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# Heterogeneous Nanostructures for Plasmonic Interaction with Luminescence and Quantitative Surface-enhanced Raman Spectroscopy

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## ABSTRACT

NIR-to-visible up-conversion nanomaterials have been investigated in many promising applications including next-generation displays, solar cells, and biological labels. When doped with different trivalent lanthanide ions, NaYF<sub>4</sub> nanoparticles can produce up-converted emission from visible to infra-red wavelengths. However, the quantum yield of this class of materials is low. Noble metals in the vicinity of the phosphor can increase the phosphorescence by local field enhancement due to plasmonic resonances, and by modification of the radiative rate of the phosphor. Most previous studies have investigated the phenomenon by placing nanophosphors onto a metal substrate, or by fabrication of nanostructures with spacers such as polymers, dielectric materials (silica). By contrast, we have studied the interaction between the luminescence and the surface plasmon using a core-shell type nanostructure where a uniform shell of silver is shown to grown on doped-NaYF<sub>4</sub> nanophosphors by Ostwald ripening. We further demonstrate the proximity effect of metal-enhanced luminescence by exciting an undoped NaYF<sub>4</sub> shell. The result shows a significant synergistic enhancement of up-conversion luminescence due to the active shell as spacer layer. In addition, we have shown this novel nanostructure may be useful in surface-enhanced Raman spectroscopy (SERS).

**Keywords:** Hetero-epitaxial growth, up-conversion enhancement, surface plasmon, Raman spectroscopy, SERS

## INTRODUCTION

Novel heterogeneous nanostructures have often been explored to advance the technological potential of conventional nanomaterials beyond their inherent limitations. Heterogeneous nanostructures create platforms on which electronic communication can generate synergistically enhanced and/or tunable chemical-physical responses, or even lead to emergence of unusual phenomena, not otherwise accessible by any of the single components alone, or their physical mixture counterparts.[1-3] To date, several strategies to form heterogeneous nanostructures have been reported. The general strategy to synthesize multicomponent materials is first to prepare nanoparticles of one material, and then use them as nucleation seeds to deposit the other components. Significant progress has been made in the synthesis of nanoparticles with homogeneous epitaxial shells. However, synthesis of nanoparticles that combine components with very different lattice parameters is still challenging. Most of the reported methods that have achieved high-quality monocrystalline heterostructures are all based on epitaxial growth, which requires moderate lattice mismatches (< 2%) between the two different materials.[1] The lattice mismatch is a major constraint to grow core-shell nanostructures – core nanoparticles possess highly curved surfaces that present many different crystallographic facets. In addition to such lattice-matching requirements, the issues related to differences in crystal structure, bonding, and other properties have been found to inhibit epitaxial growth of dissimilar hybrid materials. Attempts to use epitaxy to achieve hybrid core-shell nanostructures have mostly resulted in either polycrystalline shells or anisotropic structures with segregation of the core and shell. In this study, we report a non-epitaxial growth of a metal (i.e. Ag) shell grown on core nanoparticles (i.e. NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup>) exploiting Ostwald ripening to create a heterostructure formation. Ostwald ripening is the phenomenon in which smaller particles in solution dissolve and deposit on larger particles in order to reach a thermodynamically stable state.

In a typical nanoparticle synthesis, a large number of nuclei crystallize at early stages of the synthesis from the “monomers” of the solution. The nuclei subsequently grow by consuming remaining monomers in solution and start to form particles. Therefore, as particles grow larger, the monomer concentration drops. However, at sufficiently low

monomer concentration, the smaller particles of the size distribution start to dissolve back in the solution and release monomers to maintain equilibrium. The larger particles consume the released monomers and thereby increase in size, whereas the smaller particles continue to decrease in size and finally dissolve completely. Under these conditions, the concentration of monomers ultimately becomes quasi-stationary; that is, the concentration decreases only very slowly with time, asymptotically approaching the equilibrium value observed over a precipitate of the bulk solid. This growth stage, called Ostwald ripening, can be mathematically described within the framework of LSW (Lifshitz-Slyozov-Wagner) theory.[4] Ostwald ripening results in a broad particle size distribution containing a small fraction of particles which are close to complete dissolution. However, the broad size distribution can be avoided if a high concentration of monomers can somehow be maintained in solution (i.e. supersaturation of monomers). Dagtepe et al.[5] have theoretically investigated the Ostwald ripening of bimodal size distributions, that is, the special case where the monomer precursor consists of very small particles of the same material as the growing nanocrystals. If the two particle fractions of the bimodal distribution are sufficiently well-separated in size, the dissolution rate of the smaller particles is high enough to achieve supersaturation conditions for the larger particles and a narrow size distribution is obtained. In our experiment, we have conceptualized this notion of bimodal size-driven Ostwald ripening to achieve heterogeneous growth where ~5 nm Ag nanoparticles were injected in to a solution of ~22 nm core NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> to yield ~27 nm core-shell nanoparticles.

Lanthanide fluoride based up-conversion nanoparticles (UCNPs) in particular NaYF<sub>4</sub>:Ln<sup>3+</sup> (Ln = doped lanthanides ions) have drawn considerable attention in many biological applications due to their high photo-stability, low excitation energy, low toxicity and ability to be excited and to emit in the near infrared (NIR) region.[6-9] Despite such advantages, the application of UCNPs has been limited due to their low emission efficiency (< 1%). A number of efforts have been reported to increase the excitation and emission efficiency of up-conversion nanoparticles. One distinct approach is to introduce metal nanoparticles such as Ag and Au for their inherent surface plasmon resonances (SPR).[10-18] The origin of plasmonic enhancement can be primarily attributed to (i) an increase in the local excitation rate caused by local field enhancement associated with plasmon resonance, and (ii) an increase in the emission rate, which is an enhancement of the emission efficiency due to the coupling of the up-conversion emission with the plasmon resonance that is present in close proximity, which effectively increase both the non-radiative and radiative decay rate. However, it has been reported that a fluorophore directly in contact with a metal is quenched, while the maximum fluorescence enhancement is observed only from molecules at a discrete distance from the metals.[11] Most of the previous studies investigating metal induced enhancement were done by placing nanoparticles on the substrates,[19] trapping up-converting nanoparticles in photonic crystals[20], or imbedded in glasses. For solution-based nanocomposites, some previous reports on core-shell nanocomposites containing up-conversion nanoparticles and metal nanoparticles have used polymer molecules or silica as spacers to modulate the luminescence.[18, 21] However, most of these system lacks the ability to tune the spacing of spacer layer in colloidal system so that the impact of the interaction distance can be clearly discerned.

In this study, we have developed a novel method to grow a Ag shell directly on NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanoparticles, overcoming the lattice mismatch. To study the modulation of up-conversion luminescence, we have fabricated a NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup>@NaYF<sub>4</sub>@Ag core-shell-shell architecture while the tunable undoped-NaYF<sub>4</sub> can act as a spacer between the core and Ag shell. The advantage of adding the undoped-NaYF<sub>4</sub> is that it can show a synergistic effect of luminescence enhancement, simultaneously acting as a surface passivator as well as providing the right spacing between the metal and emitters. Results show that the undoped-NaYF<sub>4</sub> spacer resulted in an enhancement of ~25.5 at a distance of 7 nm. We also observed that when the Ag shell is in direct contact with the core NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup>, luminescence was quenched by a factor of 2.4. This study provides direct evidence of luminescence quenching for noble metal in contact with phosphors in colloids as well as spacer-dependent enhancement.

## METHODOLOGY

**2.1 Chemicals.** All chemicals were used as received without further purifications. Yttrium chloride hexahydrate (> 99.99%), ytterbium chloride hexahydrate (> 99.9%), erbium chloride hexahydrate (> 99.99%), oleic acid (tech., 90%), 1-octadecene (tech., 90%), ammonium fluoride (> 99.99%), silver nitrate (≥ 99.0%), oleylamine (tech.), phenyl ether (99%), hexane (ACS reagent, ≥ 98.5%) were purchased from Sigma-Aldrich. Sodium hydroxide (pellets, reagent ACS) was purchased from ACP Chemicals Inc. Methanol (ACS, VWR), ethanol (ACS, VWR), chloroform (ACS, Fisher) were of analytical reagent grade.

**2.2 Synthesis of core/shell Nanoparticles.** In a typical synthesis of ~22 nm NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanoparticles, 0.8 mmol of YCl<sub>3</sub>·6H<sub>2</sub>O, 0.18 mmol of YbCl<sub>3</sub>·6H<sub>2</sub>O and 0.02 mmol of ErCl<sub>3</sub>·6H<sub>2</sub>O were added to a mixture of 6 ml oleic acid and 15 ml 1-octadecene, and heated to 130 °C under vacuum for 2 h. The solution was brought back to room temperature and a solution of 2 mmol NaOH and 2.5 mmol NH<sub>4</sub>F dissolved in 10 ml methanol was added. The resulting mixture was further stirred for 1 h at room temperature and then slowly heated to 70 °C to remove methanol. Once methanol was removed, the clear solution was heated to 300 °C under an argon blanket and stirred for 1 h. Once the reaction was complete, the solution was cooled down to room temperature and precipitated with ethanol. The nanoparticles were then washed several times with ethanol and collected by centrifugation (5000 rpm, Fisher Scientific Centrifuge). The washed nanoparticles were dispersed in 6 ml chloroform for further steps. To grow undoped-NaYF<sub>4</sub> shells on the core NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs, a successive layer-by-layer strategy of tunable shell growth was adopted, as reported by Li et al.[22]

A total of 0.3 mmol of silver nitrate, 2 mL oleylamine, 1mL oleic acid and 10 mL phenyl ether were mixed in a 100 mL flask. The mixture was heated to 150 °C with magnetic stirring under argon blanket. The solution was kept at this temperature for 0.5 hours then cooled to room temperature. The resultant ~5 nm silver nanoparticles were washed several times with ethanol and dispersed in 2 ml 1-octadecene solution.

For core/shell nanoparticles, 1 mmol of synthesized NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> core nanoparticles were taken into 1-octadecene and raise the solution temperature to 160 °C under argon. At that temperature, 0.3 mmol of silver nanoparticles dispersed in 1-octadecene solution was quickly injected into the reaction solution. The Ag nanoparticles dissolve, while the large NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanoparticles ripen to yield core/shell nanoparticles with time. After 1 h the reaction was stopped, washed with ethanol, then dispersed in hexane .

## RESULTS AND DISCUSSION

The transmission electron microscope (TEM) images of the nanoparticles are shown in Figure 1. Figure 1a and Figure 1b show the as-synthesized Ag and NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanoparticles respectively. Figure 1c shows the core-shell nanoparticles formed after the Ostwald ripening process where all the small nanoparticles were dissolved to form a thin shell (~2-4 nm) around the core the nanoparticles. Each of the nanoparticles are fully covered with a uniform silver shell. We further characterized the sample with a high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) to find the core-shell structure. HAADF STEM produces different contrast based on the atomic number (Z); the imaging is often referred to as Z-contrast imaging because the intensity of an image is approximately proportional to Z<sup>2</sup> (Z: atomic number). To establish the presence and the spatial distribution of silver, we adopted the Z-contrast approach as two elements that constitute the core (Y) and the shell (Ag) are sufficiently distant in the periodic table and atomic number to give good contrast and to determine the position and distribution of silver. Figure 1d shows the Z-contrast images from a scanning transmission electron microscopy (STEM). The silver shell was visible on top of the NP core. Due to the atomic number difference between the yttrium core and the silver, the silver shell appears with a lighter contrast. However, we believe the silver shell formed were amorphous which probably makes them look lighter. To understand the crystallinity of the synthesized nanoparticles, we obtained X-ray diffraction (XRD) patterns. As shown in Figure 2, the XRD pattern of the synthesized silver nanoparticles shows regular silver peaks; however, the XRD pattern of the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup>@Ag core/shell nanoparticles did not show any peaks of silver.

To study the plasmonic interaction of silver shell and the up-converting nanoparticles, we coated the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanoparticles with a undoped- NaYF<sub>4</sub> shell as described. The synthetic method published by Li et al. [22] provides a good control over shell thickness. To begin, about 7 nm shell of undoped-NaYF<sub>4</sub> size was grown on the core NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanoparticles; then a metal shell of silver (~ 2 nm thick) was added. As shown in Figure 3, the luminescence intensity went down by about 2.4 times when the silver shell was in direct contact with the phosphors

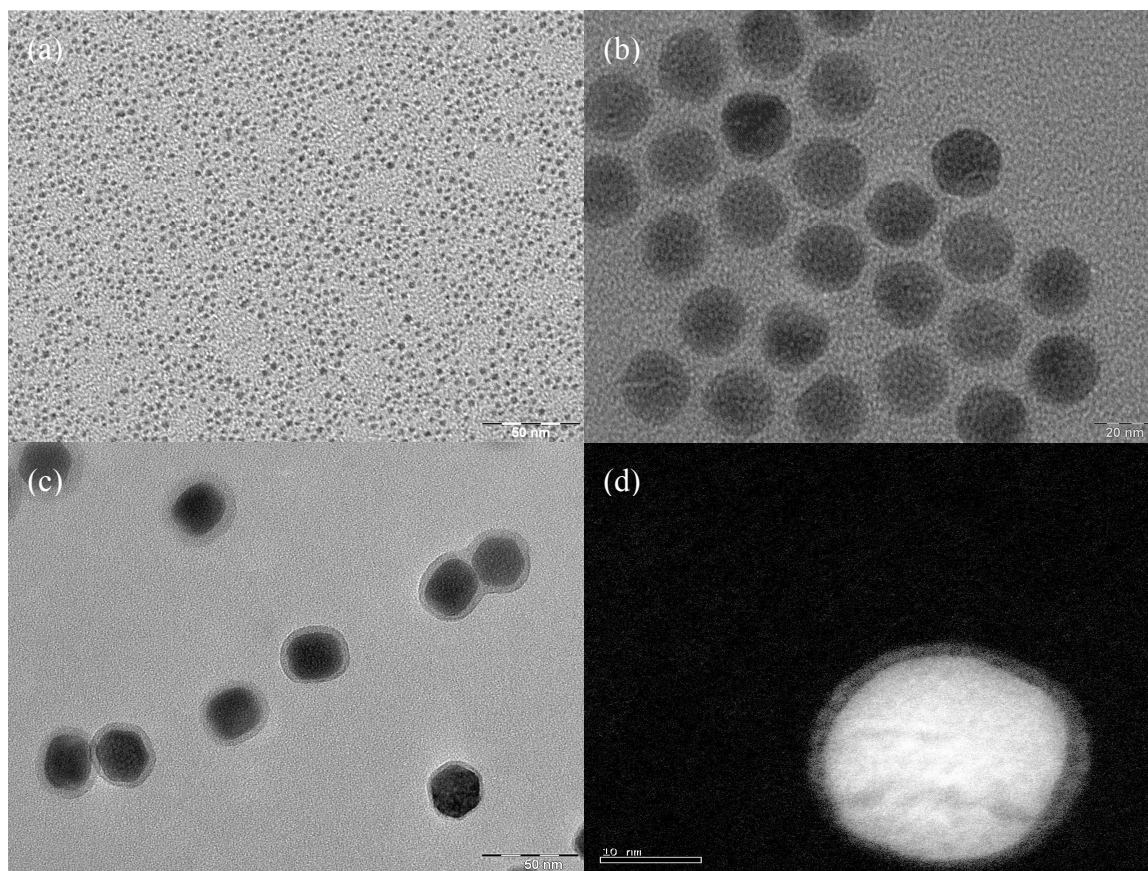


Figure 1. TEM image of (a)  $\sim 5$  nm Ag nanoparticles; (b)  $\sim 22$  nm  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  core nanoparticles; (c)  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}@\text{Ag}$  core-shell nanoparticles; and (d) HAADF STEM image of the  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}@\text{Ag}$  core-shell nanoparticles.

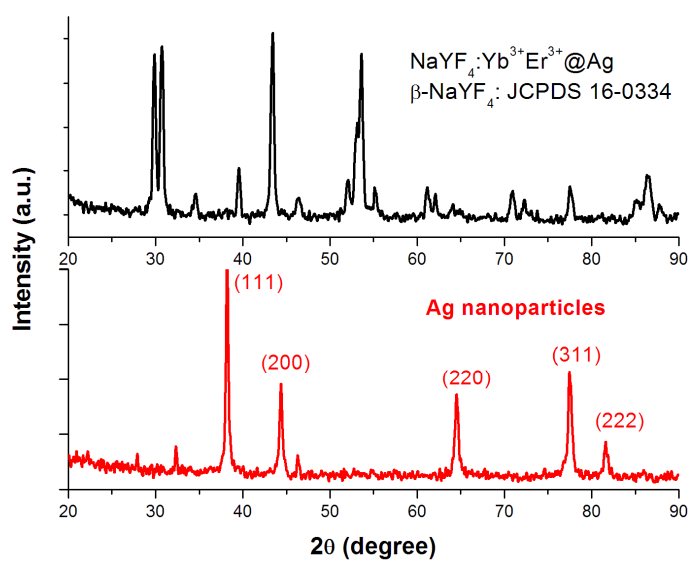


Figure 2. XRD pattern of Ag nanoparticles (bottom), and  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}@\text{Ag}$  core-shell nanoparticles



nanoparticles. However, it the luminescence was enhanced significantly by  $\sim 25.5$  fold when a 7 nm shell of undoped  $\text{NaYF}_4$  was placed between them. This result suggests that the doped emitter ions are mostly present around the surface of the phosphors and emission from the emitter ions is quenched, probably due to rapid radiation-less energy transfer to the metal. However, maximal fluorescence enhancement is observed only from molecules at certain distances from the surface. We have not optimized the separation distance yet – no other spacer distance data are available in the current study. The 7 nm shell is based on a study reported by Yuan et al.[19] where the authors achieved a maximum enhancement at around 10 nm. However, compared to them (14.4 fold enhancement by putting a silica shell and Ag nanoparticles), our results show significant improvement. We believe that the enhanced effect is due to the  $\text{NaYF}_4$  layer shell, which synergistically enhances luminescence by covering the emitters with a suitable epitaxial layer, and provides the required spacing to reduce or eliminate quenching.

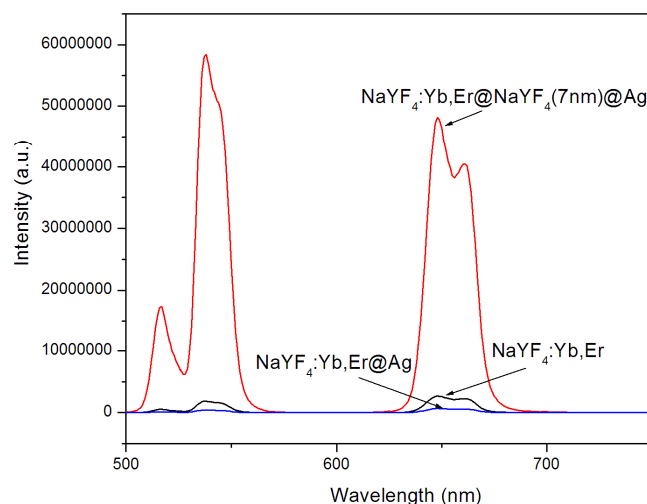


Figure 3. Up-conversion luminescence spectra of the (i) core  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanoparticles, (ii)  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}@\text{Ag}$  nanoparticles and (iii)  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}@\text{NaYF}_4@\text{Ag}$  nanoparticles.

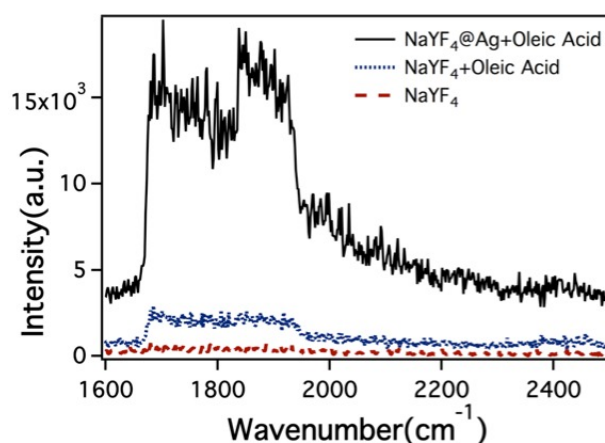


Figure 4. Raman spectra of oleic acid on the surface of  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  and  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}@\text{Ag}$ .

The applicability of the silver coated  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  for dual spectroscopy was demonstrated by measuring the surface enhanced Raman spectra of the oleic acid. Figure 4 shows the C=C and C=O Raman stretching frequencies that fall in the window  $1650\text{--}1850\text{ cm}^{-1}$ . The Raman signal due to the presence of Ag on the surface of  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  was enhanced 7 fold in comparison to  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  without Ag. We are currently undertaking quantitative SERS experiments. We believe, this novel nanoparticles open up possibilities for both label and label-free *in vitro* application.

## CONCLUSIONS

In summary, we have developed a novel method of achieving a new photonic material i.e. silver shell on up-converting NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> phosphors. The new synthesis method offers an added advantage by adding an undoped-NaYF<sub>4</sub> nanoparticles as a spacer layer between the metal and the phosphor surface which helps to achieve a significant enhancement of emission compared to previous works. Coupled to the up-conversion enhancement is the surface enhanced Raman signal. This nanoparticle opens up exciting new possibilities with sensitive label and label-free dual mode spectroscopy. We believe that this new method can be extended to other systems with a further optimized design to yield efficient luminescent materials for a range of applications.

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