



RAPID COMMUNICATION

High performance porous nickel cobalt oxide nanowires for asymmetric supercapacitor



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Abstract

In this work, we present the formation of porous NiCo oxide nanowires from single crystal nickel cobalt bimetallic carbonate hydroxide nanowires (NiCo cNW) for supercapacitor applications. High aspect ratio NiCo cNWs are found to evolve from highly crystalline nickel cobalt layered double hydroxides through a dodecyl anion assisted crystallization-dissolution-recrystallization process. The porous nickel cobalt oxide ($\text{Ni}_x\text{Co}_{3-x}\text{O}_4$) nanowire array is formed by the heat treatment of nickel cobalt bimetallic carbonate hydroxide nanowires on nickel foam (NF) for the assembly of supercapacitors. This binder free electrode shows a high specific capacitance of 1479 F g^{-1} at 1 A g^{-1} and 792 F g^{-1} at 30 A g^{-1} , indicating an excellent rate capability. Asymmetric device is constructed from $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ on NF and activated carbon (AC) with an operation potential from 0 to 1.6 V. It shows a high specific capacitance of 105 F g^{-1} at a current density of 3.6 mA cm^{-2} , while it maintains 58.7 F g^{-1} at 89.4 mA cm^{-2} . In addition, the asymmetric device shows good stability towards long time charge-discharge cycles.

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Introduction

Supercapacitors, a promising energy storage device, have received tremendous attention because of their high power density and excellent cycling life [1,2]. Early transition metal oxides such as MnO_2 [3], V_2O_5 [4], NiO [5–7], and Co_3O_4 [8], are a group of very promising supercapacitor electrode materials to replace expensive and toxic RuO_2 [9,10]. Among various materials, spinel type nickel cobalt oxide ($\text{Ni}_x\text{Co}_{3-x}\text{O}_4$, $0 < x \leq 1$) is of particular interest.

It offers many advantages such as abundant electrochemical reaction, low cost and environmentally benignity [11]. Moreover, it has much higher electrical conductivity ($\sim 10^{-1}$ – 10 S cm^{-1}) than popular materials like MnO_2 ($\sim 10^{-6}$ – $10^{-5} \text{ S cm}^{-1}$), NiO and Co_3O_4 ($\sim 10^{-3}$ – $10^{-2} \text{ S cm}^{-1}$) [12,13]. However, previous attempts to fabricate $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ supercapacitor electrode materials encountered several major problems such as low capacitance [14,15], poor cycling stability [16], and low active material loading mass [11]. The main causes for the unsatisfactory performance can be attributed to three aspects: (1) the use of insulating polymer binders [11,14–16], which trades off the electric conductivity; (2) the thick slurry layer in electrode fabrication process leads to peeling of active material

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during cycling [16]; (3) random assembly of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocrystals are not favorable for electron conduction during electrode reaction. Thus, it is of great importance to realize effective synthesis strategies for the growth of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ materials to achieve enhanced electrochemical performance.

It is of great interest to design and fabricate one dimensional (1D) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanostructure to fully exploit their potential in electrochemical energy storage (theoretical specific capacitance over 3000 F g^{-1}). 1D nanostructures directly grown on current collector enhances the energy storage properties owing to its fast redox reaction and short electrolyte diffusion path [3,17,18]. Moreover, the exclusion of insulating binders greatly enhances the rate performance. However, there were only a few attempts to synthesize 1D structure of $\text{Ni}_x\text{Co}_{1-x}\text{O}_4$. Li et al. synthesized Co_3O_4 and $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ microwires with a diameter over 500 nm using ammonia evaporation method [19,20]. Similar method was adopted to fabricate Co_3O_4 nanowire and/or its hybrid material [21-23]. However, the resultant nanowire diameter is still large and this limits the material utilization in bulk region. Meanwhile, the excessive use of ammonium hydroxide during the synthesis is also not environmental friendly. An alternative method for $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ polycrystalline nanowire synthesis was reported by Xiao et al., using a urea induced bimetallic carbonate hydroxide nanowire formation method [24]. The transformation into polycrystalline $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is achieved by thermal treatment. Well-separated nanowires can be formed on specific substrates [25]. However, the yet poor electrochemical performance (specific capacitance only 658 F g^{-1} at 1 A g^{-1}) of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ bulky structure still limits the real application. Previous reports on the fabrication of 1D $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanostructures either shows unsatisfactory large diameter, or low aspect ratio with bulky structure, which hinders electron conduction and electrolyte diffusion. Therefore, to realize high performance $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ 1D material is highly desirable for the development of high performance supercapacitor.

Hexamethylteramine (HMTA) is widely used as hydrolysis reagent to produce highly crystalline bimetallic layered double hydroxides (LDHs), which generally possess a sheet like morphology [26-28]. In this contribution, we present an unconventional transformation of single crystalline Ni Co LDHs into Ni Co bimetallic carbonate hydroxide nanowires through a crystallization-dissolution-recrystallization process without the assistance of specific substrate. Sodium dodecyl sulfate is found to be crucial to initiate such transformation. High aspect ratio polycrystalline $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ ($x=0.6$) nanowires are achieved from nickel cobalt bimetallic carbonate hydroxide nanowires by heat treatment. Polycrystalline $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires directly grown on nickel foam (NF) are fabricated to demonstrate the advantage of high aspect ratio 1D structure in electrochemical application. Such binder free and highly conductive $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ electrode exhibits a high specific capacitance of 1479 F g^{-1} at 1 A g^{-1} and 792 F g^{-1} at 30 A g^{-1} with high loading mass. As a result, high performance asymmetric supercapacitor device is successfully assembled based on $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ on NF and activated carbon (AC). It shows a high specific capacitance of 105 F g^{-1} at a current density of 3.6 mA cm^{-2} , while it maintains 58.7 F g^{-1} at 89.4 mA cm^{-2} . In addition, the asymmetric device shows good stability towards

long time charge-discharge cycles. This new strategy provides a perfect platform for further electrochemical applications, such as energy storage, electrochemical catalysis.

Materials and methods

Materials

All chemicals were purchased from Sigma and were used without further purification. The nickel foam was purchased from Changsha Liyuan New Materials Co. A piece of pre-cleaned nickel foam substrate ($1 \text{ cm} \times 1 \text{ cm}$) was used as a substrate for the growth of materials. $0.1552 \text{ g Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.53 mmol), $0.0776 \text{ g Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.26 mmol), $0.0700 \text{ g hexamethylenetetramine}$ (HMTA, 0.5 mmol) and $0.0288 \text{ g sodium dodecyl sulfate}$ (SDS, 0.1 mmol) were added subsequently into 20 ml DI water under continuous stirring. After complete dissolution, the pink transparent solution was transferred into a $40 \text{ ml Teflon lined autoclave}$ and kept at $140 \text{ }^\circ\text{C}$ for 14 h . After reaction, the substrate was collected and washed with DI water and ethanol several times. After drying in oven at $60 \text{ }^\circ\text{C}$ for 4 h , the substrate was sintered to $300 \text{ }^\circ\text{C}$ at a ramp of $2 \text{ }^\circ\text{C min}^{-1}$ and maintained for 4 h . This sample was labeled as NW-NF and was used for electrochemical characterization.

Method

The products were characterized using X-ray powder diffractometry (XRD; Shimadzu XRD-6000, Cu K α radiation) at a scan rate of 2° min^{-1} , scanning electron microscopy (FESEM; JEOL, JSM-7600F), transmission electron microscopy (TEM; JEOL, JEM-2100) and electron dispersive X-ray spectroscopy (EDX). N_2 adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements using TriStar II surface area and porosity analyzer.

The electrochemical tests of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ on NF were first conducted using a three electrode system in 2 M KOH using Autolab PGSTAT 30 potentiostat. The reference electrode was Ag/AgCl electrode and counter electrode was Pt plate. The loading mass of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ was acquired by measuring electrode with a microbalance with accuracy of 0.01 mg . Typically, the loading mass of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ was around 2.50 mg cm^{-2} . Asymmetric supercapacitor device was assembled into a coin cell with optimized $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ to activated carbon weight ratio using filter paper as separator. The mass of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ was around 3.50 mg cm^{-2} and the mass of activated carbon is around 14.00 mg cm^{-2} .

Results and discussion

Structural characterization

The crystal structure of porous ternary oxide nanowire is first investigated by XRD. As shown in Figure 1a, the diffraction peaks of nanowire sample match well with the spinel structure of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ (PDF #200781: $a=8.11 \text{ \AA}$). The chemical composition of the sample is further examined by TEM based EDX, as shown in Figure 1b. The presence of Ni and Co elements confirms the Ni substitution of Co in spinel

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