

Brief Communication

Synthesis and characterization of Gd(OH)₃ nanobundles

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Abstract

Gd(OH)₃ nanobundles, which consisted of bundle-like nanorods, have been prepared through a simple and facile hydrothermal method. The crystal, purity, morphology and structural features of Gd(OH)₃ nanobundles are investigated by powder X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and energy dispersive X-ray (EDX). A possible formation mechanism of Gd(OH)₃ nanobundles is briefly discussed.

Introduction

Since the discovery of carbon nanotubes in 1991 (Iijima, 1991), one-dimensional (1-D) structures with nanoscale diameters such as nanowires, nanorods, nanofibers, and nanotubes are currently the focus of much attention because of their special physical and chemical properties (Rao et al., 1997). Rare earth compounds have been used in high performance luminescent devices, magnets, catalysis and other functional materials, because of their outstanding optical, electronic and magnetic properties resulting from the 4f electrons (Adachi & Imanaka, 1998). Along with chemical composition and crystal structure, shape and dimensionality are now regarded as particularly important factors that influence physical and chemical properties of materials, thus if rare earth compounds were fabricated in the form of 1-D nanostructure, they would have new unique properties and a wide range of applications.

Many rare earth compounds with 1-D nanostructure have been prepared, such as rare earth (Er, Tm, Yb, Lu) oxide nanotubes prepared by using dodecylsulfate as a template (Yada et al., 2002), Tb(OH)₃ and Y(OH)₃ single crystalline nanotubes (Fang et al., 2003a), lanthanide orthophosphate nanowires (Fang et al., 2003b), β-La₂S₃ nanorods (Tang et al., 2002), Eu₂O₃ nanorods (Pol et al., 2002), lanthanide hydroxide nanowires (Wang & Li, 2002), La(OH)₃ nanorods (Deng et al., 2003), and Gd(OH)₃ nanorods (Du & Van Tendeloo, 2005). Gadolinium hydroxide has been used as the catalyzer and sorbent, and the precursor for the preparation of Gd₂O₃ by thermal dehydration (Du & Van Tendeloo, 2005). Recent studies on the preparation of Mg(OH)₂ nanorods have shown that the 1-D nanostructure can be prepared by planar molecule complex serving as a molecule template in control of the Mg(OH)₂ crystal growth (Li et al., 2000), which lead us to believe that 1-D the rare earth nanostructure might be prepared via planar molecule

complex of rare earth oxalate (Hansson, 1970) precursor. Rare earth hydroxides with bundle-like are few reported, to the best of our knowledge, there has been no report of $\text{Gd}(\text{OH})_3$ nanobundles, through facial hydrothermal synthetic method so far. Here we first report that $\text{Gd}(\text{OH})_3$ and $\text{Sm}(\text{OH})_3$ nanobundles were prepared by a direct conversion method of rare earth oxalate precipitation, without the additional introduction of other templates or surfactant and catalysts.

$\text{Gd}(\text{OH})_3$ and $\text{Sm}(\text{OH})_3$ nanobundles were composed of many parallel nanorods, rather than disordered aggregative nanorods. In this paper, we first proposed mechanism of planar network structure template to explain the formation of novel nanobundles.

Experimental procedure

All chemicals used were analytic grade reagents without further purification. **A: preparation of gadolinium oxalate hydrate:** at first, Gd_2O_3 was dissolved in 1:1 HNO_3 , then the solution was heated to remove the residue HNO_3 , and cool down to the room temperature. Then the solution was diluted in distilled water and pH of solution was adjusted to pH 2 using 1:1 HCl . Then aqueous solution of 10% $\text{H}_2\text{C}_2\text{O}_4$ was added to above solution, subsequently, the precipitate was separated, washed with distilled water thoroughly and dried at 80°C for 4 h in air. **B: preparation of the $\text{Gd}(\text{OH})_3$ nanobundles:** as a typical procedure, 1.0 g gadolinium oxalate hydrate was dispersed into 25 ml distilled water, then 15 ml 0.2 M NaOH solution was added to the suspension solution. The suspension solution was sealed into a teflon lined autoclave and kept at 180°C for 8 h, then cool down to room temperature. The precipitates were filtered off and washed with distilled water. After drying in air at 70°C for 2 h, white powder was collected for characterization. $\text{Sm}(\text{OH})_3$ nanobundles also were prepared by the same method.

The samples were characterized by power X-ray diffraction (XRD) on Rigaku D/max-IIB X-ray diffractometer, using $\text{CuK}\alpha$ radiation. XRD patterns were recorded from 10 to 90° with a scanning step of 0.02° . Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were taken with a JEOL JEM-2010 transmission electron microscope, with an

accelerating voltage of 200 kV. The morphologies of the sample were characterized by a PHILIPS XL30 ESEM FEG scanning electron microscope (ESEM), and energy dispersive X-ray (EDX) spectrum of the $\text{Gd}(\text{OH})_3$ nanobundles sample was obtained also using the same instrument.

Result and discussion

Figure 1 shows powder XRD pattern of the as-prepared $\text{Gd}(\text{OH})_3$ nanobundles. All of the reflections of the XRD patterns of the as-synthesized $\text{Gd}(\text{OH})_3$ nanobundles can be easily indexed to a pure hexagonal crystalline $\text{Gd}(\text{OH})_3$ with calculated lattice constants of $a=6.336\text{ \AA}$ and $c=3.624\text{ \AA}$ (JCPDS 83-2037), indicating the formation of single-phase $\text{Gd}(\text{OH})_3$. No impurity can be detected in the XRD analysis.

The typical ESEM morphologies of the as-synthesized product shown in Figure 2 reveal that $\text{Gd}(\text{OH})_3$ products exist in the form of nanobundles, and each nanobundle were composed of 4–8 parallel nanorods with diameters of 30–60 nm, and lengths of 0.5–2 μm . It can be seen that these nanobundles are very dispersive, and size distribution is also very uniform, which is consistent with the TEM observation. The morphology and structure of the products were further examined with TEM (Figure 3a), all the samples dispersed on the copper grids coated with a layer of amorphous carbon show nanobundles morphologies with uniform diameters 40–50 nm, and length up to about 1 μm , which is good agreement with the result of above ESEM image. Images of these nanobundles (Figure 3a) reveal bundle-like nanorods. It is also interesting to find that these nanorods tend to assemble to form parallel bundles. Figure 3b is the corresponding SAED pattern, taken on the single $\text{Gd}(\text{OH})_3$ nanobundles. It looks from the SAED pattern that the pattern was consisted of two sets of SAED patterns which could be obtained when the electron beam was focused on several individual nanorods with different axis zones, it was that because the $\text{Gd}(\text{OH})_3$ crystal was bundle-like morphology, it was difficult of electron beam was focused on single nanorod. Therefore, the nanorod itself is a single crystal, while the nanobundle is polycrystalline.

Energy-dispersive X-ray spectroscopy (EDX) analysis (Figure 4) shows the sample contains Gd and O; no Na is detected, indicating the final

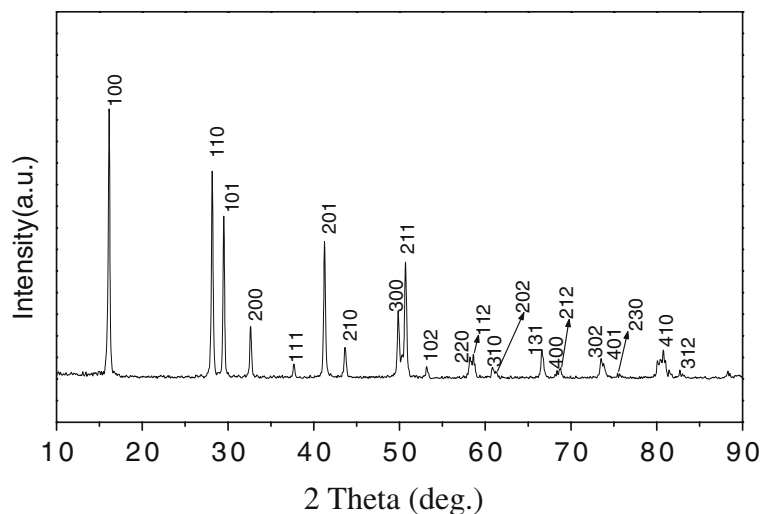
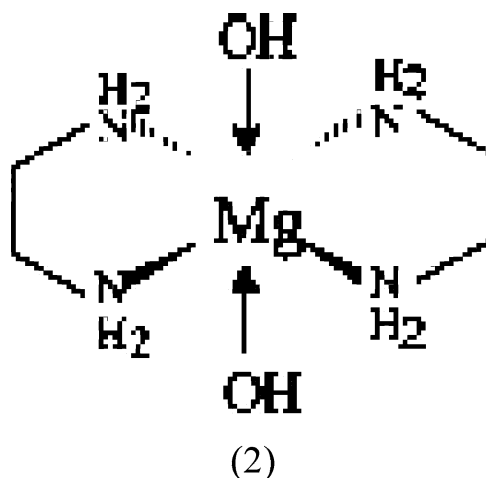


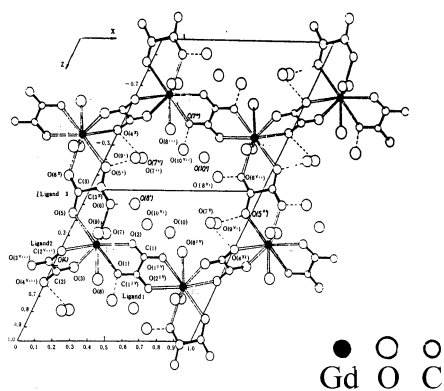
Figure 1. XRD patterns of the obtained $\text{Gd}(\text{OH})_3$ nanobundles.

product is free of elemental Na and have a high purity. (The peaks corresponding to the Si atom and Au atom respectively come from the silicon substrate and spraying gold.)

In our synthetic experiments, the planar network structure of the complex 1 (Hansson, 1970) played an important role in controlling nucleation and growth of $\text{Gd}(\text{OH})_3$ nanobundles. Oxalate ion might act as a bidentate ligand to form the stable Gd^{3+} complex 1, which might be arranged in a similar way to the structure shown in complex 2 (Li et al., 2000). In complex 2, OH attacked the planar complex, which caused $\text{Mg}(\text{OH})_2$ nanorods structure was formed.



Mg^{2+} -ethylenediamine complexes



The crystal structure of gadolinium oxalate

Similarly, in the complex 1, each Gd atoms were coordinated by three $\text{C}_2\text{O}_4^{2-}$ ions forming a planar network structure. There were three coordinated H_2O molecules in both sides of the molecular plane. When H_2O and $\text{C}_2\text{O}_4^{2-}$ were replaced by OH, because of spatial steric effect, OH attacked the complex only from the direction of perpendicular to the plane, it is easy to form rod-like structure, which was helpful to control one-dimensional nanomaterials growth, and between Gd atom and Gd atom were coordinated by $\text{C}_2\text{O}_4^{2-}$ to form network structure causing $\text{Gd}(\text{OH})_3$ nanorods structure to constructed into

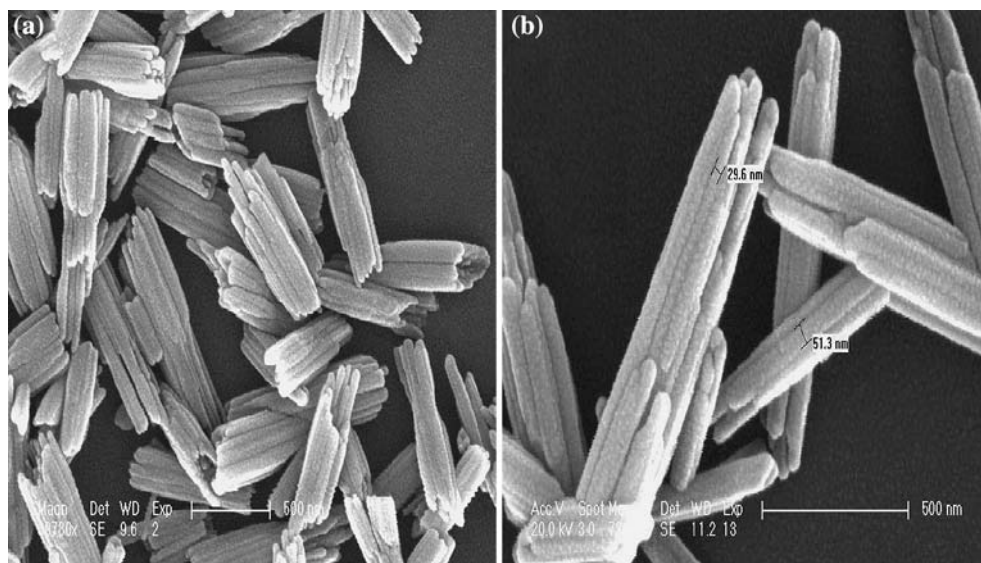


Figure 2. (a) ESEM images of the $\text{Gd}(\text{OH})_3$ nanobundles, and (b) Enlarged ESEM images of the $\text{Gd}(\text{OH})_3$ nanobundles.

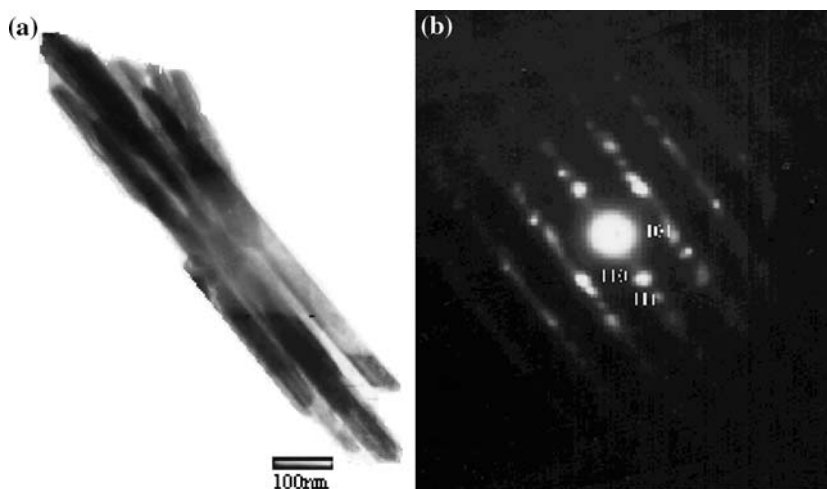


Figure 3. (a) TEM images of the $\text{Gd}(\text{OH})_3$ nanobundles, and (b) SAED patterns of $\text{Gd}(\text{OH})_3$ nanobundles.

nanobundles structure. In the complex 2, Mg^{2+} -ethylenediamine complexes also was planar structure, but it was not planar network structure, the $\text{Mg}(\text{OH})_2$ product was rod-like structure rather than bundle-like structure.

To improve our comprehensive of the nanobundles formation mechanism in the conversion synthesis, we synthesized $\text{Gd}(\text{OH})_3$ by replacing gadolinium oxalate by $\text{Gd}(\text{NO}_3)_3$ and GdPO_4 , which were not planar network structure. The results showed that the $\text{Gd}(\text{OH})_3$ product grew into

the agglomerates rather than nanobundles. The above results implied that planar network structure of oxalate precursor might be favorable for forming a bundle-like morphology. The results was further validated by another oxalate. We also synthesized $\text{Sm}(\text{OH})_3$ by $\text{Gd}_2(\text{C}_2\text{O}_4)_3$ was substituted for $\text{Sm}_2(\text{C}_2\text{O}_4)_3$. XRD showed that the obtained samples were pure hexagonal $\text{Sm}(\text{OH})_3$ phase, and ESEM showed that the obtained samples were bundle-like $\text{Sm}(\text{OH})_3$ (Figure 5). The mechanism of the formation is complex and needs

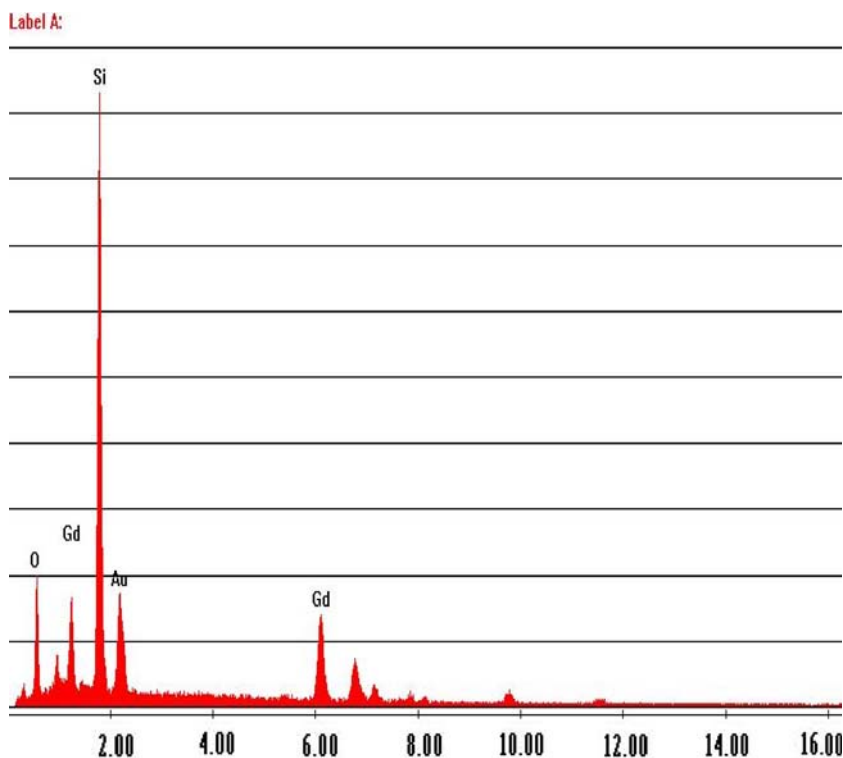


Figure 4. EDX image of $\text{Gd}(\text{OH})_3$ nanobundles.



Figure 5. ESEM images of the $\text{Sm}(\text{OH})_3$ nanobundles.

further investigation. Preparation and characterization of other rare earth hydroxide nanobundles are undergoing.

Conclusion

In summary, we have developed a simple and novel route to prepare $\text{Gd}(\text{OH})_3$ and $\text{Sm}(\text{OH})_3$ nanobundles by hydrothermal method. The nanobundles were prepared because of the planar network structure of gadolinium oxalate, which was first brought forward by us. This simple approach may provide a novel route for large-scale synthesis of this nanostructured material in a controlled manner for many important applications in nanotechnology.

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