Research paper

Belt-like nickel hydroxide carbonate/reduced graphene oxide hybrids: Synthesis and performance as supercapacitor electrodes

Chunyan Xi[a], Guoxing Zhu[a,*], Yuanjun Liu[b], Xiaoping Shen[a,*], Wenjuan Zhu[c], Zhenyuan Ji[a], Lirong Kong[a]
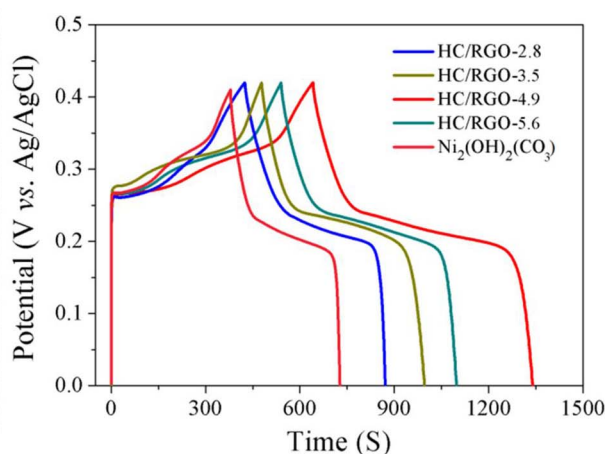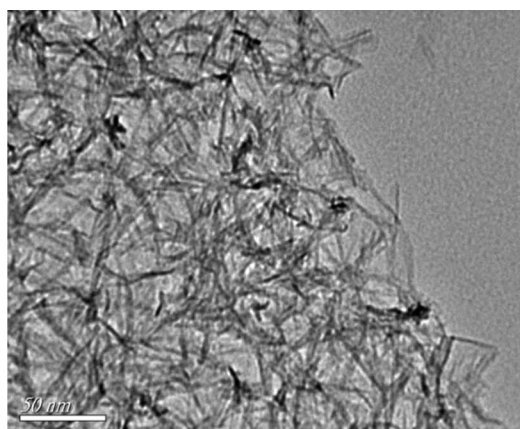
[a] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China
[b] School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212018, China
[c] School of Chemistry and Chemical Engineering, Hefei Normal University, Hefei 230601, China

GRAPHICAL ABSTRACT

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ABSTRACT

Supercapacitors with superior performance and long cycling ability are attractive for the next-generation energy storage devices. Herein, an unique hybrid of nickel hydroxide carbonate nanobelts densely and strongly anchored on reduced graphene oxide nanosheets (HC/RGO) has been designed and synthesized through a facile hydrothermal approach. The as-prepared HC/RGO composites display a nearly two-dimensional architecture. Electrochemical investigation shows that the HC/RGO composite electrode has a maximum specific capacitance of 1662.4 F/g (3.5 F/cm^2) at 1.0 A/g with excellent rate capability (64.7% capacitance retention when increasing the current density from 1.0 to 10.0 A/g) and good cyclic stability. The outstanding electrochemical property of HC/RGO composite electrode is possibly attributed to the intrinsic nature of $Ni_2(OH)_2(CO_3)$, the conductive RGO support, and the ultrathin thickness of $Ni_2(OH)_2(CO_3)$ nanounits which can accelerate the electron transport and facilitate the redox reactions. This hydroxycarbonate-based hybrids with excellent electrochemical performance provide an new avenue for designing high-performance supercapacitor electrodes.

* Corresponding authors.
  E-mail addresses: zhuguoxing@ujs.edu.cn (G. Zhu), xiaopingshen@163.com (X. Shen).

1. Introduction

The demand for power sources of portable electronic devices has increased in recent years with the dramatic growth of portable and smart electric products. Supercapacitors, which bridge the storage gap between high-energy batteries and high-power dielectric capacitors, have been considered as an important class of energy source because of their high power density and high cycle efficiency [1–3]. There are two types of supercapacitors based on different energy storage mechanism, electrical double-layer capacitors or pseudocapacitors [4]. The later one takes advantage of the reversible Faradic reactions occurring at the electrode surface and offers better electrochemical performances than the former [5,6]. Transition metal oxides (*e.g.*, MnO_2, RuO_2, NiO), hydroxides (*e.g.*, $Ni(OH)_2$, $Co(OH)_2$), sulfides (*e.g.*, Ni_2S_3, $CoNi_2S_4$), and polymers (*e.g.*, polyaniline) are often used to build pseudocapcitors due to their low cost, low toxicity, high theoretical capacitance, and great flexibility in structure and morphology [7–10].

Among the materials for pseudocapcitors, nickel-based compounds are highly considered to be ideal materials because of the high theoretical capacitance, environmental friendliness, and good electrochemical performance. Up to date, various nickel-based compounds, such as NiO [11–13], $Ni(OH)_2$ [14–16], Ni_3S_2 [17,18], $NiCo_2O_4$ [19,20], $NiCo_2S_4$ [21,22] *etc*, have been extensively studied in search of the alternative inexpensive electrode materials with high electrochemical performance [23–29]. However, most pseudocapacitive materials including the nickel-based compounds often exhibit low electrical conductivity hindering the transfer of electrons and poor stability during the charge-discharge process [30,31]. In order to overcome this limitation, much work has focused on the incorporation of nickel-based compounds onto nanostructured carbon materials including carbon nanotubes, activation carbon, and graphene [32–34]. Due to the outstanding feature of high conductivity, large specific surface, and excellent mechanical properties, graphene nanosheets is a kind of excellent backbone to hold the electrochemical active materials for capacitor electrodes [35,36]. In these composites, the graphene nanosheet surface was anchored with electrochemical active materials, which prevent the restacking of graphene nanosheets, therefore minimizing their aggregation and maximizing the electrochemically accessible area [37,38]. At the same time, graphene nanosheets provide excellent charge transport avenue for electrochemical active materials. Thus, enhanced electrochemical performances are often demonstrated in these composites [39,40]. Various kinds of graphene-based composites as supercapacitior electrodes have been reported. For example, Trung et al. prepared a 3D-RGO/NiO electrode, which exhibits a high specific capacitance value of 1328 F/g at a current density of 1 A/g and an excellent cycling stability with 87% retention of the capacitance after 2000 cycles of galvanostatic charge-discharge [41]. Dong et al. synthesized a graphene-based composite with free-standing α-$Ni(OH)_2$ nanosheets growing on reduced graphene oxide (RGO) by a one-step solution method. The specific capacitance was reported to be 1044 F/g at a large current density of 15 A/g (84.7% of 1233 F/g at 5 A/g) [9]. Similarly, $NiCo_2O_4$/RGO-based composite also exhibits a high specific capacitance of 1222 F/g at 0.5 A/g with an outstanding rate capability [42].

Recently, we have demonstrated that $Ni_2(OH)_2(CO_3)$ material would be a potential material for energy storage devices [23]. For further improving the electrochemical performance of $Ni_2(OH)_2(CO_3)$ material, some substrates were selected to form composites with it. Tang et al. prepared $Ni_2(OH)_2(CO_3)$/ZIF-8 composite with ZIF-8 as host by a solvothermal method. The $Ni_2(OH)_2(CO_3)$/ZIF-8 composite exhibits a specific capacitance of 851 F/g at a scan rate of 5 mV/s and good stability over 5000 cycles [43]. Gao et al. selected graphene nanosheets as the host, which were modified by sulfonated salicylic acid before loading with $Ni_2(OH)_2(CO_3)$ nanoparticles. The specific capacitance of the formed $Ni_2(OH)_2(CO_3)$ nanoparticles/sulfonated salicylic acid functionalized graphene composite is highly improved, which

exhibits specific capacitance of 1508 F/g at a current density of 1 A/g, much higher than 1039 F/g for pure $Ni_2(OH)_2(CO_3)$ nanoparticles [44]. These studies evidenced that loading of $Ni_2(OH)_2(CO_3)$ product on suitable substrate materials will effectively improve their specific capacitance value. However, these study also leaves a huge developing room for further improving the electrochemical performance of $Ni_2(OH)_2(CO_3)$ material, since the different hybrid microstructure, different composition ratio, different size in the $Ni_2(OH)_2CO_3$/substrate composites will influence their performance as capacitor electrodes [16,45].

In this study, a novel hierarchical hybrid consisting of belt-like $Ni_2(OH)_2(CO_3)$ decorated on two dimensional RGO nanosheets was prepared. Its superior performance as supercapacitor electrode was identified in this work. The obtained $Ni_2(OH)_2(CO_3)$/RGO hybrid product demonstrates high specific capacitance and good cycling ability. The strategy of effectively decorating of belt-like $Ni_2(OH)_2(CO_3)$ nanounits on light weight but conductive carbon support would also be extended to other hydroxycarbonate-based materials for the next-generation high-energy supercapacitors.

2. Experimental

2.1. Materials

Natural flake graphite with a particle size of 150 μm (99.9% purity) was purchased from Qingdao Guyu Graphite Co., Ltd. All other chemical reagents in our experiments were purchased from Sinopharm Chemical Reagent Company. The chemicals used in this research are of analytical grade and used without any further purification.

2.2. Synthesis of HC/RGO composites

Graphite oxide was prepared by a modified Hummers' method [46]. In a typical synthesis process, 25 mg of the obtained graphite oxide was dispersed into 50 mL of distilled water. With the assistance of strong ultrasonication for about 2 h followed by vigorous stirring for another 2 h, a homogeneous graphene oxide (GO) dispersion was obtained. 4.9 g of $Ni(NO_3)_2 \cdot 6H_2O$ and 0.53 g of urea solid were then added to the GO dispersion. The obtained mixture was stirred till $Ni(NO_3)_2 \cdot 6H_2O$ and urea were absolutely dissolved. After that, the mixture (only taking 40 mL) was transferred into a 50 mL Teflon-lined stainless autoclave and was heated at 120 °C for 5 h. The obtained solid product was then collected, washed with distilled water and absolute ethanol for several times, and dried in a vacuum oven at 45 °C for 24 h, which was denoted as HC/RGO-4.9. For comparison, HC/RGO-2.8, HC/RGO-3.5, and HC/RGO-5.6 were also prepared with the feeding amount of 2.8 g, 3.5 g, 5.6 g of $Ni(NO_3)_2 \cdot 6H_2O$, and 0.3 g, 0.38 g, 0.6 g of urea, respectively. For preparing of these control samples, the ratio of $Ni(NO_3)_2 \cdot 6H_2O$ to urea is constant. Pure $Ni_2(OH)_2(CO_3)$ and RGO were also prepared in the same way as HC/RGO-4.9 composite in the absence of graphite oxide or in the absence of $Ni(NO_3)_2 \cdot 6H_2O$ and of urea.

2.3. Characterization

Crystal phase structures of the synthesized samples were characterized by powder X-ray diffraction (XRD) on a Bruker D-8 Advance diffractometer using Cu Kα (λ = 1.5418 Å) radiation. The morphology and microstructure analyses were conducted on a Hitachi S-4800 or JEOL JSM-7800F field emission scanning electron microscope (FE-SEM), a JEM-2010 high-resolution transmission electron microscope (TEM). Raman spectrum was recorded on a JY HR-800 Raman spectrometer with a 453 nm laser excitation. Fourier transform infrared spectra (FTIR) were recorded on a Nicolet Nexus 470 FTIR spectrophotometer using a KBr disk. X-ray photoelectron spectra (XPS) were detected by X-ray photoelectron spectroscopy (Thermo ESCALAB 250) with Al Kα (hν = 1486.6 eV) X-ray radiation source. The XPS spectra