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Synthesis, Characterization, and Spectroscopy of NaGdF$_4$: Ce^{3+}, Tb^{3+}/NaYF$_4$ Core/Shell Nanoparticles

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There is a growing interest in materials chemistry for the development of new luminescence nanomaterials such as lanthanide-doped nanoparticles (NPs). NPs of this type have been considered for use in luminescence devices,[1] optical amplifiers,[2] and as labels for biomolecules.[3−6] Lanthanide ions are widely used as the emitting species in many traditional phosphors.[7] In particular, the Ce^{3+}, Tb^{3+} ion couple is utilized in a number of traditional phosphors for the generation of green light.[8] Hence, numerous dispersible NPs doped with the Ce^{3+} and Tb^{3+} ions have been synthesized through a varity of techniques.[9−13] In this paper, we present the synthesis of Ce^{3+} and Tb^{3+}-doped NaGdF$_4$ NPs that are dispersible as colloidal solutions in nonpolar organic solvents such as hexane and chloroform. The NPs were characterized using transmission electron microscopy (TEM), selected area electron diffraction (SAED), and powder X-ray diffraction (XRD). The luminescence properties of the colloidally dispersed NPs were also investigated under ultraviolet excitation. The synthesis of core/shell NPs is also presented as a method of increasing the efficiencies of the synthesized materials.

The method used for the synthesis of NaGdF$_4$ NPs has been adapted from the synthesis of LaF$_3$ nanoplates and NaYF$_4$ NPs.[14−16] The lanthanide trifluoroacetate precursors were prepared from the corresponding lanthanide oxides and carbonates and trifluoroacetic acid. The noncoordinating, high-boiling solvent octadecene was selected as the growth medium for the NPs. Oleic acid and oleylamine were employed as the coordinating organic ligands, which attach to the particle surface during the crystal growth and keep the NPs well-separated from each other. The reagents were added to a three-neck round-bottom flask and heated to 100 °C under a vacuum with stirring for 30 min to remove water and oxygen. The resulting solution was heated to 270 °C at a rate of 10 °C/min under argon and kept at this temperature for 45 min. The mixture was then allowed to cool to room temperature; the NPs were then precipitated using ethanol and isolated via centrifugation.

Figure 1 shows the characterization data of the NaGdF$_4$: Ce^{3+},Tb^{3+} NPs. From the TEM images (Figure 1A), it can be observed that the NaGdF$_4$ particles are approximately 4−5 nm in diameter and appear spherical in shape. The high-resolution TEM image in the inset of Figure 1A clearly demonstrates the high crystallinity of the particles. Lattice fringes corresponding to the (111) lattice plans of the cubic NaGdF$_4$ structure can be observed on the individual particles. All of the particles observed in the HRTEM images are composed of single crystallites.

To determine the crystal system of the NPs, we used XRD and SAED techniques. The XRD (Figure 1B) and SAED (Figure 1C) patterns also demonstrate the highly crystalline nature of the synthesized NPs. Both the XRD and SAED patterns obtained clearly match the reported pattern for cubic NaGdF$_4$ (JCPDS 27-0697) as seen in Table S1 (see the Supporting Information). Using the (111) peak of the diffraction patterns, we calculated an average crystallite size of 5 nm with the Debye−Scherrer formula, which corresponds well with TEM data.

Figure 2A shows the excitation and emission spectra of the NaGdF$_4$: 15% Ce^{3+}, 5% Tb^{3+} sample dispersed as a 1 wt % colloid in hexane. The spectra of the NaGdF$_4$: Ce^{3+}, Tb^{3+} NPs closely match what has been reported previously for the Tb^{3+} ion in fluoride-based NPs.[9−12] The excitation spectrum of the NaGdF$_4$: 15% Ce^{3+}, 5% Tb^{3+} sample (left of Figure 1A) is dominated by the 4f−5d absorption of Ce^{3+}, whereas the emission spectrum is characteristic of the Tb^{3+} ion. Excitation energy is absorbed by the Ce^{3+} 4f → 5d transition and then transferred via the Gd^{3+} lattice to a Tb^{3+} ion, where the energy is released as visible emissions (Figure 2B). The visible emissions can easily be assigned to transitions between the 4f energy levels of the Tb^{3+} ion (panels A and B of Figure 2). Finally, Figure 2C shows the luminescence of some of the freshly made 1 wt % solutions of the NPs under 254 nm ultraviolet light. It was observed that the luminescence intensity of the freshly made particles increases with increasing cerium concentration up to 20%.

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(1) Sivakumar, S.; van Veggel, F. C. J. M.; Raudsepp, M. *J. Am. Chem. Soc.* **2005**, *127*, 12464.
(2) Kumar, G. A.; Chen, C. W.; Ballato, J.; Riman, R. E. *Chem. Mater.* **2007**, *19*, 1523.
(3) Evanics, F.; Diamente, P. R.; van Veggel, F. C. J. M.; Stanisz, G. J.; Prosser, R. S. *Chem. Mater.* **2006**, *18*, 2499.
(4) Sivakumar, S.; Diamente, P. R.; van Veggel, F. C. J. M. *Chem.*−*Eur. J.* **2006**, *12*, 5878.
(5) Diamente, P. R.; Burke, R. D.; van Veggel, F. C. J. M. *Langmuir* **2006**, *22*, 1782.
(6) Diamente, P. R.; van Veggel, F. C. J. M. *J. Fluoresc.* **2005**, *15*, 543.
(7) Ronda, C. R.; Justel, T.; Nikol, H. *J. Alloys Compd.* **1998**, *275*−*277*, 669.
(8) Feldmann, C.; Juestel, T.; Ronda, C. R.; Schmidt, P. J. *Adv. Funct. Mater.* **2003**, *13*, 511.
(9) Wang, F.; Zhang, Y.; Fan, X.; Wang, M. *J. Mater. Chem.* **2006**, *16*, 1031.
(10) Wang, Z. L.; Quan, Z. W.; Jia, P. Y.; Lin, C. K.; Luo, Y.; Chen, Y.; Fang, J.; Zhou, W.; O'Connor, C. J.; Lin, J. *Chem. Mater.* **2006**, *18*, 2030.
(11) Guo, H. *Appl. Phys. B* **2006**, *84*, 365.
(12) Stouwdam, J. W.; van Veggel, F. C. J. M. *Langmuir* **2004**, *20*, 11763.
(13) Koempe, K.; Borchert, H.; Storz, J.; Lobo, A.; Adam, S.; Moeller, T.; Haase, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5513.
(14) Mai, H.-X.; Zhang, Y.-W.; Si, R.; Yan, Z.-G.; Sun, L.-d.; You, L.-P.; Yan, C.-H. *J. Am. Chem. Soc.* **2006**, *128*, 6426.
(15) Boyer, J.-C.; Vetrone, F.; Cuccia, L. A.; Capobianco, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 7444.
(16) Zhang, Y.-W.; Sun, X.; Si, R.; You, L.-P.; Yan, C.-H. *J. Am. Chem. Soc.* **2005**, *127*, 3260.

10.1021/cm070865c CCC: $37.00

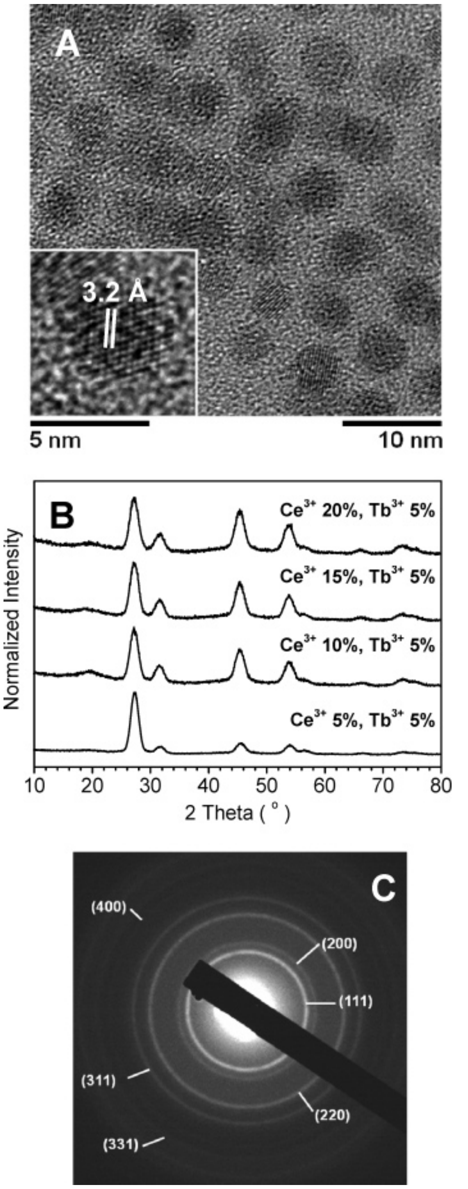

Figure 1. Characterization data for core-only NPs. (A) TEM image of NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+}. Inset, HRTEM image of a single NP. (B) Powder XRD patterns for particles with different cerium concentrations. (C) SAED pattern of the NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+} NPs.

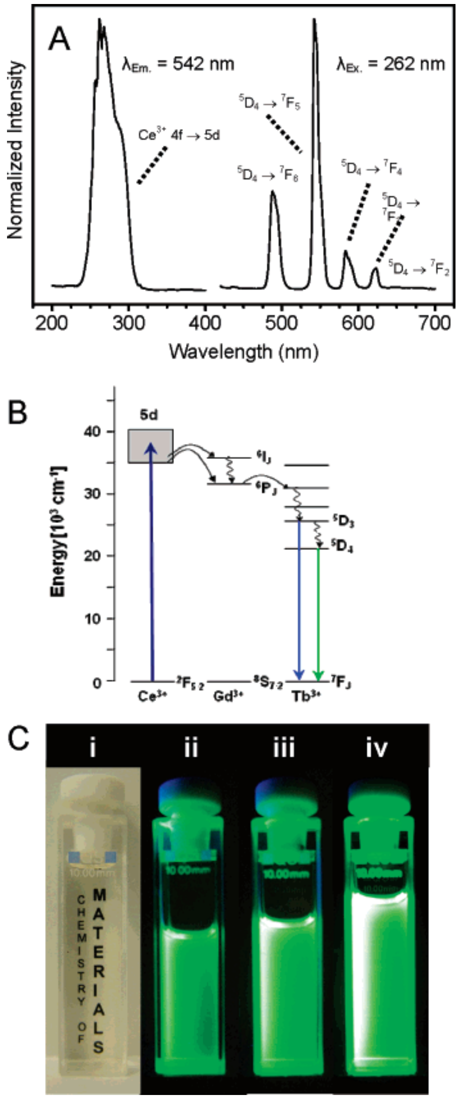

Figure 2. (A) Excitation and emission spectra of NaGdF$_4$: 15% Ce^{3+}, 5% Tb^{3+} NPs dispersed as a 1 wt % solution in hexane. (B) Mechanism responsible for Tb^{3+} emissions. (C) Photographs of a 1 wt % solution of freshly prepared NaGdF$_4$: 10% Ce^{3+}, 5% Tb^{3+} NPs in hexane under (i) ambient and (ii) 254 nm UV light. Photographs of 1 wt % solutions of freshly prepared (iii) NaGdF$_4$: 15% Ce^{3+}, 5% Tb^{3+} and (iv) NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+} NPs in hexane under 254 nm UV light.

The NPs and their colloidal solutions tend to yellow over time with an accompaning decrease in their luminescence efficiency. This phenomenon was attibuted to the oxidation of Ce^{3+} to Ce^{4+}. For efficient green Tb^{3+} luminescence, the energy from the ultraviolet excitation light has to be first absorbed by Ce^{3+} and then transferred to Tb^{3+}. The Ce^{4+} ion is not capable of acting as a sensitizer in this way. To prevent this oxidation, we added a NaYF$_4$ shell to the core particles during the synthesis. Addition of an undoped shell has the added benefit of protecting the luminescent lanthanide ions from the high vibration energies of the organic solvent and other quenching sites located at the surface of the NPs. For this reason, a shell of NaYF$_4$ was employed instead of NaGdF$_4$. As mentioned previously, the excitation energy is transferred to the Ce^{3+} ions via the Gd^{3+} lattice. If NaGdF$_4$ was utilized as the shell material, it would still allow for energy transfer of the exciting energy up to the surface of the nanoparticles. Core/shell structures have been utilized in the past for other Ce^{3+}/Tb^{3+}-doped NPs for similar reasons.[10,12,13,17] For the core/shell particles, the same synthetic procedure was utilized as above except a second reaction mixture containing yttrium and sodium trifluoroacetates was added over a 10 min period after the first 45 min of reaction time. The resulting reaction mixture was maintained at 270 °C for an additional 30 min.

Figure 3 clearly demonstrates the advantages of employing a core/shell structure over the core-only particles. Figure 3A shows the emission spectra of four core-only NaGdF$_4$: Ce^{3+}, Tb^{3+} samples and a NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+}/NaYF$_4$ core/shell sample 1 week after their synthesis. The emission intensity decreases in the core-only particles with increasing cerium concentration (Figure 3A). Upon addition of the undoped NaYF$_4$ shell to the core particles, the intensity of the emission is increased considerably (Figure 3A). This

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(17) Koempe, K.; Lehmann, O.; Haase, M. *Chem. Mater.* **2006**, *18*, 4442.

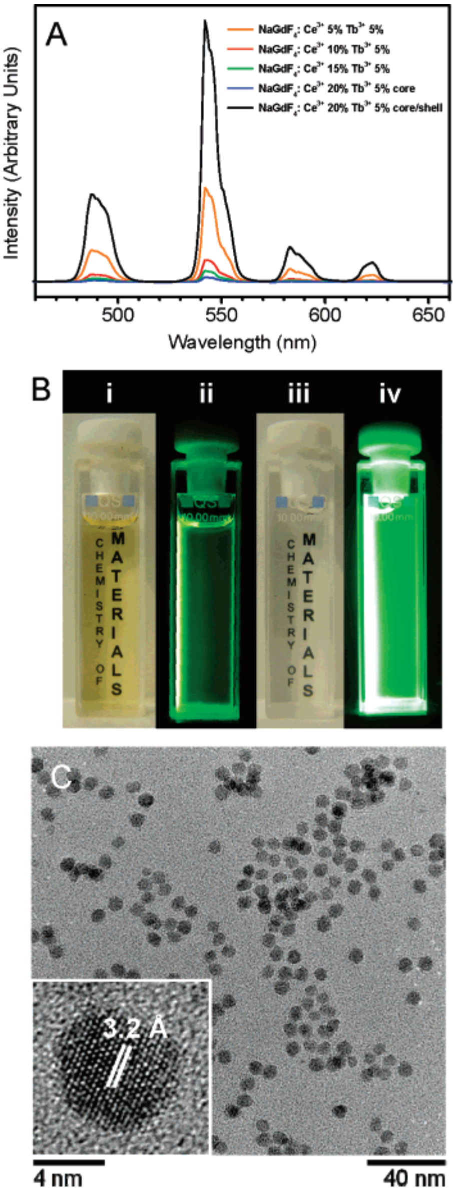

Figure 3. (A) Emission spectra of 1 wt % solutions in hexane of NaGdF$_4$: Ce^{3+}, Tb^{3+} core and NaGdF$_4$:Ce^{3+} 20%,Tb^{3+} 5%/NaYF$_4$ core/shell NPs. (B) Photographs of a 1 wt % solution of aged NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+} NPs in hexane under (i) ambient and (ii) 254 nm UV light and NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+}/NaYF$_4$ NPs under (iii) ambient and (iv) 254 nm UV light. (C) TEM image of NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+}/NaYF$_4$ sample. Inset, HRTEM image of a single NP.

dramatic increase in luminescence efficiency is attributed to the fact that the NaYF$_4$ shell protects the NaGdF$_4$: Ce^{3+},Tb^{3+} NPs from cerium oxidation. The core-only colloidal solutions tend to turn yellow after only a few days (Figure 3B(i)), accompanied by a drastic decrease in their overall luminescence (Figure 3B(ii)). In contrast, the colloidal solutions containing the core/shell particles remained colorless (Figure 3B(iii)), and no changes in their luminescence intensity were observed (Figure 3B(iv)) over the same time period. Even when freshly made solutions of NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+} core and NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+}/NaYF$_4$ core/shell NPs are compared, a dramatic increase in overall luminescence is observed in the core/shell sample. The addition of an undoped shell effectively reduces nonradiative quenching of the lanthanide ions by surface defects and surounding solvent molecules. Moreover, there is no significant differences in the TEM and the XRD patterns of the core-only and the core/shell particles. The latter just appear to have a slightly larger diamter of 7−8 nm (Figure 3C).

The quantum yield of the core/shell NPs was also determined in solution by comparison to a Rhodamine 6G laser dye in order to demonstrate their efficiency. A quantum yield of ∼30% for the Tb^{3+} emissions was determined for a dilute solution of NaGdF$_4$: 20% Ce^{3+}, 5% Tb^{3+} core/shell NPs in hexane. Although this value is not close to that of 70% reported for core/shell NPs previously,[13] further refinement of the lanthanide doping levels is currently under investigation.

In conclusion, we have synthesized NaGdF$_4$ NPs doped with cerium and terbium that form colloidal solutions in nonpolar organic solvents and show green luminescence under UV excitation. The NPs have been characterized using TEM, powder XRD, SAED, and luminescence spectroscopy. Core/shell NPs have also been synthesized that demonstrate a higher quantum efficiency under ultraviolet light and a greater resistance to cerium oxidation when compared to the core-only NPs.

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Supporting Information Available: Synthesis of NaGdF$_4$: Ce^{3+}, Tb^{3+} NPs. Powder XRD data. This material is available free of chrage via the Internet at http://pubs.acs.org.

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