STUDIES OF ORDERED NANOPARTICLE MONO- AND MULTILAYERS

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Abstract

Surfactant stabilized colloidal nanoparticles represent an important class of nano-materials due to their low size dispersion and moderate production costs. The production of monodisperse (< 12%) metal nanoparticles (diameter 6-12 nm) was elaborated. Large area ordered nanoparticle mono (2D)- and multilayer (3D) assemblies (up to 25 cm²) were prepared by a modified Langmuir-Schaefer deposition. The grazing-incidence small-angle X-ray scattering (GISAXS) technique was applied for analysis of the 2D and 3D nanoparticle assemblies. Appropriate simulation software has been developed for GISAXS evaluation including 3D nanoparticle assemblies. Using the GISAXS technique the vertical correlation of the nanoparticle position in the nanoparticle multilayer was studied. The examples of the presence and absence of the vertical ordering in nanoparticle multilayers are presented.

Keywords: nanoparticle, multilayer, Langmuir-Schaefer, GISAXS

1. INTRODUCTION

The surfactant stabilized colloidal nanoparticles represent an important class of nano-materials due to their low size-dispersion and moderate production costs. Moreover, colloidal nanoparticles can serve as building blocks for complex thin film structures. They self-assemble into ordered 2D and 3D arrays (monolayers and multilayers, respectively) under specific conditions. Large self-assembled two- and three-dimensional arrays of colloidal nanoparticles have been fabricated. Potential applications are ranging from high-capacity storage media up to the new emerging field of plasmon nano-optics [1].

The self-assembling is a complex process in which an interplay between localized interactions such as van der Waals attraction and hard-core (steric) repulsion (combined with long-range magnetic dipolar interaction if the particles are magnetic) determine the assembling process. At present, a large variety of possible resulting patterns of the self assembled nanoparticle arrays is a serious limitation for targeted technological applications of self assembling. For preparation of ordered nanoparticle arrays various deposition methods have been elaborated up to now. Among them the Langmuir-Blodgett and/or Langmuir - Schaefer methods have a potential to control the deposition process over a large area [2]. We applied a modified vertical Langmuir Schaefer technique which allows an improved control of the homogeneity and ordering of nanoparticle arrays over large areas [3].

The real-space imaging techniques like scanning electron microscopy and/or atomic force microscopy are suitable only for the final inspection of nanoparticles immobilized in the layers on solid surfaces. However, the real-time monitoring and controlling of the deposition process and manipulation of the nanoparticle assemblies requires a fast, non-destructive and vacuum-free technique. It was demonstrated that the grazing-incidence small-angle X-ray scattering (GISAXS) is the most suitable technique for analysis of the nanoparticles arrays [4]. Using the static and scanning GISAXS techniques the nanoparticle self-assembly process in the drying
nanoparticle colloidal drop was studied. The measurements confirm that the three-phase line boundary of the drying drop is the nucleation center for the nanoparticle self-assembly [5,6].

The key topics addressed in this paper are the preparation, manipulation and analysis of nanoparticles organized into self-assembled 2D and 3D arrays.

2. **EXPERIMENTAL**

Silver nanoparticles of the diameter 6-12 nm with low size dispersion (10%) have been synthesized using a simple precursor, silver nitrate, at higher temperature (170°C) under atmospheric pressure in the presence of inert gas (Ar). During synthesis oleic acid and/or oleylamine as a capping reagents were used.

Fe$_3$O$_4$ and CoFe$_2$O$_4$ nanoparticles of the diameter 6-9 nm with size dispersion 12% were synthesized by a high-temperature solution phase reaction of metal acetylacetonates (Fe(acac)$_3$, Co(acac)$_2$) with 1,2-hexadecanediol, oleic acid and oleylamine in phenyl ether [7].

For our nanoparticles toluene was used as a solvent. The particle size and its dispersion were measured by dynamic light scattering (Malvern Zetasizer Nano series) and by small angle X-ray scattering (SAXS) methods.

The SAXS measurements were realized at a novel SAXS/GISAXS laboratory set-up at the Institute of Physics, SAS, employing a microfocus sealed X-ray tube with integrated focusing optics (Incoatec, $\mu$S$^T^M$) at the working wavelength of Cu-K$_\alpha$ line ($\lambda=0.154$ nm). A 2D X-ray detector (Dectris, Pilatus 100K) was used to record SAXS pattern.

Large area ordered nanoparticle mono- and multilayer assemblies (up to 25 cm$^2$) were prepared by a modified Langmuir-Schaefer deposition technique using a computer-controlled Langmuir-Blodgett (LB) trough (Nima Technology). In this method Si substrate was placed horizontally inside the trough before the particles were distributed onto the water subphase. The nanoparticles dissolved in chloroform were spread by a microsyringe onto air/water interface of a LB trough and the nanoparticle layer was compressed to a monolayer phase. The ordered monolayer was transferred on the Si substrate by a regulated removal of the subphase at a surface pressure of 20 mN/m. The nanoparticle multilayers were prepared using the method described above, adding layer by layer one after another.

The experiments were performed on the GISAXS beamline BW4 at the Hamburger Synchrotronstrahlungslabor. The size of the focused beam at the substrate position, as determined from 1/e of the maximum intensity, was 65x35 μm$^2$ size (horizontal × vertical). The X-ray wavelength was set to 0.138 nm. The scattered X-ray radiation was detected by a two-dimensional X-ray CCD camera. Each CCD pattern was acquired for 2.6 s if not stated otherwise [8].

The second part of our experiments was performed on our Lab-GISAXS installation with temporal resolution of 25 ms was built in our laboratory to study in situ the nanoparticle self-assembling and re-assembling at the solid-air and water-air interfaces. The SAXS and GISAXS measurements were performed at a novel laboratory set-up constructed in our laboratory. The device consists of a microfocus X-ray source with integrated focusing Montel optics (Incoatec Microfocus Source, Cu-K$_\alpha$, 0.154 nm) and a silicon based 2D X-ray detector (Pilatus 100K). The focal spot diameter (FWHM) is 250 μm and the maximum flux amounts to 3.10$^8$ photon/s. The GISAXS pattern was calibrated by silver behenate which is a typical reference for small-angle scattering patterns [9].

3. **RESULTS AND DISCUSSION**

In Fig. 1a it shown the SEM micrograph of 2D ordered array (a monolayer) of iron oxide nanoparticles deposited by the modified Langmuir Schaefer method onto Si substrate. The corresponding GISAXS pattern is shown in
Fig. 1b. The $q_y$ and $q_z$ components of the scattering vector are parallel and perpendicular to the substrate surface, respectively. The side maxima on the reciprocal space map indicate the lateral ordering of the nanoparticle monolayer [5,6]. From the simulation of the measured GISAXS pattern the following parameters were obtained: the average particle diameter of $6.1\pm0.6$ nm, the average interparticle distance of $7.5\pm1$ nm, and the lateral correlation length of the particle distribution of $87$ nm are obtained [5].

![SEM micrograph of FeO nanoparticle monolayer (left) and corresponding GISAXS spectrum (right).](image)

Employing the same modified Langmuir-Schaefer deposition technique the nanoparticle multilayers were prepared. The presence of a layered structure was confirmed by X-ray reflectivity [3] and GISAXS measurements. Presence of the vertical correlation of the nanoparticle positions was analyzed by GISAXS. This method enables us to distinguish a nanoparticle multilayer composed from laterally ordered monolayers with no vertical correlation of nanoparticle positions and an artificial crystal with vertical ordering of nanoparticles. Two different types of stacking can be observed, AA – particles of the neighbouring layers have the same x-y positions and/or AB – particles in a layer are located between the particles of the underlying layer. In Fig. 2 it is shown a the GISAXS spectrum of the Fe-O nanoparticle multilayers composed of 6 layers. The presence of a broad maximum around $q_z=1.6$ nm$^{-1}$ point at the absence of vertical ordering in the nanoparticle multilayer. This was confirmed by the simulation of the GISAXS pattern (not shown).

![GISAXS pattern of the six-layered nanoparticle multilayer prepared by a modified Langmuir Schaefer deposition technique and measured at angle of incidence $0.7^\circ$ (b) Corresponding vertical line profiles acquired at $q_y=0.0$ nm$^{-1}$ and at first lateral peak position at $q_y=0.87$ nm$^{-1}$.](image)
In the next step we studied the formation of mono- and multi-layer nanoparticle films in-situ directly at Langmuir-Blodgett trough. The experiments were performed at beamlines at HASYLAB (BW1) and ESRF (ID10B) (Fig. 3a). The time-resolved studies with gradually increasing surface pressure showed the formation of monolayer from the spatially isolated but already ordered islands of nanoparticles. The collapse of a monolayer was accompanied by the formation of a double layer which was proved by a distinct diffraction spots in GISAXS pattern. Simultaneously we were able to track precisely the inter-particle distance and correlate this to the mechanical properties of nanoparticle layer (Fig. 3b).

**Fig. 3 a)** The GISAXS pattern of Ag nanoparticle monolayer at the water interface. **b)** Using time-resolved GISAXS we monitored the compression and decompression of nanoparticle film via the position of the first side maxima in GISAXS pattern that directly corresponds to the inter-particle distance. The maximum in layer’s elastic modulus indicates the 2D->3D nanoparticle film transition.

In Fig. 4 it is shown the GISAXS pattern of a nanoparticle multilayer (number of layers ≥2) formed at the water/air interface after compression a decompression of the nanoparticle film. Distinct spots in the GISAXS pattern indicate the existence of a 3D ordered structure formed by nanoparticles.

**Fig. 4** The GISAXS pattern taken at the angle of incidence of 0.1 of a nanoparticle multilayer formed at the water/air interface after compression a decompression of the nanoparticle film.
4. CONCLUSIONS

The ordered nanoparticle mono- and multilayers prepared by a modified Langmuir Schaefer deposition technique were analyzed. For a monolayer the local ordering of the nanoparticle arrays was confirmed by the SEM micrographs and GISAXS technique. For a nanoparticle multilayer consisting from 6 layers subsequently deposited by the same procedure as the nanoparticle monolayer the lateral ordering of nanoparticles in each layer was found. However, the vertical correlation of nanoparticles was not observed in the GISAXS patterns.

The formation of a nanoparticle multilayer was studied by in situ GISAXS during the compression and decompression of the nanoparticle film at the water /air interface. The maximum in layer’s elastic modulus indicated the 2D->3D nanoparticle film transition. Formation of the nanoparticle multilayer with vertical ordering was confirmed by GISAXS.

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LITERATURE