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# Synthesis of TbO<sub>x</sub> Nanoparticles from the Thermal Decomposition of Tb(III) Complexes\*

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Terbium oxide nanoparticles, TbO<sub>x</sub> nanoparticles, were synthesized by the thermal reaction of Tb(III) complexes as a single-source precursor with acetylacetonone (acac) or hexafluoroacetylacetonone (hfa). Thermal decomposition processes of Tb(III) complexes for preparation of TbO<sub>x</sub> nanoparticles were characterized by the thermogravimetric analysis (TGA). The prepared TbO<sub>x</sub> nanoparticles were identified using XRD and TEM measurements.  
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## I. INTRODUCTION

Semiconductor nanoparticles have attracted considerable attention in the area of advanced materials science because of their remarkable luminescent, catalytic and magnetic properties [1-9]. Various types of preparation method of semiconductor nanoparticles have been reported for the past few decades. In particular, the thermal reaction of single-source precursor method has been utilized for the synthesis of nanoparticles in the presence of a suitable capping agent. The single-source precursor method permits to control the particle size and shape, and prevent particle aggregation by introduction of surface modification reagents. O'Brien and coworkers have synthesized CdSe nanoparticles using single-source precursor method, and successfully tuned luminescent color related to the diameter of CdSe nanoparticles, the quantum size effect [10]. Singh and coworkers have also reported synthesis of Pd<sub>17</sub>Se<sub>15</sub> nanoparticles using Pd-Se complex and their efficient catalyst for C-O coupling reactions [11]. Recently, we have reported the synthesis of monodisperse EuS nanoparticles using Eu(III) dithiocarbamate complex, and demonstrated characteristic magneto-optical properties of EuS nanoparticles depending on their particle size, shape and surface environments [12-14].

Here, we focused on nanoparticles containing terbium ions. Various types of nanoparticles containing terbium ions, for example, terbium-doped yttrium aluminum garnet (YAG:Tb) nanoparticles [15], terbium-doped ZnO nanoparticles [16] and TbPO<sub>4</sub> nanoparticles [17], have been reported. They exhibit characteristic optical and magnetic properties based on the degenerate 4f orbitals in terbium ions. Terbium oxide (TbO<sub>x</sub>) nanoparticles have also been reported [18, 19]. Chen and coworkers have reported synthesis of Tb<sub>2</sub>O<sub>3</sub> nanoparticles by the method of pulsed-laser beam ablation at the interface of Tb<sub>2</sub>O<sub>3</sub>

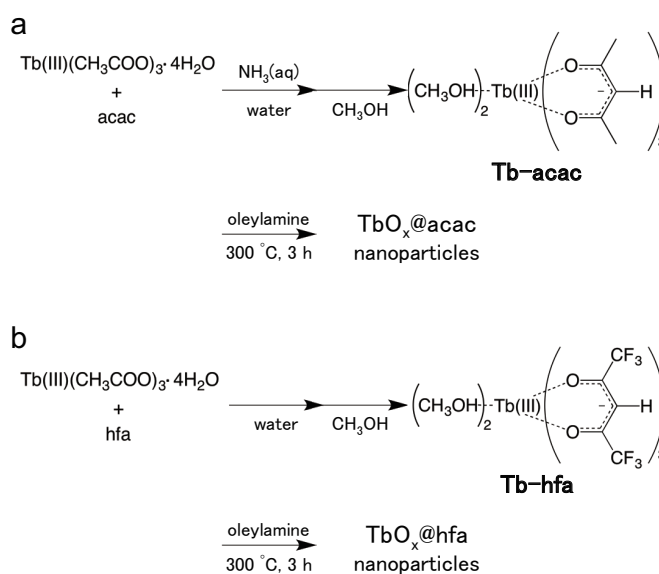


FIG. 1. Reaction schemes of (a) TbO<sub>x</sub>@acac and (b) TbO<sub>x</sub>@hfa nanoparticles.

target with acetylacetonone (acac) and 2,2'-bipyridyl (bpy) molecules [20]. The acac and bpy molecules show effective coordination ability as an organic ligand for single-source precursor. Dickerson and coworkers have used the thermal decomposition of single-source precursor, terbium oleate, at 350°C for preparation of monodisperse Tb<sub>2</sub>O<sub>3</sub> nanoparticles [21].

In this study, we have attempted to synthesize terbium oxide nanoparticles using the thermal decomposition of terbium(III) complexes as a single-source precursor, tris(acetylacetonato)dimethanolterbium(III) (Tb(III)(acac)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>, Tb-acac) and tris(hexafluoroacetylacetonato)dimethanolterbium(III) (Tb(III)(hfa)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>, Tb-hfa) (Fig. 1). Terbium oxide nanoparticles composed of Tb(III) or (IV) ions, TbO<sub>x</sub> nanoparticles, were synthesized by the thermal reactions of Tb(III) complexes in oleylamine at 300°C. Thermal decomposition processes of Tb(III) complexes for preparation of TbO<sub>x</sub> nanoparticles were characterized by the thermogravimetric analysis (TGA). The prepared

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TbO<sub>x</sub> nanoparticles were identified using XRD and TEM measurements. In the present study, we report on the influence of coordination ability of ligand for formation of TbO<sub>x</sub> nanoparticles.

## II. EXPERIMENTAL

### A. Materials

Terbium(III) acetate tetrahydrate (Tb(III)(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·4H<sub>2</sub>O) was purchased from Wako Pure Chemical Industry, Ltd. Acetylacetone (acac, CH<sub>3</sub>C(O)CH<sub>2</sub>C(O)CH<sub>3</sub>), hexafluoroacetylacetone (hfa, CF<sub>3</sub>C(O)CH<sub>2</sub>C(O)CF<sub>3</sub>) and oleylamine were obtained from Tokyo Chemical Industry Co., Ltd. All other chemicals and solvents were reagent grade and were used without further purification.

### B. Synthesis of precursor

#### 1. Synthesis of [Tb(acac)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>], Tb-acac

Terbium(III) acetate tetrahydrate (5.00 g, 12.3 mmol) was dissolved in distilled water (40 mL) by stirring. Acetylacetone (3.74 g, 37.4 mmol) was added dropwise to the above solution. The pH value of this solution was adjusted at pH 7 by adding NH<sub>3</sub> aqueous solution. The mixture produced a white precipitate after stirring for 3 h. The resulting precipitate was separated by filtration and washed 2 times with distilled water. Re-precipitation from methanol gave a white precipitate of [Tb(acac)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>]. IR (ATR):  $\nu_{\text{bar}} = 1650(\text{C}=\text{O})$ ,  $1390(-\text{CH}_3)$ ,  $1020(-\text{CH}_3)$ ,  $920(\text{C}-\text{CH}_3)$  cm<sup>-1</sup>; ESI-MS:  $m/z$ : calcd for C<sub>12</sub>H<sub>22</sub>O<sub>6</sub>Tb [M-(acac)]<sup>+</sup>: 421.07; found: 421.10.

#### 2. Synthesis of [Tb(hfa)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>], Tb-hfa

Terbium(III) acetate tetrahydrate (5.00 g, 12.3 mmol) was dissolved in distilled water (40 mL) by stirring. Hexafluoroacetylacetone (7.78 g, 37.4 mmol) was added dropwise to the above solution. The mixture produced a white green precipitate after stirring for 3 h. The resulting precipitate was separated by filtration and washed 2 times with distilled water. Re-precipitation from methanol gave a white precipitate of [Tb(hfa)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>]. IR (ATR):  $\nu_{\text{bar}} = 1650(\text{C}=\text{O})$ ,  $1255-1141(\text{C}-\text{F})$  cm<sup>-1</sup>; ESI-MS:  $m/z$ : calcd for C<sub>12</sub>H<sub>10</sub>F<sub>12</sub>O<sub>6</sub>Tb [M-(hfa)]<sup>+</sup>: 636.95; found: 637.01.

### C. Synthesis of terbium oxide (TbO<sub>x</sub>) nanoparticles (TbO<sub>x</sub>@acac and TbO<sub>x</sub>@hfa)

Under N<sub>2</sub> atmosphere, precursor Tb(III) complex (Tb-acac or Tb-hfa, 1.02 mmol) was dissolved into oleylamine (15 mL, 45.6 mmol), and the mixture was heated at 300°C and stirred for 3 h. Then, the resulting liquid was centrifuged at 4000 rpm for 10 min. The precipitation was added to *n*-hexane (10 mL) and centrifuged at

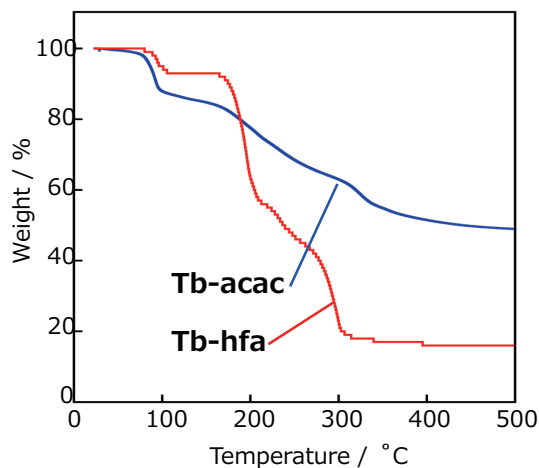


FIG. 2. Thermogravimetric profiles of Tb-acac (blue) and Tb-hfa (red).

4000 rpm for 10 min, and the clear liquid of oleylamine capped TbO<sub>x</sub> nanoparticles was obtained.

### D. Characterizations

Infrared spectra were recorded on a ThermoNicolet Avatar 320 FTIR spectrometer. Mass spectra were measured using a JEOL JMS-T100LP. High-resolution images of TbO<sub>x</sub> nanoparticles were obtained with a TEM, JEOL 2010 FASTEM (200 kV).

## III. RESULTS AND DISCUSSION

Synthesis of Tb(III) complexes, [Tb(acac)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>] (Tb-acac) and [Tb(hfa)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>] (Tb-hfa), were synthesized using the same method as previously reported [22] (Fig. 1). Their chemical structures were identified using IR and ESI-MS spectra. Thermogravimetric (TG) profiles of Tb(III) complexes are shown in Fig. 2. The first weight losses of Tb-acac and Tb-hfa at around 100°C (14% and 7%, respectively) are caused by the elimination of coordinated methanol molecules. The weight of Tb-acac was gradually decreased in increasing with the temperature between 100 and 500°C. In contrast, the weight of Tb-hfa was constant in the range between 100 and 150°C. We also observed that the weight of Tb-hfa was effectively decreased at 150°C. These results indicate that Tb-hfa is a promising single-source precursor for preparation of terbium oxide nanoparticles at around 300°C.

TbO<sub>x</sub> nanoparticles, TbO<sub>x</sub>@acac and TbO<sub>x</sub>@hfa, were synthesized by the thermal reaction of Tb-acac and Tb-hfa at 300°C, respectively (Fig. 1). The prepared powders were separated by centrifugation and washed with *n*-hexane. After washing, powder of TbO<sub>x</sub>@acac and TbO<sub>x</sub>@hfa were obtained. The prepared TbO<sub>x</sub> nanoparticles were analyzed by the transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). Figure 3a and b show TEM images of TbO<sub>x</sub>@acac and TbO<sub>x</sub>@hfa nanoparticles. TEM image

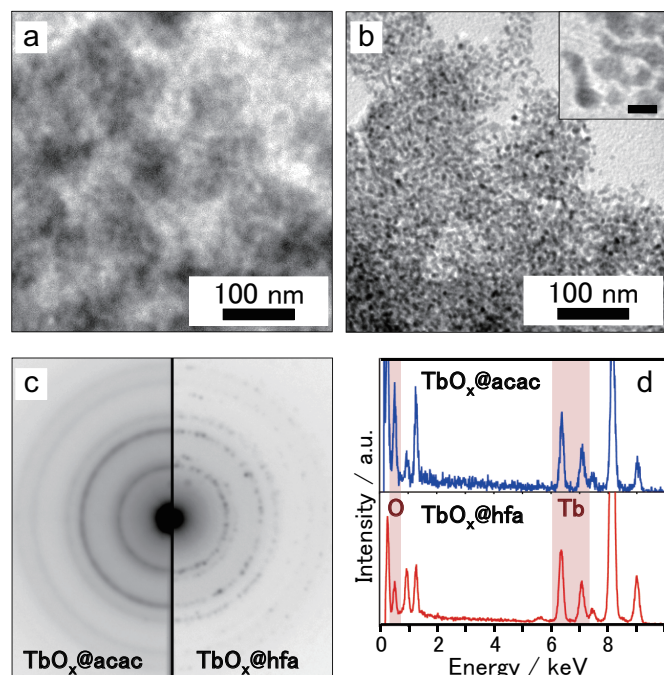


FIG. 3. TEM images of (a)  $\text{TbO}_x\text{@acac}$  and (b)  $\text{TbO}_x\text{@hfa}$  nanoparticles. Inset figure: length of scale bar = 10 nm. (c) The electron diffraction patterns of  $\text{TbO}_x\text{@acac}$  (left) and  $\text{TbO}_x\text{@hfa}$  (right) nanoparticles. (d) EDS analysis of  $\text{TbO}_x\text{@acac}$  (blue) and  $\text{TbO}_x\text{@hfa}$  (red) nanoparticles.

of  $\text{TbO}_x\text{@acac}$  nanoparticles provides cloud-like aggregations without clear shapes. On the other hand, TEM image of  $\text{TbO}_x\text{@hfa}$  nanoparticles shows smaller spherical particles. Their average particle size was found to be 7.1 nm. The electron diffraction pattern of  $\text{TbO}_x\text{@acac}$  is the same as that of  $\text{TbO}_x\text{@hfa}$  (Fig. 3c). These electron diffraction patterns are similar to that of  $\text{Tb}_2\text{O}_3$ ,  $\text{Tb}_4\text{O}_7$  and  $\text{TbO}_2$  compounds. EDS analysis indicates that their particles are composed of terbium and oxygen atoms

(Fig. 3d). From these results, we successfully prepared  $\text{TbO}_x$  nanoparticles using single-source precursors,  $\text{Tb-acac}$  and  $\text{Tb-hfa}$ . The size and shape of  $\text{TbO}_x$  nanoparticles are dependent of the thermogravimetric data for single-source  $\text{Tb(III)}$  complex. The decomposition temperature of  $\text{Tb(III)}$  complex is directly linked to the coordination ability of the ligands. According to the previous reports, the coordination ability of the acac and hfa ligands (binding constants of lanthanide complex) is estimated to be  $\log \beta_{1,\text{acac}} = 8.3$  and  $\log \beta_{1,\text{hfa}} = 4.7$ , respectively[23]. We consider that  $\text{Tb(III)}$  complex including hfa ligand with small binding constant is suitable for preparation of smaller and spherical  $\text{TbO}_x$  nanoparticles.

#### IV. CONCLUSIONS

$\text{TbO}_x$  nanoparticles was successfully synthesized by the thermal decomposition of single-source precursor. The thermogravimetric profiles show that  $\text{Tb-hfa}$  was effectively decreased at  $150^\circ\text{C}$  and a promising single-source precursor for preparation of terbium oxide nanoparticles at around  $300^\circ\text{C}$ . The TEM image of  $\text{TbO}_x\text{@hfa}$  shows cloud-like aggregations without clear shapes, in contrast, that of  $\text{TbO}_x\text{@acac}$  shows smaller spherical particles. Prepared  $\text{TbO}_x$  nanoparticles was expected to be useful for application in the field of optic and magnetic material sciences.

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