Lutetium doping for making big core and core-shell upconversion nanoparticles

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ARTICLE

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A novel strategy for making big core and core-shell upconversion nanoparticles (UCNs) by Lutetium doping has been developed. The size of the core UCNs is easily tuned in the increasing direction with enhanced luminescence by rational Lutetium doping. Use of $NaLuF_4$ as the shell material, provides a promising solution to the difficulty of coating shell onto big core UCNs with tremendous thickness. This can lead to the fabrication of UCNs with well-designed core-shell structures, with multiple layers and desired thickness, for various applications such as optical encoding, multiplexed biodetection, microarrays, and flow cytometry.

Introduction

Upconversion nanoparticles (UCNs) have drawn wide research interest in the past decade owing to their unique properties that surpass conventional fluorophores like organic dyes and quantum dots. Their nil auto-fluorescence background, deeper penetration of excitation light, low phototoxicity and excellent photostability make UCNs a revolutionary nanomaterial for applications like bio-imaging[1, 2], photodynamic therapy[3-5], photo-activation[6-8], and bio-detection[9, 10]. Plenty of efforts have been devoted to engineer UCNs with tunable size and luminescence characteristics according to the application it is being used in.[11-14] The size of UCNs is usually tuned by delicately manipulating the synthesis conditions (reaction temperature, solvent composition, and reaction time) during nucleation and growth of the nanocrystal.[15, 16] Apart from these, rational doping of lanthanide ions have also been reported as an effective way to tune the size of UCNs.[11, 14] Doping of various lanthanide ions with similar ionic radii into the $NaYF_4$ nanocrystal has been proved to provide very effective host materials for UCNs since they take the position of Yttrium (Y^{3+}) in the crystal lattice. Whereas the small difference in radius between the doped ions and Y^{3+}, will promote or delay the nucleation and phase transition of $NaYF_4$ nanocrystals from cubic phase to hexagonal phase during synthesis.[11] Generally, the hexagonal phase $NaREF_4$ (RE-Rare Earth) is more thermodynamically stable than the cubic phase,[17] and hence easier phase transition will promote nucleation. Moreover, the difference in radius between the doped ions and Y^{3+} will also affect the electron charge density on the nanoparticle surface, which determines the crystal growth rate. Through density functional theory (DFT) calculation, Liu *et al.* demonstrate that the electron charge density of the crystal surface was increased after a larger Gd^{3+} ion replaced the Y^{3+} ion in the $NaYF_4$ crystal lattice, which thus repelled the negatively charged F^- ions and suppressed the growth of the nanoparticle to produce a smaller nanoparticle size.[11] On the contrary, when Y^{3+} is replaced by a smaller radius ion, the electron charge density on the surface of growing nanoparticle will be decreased, thus resulting more attraction of F^- ion to the particle surface to form a larger sized UCNs. Considering that Gadolinium (Gd^{3+}) also lacks of energy levels that interfere with energy transfer in UCNs, it is the most commonly used ion to decrease the size of UCNs, without significant change in its fluorescent properties.[11, 18, 19] However, increasing the size of UCNs by lanthanide doping, without changing their fluorescent properties has been met with very little success. Although it has been reported that by increasing the concentration of Yb^{3+}, whose ionic radius is smaller than Y^{3+}, the size of UCNs will grow.[14, 20] Yb^{3+} is also the sensitizer ion in the energy transfer process, whose concentration affects the fluorescent properties of UCNs significantly. Moreover, due to back-energy transfer from activator ions to the sensitizer Yb^{3+} ions, increase of Yb^{3+} concentration will not only change the ratio of peaks in the spectrum, but also decrease the upconversion efficiency. Thus tuning the size of UCNs in the increasing direction by rational doping is still very challenging

Another important strategy employed to increase the size and luminescence intensity of UCNs is to synthesize UCNs with core-shell architecture.[12, 21-26] The key point to fabricate core-shell structure is the separation of nucleation and growth, failure of which leads to the formation of new nuclei which grows in to new core particles instead of forming the shell.[27] Currently, two methods are generally used to fabricate core-shell UCNs namely heating-up method[24, 28, 29] and hot-injection method[30-33]. In the heating-up method, the core nanoparticles are synthesized beforehand. When coating the shell, the core nanoparticles are introduced into the reaction solution containing the shell precusors, acting as the nuclei for the shell precusors to deposit and grow into the shell layer. In the hot-injection method, shell precusors are first dissolved in high boiling solvents (usually oleic acid, oleylamine, and octadecene). When the core nanoparticles are synthesized in the hot reaction solution without cooling down, the high boiling point solvents containing the shell precusors are injected into the hot reaction solution. The shell precusors, which are the ion mononers[31, 33] or small sacrificial alpha-$NaYF_4$ nanoparticles[30, 32] grow onto the core particles and form the shell layer in the growth process or Ostwald-ripening process, respectively. Core-shell UCNs with lots of different structures have been fabricated through the above methods, but the size of the core particles are usually less than 30 nm, and the shell thickness is usually less than 10 nm.[24, 29, 31, 32, 34, 35] It is still challenging to coat shell onto big core nanoparticles with tremendous shell thickness. In the previous attempts, $NaYF_4$ or $NaGdF_4$, were chosen as the shell precusors to ensure the efficient photo-upconverting process in the shell host. However, $NaYF_4$ and $NaGdF_4$ easily form new nuclei when added into the reactions, rather than deposit and form shell onto the already-made core particles, especially when the core particles are big in size, having smaller surface-to-volume ratio and less surface defects for shell precusors to deposit. Thus the concentration of the shell precusors should be kept low to avoid the nucleation process but this in-turn limits the thickness of the shell. Hence the coating of shells with tremendous thickness also remains an unsolved problem till date.

In this study, we demonstrate a promising solution to these two major problems mentioned above to produce nanoparticles with larger size and enhanced fluorescence. Here, we report for the first time, the use of lutetium for doping in UCN core to increase their size and also used to coat shells of tremendous thickness on to the UCN core. This methodology enables the efficient tuning of the size of UCNs in the increasing direction and also enhances their fluorescence emission characteristics significantly.

Lutetium provides a promising solution to the problem of increasing the size of UCNs by rational doping and coating shell with tremendous thickness onto big core UCNs. Similar to Y^{3+}, whose energy levels are simple and do not interfere with the energy transfer in upconversion, Lu^{3+} also doesn't have unpaired electrons in the 4f orbits, thus isolating the energy transfer between the sensitizers and activators and constitutes as a perfect host material for UCNs.[9, 36-41] Lu^{3+} has a smaller ionic radius than Y^{3+}. When forming the $NaREF_4$ nanocrystal, the smaller ionic radius makes it more difficult to form stable hexagonal nucleus, thus nucleation process is supressed. And when Y^{3+} is replaced by smaller Lu^{3+}, the electron charge density on the surface of growing UCNs decreases, allowing more attraction of F- ion to the particle surface, thus benifiting the growth process to form a larger sized UCNs. This is desirable for making big nanoparticles and coating shell onto the core particles (Figure 1). In this work, the ability of Lu^{3+} to increase the size of UCN core is studied for the first time. UCNs with tunable size and constant emission peaks ratios are produced by doping different concentrations of Lu^{3+}. As a proof of concept to show the advantages of $NaLuF_4$ as a shell material, the effects of $NaLuF_4$ and $NaYF_4$ shell coating onto big $NaYF_4$ core UCNs with different core/shell ratios are compared using the heating-up method.

Experimental

Synthesis of $NaYF_4$:Yb,Er UCNs with Lu^{3+} doping

All the chemicals were purchased from Sigma-Aldrich and used without further purification. Typically, $NaYF_4$: 20%Yb, 2%Er nanoparticles with 10% Lu^{3+} were synthesized following protocols reported previously with modifications.[16] 0.68 mmol YCl_3, 0.1 mmol $LuCl_3$, 0.20 mmol $YbCl_3$ and 0.02 mmol $ErCl_3$ were mixed with 6 ml oleic acid and 15 ml 1-octadecene in a 100 ml flask. The solution was heated to 150 °C to form a homogenous solution, and then cooled down to room temperature. A solution of 4 mmol NH_4F and 2.5 mmol NaOH in 10 ml of methanol was added into the flask and stirred for 30 min. Subsequently, the solution was heated to 100 °C to remove the methanol. After methanol was evaporated, the solution was heated to 300 °C and incubated at that temperature for 1 hour under an argon atmosphere and then cooled to room temperature. The UCNs were precipitated with 10ml of acetone, collected after centrifugation, then washed thrice with ethanol/water (1:1 v/v) and finally dispersed in cyclohexane for subsequent use. $NaYF_4$: Yb, Er UCNs with different Lu^{3+} doping concentration is synthesized similarly, but by changing the amount of lanthanide chlorides stoichiometrically.

Synthesis of $NaYF_4$:Yb,Er core UCNs

Core UCNs with different Yb concentrations are synthesized similarly as above, by stoichiometrically changing the amount of lanthanide chlorides and without Lu^{3+} doping.

Synthesis of $NaYF_4$:Yb,Er@$NaLuF_4$:Yb,Tm core-shell UCNs

0.745 mmol $LuCl_3$, 0.25 mmol $YbCl_3$ and 0.05 mmol $TmCl_3$ were mixed with 6 ml oleic acid and 15 ml 1-octadecene in a 100 ml flask. The solution was heated to 150 °C to form a homogenous solution, and then cooled down to room temperature. Solution of the $NaYF_4$: Yb, Er core nanocrystals dispersed in cyclohexane that were obtained from the previous step was added to the flask. The solution was maintained at 70 °C to remove the cyclohexane solvent and then subsequently cooled down to room temperature. A solution of 4 mmol NH_4F and 2.5 mmol NaOH in 10 ml of methanol was added into the flask and stirred for 30 min. Subsequently, the solution was heated to 100 °C to remove the methanol. After methanol was evaporated, the solution was heated to 300 °C and incubated at that temperature for 1 hour under an argon atmosphere and then cooled to room temperature. The nanocrystals were precipitated with 10ml of acetone, collected after centrifugation, then washed thrice with ethanol/water (1:1 v/v) and finally dispersed in cyclohexane for subsequent use. UCNs of different core-shell ratio is synthesized similarly, but by changing the amount of core UCNs added into the reaction stoichiometrically and prolonging the incubation time. $NaYF_4$:Yb,Er@$NaYF_4$:Yb,Tm core-shell UCNs are synthesized similarly by the replacement of $LuCl_3$ with YCl_3 as the shell precursor.

Characterizations

Transmission electron microscopy (TEM) images were recorded on a JEOL 2010F transmission electron microscope (Jeol Ltd., Tokyo, Japan) operating at an acceleration voltage of 200 kV. Fluorescence spectra of were recorded on a Hitachi F-500 fluorescence spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan) equipped with an NIR continuous wave laser with emission at 980 nm (Photonitech (Asia) Pte. Ltd., Singapore). The DLS size distribution statistics were measured with a Malvern zetasizer nano series (Malvern Instruments Ltd., Worcestershire, UK). Elements analysis was performed by analyzing of the HNO_3 digestion of the UCNs samples in an Optima 5300 DV ICP-OES system. XRD measurement was carried out using a Bruker D5005 X-ray diffractometer (Siemens AG, Munich, Germany) furnished with Cu Ka radiation under 40 kV. Fourier transform infrared (FTIR) were performed using IRPrestige-21 Fourier transform infrared spectrophotometer (Shimadzu Corp., Japan).

Results and discussion

NaY/LuF_4: Yb, Er UCNs doped with different concentrations of Lu^{3+} have been synthesized under the same experimental conditions, except for varying the doping concentration of Lu^{3+}. Element analysis by ICP-OES demonstrates that the elemental content of the synthesized NaY/LuF_4: Yb, Er UCNs generally agrees with the concentration of lanthanides in the raw materials (Table S1). XRD characteraziation of the UCNs demonstrates that pure hexagonal phase were obtained in the NaY/LuF_4: Yb, Er with different concentration of Lu^{3+} doping. The XRD peaks sequentially shift towards high-angle as the Lu^{3+} concentration increases (Figure S1). This peak shifting confirms the shrink of the crystal lattice due to the replacement of Y^{3+} by smaller radius Lu^{3+}. Size of the UCNs were characterized by TEM. As shown in Figure 2a-e, the size of the UCNs obtained were from 20 nm to 100 nm as the doping concentration of Lu was increased from 0% to 50%. As discussed above, with the increase in Lu^{3+} concentration, the nucleation process is suppressed and the growth process is benefited, thereby making the nanoparticles grow bigger eventually. The size of the above samples measured by Dynamic light scattering (DLS) is also given in Figure 2f and the trend agrees well with the size increment by Lu^{3+} doping as observed in the TEM images. It has been noted that the absolute size value measured by DLS is larger than that observed from a TEM image, since the former one measures the hydrodynamic radius while the later one captures the actual radius of the nanoparticles. The luminescence spectra (Figure 2h) shows that the luminescence intensity increases as the concentration of Lu^{3+} increases. This is because, as the size of UCNs increases, more sensitizer and activator ions are isolated from the surface defects.[42] While the red to green and blue to green ratios of the emission peaks still remain the same across the samples (Figure 2i). This confirms that Lu^{3+} doesn't interfere with the energy transfer from Yb^{3+} to Er^{3+} or back energy transfer from Er^{3+} to Yb^{3+} (Figure 2g). Thus, UCNs with tunable size but similar fluorescent properties can be obtained effectively by Lu^{3+} doping.

Another attractive property of $NaLuF_4$ is that it enables shell coating onto big core UCNs with tremendous shell thickness. We first compare the coating of $NaLuF_4$ amd $NaYF_4$ shell with 1:1 core/shell ratio onto big $NaYF_4$ UCNs under different incubation time. $NaY_{0.5}Yb_{0.5}F_4$:Er core UCNs with 50% Yb doping and the diameter of around 40 nm (Figure 3a) were synthesized, which are bigger than the conventional $NaYF_4$:Yb,Er UCNs with 20% Yb doping and the diameter of around 20 nm, and also bigger than the core particles in the previous studies on core-shell UCNs. The shell was coated onto the core UCNs through the heating-up method, and incubated at 300 ^{o}C for 1 hour or 4 hours. With one hour incubation time, the $NaYF_4$ shell was not fully coated onto the big core UCNs, instead small new core particles were formed (Figure 3b). Only by prolonging the incubation time to 4 hours through the Ostwald-ripening process, the small newly-formed core particles dissolved and grew onto the big core-shell particles as the shell (Figure 3c). However, $NaLuF_4$ fully coated on to the big core UCNs without new nucleations efficiently within one hour incubation time (Figure 3d). As described above, this is due to the relative low stability of $NaLuF_4$ nucleus, which suppresses the nucleation of the shell precusor, and the decreased electron charge density on the surface of the $NaLuF_4$ coated nanoparticles, which is benificial for shell growth. The luminescence spectra (Figure 3f) also indicated that $NaLuF_4$ is more preferable to use as the shell host than $NaYF_4$, by giving stronger emission from samples incubated for both 1 hour and 4 hours. To compare the lumincescence of shell host, the activator doped in the shell was different from that doped in the core, namely Tm and Er for the shell and core, respectively (Figure 3e). The Er emissions at 545 nm were almost equal across the samples, since the amount of the core UCNs were the same. While the Tm emissions from

$NaLuF_4$:Yb,Tm shell was much stronger than that from $NaYF_4$:Yb,Tm shell, indicating $NaLuF_4$ is more effective than $NaYF_4$ acting as shell host. It has been noticed that, the Tm emissions from the samples with longer incubation time were stronger than those with shorter incubation time. This may be attributed to the crystal growing to perfection with increasing incubation time.

Thicker shell has also been obtained by adding in more $NaLuF_4$ shell precursor. By using $NaLuF_4$ as the shell precursor, we successfully coated a shell with tremendous shell thickness at 1:5 and 1:10 core/shell ratio, and grew the size of nanoparticle from 40 nm of the core to 200 nm and 300 nm of the core-shell nanoparticles (Figure 4c,d and Figure S2e,f). However, the coating of $NaYF_4$ shell with 1:5 and 1:10 core/shell ratio was not successful. The size of the nanoparticles were less than 70 nm, and instead of coating the shell, plenty of new core nanoparticles were formed, which were bigger than the newly-formed particles with 1:1 core/shell ratio coating, and not dissolvable even when the incubation time was prolonged to 4 hours (Figure 4a and b). It has been noticed that the size of the newly-formed particles were around 30 nm, which was as big as the core nanoparticles synthesized conventionaly without adding the prepared core UCNs, thus indicating that the spontaneous nucleation of the $NaYF_4$ shell precusor significantly surpasses the deposition and shell growth onto the prepared core UCNs. However, under the same core/shell ratio and reaction conditions, $NaLuF_4$ completely grew as the shell onto the prepared core UCNs, without any new core particles being formed, demonstrating $NaLuF_4$ as an ideal material for $NaREF_4$ UCNs shell coating. The luminescence intensity of the core-shell nanoparticles increased as the thickness of the shell increased (Figure 4e). However, it has been noticed that, the Tm emissions of the $NaYF_4$ shell with 1:5 and 1:10 core/shell ratio was only equivalent to the emission of $NaLuF_4$ shell with 1:1 core/shell ratio, while the emissions of the $NaLuF_4$ shell with 1:5 core/shell ratio were significantly stronger and became even stronger with 1:10 core/shell ratio. It provides not only a way to enhance the luminescence intensity of the nanoparticles by shell coating, but also a stratergy to produce ratiometric optical encoding in a wide range. By coating a luminescent shell (with different emissions from the core) with different thickness and using the fluorescence of the core as a constant reference, ratiometric differentiable optical codes can be produced in a large number, owing to the feasibility of shell coating with tremendous thickness.

We also tested coating a $NaLuF_4$ shell onto even bigger core hexagonal nanoplate with the diameter of around 100 × 60 nm (Figure S3a). $NaLuF_4$ shell with 1:5 and 1:10 core/shell ratio can still be successfully coated onto the bigger core. This was confirmed by TEM and DLS measurement (Figure S3b-d). The luminescence intensity of the shell increased with the thickness of the shell (Figure S3e).

Conclusions

We have developed a strategy for tuning the size of UCNs in the increasing direction without changing the emission peak ratios by Lu^{3+} doping. In addition, it has been demonstrated that $NaLuF_4$ is an excellent material for shell coating onto $NaREF_4$ core UCNs, by providing a promissing solution to the difficulties of shell coating onto big core UCNs and coating shell with tremendous thickness. The advantages of utiziling $NaLuF_4$ for shell coating, provide much more freedom for engineering of UCNs with desirable properties such as enhanced lumincecence intensity, tunable emissions and excitations. This can lead to the fabrication of UCNs with well designed core-shell structure with multiple layers and desired thickness, which is a imminent necessity for various applications such as optical encoding, multiplexed biodetection, microarrays, and flow cytometry.

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Notes and references

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1. J. Zhou, Z. Liu and F. Y. Li, *Chem Soc Rev*, 2012, **41**, 1323-1349.
2. Y. F. Wang, G. Y. Liu, L. D. Sun, J. W. Xiao, J. C. Zhou and C. H. Yan, *Acs Nano*, 2013, **7**, 7200-7206.
3. S. S. Lucky, N. Muhammad Idris, Z. Li, K. Huang, K. C. Soo and Y. Zhang, *ACS Nano*, 2015, **9**, 191-205.
4. X. F. Qiao, J. C. Zhou, J. W. Xiao, Y. F. Wang, L. D. Sun and C. H. Yan, *Nanoscale*, 2012, **4**, 4611-4623.
5. X. Wang, K. Liu, G. Yang, L. Cheng, L. He, Y. Liu, Y. Li, L. Guo and Z. Liu, *Nanoscale*, 2014, **6**, 9198-9205.
6. J. Shen, G. Chen, T. Y. Ohulchanskyy, S. J. Kesseli, S. Buchholz, Z. Li, P. N. Prasad and G. Han, *Small*, 2013, **9**, 3213-3217.
7. M. K. G. Jayakumar, A. Bansal, K. Huang, R. Yao, B. N. Li and Y. Zhang, *ACS Nano*, 2014, **8**, 4848-4858.
8. M. K. G. Jayakumar, N. M. Idris and Y. Zhang, *Proceedings of the National Academy of Sciences of the United States of America*, 2012, **109**, 8483-8488.
9. P. Huang, W. Zheng, S. Zhou, D. Tu, Z. Chen, H. Zhu, R. Li, E. Ma, M. Huang and X. Chen, *Angewandte Chemie International Edition*, 2014, **53**, 1252-1257.
10. F. Zhang, Q. H. Shi, Y. C. Zhang, Y. F. Shi, K. L. Ding, D. Y. Zhao and G. D. Stucky, *Advanced Materials*, 2011, **23**, 3775-3779.
11. F. Wang, Y. Han, C. S. Lim, Y. H. Lu, J. Wang, J. Xu, H. Y. Chen, C. Zhang, M. H. Hong and X. G. Liu, *Nature*, 2010, **463**, 1061-1065.
12. F. Wang, R. R. Deng, J. Wang, Q. X. Wang, Y. Han, H. M. Zhu, X. Y. Chen and X. G. Liu, *Nat Mater*, 2011, **10**, 968-973.
13. J. Shen, G. Chen, A.-M. Vu, W. Fan, O. S. Bilsel, C.-C. Chang and G. Han, *Advanced Optical Materials*, 2013, **1**, 644-650.
14. S. Hao, W. Shao, H. Qiu, Y. Shang, R. Fan, X. Guo, L. Zhao, G. Chen and C. Yang, *Rsc Adv*, 2014, **4**, 56302-56306.

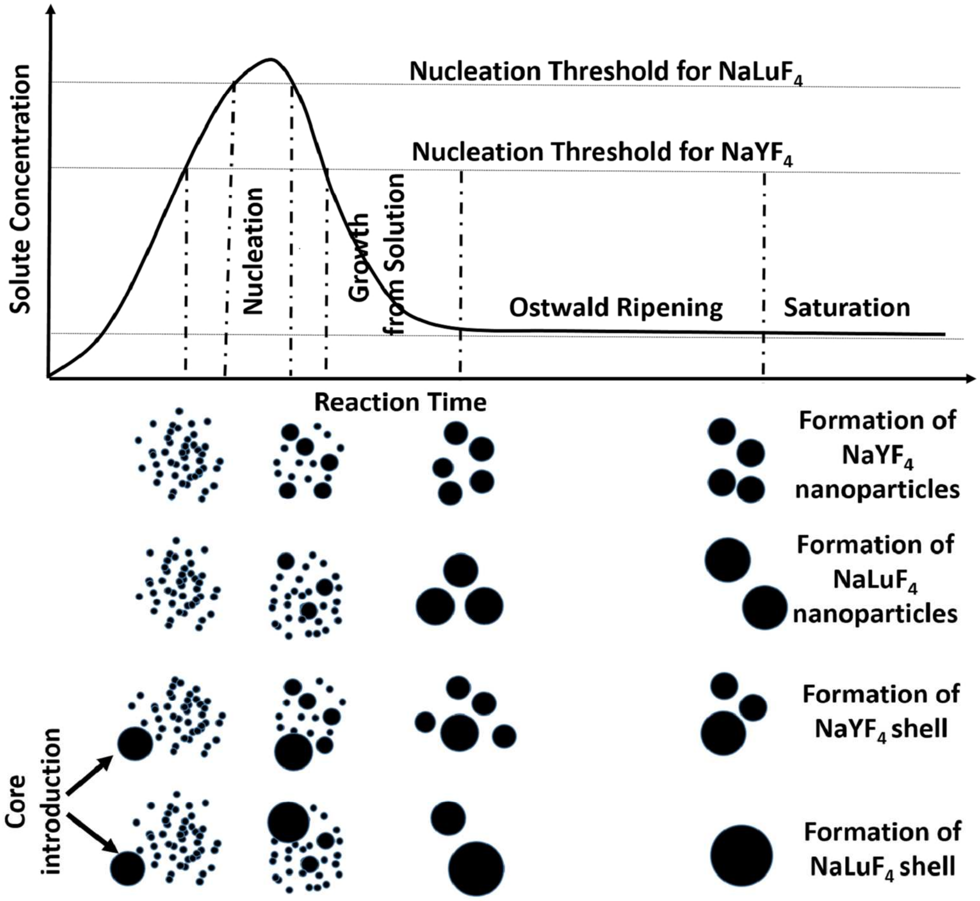
15. H.-X. Mai, Y.-W. Zhang, L.-D. Sun and C.-H. Yan, *The Journal of Physical Chemistry C*, 2007, **111**, 13730-13739.
16. Z. Li and Y. Zhang, *Nanotechnology*, 2008, **19**, 345606-345610.
17. H.-X. Mai, Y.-W. Zhang, R. Si, Z.-G. Yan, L.-d. Sun, L.-P. You and C.-H. Yan, *Journal of the American Chemical Society*, 2006, **128**, 6426-6436.
18. Z. Chen, Z. Y. Liu, Y. Liu, K. Z. Zheng and W. P. Qin, *Journal of Fluorine Chemistry*, 2012, **144**, 157-164.
19. N. J. J. Johnson, W. Oakden, G. J. Stanisz, R. S. Prosser and F. C. J. M. van Veggel, *Chemistry of Materials*, 2011, **23**, 4877-4877.
20. F. Wang and X. G. Liu, *Journal of the American Chemical Society*, 2008, **130**, 5642-5643.
21. X. Liu, X. Kong, Y. Zhang, L. Tu, Y. Wang, Q. Zeng, C. Li, Z. Shi and H. Zhang, *Chem Commun (Camb)*, 2011, **47**, 11957-11959.
22. M. M. Lezhnina, T. Jüstel, H. Kätker, D. U. Wiechert and U. H. Kynast, *Advanced Functional Materials*, 2006, **16**, 935-942.
23. Q. Cheng, J. Sui and W. Cai, *Nanoscale*, 2012, **4**, 779-784.
24. Q. Dou, N. M. Idris and Y. Zhang, *Biomaterials*, 2013, **34**, 1722-1731.
25. B. Zhou, L. Tao, Y. H. Tsang and W. Jin, *J Mater Chem C*, 2013, **1**, 4313-4318.
26. Y.-F. Wang, L.-D. Sun, J.-W. Xiao, W. Feng, J.-C. Zhou, J. Shen and C.-H. Yan, *Chemistry – A European Journal*, 2012, **18**, 5558-5564.
27. C. B. Murray, C. R. Kagan and M. G. Bawendi, *Annual Review of Materials Science*, 2000, **30**, 545-610.
28. H. S. Qian and Y. Zhang, *Langmuir*, 2008, **24**, 12123-12125.
29. H. Wen, H. Zhu, X. Chen, T. F. Hung, B. Wang, G. Zhu, S. F. Yu and F. Wang, *Angewandte Chemie International Edition*, 2013, **52**, 13419-13423.
30. N. J. Johnson, A. Korinek, C. Dong and F. C. van Veggel, *J Am Chem Soc*, 2012, **134**, 11068-11071.
31. X. M. Li, D. K. Shen, J. P. Yang, C. Yao, R. C. Che, F. Zhang and D. Y. Zhao, *Chemistry of Materials*, 2013, **25**, 106-112.
32. N. J. Johnson and F. J. M. van Veggel, *Nano Research*, 2013, **6**, 547-561.
33. Q. Zeng, B. Xue, Y. Zhang, D. Wang, X. Liu, L. Tu, H. Zhao, X. Kong and H. Zhang, *CrystEngComm*, 2013, **15**, 4765-4772.
34. D. Chen and P. Huang, *Dalton Transactions*, 2014, **43**, 11299-11304.
35. Q. Q. Su, S. Y. Han, X. J. Xie, H. M. Zhu, H. Y. Chen, C. K. Chen, R. S. Liu, X. Y. Chen, F. Wang and X. G. Liu, *Journal of the American Chemical Society*, 2012, **134**, 20849-20857.
36. T. Yang, Y. Sun, Q. Liu, W. Feng, P. Yang and F. Li, *Biomaterials*, 2012, **33**, 3733-3742.
37. F. Shi, J. Wang, X. Zhai, D. Zhao and W. Qin, *CrystEngComm*, 2011, **13**, 3782-3787.
38. D. Zhao, H. Chen, K. Zheng, X. Chuai, F. Yu, H. Li, C. Wu, G. Qin, W. Di and W. Qin, *Rsc Adv*, 2014, **4**, 13490-13494.
39. J. Wang, H. Song, W. Xu, B. Dong, S. Xu, B. Chen, W. Yu and S. Zhang, *Nanoscale*, 2013, **5**, 3412-3420.
40. Q. Liu, Y. Sun, T. S. Yang, W. Feng, C. G. Li and F. Y. Li, *Journal of the American Chemical Society*, 2011, **133**, 17122-17125.
41. L. L. Wang, M. Lan, Z. Y. Liu, G. S. Qin, C. F. Wu, X. Wang, W. P. Qin, W. Huang and L. Huang, *J Mater Chem C*, 2013, **1**, 2485-2490.
42. F. Wang, J. A. Wang and X. G. Liu, *Angewandte Chemie-International Edition*, 2010, **49**, 7456-7460.

Figure 1. Schematic comparing the formation of $NaYF_4$ and $NaLuF_4$ nanoparticles, and shell on core nanoparticle using LaMer model.

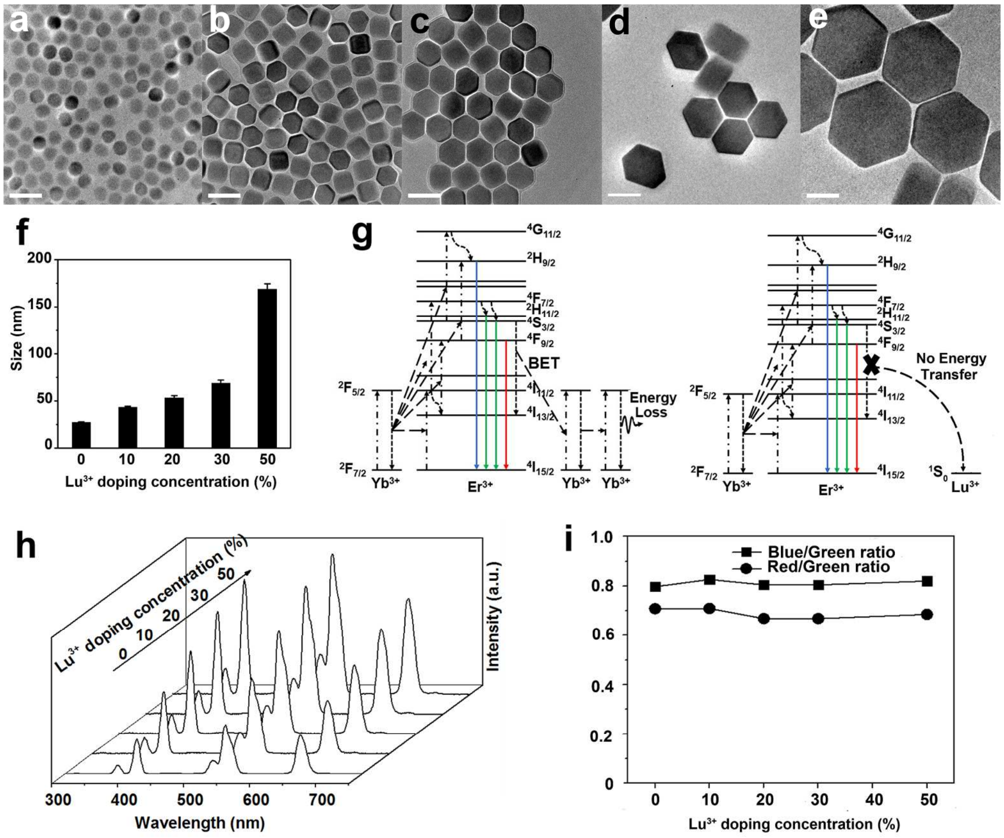
Figure 2. Tuning size of $NaYF_4$:Yb,Er UCNs by Lu^{3+} doping. a-e) TEM images of $NaYF_4$:Yb,Er UCNs doping with Lu^{3+} at different concentration, 0%, 10%, 20%, 30%, and 50%, from a to e, respectively; scale bar is 50 nm. f) Average size of the above samples measured by DLS. g) Diagram of energy transfer in $NaYF_4$:Yb,Er UCNs comparing tuning UCNs size through increasing Yb^{3+} concentration (left) and doping Lu^{3+} ions (right). h) Luminescence spectra of $NaYF_4$:Yb,Er UCNs with different concentration of Lu^{3+} doping. i) Luminescence intensity ratio of blue/green and red/green in $NaYF_4$:Yb,Er UCNs with different concentration of Lu^{3+} doping.

Figure 3. Comparing of $NaYF_4$ and $NaLuF_4$ shell coating onto core UCNs under different incubation time. TEM image of core UCNs (a), core-shell UCNs with $NaYF_4$ shell incubated for 1 hour (b) and 4 hours (c), core-shell UCNs with $NaLuF_4$ shell incubated for 1 hour (d); scale bar is 50 nm. Different activator ions, Er and Tm, are doped separately into core and shell, respectively (e). f) Luminescence spectra of core-shell UCNs with $NaYF_4$ or $NaLuF_4$ shell incubated for 1 hour and 4 hours. The core/shell ratio of the above samples are 1:1.

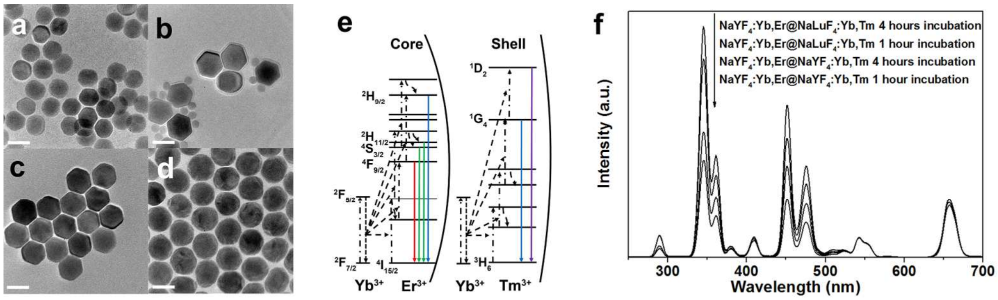
Figure 4. Comparing of $NaYF_4$ and $NaLuF_4$ shell coating onto core UCNs with different core/shell ratio. TEM image of core-shell UCNs with $NaYF_4$ shell at 1:5 (a) and 1:10 (b) core/shell ratio, core-shell UCNs with $NaLuF_4$ shell at 1:5 (c) and 1:10 (d) core/shell ratio; scale bar is 100 nm. e) Luminescence spectra of core-shell UCNs with $NaYF_4$ or $NaLuF_4$ shell with different core/shell ratio; Er and Tm are doped in core and shell, respectively. f) Optical images of the core-shell UCNs with $NaLuF_4$ shell at different core/shell ratio, under the excitation of 980 nm laser. The incubation time of the above samples are 4 hours.



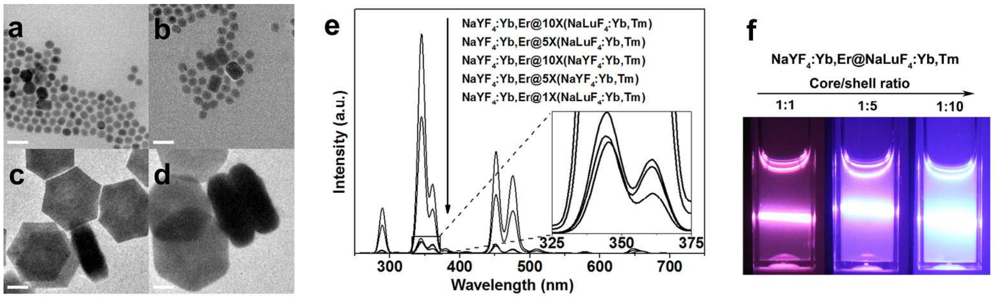
465x423mm (96 x 96 DPI)



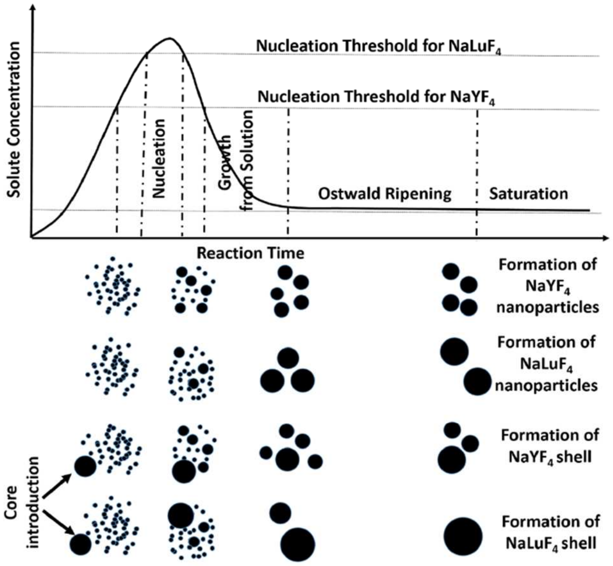
508x423mm (96 x 96 DPI)



508x148mm (96 x 96 DPI)



508x149mm (96 x 96 DPI)



Graphical Abstract. Fabricating big sized core and core-shell UCNs through Lutetium doping.