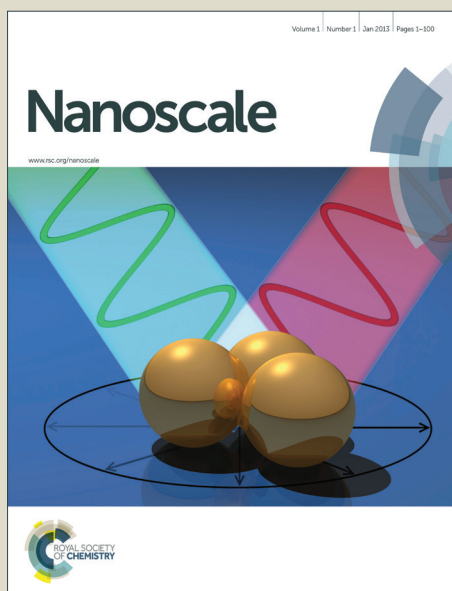


Nanoscale

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Active-Core/Active-Shell Structure with Enhanced Quantum-cutting Luminescence in Pr³⁺-Yb Co-Doped Monodisperse Nanoparticles

Cite this: DOI: 10.1039/x0xx00000x

Wenjuan Zhu,^a Daqin Chen,^{a,b*} Lei Lei,^a Ju Xu,^a Yuansheng Wang^{a*}Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Monodisperse Pr³⁺/Yb³⁺: NaGdF₄@NaYF₄ active-core/inert-shell nanoparticles, which exhibit efficient near-infrared quantum-cutting luminescence, are successfully prepared. In order to relieve the adverse effect caused by concentration quenching in the core, the extra Yb³⁺ ions are introduced into the shell, forming an active-core/active-shell structure which leads to a much intensified near-infrared emission.

One of the main difficulties in improving the energy efficiency of crystalline silicon (c-Si) solar cells is the mismatch between the incident sunlight spectrum and the absorption spectrum of the c-Si semiconductor. For photon with energy higher than the semiconductor band gap, the excess energy is not effectively used but converted into heat, resulting in the so-called lattice thermalization loss.¹⁻⁵ Quantum-cutting (QC) is defined as the “cutting” of one high energy photon into at least two lower energy photons.⁶ It has been widely recognized that the thermalization energy loss of c-Si solar cell could be minimized by the usage of a QC down-converter.⁷⁻¹⁰

In the past years, many groups have devoted themselves to studying QC effects using the Ln³⁺-Yb³⁺ (Ln=Tb, Er, Pr, Ce, Ho, Nd, Tm) rare earth couples.¹¹ QC of rare earth ions has been realized in the host matrixes such as crystals, glass ceramics and glasses.¹² However, to be applied in a c-Si solar cell, the QC down-converter should be coupled on the front surface of the cell.¹³ It is therefore necessary to minimize scattering of the incident light. As a consequence, the host material with small and uniform sized nanoparticles (NPs) should be adopted.¹⁴ However, owing to the large specific surface area, there are a big amount of surficial defects in NPs which may bring in a quenching for the QC luminescence. In this work, we construct the Pr³⁺/Yb³⁺: NaGdF₄@NaYF₄ core-shell nano-structure to modify the QC luminescence of Pr³⁺-Yb³⁺ couples doped in the NaGdF₄ core, using the NaYF₄ shell to protect the active ions in the core from the surface oscillation induced non-radiative

decay.¹⁵ The adoption of Pr³⁺-Yb³⁺ couple is based on the consideration that Pr³⁺ has a suitable intermediate ¹G₄ state at 9885 cm⁻¹, which may enable Yb³⁺ sensitization proceeded by a two-step sequential energy transfer from Pr³⁺ to Yb³⁺, instead by a second-order cooperative one. Furthermore, the absorption bands of Pr³⁺ cover a broad spectral window in the blue region due to the successive energy levels of Pr³⁺: ³P_J (J=0, 1 and 2), which may benefit to the harvest of short wavelength light. Nanofluoride is chosen as the host not only because of its low phonon energy, but also its desirable chemical stability.¹⁶ As is known to all, when Yb³⁺ concentration in the core increases to a certain extent, it can induce concentration quenching, reducing seriously the Yb³⁺ emission intensity. To prevent this adversity, in our study, the active-core/active-shell structure is further designed and fabricated to accommodate the distribution of Yb³⁺ by introducing the extra Yb³⁺ ions into the shell. It is experimentally demonstrated that such strategy does lead to a much intensified near-infrared (NIR) QC luminescence in the NaGdF₄@NaYF₄ core-shell system.

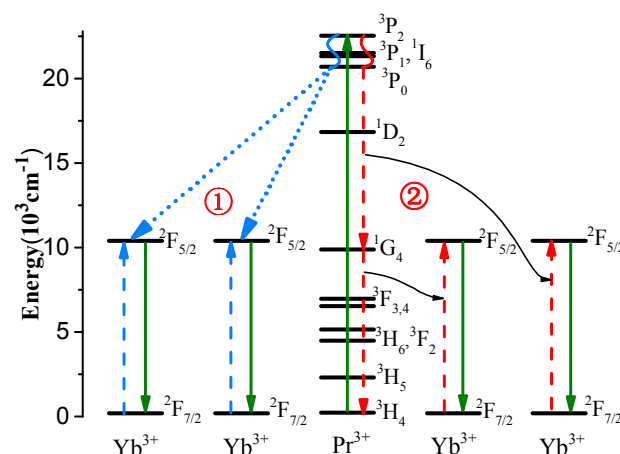


Fig. 1 Schematics showing energy levels and quantum-cutting mechanisms of the $\text{Pr}^{3+}\text{-Yb}^{3+}$ couples. Mechanism ①: $\text{Pr}^{3+}: {}^3\text{P}_0 \rightarrow \text{Yb}^{3+}: {}^2\text{F}_{5/2} + \text{Yb}^{3+}: {}^2\text{F}_{5/2}$; Mechanism ②: $\text{Pr}^{3+}: {}^3\text{P}_0 + \text{Yb}^{3+}: {}^2\text{F}_{7/2} \rightarrow \text{Pr}^{3+}: {}^1\text{G}_4 + \text{Yb}^{3+}: {}^2\text{F}_{5/2}$, $\text{Pr}^{3+}: {}^1\text{G}_4 + \text{Yb}^{3+}: {}^2\text{F}_{7/2} \rightarrow \text{Pr}^{3+}: {}^3\text{H}_4 + \text{Yb}^{3+}: {}^2\text{F}_{5/2}$.

The energy levels of Pr^{3+} and Yb^{3+} are schematically shown in Fig. 1. Upon excitation of Pr^{3+} from the ground state to the ${}^3\text{P}_J$ ($J=0, 1, 2$) levels, energy release of the ${}^3\text{P}_0$ excited state can be realized through two possible routes. For the first route, the ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ transition (483 nm, or 2.57 eV) results in the emission of two NIR photons (980 nm, or 1.27 eV) coming from the ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition of Yb^{3+} . For the second route, energy release of ${}^3\text{P}_0$ proceeds through two consequent steps with ${}^1\text{G}_4$ acting as the intermediate level, i.e., $\text{Pr}^{3+}: {}^3\text{P}_0 + \text{Yb}^{3+}: {}^2\text{F}_{7/2} \rightarrow \text{Pr}^{3+}: {}^1\text{G}_4 + \text{Yb}^{3+}: {}^2\text{F}_{5/2}$ followed by $\text{Pr}^{3+}: {}^1\text{G}_4 + \text{Yb}^{3+}: {}^2\text{F}_{7/2} \rightarrow \text{Pr}^{3+}: {}^3\text{H}_4 + \text{Yb}^{3+}: {}^2\text{F}_{5/2}$.

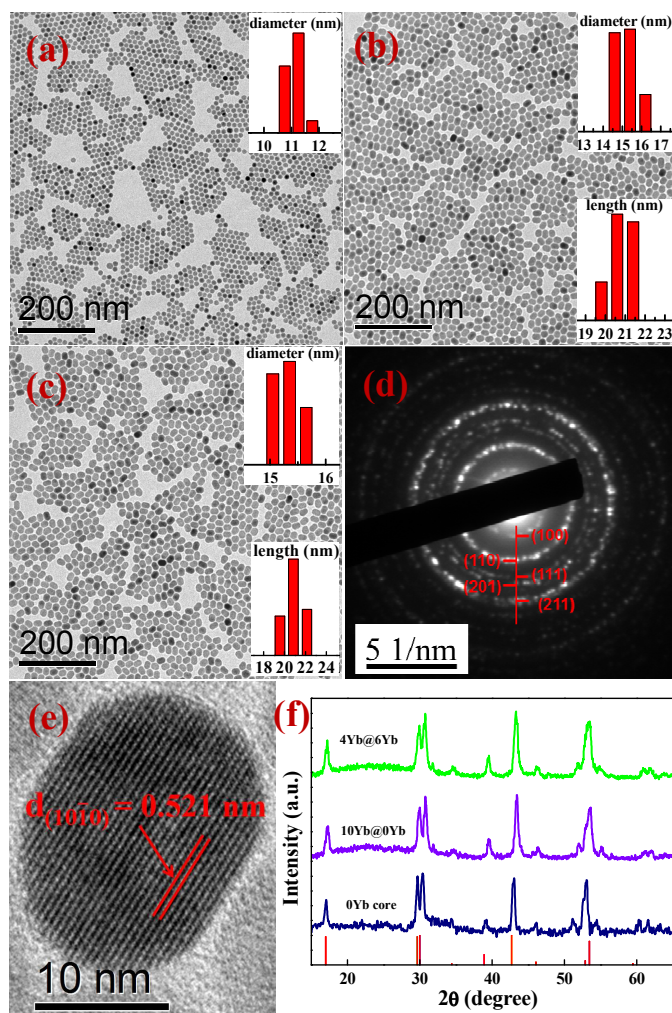


Fig. 2 TEM micrographs of (a) 0.1Pr^{3+} : NaGdF_4 core NPs, (b) $0.1\text{Pr}^{3+}/10\text{Yb}^{3+}$: $\text{NaGdF}_4@ \text{NaYF}_4$ active-core/inert-shell NPs, and (c) $0.1\text{Pr}^{3+}/4\text{Yb}^{3+}$: $\text{NaGdF}_4@6\text{Yb}^{3+}$: NaYF_4 active-core/active-shell NPs; (d) SAED pattern from particles in (c); (e) HRTEM image of a particle in (c); (f) XRD patterns of the above three samples.

To study QC effect of the $\text{Pr}^{3+}\text{-Yb}^{3+}$ couple, a series of $\text{Yb}^{3+}/\text{Pr}^{3+}$: NaGdF_4 NPs were prepared with low Pr^{3+} (0.1 mol%) and various Yb^{3+} (0, 1, 2, 4, 6, 10 mol%) concentrations. As

exhibited in the representative transmission electron microscopy (TEM) image (Fig. 2a), the monodisperse $\text{Yb}^{3+}/\text{Pr}^{3+}$: NaGdF_4 NPs are nearly spherical in shape with a diameter of 11 nm. X-ray diffraction (XRD) pattern (Fig. 2f) confirms that they are pure hexagonal NaGdF_4 phase (JCPDS 27-0699). In a further step, the synthesized $\text{Yb}^{3+}/\text{Pr}^{3+}$: NaGdF_4 NPs were used as seed crystals to grow NaYF_4 shells, resulting in the formation of monodisperse and uniform sized $\text{Pr}^{3+}/\text{Yb}^{3+}$: $\text{NaGdF}_4@ \text{NaYF}_4$ active-core/inert-shell NPs, which are rod like with a mean length of 21 nm and a mean diameter of 15 nm, as exhibited in Fig. 2b. Furthermore, high-angle annular dark-field (HAADF) TEM observation, which is sensitive to the atomic number (Z) difference in the sample, is adopted to characterize the core-shell structure. As shown in Fig. 3, owing to the much larger atomic number of Gd ($Z=64$) than that of Y ($Z=39$), a significant difference in contrast between core (bright) and shell (dark) is obviously observed, confirming the successful growth of NaYF_4 shell on the NaGdF_4 core. To relieve concentration quenching, instead of the NaYF_4 inert-shells, the Yb^{3+} : NaYF_4 active-shells were grown on the $\text{Yb}^{3+}/\text{Pr}^{3+}$: NaGdF_4 active-cores, with the resulted active-core/active-shell NPs (Fig. 2c) having the same size as the active-core/inert-shell NPs (Fig. 2b). Fig. 2e is the high-resolution TEM (HRTEM) image of an active-core/active-shell particle. Selected area electron diffraction (SAED) pattern (Fig. 2d) as well as XRD patterns of the core-shell samples demonstrates that they also exhibit hexagonal phase structure.

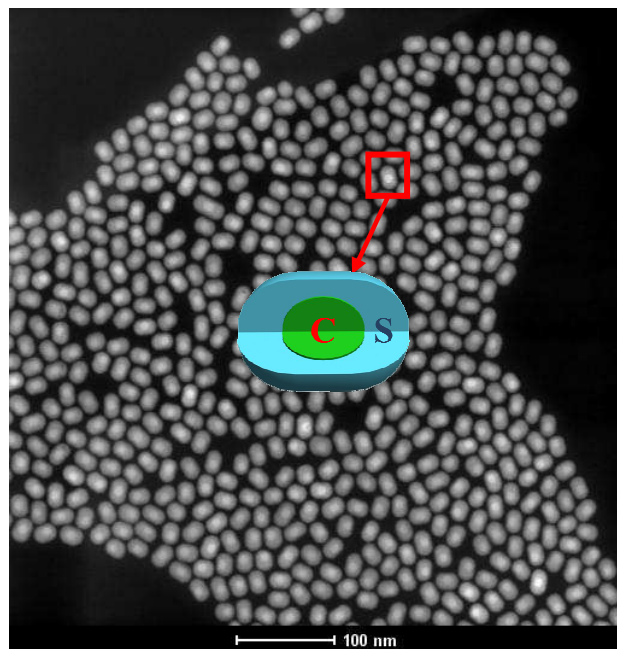


Fig. 3 HAADF image of the $0.1\text{Pr}^{3+}/10\text{Yb}^{3+}$: $\text{NaGdF}_4@ \text{NaYF}_4$ active-core/inert-shell NPs.

Photoluminescence excitation (PLE) spectra of the $\text{Pr}^{3+}/\text{Yb}^{3+}$: $\text{NaGdF}_4@ \text{NaYF}_4$ NPs preliminarily demonstrate the occurrence of QC effect. In the PLE spectra of Yb^{3+} emission at 979 nm shown in Fig. 4a, there are three characteristic peaks at 445 nm, 467 nm and 483 nm, along with a relatively weak band at 589

nm, which are assigned to the transitions of $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^3\text{P}_1$, $^3\text{P}_0$ and $^1\text{D}_2$ of Pr^{3+} respectively. Compared to the sample without Yb^{3+} , the excitation intensity of the 10 mol% Yb^{3+} doped sample is much enhanced. The transitions of Pr^{3+} occurring in the excitation spectra of Yb^{3+} emission indicates the presence of energy transfer from Pr^{3+} to Yb^{3+} . Photoluminescence (PL) spectra of the $0.1\text{Pr}^{3+}/x\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$ ($x=0, 10$ mol%) core-shell NPs, upon excitation at 445 nm of the Pr^{3+} : $^3\text{H}_4 \rightarrow ^3\text{P}_2$ transition, are presented in Fig. 4b. Because of the narrow energy gap between $^3\text{P}_2$ and $^3\text{P}_0$ levels, non-radiative relaxation from $^3\text{P}_2$ to $^3\text{P}_0$ proceeds easily. So the transitions from $^3\text{P}_0$ to the lower levels are dominant and the most intense emission is centered at 483 nm owing to the transition from $^3\text{P}_0$ to the ground state $^3\text{H}_4$. Remarkably, in the sample without Yb^{3+} the characteristic $^3\text{P}_0$ emissions of Pr^{3+} are intense, while in the sample doped with 10 mol% Yb^{3+} they become very weak, and on the contrary, an intense Yb^{3+} : $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ emission at 979 nm occurs. Since Yb^{3+} could not be excited directly by 445 nm photons, the appearance of its NIR emission further evidences the energy transfer from Pr^{3+} to Yb^{3+} .

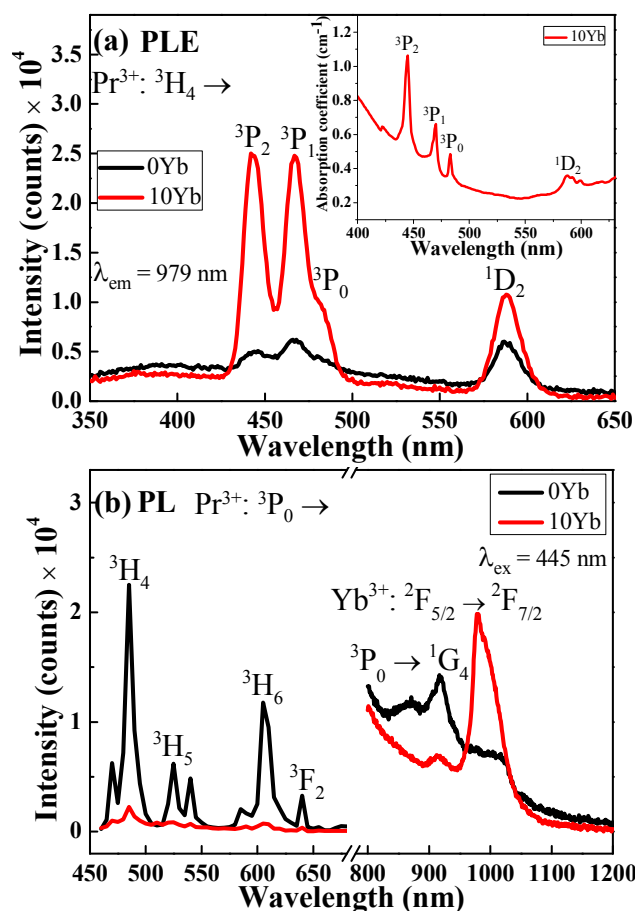


Fig. 4 (a) PLE spectra of the 0.1Pr^{3+} : $\text{NaGdF}_4/\text{NaYF}_4$ and $0.1\text{Pr}^{3+}/10\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$ samples; inset shows absorption spectra of the latter sample. (b) Visible and NIR PL spectra of these two samples.

In order to further prove the existence of energy transfer, PL decay curves corresponding to the Pr^{3+} : $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition (483

nm) for the different samples were measured, as shown in Fig. 5. For the Pr^{3+} : $\text{NaGdF}_4/\text{NaYF}_4$ core-shell sample without Yb^{3+} , the PL decay curve can be well-fitted to a single-exponential decay with a lifetime of 27.1 μs . However, when doping 10 mol% Yb^{3+} , the decay time shortens rapidly from 27.1 μs to 12.6 μs . As revealed in the inset of Fig. 5, with increasing of Yb^{3+} content, the lifetime monotonously decreases while the efficiency of energy transfer from Pr^{3+} to Yb^{3+} monotonously increases resulted from the existence of extra decay pathways induced by Yb^{3+} doping.

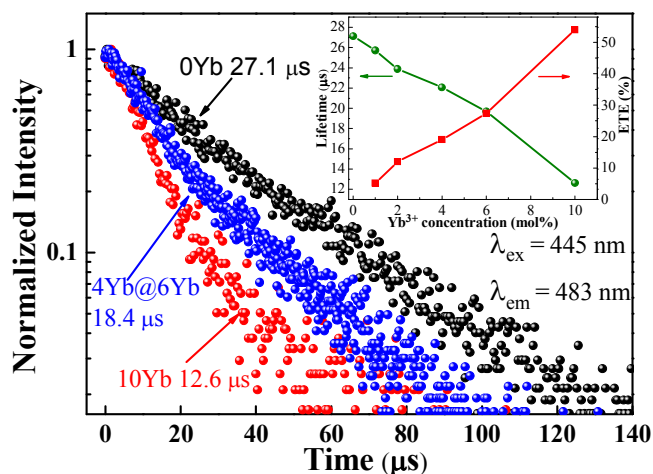


Fig. 5 Normalized decay curves of $^3\text{P}_0$ level in the $0.1\text{Pr}^{3+}/x\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$ ($x=0, 10$ mol%) and $0.1\text{Pr}^{3+}/4\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$ samples under excitation at 445 nm; inset shows the decay lifetime of Pr^{3+} emission at 483 nm and energy transfer efficiency (ETE) as the function of Yb^{3+} concentration.

NIR PL spectra for the $0.1\text{Pr}^{3+}/x\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$ samples with various Yb^{3+} doping contents are shown in Fig. 6a. The NIR luminescence at 979 nm rapidly intensifies when Yb^{3+} content increases from 0 to 4 mol%, then weakens with further increasing of Yb^{3+} content owing to concentration quenching. In order to relieve the adverse concentration quenching effect, extra Yb^{3+} ions were introduced into the shell to reduce the Yb^{3+} concentration in the core. As clearly exhibited by Fig. S1 (ESI), all the active-core/active-shell NPs doped with different Yb^{3+} concentrations are in good dispersity and their sizes are almost the same.

As shown in Fig. 6b and Fig. 6c, the 979 nm emission intensities of the active-core/active-shell NPs ($0.1\text{Pr}^{3+}/4\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$ and $0.1\text{Pr}^{3+}/4\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$) are much stronger than those of the active-core/inert-shell ones ($0.1\text{Pr}^{3+}/6\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$ and $0.1\text{Pr}^{3+}/10\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$). The NIR luminescence of Yb^{3+} in NaYF_4 is resulted from the energy transfer from Pr^{3+} in the core to Yb^{3+} in the shell. As shown by decay curves in Fig. S3 (ESI), the lifetime of $^3\text{P}_0$ level for the $0.1\text{Pr}^{3+}/4\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$ NPs with inert-shells is longer than that for the $0.1\text{Pr}^{3+}/4\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$ NPs with active-shells, which evidences that Yb^{3+} doping in the shell provides extra path for the energy transfer from Pr^{3+} to Yb^{3+} , leading to a much intensified NIR QC luminescence. As shown in Fig. 5, lifetime of the active-shell NPs ($0.1\text{Pr}^{3+}/4\text{Yb}^{3+}$: $\text{NaGdF}_4/\text{NaYF}_4$) is longer than that of the corresponding inert-shell NPs

(0.1Pr³⁺/10Yb³⁺: NaGdF₄@NaYF₄), indicating that the efficiency of energy transfer from Pr³⁺ to Yb³⁺ in the former is lower than that in the latter. However, the Yb³⁺ emission in the former is much stronger than that in the latter (Fig. 6c). These results clearly demonstrates that the concentration quenching is indeed reduced by the designed active-core/active-shell architecture. In the active-core/active-shell NPs, the Yb³⁺ ions in the core and those in the shell are spatially separated. In other words, the shell provides another space for the extra Yb³⁺ ions to carry on radiative emitting.

Fig. 6d shows PL spectra of the 0.1Pr³⁺/4Yb³⁺: NaGdF₄@xYb³⁺: NaYF₄ (x=0, 1, 2, 6 mol%) samples. Obviously, the Yb³⁺ luminescence at 979 nm gradually intensifies with Yb³⁺ content increasing from 0 to 2 mol%, however, it turns to be weakened when the Yb³⁺ content further increases. Therefore, the 0.1Pr³⁺/4Yb³⁺: NaGdF₄@2Yb³⁺: NaYF₄ sample yields the optimal luminescence. The reduction of PL intensity is also caused by concentration quenching, so increasing shell thickness should be a reasonable approach to further intensify the QC emission of Yb³⁺.

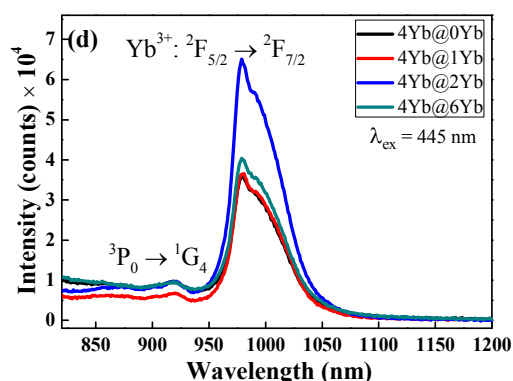
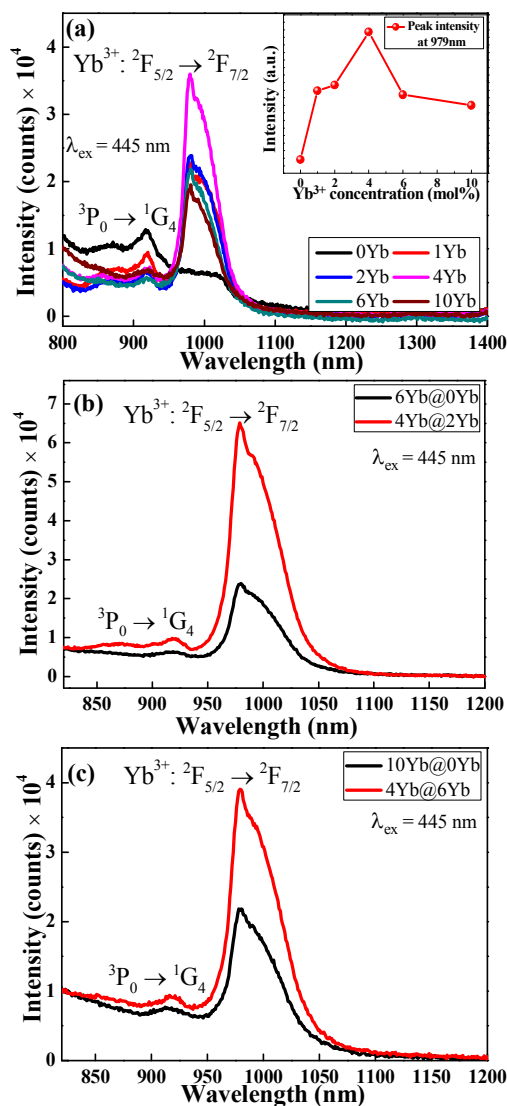


Fig. 6 (a) NIR PL spectra of the 0.1Pr³⁺/xYb³⁺: NaGdF₄@NaYF₄ samples with various Yb³⁺ doping contents; inset shows PL intensity as a function of Yb³⁺ content. (b) Comparison of NIR PL spectra for the 0.1Pr³⁺/4Yb³⁺: NaGdF₄@2Yb³⁺: NaYF₄ and 0.1Pr³⁺/6Yb³⁺: NaGdF₄@NaYF₄ samples. (c) Comparison of NIR PL spectra for the 0.1Pr³⁺/4Yb³⁺: NaGdF₄@6Yb³⁺: NaYF₄ and 0.1Pr³⁺/10Yb³⁺: NaGdF₄@NaYF₄ NPs samples. (d) PL spectra for the 0.1Pr³⁺/4Yb³⁺: NaGdF₄@xYb³⁺: NaYF₄ (x=0, 1, 2, 6 mol%) samples.

The efficiency (η_{ETE}) of energy transfer from Pr³⁺ to Yb³⁺ to induce Yb³⁺ emission can be determined by the following conventional formula:¹⁷

$$\eta_{\text{ETE}} = 1 - \frac{\tau_{\text{Pr-Yb}}}{\tau_{\text{Pr}}} \quad (1)$$

Where $\tau_{\text{Pr-Yb}}$ and τ_{Pr} are the decay time of Pr³⁺ transitions at 483 nm in the samples with and without Yb³⁺. The quantum efficiency (η_{QE}), usually defined as the ratio of the number of emitted photons to the number of absorbed photons, is described by formula (2) below:

$$\eta_{\text{QE}} = \eta_{\text{Pr}}(1 - \eta_{\text{ETE}}) + 2\eta_{\text{ETE}} = 2 - \frac{\tau_{\text{Pr-Yb}}}{\tau_{\text{Pr}}} \quad (2)$$

where η_{Pr} is the QE value of Pr³⁺. As revealed by PL decay curves for the Pr³⁺: ³P₀→³H₄ transition at 483 nm in the sample without Yb³⁺, shown in Fig. S4 (ESI), the lifetime measured at 77K is almost the same as that measured at room temperature, which evidences that the probability of non-radiative transitions of Pr³⁺ is quite low and therefore η_{Pr} can be assumed to be 1. Based on formula (2), the quantum efficiency for the NIR QC luminescence in the 0.1Pr³⁺/4Yb³⁺: NaGdF₄@NaYF₄ active-core/inert-shell sample is evaluated to be 119%, while that in the 0.1Pr³⁺/4Yb³⁺: NaGdF₄@2Yb³⁺: NaYF₄ active-core/active-shell sample reaches 127%.

Conclusions

In summary, efficient near-infrared quantum-cutting luminescence in the Pr³⁺/Yb³⁺: NaGdF₄@NaYF₄ nanoparticles has been demonstrated for the first time. Upon excitation of Pr³⁺ ions with blue light at 445 nm, an intense emission centered at 979 nm corresponding to the ²F_{5/2}→²F_{7/2} transition of Yb³⁺ is observed. The emission intensity depends on the Yb³⁺ doping content. Impressively, when the extra Yb³⁺ ions are incorporated

into the shell, forming the active-core/active-shell structure in the nanoparticles, the concentration quenching effect is depressed and a much intensified near-infrared luminescence is achieved. Using the conventional formulas, quantum efficiency of the sample with active-shell is evaluated to be 127%, which is 8% higher than that of the sample with inert-shell.

Acknowledgements

This work was supported by National Natural Science Foundation of China (51172231, 21271170, 11204301, 51202244 and 11304312), Key Laboratory of Design and Assembly of Functional Nanostructures, Chinese Academy of Sciences (2013DP173231), and Natural Science Foundation of Fujian for Distinguished Young Scholars (2012J06014).

Notes and references

^a State Key Lab of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences; University of Chinese Academy of Sciences, Fuzhou, 350002, P. R. China.

^b College of Materials & Environmental Engineering, Hangzhou Dianzi University, Hangzhou, 310018, P. R. China.

E-mail: dqchen@hdu.edu.cn (DQ Chen), Tel/Fax: +86-591-83751401
yswang@fjirsm.ac.cn (YS Wang), Tel/Fax: +86-591-83705402

†Electronic Supplementary Information (ESI) available: Experimental section and Figure S1-S4. See DOI: 10.1039/c000000x/

- H. Q. Wang, M. Batentschuk, A. Osvet, L. Pinna and C. J. Brabec, *Adv. Mater.* 2011, **23**, 2675–2680.
- B. S. Richards, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 1189–1207.
- R.T. Wegh, H. Donker, E.V.D. van Loef, K.D. Oskam and A. Meijerink, *Journal of Luminescence*, 2000, **87-89**, 1017–1019.
- D. Q. Chen, Y. S. Wang, M. C. Hong, *Nanoenergy*, 2012, **1**, 73–90.
- C. Strümpel, M. McCann, G. Beaucarne, V. Arkhipov, A. Slaoui, V. Švrcek, C. del Cañizo and I. Tobias, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 238–249.
- X. Y. Huang, S. Y. Han, W. Huang, X. G. Liu, *Chem. Soc. Rev.*, 2013, **42**, 173–201.
- B. S. Richards, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 2329–2337.
- G. J. Gao, L. Wondraczek, *Optical Materials Express*, 2013, **3**, 633–644.
- D. Timmerman, I. Izeddin, P. Stallinga, I. N. Yassievich and T. Gregorkiewicz, *Nature Photonics*, 2008, **2**, 105–109.
- B. M. van der Ende, L. Aarts and A. Meijerink, *Adv. Mater.*, 2009, **21**, 3073–3077.
- (a) K. M. Deng, T. Gong, L. X. Hu, X. T. Wei, Y. H. Chen and M. Yin, *Optics Express*, 2011, **19**, 1749–1754. (b) L. C. Xie, Y. H. Wang and H. J. Zhang, *Applied Physics Letters*, 2009, **94**, 061905. (c) V. D. Rodríguez, V. K. Tikhomirov, J. Méndez-Ramos, A. C. Yanes and V. V. Moshchalkov, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 1612–1617. (d) H. Lin, S. M. Zhou, H. Teng, Y. K. Li, W. J. Li, X. R. Hou and T. T. Jia, *Journal of Applied Physics*, 2010, **107**, 043107. (e) D. Q. Chen, Y. L. Yu, H. Lin, P. Huang, Z. F. Shan and Y. S. Wang, *Optics Letters*, **35**, 220–222. (f) L. N. Guo, Y. H. Wang, W. Zeng, L. Zhao and L. L. Han, *Phys. Chem. Chem. Phys.*, 2013, **15**, 14295–14302. (g) Q. Y. Zhang, G. F. Yang, and Z. H. Jiang, *Applied Physics Letters*, **91**, 051903. (h) B. Fan, C. Chlique, O. Merdignac-Conanec, X. H. Zhang and X. P. Fan, *J. Phys. Chem. C*, 2012, **116**, 11652–11657. (i) G. G. Zhang, C.M. Liu, J. Wang, X. J. Kuang and Q. Su, *J. Mater. Chem.*, 2012, **22**, 2226–2232. (j) L. N. Guo, Y. H. Wang, J. Zhang, Y. Z. Wang and P. Y. Dong, *Nanoscale Research Letters*, 2012, **7**, 1–7. (k) Q. Q. Duan, F. Qin, Z. G. Zhang and W. W. Cao, *Optics Letters*, 2012, **37**, 521–523.
- (a) X. J. Zhou, Y. J. Wang, X. Q. Zhao, L. Li, Z. Q. Wang and Q. X. Li, *J. Am. Ceram. Soc.*, 2014, **97**, 179–184. (b) D. Q. Chen, Y. S. Wang, Y. L. Yu, P. Huang and F. Y. Weng, *Optics Letters*, 2008, **33**, 1884–1886. (c) G. Özen, O. Forte, and B. Di Bartolo, *Journal of Applied Physics*, 2005, **97**, 013510. (d) X. B. Chen, J. G. Wu, X. L. Xu, Y. Z. Zhang, N. Sawanobori, C. L. Zhang, Q. H. Pan and G. J. Salamo, *Optics Letters*, 2009, **34**, 887–889. (e) Q. Luo, X. S. Qiao, X. P. Fan and X. H. Zhang, *Optics Letters*, 2011, **36**, 2767–2769. (f) A. Guille, A. Pereira, C. Martinet and B. Moine, *Optics Letters*, 2012, **37**, 2280–2282. (g) X. F. Liu, Y. B. Qiao, G. P. Dong, S. Ye, B. Zhu, G. Lakshminarayana, D. P. Chen and J. R. Qiu, *Optics Letters*, 2008, **33**, 2858–2860. (h) Y. S. Xu, F. Huang, B. Fan, C. G. Lin, S. X. Dai, L. Y. Chen, Q. H. Nie, H. L. Ma and X. H. Zhang, *Optics Letters*, 2014, **39**, 2225–2228.
- T. Trupke and M. A. Green, *Journal of Applied Physics*, 2002, **92**, 1668–1674.
- C. Lorbeer, J. Cybinska and A. Mudring, *Chem. Commun.*, 2010, **46**, 571–573.
- (a) F. Vetrone, R. Naccache, V. Mahalingam, C. G. Morgan and J. A. Capobianco, *Adv. Funct. Mater.*, 2009, **19**, 2924–2929. (b) D. Q. Chen, L. Lei, A. P. Yang, Z. X. Wang and Y. S. Wang, *Chem. Commun.*, 2012, **48**, 5898–5900. (c) Y. Wang, K. Liu, X. M. Liu, K. Dohnalová, T. Gregorkiewicz, X. G. Kong, M. C. G. Aalders, W. J. Buma and H. Zhang, *J. Phys. Chem. Lett.*, 2011, **2**, 2083–2088. (d) D. Q. Chen and P. Huang, *Dalton Trans.*, 2014, DOI: 10.1039/C4DT01237B. (e) C. Zhang and J. Y. Lee, *ACS Nano*, 2013, **7**, 4393–4402. (f) L. Lei, D. Q. Chen, P. Huang, J. Xu, R. Zhang and Y. S. Wang, *Nanoscale*, 2013, **5**, 11298–11305.
- (a) X. Zhang, P. P. Yang, C. X. Li, D. Wang, J. Xu, S. Gai and J. Lin, *Chem. Commun.*, 2011, **47**, 12143–12145. (b) F. Shi, J. S. Wang, D. S. Zhang, G. S. Qin and W. P. Qin, *J. Mater. Chem.*, 2011, **21**, 13413–13421. (c) M. Y. Ding, D. Q. Chen, T. J. Chen, C. H. Lu, Y. R. Ni and Z. Z. Xu, *Mater. Lett.*, 2014, **128**, 101–104. (d) H. X. Mai, Y. W. Zhang, R. Si, Z. G. Yan, L. D. Sun, L. P. You and C. H. Yan, *J. Am. Chem. Soc.*, 2006, **128**, 6426–6436.
- Y. T. An, C. Labbé, J. Cardin, M. Morales and F. Gourbilleau, *Adv. Optical Mater.*, 2013, **1**, 855–862.