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Kinetics of II-VI and III-V Colloidal Semiconductor Nanocrystal Growth: "Focusing" of Size Distributions

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The development of reliable and reproducible methods for producing large amounts of uniformly sized inorganic nanocrystals has been a major goal in materials chemistry research over the last several years. In the case of semiconductors, the most successful preparations involve growth in solution from molecular precursors.[1−4] Both II-VI (CdS, CdSe)[5−7] and III-V (InP, InAs)[8−16] nanocrystals have been prepared using such methods, yielding highly crystalline and processable nanoparticles. Two broad strategies have been employed previously for preparing narrow size distributions in these types of preparations. In the first case, nucleation and growth of nanoparticles are allowed to take place over an extended period of time at a moderate temperature (180−300 °C),[5] yielding a wide range of sizes. This broad distribution can then be sorted.[6] The second approach involves separation of nucleation from growth by injecting rapidly at higher temperature (350 °C) to induce nucleation and then reducing the temperature during the growth phase,[7] yielding particles of one size. Unfortunately, this approach depends critically on the precise kinetics of the initial nucleation and growth and has not been possible in the III-Vs.

In micron-sized colloidal systems, Reiss demonstrated theoretically that diffusion-limited growth can lead to narrowing of size distributions with time by considering the diffusion area vs size.[17] The kinetics of crystal growth will also be influenced strongly by the variation of the surface energy with size, provided the crystallites are small enough that the Gibbs−Thomson effect is significant.[18−20] In this paper we demonstrate that these effects do indeed influence the kinetics of II-VI and III-V nanocrystal growth.

In the cases of CdSe and InAs, the band edge luminescence energy is well-known to depend strongly on the size, and we use this property to assess the time evolution of the growth process. The variation of the luminescence energy of the nanocrystals versus size was calibrated previously by transmission electron microscopy.[5,7,9]

A given PL spectrum was translated into a size distribution curve by assuming a δ function emission for each single size and the same emission efficiency for different sizes. Both of these assumptions mean that the reported size distributions are systematically larger than the real ones. In addition, we report only the average size (first moment) and the variance (second moment) but not the third moment or degree of asymmetry of the distribution. A more accurate method of sizing would be required to determine the third moment.

The temporal evolution of the size distribution for one CdSe nanocrystal growth experiment is shown in Figures 1 and 2, left.[21] The size distribution starts out with a standard deviation of 20%. Over the next 190 min, there are two distinct kinetic regimes: during the first 22 min, the average size increases relatively rapidly (from 2.1 to 3.3 nm diameter), and the size distribution is "focused" from 20% to 7.7%. Subsequently, the nanocrystals grow more slowly (from 3.3 nm to 3.9), and the nanocrystal size distribution broadens to 10.6%. A second injection of molecular precursors increases the growth rate and refocuses the size distribution to 8.7%. Particle yield data revealed that the number of particles keeps constant during "focusing" and "refocusing" and decreases during "defocusing". The monomer concentration, determined by particle yield, exhibits a dramatic drop during focusing and refocusing and keeps approximately constant during the defocusing. Similar growth kinetics are observed for InAs (Figure 2, right).[22] The nanocrystal yield from the reaction is high, and the resulting particles are faceted (Figure 3).

Nucleation takes place rapidly right after injection and continues until the temperature and monomer concentration drop below a critical threshold. The kinetics of nucleation are difficult to study, whereas the subsequent growth stage is more readily examined. At a fixed monomer concentration, assuming diffusion is the rate limiting step, the size dependent growth rate can be obtained by considering the Gibbs−Thomson equation[20]

$$S_\mathrm{r} = S_b \exp(2\sigma V_\mathrm{m}/rRT)$$

S_r and S_b are the solubility of the nanocrystal and the corresponding bulk solid; σ is specific surface energy; r is the radius of the nanocrystal; V_m is the molar volume of the materials; R is the gas constant; and T is the temperature.

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(21) **Synthesis of CdSe nanocrystal samples**: Four grams of trioctylphosphine oxide (TOPO) was heated to 360 °C with Ar flowing. Cold stock solution (2.4 mL) (Se:Cd(CH$_3$)$_2$:tributylphosphine = 2:5:100 by mass) was quickly (<0.1 s) injected into the rapidly stirred, hot TOPO solution. The temperature was lowered to 300 °C by the injection. At various time intervals, 0.2 mL of aliquots of the reaction mixture was removed and precipitated in 2 mL of methanol. The mass and particle yield of the aliquots was measured after purification from excess TOPO, byproducts, and solvent. The UV−vis and PL (photoluminescence) spectra of the aliquots were recorded by redissolving the nanocrystals in toluene. The optical density (OD) of all the samples was kept at 0.09 ± 0.02 for the PL measurements. One hundred ninety minutes after the first injection, 0.8 mL of stock was slowly injected into the reaction mixture.

(22) **Synthesis of InAs nanocrystal samples**: A concentrated solution of InCl$_3$·TOP (trioctylphosphine, distilled) was prepared by heating 0.33 g of InCl$_3$/mL TOP at 260 °C under argon. The solution was cooled and taken into the drybox for storage. Two grams of TOP was heated to 300 °C. One milliliter of cold stock solution (TMS$_3$As:InCl$_3$:TOP = 1:1.1:2.8 by mass) was rapidly (<0.1 s) injected into the hot TOP, lowering the temperature to 250 °C initially. Growth continued at 260 °C. Aliquots were removed at various time intervals and diluted in toluene. UV−vis and PL spectra were recorded in toluene. Additional injections: 0.5 mL after 23 min, 0.8 mL after 158 min.

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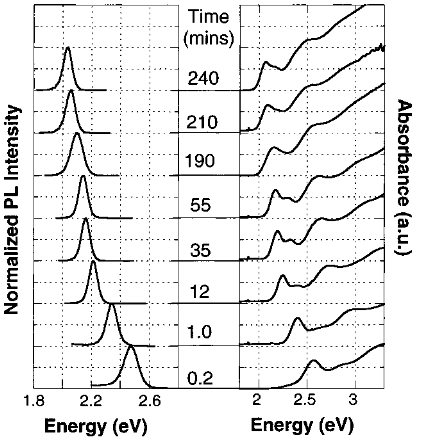

Figure 1. Room-temperature PL and absorption spectra from the sample of CdSe nanocrystals. Note that a secondary injection of monomer occurs at 190 min.

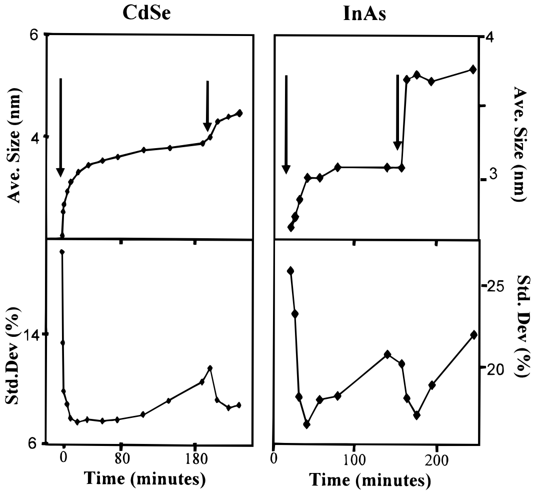

Figure 2. Left: The mean size and the size distribution extracted from the data in Figure 1. Right: The same data extracted from the PL for a synthesis of InAs. Arrows indicate injections.

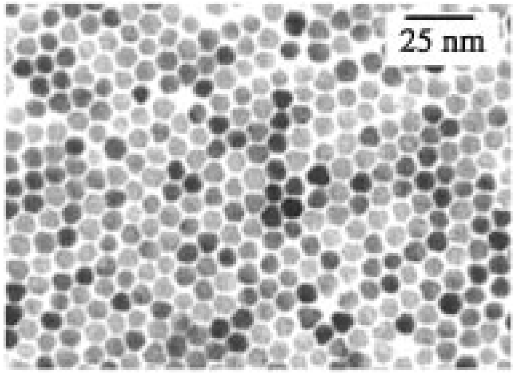

Figure 3. Transmission electron micrograph of 8.5 nm diameter CdSe nanocrystals prepared by the method of distribution focusing.

If $2\sigma V_m/rRT \ll 1$, the diffusion controlled growth rate of the particle with size r is

$$dr/dt = K(1/r + 1/\delta)(1/r^* - 1/r)$$

Here, K is a constant proportional to the diffusion constant of the monomer. δ is the thickness of the diffusion layer. At a fixed concentration, r^* is the critical radius for which the solubility of the nanocrystal is exactly the concentration of the monomers in solution (zero growth rate). Figure 4 is a plot of the above growth rate function when the diffusion thickness is infinite.

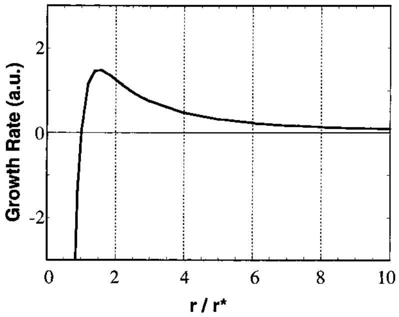

Figure 4. Variation of the growth rate versus size, according to model of Sugimoto.[20]

In this picture, at any given monomer concentration, there exists a critical size, which is at equilibrium. Nanocrystals smaller than the critical size have negative growth rates (dissolve), while larger ones grow at rates dependent strongly on size. Focusing of the size distribution occurs when the nanocrystals present in solution are all slightly larger than the critical size. Under these conditions, the smaller nanocrystals in the distribution grow faster than the larger ones. When the monomer concentration is depleted due to growth, the critical size becomes larger than the average size present, and the distribution broadens because some smaller nanocrystals are shrinking and eventually disappear, while larger ones are still growing. This is Ostwald ripening or defocusing. The distribution is refocused by injection of additional monomer at the growth temperature, which shifts the critical size back to a smaller value. By varying the initial concentration of the monomer, the focusing time as well as the focused size changes, because the time for depleting the monomer concentration changes. For example, in the case of CdSe nanocrystals, just decreasing the volume of the first injection by about 15% and keeping all the other conditions the same, the focusing time was shortened from 22 to 11 min. The focused size decreased from 3.3 to 2.7 nm. In the reaction described in this paper, the Cd to Se molar ratio in the stock solution was about 1.4:1. At a Cd:Se ratio of 1.9:1, after reaching the focused size, the nanocrystals can be maintained at the growth temperature for hours before defocusing occurs. On the other hand, at a ratio of 1.1:1, defocusing is rapid, and the only way to get a tight size distribution is to almost double the concentration of both Cd and Se, which again reduces the critical size.

The effects seen in CdSe and InAs also apply to CdS and InP and presumably to the entire class of II-VI and III-V semiconductors.

During an actual experiment, the concentration of monomer changes continuously, so that the critical size and the relative growth rates of the different sizes are also changing. This suggests that an optimal growth sequence involves continuous monitoring and adjustment of the monomer concentration, so that the average size present is always just slightly larger than the critical size. This type of automation can reproducibly and reliably generate preparations of large amounts of uniform nanoparticles.

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Supporting Information Available: Table of PL peak positions vs sizes of both CdSe and InAs nanocrystals calibrated by TEM and UV-vis and PL spectra of the InAs nanocrystal synthesis (3 pages, PDF/print). See any current masthead page for ordering information and Web access instructions.

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