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Hydrothermal synthesis of a flower-like nano-nickel hydroxide for high performance supercapacitors

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ABSTRACT

To construct suitable nanostructures for electronic and ionic transport in the electrode of a supercapacitor, a flower-like nanostructured nickel hydroxide ($Ni(OH)_2$) was synthesized by a facile hydrothermal process in this study. For comparison, an additional two $Ni(OH)_2$ samples were synthesized to investigate the formation mechanism of the flower-like $Ni(OH)_2$. Physicochemical characterizations indicate that the $Ni(OH)_2$ nanoflower was formed by stacked hexagonal β-phase of the $Ni(OH)_2$ nanoflakes. The dissolution-recrystallization of $Ni(OH)_2$ and the stacking of nanoflakes play important roles in the formation of $Ni(OH)_2$ nanoflowers. Due to the higher conductivity and the suitable macropores for ionic transport, the nanoflower-like $Ni(OH)_2$ exhibits a high specific capacitance of 2653.2 F g^{-1} at 2 A g^{-1} and 1998.5 F g^{-1} at 40 A g^{-1}. An asymmetric supercapacitor, which was assembled with $Ni(OH)_2$ as the positive material and HNO_3-treated activated carbon as the negative material, exhibited a high cell voltage of 1.6 V. Due to the high specific capacitance and high cell voltage, the as-prepared asymmetric supercapacitor exhibited a high energy density of 32.7 Wh kg^{-1} at 71.5 W kg^{-1} and 25.5 Wh kg^{-1} at 1.28 kW kg^{-1}.

1. Introduction

Supercapacitors, which are also known as electrochemical capacitors, have many advantages for energy applications because of their high power density and long cycle life as well as being environmentally friendly. In addition, they can bridge the power and energy gaps between traditional physical capacitors and secondary batteries/fuel cells. Therefore, supercapacitors have been widely used in electric vehicles and advanced energy storage devices. According to the energy storage mechanism, supercapacitors can be divided into two categories where electrical double-layer capacitors (EDLCs) store energy via fast charge adsorption/desorption on the surface of the electrodes [1,2] and pseudo-capacitors store energy via surface Faradaic reactions between electrode materials and electrolyte ions [3,4]. Carbon materials, such as activated carbon [5,6], carbon nanotube [7] and graphene [1,8,9], are widely used for EDLC electrodes. Transition metal oxides [10–12], hydroxides [13,14] and conductive polymers [15,16] are the prominent pseudo-capacitive materials.

Limited by the specific surface area and energy storage mechanism, carbon materials commonly exhibit specific capacitances lower than 200 F g^{-1} [5–8]. By contrast, the fast Faradaic reactions of transition oxides and hydroxides result in substantially larger specific capacitances compared to carbon materials [10–14,17–21]. Due to the high specific capacitances and long cycle performances, nickel hydroxides have been the focus of research for supercapacitors [14,20–22]. Sun et al. [21] prepared a $Ni(OH)_2$/graphene composite using a mechanically assisted solid-state reaction method that exhibited a specific capacitance of 1568 F g^{-1}. Yan et al. [22] synthesized $Ni(OH)_2$/graphene composite via a microwave heating approach, which exhibited a specific capacitance of 816 F g^{-1}. Chen et al. [23] fabricated $Ni(OH)_2$ nanoparticles confined in graphene films to form a $Ni(OH)_2$/graphene composite with a high rate performance and long cycle life. The high capacitance of $Ni(OH)_2$ and the high conductivity of graphene for electronic and ionic transport are important contributions to the high performance of these $Ni(OH)_2$/graphene composites. However, for the lower specific capacitances of carbon materials, the specific capacitances of these composites are limited by the hydroxide ratios in the total mass of the composite. To further improve the capacitances, an ingenious structure suitable for the fast electronic and ionic transport in pure $Ni(OH)_2$ is strongly desired. A three-dimensional flower-like nanostructure, which possesses both macropores and

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highly crystalline film-like flake, is an ideal structure for ionic and electronic transport. The macropores will provide channels for ionic transport, and the highly crystalline flake will be suitable for electronic transfer.

In this study, a flower-like nanostructured $Ni(OH)_2$ was synthesized by a facile hydrothermal process. The phase structure and morphology of the as-prepared $Ni(OH)_2$ were characterized via X-ray diffraction, transmission electron microscopy, scanning electron microscopy and high-resolution transmission electron microscopy. The formation mechanism of the $Ni(OH)_2$ nanoflower was proposed by comparing the $Ni(OH)_2$ samples obtained via different processes. Due to its suitable structure for supercapacitor, the flower-like $Ni(OH)_2$ nanomaterial exhibits high specific capacitance and a high rate performance. The asymmetric supercapacitor, which was assembled with $Ni(OH)_2$ as the positive material and HNO_3-treated activated carbon as the negative material, exhibits high energy density and high power density.

2. Experimental

2.1. Preparation of nickel hydroxides

Flower-like nickel hydroxide was prepared by a facile hydrothermal process as described below. A total of 20 mL of an 85 mM $Ni(NO_3)_2$ solution was added to a beaker. An ammonia solution was added dropwise with stirring until the pH reach a value of 9. Then, the blue floccule mixture was transferred to a 100-mL autoclave and allowed to react at 120 °C for 4 h. The nickel hydroxide, which is referred to as $Ni(OH)_2$-TH-NH_3, was obtained after separating, washing and drying. For comparison, the blue floccule that was obtained without the use of a hydrothermal process was separated, washed and dried to yield an additional $Ni(OH)_2$ sample, which is referred to as $Ni(OH)_2$-CP-NH_3. The third $Ni(OH)_2$ sample, which is referred as $Ni(OH)_2$-CP-KOH, was obtained via coprecipitation methods with potassium hydroxide (KOH) as the precipitation agent. A total of 20 mL of an 85 mM $Ni(NO_3)_2$ solution was added to a beaker. A 10 mM KOH solution was added dropwise with stirring until the pH reached a value of 9. After separating, washing and drying, $Ni(OH)_2$-CP-KOH was obtained.

2.2. Physiochemical characterization of nickel hydroxides

The X-ray diffraction (XRD) analyses of nickel hydroxides were performed using a PANalytical X'Pert-Pro X-ray diffractometer with Ni-filtered Cu Kα radiation (λ = 1.54056 Å). The morphologies of the nickel hydroxides were characterized using a transmission electron microscope (TEM, HT 7700 model, Hitachi Corp., Japan), a high-resolution transmission electron microscope (HRTEM, JEM 2010 model, JEOL Ltd. Corp., Japan) and a scanning electron microscope (SEM, KYKY-2800B, Beijing, China).

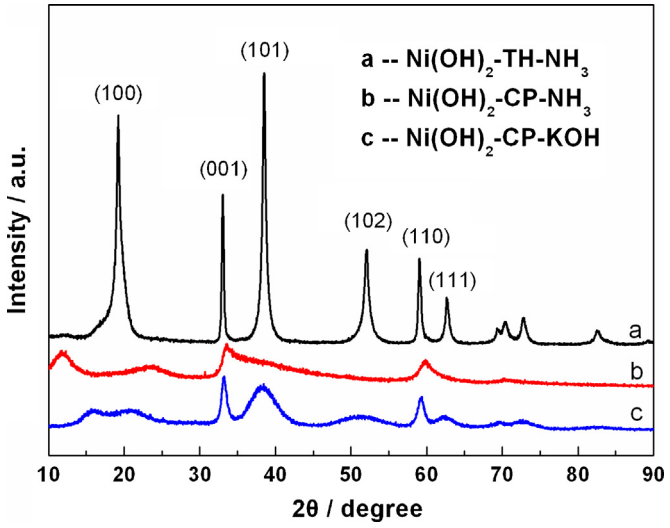

Fig. 1. XRD patterns of $Ni(OH)_2$-TH-NH_3, $Ni(OH)_2$-CP-NH_3 and $Ni(OH)_2$-CP-KOH.

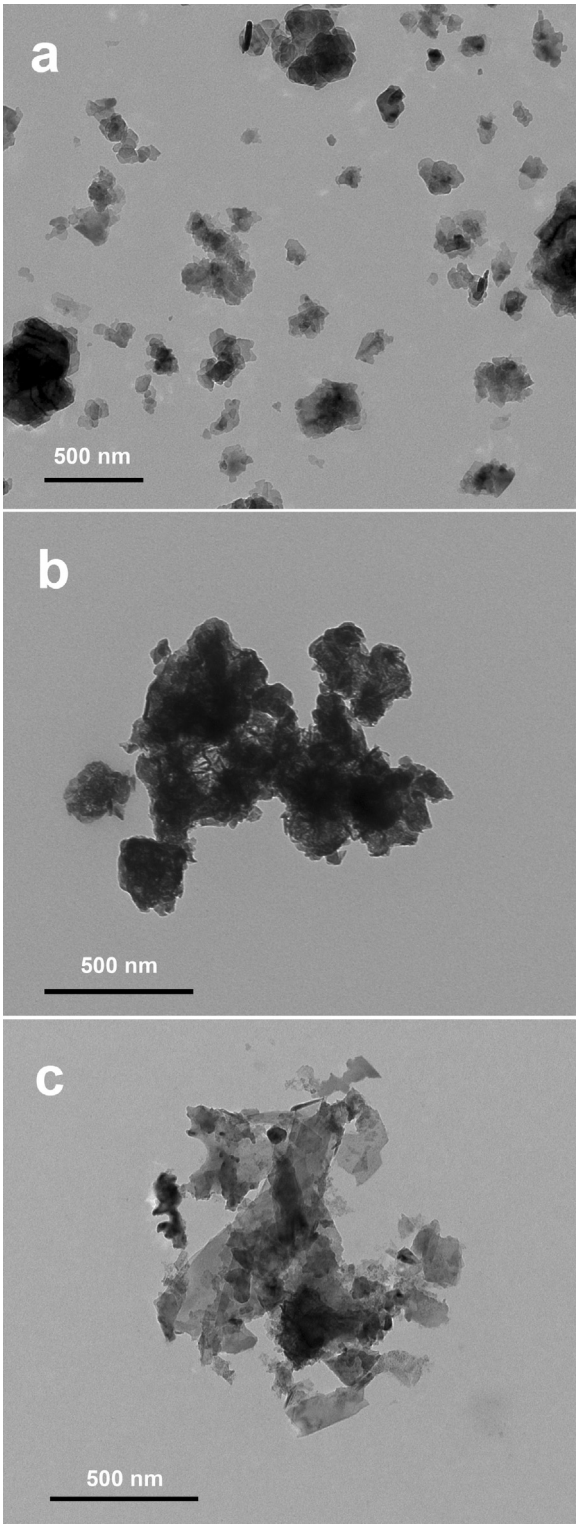

Fig. 2. Typical TEM images of $Ni(OH)_2$-TH-NH_3 (a), $Ni(OH)_2$-CP-NH_3 (b) and $Ni(OH)_2$-CP-KOH (c).