In situ μGISAXS investigation of adsorption kinetics in a microfluidic channel


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Nanostructured polymer films can be used as a template for controlled deposition of hard inorganic materials [1-3]. The ordered patterning of metal nanoparticles on solid surfaces is important for possible applications in nanocatalysts, nanoelectronics, bioelectronics, magnetic recording devices, and gas sensors. The self-assembly and easy processing of polymers has enabled the low-cost fabrication of integrated micro- and nanosystems with a high degree of complexity and functionality. In order to understand the growth of the nanocomposite materials and its inherent polymer and metal layers, it is mandatory to know, how the polymer templates influences the metal film morphology and the growth kinetics during flow stream deposition. In general, the specific nature of the selective gold-polymer interaction causes self-assembly is still not completely understood.

In situ grazing incidence small-angle X-ray scattering with a microfocused beam (μGISAXS) is a powerful tool to investigate surface properties of thin polymer and nanocomposite films and growth kinetics during nanoparticle deposition [2,3,5,6]. Several deposition techniques for the patterning of metal nanoparticles within polymer films have been studied. For example, one method uses the self-organization characteristic of evaporated or sputtered nanoparticles on a self-assembled polymer film to create nanostructures by selective adsorption [2,3].

Initial measurements performed at BW4 beamline at HASYLAB (DESY) serve as basis for our experiment. Moulin et al. designed a fluidic cell based on low absorbing cyclic olefins (TOPAS), which allows the GISAXS characterization of the interfacial flow in a channel (18x1x0.1) mm³ and enables the study of the solid-liquid interface during the continuous flow stream of an aqueous solution with a broad range of flow rates [4]. Metwalli et al. demonstrated the flow stream deposition technique by the deposition of gold nanoparticles onto a microphase-separated cylinder forming polystyrene-blockpolyethyleneoxide P(S-b-EO) diblock copolymer film [5]. After feasibility study at BW4 to test process conditions of our microfluidic setup we performed a first successful round of microfluidic experiments at P03 [7].

The experimental setup is shown in figure 1(A). The experimental parameters were $D_{SD} = 4$ m, $\lambda = 0.941$ Å, $\alpha_i = 0.4^\circ$, beam size = (22 x 13) µm². We used the PILATUS 300K detector routinely installed at the MiNaXS beamline P03. We used an acquisition time of 0.1 s at an interval of 2 s to avoid beam damage. The flight path between microfluidic cell and detector was evacuated. Two separate point-like beam stops were used to shield the direct and the specular reflected beam to avoid saturation of the detector. A programmable nanolitre flux generator enables the remote controlled performance of the flow stream deposition experiment, where the flow rate was adjusted to 0.02 ml/min.
Figure 1. (A) The microfluidic setup during the first experiments at P03. Aqueous gold nanoparticle solution in a syringe was transported at a controlled flow rate via tubes to the microfluidic cell. (B) and (C) µGISAXS patterns taken before and after a microfluidic experiment with gold nanoparticles (10 nm diameter). The broadening of the Yoneda peak in the lower part of the image indicates the presence of nanoparticles. (D) Out-of-plane cuts (horizontal line cuts) at the Yoneda peak taken from the µGISAXS patterns (B) and (C) before (blue) and after (red) the experiment. The form factor of the gold nanospheres is clearly detectable around 0.6 nm\(^{-1}\).

In our experiment described here, we used the well-established flow stream deposition technique to investigate in-situ the adsorption kinetics of gold (Au) nanospheres on thin colloidal polystyrene (PS) films as a function of differences in their surface chemistry. The aim of the experiment was to describe a novel fabrication method of gold decorated nanospheres by chemisorption. In figure 1B) we present the µGISAXS data before deposition of the Au nanoparticles. Clearly, little diffuse scattering around the separated Yoneda peaks is visible, indicating the lack of smaller structures, as the diameter of the (PS) colloids of the template is 50 nm. Fig 1C) shows the µGISAXS pattern after deposition. It reveals an adsorptive growth of gold nanoparticles on top of the polystyrene colloids, as strong diffuse intensity around the Yoneda peaks of silicon and polystyrene is visible. This contribution stems from the spherical form factor of the Au nanoparticles. Fig 1D) shows the out-of-plane cuts at the Yoneda peak of Si. The form factor of the spherical Au nanoparticles is clearly detectable around 0.6 nm\(^{-1}\).

To summarize, our study hints that gold nanoparticles adsorb to the brush-like anionic surface of the PS colloidal spheres. Additional SEM images (not shown here) corroborate our findings. This shows the opportunity to fabricate gold decorated spheres as a nanocomposite model system with the flow stream deposition technique [5].

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References