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Nickel cobaltite nanograss grown around porous carbon nanotube-wrapped stainless steel wire mesh as a flexible electrode for high-performance supercapacitor application

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ABSTRACT

Nickel cobaltite nanograss with bimodal pore size distribution (small and large mesopores) is grown on various electrode substrates by one-pot hydrothermal synthesis. The small pores (<5 nm) in the nanograss of individual nanorods contribute to large surface area, while the large pore channels (>20 nm) between nanorods offer fast transport paths for electrolyte. Carbon nanotubes (CNTs) with high electrical conductivity wrap around stainless steel (SS) wire mesh by electrophoresis as an electrode scaffold for supporting the nickel cobaltite nanograss. This unique electrode configuration turns out to have great benefits for the development of supercapacitors. The specific capacitance of nickel cobaltite grown around CNT-wrapped SS wire mesh reaches 1223 and 1070 F g^{-1} at current densities of 1 and 50 A g^{-1}, respectively. CNT-wrapped SS wire mesh affords porous and conductive networks underneath the nanograss for rapid transport of electron and electrolyte. Flexible CNTs connect the nanorods to mitigate the contact resistance and the volume expansion during cycling test. Thus, this tailored electrode can significantly reduce the ohmic resistance, charge-transfer resistance, and diffusive impedance, leading to high specific capacitance, prominent rate performance, and good cycle-life stability.

1. Introduction

Recently, much effort has been made aiming to explore the high-performance supercapacitors due to the high power demand of the new electrical systems [1]. Traditional electric double-layer capacitors (EDLCs) store charges in electric double layer at the interface between electrode and electrolyte. Electrochemical supercapacitors (ECs) not only store charge like the EDLCs, but they also exhibit faradaic reactions between electrode and electrolyte in the appropriate potential window. Through redox faradaic reactions, ECs can store much more charge than traditional EDLCs. Some materials like carbon-based materials, metal oxides, metal sulfides, and conducting polymers have turned out to be highly perspective active electrode materials for ECs [1–4]. Among these candidate materials, nickel and cobalt-based oxides such as nickel cobaltite ($NiCo_2O_4$) are promising for application in alkaline ECs due to their high specific capacitance, superior stability, and good corrosive resistance in the alkaline electrolyte [5–8].

Nickel cobaltites with spinel structure exhibit better electrochemical activity and electrical conductivity than the pure nickel and cobalt oxides, making them suitable for application in ECs with alkaline media [5,7]. To achieve both high energy density and power density, it is generally essential that the electrode materials exhibit good electrical conductivity, huge surface area, and applicable pore size distribution [9–12]. Micropores may provide huge surface area to the electrode material, but narrow micropores cannot be fully accessed by the electrolyte. The use of mesoporous nickel cobaltite materials circumvents the difficulty in electrolyte penetration and spreading in ultrafine pores [9,13]. Nanostructured nickel cobaltites display superior capacitive performance than the bulk ones, primarily resulting from their large surface area and suitable pore size for facilitating the transport of electrolyte ions [14]. Nickel cobaltites with various types of configuration such as nanosheet [15–23], nanoplate/nanoflake [24–29], nanoflower [30,31], nanotube/nanorod [32–36], nanowire [37–42], and urchin-like nanostructures [43–46] have been demonstrated to have a strong positive impact on their capacitive performance. Thus, shape control of nickel cobaltite nanomaterials plays the key role in the success of the supercapacitor technology [40,47,48]. In addition, the electrical conductivity of electrode contributed from the active material and supporting substrate (current collector)

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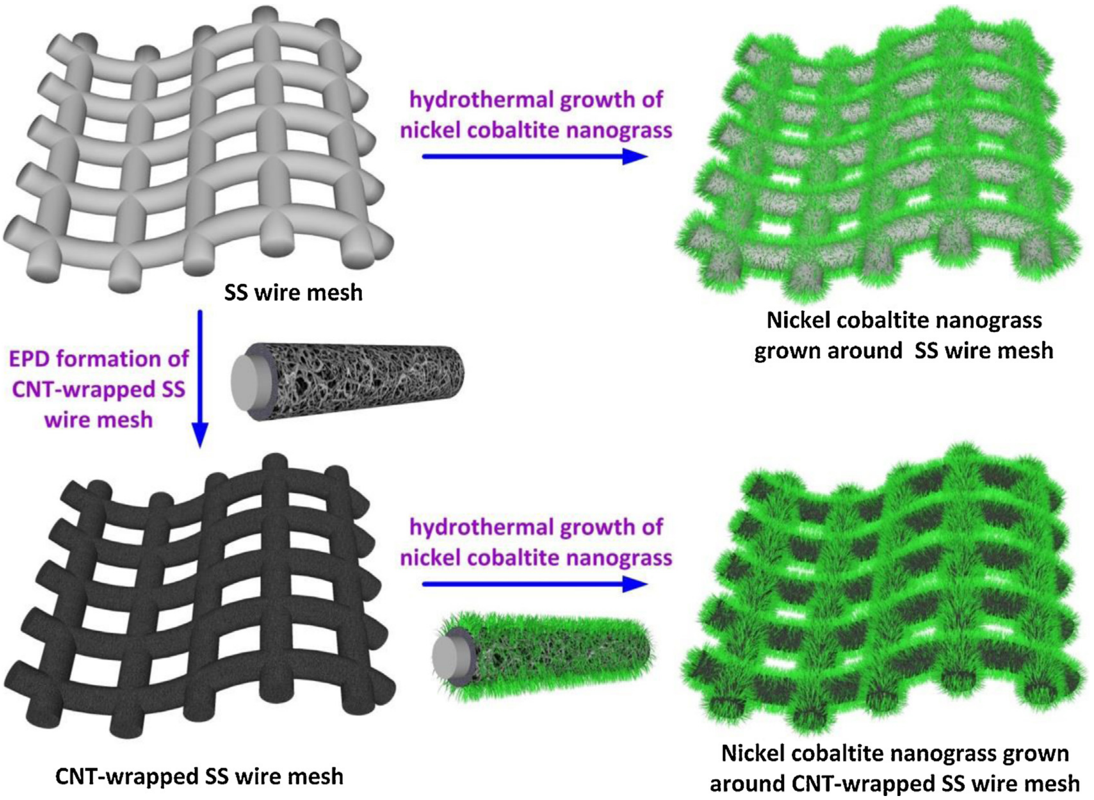
also acts a critical factor in determining the internal resistance of ECs and the utilization of active material. There are several strategies for increasing electrical conductivity of electrode, the most straightforward being the composite electrode introduced by adding the carbon materials that have high electrical conductivity such as activated carbon [49,50], carbon nanotube (CNT) [51,52] and graphene [53–55]. Nickel cobaltites grown on highly conductive and porous Ni foam and graphene foam also reveal an enhanced supercapacitive performance [56,57].

In this work, an innovative electrode substrate featuring CNT-wrapped stainless steel (SS) wire mesh is explored for supporting the nickel cobaltite nanograss as a high-performance electrode for ECs. SS wire mesh has the benefits of low cost, high flexibility, good resistance to corrosion, and easy production. Scheme 1 illustrates the formation of nickel cobaltite nanograss around SS wire mesh and CNT-wrapped SS wire mesh. Three-dimensional (3D) porous CNT film with interconnected networks could be homogeneously wrapped around the SS wire mesh by electrophoretic deposition (EPD). Nickel cobaltite nanograss with individual nanorods is grown around the CNT-wrapped SS wires by hydrothermal reactions. Highly conductive and porous CNT film provides conductive networks for fast transport of electron and accommodates large amounts of electrolyte for facile transport of electrolyte. Nickel cobaltite nanograss with bimodal pore size distribution (narrow and wide mesopores) provides large capacitance through the redox faradaic reactions between individual nanorods and ions. Thus, the nickel cobaltite nanograss with CNT-wrapped SS wire mesh electrode is expected to exhibit high specific capacitance, good rate performance, and long cycle life.

2. Experimental

Type 304 SS sheet and wire mesh (with a spacing size of 0.15 mm) were employed as the substrate to support the active materials. SS substrates (2 cm × 2 cm) were rinsed with acetone and then vigorously washed with de-ionized water. Multiwalled CNTs with an outer diameter of 20–40 nm and a length of 0.5–200 μm were purchased from ECHO Chemical Co. Ltd. (Taiwan). The raw CNT powder was etched with boiling nitric acid solution (15 M) under reflux for 1 h. The CNTs were then extensively washed with de-ionized water several times until the solution became neutral. CNT-wrapped SS wire mesh was prepared by EPD in a suspension composed of CNT powder (50 mg), 0.1 mM $Ni(NO_3)_2{\cdot}6H_2O$, and isopropyl alcohol (50 mL). The nickel nitrate functioned as a charging agent for facilitating the dispersion and EPD of CNTs. EPD was carried out by applying a potential difference of −60 V between the working (negative electrode, SS) and counter (positive electrode, Pt) electrodes for 20 s at ambient temperature using a source meter (Keithley, 2400). The working electrode was placed in between two parallel Pt counter electrodes. After EPD, the SS mesh with attached CNT film was rinsed with de-ionized water and then dried at 300 °C in air for 1 h. The mass loading of CNT film was measured to be 0.3 mg. Nickel cobaltite nanograss was grown on the SS sheet, SS mesh, and CNT-wrapped SS mesh by means of a hydrothermal method. In a typical procedure, a solution (30 mL) containing $NiSO_4{\cdot}6H_2O$ (2.5 mM), $CoSO_4{\cdot}6H_2O$ (5.0 mM), and urea (25.0 mM) was prepared with deionized water under continuous magnetic stirring at ambient temperature for 10 min to form a homogenous solution. The solution mixture was transferred into a Teflon-lined SS (type 304) autoclave. Two sheets of electrode substrate (SS sheet, SS mesh, or CNT-wrapped SS mesh) were put into the autoclave for hydrothermal synthesis. The autoclave was tightly capped, and then heated to 95 °C at a heating rate of 10 $°C\,min^{-1}$ and held at that temperature for 6 h in an electric oven. After cooling to ambient temperature at a cooling rate of 1 $°C\,min^{-1}$, the autoclave was stored at ambient temperature for 13 h before it was opened. The electrodes with attached nickel-cobalt hydroxide products were



Scheme 1. Schematic illustrating the formation of nickel cobaltite nanograss around SS wire mesh and CNT-wrapped SS wire mesh for high-performance supercapacitors.