

## Time-Resolved Small-Angle X-ray Scattering Studies of Nanocrystal Superlattice Self-Assembly

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Received December 17, 1997

A large number of methods have been developed for preparing size-monodisperse nanocrystals.<sup>1–8</sup> While the lattice structure of these essentially defect free particles is the same as that of the bulk material, their physical properties may be significantly size dependent due to confinement effects. For example, electron–hole pair confinement in a semiconductor nanocrystal leads to a blue-shift in the onset of band gap absorption,<sup>9</sup> while single electron tunneling in a metal nanocrystal leads to staircase current–potential behavior.<sup>3</sup> The study of nanocrystals and the size dependence of their physical properties has provided important insights into the evolution of bulk properties in solids.

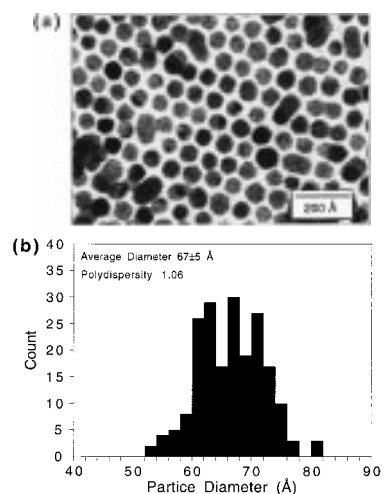
A growing number of methods have also been developed for the self-assembly of two- and three-dimensional nanocrystal superlattices possessing long-range structural order (Au,<sup>3</sup> Ag,<sup>5,10</sup> CdSe,<sup>11,12</sup> Ag<sub>2</sub>S,<sup>13</sup> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub><sup>14</sup>). In a few instances, the collective optical and electronic properties of superlattices have been reported (Au<sup>3</sup> and CdSe<sup>11,12</sup>). As the optical and electronic properties of the constituent nanocrystals are size dependent, it should be possible to tune the collective properties of these superlattices. This expectation has led to suggestions that nanocrystal superlattices will find applications in quantum computers, high-efficiency lasers, ultrafast switching devices, and light-emitting diodes.<sup>1–9</sup>

To date, no studies of the dynamics of superlattice self-assembly have been reported. Accordingly, time-resolved small-angle X-ray scattering (SAXS) has been used to study the self-assembly of a face-centered cubic (fcc) superlattice of size-monodisperse dodecanethiol stabilized silver nanocrystals. By adopting this approach it has been possible to study the dynamics of superlattice self-assembly and relaxation.

Dodecanethiol stabilized Ag nanocrystals were prepared following the method of Brust et al.<sup>15,16</sup> Size-selective precipitation,<sup>17</sup> using the solvent/nonsolvent pair chloroform/ethanol,

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**Figure 1.** (a) TEM image of a monolayer of dodecanethiol stabilized silver nanocrystals formed by evaporation of a drop of a chloroform dispersion (0.1 mg/mL) on a carbon coated copper grid. (b) Distribution of nanocrystal diameters in sample a.

narrowed the size distribution to the extent that the standard deviation ( $\sigma$ ) about the mean particle diameter was  $\pm 7\%$  and the polydispersity 1.06.<sup>18</sup> These nanocrystals were redissolved in chloroform (0.1 mg/mL) and a drop of the resulting dispersion was placed on a carbon coated Cu grid. As may be seen from the corresponding TEM (Figure 1a), solvent evaporation is accompanied by the self-assembly of a hexagonally close-packed (hcp) monolayer. Analysis of the above image yields an average particle diameter of  $67 \pm 5$  Å (Figure 1b) and an average interparticle distance (center-to-center) of  $83 \pm 6$  Å. The interparticle spacing (16 Å), as previously reported,<sup>19</sup> is about half that expected on the basis of the reported thickness of a monolayer of dodecanethiol adsorbed at a flat Ag surface (15 Å).<sup>20</sup>

A <sup>1</sup>H NMR spectrum of the surface modified nanocrystals in chloroform-*d* (not shown) confirms that all the dodecanethiol present in solution is adsorbed at the surface of a silver nanocrystal. Specifically, the  $\alpha$  ( $\delta$  2.52, quartet),  $\beta$  ( $\delta$  1.61, quintet), and  $\gamma$  ( $\delta$  1.31, unresolved multiplet) methylene group resonances of dodecanethiol in solution are not observed, while the resonances assigned to the remaining methylene groups ( $\delta$  1.3, unresolved multiplet) and the terminal methyl group ( $\delta$  0.91, triplet) are significantly broadened. These findings are characteristic of alkanethiols adsorbed at a nanocrystal.<sup>19</sup>

Elemental analysis gives the mass ratio of organic to metal which, when taken with the average particle diameter, yields the number of dodecanethiol molecules adsorbed at the surface of a silver nanocrystal.<sup>21</sup> On this basis, the area occupied by an

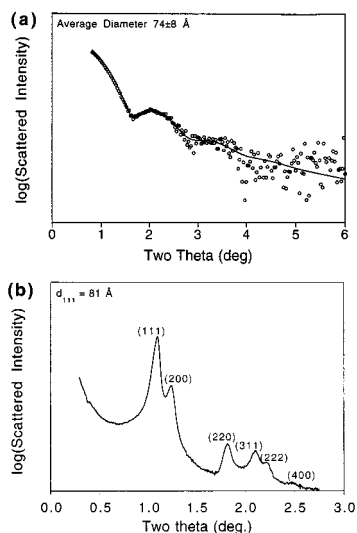
(17) An optically clear, concentrated nanocrystal dispersion in chloroform was rapidly stirred while ethanol was added dropwise until opalescence persists. The ethanol increased the polarity of the solvent and caused the preferential precipitation of the large particles. The above precipitate was isolated by centrifugation at 10 000 rpm for 15 min. The tightest size distributions were obtained by subjecting the supernatant to one more size selective precipitation and collecting the precipitate.

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(21) Elemental analysis of the dodecanethiol stabilized silver nanocrystal samples, prior to size-selective precipitation, yields the following percentage composition: C, 12.30; H, 2.85. On this basis it is calculated that 17% of the dry weight of the modified nanocrystals is that of the surface adsorbed dodecanethiol.



**Figure 2.** (a) SAXS of dodecanethiol stabilized silver nanocrystals (open circles) dispersed in hexane (0.1 mg/mL). Also shown is a simulation (full line) of these data. (b) SAXS of superlattice formed by evaporation of a drop of a more concentrated (1.0 mg/mL) dispersion similar to the one in sample a on a mica substrate.

adsorbed dodecanethiol is approximately  $14 \text{ \AA}^2$ , a value significantly less than that predicted and measured for a close-packed monolayer of dodecanethiol adsorbed at an atomically flat silver surface ( $17.5 \text{ \AA}^2$ ).<sup>17,22</sup> This closer-packing of the adsorbed dodecanethiol molecules is most likely a consequence of the curvature of the silver nanocrystal.<sup>19</sup>

The nanocrystals whose characterization has been described above were dispersed in hexane (0.1 mg/mL) and the log of the intensity of the scattered X-ray radiation plotted against  $2\theta$  (Figure 2a). At least three maxima are observed, supporting the assertion that these nanocrystals possess a relatively narrow size distribution.<sup>12</sup> More quantitatively, the average size and size distribution may be determined by using the form factor  $P(qR)$  for scattering from a sphere (eq 1), where  $\lambda$  is the wavelength ( $1.54 \text{ \AA}$ ) of the X-ray source and  $R$  is the nanocrystal radius.<sup>23</sup>

$$P(qR) = \left[ 3 \left( \frac{\sin(qR) - qR \cos(qR)}{(qR)^3} \right) \right]^2; \quad q = \frac{4\pi}{\lambda} \sin \theta \quad (1)$$

For dilute dispersions, where interparticle scattering effects are absent, the scattering intensity  $I(q)$  is proportional to  $P(qR)$  (eq 2), where  $n(R)$  is taken as a normalized distribution with a mean

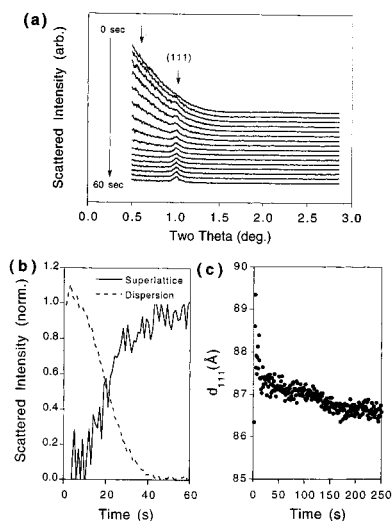
$$\frac{I(q_1)}{I(q_2)} = \frac{\int_0^\infty n(R)P(q_1R)M(R)^2 dR}{\int_0^\infty n(R)P(q_2R)M(R)^2 dR} \quad (2)$$

radius  $\bar{R}_n$  and variance  $\sigma^2$ , and  $M(R)$  is the molecular weight of a nanocrystal with radius  $R$ . Fitting the above equation to the measured data is achieved for  $\bar{R}_n$  of 74 and  $\sigma$  of 8 Å in good agreement with the number average value obtained by TEM ( $67 \pm 5 \text{ \AA}$ ).

Two-hundred microliters of the same sample was placed on a mica substrate and allowed to evaporate. The sharp diffraction peak in the corresponding SAXS confirms formation of a fcc superlattice possessing long-range order and a  $d_{111}$  spacing of 81 Å (Figure 2b). The implied interparticle (center-to-center) distance and spacing of 95 Å and 21 Å, respectively, are somewhat larger values than obtained by TEM (16 Å).

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**Figure 3.** (a) SAXS of dodecanethiol stabilized silver nanocrystals dispersed in hexane (1.0 mg/mL) at the indicated times during solvent evaporation. (b) Time evolution of scattered intensity in sample a at  $2\theta$  equal to  $0.6^\circ$  and  $1.1^\circ$  normalized with respect to initial and final scattered intensities, respectively. (c) The  $d_{111}$  spacing calculated from the SAXS in sample a.

Since high-quality SAXS data were obtained for both a nanocrystal dispersion and a superlattice, it was hoped that time-resolved SAXS could be used to study the dynamics of superlattice formation. Accordingly, the scattering profile of an evaporating dispersion of silver nanocrystals (1 mg/mL) was accumulated during 1 s intervals over 250 s.<sup>24</sup> Clearly, the intensity of low-angle scattering from nanocrystals randomly dispersed in hexane decreases, while the intensity peak assigned to diffraction from the (111) plane in the superlattice increases (Figure 3a). In fact, the amplitude of the scattered intensity from the dispersed particles and the (111) plane of the superlattice are inversely correlated (Figure 3b). It is noted that after correcting for scattering by nanocrystals randomly dispersed in hexane the (111) peak maximum in  $2\theta$  increases from  $1.95^\circ$  to  $2.04^\circ$  over 250 s (Figure 3c).<sup>25</sup> This corresponds to a decrease in the  $d_{111}$  spacing from 89 to 87 Å and is most likely due to solvent molecules evaporating from the superlattice interstices. It is noted that if the gradual decrease in the  $d_{111}$  spacing is extrapolated to 20 min, a value of 81 Å will be obtained. Significantly, this value agrees with that obtained for the superlattice prepared 20 min prior to measurement (Figure 2b).

These findings indicate that superlattice growth in the (111) direction can be monitored in real-time. They also suggest that solvent molecule inclusion accompanies superlattice self-assembly, leading to a larger spacing in the (111) direction, but that these solvent molecules subsequently evaporate. More generally, they establish the feasibility of an approach that would be expected to yield detailed information about the relationship between the structure and collective properties of a superlattice and the dynamics of self-assembly. Using this information, new routes to new superlattice materials possessing desired collective properties may be envisaged.

**Acknowledgment.** The authors thank Dr. E. Komanschek at the Central Laboratory of the Research Councils, Daresbury. We also thank the Commission of the European Union for funding access to the synchrotron radiation source at this laboratory through the Large Scale Facilities Program.

JA974273E

(24) Approximately 100  $\mu\text{L}$  of a hexane dispersion (1 mg/mL) was placed between two mica slides supported in a holder which was placed in the path of the SAXS source. One of the mica slides had been partially cut away in order to permit solvent evaporation.

(25) The position of the  $d_{111}$  peak maxima were determined from the second derivative of the scattering profile by taking the average of the two zero-crossing points. Connolly, M. Adsorption on Copper Surfaces. Ph.D. Thesis, Dublin University, 1989; Appendix B.