



# Template-free hydrothermal synthesis of nickel cobalt hydroxide nanoflowers with high performance for asymmetric supercapacitor



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## ABSTRACT

In this work, various nickel cobalt double hydroxide nanoflowers with different Ni/Co ratios (denoted as  $\text{Ni}_x\text{Co}_{(1-x)}(\text{OH})_2$ ), assembled by filmy nanoflakes, are prepared via a facile template-free hydrothermal process. The sizes of these nanoflowers are easily tuned by the Ni/Co ratio in the precursors. The formation mechanism of flower-like nickel cobalt hydroxide, based on the synergistic effect of ammonia complexation, Ni/Co ratios, precipitators and solvents in the template-free hydrothermal system, is demonstrated in detail. As the battery materials, the as prepared flower-like nickel cobalt double hydroxides exhibit excellent specific capacities and high rate performance.  $\text{Ni}_{0.28}\text{Co}_{0.72}(\text{OH})_2$  displays the highest capacity of  $206.7 \text{ mA h g}^{-1}$  at  $1 \text{ mV s}^{-1}$  and  $174.3 \text{ mA h g}^{-1}$  at  $1 \text{ A g}^{-1}$ , respectively. The capacity retention of  $\text{Ni}_{0.28}\text{Co}_{0.72}(\text{OH})_2$  is 59.1% (from 206.7 to  $122.2 \text{ mA h g}^{-1}$ ) at the potential scan rate from 1 to  $25 \text{ mV s}^{-1}$ . Due to the high rate performance corresponding to high power energy,  $\text{Ni}_{0.28}\text{Co}_{0.72}(\text{OH})_2$  is used as positive material to assemble the hybrid device (asymmetric supercapacitor) with activated carbon as negative material. The as-prepared asymmetric supercapacitor exhibits  $19.4 \text{ Wh kg}^{-1}$  at  $80.5 \text{ W kg}^{-1}$ , and even  $20.6 \text{ Wh kg}^{-1}$  at  $3.93 \text{ kW kg}^{-1}$ .

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## 1. Introduction

Supercapacitors, also known as electrochemical capacitors, have been attracting much attention in recent years due to their significant potential for energy storage and electric vehicles. Many advantages such as high power density, long cycle life and environmentally friendly make supercapacitors useful for electrochemical energy storage. Furthermore, supercapacitors can fill the energy and power gaps between conventional electric double-layer capacitors and second batteries. Carbon materials [1–3], transition metal oxides/hydroxides [4–7] and conducting polymers [8,9] are widely used as electrode materials for supercapacitors. Carbon materials could store energy through fast adsorption/desorption of electrolyte ions on the surface of active electrode materials. For this mechanism, carbon materials can only display specific capacitance lower than  $300 \text{ F g}^{-1}$ , which are limited by their specific surface area [2,10–12]. Transition metal oxides or

hydroxides [6,7,13–16], as the conventional battery materials, mainly storing energy by the Faradic reactions between electrolytes and active materials, can exhibit remarkably a high capacity. Therefore, assembling a hybrid device [5], which is called asymmetric supercapacitor with transition metal oxides or hydroxides as positive materials and carbon materials as negative materials, is a good strategy to enhance the capacitance of supercapacitor.

Among various transition metal oxides or hydroxides used in asymmetric supercapacitors or batteries, nickel hydroxide has been attracting more interests due to its low cost and high theoretical specific capacitance or capacity [5,6,16,17]. However, the poor electrical conductivity of nickel hydroxide limits its high-rate performance and cycle life. Addition of cobalt into the nickel hydroxide can increase the electrical conductivity of the final nickel cobalt double hydroxide [15,18,19]. Moreover, cobalt hydroxide has been widely reported as good pseudocapacitive material exhibiting high specific capacitance [20–22]. Therefore, the well-designed nickel cobalt double hydroxides are expected to possess enhanced specific capacities with high rate performance and long cycling life [23–29].

Developing a well defined three-dimension (3-D) nanostructure with high specific surface area for fast Faradic

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reaction and suitable porous structure for short ionic transportation is the key challenge for nickel cobalt hydroxides in the application of supercapacitors or batteries. Electrodeposition [23–25] is one of the strategy to obtain suitable 3-D structured nickel cobalt hydroxides. Chen et al. [23] directly prepared the interconnected nickel cobalt hydroxides nanoplatelets on the nickel foam with interwoven pores. Kulkarni et al. [24] also obtained aligned nickel cobalt double hydroxides with interwoven pores which are suitable for the short ion transportation. However, the yield of the hydroxides and the active materials loading on the electrodes would be markedly limited by the natural characteristic of electrodeposition (complex multiphase reactions, low micro space utilization, and so on). Designing the structure and morphology by structure-directed co-precipitation through soft templates is another strategy to obtain well-defined 3-D nickel cobalt double hydroxides [26–29]. Chen et al. [26] and Pu et al. [27] constructed highly porous hybrid films composed of ultrathin Ni–Co double hydroxide nanosheets supported on the three-dimensional macroporous nickel foam by hydrothermal co-deposition method with cetyltrimethyl ammonium bromide and hexamethylenetetramine as the nanostructure growth assisting agent, respectively. Nevertheless, the high dosage of expensive soft templates and the complex post treatment to remove these templates will also limit the high-yield preparation of these nickel cobalt hydroxides for practical application. Therefore, developing a template-free method to obtain well-defined 3-D structured nickel cobalt hydroxides and tuning their morphology, size and structure is an interesting work. Furthermore, the synthesis conditions in template-free hydrothermal system (including Ni/Co ratios in precursors, precipitators and solvents), which were limited concerned about in literatures, are important for the morphology and size control of nickel cobalt hydroxides.

Herein, a facile template-free hydrothermal process, with ammonia as accelerating agent for the dissolution–recrystallization of hydroxides, was developed to obtain flower-like nanostructured nickel cobalt hydroxides. Large-scale product could be obtained easily in this facile process. The formation mechanism of flower-like nickel cobalt hydroxide, based on the synergistic effect of ammonia complexation, Ni/Co ratios, precipitators and solvents in the template-free hydrothermal system, is demonstrated in detail here. Furthermore, the effect of Ni/Co ratios on both physicochemical and electrochemical properties of nickel cobalt hydroxides is also discussed carefully. Due to the unique nanostructure of well-defined 3-D nanoflowers with high surface area from filmy nanoflakes and suitable mesopores from interwoven flake-stacking, the as-prepared nickel cobalt hydroxides exhibit high specific capacity as battery materials with good high-rate performance corresponding to high power density. The asymmetric supercapacitor, assembled with nickel cobalt hydroxides as positive electrode and activated carbon as negative material, exhibits high energy density with high power density.

## 2. Experimental section

### 2.1. Preparation of nickel cobalt hydroxides

Nickel cobalt hydroxides were prepared via hydrothermal process with ammonia as the precipitation agent. Nickel nitrate and cobalt nitrate were dissolved to obtain the 0.85 mM  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  solutions, respectively. Designed amount of  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  solutions according to the Ni/Co ratios in the final hydroxides were mixed in a beaker. Floccule-like suspension was obtained by adding 1.0 M ammonia solution drop by drop into the beaker with stirring. The suspension was transferred into a 100 mL autoclave and then heated in an oven for 2 h at 120 °C. These nickel cobalt hydroxides were denoted as  $\text{Ni}_x\text{Co}_{(1-x)}(\text{OH})_2$ .

To investigate the effect of precipitator on the morphologies of double hydroxides and explore the formation mechanism of flower-like hydroxides without template, the nickel cobalt hydroxides with Ni/Co ratio of 1:1 were prepared by similar hydrothermal processes above except with alternative KOH,  $\text{NaCO}_3$  and urea as precipitator, respectively. Furthermore, the similar solvothermal process with ethylene glycol as solvent and ammonia as precipitator was also carried out to obtain the nickel cobalt hydroxide with Ni/Co ratio of 1:1 for comparison.

### 2.2. Physicochemical characterizations of nickel cobalt hydroxides

The real Ni/Co ratios in various nickel cobalt hydroxides were measured by AA-6800F/G atomic absorption spectrophotometer (AAS). 10 mg  $\text{Ni}_x\text{Co}_{(1-x)}(\text{OH})_2$  sample was dissolved in 50 mL 2 M nitric acid solution, and then 2 mL of the obtained nickel cobalt nitrate solution was diluted to 50 mL to obtain the solution for the AAS measurement. Furthermore, the composites of nickel cobalt hydroxides were also measured by EDAX AMETEK MATERIALS ANALYSIS DIVISION energy dispersive spectrometer. Powder X-ray diffraction (XRD) analysis was carried out by D-max-2500 X-ray diffractometer (Rigaku Corp., Japan) with Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The patterns were recorded at the  $2\theta$  range of 10–90° with step size of 0.02°. The thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed from room temperature to 700 °C at sweep rate of 10 °C  $\text{min}^{-1}$  in air atmosphere by DTG-60A apparatus. The Fourier transform infrared spectroscopy (FTIR) measurement was conducted by Nicolet 380 FT-IR spectrometer (Thermo Fisher Scientific Corp. USA). The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were performed by ASAP 2020 V3.01 G system. The morphologies of hydroxides were measured by HT 7700 model transmission electron microscope (TEM) operating at 100 kV, 10  $\mu\text{A}$  and KYKY-2800B scanning electron microscope (SEM) operating at 15.0 kV. The TEM images were acquired by high-contrast mode through slow scan CCD camera.

### 2.3. Electrode preparation and electrochemical measurements

The electrochemical performance of nickel cobalt hydroxides was evaluated by cyclic voltammetry (CV) and galvanostatic charge–discharge (GC) on the CHI 660A workstation (CH Instrument Corp. USA) and the Land CT 2001A (Land Instrument Corp., Wuhan, China), respectively. Nickel cobalt hydroxides coated Ni foam ( $1 \times 1 \text{ cm}^2$ ), Pt foil ( $1 \times 1 \text{ cm}^2$ ) and Hg/HgO electrode were used as working electrode, counter electrode and reference electrode of three-electrode measurement system, respectively. The active materials coated Ni foam working electrode was prepared as follows: 80 wt.% of  $\text{Ni}(\text{OH})_2$  sample, 15 wt.% of acetylene black and 5 wt.% of polyvinylidene difluoride were mixed in the ethanol to form a homogeneous slurry. The obtained slurry was coated on the clean Ni foam ( $1 \times 1 \text{ cm}^2$ ) and dried in a vacuum at 80 °C for 12 h. The active material loading on the electrode is about 4.0  $\text{mg cm}^{-2}$ . The working electrodes were obtained by pressing the active material coated Ni foam at 10 MPa. All the electrolytes in these measurements were 6.0 M KOH solution.

An asymmetric supercapacitor was assembled with the as-prepared nickel cobalt hydroxide as positive material and commercial activated carbon black (KetjenBlack EC 600J) as negative material. The preparation of negative electrode is similar to that of positive electrode, which is mentioned above. The active material loadings in positive electrode and negative electrode are 4.4 and 8.4  $\text{mg cm}^{-2}$ . The asymmetric supercapacitor, denoted as NCOH//AC supercapacitor, was assembled with surface modified polypropylene–polyethylene composite membrane as separator.

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