

Pr³⁺/Yb³⁺:NaGdF₄@Yb³⁺:NaYF₄ Core/Shell Nanocrystals: Synthesis, Microstructure and Quantum-Cutting Luminescence

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One of the major issues restricting energy efficiency of the c-Si solar cell is the mismatch between the solar spectrum and the bandgap of silicon semiconductor (~1.1 eV). For the photon with energy higher than the bandgap, the excess energy is dissipated through thermalization of charge carriers [1,2]. One promising solution to reduce this energy loss is the spectral modulation via quantum-cutting (QC), *i.e.*, “cutting” one blue incident photon into two near-infrared (NIR) ones to match with the c-Si bandgap.[3,4] To this end, Pr³⁺/Yb³⁺:NaGdF₄@Yb³⁺:NaYF₄ core/shell nano-structure is designed and fabricated to achieve efficient QC luminescence in the present work.

In a typical experiment, a certain amount of GdCl₃, YbCl₃ and PrCl₃ were mixed with OA (6mL) and ODE (12 mL) in a 100 mL three-neck round-bottom flask. The resulting mixture was heated to 150 °C under N₂ flow with constant stirring for 30 min to form a clear solution, and then cooled down to room temperature. Thereafter, methanol solution (10 mL) containing NH₄F (4 mmol) and NaOH (2 mmol) was added and the solution was stirred at 65 °C for 30 min. After methanol was evaporated, the solution was heated to 300 °C, under N₂ flow with vigorous stirring for 30 min and then cooled down to room temperature naturally. The obtained NPs were precipitated by addition of ethanol (15 mL), collected by centrifugation, washed with moderate cyclohexane and ethanol several times, and finally re-dispersed in cyclohexane for further use.

The transmission electron microscopy (TEM) image of Yb³⁺/Pr³⁺:NaGdF₄ nanoparticles (NPs) exhibits hexagonal in shape with a diameter of ~11 nm (Fig.1a). The high-resolution TEM (HRTEM) image demonstrates the single-crystalline nature with the interplanar spacing of 0.515 nm coinciding with (100) plane of NaGdF₄ (inset of Fig.1a). The synthesized Yb³⁺/Pr³⁺:NaGdF₄ NPs were further used as seed crystals to grow NaYF₄ shells, leading to the formation of monodispersed and uniform sized Pr³⁺/Yb³⁺:NaGdF₄@Yb³⁺:NaYF₄ active-core/active-shell NPs, which are rod-like with a mean diameter of 15 nm and a mean length of 21 nm (Fig. 1b). High-angle annular dark-field (HAADF) STEM observation, which is sensitive to the atomic number (Z) difference in the sample, was adopted to characterize the core-shell structure. Owing to the much larger atomic number of Gd (Z=64) than that of Y (Z=39), a significant difference in contrast between the core (bright) and the shell (dark) is obviously observed, confirming the successful growth of the NaYF₄ shell on the NaGdF₄ core (Fig. 1c).

Upon 445 nm excitation, intense characteristic ³P₀ emissions of Pr³⁺ were detected in photoluminescence (PL) spectrum of the Pr³⁺:NaGdF₄@NaYF₄ core-shell NPs; while in the sample doped with Yb³⁺ they become very weak, and in contrast, an intense Yb³⁺:²F_{5/2}→²F_{7/2} emission at 979 nm occurs, which indicates the occurrence of energy transfer from Pr³⁺ to Yb³⁺ (Fig. 2a). The energy release of Pr³⁺:³P₀ proceeds through two consequent steps with ¹G₄ acting as the intermediate level, *i.e.*, Pr³⁺:³P₀ + Yb³⁺:²F_{7/2} → Pr³⁺:¹G₄ + Yb³⁺:²F_{5/2}, followed by Pr³⁺:¹G₄ + Yb³⁺:²F_{7/2} → Pr³⁺:³H₄ + Yb³⁺:²F_{5/2}, resulting in the QC luminescence. Interestingly, QC luminescence is greatly intensified when doping a part of

Yb^{3+} into the shell (Fig. 2b). This result reveals that the concentration quenching is reduced in the designed active-core/active-shell architecture, since the shell provides another space for the extra Yb^{3+} ions to perform radiative emitting.

In summary, the efficient NIR QC luminescence by converting one 445 nm photon into two 979 nm photons is realized in the $\text{Pr}^{3+}/\text{Yb}^{3+}:\text{NaGdF}_4 @ \text{Yb}^{3+}:\text{NaYF}_4$ NPs. Thanking to the rational distribution of the active rare earth ions by introducing the extra Yb^{3+} ions into the shell, the adverse concentration quenching effect is greatly suppressed, which leads to a much intensified NIR QC luminescence. Hopefully, the studied material may find potential application as a frequency converter to reduce the thermalization loss in c-Si solar cells. [5]

References:

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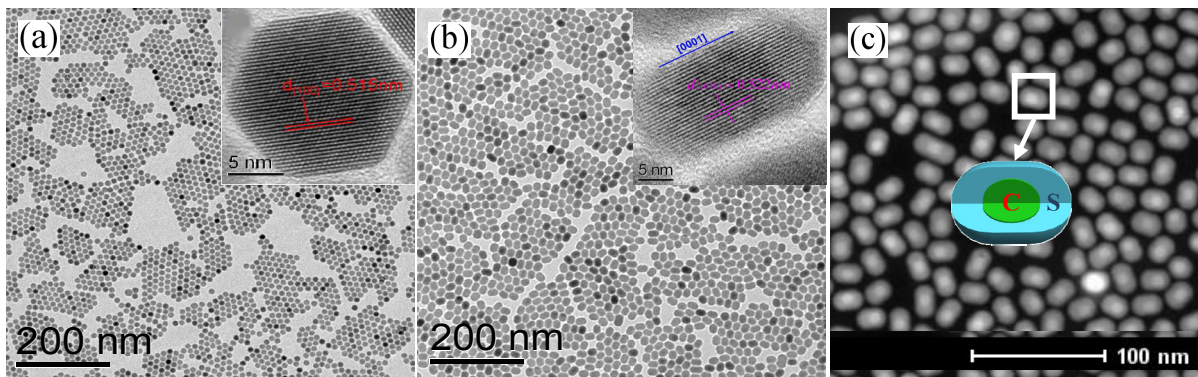


Figure 1. (a) TEM micrograph of $\text{Pr}^{3+}:\text{NaGdF}_4$ core NPs; (b) TEM micrograph of $\text{Pr}^{3+}/\text{Yb}^{3+}:\text{NaGdF}_4 @ \text{Yb}^{3+}:\text{NaYF}_4$ core/shell NPs; (c) HAADF-STEM image of the sample in (b) showing core/shell structures. Insets in (a) and (b) are the corresponding HRTEM images.

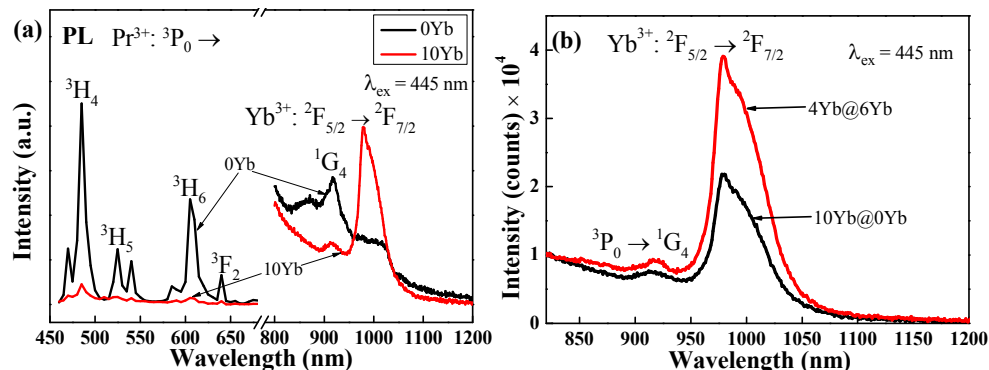


Figure 2. (a) Visible and NIR PL spectra of the $0.1\text{Pr}^{3+}:\text{NaGdF}_4 @ \text{NaYF}_4$ and $0.1\text{Pr}^{3+}/10\text{Yb}^{3+}:\text{NaGdF}_4 @ \text{NaYF}_4$ samples. (b) Comparison of NIR PL spectra for the $0.1\text{Pr}^{3+}/4\text{Yb}^{3+}:\text{NaGdF}_4 @ 6\text{Yb}^{3+}:\text{NaYF}_4$ and $0.1\text{Pr}^{3+}/10\text{Yb}^{3+}:\text{NaGdF}_4 @ \text{NaYF}_4$ NPs samples.