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BY ATOMIC FORCE MICROSCOPY**

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Surface structure of MX-Chains studied by atomic force microscopy

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Abstract

The surfaces of mixed-valence halogen-bridged transition metal linear chain compounds $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2(\text{X}_{1-y}\text{X}'_y)_2](\text{ClO}_4)_4$ ($\text{X}, \text{X}' = \text{Cl}, \text{Br}, \text{or I}$; $\text{en} = \text{C}_2\text{H}_8\text{N}_2$; $y = 0.0 - 1.0$) were examined by atomic force microscopy (AFM). The AFM images are consistent with the surfaces expected from the bulk crystal structure. The surface unit-cell parameters of the images correspond to the lattice constants of the bulk crystals. The patterns of the atomic-scale AFM images are dominated by the most protruded H atoms of the en ligands and the most protruded O atoms of the ClO_4^- anions.

Introduction

The halogen-bridged platinum complexes $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2(\text{X}_{1-y}\text{X}'_y)_2](\text{ClO}_4)_4$ ($\text{en} = \text{C}_2\text{H}_8\text{N}_2$; $y = 0.0 - 1.0$; $\text{X}, \text{X}' = \text{Cl}, \text{Br}, \text{or I}$), generally referred to as "PtX", are among the most widely studied compounds of the MX class of low-dimensional solids. These highly anisotropic materials are susceptible to a Peierls distortion and characterized by one-dimensional metal-halide chains, with the metal atoms in alternating valence states often described as a charge density wave (CDW). The electronic and optical properties of these compounds have been studied both experimentally and theoretically [1].

The surfaces of MX solids have not been characterized so far. Scanning tunneling and atomic force microscopy (STM/AFM) are powerful techniques for surface analysis since they provide atomic or molecular resolution images of surfaces. STM is applicable for conducting and semiconducting materials, as it probes the tunneling current between the sample and tip. AFM is applicable also to insulators because it senses the repulsive forces between the sample and tip in a contact mode AFM. Since the PtX compounds do not provide tunneling currents sufficient enough for STM measurements we characterized the surfaces by AFM. In this contribution the atomic-scale AFM images of the surfaces of various PtX crystals are discussed.

Experimental

The PtX crystals were obtained by methods described previously [2]. The samples were examined without any surface treatment before imaging. The experiments were performed at ambient conditions with a commercial scanning probe microscope, Nanoscope III. We used pyramidal shaped Si_3N_4 tips. The images were registered in the height and force imaging mode. Molecular resolved images were processed by using the two-dimensional fast Fourier transform. More experimental details can be found elsewhere [3].

Results and discussion

Atomically flat surfaces are required in order to obtain molecular resolved AFM images. Not all the surfaces of the PtX samples meet this requirement. As an example a large-scale image of the bc-surface of PtBr is shown in Fig. 1a. The image shows atomically flat terraces with several steps. On such flat surfaces molecular-resolved images can be obtained routinely.

In contrast to PtBr and PtI, the main surfaces of PtCl do not reveal atomically flat terraces but rather rough surfaces. We believe that due to this fact no molecular resolved AFM images were obtained so far of this compound. It should be noted that not all surfaces of even the same compound show the same quality. Atomically flat terraces were observed only on the main, largest faces, while other faces appeared to be rough and no molecular resolved images were obtained on them.

An atomic-scale AFM image of the bc-surface of PtI is shown in Fig. 1b. The image consists of two different rows of patterns aligned along the b-direction. The unit cell parameters of the image are $b = 5.7 \pm .2 \text{ \AA}$, $c = 7.4 \pm .3 \text{ \AA}$ and $90^\circ \pm 3^\circ$. These values are in good agreement with the bc-plane parameters of the bulk crystal ($b = 5.805 \text{ \AA}$, $c = 7.448 \text{ \AA}$ and 90° [4]). It is worth to compare the AFM image to the bc-plane expected from the bulk crystal structure presented in Fig. 1c. The chains run along the b-axis, and the ClO_4^- counterions lie between the chains making N-H...O and C-H...O hydrogen bonds with their en ligands. Fig. 1c shows that the most protruded atoms of the bc-surface are the H atoms of the en ligand and the O atoms of the ClO_4^- anions. From the comparison of the AFM image with the surface structure of the bc-plane the rows revealed in the AFM image can be interpreted as visualization of the chains and the counterions. A more detailed study [5] by calculating the total electron density plots for the bc-plane surface shows that the ethylene H atoms contribute more to the AFM image than the O atoms of the ClO_4^- anions because the H atoms lie higher than the O atoms by $0.6 \text{ \AA}$. Thus, the bigger and brighter spots of the AFM image can be assigned to the H atoms of the ethylene groups and the smaller spots to the O atoms of the ClO_4^- anions.

A structural study of the mixed PtI/PtCl solids showed that the crystal structure is determined by the major constituent [2], so that the crystals with 70% PtI contributions have the structure of the pure PtI system. This also confirmed by the atomic scale image of the bc-surface of the mixed $\text{PtI}_{0.7}\text{PtCl}_{0.3}$ compound presented in Fig. 1d. Similar to the AFM image of the pure PtI the image consists of two different rows of patterns aligned along the b-direction. The main repeat distances of the AFM image of $\text{PtI}_{0.7}\text{PtCl}_{0.3}$ ($b = 5.7 \pm .1 \text{ \AA}$, $c = 7.4 \pm .3 \text{ \AA}$ and $91^\circ \pm 3^\circ$) are consistent with the unit cell bc-plane parameters of the bulk crystal of PtI. Thus, the AFM images of the bc-surface of PtI and $\text{PtI}_{0.7}\text{PtCl}_{0.3}$ reveal the features of the bc-

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Fig. 1: a) Large-scale image of PtBr ($220 \times 220 \text{ nm}^2$). b) Atomic-scale image of the bc-plane of PtI ($6 \times 6 \text{ nm}^2$). c) Molecular arrangement of the bc-plane of PtI taken from bulk crystal data. The numbers indicate the relative height difference (in pm) between the most protruded H atoms of the en ligands and the protruded O atoms of the ClO_4^- anions. d) Atomic-scale image of the bc-plane of $\text{PtI}_{0.7}\text{PtCl}_{0.3}$ ($13 \times 13 \text{ nm}^2$). e) Molecular arrangement of the ab-plane of PtBr taken from bulk crystal data. f) Atomic-scale image of the ab-plane of PtBr ($9 \times 9 \text{ nm}^2$). The unit cell is given in all atomic-scale images.

plane expected from the bulk crystal structure.

In PtBr the chains are aligned along the b-axis, and the counterions lie between the chains as in PtI. In contrast to PtI, however, there are two crystallographically inequivalent ClO_4^- anions per unit cell (Fig. 1e). Fig. 1e shows the molecular arrangement in the ab-plane of PtBr expected from the bulk crystal structure. The most protruded atoms are the H atoms of the en ligands and the O atoms of the counterions. The most protruded O atoms of the two ClO_4^- anions have a height difference of approximately $0.6 \text{ \AA}$, and the most protruded atoms of the higher-lying ClO_4^- anions lie about $0.2 \text{ \AA}$ lower than the most protruded H atoms of the en ligands.

An atomic-scale AFM image of PtBr is given in Fig. 1f. The unit cell parameters of the image ($a = 7.6 \pm 0.3 \text{ \AA}$, $b = 10.8 \pm 0.4 \text{ \AA}$ and $92^\circ \pm 4^\circ$) are consistent with the ab-plane of the bulk crystal ($a = 7.972 \text{ \AA}$, $b = 10.874 \text{ \AA}$ and 90° [7]). The image reveals two different rows of patterns of different heights aligned along the b-direction. The bright spots within each row have the same heights and form a straight line. A similar AFM image was also observed for the ab-surface of $\text{PtI}_{0.2}\text{PtBr}_{0.8}$. This is not in agreement with the topography expected from the bulk crystal structure (Fig. 1e). The two ClO_4^- anions appear in equal brightness despite the difference in their corrugation of about $0.6 \text{ \AA}$. Recent AFM studies [3] showed that AFM is quite

sensitive to height corrugations in the range of $0.3 - 1.0 \text{ \AA}$. The found discrepancy is most likely caused by an rearrangement of the ClO_4^- anions. A detailed analysis [5] of the hydrogen bond contacts suggests that the lower-lying counterions optimize their hydrogen bond interactions by such a rearrangement. In conclusion the presented results demonstrate the AFM abilities in characterization of surface topography of MX-chain solids.

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