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Controllable preparation of multi-dimensional hybrid materials of nickel-cobalt layered double hydroxide nanorods/nanosheets on electrospun carbon nanofibers for high-performance supercapacitors

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ABSTRACT

Hybrid nanomaterials with hierarchical structures have been considered as one kind of the most promising electrode materials for high-performance supercapacitors with high capacity and long cycle lifetime. In this work, multi-dimensional hybrid materials of nickel-cobalt layered double hydroxide (Ni-Co LDH) nanorods/nanosheets on carbon nanofibers (CNFs) were prepared by electrospinning technique combined with one-step solution co-deposition method. Carbon nanofiber membranes were obtained by electrospinning of polyacrylonitrile (PAN) followed by pre-oxidation and carbonization. The successful growth of Ni-Co LDH with different morphologies on CNF membrane by using two kinds of auxiliary agents reveals the simplicity and universality of this method. The uniform and immense growth of Ni-Co LDH on CNFs significantly improves its dispersion and distribution. Meanwhile the hierarchical structure of carbon nanofiber@nickel-cobalt layered double hydroxide nanorods/nanosheets (CNF@Ni-Co LDH NR/NS) hybrid membranes provide not only more active sites for electrochemical reaction but also more efficient pathways for electron transport. Galvanostatic charge-discharge measurements reveal high specific capacitances of 1378.2 $F g^{-1}$ and 1195.4 $F g^{-1}$ (based on Ni-Co LDH mass) at 1 $A g^{-1}$ for CNF@Ni-Co LDH NR and CNF@Ni-Co LDH NS hybrid membranes, respectively. Moreover, cycling stabilities for both hybrid membranes are significantly enhanced compared with those of Ni-Co LDH NR and NS powders. This facile method provides a new strategy for designs and applications of binary transition metal oxides/hydroxides deposited on various substrates for next-generation energy storage devices.

1. Introduction

Nowadays, high-performance energy storage technologies are widely explored in order to remit the increasingly tensive energy situation [1,2]. Supercapacitors, also called as electrochemical capacitors, have attracted extensive attention because of their fast charge-discharge process, long lifespan and high power density [3–7]. In general, supercapacitors can be divided into two categories of electrical double-layer capacitors (EDLCs) and pseudocapacitor based on their charge-discharge mechanism [6,8]. Electrode materials for EDLCs, such as reduced graphene oxide, carbon nanotubes and graphitized carbon, usually own good cycle lifetime but low specific capacity to meet the ever-growing needs for high-performance energy devices [9–11]. Transition-metal oxides/hydroxides, such as RuO_2, MnO_2, NiO, $Ni(OH)_2$, Co_3O_4, Fe_3O_4 and their binary systems are typical electrode materials for pseudocapacitors with a relatively high specific capacity [12–18]. Nickel-cobalt layered double hydroxides (Ni-Co LDHs) are one kind of the most promising candidates among binary metal hydroxides due to their low cost, high redox activity and electrical conductivity [19–22]. Moreover, abundant OH^- ions in hydrotalcite-like structure of Ni-Co LDHs can drastically increase the ion exchange rate during the electrochemical charge-discharge processes. Xie et al. synthesized Co-Ni layered double hydroxide (Co_xNi_{1-x} LDH) nanoparticles by a poly (vinyl pyrrolidone)-assisted chemical co-precipitation method, which exhibited the highest specific capacitance of 2614 $F g^{-1}$ when the atomic ratio of Co to Ni was equal to 0.57:0.43 [23]. Hsu et al. obtained mesoporous Ni-Co oxy-hydroxides through the microwave assisted hydrothermal annealing method, showing a specific capacitance of 636 $F g^{-1}$ under the calcination temperature of 200 °C [24]. Though high specific capacitance was achieved, the low electrochemical stability can hardly be avoided for bulk Ni-Co LDH due to the conglomeration of nanoparticles, which severely limits their wider applications.

It has been proven that hybrid structures of Ni-Co LDHs and carbonaceous materials, such as CNT/Ni-Co oxides composites

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[25], reduced graphene oxides/Ni-Co nanostructures [26,27], glassy carbon/Co-Ni films [28], can greatly contribute to the optimization of electrode properties with better rate/cycling stability and higher specific capacitance. Salunkhe et al. developed nickel-cobalt binary metal hydroxide nanorods coated multi-walled carbon nanotube hybrid material through a chemical synthesis method [29]. The as-obtained hybrid showed enhanced supercapacitive performance and cycling ability. Huang et al. synthesized a series of three-dimensional nanocomposite electrodes by facile electro-deposition of cobalt and nickel double hydroxide nanosheets on porous $NiCo_2O_4$ nanowires which were grown on carbon fiber paper for high-performance supercapacitors, showing high rate capability and excellent cycling stability [30]. Chen et al. also fabricated Ni-Co LDHs on macroporous nickel foam by one-step hydrothermal co-deposition method [31]. The as-obtained Ni-Co LDH hybrid films exhibit ultra-high specific capacitance of 2682 F g^{-1} at 3 A g^{-1} (based on active materials) and energy density of 77.3 Wh kg^{-1} at 623 W kg^{-1}, making the Ni-Co LDH hybrid films promising electrode materials for high-performance supercapacitors. Despite the excellent electrochemical performance, most of the above hybrid materials need to be blended with conductive and binding agents as electrodes. The electrode materials thus obtained can hardly be flexible enough to meet tough environmental situations. In addition, the cumbersome process with introduction of excess binding agents may severely affect the electrochemical performance. Therefore, it is necessary to develop flexible electrode materials for high-performance supercapacitor applications.

As an effective method to build one-dimensional nanostructures, electrospinning technique attracts lots of attention, through which micron-sized or even nano-sized fibers can be easily generated [32–39]. Free-standing electrospun nanofiber membranes have many outstanding characteristics such as large specific surface area, controllable diameter and excellent flexibility, making them ideal candidates for tissue engineering, drug carrier, heavy metal removal, as well as electrode materials for Li-ion batteries and supercapacitors [40–43]. Kim et al. synthesized the carbon nanofiber webs from polyacrylonitrile solutions, which possess high specific surface area and huge conductive network of nano-sized fibers as a new type supercapacitor electrode [44]. Therefore, electrospun carbon nanofiber (CNF) membrane will be a promising template for the next-generation energy storage materials.

In this study, PAN nanofiber membranes were firstly fabricated by electrospinning with an average diameter of 300-450 nm, followed by a two-stage heat treatment of pre-oxidation and high temperature carbonization to obtain CNF membranes. With virtue of two different auxiliary agents (urea and hexamethylenetetramine), Ni-Co LDH nanorods (Ni-Co LDH NR) and ultrathin Ni-Co LDH nanosheets (Ni-Co LDH NS) were successfully grown on the surface of CNFs to form multi-dimensional structure of CNF@Ni-Co LDH hybrids by a one-step solution co-deposition method. The hierarchical nanostructures of CNF@Ni-Co LDH hybrid membranes can effectively improve the dispersion of Ni-Co LDH nanoparticles, increase the specific surface area and provide more active sites for electrolyte ion adsorption and transport. Electrochemical results show remarkably enhanced capacitive performance with the specific capacitance of 1378.2 F g^{-1} and 1195.4 F g^{-1} (based on the mass of Ni-Co LDHs) at 1 A g^{-1} for CNF@Ni-Co LDH NR and CNF@Ni-Co LDH NS membranes, respectively. Therefore, this method suggests a facile and universal approach to construct binary transition metal oxides/hydroxides and carbonaceous hybrid materials with hierarchical nanostructures for high-performance supercapacitor electrodes.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, Mw = 150,000 g mol^{-1}) was purchased from Sigma-Aldrich. Nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$) was purchased from Aladdin Chemical Reagent Co. Cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$), urea, hexamethylenetetramine (HMT), *N,N*-dimethylformamide (DMF), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were all purchased from Sinopharm Chemical Reagent Co. All of the chemicals were of analytic grade and used without further purification.

2.2. Preparation of electrospun CNF membranes

PAN was dissolved in DMF under magnetic stirring at room temperature for 12 h to prepare a 10 wt % spinning solution, which was loaded into a 5 mL syringe with a stainless steel needle having an inner diameter of 0.5 mm. A high voltage of 15 kV and a feeding rate of 1 mL h^{-1} were applied to the spinneret. The electrospun PAN nanofibers were collected onto the rotating aluminum collector, which was placed 15 cm away from the spinneret. The collected PAN nanofiber membranes underwent pre-oxidation by the following program: heating up to 250 °C at a ramp rate of 2 °C min^{-1}, followed by holding at 250 °C for 2 h. Afterwards, PAN

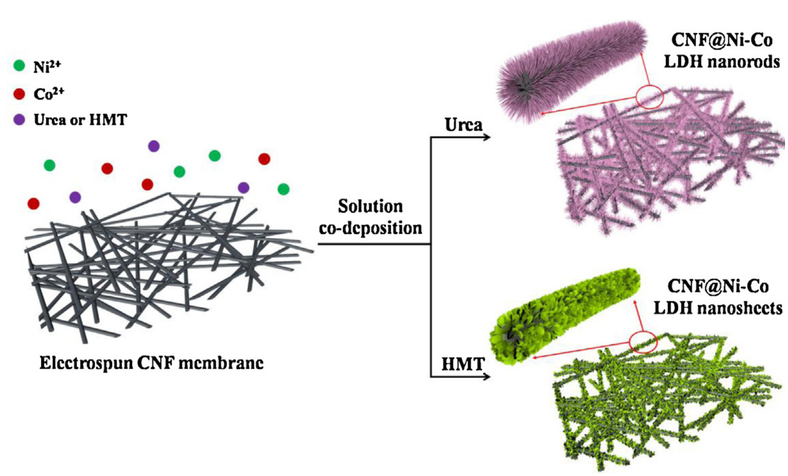

Fig. 1. Schematic illustration of the preparation of CNF@Ni-Co LDH NR and CNF@Ni-Co LDH NS hybrid membranes.