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Preparation and electrochemical performance of alpha-nickel hydroxide nanowire

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ABSTRACT

Alpha-nickel hydroxide nanowire with diameter of 60 nm was successfully synthesized by conversely migrates technique. Structural and morphological characterizations were performed using power X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The capacitive properties were evaluated by cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy technique in 6 M KOH aqueous electrolyte. A maximum specific capacitance of 833 F g^{-1} was obtained at constant current of 5 mA, indicating that the α-nickel hydroxide nanowire is a promising electrode material for electrochemical capacitors.

1. Introduction

Recently, Nanostructered $Ni(OH)_2$ has attracted extensive attention due to their potential in improving the electrochemical capacitive behaviors and the performance of batteries [1]. It has been shown that $Ni(OH)_2$ exists in two common forms, α and β and α-$Ni(OH)_2$ generally exhibits superior electrochemical properties compared with the β-form. This is because the γ-phase NiOOH contains nickel species in an oxidation state of 4+ (Ni^{4+}) [2], and the average oxidation state of nickel in this phase is 3.3–3.7. This means that more than one electron is involved in the electrochemical redox reaction. However, the α-$Ni(OH)_2$ is a metastable phase and is difficult to synthesize because it changes rapidly to the β-phase during synthesis or on storage in a strong alkali. Hence, the synthesis of nanosized α-nickel hydroxide is of utmost importance. Numerous efforts have been made to stabilize the α-$Ni(OH)_2$ by partial substituting Al [3], Zn [4] or Mn [5] ions for Ni ions. The available capacity and energy density, however, usually decrease with increasing the percentage of substitution since the substitution element does not take part in electrochemical redox reaction.

As inspired by both the potential applications of $Ni(OH)_2$ and the novel properties of nanoscale materials, considerable effort recently has been focused on the synthesis of nickel hydroxide nanostructures with different morphologies, such as plateletlike [6], Flowerlike [7], nanoparticle [8], microspheres [9], nanotub [10] and nanorode [11]. Among the different shapes, one-dimensional nanostructured of $Ni(OH)_2$ has received increased interest because it can provide short diffusion path lengths to ions and excitons, leading to high charge/discharge rates. Martin's group has demonstrated that high surface area nanowire of SnO_2 and V_2O_5 have significantly improved rate capability compared with thin films of the same material [12,13].

More recently, some methods have been developed to prepare $Ni(OH)_2$ nanocrystals with one-dimensional nanostructured morphologies. Cai et al. [10] prepared $Ni(OH)_2$ meso-/nanotubes by chemical deposition using anodic alumina membrane as template. Yang et al. [14] synthesized nickel hydroxide nanoribbons via hydrothermal treating. Liang and Li [11] reported the synthesis of $Ni(OH)_2$ nanorods with 40–90 nm in diameters by hydrothermally treating the mixture of $NiCl_2$ and aqueous ammonia at 180 °C. However, some of the above-mentioned methods complicate the synthetic processes, and the achieved products are β phase. Up to now, there are few of the works on the fabrication of $Ni(OH)_2$ nanowires [15], especially α-$Ni(OH)_2$ nanowires. Moreover, to the best of knowledge, the electrochemical properties of α-$Ni(OH)_2$ nanowires have not been studied so far.

In theory, a large number of intersecting nanowires can form three-dimensional network structure, which will result in a shorter current conducting pathway in the active material and a better degree of contact between the nickel electrode and the electrolyte. In our previous work, the Ag nanowire was used as electrochemical capacitor electrode, which showed excellent electrochemical performance [16]. In this work, α-$Ni(OH)_2$ nanowires were synthesized without substitution by conversely migrate technique [17],

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their morphology and crystal were characterized by FESEM and XRD respectively. Cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge/discharge techniques were carried out to examine the electrochemical performance of them.

2. Experimental

All of the chemical reagents used in this work were analytical grade; they were obtained from the commercial market and used without further purification. The anodic alumina oxide templates were formed by a two-step anodization process as described previously by Jessensky et al. [18,19]. Here, the pores of the AAO prepared are about 60 nm in diameter and about 50 μm in length with interpore spacing of 100 nm. In course of our experiment the Ni^{2+} in 0.5 M $Ni(NO_3)_2$ solution and OH^- in 1 M ammonia solution was transported into the nanochannels of the AAO by diffusing conversely. In this case the nanochannels of the AAO template acted as a micro-cell inside which the $Ni(OH)_2$ precipitations with one dimension form were formed. After 3 h, the template fully filled with $Ni(OH)_2$ precipitations was washed repetitiously with distilled water to completely remove reaction residuals from the template. Finally the template was dried under vacuum at 60 °C for 1 h, and then it was placed in 3 M NaOH solution to dissolve away the framework of the template and reveal all the $Ni(OH)_2$ nanowires. After purified by repeatedly washing, the products were completely transferred into a vessel filling with ethanol.

The morphology of the samples was observed by field emission scanning electron microscopy (JSM-6701F, Japan). X-ray diffraction (XRD) data were collected using a Rigaku D/MAX-2400 diffractometer (Japan) with Cu Kα radiation ($\lambda = 1.5418$ Å) operating at 40.0 kV, 60.0 mA.

Electrodes for electrochemical capacitors were prepared by mixing the active materials with 10 wt% acetylene black, 10 wt% conducting graphite and 5 wt% polytetrafluoroethylene (PTFE) of the total electrode mass. A small amount of ethanol was added to this composite to make a more homogenous mixture, which was pressed on nickel foam sheet.

Electrochemical measurements of the samples were carried out on a CHI660B electrochemical working station (CH Instrument). A typical three-electrode cell was employed. The electrolyte was 6 M KOH solution. The prepared electrode with a geometric area of 1 cm^2 was used as the working electrode. A platinum foil served as the counter electrode, and an Hg/HgO electrode as the reference electrode. Cyclic voltammetry and galvanostatic charge–discharge method were used to measure capacitive properties of the electrodes. All solutions used in this work were prepared with double-distilled water. All electrochemical experiments were carried out at room temperature and the potentials were referred to Hg/HgO.

3. Results and discussion

The power XRD pattern of the as-prepared $Ni(OH)_2$ is shown in Fig. 1. The result demonstrate that nickel hydroxide exist as $Ni(OH)_2{\cdot}0.75H_2O$. The sample exhibits α-$Ni(OH)_2$ with a rhombohedral P3 structure. As we know, α-$Ni(OH)_2$ was hydrated structure with a long triple-layered unit cell, in which anions were intercalated in the interlayer regions. When Al^{3+} was introduced in the lattice of α-$Ni(OH)_2$, anions strongly anchored the positively charged brucite-type layer and stabilized the structure in a variety of stressful conditions [20]. In this case the nanochannels of the AAO template acted as a micro-cell inside which the α-$Ni(OH)_2$ precipitations with one dimension form were formed as a result of aluminum guidance function. Thus, a certain amount of Al^{3+} inevitably enters into the lattice inside, which could successfully stabilize the α-$Ni(OH)_2$ structure in strong alkaline medium [21].

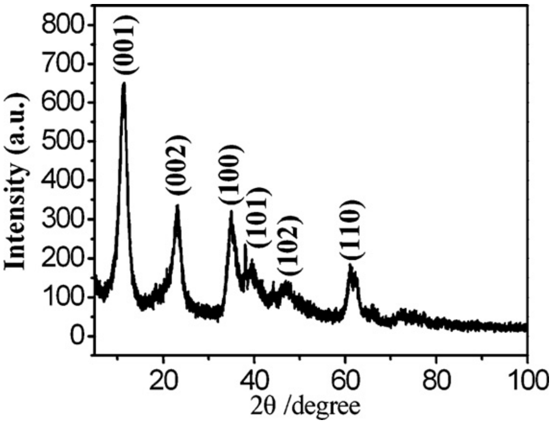

Fig. 1. XRD pattern of α-$Ni(OH)_2$ nanowires.

Fig. 2a shows the surface morphology of the typical α-$Ni(OH)_2$ nanowires at different magnifications. The lengths of the most nanowires are more than 5 μm, and aspect ratios are in ranging from 80 to 100. The inset in the top right corner of Fig. 2a is an FESEM image of $Ni(OH)_2$ nanowires at a higher magnification. All of them have a uniform diameter of about 60 nm, which is approximately consistent with pore diameter of the used AAO template. However, a small amount of nanorods is also observed in the sample, which may be due to some negative factors such as obstruct of nano-channels in the reaction process, or break of nanowires in the cleaning, separating and dispersing process. Fig. 2b reveals a cross section of an AAO template embedded with $Ni(OH)_2$ where the alumina matrix of the template has been partially dissolved away. This shows that the $Ni(OH)_2$ nanowires are arranged roughly parallel to one another with a smooth surface alignment. It is correlative to that the AAO template had an array of densely parallel nanoholes arranged in a hexagonal fashion.

Fig. 3 shows the CV curves of the α-$Ni(OH)_2$ nanowire electrode at different scan rates in 6 M KOH electrolyte solution. As can be seen in Fig. 3, the CV curve only consists of a pair of strong redox peaks, which appreciably differ from that the literature reported [22]. The two strong redox reaction peaks are responsible for the pseudo capacitive capacitance. The anodic peak is due to the oxidation of $Ni(OH)_2$ to NiOOH and the cathodic peak is for the reverse process. This indicates that the capacitance characteristics are mainly governed by Faradaic reactions and not by pure electric

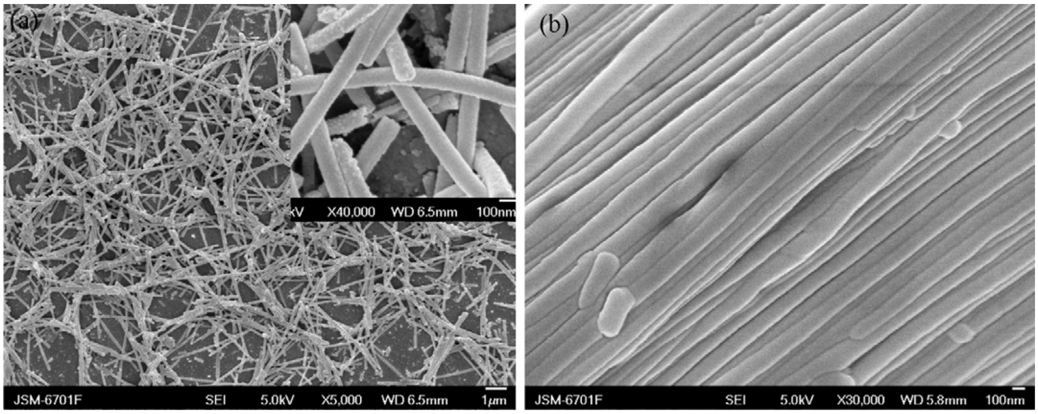

Fig. 2. (a) A FESEM image showing the morphology of $Ni(OH)_2$ nanowires, the inset is an FESEM image of $Ni(OH)_2$ nanowires at a higher magnification. (b) FESEM image of a cross section of $Ni(OH)_2$ nanowire arrays after partially removing the AAM.