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Template induced sol–gel synthesis of highly ordered $LaNiO_3$ nanowires

Zhi Yang, Yi Huang, Bin Dong, Hu-Lin Li*

College of Chemistry and Chemical Engineering, Lanzhou University, No. 222, Tianshui South Road, Gansu Province, Lanzhou City 730000, People's Republic of China

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Abstract

The highly ordered $LaNiO_3$ nanowires of the rare-earth perovskite-type composite oxide were controlled synthesized within a porous anodic aluminum oxide (AAO) template by means of sol–gel method using nitrate as raw materials and citric acid as chelating agent. The results of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that the obtained $LaNiO_3$ nanowires had a uniform length and diameter, which were determined by the thickness and the pore diameter of the applied AAO template. The results of X-ray diffraction (XRD) and the selected-area electron diffraction (SAED) indicated that the $LaNiO_3$ nanowires were perovskite-type crystalline structures. Furthermore, X-ray photoelectron spectroscopy (XPS) and the energy dispersive X-ray (EDX) spectroscopy demonstrated that the stoichiometric $LaNiO_3$ was formed.

Keywords: $LaNiO_3$ nanowires; Sol–gel; Template synthesis

1. Introduction

Because of their restricted size and high surface area, one-dimensional nanomaterials exhibit novel physical properties and play an important role in fundamental research as well as practical application. Plenty of efforts have been expended on the synthesis of nanoscale materials of various compounds. Recently, much attention has been paid to the preparation of composite oxides nanowires for their interesting and distinctive physical and chemical properties that are different from those of conventional bulk materials. Several composite oxide nanowires such as $La_{1-x}Ca_xMnO_3$ [1], $La_{0.67}Ca_{0.33}MnO_3$ [2], $LiNi_{0.5}Mn_{0.5}O_2$ [3], $LiMnO_2$ [4], and $LiCoO_2$ [5] have been successfully synthesized. In this paper, we select perovskite-type composite oxide $LaNiO_3$ as a subject, which is well-known material and which has thus received intensive investigations over the years.

Functional perovskite composite oxides such as $LaNiO_3$ and related compounds, are very promising materials due to their innovative use in advanced technologies. These perovskite-type oxides are active oxidation catalysts [6–8], conductive thin films [9–11] and electrode materials [12,13]. The synthesis of $LaNiO_3$ and related compounds have been achieved by many methods, including sol–gel [14–16], sonochemical synthesis [17], metalorganic decomposition [18], pulsed laser ablation [19], and metal-organic CVD method [20].

Recent publications mainly focus on the preparation and properties of the $LaNiO_3$ films and powders. In contrast, the investigations on wire-like $LaNiO_3$ nanostructures are quite limited. The properties of the final materials obtained are strongly dependent on the preparation method. Shankar et al. [2] have stated that the $La_{0.67}Ca_{0.33}MnO_3$ nanowires fabricated by AAO, a composite oxide nanowire, were ferromagnetic at room temperature and exhibited enhanced ferromagnetic

*Corresponding author. Fax: +86 931 891 2582.
E-mail address: lihl@lzu.edu.cn (H.-L. Li).

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transition temperature well in excess of 300 K, which was substantially higher than that of single crystalline $La_{0.67}Ca_{0.33}MnO_3$. For most applications, the controlled synthesis of homogeneity, high purity and high surface areas $LaNiO_3$ materials is necessary for obtaining reproducible properties. $LaNiO_3$ nanowires have higher surface areas compared to $LaNiO_3$ films and powders, and hence should enhance the effectiveness of the material in many applications, e.g., catalysis and gas sensitivity. Up to now, the synthesis of nanowires of multi-component oxides is still a challenging issue.

As an important way to prepare one-dimensional nanomaterials, template methods have attracted more and more attention in preparing ordered carbon nanotube, semiconductor nanowire arrays, magnetic nanowire arrays, etc. As the pore density is high, the pore distribution is uniform and the diameter of the pores is easily controlled by anodizing conditions [21]; porous anodic alumina oxide (AAO) templates are considered as particularly attractive templates for fabricating nanowires. Sol–gel method has become a popular method for preparation of inorganic materials and has a number of advantages over more conventional synthetic procedures such as high purity, homogeneous multi-component and easy chemical doping of the materials prepared. Sol–gel deposition has been widely used to fabricate nanowire arrays in the nanochannels of the template [22,23]. This method typically entails hydrolysis of a solution of a precursor molecule to firstly obtain a suspension of colloidal particles (the sol) and then a gel composed of aggregated sol particles. The gel is then thermally treated to yield the desired material.

Herein we have perfectly combined the concepts of sol–gel synthesis and template preparation of nanomaterials for the first time to yield a novel general route for fabricating highly ordered $LaNiO_3$ nanowires, which are distinctly different from the results of conventional methods. This was accomplished by conducting sol–gel synthesis within the pores of nanoporous membranes; mono-dispersed $LaNiO_3$ nanowires were obtained. This process uses inexpensive raw materials and can be performed at room temperature.

2. Experimental section

2.1. Membrane preparation

High-purity aluminum foil (99.999%) employed in this experiment was ultrasonically degreased in acetone for 10 min, etched in $1.0\,mol\,L^{-1}$ NaOH at room temperature for 3 min to remove the native oxide, washed thoroughly with distilled water, electropolished in a mixed solution of $HClO_4:CH_3CH_2OH = 1:4(V/V)$ for 5 min to provide a smooth surface and promptly rinsed with distilled water. Afterwards, the resulted clean aluminum foil was anodized at $80\,V_{dc}$ for 2 h in $0.5\,mol\,L^{-1}$ phosphoric acid solution. Each sample was then placed into saturated $HgCl_2$ solution for 1 h to separate the template membrane from the aluminum substrate. The membrane was rinsed with distilled water and immersed in $0.5\,mol\,L^{-1}$ H_3PO_4 solution for about 15 min at 328 K in order to dissolve the barrier-type part of nanoholes on the bottom. The obtained AAO template had a highly ordered porous structure with very uniform and nearly parallel pores, which could be organized in an almost precise hexagonal structure. The AAO template was characterized by using atomic force microscopy (AFM, Solver P47, Russia) and SEM (JSM-5600LV, Japan).

2.2. Preparation of $LaNiO_3$ nanowires

The $LaNiO_3$ perovskite precursors in this work were prepared by the citrate-based sol–gel method. Analytical grade lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), citric acid ($C_6H_8O_7 \cdot H_2O$) and ammonia water ($NH_3 \cdot H_2O$) were used as raw materials. According to the stoichiometric composition reactants, specified amounts of $La(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were first dissolved in deionized water, then an amount of citric acid was added to the above solution. The molar amount of citric acid was equal to the total molar amount of metal nitrates in the solution. Ammonia water was slowly added to adjust the pH value of the solution in the range of 6–7 and stabilize the nitrate–citrate solution. During this procedure, the solution was kept at a temperature of 333 K and continuously stirred. Thus a transparent and homogeneous sol was obtained.

The AAO template membrane was immersed into this sol for the desired amount of time and then removed. Excess sol on the membrane surface was wiped off using a laboratory tissue, followed by drying under vacuum at 323 K for 2 h. The membrane surface was carefully wiped again to remove salts crystallized on the surface and then heat treated at 923 K for 3 h in the open furnace. As a result, $LaNiO_3$ nanowires were formed inside the pores of the AAO template.

2.3. Characterization of $LaNiO_3$ nanowires

The structure and morphology properties of $LaNiO_3$ nanowires were characterized by several techniques. The SEM samples were obtained as follows: the alumina membrane was attached to an SEM sample stub with carbon conductive paint and then several drops of $3\,mol\,L^{-1}$ NaOH were added to the sample to dissolve the partial membrane. Prior to characterization, Au was sputtered onto the samples surface in order to increase their conductivity. The concentrations of La and Ni elements in the $LaNiO_3$ nanowires were determined by