Laterally Inhomogeneous Self-Ordered Structures on Surfaces Investigated by GISAXS Microtomography

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Grazing-incidence small-angle x-ray scattering (GISAXS) is a standard tool for the analysis of surfaces and thin layers containing nanometer-sized structures. In order to obtain a two-dimensional map of their local morphology, we performed GISAXS microtomography on dried drops of colloidal suspensions. In particular, we investigated the self-organization of drying suspensions of TiO_2 on polyethylene surfaces. Hierarchically structured titania films and their mesoporous structure on the nanoscale have a large variety of applications, e. g., in photovoltaics, photocatalysis, and gas sensing. They are prepared by combining sol-gel chemistry with an amphiphilic diblock copolymere as a structure-directing agent. The sample presented here is a dried drop of nanostructured titania (TiO_2), consisting of a sponge-like structure with an expected pore size of 30 - 40 nm. Figure 1(a) shows an optical micrograph of this laterally inhomogeneous sample. Prior to depositing the drop, the Si substrate was spin coated with the same solution.

GISAXS microtomography is ideally suited to investigate the local structure of such an inhomogeneous object. The feasibility of this method was recently demonstrated [1,2] with polystyren nanoparticles of well-known sizes [3]. It was developed based on a similar tomographic reconstruction technique for small-angle x-ray scattering (SAXS) that has been demonstrated on injection moulded polyethylene, collagen fibres, nanoporous glass, and freeze-dried biological samples [4,5,6]. While for SAXS tomography the kinematical theory of diffraction can be applied in most cases, the interpretation of GISAXS patterns relies on the distorted wave Born approximation (DWBA). In general, GISAXS data does not allow for tomographic reconstruction. However, for example, a tomographic reconstruction is possible for films with a local fibre texture about the surface normal. In this study, we derived a method to verify the validity of a tomographic reconstruction [1] [Fig. 1(b)]. For green pixels in Fig. 1(b), the tomographic model is consistent, while for yellow and red pixels the tomographic reconstruction is not possible due to a low signal or inconsistencies, respectively.

The experiment was performed at beamline BW4 [7]. The sample was scanned in 73 translational steps of $\Delta y = 25\,\mu m$ each and 113 rotational steps over 180°, recording at each position of the scan a GISAXS pattern with $t = 3\,s$ aquisition time [2].

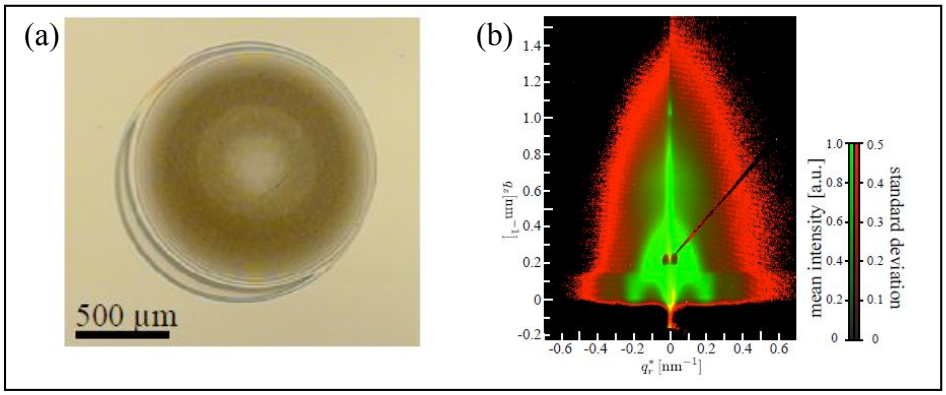

Figure 1: (Color) (a) Optical micrograph of the dried drop of nanostructured titania. (b) Consistency check of the tomographic data set as described in [1].

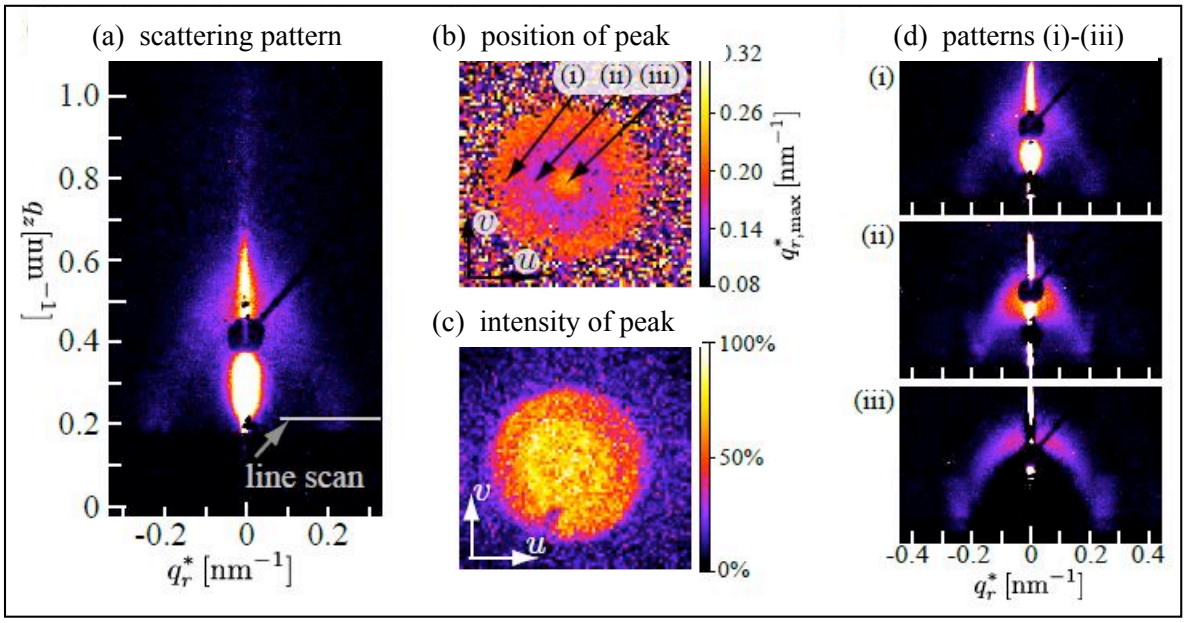

Figure 2: (Color) Example data analysis of a GISAXS microtomogram [1]. (a) Reconstructed GISAXS pattern with marked line scan. (b) The peak position and (c) the peak intensity along this line scan at each position in the drop. (d) Reconstructed GISAXS patterns of at the positions (i), (ii), and (iii) shown in (b).

The resulting tomogram consists of 74 x 114 = 8436 GISAXS patterns recorded with a mar165 detector. The incident angle was set to $\alpha_i = 0.3°$ and the sample-to-detector distance was $L_{SD} = 2101$ mm. Figure 2 shows a typical example of how the tomographic GISAXS data are analysed. Figure 2(a) displays one of the 5476 single reconstructed GISAXS patterns. From these patterns, certain features can be extracted for detailed analysis, e. g., the position and intensity of a side lobe of the GISAXS pattern along the line scan shown in Fig. 2(a). These two quantities are mapped as a function of position in the drop in Figure 2(b) and (c), respectively. In addition, the full GISAXS data is available at each location in the drop, as shown in Figure 2(d) for three locations pointed to by the arrows in Fig. 2(b). Four complete tomograms of dried drops of nanostructured TiO_2 were recorded and are currently evaluated.

This experiment successfully concludes the methodological developments of SAXS and GISAXS microtomography at BW4.

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