ESRF	**Experiment title:** **In-situ XAFS and WAXS/SAXS Monitoring of Surfactant Assisted Nanoparticle Synthesis**	**Experiment number**: CH-3233
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Shifts: 12	**Local contact:** Dr M. Silveira	*Received at ESRF:*

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1 Objective

The main purpose of this work was to strive for new insight into the surface structure and surface chemistry of metal sulfide nanoparticles. This was proposed to be done on two levels:

1. Comparative XAFS study of various metal sulfide nanoparticle morphologies.
2. In situ XAFS monitoring of nanoparticle synthesis.

2 Experimental

2.1 XAFS of Previously Prepared Powder Samples

For each metal sulfide, the examined samples consisted of a bulk commercial powder as the standard, in addition to powders of the distinct nanoparticle morphologies. Generally, the samples were examined in capillaries, although whenever this was not possible, the powders were diluted with boron nitride and

examined as pressed pellets. The nanoparticle morphologies for each metal sulfide, as can be seen in the TEM micrographs in Figure 2.1, were:

- For ZnS: curved wires, straight wires and rods.
- For CdS: tripods and prolate rods.
- For PbS: ordered, small and large cubes.

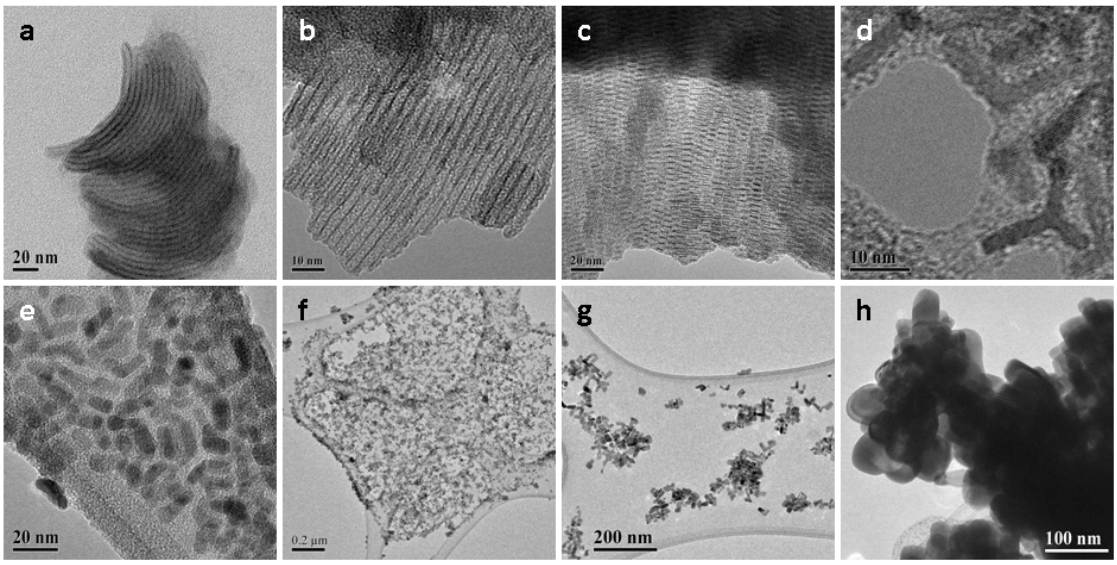

Figure 2.1: BF TEM images of metal sulfide nanoparticles: (a) curved ZnS wires, (b) straight ZnS wires, (c) ZnS rods, (d) CdS tripods, (e) prolate CdS rods, (f) ordered PbS cubes, (g) small PbS cubes and (h) large PbS cubes.

2.2 In-situ XAFS Experiments

In order to analyze the synthesis process, a scaled-down experimental setup was developed. This was done by filling a vertically aligned capillary with a mixture of ODA surfactant and metal ethylxanthate precursor, followed by recreating the synthesis thermal conditions using a high temperature accuracy blow heater. For greater semblance to the original synthesis procedure, the surfactant-to-precursor ratios and thermal cycle programs were chosen according to the conditions of previously synthesized nanoparticle morphologies. To monitor the experiment as closely as possible, fast XAFS spectra and XRD diffractograms were collected (~1 minute of data collection for each), corresponding to the best possible time resolution.

3 Results

3.1 XAFS of Previously Prepared Powder Samples

3.1.1 ZnS Nanoparticles

Processing the XAFS data of ZnS nanoparticles resulted in a meaningful fine structure as can be seen in FIGURE.

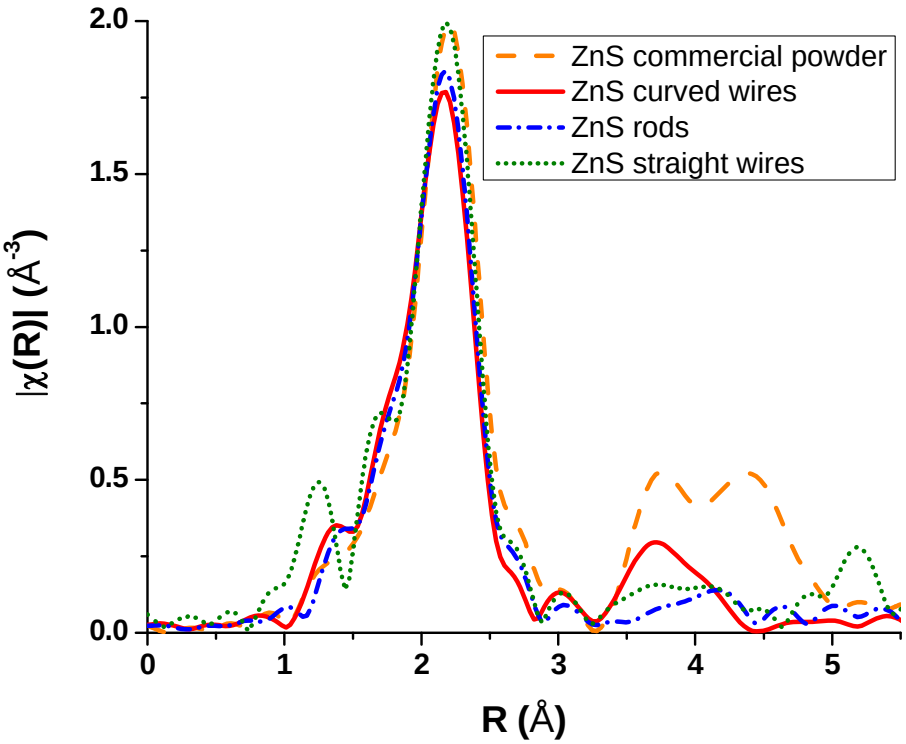

Figure 3.1: χ(R) plot of ZnS powders: the bulk commercial powder is marked in dashed orange, the curved nanowires morphology is marked in solid red, the straight nanowires morphology is marked in dotted green and the nanorods morphology is marked in dot-dashed blue.

Notable are:

- The variance in the height of the R≈2.2Å peak, indicating a variance of coordination.
- The peaks in the range of R≈3.5Å to R≈4.5Å, vary significantly and are the prime candidates for further analysis.

3.1.2 CdS Nanoparticles

Processing the XAFS data of CdS nanoparticles resulted in a meaningful fine structure as can be seen in Figure 3.2.

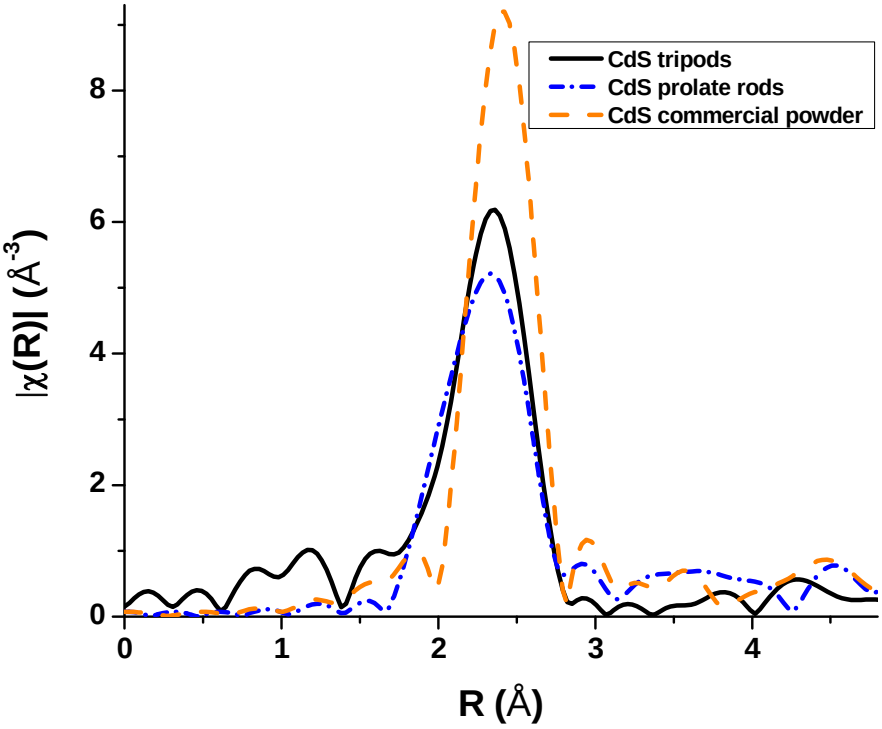

Figure 3.2: χ(R) plot of CdS powders: the bulk commercial powder is marked in dashed orange, the prolate nanorods morphology is marked in solid black and the nanotripods morphology is marked in dot-dashed blue.

Notable are:

- The variance in the height of the R≈2.4Å peak, indicating a variance of coordination.
- The peaks in the range of R=3Å to R=4.5Å, are the prime candidates for further analysis.

3.1.3 PbS Nanoparticles

The PbS nanoparticles XAFS data processing yielded very little meaningful fine structure. The one meaningful comparison can be seen in Figure 3.3.

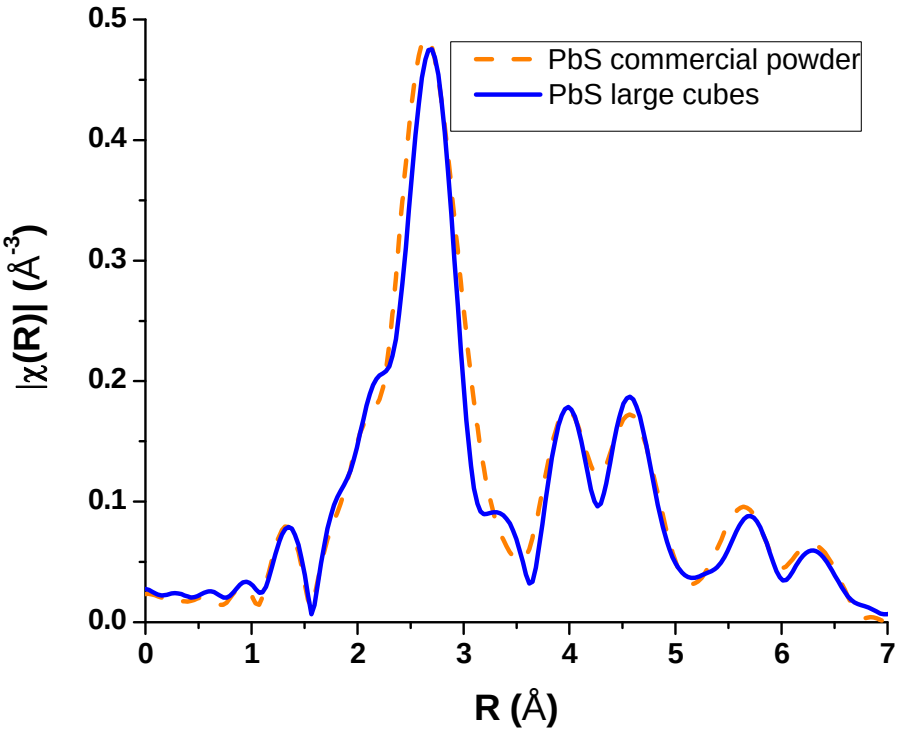

Figure 3.3: χ(R) plot of PbS powders: the bulk commercial powder is marked in dashed orange, the large agglomerated nanocubes morphology is marked in solid blue.

Note the additional peak at R≈3.3Å in the large agglomerated nanocubes XAFS.

3.2 In situ XAFS Experiments

3.2.1 ZnS Nanoparticles

During each of the multiple *in situ* experiments, tens of XAFS spectra were collected. Figure 3.4 demonstrates a sample progression of XAFS data for an experiment which was analogous to curved nanowires synthesis conditions.

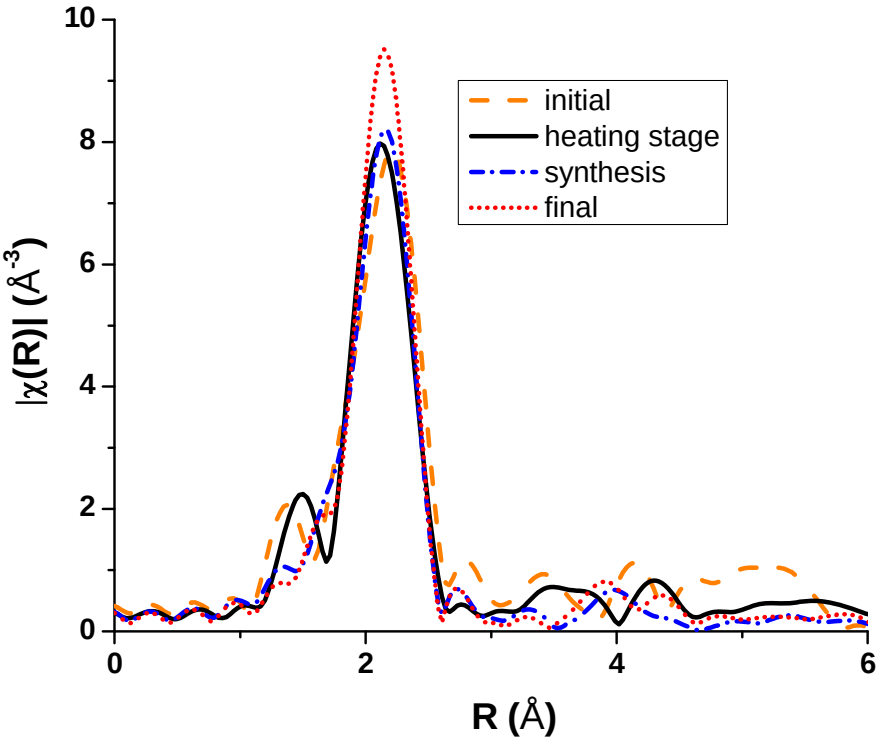

Figure 3.4: χ(R) plot of ZnS synthesis experiment anlogous to curved wires synthesis conditions: the initial powder mixture is marked in dashed orange, the heating stage is marked in solid black, the synthesis stage is marked in dot-dashed blue and the final state is marked in dotted red.

Notable are:

- The higher symmetry of the final state.
- The fine structure varies at different synthesis stages.

3.2.2 CdS Nanoparticles

As in the case of ZnS, tens of XAFS spectra were collected for each of the multiple in situ experiments. Figure 3.5 demonstrates a sample progression of XAFS data for an experiment which was analogous to nanotripods synthesis conditions.

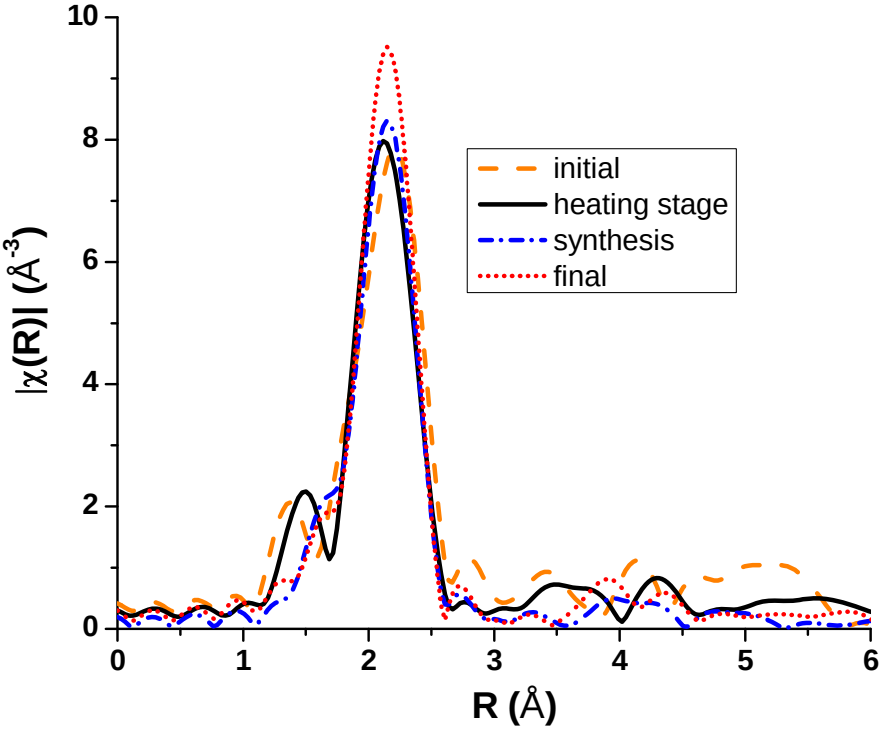

Figure 3.5: χ(R) plot of CdS synthesis experiment anlogous to tripods synthesis conditions: the initial powder mixture is marked in dashed orange, the heating stage is marked in solid black, the synthesis stage is marked in dot-dashed blue and the final state is marked in dotted red.

Notable are:

- The higher symmetry of the final state.
- The fine structure varies significantly at different synthesis stages.

3.2.3 PbS Nanoparticles

We are making efforts to process the *in situ* PbS XAFS data to obtain meaningful figures.

4 Summary and Future Work

- XAFS spectra have been obtained and processed for ZnS, CdS and, to a lesser degree, PbS nanoparticles.
- By way of internal comparison between the various morphologies and bulk powder, meaningful variance of the fine structure has been demonstrated. The *in situ* XAFS also possess meaningful fine structure, although to a lesser extent.
- The next step is the modeling and fitting of crystal data, in order to analyze the processed XAFS data for the powder samples.
- A working model will provide the possibility for pinpointing and analyzing the chemical and structural changes observed in the in situ XAFS.
- Additional effort will be directed towards attempting to improve the data processing for PbS XAFS, in order to obtain more meaningful results.