Flow induced surface attachment of gold nanoparticles - an in situ x-ray investigation with micro-fluidic cell

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The deposition of metallic nano-particles onto solid surfaces is of interest in a wide range of topics from nanoelectronics and nanosensors to nanocatalysts. One way of to achieve patterns of ordered nanoparticles is to apply a continuous flow over the substrate via a micro-fluidic channel [1, 2]. X-rays are a useful probe for the investigation of flow and processes in micro-fluidic systems. In transmission geometry (SAXS, small angle x-ray scattering) growth processes or the orientation of nanoparticles can be followed. With the application of a reflection geometry in GISAXS (grazing incidence small angle x-ray scattering) and a special designed fluidic cell also surface sensitive investigations are possible [1]. With this method the selective immobilization of gold nanoparticles on one block of a micro-phase separated block-copolymer surface was investigated in-situ leading to the growth of gold nanowires [2].

Figure 1: Set-up of micro-fluidic cell  a: installation at MiNaXS beamline; arrow indicates the incoming x-ray beam  b: top part cell design with Luer connectors for one inlet and two outlets.

In figure 1a the set-up of the micro-fluidic cell at the micro- and nanofocus x-ray scattering beamline (MiNaXS/P03) at the synchrotron source PETRA III is shown. The x-ray beam was focused to a size of 35 µm x 22 µm by beryllium compound refractive lenses. The arrow in figure 1a depicts the x-ray beam from the position of guard slits to the position hitting the micro-fluidic cell. The fluidic cell for GISAXS investigations comprises a top part made of a copolymer based on cyclic olefines shown in figure 1b. The material is transparent to visible light and has a relative low absorption in the x-ray range used in the experiments. The top part is connected to the surface to be investigated (e.g. a thin polymer film on a glass slide with a metallic clamp as shown in figure 1a). The channel geometry (1 mm wide and 1.3 mm deep) enables the study of the solid-liquid interface during the continuous flow stream of a solution with a broad range of flow rates. There are two inlets allowing for mixing experiments and chemical reactions.
In this study the attachment of high aspect ratio gold nanorods to surfaces of calcium-alginate is investigated. Spin-coating of thin films of sodium-alginate and subsequent cross-linking with divalent calcium ions leads to water insoluble films. The high aspect ratio gold nanorods with a size of 25 nm x 256 nm are stabilized with cetyltrimethylammoniumbromide (CTAB). The polyanion alginate serves as a counterpart to the nanoparticles with net-positive charge. Only one of the inlets of the micro-fluidic cell is used to pump the aqueous nanoparticle dispersion with 0.05 ml/min. A scan of the micro-fluidic channel (along y-direction in figure 1b) is carried out, collecting scattering data for 0.5 s at 70 positions in 250 µm distance from each other. The duration of one scan is 180 s. The flow experiment is run for 1 h with 20 subsequent scans along the channel. This procedure offers a time as well as a position resolved investigation of the nanoparticles attachment at the same time.

Figure 2: 2d detector patterns for flow experiment with gold nanorods on alginate surface; arrows indicate Bragg reflection spots.

In figure 2 the 2d GISAXS detector patterns are shown for one of the positions on the channel. The 2d patterns are marked with the number of the scan. The first scan shows the GISAXS pattern of the dry alginate film. The characteristic features arising with flow of the nanoparticle dispersion are Bragg reflections indicated with arrows in the 4th scan of figure 2. The Bragg reflections are accompanied by a ring shaped intensity centered by the direct beam. With following scans (6th and 20th run are shown in figure 2) the Bragg reflections as well as the ring shaped intensity are more pronounced and observed at smaller q-values. The scattering patterns with Bragg reflections indicate domains of 2d cylindrical hexagonal structures oriented parallel to the surface.

Figure 3: Contour plots of vertical cut of 2d detector pattern for 70 positions on the micro-fluidic channel.

In figure 3 the GISAXS data dependent on the position of the micro-fluidic channel are illustrated with a contour plot of a vertical (detector) cut for the 70 positions on the channel investigated. The contour plots are shown for the 4th and the 20th run. Whereas in the 4th run one Bragg reflection is clearly observable, in the 20th run this reflection is shifted to smaller q_z to the area which is not accessible by the detector because of the frame bordering two modules (see also 20th run in figure 2). Further data evaluation and the additional use of real space imaging techniques for the nanoparticle covered alginate surface after the flow experiment will allow for the description of the attachment of gold nanorods dependent on time and position on the fluidic channel.

This work has been financially supported by the BMBF (grant number 05K10WOA).

References