EUROPEAN SYNCHROTRON RADIATION FACILITY

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 report should be submitted electronically to the User Office via the User Portal: *https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** **SAXS/WAXS for monitoring structure evolution in ultranarrow alkylamine-coated ZnS nanoparticle suspensions**	**Experiment number**: MX-2333
Beamline: BM 29	**Date of experiment**: from: 18/02/2022 to: 19/02/2022	**Date of report**: 23/04/2022
Shifts: 3	**Local contact(s)**: Petra Pernot	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Scientific background:

Zinc sulfide (ZnS) is a direct compound semiconductor that has a wide bandgap of 3.91 eV, a high index of refraction and high transmittance in the visible range. ZnS nanoparticles are useful as photo-catalysts and devices such as fluorescent displays, electroluminescent devices, light-emitting diodes, infrared windows, lasers and sensors. We synthesize in the lab highly uniform, ultranarrow ZnS nanowires and nanorods using zinc-ethylxenthate precursor molecule and octadecylamine as both a surfactant and solvent [1,2]. TEM characterization of *dried* suspensions showed that the particles form ordered arrays with a typical particle-particle distance of ca. 5 nanometers (Figure 1).

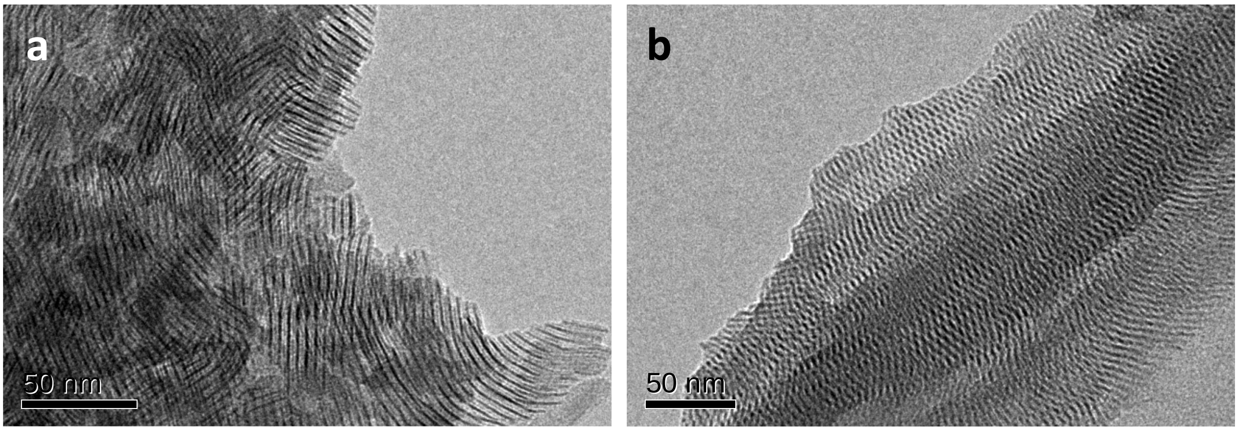

Figure 1. Bright field TEM images of (dried) ZnS nanoparticle assemblies (a) nanowires (b) nanorods.

Photoluminescence results of ZnS nanowires and nanorods in chloroform suspension show that the **emission increases upon decreasing the concentration**, which is not an obvious result (Figure 2). Therfore, we aimed to reveal the structure of these assemblies in the suspenion with various concentrations for understanding their optical properties.

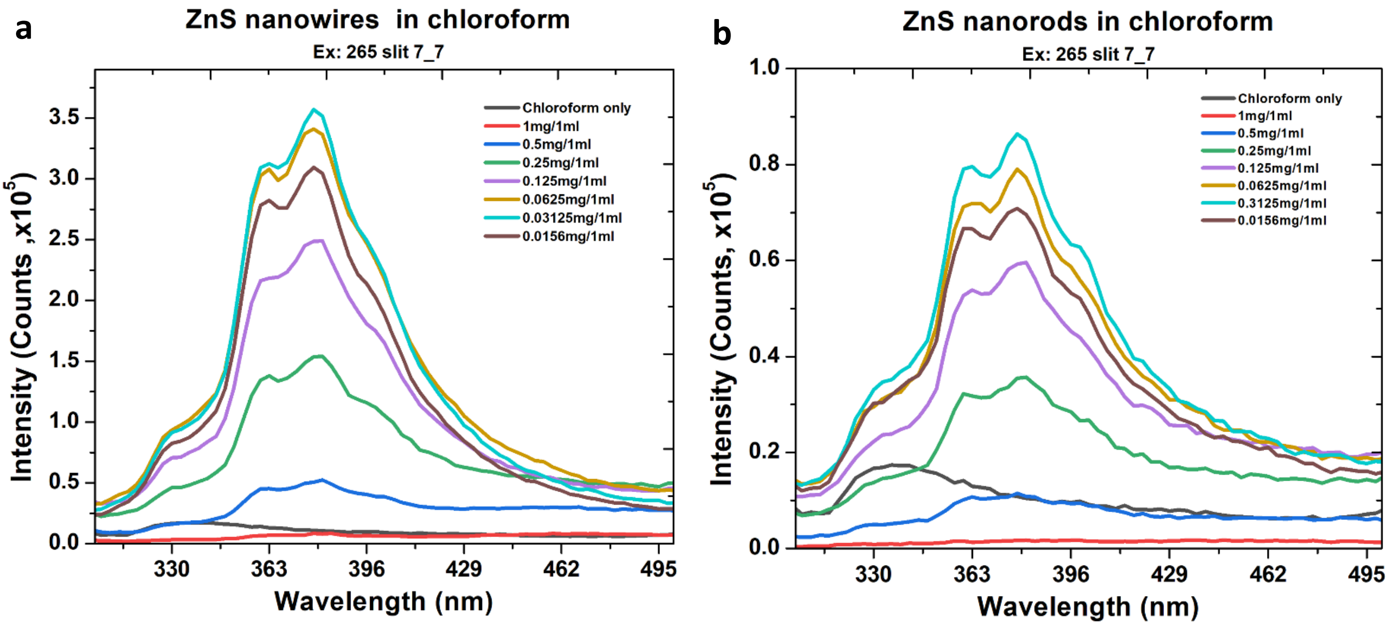

Figure 2. Photoluminescence results of ZnS (a) nanowires and (b) nanorods in chloroform suspension.

Results:

Our main goal was to investigate the structure evolution in suspensions of the highly uniform ZnS nanowires and nanorods in different various conditios: concentrations, temperatures and solvents for suspensions. Using SAXS at BM-29 we measured the ZnS nanowires and nanorods in different concentrations and temperatures. The results of the ZnS nanowires and nanorods in chloroform with different concentrations shows a clear trend of peak enhancement with the increase in the concentration, as expected (Figures 3 and 4, respectively). For both nanowires and nanorods the results indicates a liquid crystal behaviour. The three peaks in the wires results are of 1st, 2nd and 3rd diffraction order, respectively, where the first order peak represents the spacing between the particles. As for the nanorods, the second and third peaks ***are not*** of higher diffraction orders of the first peak as in the case of wires. For determenation and full understanding of the ZnS nanoparticles liquid-crystal structure, WAXS and SAXS with high brilliance will be employed at ID-02 for studying suspensions with low concentrations.

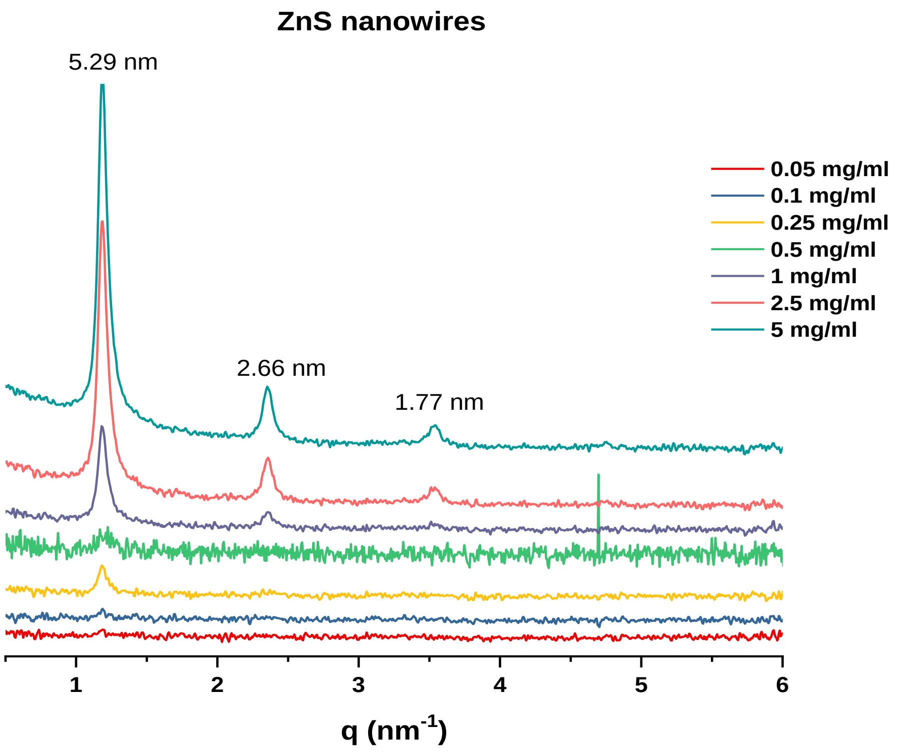

Figure 3. SAXS results of ZnS nanowires in chloroform suspension with different concentrations.

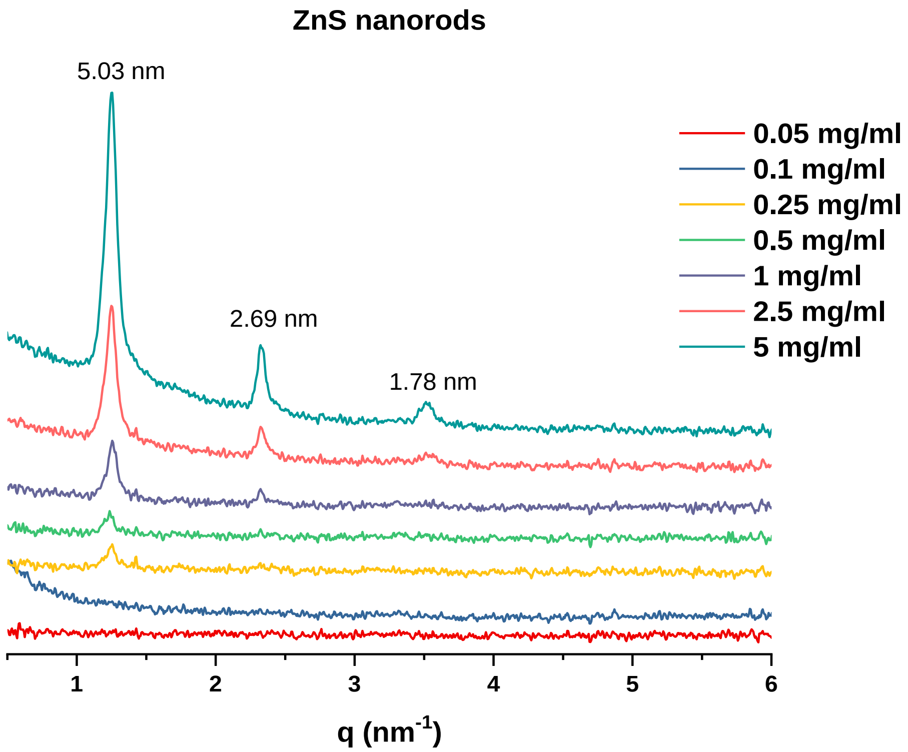

Figure 4. SAXS results of ZnS nanorods in chloroform suspension with different concentrations.

The temperature dependent SAXS results of the nanowires and nanorods in chloroform suspension at constant concentration of 5mg/ml are shown in Figures 5a and 6a, respectively. The analysis of the SAXS peaks was done using Lorentz fitting in OriginLab software. For both the wires and rods the peak height is decreasing with temperature. The large error bars of the third peak can be related to its relatively weak intensity and the relative low brilliance of BM29 (Figures 5b and 6b, respectively). In addition, the d-spacing of both the wires and the rods is increasing with temperature due to thermal expansion, which is somewhat more significant in the rods compared to the wires (Figure 7a,b respectively).

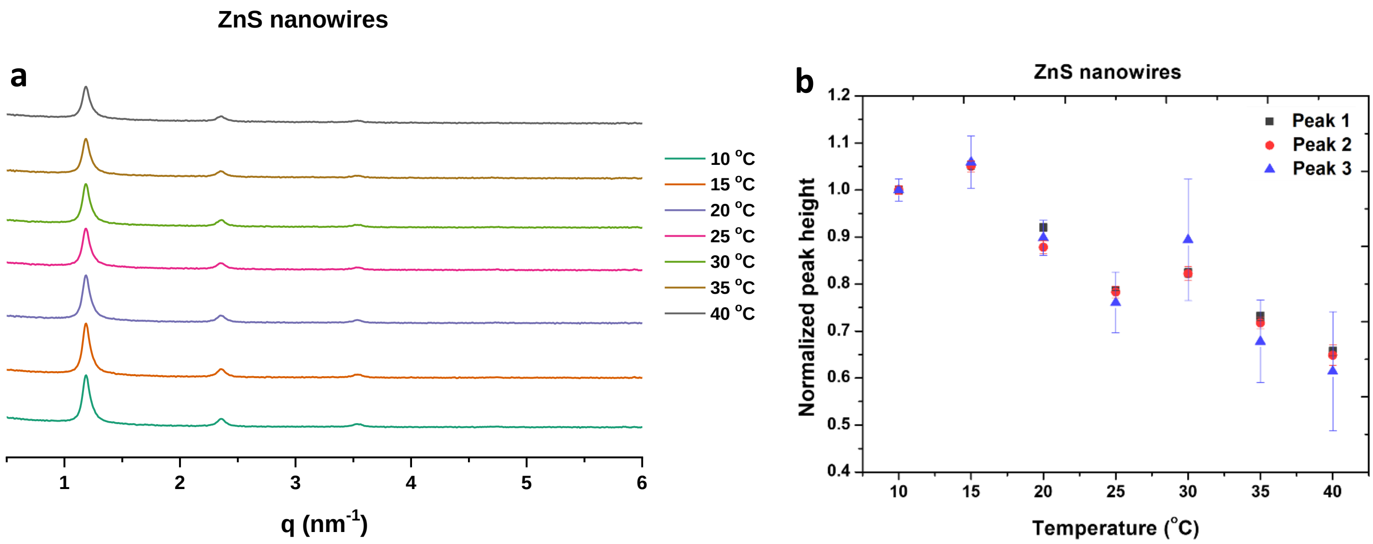

Figure 5. Temperature dependent (a) SAXS results, (b) analyzed results of peak hieght, in chloroform suspension.

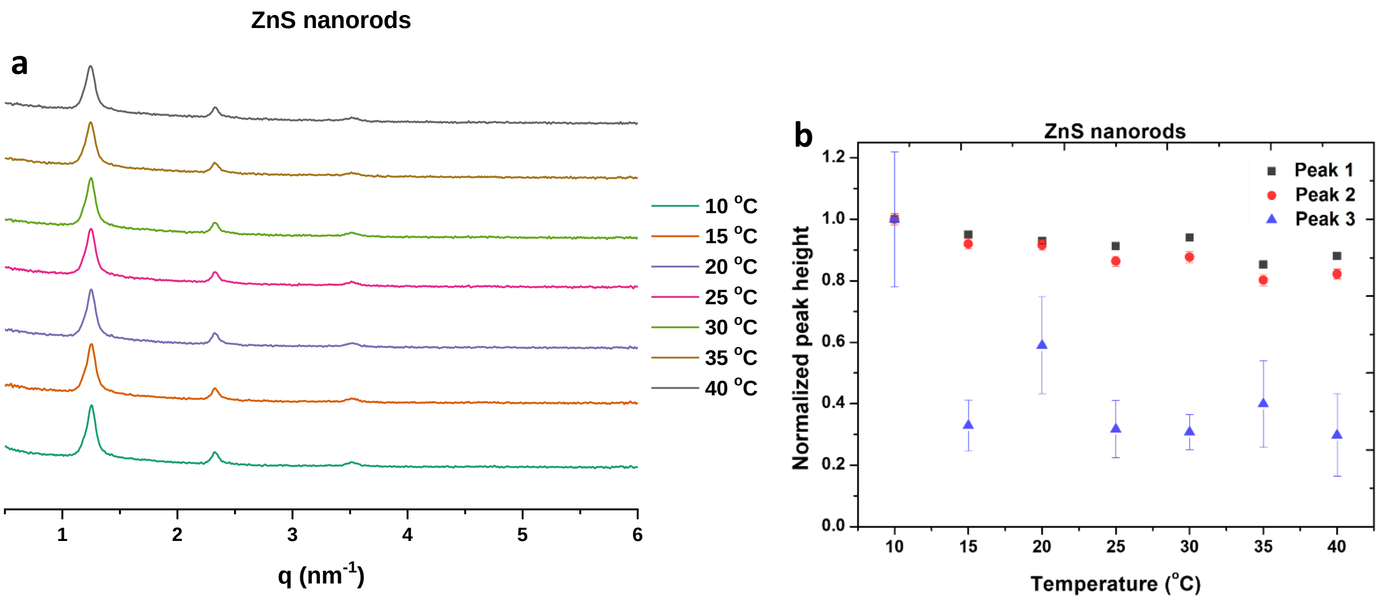

Figure 6. Temperature dependent (a) SAXS results (b) analyzed results of peak hieght , in chloroform suspension.

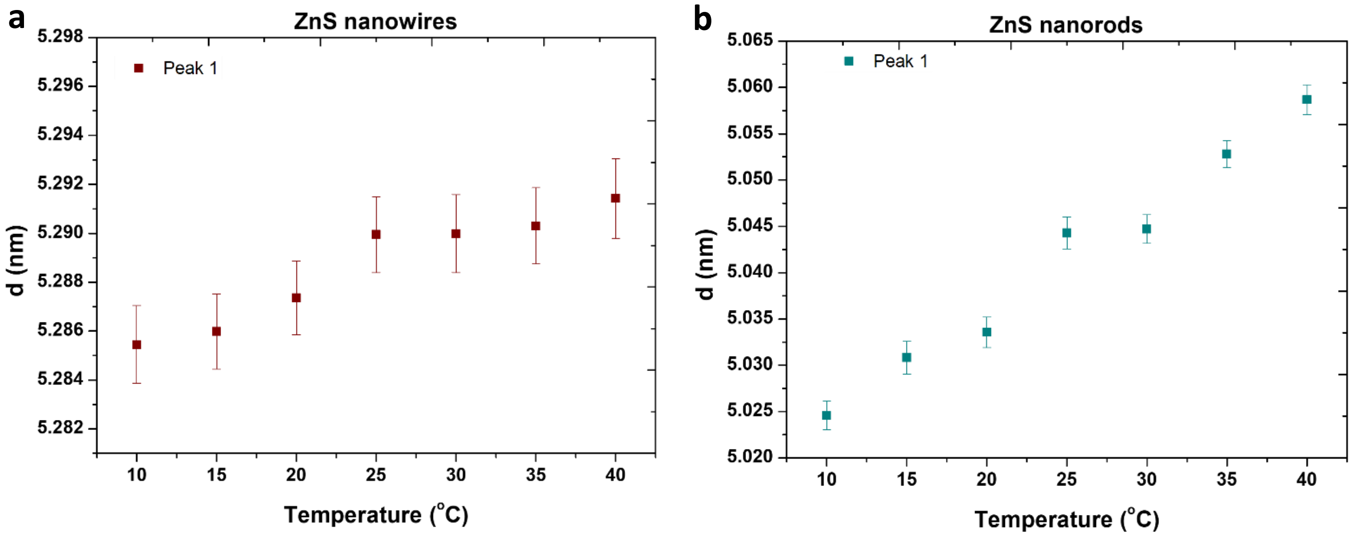

Figure 7. Temperature dependence of measured d-spacing for ZnS (a) nanowires (b) nanorods, in chloroform suspension.

Conclusions:

The results from these short and preliminary experiments show that both ZnS nanowires and nanorods form liquid-crystal like structures in suspension. The structure formed by the nanoparticles is apparently not affected by concentration, whereas the spacing between the nanoparticles is linearly changing with temperature.

References:

1. N. Belman, J.N. Israelachvili, Y. Li, C.R. Safinya, J. Bernstein and Y. Golan, "Reaction of Alkylamine Surfactants with Carbon Dioxide: Relevance to Nanocrystal Synthesis" *Nano Lett.* 9 (2009) 2088.
2. N. Belman, J.N. Israelachvili, Y. Li, C.R. Safinya, V. Ezersky, A. Rabkin, O. Sima and Y. Golan, "Hierarchical Superstructure of Alkylamine-Coated ZnS Nanoparticle Assemblies" *Phys. Chem. Chem. Phys.* 13 (2011) 4974.