SYNTHESIS AND CHARACTERIZATION OF LUMINESCENT OXIDE NANOCRYSTALS

By

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To God, my family and friends, this work is dedicated
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SYNTHESIS AND CHARACTERIZATION OF LUMINESCENT OXIDE NANOCRYSTALS

By
Sooyeon Seo
August 2007

Chair: Paul H. Holloway
Major: Materials Science and Engineering

Oxide nanocrystals with controlled geometries exhibit unique shape dependent optical and structural properties. Shape-controlled synthesis of rare earth doped gadolinium oxide (Gd$_2$O$_3$:Eu$^{3+}$, Tb$^{3+}$ or Er$^{3+}$) and zinc gallate (ZnGa$_2$O$_4$:Eu$^{3+}$) nanocrystals by non-hydrolytic high temperature (~300°C) methods are reported. Various shapes of Gd$_2$O$_3$ nanocrystals were synthesized, including spheres and plates and advanced shapes such as curved rods and triangles. The nanocrystal shape was shown to be a function of the synthesis parameters, such as metal precursors (acetate, acetyl acetonate, chloride or octanoate) and surfactant type (tri-octyl phosphine oxide-TOPO, or hexadecanediol-HDD) and concentration (metal precursor: surfactant molar ratios of 1:2 to 1:5), as well as heating rate (5-25°C/min.) between pre-heat (200°C) and reaction (290°C) temperatures. The effects of these parameters upon nanocrystal shape were explained based on nucleation and growth of oxide nanocrystals. The photoluminescence intensity from Gd$_2$O$_3$:Eu$^{3+}$ was shown to increase as the concentration of dopant incorporated into the nanocrystals increased. The doping efficiency, defined to be the percentage of dopant incorporated into the nanocrystals, ranged from 0.57-6.1 mol%, was a function of shape of the Gd$_2$O$_3$:Eu$^3$ and was discussed in terms of the rate of reaction, product yield and crystal structure.
To be used for labeling biomolecules such as DNA, RNA, or proteins, water soluble luminescent nanocrystals are required. Doped Gd$_2$O$_3$ nanocrystals prepared by the non-hydrolytic hot solution method are hydrophobic and are not soluble in water due to organic surfactant encapsulation. A general strategy to convert hydrophobic luminescent nanocrystals (e.g. Gd$_2$O$_3$) to water soluble particles by over-coating the hydrophobic surface with amphiphilic polymers is reported. Specifically, octylamine modified surfaces were coated with poly (acrylic acid) and water dispersions of Gd$_2$O$_3$:Eu$^{3+}$ were still stable at room temperature after four months.

The non-hydrolytic hot solution synthesis technique was used to grow monodispersed ternary oxide nanospheres (~5nm) of ZnGa$_2$O$_4$: Eu$^{3+}$ from a variety of metal precursors. Using Gd acetate dehydrate, large (~20nm) complex shaped (triangle and rectangle) ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals were obtained. Based on X-ray diffraction data, the nanocrystals had a cubic spinel structure with no impurity phases. The size of the ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres could be varied by changing the molar ratio of Zn to surfactants, with higher concentrations of surfactant resulting in smaller nanocrystals. Analysis of the PL emission suggests that the Eu$^{3+}$ ions were incorporated into the ZnGa$_2$O$_4$ host.
CHAPTER 1
INTRODUCTION

In the nanoscale regime, the chemical and physical properties of inorganic crystals are highly dependent on geometrical factors such as size and shape [1, 2]. Precise control of such factors allows one not only to observe unique properties of the nanocrystals but also to tune their chemical and physical properties as desired. During the past decades, researchers have explored efficient synthetic routes to produce well-defined inorganic nanocrystals with a controlled size and shape. Some advanced nanocrystal structures with interesting geometries including wires [3, 4], tubes [4, 5], ribbons [6, 7], and more complex shapes [7, 8] were produced with gas phase approaches. On the other hand, the colloidal approach in liquid media provides a convenient and reproducible route for the fabrication of nanocrystals with controlled size and shape. This enables the resulting nanocrystals not only to be precisely tuned at the sub-10 nm scale but also to be easily dispersed in organic or aqueous media for numerous potential applications in electronic and biological systems. Along with size control, anisotropic shape control of nanocrystals has been attained through liquid methods [9-17].

The nonhydrolytic molecular precursor decomposition method is an effective route for the controlled synthesis of both isotropic and anisotropic colloidal nanocrystals [11]. Nanocrystals obtained by such nonhydrolytic synthetic methods in general possess excellent crystallinity and monodispersity in terms of size and shape. Although there are increasing numbers of examples of colloidal semiconductor nanocrystals with anisotropic shapes, from simple one-dimensional rods and wires to advanced multipods and stars, reports of shape-guided rare earth doped oxide nanocrystals are very limited. To obtain luminescent oxide nanocrystals with the desired shape and to investigate the relationship of the controlled structures with the luminescent efficiency,
systematic understanding of shape-guiding processes is necessary to provide the insight for efficient doping.

In this dissertation, Chapter 2 reviews the fundamental physics, synthetic methods, shape controlled nanocrystals, proposed mechanisms and application in cell biology. In Chapter 3, the preparation of rare earth doped gadolinium oxide nanocrystals with a nonhydrolytic synthetic route resulting in various shapes is discussed. The effects of reaction variables on shape-guiding growth were also studied, as were their crystallographic and luminescent properties. In Chapter 4, a general strategy is introduced to make luminescent Gd₂O₃ nanocrystals water soluble by over-coating hydrophobic surfaces with amphiphilic polymer. The conversion of hydrophobic nanocrystals into hydrophilic particles is prerequisite for biological applications. As a labeling material for biomolecules, especially for the sensitive determination of molecules such as DNA, RNA, or proteins, well-controlled nanocrystals are required in the nanoscale regime. In Chapter 5, ternary (ZnGa₂O₄: Eu³⁺) oxide nanocrystals have been grown in the shape of spheres and plates and advanced shapes such as curved rods and triangles. The size of the ZnGa₂O₄: Eu³⁺ nanocrystals can be controlled by varying the concentration of organic surfactants. Finally, conclusions and future work are summarized in Chapter 6.
2.1 Fundamentals of Colloidal Nanocrystals

2.1.1 Chemistry and Physics of Nanocrystals: Size and Shape Issues

Nanomaterials are small-scaled with at least one dimension between 1nm and 100 nm, and include a range of shapes, such as nanospheres, nanocubes, nanorods, nanosheets and nanotubes [6, 18-21]. They exhibit novel optical, electronic, magnetic, chemical and mechanical properties that are different from their bulk counterparts from which they can be derived. Nanocrystals have attracted broad attention in a variety of fields including catalysis, photovoltaics, and coatings as well as in the emerging fields of nanomedicine where they can be used as imaging agents and drug-delivery vectors. Also, inorganic nanomaterials that will be the key component of futuristic nano-devices have recently emerged as a promising candidate to overcome many of the limitations of current technologies.

Crystals consist of a periodic array of specific repeating atoms or molecules. The individual repeating molecules have quantized electronic structures while crystals have continuous electronic band structures that result from the overlap and combination of atomic and/or molecular orbitals of the repeating atoms or molecules. Therefore, isolated atoms and molecules exhibit quantum mechanical properties, while the chemical and physical properties of bulk crystals obey the laws of classical and quantum mechanics. However, when the crystal size decrease into the nano-scale regime (1~100 nm), the electronic band of the crystals is further quantized and the resulting nanocrystals behave as an intermediate between molecules and crystals [22-24].

In semiconductor quantum dots (QDs), the density of electronic energy levels as a function of the size varies systematically, which is known as quantum size effects [25-27]. The surface of
nanocrystals plays a key role in their electronic and optical properties due to the high surface to volume ratio of semiconductor nanocrystals. Also, the melting temperature of nanocrystals decreases when the nanocrystal size is reduced [28].

These nanoscale phenomena are strongly related to the crucial parameters of size and shape. Early investigations focused on the nanoscale size effects since the physical properties of nanocrystals are influenced by the size of nanocrystals [25, 26]. It has been demonstrated both theoretically and experimentally that the quantized electronic band structure of a crystal is changed as the crystal size is reduced, resulting in an increase in the band-gap energy [23]. Figure 2-1 demonstrates the size-tunable fluorescence properties and spectral range of six CdSe quantum dot (QD) nanocrystals with different core sizes [29].

Figure 2-1. Size-tunable fluorescence and spectral range of CdSe QDs with different core size. All samples were excited at 365 nm with a UV source [13].

Similarly, the shape of nanocrystals plays a crucial role in the determination of their properties [30, 31]. The density of energy states (DOS) for inorganic crystals, which is predicted by a simple particle in a box type model, evolves from near-continuous energy levels into quantum states separated by large energies as the dimensionality is decreased from three to zero (Figure 2-2).
Figure 2-2. Energy vs. density of electronic states (DOS) for inorganic crystals of 3, 2, 1, and 0-dimensions [1]

The band-gap energy ($E_g$) of nanocrystals is also influenced by their shape. The band-gap energy diagram of CdSe nanocrystals with various diameters and lengths, shown in Figure 2-3, clearly exhibits shape effects [30]. The UV-Vis absorption and photoluminescence spectra on CdSe rods with different aspect ratio have peak widths comparable to those of spherical quantum dots (Figure 2-4) [31].

Figure 2-3. Band gap of CdSe quantum rods versus length and width viewed from two different angles [30]. The mesh is the best fit to real data (red dots).
Figure 2-4. TEM images (A-C) and UV-VIS absorption (solid lines) and photoluminescence (dotted lines) spectra (D- F) of three nanorod CdSe samples. The nanorods have diameters of ~4.2 nm and lengths of 11 (A and D), 20 (B and E), and 40 nm (C and F) [31].

Other properties, such as magnetic properties, of crystals are also strongly dependent on the shape of nanocrystals [32]. In the case of cobalt nanospheres that are ~ 4 nm in diameter, the blocking temperature of the nanospheres is 20 K. However, when nanocrystals with a nanodisc shape (height ~ 4 nm) are formed, a huge increase in the blocking temperature is observed due to enhanced anisotropy. Similarly, the magnetic coercivity of the discs has a higher value relative to that of a sphere (Figure 2-5). Enhanced shape anisotropy induces a preferential alignment of the magnetic spins along the long axis of the discs.
2.1.2 Synthetic Processes for Colloidal Nanocrystals

Synthetic procedures for nanocrystal preparations have been performed by both ‘bottom-up’ and ‘top-down’ approaches, but the ‘bottom-up’ approach have become favored. In the bottom-up approach, small building blocks are assembled into larger structures; this approach includes liquid phase colloidal synthesis in aqueous and nonhydrolytic media. The liquid-phase colloidal synthetic approach can provide access to extremely fine structure for the convenient and reproducible shape-controlled synthesis of nanocrystals, and allows the nanocrystals to be dispersed in either an aqueous [33-39] or a nonhydrolytic media [10, 11, 40-56]. Moreover, these colloidal nanocrystals are often referred to as ‘molecular nanocrystals’ and can be modified by chemical hybridization with other functional materials for applications in electronics and biological systems.

Liquid phase synthesis relies on chemical reduction of metal salts, electrochemical pathways, or the controlled decomposition of metastable organometallic compounds by coprecipitation. Coprecipitaion process for colloidal nanocrystals growth tend to exhibit the following characteristics [21]:

Figure 2-5. Blocking temperature and magnetic coercivity of 4 nm cobalt nanospheres and nanodiscs [32].
(i) The products of the precipitation reactions are sparingly soluble species formed under conditions of high supersaturation.

(ii) Nucleation is a key step of the precipitation process and conditions are required such that a large number of nanoparticles are nucleated.

(iii) Secondary processes, such as Ostwald ripening and aggregation, will strongly affect the size, morphology, and properties of the nanoproducts.

(iv) The surfaces of nanocrystals may be stabilized by a large variety of molecules, for example, donor ligands, polymers, and surfactants are used to control any growth of the nanoparticles and to prevent them from agglomerating.

A crystal-growth diagram is illustrated in Figure 2-6. When the monomer concentration reaches a supersaturation level, nucleation occurs and the monomer is continuously incorporated onto the seeds resulting in the growth of the nanoparticles and a gradual decrease of monomer concentration. During these nucleation and growth stages, control of growth parameters and crystalline phase is critical in determining the final size and shape of the nanocrystals [57].

Figure 2-6. Crystal-growth diagram. $C_{\text{sat}}$ = saturation monomer concentration above which nucleation takes place, and $C_{\text{equil}}$ = equilibrium monomer concentration below which growth ceases [43].

In earlier methods of colloidal nanocrystals synthesis, the nanocrystals were usually grown at room temperature in hydrolytic (i.e. aqueous) media in the presence of structured micelles [34,
Several semiconductor [37, 38, 58, 59, 61] and metal oxide [34, 60, 61] nanocrystals were grown by this method starting from ionic precursors inside organic micelles. The disadvantage of these aqueous solution syntheses is that the pH value of the reaction mixture must be adjusted in both the synthesis and purification steps, and the nanoparticles often exhibit relatively poor crystallinity and/or polydispersity in their size and shape [36, 38, 62].

As a method to reduce these problems, nonaqueous high temperature thermal reaction methods with organic surfactants have been developed. Nanocrystals produced by this nonaqueous colloidal route often exhibit excellent crystallinity and monodispersity. Moreover, this route has several advantages for the shape-controlled synthesis of nanocrystals including separation between the nucleation and growth steps, and easier control of growth parameters by changing variables such as the type of surfactant molecules, monomer concentration, and temperature.

The work of Steigerwald and co-worker on the use of organometallic precursors in the nonaqueous solution phase synthesis of nanocrystals provides guidance in nanocrystals synthesis [38]. Murray and co-workers [63] introduced dimethyl cadmium (Me₂Cd) and trioctyl phosphine selenium (TOP-Se) as precursors to synthesize high quality CdSe quantum dots as shown in Figure 2-7. In the organometallic precursor method, the coordinating solvent (e.g. trioctylphosphine oxide-TOPO, TOP and trioctylamine (TOA) provide the crucial environment for the growth process, stabilizing the resulting colloidal dispersion. The coordinating ligands, i.e. surfactants, play a crucial role in mediating the growth of the particles. A variety of organometallic precursors and high boiling point coordinating solvents are potential candidates for these types of synthesis.
Figure 2-7. Illustration of the organometallic precursor method for synthesis of CdSe quantum dots

The traditional organometallic approach has some disadvantages, such as the fact that the starting materials are generally toxic, expensive, and sometimes unstable and explosive. Therefore, an inert atmosphere and temperature control during storage and reaction is often required for the chemical precursors. As an alternative route, the advantages of the traditional organometallic method may be retained by using less expensive precursors that do not require sophisticated equipment and procedures. A wide variety of precursors have been identified as possible candidates, including metal acetates [54] and metal acetylacetonates [40, 64-67]. This synthetic route provides:

(i) Less expensive and simpler approaches, since this method is a one step synthesis. Nanocrystals, generally monodispersed and highly crystallized, can be achieved without further size selection.

(ii) High yield, since in a typical reaction the product yield is higher than 50% for monodisperse nanocrystals.

(iii) Diversity; this route has been used to grow transition metal (Fe, Mn, and Zn [68, 69]), and rare earth (Gd [70, 71]) oxide nanoparticles.

(iv) Environmentally friendly; precursors such as metal acetates and metal acetylacetonate are regarded as “green chemicals”, and the by-products of the thermal decomposition are mostly CO₂ and H₂O [69, 72]
2.2 Shape Control of Colloidal Nanocrystals

Nanocrystals may be regarded as ‘artificial atoms’ and are the basic units for nano-scale devices. The design and operation of these devices will be more easily accomplished using nanocrystals with distinct sizes and shapes. The shape control of nanobuilding blocks is crucial for the success of future nano-devices. Inorganic nanocrystals can be classified according to dimensionality and crystal symmetry (Figure 2-8). Highly symmetric isotropic spheres, cubes, decahedrons, and tetrahedrons can be classified as zero-dimensional (0D) nanostructures and are the most familiar shapes in the nano world. Nanospheres of semiconductors, metal oxides, and metals have been synthesized through a variety of chemical methods. Rods, cylinders and wires are examples of one-dimensional (1D) nanoblocks. Since CdSe nanorods were first reported by Alivisatos and co-workers [11], many studies on the synthesis of 1D nanostructures have been reported [44, 45, 56, 68, 69, 73, 74]. 1D nanostructures exhibit novel optical and magnetic properties arising from shape anisotropy as illustrated in Figure 2-2 above.

Disc and plates with polygon shapes belong to 2-dimensional (2D) nanostructures. In addition to such primitive shapes of inorganic nanocrystals, advanced shapes of nanocrystals have been developed. Multipod structures of semiconductors including bipods, tripods and tetrapods, and star-shaped nanocrystals are examples [12, 15, 75, 76].
2.2.1 **Zero-Dimensional (0D) Spheres and Polyhedrons of Nanocrystals**

Zero-dimensional (0D) shapes, including spheres and cubes, have been extensively studied. Initially, Brus and co-workers successfully synthesized various II-IV semiconductor nanospheres with high colloidal stability in coordinating solvent, but size tunability and monodispersity of nanocrystals were poor [25]. Bawendi and co-workers developed more advanced methodologies to prepare various sized 0D CdSe nanocrystals via the method of injecting a precursor solution of dimetyl cadmium into trioctylphosphine oxide (TOPO). The size of nanocrystals varied from 1.2 to 12 nm with high monodispersity and crystallinity and the nanocrystals obtained were highly soluble in various organic solvent. Optical spectra exhibit size dependent quantum confinement effects indicating high monodispersity and high crystallinity of nanocrystals, as shown above in Figure 2-1 [23].

Controlled growth of isotropic 0D spherical or cube nanocrystals of CoFe$_2$O$_4$ has been reported [40]. The data indicate that the heating rate and growth temperature control the shape of CoFe$_2$O$_4$. A slow heating rate produced a low concentration of metal cations from
decomposition of the precursors, and resulted in growth of cubic CoFe$_2$O$_4$ nanocrystals having facets with low surface energy. A faster growth rate at a higher temperature with more metal cations available resulted in crystal growth being much less selective in directions and hence produced spherical CoFe$_2$O$_4$ nanocrystals (Figure 2-9). The shape of the nanocrystals could be reversibly changed between spherical and cubic. As illustrated in Figure 2-5 above, the shape of such nanocrystals strongly affect the magnetic coercivity due to surface anisotropy, and therefore have tremendous potential for high-density information storage.

![Figure 2-9. High resolution transmission electron microscope (HRTEM) images of (a) an ~8 nm spherical CoFe$_2$O$_4$ nanocrystals and (b) multiple and (c) single ~12 nm CoFe$_2$O$_4$ cube nanocrystals [40].](image)

Other 0D shapes of transition-metal oxide nanocrystals have been reported by Cheon and co-workers (Figure 2-10) [45]. Structurally well-defined iron oxide nanocrystals with shapes consisting of diamonds, triangles, and spheres were obtained from the thermal decomposition of Fe(CO)$_5$ in dodecylamine surfactant and subsequent air oxidation. Triangle, diamond, sphere and hexagon shapes are the 2D projections of 3D structures of tetrahedra, truncated octahedra, and icosahedra, respectively.
2.2.2 One Dimensional (1D) Rods and Wires of Nanocrystals

One dimensional (1D) rod growth is a fundamental step for anisotropic shape control. Growth of nanocrystals with more complex structures are possible is based on an understanding of the mechanisms guiding growth of nanorods. Basically, 1D nanostructures of semiconductors and metal oxides exhibit unique optical [11, 12] and magnetic properties [77, 78] due to their anisotropic shape.

2.2.2.1 1D Semiconductors

Non-hydrolytic synthesis are mainly utilized for high quality nanorod synthesis. Alivisatos and co-workers first reported CdSe nanorods from a thermal reacton of Me2Cd and TOP-Se in a hot surfactant mixture of TOPO and hexylphosphonic acid (HPA) [11]. In this synthesis, 1D rod shaped structures result from preferential growth along the [001] direction of wurtzite CdSe that is promoted by selective adsorption of HPA molecules on specific faces. With increasing HPA concentration, the nanocrystal shape evolves from spheres to short rods to long rods with aspect ratios of 5-20. (Figure 2-11).
By varying monomer concentration in addition to change of surfactants, this approach enabled large scale production of CdX (where X= S, Se, Te) nanorods with better control of their aspect ratio. The synthetic method has been successfully applied for the fabrication of other semiconductors, including ZnO [48], ZnS [79, 80], ZnSe [75, 79], CdS [13, 80], CdTe [43] and PbSe [47].

Weller and co-workers have proposed a mechanism of growth of ZnO nanorods via oriented attachment of dimers and oligomers in a hydrolytic synthesis [48]. Specifically, zinc acetate produces zinc oxide nanospheres through hydrolysis and aging. The growth of individual nanorods occurs by oriented and partially fused dimers and oligomers in order to remove high energy surfaces. The oriented attachment of preformed quasi-spherical ZnO nanoparticles results in almost perfect rods (Figure 2-12).
Unlike II-IV semiconductor nanocrystals which have been well studied, study of III-V semiconductor nanocrystals has been limited. This is most likely due to their greater degree of covalent bonding and the lack of non-toxic precursors. Moreover, except for column III nitrides, III-V semiconductors favor isotropic zinc blende crystal structures and thus 0D nanocrystal growth is preferred rather than 1D rod growth. Cheon and co-workers have shown that the crystalline phase of gallium phosphide nanocrystals can be controlled by adopting suitable surfactants [81]. Zinc blende GaP is the thermodynamically stable low temperature phase, while wurtzite GaP is the high temperature stable phase that may be metastable at low temperatures and has desired electronic properties. When sterically limiting amine surfactants (e.g. trioctylamine-TOA) are used as capping molecules, formation of nanospheres GaP is favored. However, when sterically less bulky, linear alkyl amines (e.g. hexadecylamine-HDA) are used, the staggered conformation is not favored. Wurtzite GaP nanorods were formed when a mixed surfactants of TOA and HDA was used. The resulting nanocrystals showed unique shape-dependent spectroscopic features. The absorption spectra exhibited shoulders at 3.48 eV for spheres and 3.46 eV for rods. The photoluminescence peak was at 2.94 eV for 8 nm GaP nanospheres, but was red shifted to 2.79 eV for 8 × 45 nm rods. (Figure 2-13).

![GaP nanocrystals](image)

Figure 2-13. GaP nanocrystals. HRTEM images of (a) zinc blende nanospheres and (b) wurtzite nanorods, and absorption and photoluminescence colors from (c) nanospheres and (d) nanorods [81].
2.2.2.2 1D Metal Oxide Nanocrystals

Nanoscale transition metal oxides have attracted considerable interest due to their optical, magnetic, electrical and catalytic properties [82]. Penn and Banfield reported naturally aligned titania nanocrystals grown with a hydrothermal process with an oriented attachment mechanism [83-85]. In this procedure, titanium alkoxide precursors produced diamond shaped anatase titania nanocrystals. The nanocrystals were truncated with three different crystalline facets parallel to {001}, {112}, and {101} crystal planes. Because the (001) face has the largest number and the (101) face has the lowest number of dangling bonds, the surface energy of the (001) face is higher than that of the (101) face. When a significant thermal energy was supplied to the system, oriented attachment occurred most commonly on {112}, occasionally on {001}, and rarely on {101} faces. The mechanism resulted in a lower total free energy by reducing the surface area where the crystallites were joined. This mechanism is distinct from Ostwald ripening, which involves the dissolution of fine particles and growth of larger particles. Clearly, both mechanisms can operate in such a titania system.

![Figure 2-14. TiO$_2$ nanocrystals formed from single crystal via oriented attachment [85].](image)

Recently, Seo and co-workers have synthesized various 1D nanostructures of transition metal oxide (e.g. W$_{18}$O$_{49}$, TiO$_2$, Mn$_3$O$_4$ and V$_2$O$_5$) using a thermal crystal growth process from a mixture of metal chloride and surfactants [74, 86]. (Figure 2-15) These metal oxide nanorods have crystallographically anisotropic structures where surface energy is thought to be a crucial
factor. Both tetragonal TiO$_2$ and Mn$_3$O$_4$ nanocrystals have a \{001\} surface with higher energy, whereas monoclinic W$_{18}$O$_{49}$ nanocrystals possess a \{010\} surface with higher energy. Because the growth rate is exponentially proportional to the surface energy under the kinetic growth process—this depends on the model used to predict growth, the energy difference between the higher versus lower energy surfaces will promote preferential growth along the \langle001\rangle directions of TiO$_2$ and Mn$_3$O$_4$, and along the \langle010\rangle direction of W$_{18}$O$_{49}$, i.e. rods aligned along the higher energy crystallographic direction.

![Figure 2-15. TEM images of nanorods of (a,b) tungsten oxide (c,d) manganese oxide and (e,f) titanium dioxide [74].](image)

O’Brien and co-workers have synthesized other 1D metal oxide nanocrystals using nonhydrolytic methods. Zinc oxide nanorods with a high degree of crystallinity and a narrow size distribution were assembled into close-packed “stacks” aligned with the long axis parallel to each other (Figure 2-16).
2.2.3 Two Dimensional (2D) Discs and Prisms of Nanocrystals

Synthesis of nanocrystals with controlled shapes has concentrated on the 1D nanostructures, while studies of 2D nanocrystals have been limited. In a kinetically driven growth regime, 1D nanorod growth is promoted when preferential growth along a specific direction is faster. Likewise, when growth along a specific axis is inhibited, the formation of 2D (e.g. disc shaped) nanocrystals may result. Alivisatos and co-workers reported the formation of disc shaped cobalt nanocrystals by rapid decomposition of cobalt carbonyl in the presence of linear amines [51]. The nanodiscs self-assembled into long ribbons by discs stacking face-to-face, perhaps assisted by the magnetic interaction between individual nanodics. (Figure 2-17) Selective adsorption by alkylamines inhibit the growth along the [001] direction while allowing growth along the perpendicular directions resulted in the growth of nanodiscs.

Figure 2-16. TEM image of self-assembled 2 nm diameter ZnO nanorods. Inset: higher magnification image showing the oriented stacks of 1D ZnO.

Figure 2-17. TEM image of Co nanodisks either self-assembled into ribbons (edge-on view) or lying flat (right) on the sample support surface [51].
Ghezelbash and co-workers demonstrated a solventless thermolysis approach to synthesize Cu$_2$S [87, 88] and NiS [89] nanodiscs. In the presence of alkanethiol surfactants, preferential growth along the [100] and [110] directions and inhibition of growth along [001] direction results in the formation of Cu$_2$S nanodiscs (Figure 2-18 (a)). Similarly, rhombohedral NiS nanoprisms results from inhibition of growth along the [110] direction and fast growth along the perpendicular <111> directions (Figure 2-18 (b)).

![Figure 2-18. TEM images (a) Cu$_2$S nanodics [87], (b) NiS nanoprisms [89].](image)

Besides control of surfactant, temperature and time, a photo-induced method for converting of silver nanospheres into triangular nanoprisms was reported [90]. Photons result in a colloid with distinctive optical properties that result in the nanoprism shape. Unlike spherical particles that are derived from Rayleigh light-scatter in the blue, these nanoprisms exhibit scattering in the red, which could be useful in developing multicolor diagnostic labels. (Figure 2-19)

![Figure 2-19. TEM images and schematic of morphology changes: (a) nanospheres before irradiation, (b) nanoprisms after 70 hours of irradiation, and (c) the color of light Rayleigh scattered by nanoprisms and nanospheres](image)
Recently, nanoplates of lanthanide oxide nanocrystals have been reported [70, 71]. Square plate-shaped Gd$_2$O$_3$ were produced through thermal decomposition of Gd acetate precursor in the presence of a noncoordinating solvents (octadecene) and oleic acid in coordinating oleylamine [70]. These nanoplates were highly crystalline with a cubic structure, and the sides of square nanoplates were parallel to (100) and (010) faces while the top and bottom faces were parallel to the (001) plane. The nanoplates were only one unit cell of Gd$_2$O$_3$ thick along the c-axis, with the top and bottom (001) faces modified by the organic ligands (Figure 2-20 (a,b)).

This important family of rare earth compounds was synthesized by thermolysis of their benzolacetonate complexes in a oleic acid/oleylamine solvent [52]. Due to selective adsorption of capping ligands on certain cubic faces during crystal growth, nanocrystals with different morphologies, such as nanoplates and nanodiscs, were created (Table 2-1 and Figure 2-21 (c-e)).

![Image](image_url)

Figure 2-20. Two dimensional (2D) lanthanide oxide nanocrystals: (a) Gd$_2$O$_3$ nanoplates, (b) model for the nanoplates assembly [70], (c) Eu$_2$O$_3$ nanodisks, (d) Er$_2$O$_3$nanodisks, and (e) Pr$_2$O$_3$ nanoplates [52].
Table 2-1. Rare earth oxides synthesized by thermolysis of Ln(BA)$_3$(H$_2$O)$_2$ or Ce(BA)$_4$ where Ln=La to Y and BA = benzolacetonate, in oleic acid (OA)/Oleylamine (OM) at 250-330 °C for 20-60 min [52].

<table>
<thead>
<tr>
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</tr>
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<td>250</td>
<td>20</td>
</tr>
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<td>3:5</td>
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<td>60</td>
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<td>60</td>
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<td>Y$_2$O$_3$</td>
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2.2.4 Advanced Shapes of Nanocrystal

If the assembly of shaped components (0D, 1D and 2D) can be controlled, the construction of advanced nanostructures can be achieved. [13-15, 76, 91] Alivisatos and co-workers achieved the formation of arrow, teardrop, tetrapod, and branched tetrapod shaped nanocrystals of CdSe using mixtures of hexadexylphosphonic acid (HPA) and trioctylphosphine oxide (TOPO) [14]. The three fundamental parameters that were varied to control the shape of CdSe nanocrystals were (i) the ratio of the surfactants (HPA/TOPO), (ii) the volume of the initial injection, and (iii) the time dependence of the monomer concentration. Tetrapods of MnS [13] and CdTe [15] were also reported. This fundamental branched structures results from nucleation of the cubic zinc blende phase with subsequent anisotropic growth of the hexagonal wurtzite phase. In case of branched nanostructures, anisotropic colloidal heterostructures are fabricated by sequential growth of semiconductor dots and rods of different materials, with the potential for branched connectivity in each generation. Branching is introduced through crystal phase control, so the large class of semiconductors exhibiting zincblende-wurtzite polytypism [92] could be incorporated into branched heterostructures by these methods.
Figure 2-21. Tetrapod shaped nanocrystals of (a) CdSe, (b) MnS, and (c) proposed model of CdTe

The tetrapod shape potentially has very interesting optical properties, since in a rod or tetrapod nanocrystals, most of the confinement energy is along the diameter of the hexagonal arms [30]. Tetrapods having comparable arm lengths but different diameters in fact show remarkable differences in their bandgap energy, whereas spectra of tetrapods with comparable diameters but different arm lengths are almost identical, as shown in Figure 2-23 [15].

Figure 2-22. Influence of the shape of CdTe tetrapods on optical absorption spectra. (a) tetrapods having comparable arm diameters but different diameters; (b) tetrapods having comparable arm diameters but different lengths [15].

Cheon and co-workers [93] found that more complex shapes could be synthesized, including 1D rods, highly faceted stars, truncated octahedrons and cubes. As shown in Figure 2-
24, a variety of rod-based nanocrystals including PbS tadpole shaped monorods, I-shaped bipods, L-shaped bipods, T-shaped tripods, cross shaped tetrapods, and pentapods were obtained.

Figure 2-23. PbS nanocrystals with shapes corresponding to (a) rod-based multipods at 140 °C, (b) tadpole-shaped monopod, (c) I-shaped bipod, (d) L-shaped bipod, (e) T-shaped tripod, (f) cross-shaped tetrapod, (g) pentapod, (h) star-shapes at 180 °C, (j) truncated octahedrons at 250 °C, and (k) conversion of cubes to star-shape to 1D rod-based multipods by control of the growth parameters [83].

Recently, nanowires synthesis using oriented attachment was used to produce PbSe nanowires with control of wire dimensions and morphology [94]. In addition to straight nanowires, zigzag, helical, branched, and tapered nanowires as well as single crystal nano rings (Figure 2-25) could all be prepared by adjustment of the reaction conditions. The inherent anisotropy of the crystal structure or crystal surface reactivity was identified as the driving force for the one dimensional growth. Dipolar interaction was concluded to be the most probable driving force causing PbSe nanocrystals to assemble into chains.
Figure 2-24. PbSe nanocrystals showing (a) zigzag nanowires packing of octahedral building blocks, (b) star shaped nanocrystals, (c) radially branched nanowires, and (d) nanorings through oriented attachment [94].

2.3 Proposed mechanism for shape-control growth of nanocrystals

The state of mechanistic investigation of nanocrystals formation is primitive. Specifically, there are no prior kinetic and mechanistic studies of the formation pathway of compositionally and geometrically well-defined nanocrystals for generalization. Matijevic [35] noted that it is not clear why in some instances the final particles are spherical and in others they appear in different geometric forms, yet are of the same chemical composition.

In the 1950s, Lamer and co-workers studied extensively the formation of colloids and clusters in homogeneous, initially supersaturated solutions. Their widely cited LaMer mechanism assumes that homogeneous nucleation occurs forming nuclei of the critical size. Further growth on the nucleus is spontaneous but diffusion-limited [95]. This mechanism predicts that as the precursor is consumed, its concentration fall below saturation, and hence no
more nucleation takes place, thereby achieving the needed separation of nucleation and growth in time that is required for the formation of a monodispersed size distribution. Even though the LaMer mechanism has been successfully applied in attempts to tune the main variables (i.e. concentration of reactants), separation of nucleation and growth in reaction time is critical for synthesis of monodisperse nanocrystals regardless of whether or not the LaMer mechanism is correct in a given case.

In a separate study, the most preferred classic model for shape control is the Wulff facets arguments, or Gibbs-Curie-Wulff theorem, which suggests that the shape of a crystal is determined by the surface energy of each face or facet of the crystal [96]. However, recent studies reveal that these classic thermodynamic arguments are not sufficient to understand the shape evolution of nanocrystals, and other factors are influential.

2.3.1 Kinetically Induced Anisotropic Control

Recent shape control research in nanocrystals illustrate that the kinetically induced anisotropic growth from molecular precursors is highly effective for producing advanced shapes of nanocrystals. Important factors for determining the shape of nanocrystals include reaction temperature and time, the surfactants used for capping, and precursor concentrations during nucleation and growth.

2.3.1.1 Crystalline Phase Control of Nucleating Seeds by Temperature

Nucleating seeds of nanocrystals can potentially have a variety of crystalline phase that affect the final shape of nanocrystals. The stable phase of nanocrystals is highly dependent on its environment, such as the temperature and the choice of capping molecules. For example, by adjusting the initial temperature during the nucleation process, the crystalline phase of nanocrystals can be controlled. An isotropic unit cell structure of the seed generally induces the isotropic growth of nanocrystals from the seed, and therefore 0D nanostructures would be
expected. In contrast, anisotropic unit cell structures of the seed can induce anisotropic growth along reactive crystallographically directions, and anisotropic shapes of nanocrystals would be expected.

In case of MnS semiconductor nanocrystals [76], nuclei with the rock-salt phase are more stable at high temperature (> 200 °C), whereas the wurtzite structure is preferred at temperature below 200 °C [97]. At high temperature (∼ 200°C) the seeds of rock-salt MnS induced isotropic growth along eight \{111\} directions, and 30 nm sized nanocubes were obtained. In contrast, at low temperature (∼ 120 °C), the nucleation with the hexagonal wurtzite structure resulted in anisotropic growth along the c-axis of wurtzite and therefore very thin nanowires of 2 nm in diameter with an aspect ratio of ∼ 80 were observed.

Similarly, crystalline phase effects of the seeds can be observed in the case of CdS nanocrystal growth [13]. CdS has two distinct crystalline phases; an isotropic zinc blende phase is stable below 250°C, and hexagonal wurtzite is preferred at high temperature (∼ 300°C). At high temperature, formation of 1D CdS rods is observed from high temperature stable wurtzite structured seeds, similar to the MnS nanowire growth. However, at lower temperatures, the formation of tetrahedral shapes of zinc blende seeds truncated with four \{111\} faces is observed. The subsequent epitaxial growth of wurtzite pods along the c-axis from the four equivalent \{111\} faces of the seed results in the formation of CdS tetrapods.

Figure 2-25. Shape evolution of MnS nanocrystals controlled by the growth temperatures: wires at 120 °C, (b) spheres at 180°C, and (c) cubes at 250 °C [97].
Variation of the shapes of CdS nanocrystals by changing growth temperature from (a) 300°C-nanorods, (b) 180 °C-bipods and tripods, and (c) 120 °C-tetrapods.

Figure 2-27 summarizes the dependence of final shape on the crystalline phase of nuclei in MnS and CdS nanocrystals [9].

![Figure 2-27](image)

Temperature-mediated crystalline phase control of (a) MnS and (b) CdS nanocrystals [88].

2.3.1.2 Surface energy modulation by capping surfactants

In addition to controlling the crystalline phase of the nucleating seeds, the surface energy of the nanocrystals can be modulated by introducing surfactants that adsorb onto surfaces of growing crystallites [11, 12, 74, 89]. El-sayed’s group [98] and Reets’s group [99] have performed pioneering work to understand the growth mechanisms for control of the shape of
transition metal nanocrystals. They report that control of the shape of transition metal nanocrystals was due to stabilizing reagents bound to the surface of the nanocrystals.

Peng [11] and Alivisatos [14] explored the growth of CdSe nanocrystals and reported monomer concentrations in the growth solution was the determining factors in shape control and shape evolution. The chemical potential of elongated nanocrystals should be slightly higher than that of a spherical nanocrystal. As a result, the growth of such anisotropic structures should require a relatively high chemical potential in the solution, i.e. a relatively high monomer concentration. This condition provides the external environment for the formation of elongated [42] or other anisotropic shapes [13, 14]. At high monomer concentrations, the differences in the growth rate of different faces can lead to anisotropic shapes. The relative growth rate of the different faces can be controlled by the concentration, size and shape, and adsorption strength of capping surfactants, such as trioctylphosphine oxide (TOPO) and hexylphosphonic acid (HPA) [11]. On the other hand, for a low monomer concentration and low chemical potential, Ostwald ripening occurs and small nanocrystals dissolve at the expense of larger ones. Such slow growth conditions favor the formation of a spherical shape. HPA leads to an increased growth rate of the (001) face of CdSe relative to all other faces since HPA selectively binds to (100) and {110} surfaces and reduces the growth rate of these two surfaces. At low concentration of HPA or in the absence of HPA, only spherical nanocrystals are formed. With higher HPA concentrations, nanorods are obtained with their axis along the [001] direction.

More complicated shape control was subsequently observed with the formation of CdSe tetrapods [14].
Figure 2-28. Anisotropic growth along [001] direction of CdSe nanocrystals. The surface growth rate was effected by selective capping by surfactants to produce (a) short rods (b) medium rods, and (c) long rods [14].

There are other examples of preferential ligand binding to the specific facets, as in the case of Co [49] and CuS [87] where amine preferentially binds to the {001} facets to induce [100] and [110] direction leading to disk-shaped growth.

Figure 2-29. Disc-shaped nanocrystals of (a) Co and (b) CuS produced by preventing growth along the [001] direction due to selective capping by surfactants [35, 76].

2.3.1.3 Growth Regime Control by Monomer Concentration and Temperature

The monomer concentration and thermal energy (kT) strongly affects the final structure of the nanocrystals through a delicate balance between the kinetic and thermodynamic growth regimes. Isotropic growth of nanocrystals is preferred under the thermodynamic growth regime that is characterized by a sufficient supply of thermal energy (kT) and a low flux of monomers. In contrast, anisotropic growth along a specific direction is facilitated under a kinetic growth regime that is promoted by a high flux of monomers. After the intrinsic surface energy of the
crystallographic face of the seed is determined, the surface properties can be tailored by the types and the amounts of adsorbed capping surfactants. The growth processes should be quenched at appropriate times, since long growth times can result in thermodynamically stable shapes of nanocrystals.

The architectural features of the PbS nanocrystals are good examples to illustrate the effects of growth regime. PbS nucleates as tetradecahedron truncated with eight {111} faces and six {100} faces [93]. When excess thermal energy is supplied at a high growth temperature (~300°C), the thermodynamic regime governs the growth process. In this growth regime, nearly isotropic growth from the seeds is favored, and therefore cube shapes of PbS are obtained. However, under the conditions of low temperature (~140°C) and in the presence of surfactant (i.e. dodecanethiol), the growth process shifts into the kinetic growth regime and anisotropic growth on the high surface energy {100} faces is preferred and 1D rod-based multipod structures are obtained, as illustrated in Figure 2-31 [9].

![Figure 2-30. Shape control of PbS nanocrystals dependent on the growth regime [9].](image_url)
For an intermediate growth temperature (~180 °C), star-shaped nanocrystals, as a transient shape between isotropic and multi-pod shapes, are obtained. The enhanced growth rate on the \{100\} faces induces shrinking of the six \{100\} faces into sharp triangular corners which finally results in a star-shaped nanocrystals.

The growth temperature affects the doping of nanocrystals as well as the anisotropic shapes. The formation of magnetic semiconductor (e.g. Cd$_{1-x}$Mn$_x$Se) nanocrystals with a homogeneously distributed high level of Mn dopants has been difficult because of surface segregation of Mn dopants from the host matrix during high temperature thermodynamically driven synthesis [100]. However, low temperature kinetic growth allows not only the homogeneous doping of Mn atoms at high levels (up to ~12%), but also the 1D growth of monorod of Cd$_{1-x}$Mn$_x$S (0.02 ≤ x ≤ 0.12) [93].

### 2.3.2 Oriented Attachment

As reported above in section 2.2.2, Penn and Banfield [83, 84, 101] observed that anatase and iron oxide nanoparticles with sizes of a few nanometers coalesce under hydrothermal conditions by a mechanism they call “oriented attachment”. The mechanism is based on the fact that the surface area is reduced by attachment which reduce the total energy of the nanocrystals. Attachment of nanocrystals were pointed out above for both hydrolytic growth of CdTe [16] nanowires and nonhydrolytic growth of ZnO [48], ZnS [56], and PbSe [94] nanorods. In this process, nanocrystals are first formed by at high chemical potential due to a high monomer concentration. These nanocrystals form chain-like structure due to induced dipole-dipole interactions at the early stage of growth. In the final stage of 1D growth via the oriented attachment process, Ostwald ripening smooths the irregular surface to produce nanocrystals with a smooth surface. Synthesis by the oriented attachment mechanism can produce nanowires with
controlled wire dimensions and morphology, such as nanorings or straight, zigzag, helical, branched, or tapered nanowires.

Figure 2-31. Growth of 1D nanocrystals by the oriented attachment mechanism. (a) aligned TiO2 nanocrystals [85]; (b) alignment of PbSe nanocrystals [94]; (c) ZnS nanorods containing some fraction of spherical nanocrystals; (d) ZnS nanorods obtained after the aging; (e) summary of steps in oriented attachment mechanism for ZnS nanorods in (c): kinetic formation of primary nanocrystal → interparticle ripening → oriented attachment → Ostwald ripening to form smooth surface nanorods [56].

2.4 Application of Nanocrystals in Biomedicine

Nanocrystals offer some attractive possibilities in biomedicine. First, they have controllable sizes ranging from a few nanometers up to tens of nanometers, which are smaller than or comparable to those of a cell (10-100 μm), a virus (20-450 nm), a protein (5-50 nm) or a gene (2 nm wide and 10-100 nm long). This means that they can get close to biological molecules of interest. Indeed, they can be coated with biological molecules to make them interact with or bind to a biological entity, thereby providing a controllable means of tagging. Second, inorganic nanocrystals exhibit unique properties and many new nanocrystal labels have been
introduced for biomedical applications. Magnetic separation and fluorescent labeling are the two most widely used nanotechniques in bioscience. The present work attempts to prepare a new type of nano-sized hybrid particle that exhibits both a magnetic response and fluorescence for bio-detection.

Colloidal quantum dots are robust and very stable light emitters that can be broadly tuned in emission wavelength through size variation. It was quickly realized that colloidal quantum dots (QDs) were about the size of a typical protein, and thus it was possible to introduce QDs into cells.

2.4.1 Biocompatible Magnetic Nanocrystals for MR Contrast Effects

Nanocrystal biomedical applications based on magnetic properties include utilization as a magnetic probe for detection and imaging and as a magnetic vector for cell separation and drug delivery. In particular, they are employed for magnetic separation, in vivo magnetic drug targeting, and magnetic resonance imaging (MRI) [102-107].

Modern MRI is one of the most powerful medical diagnostic tools due to its non-invasive nature and multi-dimensional tomographic capabilities coupled with high spatial resolution. MRI relies on the counterbalance between the exceedingly small magnetic moment on a proton, and the exceedingly large number of protons present in biological tissue, which leads to a measurable effects in the presence of large magnetic fields. Under an applied magnetic field, induced magnetic spins in magnetic nanocrystals perturb the nuclear spin relaxation processes of protons in surrounding water molecules. This effect leads to shorter spin-spin relaxation time (T2) of the proton, which results in contrast for MR images. When magnetic nanocrystals are conjugated with biologically active materials, the resulting nanocrystal-biomolecule conjugates have the multi-functionalities of both MR contrast effect and selective attachment to target molecules.
Santra and Holloway [108] reported highly water-dispersible, multifunctional, CdS:Mn/ZnS core-shell Qdots using water-in-oil(W/O) microemulsion method. These Qdots are fluorescent, radio-opaque, paramagnetic, and suitably stable in an \textit{in vivo} environment [109].

Paramagnetic metal ions (Cr$^{3+}$, Mn$^{2+}$, Fe$^{3+}$ and Gd$^{3+}$) show suitable effects which depend on the number of unpaired electrons in the ion. Among these ions, the prominent feature of Gd$^{3+}$ is the high number (seven) of unpaired electrons. The Gd$^{3+}$ ion retains a number of unpaired spins when bound to the organic ligand. The free Gd$^{3+}$ ion is extremely toxic, but a large fraction of the complexes are very stable and thus exhibit much less toxicity. The Gd-DTPA complex has been approved for clinical use and is now marketed in USA under the name “Magnevist” [110-112]. Although many researchers are investigating stability of the series of complexes versus acute toxicity \textit{in vivo}, the search for new ligands for complexation is still a hot area for investigation. Criteria include thermodynamic stability, rates of excretion, toxicity and biodistribution.

Iron oxide nanocrystals are the most commonly used superparamagnetic contrast agents. Various sizes of iron oxide nanocrystals with a narrow size distribution were produced using a high temperature injection methods [113]. The nanocrystal surface was treated with 2,3-dimercaptosuccinic acid (DMSA) which makes them stable in a water dispersion. The watersoluble iron oxide nanocrystals exhibit excellent size-dependent magnetism and MR contrast effects. Increasing the size of nanocrystals from 4 to 6, 9, and 12 nm, the mass magnetization at 1.5 T increased from 25 to 43, 80, and 102 emu/(g Fe), respectively, and higher MR contrast effects can be seen in Figure 2-32.
2.4.2 Luminescent Nanocrystals for Fluorescence labels

Another important application of nanocrystals in cell biology is their use as fluorescence markers to label structures and molecules in cells. Fluorescence labelling is used to visualize structural units that, due to lack of contrast or resolution, cannot be distinguished [114-116]. This is achieved by attaching a ligand to the nanoparticle label and this conjugate binds with high specificity to its target receptor, which can be visualized by the fluorescence of the label (see Figure 2-33). The receptor molecule typically is an antibody for the structure to be labelled. A popular receptor pair is avidin and streptavidin, and the structure to be labelled is incubated with the biotinylated streptavidin antibody which is then recognized by the fluorescence-avidin construct.

Alivisatos [117] and Nie [118] reported the use of colloidal QDs for biological labeling and suggested that the photochemical stability and the versatility could make them extremely useful. Recently, a wide range of applications for QDs have been seen as cell labeling [119], cell
tracking [120], cell signaling [121], in-vivo imaging [122], near infra-red imaging [123] and DNA detection [124].

Figure 2-33. Schematic representation of the use of QDs for bio-labelling. (a) Water soluble QD comprise a core and hydrophilic shell; (b) QD conjugate with biological molecule (drawn in red); (c) Bioconjugated QD that binds specifically to designated receptors

Luminescent colloidal QDs offer many advantages compared to organic dyes as fluorescence labels for biological staining and already been used in labelling experiments. QD properties of interest to biologists include high quantum yield and exceptional resistance to photochemical degradation and photobleaching. Upon optical excitation, organic fluorophores can undergo irreversible light-induced reactions such as photo-oxidation. Reacted molecules are no longer fluorescent, i.e. they have been ‘photobleached’. The fluorescence emission spectra of QDs are typically narrow, symmetric and do not exhibit tail to longer wavelength (i.e. red tail), therefore many different colors from size-tune fluorescent emission can be distinguished without spectral overlap (see Figure 2-34). For biological fluorescence labelling, more colors mean that a larger number of structures can be simultaneously labelled, each with a different color (see Figure 2.35) [125-127]. The detection of multiple molecules (markers) in a cell or tissue by QDs color emission can improve diagnostic efficiency. The decay time of the fluorescence of nanocrystals is typically longer (ns to µs) than the decay time of autofluorescence (ps to ns), therefore time-gated imaging can be used to reduce the autofluorescence background in fluorescence imaging of cells [128]. Besides spherical nanocrystals, assymmetric nanorods can
also be synthesized as discussed above. Due to their anisotropic shape their emitted fluorescence light can be polarized which enables detection of the orientation of labelled structures [31].

Figure 2-34. Representative QD core materials scaled as a function of their emission wavelength over spectrum. Representative areas of biological interest are presented corresponding to the pertinent emission highlighting [129].

Figure 2-35. (a) Multicolor staining of HeLa cell with red and green QDs. [130] (b) In vivo labeling of a Xenopus embryo with green-micelle-coated QDs. [122] (c) Image of QDs targeting prostate cancer in vivo in a mouse bearing a xenograft tumor targeted using orange-red emitting QD probes [131].

Recently, QDs fluorescing in the infrared have been demonstrated as a contrast label for optical detection. QDs with infrared fluorescence are of particular interest if their emission wavelength is chosen in a spectral window where absorption by the biological molecules (e.g. water and hemoglobin) is low [132]. Kim and co-workers have demonstrated the use of QDs for
sentinel-lymph-node mapping in pigs, which helps guide surgeons in the removal of tumor cells [123]. Compared to the currently used visible fluorescence contrast agent, infrared fluorescence can be imaged through the skin, which allows the surgeon to identify the position of the QDs in the lymph channels in real time and reduce the size of the incision and allow determination of the complete removal of the lymph node.

While the above discussion reveals some of the positive attributes for QDs in bio-applications, there are still many questions about the toxicity of inorganic QDs containing Cd, Se, Zn, Te, Hg and Pb. These elements can be potent toxins, depending on dosage, that can accumulate in and damage the tissue. Living cells have been demonstrated to ingest QDs, allowing their potential use as contrast agents in animals and humans that may remain in the living tissue for months and presumably even for years [133]. Studies on non-toxic QDs such as oxide compounds would be desirable. This is one of the objectives of this dissertation.
CHAPTER 3
SYNTHESIS AND CHARACTERIZATION OF LUMINESCENT GADOLINIUM OXIDE NANOCRYSTALS

3.1 Introduction

Rare earth doped compounds have attracted extensive attention as luminescent components in many applications. In addition, shape control of colloidal nanocrystals is possible and result in many advanced shapes of nanocrystals. For example, rare earth doped one dimensional (1D) structures such as LaPO₄: RE (RE= Eu³⁺, Tb³⁺) nanowires [134], Y₂O₃:RE nanotubes [135] and Gd₂O₃: Eu³⁺ nanoplates [71] have been reported. However, the luminescent properties of nanocrystals with different shapes were not compared.

Eu³⁺ doped Gd₂O₃ nanocrystals have shown red luminescent peaks due to the electric-dipole ⁵D₀-⁷F₂ transitions on the trivalent europium ion (Eu³⁺, 4f⁶) [136]. Gd₂O₃: Eu³⁺ nanocrystals obtained by nonhydrolytic thermal reactions in the presence of organic surfactants exhibit excellent crystallinity, monodispersivity and good luminescent efficiency. Moreover, this synthetic route allows control of the growth and shape of nanocrystals by variables such as the type of metal precursors, organic surfactants molecules, monomer concentration ratio, and heating rate. In this chapter, the luminescent properties of Gd₂O₃: Eu³⁺ are reported and discussed versus the crystal structure, shape of nanocrystals and the quantities of Eu³⁺ dopant incorporated into the Gd₂O₃.

3.2 Experimental Section

3.2.1 Materials

The following precursor compounds and solvents were purchased from Aldrich: Gd (III) acetate hydrate , Gd(III) acetylacetonate hydrate, Eu(III) acetate hydrate , oleic acid (90%) ,
tech.), Tb(III) acetate hydrate (90% , tech.) , Er(III) acetate hydrate (90% , tech.), oleic acid (90% , tech.), oleylamine (70%) benzyl ether (99%) , 1,2-hexadecanediol (HDD, 97%), trioctylphosphine oxide (TOPO, 99%) , and octadecene (90%). All chemicals were used without further purification. Absolute ethanol, benzyl ether and hexane were used as received.

3.2.2 Synthesis of platelet Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals

The general scheme to grow Gd$_2$O$_3$ nanocrystals is shown in Figure 3.1. In a one pot reaction to produce Gd$_2$O$_3$: Eu$^{3+}$, Gd-acetate (2mmol), Eu-acetate (0.2 mmol), oleic acid (6mmol), oleylamine (3mmol), benzyl ether (10mmol) and TOPO (4 mmol) were mixed and magnetically stirred under a flow of nitrogen. In a typical reaction to produce Gd$_2$O$_3$: Eu$^{3+}$, 2mmol of Gd-acetate, 0.2 mmol Eu-acetate were mixed with 6mmol oleic acid, 6mmol oleylamine, 4mmol TOPO and 10mmol benzyl ether in a three-neck reaction flask under nitrogen. In both cases, the mixture was heated at 200$^\circ$C for 30 min, resulting in a transparent brownish solution that was then heated to 290$^\circ$C with a heating rate of 5-25$^\circ$C /min and maintained for 2-3h under the N$_2$ blanket.

In a second procedure using two pots, a mixture of 2mmol of Gd-acetate, 0.2mmol Eu-acetate were mixed with 6mmol oleic acid and heated to 200$^\circ$C for 30 min in a vial resulting in a homogeneous brownish solution. At the same time, 10ml of benzyl ether and 4mmol of TOPO were mixed in a three-neck flask and heated to 200$^\circ$C for 30 min. After 30 min, the Gd-oleate solution was rapidly injected into the benzyl ether/TOPO mixture and the temperature was raised to ~ 290$^\circ$C with a heating rate of 5-25$^\circ$C /min, and kept at that temperature under a N$_2$ blanket for 150min.

After reflux, the brownish transparent mixtures were cooled to room temperature by removing the heat source in the case of either the one pot or two pot processes. Under ambient
conditions, ethanol was added to the mixture, and Gd$_2$O$_3$ nanocrystals were precipitated and separated via four centrifugations (9000 rpm, 10 min) to remove any residue. The purified Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals, capped with organic species, were well dispersed by organic solvents such as hexane, chloroform and toluene. The properties of the resulting nanocrystals from the one versus two pot reaction were identical with respect to size, shape and product yield. The data reported below are all from the one pot approach.

3.2.3 Synthesis of spherical Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals

To produce spheres of Gd$_2$O$_3$: Eu$^{3+}$, Gd(acac)$_3$ (1mmol), Eu-acetate (0.2 mmol), oleic acid (3mmol), oleylamine (3mmol), benzyl ether (5mmol) and either hexadecanediol (HDD, 2.5mmol) or TOPO (2 mmol) were mixed and magnetically stirred under a flow of nitrogen. After preheating at 200°C for 30 min, the mixture was heated to ~ 290°C and kept at that temperature for 150min. Cooling and purification of the nanospheres were performed in the same way as described above for synthesis of platelet Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals. The effects of other precursors, such as Gd-chloride and Gd-octanoate, and growth solvents, such as octadecene, on the shape of the rare earth doped Gd$_2$O$_3$ nanocrystals were investigated as reported below.

Most batches of Gd$_2$O$_3$: Eu$^{3+}$ were processed using two-coordinating solvents (e.g. TOPO/TOA, TOPO/benzyl ether, or HDD/benzyl ether) with oleic acid for better homogeneous mixtures of the starting materials. For other dopant elements (Er$^{3+}$ and Tb$^{3+}$), the same protocols were used. For controlling the shape of Gd$_2$O$_3$ nanocrystals, several critical parameters were found, including the type of Gd precursor, organic surfactants, the ratio of Gd-precursor/dominant organic surfactant, and the heating rate as reported below.
Figure 3-1. Synthesis of Gd$_2$O$_3$: Eu$^{3+}$ nanospheres by the nonhydrolytic hot solution route.

3.2.4 Characterization of Rare Earth Doped Gd$_2$O$_3$ Nanocrystals

Nanocrystals for examination by transmission electron microscopy (TEM) were dispersed in hexane and drop-cast onto a copper grid with a carbon film containing holes. The solvent was evaporated in ambient air. For Fourier-transform infrared (FTIR) measurements, the powder was ground together with KBr in a mortar and pestle, then pressed into pellets. For ICP analyses of concentrations, Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals were dissolved in nitric acid. For thermogravimetric analysis (TGA), Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals were heated after ambient drying to remove the solvent. Photoluminescence (PL) and UV-absorption were measured from Gd$_2$O$_3$:RE nanocrystals dispersed in hexane contained in a quartz cuvette. For near infrared (NIR) emission, Gd$_2$O$_3$ nanocrystals were dried and measured as green powder pellets.

X-ray diffraction (XRD) patterns to determine the crystal structure were obtained using Philips APD 3720 X-ray diffractometer with Cu K$_{α}$ radiation source ($λ$ = 0.5418 nm). A JEOL 2010F transmission electron microscope operated at 200 kV was used for collection of images and determination of the size and shape of the nanocrystals. Absorption spectra were collected...
with a Shimadzu UV-2401PC spectrophotometer. Photoluminescence (PL) was measured at room temperature from nanocrystals suspended in hexane using a Fluorolog Tau 3 spectrofluorometer (Jobin Yvon Spex Instruments, S.A. Inc) with a 450 W xenon excitation lamp. Life time was measured with FP-6500 spectrofluorometer (JASCO). Near-infrared (NIR) emission spectra of Gd$_2$O$_3$: Er$^{3+}$ nanocrystals were collected using a 488 nm Ar laser line for excitation and a Ge detector. Thermo-gravimetric analysis (TGA, Seiko TG/ATD 320U, SSC 5200) was used to investigate the temperatures for decomposition of Gd precursors and to determine the amount of surfactant bound on the particle surface. For TGA, the samples were heated up to 800°C in air at a rate of 10°C min$^{-1}$. FTIR spectra from the Gd$_2$O$_3$ nanocrystals were recorded with a Thermo Electron Magna 760 FT-IR microscope in order to confirm the nature of the coating and its bonding to the surface. The concentration of Eu$^{3+}$ dopants in Gd$_2$O$_3$ nanocrystals, as prepared, was determined by inductively coupled plasma (ICP, Perkin-Elmer Plasma 3200).

3.3 Results and Discussion

3.3.1 Nanoplates and Nanospheres of Gd$_2$O$_3$: Eu$^{3+}$

As described above, nanoplates of Gd$_2$O$_3$: Eu$^{3+}$ were synthesized using Gd-acetate as the precursor and using thermal decomposition under nitrogen flow at 290 °C after preheating at 200°C. Gd-acetate is completely soluble in the oleic acid, TOPO and benzyl ether mixture at 200°C. The temperature leads to decomposition of Gd-acetate to a Gd$_2$O$_3$-organic surfactant complex with reaction products of CO$_2$ and acetone [72].

High resolution TEM (HRTEM) images in Figure 3.2 (a-b) show that square nanoplates of Gd$_2$O$_3$: Eu$^{3+}$ were formed with 10nm of edge length and 1nm thickness. Over most of the area, the nanoplates were aligned with one edge parallel to the surface and their
surface self-aligned parallel to their neighbor platelets. To verify that the images in Figure 3.2(a) and (b) were from aligned plates rather than e.g. rods, tilted TEM images were taken in Figure 3.2(c) and (d), and the change in contrast is consistent with plates rather than rods of the same length. The image shows that the standing plates varied in thickness when tilted in the short direction and remained of constant edge length when tilted in the long one. The size distributions of the platelet edge length is more broad (5-10 nm), while the thickness is monodispersed at 1 nm.

Figure 3-2. HRTEM images of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals (a-b) nanoplates (c) the images correspond to no tilt and (d) correspond to tilt. Labelled face is (001) and edges are (100, 010).

As shown in Figures 3-2 and 3-3, the Gd$_2$O$_3$: Eu$^{3+}$ nanoplates self-assemble into “stacks”, in which they are aligned with their square planes parallel to each other. The thickness of and spacing between nanoplates was very uniform at 1 nm and 1.3 nm. This spacing of 1.3 nm is consistent with small angle x-ray diffraction data which reduce to a interplate spacing of 1.2
nm. Face-to-face platelet stacking has also been reported for Cu$_2$S [137] and Co[51] nanodisks. The existence of a nematic phase due to the entropy of oriented packing was first suggested by Onsager [138], and has been confirmed by computer simulations of platelets and experimental data for submicrometer hard disk colloids [139]. The van der Waals attraction is also greater for nanoplates oriented face-to-face relative to nanoplates oriented edge-to-edge due to the much greater interfacial contact area provided by the face-to-face configuration [140]. As suggested by Cao, et al [70], face-to-face stacking for Gd$_2$O$_3$ might also be assisted by electric dipole interactions since the faces of the nanoplates are the {001} and the edges are {100} and {010} crystal faces.

Figure 3-3. HRTEM images of self-assembled ‘stacks’ of nanoplates of Gd$_2$O$_3$: Eu$^{3+}$ shown at three different magnifications.

Using the same temperatures and times for reactions but using a precursor of Gd (acac)$_3$ (1mmol) and hexadecanediol (2.5mmol) as a surfactant, nearly monodisperse 2-4 nm diameter nanospheres of Gd$_2$O$_3$: Eu$^{3+}$ were grown. Although the mechanism leading to Gd$_2$O$_3$ nanocrystals is not clear, decomposition of the acetylacetonate ligand in the Gd(acac)$_3$ precursor is the only possible oxygen source. Nanospheres of several metal oxides [40, 54, 64-66] have been prepared by thermal decomposition of metal acetylacetonates under an inert atmosphere, and several authors have proposed that decomposition of the acac ligand leads to formation of
carbon dioxide that oxidizes the Gd. When TOPO (1mmol) was used as solvent instead of hexadecanediol (2.5mmol), the same size of Gd$_2$O$_3$: Eu$^{3+}$ nanospheres were obtained.

![HRTEM images](image)

**Figure 3-4.** HRTEM images of nanospheres of Gd$_2$O$_3$: Eu$^{3+}$ from thermal decomposition of Gd(acac)$_3$ (1mmol) precursor in the presence of (a) hexadecanediol (2.5mmol) or (b) TOPO (1mmol).

Regardless of the shape of nanocrystals (platelet versus sphere), heating the mixture to 200$^\circ$C for 30 min before heating to reflux at 290$^\circ$C is important for monodispersity and high product yield ($\sim$ 80 %). Directly heating the mixture to 290$^\circ$C from room temperature resulted in Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals with a wide size distribution and relatively low ($\sim$ 60 %) product yield. These observations suggest that the nucleation of Gd$_2$O$_3$: Eu$^{3+}$ at the higher temperature is a slower, continuous process, and subsequent growth leads to a large size distribution.

For many colloidal nanocrystals, particle size can be increased by longer growth times [54] and larger metal precursor/surfactants ratios [67], often described by the Lifshitz-Slyozov-Wagner (LSW) model which predicts the time dependence of the particle size. Particle growth is driven by the dependence of the solubility of a solid phase on the particle size according to the Gibbs-Thomson relation, assuming that the particles are spherical [141-143]. However, the particle size of Gd$_2$O$_3$: Eu$^{3+}$ did not increase at longer growth times. The independence of the nanoparticle size from growth time is attributed to the monodispersivity the nanocrystals. At long
times, growth of the nanoparticles would be expected from Ostwald ripening [144]. In addition, changes in the metal precursor/surfactants ratio changed the shape of particle more than the size.

3.3.2 Shape control of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals

3.3.2.1 Effects of Gd-precursor

Thermal decomposition of various Gd precursors in oleic acid, oleylamine, benzyl ether and TOPO leads to the formation of different morphologies of nanocrystals. Figure 3-5 shows HRTEM images of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals grown from different Gd precursors at 290°C. As shown above, Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals obtained from Gd(acac)$_3$ are 2-4 nm nanosphere (Figure 3-5(a)), in contrast to nanoplates of Gd$_2$O$_3$: Eu$^{3+}$ grown from Gd-acetate precursor (Figure 3-2, 3-3, and 3-5(b)). Gd-chloride precursors led to growth of 2-4 nm nanospheres (Figure 3-5 (c)), but the product yield was lower (~35%) than from Gd(acac)$_3$. Interestingly, Gd-octanoate precursors produced Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals with both sphere and plate shape (Figure 3-5 (d)). The two different shaped nanocrystals separated and the platelet Gd$_2$O$_3$: Eu$^{3+}$ self-assembled into ‘stacks’, similar to those shown in Figures 3-2 and 3-3.

In studies of the shape of nanocrystals, the effects of metal precursors have rarely been reported. One reason is the difficulty in finding different precursors compatible with the appropriate organic surfactants. The combined effects of both the precursor and organic surfactants determine the crystal nucleation, growth and shape. While it is not possible to suggest a priori specific precursor favorable for anisotropic growth, the reactivity of the precursor is expected to affect the size and shape of nanocrystals. In case of a highly reactive precursor, a relatively large number of nuclei could be expected due to fast nucleation and depletion of the precursor to reduce further growth. On the other hand, a less reactive precursor a should form a relatively small number of nuclei in the same period of time, and these nuclei will not reduce the concentration of the precursor monomers as much, allowing growth of elongated shape in some
cases [11, 42, 145]. In the present study, a Gd-acetate precursor resulted in platelet Gd₂O₃: Eu³⁺ nanocrystals, while Gd(acac)₃ resulted in the formation of spherical Gd₂O₃: Eu³⁺ nanocrystals in the presence of organic surfactant such as TOPO or hexadecanediol. The thermal decomposition of these two precursors investigated with TGA are reported below and will be related to their relative reactivity during growth.

![HRTEM images of different shaped Gd₂O₃: Eu³⁺ nanocrystals](image)

**Figure 3-5.** HRTEM images of different shaped Gd₂O₃: Eu³⁺ nanocrystals from (a) Gd(acac)₃, (b) Gd-acetate, (c) Gd-chloride, or (d) Gd-octanoate precursors

3.3.2.2 Effects of Surfactants

Organic surfactants play an important role in the shape of the nanocrystals. The reaction occurred in a mixture of coordinating and noncoordinating organic surfactants. When Gd(acac)₃ was used as the precursor, the use of hexadecanediol (HDD) resulted in spherical Gd₂O₃: Eu³⁺ nanocrystals at a Gd(acac)₃/HDD ratio of 1:2.5, as shown in Figure 3-6(a). In all syntheses, oleic acid, oleylamine and benzyl ether were co-introduced with the main surfactant (i.e. HDD, TOPO or octadecene). When HDD was replaced with TOPO, both of nanospheres and nanoplates were simultaneously formed with a Gd(acac)₃/TOPO ratio of 1:1 (Figure 3-6(b)). The nanoplates were stacked without a preferred direction, but non-stacked individual nanoplates
lying on their faces were rarely observed. Using Gd octanoate precursor and TOPO produced mixed shapes of spheres and plates of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals (Figure 3-6(c)). Finally, varied complex shapes of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals (~10 nm spheres, plates, rings and triangles) were formed from a Gd octanoate precursor when TOPO was replaced with octadecene as the main organic surfactant (Figure 3-6(d)) and reacted for short times (1 h) at a growth temperature of 290°C after a 200°C nucleation.

![Figure 3-6. HRTEM images of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals synthesized from thermal decomposition of Gd(acac)$_3$ precursor (a,b) with (a) hexadecanediol (HDD-nanospheres) and (b) TOPO surfactant (nanospheres and nanoplates), and of Gd-octanoate precursor (c,d) with (c) TOPO (nanoplates) and (d) octadecene (complex larger shapes) surfactant.](image)

3.3.2.3 Effects of the Precursor/Surfactant Ratio

The concentration ratio of the Gd precursor and the main organic surfactant (i.e. Gd(acac)$_3$ /TOPO or HDD) was critical to the size and shape of the nanocrystals formed. For a Gd(acac)$_3$/TOPO molar ratio of 1:1, only nanospheres (<5nm) were observed, as shown in Figure 3-7(a). For a ratio of 1:2, a mixture of nanospheres and nanoplates was observed (Figure 3-7(b)). Nanospheres of Gd$_2$O$_3$: Eu$^{3+}$ were produced with a Gd(acac)$_3$/HDD molar ratio of 1:2.5
(Figure 3-7(c)), but curved worm-like nanocrystals appear along with the dominant formation of nanospheres at a ratio of 1:5 (Figure 3-7(d)).

![HRTEM images of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals synthesized with a Gd(acac)$_3$/TOPO molar ratio of (a) 1:1 (nanospheres), (b) 1:2 (mixed nanospheres and nanoplates), or a Gd(acac)$_3$/HDA ratio of (c) 1:2.5, (d) 1:5.](image)

Figure 3-7. HRTEM images of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals synthesized with a Gd(acac)$_3$/TOPO molar ratio of (a) 1:1 (nanospheres), (b) 1:2 (mixed nanospheres and nanoplates), or a Gd(acac)$_3$/HDA ratio of (c) 1:2.5, (d) 1:5.

Data in Figures 3-6 and 3-7 show that the type and concentration of surfactants are important factors for controlling the shape of nanocrystals. Relatively high surfactant concentrations result in high chemical potentials which are favorable for formation of anisotropic nanocrystals, regardless of the type of surfactant. In hetero-structured Gd$_2$O$_3$ nanocrystals (Figure 3-7(b) and (d)), small (<5 nm) nanospheres are surrounded by anisotropic nanocrystals. It seems logical to postulate that the small nanospheres play an important role in the growth of the larger anisotropic nanocrystals, such as plates or curved rods. The co-existence of these small nanospheres and nanorods is consistent with the “oriented attachment process” discussed in Chapter 2 [83]. As the molar ratio of Gd(acac)$_3$/HDD was changed from 1:1 to 1:3 to 1:5 (Figure 3-8), quasi-spherical nanocrystals (figure 3-8(a)) apparently attached to one another (red arrows in Figure 3-8(b)) to form long nanorods (>10nm) as shown in Figure 3-8(c). This shape
change from nanospheres to nanorods was the result of an increased concentration of HDD, and was not due to an aging process. Upon changing the concentration ratio of Gd(acac)$_3$/TOPO from 1:1 to 1:2, the shape of the Gd$_2$O$_3$: Eu$^{3+}$ changed from nanospheres to mixed spheres and plates, but did not change further at higher concentrations of the strongly bound TOPO surfactant. The nanoplates were probably formed due to the high chemical potential at the higher concentration of TOPO, not from the evolution of nanospheres.

Figure 3-8. HRTEM images of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals synthesized with ratios of Gd(acac)$_3$/HDD of (a) 1:1, (b) 1:3, or (c) 1:5 illustrating oriented attachment of nanospheres (b-red arrows) to form nanorods in (c).

3.3.2.4 Effects Rate of Heating from 200°C to 290°C

Different heating rates were investigated using a ratio of Gd(acac)$_3$/HDD of 1:5 with other reactants (oleic acid, oleylamine and benzyl ether) after preheating 200°C. If the heating rate is 25°C/min from 200°C to the reflux temperature of 290°C, a mixture of nanospheres and a few curved nanorods were obtained, as shown in Figure 3-9 (a). Slower heating rate of 5°C/min led to a lower density of curved nanocrystals, with the vast majority being nanospheres as shown in Figure 3-9 (b). The result suggest that a rapid growth rate due to larger heating rates result in a high chemical potential which favors the formation of anisotropic nanocrystals.
Figure 3-9. HRTEM images of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals synthesized with a heating rate of (a) 25°C/min (mixed curved nanoplates and nanospheres) and (b) 5°C/min (dominated by nanospheres).

3.3.3 Crystal Structures of Gd$_2$O$_3$: Eu$^{3+}$ Nanocrystals

It is known that cubic Gd$_2$O$_3$ transforms to monoclinic at 1300-1400 °C [146], with the monoclinic phase being favored at temperatures over 1400°C. These different crystallographies affect the magnetic and optical properties of Gd$_2$O$_3$ [147]. The crystallographic structure of Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals were examined using Cu K$_\alpha$ radiation, and a XRD spectrum is shown in Figure 3-10. The XRD peaks were broadened due to the small size of nanocrystals comparing to bulk Gd$_2$O$_3$: Eu$^{3+}$, especially for the nanospheres with a smaller size than the nanoplates. Although the main peak ($2\theta \approx 32.47^\circ$) of monoclinic Gd$_2$O$_3$ (JCPDS file 43-1015) was seen in both samples, most of the monoclinic peaks overlapped with those from cubic Gd$_2$O$_3$ (JCPDS file 43-1014), making it difficult to determine if only a single phase was present. However, a relatively sharp monoclinic (002) peak was seen at $2\theta \approx 32.47^\circ$ from nanoplates, consistent with these planes being the face along which the stacks self aligned. It is also possible that nanoplates contain a larger fraction of the monoclinic (versus cubic) phase compared to Gd$_2$O$_3$ nanospheres. Based on this assumption, it could be expected that the emission efficiency of Gd$_2$O$_3$: Eu$^{3+}$ nanoplates were less than that of nanospheres because monoclinic crystals show a considerably
lower luminance than cubic crystals.[148]. Interestingly, mixed shaped of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals with larger sizes over 10 nm (Figure 3-6 (d)) have very sharp peak at $2\theta \approx 28.5^\circ$ assigned to (222) plane of the cubic phase (not shown here).

![Figure 3-10. XRD pattern of Gd$_2$O$_3$: Eu$^{3+}$ (a) nanoplates and (b) nanospheres compared to the JCDPS patterns for cubic and monoclinic Gd$_2$O$_3$.](image)

3.3.4 Luminescence Properties of Gd$_2$O$_3$: Eu$^{3+}$, Tb$^{3+}$ and Er$^{3+}$ Nanocrystals

3.3.4.1 Eu$^{3+}$ Fluorescence in Oxides

Photoluminescence (PL) from Eu$^{3+}$-doped Gd$_2$O$_3$ nanocrystals showed a red color attributed to transitions from the excited $^5D_0$ level to the crystal-field-split $^7F_j$ manifolds of the 4f$^6$ electronic states. The $^5D_0 \rightarrow ^7F_j$ emission of Eu$^{3+}$ is very sensitive to the crystal field around the Eu$^{3+}$ sites. Whereas the $^5D_0 \rightarrow ^7F_{1,3}$ of Eu$^{3+}$ is an allowed magnetic-dipole transition, the $^5D_0 \rightarrow ^7F_{2,4}$ of Eu$^{3+}$ is a forbidden electric-dipole transition (parity selection rule) [136]. However, this selection rule can be relaxed for Eu$^{3+}$ in a host lattice lacking inversion symmetry, such as Gd$_2$O$_3$[148], Y$_2$O$_3$ [149] and LaPO$_4$ [134].
Figure 3-11. Optical transitions from Eu$^{3+}$ in either a C$_2$ or a S$_6$ symmetry site in Gd$_2$O$_3$ [150].

3.3.4.2 Luminescence vs. Gd$_2$O$_3$ Crystallography

The two different crystal structures of Gd$_2$O$_3$ nanocrystals strongly affect the luminescent properties, with the monoclinic system showing a considerably lower luminance than the cubic system [151]. Cubic Gd$_2$O$_3$ is a good host materials for trivalent activators (i.e. Eu$^{3+}$, Tb$^{3+}$ and Er$^{3+}$), which are believed to substitute on Gd$^{3+}$ sites. In cubic Gd$_2$O$_3$: Eu$^{3+}$, two possible symmetry sites exist for the Eu$^{3+}$ ions, namely S$_6$ and C$_2$ point group symmetry. The crystal structure of Gd$_2$O$_3$ is of the rare-earth sequioxide C-type in which each Gd$^{3+}$ ion is surrounded by six oxygen located at the corners of a cube [152]. Two of the corners are vacant and this can occur along either a body or a face diagonal of the cube, which results in two Gd$^{3+}$ site symmetries, namely S$_6$ or C$_2$, respectively. Figure 3-12 depicts the two types of crystallographic sites possible in Gd$_2$O$_3$. The unit cell consists of two types of alternating Gd$^{3+}$ layers, one composed of only C$_2$ sites and the other composed of an equal number of S$_6$ and C$_2$ sites; the ratio of C$_2$ to S$_6$ sites is 3 to 1 [153].
Figure 3-12. Two Gd$^{3+}$ symmetry sites in Gd$_2$O$_3$.

In fact, electric dipole transitions for Eu$^{3+}$ ion at S$_6$ site is forbidden because of the strict inversion symmetry. Therefore, the $^5$D$_0 \rightarrow ^7$F$_{2,4}$ transitions originates mostly from the C$_2$ site, because of its’ relatively poor inversion symmetry [136].

Monoclinic Gd$_2$O$_3$ provides three different crystallographic sites Cs for the Eu$^{3+}$ ion [154]. These three sites give rise to a majority of the $^5$D$_0$ and $^7$F$_2$ stark levels, which produce numerous peaks in the range between 600 and 630 nm, even through our measurement was not sufficient to resolve them.

Figure 3-13 shows the PL excitation (PLE) spectra for emission at 612 nm from Gd$_2$O$_3$: Eu$^{3+}$ nanoplates versus nanospheres at room temperature. For both shapes a broad excitation band extends from ~250 to ~300 nm, and is thought to result from both host and charge-transfer-band (CTB) excitation. An electronic excitation transition near 260nm is associated with the 2p orbital of O$^{2-}$ to the 4f orbital of Eu$^{3+}$, whose strength is related to the covalency between O$^{2-}$ and Eu$^{3+}$ and the coordination environment around Eu$^{3+}$ [155]. Another broad band at 280 nm is related to Gd$^{3+}$ transitions due to Gd$^{3+} \rightarrow$ Eu$^{3+}$ energy transfer. The weak, sharp lines at ~320 and
360-390 nm, shown in the inset, are associated with direct excitation of the f-f shell transitions of \( \text{Eu}^{3+} \) as labeled [150]. While the PLE spectral wavelengths and intensities were not altered, the shape of the broad CTB were different between nanoplates and nanospheres. When the CTB was decomposed into two Lorentzian component at 260 and 280 nm (not shown here), their ratio was different. This is attributed to a variation of the coordination environment around \( \text{Eu}^{3+} \) ions in these two different samples. In nanocrystals, the coordination environment around the \( \text{Eu}^{3+} \) on the surface would be different from that around interior \( \text{Eu}^{3+} \) since effects such as adsorption, dangling bonds and defects exist at the surface [156]. In nanoplates versus nanospheres, the ratio of surface to volume varies which leads to an increase in CT transitions contributed by surface \( \text{Eu}^{3+} \) ions and a decrease of those contributed by internal \( \text{Eu}^{3+} \) ions.

Figure 3-13. PL excitation spectra of \( \text{Gd}_2\text{O}_3: \text{Eu}^{3+} \) nanocrystals for the emission line at 612 nm of nanoplates and nanospheres. The inset shows the PLE spectrum from 315-400 m at a higher sensitivity so that the labeled absorption transitions of \( \text{Eu}^{3+} \) can be seen.

The emission spectra from \( \text{Gd}_2\text{O}_3: \text{Eu}^{3+} \) (10 mol%) nanospheres, nanoplates and mixed nanocrystals (spheres, platelets, triangles and rings) under 270 nm excitation is shown in Figure
3-14 (a), (b) and (c), respectively. Note that the concentration of Eu$^{3+}$ that leads to quenching in the present colloidal nanocrystals is higher (>6 mol%) than that in bulk materials (3-5 mol%) [148]. This is attributed to reduced energy transfer rates from luminescence centers to quenching centers due to the interface related size issue, and the fact that the liquid phase synthetic route appears to sweep dopant ions into the solvent during growth.

The red emission of Eu$^{3+}$ is dominated by the $^5D_0\rightarrow^7F_2$ transition at 612 nm with minor peaks from $^5D_0\rightarrow^7F_J$ ($J = 0,1,3$) transitions characteristic of the Gd$_2$O$_3$ host lattice (see Figure 3-14). Peaks for $J=0$ are observed at 578 nm, for $J = 1$ at 588 and 597 nm and for $J = 2$ at 612 and 620 nm. Emission peaks near 650 nm ($^5D_0\rightarrow^7F_3$) and near 700 nm ($^5D_0\rightarrow^7F_4$) are also shown. The f-f transitions of Eu$^{3+}$ are essentially free-ion-like in character and their relative intensities are sensitive to the crystal environment, therefore the luminescence can be used as the detector of the local crystal structure. As previously described, several split levels give emission between 600 and 630 nm in monoclinic Gd$_2$O$_3$, while emission from $^5D_0\rightarrow^7F_2$ at 612 nm is dominant from cubic Gd$_2$O$_3$. The low energy peak at 620 nm is stronger than the 612 nm peak from monoclinic Gd$_2$O$_3$: Eu$^{3+}$, and the site symmetry results in a less intense red emission [151, 157, 158]. Both the nanospheres and nanoplates of Gd$_2$O$_3$: Eu$^{3+}$ have a very strong red color and the emission peak at 612 nm is stronger than that at 620 nm. However the ratio of the peak intensities, $I_{612}/I_{620}$, is larger for nanospheres versus nanoplates, as shown in Figure 3-14(a) and (b), suggesting that both cubic and monoclinic Gd$_2$O$_3$ were present.

Focusing on the shapes of nanocrystals, the emission of $^5D_0\rightarrow^7F_2$ at 612 nm was stronger in nanospheres than nanoplates. This could result from several effects. First, the relatively high 612 nm peak suggests that Gd$_2$O$_3$: Eu$^{3+}$ nanospheres had a larger fraction of cubic versus monoclinic
phase. The relatively intense peak at 612 nm would originate from the C\textsubscript{2} site in the cubic structure, consistent with the XRD data discussed above.

Because of their geometry, nanoplates have a higher surface to volume ratio than do nanospheres. As a result, a larger fraction of Eu\textsuperscript{3+} ions are expected to be near the surface with modified site symmetry, and lower emission intensity might result.

Note that mixed shaped nanocrystals with larger size than those of nanoplates and nanospheres exhibited relatively poor luminescence (Figure 3-14) even though XRD data showed a crystalline cubic structure. These mixed shaped nanocrystals were produced by a very fast reaction of Gd-octanoate and octadecene (<1 h) while nanoplates and nanospheres were produced by slower reactions (~3 h). In a fast growth process, it is reasonable to postulate that dopant ions have less time to locate the appropriate sites in the host lattice, and instead remain in the liquid surfactants. The low intensity from cubic mixed shape nanocrystals could therefore be attributed to a low doping efficiency, consistent with ICP analysis of the Eu\textsuperscript{3+} concentration reported below.

The emission spectra of mixtures of Gd\textsubscript{2}O\textsubscript{3}: Eu\textsuperscript{3+} nanocrystals (rods + spheres and plates + spheres) are shown in Figure 3-15. As previously shown in Figure 3-7 (b, d), these mixed structures were prepared by varying the main organic surfactant. It can be seen that the emission of mixed nanorods and nanospheres (Figure 3-15(a) grown from Gd(acac)\textsubscript{3} and TOPO) was less intense than from the mixture of nanoplates and nanospheres (Figure 3-15(b) grown from Gd(acac)\textsubscript{3} and HDD). It is speculated that the reaction of Gd(acac)\textsubscript{3} and hexadecanediol allowed better incorporation of Eu\textsuperscript{3+} dopants than that of Gd(acac)\textsubscript{3} and TOPO, as discussed below.
Figure 3-14. Relative PL emission spectra of Gd$_2$O$_3$: Eu$^{3+}$ (10 mol %) of a) nanospheres (synthesized with Gd(acac)$_3$ and hexadecanediol), b) nanoplates (synthesized with Gd acetate and TOPO) in the presence of oleic acid, oleylamine and benzyl ether, and c) mixed shapes (synthesized with Gd octanoate, oleic acid and octadecene).

Figure 3-15. PL emission spectra of mixed shapes of Gd$_2$O$_3$: Eu$^{3+}$ (10 mol %) prepared with a) of Gd(acac)$_3$ / TOPO (1:2), and b) Gd(acac)$_3$ / HDD (1:5).
3.3.4.3 Nanocrystals of Gd$_2$O$_3$: Tb$^{3+}$

The luminescence spectra of Gd$_2$O$_3$:Tb$^{3+}$ nanoplates and nanospheres were investigated using 270 nm excitation. Since the luminescence of terbium originates from a level ($^5$D$_4$) strongly split by the crystal field, the emission pattern is much more complicated than for Eu$^{3+}$, and each peak in the spectrum represents a number of unresolved lines. The main intense luminescence line is at 542 nm. Like Eu$^{3+}$ doped Gd$_2$O$_3$ nanocrystals (Figure 3-14), the transition energies were the same for nanoplates and nanospheres, but the luminescent intensity of nanospheres was higher than that of nanoplates (Figure 3-16). The origin(s) of this effect is thought to be similar to that for Eu, as discussed above.

![Relative PL emission spectra of Gd$_2$O$_3$: Tb$^{3+}$ (10 mol %) nanocrystals with the shape of a) spheres (synthesized with Gd(acac)$_3$ and hexadecanediol ), and b) plates (synthesized with Gd acetate and TOPO) in the presence of oleic acid, oleylamine and benzyl ether.](image)

Figure 3-16. Relative PL emission spectra of Gd$_2$O$_3$: Tb$^{3+}$ (10 mol %) nanocrystals with the shape of a) spheres (synthesized with Gd(acac)$_3$ and hexadecanediol ), and b) plates (synthesized with Gd acetate and TOPO) in the presence of oleic acid, oleylamine and benzyl ether.
3.3.4.4 Near Infrared Emission From Gd$_2$O$_3$: Er$^{3+}$

Near infrared (NIR) emission from Er$^{3+}$ ions at 1.5 µm are well known and NIR is promising for biolabeling [117, 159] since excitation and emission have longer penetration depths in tissue [132]. Dopant Er$^{3+}$ ions were incorporated into the Gd$_2$O$_3$ nanocrystalline host and the properties tested. Growth of Gd$_2$O$_3$: Er$^{3+}$ nanocrystals with various shapes similar to those of Gd$_2$O$_3$: Eu$^{3+}$ was observed. NIR emission was detected from Er$^{3+}$ doped Gd$_2$O$_3$ nanospheres produced using the same protocol (section 3.2.3) as for Gd$_2$O$_3$:Eu$^{3+}$ as shown in Figure 3-17 (excited by 488 nm from an Ar laser). The characteristic $^4$I$_{13/2} - ^4$I$_{15/2}$ and many sublevel peaks from Er$^{3+}$ over the range 1450-1650 nm were observed.

![Figure 3-17. Near infrared (NIR) PL emission spectra from Gd$_2$O$_3$:Er$^{3+}$ nanospheres under 488 nm laser excitation.](image)

3.3.5 Eu$^{3+}$ Incorporation into Gd$_2$O$_3$ Nanocrystals

In Figure 3-14, the relative PL intensities were shown versus the shape of the Gd$_2$O$_3$ nanocrystals. Determination of the concentration of Eu in as-prepared samples by inductively coupled plasma (ICP) is very important since the concentration of Eu$^{3+}$ ions is directly related to the luminescent properties of Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals. The morphology, relative PL emission
intensity at 612 nm and Eu concentration (mol %) in samples with the same solvent volume prepared from different Gd precursors are reported in Table 3-1. Nanospheres, nanoplates and mixed samples were prepared by the same route as in Figure 3-14 under standard conditions. Gd chloride was reacted in the presence of HDD, oleic acid, oleylamine and benzyl ether under standard condition (see Table 3-1 footnote) and resulted in nanospheres of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$. All samples had the same concentration of $\text{Eu}^{3+}$ in all starting solutions (10 mol%). The results show that $\text{Eu}^{3+}$ concentration varies from 0.57 to 6.1 mol % in as-prepared nanocrystals. While the volume of solvent with dispersed nanocrystals was constant, the amount of nanocrystal varied from one condition to the next. The concentration of Eu incorporated into the nanocrystals decreased from Gd(acac)$_3$ (a-nanospheres) to Gd acetate (b-nanoplates) to Gd octanoate (c-mixed shapes), suggesting a strong correlation between the particle shape and Eu concentration. Although both Gd chloride (d) and Gd(acac)$_3$ (a) produced nanospheres, the relative PL intensities were much lower from the chloride versus the nanospheres from Gd(acac)$_3$ (Table 3-1). The reaction producing nanospheres from Gd chloride was relatively fast (~30min), the yield of product and Eu incorporation was low. As depicted, mixed shapes(c) of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystals were obtained within 1 h, which is faster reaction than ones (3 h) of nanospheres (a) and nanoplates (b).

Table 3-1. Nanocrystal shape, normalized PL intensity and Eu concentration in $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystals versus the Gd prerecursor.

<table>
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<tr>
<th>Gd-precursor</th>
<th>morphology</th>
<th>Relative PL intensity Probed at $\lambda_{\text{em}}=612$ nm</th>
<th>Eu$^{3+}$ concentration (mol % in final product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Gd(acac)$_3$</td>
<td>nanospheres</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.1</td>
</tr>
<tr>
<td>b</td>
<td>Gd acetate</td>
<td>nanoplates</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>c</td>
<td>Gd octanoate</td>
<td>mixed nanocrystals</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>d</td>
<td>Gd chloride</td>
<td>nanospheres</td>
<td>0.0036</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.57</td>
</tr>
</tbody>
</table>

* Standard condition: After the solution is preheated at 200°C for 30 min, it is heated at the rate of 25°C/min up to ~290°C under a N$_2$ blanket.
Erwin and Norris reported the efficiency of Mn doping in II-IV and IV-VI nanocrystals [160], and conclude that doping efficiency is determined by three main factors: surface morphology, nanocrystal shape and surfactants in the growth solution. Particularly, (001) facets of zinc blende nanocrystals play a special role in doping process because energies of these surfaces are strikingly larger (vs. wurtzite or rock-salt). These surfaces consist of anion dimers which provide very stable binding sites that are absent from other facets. They suggest that strong surfactants (such as phosphonic acids) can also bind Mn and compete with surface adsorption of dopants.

The normalized PL intensity at 612 nm and the Eu concentration from the same volume of solvent-dispersed nanocrystals from samples a-d (Table 3-1) are shown in Figure 3-18. There is a strong correlation between the normalized PL intensity and normalized Eu concentration multiplied by the product yield.

Figure 3-18. Normalized PL emission intensity at 612 nm, Eu concentration and HRTEM photomicrographs of Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals grown from Gd precursor a-d (see Table 3-1).
In rare earth doped oxide nanocrystal systems, several factors will control the doping efficiency, defined to be the concentration of RE incorporated into the nanocrystals. The results above indicate that the luminescent efficiency of Eu\(^{3+}\) doped Gd\(_2\)O\(_3\) nanocrystals is not only dependent on the shape of nanocrystals, but also on the reaction rate and product yield, i.e. doping efficiency is based on the kinetics of the reaction. In slow reactions, the dopants have enough time to be incorporated. The incorporated concentration of dopants in as prepared samples rises monotonically with increasing product yield. Additionally, the crystal structure of Gd\(_2\)O\(_3\):Eu\(^{3+}\) nanocrystals can affect the doping efficiency, as it is known that the cubic phase of Gd\(_2\)O\(_3\) is a better host than the monoclinic phase. But this should be considered as minor factor since mixed nanocrystals (c) have lower luminance than samples a and b, even though they are predominantly cubic phase. The results suggest that doping efficiency is affected by three factors in Gd\(_2\)O\(_3\) nanocrystals: rate of reaction, product yield and crystal structure of nanocrystals as summarized in Table 3-2.

Table 3-2. Three main factors for doping efficiency of Eu in Gd\(_2\)O\(_3\) nanocrystals (a-d)

<table>
<thead>
<tr>
<th></th>
<th>Reaction time</th>
<th>Product yield</th>
<th>Crystal structure (from XRD and PL)</th>
<th>Eu(^{3+}) concentration (mol % in final product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>~ 3 h</td>
<td>~ 80 %</td>
<td>cubic+monoclinic</td>
<td>6.12</td>
</tr>
<tr>
<td>b</td>
<td>~ 3 h</td>
<td>~ 80 %</td>
<td>cubic+ <strong>Monoclinic</strong></td>
<td>1.85</td>
</tr>
<tr>
<td>c</td>
<td>~ 1 h</td>
<td>~ 60 %</td>
<td>cubic</td>
<td>1.24</td>
</tr>
<tr>
<td>d</td>
<td>~ 0.5 h</td>
<td>~ 35 %</td>
<td>cubic+monoclinic</td>
<td>0.57</td>
</tr>
</tbody>
</table>

*Bold* represents the dominant crystal structure in sample b.

3.3.6 Thermo-gravimetric analysis (TGA)

Figure 3-19 shows TGA data from thermal decomposition in air of Gd-acetate and Gd(acac)\(_3\) precursors. The decomposition of Gd-acetate (Gd(CH\(_3\)COO)\(_3\)) (red line) takes place in three steps. A dehydration step observed at ~100°C results in a loss of ~3H\(_2\)O molecules per
monomer. The dehydration weight loss of \(3\text{H}_2\text{O}\) was estimated to be \(\sim 16.4\%\) in good agreement with measured loss of \(\sim 17.5\%\). Continued decomposition of dehydrated \(\text{Gd(CH}_3\text{COO)}_3\) proceeds in two steps, with the first step in the temperature range (300-400\(^\circ\text{C}\)) corresponding to formation of \(\text{Gd}_2\text{O}_2\text{CO}_3\) and volatile products. The second step over the temperature range of 580-650\(^\circ\text{C}\) occurred by the formation of \(\text{Gd}_2\text{O}_3\) and \(\text{CO}_2\) [161]. The TGA data from \(\text{Gd(acac)}_3\) precursor (blue line in Figure 3-19) shows dehydration at \(\sim 100\^\circ\text{C}\), followed by decomposition above \(\sim 200\^\circ\text{C}\) that proceeds continuously until \(\sim 550\^\circ\text{C}\). The reaction temperatures for the current solution synthesis scheme for nanocrystals are lower (200-290\(^\circ\text{C}\)) than the temperatures for the majority of the decomposition, therefore the reactivity of the metal precursors with the other reactants and the organic surfactants must affect the nucleation of metal oxide phase. The TGA data in Figure 3-19 show that the decomposition of \(\text{Gd(acac)}_3\) proceeds gradually, while the decomposition of \(\text{Gd acetate}\) occur abruptly at 350\(^\circ\text{C}\). The reaction using \(\text{Gd acetate}\) forms nuclei in a short period of time which implies that the system would be under kinetic control, allowing an anisotropic final product (nanoplates). The decomposition of \(\text{Gd(acac)}_3\) over an extended temperature range above 200\(^\circ\text{C}\) results in the formation of a relatively large number of nuclei and the thermodynamically controlled reaction favors the formation of isotropic nanospheres.
The amount of surfactant coating the surface is a function of the nanoparticle size and shape. The TGA data from different shapes of the Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals coated with organic surfactants are shown in Figure 3-20. The observed weight loss versus temperature was dramatic above ~250°C. The small weight loss for temperatures <250°C is attributed to desorption of physisorbed molecules from the surface. The larger weight loss at >250°C is attributed to desorption of organic surfactant molecules from the surface, which is complete at ~500°C. Note that the relative weight loss for T < 250°C was greater (6 versus 4%) and desorption of surfactant started at a lower temperature (~50 versus ~100 °C) for nanospheres versus nanoplates, respectively. Data in Figure 3-20 and Table 3-2 show a total weight loss upon heating to >600°C of 35 % and 42 % for nanoplates (5-7 nm edge and 1nm thickness) and nanospheres (2-3 nm diameters), respectively. These data suggest that the relative amount of surfactant decreased as the size of the Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals increased. The data also suggest that the surfactant is more strongly bound in stacked nanoplates than for dispersed nanospheres.
Figure 3-20. TGA data from nanoplates and nanospheres of Gd$_2$O$_3$:Eu$^{3+}$ synthesized under standard conditions listed in Table 3-1.

Table 3-3. Normalized weight loss based on TGA data in Fig 3-20.

<table>
<thead>
<tr>
<th>Sample shape</th>
<th>Size</th>
<th>First weight loss ( % )</th>
<th>Second weight loss ( % )</th>
<th>Total loss ( % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanoplates</td>
<td>5-7 nm, 1nm (edge, thickness)</td>
<td>3.9</td>
<td>31.5</td>
<td>35.4</td>
</tr>
<tr>
<td>nanospheres</td>
<td>2-3 nm</td>
<td>6.1</td>
<td>36.1</td>
<td>42.2</td>
</tr>
</tbody>
</table>

If we assume a close-packed monolayer of the surfactant on the surface of a Gd$_2$O$_3$ nanosphere of diameter d, the total weight of the nanoparticle plus the monolayer is $(1/6)\pi d^3 \rho + (\pi d^2/a)(M/N_0)$ where d = the diameter of the particle , $\rho$ = the density of the particle, a = the attachment (head) area per molecule of the surfactant, $M_w$ = the molecular weight of the surfactant, and $N_0$ = Avogadro number. Assuming that the TGA heating causes weight loss of only the surface-bound surfactant, the percentage weight loss from a particle of diameter d can be calculated using the relation [162]:

$$\text{Weight loss in } \% = 100 \times \left(\frac{\pi d^2}{a} \frac{M_w}{N_0}\right) / A$$  (1)
\[ A = \frac{1}{6} \pi d^3 \rho + \frac{\pi d^2}{a} \left( \frac{M}{N_0} \right) \]

In case of Gd\(_2\)O\(_3\):Eu\(^{3+}\) nanospheres, using \(d = 25\) Å (average diameter), \(\rho = 7.407\) g cm\(^{-3}\), \(a = 20\) Å\(^2\) (for oleic acid) and \(M_w = 282.46\) gm mol\(^{-1}\) for oleic acid, the calculated percentage weight loss using equation (1) is 43 %, in good agreement with the 42 % that was obtained experimentally. This suggests a monolayer oleic acid coated the nanosphere surface.

### 3.3.7 FTIR analysis

The capping ligands chemisorbed by the surfaces of the Gd\(_2\)O\(_3\):Eu\(^{3+}\) nanocrystals can be identified from the FTIR spectra presented in Figure 3-21. Transmittance data were collected from the solid sample such as nanoplates and nanospheres of Gd\(_2\)O\(_3\):Eu\(^{3+}\), TOPO, and hexadecanediol (HDD), and absorbance were obtained from liquid oleic acid. As reported above, nanoplates of Gd\(_2\)O\(_3\): Eu\(^{3+}\) were prepared by Gd(acac)\(_3\) precursor with TOPO and oleic acid, while nanospheres were prepared by Gd(acac)\(_3\) with hexadecanediol and oleic acid. The two absorption bands at 2937 and 2857 cm\(^{-1}\) in all five samples were attributed to the asymmetric CH\(_2\) stretch and the symmetric CH\(_2\) stretch, respectively. The C=O stretch band of the carboxyl group at 1715 cm\(^{-1}\) was detected only from oleic acid, and was absent in the data from the nanoplates and nanospheres. This suggests that oleic acid molecules are covalently bonded to the nanocrystals surface and there are no free oleic acid molecules [163]. Two bands at 1430 and 1535 cm\(^{-1}\) from nanoplates and nanospheres probably result from the symmetric and asymmetric stretching vibrations of carboxylic groups bonded symmetrically or bonded at an angle to the surface [164]. Absorptions at \(\sim 1050\) cm\(^{-1}\) probably arise from C-O single bond stretching. These data are consistent with ligands being chemisorbed onto the Gd\(_2\)O\(_3\):Eu\(^{3+}\) nanocrystals as a carboxylate.
Nakamoto categorized the interaction between a carboxylate head and a metal atom as monodentate, bridging (bidentate), chelating (bidentate), or ionic [165]. The wave number shift, Δ, between the asymmetric ν_{as}(COO⁻), and symmetric ν_{s}(COO⁻), IR bands can be used to distinguish the type of the interaction. The largest Δ (200-320 cm⁻¹) corresponds to the monodentate interaction, the smallest Δ ( < 110 cm⁻¹ ) to the chelating bidentate, and a medium range Δ (140-190 cm⁻¹ ) to the bridging bidentate. In this work, the Δ ( 1535-1430 = 105 cm⁻¹ ) suggests the chelating bidentate was formed where the interaction between the COO⁻ group and the Gd atom was covalent.

From pure TOPO, the ν (P=O) stretching absorption appears as a sharp peak at 1145 cm⁻¹, and this peak is detected from nanoplates but is absent from nanospheres of Gd₂O₃:Eu³⁺. The band at 560 cm⁻¹ is characteristic of Gd₂O₃ [166]. Thus IR adsorption bands show the Gd₂O₃: Eu³⁺ nanocrystals are coated primarily with oleic acid.

Figure 3-21. FTIR spectra from nanoplates and nanospheres of Gd₂O₃: Eu³⁺ and surfactants (hexadecanediol, TOPO and oleic acid). The oleic acid is liquid, while the other samples are solid.
3.4 Conclusions

Well dispersed, crystalline rare earth (Eu$^{3+}$, Tb$^{3+}$ and Er$^{3+}$, 10 mol %) doped Gd$_2$O$_3$ nanocrystals were synthesized at 290 °C (reaction time, ~ 3 h) by a hot solution nonhydrolytic route. The Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals were changed from nanospheres (<5nm) to nanoplates (1nm x <10nm$^2$) to mixed shaped nanocrystals (spheres, plates, rods, and triangles) by changes of Gd precursors, organic surfactants, concentrations and heating rate (between 200 and 290°C reaction temperatures). The mechanisms leading to isotropic versus anisotropic growth of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals were discussed. The PL emission and excitation properties of nanospheres, nanoplates and mixed shape nanocrystals were reported. The intensity of the Eu$^{3+}$ 5D$_0$→7F$_2$ emission at 612nm from nanospheres was more intense than that from nanoplates or mixed shape nanocrystals due to a higher concentration (6.12 %) of Eu in nanospheres versus nanoplates(1.85 %) or mixed shape nanocrystals (1.24 %). Three main factors for doping efficiency are suggested in Gd$_2$O$_3$ nanocrystals: rate of reaction, product yield and crystal structure of nanocrystals which dominantly affect the doping efficiency in order. It is note that Gd(acac)$_3$ is slowly reacted (~ 3 h) with oleic acid and HDD surfactants and induce, well doped, efficiently luminescent Gd$_2$O$_3$: Eu$^{3+}$ nanospheres with high product yield (~ 80 %). In this way, this experimental advances in rare earth doped oxide nanocrystals in controlling shape and crystal structure of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals can also be important in optimizing the luminescent efficiency from rare earth doping.
CHAPTER 4
WATER SOLUBLE SURFACE MODIFICATION OF LUMINESCENT GADOLINIUM OXIDE NANOCRYSTALS FOR BIOMEDICAL RESEARCH

4.1 Introduction

Thermal decomposition of metal precursors in stabilizing organic surfactants has been proven to produce monodispersed luminescent nanocrystals. This synthetic procedure also allows control over the shape and size of nanocrystals (see Chapter 3) with the desired optical properties, e.g. high photoluminescence yield, narrow emission peaks and stability against photobleaching [37, 38, 59, 61, 71]. Nanocrystals synthesized by this method are hydrophobic because of the coordinating agent, and are therefore insoluble in aqueous solutions making them incompatible with biological systems. To disperse them in aqueous solutions, a polar surface must be created to render them water soluble.

Several methods have been developed to modify the surface of nanocrystals for water solubility [117, 118, 167-170]. In addition to making the nanocrystals hydrophilic, the treatment should also a) prevent nanocrystals from flocculating during long-term storage, b) maintain or improve the nanocrystal’s fluorescence quantum yield, and c) maintain the sub-10 nm nanocrystal size [168]. Most surface modification methods rely on the placement of the hydrophobic surfactant coatings by ligand molecules that are reactive towards the nanocrystals surface on one end, and has a hydrophilic groups on the other end. Alivisatos, et al and Nie, et al first used such chemical exchange reactions to modify the surface chemistry of quantum dots (QDs) [117, 118]. In had method, a bifunctional molecule, such as mercaptoacetic acid (MAA), competed with TOPO (or another organic stabilizer) for binding to a metal atom on the Qdots surface. With excess bifunctional molecules in solution, the thiol (-SH) functional groups on the MAA displaces the phosphonic oxide (from the TOPO) that was initially bound to the metal atoms. If the bifunctional molecules contains a polar functional group opposite to the thiol (-SH)
functional group, the Qdots become polar and are soluble in water solutions. Some disadvantages of using MAA was rapid flocculation of the hydrophilic nanocrystals and a significant decrease in quantum yield. Particle aggregation was attributed to a weak bond between the thiol (-SH) group and the Qdots surface which allowed the hydrophilic ligand shell around the nanocrystal to disintegration [167, 169].

Another approach to make the nanocrystals water soluble is to grow a hydrophilic silica shell through surface silanization [170, 171]. At first a ligand exchange is used to substitute the original hydrophobic surfactant with another surfactant shell (e.g. mercaptopropyltrimethoxysilane) which is cross-linked for improved stability. To make this silica shell hydrophilic, molecules with methoxysilane groups at one end and hydrophilic groups at the other end are attached by siloxane bonds, resulting in a multi-layer shell. Silanized nanocrystals are extremely stable in solution, but the silanization process is laborious and the resulting shell often is inhomogeneous.

Recently, methods to coat hydrophobic nanocrystals with amphiphilic polymers has been reported [119, 125, 133, 172]. In these approaches, hydrophobic tails of the amphiphilic polymer intercalate the hydrophobic surfactant molecules on the nanocrystals surface and thus form an additional coating layer. The water solubility of polymer coated nanocrystals is ensured by hydrophilic groups that self-assemble on the polymer shell and the are cross-linked for better stability. This method is not based on ligand exchange, i.e. not based on replacing the original hydrophobic surfactant with hydrophilic molecules, but rather depends on the whole nanocrystals being covered with a cross-linked hydrophilic polymer shell. There is no direct interaction between the polymer and the nanocrystals surface atoms, and therefore the original luminescent efficiency should be preserved. In addition, the large number of hydrophobic side chains on the
amphiphilic polymer strengthens the hydrophobic structure at the surface, resulting in more stable water-soluble nanocrystals. The data indicate that this amphiphilic shell is thinner and more homogeneous than silica shells, although the multiple shells around the inorganic core make the overall diameter larger than nanocrystals made hydrophilic by surfactant exchange.

In the present study, the amphiphilic polymer coating method was applied to make luminescent Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals hydrophilic. The optical properties and size was monitored.

4.2 Experimental Sections

4.2.1 Materials

Octylamine, anhydrous N, N-dimethylformamide (DMF), 1-[3-(dimethyl-amino)-propyl]-ethylcarbodiimide hydrochloride (EDC) and poly(acrylic acid) (PAA, molecular weight 2000) were purchased from Aldrich and were used as received without further purification.

4.2.2 Synthesis of Hydrophobically Modified Poly(Acrylic Acid)

Octylamine (3.5g) in DMF solution was transferred dropwise into a stirred anhydrous DMF solution containing dry PAA powder (4g) and 1-[3-(dimethyl-amino)-propyl]-ethylcarbodiimide hydrochloride (1.2g). The reaction was allowed to continue for 24 h at room temperature. After 24h an excess of H$_2$O was added to the solution, resulting in the precipitation of the polymer. The precipitated polymer was dissolved in methanol, which was then evaporated to obtain the final purified amine modified PAA polymer product.

4.2.3 Synthesis of Hydrophilic Gd$_2$O$_3$ : Eu$^{3+}$ Nanocrystals

The Gd$_2$O$_3$ : Eu$^{3+}$ nanoplates and nanospheres were prepared by the non hydrolytic hot solution synthesis route as described in section 3.2.2 and 3.2.3. Under ambient conditions, hydrophobic Gd$_2$O$_3$ nanocrystals (20mg) were dispersed in 15ml hexane. The suspension was added dropwise while stirring into a hexane solution of the amine modified PAA (60 mg /15ml).
The hexane was removed by evaporation to yield a thin film of polymer/nanocrystals composite on the wall of the flask. The dry film was redispersed in distilled water with stirring, and aggregated material and excess polymer was removed by filtration (0.2 μm, syringe filter).

4.2.3 Characterization

The morphology of modified Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals were imaged using high resolution TEM (JEOL 2010F, 200kV). Photoluminescence (PL) was measured at room temperature from nanocrystals suspended in hexane using a Flurolog Tau 3 spectrofluorometer (Jobin Yvon Spex Instruments, S.A. Inc) with a 450 W xenon excitation lamp. For confirmation of the dispersibility in water, the Zeta potential was measured with a colloidal dynamics acoustosizer.

4.3 Results and Discussion

4.3.1 Water Soluble Surface Modification of Gd$_2$O$_3$:Eu$^{3+}$ Nanocrystals

A schematic model structure, after surface modification of Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals, is shown in Figure 4-1. In this model, the surfactant chains for hydrophobically capped Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals are pointing away from the nanocrystals surface, in a brush-like arrangement (left side of Figure 4-1). A plausible configuration for the amphiphilic polymer coating is shown on the right of Figure 4-1 where the hydrophobic alkyl chains of the octylamine-modified PAA intercalate with the surfactant coating, and the outer surface is covered by the hydrophilic ends.

![Figure 4-1. Schematic model of surface modification of Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals using octylamine modified PAA.](image)
TEM images of Gd$_2$O$_3$:Eu$^{3+}$ nanospheres before and after modification are shown in Figure 4-2. The original Gd$_2$O$_3$:Eu$^{3+}$ nanospheres were prepared using hexadecanediol, oleic acid, oleylamine and benzyl ether. Although the strong affinity of surfactants such as oleic acid increase the difficulty of modifying these hydrophobic nanocrystals to make them dispersible in aqueous solutions [173], the TEM images showed a lack of aggregation of nanoparticles. The aqueous dispersed Gd$_2$O$_3$:Eu$^{3+}$ nanospheres (Figure 4-2 (b-c)) were stable suspensions even after 3 months in lab ambient. The TEM images show that the average sizes of Gd$_2$O$_3$:Eu$^{3+}$ nanospheres are about 2-3 nm and 3-4 nm before and after modification, respectively.

![Figure 4-2. TEM images of Gd$_2$O$_3$:Eu$^{3+}$ nanospheres capped with oleic acid and HDD before (a) and after (b-c) hydrophilic modification.](image)

An amine group coordinated to the Gd atoms was also prepared to investigate the effect of the low bond strength on surface modification. These Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals were synthesized with hexadecylamine (HDA) instead of HDD and oleic acid in a relatively fast reaction (<1 h). HDA has been successfully used for the synthesis of II-VI semiconductor nanocrystals. However, HDA capped Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals exhibited poor crystallinity and were polydispersed with relatively low product yield (see Figure 4-3(a)). Although it was expected that the weak coordination of HDA to the nanocrystals would result in easier and more effective
surface modification, the poor crystallinity of unmodified nanocrystals results in poor surface modification and therefore particle agglomeration, as shown in Figure 4-3(b).

Figure 4-3. TEM images of Gd$_2$O$_3$:Eu$^{3+}$ nanospheres capped with HAD before (a) and after (b) hydrophilic modification.

Using the same approach, modification of the surface of Gd$_2$O$_3$:Eu$^{3+}$ nanoplates was attempted. As shown previously in Figure 3-3 and Figure 3-6(b), nanoplates self-assembled into closely stacked arrays. The modified hydrophilic Gd$_2$O$_3$:Eu$^{3+}$ nanoplates were aggregated, consistent with the expectation that the surfaces of the assembled nanocrystals were difficult to completely modify and produce a stable dispersion.

Figure 4-4. TEM images of Gd$_2$O$_3$:Eu$^{3+}$ nanoplates before (a) and after (b) hydrophilic surface modification.
4.3.2  Luminescence properties of hydrophilic surface modified Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals

Surface modified hydrophilic nanocrystals should at least retain the optical properties of hydrophobic capped nanocrystals. The photoluminescent spectra from Gd$_2$O$_3$:Eu$^{3+}$ nanospheres prepared with oleic acid and HDD before and after hydrophilic modification are compared in Figure 4-5. The spectral distribution did not change but the emission intensity at 612 nm decreased to 47% of the initial intensity after the hydrophilic modification.

![PL emission spectra of oleic acid and HDD capped hydrophobic (before) and PAA capped hydrophilic (after) Gd$_2$O$_3$:Eu$^{3+}$ nanospheres.](image)

**Figure 4-5.** PL emission spectra of oleic acid and HDD capped hydrophobic (before) and PAA capped hydrophilic (after) Gd$_2$O$_3$:Eu$^{3+}$ nanospheres.

HDA capped hydrophobic Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals can also be surface modified with PAA hydrophilic polymer (see Figure 4-3), and again the PL spectra are the same but the intensity after modification is only 26% of the original PL emission yield at 612 nm (Figure 4-6).

Both nanocrystals of Gd$_2$O$_3$:Eu$^{3+}$ synthesized with HDD and HDA are well dispersed in water after the hydrophilic surface modification, but both also decrease the 612 nm PL emission are observed in Figure 4-5 and Figure 4-6. These decreases are likely the result of differences in the type and binding strength of capping surfactants, such as oleic acid and amines. The largest drop in PL emission was from Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals prepared with HDA versus those
prepared with oleic acid and HDD. The larger drop for HDA capped nanocrystals is attributed to the fact that the HDA ligands are labile and these capping groups are easily removed from the Gd₂O₃:Eu³⁺ surface. As pointed out above, weak encapsulation by HAD results in poor crystallinity and unstable condition for Eu³⁺ doping, with or without the PAA surface modification.

Figure 4-6. PL emission spectra of had capped hydrophobic (before) and hydrophilic (after) Gd₂O₃:Eu³⁺ nanocrystals.

4.3.3 Dispersion Properties of Hydrophilic Surface Modified Gd₂O₃:Eu³⁺ Nanocrystals

The zeta potential of hydrophilic Gd2O3:Eu3+ (sample in Figure 4-2 (b,c)) after surface modification is shown versus pH in Figure 4-7. The pH value of the original sample was 7.35 that corresponds to a zeta potential of -45 mV, and the dispersion should be stable. For pH values between 5 and 8, the data indicate that modified Gd2O3:Eu3+nanocrystals should be well Dispersed and aggregation is not expected.
Figure 4-7. Zeta potential versus aqueous solution pH of hydrophilic PAA surface modified Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals.

4.4 Conclusions

Octylamine-modified poly(acrylic acid) (PAA) has been used to convert the hydrophobic surface of Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals synthesized by a non hydrolytic hot organic solvent technique to a hydrophilic surface. The surface conversion results in a dispersion of nanocrystals in aqueous solutions stable in lab ambient for >31 days, especially for nanocrystals synthesized using oleic acid and hexadecanediol (HDD). The quality of surface modified Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals synthesized with hexadecylamine (HDA) was not as good. For both synthesis routes, the PL spectra was unchanged by the surface modification, but the intensity was decreased to 47% and 26% of the hydrophobic capped value for synthesis with HDD and HDA, respectively.
CHAPTER 5
SYNTHESIS AND CHARACTERIZATION OF TERNARY ZNGA2O4: EU3+
NANOCRYSTALS

5.1 Introduction

An organic phase process known as thermal decomposition synthesis allows precise tuning of nanocrystals size, shape, and composition, and also allows them to be dispersed in either an aqueous or a nonhydrolytic media. This technique has been demonstrated for binary semiconductor (e.g. CdSe [23], ZnSe [174], and PbSe [175] ) and binary transition metal oxide (e.g. ZnO [68], TiO\(_2\) [74], MnO [54], Fe\(_3\)O\(_4\) [65] and Gd\(_2\)O\(_3\) [70]) nanocrystals. Recently, this synthetic route was expanded to synthesis of ternary nanocrystals with controlled stoichiometry . Zhong and co-workers synthesized Zn\(_x\)Cd\(_{1-x}\)S nanocrystals at high temperature by reacting a mixture of CdO and ZnO oleic acid complexes with sulfur in a noncoordinating solvent (octadecene) system [176]. They found that the nanocrystals show narrow and composition-dependent photoluminescence spectra. Lee, et al used hot solution synthesis to grow nanorods of Cd\(_{1-x}\)Zn\(_x\)Se [177]. They showed that the ternary nanorods could be grown from a solution containing both Cd and Zn precursors, of by solid state diffusion after growth of a CdSe core and a ZnSe shell [164]. Finally, growth of ternary compounds of MFe\(_2\)O\(_4\) (M=Fe, Co, Mn, and Mg) [64, 66] were reported by thermal decomposition synthesis. The composition of the particles was controlled by the molar ratio of Fe(acac)\(_3\) and M(acac)\(_2\) reactants, and the shape and size were changed by varying the reaction conditions. By selecting different elements for M\(^{2+}\), the MFe\(_2\)O\(_4\) could be molecularly engineered over a wide range of magnetic properties.

However, growth of doped ternary nanocrystals has not been reported, either as II-VI semiconductors or as oxide compounds. Even the number of reports of doped binary oxide nanocrystals are few (e.g. Y\(_2\)O\(_3\): Eu\(^{3+}\) [178] and Gd\(_2\)O\(_3\): Eu\(^{3+}\) [71]). In the present study, thermal
decomposition synthesis and the resulting photoluminescent properties of Eu\(^{3+}\) doped ternary ZnGa\(_2\)O\(_4\) nanocrystals is reported.

Luminescent zinc gallate (ZnGa\(_2\)O\(_4\)) has attracted a great deal of attention due to potential applications in field emission displays and electroluminescent devices [179, 180]. In principle, an oxide should show better chemical stability versus competing sulfide phosphors (ZnS: Cu,Cl and SrGa\(_2\)O\(_4\):Eu\(^{2+}\)), especially at high electron beam currents [181]. ZnGa\(_2\)O\(_4\) crystallizes as a cubic spinel with a large band gap of \(~4.4\) eV, and exhibits an intense green emission when doped with Mn and blue luminescence without doping via a self-activated center [182]. It has been suggested that white luminescence could be achieved from ZnGa\(_2\)O\(_4\) by doping with Mn\(^{2+}\) (green), Eu\(^{3+}\) (red), and Ce\(^{3+}\) (blue) [180].

5.2 Experimental

5.2.1 Materials

Zn (II) acetate hydrate, Zn (II) acetate dehydrate, Zn(II) acetylacetonate hydrate, Ga(III) acetylacetonate hydrate, Ga (III) nitrate hydrate, Eu(III) acetate hydrate, oleic acid (90%, tech.), oleyamine (90%, tech.), benzyl ether (99%), 1,2-hexadecanediol (97%), and trioctylphosphine oxide (TOPO, 99%) were purchased from Aldrich and used without further purification. Absolute ethanol, benzyl ether and hexane were also used as received.

5.2.2 Synthesis of ZnGa\(_2\)O\(_4\): Eu\(^{3+}\) Nanocrystals

Similar procedures were used to prepare all ternary ZnGa\(_2\)O\(_4\): Eu\(^{3+}\) nanocrystals.

A zinc precursor (e.g. 1mmol of Zn(II) acetylacetonate hydrate) was mixed with Ga(III) acetylacetonate hydrate(2mmol), Eu(III) acetate hydrate (0.1 mmol), oleic acid (6mmol), oleylamine (6mmol), benzyl ether (5 mmol) and hexadecanediol (5 mmol) and magnetically stirred flowing nitrogen in a three-neck reaction flask. This mixture in the flask was heated to 200°C for 30 min, then heated to 290°C at a heating rate of 25°C /min and held for 3h under the
N2 blanket. After reflux, the mixture was cooled to room temperature by removing the heat source. Under ambient conditions, ethanol was added to the mixture, and ZnGa$_2$O$_4$: Eu$^{3+}$ was precipitated and separated via centrifugation (9000 rpm, 10 min). After several purification with ethanol followed by centrifugation, purified ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres were well dispersed in organic solvents such as hexane, chloroform or toluene. For other Zn precursors, Zn (II) acetate hydrate resulted in nanospheres of ZnGa$_2$O$_4$: Eu$^{3+}$ with the same concentrations and heating sequences. When TOPO (2 mmol) was used instead of hexadecanediol (5 mmol), sphere-like ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals were again produced. However, Zn (II) acetate dehydrate reacting with Ga(III) acetylacetonate hydrate (2mmol), Eu (III) acetate hydrate (0.1 mmol), oleic acid (6mmol), oleylamine (6mmol), benzyl ether (5 mmol) and hexadecanediol (2.5 mmol) resulted in mixed-shaped large ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals.

5.2.3 Characterization of ZnGa$_2$O$_4$: Eu$^{3+}$ Nanocrystals

X-ray diffraction (XRD) (Philips APD 3720) was used to determine the crystal structure with Cu K$_\alpha$ radiation source (λ = 0.5418 nm). A JEOL 2010F transmission electron microscope (TEM) operated at 200 kV was used to determine the size and shape of the nanocrystals. Optical absorption spectra were collected with a Shimadzu UV-2401PC spectrophotometer. Photoluminescence (PL) was measured at room temperature from nanocrystals suspended in hexane using a Fluorolog Tau 3 spectrofluorometer (Jobin Yvon Spex instruments, S.A. Inc) with a 450 W xenon excitation lamp. Thermo-gravimetric analysis (TGA, Seiko TG/ATD 320U, SSC 5200) was used to investigate the amount of surfactant bound on the particle surface. In the TGA, the samples were heated up to 800°C in air at a heating rate of 10°C min$^{-1}$. 

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5.3 Results and Discussion

5.3.1 Shape Control of ZnGa$_2$O$_4$: Eu$^{3+}$ Nanocrystals

ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres were prepared with a main surfactant of either hexadecanediol (HDD) or TOPO and a mixture of oleic acid, oleylamine and benzyl ether with Zn- and Ga-precursors. The Zn- and Ga-precursors and main surfactant were varied as shown in Table 4-1 to determine their effects on formation of ternary ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres.

Table 5-1. Precursors and surfactants used to synthesize ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Ga</th>
<th>Surfactant</th>
<th>Ratio of Zn/surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Zn(acac)$_2$</td>
<td>Gd(acac)$_3$</td>
<td>hexadecanediol</td>
<td>1:5</td>
</tr>
<tr>
<td>b</td>
<td>Zn acetate hydrate</td>
<td>Ga nitrate</td>
<td>hexadecanediol</td>
<td>1:5</td>
</tr>
<tr>
<td>c</td>
<td>Zn acetate hydrate</td>
<td>Gd(acac)$_3$</td>
<td>hexadecanediol</td>
<td>1:5</td>
</tr>
<tr>
<td>d</td>
<td>Zn(acac)$_2$</td>
<td>Gd(acac)$_3$</td>
<td>TOPO</td>
<td>1:2</td>
</tr>
</tbody>
</table>

For synthesis of ZnGa$_2$O$_4$ by solid state reactions (heating to high temperatures in air), Zn/Ga ratio much higher than one must be used because of the high vapor pressure of ZnO, but nonstoichiometric product was still reported [183-185]. In the present case, the Zn:Ga ratio in the purified Zn$_x$Ga$_{2-x}$O$_4$: Eu$^{3+}$ nanocrystals was essentially identical to that in the reactant mixtures. Most samples were prepared with the ratio of Zn:Ga of 1:1. This constant ratio between reactants and products probably is a result of similar precursors and solubilities of the Zn and Ga precursors in the nonhydrolytic liquid phase, and results in easy composition adjustments.

High resolution transmission electron microscope (HRTEM) images of ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres (from combinations a-d listed in Table 5-1 and discussed in section 5.2.2) are shown in Figure 5-1. The ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals are mainly monodisperse, crystalline spherical particles, with a diameter of <5 nm. The average diameter of ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres in sample (a) are larger (~3-4 nm) than samples (b-d) (~2-3 nm).
Figure 5-1. HRTEM images of ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres prepared with the precursors and surfactants corresponding to (a-d) in Table 5-1.

When the Zn precursor was changed to Zn acetate dehydrates with a ratio of Zn/hexadecanediol (1:2.5), complex shaped triangular and rectangular ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals were observed as shown in Figure 5-2. Because of the poor contrast in the TEM images, these nanocrystals could be nanoprisms and nanoplates rather than flat triangles and rectangles.

Figure 5-2. HRTEM images of ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals prepared with Zn acetate dehydrate with the ratio of Zn:hexadecanediol of 1:2.5 under standard conditions.
5.3.2 Size Control of ZnGa$_2$O$_4$: Eu$^{3+}$ Nanocrystals

In most colloidal techniques, particle synthesis from homogeneous solution involves nucleation and growth [186]. The surfactant ligand is critical to allow particles to grow to a specific size and then to arrest growth, therefore higher concentration could be expected to better limit the growth of nanocrystals. With higher concentration of stabilizing surfactants (over a limited range), smaller nanocrystals were obtained with a Zn(acac)$_3$ / oleylamine system [67]. It was reported that injection of additional surfactants, such as thiol, would arrest the growth and result in formation of smaller ZnO nanocrystals [187].

![HRTEM images of ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals](image)

Figure 5-3. HRTEM images of ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals synthesized with a ratio of Zn(acac)$_2$ / hexadecanediol (a-b) 1:2.5, and (c-d) 1:5; (e) selected area electron diffraction (SAED) pattern from a cubic spinel crystalline phase.

HRTEM images of the ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals using a 1:2.5 molar ratio of the Zn(acac)$_2$ / hexadecanediol are shown in Figure 5-3 (a-b). Nearly monodispersed, spherical nanocrystals >4-5 nm in diameter were observed. Smaller nanocrystals of <4 nm in diameter were obtained as shown in Figure 5-3 (c-d), when a 1:5 molar ratio of Zn(acac)$_2$ / hexadecanediol was used. The selected area electron diffraction (SAED) pattern of the
nanocrystals show rings from the (220), (311) and (400) planes of cubic spinel ZnGa$_2$O$_4$ (Figure 5-3(e)).

**5.3.3 Crystal Structures of ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals**

ZnGa$_2$O$_4$ has a cubic normal spinel crystal structure with Fd3m space group that can be thought of as a combination of rock salt and zinc blende structure (see Figure 5-4) [188]. The oxygen ions are in face-centered cubic close packed configuration. The unit cell contains 8 tetrahedral cations, 16 octahedral cations and 32 oxygen anions. The normal spinel ZnGa$_2$O$_4$ has tetrahedrally coordinated Zn sites surrounded by 4 oxygens and octahedrally coordinated Ga sites surrounded by 6 oxygens.

![Figure 5-4. The cubic spinel structure of ZnGa$_2$O$_4$][189].

Figure 5-5 is XRD patterns from ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals (samples (a-b) in Figure 5-3). Although peak broadening occurred due to the small size of the nanocrystals, all of the diffraction peaks could be indexed from the cubic spinel ZnGa$_2$O$_4$ structure (JCPDF 38-1240). The main peak from (311) planes of ZnGa$_2$O$_4$ is observed at a two-theta of 35.6$^\circ$ and no peaks from Ga$_2$O$_3$ or ZnO were found, consistent with single phase of ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals. The
mean crystal size is calculated with the Scherrer’s formula to be 5.0 nm, which is consistent with the size determined from the HRTEM image (Figure 5-3 (b)).

Figure 5-5. XRD pattern of ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals (sample (a-b) in Figure 5-3).

5.3.4 Luminescence properties of ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals

The photoluminescence excitation (PLE) spectrum of ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals (sample (a-b) in Figure 5-3) are shown in Figure 4-6. The PLE spectrum of Eu$^{3+}$ ion was obtained by monitoring the Eu$^{3+}$ $^5$D$_0$$\rightarrow$$^7$F$_2$ luminescence at 612 nm, and it consists of a broad intense band with a maximum 305 nm and two excitation peaks (stronger one is at 396 nm for $^5$F$_0$$\rightarrow$$^5$L$_6$ ) of Eu$^{3+}$. The 305 nm band is due to the charge transfer band (CTB) of O$^{2-}$-Eu$^{3+}$ together with absorption of ZnGa$_2$O$_4$ host lattice, which is shown in the inset of Figure 5-6.

The emission spectrum obtained by excitation into 305 nm is composed of characteristic emission peaks of Eu$^{3+}$ ion from 580 to 700 nm, which are associated with the transition from the excited $^5$D$_0$ level to $^7$F$_j$ ( J = 1,2,3,4 ) as seen in Figure 5-7. In the spinel ZnGa$_2$O$_4$ structure, Eu$^{3+}$ ions could occupy at two sites, tetrahedral Zn$^{2+}$ sites and octahedral Ga$^{3+}$ sites. It is known that the relative intensity of $^5$D$_0$-$^7$F$_1$ transition (magnetic dipole transition) and $^5$D$_0$-$^7$F$_2$ (electric dipole
transition) depends strongly on the local symmetry of Eu$^{3+}$ ions. When ions occupy the inversion center sites, the $^5D_0-^7F_1$ transition should be relatively strong, while the $^5D_0-^7F_2$ transition is partly forbidden and should be very weak. Therefore, the ($^5D_0-^7F_2$)/($^5D_0-^7F_1$) intensity ratio, known as the asymmetry ratio, is a measure of the degree of distortion from the inversion symmetry of the local environment of the Eu$^{3+}$ in the lattice. These ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals exhibit high ($^5D_0-^7F_2$)/($^5D_0-^7F_1$) intensity ratios, i.e. large asymmetry ratios, as seen in Figure 5-7, indicating strong electric fields and low symmetry at the Eu$^{3+}$ ions sites. This result suggest that the Eu$^{3+}$ ions occupies tetrahedral Zn$^{2+}$ sites or distorted octahedral Ga$^{3+}$ sites with no inversion symmetry in ZnGa$_2$O$_4$ nanocrystals. Since the ionic radii of Zn$^{2+}$ (0.6 Å) and Ga$^{3+}$ (0.62 Å) are so similar and much smaller than that of Eu$^{3+}$ (0.947 Å), there is no basis for speculating on a site preference based on ionic size.

Figure 5-6. PLE spectrum for emission at 612 nm from ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals. The inset shows the UV absorption spectrum of undoped ZnGa$_2$O$_4$ nanocrystals.
5.3.5 Thermo-gravimetric analysis (TGA)

The TGA data from ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals (sample in Figure 5-2) are shown in Figure 5-8. These ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals are relatively large (~20 nm) complex shaped particles coated with organic surfactants. The weight loss during heating from RT to ~200$^\circ$C was ~4% which is attributed to desorption of physisorbed molecules from the organic surfactants. The 16% weight loss in heating from ~200$^\circ$C to ~300$^\circ$C was presumably due to the desorption of organic surfactants from the particle surface. Decomposition of the surfactants is complete at 410$^\circ$C and results in a weight loss of 2% between ~300$^\circ$C and 410$^\circ$C. The total weight loss from desorption of surfactants from large complexed shaped ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals is ~20%, while the total loss was 35% for nanoplates and 42% for nanospheres of Gd$_2$O$_3$:Eu$^{3+}$, as reported in Chapter 3. This result is attributed to the previous conclusion that the relative amount of adsorbed surfactants decreases as the size of the nanocrystals increases.
5.4 Conclusions

Monodispersed Eu$^{3+}$ doped ternary ZnGa$_2$O$_4$ nanospheres (~5nm) were prepared from a variety of metal precursors by a nonhydrolytic thermal decomposition route. Using Gd acetate dehydrate, large (~20nm) complex shaped (triangle and rectangle) ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals were obtained. Based on X-ray diffraction data, the nanocrystals were concluded to have a cubic spinel structure with no impurity phases. The size of the ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres could be varied by changing the molar ratio of Zn to surfactants, with higher concentrations of surfactant (1: 5) resulting in smaller nanocrystals (~< 4 nm). Analysis of the PL emission suggests that the Eu$^{3+}$ ions were incorporated into the ZnGa$_2$O$_4$ host. It is concluded that the nonhydrolytic thermal decomposition synthesis route with organic surfactants not only allows the formation of stoichiometric ternary oxides, but also results in efficient incorporation of rare earth dopants.
CHAPTER 6  
CONCLUSIONS

6.1 Synthesis and Characterization of Luminescent Gadolinium Oxide Nanocrystals

1. Well dispersed, crystalline rare earth (Eu$^{3+}$, Tb$^{3+}$ and Er$^{3+}$) doped Gd$_2$O$_3$ nanocrystals were synthesized at 290°C (reaction time, ~3 h) by a hot solution nonhydrolytic route.

2. The shape of Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals were changed from nanospheres (<5nm) to nanoplates (1nm x <10nm$^2$) to mixed shaped nanocrystals (spheres, plates, rods, and triangles) by changes of Gd precursors, organic surfactants, concentrations and heating rate (between 200 and 290°C reaction temperatures).

3. The intensity of the Eu$^{3+}$ $^5$D$_{0}$→$^7$F$_2$ emission at 612nm from nanospheres was more intense than that from nanoplates or mixed shape nanocrystals due to a higher concentration (6.12 %) of Eu in nanospheres versus nanoplates (1.85 %) or mixed shape nanocrystals (1.24 %), and due to a higher nanocrystal product yield for purified nanospheres.

4. The three main factors leading to larger amounts of dopant in Gd$_2$O$_3$ nanocrystals are a slower rate of reaction, a larger product yield and monoclinic crystal structure. Use of Gd(acac)$_3$ precursor with oleic acid and HDD surfactants led to a slow reaction (~3 h) with high product yield (~80 %) and 6.1 % Eu incorporation for bright luminescent Gd$_2$O$_3$: Eu$^{3+}$ nanospheres.

6.2 Water Soluble Surface Modification of Luminescent Gadolinium Oxide Nanocrystals for Biomedical Research

1. Hydrophobic Gd$_2$O$_3$: Eu$^{3+}$ nanocrystals were surface modified by Octylamine-modified poly(acrylic acid) (PAA), amphiphilic polymer. The surface conversion results in a dispersion of nanocrystals in aqueous solutions stable in lab ambient for >31 days, especially for nanocrystals synthesized using oleic acid and hexadecanediol (HDD).

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2. The PL spectra from Gd$_2$O$_3$:Eu$^{3+}$ were unchanged by the PAA surface modification, but the PL intensity was decreased to 47% and 26% of the hydrophobic capped value for synthesis with HDD and hexadecylamine (HDA), respectively.

6.3 Synthesis and Characterization of Ternary ZnGa$_2$O$_4$: Eu$^{3+}$ Nanocrystals

1. Monodispersed Eu$^{3+}$ doped ternary ZnGa$_2$O$_4$ nanospheres (~5nm) were prepared from a variety of metal precursors by a nonhydrolytic thermal decomposition route. Using Gd acetate dehydrate, large (~20nm) complex shaped (triangle and rectangle) ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals were obtained.

2. ZnGa$_2$O$_4$: Eu$^{3+}$ nanocrystals had a cubic spinel structure with no impurity phases from X-ray diffraction and selected area diffraction pattern.

3. The size of the ZnGa$_2$O$_4$: Eu$^{3+}$ nanospheres was controlled by changing the molar ratio of Zn to surfactants from 1:1 to 1:5, with higher concentrations of surfactant (1:5) resulting in smaller nanocrystals (~4 nm).

4. Analysis of the PL emission suggests that the Eu$^{3+}$ ions were incorporated into the ZnGa$_2$O$_4$ host. The nonhydrolytic thermal decomposition synthesis route with organic surfactants not only allows the formation of stoichiometric ternary oxides, but also results in efficient incorporation of rare earth dopants.
CHAPTER 7
FUTURE WORK

It is evident that the above approaches can lead to success in shape and size control of nanocrystals. This would be very useful in incorporating luminescent oxide nanocrystals with nonhydrolytic liquid phase synthesis. This method can be expanded to other efficient luminescent oxide systems.

As with a doping issue in this synthetic route, efficiency is not good comparing to the solid state reaction. Liquid phase synthesis has still a possibility to lost dopant ions into solvent during synthesis. The synthetic condition could be modified to make the reaction stable for better incorporation of dopant by trial of various chemical combinations. The fine control of dopants could allow the co-doped oxide nanocrystals (i.e. Gd$_2$O$_3$:Er$^{3+}$, Yb$^{3+}$ and YVO$_4$: Er$^{3+}$, Yb$^{3+}$, etc) to be synthesized through this protocol for efficient up-conversion phosphor.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

SooYeon Seo was born in Seoul, South Korea and received her early education in this city. She was allowed access to the laboratory tools in her home from an early age. This early influence of science has had a lasting impact on her interest in phenomenon in nature and led to a foundation of evolutionary thinking in her pursuit of understanding the materials, in the kinds of research questions that have intrigued her. After she received a M.A in materials science and engineering, in South Korea, she obtained her Ph.D. degree from the Department of Materials Science and Engineering, University of Florida in Gainesville, US in 2007.

SooYeon Seo’s general research interests are in the area of luminescent materials in electro- and bio- application. The general theme of her current research interests deals with synthesis and characterization of luminescent oxide nanocrystals related to the candidate for the bio-labeling application in bio-medicine. She also has other interests and has done research on such topics as the luminescent nanocrystals as well as general issues related to methodology and optical analysis in electronic and bio-applications.