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Physicochemical Evaluation of the Hot-Injection Method, a Synthesis Route for Monodisperse Nanocrystals

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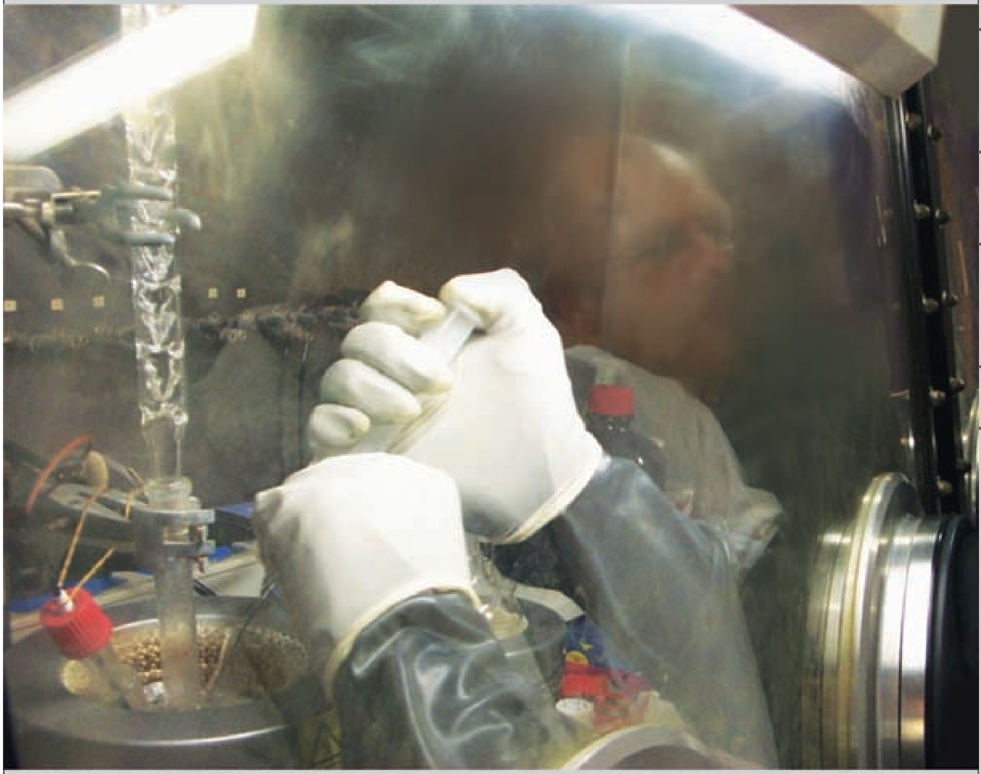

Injection of precursors (at room temperature) into liquid tri-*n*-octylphosphine oxide (at elevated temperature).

NANO MICRO small

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- quantum dots
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- synthetic methods

The quintessence of the hot-injection method, a synthesis route for monodisperse, highly luminescent semiconductor nanocrystals, is reviewed. The separate stages of nucleation and growth of the nanocrystals are discussed in the framework of classical nucleation theory and an equilibrium model proposed by Debye. We also review the numerous adaptations of the original synthesis that currently provide colloidal nanocrystals with well-defined, size-dependent optical, electrical, and magnetic properties. The availability of these remarkable materials is one of the most promising developments in nanoscience and nanotechnology.

1. Introduction

Anyone who regularly reads the current chemistry or physics literature or browses through popular science journals can hardly imagine that there have been times in which the nanometer length scale was completely ignored. In 1915, W. Ostwald alluded to this in the title of his famous book on colloidal science “Die Welt der vernachlässigten Dimensionen” (which translates as “The World of the Neglected Dimensions”).[1a] In the following decades colloid science took flight, focusing mostly on structures of the order of the wavelength of visible light, that is, 0.1 to 1 micrometer. In parallel, the chemistry and physics of ultrasmall colloidal particles, with dimensions in the nanometer range, has developed enormously since the 1980s. In this size range, the dimensions matter for nearly all material properties.[1]

The study of metallic and semiconductor crystals with dimensions in the 1–10 nm range must have had its origin in the fields of catalysis and photocatalysis (including photography) and in the remarkable size-dependent optical properties of noble metal colloids.[1] It was, however, the recognition that quantum confinement effects determine the optical properties of CdS nanocrystals[1,2] that provided the basis for worldwide efforts in the wet-chemical synthesis of semiconductor nanocrystals. Most of the work was focused on the use of ionic precursors in aqueous or polar solutions leading to charge- or sterically stabilized colloidal suspensions. The size-dependent optical and photochemical properties of these semiconductor colloids were explored extensively.[1]

In 1993, a paper entitled “Synthesis and Characterization of Nearly Monodisperse CdX (X = S, Se, Te) Semiconductor Nanocrystallites” by Murray, Norris, and Bawendi appeared in the Journal of the American Chemical Society.[3] The paper described the chemical synthesis of semiconductor nanocrystals of cadmium chalcogenides using *non-ionic* (organometallic) Cd and Se (or S or Te) precursors in a high-boiling *apolar* coordinating solvent, namely, trioctylphosphine oxide (TOPO). The method provided suspensions of II–VI semiconductor nanocrystals in organic solvents, with a bright luminescence and clearly resolved, discrete optical transitions. A collection of some illustrative results is presented in Figure 1. The optical properties of ensembles of nanocrystals (or quantum dots) could be studied in detail due to the strong exciton photoluminescence (PL) and the small inhomogeneous broadening (size dispersion $<10\%$). Furthermore, the absorption and photoluminescence excitation spectra could be related to the electronic structure of the nanocrystal quantum dots. The hot-injection organometallic synthesis method proved to be highly versatile and was adapted to prepare other nanocrystal compounds of II–VI, IV–VI, and III–V semiconductors.

Several excellent reviews covering various aspects of nanoparticle research have been published recently.[4] Here, we aim to highlight the essence of the original synthesis and discuss whether this can be understood with the help of existing models for nucleation and growth. Subsequently, we will briefly review the numerous adaptations to this synthesis route, proposed by many research groups to vary the size and shape of the semiconductor nanocrystals, or to prepare other semiconductor or metallic compounds with striking size-dependent properties. Finally, we discuss the importance of monodisperse and highly luminescent nanocrystals to nanoscience and photophysics.

2. The Hot-Injection Method

The method to prepare CdSe nanocrystals involved the injection of a “cold” (room temperature) solution of precursor molecules into hot liquid TOPO (300 °C).[3] The precursor solution consisted of $CdMe_2$ and Se in trioctyl phosphine (TOP). The injection leads to the instantaneous formation of nuclei of CdSe (denoted as $(CdSe)_c$). Due to a drop in temperature to about 170 °C, the formation of new nuclei is prevented. The result is a suspension of reasonably monodisperse nuclei together with considerable amounts of free Cd and Se precursors. Increasing the temperature to higher values, but below 300 °C, leads to slow growth of the exist-

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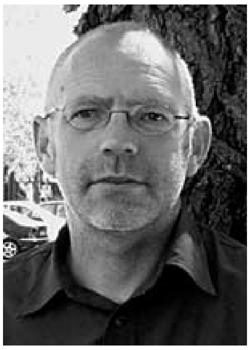
ing nuclei but not to new nucleation. The size of the resulting CdSe nanocrystals increases with increasing growth temperature. The omnipresent TOPO molecules (the solvent) slow down the growth considerably by coordinating the surface Cd atoms, thus forming a steric barrier for reactants. The slow growth at relatively high temperatures allows the nanocrystals to anneal and to form nearly defect-free wurtzite lattices, which are identical to the bulk lattice.[1d] It is noted that the use of alkylphosphine oxide molecules with shorter alkyl chains as the coordinating solvent leads to a much faster growth, which becomes uncontrolled at a sufficiently elevated temperature (230 °C for butylphosphine oxide).[3] After the synthesis, the nanocrystals can be separated from the growth solution by adding a nonsolvent, and can then de redissolved in a suitable organic solvent to form stable colloidal suspensions. The TOPO molecules remain attached to the surface Cd atoms, and the suspensions are sterically stabilized. Such CdSe nanocrystal suspensions have remarkable optical properties (see Figure 1).

The hot-injection solvothermal method[3] represents a clear break with previous wet-synthetic methods, in the sense that neutral organometallic precursors were used in a coordinating alkyl solution with a high boiling point, instead of ionic precursors in water or another polar solvent. The use of TOP-Se and $CdMe_2$ precursors was inspired by the work of Steigerwald and co-workers carried out in the late 1980s at Bell Laboratories, in which organometallic precursors were reacted in inverse micelles at room temperature to yield CdSe clusters and nanocrystals of various sizes.[5] The small CdSe clusters could be isolated and subsequently grown to larger sizes (3–4 nm) by treatment at higher temperatures ($\approx$200 °C) in coordinating solvents (e.g., ethylpyridine, alkylphosphine, or alkylphosphine oxides). Thus, nucleation and growth were separated resulting in a very reasonable size dispersion ($<$8 %) of CdSe nanocrystals.[5b,c] The photoluminescence quantum yield (QY) at room temperature, however, was rather low.[5c]



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3. Physicochemical Evaluation of Nucleation and Growth

In the original synthesis method,[3] the size dispersion of the CdSe nanocrystals is remarkably small ($<$10 %), and later adaptations have led to even smaller size-dispersions.[6,7] One of the reasons for this might be that nucleation and further growth of the nanocrystals occur in separate timeframes. Hot injection leads to instantaneous nucleation, quenched by fast cooling of the reaction mixture and because supersaturation is relieved by the nucleation burst. Further growth of the nuclei into mature nanocrystals occurs at a lower temperature, such that new nucleation events do not occur. Separation of nucleation and growth had already been discussed in detail in 1950 by LaMer and Dinegar with respect to the formation of sulfur crystals.[8] The authors based their model on a paper of Debye that considered thermodynamic equilibrium between a monomer precursor M (a fatty acid) and an aggregate M_n (a micelle).[9] Here we aim to discuss the hot-injection method within the framework of classical nucleation theory.[10] We use the equilibrium model between monomers and an aggregate proposed by Debye as a basis for the discussion.

According to classical nucleation theory, monomer precursors can combine to form small, unstable clusters of increasing free energy (also called embryos). In the case of CdSe clusters, we may consider the following reaction:

$$n\ \text{Cd-TOPO} + n\ \text{Se-TOP} \rightleftharpoons (\text{CdSe})_n\text{TOPO}_m + (n-m)\text{TOPO} + n\ \text{TOP} \tag{1}$$

The change in free energy $\Delta G(n)$ (with respect to that of the monomers) for the formation of a cluster with n CdSe units (formal radius r) is given by:

$$\Delta G(n) = (4/3)\pi r^3 \Delta G_\text{v} + 4\pi r^2 \gamma \tag{2}$$

where ΔG_v (<0) is the decrease in free energy per unit volume due to formation of the crystal structure, and γ (>0) is the surface free energy per unit of surface area. The free energy $\Delta G(n)$ of formation of the $(\text{CdSe})_n\text{TOPO}_m$ clusters is sketched in Figure 2a; for very small sizes, it is positive and increases with increasing size until a maximum is reached. For clusters larger than the critical size, the free energy decreases with increasing size. The clusters with maximum free energy correspond to a "transition state" in chemical language. Thus, the critical nuclei have an equal chance to decompose to the reactants, or to grow out to mature nanocrystals. The radius of the critical nuclei is obtained from $\mathrm{d}\Delta G(n)/\mathrm{d}r = 0$:

$$r_\text{c} = 2\gamma/|\Delta G_\text{v}| \tag{3}$$

The distribution in the size of these critical nuclei is given by $\Delta r_\text{c} = (2\ln 2)^{1/2}\ (3kT/8\pi\gamma)^{1/2} \approx 0.407\ (kT/\gamma)^{1/2}$; it can be small, that is, $\Delta r_\text{c}/r_\text{c} = (3\ln 2/16\pi)^{1/2}(kT\Delta G_\text{v}^{\,2}/\gamma^3)^{1/2} \approx 0.203\ (kT\Delta G_\text{v}^{\,2}/\gamma^3)^{1/2} < 0.1$, due to the large surface energy.

It is doubtful that classical nucleation theory can be quantitatively applied to the formation of nuclei in the hot-

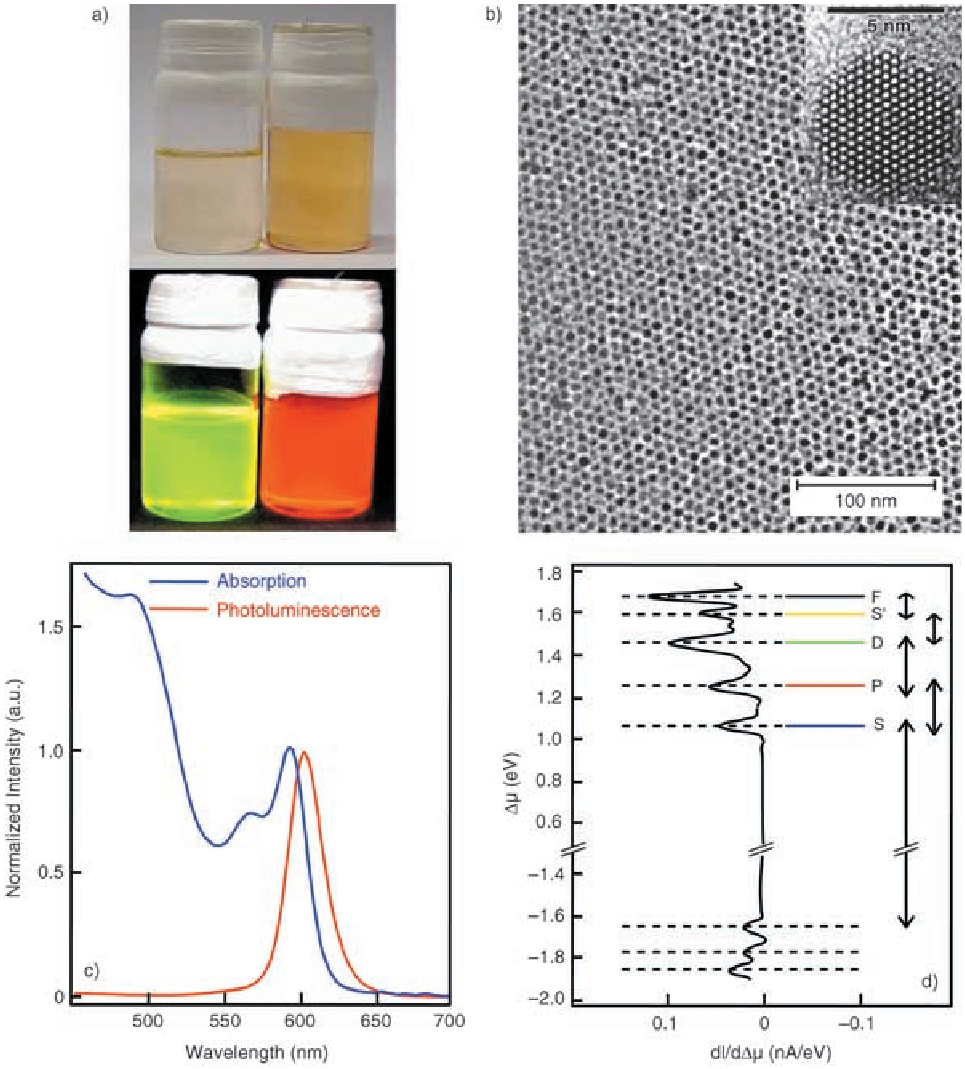

Figure 1. Remarkable properties of CdSe nanocrystals (NCs) prepared by the hot-injection solvothermal synthesis: a) Colloidal suspensions of CdSe NCs under weak daylight (top) and under UV excitation leading to brilliant luminescence (bottom); left flask: CdSe(core)/ZnSe(shell)/ZnS(shell)/TOPO-HDA NCs with a CdSe core of 2.8 nm in diameter; right flask: CdSe/TOPO-HDA (core diameter: 4.3 nm).[7] b) CdSe/TOPO-HDA NCs (6.0 nm in diameter) self-assembled on a TEM grid; and a high-resolution TEM image of a single CdSe NC (URL: www.mrsec.wisc.edu/edetc/SlideShow/shows/quantum dot.html). c) Optical absorption spectrum showing the fundamental (i.e., HOMO–LUMO) and a few higher-energy inter-band transitions of 4.3 nm CdSe/TOPO-HDA NCs, together with the exciton luminescence spectrum (in red).[7] d) Resonant tunneling spectrum obtained with a single CdSe quantum dot of 4.3 nm in diameter: the resonances at positive bias indicate the atom-like S, P, D, and F electron levels, the theoretical separations are indicated with arrows, the quantum confinement energy is in good agreement with pseudo-potential calculations. Some valence levels (e.g., HOMO, HOMO−1) are seen at negative bias.[30b]

injection method. There are a number of reasons for this. First, the $(CdSe)_nTOPO_m$ embryos are very small (see below), which means that ΔG_v should not be considered as a constant, but can vary considerably with the size and inherent structure of the growing nuclei. The magic atom numbers observed with metallic clusters are an example of this. Second, the surface tension γ will depend on the arrangement of the surface atoms and the binding with the coordinating ligands, that is, γ is not a priori constantly independent of cluster size. Steric hindrance between the bulky TOPO molecules may contribute to γ. Third, the hot-injection method is based on temperature-quenching of the nucleation (Equation (1)). This means that the size of the nuclei is not necessarily that of the critical nuclei given by Equation (3); it could be that, at the moment of quenching, the nuclei have exceeded the critical radius (see Figure 2a). While classical nucleation theory is not quantitatively applicable in the context of the hot-injection synthesis, it provides a qualitative basis for an understanding of the formation of nuclei with a small size-dispersion (see below).

In the following sections, we will assume that the critical nuclei consist of a well-defined number c of CdSe molecules. The equilibrium between the monomers and critical nuclei can thus be written as in Equation (1), with $n=c$, and with a formal equilibrium constant:

$$K_c = \frac{[(CdSe)_c][TOPO]^{c-m}[TOP]^c}{[Cd]^c[Se]^c} \qquad (4)$$

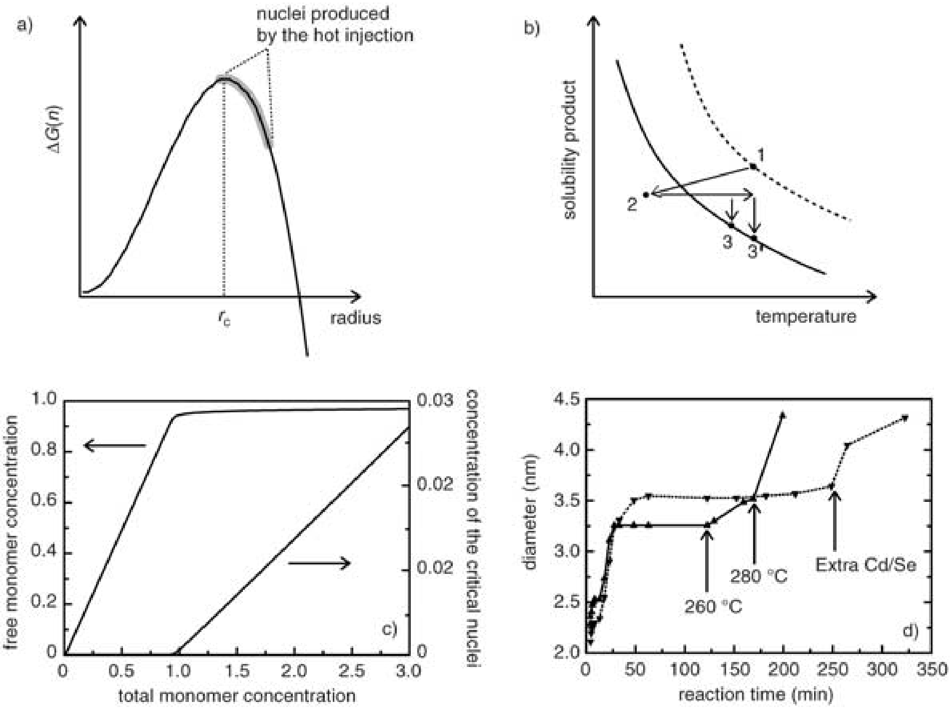

Figure 2. Essential points of the synthesis of monodisperse CdSe nanocrystals with separate nucleation and growth: a) Sketch of the free energy of formation of a cluster according to classical nucleation theory. b) Sketch of the solubility product [Cd][Se] as a function of temperature. Solid line: thermodynamic curve for the equilibrium between the monomers Cd-TOPO and Se-TOP and a macroscopic CdSe crystal. Dashed line: the solubility product for the equilibrium between the monomers and the critical nuclei $(\mathrm{CdSe})_c$ indicative of supersaturation. The points indicate: nucleation (1), cooling (1–2), and growth of the nuclei at two different temperatures (3 and 3′). c) The concentration of monomer precursors and critical nuclei $(\mathrm{CdSe})_c$ as a function of the total precursor concentration added to the reaction flask, calculated for the equilibrium given in Equation (1); $c=75$ CdSe units in accordance with experimental observations,[11] (the concentrations are given in arbitrary units). The point at which the concentration of critical nuclei rises steeply is called the critical point.[9] d) Experimental observation of the growth evolution of nuclei into mature nanocrystals at 240 °C. The diameter of the nanocrystals first increases and than becomes constant. Increase of the temperature to 260 and 280 °C (full curve) leads to further growth similarly to the addition of excess precursors (dashed curve).[7]

Equation (1) should be distinguished from the commonly known equilibrium between the Cd and Se monomers and a macroscopic CdSe crystal: due to their excess surface energy component, the nuclei have a higher free energy per unit volume than a macroscopic CdSe solid, which forms the thermodynamically stable phase. In Figure 2 b, we have sketched the solubility product [Cd][Se] of the monomers as a function temperature, assuming that the formation of a macroscopic CdSe solid from the precursors is endothermic (see below). Following LaMer and Dinegar[8] and Debye,[9] we also have added a second line (dashed) which indicates the monomer concentration product assuming an equilibrium between the monomers and the critical nuclei $(\mathrm{CdSe})_c$ as denoted in the reaction shown in Equation (1). A larger chemical potential is required to add a Cd and Se atom to such a small critical nucleus. As a consequence, this monomer product lies above the thermodynamic product [Cd][Se], and it is indicative of supersaturation. We have analytically calculated the free monomer concentration and the concentration of the critical nuclei $(\mathrm{CdSe})_c$ in the reaction flask as a function of the total concentration of added precursors (Figure 2 c). The concentration of critical nuclei remains essentially zero, up to a certain concentration of precursors, above which the concentration of the critical nuclei rapidly rises (nucleation outburst). This is in agreement with the argumentation of Debye, which showed that monodisperse aggregates are formed quantitatively from the monomers after exceeding a threshold concentration.[9] We conclude that if the reaction shown in Equation (1) leads to nuclei $(\mathrm{CdSe})_c\mathrm{TOPO}_m$ with a well-defined and relatively large number of CdSe molecular units ($c>10$), the concentration of such nuclei is directly proportional to the precursor concentration added to the reaction mixture.

The nucleation and growth steps were investigated in detail by Bullen and Mulvaney for the case of CdSe nucleation in a non-coordinating solvent.[11] This enabled the study of the nucleation characteristics with varying concentrations of capping agent. The size and concentration of the nuclei and the growing nanocrystals were estimated from optical absorption measurements.[11] It was confirmed that after initial nucleation, the number of nanocrystals during growth stays constant, that is, that new nucleation events do not occur during growth. The polydispersity in the initial size of the seeds just after nucleation can be remarkably small (size dispersion below 10 %), which means that this is very probably also the case for the critical nuclei, thus $\Delta r_c/r_c<0.1$. The critical size of $(\mathrm{CdSe})_c$ was found to correspond to a value of c of about 75. In addition, 2–8 % of the precursors were consumed in the nucleation process. This is in fair agreement with the calculated curve for $c=75$ showing that about 90 % of the precursors exist as free monomers at the point at which nucleation erupts (Figure 2 c). This means that there are enough free precursors for the further growth of the nuclei into larger nanocrystals in the second stage. It was also reported that the concentration of nuclei in the solution decreased with increasing concentration of the capping agent. This can have a kinetic reason; the coordinating molecules lower the rate of nucleation. It is, however, also in agreement with the equilibrium shown in Equation (1). It was reported that the size of the final nanocrystals increased with increased concentration of the capping molecules; this somewhat counterintuitive result is simply a consequence of the reduced concentration of nuclei, that is, the equilibrium in Equation (1) shifts towards the left. In addition, it was found that the concentration of the nuclei increased with increasing temperature of nucleation. This is in accordance with the reaction in Equation (1) being endothermic in the forward direction.

The separate stages of nucleation and growth can now be rationalized using the scheme presented in Figure 2b:

1: Injection of the precursors at 300°C; supersaturation is achieved and relatively monodisperse nuclei $(CdSe)_c$ are formed. The critical nuclei coexist with large amounts of unreacted precursors.

1→2: Drop of the temperature to 170°C due to the injection of the room temperature reactants; this leads to quenching of nucleation and growth.

3 and 3′: Increase of the temperature to values at which growth of the nuclei to larger nanocrystals occurs, without the formation of new nuclei.

We followed the size evolution of the nanocrystals during growth at different temperatures (Figure 2d).[7] After a period of growth at 240°C, the size of the nanocrystals reaches a constant. If the temperature is raised, the nanocrystals start to grow again until a larger constant size is reached. The evolution of the crystal size in response to a sudden increase in temperature was very similar to that following injection of excess precursors. This can be represented by small steps to the right (e.g., from point 3 to 3′) along the solid curve in Figure 2b. These observations indicate that equilibrium between the nanocrystals and the free monomers can occur in the TOPO solution at a given temperature and that the nucleation reaction is indeed endothermic. Of course, growth can be quenched on purpose by a decrease of the temperature before equilibrium is reached.

4. Adaptations of the Original Synthesis

There was a rapid response to the publication of the original work by Bawendi and co-workers.[3] Rarely has a paper on a new synthesis method of an already existing compound attracted so much attention. Adaptations on the synthesis of CdSe nanocrystals concerned the temperature of nucleation and growth, the use of organic capping molecules other than TOPO and TOP, the growth of inorganic shell structures around the CdSe core, and the preparation of nanocrystals with a non-spherical shape. These adaptations are summarized in Table 1. It also became clear that the use of organometallic precursors and growth at a high temperature are appropriate for the synthesis of other semiconductor nanocrystals; that is, III–V compounds (InAs, InP, GaP) IV-VI compounds PbX (X = S, Se, Te), and also metal nanocrystals. A discussion of this work is beyond the scope of this paper. We have summarized the reports in Table 2, where we focus on the routes that maintained the essence of the original method, that is, the separation of nucleation from growth by a rapid injection of a cold solution of precursors into a hot solvent followed by growth at a lower temperature. Adaptations to the original synthesis comprise:

a) Growth control with surfactants other than TOPO: The introduction of co-surfactants with linear alkyl chains that are less bulky than TOPO, such as hexadecylamine (HDA), allowed the size-distribution of CdSe nanocrystals to be narrowed during growth and led to an unprecedented degree of monodispersity without the need for post-preparative size-selection techniques.[6,7] Moreover, the surface passivation was greatly improved, increasing the photoluminescence quantum yields to 10–25%.[6] Growth with a large excess of Se and at lower temperatures (240°C) was found to favor surface ordering and reconstruction, further improving the surface properties and allowing reproducible formation of nearly monodisperse CdSe nanocrystals with band-edge PL QYs as high as 85%.[6b,7] Multicomponent surfactant mixtures have also been crucial for the preparation of other semiconductor and metal nanocrystals (see Table 2) and to achieve shape control (see below).

b) Ligand exchange after synthesis: The surface properties of the high-quality nanocrystals obtained by the hot-injection solvothermal approach can be further modified by post-preparative ligand exchange, allowing the QY to be improved, the solubility to be modified (e.g., water-soluble CdTe QDs with a high QY have been obtained by exchanging the original capping layer for thiols[14]), or bioactivity to be achieved.[4f,g,15]

c) Inorganic passivating shells: The original method yielded CdSe nanocrystals with rather low photoluminescence quantum yields (≤10%). Although organically capped nanocrystals with PL QYs as high as 85% can now be synthesized,[6,7] their photostability under ambient conditions is rather poor since the organic shells are flexible, allowing chemical species, such as water and oxygen, to reach the nanocrystal surface. The (photo)stability (and photoluminescence quantum yields) can be improved by growing an inorganic shell of a wider-bandgap semiconductor around the nanocrystals, yielding so-called core–shell quantum dots (heteroepitaxy).[12c–g] An early example of a core–shell synthesis was the water based synthesis of $CdS/Cd(OH)_2$ nanocrystals, which possess a high photoluminescence quantum yield.[16] In the case of the organometallic synthesis route, CdSe/ZnS core–shell nanocrystals were the first to be reported[12c,d] and are still the most stable core–shell nanocrystals.[12g] However, the large mismatch (≈12%) between CdSe and ZnS lattice parameters induces strain at the core–shell interface. For ZnS shells thicker than ≈2 monolayers this leads to the formation of defects that decrease the QY and the stability.[12g] The lattice mismatch is smaller for CdS and ZnSe shells and a higher QY can be obtained for CdSe/CdS and CdSe/ZnSe core–shell quantum dots,[12e–g] but with a lower stability due to the smaller bandgap difference between the shell and core materials. Recently CdSe/ZnSe/ZnS, CdSe/CdS/ZnS, and CdSe/(Cd,Zn)S/ZnS core/shell/shell nanocrystals have been reported, providing luminescence QY and photostability exceeding those of the CdSe nanocrystals capped with a single shell.[12g,m] Shells of different materials (such as silica or polymers) can also be grown around nanocrystals to simultaneously provide stability and water solubility.[4f,g,15]

d) Synthesis of nanocrystals with a non-spherical shape: If the overall growth rate is slow, the nanocrystals possess a nearly spherical, but still faceted shape minimizing the over-

Table 1. Modifications to the original hot-injection solvothermal method[3] for the synthesis of colloidal CdSe nanocrystals: (NC = nanocrystal; T_{inj} = injection temperature, T_{gr} = growth temperature; V_{inj} = injection volume; [CdSe] = concentration of CdSe monomers in the growth solution; QY = photoluminescence quantum yield at room temperature; TOPO = tri-*n*-octylphosphine oxide; TOP = tri-*n*-octylphosphine; HDA = hexadecylamine; TBP = tri-*n*-butylphosphine; ODA = octadecylamine; SA = stearic acid; PA = phosphonic acids; TDPA = tetradecylphosphonic acid; HPA = hexylphosphonic acid; OD = 1-octadecene).

Modification	Effect	Ref.
Higher T_{inj} (350 °C) and T_{gr} (300 °C); smaller V_{inj} ; lower [CdSe] (0.015 mol kg^{-1})	Spherical NCs without stacking faults and narrower size-dispersion, sizes: 1.8–6.0 nm	12a
Solvent: TOPO/TOP/HDA; higher T_{gr} (250–310 °C); [CdSe]: 0.1 mol kg^{-1}	No stacking faults; monodisperse samples without size-selection, higher QY (10–25 %)	6
Solvent: TOPO/TOP/HDA; higher Se/Cd (5); T_{gr}: 240 °C; [CdSe]: 0.07 mol kg^{-1}	Monodisperse samples without size-selection, higher QY (50–85 %); high reproducibility, radiative exciton lifetimes	7
Solvent: TOPO/TBP/HDA/ODA; higher T_{inj} (320 °C) and T_{gr} (290 °C); higher Se/Cd ($\leq$10); [CdSe]: 0.04 mol kg^{-1}	Monodisperse samples without size-selection, higher QY (40–85 %)	6b
Overgrowth of a ZnS shell by a 2-step single-pot method	CdSe/ZnS core/shell NCs; higher QY (30–50 %) and superior photostability, but broader size-dispersion and poorer reproducibility	12c
Overgrowth of a ZnS shell by a 2-step 2-pot method	CdSe/ZnS core/shell NCs; higher QY (30–50 %), superior photostability	12d
Overgrowth of a CdS shell by a 2-step 2-pot method	CdSe/CdS core/shell NCs; higher QY (50–80 %), superior photostability but lower than for ZnS shell	12b,e
Overgrowth of a ZnSe shell by a 2-step 1-pot method	CdSe/ZnSe core/shell NCs; higher QY (40–85 %), superior photostability but lower than for ZnS shell	12f
Sequential overgrowth of a double shell	CdSe/(Cd,Zn)S/ZnS, CdSe/ZnSe/ZnS, CdSe/CdS/ZnS, core/shell/shell NCs; higher QY (up to ≈90 %), superior photostability (higher than for CdSe/ZnS core/shell), improved reproducibility, narrow size-distribution (< 10 %)	12g,m
Precursors: CdO or Cd(Ac)$_2$ + acid/ligand (SA, PA, TDPA). Growth solvents: fatty acids, amines, octadecene	Growth kinetics depends on precursor, solvent and T_{gr}. Suitable combinations of precursor/solvent yield size distribution 5–10 % and QY up to 30 % (TOPO still added as co-solvent). Non-coordinating solvents such as OD require stable complex as precursor (TDPA-Cd; Cd oleate, Cd stearate)	11, 12b,g,h
Solvent: TOPO/TOP + strong Cd ligand (TDPA or HPA). T_{inj}: 280–350 °C. T_{gr}: 250–300 °C. [CdSe]: 0.06–0.4 mol kg^{-1}	Shape control: dots, rods, bipods, tripods, tetrapods	12i–l
Addition of TDPA to the Se-precursor mixture	Addition of TDPA to the Se-precursor mixture yields CdSe nanocrystals with zinc blende lattice structure	12n

Table 2. High-quality nanocrystalline quantum dots prepared by the hot-injection solvothermal approach. The nanocrystals are (nearly) spherical, unless otherwise stated.

Material	Size/(σ)[a]	Properties	Ref.
CdSe	2–15 ($\leq$5 %)	Wurtzite, λ_{em}: 520–660 nm, QY: up to 85 %; size and shape control	Table 1
CdSe	2.5–4 (6–7 %)	Zinc blende, λ_{em}: 510–590 nm, QY > 25 %	Table 1
CdSe/shell	2–15 ($\leq$10 %)	Same as the CdSe core, but improved QYs and stability; shell: CdS, ZnSe, or ZnS	Table 1
CdS/ZnS	4–5 (8 %)	Wurtzite, λ_{em}: 460–480 nm, QY: 20–30 %, higher stability than CdS	13a
CdTe	2.5–7 ($\leq$10 %)	Zinc blende; λ_{em}: 550–650 nm, QY: 35–65 %	13b
	2–11 ($\leq$10 %)	Zinc blende or wurtzite, Shape control (dots, rods, tetrapods); λ_{em}: 530–760 nm, QY: 20–70 %	13c
$Cd_{1-x}Zn_xSe$	5–8 ($\leq$5 %)	Wurtzite λ_{em}: 470–580 nm, QY: 70–85 %, higher stability than CdSe	13d
$CdSe_{1-x}Te_x$	2–8 ($\leq$10 %)	Wurtzite λ_{em}: up to 850 nm, QY: 60 %	13e
ZnSe	3–6 (10 %)	Zinc Blende; λ_{em}: 460–480 nm, QY: 20–50 %	13f
ZnO	3–5 ($\leq$10 %)	Wurtzite; λ_{em}: 335–350 nm (exciton) and ≈550 nm (defect-related)	13g
PbS	3–10 ($\leq$15 %)	Rock-salt structure, λ_{em}: 1.0–1.4 μm, QY: up to 20 %	13h
	4–50 (12 %)	Shape: rods, multipods, octahedrons, cubes, stars	13q
PbSe	3–9 ($\leq$5 %)	Rock-salt structure, λ_{em}: 1.2–2 μm, QY: 85 %	13i, j
	10–500	Shape: nanowires (straight, zigzag, helical, branched), multipods, rods, cubes, nanorings	13k,r
PbTe	8–15 ($\leq$15 %)	Rock-salt structure; shape: spherical or cubic	13m
InP	2–7 ($\leq$10 %)	Zinc blende ; λ_{em}: 520–750 nm, QY: 20–40 %	13n
	3–30	Shape: rods and wires; λ_{em}: 600–800 nm	13o
InAs/ZnSe	2.4–6 (8 %)	Zinc blende λ_{em}: 0.8–1.4 μm, QY: 20 %	13p
Co	2–12 (< 5 %)	Magnetic	13i
FePt	3–10 (< 5 %)	Magnetic	13l
$CoPt_3$	1.5–7 (< 5 %)	Magnetic	13s

[a] Particle size in nanometers; σ = size dispersion.

all surface area per unit volume.[12i–k] Shapes that strongly deviate from spherical can be obtained by manipulation of the growth conditions such that the growth rate of the different crystal facets becomes substantially different. For nanocrystals with a strongly anisotropic crystal structure (e.g., wurtzite), this can be achieved by using a high precursor concentration. This leads to a faster growth rate along the *c* axis and rod-shaped nanocrystals. In order to maintain control over the growth at high precursor concentration, the addition of strong cadmium-coordinating ligands (e.g., hexylphosphonic acid) is required. Shape control can be achieved also for nanocrystals with isotropic crystal structures such as PbSe or PbS (rocksalt) (see Table 2) by using growth conditions (i.e., surfactant composition, concentration, temperature) that either limit/accelerate the growth rate of a particular face or induce smaller nanocrystals to attach to each other along preferential crystallographic directions.[13i–k, r] It is worth noting that shape control is possible only under kinetically controlled conditions. Possibly, there is a heterogeneous equilibrium of the coordinating molecules (chemisorbed versus dissolved) that is different for different crystal facets. The same principles employed for shape control have recently allowed the preparation of nanocrystal heterostructures (PbSe/CdSe nanorod–PbSe dumbbell heterotrimers[17]).

e) Alternative precursors and/or solvents**:** A major drawback of the traditional hot-injection solvothermal method is the use of expensive, hazardous, and toxic organometallic precursors and coordinating solvents, which has motivated many groups to develop alternative solvothermal methods based on cheaper and less hazardous chemicals[11, 12b,g,h,m]. The precursors are typically metal (e.g., Cd^{2+}) complexes with organic acids (such as alkylphosphonic or fatty acids), which are prepared in situ from CdO or cadmium acetate, and solutions of elemental selenium (or sulfur). Alternative solvents include fatty acids, amines, or even noncoordinating solvents such as octadecene. The alternative methods are cheaper, easier, and less hazardous and have made it possible to carry out large-scale (multigram) syntheses of, for example, CdSe/CdS core/shell nanocrystals.[12b]

An obvious alternative approach, in particular for nanocrystals intended for biomedical applications, would be synthesis in aqueous media, since this yields nanocrystals that are naturally hydrophilic and therefore more likely to be biocompatible. However, despite the frantic level of activity in the field of biomedical labeling[4f, g, 15] and several promising recent developments in water-based synthesis (see below),[18a–d] nanocrystals synthesized in water have yet to find their place in successful application in biological environments.[4f, g, 15] Arrested precipitation in water in the presence of stabilizers is probably the faster and simpler method to prepare semiconductor nanocrystals, and yielded the first high-quality CdS nanocrystals, small enough to show quantum confinement effects.[1] Development of aqueous synthetic routes to semiconductor nanocrystals has remained a very active research field over the last 20 years for the preparation of many different compounds (see Refs. [4d, e] for recent reviews). In many cases, however, the nanocrystals show a rather low exciton photoluminescence quantum yield, sometimes dominated by defect-related emission (e.g., CdS,[18a] CdSe,[18f,g] CdTe,[18h] and ZnSe[18i]). This limited success might be related to the lower growth temperatures attainable in aqueous media, which leads to lower crystallinity and more defects, and to a poorer surface passivation due to the lack of suitable water-soluble surfactants. Furthermore, water itself might be a chemical reactant, changing the surface chemistry of the nanocrystals (e.g., CdSe). Nevertheless, there are recent developments yielding high-quality thiol-capped CdTe,[18a,b,d] HgTe,[18a,b] and ZnSe[18c] nanocrystals with size-dispersion, crystallinity and photoluminescence properties (spectral position and QY) comparable to those synthesized by the hot-injection solvothermal methods (namely, size-dispersion $\leq 10\%$, nearly absent defect-related PL, and PL QYs between 40–60% for CdTe and 20–30% for ZnSe).

5. Importance for Nanoscience and Photophysics

In the 1980s, synthesis routes in polar solvents at room temperature were used for the preparation of semiconductor nanocrystals. Although exciton and sub-bandgap luminescence and effects due to quantum confinement were reported, the emphasis of most of the research was on photo(electro)chemistry and catalysis.[1] The hot-injection solvothermal method and its modifications yielded semiconductor nanocrystals with a high luminescence quantum yield and a reasonably small dispersity in size and shape. The small size and shape variations are a key to the self-assembly of nanocrystal building blocks into two-dimensional and three-dimensional arrays. Both the small size-dispersion and the high photoluminescence quantum yield are required for a fundamental study of the photophysics of nanocrystal quantum dots. Since 1990, the chemistry and physics of colloidal nanocrystal quantum dots is one of the most rapidly expanding fields of research, which is leading to many scientific discoveries and technological innovations. In Table 3, we have summarized some of these that are directly related to the narrow size-dispersion and/or strong photoluminescence; a complete discussion is beyond the scope of the present paper. Here, we will briefly touch on a few aspects.

a) Self-assembly of nanocrystals into ordered arrays: In the original paper of Bawendi and co-workers,[3] a TEM picture of a dense monolayer of nearly monodisperse CdSe nanocrystals showing local order was presented. In a following paper, three-dimensional close-packed superlattices were demonstrated.[19a,b] The assembly is driven by the van der Waals interactions between the nanocrystal cores, and between the capping molecules. Interdigitation of the capping molecules can also occur. We remark here that uncharged nanocrystals with a small size-dispersion are required to obtain such dense, well-ordered superlattices. Recently, ordered AB_2 and AB_{13} binary arrays of semiconductor and magnetic nanocrystals have been reported.[19d] Thus, nanocrystals can be considered as building blocks for larger architectures. In these novel materials, both the properties of the building blocks and the electronic and magnetic inter-

Table 3. Breakthroughs made possible by the superior properties of semiconductor nanocrystals grown by hot-injection solvothermal synthesis.

System		Ref.
	Self-assembly of nanocrystals	
Semiconductor nanocrystals, magnetic nanocrystals	Ordered 2D and 3D nanocrystal arrays obtained by solvent evaporation or addition of a non-solvent	12k, 13l,s, 24a,b, 31a
	Binary arrays of nanocrystals	19d,e
	Ordered 2D arrays obtained in a Langmuir trough	19f,g 24c,d
	Photophysics: Measurement and results	
Colloidal suspension of nanocrystalline quantum dots	Light absorption spectroscopy in near UV–near IR, showing discrete inter-band optical transitions	20
	Luminescence excitation spectroscopy showing a multitude of optical transitions and their relative strength	20
Ensembles of nanocrystalline quantum dots	Fluorescence line-narrowing spectroscopy: exciton Stokes shift and triplet–singlet splitting	21
	Time-resolved luminescence spectroscopy: lifetime of exciton singlet and triplet states over entire temperature range (1.2–300 K)	22,23
	Time-resolved luminescence spectroscopy: temperature anti-quenching	23
	Exciton energy transfer	24
	Photonic effects: refractive index, microcavity	25
	Photonic effects in 3D photonic crystals	26
Suspensions and ensembles of nanocrystalline quantum dots	Light-absorption spectroscopy in the near infrared of quantum dots occupied with electrons (holes) detecting the transitions between the discrete conduction (hole) levels (intraband relaxation)	13j, 27
Ensembles of nanocrystalline quantum dots	Ultrafast spectroscopies detecting the decay of higher excitonic states, the kinetics of Auger recombination, and the decay of multi-exciton states	28
Single quantum dot	Single exciton lifetime	29a,b
	Single nanocrystal quantum yield	29c
	Excitation spectroscopy	29d
	Photon antibunching	29e
	On–off behavior (blinking), Stark effects, charging effects	29f–h
	Charge and photoionization (electrostatic force microscopy)	29i
	Electrical properties: Measurement and results	
Single quantum dot (CdSe, InAs, PbSe,...)	Tunneling spectroscopy of the electron and hole energy levels and Coulomb interactions in a single dot	30
Quantum dot solids (CdSe, PbSe, ZnO)	Controlled electrochemical gating, measurement of electron (hole) transport and optoelectronic properties	31a–c
CdSe quantum dot	Gate-controlled single-hole transport through a quantum dot	31d

actions can be tuned by variation of the chemistry, the size and the distance between the crystals. In addition, the occupation of the energy levels can be controlled, for instance by electrochemical gating. The study of quantum dot solids has led to exciting physics, for example, exciton energy transfer,[24] electron transport determined by quantum properties,[31] and low-threshold lasing.[32a,b] This line of research can be expected to lead to novel materials with tunable optoelectronic properties.

b) Exciton dynamics in semiconductor nanocrystals: There is a scientific quest for the true radiative lifetime of the exciton in semiconductor nanocrystals. An increasing number of works report single-exponential decay of the photoluminescence with suspensions of semiconductor nanocrystals, and the reported exciton lifetimes seem to converge. For instance, for CdSe nanocrystals in organic solutions consistent values of the exciton lifetime of around 25 nanoseconds are reported at room temperature. Interestingly, this conclusion is obtained from measurements on ensembles,[25a] as well as on single CdSe nanocrystals.[29a] The fact that the true radiative decay time can be obtained has given a new impetus to the study of the photophysics of nanocrystal quantum dots. Examples are studies of the influence of the refractive index[25a] and the density of photon modes in a photonic crystal on the rate of spontaneous emission of CdSe and CdTe quantum dots.[26] The exciton dynamics have been studied over a wide temperature range from 2 to 330 K for both ensemble and single CdSe nanocrystals.[22,23,29b] The energetics and dynamics of a triplet dark state in thermal equilibrium with the singlet state has been studied in detail. In addition, remarkable results have been reported recently suggesting that subtle effects of strain in the surface capping can have a strong effect on the photoluminescence quantum yield and the exciton decay (temperature anti-quenching).[23] We believe that the study of the optoelectronic properties of individual nanocrystals in a well-controlled environment will form one of the most exciting branches of nanophysics in the coming decade.

6. Conclusions

Hot-injection synthesis provides a versatile methodology for the preparation of highly luminescent colloidal nanocrystals with tunable size, shape, and surface passivation. The reason for the success of this approach lies in the use of non-ionic precursors in high-boiling organic solvents. This makes it possible to grow the nanoparticles relatively slowly at a high temperature, which yields defect-free, well-passivated nanocrystals.

The second important aspect of this type of synthesis is the separation of the nucleation and growth stages. Due to this, a high degree of monodispersity can be achieved without the use of post-synthesis size-selective techniques. We have discussed the nucleation and growth processes in the framework of classical nucleation theory, assuming an equilibrium between the precursors and critical nuclei that have a well-defined number of molecular units.

The ability to manipulate precisely the size, the shape, and the surface of nanocrystals has opened up a number of potential applications for these new materials: light-emitting diodes,[13a,33] low-threshold lasers,[12l,32] solar cells,[34] optical amplifiers for telecommunications,[35] and biomedical tags.[4f,g,15] Considering the astonishing rate at which progress is being made on several fronts, we may expect that the impact of this field of nanoscience on our daily lives will grow markedly in the near future.

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