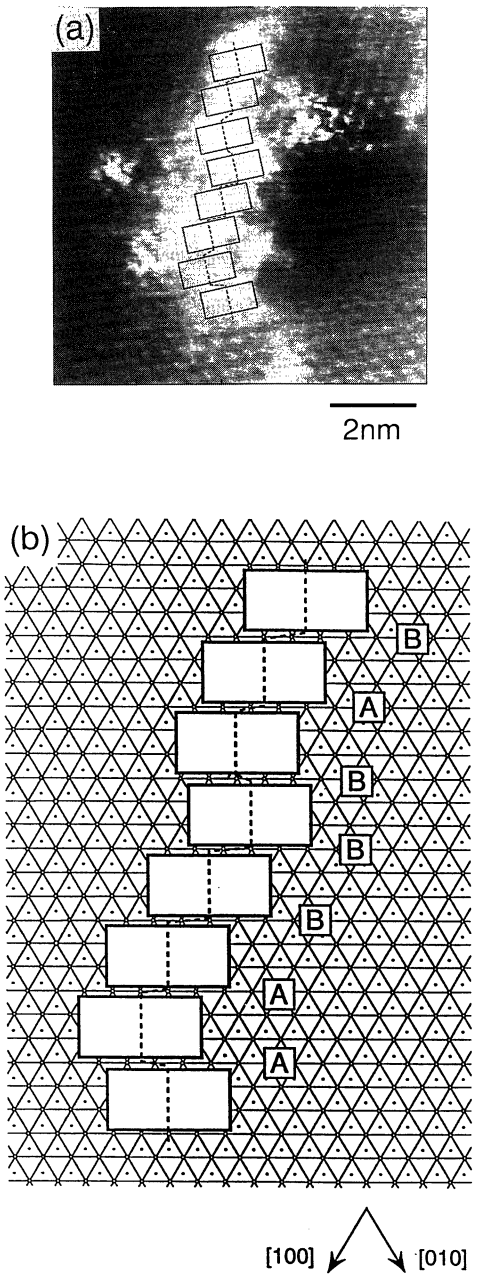

Fig. 5. STM image of molecular tube on MoS_2 (a) and its schematic structure (b).

Figure 5(a) shows an STM image of a molecular tube (Vt=190 mV, Is=1.2 nA), where the chain of CyDs is schematically superposed. In order to focus on the atomic structure of MoS_2, the STM image of the molecular tube is rather blurred. However, as shown in Fig. 5(b), the positional relationship between CyDs and the MoS_2 substrate is in good agreement with the lattice-matching model shown in Fig. 3. Both conformations, type A and type B in Fig. 3(b), are included here, as indicated by "A" and "B". The STM image of the molecular tube obtained here has a rather zigzag structure, and the difference between the adjacent CyD axes ranges from ~0.16 to ~0.47 nm. The distortion may be related to the structure of the CyD tube or interaction between CyD and the MoS_2 substrate. Molecular tubes with CyDs ordered in a straight chain were also observed, and detailed analysis of this molecular tube is now in progress.

4. Conclusions

α-CyDs were stably observed on MoS_2 for both molecular necklace and molecular tube structures, which was explained well by the lattice-matching model of α-CyD commensurate with the surface structure of the MoS_2 substrate. MoS_2 is considered to be one of the most promising candidates as the substrate material on which CyDs and molecular tubes can be studied and fabricated.

Acknowledgements

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