

Summary

Surface nanopatterns are interesting for several reasons. They can be used to functionalize substrates, to build electronic nano-circuits or to be employed as wells to trap (bio) molecules. In our study we are interested in creating ordered arrays of molecules with nanometer periodicity for templating. A nanopattern on a surface can be used to induce order in subsequently deposited material. Our aim is to use these templates to enhance protein crystal growth. Regular crystal surfaces have too small repetitive units, therefore we chose ordered macromolecular monolayers on crystalline surfaces as candidate templates.

As described in the introductory chapter many processes and interactions occur at a surface. All these influence the formation of macromolecular monolayer templates. A variety of these aspects is studied in this thesis, in order to be able to create a stable template for crystal growth.

In chapter 2 we describe the processes taking place during removal of a crystal surface from solution. The deterioration of crystal surfaces during removal from solution prior to observation (the shut-off effect) poses a serious problem for ex situ (atomic force) microscopy studies. The influence of the following parameters: size, orientation, lifting rate, humidity, airflow, rinsing and pollution on surface quality are investigated for our model system of potassium alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$) crystals. Based on this a descriptive model for the processes occurring during removal is obtained. Implications for other systems are presented in order to minimize the difference between in situ and ex situ surfaces. This difference is minimized for potash alum if a crystal is lifted slowly from its solution with its surface of interest in a vertical position at a humidity below room humidity and in the absence of air flow.

A completely different aspect of surface self-assembly is treated in chapter 3. Here the structure of and (re) arrangement at muscovite mica surfaces in three different potassium rich circumstances is investigated using surface X-ray diffraction. For these three circumstances we have measured specular and in-plane crystal truncation rods using synchrotron radiation. We show that 'dry' mica is covered with half a monolayer of downwards relaxed potassium ions positioned in the middle of the surface cavities and water layers on top, which are strongly ordered. Mica in contact with potassium rich solvents results in two half monolayers of potassium ions covering the surface of which one half layer is relaxed downwards into the cavities and the other upwards.

The position of these potassium ions influences the self-assembly of macromolecules on top of the crystal. In chapter 4 the ordering of a phthalocyanine molecules modified with ether tails on the mica surface is studied *ex situ* as well as *in situ*. Using AFM and surface X-ray diffraction an ordered layer of approximately 1 nm thickness is found *ex situ*. *In situ*, however, no in plane ordering exists. The material is attracted towards the substrate surface, but instead of ordering it aggregates in a liquid-like fashion. This is likely caused by the fact that the water present in the ethanol solution has a stronger interaction with the potassium ions on the mica surface than the ether tails of the phthalocyanine.

In chapter 5 the growth of a free base C_{11} -tailed porphyrin on an organic crystalline substrate with low surface symmetry is studied. Layers of this porphyrin are deposited from n-heptane solution onto single crystalline potassium acid phthalate substrates and the self-assembled structures obtained are characterized by atomic force microscopy and X-ray diffraction. Depending on the concentration of the porphyrin solution, different anisotropic structures are found, which are epitaxially related to the substrate. For undersaturated solutions patterns of approximately 2.5 nm thickness are formed, which correspond to porphyrin molecules stacking approximately perpendicular to the substrate surface. From supersaturated solutions multilayers are formed. At the highest concentrations nanosized needles develop with a different molecular layer spacing, which cover the whole substrate, creating a 'monocrystalline' film with a length scale of several millimeters.

The last chapter describes a porphyrin monolayer on graphite consisting of two different packings, which is used as a template for protein nucleation. We show that the layer can be imaged using ambient tapping mode atomic force microscopy and study the deposition of 2D and 3D protein structures on this layer. For 2D deposition we show that the proteins attach firmly to the porphyrin template and that the 2D structures can be influenced by the underlying template. 3D crystal growth on the porphyrin template shows promise for protein nucleation enhancement, but additional experiments are needed to confirm this.