

Determination of Core/Double-Shell Architecture of a Single Tetragonal Bipyramidal Nanophosphor for Intense Dual-Mode Luminescence

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Trivalent lanthanide ion-doped inorganic nanophosphors have been spotlighted due to their unique optical properties including sharp peak emission, long life time, large Stokes/anti-Stokes shift, high photostability, and non-blinking luminescence [1-3]. Unlike bulk phosphors, which exhibit either downconversion luminescence (DCL) or upconversion luminescence (UCL), nanophosphors can emit both DCL and UCL simultaneously from a single particle by co-doping or creating core-shell structures [4]. In such system, however, activator ions usually suffer deterioration of their luminescence due to surface quenching by surface defects, ligands, and solvents [5]. Thus, to achieve intense dual-mode luminescence, the surface quenching needs to be effectively suppressed. Exploration of a new phosphor composition showing high luminescence efficiency is also encouraged.

Here, we report structural characterization of highly bright dual-mode green-emitting $\text{Li}(\text{Gd},\text{Y})\text{F}_4:\text{Yb},\text{Er}/\text{LiYF}_4:\text{Ce},\text{Tb}/\text{LiYF}_4$ nanophosphors with core/double-shell architecture. A new efficient green DCL $\text{LiYF}_4:\text{Ce},\text{Tb}$ nanophosphor was developed for the inner shell. The structure of nanophosphors is clearly determined by an aberration-corrected scanning transmission electron microscopy (STEM) equipped with a high-efficiency energy dispersive X-ray spectroscopy (EDX) system, with the aid of a simple line profile calculation. In spite of the tetragonal bipyramidal shape of the nanophosphors and there being no unique element present in any one of the shells, direct and detailed characterization of the core/double-shell structures and dopant distribution is achieved. The results could facilitate controlling the optical functionality of a single nanophosphor by designing materials architecture.

High-angle annular dark-field (HAADF) STEM imaging and STEM-EDX experiments were performed using an aberration-corrected FEI Titan G2 60-300 (S)TEM equipped with a Super-X EDX system, operated at 80 kV. Details of the synthesis of core/double-shell nanophosphors are found in Ref. [6].

Highly efficient $\text{LiYF}_4:\text{Ce},\text{Tb}$ is adapted to form a DCL inner-shell on UCL $\text{Li}(\text{Gd},\text{Y})\text{F}_4:\text{Yb},\text{Er}$ core. To suppress the surface quenching effect, an inert inorganic outer-shell was coated and it further enhances the dual-mode luminescence (Fig. 1). The synthesized core/double-shell nanophosphors have a $\{112\}$ -bound tetragonal bipyramidal morphology with sides of $51 \pm 2 \text{ nm} \times 52 \pm 1 \text{ nm}$. Although, a glimpse of core/double-shell structures was caught in EDX spectrum imaging (Fig. 2a), the designed core/double-shell architectures were explicitly corroborated using EDX elemental line profiling. Because the nanophosphors are not sphere-shaped, the line profiling was conducted across five primary crystallographic orientations and all experimental data were compared to the calculated profiles (Fig. 2). Structure and dopant distribution of the

core/double-shell nanophosphors as well as their optical properties are discussed in detail [7].

References:

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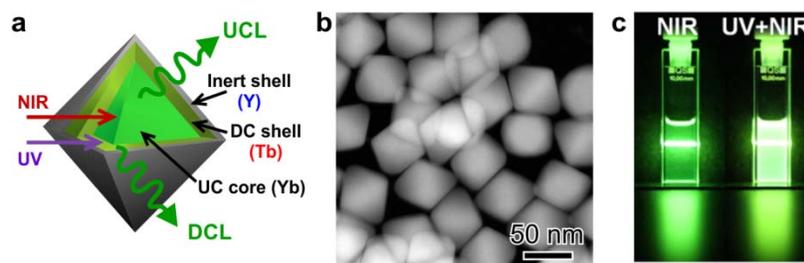


Figure 1. (a) The schematic illustrates a bright dual-mode luminescent core/double-shell nanophosphor. (b) The HAADF-STEM image shows that the nanophosphors are {112}-bound with blunt vertices. (c) Nanophosphor solution under 980 nm near infrared (NIR) laser and combined ultraviolet (UV) and NIR illumination.

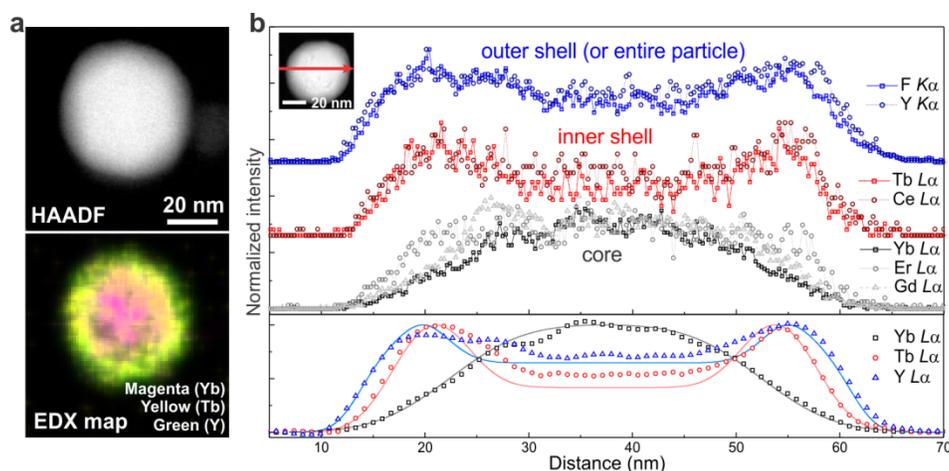


Figure 2. (a) HAADF-STEM image from a core/double-shell nanophosphor and its composite EDX map. (b) Raw line profile data for elements, which are present in each region of a single nanophosphor, are shown in the upper panel, and simulated EDX elemental profiles (lines) with a dimension of 36/5/3 nm were superimposed on the experimental data (symbols) in the lower panel, showing good agreement with the designed core/double-shell architecture.