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SNOM: a new photophysical tool

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Abstract

Scanning near-field optical microscopy (SNOM) is used as a new photophysical tool for the elucidation of the surface hydration processes of crystalline phthalimide (**1**) by determination of the chemical contrast. Surface hydration and hydrolytic ring opening to give phthalamic acid (**2**) are distinguished at the nanoscale. The long-range molecular movements are interpreted in terms of the crystal packing.
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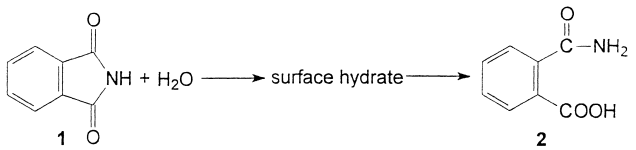
Keywords: SNOM; AFM; Local chemical contrast; Hydration of phthalimide; Crystal surface phenomena; Nanosciences; Long-range molecular movements

1. Introduction

Scanning near-field optical microscopy (SNOM) on rough surfaces is a new photophysical tool for the recording of chemical contrast at the submicroscopic level [1]. It complements submicroscopic techniques such as atomic force microscopy (AFM) that record topography and its changes down to the molecular and submolecular scale. The high importance for most surface phenomena is apparent not only in photochemistry [2], biology or material sciences. A particular problem in such surface sciences is the local identification of different species in minute quantities if only few molecular layers are involved. We report here on two distinct surface changes if phthalimide crystals (**1**) are exposed to vaporized water and their analysis by SNOM. These processes deserve scrutiny as they may complicate the study of solid state syntheses [3].

2. Experimental details

A reflection back to the fiber SNOM setup under shear force AFM control with uncoated fiber tips, that were pulled to opening angles $<10^{\circ}$ and end radii of 15–20 nm, was used. This setup is appropriate even on rough surfaces that are scanned at constant shear force [1,4,5] and (topographical) artefacts are carefully avoided [6]. Both an argon-ion (488 nm) and a helium–neon laser (633 nm) were used for the recording of chemical contrast. The near-field enhancement factors in the presented measurements were 2.8 and 3.0. Single crystals of **1** were grown from acetone.



3. Results and discussion

The (0 0 1) surface of phthalimide crystals (P21/n from acetone [7]) changes when left in moist air and similarly but more rapidly when stored in a vacuum near the saturation pressure of water at room temperature. The sequence of events may be easily followed with contact AFM. The initial surface in Fig. 1 is very flat ($R_{ms} = 0.349$ nm; some pre-exposure is apparent), the step heights are at the monomolecular range and some peaks with heights of 2.3–3.0 nm persist in moist air. However, numerous monolayer-sized steps and deeper ditches align along the long crystal axis [0 1 0] upon the moderate exposure to moisture. More extended exposure to moisture (weeks) or exposure to undiluted vapor of water retained the direction of preference (the ditch in Fig. 1c is ca. 10 nm deep) but additionally volcano-like hills of considerable height (180 nm in Fig. 1c) were formed. Apparently, two different processes with long-range molecular movements are seen. The most likely interpretation is surface hydration for the terraces/ditches and hydrolytic ring opening to give phthalamic acid (**2**) for the volcanoes.

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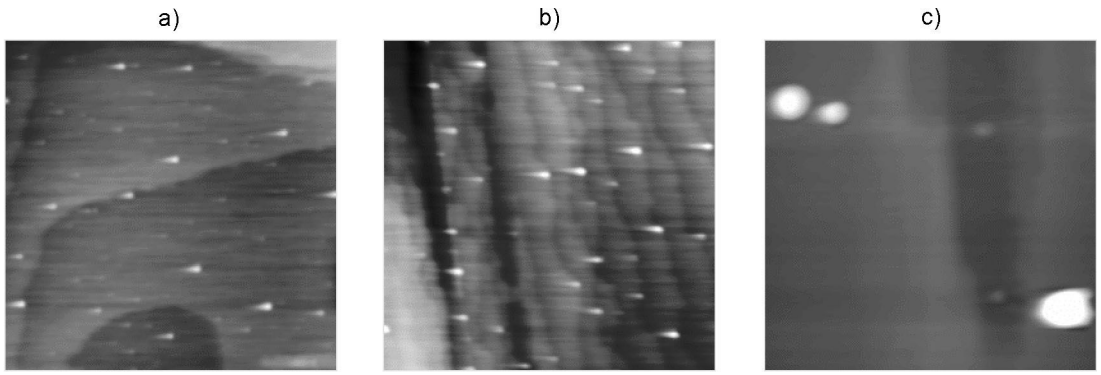

Fig. 1. 5 μm AFM topographies on (0 0 1) of phthalimide (**1**) at room temperature: (a) from acetone ($z = 10$ nm); (b) after 2 days in air (relative humidity was 50–60%; $z = 10$ nm); (c) after 16 h in water vapor ($z = 200$ nm).

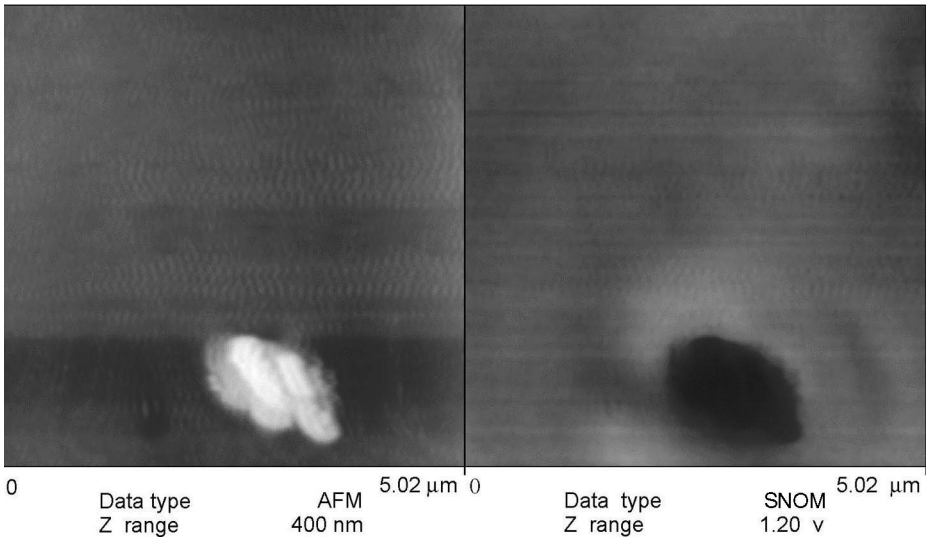

Fig. 2. Shear-force AFM and simultaneous reflection-back-to-the-fiber SNOM on (0 0 1) of a phthalimide crystal (**1**) that was exposed to water vapor. Optical contrast at 488 nm.

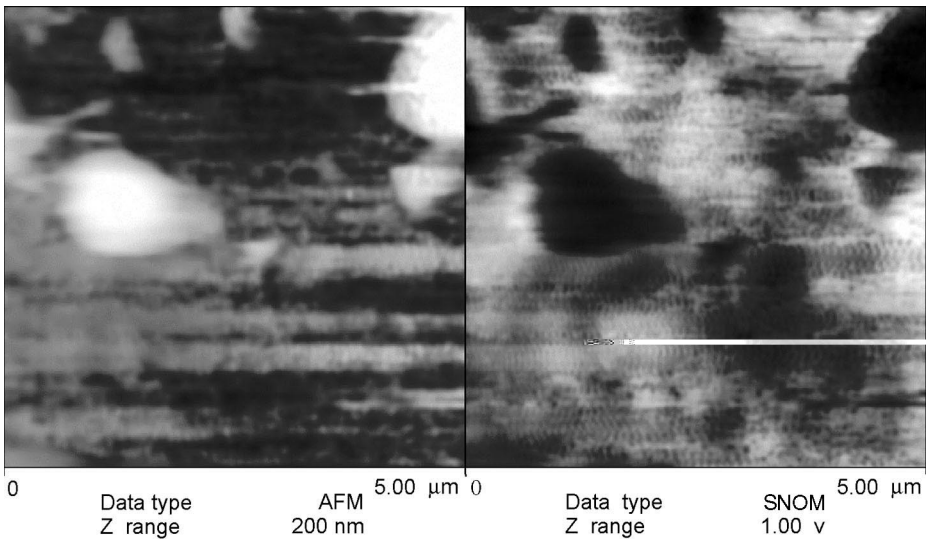

Fig. 3. Simultaneous AFM/SNOM on (0 0 1) at a more advanced state of exposure of crystal **1** to water vapor. Optical contrast at 633 nm.

part to the lower right and at further locations. There seems to be a tendency for bright contrast in the depths, where the water content may be higher. Again, the perfect correspondence of optical contrast and topography guarantees the validity of the data [6], that can be interactively explored using the VRML full data [8].

Phthalamic acid (**2**) is the product of base catalyzed hydrolysis of **1** in solution, followed by acidification [9] and there remain no other reasonable possibilities for the interpretation of the SNOM data. Thus, the correlation of the AFM/SNOM data with the crystal structure of **1** [7] is of importance. The 3D images in Fig. 4 show the stacking of hydrogen bridged dimers of **1** parallel to (0 0 1). A further glide plane is (1 0 1) that runs parallel to the *b*-axis and therefore explains the direction of preference in the AFM images of Figs. 1 and 3.

One half of the carbonyl groups of **1** remain unbridged. It is therefore comprehensible that the surface may be hydrated and reconstructed, initially in monolayers. Furthermore, the molecules **2** once formed have to move above the (0 0 1) surface and leave the lattice, as they do not geometrically fit. An obvious way is along the (1 0 1) glide plane, but that is not smooth and makes such movement difficult. The best way for the system is to start at nucleation centers and build islands around it. Thus, the occurrence of isolated volcanoes reflects nicely the correlation to the crystal structure.

4. Conclusions

The applications of SNOM, that use the recently found and secured near-field enhancement effect (reflected light at shear force distance) [5], are by no means restricted to photochemistry [2]. The present model for the application of the new photo-tool points to numerous applications in all fields of surface sciences where the submicroscopic elucidation of local surface structure and surface change gains more and more importance [1]. SNOM on rough surfaces opens exciting new possibilities for supermicroscopy with light in the near-field at distances of interaction that are well below 10 nm, including local near-field fluorescence and Raman spectroscopy [10]. The present results show, that AFM studies of surfaces at high resolution under ambient conditions should be complemented by SNOM at constant shear-force, particularly if complications by surface hydrations are to be expected.

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