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Citation: *Appl. Phys. Lett.* **88**, 143104 (2006); doi: 10.1063/1.2187518

View online: <http://dx.doi.org/10.1063/1.2187518>

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Luminescent enhancement in europium-doped yttria nanotubes coated with yttria

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(Received 20 November 2005; accepted 2 February 2006; published online 3 April 2006)

Europium-doped yttria nanotubes were coated with yttria by a simple two-step hydrothermal method, forming the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$ core-shell composite. Remarkable improvement of photoluminescence was observed in the core-shell composite under both violet and ultraviolet excitations. These characteristics were attributed to the reduced influence of surface defects on host excitation, charge transfer transitions, and $f-f$ inner-shell transitions of the Eu^{3+} ions. Due to striking red luminescence under ultraviolet excitation, the core-shell structure has potential application in plasma display panel devices. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2187518]

Recently, rare-earth-doped low-dimensional nanosized phosphors have received extensive attention due to their potential applications in the fields of optoelectronic devices,^{1,2} low-threshold laser,³ biological fluorescence labels, etc.^{4,5} However, because of the high ratio of surface to volume, there exist numerous surface dangling bonds, adsorptions and defect states, etc., which generally act as nonradiative relaxation channels, dramatically reducing luminescence lifetime and quantum efficiency (QE). This has a negative impact on their applications. So strategies have been developed to improve the QE of nanocrystals (NCs) by suppressing energy loss processes at the particle's surface.⁵⁻⁷ A convenient and straightforward method is to grow an undoped crystalline shell of material around the starting NCs, forming the so-called core-shell structures.⁸⁻¹⁰ On one hand, in the core-shell structure the surface defects around the luminescent ions can be modified. On the other hand, the distance between the luminescent ions and the surface defects or luminescence quenchers is increased, thus reducing the nonradiative pathways. Up to now, many reports are available regarding ways to improve the luminescent characteristic of semiconductor nanocrystals.⁸ A few of them are to improve the photoluminescence of rare-earth-doped nanomaterials by self-coating, such as $\text{LaPO}_4:\text{Eu}^{3+}/\text{LaPO}_4$ and $\text{LaF}_3:\text{Eu}^{3+}/\text{LaF}_3$ core-shell structures.^{10,11}

As the main and unsurpassed red emitting materials in fluorescent lamps and projection television tubes, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors inevitably gather more attention. In the past few years, a lot of work has been performed on $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NCs to improve its photoluminescent property further.¹²⁻¹⁴ Nevertheless, the coating of lanthanide oxide including $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NCs have been rarely reported. Nanotubes (NTs) have open ends, which have provided the possibility for wetting processing of inner parts with capillary action as the driving force. At the same time, NTs are generally hydrophilic. By immersing the NTs into the solution containing

functional molecules, these NTs could be coated with the functional groups.^{15,16} Here, we demonstrate a simple two-step hydrothermal method to prepare the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$ core-shell NCs based on $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NTs. In the core-shell NCs, remarkable luminescence enhancement under ultraviolet (UV) and vacuum ultraviolet (VUV) excitation was observed.

In the first hydrothermal step, appropriate amounts of high purity Y_2O_3 and Eu_2O_3 (1: 0.01 mol ratio) were dissolved in concentrated HNO_3 first. Then the final pH value was adjusted to^{12,13} with a NaOH solution (0.2M). After a thorough stirring, the colloid solution was transferred into several closed Teflon-lined autoclaves and subsequently heated to 150 °C for 12 h. The obtained suspension was centrifuged and the supernatant was discarded. The resultant precipitate was washed with de-ionized water several times, and then one half of the precipitate was dried at 70 °C. Following the above procedure, the $\text{Y}(\text{OH})_3$ powders were obtained and converted into Y_2O_3 after annealing at 500 °C for 2 h. In the second hydrothermal step, the remaining one half of the precipitate and appropriate amounts of $\text{Y}(\text{NO}_3)_3$ solution were removed to a stainless beaker with a volume of 250 mL. After ultrasonically dispersing for about 1 h, ammonia solution (0.2M) was slowly added, and the final pH value was adjusted to.^{10,11} The as-obtained colloidal precipitate was transferred into several autoclaves and kept at 150 °C for 12 h. The precipitate was then centrifuged, washed, dried and annealed at 500 °C for 2 h. The instruments and conditions for the characterization and spectral measurements are the same as those described previously.¹⁷

Figure 1(a) shows transmission electron microscopy (TEM) images of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NTs before coating. It is obvious that the central parts of these cylindrical samples are brighter in contrast to their edges, confirming their hollow-tube nature. The products predominantly consist of nanotubes with outer diameters of 70–90 nm and lengths of $\sim 2 \mu\text{m}$. Figure 1(b) depicts the magnified image of the tube structures shown in Fig. 1(a). It is apparent that the tips of the tubes are open and the walls are 10–20 nm in thickness and the surfaces are without amorphous layers. The inset of

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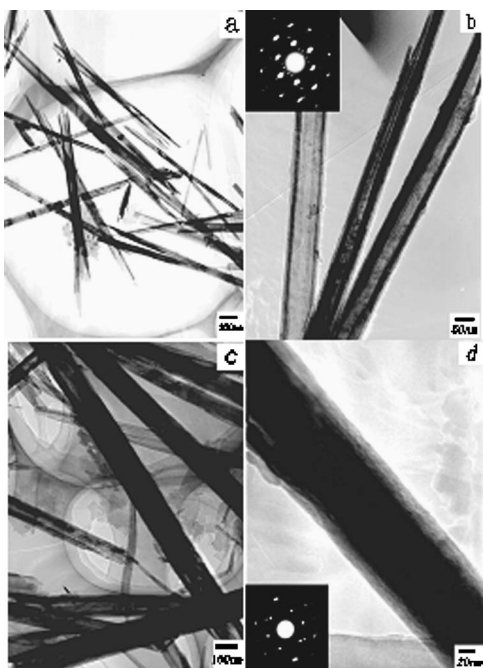


FIG. 1. (a) TEM images of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NTs, (b) The enlarged images of the NTs, (c) TEM images of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ core-shell NCs, and (d) The enlarged images of the core-shell structure.

Fig. 1(b) shows the electron diffraction pattern taken from a single coated tube, which reveals its single crystalline nature. Figure 1(c) is the TEM image of the coated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NCs and Fig. 1(d) displays typical $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$ core-shell NCs found in the composite. It can be observed that for most of the nanotubes the inner sides have been completely filled and the outer sides have been fully coated with yttria layers. Fig. 1(d) more clearly shows that the tube has been changed to solid inner and the thickness of the coated outer layer is usually 10–20 nm, which can be identified by the brighter edge.

Figure 2 shows the x-ray diffraction (XRD) patterns of the two different samples. It can be identified that the crystal structures of them both belong to the pure cubic phase. The calculated crystal cell parameter ($a=1.064$ nm) for the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ core NTs is a little larger than that ($a=1.060$ nm) for the typical card (JCPDS No. 79-1257), which may result from the substitution of the smaller Y^{3+} ions with the larger Eu^{3+} ions.¹⁸ In the core-shell structure, the crystal cell parameter a decreases to 1.060 nm again.

Figures 3(a) and 3(b) display, respectively, the excitation and emission spectra (Hitachi F-4500) of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NTs and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$ core-shell NCs at room temperature. In Fig. 3(a), the band extending from 200 to 300 nm is known to be a charge transfer (CT) one, which relates to the electronic transition from the $2p$ orbital of O^{2-} to the $4f$ orbital of Eu^{3+} . The sharp lines correspond to direct excitation of the $f-f$ inner-shell transitions, as labeled in the figure. Figures 3(a) and 3(b) demonstrate that the luminescent intensity in the core-shell composite increases remarkably over that in the NTs, for either the CT or the $f-f$ inner-shell excitations. However, the intensity ratio for the CT excitation to $f-f$ inner-shell excitation in the two samples has little variation. Figures 3(c) and 3(d) show the fluorescence decay curves for the ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ and ${}^5\text{D}_1\text{-}{}^7\text{F}_1$ transitions, respectively. In the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NTs, the ${}^5\text{D}_1\text{-}{}^7\text{F}_1$ transitions decay nonex-

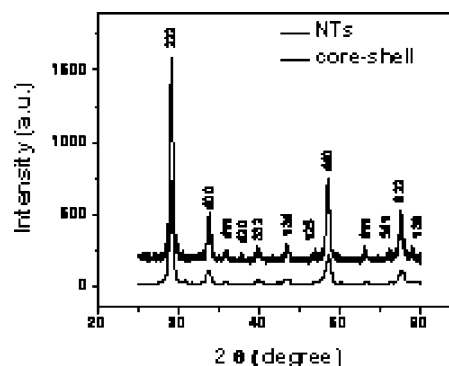


FIG. 2. XRD patterns of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NTs and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$ core-shell NCs.

ponentially and much faster than that in the core-shell structure. The two decay time constants are determined to be $\tau_1=65.9$ μs (with an intensity ratio of 49.6%) and $\tau_2=4.8$ μs (50.4%) by a biexponential fitting. In the core-shell structure, the decay curve of ${}^5\text{D}_1\text{-}{}^7\text{F}_1$ almost goes with a single exponential line, with a time constant of 94.6 μs . In contrast, the nonexponential decay in the core can be attributed to the energy transfer (ET) from the excited state of Eu^{3+} ions to surface defect states, which should have a much larger rate than radiative transitions.^{11,19} For the ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ transition, the fluorescence decay is single exponential for both the samples, with a time constant of 1.7 ms in the NTs and of 2.1 ms in the core-shell structure. The above results demonstrate that the coating can reduce the nonradiative relaxation of the $f-f$ inner-shell transitions for Eu^{3+} considerably, especially for the higher excited states.

Figures 4(a) and 4(b) show, respectively, the excitation and emission spectra under VUV deuterium-lamp excitation. In the excitation spectra, three bands are observed, located at 246, 211, and 172 nm, respectively. The former two bands are assigned to the CT transition and the self-trapped exciton transition of Y_2O_3 (SET), respectively, as reported in Ref. 20. The 172 nm band, which was seldom described in any literature might be attributed to the excitation of the Y_2O_3 host. The energy of host excitation (HE) should have equal or larger energy than band gap (6.2 eV for the bulk Y_2O_3). Corresponding to the excitation of the Y_2O_3 host, the emis-

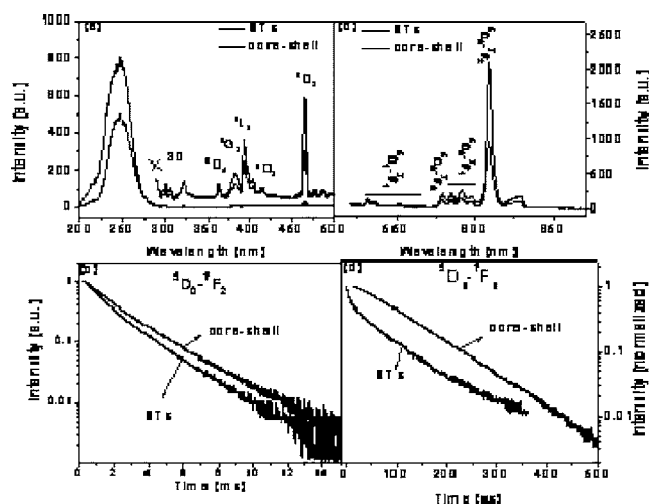


FIG. 3. (a) Excitation spectra ($\lambda_{\text{em}}=611$ nm), (b) emission spectra ($\lambda_{\text{ex}}=246$ nm), (c) the fluorescence decay curves of ${}^5\text{D}_0$ state ($\lambda_{\text{em}}=611$ nm) and (d) the fluorescence decay curves of ${}^5\text{D}_1$ state ($\lambda_{\text{em}}=537$ nm).

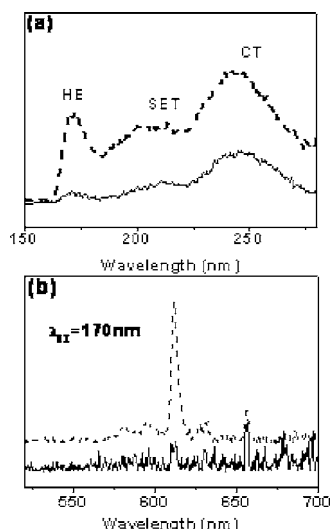


FIG. 4. Fluorescence spectra of Y₂O₃:Eu³⁺ NTs (solid lines) and Y₂O₃:Eu³⁺/Y₂O₃ (dashed lines) core-shell NCs under VUV deuterium-lamp excitation, (a) the excitation spectra and (b) the emission spectra.

sion intensity of the ⁵D₀-⁷F₂ transitions in the core-shell structure increases dramatically over that in the core. This indicates that the coating not only modified the *f-f* inner-shell transitions, but also modified the ET transitions from Y₂O₃ host to the Eu³⁺ ions significantly, which has the potential application in plasma display panel (PDP) devices. In core Y₂O₃:Eu³⁺ NCs, due to the existence of surface yttrium dangling bonds, some negative groups such as OH⁻, CO₃²⁻ are largely involved by surface contamination.^{21,22} Therefore, we have reason to consider that the bonding groups such as Eu³⁺-O²⁻-Y³⁺-OH⁻ or Eu³⁺-O²⁻-Y³⁺-CO₃²⁻ exist on the surface of the NCs. Consequently, most of the energy for O²⁻-(valence band)-Y³⁺ (conduction band) are nonradiatively transferred to the nearby OH⁻ and CO₃²⁻ groups, which have large vibration energy, instead of the nearby Eu³⁺ ions. As a consequence, the ET transitions from the Y₂O₃ host to the Eu³⁺ ions are strongly quenched. In the core-shell structure, this pathway is blocked due to the shielding of Eu³⁺ ions from surface adsorbing bonds.

Figure 5 shows the dependence of normalized emission intensity at 611 nm on the time under UV irradiation in the

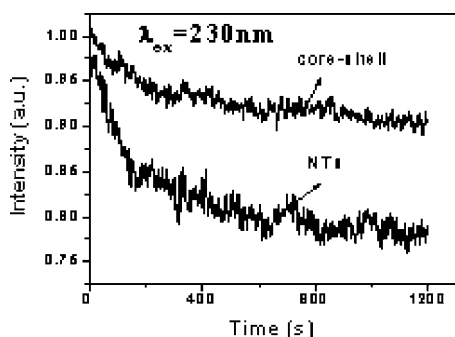


FIG. 5. Dependence of normalized intensity at 611 nm on irradiation time of 230 nm light in different samples.

two samples. It is obvious that the relative change in the luminescence intensity in the core NTs is much larger than that in the core-shell structure. The light-induced luminescence intensity change can be attributed to the rearrangements of local environments surrounding Eu³⁺ ions.²³ In the core-shell structure, the fluorescence stability under the exposure of UV light is also improved greatly.

In conclusion, the inner and outer surfaces of Y₂O₃:Eu³⁺ nanotubes were coated with yttria by a simple two-step hydrothermal method. In the Y₂O₃:Eu³⁺/Y₂O₃ core-shell structure, remarkable improvement of photoluminescence under UV and VUV excitation was observed due to a significant reduction of the surface defects. The striking red emission under the VUV excitation in the core-shell structure has potential application in nanosized PDP devices.

The authors acknowledge the financial support of the National Natural Science Foundation of China, Grant No. 10374086 and Grant No. 10504030 and the Talent Youth Foundation of JiLin Province, Grant No. 20040105.

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