VIP Doped Nanoparticles

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Direct Evidence of a Surface Quenching Effect on Size-Dependent Luminescence of Upconversion Nanoparticles**

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Lanthanide-doped upconversion (UC) nanoparticles have shown considerable promise in biological labeling, imaging, and therapeutics.[1] However, although current synthetic approaches allow for preparation of ultrasmall UC nanoparticles with precise control over particle morphology and emission color,[2] smaller nanoparticles come at the expense of weaker emissions, which is a constraint that is practically impossible to surpass. Many fundamental aspects of the UC luminescence in these nanomaterials still lack sufficient understanding. In particular, several groups have observed varied relative intensity of the multi-peak UC emissions with varying particle size.[3] The UC luminescence primarily originates from intra-configurational $4f^n$ electron transitions within the localized lanthanide dopant ions. Due to a small Bohr radius of the exciton in UC hosts and weak interactions between $4f^n$ electrons of the lanthanide dopant ions and the host matrix, the size-dependent UC luminescence can hardly be explained by classic theories, such as quantum confinement and surface plasmon resonance related to optical properties of semiconductor and metal nanoparticles.[4]

Although phonon confinement[3a–d] has been used to account for the size-dependent UC luminescence, it has been a matter of much debate, owing to the constraints typically associated with solid-state sample measurements at extreme conditions (for example, low temperatures of ca. 10 K) and exclusion of vibrational energies and optical traps arising from particle surface. To this end, a surface quenching effect[3f–i] is proposed and correlated with size-dependent UC luminescence. However, the surface quenching effect has not been conclusively established, largely because of the lack of direct evidence on surface-quenching-induced luminescence modulation of different-sized particles. Herein, we present a comparative spectroscopic investigation of a series of Yb/Tm co-doped hexagonal-phase $NaGdF_4$ nanoparticles (10, 15, and 25 nm) with or without a thin (ca. 2.5 nm) surface protection layer. We show that, through the thin layer coating, the characteristic optical features (such as relative emission intensities) of these nanoparticles can be retained, thereby providing direct evidence to support the surface quenching effect responsible for the size-dependent UC luminescence.

Hexagonal-phase $NaGdF_4$ was chosen as the model host system owing to its ability to render high UC efficiency and the benefits of producing relatively small (< 20 nm) and uniform nanoparticles.[2a,5] Furthermore, the Gd^{3+} host ion that features half-filled 4f orbitals is relatively inert in the luminescence process and thus has negligible interaction with the dopant ions.[2a] To provide a direct comparison over a broad wavelength range between the relative emission intensity of the particles, the Tm^{3+} ion with a ladder-like arrangement of energy levels was selected as the activator capable of generating upconverted emission peaks that span from ultraviolet (UV) to near-infrared (NIR) spectral regions (Figure 1 a).

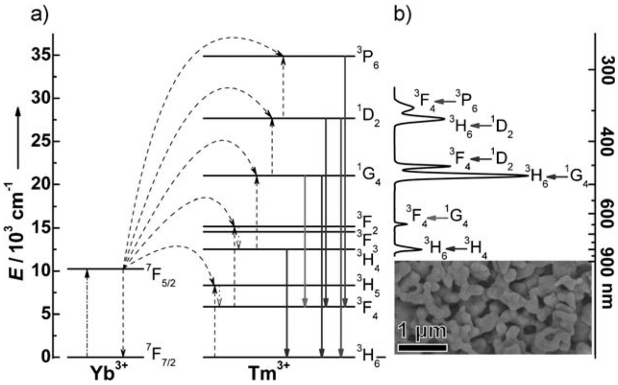

Figure 1. a) Proposed energy-transfer mechanisms, showing the UC processes in $NaGdF_4$:Yb/Tm nanoparticles. Key to arrows: –•–• photon excitation, ——— energy transfer, ----- multiphonon relaxation, —— emission processes. b) A typical emission spectrum of the as-prepared bulk $NaGdF_4$:Yb/Tm (25/0.3 mol%) under excitation of a 980 nm CW diode laser at a power density of 10 W cm^{-2} (inset: scanning electron microscope image of the sample).

To probe the surface quenching effect on size-dependent luminescence of UC nanoparticles, we first synthesized $NaGdF_4$:Yb/Tm (25/0.3 mol%) materials in bulk form (>100 nm) and in the form of nanoparticles of different size (10, 15, and 25 nm). All samples were determined as hexagonal-phase $NaGdF_4$ by X-ray powder diffraction (Supporting Information, Figure S1). Upon NIR excitation, Tm^{3+} ions in bulk $NaGdF_4$ phosphors exhibit a characteristic emission ($^1G_4 \rightarrow {}^3H_6$) in the blue spectral region with an intensity that is significantly higher than that in the NIR spectral region ($^3H_4 \rightarrow {}^3H_6$; Figure 1 b). In contrast, the nanoparticle counterparts containing an identical dopant compo-

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sition show a substantial change in the relative intensity of the blue to NIR emissions (Figure 2a). Furthermore, constantly decreased relative intensity ratios of the blue to NIR emissions are observed with decreasing particle size (Figure 2a).

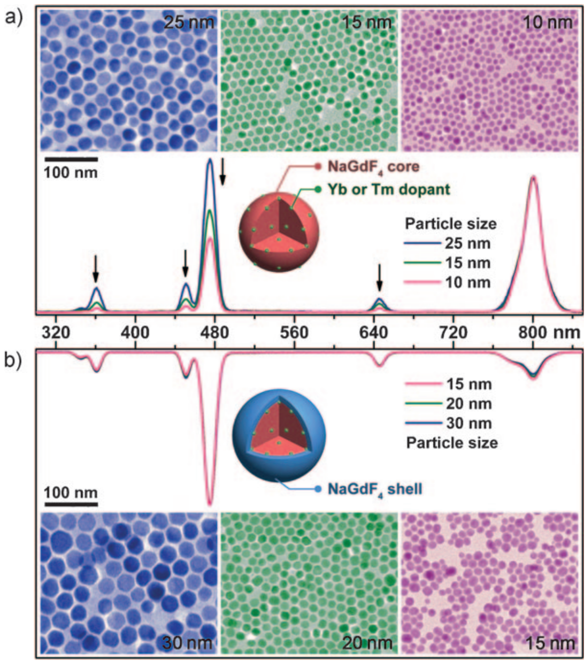

Figure 2. a) Room-temperature UC emission spectra of a series of $NaGdF_4$:Yb/Tm (25/0.3 mol%) nanoparticles in 4 mM cyclohexane solutions (insets: corresponding TEM images of the nanoparticles). b) Emission spectra of a series of nanoparticles modified with a thin layer (ca. 2.5 nm) of $NaGdF_4$ in 8 mM cyclohexane solutions (insets: corresponding TEM images of the core/shell nanoparticles). The spectra in (a) and (b) were normalized to Tm emissions at 800 and 480 nm, respectively. All spectra were recorded under excitation of a 980 nm CW diode laser at a power density of 10 $W cm^{-2}$.

We attribute the change in the relative intensity of upconverted emissions as a function of particle size to the surface quenching effect. Each emission peak corresponds to a sum of optical emissions contributed from dopant ions at the surface and in the interior of the particles. When compared to the interior dopant ions, the surface dopant ions should show weakened emission peaks owing to quenching of the excitation energy by surface defects, impurities, ligands, and solvents.[6] More importantly, the depletion of low-lying intermediate levels (for example, $^3H_4$ of Tm^{3+}) by surface quenching will suppress the population in high-lying levels (e.g., $^1G_4$ of Tm^{3+}) by subsequent excited state absorption or energy transfer. Therefore, the emission in the UV/Vis region involving a higher number of excitation steps should be more susceptible to surface quenching than that in the NIR region involving less number of excitation steps. As the particle size decreases, the concentration of the surface dopant ions increases, leading to a variation of the relative emission intensity.

To validate our hypothesis, we further modified the three sets of nanoparticles with a thin surface protection layer (ca. 2.5 nm) of $NaGdF_4$ through an epitaxial growth method (Figure 2b, inset).[7] Surprisingly, the core/shell nanoparticles resulting from the 10 nm core show significantly enhanced relative intensity of the blue to NIR emissions (Figure 2b). Despite the large disparity in particle sizes (15, 20, and 30 nm), the emission spectra obtained from these core/shell nanoparticles are essentially identical. They also closely resemble the emission spectrum of the corresponding bulk phosphors. Taken together, these results strongly indicate that the variation in particle size (or phonon confinement) has extremely limited impact on the relative emission intensity of the nanoparticles, thus confirming the prominent role of surface quenching effect on the UC emission.

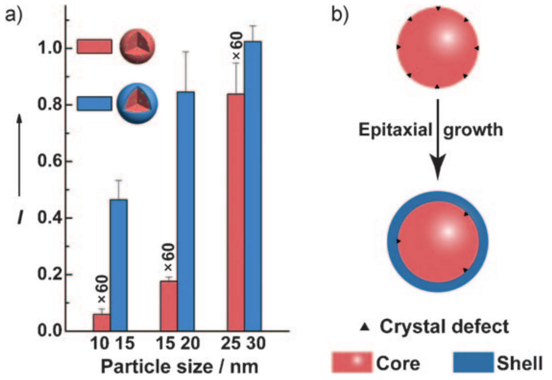

Figure 3. a) UC emission intensity comparison of $NaGdF_4$:Yb/Tm (25/0.3 mol%) nanoparticles of different size, without and with a thin protection layer, in cyclohexane solutions (4 mM and 8 mM for core and core/shell particles, respectively). The emission intensities were calculated by integrating the spectral intensity of the emission spectra over a wavelength range of 300–850 nm. The intensities are averaged values obtained from duplicated experiments. All samples were excited with a 980 nm diode laser at a power density of 10 $W cm^{-2}$. b) How surface defects of the core particle may be partially retained as volume defects in the resulting core/shell particles.

Notably, we observed significant enhancement in overall emission intensity of the core/shell particles (Figure 3a), which can be ascribed to the surface passivation effect.[8] Remarkably, upon surface coating a more than 450-fold increase in the emission intensity for the 10 nm nanoparticles was estimated. Another notable feature of the emission spectra from different sets of core/shell nanoparticles was the decrease in overall emission intensity as the particle size decreases. The relatively weak luminescence from smaller nanoparticles is attributed to increased local concentration of crystal defects that dissipate excitation energy of the dopant ion. During the epitaxial growth of the $NaGdF_4$ shell layer, surface defects of the particles may be partially retained, resulting in the formation of volume defects in the core/shell particles (Figure 3b). Since the surface area per volume (or the density of surface defects) increases with decreasing particle size, smaller core/shell particles will retain a higher density of volume defects, contributing to suppressed UC emission intensity.

To shed more light on the effect of surface quenching, we transferred the 15 nm particles and corresponding 20 nm core/shell particles into polyoxyethylene (5) nonylphenylether (CO-520)/ethanol solutions with different amounts of water molecules. Because of the high energy (ca. 3500 cm^{-1}) of the stretching vibration, the water molecule is known as a surface oscillator that significantly quenches the luminescence of lanthanide dopant ions.[6c] As the concentration of water molecules increases, we observed a marked decrease in UV/Vis to NIR emission ratios for the nanoparticles without surface coating (Figure 4a). In stark contrast, the relative emission intensities of the core/shell nanoparticles are essentially unaltered owing to the effective protection of dopant ions by the inert shell (Figure 4b). This direct data comparison further confirms that the size-dependent UC luminescence is primarily due to the surface quenching effect.

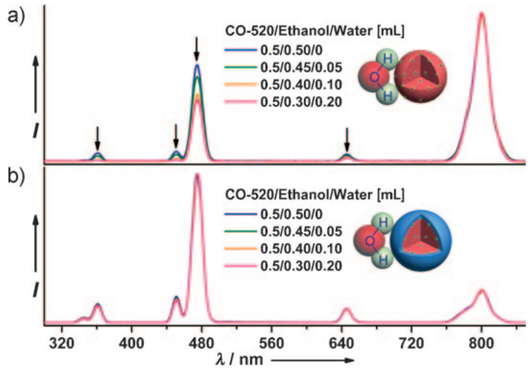

Figure 4. Room-temperature UC emission spectra of a) the 15 nm $NaGdF_4$:Yb/Tm (25/0.3 mol%) particles and b) corresponding 20 nm core/shell particles obtained in CO-520/ethanol/water solutions at different concentrations of water. The spectra in (a) and (b) were normalized to Tm emissions at 800 and 480 nm, respectively. All spectra were recorded under excitation of a 980 nm CW diode laser at a power density of 10 W cm^{-2}.

Importantly, the 20 nm core/shell nanoparticles were found to be substantially more resistant to quenching by water molecules than the unmodified nanoparticle counterparts. In the presence of a water content of 20 vol% the core/shell nanoparticles lost around 35% of the overall emission intensity, in sharp contrast to 80% for the unmodified nanoparticles (Figure 5a). Control experiments show that the absorption of NIR excitation by the solvent molecules[9] only accounts for about 10% of the loss in overall emission intensity (Figure 5b), which confirms surface quenching effect of water molecules. The result also implies that the core particles are either incompletely coated with a thin layer of $NaGdF_4$ or coated with a porous layer of $NaGdF_4$. Nevertheless, these data suggest that the core/shell particles should provide more reliable optical signals than the unmodified particles for practical applications in biological settings where solvent-induced luminescence quenching often results in false-positive assays.

We would like to emphasize that the thin surface coating does not prevent the resulting core/shell nanoparticles from effective use in lanthanide resonance energy transfer (LRET) studies (Figure 5c). As a proof-of-concept experiment, we added 0.1 mM fluorescein isothiocyanate to a solution of CO-520/ethanol containing as-synthesized 8 mM core/shell nanoparticles (20 nm). Upon NIR excitation, we observed the significant suppression of upconverted emissions, accompanied by a strong emission from the dye molecule. By measuring the decrease in emission intensity of the nanoparticles, we estimated the LRET efficiency to be 90%. The high efficiency was obtained due to the inherent large energy transfer distance range (>10 nm) of LRET-based techniques.[10]

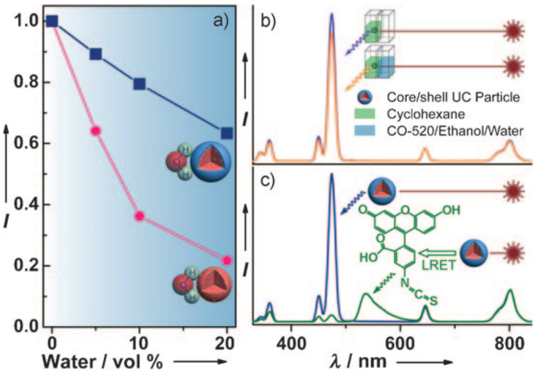

Figure 5. a) Comparison of emission intensity loss for 15 nm core particles and corresponding 20 nm core/shell particles in polar solvents with different amounts of water. b) Comparison of emission spectra of the particles in cyclohexane solution under direct NIR excitation and with the NIR excitation blocked by a solution of CO-520/ethanol/water (50:30:20 vol%). c) Emission spectra of a solution of CO-520/ethanol (1:1 v/v) containing the core/shell UC particles (8 mM) in the absence and presence of fluorescein isothiocyanate (0.1 mM), respectively. All samples were excited with a 980 nm diode laser at a power density of 10 W cm^{-2}.

In conclusion, we have presented direct evidence for the surface quenching effect associated with the size-dependent luminescence of UC nanoparticles. We show that the use of an inert thin-shell coating preserves the optical integrity of the nanoparticles and largely minimizes surface quenching-induced emission losses. Moreover, the shell coating offers the possibility of fine-tuning UC emissions in nanoparticles (Supporting Information, Figure S2). This study suggests that the use of thin-shell coating provides the UC nanoparticles with a platform to best achieve a reliable performance in the context of highly complex bioimaging applications.

Experimental Section

$GdCl_3 \cdot xH_2O$ (99.99%), $YCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.99%), $ErCl_3 \cdot 6H_2O$ (99.9%), NaOH (98+%), NH_4F (98+%), 1-octadecene (90%), oleic acid (90%), fluorescein isothiocyanate, and polyoxyethylene (5) nonylphenylether were all purchased from Sigma–Aldrich and used as starting materials without further purification.

In a typical procedure for the synthesis of 25 nm $NaGdF_4$:Yb/Tm nanoparticles, 1 mL aqueous solution of $LnCl_3$ (0.4 M, Ln = Gd, Yb, Tm) was added to a 50 mL flask containing oleic acid (4 mL). The mixture was heated at 150 °C for 30 min to remove the water content from the solution. A solution of 1-octadecene (6 mL) was then quickly added to the flask and the resulting mixture was heated at 150 °C for another 30 min before cooling to 50 °C. Shortly thereafter, a methanol solution (5 mL) containing NH_4F (1.1 mmol) and NaOH

(1 mmol) was added and the solution was stirred for 30 min. After the methanol was evaporated, the solution was heated to 280 °C under argon for 1.5 h and then cooled to room temperature. The resulting nanoparticles were precipitated by addition of ethanol, collected by centrifugation, washed with methanol and ethanol several times, and finally redispersed in cyclohexane. $NaGdF_4$:Yb/Tm nanoparticles, with particle sizes of 15 and 10 nm, were synthesized by using an identical procedure, except for the use of 1.2 and 1.5 mmol of NH_4F in the synthesis, respectively.

The $NaGdF_4$ shell precursor was first prepared by mixing an aqueous solution (1 mL) of $GdCl_3$ (0.4 M) and oleic acid (4 mL) in a 50 mL flask and subsequently heating at 150 °C for 30 min. 1-Octadecene (6 mL) was then added and the mixture was heated at 150 °C for another 30 min before cooling to 50 °C. $NaGdF_4$:Yb/Tm core nanoparticles in cyclohexane (4 mL) were added along with a methanol solution (5 mL) of NH_4F (1.1 mmol) and NaOH (1 mmol). The resulting mixture was stirred at 50 °C for 30 min, after which time the solution was heated to 280 °C under argon for 1.5 h and then cooled to room temperature. The resulting nanoparticles were precipitated by addition of ethanol, collected by centrifugation, washed with methanol and ethanol several times, and re-dispersed in cyclohexane.

In a typical procedure for the synthesis of the bulk phosphors, an aqueous solution (10 mL) charged with $LnCl_3$ (2 mmol; Ln = Gd, Yb, Tm) and NaF (20 mmol) was sealed in a 20 mL Teflon-lined autoclave and then heated at 200 °C for 48 h. The as-synthesized phosphors were collected by centrifugation, washed twice with deionized water, and dried in an oven at 50 °C for 12 h. Subsequently, the product was annealed at 400 °C for 4 h and characterized without further purification.

Aqueous dispersion of nanoparticles: $NaGdF_4$:Ln^{3+} nanoparticles in 5 mL cyclohexane were mixed with 5 mL polyoxyethylene (5) nonylphenylether (CO-520), followed by removal of the cyclohexane at 75 °C for 1 h while stirring. The resulting mixture was then mixed with 5 mL of ethanol/water solutions for optical characterization.

TEM measurements were carried out on a JEL-1400 transmission electron microscope (JEOL) operating at an acceleration voltage of 120 kV. XRD analysis was carried out on an ADDS wide-angle X-ray powder diffractometer with $Cu_{K\alpha}$ radiation (40 kV, 40 mA, $\lambda = 1.54184$ Å). Luminescence spectra were obtained with a DM150i monochromator equipped with a R928 photon counting photomultiplier tube (PMT), in conjunction with a 980 nm diode laser. The spectra for all nanoparticles were recorded from samples dispersed in solutions. The concentrations of lanthanide ions were fixed at 0.4 mM and 0.8 mM for core and core/shell particles, respectively. The spectrum for the bulk phosphors was recorded from solid samples immobilized on a microscope glass slide.

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