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Solvothermal synthesis of pompon-like nickel-cobalt hydroxide/graphene oxide composite for high-performance supercapacitor application

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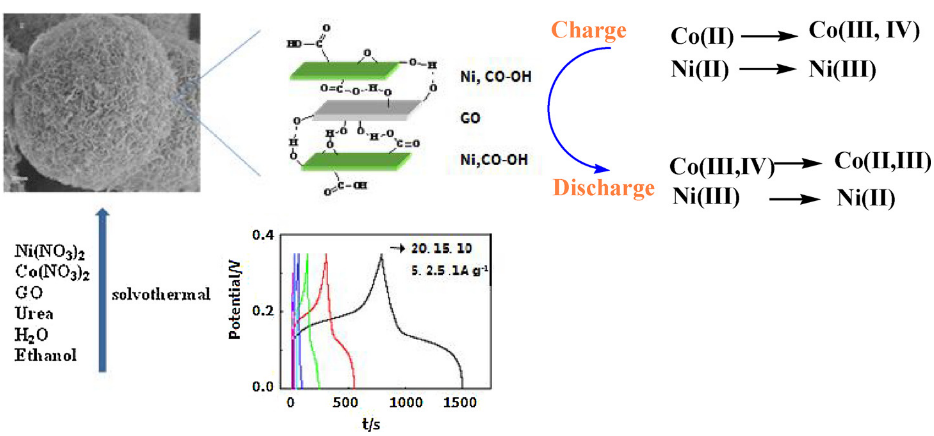
GRAPHICAL ABSTRACT

Pompon-like Ni-Co double hydroxides/graphene oxide hybrid prepared by solvothermal process possesses high specific capacitance of 2050.6 F g^{-1} at 1 A g^{-1}, energy density of 87.2 W h Kg^{-1} and power density of 438.7 W Kg^{-1} as well as good cyclic stability.



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ABSTRACT

Novel pompon-like nickel-cobalt double hydroxide/graphene oxide ($Ni(OH)_2/Co(OH)_2/GO$) composites were successfully synthesized via a simple one-step solvothermal process. Their structure, morphology, surface and electrochemical properties were characterized by scanning electron microscopy(SEM), transmission electron microscopy(TEM), X-ray diffraction(XRD), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge(GCD) curves. The composite electrodes showed typical pseudocapacitance performances. When addition amount of graphene oxide was 10mg, resulted composite exhibited a high specific capacitance (2050.6 F g^{-1} at 1 A g^{-1}) and good cycling stability with a capacitance retention of 84% after 1000 cycles. Appropriate amount of graphene oxide not only served as a structural director but also enhanced the conductivity and stability of the resulted composite. The attractive performances and facile fabrication made the prepared $Ni(OH)_2/Co(OH)_2/GO$ composite become a promising candidate for low-cost high-performance energy storage device.

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1. Introduction

Supercapacitors, also known as electrochemical capacitors, are a new type of energy storage devices based on the electrochemical process of the electrode/solution interface. For specific energy storage mechanism, supercapacitor possesses higher power density than battery and higher energy density than tranditional capacitors [1]. At the same time, compared with the traditional capacitors and chemical batteries, supercapacitors have higher charge-discharge rate, wider applied temperature range, higher stability, longer cycle life as well as no pollution to the environment. So it is one of the most important green energies in the future.

According to the different energy storage mechanism, the supercapacitor can be divided into two categories: The first is electric double-layer capacitor(EDLC) which stores energy through accumulating charge in the electrode/electrolyte interface and the second is pseudo-capacitance capacitor or Faraday capacitor which stores energy by the fast and reversible redox reaction at electrochemically active sites [2–4]. Tranditional pseudo-capacitor electrode materials mainly include transition metal oxides and hydroxides, which possess several oxidation states favorable for rapid redox reactions, leading to highly efficient energy storage and conversion. Among them, $Ni(OH)_2$ possesses relatively low cost, big specific capacitance and high redox activity, so it has become one of the electrode materials of top choice. But the single metal oxides or hydroxides usually suffer from low conductivity and unfavorable stability. It has been reported that incorporation of cobalt into nickel hydroxide can improve the electrochemical and conductive properties [5–13]. During the charge-discharge processes, highly conductive CoOOH will be formed which can enhance the rate capability of the resulting materials. At the same time, its synthesis method is simple and the morphology is controlled too [14]. However, even so, the resulted conductivity is still unsatisfactory.

As we know, nanostructured carbon-based material, such as graphene which presents many edges, like notably high electrical conductivity, large SSA (specific surface area) (over $2600\,m^2\,g^{-1}$) and small quality, makes itself excellent EDLC material and good support for pseudocapacitors in energy storage [15]. B. Wei et al. [16] reported the MnO_2/rGO composites displayed an excellent cycling (2.3% loss after 1000 cycles). Y. Xu et al. [17] reported a $NiCo_2O_4$/GO composite showed a high capacitance of $1211.25\,F\,g^{-1}$. Especially, GO with a layer structure has many carboxyl, hydroxyl and epoxy groups, which are arranged in the basal plane and in the borders of the nanosheets. These functional groups provide a good compatibility between GO and other materials through covalent or non-covalent interactions to improve the stability of the resultant composites [18–20]. The presence of oxygenated functional groups in the GO can be still exploited to facilitate the transference of protons [21,22], which can lead to a considerable increase in the conductivity for application in fuel cells. Therefore, GO can be used as a compatibilizing component to accommodate active species and fabricate layer composition structures [23,24].

So far, different combinations of graphene have been done for electrode preparation in order to obtain a high performance supercapacitor, for example, polymer/graphene oxide (GO) nanofibers or nanowires [25,26], graphene/transition metal oxide nanocomposites [17,27] and reduced graphene oxide/transition metal double hydroxide nanocomposites [28–30], etc.

Kim et al. [28] synthesized reduced graphene oxide (RGO)/nickel cobalt (NiCo) double hydroxide nano-piece network composites by one-pot microwave-assisted method. When the weight ratio of nickel to cobalt was 2:1, the highest specific capacitance was $1622\,F\,g^{-1}$ at a scan rate of $5\,mV\,s^{-1}$. Chent et al. [29] prepared Ni/Co hydroxide nanowire/rGO hybrid networks by hydrothermal and in suit electrochemical reduction method. The specific capacitance achieved $1434\,F\,g^{-1}$ at $0.5\,A\,g^{-1}$. Ma et al. [30] synthesized ultrathin nanolayered Ni−Co binary hydroxides/rGO hybrid material by a simple one-pot hydrothermal method and the highest specific capacitance was $1691\,F\,g^{-1}$ at $0.5\,A\,g^{-1}$. The Ni,Co−OH/rGO//hierarchical porous carbon asymmetric supercapacitor can reached high energy density of $56.1\,W\,h\,kg^{-1}$ at power density of $76\,W\,kg^{-1}$. It is evident that chemical states of graphene and the structures of the composites were very important for electrochemical performances.

In this present paper, $Ni(OH)_2$/$Co(OH)_2$/graphene oxide composites were synthesized by simple solvothermal method and their electrochemical properties were investigated in detail. We expect to enhance the conductivity of the resulted composites based on excellent conductivity of graphene oxide(GO) and to improve the cyclic stability of the resulted materials with the aid of the strong interaction between the functional groups of GO and hydroxides of the metal hydroxides. The results showed that the prepared composition materials indicated excellent pseudo-capacitor performances.

2. Experimental

2.1. Reagents and apparatus

Sodium nitrate was purchased from Kaitong Chemistry Co., Ltd. (Tianjin), Potassium permanganate was obtained from Guanghua Chemistry Co., Ltd.(Guangdong), hydrogen peroxide(30 wt%) was purchased from Sinopharm Chemical Reagent Co., Ltd.(Shanghai), nickel nitrate hexahydrate and cobalt nitrate hexahydrate were purchased from Aladdin Chemistry Co., Ltd.(Shanghai) Urea was bought from Beijing Chemical Industry Group Co., Ltd. Conductive carbon black was obtained from Cabot Corporation. Polytetrafluoroethylene (PTFE) was acquired from Sigma-Aldrich.

All the chemical reagents were analytically pure and used without further purification. Deionized water used in the experiment was prepared in laboratory.

The powder X-ray diffraction (XRD) patterns of the products were measured using an X-ray diffractometer (Empyrean, Holland), Raman spectra were recorded on a RFS100/S Fourier transform Raman spectrometer (Bruker, Germany), Fourier transform infrared spectra(FT-IR) were recorded from a FTS-3000 spectrometer (Digilab, Finland), microstructures and morphologies were observed on a JSM-6701F field emission scanning electron microscope (JOEL, Japan) and a JEM-1200EX transmission electron microscope (JOEL, Japan) respectively. Elemental chemical states on the surface of the materials were measured by an ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS, ThermoFisher Scientific, USA).

2.2. Preparation of the materials

Graphene oxide(GO) was prepared using a modified Hummers method [31]. And then, given amount (0.005 g, 0.01 g and 0.03 g) of GO was added in 60 ml 50% ethanol and ultrasonically dispersed to obtain a uniform suspension. Subsequently, 0.56 g of $Ni(NO_3)_2{\cdot}6H_2O$, 0.28 g of $Co(NO_3)_2{\cdot}6H_2O$ and 0.95 g of urea were added to the above suspension under vigorously stirring. And then the mixture was transferred into an autoclave and the reaction temperature was maintained at 120 °C for 4 h. Lastly, the resulting product was washed several times with deionized water and ethanol respectively and dried in a vacuum oven at 60 °C. These composites with different quality of GO were named Ni,Co-OH/GO-1, Ni,Co-OH/GO-2 and Ni,Co-OH/GO-3, respectively corresponding mass fraction of GO 1.83%, 3.66% and 10.99%.

For comparison, we also prepared the pure nickel-cobalt hydroxide using a similar process except without the addition of GO.

2.3. Electrode preparation and electrochemical characterization

Electrochemical measurements were performed using a CHI 660E electrochemical workstation with a convenient three-electrode system