Ordering During Directional Drying in Colloidal Films: An in situ Grazing Incidence X-ray Scattering Study


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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, 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].

The technique is based on a drying process, the so-called directional drying, involving the natural propagation of drying fronts across the liquid film. Solidification starts from the film edge and progresses towards the middle, whereas three distinct transitions are identified: ordering, aggregation and dewetting [3]. Roth et al. investigated recently the air-water-substrate boundary of a horizontally drying droplet of colloidal solution obtaining a quantitative view of the solidification and ordering [4]. However, the directional drying during dip-coating involves the drawing speed as additional parameter. For a full understanding of the drying process, several parameters are of interest, i.e. film height, particle concentration and structure height at any given time during drying at a fixed spot on the sample surface are of interest. Based on this complex knowledge, the evaporation profile over the liquid film and occurring flows could be extracted.

The investigation of the vertical drying process during dip-coating is performed by microbeam grazing incidence small angle X-ray scattering (µGISAXS) as non-destructive, surface sensitive probe revealing the structure at the vicinity of the drying fronts as shown in the scheme in Figure 1. With the selected measurement configuration, a fixed spot on the sample surface is probed and the structural information at the time the drying fronts pass through the beam-illuminated area is obtained [5].

Recent experiments have been performed at beamline P03 MiNaXS of the PETRA III storage ring using a micro-focused beam (λ = 0.096 nm) with a size 6 x 4 µm² (h x v) enabling improved lateral resolution [6]. The distance between the sample and detector was set to DSD = 4590 mm.
Figure 2 presents the results of the simultaneous GISAXS measurements of the dip-coating process of a model system of polystyrene nanoparticles ($2R = 194$ nm) in an aqueous suspension with a drawing speed of 2.25 mm/min at 10 frames per second (fps). The final scattering pattern at time $t = \tau$ in Figure 2(a) clearly indicates the successful deposition of the thin colloidal film with a highly ordered hexagonal array of PS nanoparticles.

![Figure 2](image)

Figure 2: (a) 2d GISAXS data of the final dip-coated thin film of PS nanoparticles. (b) Extracted characteristic in-plane length scale $\Lambda$ as a function of the drying time $t$.

The evolution ($t_0 \rightarrow \tau$) to the final particle arrangement is represented by the extracted characteristic in-plane length scale $\Lambda$ as a function of the drying time $t$ as shown in Figure 2(b). The appearing peak at $q = 0.0224$ nm$^{-1}$ becomes more pronounced and shifts towards $0.0395$ nm$^{-1}$ (horizontal dashed lines), hence decreasing the characteristic in-plane length scale $\Lambda$ from 280 nm down to 159 nm. Furthermore, distinct transition regions (vert. dashed lines) upon solvent evaporation are clearly identified by the change in slope of $\Lambda(t)$ [7].

The successful experiments at MiNaXS on the pattern formation of drying colloidal suspensions illustrate strikingly the very high potential of advanced scattering experiments in grazing incidence. The experimental setup provides the required high precision for gracing incidence sample alignment and enables real-life conditions under controlled environment. Due to the improved time-resolution by a factor of 100 (0.1 fps$\rightarrow$10 fps), the identification of distinct transition regions is possible [5, 7]. However, further analysis, i.e. peak heights and widths, yields concentration profile is required and a more detailed investigation of the process key parameters will be performed with purely colloidal suspensions as well as the successive patterning of these prepared colloidal templates with different species of nanoparticles.

References