Facile Synthesis of Co_3O_4 Nanowires Grown on Nickel Foam with High Electrochemical Capacitance

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Summary: Co_3O_4 nanowire arrays freely standing on nickel foam were prepared by a hydrothermal method. The detailed microstructure and morphology of Co_3O_4 nanowire were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) etc. The results indicated that the Co_3O_4 nanowires have diameters of around 80 nm and composed of many nanoparticles with diameters of about 20 nm. The electrochemical results show that Co_3O_4 nanowires demonstrate enhanced specific capacitance (616 F g^{-1}) and electrochemical reversibility, and the specific capacitance of nanowires only decreased 19% after 3000 charge-discharge cycles

Keywords: Cobalt oxide; Nanowires; Supercapacitor; Nickel foam.

Introduction

Supercapacitors, namely electrochemical capacitors, have attracted much more attention due to their higher power density, longer cycle life and fast charge/discharge process compared to the commercial chemical batteries [1-3]. The electrode material is one of the important factors to affect the performances of supercapacitors. The electrode materials can be classified into three types: carbon, metal oxides, and conducting polymers. Many efforts have been made to research metal oxides, due to their much higher specific surface area and electrical conductivity. RuO_2 have been used as pseudocapacitive electrode materials once upon a time, however the high cost limit their commercialization. Therefore, the development of electrode materials with low cost and high performance has attracted considerable attention. Transition metal oxides such as NiO, MnO_2, Co_3O_4 and Fe_2O_3 have been widely studied [4-6]. Among them, Co_3O_4 are reported to be promising electrode materials due to their great reversibility, high theoretical specific (3560 F g^{-1}), high redox activity and quite ordered structures [7]. For instance, Li et al synthesized Co_3O_4 thin film by a chemical bath deposition, which showed a large specific capacitance of 227 F g^{-1} at 0.2A g^{-1}, and when the specific current increased to 1.4A g^{-1} the specific capacitance only decreased 33% [8]; Zhang et al prepared porous Co_3O_4 nanoflake array film grown on nickel foam by a hydrothermal synthesis. The results showed that the specific capacity was 210, 289 and 351 F g^{-1} at 2 A g^{-1} tested at 5 ºC, 25 ºC and 60 ºC, respectively, and the remaining specific capacity is 187, 342 and 124 F g^{-1} tested at 5 ºC, 25 ºC and 60 ºC. After 4000 cycles at 2 A g^{-1}[9]; Liao et al synthesized novel flower-like porous Co_3O_4 hierarchical microspheres by a facile hydrothermal strategy and template-free method. The results demonstrated that Co_3O_4 exhibited a large specific capacitance of 541.9 F g^{-1} and 483.8 F g^{-1} at 5 mV s^{-1} and 1 A g^{-1}, respectively [10]. Furthermore, after a 2000 cycles test, the specific capacity reduced to 89.5%. In addition to all these achievements, many researches have made a great contribution in the study of Co_3O_4 materials, but the results are still unsatisfying. Therefore, how to improve the specific capacitance is still a challenge.

In this paper, Co_3O_4 nanowires grown on nickel foam were prepared by hydrothermal method. The results indicated that the nanowires showed a larger specific surface area and good electrochemical performance, and that was a promising electrode material.

Experimental

All the reagents were analytical grade and were used without further purification.

Co_3O_4 nanowire arrays supported on nickel foam were prepared via a hydrothermal method [11-14].The process of the preparation of Co_3O_4 nanowire can be described briefly. 2g $Co(NO_3)_2\cdot 6H_2O$, 1g Hexa decyl trimethyl ammonium Bromide (CTAB) , 6 ml water and 30 ml absolute methanol were mixed together under vigorous magnetic stirring. The obtained solution was then transferred into a 40 ml Teflon- lined stainless steel autoclaves. A piece of nickel foam (1

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cm×1 cm) was added to the solution, and then the autoclave was put in an oven at 180ºC for 24 h to allow the growth of Co_3O_4 nanowires.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-IIIB diffractometer using Cu Kα radiation (λ=1.5406 Å). The morphology of the samples was inspected with a field-emission scanning electron microscope (SEM, Philips XL 30). Transmission electron microscopy (TEM) and images were obtained from a FEI Tecnai G2 S-Twin transmission electron microscope with a field emission gun operating at 200 kV.

The electrochemical properties of the products were investigated under a three-electrode electrochemical cell. The nickel foam supported Co_3O_4 nanowires were used as the working electrode, platinum foil acted as counter electrode, and a saturated calomel electrode (SCE) were used as reference electrodes. KOH (6.0 M) aqueous solution was used as the electrolyte. Cyclic voltammetry (CV) tests were measured between 0 V and 0.5 V (vs. SCE) at scan rates of 5, 10, and 20 mV s^{-1}. Galvanostatic charge/ discharge curves were done in the potential range of 0-0.5 V (vs. SCE) at current densities of 5, 10, and 20 mA·cm^{-2}, and EIS measurements were also carried out in the frequency range from 100 kHz to 0.05 Hz.

Results and Discussion

Fig. 1 shows the XRD patterns of Co_3O_4 nanowire. The main peaks at 2θ values of 19.00◦, 31.14◦, 36.58◦, 38.45◦, 59.30◦and 65.20◦belong to the crystal planes of (111), (220), (311), (222), (511) and (440), which indicates that pure Co_3O_4 (JCPDS card No. 42-1467) formed. While the peaks at 2θ values of 44.68◦and 55.57◦correspond to Ni substrate (JCPDS no. 01-1258).

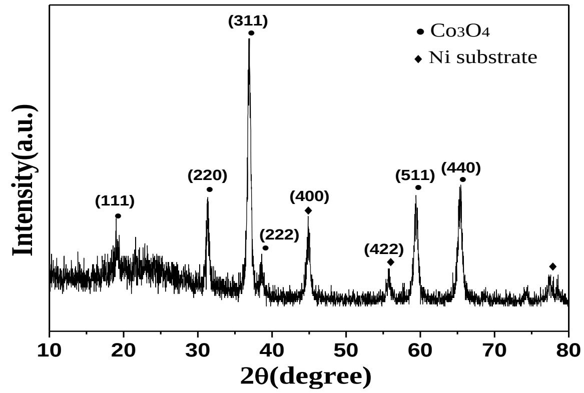


Fig. 1: XRD patterns of Co_3O_4 nanowire.

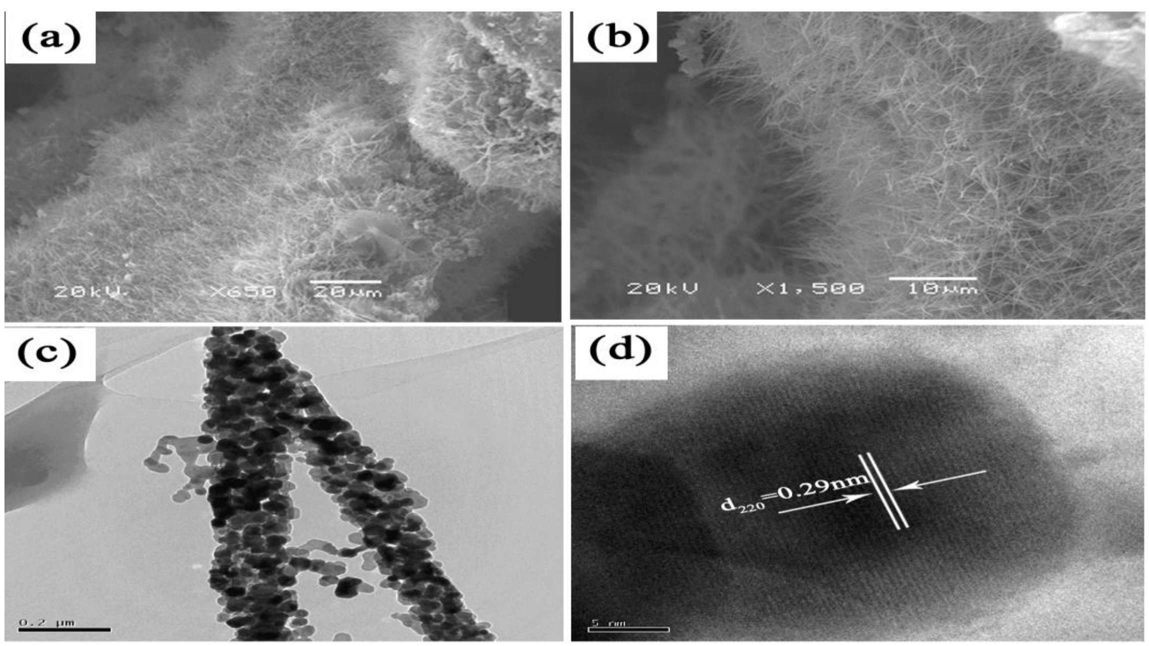


Fig. 2: SEM and TEM images of different samples: (a) SEM image of Co_3O_4 nanowire; (b) Magenified SEM image of Co_3O_4 nanowire; (c) TEM image of Co_3O_4 nanowire; (d) HRTEM image of Co_3O_4 nanowire.

Fig. 2 (a) (b) shows SEM image of Co_3O_4 nanowire, it can be seen that Co_3O_4 nanowire grow on nickel foam with diameters range from 80 to 100 nm. The morphologies of Co_3O_4 nanowire are further characterized by TEM (Fig. 2 (c)). It indicates that the Co_3O_4 nanowires are composed of nanoparticles with diameters of about 20 nm. The lattice fringe in Fig. 2 (d) with interplanar spacing of 0.29 nm is assigned to the (220) planes of the Co_3O_4 crystal [15].

A possible mechanism of Co_3O_4 is suggested as follows:

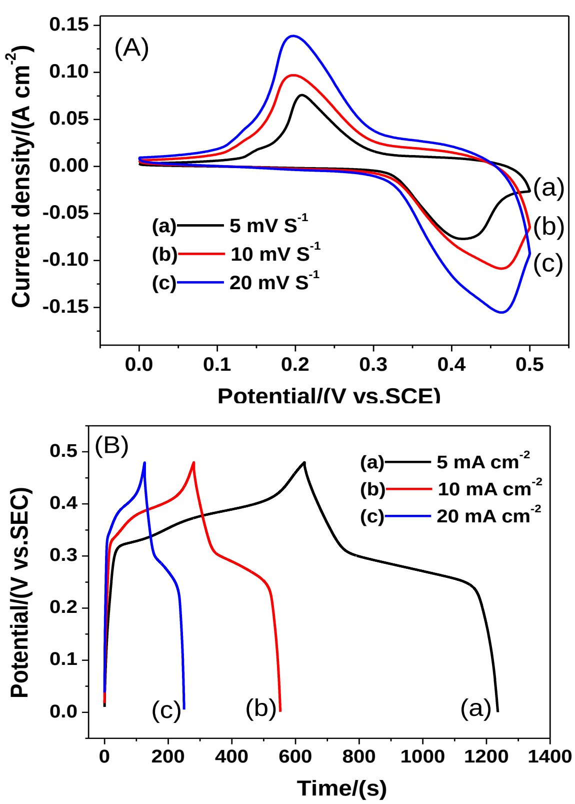
$$CH_3OH + H_2O \longrightarrow CH_3OH_2^+ + OH^-$$

$$Co(NO_3)_2 \longrightarrow Co^{2+} + NO_3^-$$

$$Co^{2+} + OH^- \longrightarrow Co(OH)_2$$

$$Co(OH)_2 + O_2 \longrightarrow Co_3O_4 + H_2O$$

Hydroxyl ions is produced from methanol, and cobalt ions (Co^{2+}) from the $Co(NO_3)_2$ solution react with hydroxyl ions to form $Co(OH)_2$. Co_3O_4 is generated after calcined.



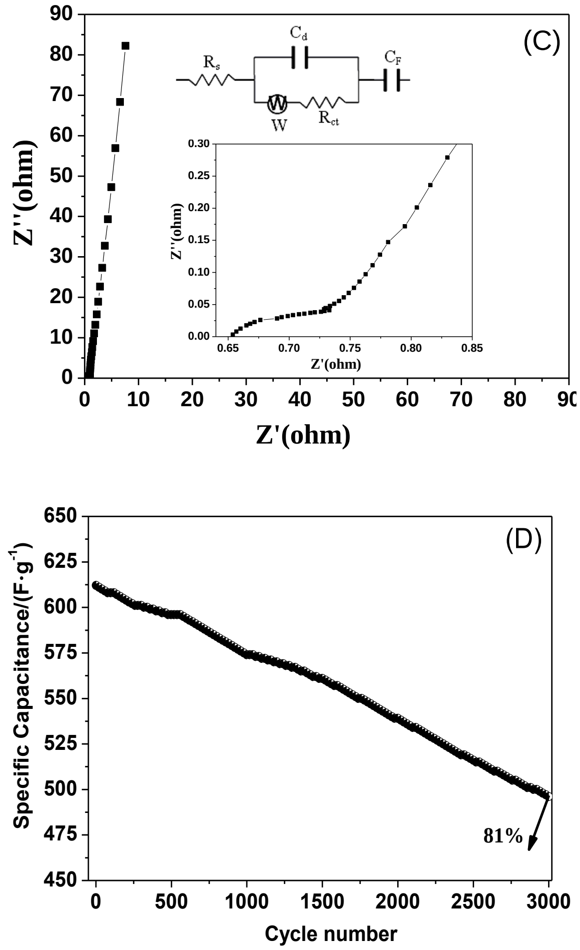


Fig.3: CV curves of Co_3O_4 nanowire at different scan rates of 5, 10 and 20 mV ·s^{-1}, calcined at 500 °C, in 6.0 M KOH solution (A); Galvanostatic charge/discharge curves of Co_3O_4 nanowire at different current density of 5, 10 and 20 mA·cm^{-2} (B); Electrochemical impedance spectras (EIS) of Co_3O_4 nanowire and equivalent circuit (C); Cycling performance of Co_3O_4 nanowire at constant current of 5 mA·cm^{-2}(D).

Fig. 3 (A) shows CV curves of Co_3O_4 nanowire at different scan rates of 5, 10 and 20 mV ·s^{-1}. Two pairs of redox peaks are observed, which attributed to the transition of Co(II)/Co(III) and Co(III)/Co(IV). The possible redox reactions can be described as follows: [16-17]

$$Co_3O_4 + OH^- + H_2O \longleftrightarrow 3CoOOH + e^-$$

$CoOOH+OH^- \longleftrightarrow CoO_2+H_2O+e^-$

with the increase of the scan rate, the anodic peaks shifted toward positive potential and cathodic peaks shifted toward negative, indicating the quasi-reversible feature of the redox couples [18-19]. Fig.3 (B) indicates galvanostatic charge/discharge curves of Co_3O_4 nanowire at various current density of 5, 10 and 20 mA·cm^{-2}. The specific capacitance can be caculated according to the following equation [20].

$$C_m = \frac{I \times \Delta t}{\Delta V \times m} \quad (1)$$

where C_m is the specific capacitance of the electrode (F g^{-1}), I is the charge/discharge current (A), Δt is the discharge time (s), ΔV is the potential drop during discharge, and m is the mass of active electrode materials. According to Eq (1), the specific capacitance values of the Co_3O_4 nanowires are calculated to be 616, 540 and 480 F g^{-1} at the current density of 5, 10 and 20 mA·cm^{-2}, respectively. The large values of capacitance can be attributed to the large specific surface area of the nanowires [21]. With the increasing of the current density, the specific capacitance values decreased. This indicates that the insertion and extrusion of OH^- is slow when the current density is lower, and more active surface area can be provided for Faradaic reactions.

Fig.3 (C) shows the electrochemical impedance spectras (EIS) of Co_3O_4 nanowire. The equivalent circuit in accordance with the Nyquist plot is presented in Fig.3 (C) (upper right inset). The value of R_s (the solution resistance of the electrochemical system) can be read from the intersection With the X axis, and then the R_s of Co_3O_4 nanowire is 0.65Ω. The value of R_{ct} (Faradaic interfacial charge transfer resistance [22]) can be read from the semicircle of EIS, so the R_{ct} of Co_3O_4 nanowire is 0.1Ω.

Fig.3 (D) indicates cycling performance of Co_3O_4 nanowire at constant current of 5 mA·cm^{-2}. It can be seen that the specific capacitance only decreased 19% after 3000 test cycles, which demonstrates that the Co_3O_4 nanowire has a stronger stability, and it is appropriate for long time capacitor applications in KOH solution.

Conclusions

Co_3O_4 nanowire arrays freely standing on nickel foam were prepared by a hydrothermal method. The results indicated that the Co_3O_4 nanowires have diameters of around 80 nm and composed of many nanoparticles with diameters of about 20 nm. The electrochemical properties suggest that Co_3O_4 nanowire has good electrochemical reversibility and displays superior capacitive performance with large capacitance (616 F g^{-1}), as well as excellent cycling stability after 3000 cycles.

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