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Template synthesis of $LaMnO_{3+\delta}$ ordered nanowire arrays by converse diffusion or convection

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Abstract

A method, whereby metal ions and precipitation reagents were transported in the nanochannels of anodic alumina membrane (AAM) templates by converse diffusion or convection and reacted in situ to form into one-dimensional nanostructure of the precursor, was developed. A high-aspect ratio nanowire array of the $LaMnO_{3+\delta}$ was prepared by this method. Electron microscope images showed that the $LaMnO_{3+\delta}$ nanowire array was abundant, uniformly distributed and well-ordered in large area. The individual nanowires are about 60 nm in diameter and their length corresponds to the thickness of the applied AAM template. The analysis of X-ray diffractions demonstrated that the $LaMnO_{3+\delta}$ nanowires are pseudocubic with typical perovskite lattice parameter.

Keywords: A. Oxides; B. Chemical synthesis; C. Electron microscopy; C. X-ray diffraction

1. Introduction

$LaMnO_3$ belongs to a class of the perovskite oxides that attract the scientific interest by more than 50 years due to novel physical and chemical properties. More recently, the interest to the manganite perovskite materials has increased considerably after revealing its colossal magnetoresistance properties [1,2]. Great effort has been made for both their potential application of the efficient technological devices and the theoretical and experimental understanding of the magnetism and the electronic structure [3–5]. In addition, manganite perovskite oxides are characterized by great stability at high temperature, high mobility of oxygen, and stabilization of unusual cation oxidation states in the structure. Both latter properties lead to oxygen non-stoichiometry that makes them suitable for the catalytic oxidation, including hydrogenation and hydrogenolysis of hydrocarbons, CO oxidation, ammonia oxidation, and catalytic combustion [6–8]. Manganite perovskite-type oxides also prove to be promising materials for application as electrode materials in solid oxide fuel cells, exhaust gas sensors in automobiles, membranes for separation processes and as catalysts [9–11]. Recently, a lot of attention has been paid to the method of fabricating these materials, as the properties depend very much on the synthesis. The compounds of the $LaMnO_3$ family prepared by traditional solid-phase reaction exhibit usually small specific areas. In order to overcome it the new methods such as gel–sol and coprecipitation were used to obtain nanoparticles of the perovskite oxides [12,13]. In this paper, a new method was developed to fabricate the $LaMnO_{3+\delta}$ nanowire array by the anodic alumina membrane (AAM) templates.

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One-dimensional (1D) nanostructures (nanowires or quantum wires) are ideal systems for investigating the dependence of electrical transport and mechanical properties on size and dimensionality. They are expected to play an important role as both interconnects and functional components in the fabrication of nanoscale electronic and optoelectronic devices. Many unique and fascinating properties have already been proposed or demonstrated for this class of materials, such as superior mechanic toughness [14], higher luminescence efficiency [15], enhancement of thermoelectric figure of merit [16], and lowered lasing threshold [17]. Although there is no general guideline that could be consulted for the design of any kind of desired novel nanowires (or nanorods), there are some major synthetic methods that are often successfully employed for nanowire formation [18,19]: gas-phase reaction methods, solvothermal routes, template-directed as well as liquid–crystal assisted syntheses, various solution-based techniques, and sonochemically driven reactions are widely used. A wealth of templates including step edges present on the surfaces of a solid substrate [20], channels within a porous material [21], mesoscale structures self-assembled from organic surfactants [22] or block copolymers [23], biological macromolecules such as DNA strains or rod-shaped viruses [24], and existing microstructures synthesized using other approaches [25] have been proven to be versatile for preparing ordered nanostructures. Among these templates, the anodic alumina porous membranes (AAM) have received considerable attention in synthetic nanostructure materials due to its several unique structure properties, such as controllable pore diameter, extremely narrow size distribution for pore diameters and their intervals, and ideally cylindrical shape of pores [26,27], besides they also exhibit good chemical and thermal stability, making them a suitable material for a variety of deposition method and conditions. Thus, they have been extensively used to fabricate nanometer-size fibrils, rods, wires, and tubules of different solid materials by a variety of synthetic strategies. Some metal and alloy nanowire arrays were synthesized by electrochemical deposition with AAM templates [28]. Several researches used sol–gel method to produce inorganic oxide nanowires inside pores of template [29]. Although it is relatively advantageous in fabrication of the nanoparticles, this method will encounter serious difficulty in preparing nanowires with high-aspect ratio because it is hard to pour the viscous sol in the nanochannels with a small pore diameter. So it is necessary to make an effort to obtain more effective route that the precursor generates in situ and forms into the nanostructure in the nanochannels of the anodic alumina membrane. In this paper, we report a new technique to synthesize the long, straight, and uniform $LaMnO_{3+\delta}$ nanowires. In this technique, the mixed solution containing La^{3+} and Mn^{3+} and precipitation reagents were transported in the nanochannels of AAM templates by converse convection or diffusion and reacted in situ to form into one-dimensional nanostructure of the precursor. Subsequently, they were changed into $LaMnO_{3+\delta}$ nanowires at high temperature.

2. Experimental

2.1. Preparation of anodic alumina membrane

The AAM templates were produced from pieces of high-purity aluminum foil (30 mm × 12 mm, 99.99%) via two-step anodization processes. Before anodization, the aluminum sheets were degreased, etched in alkaline solution, carefully rinsed, dried, and then annealed under nitrogen ambient at 673 K to remove mechanical stresses and recrystallize. To obtain the smooth surface the aluminum sheets were electropolished in a mixed solution of $HClO_4$:CH_3CH_2OH = 1:4. In the first step of the anodization process, aluminum foils were anodized at constant voltages of 40 V in 0.3 M $H_2C_2O_4$ aqueous solution at 273–278 K for 24 h, then the alumina layer obtained was removed in a mixture of phosphoric acid (6 wt%) and chromic acid (1.5 wt%) at 333 K for 3 h, afterwards, the foils were re-anodized at the same conditions as these used in the first step for 48 or 72 h. Next, the whole sample was immersed in saturated Hg_2Cl_2 solution to separate anodic oxide film from aluminum substrate. A subsequent etching treatment was carried out in a 6 wt% phosphoric acid solution at 310 K for 1 h to remove the barrier layer on the bottom side of the AAM, resulting in the freestanding template.

2.2. Preparation of $LaMnO_{3+\delta}$ nanowires

In the course of experiment, the prepared template was used as membrane to separate a vessel into the two parts. One of compartments was filled with the stoichiometric mixture solution composed of lanthanum nitrate and manganese nitrate, and the other was filled with 0.2 M ammonia carbonate solution. The metal ions and carbonate ions migrated conversely in the nanochannels of AAM templates and reacted in situ to form into one-dimensional

nanostructure. After the reaction lasted about half an hour, the template was transferred into the vessel filled with distilled water to completely remove reaction residuals. Finally, the template was dried under vacuum at 333 K for 1 h and then heated at 923 K for 6 h forming arrays of $LaMnO_{3+\delta}$ nanowires inside the pores of AAM templates.

2.3. Characterization of nanowires

A TEM (JEM1200EX, Japan) was used to investigate morphology of nanowires. For TEM measurement the treatment of samples is important. A piece of AAM template embedded with $LaMnO_{3+\delta}$ nanowires was placed in 3 M NaOH solution to dissolve away aluminum oxide framework. After centrifugal sedimentation the solution was removed slowly using a syringe and then an amount of distilled water was carefully added to rinse products. The process was repeated three times. The residuals were completely transferred into 1 mL of ethanol. A carbon grid was dipped in this dispersed solution and allowed to dry before TEM observation.

SEM images of the resultant $LaMnO_{3+\delta}$ nanowires were obtained with a JSM-6500LV electron microscope. The specimens for SEM were prepared as follows. A piece of AAM template embedded with $LaMnO_{3+\delta}$ nanowires was fixed to a SEM stub and then about 0.1 mL of 3 M NaOH solutions was dropped into the sample to partially dissolved alumina film and uncover nanowires from the template. After carefully rinsing with distilled water and drying in air, the samples were coated with gold thin layer by evaporating at vacuum to form conducting film.

X-ray diffraction (XRD) measurement was performed by a Rigaku D/MAX2400 diffractometer with Cu Kα radiation to investigate the phase structure and crystal orientation of the $LaMnO_{3+\delta}$ nanowire array.

3. Results and discussion

Growth of anodic porous alumina has been investigated in detail in various electrolytes [26,27]. Self-organized growth leads to a uniform array of hexagonal cells, each containing a cylindrical pore separated from aluminum metal by a barrier layer. The structural properties of the pores depend intensively on the anodization conditions. The AAM templates prepared in the oxalic acid solution have the periodic pore arrangement with a pore diameter average of 60 nm and a pore density of about 10^9–10^{10} cm^{-2}. Almost perfect hexagonal ordered domains can be seen over a wide range of pore distances. Before used as the templates, anodic alumina membrane needs to be etched in an acid solution to perforate the barrier layer. It is aware that etching process also induces the pore walls to be thin unevenly. So the exact control of etching time, concentration, and temperature is essential to preparing the anodic alumina templates with uniform pore diameter. The TEM image of the $LaMnO_{3+\delta}$ nanowires prepared by using the AAM template with these uniform pore structures are shown in Fig. 1, indicating that individual nanowires are around 60 nm in diameter and near to 7.5 μm in length. Seen from Fig. 1b, two nanowires are arranged in a y-type. Fig. 1c shows that several parallel and uniform nanowires form a nanowire array corresponding to the parallel pore channels of the templates. This arrangement may be relative to the coagulation of nanowires. As shown in figures the fabricated nanowires are dense and uniform, and their length and diameter depend on the size of the nannochannel of the used template.

SEM images of nanowire array prepared by using this method are shown in Fig. 2. Few microscopic defects are observed in the figures. Fig. 2a reveals a cross-section where the alumina matrix of the AAM template has fully been dissolved away. As shown, the $LaMnO_{3+\delta}$ nanowires deposited inside the nanochannel of the AAM template are in order aligned and uniformly distributed. It is correlative to the AAM template with densely parallel nano-holes arranged in a hexagonal fashion. Fig. 2b shows a split where the alumina matrix of the AAM template has been partly dissolved and large quantities of $LaMnO_{3+\delta}$ nanowires remain. Fig. 2c is a planform of the $LaMnO_{3+\delta}$ nanowire array, taken at lower magnification. It is seen from the large visual field that $LaMnO_{3+\delta}$ nanowires fabricated in our experiment are abundant, uniform, and well-ordered in large area. As shown in the micrographs, the nanowires are upstanding in high order, but the top of them is inclined to agglutinate together. When the alumina matrix of the AAM template was dissolved away, the nanowires embedded in the template were gradually released from top to bottom. Thus, the topside half of nanowires uncovered from the templates is more freestanding than their bottoms because of residuals of the alumina matrix. This situation leads to interesting sight in the figures. It is conceivable that these phenomena may result from the high surface energy of the nanowires. From these it can be found that the $LaMnO_{3+\delta}$ nanowires are produced in plenty inside the pore channels of the templates. Therefore, it can be reckoned that the density of the nanowire array is approximately equal to that of the pore of the templates (about 10^{10} cm^{-2}). In addition,

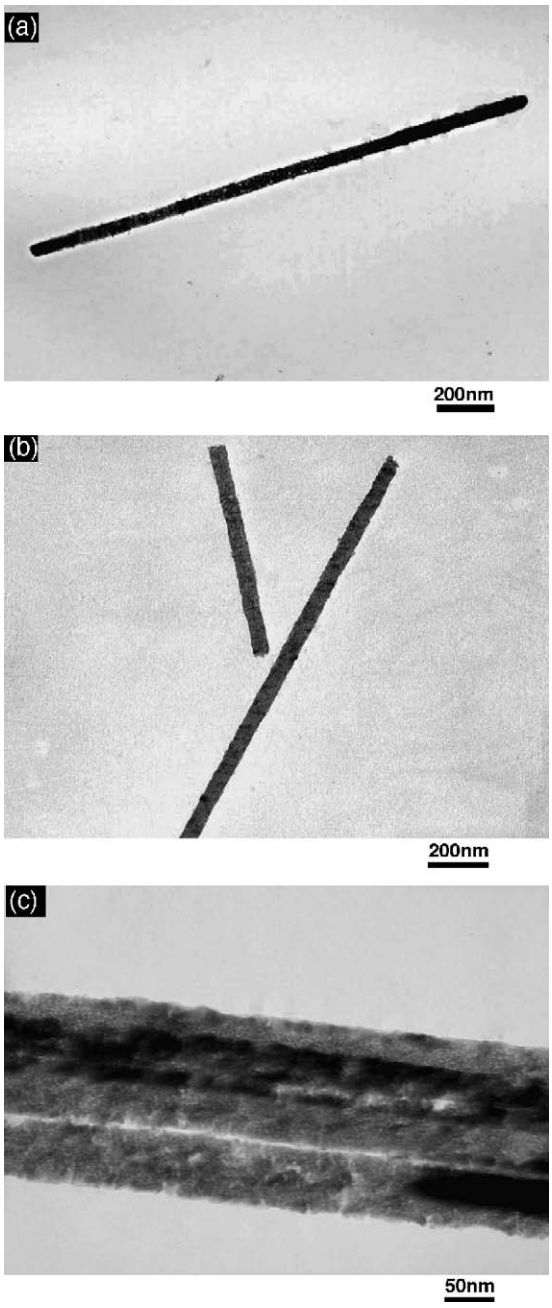

Fig. 1. TEM photographs: (a and b) freestanding $LaMnO_{3+\delta}$ nanowires and (c) parallel $LaMnO_{3+\delta}$ nanowire array.

it can be estimated that the length of them are more than 40 μm and the diameter is equivalent to the pore diameter of the template.

The structural chemistry of perovskite lattices is very complex, and there are a whole series (with hundreds of individual members) of hexagonal, rhombohedral, orthorhombic, and tetragonal distortions possible. The structural investigations [30] of the stoichiometric $LaMnO_{3+\delta}$ showed that oxidation of Mn ions over the level 3+ in stoichiometric $LaMnO_3$ induces vacancies on La and Mn sites, which are present therein in equal quantities. Thus, the entire structure skeleton is forced into becoming cation deficient. In other words, $LaMnO_{3+\delta}$ is not a compound with precise stoichiometry. Therefore, $LaMnO_{3+\delta}$ can exist in different structure forms, depending on the La/Mn ratio,

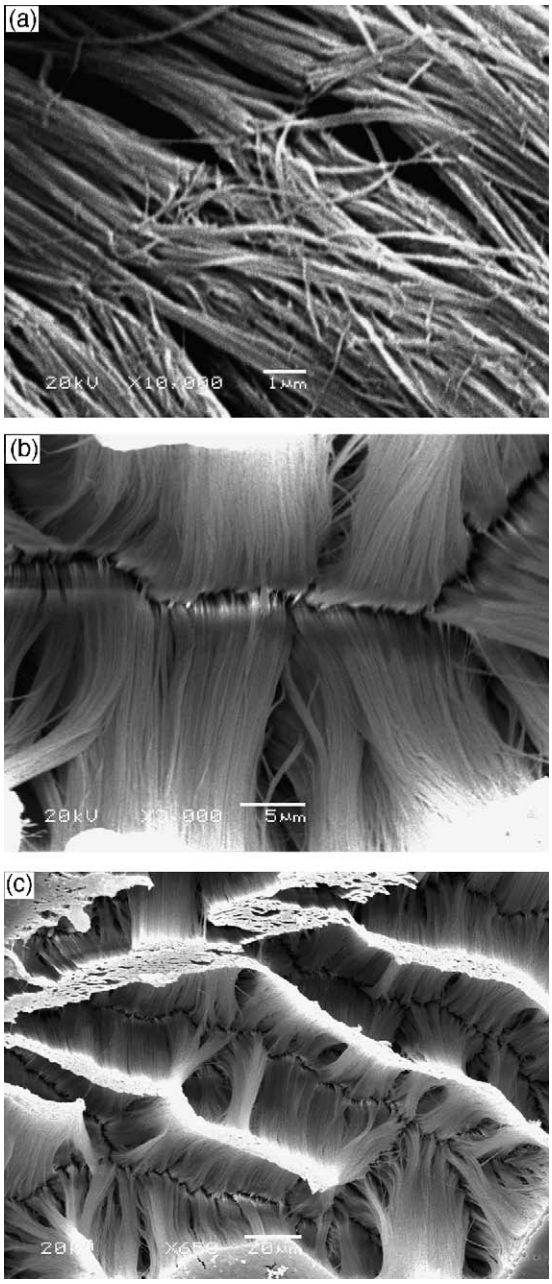

Fig. 2. SEM images of $LaMnO_{3+\delta}$ nanowire array: (a) cross-section view, (b) top view in low magnification, and (c) top view in high magnification.

temperature, and oxygen pressure. Within the temperture range 833 $\leqq$ 1473 K, and under the oxidizing conditions prevalent in air, $LaMnO_{3+\delta}$ exhibits three polymorphic forms; the rhombohedral existing up to ~1130 K, the nearly tetragonal appearing between ~1130 and ~1300 K, and the orthorhombic one stable above ~1300 K [4]. In our experiment, the precursors with molar La/Mn ratio = 1 was shaped in the nanochannels of the AAM template, and then they were changed into the $LaMnO_{3+\delta}$ nanowires at 923 K. The XRD spectrum of $LaMnO_{3+\delta}$ nanowires embedded in the template is shown in Fig. 3. The major diffraction peaks of $LaMnO_{3+\delta}$ are observed and their positions are in agreement with the JCPDS standard (card no.: 50-298). The pattern is pseudocubic with typical perovskite lattice parameter since different components are not resolved and different distortions are equally possible based these data. Although the nanowires are prepared at relatively low temperature, which is favorable to rhombohedral-phase,

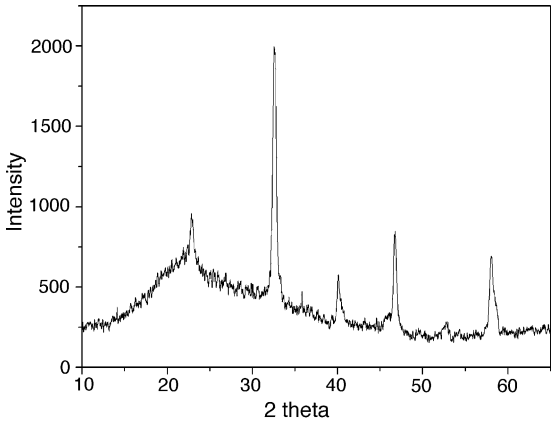

Fig. 3. X-ray diffraction spectra of $LaMnO_{3+\delta}$ nanowire array embedded in the AAM template.

precursors formed within the nanochannels of AAM templates may exhibit abnormal pyrogenation and phase transition because nanomaterials are more easily melted than the bulk materials. In addition, the specific field of nanowires could stabilize orthorhombic modifications. It should be pointed out that the observed reflections show some specific features of nanowire. For example, the major peak broadening may be due to diminutiveness in diameter of nanowires or size of crystal particles of which nanowires are composed. Furthermore, the anisotropic peak broadening and intensifying results from the preferred orientation of nanowires.

4. Conclusion

We have developed the new technique that the precursor is generated in situ, formed into one-dimensional nanostructure in the nanochannels of the AAM template, and then changed into the $LaMnO_{3+\delta}$ nanowires at 923 K. The analysis of the X-ray diffraction demonstrated that $LaMnO_{3+\delta}$ nanowires are pseudocubic with typical perovskite lattice parameter. Electron microscope images showed that nanowire array was abundant, uniformly distributed, and well-ordered in large area. It is estimated from the electron microscope photographs that the diameter of the individual nanowire is about 60 nm and the length was corresponding to the thickness of the applied AAM template.

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