Solar Energy Materials and Solar Cells 174 (2018) 325–332

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

A novel and facile step-by-step hydrothermal fabrication of peony-like $Ni_{0.4}Co_{0.6}(OH)_2$ supported on carbon fiber cloth as flexible electrodes for advanced electrochemical energy storage

Xinming Wu*, Lian Meng, Qiguan Wang, Wenzhi Zhang, Yan Wang

School of Materials Science and Chemical Engineering, Xi'an Technological University, Xi'an 710032, PR China

ARTICLE INFO

Keywords:
Nickel/cobalt double hydroxide
Carbon fiber cloth
Flexible
Supercapacitor

ABSTRACT

Nickel/Cobalt double hydroxide has attracted increasing attention as promising electrode material in supercapacitor field, but its poor adhesion in most conductive substrates largely thwarts the capacitance and cycling stability performance. In this work, an effective strategy was developed to synthesis $Ni_{0.4}Co_{0.6}(OH)_2$ onto carbon fiber cloth (CFC) and obtained a flexible peony-like electrode ($Ni_{0.4}Co_{0.6}(OH)_2$/CFC) by a simple step-by-step hydrothermal method without any adscititious alkali source and oxidant. Electrochemical studies showed that this type of $Ni_{0.4}Co_{0.6}(OH)_2$/CFC exhibited an extraordinary capacitance of 1816 F g^{-1} (605 F cm^{-2}) at the current density of 1.0 A g^{-1} and excellent cycling stability with capacitance retention of 98.3% after 5000 charge/discharge cycles. After assembled to be a symmetric flexible solid supercapacitor, its electrochemical performances remained stability under flat, folded, twisted and rolled states. The remarkable electrochemical and flexible properties of $Ni_{0.4}Co_{0.6}(OH)_2$/CFC developed in this study are obviously superior to those previously reported $Ni_{0.4}Co_{0.6}(OH)_2$-based supercapacitors.

1. Introduction

With the vigorous development of portable electronic devices and technology update, it assumes enormous importance to develop low-cost, flexible and high electrochemical performance energy storage devices [1–3]. Supercapacitor, with its high power density and long cycle life, draws tremendous interests of researchers [4–6]. Meanwhile, flexible solid-state supercapacitor is considered as the most promising candidate for lightweight, safe and eco-friendly electrochemical energy storage devices. To achieve high electrochemical and flexible performance, high capacitance electrode materials and flexible conductive substrate are, among others, two major prerequisites for the active materials used in the flexible supercapacitors [7].

Both $Ni(OH)_2$ and $Co(OH)_2$ are given priorities while considered as supercapacitor materials, owing to their high theoretical specific capacitances [8–10]. Nevertheless, $Ni(OH)_2$ and $Co(OH)_2$ are both P-type semiconductor with a rather low electrical conductivity ($\sim 10^{-5}$ to 10^{-9} S cm^{-1}). As previous studies reported, binary or ternary system of Ni or Co hydroxide composites can enhance electrochemical properties while compared with single metal hydroxides [11–15]. Most typically, $NiCo(OH)_2$ shows higher specific capacitance than $Ni(OH)_2$ or $Co(OH)_2$. Besides, morphology and structure are also key points for $NiCo(OH)_2$. When it comes to the synthetic methods, many have been reported, such as chemical deposition, hydrothermal method and high temperature vapor deposition. Unfortunately, electrochemical deposition has the disadvantages of small deposition scale, high-cost and difficulty cleaning for electrode [16], and high temperature vapor deposition is limited by its expensive cost and large energy consumption [17]. Thus, it is crucial to find a suitable synthetic method for $NiCo(OH)_2$. Recent research has introduced template method to obtain $NiCo(OH)_2$ electrode material with high specific capacitance and special structures, such as hydrangeas-like [18,33], flower-like [19], nanorod and porous structures [20–22]. In practical application, $NiCo(OH)_2$ powder, conductive agent and adhesive are deposited on substrates together. But these kinds of substrates are always foam nickel, foam graphene and other conductive substrates, which usually limits the performances at high capacitance and cycling stability of $NiCo(OH)_2$. How to make special structural $NiCo(OH)_2$ directly deposited on conductive substrates is the current challenge we are facing. Therefore, it is of great importance to design and fabricate high quality and high capacitance $NiCo(OH)_2$ electrode materials which also with good chemical compatibility to the surface of flexible conductive substrates.

In this work, with low-cost hydrothermal method, we successfully fabricated peony-like $Ni_{0.4}Co_{0.6}(OH)_2$ which direct grows on carbon

* Corresponding author.
E-mail address: Aimar_wu@aliyun.com (X. Wu).

http://dx.doi.org/10.1016/j.solmat.2017.09.021
Received 31 May 2017; Received in revised form 9 September 2017; Accepted 11 September 2017

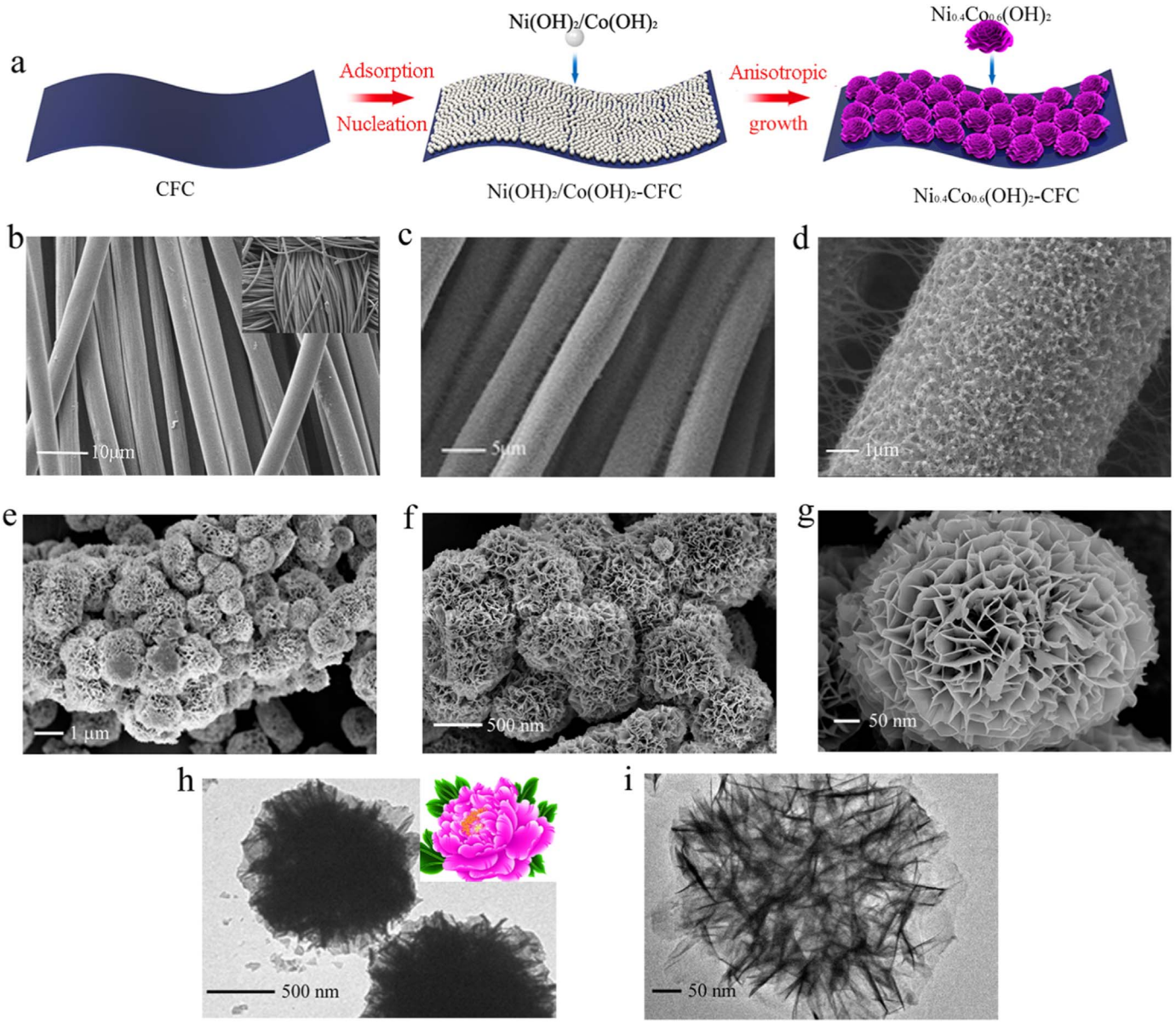

Fig. 1. Schematic illustration showing the procedure for preparation of $Ni_{0.4}Co_{0.6}(OH)_2$/CFC (a); SEM micrograph of CFC(b), SiO_2-CFC(c-d) and $Ni_{0.4}Co_{0.6}(OH)_2$/CFC (e-g); TEM micrograph of $Ni_{0.4}Co_{0.6}(OH)_2$/CFC (h-i).

fiber cloth substrates (Fig. 1(a)). This novel method neither needs alkali source to produce hydroxyl ions and oxidant to produce trivalent cations, nor special steps to remove templates. The as-prepared Ni-Co $(OH)_2$/CFC shows a 3D structure with well-defined hollow interior and peony-like exterior, provides excellent electrochemical performance for supercapacitors including high specific capacitance and long-term cycling stability. Simultaneously, as all-solid-state supercapacitor, it exhibits excellent electrochemical stability under flat, folded, twisted and rolled states.

2. Experimental

2.1. preparation of peony-like $Ni_{0.4}Co_{0.6}(OH)_2$/CFC

The $Ni_{0.4}Co_{0.6}(OH)_2$ was prepared by the method reported in literature [30]. Briefly, 1.37 g $Ni(NO_3)_2{\cdot}6H_2O$ and 2.06 g $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 150 ml ethanol (70 wt% in water) and ultrasonically dispersed for 30 min and the starting ratio of Ni^{2+}/Co^{2+} was fixed at 2:3. The homogeneous solution was then transferred into a Teflon-lined stainless steel autoclave (100 ml in capacity). After that, the treated-CFC sample (using dilute nitric acid and alcohol for half an hour) was added in this solution and the autoclave was sealed and heated at 120 °C for 8 h. When the first stage of the reaction was complete, continue to raise the temperature to 160 °C to allow the reaction to last 4 h. After cooling to room temperature, the sample was washed several times with deionized water and dried at 80 °C for 24 h. By calculation, 1.1 g $Ni_{0.4}Co_{0.6}(OH)_2$ obtained from the surface of CFC.

2.2. Solid-state supercapacitor preparation

The following steps are the preparation procedures for the solid-state supercapacitor. First, the H_3PO_4-PVA gel electrolyte was prepared as below: 1 g KOH was added into 10 ml deionized water, then 1 g PVA was added in. The mixture was stirred at 80 °C until it became transparent. Second, the two pieces of $Ni_{0.4}Co_{0.6}(OH)_2$/CFC was ready (an area mass of approximately 0.37 g cm^2). Third, the prepared KOH-PVA gel electrolyte was slowly separately poured onto two films and dried at 60 °C for 8 h. Next, two electrodes were pressed together under a