

Synthesis of Lanthanide Fluoride Nanoparticles of Varying Shape and Size

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Yttrium fluoride nanoparticles of varying crystallinity, shape, and size are prepared by precipitation in reverse microemulsions of water in cyclohexane stabilized with polyoxyethylene isoctylphenyl ether. YF₃ particles obtained by the classical microemulsion method are found to be monodisperse amorphous spheres, with controllable diameters between 6 and 50 nm. Particles of the same material obtained by a relatively minor variation of this method are found to be monocrystalline. Typically, mixtures of monodisperse regular hexagonal and triangular single crystals are observed. The size of the crystalline particles can be varied between about 25 and 350 nm. The formation of single crystals can be attributed to the slower incorporation of the precipitant into the micelles when introduced in this fashion.

Introduction

Recent scientific literature demonstrates a growing interest in new methods of nanoparticle synthesis, driven primarily by an ever increasing awareness of the unique properties and technological importance of nanostructured materials. Major issues associated with nanoparticle preparation include the control of particle size and internal structure. The fabrication of nanoparticles within reverse microemulsions^{1–4} has been shown to be a convenient route to monodisperse particles of controllable size. This method exploits two useful properties of reverse microemulsions: the capacity to dissolve reactants in the water core and the constant exchange of the aqueous phase among micelles. Within the microemulsion, micelles are in constant Brownian motion and thus collide frequently. A small fraction of these collisions result in micelle fusion which give rise to short-lived dimers.⁵ The dimers subsequently separate to form new micelles containing a mixture of the solutions enclosed in the two original micelles. Thus, by mixing microemulsions containing different reactants, it is possible to perform chemical reactions inside the reverse micelle water pool, using it as a nanoreactor.⁶ If this reaction results in a solid compound, nanoparticles are created and their growth is limited by the micelle size. This method has been studied for some years and has been widely used for metal,^{2,3} semiconductor,⁴ and oxide⁷ nanoparticle synthesis. To the best of our knowledge, it has not yet been applied to the preparation of nanoparticles of lanthanides salts.

The unique luminescence properties of lanthanide ions incorporated in glass matrixes have long been recognized.^{8,9} Recent structural studies^{10–12} suggest that lanthanide fluorides, including YF₃, may be useful as new laser materials. In this paper, we present the synthesis of YF₃ nanoparticles by the reverse micelle method. We show that both amorphous and single-crystal particles can be obtained and that particle size can be controlled. Monocrystalline YF₃ nanoparticles are found to present a surprising variety of regular shapes.

Experimental Section

The nanoparticles were prepared using the two methods outlined below. All chemicals were supplied by Aldrich and used as received without further purification.

Classical Microemulsion Method. Amorphous yttrium fluoride nanoparticles were prepared using the previously described microemulsion method.^{13,14} Microemulsions were first prepared by mixing varying amounts of an aqueous solution, containing either yttrium chloride (YCl₃) or ammonium hydrogen difluoride (NH₄HF₂), with 2 g of the surfactant igepal CO520 (also known as NP-5 or polyoxyethylene(5)isoctylphenyl ether) and 15 mL of cyclohexane. Homogeneous microemulsions were obtained by mixing with a magnetic stirrer followed by 20 min in an ultrasonic bath. Equal quantities of the two separate microemulsions containing YCl₃ and NH₄HF₂ were then mixed together, with agitation at ambient conditions, to produce the YF₃ particles. The resulting suspension was clear to the eye. Particles were prepared in systems of differing water content by varying the volume of aqueous solution incorporated in the microemulsions from 0.1 mL to 2.0 mL while

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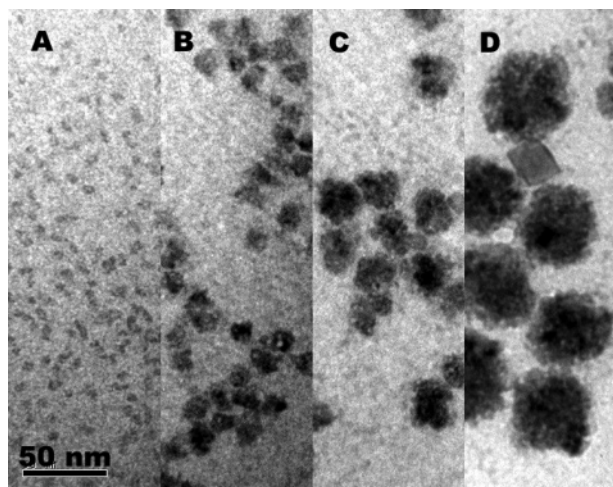


Figure 1. YF_3 nanoparticles obtained by the mixing of two microemulsions containing YCl_3 and NH_4HF_2 , respectively, at water-to-surfactant molar ratios equal to (a) 1.2, (b) 6.1, (c) 12.2, and (d) 24.4.

maintaining constant quantities of surfactant and cyclohexane. The concentrations of the aqueous solutions were varied from 0.2 to 0.01 M in order to produce the same quantity of particles at different water contents.

Single Microemulsion Method. Monocrystalline yttrium fluoride nanoparticles were prepared by a minor modification of the method described above. A microemulsion was first prepared by mixing 0.5 mL of 0.04 M aqueous YCl_3 and 2 g of igeal CO520 in 15 mL of cyclohexane. As above, the microemulsion was mixed with a magnetic stirrer followed by 20 min in an ultrasonic bath. With vigorous stirring at ambient conditions, 0.5 mL of aqueous 0.04 M NH_4HF_2 was then added directly to the microemulsion. The resulting suspension of YF_3 nanocrystals appeared clear. A decrease in the surfactant concentration from 0.3 to 0.02 M resulted in the formation of larger particles.

Transmission electronic microscopy (TEM) images and electron diffraction patterns were recorded with a JEOL JEM-1230 at an accelerating voltage of 120 kV. Samples were prepared by allowing a drop of the YF_3 suspensions, as obtained by the syntheses described above, to dry directly on a Formvar coated nickel microscope grid. Size measurements were made of randomly selected particles on TEM images. Electron probe microanalysis (EPMA) measurements were performed with a CAMECA SX-100. EPMA specimens were prepared by evaporating drops of the particle suspensions on aluminum foil. Excess surfactant was removed before analysis by washing with methanol.

Results and Discussion

Particles Obtained by the Classical Microemulsion Method. TEM images of the particles obtained by the mixing of two microemulsions, containing YCl_3 and NH_4HF_2 , respectively, are shown in Figure 1, for four different water contents. These images indicate that primarily spherical nanoparticles are obtained in all cases. Electron diffraction measurements reveal only diffuse halos, indicating the amorphous nature of the particles.

The mixing of YCl_3 and NH_4HF_2 via micelle fusion should lead to the precipitation of insoluble YF_3 . Unfortunately, the small size of the particles obtained by this process prohibits the determination of their chemical composition by electron probe microanalysis. Similarly, their amorphous nature renders identification by electron diffraction equally inac-

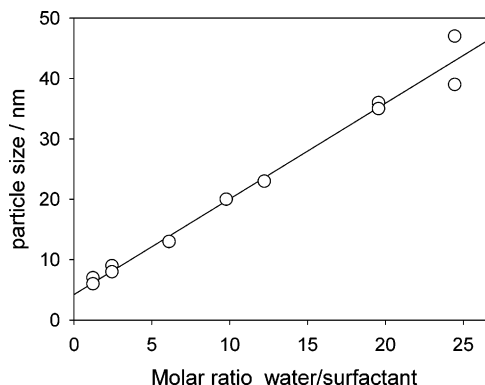


Figure 2. Size of nanoparticles obtained by mixing of two separate microemulsions containing YCl_3 and NH_4HF_2 , respectively, as a function of the water content in each of the microemulsions. Particle sizes were determined from TEM images.

cessible. The identification of the nanoparticles as YF_3 is therefore only possible through indirect experiments. TEM images recorded for electron microscope grids prepared by the evaporation of a single microemulsion containing only YCl_3 are found to be featureless. It can be thus concluded that the nanoparticles shown in Figure 1 are not simply formed from soluble salts within the micelles during the evaporation of the volatile microemulsion components. For this reason, we have tentatively identified the particles as being composed of YF_3 . Clearly the other inorganic components of the mixture (presumably NH_4Cl) remain within the samples. At this time, we can only speculate that the soluble components are present on the TEM grid as featureless thin films.

Importantly, particle size is found to vary systematically with the water content of the system, as expected from previous results.^{1,15} The quantity of reactants available for a reaction occurring within a micelle is limited by the concentrations of the enclosed solutions and the size of the micelles themselves. The concentrations can obviously be easily controlled. Furthermore, the total volume of the micelles is determined by the water content, whereas the total surface area of the micelles is limited by the amount of available surfactant.^{1,5} Thus, by varying the water/surfactant molar ratio, it is possible to change the micelle size and, therefore, the particle size. Figure 2 illustrates that the average particle size is indeed found to vary systematically with the molar ratio of water to surfactant in the microemulsion. The range of particle sizes attainable with this method is, however, limited by the range of water contents for which the microemulsions are stable. Furthermore, at high water content, the polydispersity of the particles is observed to increase. This method therefore allows for the convenient preparation of relatively monodisperse amorphous YF_3 nanoparticles of controlled size between 6 and 47 nm.

Particles Obtained by the Single Microemulsion Method. TEM images of YF_3 nanoparticles obtained by the direct addition of a solution of NH_4HF_2 to a microemulsion containing YCl_3 are shown in Figure 3. As illustrated, a variety of well-defined particle shapes are observed. TEM analysis of many samples indicates that the majority of the

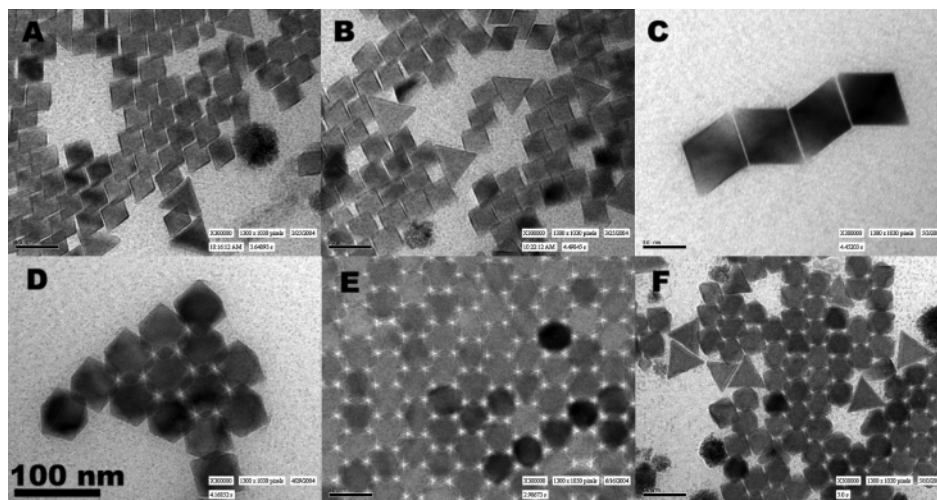


Figure 3. Different morphologies of LnF_3 nanoparticles obtained by adding aqueous NH_4FHF to a microemulsion containing LnCl_3 : (a) and (b) typical mixtures of predominant YF_3 particles morphologies, (c) YF_3 quadrilateral shaped particles, (d) YF_3 hexagonal particles, (e) self-assembly of YF_3 hexagonal particles, and (f) ErF_3 particles.

shapes observed are hexagonal, while a significant minority of triangles and quadrilaterals are observed. Rotation of the sample grid indicates that the hexagonal and quadrilateral shapes represent, in fact, different faces of the same particle morphology. Triangular shapes appear to arise from a different crystal habit. The formation of the various particle shapes is quite reproducible, with all habits being present in different batches of particles prepared by the same procedure. The proportions of the various particles do seem to vary somewhat from one preparation to another, but this is difficult to quantify because of the partial nature of sampling by TEM. Particle size was found to increase with decreasing surfactant concentration, and hexagonal particles with diameters reaching 350 nm were obtained for electron probe microanalysis.

The chemical compositions of nanoparticles were determined by electron probe microanalysis (EPMA). Measurements were made on 350-nm hexagonal particles, obtained from microemulsions with reduced surfactant content. Microprobe analysis is restricted to larger particles because of the poor resolution of the apparatus. We are, however, confident that these results can be extended to smaller particles since electron diffraction measurements, presented below, confirm identical crystal structures for the smaller particles. EPMA analyses qualitatively revealed the presence of yttrium and fluorine. Importantly, no chloride was detected. These measurements thus permit the identification of particles as YF_3 , as confirmed by the electron diffraction measurements presented below.

The well-defined shapes of the particles illustrated in Figure 3 indicate the crystalline nature of the particles. Figure 4 shows the diffraction rings generated by an ensemble of particles containing all of the different shapes. The d spacings evaluated from the positions of the diffraction rings are reported in Table 1 and found to be in good agreement with the known data¹⁶ for orthorhombic YF_3 , thus confirming the chemical identification indicated by EMPA measurements. The crystalline nature of the particles is also confirmed by the electron diffraction pattern of a single particle shown in Figure 5, which clearly arises from a single crystal. Importantly, identical diffraction patterns are obtained from

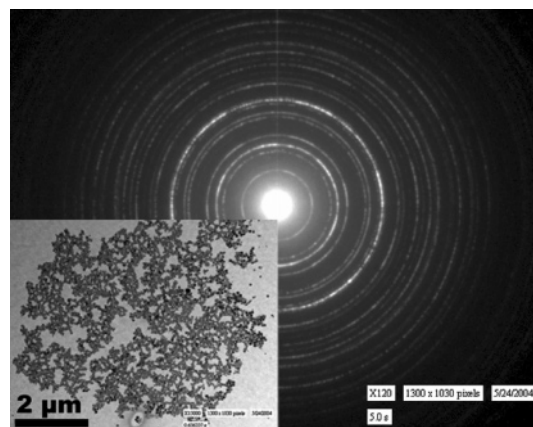


Figure 4. Electronic diffraction rings pattern from an ensemble of yttrium fluoride nanoparticles of various morphologies.

Table 1. Interplanar Spacing (Å) of Yttrium Fluoride Experimentally Determined from the Electronic Diffraction Pattern Presented in Figure 4^a

experimental electronic diffraction	literature ¹⁶ X-ray diffraction
5.46	
3.59	3.612 (101)
3.19	3.197 (111)
2.76	2.886 (210)
2.19	2.196 (002)
2.09	2.076 (102)
1.91	1.910 (301)
1.84	1.840 (311)
1.59	1.5914 (400)
1.38	1.3713 (421)
1.32	1.3217 (142)
1.26	1.2666 (412)

^a Literature X-ray diffraction data¹⁶ are provided for comparison.

hexagonal and triangular particles. This observation indicates that the two habits arise from the same polymorph of YF_3 and that the diffraction pattern, in fact, originates from the same diffraction plane. Thus far, however, we have been unable to index the single-crystal diffraction pattern of Figure 5 with the literature assignments for orthorhombic YF_3 .

(16) JCPDS International Centre for Diffraction Data, Powder Diffraction File, 32-1431, 1988.

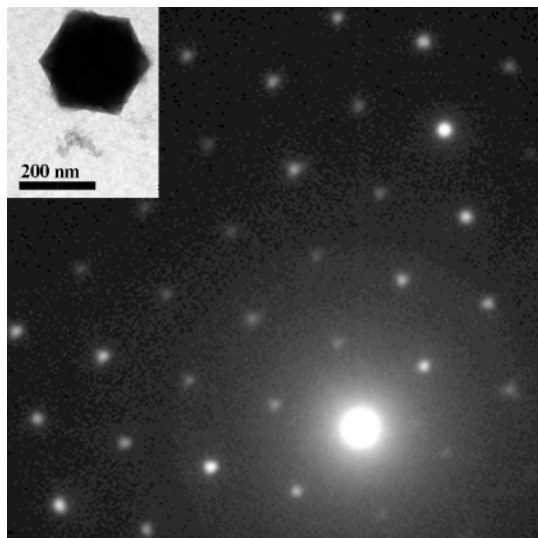


Figure 5. Electronic diffraction pattern from a single hexagonal shaped crystal.

Furthermore, the observation of hexagonal and triangular crystal habits, as well as the single crystal diffraction pattern of Figure 5, suggests rather a trigonal structure analogous to that recently reported by Yan et al.¹⁷ for LaF_3 triangular particles. Further work, aimed primarily at obtaining complete single-crystal diffraction patterns through higher-resolution TEM, is required before a more complete analysis of the crystal structure of the particles can be provided.

Comparison of the images presented in Figures 3 with those of Figure 1 indicates that very different particles are produced by the two methods of preparation. The amorphous nature of the particles obtained by the first method (mixing of two microemulsions) suggests that precipitation of YF_3 occurs rapidly in this case. Conversely, the single crystals obtained by the second method (the addition of a solution of NH_4HF_2 to a microemulsion containing YCl_3) suggest a slower crystallization process. The incorporation of an added aqueous phase into existing micelles would in fact be expected to be less rapid than the quasi-instantaneous solution exchange that occurs upon micelle fusion. Even if the frequency of micelle fusion is relatively low, when fusion occurs, the mixing of the contents, and thus the precipitation of the insoluble salt, will be rapid.

The possibility that particle crystallization may occur outside the micelles in the second method can also be considered. However, the dependence of particle size on surfactant concentration, and hence on micelle size, seems to suggest otherwise. In addition, the constant distance of separation observed between the single crystal particles shown in Figure 3 suggests a surfactant coating on the surface of the crystals. Such a coating would be expected to result only from particle growth within the micelles.

A final noteworthy feature of the nanoparticles obtained in this work is their propensity to self-assemble over relatively large distances. This is illustrated by the various images presented in Figure 3, with Figure 3e exhibiting the most striking case. The self-assembled particles seem to be separated by an equivalent distance, suggesting the particles are coated with surfactant. This feature could be useful, as we plan to eventually disperse these particles in polymer matrixes.

The same synthetic route has been employed for other lanthanides fluorides, including ErF_3 (shown in Figure 3h) and YbF_3 , and similar regularly shaped nanoparticles were obtained. We therefore believe that this method may be extended to all lanthanides fluorides, and perhaps even to other compounds.

Conclusions

Yttrium fluoride nanoparticles can be conveniently prepared by the reverse micelle method. Particles prepared by the mixing of two microemulsions results in the precipitation of amorphous spherical particles. Furthermore, particle size can be controlled by varying the water-to-surfactant ratio. A second method of preparation, consisting of the direct addition of a fluoride solution to a microemulsion containing YCl_3 , results in monodisperse single crystals. Two different crystal habits are found, both of which present the same crystal structure.

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