

Acid-Based Synthesis of Monodisperse Rare-Earth-Doped Colloidal SiO₂ Spheres

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Introduction

Monodisperse colloidal spheres in solution can self-organize into an ordered structure if their size polydispersity is low enough. In such a colloidal crystal the dielectric constant shows a periodic variation with position. If the length scale of this periodic variation is comparable to the wavelength of visible or near-infrared wavelengths, the structure can Bragg-reflect the light, leading to interesting optical properties. The properties of such a photonic crystal can be studied by placing luminescent probes inside the crystal.¹ For example, fluorescently labeled spheres can be used to study colloidal crystals in real space by confocal microscopy.² Commonly, laser dyes are used for this purpose and are chemically incorporated into the SiO₂ particles during synthesis.^{3,4} However, to study the effect of the photonic crystal on spontaneous emission or to probe the local optical density of states, dyes are impractical, as their emission spectrum is often broader than the photonic feature under study.^{4,5} In contrast, rare earth (RE) ions incorporated in SiO₂ display narrow-line intra-4f transitions that are first order independent of the local environment. In addition, the luminescence from RE ions is often improved by thermal treatments, extending the experimental range of RE luminescent probes to sintered colloidal crystals. Also, RE ions do not exhibit photo bleaching commonly observed for laser dyes. Thus, RE-doped colloids appear to be ideal probes in photonic crystals.

So far, ion implantation was used to dope monodisperse spherical SiO₂ particles with Er³⁺.⁶ However, this technique only yields a limited amount of particles. In this communication we describe a new method to dope SiO₂ particles with RE ions via an acid-based wet

chemical synthesis route by adding the appropriate RE-chloride to the reaction mixture. This method was explored recently to synthesize Pr³⁺ and Er³⁺ silica microspheres.⁷ In addition, we also describe a seeded growth process in which a thin shell of Er³⁺-doped silica is grown on existing, monodisperse silica colloids. The growth and luminescence properties of the particles are studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Rutherford backscattering spectrometry (RBS), and photoluminescence (PL) spectroscopy.

Experimental Section

All chemicals were used as received without further purification. Tetraethoxysilane (TEOS) (purity = 99%) was supplied by Fluka Chemie AG, KOH was supplied by Aldrich, and glacial acetic acid was supplied by Biosolve. Ethanol (Merck) was of analytical grade. ErCl₃, EuCl₃·6H₂O, and TbCl₃·6H₂O (purity = 99.9%) were all supplied by Acros Organics.

SiO₂ colloids were produced by adding TEOS to a mixture of glacial acetic acid and water under continuous stirring for 30 min at room temperature. The molar composition of TEOS:CH₃COOH:H₂O was 1:4:4, which results in dense (2.14 ± 0.02 g cm⁻³) spherical SiO₂ colloids.^{8,9} Rare-earth (RE) ions were incorporated into the SiO₂ by replacing the water with an aqueous solution of 1 wt % ErCl₃, EuCl₃·6H₂O, or TbCl₃·6H₂O, respectively. After synthesis, the SiO₂ particles were separated from the solution by centrifuging at 1000 rpm and washed at least twice with pure ethanol. Seeded growth experiments were conducted using a slightly different molar composition, TEOS:CH₃COOH:H₂O of 1:8:8, and using a 0.2 wt % ErCl₃ solution. The total reaction time in this case was 45 min. The SiO₂ seed particles were made in a microemulsion^{10,11} and subsequently grown larger in a base-catalyzed seeded growth procedure.^{11,12}

SiO₂ particles were deposited on a Si substrate that was cleaned for 2 min in a KOH in ethanol solution. This was done by evaporating the ethanol from a droplet of the particles in suspension on the substrate. Particles were annealed at 900 °C for 30 min under flowing oxygen (4 L min⁻¹). Photoluminescence (PL) measurements were done on the particles on a Si substrate as well as on quartz cuvettes containing suspensions of the particles in a mixture of dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) (*n_D* = 1.45) that roughly index matches the particles to suppress strong light scattering.

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The 465.8-nm (Eu^{3+}) and 488.0-nm (Er^{3+} , Tb^{3+}) lines of an Ar ion laser, modulated on–off at frequencies of 7–11 Hz with an acousto-optic modulator, were used as an excitation source. The luminescence was focused on the entrance slits of a 48-cm grating monochromator and detected by a liquid-nitrogen-cooled Ge detector ($\lambda = 800\text{--}1700\text{ nm}$) or an AgOCs photomultiplier tube ($\lambda = 400\text{--}1100\text{ nm}$) employing standard lock-in techniques. Decay curves were recorded using a digitizing oscilloscope in combination with the Ge detector for Er^{3+} (time response $30\ \mu\text{s}$) or a multichannel scaler system in combination with the photomultiplier tube for Eu^{3+} and Tb^{3+} (time response 100 ns , limited by the AOM).

Scanning electron microscopy (SEM) images were taken at a resolution better than 5 nm using 5-keV electrons. Transmission electron microscopy (TEM) images were taken using 200 keV with particles dried from the suspension on standard Cu TEM grids. To determine the elemental composition of the rare-earth-doped colloids, Rutherford backscattering spectroscopy (RBS) of 2-MeV He^+ particles was used at a scattering angle of 165° .

Particle Synthesis

Colloidal SiO_2 particles can be formed by either an acid-catalyzed reaction^{8,9} or a base-catalyzed (Stöber) reaction.¹³ The base-catalyzed reaction, using ammonia, ethanol, water, and tetraethoxysilane (TEOS), can be controlled to yield spherical SiO_2 particles with low size polydispersity. Seeded growth has been applied on these particles to grow larger particles, to incorporate laser dyes, and to grow core–shell particles.^{12,3,4} Unfortunately, the incorporation of RE ions by dissolving a RE salt in ethanol fails for the base-catalyzed reaction because the RE ion immediately forms an insoluble RE hydroxide.¹⁴ Attempts to synthesize RE-doped particles by using either triaminopropyltriethoxysilane or *N*-(trimethoxysilylpropyl)ethylenediamine, triacetic acid, sodium salt ($\text{C}_{11}\text{H}_{19}\text{N}_2\text{Na}_3\text{O}_9\text{Si}$, Gelest, 50% in water) were unsuccessful for the same reason.¹⁴

A well-established process to obtain RE-doped SiO_2 layers is spin coating of sol–gel solutions containing RE ions. This acid-catalyzed process relies on the formation of a gel from a reaction mixture containing TEOS, ethanol, water, and an acid.^{15,16} In an early stage of this reaction, spherical particles can be separated from such an acid-catalyzed reaction mixture of TEOS, glacial acetic acid, and water.^{8,9} The reaction results in the formation of micrometer-sized spherical particles that are quite polydisperse. We have used this reaction, modified by the addition of ErCl_3 , to form bulk Er-doped SiO_2 colloids.

Figure 1a shows a SEM image of these particles after annealing ($900\text{ }^\circ\text{C}$, 30 min). The inset shows a TEM image of one of the particles. Analyzing ≈ 100 particles reveals a broad size distribution (not shown) characterized by a mean diameter of $2.2\ \mu\text{m}$ and a size polydis-

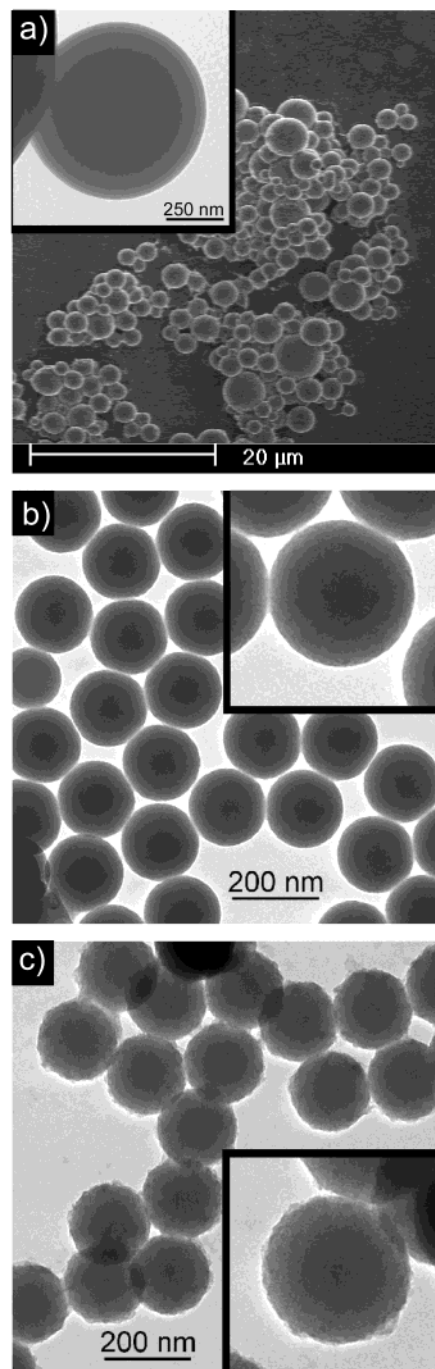


Figure 1. (a) SEM image of colloidal SiO_2 particles grown by the acid-based route, (b) TEM images of particles used for seeded growth experiments, and (c) TEM images of seed particles after seeded growth using the acid-based reaction. The insets zoom in on single particles and reveal an increase in both particle diameter and surface roughness by the seeded growth.

persity of $\sigma = 40\%$. The distribution is not Gaussian-shaped and exhibits a tail extending to a diameter of $\approx 6\ \mu\text{m}$. Note that in this analysis the number density of small particles may be underestimated as they may not all be collected from the solution in the centrifugation step. After separation, the remaining reaction mixture develops into a stiff, ringing gel in a few days time, clearly demonstrating the fact that the particles studied form in an early stage of the reaction. Particle suspensions washed only once in pure ethanol eventu-

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ally form a gel as well, albeit on a much longer time scale. The particles in this study were all washed at least twice, resulting in stable suspensions of particles in ethanol. No gelation was observed in these suspensions.

To use Er-doped colloids in photonic crystals and colloidal crystallization studies, the size polydispersity needs to be low and controllable. We achieve this by using a seeded growth process starting from 183-nm-diameter (undoped) silica seed particles. Figure 1b,c shows TEM images of silica particles used before (b) and after (c) seeded growth in the Er-doped solution. The seeds used were grown by a base-catalyzed reaction starting from particles grown in a microemulsion, leading to the formation of 183-nm-diameter particles with a 1% size polydispersity (Figure 1b). After seeded growth (Figure 1c) the particle diameter increased to 194 nm by 11 ± 2 nm, and the size polydispersity increased to $\approx 3\%$.¹⁷

These data show that the particle diameter has increased by 11 ± 2 nm using the seeded growth process. Furthermore, as the insets in Figure 1b,c show, the roughness of the particle surface increases by seeded growth, the roughness being typically 2–3 nm. As the roughness in a base-catalyzed seeded growth process is usually smaller,¹² this indicates that the acid-catalyzed reaction leads to a different growth mechanism. To obtain a successful seeded growth, the reaction conditions were chosen such that the reaction speed was lower than that for the synthesis of the bulk Er-doped (polydisperse) particles in Figure 1a, while the ErCl_3 concentration was kept low to avoid clustering of seed particles. When the seeded growth was carried out under the same conditions as those used for the bulk particles, nucleation of new particles also occurred. The inset in Figure 1a shows that the roughness of the bulk Er-doped particles grown by the acid-based reaction is much lower, which indicates that reduction of the surface roughness of particles grown by seeded growth may be possible by careful tuning of the reaction conditions.

The absence of large clusters of particles in Figure 1c indicates that seeded growth in the Er solution occurs on individual particles. Further evidence that mostly single particles are present in the solution is provided by the fact that uniform layers of the particles can be deposited on Si substrates by depositing a droplet of the solution on the substrate. Directly after synthesis the particles were mostly unaggregated. Storing the particles for a few weeks, however, leads to large aggregates of particles which may be related to the reduced surface potential of the particles. In principle, self-assembly of the particles to form colloidal crystals and long-term storage could be possible if the particles are covered with a thin outer shell of pure, undoped silica. We note that the effect of (charged) RE ions on the stability of the particle suspension has been observed before. For instance, it is known that RE ions influence the viscosity of sol–gel solutions used in spin-coating studies.¹⁸

(17) Estimates of the average diameter and variance of the size distribution were obtained by analyzing ≈ 20 particles. Using the Student's t distribution and a 95% confidence interval, we estimate that the real average lies between 182.7 and 184.0 nm before seeded growth and between 192.0 and 196.2 nm after seeded growth. See e.g. Barlow, R., *Statistics*, Wiley: New York, 1989.

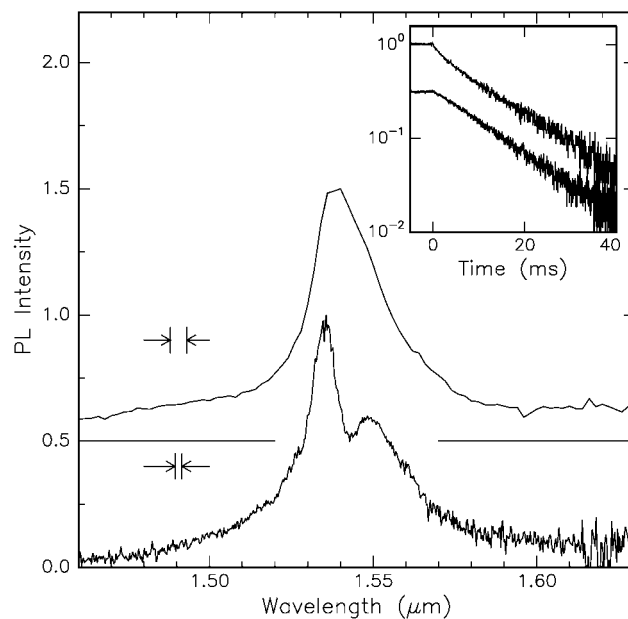


Figure 2. Normalized PL spectra of bulk Er-doped particles (lower spectrum) and Er-doped particles obtained by seeded growth (upper spectrum, offset for clarity) after annealing for 30 min in pure oxygen at 900 °C. The arrows indicate the spectral resolution. The inset shows PL decay traces measured for the seeded growth particles (upper trace) and bulk-doped particles (lower trace) at the peak emission wavelength.

RBS was done on bulk Er-doped SiO_2 particles on a Si substrate to determine the elemental composition of the colloids (data not shown). It was found that the Si:O ratio is close to the stoichiometric value for pure SiO_2 . No carbon (detection limit 3 at. %) was observed in RBS. The Er concentration measured is typically 0.15–0.18 at. %. In studies on spin-coated SiO_2 layers containing Er ions it was found that the Er:Si ratio in the deposited layer is roughly equal to the Er:Si ratio in the solution.^{16,18} The solutions in our work have an Er:Si ratio of 1:60, while the Er:Si ratio in the particles is roughly 1:200, which is significantly lower. At present both the exact growth mechanism of the acid-catalyzed silica growth and the incorporation mechanism of the Er ions are not known and need further study.

Photoluminescence

Figure 2 shows the normalized PL spectra of the bulk Er^{3+} -doped particles (see Figure 1a) and Er^{3+} -doped particles obtained by the seeded growth process (see Figure 1c), both annealed at 900 °C for 30 min in a 100% oxygen flow. Annealing of the particles in a vacuum furnace leads to a discoloration most likely because of a small amount of carbon formed by cracking of the remaining organic groups in the SiO_2 network at high temperatures. By annealing in pure oxygen, any remainder of organic groups is burnt away and the particles do not change color upon annealing. No Er^{3+} -related luminescence is observed from SiO_2 particles that are not annealed. This is most likely caused by the presence of C–H and O–H groups in the silica network of which the first vibrational overtones are known to

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be resonant with the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} at $1.5 \mu\text{m}$, causing the Er^{3+} luminescence to be quenched.

The PL spectra in Figure 2 show typical luminescence from the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions in SiO_2 , peaking at $1.536 \mu\text{m}$. No luminescence related to other Er transitions was observed in the wavelength range from 550 to 1100 nm. The inset shows PL decay traces measured at the peak luminescence wavelength. The measured decay traces show single-exponential behavior characterized by a lifetime of 13.5 ms (decay rate 75 s^{-1}) for both samples. The measured decay of the particles obtained by seeded growth shows an initial fast decay component, attributed to the small background observed in the PL spectrum, and is therefore not related to Er^{3+} .

Comparing the PL lifetimes with earlier results on Er^{3+} -doped colloidal particles by ion implantation, and taking into account the variation in local optical density of states in the spherical particles,¹⁹ we estimate the PL quantum efficiency to be $\approx 70\%$ (the radiative decay rate of Er^{3+} in bulk SiO_2 is 54 s^{-1} ^{6,19}). In a comparison of PL measurements for bulk-doped (polydisperse) Er-doped particles and the particles fabricated by seeded growth, with only a 5–6-nm-thick Er-doped shell, it was found that the latter showed much lower absolute PL intensity. As the quantum efficiency (PL lifetime) for both types of particles is similar, the reduction in PL intensity for the particles made by seeded growth is mainly attributed to the much lower total Er content of the particles made by seeded growth.

The monodisperse Er^{3+} -doped particles synthesized here might find use as optical probes in photonic crystals with a band gap centered around the important telecommunication wavelength of $1.5 \mu\text{m}$. For applications in the visible range of the spectrum, other rare-earth ions, for example, Eu^{3+} and Tb^{3+} , are of interest. We have synthesized bulk Eu^{3+} - and Tb^{3+} -doped particles using the acid-based process using the corresponding RE-chloride. PL spectra of such polydisperse particles suspended in an index-matching mixture of dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) are shown in Figure 3 for Tb^{3+} (a) and Eu^{3+} (b) ions. The Tb^{3+} ions are pumped directly into the 5D_4 level ($\lambda = 488 \text{ nm}$) and show typical Tb^{3+} luminescence from transitions to the 7F_5 , 7F_4 , 7F_3 , and 7F_0 levels as indicated in the level diagram in Figure 3. The luminescence from the 5D_4 to 7F_1 and 7F_2 transitions is too weak to be observed. Luminescence from the 5D_4 manifold down to the ground state of Tb^{3+} cannot be measured because it coincides with the laser line used for excitation. Exciting the Eu^{3+} ions into the 5D_2 level ($\lambda = 465.7 \text{ nm}$) leads to characteristic peaks in the luminescence related to transitions from the 5D_0 level to the 7F_4 , 7F_3 , 7F_2 , 7F_1 , and 7F_0 levels, as shown in Figure 3b.

The PL spectra in Figure 3 are measured on particles that were not annealed after synthesis. Decay traces of the luminescence from the 5D_4 level of Tb^{3+} and the 5D_0 level of Eu^{3+} show single-exponential decay curves. The measured lifetimes are summarized in Table 1 together with the measured lifetime of the Er^{3+} -doped colloids. The measured lifetime of the Tb^{3+} 5D_4 level increases

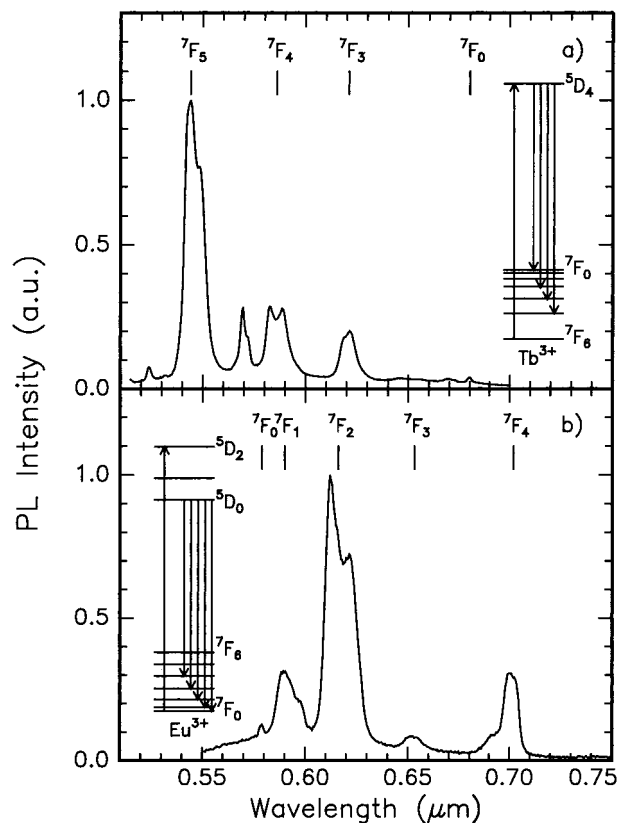


Figure 3. PL spectra of (a) unannealed Tb^{3+} and (b) Eu^{3+} -doped SiO_2 particles suspended in an index-matching DMSO/DMF mixture. Excitation wavelengths of 488 nm (Tb^{3+}) and 465.7 nm (Eu^{3+}) were used. Level diagrams for Tb^{3+} and Eu^{3+} are shown as insets and the transitions from the initial 5D_4 (Tb^{3+}) and 5D_0 (Eu^{3+}) states to the final states are indicated by the arrows.

Table 1. Measured PL Lifetimes of Er^{3+} , Eu^{3+} , and Tb^{3+} Ions^a

RE ion	not annealed	900 °C 30 min	DMSO/DMF solution
Er^{3+}		13.2 ms	
Eu^{3+}	0.15 ms	1.00 ms	1.29 ms
Tb^{3+}	0.66 ms	1.15 ms	2.43 ms

^a Lifetimes of the RE ions are tabulated for unannealed particles on a Si substrate, particles annealed for 30 min at 900 °C under flowing O_2 and particles suspended in a DMSO/DMF mixture. Er^{3+} luminescence was observed only for the annealed particles.

from 0.15 to 1.00 ms upon annealing at 900 °C and increases even further to 1.29 ms when the silica spheres are suspended in an index-matching DMSO/DMF mixture. A similar trend is observed for the 5D_2 level of Eu^{3+} ; in this case the lifetime of unannealed colloids is 0.66 ms and increases to 1.15 and 2.43 ms for annealed particles and particles in DMSO/DMF, respectively. As noted before, Er luminescence was observed for annealed particles only. The increased lifetime for Tb^{3+} and Eu^{3+} upon annealing is ascribed to the removal of quenching sites such as (point) defects in the silica glass network or impurities such as $-\text{OH}$ and $-\text{CH}$.²⁰ Indeed, the observed lifetime increase upon suspending the colloids in DMSO/DMF may be ascribed to the removal of $-\text{OH}$ groups that interact with the RE ions.

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Finally, we note that, during RBS measurements, using a 20 nA, 2-MeV He⁺ beam in a 1-mm-diameter spot, both the Eu³⁺- and Tb³⁺-doped colloids show red and green ionoluminescence, respectively, that is clearly visible to the naked eye. This shows that the RE ions in the SiO₂ particles can be excited by other means than optical pumping, paving the way to use, for instance, cathodoluminescence techniques to probe the properties of photonic crystals.

Conclusions

In conclusion, we have successfully applied seeded growth in the synthesis of 194-nm-diameter, monodisperse, Er³⁺-doped colloidal particles using an acid-based reaction. Without using seeded growth, bulk Er-doped spherical particles with an average diameter of 2.2 μm and a ≈40% polydispersity are formed. The typical Er concentration is 0.15–0.18 at. %. Identical photoluminescence spectra were observed from both the polydis-

perse and seeded growth particles after annealing for 30 min at 900 °C in flowing O₂. The luminescence lifetime is 13.2 ms, corresponding to a quantum yield as high as 70%. Visible luminescence from bulk-doped (polydisperse) Eu³⁺- and Tb³⁺-doped particles was observed, with lifetimes in the millisecond range for both annealed and unannealed particles. The particles described in this chapter might find future application as optical probes inside photonic crystals.

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