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# Formation and Properties of 1-D Alumina Nanostructures Prepared via a Template-free Thermal Reaction

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**Abstract**

A facile template-free thermal reaction was applied to prepare one dimensional (1-D) alumina nanostructures. Through utilizing the anisotropic modules existing in layered structures, the 1-D alumina nanostructures could be controlled to form nanotubes or nanorods with various configuration. The characters were then carefully studied and discussed based on the observation of TEM, XRD and photoluminescence.


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*Keywords:*1-D Alumina nanostructure； template-free；anisotropic module； disparate circumstance

## 1. Introduction

Since the discovery of carbon nanotubes by Iijima [1], wherein the graphene sheets roll and fold onto themselves to form hollow structures, a large number of inorganic nanotubes have been synthesized [2]. In the family of metal oxides, several strategies were employed to fabricate 1-D nanostructures [3, 4]. For examples, $VO_x$ nanotubes were

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prepared by means of hydrothermal treatment and primary amines [5, 6]; ZnO and TiO2 nanorods were prepared via wet chemistry [7] and electrophoretic deposition process, repectively [8]; $Fe_2O_3$, $SiO_2$, $TiO_2$, $ZrO_2$ nanotubes were prepared through the method of sol-gel technique [9, 11], electrochemical method [12] or AAO template [13,14]; and Ajayan [15]. Rao reported the synthesis of $SiO_2$, $Al_2O_3$, $MoO_3$ and $RuO_2$ nanotubes through using partially oxidized carbon nanotubes as templates. Various alumina nanostructures such as nanofibers [16], nanotubes [17], nanobelts [18] and hollow nanosphere [19] prepared via template methods were also reported. On summary of the reported works, the template is of great importance for forming tubular structures, but always results in annoying post-treatments. Many nanotubes lost their tubular structures after extracting the template, such as the case of $VO_x$ nanotubes through calcination over 523K [10]. It is in great need of some simple and template-free strategies to fabricate metal oxide nanotubes.

Inspired by the formation of carbon nanotubes, a large number of layered inorganic materials have been fabricated to form 1-D nanostructures [20]. It is known that the motivity of rolling and folding results from its reducing surface tension of strained surface layer once it is freed from the layer beneath [21] and the response of anisotropic modules existing in layers to outer circumstance, which drives the layered inorganic materials to form various nano-structures. For instance, the carbon sheets could be controlled to roll along certain direction to form armchair, zigzag or chiral nanotubes [22]. In previous works, we reported a separated two-phase interface hydrolysis method to prepare metal oxide nanoparticles. During the reaction, the organic solution offered confined space to restrict the growth of ultra fine particles [23]. On the other side, the reaction interestingly introduces a disparate circumstance mixed by water and oil when the temperature is over their boiling points. We expected that the layered materials could respond to hetero-circumstance and form some novel structures. In this contribution, we report the formation and properties of 1-D alumina nanostructures, including nanotubes/nanorods of boehmite (AlO(OH)) and gamma alumina ($\gamma$-$Al_2O_3$) via this facile template-free two-phase interface reaction. Reveled by high-resolution transmission electron microscope (HRTEM), the constitution of as-prepared boehmite nanotubes/nanorods was observed, which exhibits the analogical formation procedure as carbon nanotubes. Besides, the as-prepared 1-D alumina nanostructures showed well photoluminescence. This method provides a promising template-free synthetic strategy for preparing 1-D nanostructures through layered materials' rolling and folding.

## 2. Experimental

### *2.1. Synthesis*

The essence of this facile synthetic procedure is the combination of oil/water at quasi-gas state, which offers a hetero-cirmcumstance for the interface hydrolysis. The preparation process of 1-D alumina nanostructures can be described as follows: 20g of water and the organic solution containing 20g of aluminum butoxide in 20g of toluene were put separately in different teflon-lined chambers within one steel-lined autoclave. Under thermal reaction (over

toluene's b.p. 110°C), the water and organic phases diffused and encountered at an interface area. And the hydrolysis reaction occurred immediately within the oil/water hetero-circumstance. Then, the layered boehmite grew and rolled to form 1-D nanostructures due to the response of anisotropic modules existing in boehmite layers to hetero-cirmcumstance. The $\gamma$-$Al_2O_3$ nanorods were then obtained through calcination under 600 °C.

### *2.2. Characterization*

The samples were characterized using X-ray diffraction(XRD) and transmission electron microscopy(TEM) in combination with electron diffraction. Powder XRD patterns were obtained with a Bruker D8 X-ray diffractometer equipped with monochromated Cu Kα radiation, in the range $0° < 2\theta < 40°$. TEM was performed using a FEI Tecnai 20 S-TWIN electron microscope, operating at accelerating voltage of 200KV equipped with a LaB6 electron gun. Images were recorded using a Gatan 794 CCD camera. The specimen was prepared by depositing the powder onto a holey carbon film, supported on a standard 200 mesh ϕ 3mm TEM Cu grid, before transferring it into the microscope specimen chamber. The properties of photoluminescence (PL) were studied by a SHIMADZU UV-3600 UV-VIS-NIR Spectrophotometer.

## 3. Results and discussions

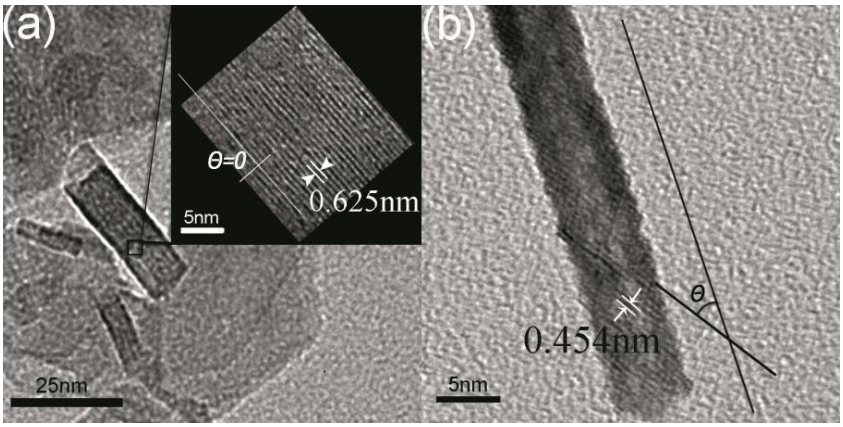


Fig.1. HRTEM images of (a) as-prepared boehmite nanotube and (b) nanorod

Fig.1. shows the typical HRTEM images of boehmite nanotubes/nanorods with distinct lattices on their surfaces. It can be seen that the open ended nanotube in Fig.1.(a) has about 30nm in length and 10nm in diameter. The parallel lattices on nanotube are parallel to axial direction with the θ of 0°. The nanorod in Fig.1.(b) has much more aspect ratio with over 30nm in length and about 5nm in diameter. The parallel lattices on nanorod have the transformable angle of θ to axial direction. Meanwhile, the parallel lattices in Fig.1.(a) have 0.625nm in width and

the diagonal lattices in Fig.1.(b) have 0.454nm in width. The formation mechanism of 1-D nano-structure with distinct lattices on their surfaces was revealed by further TEM observation.

Low resolution TEM image of the products after four hours' reaction (Fig.2.(a)) shows the state of co-existence of layered and tubular structures. The cycles of diffraction certify their structure of boehmite. Interestingly, the formation of hollow structures, through rolling and folding sheets onto themselves, could be verified by the direct observation of a rolled nanotube with disfigurements on one end. One nanotube ①-③ in Fig.2.(b) indicates the different rolling layers. It can be seen that such nanotube has two inner layers appearing on the position of disfigurement. And based on the view of the disfigurement direction, the fold could be deduced to roll anticlockwise. Fig.2.(c) shows the simulated structure of boehmite viewed from *x* direction and rolling method of layers. The distances of opposite and adjacent Al atoms on two chains could be calculated as 0.626nm and 0.445nm, which might be the reason affecting the observation from the images in Fig.1. Then, a speculation could be deduced as follows: during the two phase interface hydrolysis reaction, the layered boehmite first formed; and due to the oil/water hetero-circumstance, the sheets have chance to roll and fold onto themselves. As the formation process of carbon nanotubes, a schematic diagram is illustrated in Fig.2.(c), aiming the formation mode of boehmite 1-D nanostructure. One simulated layered structure of boehmite could be recognized based on the view along *x*-axis. The boehmite sheet, which is vertical to *x*-axis in *yz*-plane, is composed of Al-O-H chains by mimicking the observation shown in Fig.1.(a). The chains are parallel to *z*-axis and vertical to *y*-axis.

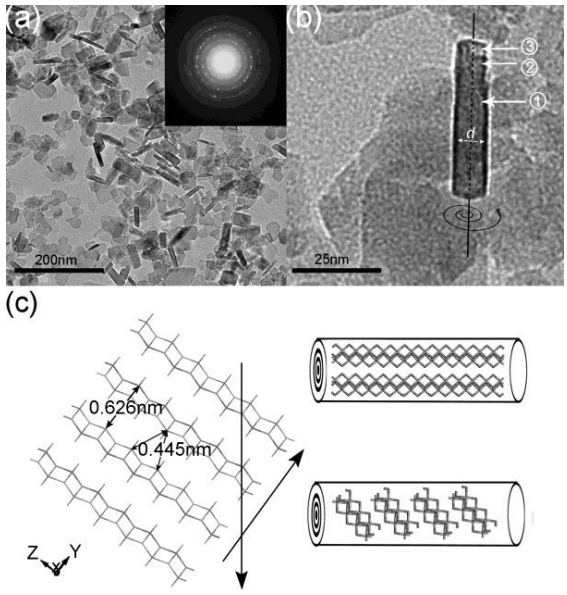


Fig.2. TEM image of (a) as-prepared nano-boehmite (b) one nanotube
(c) Schematic diagram of the possible formation mechanism for boehmite 1-D nanostructure.

Depending on two folded manners, the 1-D nano-structure transforming from boehmite sheets could be classified as follows: while the sheet rolls along *y*-axis, the lattices on nanotube are parallel to axial direction with the angle of $0^o$ (this type nanotube could be named as parallel type, p-type); while the sheet rolls along axis between *y* and *z*, the lattices on nanotube have the transformable angle of θ to axial direction (this type nanotube could be named as helix type, h-type). The difference of formation for nanotube and nanorod could be deduced resulting from the opportunity of rolling or folding of sheets: the sheet folds to nanorod when the rolling occurs at the start of sheet's formation, but folds to nanotube when rolling happens at the end of sheet's formation. The nano $\gamma$-$Al_2O_3$ was obtained by heating as-prepared nano-boehmite to $600^oC$ for 3-6 hours. As shown in Fig.3., the nano $\gamma$-$Al_2O_3$ exhibits interestingly porous and tubular morphology. The pores might result from the hetero-adsorption of oil and water on the surfaces. After calcination, the hetero-damage on the positions adsorbed with oil or water results in the formation of pores.

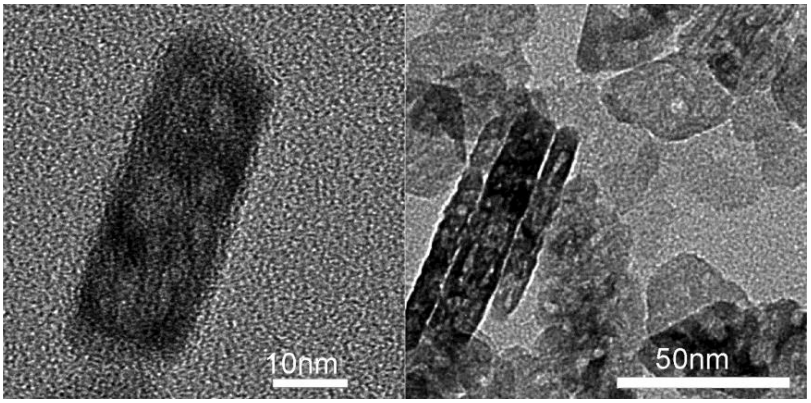


Fig.3. TEM images of as-prepared nano γ-$Al_2O_3$.

The crystallinity of products is further investigated by powder X-ray diffraction measurement (Fig.4.). The characteristic peaks of orthoclastic AlO(OH) and γ-Al2O3 can all be indexed, It could be well indexed to JACDS 83-1506 and 80-1385 as indicated.

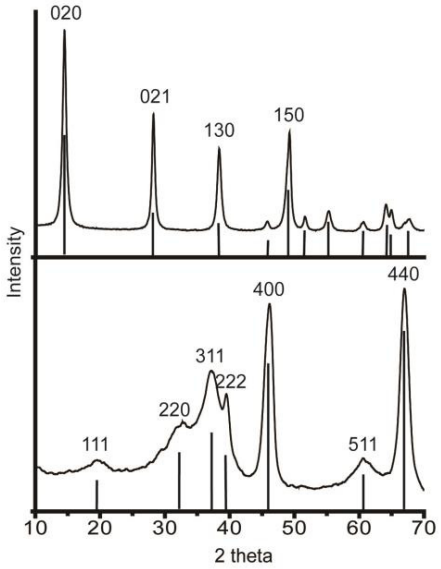


Fig.4. XRD patterns of as prepared nano AlO(OH) (upper) and γ-$Al_2O_3$ (below)

As adsorbents and catalyst components, AlO(OH) and $\gamma$-$Al_2O_3$ are widely applied in many industrial fields, such as cracking and hydrocracking of petroleum [24], the purification of gas oil fractions [25], and the steam reforming of hydrocarbon feedstocks to produce hydrogen [26]. But, the properties of photoluminescence (PL) were rarely observed or studied. Herein, the boehmite and $\gamma$-$Al_2O_3$ 1-D nano-structures exhibit some interesting PL characters which are also carefully investigated. The curves of UV-Vis absorption spectra are shown in Fig.5. The obvious absorption peaks corresponding to 242, 291 and 344nm of nano-boehmite and 225 and 280nm of $\gamma$-$Al_2O_3$ in ultraviolet region can be observed. It was reported that $Al_2O_3$ micro-powders had no PL emission, but $Al_2O_3$ nanobelts with several micrometers long, 0.1-1μm wide and 10-50nm thick had PL emission [18]. The reason roots from $F^+$ (oxygen vacancies with one electron) centers [27] in alumina nanobelts, which causes ultraviolet or violet PL bands [28]. It could be speculated that the nano-boehmite and $\gamma$-$Al_2O_3$ have the same motivity of absorption (242 and 225nm), i.e. the oxygen vacancies; and particular absorptions locating at 291 and 344nm of nano-boehmite and at 280nm of $\gamma$-$Al_2O_3$ probably result from more complicated folded 1-D structures.

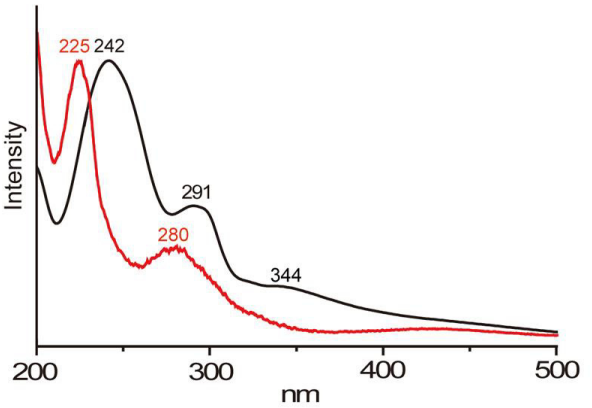


Fig. 5. Curves of UV-Vis absorption of as-prepared boehmite nanotubes and γ-Al2O3 nanorods.

In summary, a facile one-step synthesis method is described to prepare alumina 1-D nanostructues via a template-free solvothermal reaction. Due to the anisotropic circumstance within one system, as well as the advantages of the interface reaction, the sheets are drived further to roll and fold onto themselves to form nanotubes/nanorods. The advantages of template-free synthesis would be summarized as simple and low cost, high production yield and recyclable reaction. It is shown that this method is promoting to prepare 1-D nanostructues based on the layered materials, e.g. layered metals, metal sulfides, metal selenides, etc.

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## References

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[1] S. Iijima, Helical microtubules of graphitic carbon, Nature. 354 (1991) 56-58.
[2] C.N.R. Rao & M. Nath, Inorganic nanotubes. Dalton Trans. (2003)1-24.
[3] H. Wu, F. Bai, Z. Sun, R.E. Haddad, D.M. Boye, Z.Wang and M. Fan, Pressure-Driven Assembly of Spherical Nanoparticles and Formation of 1D-Nanostructure Arrays, Angew. Chem. Int. Ed. 49(2010) 8431-8434.
[4] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim & Y. Yan, One-Dimensional Nanostructures: Synthesis, Characterization, and Appli- cations, Adv. Mater. (2003)353-359.
[5] Jacques Livage, Hydrothermal Synthesis of Nanostructured Vanadium Oxides, Materials. 3(2010) 4175-4195.
[6] M.E. Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich & H.U. Nissen, Redox-Active Nanotubes of Vanadium Oxide, Angew. Chem. Int. Ed. 37(1998)1263-1265.
[7] X. Hou, L. Wang, B. Yu, F. Zhou & W. Liu, Synthesis of branched ZnO nanorods on various substrates via a wet-chemistry route, Particuology. 8(2011) 458-462.
[8] R. Mohammad Mohammadi, F. Ordikhani, D. Fray & F. Khomamizadeh, Template-based growth of titanium dioxide nanorods by a particulate sol- electrophoretic deposition process, Particuology. 9(2011) 161-169.
[9] B. Lv, Y. Xu, D. Wu & Y. Sun, Preparation and properties of magnetic iron oxide nanotubes, Particuology, 6(2010) 334-339.
[10] F. Krumeich, H. J. Muhr, M. Niederberger, F. Bieri, B. Schnyder & R. Nesper, Morphology and topochemical rections of novel vanadium oxide nanotubes, J. Am. Chem. Soc. 121(1999) 8324-8325.
[11] A. Mohammadpour et al., Multipodal and Multilayer TiO2 Nanotube Arrays: Hierarchical Structures for Energy Harvesting and Sensing, MRS Proceedings. 1552 (2013).

[12] Kasuga, T., Hiramatsu, M., Hason, A., Sekino, T. & Niihara, K. (1998) Formation of Titanium Oxide Nanotube. Langmuir, 14, 3160-3163.
[13] L. Yuan et al., Controlled synthesis of anatase TiO2 nanotube and nanowire arrays viaAAO template-based hydrolysis, J. Mater. Chem. A. 1(2013) 2552-2557.
[14] P. Hoyer, Formation of a Titanium Dioxide Nanotube Array, Langmuir. 12(1996) 1411-1413.
[15] P.M. Ajayan, O. Stephan, P. Redlich & C. Colliex, Carbon nanotubes as removable templates for metal oxide nanocomposites and nanostructures, Nature. 375(1995) 564-567.
[16] H. Zhu, J.D. Riches & J.C. Barry, γ-Alumina Nanofibers Prepared from Aluminum Hydrate with Poly(ethylene oxide) Surfactant, Chem. Mater. 14(2002), 2086-2093.
[17] L. Pu, X. Bao, J. Zou & D. Feng, Individual Alumina Nanotubes, Angew. Chem. 113(2001) 1538-1542.
[18] X. Peng, L. Zhang, G. Meng, X. Wang, Y. Wang, C. Wang & G. Wu, Photoluminescence and Infrared Properties of α-Al2O3 Nanowires and Nanobelts, J. Phys. Chem. B. 106(2002) 11163-11167.
[19] Y. Hu, H. Ding & C. Li, Preparation of hollow alumina nanospheres via surfactant-assisted flame spray pyrolysis, Particuology. 9(2011) 528-532.
[20] M. Basumallick & C.N.R. Rao, Oxide nanotubes prepared using carbon nanotubes as templates, J. Mater. Res. 12(1997) 604-606.
[21] O.G. Schmidt & K. Eberl, Nanotechnology: Thin solid films roll up into nanotubes, Nature. 410(2001) 168-173.
[22] G.R. Patzke, F. Krumeich & R. Nesper, Oxidic Nanotubes and Nanorods—Anisotropic Modules for a Future Nanotechnology, Angew. Chem. Int. Ed. 41(2002) 2446-2451.
[23] K. Tang, J. Zhang, W. Yan, Z. Li, Y. Wang, W. Yang, Z. Xie, T. Sun, & H. Fuchs, One-Step Controllable Synthesis for High-Quality Ultrafine Metal Oxide Semiconductor Nanocrystals via a Separated Two-Phase Hydrolysis Reaction, J. Am. Chem. Soc. 130(2008) 2676-2080.
[24] H. Knozinger & P. Ratnasamy, Acidic And Basic Properties Of Aluminas In Relation To Their Properties As Catalysts And Supports, Catal. Rev. Sci. Eng. 17 (1978) 31-70.
[25] R. Prins, Catalytic Hydrodenitrogenation, Adv. Catal. 46(2001) 399-464.
[26] T. Maillet, J. Barbier, P. Gelin, H. Praliaud & D.J. Duprez Effects of Pretreatments on the Surface Composition of Alumina-Supported Pd–Rh Catalysts, J. Catal. 202(2001) 367-378.
[27] P.W. Levy, Color Centers and Radiation-Induced Defects in Al2O3, Phys. Rev. 123(1961) 1226.
[28] D. Evans & M. Stapelbroek, Optical properties of the F+ center in crystalline Al2O3, Phys. Rev. B. 18(1978) 7089-7098.