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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **Assembly of nanoparticles into supraparticles inside microemulsions**	**Experiment number**: SC-3119
Beamline: ID02	**Date of experiment**: from: 29 Apr 2011 to: 02 Mai 2011	**Date of report**: April 17, 2012
Shifts: 9	**Local contact(s)**: Michael Sztucki (email: sztucki@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The aim of the experiment was to analyze the assembly of metal nanoparticles that are confined in shrinking emulsion droplets and clarify the mechanism of formation of supraparticles using synchrotron small-angle x-ray scattering (SAXS).

Gold nanoparticles with 6 nm core diameter and size dispersion below 10% were introduced into the disperse phase of an emulsion. Microemulsions of their suspensions were prepared in water using mechanical shearing. We performed an assembly experiment by gently evaporating the dispersed solvent directly at the synchrotron, drew samples of the emulsion and charaterized them in scattering experiments at different evaporation times.

A sealed vessel containing the emulsion was submerged into a thermostated bath and kept at 298 K. The vessel was connected to a nitrogen stream that bubbled through the emulsion to permit evaporation of the dispersed solvent. During the evaporation of the particle-containing emulsion, a sample of 0.3 µL emulsion was removed every 10 min, introduced into a flow-through capillary cell and characterized in a SAXS measurement. The procedure was repeated until complete evaporation of the solvent was reached. We used the same cell during all experiments to enabled reliable subtraction of the background. The experiments were repeated with two different sample-detector distances to cover a wide *q* range.

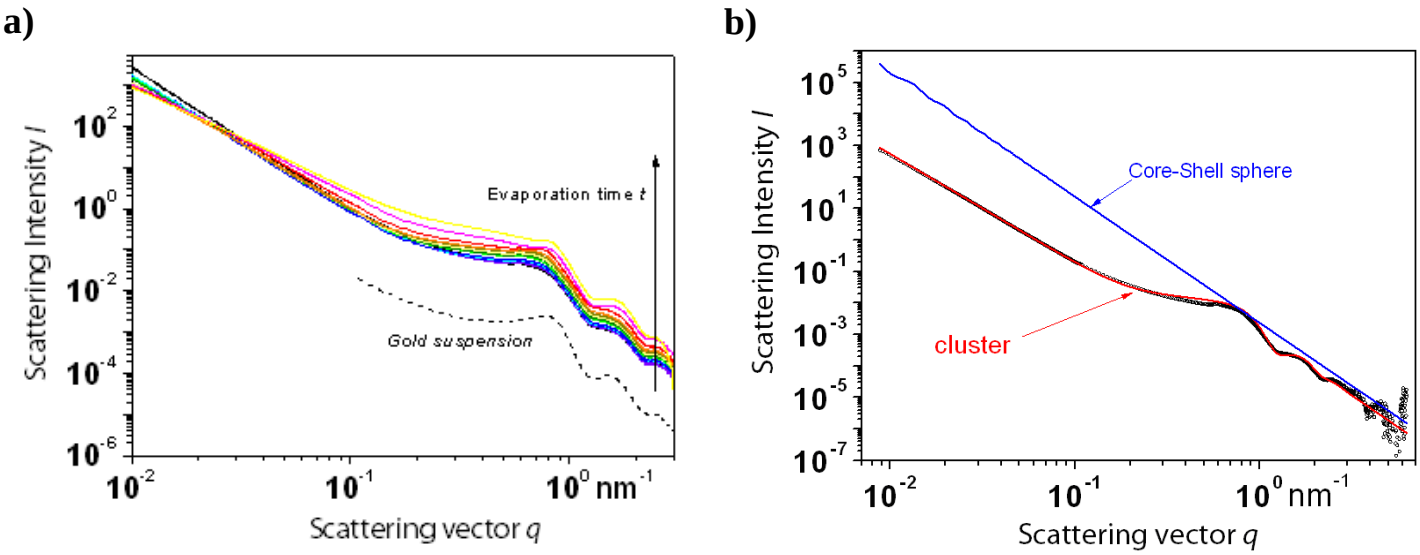

Figure 1 : Small angle X-ray scattering of samples retrieved during evaporation of the solvent. The blue curve corresponds to the measurement a t = 0 min (beginning of evaporation) and the yellow corresponds to a measurement at the end of the evaporation at t = 160 min (a). The oscillations observed are in the same region as those observed in the reference suspension containing only gold nanoparticles (dotted line). The scattering of the particle-containing emulsion can be fit using a cluster model, while a core-shell model does not fit the data (b).

Reference measurements on pure nanoparticle suspensions confirmed the geometry of the particle cores with a radius of 3.55 nm ± 0.33 nm. Figure 1a shows the evolution of the scattering intensity from the nanoparticle-containing emulsion during evaporation of the solvent. We observed a steady decrease of $I(0)$ which probably indicates the shrinking of the droplets. Strong oscillations in the high q region ($q > 0.5$ nm^{-1}) are observed, while no oscillations are visible at lower $q < 0.1$ nm^{-1}. The oscillations in the high q region is similar to that observed in the reference gold nanoparticle dispersion (Figure 1a, dotted line). They reflect the unchanged nanoparticles.

Particles that are confined inside emulsion droplets often segregate to the oil-water interface to form Pickering emulsions. To assess whether this occurs in the emulsions here, we attempted fitting the data using two differents models: a cluster model and the core-shell model. Figure 1b illustrates that the cluster model fits the scattering data best. A Pickering emulsion with the nanoparticles at the liquid-liquid interface would lead to a core-shell type of scatterers. Such geometries cause oscillations in the low q-range even if the droplets are broadly distributed in size, a signature that we did not observe in any of our evaporation experiments.

The Form Factor of the nanoparticles $F(q)$ from the reference measurements lets us evaluate the scattering intensity $I(q)$ in oder to obtain a structure factor as $S(q) = I(q)/F(q)$. Towards the end of the process, a peak appears on the structure factor curve that shifts to increasing q upon further evaporation (Figure 2). We attribute this peak to the formation of nanoparticle cluster precursors with decreasing particle-particle distances.

We also performed experiment on dried clusters. Drops of the supraparticle-containing dispersion were placed on the surface of a mica window and allowed to dry in air. The windows were placed in a four-position sample changer with their surface normal to the beam.

The small-angle X-ray scattering image shows a ring, some reflexes on the ring and some weaker reflexes at slightly lower q. The ring represent crystalline regions in the supraparticles with different orientations, while reflexes probably represent the deviating interparticle spacing at boundaries inside the clusters.

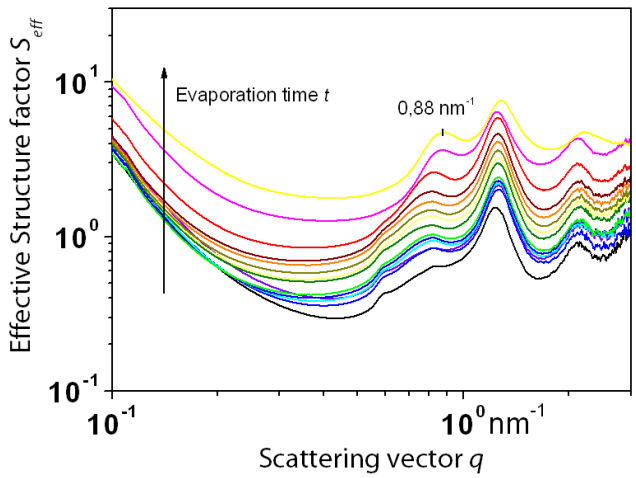

Figure 2: Evolution of the effective structure factor during evaporation of the solvent. The effective structure factor $S_{eff}(q)$ was calcuated from the Form Factor F(q) of the nanoparticles from the reference measurements as $S_{eff}(q) = I(q)/F(q)$. The peak that occurs towards the end of the evaporation indicates increasingly dense, interacting particles.

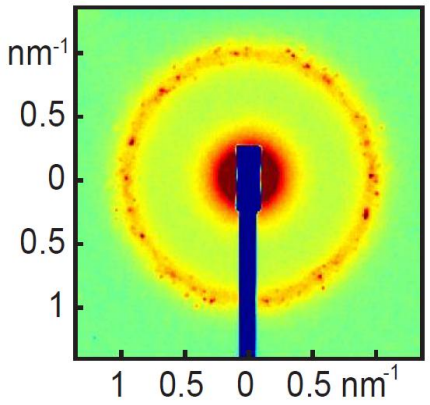

Figure 3: SAXS pattern from dried nanoparticle clusters. Emulsion-templated assembly yields supraparticles with regular structures that exhibit Bragg peaks and reflexes different from densely packed particle agglomerates.