Fabrication and Luminescent Characteristics of $Y_2O_3:Eu^{3+}$ Nanotubes by Hydrothermal Treatment

Tetsuro Jin,*[1] Erika Jin,[2] Mamoru Sano,[2] Bo Chi,[1] and Tetsuo Yazawa[3]
[1]*National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577*
[2]*Depretment of Biology, Kyoto Prefectural University of Medicine, Taishogun nishitakatsukasa-cho 13, Kita-ku, Kyoto 603-8334*
[3]*Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji 671-2201*

(Received December 26, 2007; CL-071439; E-mail: tetsu-jin@aist.go.jp)

$Y_2O_3:Eu^{3+}$ nanotube phosphors were prepared using polyethylene glycol via a hydrothermal treatment and a subsequent heat treatment. Scanning electron microscopy indicated that the crystal was a tube with an outer diameter of 80 nm. A higher emission intensity was observed with nanotubular Y_2O_3 doped with 7.5 mol % Eu^{3+} ions after heated more than 900 °C compared with that of the commercial one. In addition, the examination of toxicity using cell line suggested that the toxicity of the lanthanide oxide nanotubes indeed was much less than the case of asbestos.

Since discovery of carbon nanotubes,[1] much interest has focused on the field of 1-dimensional (1D) nanomaterials. 1D nanotubes have potential applications in several fields such as catalysis, composite materials, and intramolecular junctions.[2] Recently, various oxide 1D materials such as TiO_2 and RE_2O_3 (RE; Rare Earths) have been vigorously synthesized by templating processes[3–6] because these tubular oxides should show some remarkable characteristics such as the electronic and chemical properties of carbon nanotubes.[7,8] On the other hand, yttrium oxide doped with trivalent europium ions, $Y_2O_3:Eu^{3+}$, is a typical lanthanide oxide phosphor, which has practical use as a red emitter material in displays because of the clear brightness, good chemical and physical stability. The nanoparticles of lanthanide phosphors smaller than 10 nm, however, do not show a higher emission intensity than typical lanthanide phosphors, which are on the micrometer level.[9] While, changing the morphology as the particle size increases to several tens of nm improves the emission intensities. Recently, yttrium hydroxide and oxide have been hydrothermally prepared via a metastable precursor, a PEG–$Y(NO_3)_3$ complex. The final products were nanotubes, which have outer diameters ranging from 80 to 200 nm and wall thicknesses of ca. 30 nm.[10] Thus, it is possible to enhance the emission of $Y_2O_3:Eu^{3+}$ nanotubes prepared with the method described herein more than that of commercial phosphors. In this study, a hydrothermal preparation of trivalent europium-doped yttrium hydroxide nanotubes was performed and calcined to obtain $Y_2O_3:Eu^{3+}$ nanotubes. The size, morphology, and luminescent characteristics of the obtained nanotubes are discussed. In addition, the examinations of toxicity against human beings were also performed using human mesothelial cell line (MeT-5A).

Lanthanide oxide nanotubes were prepared using a PEG template and the method of Tang et al.[10] The starting materials were $Y(NO_3)_3$ (hexahydrate, 99.9%), $Eu(NO_3)_3$ (hexahydrate, 99.9%), and polyethylene glycol (PEG, average molecular number: 6000, 99.99%). 1 mmol of $Y(NO_3)_3$, 1.0 g of PEG-6000, and 20 mL of water were dissolved into distilled water and then stirred in a typical preparation. The Eu^{3+} ions doped ranged from 1 to 10 mol % in Y_2O_3. The transparent solution was added to an aqueous alkali solution and the obtained white mixture (pH value >10) was stirred. The mixture was poured into a Teflon-lined stainless autoclave. The autoclave was treated at more than 150 °C for 24 h and subsequently cooled to room temperature. Furthermore, the nanotubes were heated in air at 900 °C for 2 h. X-ray diffraction (XRD) using a Shimadzu XRD-6000 with Cu Kα radiation was used. The morphologies of the $Y_2O_3:Eu^{3+}$ nanotubes were collected by a conventional field emission scanning electron microscope (FE-SEM, Hitachi S-5000) and a transmission electron microscope (TEM, Hitachi H-9000NA). The emission and excitation spectra were recorded at room temperature using a Hitachi F-4500 spectrophotometer. The lifetimes were measured for the emission from the $^5D_0$–$^7F_2$ levels using a 7.5 mol % Eu^{3+}-doped tubular Y_2O_3. Excitation to these levels was performed using an optical parametric oscillator pumped with a Q-switched Nd:YAG laser. The emission intensity of the $Y_2O_3:Eu^{3+}$ nanotube was estimated by comparison with the area of the emission spectrum recorded under an optimum excitation. A commercial $Y_2O_3:Eu^{3+}$ phosphor (LP-RE1) was purchased from Kasei Optnics. A commercially available human mesothelial cell line (MeT-5A) was used for the examination of toxicity of the tubular phosphor. Met-5A cells were plated on coverslips previously coated with 2% poly-L-lysine and grown for 24 h. Then, they were exposed to $Y_2O_3:Eu^{3+}$ nanotubes and crocidolite asbestos fibers as a contrast concentration (25 $\mu g\,cm^{-2}$) for 18 h. Cells were stained by TUNEL stain for detecting of apoptotic cells. Apoptotic cells staining TUNEL (Roshe, Apoptosis Detection Kit) were counted more than 100 cells, and then the frequency of apoptosis was calculated.

X-ray diffraction studies have been conducted on the nontreated powder and on powders heated at 375 and 900 °C for 2 h. All the X-ray diffraction peaks of $Y(OH)_3:Eu^{3+}$ can be indexed as a hexagonal UCl_3-type crystal structure (JCPDS No. 24-1422) without impurities. Furthermore, after the heat treatment above 375 °C, the sample turns into $Y_2O_3:Eu^{3+}$, which can be indexed as a cubic phase (JCPDS No. 20-1412) without an impurity phase.

Figure 1 shows the morphology of a typical $Y_{1.925}O_3:_{0.075}Eu^{3+}$ nanotube observed by FE-SEM and TEM. The FE-SEM image shows that the $Y_{1.925}O_3:_{0.075}Eu^{3+}$ phosphor formed a nanotube with inner diameter of ca. 40 nm and an outer diameter of 80 nm. This is also supported by the inserted image (c). Furthermore, we can see the tubular structure of the lanthanide nanotube on TEM image.

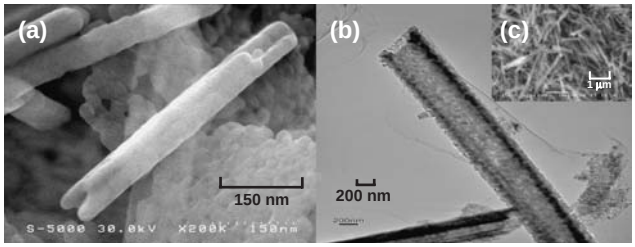

Figure 1. The images of (a) FE-SEM, (b) TEM, and (c) SEM taken at low magnification for a $Y_{1.925}O_3$:$_{0.075}Eu^{3+}$ nanotube treated at 900 °C.

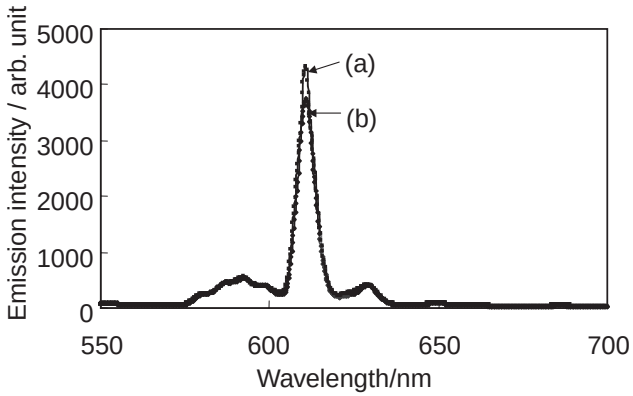

Figure 2. Emission spectra of (a) $Y_{1.925}O_3$:$_{0.075}Eu^{3+}$ nanotubes heated at 900 °C and (b) commercial Y_2O_3:Eu^{3+}. The phosphors were excited at 254 nm.

The $^5D_0$–$^7F_2$ transition for a $Y_{1.95}O_3$:$_{0.05}Eu^{3+}$ nanotube phosphor decays exponentially. The fitting of the curve indicates that the emission lifetime of $^5D_0$–$^7F_2$ is 1.12 ms. In a similar manner, the emission lifetimes of $^5D_0$–$^7F_2$ for nanotubes such as $Y_{1.925}O_3$:$_{0.075}Eu^{3+}$ and a commercial Y_2O_3:Eu^{3+} were determined, and the values of them are 1.13 and 1.29, respectively. The emission lifetime of the $^5D_0$–$^7F_2$ for $Y_{1.925}O_3$:$_{0.075}Eu^{3+}$ nanotube is approximately 13% shorter than that of a commercial one with a similar composition. As shown in Figure 2, the emission intensity of the nanotube phosphor (a) increases more than that of a commercial Y_2O_3:Eu^{3+} (b). From these findings, it is concluded that the radiative transition rate simply increases in the system of the nanotube. Furthermore, the increased emission intensity rate for the nanotube phosphor compared to the commercial one is ca. 10%. This result also supports the enhanced radiative transition rate in the Y_2O_3:Eu^{3+} nanotube system.

Although there is no toxic species in the composition ($Mg_6Si_4O_{10}(OH)_8$),[11] asbestos become showing toxicity against human cells by the rod-like morphology. In vitro studies on mesothelial cells exposed to asbestos fibers showed inhibition of growth, disruption of mitosis, induction of DNA, and chromosomal damage.[12]

Figure 3 shows that the fluorescent microscope images of Met5A apoptosis exposed to the nanotubes and asbestos of 25 μg cm^{-2} concentration. It was found that the frequency for apoptosis was 35% in the case of asbestos though the frequency of the control and the nanotubes was several %. It indicated that

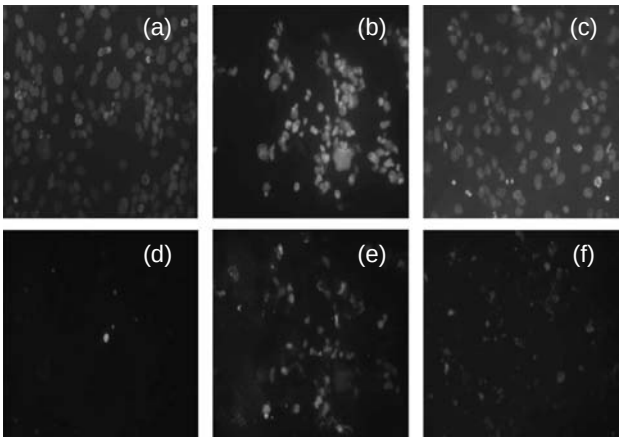

Figure 3. The images of TUNEL staining of Met5A. Upper column shows fluorescently stained nuclei of Met5A cells, and lower shows apoptotic cells by TUNEL stain, (a), (d); control, (b), (e); cultured with asbestos, and (c), (f); with $Y_{1.925}O_3$:$_{0.075}Eu^{3+}$ nanotube phosphor.

the toxicity of the nanotubes was extremely little compared with asbestos.

As conclusion, nanotubular Y_2O_3 doped with Eu^{3+} ion was successfully synthesized via $Y(OH)_3$:Eu^{3+} by a hydrothermal treatment and subsequent heating at 900 °C in air. Remarkably, the emission output from the europium trivalent ions in the yttrium oxide nanotube was intensified more than that of a commercial one. Furthermore, the oxide nanotube showed exceedingly lower toxicity for human cells than that of asbestos.

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