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Morphology of Rare-earth (Y, Sm) Nanostructures Synthesized by the Surfactant-assembled Method

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Nanostructures such as nanorods or nanowires in various morphologies have been fabricated from yttrium oxide, nitrate, and chloride, along with samarium oxide relying on a template organized from self-assembled surfactants. It is found that the different interaction mechanism between the template and rare-earth material gives rise to the various morphologies in the nm–µm domain, under observation by scanning electronic microscopy.

Development of 1D-nanostructures (NSs), likewise nanotubes (NTs), nanorods (NRs), and nanowires, has attracted attention because of their useful chemical and physical properties which are inherently different from the bulk state. Besides the carbon-frame structures commonly used for NTs, rare-earth elements have also been employed recently due to their potential applications for luminescent, electronic, or magnetic devices. Yada et al. have synthesized rare-earth (Er, Tm, Yb, and Lu) oxide NTs by applying organic surfactant-assembly where sodium dodecyl sulfate (SDS) was used.[1] On the other hand, Tang et al. have composed Y_2O_3 and $Y(OH)_3$ NTs by means of hydrothermal method.[2] Targeting the development of luminescent modules, europium-doped NTs (Y_2O_3:Eu) have been presented by surfactant-assembly[3] and hydrothermal[4] methods. The hydrothermal method has also provided nanoparticles, nanoflakes, and NRs starting from Y_2O_3.[5]

Here we summarize synthetic methodologies for rare-earth NSs developed previously. In the case of the surfactant-assembled method,[2,3] organic surfactants form micelles in an aqueous phase under self-assembly. Micelles serve as a template involving rare-earth raw materials. Final NSs are produced after calcination, removing organic ingredients. Meanwhile, with conventional hydrothermal methods[2,4,5] raw rare-earth materials are first treated as sol–gel. Then the sample is processed under adequate temperature and pressure with an autoclave. Within this routine, a mechanism accounting for the NT formation has been presented, which is called a "roll-up" model.[2]

Despite the series of elaborated works regarding Y_2O_3 and $Y(OH)_3$ NTs,[2] Y_2O_3:Eu NTs,[3,4] and rare-earth oxide NTs having a frame other than yttrium,[1] few reports have been presented for YCl_3 and $Y(NO_3)_3$, or rare-earth oxides except those produced elsewhere.[1] In this paper we have, therefore, studied the synthetic methods and morphologies of NSs for rare-earth compounds, which have been ambiguous, by means of surfactant-assembly method in association with homogeneous precipitation.

In the present series of experiments, Y_2O_3 (Wako, 99.99%), $Y(NO_3)_3 \cdot nH_2O$ (with $n \approx 5$) (Wako, 99.9%), $YCl_3 \cdot 6H_2O$ (Wako, 99.9%), and Sm_2O_3 (Kanto, 99.95%) were used as received. Note that we hereafter omit the expressions of hydrates, for the sake of brevity, for nitrate and chloride. While an aqueous solution of SDS was kept at 40 °C, a rare-earth starting material was added until saturation, without relying on acid pre-solutions. The concentration of the SDS solution was adjusted to $0.09\,\mathrm{mol\,dm^{-3}}$. Urea was supplied bit by bit, so as to maintain pH of the solution just around 9.0 ± 0.2 and the designated temperature (40 °C) while stirred. The hydrolysis of urea in the solution produced homogeneously needle-like precipitates with the length of a few centimeters, associated with the self-assembly of SDS. The precipitates were filtered and washed with water and then dried in air to remove water. The separated material was sintered in a furnace at 500 °C for 3 h referring to the literature.[3] Once after cooling to room temperature, the material was annealed at 800 °C for 2 h to remove organic substances.

Figure 1 illustrates morphologies of the materials produced in the present work observed by field emission scanning electronic microscopy (FE-SEM) (JEOL JSM-7001FA or Hitachi S-4300). For the sample synthesized from Y_2O_3 (Figure 1a), rod-like structures are obtained with the typical length of 5–10 µm. The diameter has rather broader distribution between 0.2–1 µm; however, the majority is grouped around 0.5 µm. On the other hand, $Y(NO_3)_3$ NS (Figure 1b) has totally

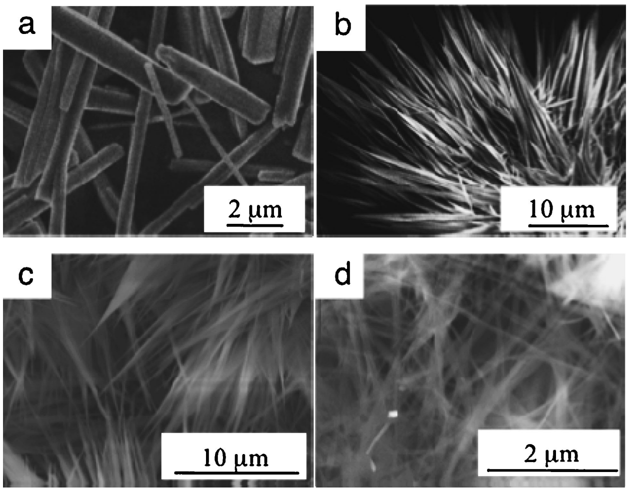

Figure 1. FE-SEM images of nm–µm structures with rare-earth elements synthesized in this work. The starting material is (a) Y_2O_3, (b) $Y(NO_3)_3$, (c) YCl_3, and (d) Sm_2O_3, respectively.

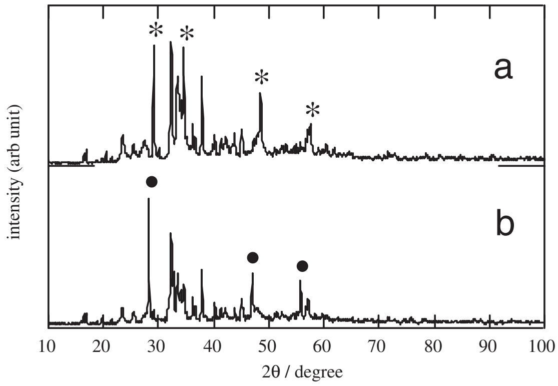

Figure 2. X-ray diffraction patterns obtained for the materials synthesized from (a) $Y(NO_3)_3$ and (b) Sm_2O_3, respectively. The asterisks and filled circles in (a) and (b) denote the peaks with possible similarity to those observed for Y_2O_3 NTs reported in the literature.[2]

different morphology compared with Y_2O_3 NS. The entire morphology of $Y(NO_3)_3$ NS looks like blooming with needles, each of which has the length and diameter of approximately 10 and 0.5 µm, respectively. YCl_3 NS (Figure 1c) is composed of tapered needles with a similar dimension of the component of $Y(NO_3)_3$ NS. However, YCl_3 NS has no longer a blooming morphology. On the other hand, Sm_2O_3 NS (Figure 1d) exhibits nest-like morphology with a typical length and diameter of 3 and 0.3 µm, respectively.

Figure 2 shows X-ray diffraction (XRD) patterns of (a) $Y(NO_3)_3$ and (b) Sm_2O_3 NS, using Cu Kα radiation (Rigaku RINT-2500V). Concerned with the analysis of XRD reflections obtained presently, we refer to the data of Y_2O_3 NT measured by Tang et al.[2] In their paper,[2] on the basis of distinct reflections at 21, 29, 34, 48, and 57° they have attributed the structure of Y_2O_3 NT to a pure cubic phase [space group $Ia3$], with $a = 1.0604$ nm. In the case of $Y(NO_3)_3$ NS obtained presently (Figure 2a), the peaks designated with asterisks appear at somewhat similar positions to the reference data of Y_2O_3 NT[2] with departures of a few degrees to the lower angle. Moreover, the pattern of $Y(NO_3)_3$ NS displays a greater number of reflections compared with Y_2O_3 NT.[2] We, therefore, assume that the crystal structure of $Y(NO_3)_3$ NS has lower symmetry with a larger unit cell compared with Y_2O_3 NT reported elsewhere.[2] Stated alternatively, lower symmetry suggested for $Y(NO_3)_3$ NS compared with that of Y_2O_3 NT in the literature[2] can also be ascribed to the differences of the ingredient as nitrate and oxide, and morphologies in the nm–µm scale as were observed by FE-SEM. On one hand, a superlattice structure can be also possible for $Y(NO_3)_3$ NS. With respect to the XRD pattern for YCl_3 NS synthesized presently, similar results were obtained as the case of $Y(NO_3)_3$ NS.

The XRD pattern for Sm_2O_3 NS (Figure 2b) exhibits less similarity to Y_2O_3 NT even compared with $Y(NO_3)_3$ NS. The reflections marked with circles (Figure 2b) indicate possible similarity to Y_2O_3 NT[2] which have more discrepancies toward the lower angle compared with $Y(NO_3)_3$ NS synthesized presently. We thus suggest that the basic structure of Sm_2O_3 NS can rather differ from that of Y_2O_3 NT.[2]

Regarding the present synthetic conditions, we have found that the formation of the needle-like precipitation of surfactant assemblies in a visible length is essential to produce NSs. In order to optimize the synthetic conditions, the SDS concentration in the aqueous solutions was prepared to 10 CMC (critical micelle concentration) irrespective of the rare-earth raw materials. We note that NSs were not obtained when we chose the other concentration conditions varied from 5 to 20 CMC. Temperature of the solution was also optimized to be 40 °C, while the other temperature conditions up to 80 °C did not produce suitable NSs.

Inside the assembly of SDS, the amphiphilic structure of the surfactant interacts with the rare-earth material dispersed preliminary in the aqueous phase. Given the experimental results, we propose that among the rare-earth materials employed presently, the interaction mechanism between $Y(NO_3)_3$ and the surfactant cage may be rather different from the others. As a matter of fact, $Y(NO_3)_3$ indicated slightly hydrophilic behavior while the other materials showed less solubility in the present synthetic routine. The saturated concentration in the present aqueous system of $Y(NO_3)_3$ was 0.04 mol dm^{-3} which was an order of magnitude higher compared to others. This is a plausible explanation for the specific morphology like blooming with needles observed for $Y(NO_3)_3$ NS. The difference of morphology between Y_2O_3 NT and YCl_3 or Sm_2O_3 NS may be explained by a similar mechanism.

In summary, on the basis of the surfactant-assembled method we have synthesized NSs starting from $Y(NO_3)_3$, YCl_3, and Sm_2O_3 which have been scarcely reported previously. The difference of the morphology of NS is attributed to the different interaction between the surfactant template and rare-earth materials. An elaborated design of the template structure will promise a detailed control of NS morphologies.

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