Facile Synthesis of Co_3O_4 Nanowires on Nickel Foam for Supercapacitor Electrodes

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Abstract: One-dimensional Co_3O_4 nanowires have been successfully fabricated on nickel foam hydrothermal method and followed by a calcinating process. Electrochemical data reveals that the as-synthesized Co_3O_4 nanowires can deliver a specific capacitance (SC) of 1631 F g^{-1} at a current density of 0.5 A g^{-1} and remain 771 F g^{-1} at 10 A g^{-1} in a 1 M KOH aqueous solution. This outstanding electrochemical performance can be explained to the high conductivity and high pseudocapacitive contributions from the nanowires.

***Keywords*:** Co_3O_4 nanowires, Hydrothermal method, Nickel foam, Supercapacitor

INTRODUCTION

Development of advanced nanostructured materials which is critical to research in the field of electrochemical energy storage systems has recently gained momentum [1]. This situation involved in portable consumer electronics and hybrid electric vehicles, to industrial scale power and energy management. Research on both high energy density and high power density requirement has lead to an energy storage device [2]. Thanks to their capability to deliver high power performance and extremely long cycle life, supercapacitors was found to meet this requirement. Supercapacitors can be integrated or replaced batteries in the energy storage system [3]. Researchers are trying to extend the energy storage capacity (i.e. capacitance and operating voltage) and lifetime and simultaneously reduce the price of such capacitors. To achieve these purpose, transition metal oxides/hydroxides (MnO_2, RuO_2, NiO, Co_3O_4, V_2O_5, $Co(OH)_2$, $Ni(OH)_2$ etc.) are extensively investigated as electrode materials for their higher energy density and specific capacitance values than carbon materials due to their faradaic redox reactions [4]. Among them Co_3O_4 has maximum theoretical pseudocapacitance of about 3560 F g^{-1} [5]. The metal oxide/hydroxide electrode materials storage charges not only the electrostatically as in the carbon materials but also the electrochemical redox reactions between the electrode material and the electrolyte ions [6]. Moreover, capacitance and charge storage mechanism in supercapacitors depends on the electrode materials. Nanoscale; increases the surface area of the electrode material as well as increases the active sites between the electrode material and the electrolyte solution and shortens the ionic diffusion pathways during the redox reaction [4].

MATERIALS AND METHODS

In this work, we synthesized Co_3O_4 nanowires on nickel foam by hydrothermal method. The solutions were obtained by mixing 2 mmol of cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) and 8 mmol of ammonium fluoride (NH_4F) and 8 mmol urea (CH_4N_2O) separately in 40 ml ultra-pure water for 1 h in the magnetic stirrer. The prepared solution and the 3D-nickel foam substrate were placed in separate teflon-lined, stainless-steel autoclave and heated to 120°C for 12 h. Then the sample was annealed in tube furnace for 3 h in a 300°C air environment. The crystal structures and morphologies of the Co_3O_4 nanowires were determined by using X-Ray Diffraction (PANalytical Empyrean, Cu-Kα, λ=1.54060 Å), Field Emission Scanning Electron Microscopy (FESEM: FEI Quanta 450 FEG), Energy Dispersion X-Ray Spectroscopy (EDAX, AMETEK Materials Analysis Division), and Raman Spectroscopy (WITec alpha300R, λ=532 nm). The electrochemical performance was determined by Cyclic Voltammetry (CV) and Galvanostatic Charge Discharge (GCD) analyses using a Gamry Reference 3000 potentiostat instrument.

The electrochemical measurements were performed using 1 M KOH aqueous electrolyte solution. Platinum foil (5×1 cm^2 in area) and the saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The Ni-foam-supported Co_3O_4 nanowires electrode (5×1 cm^2) were immersed in electrolyte and were used directly as a working electrode. The electrochemical measurements were performed in a three-electrode electrochemical cell at room temperature. The specific capacitance (C) was calculated by equation (1):

$$C = \frac{Ixt}{mxV} \tag{1}$$

where *I* is the constant discharge current, *t* is the discharge time, *V* is the potential window and *m* is the mass of the active material. The mass of the active material of the sample was 1.4 mg cm^{-2}, and the specific capacitance and the current density values were calculated according to this mass.

RESULTS AND DISCUSSION

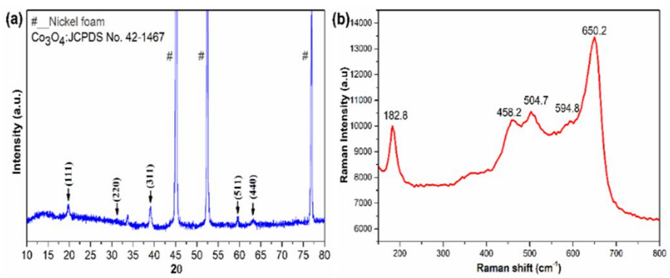

Fig. 1. (a) XRD pattern and (b) Raman analyzes of Co_3O_4 nanowires.

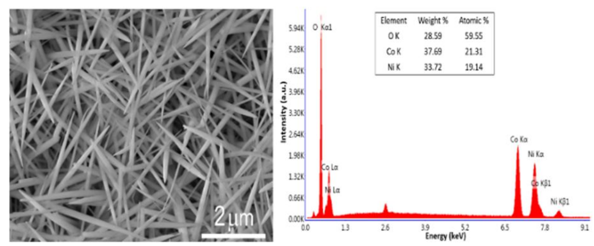

Fig. 2. FESEM image and EDS analyzes of of Co_3O_4 nanowires.

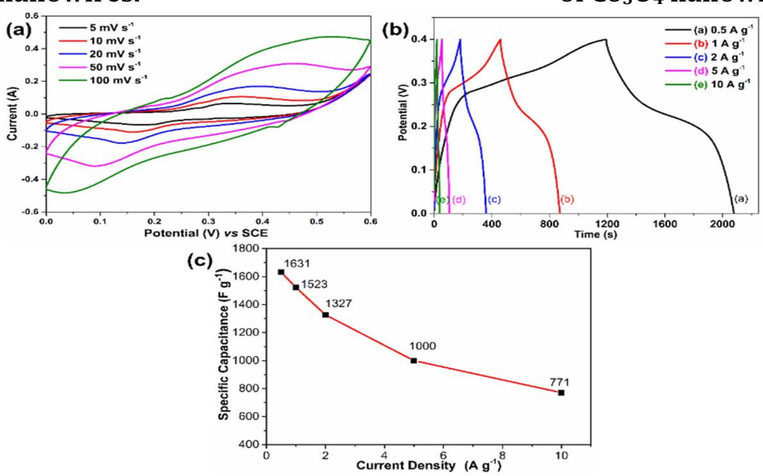

Fig. 3. (a) The CV curves at different scan rates, (b) the GCD curves at different current densities, (c) the specific capacitance vs. current density.

CONCLUSIONS

In conclusion, Co_3O_4 nanowires were synthesized on Ni foam by the hydrothermal method. According to GCD measurements at 0.5 A g^{-1} current density, specific capacitance was obtained 1631 F g^{-1} for Co_3O_4 nanowires. This electrode design can be extended to grow other mesoporous metal oxides on the substrate to fabricate high-performance supercapacitor electrode.

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