

UC San Diego

UC San Diego Previously Published Works

Title

Influence of morphological transformation on luminescence properties of europium-doped gadolinium oxide nanostructures

Permalink

<https://escholarship.org/uc/item/1xk6t7c0>

Journal

Journal of Nanophotonics, 4(1)

ISSN

1934-2608

Authors

Zhang, Kai
Dondapati, Hareesh

Publication Date

2010-09-01

DOI

10.1117/1.3501312

Peer reviewed

Journal of Nanophotonics

SPIEDigitalLibrary.org/jnp

Influence of morphological transformation on luminescence properties of europium-doped gadolinium oxide nanostructures

Kai Zhang
Hareesh Dondapati
Terence Holloway
Wei Cao
Arik Kar
Amitava Patra
Aswini K. Pradhan



Influence of morphological transformation on luminescence properties of europium-doped gadolinium oxide nanostructures

Kai Zhang,^a Hareesh Dondapati,^a Terence Holloway,^a Wei Cao,^b
Arik Kar,^c Amitava Patra,^c and Aswini K. Pradhan^a

^a Norfolk State University, Center for Materials Research, 700 Park Avenue,
Norfolk, Virginia 23504, USA

^b Old Dominion University, 12050 Jefferson Avenue, Newport News, Virginia 23606, USA

^c Indian Association for the Cultivation of Science, Department of Materials Science,
Jadavpur, Kolkata 700032, India

apradhan@nsu.edu

Abstract. Low dimensional europium (Eu³⁺)-doped gadolinium oxide (Gd₂O₃) lanthanide nanostructures are synthesized by an effective and simple coprecipitation process followed by subsequent heat treatments. Transmission electron microscope (TEM) images indicate Eu³⁺-doped Gd₂O₃ nanostructures undergo significant morphological changes from nanorods to nanoparticles during thermal treatments. Nanostructures with different morphology, including nanotubes, strongly influence the photoluminescence properties. The dependence of luminescence lifetime on morphological nature of the nanostructures demonstrates that the one dimensional nanostructures such as nanorods and nanotubes have higher emission intensity with shorter lifetime. Our analysis suggests that the morphological transformation of the nanostructures plays the most important role in the behavior of radiative and nonradiative relaxation mechanisms, resulting in the overall photoluminescence properties.

Subject terms: nanostructures; morphological transformation; photoluminescence properties.

1 INTRODUCTION

Nanoscale structures, which include nanoparticles, nanorods, nanowires, nanotubes, and nanobelts [1-5], have been considerably investigated due to their unique optical and electronic properties and prospective application in diverse fields, such as high quality luminescent devices, catalysts, sensors, biological labeling, and other new functional optoelectronic devices. The precise architectural manipulation of nanomaterials with well-defined morphologies and accurately tunable sizes remains a focus of research and a challenging issue due to the fact that the properties of the materials closely interrelate with geometrical factors such as shape, dimensionality, and size. The properties and performances of nanostructures strongly depend on their dimensions, sizes, and morphologies [6]. Therefore, synthesis and growth of morphology controlled in the crystallization process of nanostructures is of critical importance for the development of novel technologies.

Rare-earth-doped oxides are a kind of promising new class of luminescent material due to their electronic and optical properties that arise from their 4f electrons. Therefore, much attention has been paid to their luminescent characteristics such as their large Stokes shift, sharp emission visible spectra, long fluorescence lifetime (1 to 2 ms), and lack of photobleaching compared with dyes [7,8]. These materials, especially in the nanostructure, have been widely used in the lighting industry and biotechnology, including plasma display panels, magnetic resonance imaging enhancement, and microarray immunoassays for

fluorescence labels [9-12]. Since the morphology and dimensionality of nanostructures are vital factors, which particularly have an effect on the physical, chemical, optical, and electronic properties of materials, it is expected that rare-earth-doped oxides synthesized in nanoscale form of may take on novel spectroscopic properties of both dimension-controlled and modified ion-phonon confinement effects compared to their bulky counterparts. Gd_2O_3 as a rare-earth oxide is a useful paramagnetic material and good luminescent rare-earth-doped host. Eu^{3+} ions can be doped into Gd_2O_3 easily, since they are all trivalent ions and have the same crystal structure. Furthermore, $^5\text{D}_0$ - $^7\text{F}_2$ of Eu^{3+} transitions exhibit red characteristic luminescence at a wavelength of 611 nm. Therefore, lanthanide-oxide-doped nanostructures can be used as electrical, magnetic, or optical multifunction materials.

Recently, considerable efforts have been made to synthesize low dimensional nanostructures [2, 3, 13]. However, these processes must have hydrothermal routines, templates, and catalysts. The nanostructure formed depends somehow on the pressure, template, and catalysts. This results in experimental complexity, impurities, defects, and high costs. In addition, these methods especially could not meet large scale production in industry. Therefore, it is necessary to find new methods to synthesize shape, size, and dimensionality controlled lanthanide-doped oxides. Also, because of their distinct low effective density, high specific surface area, and encapsulation ability in hollow nanotubes, these nanostructures are exceptionally promising in various fields such as confined catalysis, biotechnology, photonic devices, and electrochemical cells [14-16]. Although lanthanide oxides are excellent host lattices for the luminescence of various optically active lanthanide ions [17], Gd_2O_3 is a promising host matrix for down- and up-conversion luminescence because of its good chemical durability, thermal stability, and low phonon energy [18].

We report on a novel method to prepare Eu^{3+} -doped Gd_2O_3 nanostructures through a large scale and facile solution based coprecipitation chemical route, followed by subsequent annealing heat treatment processes. In this process, the nanostructures were obtained without using any template, catalyst, or pressure. To the best of our knowledge, this is the first technique that is simple, low cost, and has high efficiency for synthesizing Eu^{3+} -doped Gd_2O_3 nanostructures. Moreover, we demonstrate the emission characteristic and lifetime dependence on the morphology of nanostructures produced by different annealing temperatures. In addition, these nanostructures were compared to 1-D nanotube counterparts to investigate the dependence of optical properties on the morphological transformation of Eu^{3+} -doped Gd_2O_3 nanostructures. The present work may open new possibilities to synthesize nanostructures with varying morphological shapes of other oxides and extend their applications.

2 SAMPLE PREPARATION

All chemicals (Alfa-Aesar, Ward Hill, Massachusetts) used in this study were of analytical reagent grade, used without further purification. Gd_2O_3 doped with Eu^{3+} nanostructures were synthesized according to a coprecipitation wet chemical solution method. In this process, 0.5-M aqueous solution was prepared by dissolving $\text{Gd}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ in deionized H_2O . The nitrate solutions with a cationic molar ratio of Gd to Eu of 0.95: 0.05 were mixed together and stirred for 30 min. The aqueous solution of 0.2-M NH_4HCO_3 was prepared and mixed with the nitrate solution drop-wise while stirring to form the precipitate. It is noted that in this experiment extra 10 mol% NH_4HCO_3 was added to ensure all the rare-earth ions reacted completely to obtain rare-earth carbonates. The white precipitate slurry obtained was aged for 24 h at room temperature with continuous stirring. Then the precipitates were centrifugated and washed with deionized water for five times to completely remove NO_3^- , NH_4^+ , and HCO_3^- , followed by drying at about 75°C in the stove. After drying, the white precursor was ground several times. It is noted that the dried precursor powders were very loosely agglomerated and can be pulverized very easily. To get Gd_2O_3 doped with Eu^{3+}

nanostructures, the as-synthesized samples were further calcined at 600, 800, and 1000°C in air for 2 h in the furnace, respectively.

Eu³⁺-doped Gd₂O₃ nanotubes were synthesized according to a modified wet chemical method [19]. A mixture of 30 ml of 0.08-M Gd(NO₃)₃ and Eu(NO₃)₃ with a nominal molar ratio of Eu/Gd 5 atom %, in a form of clear solution, was added into flasks through ultrasound for 10 min. 30 ml of 25 wt % of ammonia solution was added quickly into the solution under vigorous stirring for 20 min. Meanwhile, the pH value of the mixture was measured, which came to a value of about 10. The mixture was heated under vigorous stirring in a 70 °C silicon oil bath for 16 h. After this procedure, a white precipitate precursor was obtained. The final as-prepared precipitates were separated by centrifugation, washed with deionized water and ethanol four times, respectively, and dried for 12 h at 65 °C in air to get an as-grown sample. To get a Gd₂O₃ product, the as-synthesized samples were further annealed in air for 2 h at 600 °C in the furnace.

Several characterization techniques have been carried out to determine the nanostructure formation. The phase purity and crystallinity of products were examined by x-ray diffraction (XRD) performed on a Rigaku (Japan) powder x-ray diffractometer with copper K α incident radiation ($\lambda=1.5405$ Å). The morphology and structure of the samples were inspected using a field emission scanning electron microscopy (FE-SEM, LEO 1550) and high resolution transmission electron microscopy (HRTEM) of JEOL JEM 2100 field emission electron microscope systems. Photoemission spectra were recorded by a Hitachi F-7000 fluorescence spectrophotometer equipped with a 150-W xenon lamp as the excitation source. Time-correlated photon counting measurements of the samples were made with a nano-LED in a Horiba Jobin Yvon (Edison, New Jersey) IBH Fluorocube apparatus. The fluorescence decays were collected at a Hamamatsu MCP photomultiplier (C487802). All measurements were performed at room temperature.

3 RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the samples after different temperature calcination of as-prepared precursors. All the diffraction peaks can fully be indexed into the cubic structure of the Gd₂O₃ phase [space group: $Ia\bar{3}$ (206)], which is consistent with PDF 76-0115. No other second phase peaks can be detected, suggesting that the as-synthesized precursors transformed totally into the oxides of Gd₂O₃, and Eu³⁺ ions were effectively doped into Gd₂O₃ cubic lattices to form solid solutions after annealing at 600, 800, and 1000°C, respectively [19].

The lattice parameter of the annealed products were calculated in terms of the cubic symmetry formula $1/d^2 = (h^2 + k^2 + l^2)/a^2$, where d is the interplanar distance, h , k , and l are the miller indices, and a is the lattice parameter. Based on the (222) crystallographic planes, the lattice parameter is $a = 1.079$ nm, which closely matches the reference value of $a = 1.081$ nm. It is also noted that the peak intensity of the XRD is sharper and stronger with the increase of the annealing temperature, revealing that the high crystallinity of Eu³⁺-doped Gd₂O₃ is produced at higher annealing temperatures.

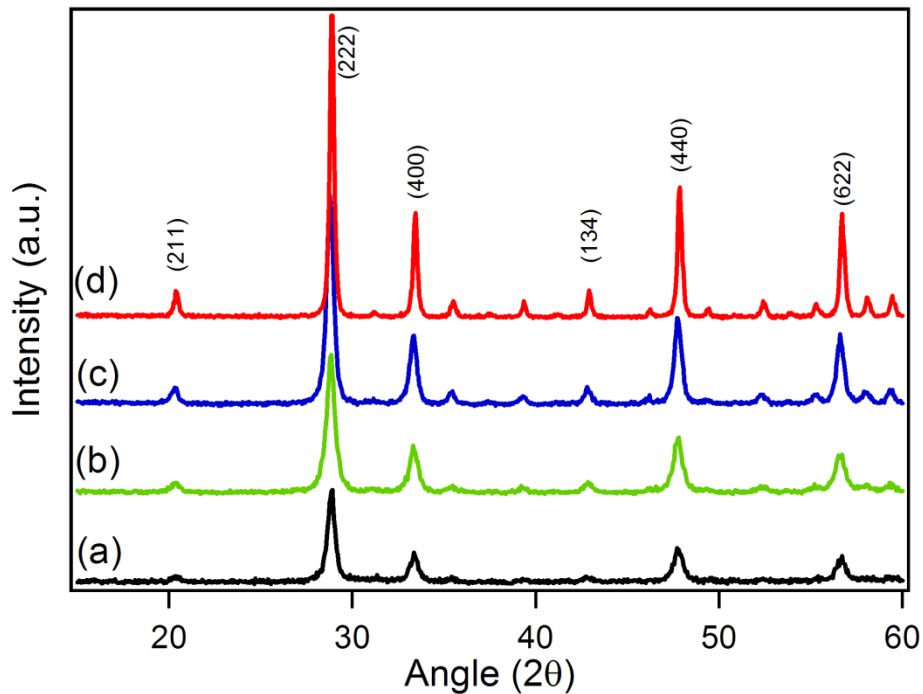


Fig. 1. x-ray diffraction of Eu^{3+} -doped Gd_2O_3 samples for (a) the nanotubes annealed at 600°C , (b) the nanorods annealed at 600°C , (c) the nanorods annealed at 800°C , and (d) the nanoparticles annealed at 1000°C for 2 h, respectively.

The morphology of Eu^{3+} -doped Gd_2O_3 nanorods obtained after calcination at 600°C for 2 h strongly depends on the heat treatment temperature. The formation of nanorods with low aspect ratio is preferred at 600°C . It can be seen from the micrograph that all the nanorods display uniform morphology, having sizes 10 nm in diameter and more than 300 nm in length [Fig. 2(a)]. In contrast, the nanorods grow bigger in diameter (about 25 nm) and shorter in length (about 100 nm) after heat treatment at 800°C , as shown in Fig. 2(c). However, it is evident that Eu^{3+} -doped Gd_2O_3 nanorods maintain the anisotropic shape during heat treatment from 600 to 800°C . It can also be observed that the formation of nanorods is related to the fact that growth direction is preferred along the [211] crystallographic orientation. This is because the spacing between fringes along nanorod axes is about 0.40 nm, which is close to the interplanar distance of the cubic (211) plane, as shown in Figs. 2(b) and 2(d). Figure 2(e) presents the TEM images of Eu^{3+} -doped Gd_2O_3 nanoparticles with sizes 60 nm in diameter obtained by heat treatment at 1000°C . The morphology of an Eu^{3+} -doped Gd_2O_3 nanostructure dependent on the heat treatment temperature is possibly attributed to metastable states that are able to recrystallize at 1000°C . A favorable growth pattern parallel to the (222) plain corresponding to interplanar spacing of 0.3 nm dominates the recrystallization of nanorods and transfigures to form nanoparticles as shown in Fig. 2(f).

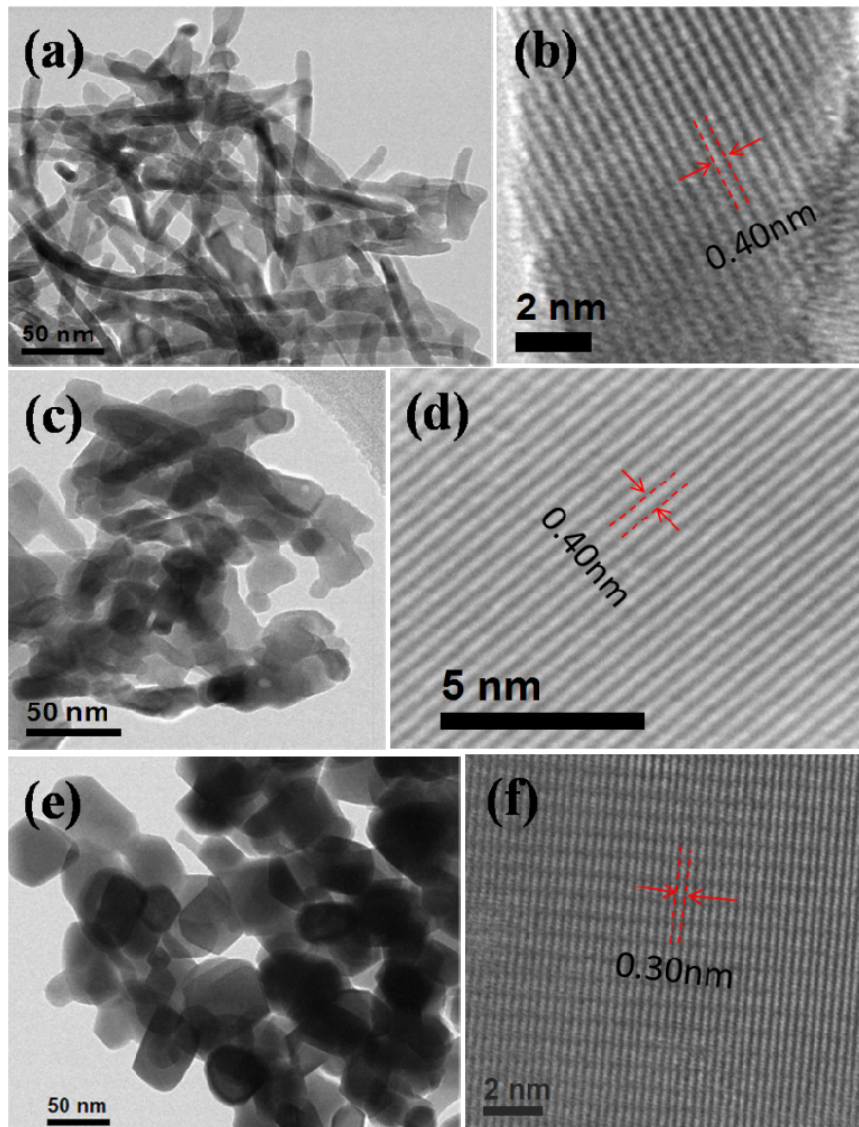


Fig. 2. Eu^{3+} -doped Gd_2O_3 nanostructure TEM photographs of low and high magnification after annealing at (a) and (b) 600°C , (c) and (d) 800°C , and (e) and (f) 1000°C , respectively. (b), (d), and (f) represent the HRTEM images of respective nanostructures.

Representative TEM and SEM images of Eu^{3+} -doped Gd_2O_3 nanotubes are shown in Fig. 3. It can be observed that these nanostructures demonstrate tubular shapes with a length in the range of about 0.7 to 1 μm and a wall thickness of 20 nm. It also reveals that these 1-D nanostructures have open ends, smooth surfaces, and straight morphology, as shown in Figs. 3(a) and 3(b). Figure 3(c) demonstrates the large number of FE-SEM images of uniform

nanotubes. The open end and the associated fine feature, such as uniform size and shape, of these nanotubes are shown in the inset of Fig. 3.

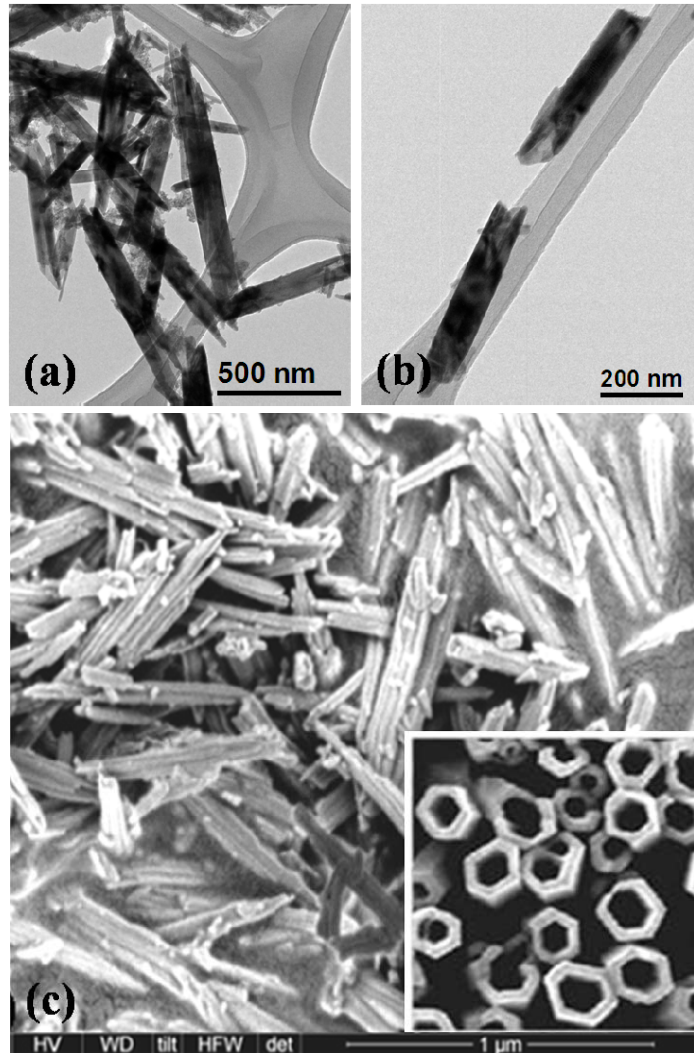


Fig. 3. (a) and (b) show low magnification TEM photographs and (c) FE-SEM images of Eu^{3+} -doped Gd_2O_3 nanotubes after annealing at 600°C . The inset in (c) demonstrates the nanotube feature of Eu^{3+} -doped Gd_2O_3 .

The optical properties and characteristics of nanostructures used in the photonic application are typically determined by their dimensions, sizes, and morphologies. The intensity of photoluminescence of Eu^{3+} -doped Gd_2O_3 nanorods strongly depends on the annealing temperature at which the morphology of nanostructures is modified. Figure 4 shows the emission spectra of Eu^{3+} -doped Gd_2O_3 nanorods excited by 263-nm ultraviolet light. The emission spectra exhibit a strong red emission characteristic of the ${}^5\text{D}_0$ - ${}^7\text{F}_2$ (around 613 nm) transition, which is an electric-dipole-allowed transition. The weaker bands around

581, 589, 593, 600, and 630 nm are ascribed to ${}^5D_0-{}^7F_1$, ${}^5D_1-{}^7F_2$, ${}^5D_0-{}^7F_0$, ${}^5D_0-{}^7F_1$, and ${}^5D_0-{}^7F_2$, respectively [13]. The emission spectra indicate that the Eu^{3+} -doped Gd_2O_3 nanostructures represent strong, narrow, and sharp emission peaks. As shown in this figure, the intensity of emission at 613 nm of nanorods increases when the annealing temperature increases from 600 to 800°C, modifying the morphology of the nanorods as described earlier. However, when the annealing temperature reaches 1000°C, the emission intensity is reduced significantly, even less than the one annealed at 600°C. The performance change of photoluminescence in these nanostructures can be attributed to the morphological transformation of the nanostructures as described below. At low annealing temperature, the Eu^{3+} -doped Gd_2O_3 exhibits nanorod morphology, with more surface area containing a larger number of luminescent centers. However, when the temperature was increased to 1000°C, the nanorods transformed to nanoparticles, which have more surface area altogether. This increase in surface area resulted in more defects, especially surface defects and strains, located on the surface of the nanoparticles. Although high annealing temperature can increase crystal perfection, the defects on the surface of these nanoparticles can overwhelm, causing reduced photoluminescence. This is further supported by the decay curves and is discussed in the later section of this work. To systematically investigate the correlation of morphology and optical characteristics of Eu^{3+} -doped Gd_2O_3 samples, the 5 at.% Eu^{3+} -doped Gd_2O_3 nanorods fabricated at 600°C were compared with 5 at.% Eu^{3+} -doped Gd_2O_3 nanotubes, as shown in Fig. 5. It is obviously revealed that the emission intensity of nanotubes is larger than the nanorods of Eu^{3+} -doped Gd_2O_3 samples, since nanotubes have more surface area than the nanorods. It is worth mentioning that the emission measurements were performed with very similar conditions and volume fractions of the nanomaterials used in this study.

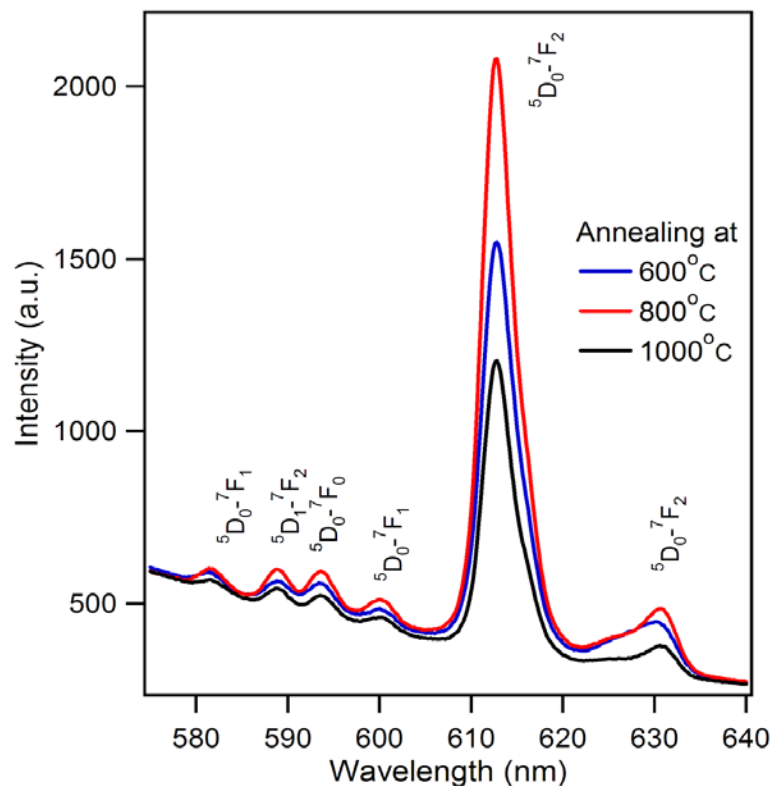


Fig. 4. Photoluminescence spectra of Eu^{3+} -doped Gd_2O_3 nanostructure annealing at 600, 800, and 1000°C, respectively.

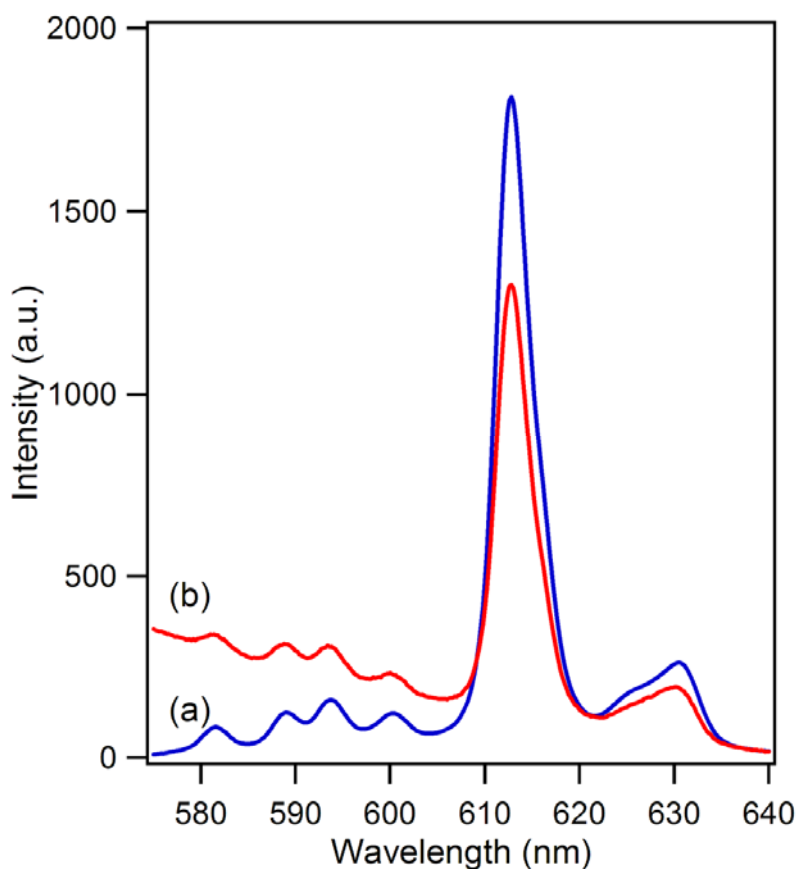


Fig. 5. Photoluminescence spectra comparison of Eu^{3+} -doped Gd_2O_3 (a) nanotubes and (b) nanorods annealed at 600°C , respectively.

Figure 6 shows the photoluminescence decay curves and lifetime of Eu^{3+} (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, 613 nm)-doped Gd_2O_3 nanorods annealed at 600 and 800°C , nanoparticles synthesized at 1000°C , and nanotubes annealed at 600°C , respectively. These four emission decay curves can be fitted to a single exponential function as $I = I_0 \exp(-t/\tau)$. The lifetime of Eu^{3+} ions are analyzed and found to be 1.47, 1.33, 1.59, and 1.31 ms by this fitting. The different lifetimes of Eu^{3+} -doped Gd_2O_3 nanostructures can be explained according to the luminescent efficiency formula as follows: $\eta_R = 1/(1 + \tau_R/\tau_{NR})$, where η_R represents luminescence efficiency, and τ_R and τ_{NR} are the radiative and nonradiative lifetimes, respectively [20]. The efficient luminescence intensity of annealed Eu^{3+} -doped Gd_2O_3 nanostructures have a radiative lifetime that should be much shorter than the nonradiative lifetime. The experimental evidence on Eu -doped rare-earth oxide shows that the fluorescence decay of the Eu^{3+} ${}^5\text{D}_0$ state is due to radiative transition at a low temperature (1.5 K) [21]. However, room temperature fluorescence lifetime decreases only a few percent relative to its value at 1.5 K, elucidating the fact that the room temperature lifetime is due to a radiative relaxation process. In nanoparticles, Eu^{3+} ions are isolated from the surrounding medium where the influence of the surrounding molecules with refractive index [21] and the pressure difference on the Eu^{3+} environment may cause additional effects. The total relaxation rate can be expressed as $1/\tau = \sum \tau_{NR} + \sum A + P_{CR}$ [22], where $\sum A$ is the total radiative emission rate, $\sum \tau_{NR}$ is the nonradiative emission rate, and P_{CR} is the rate of cross-relaxation between adjacent ions. The term $\sum A$ basically depends on the

crystal structure and symmetry, while the term $\sum \tau_{NR}$ basically depends on the host phonon spectrum (cut-off phonon energy). The lifetime may change because of modification in the crystal structure [22], which is unlikely, as no such structural changes were observed. The contribution of concentration-induced cross-relaxation between the ${}^5D_1 \rightarrow {}^5D_0$ and ${}^7F_3 \rightarrow {}^7F_0$ transitions cannot be ruled out. However, the lifetime in these nanostructures is certainly influenced by the morphology of the samples.

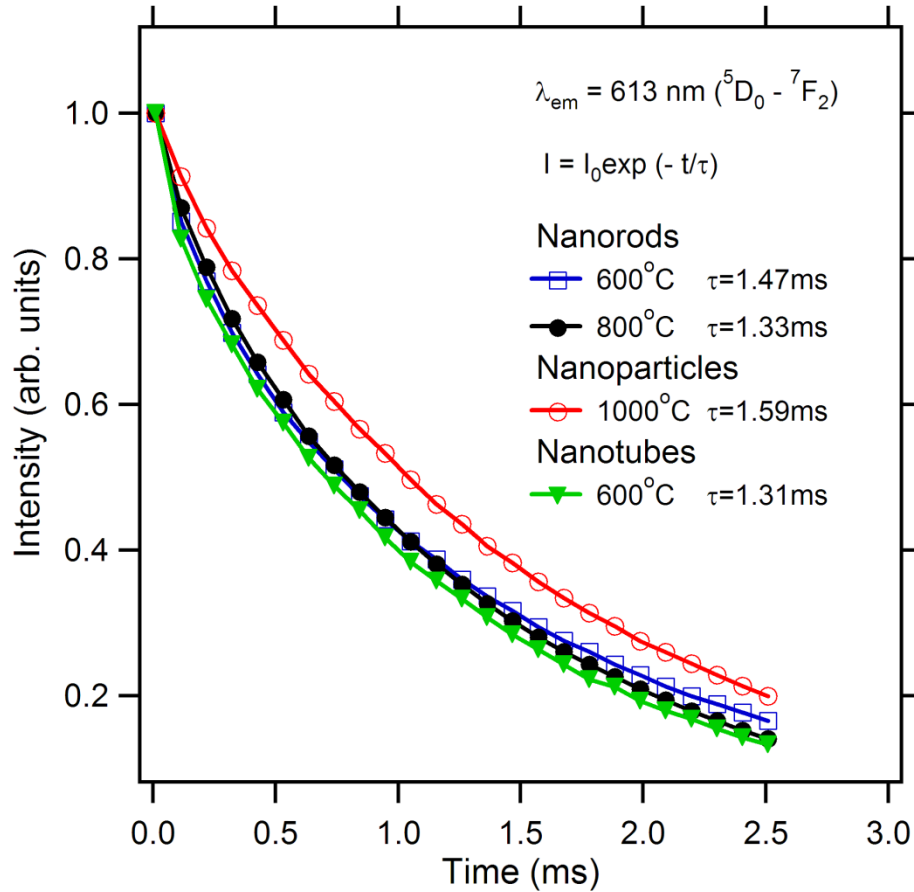


Fig. 6. Photoluminescence decay curves and lifetimes for Eu^{3+} -doped Gd_2O_3 nanotubes fabricated at 600 and 800°C, nanoparticles synthesized at 1000°C, and nanotubes annealed at 600°C, respectively.

4 CONCLUSIONS

In summary, we synthesize large scale zero and one-dimensional Eu^{3+} -doped Gd_2O_3 nanostructures by a simple coprecipitation process, followed by subsequent annealing. This process is very effective and simple, and can be utilized to synthesize some other lanthanide-doped rare-earth oxide nanostructures as a significant extension. The crystal structure, morphology, photoluminescence, and lifetime are characterized by XRD, SEM, TEM, and fluorescence spectrophotometers, respectively. Eu^{3+} -doped Gd_2O_3 nanostructures are highly crystallized after the annealing process. The Eu^{3+} -doped Gd_2O_3 morphology is strongly dependent on annealing temperature and consequently has an influence on the

photoluminescence behavior. The obtained Eu^{3+} -doped Gd_2O_3 nanostructures emit strong red luminescence with a 613-nm wavelength. The dependence of luminescence lifetime on shapes of the nanostructures demonstrates that the 1-D nanostructures have shorter lifetimes with higher emission intensity. Our analysis suggests that the morphological transformation of the nanostructures plays the most important role in the relaxation process, which impacts the overall photoluminescence properties. This increase in surface area results in more defects, mainly due to surface defects and strains in nanoparticles. The defects can reduce photoluminescence irrespective of increase in crystal perfection due to annealing at high temperatures.

Acknowledgments

This work is supported by the National Science Foundation for Research Infrastructure in Science and Education (RISE), grant number HRD-0734846.

References

- [1] K. Zhang, T. Holloway, M. Bahoura, A. K. Pradhan, R. Prabakaran, J. Pradhan, S. Smith, J. C. Hall, G. T. Ramesh, D. R. Sahu, and J.-L. Huang, "Europium doped Gd_2O_3 and FeCo nanoparticles for biomedical application," *Proc. SPIE* **7291**, 729104 (2009) [doi: 10.1117/12.817306].
- [2] C. Chang, F. Kimura, T. Kimura, and H. Wada, "Preparation and characterization of rod-like $\text{Eu}:\text{Gd}_2\text{O}_3$ phosphor through a hydrothermal routine," *Mater. Lett.* **59**, 1037-1041 (2005) [doi:10.1016/j.matlet.2004.10.077].
- [3] S. Li, H. Song, H. Yu, S. Lu, X. Bai, G. Pan, Y. Lei, L. Fan, and T. Wang, "Influence of annealing temperature on photoluminescence characteristics of $\text{Gd}_2\text{O}_3:\text{Eu}/\text{AAO}$ nanowires," *J. Lumin.* **122-123**, 876-878 (2007) [doi:10.1016/j.jlumin.2006.01.314].
- [4] Y. Mao, J. Y. Huang, R. Ostroumov, K. L. Wang, and J. P. Chang, "Synthesis and luminescence properties of Erbium-doped Y_2O_3 nanotubes," *J. Phys. Chem. C* **112**, 2278-2285 (2008) [doi: 10.1021/jp0773738].
- [5] Y. He, Y. Tian, and Y. Zhu, "Large-scale-synthesis of luminescent $\text{Y}_2\text{O}_3:\text{Eu}$ nanobelts," *Chem. Lett.* **32**, 862-863 (2003) [doi:10.1246/cl.2003.862].
- [6] L. Liu, E. Ma, R. Li, G. Liu, and X. Chen, "Effects of phonon confinement on the luminescence dynamics of Eu^{3+} in Gd_2O_3 nanotubes," *Nanotechnol.* **18**, 015403-015407 (2007) [doi: 10.1088/0957-4484/18/1/015403].
- [7] M. Nichkova, D. Dosev, R. Perron, S. J. Gee, B. D. Hammock, and I. M. Kennedy, " Eu^{3+} -doped Gd_2O_3 nanoparticles as reporters for optical detection and visualization of antibodies patterned by microcontact printing," *Anal. Bioanal. Chem.* **384**, 631-637 (2006) [doi:10.1007/s00216-005-0246-8].
- [8] H. Wang, M. Uehara, H. Nakamura, M. Miyazaki, and H. Maeda, "Synthesis of well-dispersed $\text{Y}_2\text{O}_3:\text{Eu}$ nanocrystals and self-assembled nanodisks using a simple non-hydrolytic route," *Adv. Mater.* **17**, 2506-2509 (2005) [doi: 10.1002/adma.200500503].
- [9] S. Y. Seo, K. S. Sohn, H. D. Park, and S. Lee, "Optimization of Gd_2O_3 -based red phosphors using combinatorial chemistry method," *J. Electrochem. Soc.* **149**, H12-H18 (2002) [doi:10.1149/1.1425800].
- [10] R. M. Petoral, Jr., F. Söderlind, A. Klasson, A. Suska, M. A. Fortin, N. Abrikosova, L. Selegård, P. Käll, M. Engström, and K. Uvdal, "Synthesis and characterization of Tb^{3+} -doped Gd_2O_3 nanocrystals: a bifunctional material with combined fluorescent labeling and MRI contrast agent properties," *J. Phys. Chem. C* **113**, 6913-6920 (2009) [doi:10.1021/jp808708m].

- [11] J.-L. Bridot, A.-C. Faure, S. Laurent, C. Rivière, C. Billotey, B. Hiba, M. Janier, V. Jossierand, J.-L. Coll, L. Vander Elst, R. Muller, S. Roux, P. Perriat, and O. Tillement, "Hybrid gadolinium oxide nanoparticles: multimodal contrast agent for in vivo imaging," *J. Am. Chem. Soc.* **129**, 5076-5084 (2007) [doi:10.1021/ja068356j].
- [12] M. Nichkova, D. Dosev, S. J. Gee, B. D. Hammock, and I. M. Kennedy, "Microarray immunoassay for phenoxybenzoic acid using polymer encapsulated Eu:Gd₂O₃ nanoparticles as fluorescent labels," *Anal. Chem.* **77**, 6864-6873 (2005) [doi:10.1021/ac050826p].
- [13] G. X. Liu, G. Y. Hong, X. T. Dong, and J. X. Wang, "Preparation and characterization of Gd₂O₃:Eu³⁺ luminescence nanotubes," *J. Alloys Compd.* **466**, 512-516 (2008) [doi:10.1016/j.jallcom.2007.11.108].
- [14] X. L. Xu and S. A. Asher, "Synthesis and utilization of monodisperse hollow polymeric particles in photonic crystals," *J. Am. Chem. Soc.* **126**, 7940-7945 (2004) [doi: 10.1021/ja049453k].
- [15] X. W. Lou, Y. Wong, C. Yuan, J. Y. Lee, and L. A. Archer, "Template-free synthesis of SnO₂ hollow nanostructures with high lithium storage capacity," *Adv. Mater.* **18**, 2325-2329 (2006) [doi: 10.1002/adma.200600733].
- [16] W. Wei, G. H. Ma, G. Hu, D. Yu, T. Mcleish, Z. G. Su, and Z. Y. Shen, "Preparation of hierarchical hollow CaCO₃ particles and the application as anticancer drug carrier," *J. Am. Chem. Soc.* **130**, 15808-15810 (2008) [doi: 10.1021/ja8039585].
- [17] Y. B. Mao, T. Tran, X. Guo, J. Y. Huang, C. K. Shih, K. L. Wang, and J. P. Chang, "Luminescence of nanocrystalline erbium-doped yttria," *Adv. Funct. Mater.* **19**, 748-754 (2009) [doi:10.1002/adfm.200800880].
- [18] J. Yang, C. X. Li, Z. Y. Cheng, X. M. Zhang, Z. W. Quan, C. M. Zhang, and J. Lin, "Size-tailored synthesis and luminescent properties of one-dimensional Gd₂O₃:Eu nanorods and microrods," *J. Phys. Chem. C* **111**, 18148-18154 (2007) [doi: 10.1021/jp0767112].
- [19] G. Jia, K. Liu, Y. Zheng, Y. Song, M. Yang, and H. P. You, "Highly uniform Gd(OH)₃ and Gd₂O₃:Eu³⁺ nanotubes: facile synthesis and luminescence properties," *J. Phys. Chem. C* **113**, 6050-6055 (2009) [doi:10.1021/jp9002164].
- [20] M. Fox, *Optical Properties of Solids*, Oxford Univ., New York (2001)
- [21] R. S. Meltzer, S. P. Feofilov, B. Tissue, and H. B. Yuan, "Dependence of fluorescence lifetimes of Y₂O₃:Eu³⁺ nanoparticles on the surrounding medium," *Phys. Rev. B* **60**, R14012-R14015 (1999) [doi: 10.1103/PhysRevB.60.R14012].
- [22] P. Ghosh and A. Patra, "Role of surface coating in ZrO₂/Eu³⁺ nanocrystals," *Langmuir* **22**, 6321-6327 (2006) [doi:10.1021/la0604883].