



Balanced mesoporous nickel cobaltite-graphene and doped carbon electrodes for high-performance asymmetric supercapacitor



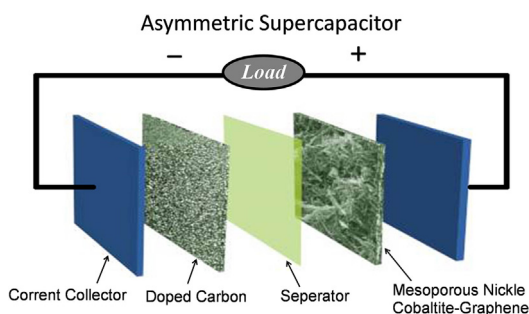
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HIGHLIGHTS

- Rod-like NiCo_2O_4 decorated on graphene has been prepared by a hydrothermal route.
- Balanced positive and negative electrodes were used to assemble high energy capacitor.
- The work provides a potential way for designing superior energy storage device.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 March 2017
Received in revised form 12 May 2017
Accepted 28 May 2017
Available online 29 May 2017

Keywords:

Nickel cobaltite
Graphene
Doped carbon
Asymmetric supercapacitor
Energy storage

ABSTRACT

Mesoporous rod-like nickel cobaltite decorated on graphene has been fabricated by a facile hydrothermal method. Due to multiple redox reactions on nickel cobaltite, a high capacitance of 845 F g^{-1} can be obtained. In order to get high energy and power densities, an asymmetric supercapacitor has been assembled by using mesoporous nickel cobaltite-graphene nanocomposite as the positive electrode and doped carbon as the negative electrode. Benefitting from the balanced capacity on positive and negative electrode, the fabricated asymmetric supercapacitor exhibit a remarkable energy density of 52.2 Wh kg^{-1} and excellent cycling life with 97.3% capacitance retention ratio after 10,000 cycles. The outstanding electrochemical performance can be attributed to the synergetic contribution of these two electrodes, which gives a promising way for designing high performance energy storage device.

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1. Introduction

With the increasing interests of hybrid vehicles, portable electronics, and capable devices, the demand for the electrochemical energy storage systems with high power and energy is emergency [1–3]. Supercapacitors, known for the high power, long cycle life and good environmental friendliness, have attracted great attention [4–6]. There are two main types of supercapacitors: electrochemical double-layer capacitors (EDLCs) and

pseudocapacitors. The charge storage mechanism for EDLCs is based on the reversible ion adsorption/desorption at the electrolyte/electrode interfaces, while the charge storage mechanism for pseudocapacitor is based on the highly reversible redox reaction on the surface or the inside of electrode materials [2,3,7]. Carbonaceous material is the dominant electrode for EDLCs [7,8], and metal oxides and conductive polymers are typical electrodes for pseudocapacitors [9,10].

Great efforts have been made in fabricating inexpensive metal oxide electrodes, such as MnO_2 , Fe_3O_4 , Co_3O_4 , NiCo_2O_4 , NiO , and $\text{Ni}(\text{OH})_2$ [11–27]. Among them, nickel, cobalt, and manganese-based oxides are promising electrode materials for supercapacitors

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due to their low cost, environmental friendly, natural abundance, and super high theoretical specific capacitance ($1370\text{--}3560\text{ F g}^{-1}$) [23,26]. More importantly, NiCo_2O_4 possesses much better electrical conductivity and higher redox activity compared to nickel oxides and cobalt oxides, which makes it a cost-effective alternative for pseudocapacitors [28]. Although metal oxides exhibit high capacitance of $1000\text{--}3000\text{ F g}^{-1}$ [10,22,29], their poor rate capability and cycle stability limit the large-scale application. The design of nanostructured metal oxide is one of the most effective approaches to solve these problems [2,5,30]. However, most metal oxides also faces the disadvantage of poor conductivity [24,26]. The incorporation of carbon material is a common and promising way to increase the conductivity, and the existence of carbon network can also act as a support to disperse metal oxide at the nanoscale, which can further improve the power characteristics [31,32]. Another thing worth mentioning is that the useful electrochemical potential window for metal oxide-based pseudocapacitors is usually narrow, *i.e.* smaller than 0.6 V for nickel/cobalt-based oxide [31,33–35]. Therefore, the promising application of metal oxides is in asymmetric devices, which combines the pseudocapacitance-based metal oxide as the positive electrode and EDLC-based carbon as the negative electrode. The combination of different charge storage mechanisms in asymmetric devices can make use of the different electrochemical potential windows of the two electrodes, leading to a wider operating voltage window, and this is the main reason for the higher energy density can be obtained for asymmetric devices [36–38].

As for asymmetric capacitors, the charge (q) stored at the positive (q_+) and negative (q_-) electrodes should be equivalent, which is correlated with the specific capacity (Q) and the mass (m) of the electrode ($q = Q \times m$). In order to achieve $q_+ = q_-$, the mass ratio of the positive and negative electrode can be expressed as: $m_+/m_- = Q_-/Q_+$, where m_+ and Q_+ are the mass and capacity for positive electrode, and m_- and Q_- are the mass and capacity for negative electrode. It is generally accepted that the maximum specific capacitance of the asymmetric capacitors can be obtained when $Q_+ = Q_-$ and $m_+ = m_-$ [29,36,39]. It is well known that the specific capacitance of metal oxides is much higher than that of carbons, so the used mass of negative electrode is much larger than that of the positive electrode, which usually results in a relatively lower capacitance and energy density for asymmetric capacitors [2,10,31]. Therefore, there is a great demand for improving the capacitance of carbon electrode.

Herein, we assemble a novel asymmetric device based on mesoporous nickel cobaltite-graphene positive electrode and doped carbon negative electrode (Fig. 1). A hydrothermal method was used to fabricate the mesoporous nickel cobaltite-graphene nanocomposite, and the incorporation of graphene increases the conductivity of the composite and ensures the distribution of nickel cobaltite at the nanoscale, leading to excellent electrochemical performance [40,41]. In order to balance the capacity of the positive electrode with the same mass loading, we chose a nitrogen and oxygen codoped porous carbon as the negative electrode. The asymmetric capacitor fabricated with the positive to negative mass ratio of 1:1 can deliver a high energy density of 52.2 Wh kg^{-1} at a power density of 187 W kg^{-1} . It is worth to note that previous literatures reported lots of metal oxides with much higher capacitance than our synthesized mesoporous nickel cobaltite-graphene electrode, however, as would be demonstrated later, the reported energy density of the fabricated asymmetric cells is inferior or comparable to our assembled asymmetric capacitor. This explanation can be found in the lack of suitable carbon electrode, and most of the capacitance for the positive electrode is wasted. Therefore, this work gives a case study to make the positive and negative electrodes ideally balanced for fabricating high-performance asymmetric devices.

2. Experimental

2.1. Synthesis of mesoporous nickel cobaltite-graphene nanocomposite

Generally, a mixture of graphene oxide dispersion (produced by XF Nano, INC), nickel nitrate hexahydrate, cobalt nitrate hexahydrate and urea (the molar ratio of urea/($\text{Ni}^{2+} + \text{Co}^{2+}$) is 10:1) was transferred into an autoclave after being stirred for 20 min, and then heated to $180\text{ }^\circ\text{C}$ for 24 h. After the autoclave was cooled down to ambient temperature, the precursor was dried by vacuum freezing. Finally, the as-received precursor was annealed at $350\text{ }^\circ\text{C}$ in air for 2 h. The obtained Nickel Cobaltite-Graphene samples were termed as NCG- x , where x indicates the starting molar ratio of cobalt nitrate over nickel nitrate. For comparison, nickel oxide-graphene (denoted as NG) or cobalt oxide-graphene (denoted as CG) was also prepared by using the same procedure without the addition of cobalt or nickel salt.

2.2. Synthesis of doped carbon

Synthesis of the doped carbon was described in detail in our previous work [42]. Briefly, a mixture of (2-benzimidazolyl) acetonitrile and KOH (the mass ratio of KOH to acetonitrile is 4:1) was firstly grounded in an agate mortar. And then the mixture was carbonized and activated under nitrogen atmosphere at $700\text{ }^\circ\text{C}$. After washing with 2 M HCl solution and deionized water, the doped carbon (abbreviated as DC) was collected and dried under $80\text{ }^\circ\text{C}$.

2.3. Material characterization

The microstructures and morphologies of the samples were measured by transmission electron microscopy (TEM, JEOL 2010F, 200 kV), scanning electron microscope (SEM, Hitachi S4800, 15 kV) and X-ray diffraction (XRD, Bruker D8 Advance, $\text{Cu K}\alpha$ radiation). Nitrogen adsorption and desorption isotherms were examined by Micromeritics 3 Flex™ surface characterization analyzer at 77 K . X-ray photoelectron spectroscopy (XPS) was obtained using a Thermo ESCALAB 250XI spectrometer with a monochromatic source of $\text{Al K}\alpha$ radiation. Thermal gravimetric analysis (TGA) was measured by Mettler TG/DSC 2HT/1600 from $20\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ in air at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Raman spectra were tested by a microscopic confocal Raman spectrometer (Lab RAM HR800).

2.4. Electrochemical measurement

A slurry was prepared by mixing 80 wt% active materials, 10 wt% polyvinylidene fluoride (PVDF) and 10 wt% Super P with absolute alcohol, and then grounded with agate mortar. The slurry was coated on a nickel foam ($1 \times 1\text{ cm}^2$) to make the electrode, and then pressed at 10 MPa . The mass loading of active materials was about 8 mg cm^{-2} for all the electrochemical test. The electrochemical performance was carried out on both a three-electrode system and a two-electrode asymmetric system at room temperature. For a three-electrode configuration, the as-prepared electrodes were used as the working electrodes, and a Pt wire and Hg/HgO electrode were used as the counter and reference electrodes. For the two-electrode configuration, an asymmetric supercapacitor with mesoporous nickel cobaltite-graphene positive electrode and doped carbon negative electrode was assembled. For both systems, 2 M KOH was used as the electrolyte. Cyclic voltammograms (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) were all tested on Gamry Interface 5000 workstation.

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