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A general melt-injection-decomposition route to oriented metal oxide nanowire arrays

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ABSTRACT

In this manuscript, a general melt-injection-decomposition (MID) route has been proposed and realized for the fabrication of oriented metal oxide nanowire arrays. Nitrate was used as the starting materials, which was injected into the nanopores of the anodic aluminum oxide (AAO) membrane through the capillarity action in its liquid state. At higher temperature, the nitrate decomposed into corresponding metal oxide within the nanopores of the AAO membrane. Oriented metal oxide nanowire arrays were formed within the AAO membrane as a result of the confinement of the nanopores. Four kinds of metal oxide (CuO, Mn_2O_3, Co_3O_4 and Cr_2O_3) nanowire arrays are presented here as examples fabricated by this newly developed process. X-ray diffraction, scanning electron microscopy and transmission electron microscopy studies showed clear evidence of the formations of the oriented metal oxide nanowire arrays. Formation mechanism of the metal oxide nanowire arrays is discussed based on the Thermogravimetry and Differential Thermal Analysis measurement results.

1. Introduction

Metal oxides are very important in material science and technology. Many fascinating properties have been discovered in metal oxides which lead them to excellent applications in water splitting [1], renewable battery [2–4], catalyst [5–8], optical sensor [9], multiferroics [10–12], capacitor [13], solar cell [14], fuel cell [15] and energy cell [16]. Meanwhile, nanowires have attracted a great deal of interests because of their unique properties as well as their wide potential applications in a large range, such as nanolaser [17], nanogenerator [18], negative refractive metamaterial [19] and nanowire solar cell [20]. Up to now, many kinds of process, including lithography [21], thermal evaporation [22], aerotaxy-based growth [23], solid state reaction [24] and hydrothermal method [25], have been successfully developed to prepare different kinds of nanowires. Most of the obtained nanowires distribute randomly [26–30]. Only few of them can form oriented nanowire arrays, such as ZnO and GaAs. The template method, especially that based on the AAO membrane which is fabricated by electrochemical oxidization of aluminum, supplies us a simple, facile and effective strategy to synthesize oriented nanowire arrays [31,32]. The AAO membrane not only provides an optimal condition for the synthesis of nanowires but also arranges them into arrays automatically, which makes them more convenient to be used in the future applications. Many techniques have been developed to fabricate nanowire arrays in the AAO membrane, such as chemical vapor deposition [33], sol-gel technique [34], pressure injection [35], electrochemical deposition [36] and oxidation after electrochemical deposition [37]. Although some metal oxide nanowires have been fabricated under the assistance of the AAO membrane, it is still a big challenge to find out a more general route to fabricate oriented metal oxide nanowire arrays.

It is known to us that the diameter of the pores of the AAO membrane is in nanoscale. The capillary action should be very strong in such narrow channels according to the Jurin's law [38]. Generally speaking, the nitrate has relative low meting point and can decompose to metal oxide at not very high temperature. This offers us a new opportunity to the fabrication of metal oxide nanowire arrays by decomposing of nitrate in the AAO nanopores after injection of it in its liquid state. In the nanowire fabrication, the AAO nanopores act not only as the morphology controllers but also as the nanoreactors. In the present work, by using their corresponding nitrates as the starting materials, four examples of metal oxide nanowire arrays (CuO, Mn_2O_3, Co_3O_4 and Cr_2O_3) have been prepared by this effective MID route.

2. Experimental procedure

The oriented metal oxide (CuO, Mn_2O_3, Co_3O_4 and Cr_2O_3) nanowire arrays were prepared through this developed MID route

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under the assistance of the AAO membranes. All chemical reagents used in our experiment were of analytical grade and were used as received without further purification.

2.1. Preparation of the AAO membranes

The AAO membranes were prepared by a fast two-step anodization method as reported in previous work [39]. Briefly, after annealed at 600 °C for 5 h in open air to eliminate its inner stress, the high purity aluminum foil (purity 99.99%) was ultrasonic degreased with acetone and then corroded by a 0.1 mol/L NaOH solution for 30 s. In the first step, the as-treated aluminum foil was anodized in a 0.3 mol/L $H_2C_2O_4$ aqueous solution at 0 °C under a constant DC voltage of 50 V for 10 min. In the second step, the DC voltage was uniformly increased to 120 V within 2 min and maintained for another 90 min. After the two-step anodization, the AAO membranes were immersed into a 0.8 mol/L phosphoric acid solution at 30 °C for 40 min to widen their pores. Finally, the AAO membranes were rinsed with distilled water for many times and dried in an oven at 60 °C for about 24 h.

2.2. Synthesis of metal oxide nanowire arrays

The MID synthesis process mainly includes three steps: melting of the nitrate, capillary injection of the liquid nitrate into the nanopores of the AAO membrane and decomposition of the nitrate within the nanopores. The AAO membrane with the remaining aluminum substrate was transferred upwards into the bottom of a porcelain crucible with a volume of 50 ml. Appropriate amount of respective nitrate, that are $Cu(NO_3)_2{\cdot}3H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Cr(NO_3)_2{\cdot}9H_2O$, was grinded thoroughly in an agate mortar and later was put onto the AAO membrane in the porcelain crucible. Subsequently, the porcelain crucible was heated in a muffle furnace, whose temperature was increased from room temperature to 620 °C with a slow rate of 5 °C/min and maintained for 10 h. Finally, after cooled down to room temperature naturally, the AAO membrane was taken out carefully and the resultant material covered on its surface was cleaned completely for further characterization.

2.3. Characterization

The morphologies of the AAO membranes were performed by a scanning electron microscope (SEM, Environment Quanta 200). The phase structure of the metal oxide nanowire arrays was collected by an X-ray diffractometer (XRD, TD-3500) with Cu Kα radiation (λ = 1.542 Å) at an operating voltage of 30 kV and current of 20 mA with a slow scanning rate of 2.4°/min. The morphologies of the as-obtained nanowire arrays were investigated by both transmission electron microscope (TEM, JEM-1200EX) and SEM respectively. Thermogravimetry and Differential Thermal Analysis (TG-DTA, NETZSCH STA 449C) were applied to analyze the growth process of the used respective nitrate under the atmosphere condition.

3. Results and discussion

One of the most important advantages of the AAO membranes is their easily tunable pore diameter in a wide range. Fig. 1 presents the typical SEM images of the morphologies of the used AAO membranes after pore widening. Fig. 1(a) gives the clear top-view image of the AAO membranes, from which it can be concluded that the pores are rather uniform in size and their average diameter after widening for 40 min at 30 °C in a 0.8 mol/L phosphoric acid solution is about 150 nm. Meanwhile, it was also ascertained by SEM that the thickness of the AAO membranes is up to about 50 μm. Fig. 1(b)

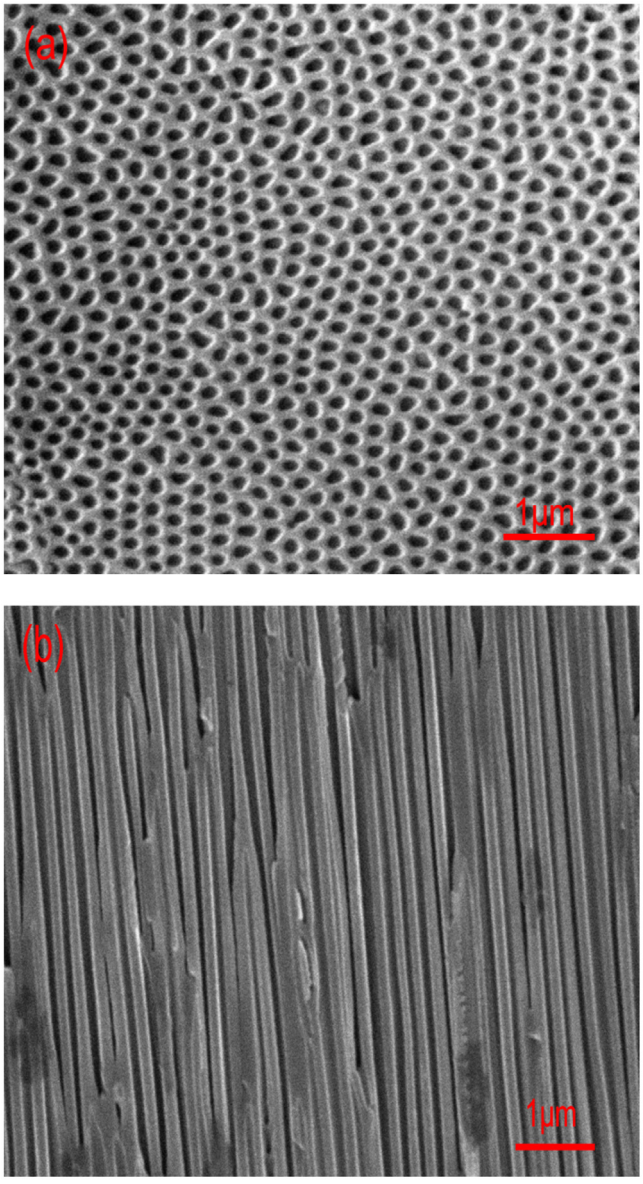

Fig. 1. Top-view (a) and side-view (b) SEM images of a blank AAO membrane after pore widening for 40 min at 30 °C in a 0.8 mol/L phosphoric acid solution. The pores are rather uniform in size and the average diameter is around 150 nm. The thickness of the AAO membranes is up to about 50 μm.

shows the typical side-view image of the AAO membranes, from which it can be seen that all of the nanochannels run parallel and straight. Thus, the hollow, parallel and straight nanochannels can be exploited to prepare oriented nanowire arrays.

The crystal structures of the four as-prepared samples have been carefully investigated by using XRD at a relative slow scanning rate and the results are depicted in Fig. 2. From the figure, it is found that all the clear reflection peaks can be assigned to the monoclinic CuO [**JCPDS card No: 74-1021**], the orthorhombic Mn_2O_3 [**JCPDS card No: 24-0508**], the cubic Co_3O_4 [**JCPDS card No: 74-2120**] and the hexagonal Cr_2O_3 [**JCPDS card No: 84-0314**] respectively. Importantly, it's also evident that there are no extra peaks belong to other oxides, indicating that the as-synthesized samples are relative pure. One should notice that the AAO membranes are still in their amorphous states after annealed at 620 °C [40] and therefore, there are no additional peaks correspond to them. The sharp and strong peaks at 44.8° can be indexed to the (200) plane of the remaining aluminum substrates [**JCPDS card No: 99-0005**].