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Structural and spectroscopic characteristics of terbium hydroxide/oxide nanorods and plates

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Abstract

Tb(III) complexes with morphologies of nanorods and plates were prepared by a hydrothermal method. Post-thermal treatment was then applied to obtain Tb(IV) oxides with the same morphologies. Their nanostructures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) crystallography, UV–vis absorption, FT-IR, Raman, X-ray photoelectron spectroscopy (XPS), and photoluminescence imaging spectroscopy. Strong photoluminescence signals between 470 and 720 nm were attributed to the $^5D_4 \rightarrow {}^7F_J$ (J =6, 5, 4, 3) transitions of Tb(III). The Tb(III) complex and $Tb(OH)_3$ were found to be converted to Tb(IV) oxide upon thermal annealing at 700 °C. The oxidation state of Tb(III) was changed to non-luminescent Tb(IV), as clearly evidenced by UV–vis absorption, change in sample color, XPS, photoluminescence and XRD patterns.

Keywords: $Tb(OH)_3$; Tb(IV) oxide; Nanorod; Nanoplate; Photoluminescence imaging

1. Introduction

Terbium (Tb) with an oxidation state of 3+ has been extensively employed for the development of green phosphor materials. Tb(III) has commonly been doped into a support material (e.g., metal oxides) and sensitized by host light absorption [1–12]. As a result, Tb(III) emits photons with unique wavelengths between 470 and 720 nm, which are attributed to the $^5D_4 \rightarrow {}^7F_J$ (J =6, 5, 4, 3) transitions. Tb complexes, Tb hydroxides and oxides have been synthesized, and their fundamental structural and spectroscopic properties were investigated [13–29]. Mu and Wang [13] prepared Ln $(OH)_3$ (Ln=La, Sm, Tb, Eu, and Gd) nanorods (120–500 nm long and 15–90 nm wide) using the CTAB micelle solution. Mahajan and Dickerson synthesized Tb oleate by a hot solution-phase technique and obtained terbium sesquioxide (Tb_2O_3, sub-3 nm) by thermal-decomposition of the oleate complex [14]. Tran et al. [15] synthesized terbium phosphate ($TbPO_4$) nanorods using a hydrothermal method and reported their photoluminescence spectra. Yang et al. [16] synthesized $Tb_{(1-x)}(OH)_3{:}xEu^{3+}$ (x=0–3 mol%) nanorods by a hydrothermal method in which they controlled the luminescent colors from green, yellow and orange to red. Flowers like Lu_2O_3 and $Lu_2O_3{:}Ln^{3+}$ (Ln=Eu, Tb, Dy, Pr, Sm, Er, Ho, Tm) microstructures were synthesized by an ethylene glycol-mediated hydrothermal method and post thermal annealing, after which their luminescent properties were examined [17]. A template method (using anodic aluminum membrane) was employed to synthesize aligned $Tb(OH)_3$ nanowire arrays [18]. Du et al. [19] prepared $Tb(OH)_3$ nanorods with diameters of 20–30 nm and lengths of ~300 nm by a hydrothermal method at 90 °C using cyclohexylamine, NaOH, and ammonia as the alkaline sources. The photoluminescence properties of the synthesized materials mentioned above have commonly been examined, and lanthanide hydroxides with nanorod morphology have been demonstrated to act as photocatalysts for dye removal [25,26].

In the present study, Tb(IV) oxide nanorods and plates were prepared by thermal annealing of synthesized Tb(III)

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complexes. Photoluminescence imaging profiles [30–33] were first fully obtained for the as-synthesized complexes. This study also showed that Tb(III) was oxidized to Tb(IV) upon thermal treatment in air, as evidenced by UV–vis absorption, change in sample color, XPS binding energy shift, and photoluminescence quenching. This study further highlights the photoluminescence profiles of Tb complexes and thermal annealing effects for future potential applications.

2. Experimental section

Tb(III) complexes with morphologies of nanorods and plates were prepared by the following hydrothermal method. Tb oxides were obtained by thermal annealing of the complexes at 700 °C for 4 h. First, 10.0 mL of 0.1 M Tb(III) nitrate pentahydrate (Aldrich, 99.9%) solution was mixed with 15.0 mL of Millipore water in a Teflon jar. An appropriate amount (from 0.5 to 2.0 mL) of ammonia (~32%, Samchun Pure Chem., Korea) solution was then added to obtain the precipitates. The solution was subsequently tightly capped and placed in an oven (120 °C) for 12 h. Following the reaction and natural cooling to room temperature, final white precipitates were collected by repeated centrifugation and washing. The collected powder sample was then dried in an ambient oven at 80 °C, after which the surface morphology was examined using a Hitachi SE-4800 scanning electron

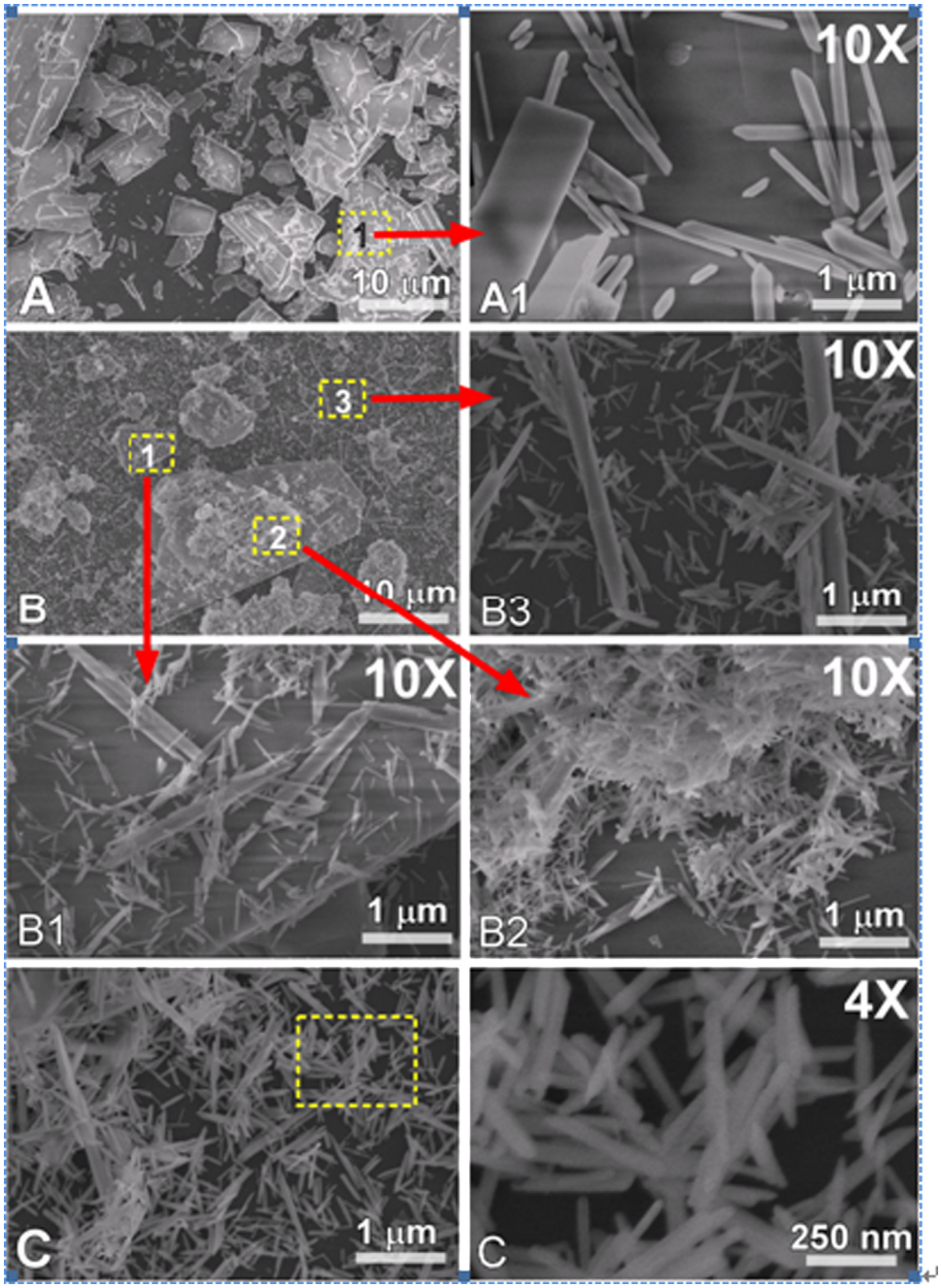

Fig. 1. SEM images of as-prepared Tb(III) complexes prepared under different conditions (A: 2.0 mL, B: 1.5 mL and C: 1.0 mL ammonia solution).

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