Facile synthesis of NaYF₄:Yb, Ln/NaYF₄:Yb core/shell upconversion nanoparticles via successive ion layer adsorption and one-pot reaction technique


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Facile synthesis of NaYF$_4$:Yb, Ln/NaYF$_4$:Yb core/shell upconversion nanoparticles via successive ion layer adsorption and one-pot reaction technique†

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The facile one-pot synthesis of NaYF$_4$:Yb, Ln/NaYF$_4$:Yb core/shell (CS) upconversion nanoparticles (UCNPs) was firstly developed through the successive ion layer adsorption and reaction (SILAR) technique, which represents an attractive alternative to conventional synthesis utilizing the chloride of Ln as the precursors, where the Ln doped NaYF$_4$ core was firstly purified and then an epitaxial shell of the desired thickness was obtained by the injection of shell precursors to a solution of the purified NaYF$_4$ core. The temperature-dependent shell growth mechanism and upconversion luminescent properties were explored thoroughly. A temperature of 280 °C proved to be the optimal shell growth temperature to prepare the compact CS structure with the highest luminescent enhanced efficiency for this preparative system. The shell thickness could be easily tuned using this SILAR technique from about 3 monolayers (ML) to 44 ML. The UC luminescent intensity was found to be increased with increasing shell thickness, and at last the effect of surface on the PL could be completely excluded by an appropriate shell thickness. Furthermore, the performance of the SILAR technique was also demonstrated by comparing Tm$^{3+}$ and Er$^{3+}$ doped separately in the core and shell with the Ln ions co-doped in the core.

Introduction

Lanthanide ion (Ln) doped upconversion (UC) luminescent nanoparticles (NPs) have received considerable attention owing to their wide applications in photoelectronic devices, bioimaging, photodynamic therapy and catalysis fields. 1–3,6 Compared with the traditional organic dyes and quantum dots, UCNPs have many advantages, including a narrower emissive band, longer luminescent lifetime, higher chemical stability, lower toxicity to cells and lower biological autofluorescence under near-infrared excitation etc. 1–3,6 Up to now, the low UC luminescence efficiency remains a key problem that needs to be resolved. Epitaxial shell growth on colloidal NPs is a widely employed strategy to enhance the inherently low quantum efficiency of the UCNPs. 7 Since growing a shell with similar lattice constants around the core could protect the luminescence lanthanide ions in the core from nonradiative decay caused by surface defects as well as vibrational deactivation from solvents or surface-bound ligands in the case of colloidal dispersions, 1,8 the shell growth technique needs to be widely explored.

The traditional Ln doped UCNPs synthesized in the oil phase often utilize the trifluoroacetate as the precursor, 5,10 where the shell can be easily prepared by the one-pot method. However, it needs a complex preparation process: the trifluoroacetate precursor should be prepared via the reaction between trifluoroacetic acid and the oxide of Ln, 8–10 which lowered the accuracy of the materials, resulting in an inferior experimental repetition rate. Furthermore, the highly luminescent UCNPs with a hexagonal phase must be prepared at temperatures greater than 330 °C and the use of a super-toxic ligand (e.g., TOPO) is often necessary. 11 The harsh ligand requirement and the higher temperature conditions make this experiment difficult to perform and environmentally hazardous, spoiling their advantages for widespread production. During the past few years, researchers generally utilized the comparatively inexpensive chloride of Ln as the precursors to prepare the hexagonal UCNPs, which presents a higher experimental repetition rate. 12–14 However, the existing two-pot shell growth process is complicated: the bare core must be purified by centrifugation and then mixed with the shell...
precursors. It is thus impossible to avoid the following drawbacks: firstly, the shell materials are likely to nucleate themselves, leading to inferior homogeneous shell coating; secondly, the thicker shell growth often needs several batches of the injection of shell precursors and duplicative purification and centrifugation process, leading to lower synthesis efficiency of the core/shell (CS) UCNPs.

The successive ion layer adsorption reaction (SILAR) technique was firstly applied in the preparation of nanosized CdSe/CdS CS and CsSe core/multishell NPs by Peng’s group and Xie et al. on the CS structure in the oil phase\textsuperscript{15,16} and our group on the preparation of CdTe/CdS CS structure in aqueous solutions.\textsuperscript{17} It is proved distinctly that the SILAR technique is a powerful method to prepare the high quality (a precise thickness control without homogeneous nucleation of the shell materials) CS NPs.\textsuperscript{15,16} The advantages of the SILAR technique are as follows: first, the synthetic CS NPs often have excellent monodispersity after a homogeneous shell growth due to the slow and controlled injection of the shell materials to the core batch, which avoids the heterogeneous shell growth induced by the temperature fluctuation or concentration difference in some areas commonly occurring in the traditional shell growth method; second, the shell thickness can be controlled precisely after an accurate calculation of shell materials; third, the different shell thickness CS NPs can be obtained in one-pot according to the individual requirement without the multiple bath experiments in the traditional two-pots method, which will save more energy and time. Recently, Zhao’s group have utilized the SILAR technique to prepare the lanthanide ions doped NaYF\textsubscript{4}/NaGaF\textsubscript{4} CS NPs, the Cryo-TEM, Cryo-HRTEM, HAADF-STEM and EELS are also introduced to sufficiently prove the existence of the CS structure, and the resulting CS NPs possessed good monodispersity (12\%) due to the homogeneous shell growth.\textsuperscript{1} However, the two-step shell growth method restricts the thicker shell growth, which is time consuming. As a result, the thicker shell CS NPs (>8 monolayers or >4 nm) have not been investigated in detail. Frank’s group have developed a novel epitaxial shell growth on lanthanide ions doped NaYF\textsubscript{4} CS NPs utilizing Ostwald ripening of small sacrificial NPs as shell precursors, and the resulting CS NPs possessed even better monodispersity (5\%) due to the homogeneous shell growth.\textsuperscript{7} However, the same problem of the preparation of thicker shell CS NPs is still not solved, what’s more, the shell thickness is based on the accurate calculation of the amounts of the sacrificial small NPs, which also need abundant energy and time. On the other hand, the calculation of the shell thickness mentioned in the above shell growth methods both use the computational formula of spherical volume, however, the hexagonal crystal structure of the space morphology of the hexagonal NaYF\textsubscript{4} NPs is clear from the TEM and XRD. Therefore, the shell growth is based on the 100 or 101 (as well as 110) space. As a result, the shell thickness, especially the thicker shell thickness should be based on the calculation of the amplification of the volume of hexagonal rods (100) or hexagonal prisms (101, 110) rather than the calculation of the volume of the sphere.

In this work, we developed a facile one-pot method for the lanthanide ions doped NaYF\textsubscript{4} core/shell UCNPs using the SILAR technique. The shell thickness could be easily tuned using this SILAR technique by simply successively introducing the shell precursor solutions. The temperature-dependent shell growth mechanism and luminescent properties of NaYF\textsubscript{4} core/shell UCNPs are explored deeply. Shell growth temperature can be reduced to 240 °C due to the superiority of the SILAR technique. The analysis from the Field Emission Scanning Electron Microscopy (FESEM), X-ray powder diffraction (XRD), photoluminescence (PL) spectra, and PL lifetime spectra indicate that the shell growth via the SILAR technique in one-pot is feasible and the optimal shell growth temperature is 280 °C, but not the common 300 °C or even higher temperature utilized in previous work.\textsuperscript{1,7,8} The shell thickness can be tuned from 3 monolayers (ML) to 44 ML via the SILAR technique in one-pot easily. Furthermore, we have doped different luminescent center lanthanide ions in core and shell separately and proved the success of the shell growth in our method by the PL spectra.

**Experimental**

**Chemicals**

The lanthanide chlorides were purchased from Aldrich in the highest purity available (>99.9\%). Oleic acid (90\%) and octadecene (90\%) were also purchased from Aldrich. NaOH (99\%), NH\textsubscript{4}F (99\%), cyclohexane (99.5\%), acetone (99.5\%), ethanol (99.5\%) and methanol (99.5\%) were all purchased from Beijing Chemical Works. All the chemicals were used as received without further purification.

**Synthesis of NaYF\textsubscript{4}:Yb, Tm core UCNPs**

The bare core UCNPs were prepared by a procedure modified from the previous method.\textsuperscript{18} Typically, in a 100 mL three-neck flask, a total of 1 mmol LnCl\textsubscript{3}:6H\textsubscript{2}O [0.78 mmol YCl\textsubscript{3}:6H\textsubscript{2}O, 0.2 mmol YbCl\textsubscript{3}:6H\textsubscript{2}O, and 0.02 mmol TmCl\textsubscript{3}:6H\textsubscript{2}O] were added, followed by the addition of 6 mL oleic acid and 15 mL octadecene. After a 30 min stirring under argon flowing at room temperature, this mixture was heated to 160 °C for 30 min to make a clear solution. It was then cooled down to room temperature, followed by the addition of solution of 2.5 mmol NaOH and 4 mmol of NH\textsubscript{4}F in 10 mL of methanol. The methanol was evaporated under heating at 70 °C in argon for 1 hour and then stirred at room temperature for another hour. The reaction mixture was then heated to 300 °C and stirred for 90 min and then cooled down to the desired temperature for the next one-pot shell growth experiment. 1 mL bare core UCNPs were picked up by syringe for the control experimental measurement. Simply, the bare core NPs were cooled to RT and then precipitated using excess acetone and isolated at 7500 rpm (a centrifugal force of 6100 g) for 6 min. The supernatant was poured off and the NPs in the bottom of the centrifuge tube were redispersed in cyclohexane, precipitated using anhydrous ethanol, and isolated again at 6000 rpm (a centrifugal force of 3900 g) for 6 min. This washing process was repeated twice. After the purification, NPs were stored as...
dispersion in cyclohexane with a concentration of 0.26 μM. From the FESEM image, the size of the bare core UCNPs was ca. 33 nm.

**Shell precursor injection solution**

The shell precursor injection solution was prepared as for the bare core precursor solutions. Typically, in a 150 mL three-neck flask, a total of 8 mmol LnCl₃·6H₂O [6.4 mmol YCl₃·6H₂O and 1.6 mmol YbCl₃·6H₂O] were added, followed by the addition of 24 mL oleic acid and 18 mL octadecene. After a 30 min stirring under argon flowing at room temperature, this mixture was heated to 160 °C for 30 min to make a clear solution. It was then cooled down to room temperature, followed by the addition of solution of 20 mmol NaOH and 32 mmol of NH₄F in 80 mL of methanol. The methanol was evaporated under heating at 70 °C in argon for 2 h and then stirred at room temperature for a further 2 h. For each injection, a calculated amount of a given injection solution was taken with a syringe at a speed of 0.1 mL per 2 min.

**Calculation for the injection**

The SILAR technique is based on the successive injections of the shell precursors into the solution containing NaYF₄ core NPs for the growth of core/shell NPs. The amount of shell precursors required for each layer was determined by the number of the surface atoms of a given size of core/shell NPs. Because it is the homogeneous shell encapsulation, the calculations were based on the hexagonal phase structure of NaYF₄ nanocrystals. The relative molar concentration of Ln ions (i) can be easily calculated according to the injected volume of shell precursor. Since the d-spacing values of <1010> and <0001> is 0.51 nm and 0.36 nm, respectively, the shell monolayer thickness should also be different for prism (0.51 nm) and rod (0.36 nm) morphology core/shell NPs. As a result, the diameter of the one monolayer passivated NaYF₄ NPs would be increased for 1.02 nm for a-axis extension and 0.72 nm for c-axis extension. The concentration of NaYF₄ was estimated according to the followed formula:

\[
m = nρV
\]

Here, \(m\) is the mass of the UCNPs, \(n\) is the amount of the whole NPs, \(ρ\) is the density of NaYF₄ (\(ρ = 4.31 \text{ g cm}^{-3}\)), \(V\) is the volume of one particle (\(V = 2.598a^2c\)). \(a\) is the length of side of the hexagonal face and \(c\) is the height of the hexagonal prism. The relative molar amount of Ln ions (\(i\)) needed for the shell growth can be easily calculated. An example of shell thickness (\(x\) ML) calculation is as follow:

\[
2.598a^2c/2.598(a + 0.51x)^2(c + 0.72x) = 1/1 + i \quad (x \leq 15)
\]

\[
2.598a^2c/2.598(a + 0.51x)^2(c + 10.8) = 1/1 + i \quad (x > 15)
\]

The schematic presentation of the hexagonal-phase core and CS NP is shown in Scheme 1. For example, in a typical experiment with 5.2 nmol of 33 nm NaYF₄ core, 0.86 mL of shell precursors is needed for the first layer of the shell growth, and additional 0.90 mL of shell precursors completes the growth of the second layer.

**Synthesis of NaYF₄:Yb, Tm/NaYF₄:Yb core/shell UCNPs by the SILAR technique at different temperatures**

After the bare core UCNPs were prepared, the reaction mixture was cooled down to the desired temperature (e.g., 220 °C, 240 °C, 260 °C and 280 °C) or held at 300 °C for the next shell growth experiment in one-pot. The shell precursor injection solution was then dropped into the three-neck flask at a speed of 0.1 mL per 2 min. 5.4 mL shell precursor solution (~10 ML) was injected and then the reaction mixture was cooled down to room temperature for the next centrifugation and purification procedure just like the purified process of the core NPs.

**Synthesis of NaYF₄:Yb, Tm/NaYF₄:Yb core/shell UCNPs by the SILAR technique with different shell thickness**

The SILAR procedure was readily extended to prepare different shell thickness CS UCNPs in one-pot. In a typical experiment with 2.6 nmol of 33 nm NaYF₄ core, the mixture was cooled from 300 down to 280 °C in an argon atmosphere for the injection and shell growth, the amounts of the injection solutions injected for each step were as follows: 1.4 mL of shell precursors is needed for the third layer of the shell growth, and an additional 2.1 mL of shell precursors completes the growth of the 7th layer, and an additional 4.1 mL of shell precursors completes the growth of the 13th layer, and an additional 9.0 mL of shell precursors completes the growth of the 26th layer, and an additional 13.5 mL of shell precursors completes the growth of the 42th layer, and so forth. With fast stirring in place, the injection solutions should be added in a dropwise manner at a speed of 0.1 mL per 2 min. After the shell precursor injection, the reaction solution was cooled down to room temperature for the next centrifugation and purification procedure in accord with the purified process of the core NPs.

**Characterization**

Steady-state photoluminescence spectra were measured using an Ocean Optics spectrophotometer. The time-resolved luminescence spectra were recorded with a 500 MHz Tektronix digital oscilloscope and the excitation was realized by a nanosecond pulse train at 980 nm from an optical parametric oscillator. The FESEM images were taken on a Hitachi, S-4800.
scanning electron microscope with an acceleration voltage of 5 kV. XRD patterns were obtained using a D8 FOCUS X-ray diffractometer purchased from the Bruker Company.

Results and discussion

It is well known that lanthanide ions doped NaYF₄ NPs with the hexagonal crystal phase have higher UC emission efficiency.⁹,¹²–¹⁴ Hence we have prepared hexagonal NaYF₄:Yb, Tm/NaYF₄:Yb core/shell UCNPs as a model system to verify the SILAR technique in shell preparation. As shown in Fig. 1, the XRD for the bare core and CS UCNPs present the same hexagonal phase crystal structure when they were prepared at temperatures higher than 240 °C. Once the shell growth temperature was lower than this temperature, e.g., 220 °C, both the hexagonal and cubic phase structure appeared simultaneously, proving the existence of the mixed phases. Combining with the basis of FESEM, the shell growth mechanism was exposed distinctly and divided by two different shell formation patterns when the temperature was higher (also including) or lower than 260 °C. As shown in Scheme 2 and Fig. 2, when the temperature was lower than 260 °C, e.g., 240 and 220 °C, the shell raw materials tend to nucleate by themselves and are adsorbed onto the surface of the core NPs to form the loosen plum blossom core/shell.

Scheme 2 UCNPs shell growth mechanism grown at different temperatures.

Fig. 1 XRD results of NaYF₄:Yb, Tm bare core (a) and the NaYF₄:Yb, Tm/NaYF₄:Yb CS NPs prepared at 220 °C, 240 °C, 260 °C, 280 °C, and 300 °C. The JCPDS file number for the cubic and hexagonal bulk structure is 77-2042 and 16-0334, respectively.

Fig. 2 FESEM results of NaYF₄:Yb, Tm bare core (a) and the NaYF₄:Yb, Tm/NaYF₄:Yb CS NPs prepared at 220 °C (b), 240 °C (c), 260 °C (d), 280 °C (e), and 300 °C (f) with different magnification powers. The lengths of the side of the hexagonal prism are calculated to be 33 ± 3 nm, 63 ± 9 nm, 49 ± 7 nm, 44 ± 4 nm and 43 ± 5 nm respectively for the bare core NPs and the CS NPs prepared at 240 °C (c), 260 °C (d), 280 °C (e), and 300 °C (f), respectively. The new nucleus of the CS NPs prepared at 220 °C (b) is 11 ± 2 nm. The scale bar is 100 nm.
like structures. The adsorbed ability practically disappears when the temperature reduces to 220 °C due to the inefficient thermal requirement. When the temperature was higher (also including) than 260 °C, e.g., 260, 280 and 300 °C, the shell raw materials tend to epitaxially grow on the surface of the core NPs to form the compact core/shell structures. This indicates that the shell growth is a strongly thermodynamics dependent process. Anyway, the shell growth temperature can be reduced to 240 °C, which is lower than the traditional shell growth temperature (≥ 300 °C) in the oil phase. This is realized based on the good control of the SILAR technique in one-pot.

However, as shown from the FESEM results, we find that the CS structure prepared at 260 °C was not as compact as the CS structure prepared at 280 °C due to the lack of enough thermal energy requirement for the compact shell growth. Although the CS NPs prepared at 300 °C also show the compact structure, this shell growth temperature, the same temperature as the core preparation, could not be chosen as the optimal one since it is widely accepted that selecting a lower shell growth temperature than the core preparation could decrease the nucleation of the shell materials as much as possible and result in the high quality CS NPs. These results implied that 280 °C might be the optimal shell growth temperature, which could be further corroborated from the steady-state and time-resolved PL spectra.

From the traditional point of view, it is accepted that elevating the growth temperature of nanocrystals trends to decrease the defects of the lattice and increase the luminescent emission efficiency. However, the experimental results refute this theory. As shown in Fig. 3, when the shell growth temperature was elevated from 220 °C to 240 °C, 260 °C, 280 °C, and 300 °C, both tri-photon (1G3–3H6) 477 nm emission and the two-photon (1H4–3H6) 801 nm UC emission of Tm ions was increased firstly and then decreased at the turn point of 280 °C. Combined with the PL decay spectra results shown in Fig. S1 and Table S1 (ESI†). The lifetime of the bare core UCNPs was increased from 330 μs (477 nm) and 599 μs (801 nm) gradually to the maximum 785 μs (477 nm) and 1328 μs (801 nm) when the shell was grown at 280 °C, then decreased to 543 μs (477 nm) and 848 μs (801 nm) when the shell growth temperature reached 300 °C. During the epitaxial growth of shell, surface defects of the UCNPs can be passivated, resulting in the obvious enhancement in UC emission and increase in lifetime. Similar results have also been emphasized by the previous work. The prolonged PL lifetime further corroborated the shell passivation effect would be strengthened when the shell growth temperature was elevated until the temperature reached 280 °C. When the temperature was higher than 280 °C (i.e., 300 °C), both the PL intensity and the luminescent lifetime decreased obviously, which was due to increased nonradiative processes induced by the thermal enrichment of the surface ligand (vide infra).

As the shell growth temperature was elevated, the effective ligand bound onto the surface of the CS NPs would increase gradually, the electron image will turn blurred, as could be transparently identified when the shell growth temperature reached 300 °C (shown in Fig. 2f). The thermogravimetry analysis (TGA) results (see Fig. S2, ESI†) could sufficiently confirm that the content percentage of surface ligand is a kind of thermodynamics process, thus the value of the CS UCNPs prepared at 280 °C was greatly lower than that of the CS UCNPs prepared at 300 °C even with the same size and CS structures. Since the UC emissive efficiency is directly in relation to the nonradiative decay caused by surface defects as well as vibrational deactivation from solvents or surface-bound ligands in the case of colloidal dispersions. The decrease in luminescence for the CS UCNPs prepared at higher shell growth temperature than 280 °C is attributed to the increase in the multiphonon relaxation of the excited levels of Tm because of the thermal inducing enrichment of ligand coordinates. The high-energy vibrations of the surface ligand would strongly quench the excited states of the Ln by multiphonon relaxation and thus impact the upconversion process significantly. Therefore, although elevating the growth temperature of nanocrystals trends to decrease the defects of lattice and increase the luminescent emission efficiency, this tendency is not monotonous. When the temperature is too high, e.g., 300 °C, the UC luminescent intensity will drop naturally.
The different shell thickness of CS UCNPs could also be readily prepared through the SILAR technique in one-pot. Since the d-spacing values of <1010> and <0001> is 0.51 and 0.36 nm, respectively, the shell monolayer thickness should also be different for hexagonal prism (0.51 nm) and rod (0.36 nm) morphology core/shell UCNPs. As is shown in Fig. 4 and Fig. S3 (ESI†), the size of the prepared CS UCNPs was enlarged as successive precursor solutions were introduced, and the CS UCNPs prepared in this work were distinctly hexagonal prism structure, as a result, the thickness of each monolayer should be 0.51 nm. As shown in Fig. 4 and Table 1, the thickness of the shell could be tuned easily in one-pot preparation from about 1.5 nm (~3 ML) to 22 nm (~44 ML), which was greatly thicker than the shell thickness (~8 ML) prepared by the recently published two-pots method.1–7 The thicker CS UCNPs had a hexagonal prism structure, which could be seen clearly from the FESEM (Fig. 4e and f). Comparing with the previously approximate calculation of the amount of the shell precursor solutions by spherical volume, our calculation (Table 1) was more accurate in predicting the shell thickness.

The upconversion luminescent property of the CS UCNPs with different shell layers prepared within the same pot was also investigated. Generally speaking, when the shell thickness increases, the distance between the surface ligand/the surface defects and the luminescent center core will be farther, leading to a weaker or even negligible influence and the stronger enhancement of UC luminescence of the core finally. As shown in Fig. 5, when the shell thickness increased, the UC PL intensity firstly increased until the shell layer reached 27 ML and then became flat. This implied that the enhancement tended to be saturated until a sufficient shell thickness was achieved. The maximum luminescent enhancement of CS to core UCNPs could be achieved at about 23 fold. The enhanced ratio of the triple-photon emission (477 nm) increased greater than that of the double-photon emission (801 nm), which was due to the more obvious influence effect of the triple-photon process of the Tm ions by the surrounding conditions.13

It is well known that if the different luminescent center lanthanide ions are co-doped in the core, the absorption (980 nm) of the sensitizer would be shared in a competitive pattern, leading to the quenching of respective luminescence, and the separation of the luminescent center lanthanide ions in different domains, e.g., core and shell, would reduce the adverse interactions with each other and hence enhance the UC luminescent efficiency of the different luminescence centers respectively.23 Here, the shell thickness was controlled by the SILAR technique as 10 ML for the next PL spectra analysis. As shown in Fig. 6, when the Er ions was doped competitively with Tm ions in core NPs with same particle size (33 nm), both the tri-photon (5G4–5H6) 477 nm UC emission and the two-photon (5H4–5H6) 801 nm UC emission of Tm ions5 were clearly quenched, which is due to the preferential energy transfer from Yb to Er ions than to Tm ions.23 When the Tm ions and Er ions were doped separately in the core and shell, both the UC emission of Tm ions (477 nm and 801 nm) and the UC emission of Er ions (542 nm and 656 nm) could be strongly detected. Furthermore, the luminescent enhancement effect of Tm ions could be found directly after the Yb, Er ions co-doped ~10 ML shell passivation (red line in Fig. 6). However, the enhancement coefficient of the Tm ions’ emission was about 2.5, which was lower than the one (3.4–3.9) after the active shell passivation (shown in Fig. 3), derived from the competitively stronger absorption ability of Er ions than Tm ions. In fact, both the 5G4–5F4 emission of Tm3+ and the 4F9/2–4I15/2 emission of Er3+ contribute to the 650 nm

![FESEM results of NaYF4:Yb, Tm bare core (a) and the NaYF4:Yb, Tm/NaYF4:Yb CS NPs with different shell thickness. The lengths of the side of the hexagonal prism are calculated to be 33 ± 3 nm (a), 36 ± 3 nm (b), 40 ± 4 nm (c), 47 ± 4 nm (d), 60 ± 5 nm (e) and 78 ± 6 nm (f) for the bare core NPs and the CS NPs with different shell layers prepared in one-pot. The scale bar is 200 nm.](Image)

**Table 1** Statistics obtained from the FESEM corresponding to the particle sizes (l) for core and CS UCNPs with different shell thickness. The predicted shell thickness by calculation of spherical volume is also listed to show the comparison of error analysis

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<td>9</td>
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emission, however, only the $^4S_{3/2} \rightarrow ^4I_{5/2}$ emission of Er$^{3+}$ (without the Tm$^{3+}$) contributes to the 540 nm emission. As a result, as shown in the blue curve of Fig. 6, although for the Er-doped UCNPs, the green 540 nm peak is stronger than the red 650 nm one, when the Tm$^{3+}$ and Er$^{3+}$ are co-doped, the 650 nm emission will be stronger than the 540 nm emission. This phenomenon further proves the superior control of doped Ln ions in the shell by the SILAR technique.

**Conclusions**

The SILAR technique reported here has proven to be versatile for the growth of Ln doped NaYF$_4$ core and core/shell UCNPs in one-pot. The intrinsic feature of the SILAR technique, a precise thickness control without homogeneous nucleation of the shell materials, have made it possible to grow high-quality CS UCNPs, which takes advantages of simplicity, low cost, and green precursors. The optimal shell growth temperature was proved to be 280 °C in this system for the formation of compact CS structure with the highest luminescent enhanced effect. As the shell thickness increased, the UC luminescent intensity of Tm ions would be improved and the maximum luminescent enhancement of CS to core UCNPs could be achieved to a saturated value of about 23 fold. The enhanced ratio of the triple-photon emission (477 nm) increased greatly to higher than that of the double-photon emission (801 nm). When the different luminescent center Ln ions were doped separately in the core and shell, the quenching effect caused by the interactions between the different Ln ions will be avoided efficiently.

**Acknowledgements**

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