# Following the formation of nanometer-sized clusters by time-resolved SAXS and EXAFS techniques

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Time-resolved *in situ* SAXS and XAS measurements were carried out to monitor the formation of nanoparticles of the sulfides of cadmium and zinc, from solutions containing the corresponding acetate, and thioacetamide under solvothermal conditions. Analysis of the SAXS data shows that particles of *ca* 5 nm in radius form within the first few minutes of the reaction and then grow uniformly to *ca* 20 nm over a period of two hours resulting in a highly mono-dispersed particle distribution. EXAFS data of the CdS particles also prepared by solvothermal methods and recorded at 20 K, support the formation of nano-meter sized particles.

## Introduction

Time-resolved measurements are essential if we are to understand the processes that take place at the initial stages of any chemical reaction. To do so, a variety of spectroscopic and structural tools are either already available or being developed. Here we focus on the use of X-ray based techniques, since both diffraction and absorption spectroscopy are well suited to determine the atomicarchitecture of materials that are undergoing reactions.<sup>1</sup> We prefer to combine these two techniques wherever appropriate, since, on the one hand, we are often concerned with systems that transform from an amorphous phase to a crystalline solid and on the other, with highly dispersed and randomly substituted crystalline solids that contain a metal or metals, and possessing no longrange order.<sup>1-3</sup> The power of these combined measurements with time-resolution on the time-scale of milliseconds to minutes have been employed successfully by us and others over the last 10 years in the study of solid-state reactions and in particular, catalyst formation, activation and during reaction.<sup>1-30</sup> Among the various solid state reactions, processes associated with crystallization of solids, nucleation and growth, in particular, have been the most challenging since it is difficult to employ a specific technique and to achieve good time-resolution in order to obtain information on the nature of the particles that promote the crystallisation process. The specific technique that is chosen depends on the type of *in situ* system that is required for the reaction. For example, for the study of solvothermal (which include hydrothermal) synthesis, using "real" autoclave systems, it is necessary to use highly-penetrating X-ray radiation, including "white beam". Indeed energydispersive diffraction is most appropriate and, more importantly, although the data are not useful for structure refinement, they are of sufficient high-quality to enable us to obtain time-resolution

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(on the scale of seconds) to determine detailed information on the kinetics of reactions.<sup>21,22,31,32</sup> Time-resolved diffraction studies, using monochromatic radiation is also possible, but with the use of miniaturized sealed systems using thin walled glass capillaries or other *in situ* cells that have path-lengths of less than 1 mm are used as opposed to the autoclaves that are normally used in conventional synthesis procedures.<sup>3,33–35</sup> The advantage in utilizing this miniaturized system is that this can be adapted for the particular *in situ* study, employing not only high-resolution diffraction measurements that enables the refinement of X-ray data but also small angle-X-ray scattering and X-ray absorption spectroscopic techniques.<sup>3</sup> Time-resolved studies using SAXS, XRD and XAS have been used extensively for the study of crystallisation of microporous materials, dense oxides and many other systems to determine the processes that take place prior to and during crystallization of inorganic solids.<sup>3,30,36–38</sup> Here we report a time-resolved study of the formation of semiconducting nano particles of the sulfides of cadmium and zinc employing SAXS, XAS and diffraction studies, under solvothermal conditions.

Most of the research has concentrated on the area of synthesis of semiconducting particles belonging to II-VI and III-V groups of the periodic table, since these materials show significant quantum confinement effects.<sup>39,40</sup> Owing to this confinement effect both electrical and optical properties of these materials vary significantly with particle size, and the ability to tune the physical properties by controlling the growth (or particle size) can find potential uses in a variety of applications. Various preparative methods have been explored to produce nano-sized particles which include control of particle growth employing matrices or stabilizers such as thiols, glasses, polymers, reverse micelles, zeolites, xerogels etc. We also focus here on the production of small cadmium- and zinc-based sulfide particles, where one of the commonly used methods for their preparation is to react cadmium or a zinc salt with a sulfur-containing organic reagent such as thiourea or thioacetamide, under solvothermal conditions. There are several ex situ investigations related to the study of the nature of the reaction conditions on the particle size and its effect on optical properties. Although there are some reports on time-resolved studies using optical spectroscopic measurements, in particular of the change in the absorption edge of a growing cadmium or zinc particle, the particle size determination is carried out only indirectly using the information derived from ex situ study.<sup>27,39-44</sup> Here we report the study of the formation of nano-sized CdS particles by reacting thioacetamide with cadmium acetate. As in many other reactions, the rate of crystallisation and the size of the particle increase with temperature. We found that particles below the size of 20 nm can be prepared by conducting the reaction at  $ca 30^{\circ}$ C over a period of two hours.

#### **Experimental**

In a typical reaction, 0.02 M of cadmium acetate dissolved in water is reacted with 0.05 M thioacetamide just before introducing the mixture into a specially designed *in situ* cell that consists of 50 µm mica as the window material. *In situ* SAXS and XAS measurements were carried out at station 8.2 and 9.3, respectively, of the SRS, Daresbury laboratory which operates at 2 GeV. Station 8.2 is equipped with Si(111) monochromator to obtain the incident beam wavelength used here of 1.54 Å, an INEL detector for measuring wide angle X-ray scattering (WAXS), a quadrant detector for measuring the SAXS data. Both these measurements were performed simultaneously at two minute time-intervals (to obtain good signal to noise) and over a period of *ca* 2 h, with a camera length of 3.5 m corresponding to a scattering vector range ( $q = 4\pi \sin\theta/\lambda = 2\pi/d$ ) of 0.006–0.2 Å<sup>-1</sup>. In a typical experiment, the required amount of the reacting liquid was inserted in to the cell and the cell was loaded immediately in a pre-heated system, kept at a specific temperature, and the scans were started immediately afterwards. However the typical time taken to start the measurement after reacting cadmium acetate and thioacetamide is approximately 3 min. The SAXS data were processed using the XOTOKO program available at the Daresbury Laboratory.

Cd and Zn K-edge XAS measurements were performed at station 9.3 of the SRS, Daresbury Laboratory. Experiments were carried out in an identical time-square way to that of the SAXS measurement. We concentrated only on the XANES region for reasons mentioned in the Results and discussion. No attempt was made to record XRD data, Data were collected employing the QUEXAFS mode and the Si(111) monochromator for the Zn K-edge and Si(220) for the Cd K-edge

and the measurement time was restricted to 3 min in order to get as close to that used for the SAXS data. The XAS data were processed employing the EXCALIB and EXBROOK suite of programs and whenever necessary EXCURV98 was used to refine the EXAFS data.

### **Results and discussion**

As mentioned in the Introduction, our aim was to follow the formation of cadmium and zinc sulfide particles from a reaction medium. First we discuss the XAS results and subsequently the SAXS data and show how we estimated the particle sizes.

Cadmium sulfide is known to be present in two different structures/types, namely sphalerite and wurtzite. In both of these the first shell around the cations comprises 4 sulfur atoms and the second neighbor consists of 12 cadmiums. However, by careful examination of the EXAFS data and their associated Fourier transforms (FTs) (see Fig. 1) for both bulk and small sulfide particles prepared using the solvothermal procedures (different temperature and time of reaction), employing ex situ methods, we find that there are no significant differences between the data for various materials, irrespective of whether they are bulk or small particles. Similar observations are made for zinc sulfide materials prepared under various solvothermal conditions. The main reason being that there appears to be a large thermal disorder associated with the Cd–Cd (or Zn–Zn) shell,<sup>45</sup> which is very well reflected in the data collected at 50 K and below, shown in Fig. 1. To determine the particle size from EXAFS, accurate estimates of the coordination number of this second shell are all important, since the first shell is always surrounded by 4 sulfurs, a typical observation made for many other oxides where the particles are terminated by the anions. This lack of information on the second shell prevented us from analyzing the EXAFS data obtained from these time-resolved measurements. However, although there are changes in the XANES (see Fig. 2) during the reaction when going from an oxygen environment to sulfur neighbors, it is difficult to conclude the nature and shape of the growing particle, since both the unreacted solution and resulting solid contribute to the XANES data. Nevertheless it was possible to monitor the extent of reaction employing the time-resolved XANES measurements. Hence measurements were restricted to the XANES data. It is clear from Fig. 2, both for cadmium and zinc containing systems, that there is a gradual change in the white line intensity (the top of the absorption edge is usually referred to as white line intensity) with time, approaching that of the sulfided form. The decrease in white line intensity is more clear for the cadmium system than for the zinc. Nevertheless, the decrease in white line intensity as a function of time suggests that this reaction results in the formation of sulfided particles.

In Fig. 3 we show the stacked time-resolved SAXS data collected during the solvothermal reaction of cadmium acetate with thioacetamide. It is clear from this figure that a gradual increase in the scattering intensity in the low q region is also accompanied by the appearance of a 'bump' which is caused by the scattering structure factor and indicates a monodisperse system. This 'bump shifts to lower q values with reaction time, indicating that small particles are gradually replaced by bigger particles. This is typically observed for many systems that represent a nucleating and growing particle processes, which ultimately yield highly monodispersed particles.

The invariant Q measures the electron density contrast  $\Delta(\rho)$  independent of particle shape or number. For a simple two-phase system, cadmium sulfide nanoparticles crystallizing out of a water solution, Q is defined by:

$$Q = \int_{q=0}^{q=\infty} I(q)q^2 dq = \phi(1-\phi)(\Delta\rho)^2$$
(1)

where  $\Delta \rho$  is the electron density difference, q the scattering vector (q = 1/d) and  $\phi$  is the fraction of one phase and a maximum is predicted when  $\phi$  is equal to 50%. Q obtained from the *in situ* SAXS is plotted against the time of the reaction in Fig. 4. Q increases rapidly to a maximum value at around t = 50 min and then begins to fall slowly and linearly as the growth process slows down, reaching its lowest value at t = 120 min, when the reaction has been stopped. By extrapolating this linear fall, it is possible to approximate the time required for converting all the cadmium sulfide particles and it is estimated to be *ca* 250 min. The maximum in Q at t = 50 min in Fig. 4 can be



Fig. 1 Comparison of Cd K-edge EXAFS of the bulk CdS sample and the one prepared under solvothermal conditions at 300 K (a) EXAFS recorded at 300 K, (b) associated FTs of the EXAFS data recorded at 300 K, (c) EXAFS recorded at 20 K and (d) associated FTs of the EXAFS data recorded at 20 K. The solid line represents the bulk CdS and the dashed curve for the one prepared under solvothermal conditions at 60  $^{\circ}$ C for 15 h.



**Fig. 2** (a) Cd and (b) Zn K-edge XANES data recorded over a period of two hours during the reaction of thioacetamide with cadmium acetate. XAS data were collected over a period of 5 min for each scan. Only a few scans are shown for clarity, along with the data of the bulk CdS and ZnS systems.



Fig. 3 Stacked SAXS data recorded every two minutes during the reaction of thioacetamide with cadmium acetate at 300 K.



Fig. 4 Q invariant calculated eqn. (1) plotted as a function time.



Fig. 5 Particle radius estimated using eqns. (2) and (3), plotted as a function of time.

interpreted as the point at which approximately half the cadmium sulfide nanoparticles have formed. From Fig. 5 we find that  $Q_{\text{max}}$  corresponds to particles with a radius of 110 Å.

From the small angle region  $(q \rightarrow 0)$  the Guinier radius can be determined by:

$$I(q) = C \exp(-\frac{R_{\rm g}^2 q^2}{3}); \ q = 2\pi/d$$
(2)

where  $R_g$  is the Guinier radius or radius of gyration, q is the scattering vector and C a scaling factor. It should be noted that the Guinier approximation is only valid only for monodispersed systems ( $Rq < 2\pi$ ).

We assume that the cadmium sulfide nanoparticles are spherical in shape and for such particles the radius r of the CdS nanoclusters is related to  $R_g$  via the following expression:

$$R_{\rm g}^2 = \frac{3}{5}r^2 \tag{3}$$

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**Fig. 6** Best fit to the (top) EXAFS data of the sample prepared at 300 K and the (bottom) associated FTs. Note that the Cd K-edge EXAFS data were collected at 20 K in order obtain the information on the second shell more accurately to determine the particle size. The analysis of the EXAFS data yielded a coordination number of *ca* 10.4 for the Cd–Cd shell; the coordination number for the bulk is 12.

During the reaction, the particle radius of the cadmium sulfide ranges from 7 nm (at time  $t_0$ ) to a maximum of 12.5 nm after 120 min. (Fig. 5) above which there is no further increase in the size.

We prepared both cadmium- and zinc-sulfided systems taking into account this *in situ* observation and prepared materials to be examined by X-ray absorption spectroscopy. The analysis of the EXAFS data recorded at 20 K (see Fig. 6) revealed that the coordination number for the second Cd–Cd shell is *ca* 10, which is smaller than that of the bulk value of 12. However, we note that a simple Gaussian description for the Debye–Waller factor is used in the present analysis which will result in the under-estimation of the particle size. Further detailed studies are in progress, in particular, the use of a cumulant method to determine accurately the coordination number and Debye–Waller factor to determine the size of the particle.

This *in situ* time-resolved study clearly allows us to track the formation of the sulfided cadmium and zinc nanoparticles.

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