Hydrothermal-synthesized NiO nanowall array for lithium ion batteries

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ABSTRACT

We report a self-supported NiO nanowall array prepared by a facile hydrothermal synthesis method. The microstructure and morphology of the sample are characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The hydrothermal-synthesized NiO nanowalls with thicknesses of $\sim$20 nm arrange vertically to the substrate forming a net-like nanowall array structure. As anode material for lithium ion batteries, the NiO nanowall array exhibits better electrochemical performances with higher coulombic efficiency and better cycling performance as compared to the dense NiO film. The NiO nanowall array shows an initial coulombic efficiency of 76%, as well as good cycling stability with a capacity of 567 mAh g^{-1} at 0.3 A g^{-1} after 50 cycles, higher than those of the dense polycrystalline NiO film (361 mAh g^{-1}). The superior electrochemical performance is mainly due to the unique nanowall array structure with shorter diffusion length for mass and charge transport.

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1. Introduction

NiO is an important material with many applications such as electrochromics [1], supercapacitors [2], and lithium–ion batteries [3–5]. Inspired by the pioneering work of Tarascon et al. [6], great efforts are devoted to nanoscale transition metal oxides for lithium–ion batteries [7–10]. Among these transition metal materials, NiO is considered to be promising anode due to its high capacity and excellent reversibility. Despite its high capacity (theoretic capacity of 718 mAh g^{-1}), the practical use of NiO for lithium–ion batteries is still hindered by large initial irreversible loss and poor capacity retention resulting from the large specific volume change causing pulverization and deterioration of active materials over extended cycling [11,12]. To overcome these problems, an effective approach is to create NiO with nanoporous structures to buffer the volume change upon cycles. Prompted by these interests, many NiO nanostructures, including nanotube [13], nanowall [14,15], nanosheet [16], nanobowel [17], nanocone[18], and mesoporous structure [19] have been synthesized by various routes and applied for lithium–ion batteries. These nanoporous structures have been demonstrated to exhibit superior performance for lithium–ion batteries due to their nanoscale porous architecture in which the Li ion diffusion path could be shortened and the inner stress caused by Li insertion/desertion could be lowered.

Recently, fabrication of vertically aligned transition metal oxide arrays directly grown on conductive substrate represents the feasi-bility of improving the electrode kinetics. In particular, self-supported nanowall structures have been considered as one of the most promising structures due to their higher surface-to-volume ratio than other one-dimensional nanostructures such as nanowires and more difficult for aggregation in comparison with nanoparticles. To date, several methods such as plasma assisted oxidation method [9], anodic electrodeposition [20], chemical bath deposition method [21], and thermal oxidation method [22,23], have been developed to prepare NiO nanowall arrays. Previously, Varghese et al. [14] reported vertically aligned NiO nanowalls on nickel foils by using a plasma assisted oxidation method and its superior electrochemical performance with a capacity of 638 mA h g^{-1} after cycling for 85 cycles. Wu and Lin [20] reported anodic electrodeposited NiO nanowalls with ultrahigh capacity of 1250 mA h g^{-1} and large initial irreversible loss of 56%. Tu's group has pioneered the NiO nanowall arrays and their composites prepared by a chemical bath deposition and their application for lithium–ion batteries [4,23]. In the present work, we report a NiO nanowall array grown on nickel foam prepared via a facile hydrothermal method and its electrochemical performance toward lithium is analyzed. The as-prepared NiO nanowall array exhibits superior performance with high specific capacity and quite good cycle life due to the unique two-dimensional porous structure.

2. Experimental

All solvents and chemicals were of reagent quality and used without further purification. The nickel nitrate, ammonium fluoride and urea were obtained from Shanghai Chemical Reagent Co. All aqueous solutions were freshly prepared with high purity water (18 MΩ cm resistance). In a typical synthesis of NiO nanowall

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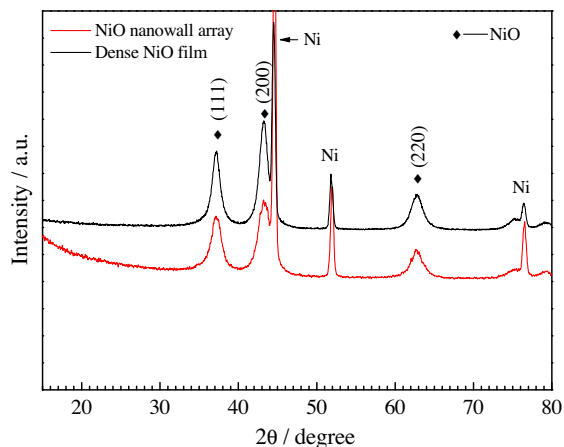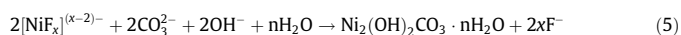E-mail address: yanxiaoyanty@126.com (X. Yan).

Fig. 1. XRD patterns of NiO nanowall array and dense NiO film grown on nickel foam.

array on nickel foam, 1 mmol Ni(NO$_3$)$_2$, 2 mmol of NH$_4$F, and 5 mmol of CO(NH$_2$)$_2$ were dissolved in 50 mL of water under stirring, respectively. Then, the homogeneous solution was transferred into a Teflon-lined stainless steel autoclave. Then a piece of clean nickel foam with a size of 3×7 cm^2 was immersed into the reaction solution. The top side was protected from solution contamination by uniformly coating with a polytetrafluorethylene tape. Hereafter, the autoclave was sealed and maintained at 110 °C for 5 h, and allowed to cool down to room temperature spontaneously. After the reaction, the substrate was taken out, completely washed with deionized water, and dried in the air. Finally, the substrate was annealed at 350 °C in argon for 2 h. The involved chemical reactions were illustrated as follows [24].

$$Ni^{2+} + xF^- \rightarrow [NiF_x]^{(x-2)-} \tag{1}$$

$$H_2NCoNH_2 + H_2O \rightarrow 2NH_3 + CO_2 \tag{2}$$

$$CO_2 + H_2O \rightarrow CO_3^{2-} + 2H^+ \tag{3}$$

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^- \tag{4}$$

$$2[NiF_x]^{(x-2)-} + 2CO_3^{2-} + 2OH^- + nH_2O \rightarrow Ni_2(OH)_2CO_3 \cdot nH_2O + 2xF^- \tag{5}$$

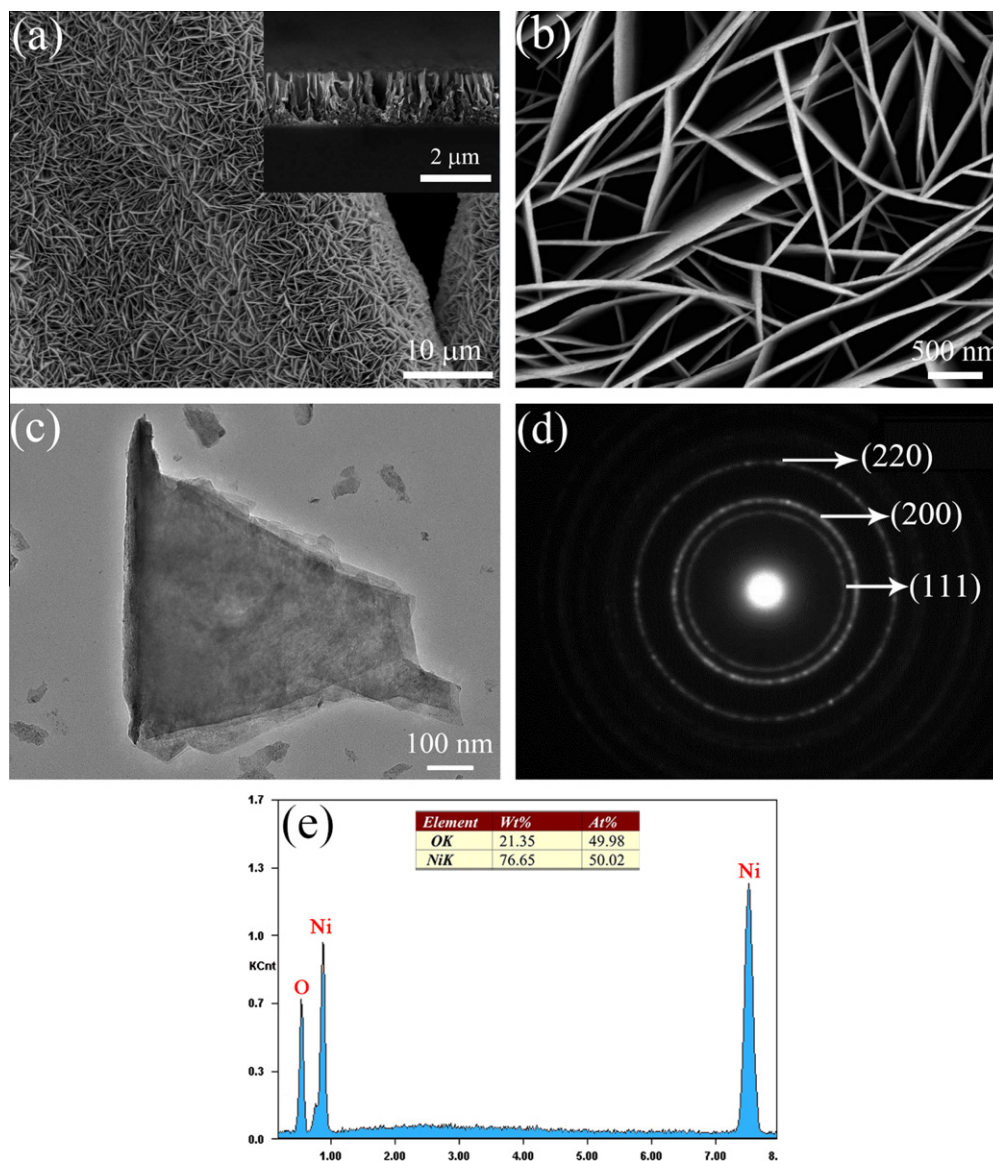The NiO forms after the annealing process as below.

Fig. 2. (a and b) SEM images of NiO nanowall array (side view of the array in inset); (c) TEM image of individual nanowall; (d) Selected area electronic diffraction (SAED) pattern of the NiO nanowall; (e) EDX spectrum of the NiO nanowalls.