Synthesis and Characterization of Lanthanide-Doped Silica Microspheres

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We report the synthesis of silica nanoparticles and microspheres doped with Pr^{3+} and Er^{3+}. Acetic acid is used to catalyze the hydrolysis and condensation of tetraethyl orthosilicate in the presence of $LnCl_3 \cdot 6H_2O$. The particles are spherical and discrete with particle sizes and size distributions controllable by variation of the reactant concentrations and reaction time. The relative standard deviation of particle diameters can be as low as 10%. The particles exhibit bright room-temperature luminescence when excited by an argon ion laser at 488 nm.

Introduction

Silica or silica-based glass doped with lanthanide ions is a visible/near-IR optically active material widely used for photonic applications, including lasers and optical fiber amplifiers.[1–3] Lanthanide-doped silica glass can be made in bulk by any of several methods including high-temperature vapor phase processing,[2,4] sol–gel chemistry,[5–7] or ion implantation.[8,9] There has been much recent interest in the synthesis of nanoscale particles doped with lanthanide ions because the optical properties of these materials may be modified as the dimensions of the host material are reduced.[10,11] In addition, producing silica colloids of predictable size and shape doped with a controllable concentration of lanthanide ions has significant potential for use in optical devices such as microlasers,[12] thin-film device structures,[13,14] active photonic band gap materials,[15,16] and luminescent markers or nanosensors.[17–20]

Currently there are few synthetic methods for preparing lanthanide-doped silica particles. The methods that currently exist allow for limited control over the physical and chemical characteristics of the doped particle. One chemical method used to incorporate neodymium or europium ions into silica microspheres produces particles with diameters ranging from approximately 5 μm to more than 1 mm.[21,22] Sonochemistry has been used to react lanthanide nitrates with tetraethyl orthosilicate (TEOS) in a basic environment, but this method produces a large fraction of nanoparticle agglomerates with irregular shapes and sizes and unpredictable doping densities.[23] Ion implantation has been used to dope films of silica nanoparticles, but only a few particles can be doped at one time, and the level of doping is not homogeneous throughout the film depth.[8,9] In this article we report the controlled growth of silica nanoparticles and microparticles doped with Pr^{3+} and Er^{3+} via solution-phase chemistry. The method results in incorporation of lanthanide ions during the acid-catalyzed growth of silica particles. Variation of reaction time and lanthanide concentration can produce batches consisting of microparticles with low polydispersity, or highly polydisperse batches of particles ranging from less than 300 nm to almost 3 μm in diameter which exhibit room-temperature photoluminescence.

Experimental Section

Materials and Instrumentation. $PrCl_3 \cdot 6H_2O$ (99.9%), $ErCl_3 \cdot 6H_2O$ (99.995%), glacial acetic acid, and TEOS (99.999%) were

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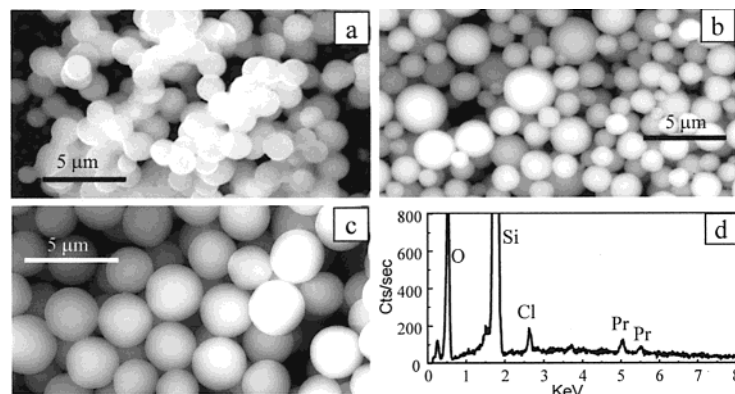
Figure 1. Scanning electron microscopy images showing (a) necked silica microparticles without added dopant, (b) Pr-doped polydisperse particles, (c) low polydispersity Pr-doped microparticles, and (d) an EDAX spectrum of the more monodisperse Pr-doped microparticles shown in c.

obtained from Aldrich Chemical Co. (Milwaukee, WI). All chemicals were used as received. Ultrapure water (18.2 MΩ cm^{-1}) from a Milli-Q system (Millipore) was used directly. Particles are synthesized directly in clear polypropylene centrifuge tubes (15 mL, Fisher). Scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDAX) were performed on a Phillips XL30 ESEM. Electron microprobe analysis was performed on a Cameca SX50 Electron Microprobe. Luminescence spectra were obtained by exciting dry powder samples in air with an Ar ion laser at 488 nm, then collecting and focusing the emitted light onto a 25-cm focal length monochromator and detecting a luminescence signal by using a lock-in amplifier (SRS850, Stanford Research Systems, CA) and standard lock-in techniques. Visible emission was detected with a photomultiplier tube (R928, Hamamatsu Corp.), and infrared emission was detected with a thermoelectrically cooled InGaAs detector (IGA-030/TE2, Electro-Optical Systems Inc.).

Particle Synthesis and Treatment. Doped silica particles can be synthesized by adding 0.5–2% $LnCl_3 \cdot 6H_2O$ to mixtures of acetic acid and water. This amount of dissolved salt gives a slight but noticeable color to the solution. After the lanthanide salt is fully dissolved in the acid–water solution TEOS, which has been stored under dry N_2, is rapidly added. A range of molar compositions [TEOS:CH_3COOH:H_2O = 1:(4.0–8.0):(1.5–5.0)] can be used to achieve discrete particles. A typical reaction uses 9 mL of acetic acid, 1.6 mL of H_2O, 0.1 g of $LnCl_3 \cdot 6H_2O$, and 4.5 mL of TEOS. The mixture is agitated for 5–30 s or until the solution turns cloudy white. At this point the mixture is allowed to react for up to 30 min. During the course of the reaction the doped particles will sediment to the bottom of the centrifuge tube. After reacting, the mixture is centrifuged and redispersed in ethanol several times. If the supernatant from the original reaction mixture is left undisturbed for several hours, it will form a clear, brittle, colored solid indicating that not all of the TEOS is used in the particle synthesis, and not all of the lanthanide salt is incorporated.

Before luminescence measurements, particles are heated to 750 °C in air for 24 h to remove any adsorbed water, alcohol, or remaining acetate groups and to promote a more complete condensation of the surface and interior silanol groups.[23,24] This thermal treatment should reduce quenching of the lanthanide luminescence by OH vibrations.[25,26]

Results and Discussion

Monodisperse silica nanoparticles are typically synthesized via the base-catalyzed hydrolysis of TEOS.[27] Lanthanide salts form insoluble lanthanide hydroxides in basic environments, therefore lanthanide salt incorporation is inconsistent with silica particles grown by means of a base-catalyzed reaction. The acid-catalyzed hydrolysis of TEOS generally results in large particles with sizes and size distributions that are difficult to control.[24,28–30] When TEOS is added to a solution of acetic acid and water, silica microparticles are produced that are connected by neck growth as shown in Figure 1a. Karmakar et al. report that, when this growth method is used, the percentage of particles attached to one another by neck growth is between 50% and 80%.[30] A more recent study suggests that large agglomerated silica particles formed during the acetic acid-catalyzed reaction may be separated from one another by washing with ethanol and acetone, and drying at 150 °C.[31]

When TEOS reacts in an acidic solution of $LnCl_3 \cdot 6H_2O$ the salt ions become included within the growing silica matrix.[20–22] As shown in Figure 1b,c the additional lanthanide salt in solution eliminates neck growth, which results in spherical, discrete particles. The formation of discrete particles instead of necked particles may result from the increase in the concentration of ions that stabilize colloids in solution. However, at a high ionic concentration only very large nonspherical agglomerates of doped silica form. This indicates that the colloidal double layer is reduced, minimizing Coulombic repulsion of the particles, and particle–particle interactions arising from van der Waals forces cause the particles to coagulate. One can observe doped particles forming and falling out of suspension within 30 s of the TEOS addition, whereas a solution of acetic acid and water without added salt may require several minutes before the added TEOS will form particles large enough to turn the solution cloudy. We have determined by elemental analysis that not only lanthanide ions are present in our particles, but chloride ions as well. As the TEOS reacts with the acetic acid, and the silica network begins to grow, both lanthanide ions and chloride ions will become trapped in favorable sites within the silica framework. Lanthanide ions will tend to cluster around isolated Ln^{3+} ions in silica glass without the addition of network modifiers such as oxides of alkali metals and alkali-earth metals that provide charge compensation and coordination balance.[2] Codoping silica with both Ln^{3+} ions and Al^{3+} ions is another way to achieve

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well-coordinated lanthanides, which should then allow the Ln^{3+} ions to be doped at higher concentrations without concentration quenching of the light emission.[2,23] Although we do observe luminescence from our doped particles, it is possible that by using a codoping technique we could achieve higher lanthanide ion concentrations and an increase in emission.

During heat treatment, evaporation of fluids from the capillaries in the interior of the particles causes the particles to shrink, in some cases, to approximately half of their unbaked sizes.[6,7] We chose to heat our particles to 750 °C to eliminate as many hydroxyl groups as possible while still leaving enough surface functionality to maintain the hydrophilic nature of the particles and allow for future surface functionalization. We have confirmed that sufficient hydroxyl functionalities remain on the surfaces of the baked particles to deposit monolayers of alkoxysilanes.

By changing the concentration of salt for a given ratio of TEOS:CH_3COOH:H_2O and varying the reaction time we are able to control the average particle size, the degree of polydispersity, and the doping density of the particles. Figure 1b shows a sample of highly polydisperse Pr-doped silica nanoparticles and microparticles from a solution of 1% $PrCl_3 \cdot 6H_2O$ and with a reaction time of 30 min. These particles range in size from less than 300 nm to approximately 2.5 μm in diameter. Figure 1c shows a sample of Pr-doped silica microparticles with an average size of 2.8 μm with a relative standard deviation of 10% and a reaction time of 5 min. The acetic acid-catalyzed reaction seems to proceed by the nucleation of an initial population of particles, which grow at approximately the same rate. This is followed by continual nucleation and growth of further particles throughout the course of the reaction. This pattern is also seen during the formation of undoped silica microparticles with acetic acid as a catalyst.[31] By stopping the reaction after the nucleation and growth of the first generation of nuclei, more monodisperse samples can be obtained.

For the samples shown in Figure 1b,c the ratio of TEOS:CH_3COOH:H_2O and the concentration of $LnCl_3 \cdot 6H_2O$ were held constant with different reaction times. The resulting doping density of Pr^{3+} in Figure 1b is 0.34 wt %, and in Figure 1c is 0.28 wt % as determined by EDAX. Figure 1d shows an EDAX spectrum of the Pr-doped particles in Figure 1c. EDAX serves as a rough estimate for the quantitative determination of elemental concentration. We have cross-checked several of our samples by using electron microprobe analysis and found good agreement with the EDAX measurements. Measurements were taken at several points on a given sample with only small variation in measured doping density between each point.

For a constant reaction time, samples of greater monodispersity are obtained by reducing the concentration of added $LnCl_3 \cdot 6H_2O$. As seen in Figure 2a,b both the average particle size and the particle size distribution increase with increasing amounts of lanthanide salt. The reaction yield is variable for a given reaction time, even with all reactant quantities held constant. This is due to the variability in the activation of the reaction by mixing the components. In general, the percent yield will be between 1% and 10% for any reaction proceeding up to 30 min. There is a minimum TEOS volume fraction of approximately 30% required before particles will nucleate. Allowing the reaction to proceed for significantly longer that 30 min will not give an appreciably higher particle yield.

The photoluminescence of Pr-doped particles as well as Er-doped particles was also measured. Figure 3a presents
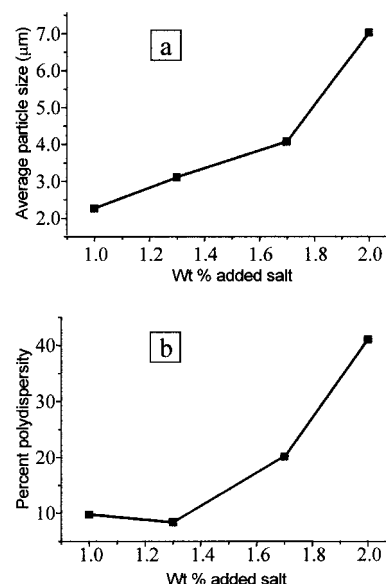

Figure 2. Relationship between the amount of added lanthanide salt: (a) average particle size and (b) percent polydispersity.
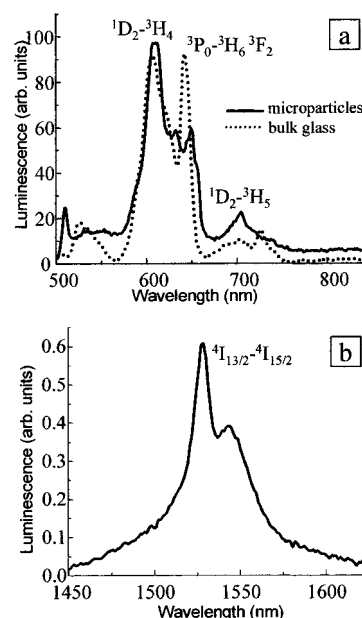

Figure 3. Photoluminescence spectra of (a) Pr-doped silica microparticles and (b) Er-doped silica microparticles.

the photoluminescence spectrum of Pr-doped silica microspheres. All spectra were taken at room temperature in air. The photoluminescence spectrum of Pr-doped microparticles exhibits the same $^1D_2$-$^3H_4$, $^3P_0$-$^3H_6$, $3P_0$-$^3F_2$, and $1D_2$-$^3H_5$ electronic transitions as Pr-doped bulk glass.[32] Differences in spectral shape arise because the bulk glass is a multicomponent glass sample composed of several different types of oxides which allows the dopant ions to be distributed differently throughout the glass matrix relative to one another than they are distributed throughout pure silica particles.[5,33] Figure 3b presents the IR emission spectrum of Er-doped silica microparticles. The $^4I_{13/2}$-$^4I_{15/2}$ transitions at 1.52 μm and 1.55 μm are present.

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Conclusions

We have developed a process for synthesizing lanthanide-doped silica nanoparticles and microparticles of controllable size, polydispersity, and doping density. Reaction time and the concentration of added lanthanide salt determine the percent polydispersity and doping density of the particle batches. These particles range in size from 300 nm to 3 μm in diameter. All particles exhibit room-temperature photoluminescence.