



X-ray scattering characterization of iron oxide nanoparticles Langmuir film on water surface and on a solid substrate



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ARTICLE INFO

Article history:

Received 29 March 2016

Received in revised form 25 July 2016

Accepted 26 July 2016

Available online 28 July 2016

Keywords:

Magnetic nanoparticles monolayer

X-ray scattering

Langmuir film

ABSTRACT

In the present study we compare a structure of a Langmuir film assembled from magnetic iron oxide nanoparticles on water surface and a structure of the same film after its transfer to a solid substrate by the Langmuir-Schaefer method. In contrast to most of related studies, where different techniques are used to characterize the films before and after the deposition, we use the same combination of X-ray reflectometry and Grazing Incidence Small-Angle X-ray scattering. In both cases – on a liquid and on a solid substrate – the film was identified as a well-ordered monolayer of the nanoparticles laterally organized in a two-dimensional hexagonal lattice. However parameters of the lattice were found to be slightly different depending on the type of the substrate. It is also demonstrated that Langmuir-Schaefer technique is the right way for deposition of such kind of the particles on a solid substrate.

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1. Introduction

Ordered arrays of magnetic nanoparticles (MNPs) are promising objects for various applications in biomedicine [1,2], catalyst [3–6], optics [7] and high-density data storage [8,7]. Furthermore, self-assembly of nanosized objects is interesting from a point of view of a fundamental understanding of the interplay between competing driving forces at the nanoscale.

Iron oxide MNPs can be assembled into a monolayer by various methods, such as drop casting [9–11], doctor blade casting [12,13] and spin coating [14,15]. Self-assembly of the nanoparticles occurs during the solvent evaporation, therefore interaction between the film and a substrate plays an important role in eventual ordering. It was recently shown, that ultimately large-area monolayers of iron oxide MNPs can be produced on water surface using Langmuir technique [16–20]. However, assembling of the monolayer on liquid surface is only first technological step. For further applications an array of MNPs should be transferred from the Langmuir trough to a solid substrate what is usually done either by Langmuir-Blodgett (LB) or by Langmuir-Schaefer (LS) techniques. X-ray reflectometry (XRR) and Grazing Incidence Small-Angle X-ray Scattering (GISAXS) are the most appropriate

experimental methods to study the nanostructure of the Langmuir films in-situ, i.e. as they form directly on the liquid surface. While scanning electron microscopy (SEM) is conventional way of characterization of the resulting LB- or LS-assembled nanoparticle films [16,18,19,21,22]. It was recently observed that a lattice constant of the same nanoparticle film obtained by GISAXS on a liquid surface and by SEM after a deposition on a solid substrate can be significantly different. The difference can be caused by several factors, including imbalance of repulsive and attractive forces [20], the transfer method [23] and physical properties of the particles [24]. Furthermore, an average structural domain size as obtained by GISAXS and SEM can have different values due to the difference in resolution and due to different areas of a sample probed by these techniques [25].

Therefore we used the same combination of XRR and GISAXS to perform analysis of MNPs organization in-plane and out-of-plane of the sample both in-situ on water subphase and ex-situ after the deposition on a solid substrate.

2. Samples

Iron oxide Fe₂O₃ maghemite nanoparticles with the size of 10 nm (denoted as IO-10) and size tolerance of 2.5 nm in chloroform solution were purchased from Ocean Nanotech. Original concentration of maghemite was 21 mg/ml (0.43% vol.). MNPs were stabilized by oleic acid (C₁₈H₃₃COOH) monolayer shell of thickness ≈ 2 nm to prevent coagulation.

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3. Experiment

The Langmuir MNP film was prepared in a custom-designed Langmuir trough, installed directly on the goniometer with the use of an active anti-vibration device Halcyonics MOD2-S. Maximum working area of the trough with fully opened barriers is 745 cm². The H₂O/IO-10 sample was prepared at room temperature by a micro syringe drop casting on different parts of the water surface in the Langmuir trough. Prior to deposition, the as-purchased sample IO-10 was diluted to concentration 1.28 mg/ml by adding pure chloroform. No sonification was applied. More diluted solution allows for more homogeneous covering of the water surface and facilitates manipulations with the micro-syringe. In total 0.3 ml of diluted sample was spread in approximately 5 min (3 μ syringes of 0.1 ml each). After the solvent evaporation the trough was sealed and filled with humid helium to minimize scattering on air and to compensate for evaporation of water. After the solvent evaporation, the film was compressed to reach a minimal area (61 \times 170 mm²) by moving one barrier. Assembly of the LB film was followed by the LS deposition technique, as shown in Fig. 1.

XRR and GISAXS measurements were carried out at ID10 beamline of European Synchrotron Radiation Facility (ESRF, Grenoble, France), which is especially designed for studies on liquid surfaces [26]. Details of a basic principles and specific experimental approach of these surface-sensitive techniques can be found elsewhere [27]. In the present experiments photons with wavelength $\lambda = 1.54$ Å were used. XRR data were acquired by a one-dimensional position-sensitive detector (PSD) Vantec and two-dimensional PSD MARCCD 133 (2048 \times 2048 pixels) was used for GISAXS measurement.

As a solid substrate we used gold covered Si crystal. A buffer titanium layer was introduced to improve adhesion of the gold layer. Top surface of gold was covered with a layer of organic molecules (1-pentadecanethiol) making it hydrophobic for better transfer of the MNP Langmuir layer which is also hydrophobic. Nominal (i.e. estimated from the deposition process) thicknesses of the gold and titanium layers were 10 nm and 5 nm respectively. In the following the substrate with deposited IO-10 layer is called sample Si/Ti/Au/IO-10.

It is worth noting that such multilayered substrate was chosen in view of our future plans to compare structure of Langmuir-Schaefer layers deposited on non-magnetic substrates and on magnetic substrates. In the later case the substrates will be similar to the present Si/Ti/Au but will contain an additional layer of cobalt between the gold and titanium layers. There gold will play a roll of capping material preventing cobalt oxidation. To separate reliably an effect of magnetic

layer on the MNPs ordering it was decided to keep all other layers identical for both magnetic and non-magnetic substrates.

4. Results and discussion

The transverse structure of the film was examined by XRR method which provides the information on electron density (ρ_e) of the film, as a function of a distance z from an interface with a substrate. Distribution $\rho_e(z)$ is obtained by fitting the model XRR curves with GenX reflectivity tool [28]. Experimental XRR data (Fig. 2) are represented as RQ_z^4 to emphasize visibility of the experimental data and the fit on all measured Q_z range.

Presence of the IO-10 particles is manifested by a local increase of the electron density ρ_e in the region 17.5 < z < 28.5 nm (Fig. 2b). Parabolic behavior of the electron density distribution in this region delivered by the fitting routine corresponds perfectly to an expected shape $\rho_e(z)$ for the case of a monolayer of spherical particles. Total thickness of IO-10 layer d for both samples is 11.7 nm, what is corresponds to the nominal diameter of the IO-10 nanoparticles with collapsed surfactant shells. The maximum value of the electron density $\rho_e = 1.17$ Å⁻³ in the center of the layer was obtained also for both samples H₂O/IO-10 and Si/Ti/Au/IO-10 samples. Thus one can conclude that the transfer has not caused any additional defects to the monolayer, such as stacking of the particles into bi- or multi-layers.

The in-plane correlations between the nanoparticles in the IO-10 film were probed by GISAXS method. A 2D GISAXS pattern for the sample H₂O/IO-10 and cuts of the intensity distribution taken at grazing incidence and scattered angles $\alpha_i = \alpha_f = 0.16^\circ$ are shown in Fig. 4a, b.

It is well-known that monolayers of iron oxide MNPs tend to form a two-dimensional hexagonal close-packed (hcp) superlattice [10,11,15–19].

A corresponding set of Bragg peaks positions in a diffraction pattern can be described by the following relation:

$$Q_y^{hk} = \frac{2\pi}{d_{hk}}, d_{hk} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + hk + k^2)}}, \quad (1)$$

where Q_y^{hk} – projection of the reciprocal space vector to the in-plane axis y , h and k are the Miller indices, d_{hk} – interplanar distance, a is lattice constant.

One of the approximations of the nanoparticle assemblies is a paracrystal model, which exhibits a correlation between neighboring

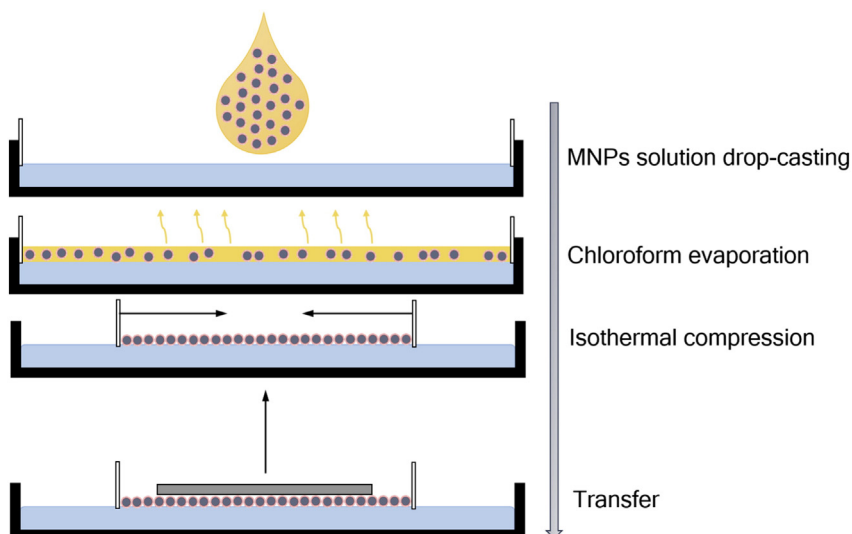


Fig. 1. Sketch of the Langmuir-Schaefer technique.

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