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Atomic-scale investigations of solid-liquid interfaces by frequency modulation atomic force microscopy

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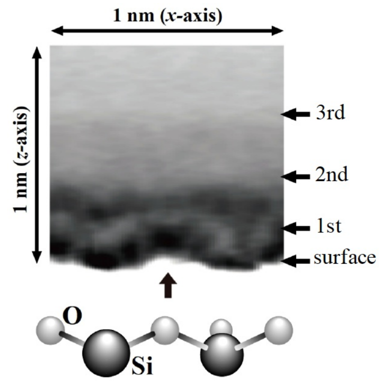
Significant progress has been made in frequency modulation atomic force microscopy (FM-AFM) in liquids over the past few years, which allows us to directly investigate solid-liquid interfaces as well as "in vivo" molecular-scale biological processes. One of the major difficulties in FM-AFM imaging in low Q-factor environments was a large increase in the phase noise of the self-oscillation loop for the cantilever. Recently we successfully reduced the phase noise by decreasing the coherence of the laser light used in the cantilever deflection sensor.

In this presentation subnanometer-resolution imaging of crystalline surfaces as well as biomolecules in liquids using the improved FM-AFM is described. FM-AFM imaging of a muscovite mica surface in pure water revealed the honeycomb structure of SiO4 tetrahedrons with a period of 0.52 nm. Recent atomic-scale study of calcite surfaces in aqueous solution is also presented. Furthermore, we also imaged a purple membrane consisting of hexagonally packed bacteriorhodopsin protein molecules in a phosphate buffer solution by FM-AFM. An array of protein trimers was clearly imaged. Furthermore, plasmid DNAs (pUC18, 2686 bp) adsorbed onto a mica surface were imaged by FM-AFM in a buffer solution containing 50 mM NiCl2. We succeeded in visualizing individual phosphate groups composing the DNA backbone chains.

In addition, we recently found that frequency shift vs distance curve measured in water by FM-AFM reflects a local hydration structure. The oscillation structures with a period of about 0.2 - 0.3 nm, which is similar to the size of the water molecule, reproducibly appeared in the frequency shift curves. This new method for the investigations of local hydration structures was combined with the force mapping method, where forces (frequency shifts) are three-dimensionally mapped by measuring the force (frequency shift) curves over the sample surface. The frequency shift signal was recorded while the AFM tip was scanned in the vertical (z) and horizontal (x) directions on a mica substrate in water. As shown in Fig.1, the results reveal that there are three/four water layer structures with slightly different spacings on the surface and that the closest layer to the surface has an atomic-scale horizontal structure reflecting the surface crystal structure of muscovite mica. The obtained hydration structure was compared with water density distributions calculated using the 3D reference interaction site model (3D-RISM) theory.

Figure 1. Two-dimensional (x and z directions) frequency shift mapping (gray contrast) in a KCl aqueous solution on a mica crystal surface.



Keywords: solid-liquid interface, hydration structure, atomic force microscopy, FM-AFM, surface atomic structure