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DIRECT OBSERVATION OF CYCLODEXTRIN INCLUSION COMPLEXES BY SCANNING TUNNELING MICROSCOPY

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On HOPG (highly oriented pyrolytic graphite), CyD-CyD interaction was dominant compared to the interaction between CyDs and the substrate, and new ordered structures were observed by scanning tunneling microscopy (STM). On the other hand, the atomic structure of the MoS_2 surface was found to exhibit lattice matching commensurate with an α-CyD molecule, and in fact, α-CyDs could be stably observed. Making use of the interaction property between α-CyD and MoS_2, STM observation was performed on α-CyD inclusion complexes with polyethylene glycol, the observed structure of which was in good agreement with the molecular necklace structure previously proposed; α-CyDs are threaded on a PEG chain.
KEYWORDS: STM, molecular necklace, molecular tube, HOPG, MoS_2.

1 INTRODUCTION

Recently, following the creation of molecular necklaces, α-cyclodextrins (CyDs) are threaded on a polymer chain of polyethylene glycol (PEG) [1], a tubular structure was synthesized by cross-linking adjacent α-CyD units in a polyrotaxane (Fig. 3) [2]. Since the diameter of α-CyD is ~0.45nm and the length of the tube can be controlled by adjusting the chain length in the range of the α-CyD cavity depth, ~0.7nm, the size of the CyD tube is extremely small compared to, for example, carbon nanotubes. In order to utilize such high potentiality of CyDs, understanding of the molecular structures on an atomic scale is urgently needed.
In this paper, we report the results of direct observation performed on CyD inclusion complexes by scanning tunneling microscopy (STM).

2 LATTICE MATCHING OF α-CYCLODEXTRIN TO SUBSTRATES

Figure 1 shows positional relationships between α-CyD and atomic structures of substrate surfaces: highly oriented pyrolytic graphite (HOPG) and molybdenum disulfide (MoS_2). As is shown in Fig.1 (a), small shift of α-CyD will create another symmetric configuration on HOPG, leading to instability of α-CyDs on this surface. On the other hand, α-CyD exhibits threefold symmetric lattice matching commensurate with the structure of S atoms on the MoS_2 substrate surface (Fig. 1(b)). Ionic interaction between hydroxyls in CyD molecules and S atoms in the surface layer of MoS_2 is expected to stabilize CyDs on this surface.

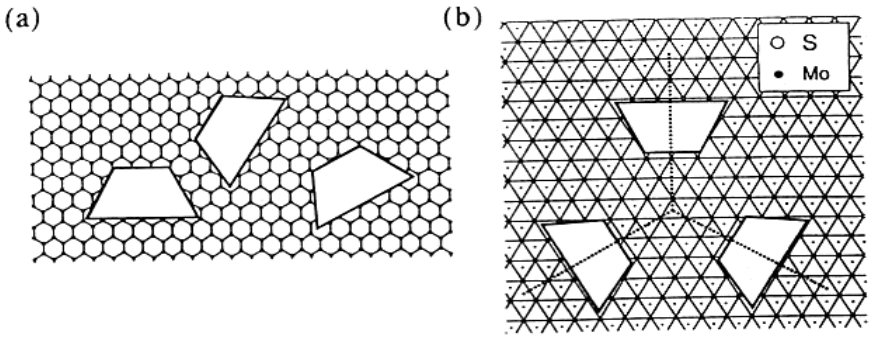

Fig. 1 Lattice Matching of α-CyD to (a) HOPG and (b) MoS_2.

3 EXPERIMENTAL

Specimens were prepared by deposition of CyD aqueous solutions (with or without guest compound) on freshly cleaved HOPG and MoS_2. STM measurements were performed in air using a PtIr tip, and all images in this paper were taken in the constant-height mode.

4 RESULTS AND DISCUSSION

4.1 CyD ON HOPG [3]

On HOPG, CyD-CyD interaction is dominant compared to the interaction between CyDs and the substrate, as mentioned in section 2. Actually, when CyD-CyD interaction was suppressed by forming, for example, CyD-adamantanemethanol inclusion complexes, the STM image became unstable and an ordered structure was not observed. However, when CyDs, without guests, were dense enough to form a monolayer, new ordered structures were observed for both α- and β-CyDs, which were attributed to the two-dimensional interaction instead of the three-dimensional one. An example of ordered α-CyDs on HOPG observed by STM is shown in Fig. 2. They have a structure intermediate between the head-to-head and head-to-tail structures, and are completely different from the herring-bone cage-type structure [4]. β-CyDs formed a similar but more tightly packed structure, which is considered to be attributable to the fact that the interaction between the two β-CyD molecules are stronger than those between the two α-CyD molecules. This conclusion agrees with the β-CyD solubility (1.85g/100ml) being considerably smaller than that of α-CyD (14.5g/100ml).

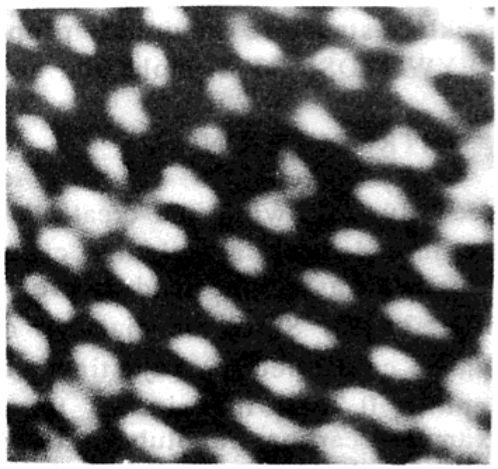

Fig. 2 α-CyD on HOPG (V_t=-24.1mV, I_s=0.91nA, 18nmx18nm).

4.2 MOLECULAR NECKLACE ON MoS_2

On the MoS_2 substrate, individual α-CyDs were stabilized, as expected. Making use of the interaction property between α-CyDs and MoS2, STM was performed on

α-CyD inclusion complexes with PEG using MoS_2 as a substrate. In order to identify each CyDs-PEG molecule, the concentration of molecules in aqueous solution was reduced sufficiently for each molecule to be isolated on the substrate. The observed structure obtained by STM was in good agreement with the molecular necklace structure previously proposed; α-CyDs are threaded on a PEG chain (Fig. 3) [1]. Ratios between the numbers of CyDs and ethylene glycols, which were controlled by changing the length of PEG chains, also agreed well with the values obtained by STM observations. For molecular necklaces about half-filled with

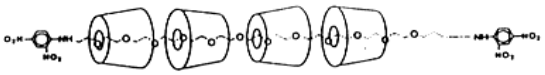

Fig.3 Schematic structure of molecular necklace.

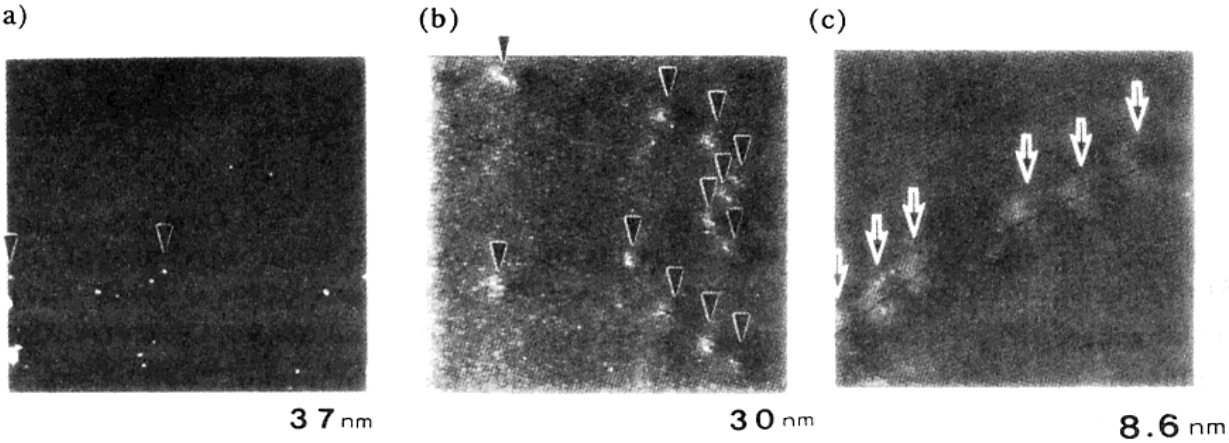

Fig. 4 Molecular necklace on MoS_2, (a) V_t=200mV, I_s=1.0nA, 37x37nm, (b) V_t=200mV, I_s=1.0nA, 30nmx30nm, (c) V_t=160mV, I_s=0.9nA, 8.6nmx8.6nm.

CyDs, CyDs were ordered in a chain structure but they did not agglomerate and were observed as individual units, as expected from the result of NMR measurement. Examples of STM images for the half filled CyDs-PEG inclusion complex are shown in Fig.4. Figure 5 shows an STM image of a molecular necklace completely filled with CyDs. Densely packed CyD structure can be seen here.

The STM image obtained for the molecular tube, i.e., an α-CyDs chain without PEG [3], was similar to that obtained for the completely filled molecular necklace, but was rather blunt, which is considered to be due to the fact that CyDs are connected to each other in a tube.

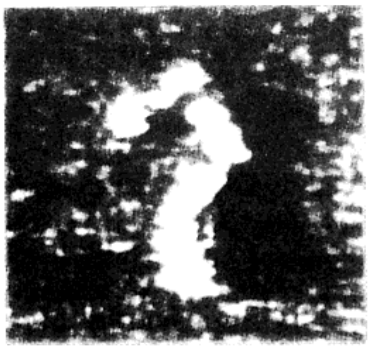

Fig. 5 Molecular necklace on MoS_2 (V_t=-200mV, I_s=0.9nA 18nmx18nm).

4.3 STRUCTURAL ANALYSIS BY LATTICE-MATCHING MODEL

Taking into consideration the structure and size of α-CyD, as shown in Fig. 6, the space which appears between two CyDs along the same axis (L in Fig.6) and the shift of axes of two CyDs (L' in Fig.6) depend on the conformation of two adjacent

CyDs, type A and type B in Fig.6. The values of L and L' can be represented by using the distances "a" and "d" between sulfur rows in [1$\bar{1}$0] and [110] directions, as L=n · d and L'=(1/2)m · a, where n and m are integers. These numbers are related with the conformations of two adjacent CyDs by n+m = even for type A, and odd for type B. Conformation of CyDs threaded by PEG were determined by our proposed lattice-matching model and details will be published elsewhere [5].

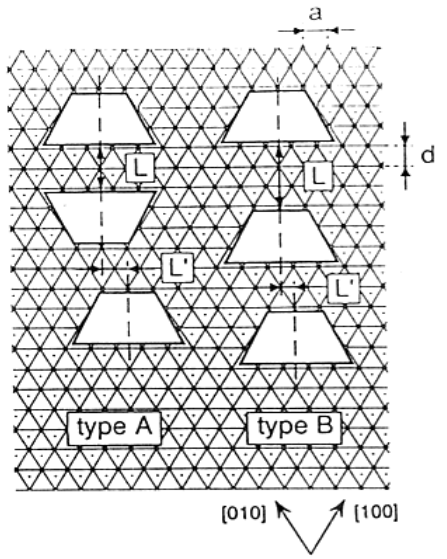

Fig. 6 Lattice-matching model of α-CyD on MoS_2.

5 CONCLUSIONS

New two-dimensionally ordered structures of CyDs caused by CyD-CyD interaction were observed on a HOPG substrate. On the other hand, the atomic structure of the MoS_2 surface was found to be commensurate with the structure of an α-CyD. Thus, making use of the interaction property between α-CyDs and MoS_2, α-CyDs-PEG inclusion complexes were successfully observed, the structure of which was in good agreement with the molecular necklace structure previously proposed.

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