Possible size control and emission characteristics of Eu³⁺-doped Y₂O₃ nanoparticles synthesized by surfactant-assembly

Yukihiko Akita,¹ Takashi Harada,¹ Ryo Sasai,² Koji Tomita,³ and Katsura Nishiyama*¹

¹Faculty of Education, Shimane University, Matsue 690–8504, Japan

²Interdisciplinary Graduate School of Science and Engineering, Shimane University, Matsue 690–8504, Japan

³Department of Chemistry, School of Science, Tokai University, Hiratsuka 259–1292, Japan

*Corresponding author (KN):

E-mail: katsura_nishiyama@edu.shimane-u.ac.jp

FAX: +81–852–32–9832

Abstract

Yttrium oxide nanoparticles doped with 2.0wt% Eu($\text{Eu}@\text{Y}_2\text{O}_3$) were synthesized via the surfactant-assembly method. The average diameter of $\text{Eu}@\text{Y}_2\text{O}_3$ (d_{av}) depends on the alkyl chain number (N) of the sodium alkyl sulfates employed as surfactants. Using surfactants with $N = 8, 10$, and 12 , $\text{Eu}@\text{Y}_2\text{O}_3$ with $d_{\text{av}} = 35, 200$, and 500 nm, respectively were obtained. Such changes in d_{av} are ascribed to the difference in the micelle aggregation numbers, supporting the use of rare-earth ions in the assembly. The $\text{Eu}@\text{Y}_2\text{O}_3$ particles synthesized presently emitted through Eu^{3+} transitions under UV excitation of Y_2O_3 , making them applicable to nanoemitters.

Keywords

nanoparticles, rare-earth emission, micelle template, nanoemitters

1. Introduction

Nanoparticles have attracted considerable attention because of their potential for application as emitting materials, catalysts, and emulsifying agents for cosmetics. With a focus on the emitting function of nanoparticles, quantum dots [1-4] and ZnO nanoparticles [5, 6] have been extensively studied so far. Quantum dots are shown to have prominent emission quantum yield (Φ_{em}) of over 80% when their surface is modified by organic materials [1]. Conventional quantum dots, however, usually comprise toxic materials such as Cd, Te, or Se, which can be a major disadvantage if they are employed for edible agricultural crops. An alternative material for emitting nanoparticles can use emitting lanthanoid ions ($Ln^{3+} = Eu^{3+}$ or Tb^{3+} , for instance) with typical 4f–4f transitions. Notably, the apparent cytotoxicity of lanthanoid materials has not been reported [7, 8]. Another advantage of Ln^{3+} emitters is that their bandwidth in the emission spectra is narrow (45 nm^{-1} at full width of half maximum (fwhm) for the $Eu^{3+} D_0 \rightarrow {}^5F_2$ transition, for example [9]) than those of quantum dots and ZnO particles (ca. 3,000–7,000 nm^{-1} , depending on the environment [3, 5]). When nanoparticles are employed in biomarkers, this feature can be very helpful for distinguishing between their signals and the broader ones originating from biomolecules.

In line with such a strategy, we recently synthesized Ln^{3+} -doped Y_2O_3 particles, which are hereafter denoted as “ $Ln@Y_2O_3$ ” [9]. When the base material, Y_2O_3 , was excited, a characteristic emission originating from Ln^{3+} was observed as a result of energy transfer. In that study, to conduct visible color-tuning, Eu^{3+} , Tb^{3+} , Dy^{3+} , and Er^{3+} were chosen as the lanthanoids for doping, and Eu^{3+} – Tb^{3+} co-doped particles were also prepared. $Ln@Y_2O_3$ was synthesized via surfactant-assembly followed by calcination, using sodium dodecyl sulfate as an anionic surfactant. Employing this protocol, an average diameter (d_{av}) of 500 nm was obtained for $Ln@Y_2O_3$ regardless of the dopant type [9]. For further application to biomarkers, however, d_{av} should be reduced down to tens of nanometers to achieve efficient spatial resolution.

Therefore, in the present study, we have been able to obtain particles with $d_{av} = 35$ nm for

Eu@Y₂O₃ through appropriate selection of the surfactant, choosing $\text{Ln}^{3+} = \text{Eu}^{3+}$. Specifically, d_{av} control was achieved by varying the micelle size formed by the surfactant. For this purpose, sodium alkyl sulfates with different alkyl-chain numbers, viz. octyl, decyl, and dodecyl, whose chemical structures are drawn in Figure 1, were used. The use of such a procedure makes it possible to discuss the detailed formation mechanism of the nanoparticles. The photochemical properties of the as-prepared Eu@Y₂O₃ nanoparticles synthesized in this study are also discussed.

Figure 1. Chemical structures of the sodium alkyl sulfates, “SNS”, with different alkyl chain numbers N .

2. Materials and methods

2.1 Materials

The synthetic routine for $\text{Ln@Y}_2\text{O}_3$ with $d_{\text{av}} = 500$ nm using surfactant-assembly in aqueous solution is reported in our previous publication[9]. A surfactant possessing a chain of length N is abbreviated as “SNS”. In this study, d_{av} control was achieved by choosing a suitable surfactant SNS ($N = 8, 10$, and 12), with technical upgrade to the calcination process. All the reagents used for synthesis, except S8S and S10S, were purchased from Wako; S8S and S10S were supplied by Alfa Aesar.

$\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ with $n \approx 5$ and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as received. The notation of hydrated water is henceforth omitted for brevity. $\text{Y}(\text{NO}_3)_3$ was dissolved in water, and 2.0 wt% $\text{Eu}(\text{NO}_3)_3$ was added as a dopant. An SNS surfactant was added to the aqueous solution, and the system was stirred at 40 °C. The SNS concentration was adjusted to 10 times the critical micelle concentration (CMC), where the CMCs for S8S, S10S, and S12S are 134, 30.0, and 8.14×10^{-3} mol dm⁻³, respectively[10].

Urea hydrolysis was used to keep the solution at pH of 9.0 ± 0.2 . With the progress of hydrolysis, white precipitates were obtained which were collected by filtration and dried in an oven at 50°C for 3 days to remove water. All precipitates, except that obtained with S12S, were calcined at 800°C for 2 h. The S12S precipitate was subjected to a pre-calcination process at 200°C for 2 h and at 500°C for 6 h, as previously described[9]. It is emphasized that pre-calcination hardly affects the properties of the nanoparticle products. We henceforth denote the $\text{Eu@Y}_2\text{O}_3$ nanoparticle synthesized with the surfactant SNS as “ $\text{Eu@Y}_2\text{O}_3\text{-}N$ ”, for the sake of simplicity.

2.2 Characterization

Emission and excitation spectra with correction were obtained with an FP-6500 or FP-8500 spectrofluorometer (Jasco). An ILF-835 integrating sphere (Jasco) attached to the FP-8500 spectrofluorometer was used to measure Φ_{em} . X-ray diffraction (XRD) measurements were carried out using a powdery X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation (30 kV, 15 mA; MiniFlex II, Rigaku). Field-emission scanning electron microscopy (FE-SEM) was conducted with a JEOL JSM-7001FA microscope.

3. Results and discussion

3.1 Structures of $\text{Eu@Y}_2\text{O}_3$

Figure 2 shows the morphologies, observed by FE-SEM, of $\text{Eu@Y}_2\text{O}_3\text{-}8$, $\text{-}10$, and $\text{-}12$ nanoparticles prepared with surfactants having different N values. The histograms of particle diameter (d) distribution, from which the d_{av} values are calculated, are presented in Figures 2a'–2c'. About 80% of d is clustered around d_{av} ; in detail, 35 ± 10 nm for $\text{Eu@Y}_2\text{O}_3\text{-}8$, 200 ± 100 nm for $\text{Eu@Y}_2\text{O}_3\text{-}10$, and 500 ± 200 nm for $\text{Eu@Y}_2\text{O}_3\text{-}12$ nanoparticles. Figure 3 correlates N and d_{av} for the $\text{Eu@Y}_2\text{O}_3$ nanoparticles, and a positive correlation is observed. The shorter the alkyl chain in the surfactant used, the smaller will be the observed d_{av} of the synthesized $\text{Eu@Y}_2\text{O}_3$ nanoparticles.

As a control experiment, a synthesis was conducted using *no* surfactant, and the product morphology is shown in Figure 2d. Rather indefinite structures were obtained. SNS is thus proven to serve as an efficient template for nanoparticle synthesis.

Figure 2. FE-SEM images of Eu@Y₂O₃- N nanoparticles depending on the alkyl chain number of the surfactant, where panels (a), (b), and (c) correspond to $N = 8, 10$, and 12 , respectively. Panel (d) shows control data for the case where no surfactant was used. For (a)–(c), the histograms of particle diameter d are given in panels (a')–(c'). The frequency is normalized so as to be 100 at the mode, where the particle numbers counted to obtain the histograms are 140 for (a') and (b'), and 125 for (c'). The data for (c') are taken from our previous study [9].

Figure 3. Correlation between the alkyl chain numbers N of the surfactants and the average diameters d_{av} of Eu@Y₂O₃- N nanoparticles synthesized accordingly. The error bars indicate standard deviations from Figures 2(a')–(c'). Dotted lines are for a guide to eyes.

XRD measurements were conducted for Eu@Y₂O₃-8, -10, and -12 nanoparticles, and for the control sample prepared without surfactants. As shown in Figure 4, the XRD patterns of Eu@Y₂O₃-10 and Eu@Y₂O₃-12 nanoparticles are rather similar. In Figure 4, the peaks labeled with bullets (•) have possible similarity to those of the Y₂O₃ cubic structure [11]. For Eu@Y₂O₃-12, we previously reported that the nitrate Y(NO₃)₃ used as the starting material undergoes oxidation during calcination, and Eu³⁺ doping, which is 2.0 wt% in preparation, hardly affects the Y₂O₃ structure [9]. Such features are also likely to be observed for Eu@Y₂O₃-10. In addition, the XRD pattern of the control material prepared *without* surfactants is also somewhat similar to the Y₂O₃ cubic structure [11].

For Eu@Y₂O₃-8 nanoparticles, patterns similar to those observed for Eu@Y₂O₃-10 and -12 particles were found to be dominant. In addition, other peaks marked with asterisks (*) are also detected, which correspond to those of the monoclinic Y₂O₃ system based on the literature ([11] and PDF #44-0399). Earlier studies reported that the Y₂O₃ crystalline structure depends on the dimensions of the particles; the cubic structure is stable for bulk Y₂O₃ materials, whereas the monoclinic phase appears in particles smaller than 10 nm [11, 12]. In the present Eu@Y₂O₃-8 particles, the distribution of *d* extends down to 10 nm (See Figure 2a'). The Eu@Y₂O₃-8 component can thus be ascribed to a mixture of cubic and monoclinic Y₂O₃ structures.

In the following, we discuss the Y₂O₃ crystalline structure under the Eu³⁺ dopant. It is a usual assumption that Y³⁺ in the Y₂O₃ structure is replaced by a dopant Ln³⁺. Cubic Y₂O₃ has two possible hexacoordinated sites where replacement with Eu³⁺ can occur [13]. To our knowledge, reliable crystallographic information files (CIF) for monoclinic Y₂O₃, based on which crystal structure images can be drawn, are not available. Hence, we use monoclinic Sm₂O₃ data as a possible alternative; the adequacy of this choice is detailed in the Supplementary Data. Supplementary Figures S1–S3 represent a bulk cubic Y₂O₃, cubic Eu₂O₃, and monoclinic Sm₂O₃ crystals, respectively, drawn based on the CIF. Regarding the O²⁻ coordination around the Sm³⁺ ion in the monoclinic Sm₂O₃ structure, both hexa- and heptacoordinated structures are found. We conjecture that monoclinic Y₂O₃

might have a similar structure. Keeping such differences in the Eu^{3+} environment doped in the Y_2O_3 structures in mind, we then consider emission properties of the $\text{Eu@Y}_2\text{O}_3$ nanoparticles in the next subsection.

Figure 4. X-ray diffraction patterns of $\text{Eu@Y}_2\text{O}_3$ -12, -10, and -8 nanoparticles (from top to bottom), and the control sample prepared without surfactants (“no surfactant”). The peaks with bullets (•) and asterisks (*) indicate signals with possible similarity to those of the cubic [14] and monoclinic [11] Y_2O_3 crystal structures, respectively.

3.2 Emission spectra and quantum yields of $\text{Eu@Y}_2\text{O}_3$

Figure 5a shows the emission spectra of the different $\text{Eu@Y}_2\text{O}_3$ nanoparticles. The excitation wavelength (λ_{ex}) was 254 nm, which corresponds to a Y_2O_3 absorption band (see Figure 5b). The emission spectra of $\text{Eu@Y}_2\text{O}_3$ -12 and -10 nanoparticles are similar to each other. The spectral similarity for these particles corresponds to their similar XRD patterns. The peaks in the spectra are attributed to the $\text{Eu}^{3+5}\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions, where $J = 0, \dots, 3$ stand for the total angular momentum [15, 16]. For the $\text{Eu}^{3+5}\text{D}_0 \rightarrow {}^7\text{F}_0$ transition appearing around 580–582 nm, two peaks are observed in all the spectra. Notably, the double-structure for the $\text{Eu@Y}_2\text{O}_3$ -8 spectrum is somewhat subtle but still recognizable. We are aware that the split appearing in emission spectra is because of the removal of degeneracy [17, 18]. However, the ${}^7\text{F}_0$ state is a singlet and has no degeneracy. In theory, the $\text{Eu}^{3+5}\text{D}_0 \rightarrow {}^7\text{F}_0$ transition, which is a transition between the $J = 0$ states, should show a single

emission band[17]. This is because both the initial and final states exhibit no Stark splitting. Therefore, the two-fold structures detected for the $^5D_0 \rightarrow ^7F_0$ transitions of Eu@Y₂O₃-12 and -10 suggest that the environment around Eu³⁺ ions in the cubic Y₂O₃ structure cannot be single; or Eu³⁺ may experience more than one environments. If Eu³⁺ were placed in a single environment in the Y₂O₃ structure, the emission from such Eu³⁺ should give a unique transition. In reality, Supplementary Figure S1 shows that two kinds of Y³⁺ sites, which can be replaced by Eu³⁺ in the present nanoparticles, are available in the cubic Y₂O₃ structure.

For $^5D_0 \rightarrow ^7F_1$ transitions in the 587–600 nm region, three peaks, corresponding to the number $2J + 1$ ($J = 1$), are clearly recognized in the spectra for Eu@Y₂O₃-12 and Eu@Y₂O₃-10 nanoparticles. For Eu@Y₂O₃-8 particles, however, three or more peaks appear in that region.

As the XRD patterns for the Eu@Y₂O₃-8 nanoparticles indicate a mixed cubic and monoclinic structure, the emission peaks may be also due to a combination of factors originating from these structures. In a similar manner, additional structures appear also in other regions of the Eu@Y₂O₃-8 spectrum, which are not detected in the spectra of Eu@Y₂O₃-12 and Eu@Y₂O₃-10. In the 611–630 nm region with $^5D_0 \rightarrow ^7F_2$ transitions, three peaks of five, corresponding theoretically to $2J + 1 = 5$ with $J = 2$ [17], are apparent for the Eu@Y₂O₃-12 and Eu@Y₂O₃-10 nanoparticle spectra. See the transitions labeled with “2” in Figure 5a. On the other hand, obviously different structures are detected for Eu@Y₂O₃-8 nanoparticles. In particular, much more complicated structures were detected in the 613–618 nm region. Such differences in the emission structure for Eu@Y₂O₃-8 than the others are also recognized in the 593–600 nm region (the $J = 1$ transition). Such complicated structures detected for the Eu@Y₂O₃-8 transitions suggest that the Eu³⁺ environment replaced in the Y₂O₃ structure should be essentially different from that for Eu@Y₂O₃-12 and Eu@Y₂O₃-10. As the cubic Y₂O₃ structure for Eu@Y₂O₃-12 and Eu@Y₂O₃-10 has two possible Y³⁺ sites (Supplementary Figure S1), Eu³⁺ in Eu@Y₂O₃-8 nanoparticles would be in more than two environments. Such aspects are in agreement with the XRD results, where the mixture of cubic and monoclinic structures is suggested for Eu@Y₂O₃-8 and the simple cubic structure is for Eu@Y₂O₃-12 and Eu@Y₂O₃-10.

Figure 5 (a) Emission spectra of Eu@Y₂O₃-12, -10, and -8 nanoparticles (from top to bottom), detected with $\lambda_{\text{ex}} = 254$ nm. The numbers $J = 0, \dots, 3$ drawn in the panel represent the possible assignments of the Eu³⁺⁵D₀→⁷F_J transitions. Assignments are based on the literature [15, 16]. Asterisks (*) given in the ⁵D₀→⁷F₀ transitions show the multiple split in the spectra. (b) Excitation spectra measured with $\lambda_{\text{mon}} = 611$ nm.

Table 1. Summary of emission quantum yields $\Phi_{\text{em}}^{(1)}$.

nanoparticles	$\Phi_{\text{em}}^{(2)}$
Eu@Y ₂ O ₃ -12	0.27 ± 0.02
Eu@Y ₂ O ₃ -10	0.28 ± 0.02
Eu@Y ₂ O ₃ -8	0.21 ± 0.02

⁽¹⁾ $\lambda_{\text{ex}} = 270$ nm for Eu@Y₂O₃-12, and 254 nm for Eu@Y₂O₃-10 and Eu@Y₂O₃-8 particles, where Φ_{em} was proved to be nearly independent of λ_{ex} if the broad Y₂O₃ absorption band (≤ 275 nm) was excited.

⁽²⁾Analyzed three times or more; the mean values and deviations are presented.

The excitation spectra of different samples are shown in Figure 5b. The monitoring wavelength was set at $\lambda_{\text{mon}} = 611$ nm in accordance with the emission maxima (Eu³⁺⁵D₀→⁷F₂ transition). The broad bands observed below 275 nm are assigned to Y₂O₃ absorption [15, 16]. Eu@Y₂O₃-8 nanoparticles exhibit a rather different spectrum compared to the others. In an analogous manner, Φ_{em} for the Eu@Y₂O₃-8 particle is somewhat smaller than for Eu@Y₂O₃-12 and Eu@Y₂O₃-10 particles (Table 1), whose Φ_{em} values are very similar.

3.3 Possible mechanisms of Ln@Y₂O₃ formation

The results obtained so far exhibit that Eu@Y₂O₃ particle size depends on the surfactants used during synthesis. The correlation between N and d_{av} , which is shown in Figure 3, seems to be rather intuitive. Figure 6 provides a graphical explanation for the formation of Eu@Y₂O₃ nanoparticles under surfactant-assembly, depending on the alkyl chain number N . With the increase in N , the aggregation number of the surfactant (n_{agg}) increases, with $n_{agg} = 41, 49$, and 76 for S8S, S10S, and S12S, respectively [10]. Such an increase in n_{agg} may make more “slots” available for interaction with Y³⁺ or Ln³⁺. After calcination, a product Ln@Y₂O₃ with a large d_{av} can be obtained.

It is noted that d_{av} decreased in a more dramatic manner (500–35 nm) than the decrease of n_{agg} . Further discussion should be made; the n_{agg} values given here [10] assume that neat water is used as the solvent, and addition of salts should increase n_{agg} . It is known that even in this case, a monotonic increase in n_{agg} should be observed with the increase in N [10]. Furthermore, in the present syntheses in the aqueous solution, the SNS concentration was adjusted to 10 times CMC (See Subsection 2.1). In our preliminary experiments using S12S and S8S, the SNS concentration was varied for 1.1, 2, and 10 times CMC. It is found that the SNS concentration scarcely affects d_{av} of the Eu@Y₂O₃ nanoparticles obtained as calcined products. We also noticed that the aqueous solutions using surfactants with 1.1, 2, and 10 times CMC stayed in their solution phases with usual viscosity. If the surfactant experienced the phase transition to form high-order aggregates such as lamellar structures, the system should have very high viscosity [19]. With these results, we believe that the diagram in Figure 6 can somewhat plausibly explain the nanoparticle formation process, at least at a qualitative level.

At the moment, we do not know the exact reason for the peculiar behavior of Eu@Y₂O₃-8 in the crystalline structure and emission properties. A possible explanation is the difference in the specific surface areas (σ); Eu@Y₂O₃-8 nanoparticles could have a σ value that is 1.5 times that of Eu@Y₂O₃-12 particles. Here we used a simple assumption that σ for spherical materials is inversely proportional to the radius, provided their density is the same. The differences in σ may alter the calcination process, which could give rise to the crystalline structures for the product materials. It is

also noted here that quantitative analyses of the differences in the excitation spectra and Φ_{em} for $\text{Eu}@\text{Y}_2\text{O}_3$ -8 are rather difficult. From an experimental aspect, for powdery and nanoscale samples as the present $\text{Eu}@\text{Y}_2\text{O}_3$ - N , photoabsorption in the particle surface may be considered to draw an entire scheme for their photoexcited states [20]. Further studies using time-resolved spectroscopy would provide more detailed insights on the specific behavior of $\text{Eu}@\text{Y}_2\text{O}_3$ -8.

Figure 6. A schematic diagram of $\text{Ln}@\text{Y}_2\text{O}_3$ formation depending on the alkyl chain number of the surfactants N . A large N leads to large $\text{Ln}@\text{Y}_2\text{O}_3$ particles.

4. Summary and future perspective

In this study, we synthesized Y_2O_3 nanoparticles doped with lanthanoid ions Eu^{3+} , which are denoted as $\text{Eu}@\text{Y}_2\text{O}_3$, via surfactant-assembly. Sodium alkyl sulfates, SNS, where N is the alkyl chain number, have been used as a template in the aqueous phase. Rare-earth nitrates were used as starting materials, and were converted to oxides after calcination. The obtained $\text{Eu}@\text{Y}_2\text{O}_3$ particles showed average diameters (d_{av}) of 500, 200, and 35 nm for particles synthesized with surfactants with $N = 8, 10$, and 12, respectively. The N dependence of d_{av} can be explained by the formation mechanism of $\text{Eu}@\text{Y}_2\text{O}_3$; rare-earth ions supplied from the starting materials may interact with the hydrophilic group of the surfactants, which are located in the exterior of the assembly. A micelle formed with an SNS having a small N gives rise to a small aggregation number for the surfactant, which leads to a small d_{av} value. A more quantitative discussion should be carried out for detailed analysis of the $\text{Eu}@\text{Y}_2\text{O}_3$ formation process. The crude model proposed here may clarify the essential features of surfactant-assembly, at least at a qualitative level.

The structures and photochemical properties of as-prepared $\text{Eu}@\text{Y}_2\text{O}_3$ have also been analyzed. The properties of $\text{Eu}@\text{Y}_2\text{O}_3$ -12 and $\text{Eu}@\text{Y}_2\text{O}_3$ -10, prepared with S12S and S10S, are rather similar, and their XRD patterns have high similarity to that of the cubic Y_2O_3 structure. However, the $\text{Eu}@\text{Y}_2\text{O}_3$ -8 (prepared with S8S) structure is attributed to a mixture of cubic and monoclinic Y_2O_3 . With UV excitation in the Y_2O_3 matrix, characteristic emission spectra originating from Eu^{3+} were observed as a result of energy transfer from the matrix to Eu^{3+} . $\text{Eu}@\text{Y}_2\text{O}_3$ -12 and $\text{Eu}@\text{Y}_2\text{O}_3$ -10 show very similar emission spectra, whereas the spectrum for $\text{Eu}@\text{Y}_2\text{O}_3$ -8 shows somewhat different characters. Such a deviation can be also due to the difference in the Y_2O_3 crystalline structure.

The emission quantum yields for $\text{Eu}@\text{Y}_2\text{O}_3$ - N are 21–28% ($N = 8$ –12). Even with the Φ_{em} obtained for the present materials, or with further improvement in Φ_{em} if needed, $\text{Eu}@\text{Y}_2\text{O}_3$ may be applicable for nanoscale emitters, such as emitting biomarkers. As a dopant, Ln^{3+} could be replaced with Tb^{3+} , Dy^{3+} , and Er^{3+} to obtain another emission colors, as we have reported for

Eu@Y₂O₃-12 in our previous study [9]. Even co-dopants, such as Eu³⁺ and Tb³⁺, can be used to realize visible color-tuning in emission[9]. For practical use of Ln@Y₂O₃ as nanoscale emitters, further elaborate studies on the emission mechanism are indeed desirable.

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Graphical abstract