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INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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 original report should be sent, together with 5 reduced (A4) copies, to the User Office.

In addition, please send a copy of your file as an e-mail attachment to reports@esrf.fr**,** using the number of your experiment to name your file. This will enable us to process your report for the ESRF Annual Report.

Reports accompanying requests for additional beam time

If your report is to support **a new proposal**, the orginal report form should be sent with the new proposal form, and a copy of your report should be attached to each copy of your proposal. 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.
- bear in mind that the report will be reduced to 71% of its original size. A type-face such as "Times", 14 points, with a 1.5 line spacing between lines for the text, produces a report which can be read easily.

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ESRF	**Experiment title:** Self-assembly of noble-metal clusters	**Experiment number**: 28-01-101
Beamline: 28	**Date of experiment**: from: 11 July 2001 to: 17 July 2001	**Date of report**: 29 April 2002
Shifts: 18	**Local contact(s)**: Dr. Simon Brown	*Received at ESRF:*

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Report:

A grazing incidence small angle X-ray scattering (GISAXS) study was carried out at the XMaS beamline in July 2001 by the University of Leicester in collaboration with the University of Liverpool. The samples consisted of silver nanoparticles (~2.0nm in diameter) in toluene. The aim of this beamtime was to initially study the aggregation of the particles in solution when subjected to an organic 'linker' molecule. In these measurements mercaptobenzoic acid was used to drive the process. Having determined the basic parameters of the particles, including the average size and distriubution, the same particles were then coated with dodecanethiol molecules that self-assemble on the silver surface. As a solution containing these clusters evaporates, the organic cage mediates a self-organising process whereby the clusters form close packed, ordered arrangements. All results were obtained by solvent evaporation on an oxidised silicon (111) sample.

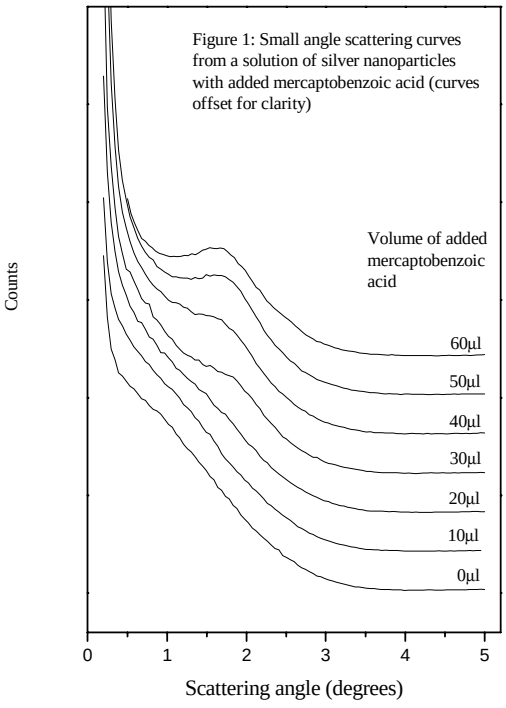

Figure 1: Small angle scattering curves from a solution of silver nanoparticles with added mercaptobenzoic acid (curves offset for clarity)

Figure 1 shows the small angle x-ray scattering curves (SAXS) measurments, from the solution of silver particles with different amounts of added mercaptobenzoic acid. For the curve with no added linker, the shape is determined entirely by the particle size and distribution. This curve can be modelled using Guinier and Porod methods, where the rate of fall-off is dependent on the size of the scattering object. These analyses indicate that the size of the silver particles used throughout this experiment are in the range of 1.4-1.6nm. As the

mercaptobenzoic acid is added, the clusters start to aggregate together forming a scattering object of interacting particles. This causes a distinct peak to appear at a scattering angle of ~1.67°, that can be interpreted as the separation of the particles in a distorted close packed structure. This yields a separation of approximately 6.7nm using Hosemann's cubic paracrystal model. These results are consistent for the interaction being driven by the mercaptobenzoic acid.

A solution of dodecanethiol was added to the naked 1.5nm silver particles, so that the quality of ordering by evaporating onto a substrate could be monitored. Previous measurements (see report 28-01-68) had indicated some temperature dependence for the ordering, whereby improved stacking perpendicular to the surface was achieved as the temperature of the substrate was reduced. Figure 2 shows the scattering in the out-of-plane direction (vertical scattering) and the in-plane direction (horizontal scattering) for the solution deposited onto the sample held at 9.4°C. This temperature was well below that required for achieving the phase transition in the previously measured gold particles. Peaks were observed at approximately 2.8° in both directions, although the background differs due to the additional scattering from the sample in the out-of-plane direction. Using the same paracrystal model as before, this corresponds to a separation of ~4nm between scattering objects. Given the size of the particles and the length of the dodecanethiol molecules, this indicates only a small amount of interdigitation between the molecules. Additional peaks were observed in the small angle region only for thick films of the silver particles deposited onto cooled substrates.

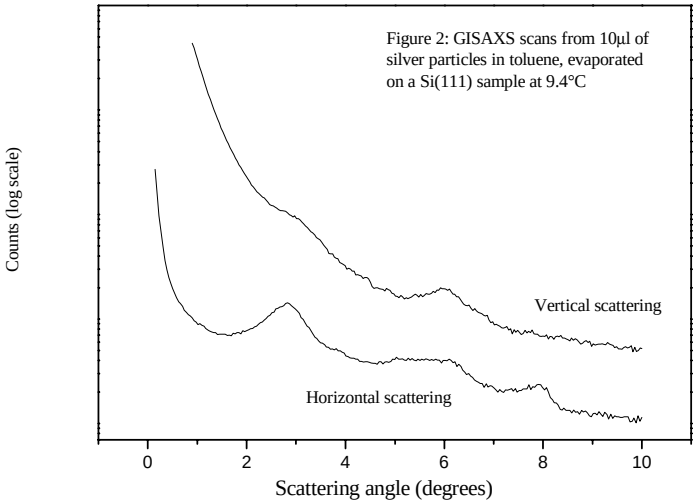

Figure 2: GISAXS scans from 10µl of silver particles in toluene, evaporated on a Si(111) sample at 9.4°C

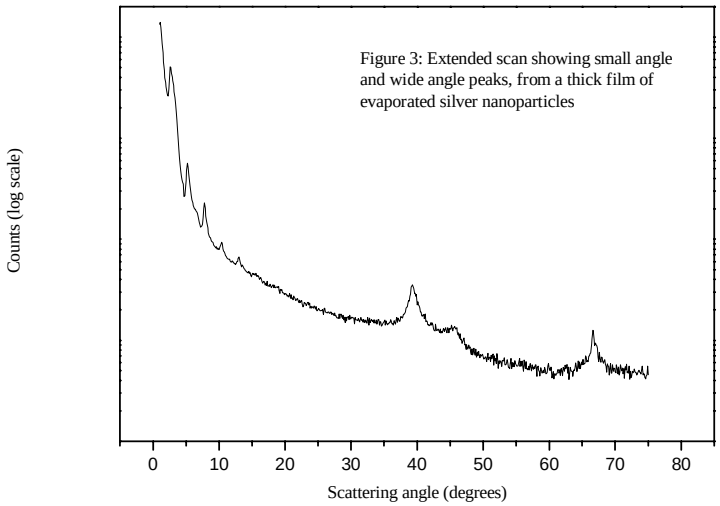

Figure 3: Extended scan showing small angle and wide angle peaks, from a thick film of evaporated silver nanoparticles

Extended measurements of a thick film of the dodecanethiol capped silver particles were made, to cover both the small angle and the wide angle scattering (figure 3). The wide angle features were interpreted using the Debye-Scherrer formula to determine the broadening of the peak, due to the crystal size. This gave a value of 5.5nm again indicating a lack of long-range order in the assembly process.

Other measurements (not shown) recorded as a function of sample temperature and concentration of solution did not show the same phase behaviour as previously observed for gold particles of size 2.5-4.5nm. This is believed to be due to the high polydispersity and small size of the silver particles used in these measurements in comparison to the gold particles that had undergone extensive size selection processes. Any deviation from a monodisperse arrangements of particles is predicted to have a serious effect on the ability of the clusters to form long-range close packed nanocrystals.

Future measurements will focus on the effects of different particle parameters on the self-organisation process. Specifically, this will include the cluster size and monodispersity, the ligand chain length and the concentration of particles. For each of these, correlations will be made with the external parameters that may affect the assembly, including sample temperature, sample orientation and surface preparation and the solvent in which the particles are dispersed.