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Supporting Information

Exploring surface-to-volume ratio in ultrasmall nanocrystals via the optical probe of Eu³⁺ ion

Huhui Fu,^a Rui Feng,^b Feilong Jiang,^a Yongsheng Liu,^{*a} and Maochun Hong^{*a}

^aState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.

^bTesting Center, Fuzhou University, Fuzhou, Fujian 350116, China.

*To whom correspondence should be addressed, E-mail: liuysh@fjirsm.ac.cn, hmc@fjirsm.ac.cn.

Experimental Section

Materials and reagents. $\text{Sc}(\text{CH}_3\text{COO})_3$, $\text{Eu}(\text{CH}_3\text{COO})_3$, LiOH , KOH , scandium oxide, oleic acid (OA), oleylamine (OM), 1-octadecene (ODE) and poly ethylene glycol-1000 (PEG_{1K}) were purchased from Sigma-Aldrich (China). Sodium acetate trihydrate and hexamethylenetetramine were purchased from Adamas Reagent, Ltd. Nitric acid, cyclohexane, chloroform and ethanol were purchased from Sinopharm Chemical Reagent Co., China. Unless otherwise noted, all the chemical reagents were used as received without further purification.

Characterization. Powder XRD measurements were performed on a powder diffractometer (MiniFlex2, Rigaku) with $\text{Cu K}\alpha 1$ radiation ($\lambda = 0.154187$ nm) from 15° to 85° at a scanning rate of 5° min^{-1} . Both the TEM and high-resolution TEM measurements were conducted on a transmission electron microscope (TEM, TECNAI G2F20) equipped with an energy dispersive X-ray spectroscopy (EDS). The SEM measurements for bulk materials were conducted on a field emission scanning electron microscope (FE-SEM, Hitachi SU8010). Photoluminescence (PL) emission/excitation spectra and PL decays were recorded on a spectrometer equipped with both continuous (450 W) xenon and pulsed flash lamps (FLS980, Edinburgh Instruments).

General procedure for preparation of $\text{Sc}_2\text{O}_3\text{:Eu}$ precursors. In a typical procedure, 4 mmol KOH , 0.8 mmol $\text{Sc}(\text{CH}_3\text{COO})_3$ and 0.2 mmol $\text{Eu}(\text{CH}_3\text{COO})_3$ were added into a 250-mL three-neck round flash containing a mixture solvent of 10 mL OA, 10 mL OM and 20 mL ODE, followed by heating to 150°C with constant stirring for 60 min under N_2 flow to form a clear yellowish solution for the following use.

General procedure for preparation of 2.6-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. In a typical procedure, 0.4 mmol $\text{Sc}(\text{CH}_3\text{COO})_3$, $\text{Eu}(\text{CH}_3\text{COO})_3$ and 2 mmol LiOH were added into a 100-mL three-neck round flash containing a mixture solvent of 10 mL OA, 10 mL OM and 20 mL ODE, followed by heating to 150°C with constant stirring for 60 min under N_2 flow to form a clear yellowish solution. Thereafter, the mixture solution was rapidly heated to 300°C under N_2 flow with constant stirring and maintained for 120 min to obtain 2.6-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. After naturally cooling down to room temperature, the resulting NCs were precipitated by addition of 40 mL ethanol, collected by centrifugation at 12000 rpm for 10 min, washed with ethanol for several times, and finally re-dispersed in cyclohexane.

General procedure for preparation of 3.6-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. In a typical procedure, 0.8 mmol $\text{Sc}(\text{CH}_3\text{COO})_3$, 0.2 mmol $\text{Eu}(\text{CH}_3\text{COO})_3$ and 4 mmol LiOH were added into a 250-mL three-neck round flash containing a mixture solvent of 10 mL OA, 10 mL OM and 20 mL ODE, followed by heating to 150°C with constant stirring for 60 min under N_2 flow to form a clear yellowish solution. Thereafter, the mixture solution was rapidly heated to 300°C under N_2 flow with constant stirring and maintained for 120 min to obtain 2.6-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ seed NCs. Thereafter, 10 mL $\text{Sc}_2\text{O}_3\text{:Eu}$ precursors were immediately injected into the reaction mixture and ripened at 300°C with constant stirring under N_2

flow for 30 min, followed by the similar injection and ripening cycles for four times to obtain 3.6-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. After naturally cooling down to room temperature, the resulting NCs were precipitated by addition of 60 mL ethanol, collected by centrifugation at 12000 rpm for 10 min, washed with ethanol for several times, and finally re-dispersed in cyclohexane.

General procedure for preparation of 4.5-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. In a typical procedure, 0.4 mmol $\text{Sc}(\text{CH}_3\text{COO})_3$, 0.1 mmol $\text{Eu}(\text{CH}_3\text{COO})_3$ and 2 mmol KOH were added into a 100-mL three-neck round flash containing a mixture solvent of 10 mL OA, 10 mL OM and 20 mL ODE, followed by heating to 150 °C with constant stirring for 60 min under N_2 flow to form a clear yellowish solution. Thereafter, the mixture solution was rapidly heated to 300 °C under N_2 flow with constant stirring and maintained for 120 min to obtain 4.5-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. After naturally cooling down to room temperature, the resulting NCs were precipitated by addition of 50 mL ethanol, collected by centrifugation at 12000 rpm for 10 min, washed with ethanol for several times, and finally re-dispersed in cyclohexane.

General procedure for preparation of 6.1-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. In a typical procedure, 0.8 mmol $\text{Sc}(\text{CH}_3\text{COO})_3$, 0.2 mmol $\text{Eu}(\text{CH}_3\text{COO})_3$ and 4 mmol KOH were added into a 100-mL three-neck round flash containing a mixture solvent of 10 mL OA, 10 mL OM and 20 mL ODE, followed by heating to 150 °C with constant stirring for 60 min under N_2 flow to form a clear yellowish solution. Thereafter, the mixture solution was rapidly heated to 300 °C under N_2 flow with constant stirring and maintained for 120 min to obtain 6.1-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. After naturally cooling down to room temperature, the resulting NCs were precipitated by addition of 50 mL ethanol, collected by centrifugation at 12000 rpm for 10 min, washed with ethanol for several times, and finally re-dispersed in cyclohexane.

General procedure for preparation of 7.6-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. In a typical procedure, 0.8 mmol $\text{Sc}(\text{CH}_3\text{COO})_3$, 0.2 mmol $\text{Eu}(\text{CH}_3\text{COO})_3$ and 4 mmol KOH were added into a 100-mL three-neck round flash containing a mixture solvent of 10 mL OA, 10 mL OM and 20 mL ODE, followed by heating to 150 °C with constant stirring for 60 min under N_2 flow to form a clear yellowish solution. Thereafter, the mixture solution was rapidly heated to 320 °C under N_2 flow with constant stirring and maintained for 120 min to obtain 7.6-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. After naturally cooling down to room temperature, the resulting NCs were precipitated by addition of 50 mL ethanol, collected by centrifugation at 12000 rpm for 10 min, washed with ethanol for several times, and finally re-dispersed in cyclohexane.

General procedure for preparation of 9.7-nm $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs. In a typical procedure, 1 mmol $\text{Sc}(\text{CH}_3\text{COO})_3$, 0.2 mmol $\text{Eu}(\text{CH}_3\text{COO})_3$ and 4 mmol KOH were added into a 250-mL three-neck round flash containing a mixture solvent of 10 mL OA, 10 mL OM and 20 mL ODE, followed by heating to 150 °C with constant stirring for 60 min under N_2 flow to form a clear yellowish solution. Thereafter, the mixture solution was rapidly heated to 320 °C under N_2 flow with constant stirring and maintained for 120 min to obtain $\text{Sc}_2\text{O}_3\text{:Eu}$ seed NCs. Thereafter, 10 mL $\text{Sc}_2\text{O}_3\text{:Eu}$ precursors

were immediately injected into the reaction mixture and ripened at 300 °C with constant stirring under N₂ flow for 30 min, followed by the similar injection and ripening cycles for four times to obtain 9.7-nm Sc₂O₃:Eu NCs. After naturally cooling down to room temperature, the resulting NCs were precipitated by addition of 60 mL ethanol, collected by centrifugation at 12000 rpm for 10 min, washed with ethanol for several times, and finally re-dispersed in cyclohexane.

General procedure for preparation of Sc₂O₃:Eu bulk materials. In a typical procedure, 0.14 g scandium oxide and 1 mL concentrated nitric acid were added into a 50 mL beaker containing 10 mL distilled water, followed by heating to 80 °C with constant stirring to form a clear solution. After being dried at 80 °C for 5 h, the obtained white powder was dissolved into 20 mL distilled water at room temperature. Subsequently, a mixture of 0.41 g sodium acetate trihydrate, 0.5 g PEG_{1K} and 1.0 g hexamethylenetetramine was added into the above solution under vigorous stirring for 30 min. The resulting mixture was then transferred into a 30-mL Teflon-lined autoclave, sealed and heated at 100 °C for 72 h. After naturally cooling down to room temperature, the white precipitates were collected via centrifugation at 12000 rpm for 5 min. After being dried at 65 °C for 24 h, the white precipitates were annealed at 800 °C in air for 4 h to obtain Sc₂O₃:Eu bulk materials.

Supplementary Figures

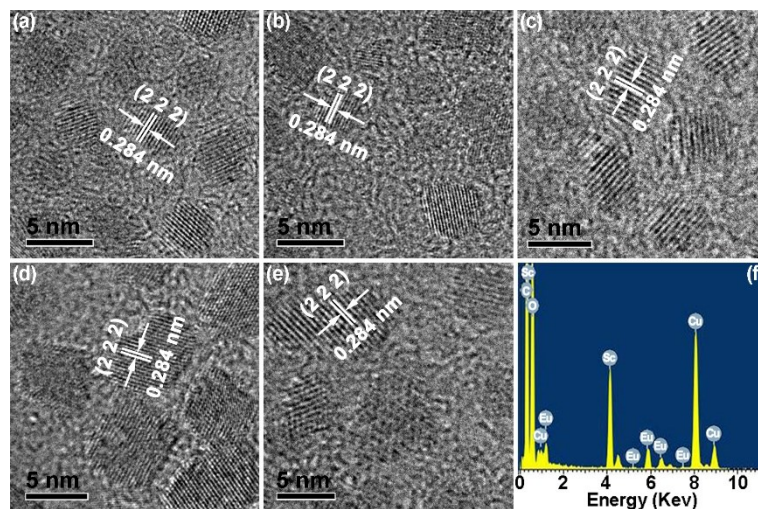


Figure S1. High-resolution TEM images for ultrasmall $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs with different nanocrystal size of (a) 3.6, (b) 4.5, (c) 6.1, (d) 7.6 and (e) 9.7 nm, respectively. Identical to the case of 2.6-nm $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs, lattice fringes in these NCs are all clear with an observed d-spacing of 0.284 nm, in good agreement with the lattice spacing for the (222) plane of cubic-phase Sc_2O_3 , indicating the high crystallinity of $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs regardless of their ultrasmall size. (f) Energy-dispersive X-ray spectroscopy (EDS) analysis for the as-synthesized ultrasmall $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs, revealing the presence of host elements of Sc, O and the dopant of Eu in these NCs.

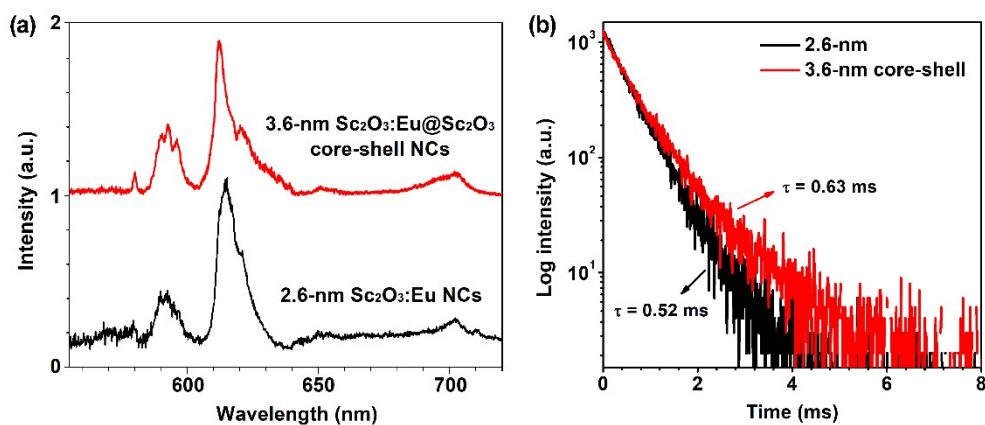


Figure S2. (a) Comparison of PL emission spectra for 2.6-nm $\text{Sc}_2\text{O}_3:\text{Eu}$ and 3.6-nm $\text{Sc}_2\text{O}_3:\text{Eu}@Sc_2\text{O}_3$ core-shell NCs and (b) their corresponding PL lifetimes. As shown in Figure S2, the PL emission spectrum of 3.6-nm $\text{Sc}_2\text{O}_3:\text{Eu}@Sc_2\text{O}_3$ core-shell NCs is observed to differ largely from that of 2.6-nm $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs in terms of line positions, shapes and relative intensities. In addition, the PL lifetime of the core-shell NCs was determined to be 0.63 ms, much larger than that of the 2.6-nm counterparts (0.52 ms). Taken together, these results unambiguously suggest that surface passivation would change the emission of Eu^{3+} .

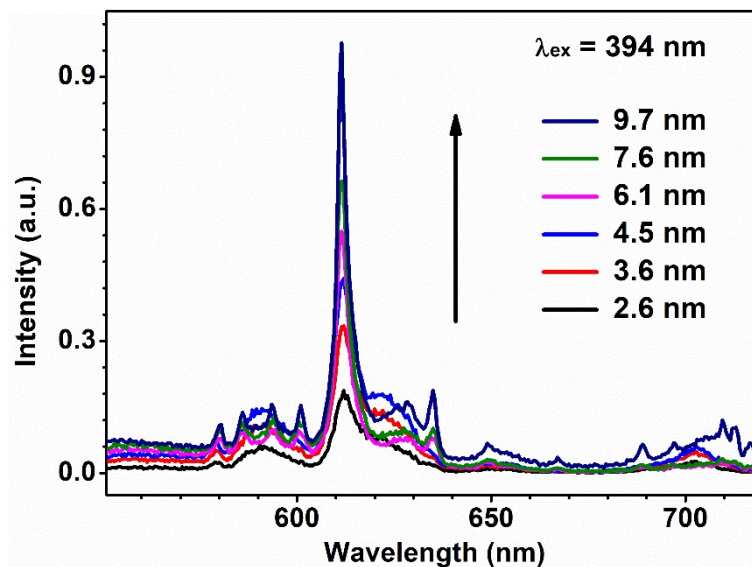


Figure S3. Comparison of PL emission spectra for the as-synthesized Sc₂O₃:Eu NCs with different nanocrystal sizes ranging from 2.6 to 9.7 nm. Note that all the PL emission spectra were measured under identical experimental conditions upon a 394-nm lamp excitation. The integrated PL emission intensity for Sc₂O₃:Eu NCs was found to gradually decrease with reducing the nanocrystal size. This downtrend of PL emission intensity for Sc₂O₃:Eu NCs is understandable, because the smaller Sc₂O₃:Eu NCs possessing larger surface-to-volume ratio are prone to undergo severer surface PL quenching effect and thus usually give rise to much weaker emission when compared to their larger counterparts.

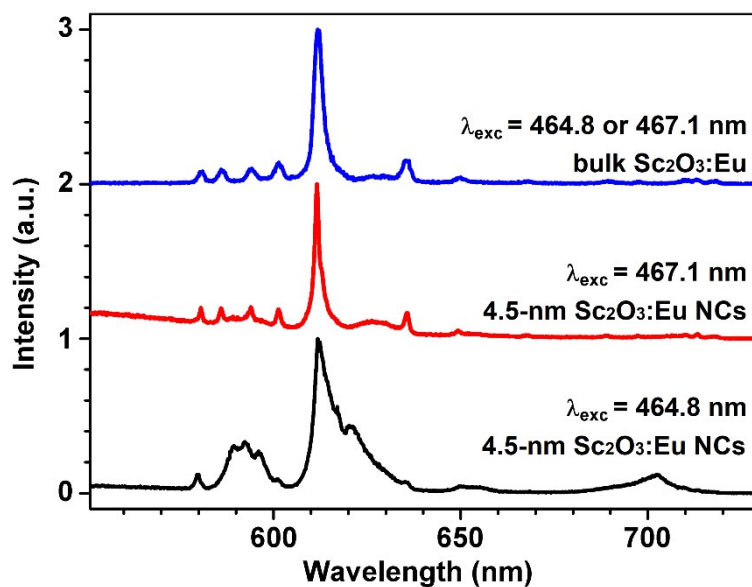


Figure S4. Comparison of PL emission spectra for 4.5-nm $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs and $\text{Sc}_2\text{O}_3:\text{Eu}$ bulk materials upon site-selective excitations at 464.8 and 467.1 nm. The PL emission spectrum of 4.5-nm $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs upon excitation at 467.1 nm is observed to be nearly identical to that of $\text{Sc}_2\text{O}_3:\text{Eu}$ bulk materials but differs markedly from that upon site-selective excitation at 464.8 nm in terms of line positions, shapes and relative intensities, clearly indicating that this subset of Eu^{3+} ions occupies a well-ordered inner crystal lattice analogous to that in bulk counterparts with a substitutional Sc^{3+} crystallographic site of C_2 symmetry.

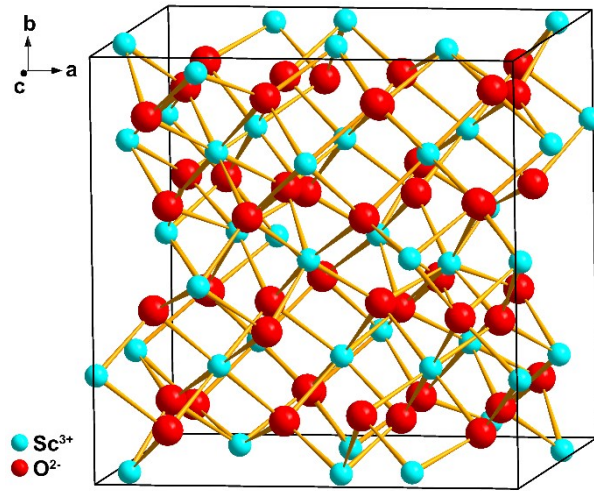


Figure S5. Schematic presentation of cubic-phase Sc_2O_3 crystal structure (JCPDS No. 74-1128). The space group of cubic Sc_2O_3 is $Ia-3$ with unit cell $a = 9.81 \text{ \AA}$ and unit cell volume $V_{\text{unit}} = 944.08 \text{ \AA}^3$, and every unit cell contains 32 Sc^{3+} and 48 O^{2-} ions. Taking 2.6-nm $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs for example, the total number of Sc^{3+} and Eu^{3+} ions per $\text{Sc}_2\text{O}_3:\text{Eu}$ nanocrystal (N_{nc}) can be roughly estimated to be 309 by using the following equation:

$$N_{\text{nc}} = \frac{4}{3}\pi r^3 / V_{\text{unit}} \times 32$$

Where r is the radius of $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs, which is 1.3 nm; V_{unit} is the unit cell volume of cubic Sc_2O_3 crystal. Note that the above calculation was conducted on the condition that the obtained $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs were assumed to be ideal spherical shape for the sake of simplicity.

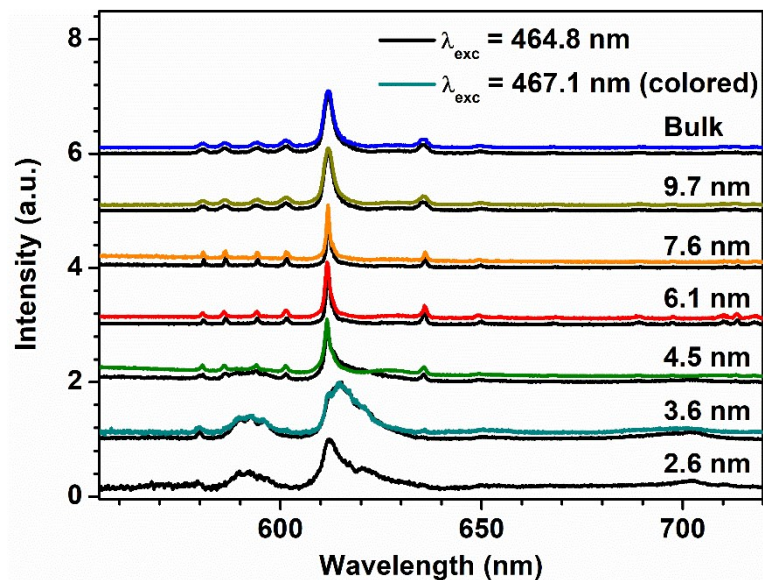


Figure S6. Comparison of PL emission spectra for $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs with different nanocrystal sizes and $\text{Sc}_2\text{O}_3:\text{Eu}$ bulk materials. When the nanocrystal size of $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs is less than 4.5 nm, dominant broad PL emission lines without apparent crystal-field splitting were detected in the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ spectra region when selectively excited at 464.8 nm, indicating that the surface Eu^{3+} ions hold a dominant position in these small $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs. By contrast, when the nanocrystal size of $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs is larger than 4.5 nm, only sharp and well resolved PL emission peaks of Eu^{3+} analogous to those of bulk materials were detected for $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs upon both 464.8-nm and 467.1-nm excitations, which suggests that almost all of Eu^{3+} ions lie in a well-ordered crystalline environment (namely, inner-lattice site) in large $\text{Sc}_2\text{O}_3:\text{Eu}$ NCs (> 4.5 nm).

Table S1. Actual Eu^{3+} doping contents determined from the inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the as-synthesized ultrasmall $\text{Sc}_2\text{O}_3\text{:Eu}$ NCs with varied nanoparticle sizes doped with 20 mol% Eu^{3+} .

Sample	Nominal Eu^{3+} doping content (mol%)	Actual Eu^{3+} doping content from ICP-AES (mol%)
2.6-nm	20	19.8 ± 0.9
3.6-nm	20	19.3 ± 1.2
4.5-nm	20	20.1 ± 0.8
6.1-nm	20	19.5 ± 0.7
7.6-nm	20	20.3 ± 0.5
9.7-nm	20	19.7 ± 1.1