The dip-coating technique is one of the commonly applied methods for the preparation of thin films or the patterning of templates from polymer solutions and particle suspensions [1]. The coating principle is based on the withdrawal of a solid substrate out of a liquid solution. The withdrawal and supposed deposition of a specific material are mainly governed by the withdrawal speed and the physical as well as chemical sample surface properties [1]. Hence these parameters determine whether the deposition yields the desired patterning result. In this regard, Ghosh et al. prepared stripe-like pattern and demonstrated the dependence of the deposition as a function of particle diameter, withdrawal speed and entrained film thickness to come up with different deposition modes [2]. In general, the pattern formation takes place at the triple phase contact line (TPCL) of air, solution and substrate. Roth et al. investigated recently the air-water-substrate boundary of a drying droplet of colloidal solution obtaining a quantitative view of the nanostructuring during solution casting [3, 4]. However, in contrast to the dip-coating process, the structuring process in solution casting is mainly evaporation driven.

We present the first results of an in-situ investigation of the dip-coating process of colloidal suspensions and nanoparticles by the advanced scattering technique grazing incidence small angle X-ray scattering (GISAXS) as shown in the scheme in Figure 1. The selected GISAXS method is predestined for this in-situ investigation, because it is a non-destructive structural probe and requires no special sample preparation [5]. The features of GISAXS as an advanced scattering method are the surface sensitivity, the selectivity to materials and the yield of excellent sampling statistics because it averages over macroscopic regions to provide information on the nanometre scale. After the in-situ GISAXS experiments, the as-prepared samples are analyzed by optical microscopy (OM) for an overall homogeneity check of the dip-coated thin film. Finally, the surface

Figure 1: Schematic representation of the experimental GISAXS geometry. In contrast to conventional GISAXS experiments, the sample surface is positioned vertically in order to perform the dipping of the sample into the solution-containing trough. The X-ray beam impinges on the sample surface with a fixed angle of incidence $\alpha_i$ adjusted by a rotatable rod on which the sample is mounted. The scattered beam is described by the exit angle $\alpha_f$ and the vertical scattering angle $\Psi$. The area detector shows the $q_y$ dependence along the vertical axis and the $q_z$ dependence along the horizontal axis. The detected two-dimensional scattering pattern shows the diffuse scattering with a broad Yoneda peak and the specular peak (shielded by a beam stop). During the in-situ dip-coating study the trough moves vertically, whereas the sample exhibits a stationary position.
structures are investigated by atomic force microscopy (AFM), yielding topographic images and thus real space information about the structure heights and widths.

The focus is on the real-time monitoring of the vertical dip-coating process to deliver an insight of the structural changes during pattern formation. With the selected measurement configuration, a fixed spot on the sample surface is probed and the structural information at the time the contact line passes through the beam-illuminated area is obtained, hence revealing the structure at the vicinity of the flowing meniscus.

First experiments have been performed at beamline BW4 of the DORIS III storage ring of HASYLAB using a moderately micro-focused beam ($\lambda = 0.1381 \text{nm}$) with a size of $23 \mu\text{m} \times 36 \mu\text{m}$ (VxH) enabling the required lateral resolution. The distance between the sample and the fast Pilatus 300k-detector was set to 2015 mm. Figure 2 presents the results of the simultaneous GISAXS measurements of the dip-coating process of pure silica nanoparticles ($2R = 30$ nm) with a drawing speed of 200 $\mu\text{m}/\text{min}$ [6].

![Figure 2: (left) 2D scattering pattern of the dip-coated thin film of silica nanoparticles as the last frame recorded during the in-situ measurement. (right) Intensity map representing the change in the Yoneda-region (blue box) as a function of time during the dip-coating process. For colour coding: blue/dark = low intensity and purple/white = high intensity.](image)

In continuation of the previous successful experiments, a more detailed investigation of the process key parameters, e.g. withdrawal speed, concentration, substrate surface modifications etc., will be performed with purely colloidal suspensions as well as the successive patterning of these prepared colloidal templates with different species of nanoparticles. Furthermore, the possibilities are discussed of obtaining 1D, 2D, and 3D structures used for different photonic and magnetic applications.

References