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Full Length Article

High-performance cobalt carbonate hydroxide nano-dot/$NiCo(CO_3)(OH)_2$ electrode for asymmetric supercapacitors

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ABSTRACT

Binder-free mesoporous $NiCo(CO_3)(OH)_2$ nanowire arrays were grown using a facile hydrothermal technique. The $Co_2(CO_3)(OH)_2$ in $NiCo(CO_3)(OH)_2$ nanowire arrays was well-decorated as nano-dot scale (a few nanometer). In addition, increasing cobalt content in nickel compound matrix, $NiCo(CO_3)(OH)_2$ nanowire arrays were separately uniformly grown without agglomeration on Ni foam, providing a high specific surface area to help electrolyte access and ion transfer. The enticing composition and morphology of the $NiCo(CO_3)(OH)_2$ nanowire exhibit a superior specific capacity of 1288.2 mAh g^{-1} at a current density of 3 A g^{-1} and excellent cycling stability with the capacity retention of 80.7% after 10,000 cycles. Furthermore, an asymmetric supercapacitor composed of the $NiCo(CO_3)(OH)_2$ composite as a positive electrode and the graphene as a negative electrode presented a high energy density of 35.5 W h kg^{-1} at a power density of 2555.6 W kg^{-1} and satisfactory cycling stability with 71.3% capacity retention after 10,000 cycles. The great combination of the active nano-dot $Co_2(CO_3)(OH)_2$ and the individually grown $NiCo(CO_3)(OH)_2$ nanowires made it a promising electrode material for asymmetric supercapacitors. A well-developed nanoarchitecture of the nano-dot $Co_2(CO_3)(OH)_2$ decorated $NiCo(CO_3)(OH)_2$ composite could pave the way for an excellent electrode design for high-performance supercapacitors.

1. Introduction

Electrical energy is extensively used in a variety of settings and provides significant convenience to our everyday lives. Consequently, the development of high-performance electrical energy storage devices has become an important issue in both industry and academia [1,2]. Generally, Li-ion batteries keep our portable devices working throughout the day, but they have the disadvantage of long charging time [3]. To overcome this disadvantage, alternative materials have been studied. Among the various candidates for energy storage devices, supercapacitors with valuable properties of rapid charging/discharging, long cycle life, good cycle stability, high power density, and the ability to deliver up to ten times more power than conventional batteries have become attractive for energy storage [4–7]. Typically, supercapacitors can be divided into two kinds according to their charge storage mechanisms: electrical double-layer capacitors (EDLCs) (by ion adsorption) [8,9] and faradaic capacitors (by rapid surface redox reaction) [10–12]. EDLCs provide high conductivity (for power density and high energy) by electrolyte ion physisorption [9,13]. However, the inferior energy densities of carbonaceous materials for EDLCs hamper their practical applications [14,15]. On the other hand, faradaic capacitor materials including transition metal oxides/hydroxides have demonstrated a high energy density that is at least one order of magnitude larger than that of EDLCs [16]. As a result, transition metal oxides and hydroxides [17–20], such as, NiO [21], RuO_2 [22], CuO [23], MnO_2 [24] and Co_3O_4 [25], $Ni(OH)_2$ [26] and their binary systems, show higher energy density and capacitance than typical carbonaceous materials [11,12,27]. Among these transition metal oxides and hydroxides, nickel- and cobalt-based oxides/hydroxide composites are widely used as a precursor to prepare electrodes for supercapacitors because of their high theoretical specific capacitance, relatively low cost, and environmentally friendly nature [28]. Recently, Salunkhe et al. exhibited mesoporous nickel-cobalt hydroxide nanorods with specific capacitance as high as 456 F g^{-1} at a scan rate of 20 mV s^{-1} [29]. Huang et al. fabricated the porous

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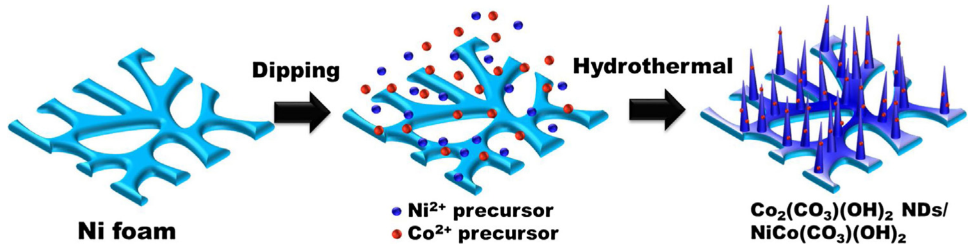

Scheme 1. Schematic diagram of the fabrication process of the $Co_2(CO_3)(OH)_2$ NDs/$NiCo(CO_3)(OH)_2$ nanowires on the Ni foam.

cobalt and nickel double hydroxide hybrid structures with specific capacitance of 1500 F g^{-1} at a current density of 2 mA cm^{-2} [30]. However, despite those many advantages, their applications for high-performance supercapacitors are limited by intrinsically low electrical conductivity. These days, carbonate/hydroxide-based transition metals have been attracted increasingly as promising electrodes for supercapacitors because of their high electrical properties of capacitive performance and additional advantages compared with oxide/hydroxide-based materials. The carbonate (CO_3^{2-}) ion substantially increases the wettability of the electrode surface due to its hydrophilic property, which has proven to be beneficial in aqueous electrolytes [31,32]. According to this feature, binary metal carbonate hydroxide materials exhibit some intriguing properties, such as effectively reducing the polarization during charging/discharging, higher reversible capacity, better structural stability and electronic conductivity owing to multiple oxidation states and rich redox reactions [33,34]. Binary metal carbonate hydroxides with divalent metal ions ($M_2(CO_3)(OH)_2$) have been widely studied and used in lots of industrial processes [35]. Among these specific metal materials, nickel- and cobalt-based carbonate hydroxide compositions are extensively used as a precursor to prepare electrodes for supercapacitors [12]. For example, Yamauchi et al. reported an NiCo-$(OH)_2$@NiCo-$(CO_3)(OH)_2$ electrode for supercapacitors, showing specific capacitance of 632 F g^{-1} at 5 mV s^{-1} [36], and Duan et al. reported a $Co_2(CO_3)(OH)_2$ array as an electrode with a specific capacitance of 1075 F g^{-1} at 5 mA cm^{-2} [37,38]. The morphologies of binary nickel–cobalt compounds are variable such as porous plates [39], nanosheets [40], nanoneedles [41], Nanowires [42], and nanoparticles [43], depending on concentration ratios and fabricating methods. In this paper, we present a facile hydrothermal method for growing 3D hierarchical hedgehog-like $NiCo(CO_3)(OH)_2$ nanowires decorated with nano-dot $Co_2(CO_3)(OH)_2$ material on Ni foam as illustrated in Scheme 1. The synthesized nanowires structure have excellent characteristics as an electrode material, such as improved conductivity, no aggregation of nanowires, a superior high surface area, and a short diffusion path of electrolyte ions. It was observed that the $Co_2(CO_3)(OH)_2$ materials as a nanoscale (ca. 2 nm) are widely distributed and embedded on the surface of the $NiCo(CO_3)(OH)_2$ nanowire composite [44]. As charge-discharge cycling increases, the performance of the nanowire electrode become deteriorated, but there is an effect of reducing structural damage by integrating and interconnecting the nano-dots and the nanowires [10,45–47]. In addition, the coherence of nano-dot $Co_2(CO_3)(OH)_2$ and $NiCo(CO_3)(OH)_2$ nanowire matrix make it increase good electron transfer between them and enhance the electrical energy performance. The $NiCo(CO_3)(OH)_2$ nanowire composite decorated with nano-dot $Co_2(CO_3)(OH)_2$ (denoted as $Co_2(CO_3)(OH)_2$ NDs/$NiCo(CO_3)(OH)_2$) structure on the Ni-foam as the electrode exhibited a remarkable maximum specific capacity (1288.2 mAh g^{-1} at a current density of 3 A g^{-1} and 492.0 mAh g^{-1} at 20 A g^{-1}) and excellent cycling stability (80.7% capacity retention after 10,000 cycles). When an asymmetric supercapacitor is assembled comprising of the $Co_2(CO_3)(OH)_2$ NDs/$NiCo(CO_3)(OH)_2$ composites as a positive electrode and graphene as a negative electrode, the energy density of the supercapacitor showed 35.5 W h kg^{-1} at a power density of 2555.6 W kg^{-1} at 2 A g^{-1}, and 13.6 W h kg^{-1} at 12262.5 W kg^{-1} at 15 A g^{-1}. These results manifest that the combination of the active nano-dots and the nanowire separation growth could be promising electrode material for high-performance supercapacitors.

2. Experimental

2.1. Materials

Ni-foam (110 PPI pore density, 320 g m^{-2} mass density, Artenano Company Limited, Hong Kong), concentrated hydrochloric acid (HCl, 37%, Daejung Chemicals, South Korea), anhydrous ethanol (SK Chemicals, South Korea), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, >97%, Sigma Aldrich), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, >98%, Sigma Aldrich), urea ($(NH_2)_2CO$, Sigma Aldrich), potassium hydroxide (KOH, Sigma Aldrich).

2.2. Electrode preparation

Fabrication of the Ni-Co electrode: Analytical-grade chemicals and Ni-foam were used. A piece of Ni-foam 2 cm x 4 cm in size was degreased with 2.0 mol L^{-1} HCl for 5 min, rinsed with DI water and ethanol for 5 min each, and dried at 60 °C in an oven for 12 h. In a typical procedure, certain values of nickel nitrate hexahydrate (6 mmol) and various ratios of cobalt nitrate hexahydrate powders (1 and 2 mmol) were dissolved in a solution containing 50 mL of DI water, and stirred magnetically for 10 min. After that, 1.3 mmol of urea is added and the total solution was stirred magnetically for 10 min again in air at room temperature. This solution was transferred to a 50 mL autoclave vessel. The Ni-foam was immersed in the aqueous solution, and the solution was heated to 160 °C for 12 h by a hydrothermal method in order to allow the growth of the $Co_2(CO_3)(OH)_2$ NDs/$NiCo(CO_3)(OH)_2$ composite material. In the synthesis, urea is the source of both the carbonate and hydroxyl anions from Eqs. (1)–(3), whereas the cobalt cations come from cobalt nitrate hexahydrate. The synthesis of the $Co_2(CO_3)(OH)_2$ material is according to Eqs. (1)–(3) [48]:

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^{+} + CO_2 + 2OH^{-} \quad (1)$$

$$CO_2 + 2OH^{-} \rightarrow CO_3^{2-} + H_2O \quad (2)$$

$$Co_2^{+} + CO_3^{2-} + 2OH^{-} \rightarrow (Co)_2(CO_3)(OH)_2 \quad (3)$$

The Ni-foam covered with the Ni-Co composite nanowires was then taken out, ultrasonically cleaned for 5 min in DI water and ethanol several times to remove surface impurities, and then dried at 60 °C for 12 h to remove the adsorbed solvents. The aqueous solution was separated by centrifugation at 4000 rpm for 2 min three times to make the powder and dried in a vacuum oven at 60 °C for 12 h.