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Facile preparation of aligned NiO nanotube arrays for electrochromic application

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ABSTRACT

Tailor-made nanotube arrays possess great potential for developing high-performance optical and electrochemical energy storage devices. Herein, we report a facile ZnO template-assisted hydrolysis method to fabricate aligned NiO nanotube arrays. The obtained NiO nanotubes are large-area and open-ended tube structures with stacked nanoparticle walls, which can shorten the diffusion distance of ions and increase surface area. As an electrochromic material, the aligned NiO nanotube arrays exhibits excellent electrochromic performances, including a larger transmittance modulation (78.5% at 550 nm), fast switching responses (3.92 s for coloration and 3.43 s for bleaching) and high CE (51.8 $cm^2 C^{-1}$ at 550 nm). Moreover, the aligned NiO nanotube arrays also depict a high stability and durability after 1000 cycles. It is also expected that this synthetic method can be extended to scale-up production of the aligned NiO nanotube arrays.

1. Introduction

In today's world, energy-saving of buildings has become increasingly important because nearly 30–40% of primary energy is consumed to maintain thermal comfort of indoor environment [1–3]. Electrochromic (EC) windows, also called smart windows, can dynamically control the amount of sunlight entered into buildings by the persistent and reversible change of color under a very small applied voltage, and therefore significantly decrease the energy consumption of buildings. Since the initial electrochromic studies by Deb in 1969, numerous organic and inorganic EC materials have been developed and applied in smart windows [4–6].

NiO is one of the most promising EC materials originating from its high EC efficiency, good cyclic reversibility and low material cost [7,8]. Among various morphologies of NiO, it is found that large area arrays with ordered nanostructures exhibit better EC properties compared with compact structure owing to their larger surface-to-volume ratio that could both increase accessible intercalation sites and shorten the diffusion distance of ions [9–11]. Therefore, the development of highly ordered nanostructures has been already regarded as a vital method for improving EC performances of NiO.

Recently, vertically oriented ZnO nanorods, a low-cost and environmentally-friendly film array, was reported to be an excellent sacrificial template material for the design and synthesis of NiO nanotube arrays [12–15]. For instance, hierarchical porous NiO nanotube arrays and Ni@NiO core-shell nanotube arrays were successfully prepared by electro-deposition (ED) methods in the presence of ED-ZnO nanorods as sacrificial templates [12,13]. Wu et al. have also synthesized an open-ended NiO nanotube arrays by hydrolysis of aqueous nickel chloride in the presence of ED-ZnO nanorod template [14,15]. However, these preparation processes (especially the preparation of the ZnO nanorod arrays), require a special ED equipment (such as electrochemical workstation) and are inappropriate for applying to nonconductive and large-sized substrates, which restrict the applicability of the NiO nanotube arrays.

Motivated by the above efforts, we herein used ZnO nanorod arrays obtained using liquid-phase deposition method as sacrificial template to fabricate aligned NiO nanotube arrays composed of NiO nanoparticles. The preparation method has great potentials for scale-up production of the aligned NiO nanotube arrays because it only needs simple and basic

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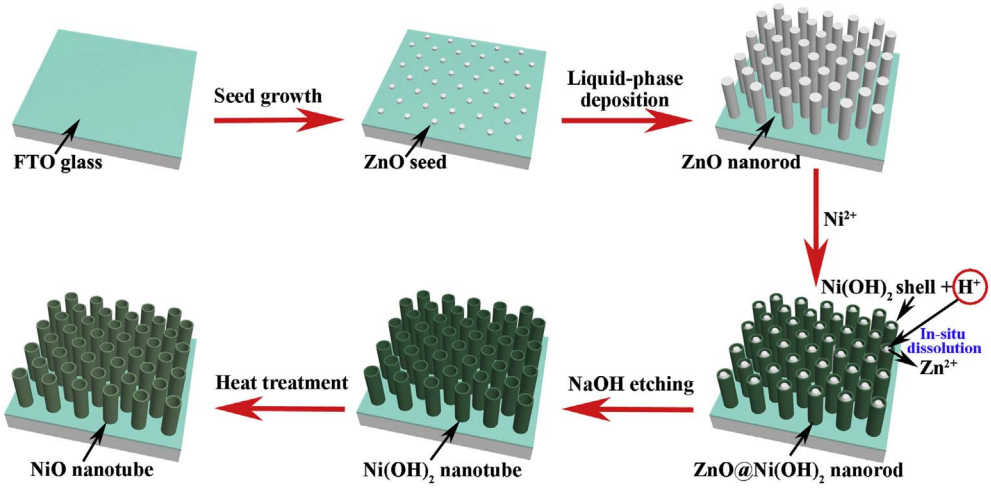

Fig. 1. Schematic illustration for the formation of the aligned NiO nanotube arrays.

experimental equipment, and can apply to various substrates. Moreover, we have also investigated the electrochromic properties of the synthesized NiO nanotube arrays in the wavelength ranges 400–1000 nm.

2. Experimental section

2.1. Synthesis

All reagents used in this study were of analytical purity without further purification. The fabrication process of the aligned NiO nanotube arrays involves several steps, which is illustrated in Fig. 1. The first step is to prepare ZnO nanorod arrays by a liquid-phase deposition method. ZnO seed layer was deposited on water/ethanol-washed FTO glass (1 × 4 cm^2) *via* a Czochralski method in ethanol solution of zinc acetate (30 mM) with a speed of 500 μm s^{-1} and then thermal treated at 270 °C for 20 min. Subsequently, the seeded FTO glass was horizontally suspended in an aqueous solution of 20 mM zinc nitrate and 20 mM hexamethylenetetramine in a watch glass with cover, and heated in an oven at 90 °C for 2 h. Finally, the ZnO nanorod arrays film was obtained after the substrate was washed using deionized water and ethanol, and then naturally dried in air.

The aligned NiO nanotube arrays film was obtained by ZnO template-assisted hydrolysis of nickel chloride. ZnO@$Ni(OH)_2$ nanorod arrays film was firstly formed by immersing the ZnO template in an aqueous solution of nickel chloride (1 M) for 10 min. The aligned NiO nanotube arrays film was obtained by dipping the ZnO@$Ni(OH)_2$ nanorod arrays into 4 M Na(OH) solution for 60 min to remove the residues of the ZnO cores, and subsequently annealed at 400 °C for 2 h.

2.2. Characterizations

Scanning electron microscope (SEM) images were gained using a FEI Helios Nanolab600i. Transmission electron microscopy (TEM) images were obtained from a Hitachi H-7650 with an accelerating voltage of 100 kV. X-ray diffraction (XRD) patterns were performed on a diffractometer (XRD, PANalytical B.V. Model X'pert Pro) at an X-ray grazing angle of 2.0°. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5700 ESCA System using Al Ka radiation (1486.6 eV). Cyclic voltammetry (CV) and chronoamperometry (CA) tests were carried out using a CHI760D electrochemical workstation in a three-compartment system with an aqueous solution of 0.1 M KOH as the electrolyte, Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. The transmission spectra of the electrochromic films in the fully colored and fully bleached states were recorded with a MAYA 2000-Pro (Ocean Optics) after the films were subjected to CV test for 10 cycles.

3. Results and discuss

3.1. Formation mechanism

As displayed in Fig. 1, the aligned NiO nanotube arrays were synthesized by three steps. Firstly, the FTO glass covered ZnO nanorod arrays was immersed in an aqueous solution of nickel chloride (1 M) to form ZnO@$Ni(OH)_2$ nanorod arrays. In brief, once the ZnO nanorods were immersed, nickel ions would prefer to adsorb on the surface of the ZnO nanorods, and simultaneously, the hydrolysis of the nickel ions commenced to form $Ni(OH)_2$ and H^+ according to the following reaction:

$$Ni^{2+} + 2H_2O \rightarrow Ni(OH)_2 + 2H^+ \quad (1)$$

The ZnO nanorods were then etched by H^+ and therefore accelerated the hydrolysis of nickel ions. The $Ni(OH)_2$ shell grew thicker with increasing the hydrolysis time until the ZnO core was entirely etched. In this study, only a small amount of ZnO core could be etched within the hydrolysis time of 10 min. After that, the residues of the ZnO cores was removed by dipping the ZnO@$Ni(OH)_2$ nanorod arrays into 4 M Na(OH) solution. Finally, the aligned $Ni(OH)_2$ nanotube arrays were turned into the aligned NiO nanotube arrays by heat treatment as follows:

$$Ni(OH)_2 \rightarrow NiO + H_2O \quad (2)$$

3.2. Morphology and structure

Surface morphologies of the films were characterized by electron microscopic studies. Fig. 2a presents SEM image of the aligned ZnO nanorod arrays. It shows dense and large-area nanorods array with well-aligned orientation perpendicular to the FTO glass, which are about 70 nm in diameter and 1.35 μm in length. After etching the ZnO template and heat treatment, uniform and dense NiO nanotubes with large-area are obtained (Fig. 2b). Moreover, these nanotubes are open-ended tubes with stacked nanoparticle walls (Fig. 2c), which can shorten the diffusion distance of ions and increase the surface area, and thereby effectively enhances the electrochromic performance. Moreover, the aligned NiO nanotubes have a diameter of 100 nm and a length of approximately 1.0 μm. The TEM image of a typical NiO nanotube is shown in Fig. 2c, which further proves the hollow nanotube structure. The length of nanotubes is less than that of the nanorods,

The crystal structures of the aligned ZnO nanorod arrays and the aligned NiO nanotube arrays grown on FTO glasses were investigated by XRD, as shown in Fig. 3. The sharp peaks at 26.46°, 33.74°, 37.71°,