

## PREPARATION OF NEODYMIUM HYDROXIDE NANORODS AND NEODYMIUM OXIDE NANORODS BY A HYDROTHERMAL METHOD

N. EKTHAMMATHAT<sup>a</sup>, A. PHURUANGRAT<sup>b,\*</sup>, B. KUNTALUE<sup>c</sup>,  
S. THONGTEM<sup>d</sup>, T. THONGTEM<sup>e,f,\*</sup>

<sup>a</sup>*Division of Chemistry, Faculty of Science and Technology,  
Bansomdejchaopraya Rajabhat University, Bangkok 10600, Thailand*

<sup>b</sup>*Department of Materials Science and Technology, Faculty of Science,  
Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand*

<sup>c</sup>*Electron Microscopy Research and Service Center, Faculty of Science, Chiang  
Mai University, Chiang Mai 50200, Thailand*

<sup>d</sup>*Department of Physics and Materials Science, Faculty of Science,  
Chiang Mai University, Chiang Mai 50200, Thailand*

<sup>e</sup>*Department of Chemistry, Faculty of Science, Chiang Mai University,  
Chiang Mai 50200, Thailand*

<sup>f</sup>*Materials Science Research Center, Faculty of Science, Chiang Mai University,  
Chiang Mai 50200, Thailand*

One dimensional Nd(OH)<sub>3</sub> nanorods were successfully prepared through a 180 °C and 20 h hydrothermal reaction. Subsequently, the Nd(OH)<sub>3</sub> nanorods were calcined at 450–600 °C for 2 h. Their phases and morphologies were characterized by XRD, SEM and TEM. The XRD patterns revealed the hexagonal Nd(OH)<sub>3</sub> phase of the precursor and the hexagonal Nd<sub>2</sub>O<sub>3</sub> phase of the final product. Upon calcination at 550 °C and above for 2 h, the hexagonal Nd(OH)<sub>3</sub> nanorods were transformed into the hexagonal Nd<sub>2</sub>O<sub>3</sub> nanorods with the shape remained unchanged. In this research, uniform Nd(OH)<sub>3</sub> nanorods and Nd<sub>2</sub>O<sub>3</sub> nanorods with the increase in size by the high temperature calcination were detected.

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### 1. Introduction

Rare earth oxides have been used in a number of applied fields such as ceramic industries, catalysts for dehydrogenation, hydrogenation and esterification reactions and catalyst carriers for their special properties arising from their 4f electrons [1–6]. Among them, neodymium oxide (Nd<sub>2</sub>O<sub>3</sub>) has been widely used in photonic applications, luminescent materials, catalysts of ammoniation and oxidative coupling of methane or catalyst promoters, and protective coatings [5, 7]. Thus the preparation and characterization of Nd<sub>2</sub>O<sub>3</sub> nanorods have attracted much attention in recent years. There have been many reports for the preparation of Nd(OH)<sub>3</sub> nanorods such as sol-gel process assisted with porous anodic aluminum oxide (AAO) template [3], sol-gel auto-combustion [6], tartrate route [7] and hydrothermal process [8].

In this research, Nd(OH)<sub>3</sub> nanorods were successfully produced through a hydrothermal method. Subsequently, the Nd(OH)<sub>3</sub> nanorods were calcined at 450–600 °C for 2 h by transforming the Nd(OH)<sub>3</sub> phase nanorods into the Nd<sub>2</sub>O<sub>3</sub> phase nanorods. Phases and morphologies of the products were further characterized by thermogravimetric analysis, X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy.

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\*Corresponding authors: phuruangrat@hotmail.com

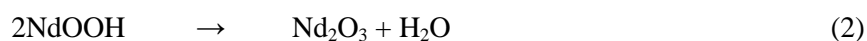
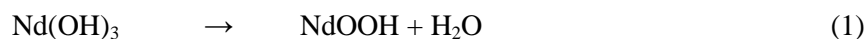
## 2. Experimental procedure

In a typical preparation, 50 ml of 0.01 M  $\text{Nd}(\text{NO}_3)_3$  aqueous solution was adjusted the pH to 10 by 3 M NaOH solution. It was transferred into a 100 ml Teflon-lined stainless-steel autoclave, which was filled with deionized water up to 80 % of its total capacity. The autoclave was tightly closed, heated at 180 °C for 20 h and cool down to room temperature. The resulting product was filtered, washed with distilled water and absolute ethanol, and dried at 80 °C for 12 h. Then the filtered self-template precursor was further calcined at the heating rate of 5 °C.min<sup>-1</sup> at high temperature of 450, 500, 550 and 600 °C for 2 h in ambient atmosphere.

The weight loss (less), purified phase, structure and morphology of the as-prepared products were characterized by a thermogravimetric analyzer (TGA -50 Shimadzu Scientific Instruments) under a stream of nitrogen at a heating rate of 10 °C/min, a Bruker AXS D8 Advance Powder X-ray diffractometer (XRD) with  $K_\alpha$  line from a copper target, a JEOL JSM-6335F field emission scanning electron microscope (FE-SEM) operating at an accelerating voltage of 15 kV with Au sputtering on the test samples, and a JEOL JEM-2010 transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV.

## 3. Results and discussion

Fig. 1 shows weight loss of the precursor at a temperature range of 45–650 °C under atmospheric condition. The total weight loss of the precursor was 15.65 % which is very close to the calculated value of 13.84 %. The weigh loss of  $\text{Nd}(\text{OH})_3$  precursor can be classified into 3 steps. First step is in the temperature range of 45–270 °C, corresponding to the evaporation of residual water adsorbing on the surface of  $\text{Nd}(\text{OH})_3$ . The second weight loss at the 270–430 °C temperature range was assigned as the dehydration and decomposition of  $\text{Nd}(\text{OH})_3$  to produce  $\text{NdOOH}$  [9, 10]. The third weight loss was at 430–650 °C, corresponding to the phase transformation of  $\text{NdOOH}$  to hexagonal  $\text{Nd}_2\text{O}_3$  structure [12, 13]. No critical weight change was detected at a temperature of and over 650 °C, indicating the thermal stability of  $\text{Nd}_2\text{O}_3$  up to 650 °C. The  $\text{Nd}_2\text{O}_3$  crystalline phase was still existence upon thermal annealing at a temperature over 650 °C. TGA curve also exhibits the multiple dehydration and decomposition processes during testing, which can generally be described by the following [9–11].



The specimen weight remained unchanged at the end of the test, implying that all chemical reactions were completed and residual ash was left behind.

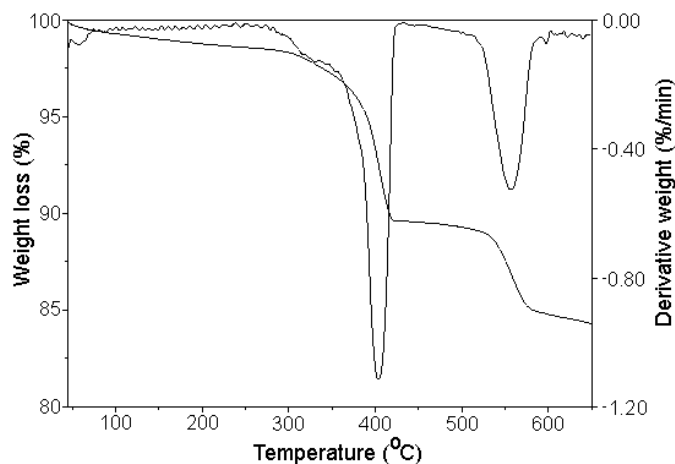


Fig. 1 Weight loss and the derivative of  $\text{Nd}(\text{OH})_3$  precursor.

Fig. 2 shows the X-ray diffraction patterns of different products. All diffraction peaks of the as-prepared precursor were indexed as pure phase of hexagonal  $\text{Nd}(\text{OH})_3$  of the JCPDS No. 70-0214 [12]. Due to the complete decomposition at  $550^\circ\text{C}$ , the hexagonal  $\text{Nd}(\text{OH})_3$  phase was fully transformed into the pure hexagonal  $\text{Nd}_2\text{O}_3$  structure in accordance with the database of JCPDS No. 75-2255 [12] caused by dehydration, decomposition and atomic arrangement. In this research, diffraction peaks of the products are very sharp and strong, indicating that they have very high crystalline degree.

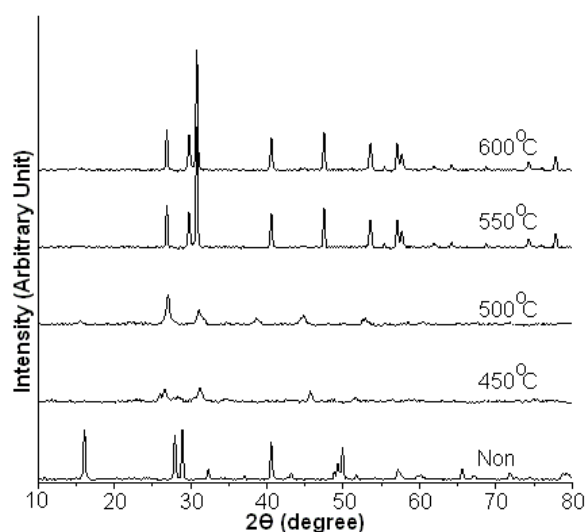


Fig. 2 XRD patterns of  $\text{Nd}(\text{OH})_3$  precursor before (Non) and after calcination at 450, 500, 550 and  $600^\circ\text{C}$  for 2 h.

Fig. 3a is a SEM image observed from the as-formed product hydrothermally produced at  $180^\circ\text{C}$  for 20 h. Clearly, the  $\text{Nd}(\text{OH})_3$  product entirely consists of uniform nanorods in high yield with diameters of about 5–10 nm and lengths of 20–30 nm. They should be noted that these nanorods are straight with very smooth surfaces. Upon calcination the  $\text{Nd}(\text{OH})_3$  product at a temperature of  $550^\circ\text{C}$  for 2 h, the final product (Fig. 3b) remained as nanorods with the size range of 200–300 nm long.

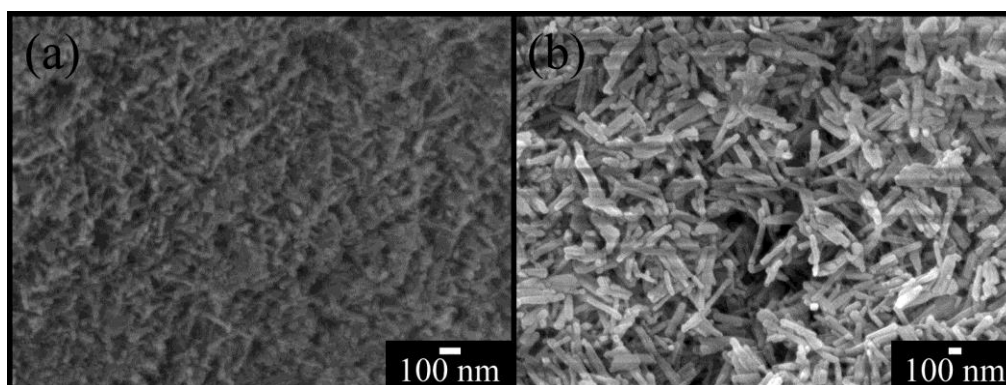


Fig. 3 SEM images of (a)  $\text{Nd}(\text{OH})_3$  and (b)  $\text{Nd}_2\text{O}_3$  obtained by  $550\text{ }^\circ\text{C}$  calcination of the precursor for 2 h.

Fig. 4 shows TEM images of the as-prepared  $\text{Nd}(\text{OH})_3$  and  $\text{Nd}_2\text{O}_3$  products. Clearly, the as-prepared  $\text{Nd}(\text{OH})_3$  product was entirely composed of relatively uniform nanorods with the lengths of 20–30 nm and diameters of about 5 nm, in consistent with the results of SEM analysis. However, the length and diameter of the as-prepared  $\text{Nd}_2\text{O}_3$  were increased with the increase in the calcination temperature from  $450\text{ }^\circ\text{C}$  to  $600\text{ }^\circ\text{C}$ . At  $450\text{ }^\circ\text{C}$  and 2 h calcination, the nanorods with 200 nm long and 20 nm diameter were produced. The length and diameter of  $\text{Nd}_2\text{O}_3$  nanorods were increased to 200–250 nm and 30–35 nm by calcination at  $500\text{ }^\circ\text{C}$  for 2 h, and to 200–400 nm and 40–60 nm by calcination at  $600\text{ }^\circ\text{C}$  for 2 h. The TEM analysis revealed that the particle size of  $\text{Nd}_2\text{O}_3$  was increased with the increasing of the calcination temperature.

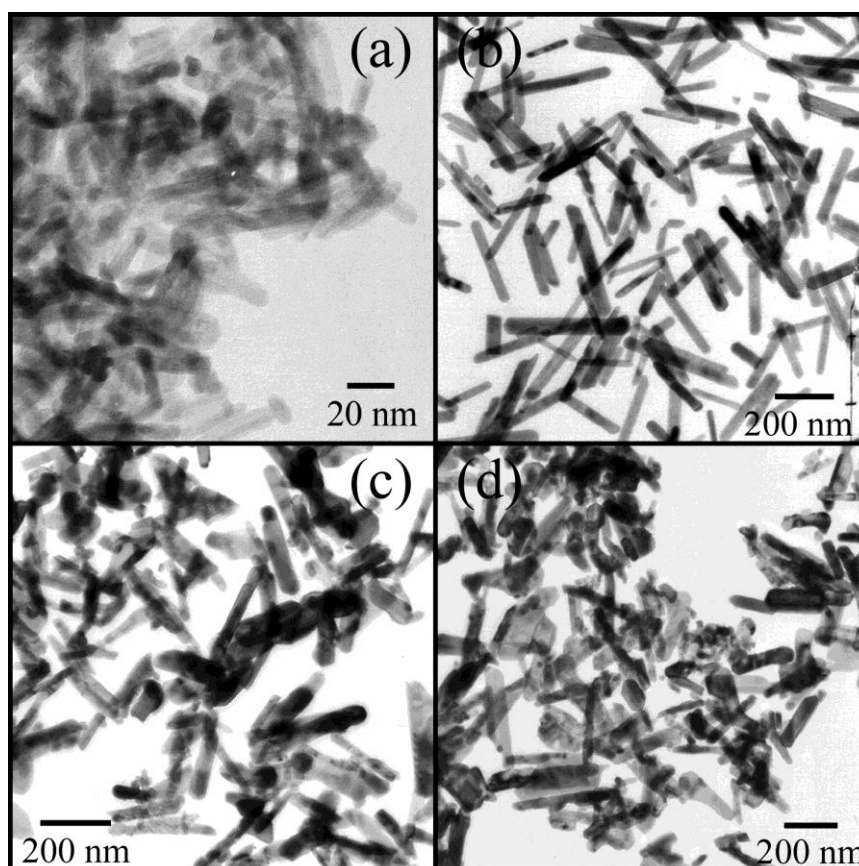


Fig. 4 TEM images of (a)  $\text{Nd}(\text{OH})_3$  prepared in the solution with the pH of 10, and followed by high temperature calcination of the  $\text{Nd}(\text{OH})_3$  precursor at (b)  $450\text{ }^\circ\text{C}$ , (c)  $500\text{ }^\circ\text{C}$  and (d)  $600\text{ }^\circ\text{C}$  for 2 h.

#### 4. Conclusions

This research was to prepare Nd(OH)<sub>3</sub> nanorods by a facile hydrothermal method in alkaline solution with the pH of 10. The pure Nd<sub>2</sub>O<sub>3</sub> nanorods were prepared by the calcination of Nd(OH)<sub>3</sub> at 550 °C and above. TGA analysis showed the evaporation, dehydration and decomposition of Nd(OH)<sub>3</sub> to form Nd<sub>2</sub>O<sub>3</sub> over the temperature range of 45–650 °C. The XRD patterns show the characteristic hexagonal Nd(OH)<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> phases before and after high temperature calcination. SEM and TEM images showed that the hexagonal Nd(OH)<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> phases are uniform nanorods with different orientations.

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#### References

- [1] N. Zhang, R. Yi, L. Zhou, G. Gao, R. Shi, G. Qiu, X. Liu, *Mater. Chem. Phys.* **114**, 160 (2009).
- [2] A.B. Panda, G. Glaspell, M.S. El-Shall, *J. Phys. Chem. C* **111**, 1861 (2007).
- [3] X. Qu, J. Dai, J. Tian, X. Huang, Z. Liu, Z. Shen, P. Wang, *J. Alloy. Compd.* **469**, 332 (2009).
- [4] T. Liu, Y. Zhang, H. Shao, X. Li, *Langmuir* **19**, 7569 (2003).
- [5] L. Qian, Y. Gui, S. Guo, Q. Gong, X. Qian, *J. Phys. Chem. Solid.* **70**, 688 (2009).
- [6] B. Zhaorigetu, G. Ridi, L. Min, *J. Alloy. Compd.* **427**, 235 (2007).
- [7] L. Kępiński, M. Zawadzki, W. Miśta, *Solid State Sci.* **6**, 1327 (2004).
- [8] W. Yang, Y. Qi, Y. Ma, X. Li, X. Guo, J. Gao, M. Chen, *Mater. Chem. Phys.* **84**, 52 (2004).
- [9] A. Phuruangrat, S. Thongtem, T. Thongtem, *Ceram. Inter.* **38**, 4075 (2012).
- [10] T. Thongtem, A. Phuruangrat, D.J. Ham, J.S. Lee, S. Thongtem, *CrystEngComm* **12**, 2962 (2010).
- [11] H. Hamano, Y. Kuroda, Y. Yoshikawa, M. Nagao, *Langmuir* **16**, 6961 (2000).
- [12] Powder Diffract. File, JCPDS Internat. Centre Diffract. Data, PA 19073–3273, U.S.A. (2001).