X-Ray diffraction studies on 3D magnetic nanoparticle assemblies

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Fundamental research on magnetic nanostructures is an important part of today's scientific effort in information technology [1]. In particular, self-assembled structures of magnetic nanoparticles are candidates for a new generation of improved magnetic storage media [2]. The understanding and control of the structure in 2D and 3D self-assembled particles is of great interest for application, as it allows low-cost mass production of very small structures. The samples that were investigated contain spherical iron oxide nanoparticles with narrow size distribution (ca. 10 nm diameter). The nanoparticles have been deposited on Si substrates by a drop casting method in a magnetic field to achieve a highly ordered arrangement. These 3D ordered arrangements of nanoparticles are called mesocrystals, in analogy to crystals formed by atoms. The mesocrystals grow as pillars on a flat silicon substrate (Fig. 1), are covered with Pt layers and extracted with a focused ion beam. They measure about 2000 nm in diameter and 500 nm in height. The superstructure of the

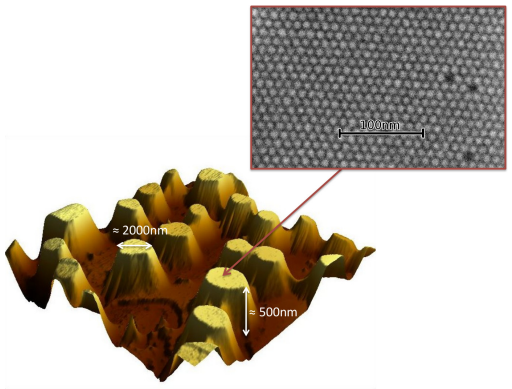

Fig. 1 SEM measurement from the top of a mesocrystal and overview of the arrangement of mesocrystals on a substrate with AFM

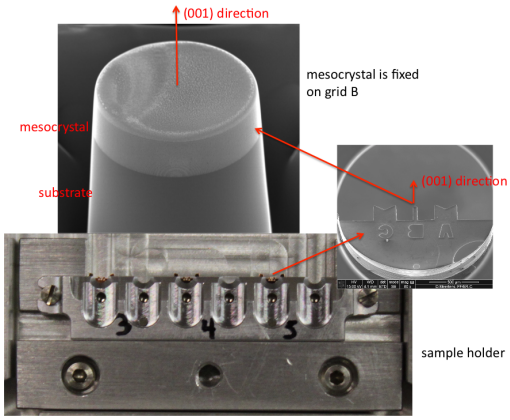

Fig. 2 Single mesocrystal extracted from a structure as in Fig. 1. The size is 2 μm in diameter and 500 nm in height.

nanoparticles was precharacterized using SEM (Fig. 2). The purpose of this study was to use a completely new approach: Performing a diffraction experiment on a single isolated mesocrystal with a microfocused x-ray beam, thus measuring the mesocrystal peaks without powder average and without background from disordered regions, as was the case in previous experiments.

A diffraction study under small diffraction angles was performed at P08 in order to determine the structure of a single highly ordered mesocrystal. A special setup was built to fix the single mesocrystals on the sample holder (Fig. 2) and goniometers were used to adjust the position with the (00l) direction of the mesocrystal lattice parallel to the axis of the phi circle (vertical to the beam), in order to rotate around the z-axis to reach different directions in the plane while keeping the l-component fixed. The detector position was fixed at 77 cm distance from the sample and the energy at 25 keV to have sufficient q-range to reach as many reflections as possible at a time and to avoid beam damage to the sample.

On the first day and night the experimental setup was built, the beamline was aligned and the sample was installed. For searching for the sample, we started with a Perkin-Elmer detektor (2048^2 pixels with 200μm size), which is not a high resolution detector, but it is optimized for the wavelength, has

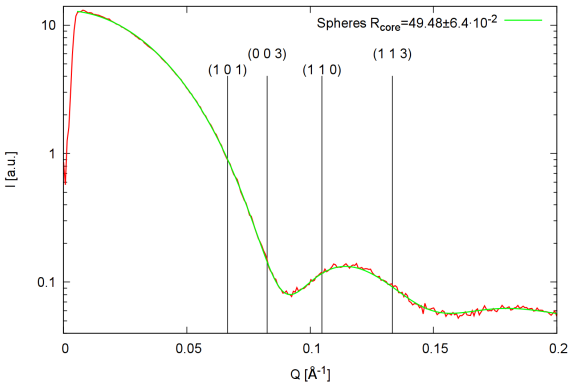

Fig. 3 SAXS measurements on Fe_2O_3 nanoparticles dissolved in toluene. The peak positions of the mesocrystal structure are indicated to illustrate the peak intensity corresponding to the formfactor. It is clearly visible, that the (101) reflection has about a factor of 8 higher intensity than the (003) (same absolute q value and thus intensity as (012)).

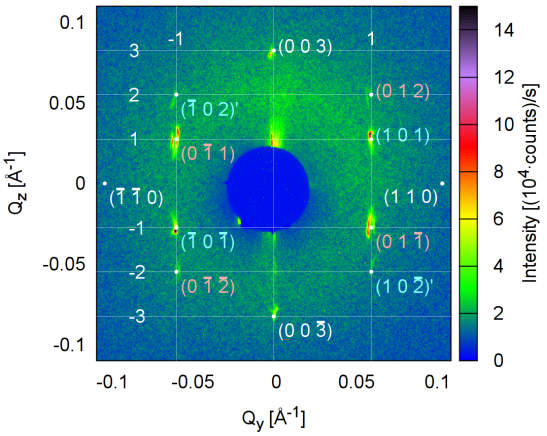

Fig. 4 Scattering from a single Mesocrystal. The peak close to the beamstop is no Bragg reflection, more s.th from the direct beam. The q-calbiration was calculated from the detector size and distance (measured with th Cu (111) powder ring). The colored peak labels correspond to one twin of the crystal.

a large area and can be read out very fast. Unfortunately no peaks from the silicon substrate could be measured with this detector, even after two days of alignment. As this approach was not successfull we switched to a combination of a NaJ point detector to measure the beam attenuation from the sample holder in combination with the high resolution detector, which was used to carry out a precise adjustment with the substrate's Si (400) reflection to define the exact out of plane direction. The same detector was used to search for the mesocrystal reflections afterwards. Reflections for one plane of the reciprocal space have been found (see Fig. 4 measured by rocking the crystal in both omega and phi during 2 hours, and subtracting background also measured for 2 hours). Repetitions of this plane every 60° have been verified, proving a three- or sixfold symmetry of the lattice. Already here proof of principle is made as the indexed peaks are consistent with the known R-3m space group and lattice parameters [3], the plane is readily identified as (h0l) and the peaks are readily indexed. The presence of both e.g. (101) and $(01\bar{1})$ shows the presence of twin domains observing -h+k+l=3n or h-k+l=3n, repectively - as often occurs in rhombohedral crystals and indicated for these samples by TEM. The similar peak shapes of $(0\bar{1}1)$ and $(01\bar{1})$, which arise from only one of the domains, are also cosistent with this. These peaks are split, suggesting for these twin domains with slightly different lattice constants. The peak with lowest q outside of (h0l) is (110), and we searched intensively for any hkl reflections but intense search in the hhl-plane 30° away form h0l yielded no results.The formfactor measurements show that the intensity of these other peaks are much weaker which makes it very hard to detect them on top of the relatively large background signal.

This challenging experiment proved the feasibility of the investigations on single, small mesocrystals of nanoparticles to open a new field for further investigations of the mesocrystal structure. The analysis of the intensities and the rocking curves is still in progress.

References

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