Electrochimica Acta 158 (2015) 35–41

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Fabrication of three dimensional carbon nanotube foam by direct conversion carbon dioxide and its application in supercapacitor

Chunlei Wang *, Fangtao Li, Haili Qu, Yanan Wang, Xiaolei Yi, Yang Qiu, Zhijun Zou, Yongsong Luo, Benhai Yu

Key Laboratory of Advanced Micro/Nano Functional Materials of Henan Province, School of Physics and Electronic Engineering, Xinyang Normal University, Xinyang 464000, PR China

ARTICLE INFO

Article history:
Received 22 January 2015
Accepted 22 January 2015
Available online 24 January 2015

Keywords:
Three dimensional carbon nanotube foam
Nickel hydroxide
Template directed chemical vapor deposition
Hydrothermal
Supercapacitor

ABSTRACT

Carbon nanotube (CNT) is an ideal electrode material for supercapacitors due to its low electronic and ionic charge-transfer resistances. Here we reported the direct synthesis 3D carbon nanotube foam (CNTF) macrostructure by conversing CO_2 through template-directed chemical vapour deposition. Using this unique network structure and outstanding electrical and mechanical properties of the CNTF, as an example, we demonstrate the excellent electrochemical properties of $Ni(OH)_2$/CNTF composite. Based on the total mass of the electrode, as high as specific capacitances of 259 and 131 $F\,g^{-1}$ are obtained at current densities of 0.5 and 10 $A\,g^{-1}$ respectively. Meanwhile, the electrode also exhibits excellent long cycle life along with 94.0% specific capacitance retained after 2000 cycle tests. Moreover, this template-directed CVD technique is versatile and scalable, and can be a general strategy for fabricating a broad class of three-dimensional macroscopic structures of determined shapes with excellent properties and new uses.

1. Introduction

Specific energy storage devices possessing merits of light weight, low cost, and even safety can meet the large scale application of consumer electronics. Among various emerging energy storage technologies, supercapacitors, also called ultra-capacitors or electrochemical capacitors, with combined high power and high energy density [1–3], have been paid much attention in world wide and will be a promising candidate for energy storage devices. In order to achieve higher capacity, long cycle lifetime, and better rate performance, many efforts have been done to develop new electrode materials for supercapacitors [4–7]. Among all these materials, the transition metal oxides/hydroxides, such as MnO_2, Co_3O_4, NiO, $Ni(OH)_2$, have aroused tremendous research interest due to their very high theoretical capacitance [8–12].

In these electrode materials, nickel hydroxide ($Ni(OH)_2$) possesses high theoretical capacity($\sim$3650 $F\,g^{-1}$) and is easy to synthesize in different morphologies, thus, it is a strong contender as a electrode material for high performance supercapacitors. Unfortunately, like other electrode materials, ($Ni(OH)_2$ usually suffers from low conductivity, large volume change during charge and discharge processes and low coulombic efficiency [13]. In order to improve the electrochemical properties of $Ni(OH)_2$ based electrodes, various $Ni(OH)_2$ nanostructures have been investigated including the $Ni(OH)_2$ carbon composites [14,15].

The carbon based materials usually with high surface area and excellent conductivity, such as activated carbon, carbon nanotubes (CNTs), graphene, and hollow carbon nanostructures, offer a number of components to be applied in supercapacitors. Especially, these materials can play a vital role in improving the efficiency in charge/discharge processes by strengthening the conductivity of the composites. For example, Wang et al. have synthesized $Ni(OH)_2$ nanoplates on graphene and the electrochemical properties of $Ni(OH)_2$ were improved greatly [16]. Zhang et al. have reported a 3D hierarchical porous α-$Ni(OH)_2$/graphite nanosheet composite and the as-prepared composite exhibited large specific capacitance, good rate capability and long cycle stability as compared to the pure α-$Ni(OH)_2$ [17]. As reported in these references, such nanostructured composites have always been spread on a metal current collector to obtain a continuous conductive structure, which will increase the mass of electrodes and decrease the overall gravimetric specific capacitance. In addition, the typical addition of polymeric binder will hinder the charge transport and further decrease effective mass of the electrode. In order to resolve such a problem, lots of experiments have been explored. Recently, Mn_3O_4

---

* Corresponding author. Tel.: +86376 6391731.
E-mail address: wanglei@xynu.edu.cn (C. Wang).

http://dx.doi.org/10.1016/j.electacta.2015.01.112
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

nanoparticles have been successfully anchored on continuous carbon nanotube network and a high rate capacity as large as 342 mAh g^{-1} at 10 C was obtained [18]; Ji et al. have fabricated 3D ultrathin-graphite foam (UGF) by chemical vapor deposition, which was used as backbone of the composite electrodes to substitute traditional current collectors [19,20].

In this work, we have successfully fabricated three-dimensional carbon nanotube foam (CNTF) by direct conversion of carbon dioxide, and the CNTF have high electrical conductivity, low density, high surface area and good mechanical properties. These properties make us realize that the CNTF can be taken as novel current collectors to replace traditional one such as nickel foam or carbon paper. Thus, we report a binder-free $Ni(OH)_2$/CNTF composite by direct growth of $Ni(OH)_2$ on the CNTF surface by hydrothermal reaction. It is surprise to find that such $Ni(OH)_2$/CNTF composites show excellent electrochemical properties. In addition to its ecofriendly credentials, the present method has the merits such as low cost, high yield, and fabrication processing simple. Therefore, this method has potential for the large-scale synthesis of three-dimensional carbon nanotube foam.

2. Experimental methods

2.1. Synthesis of three-dimensional carbon nanotube foam (CNTF)

The 3D CNTF were synthesized by direct chemical reaction of Mg with CO_2 gas. Before the reaction, a high-purity alundum (Al_2O_3) boat ($20 \times 60 \times 90\,mm^3$) loaded with about 1 g Mg ribbons and several piece of nickel foam ($0.5 \times 10 \times 20\,mm^3$) used as a template was put into a horizontal tube furnace (Φ 70 × 1000 mm, HLZG-16B, LUOYANG HENGLI FURNACE KILN CO., LTD, China) filled with argon gas. The furnace was heated to the desired temperatures 800 °C and held at this temperature for 1–2 hours under argon gas atmosphere. Then CO_2 and argon gas mixture of about 1:3 – 3:1 volume ratios was flowing at 30–80 sccm. Once the expected reaction time was reached, CO_2 gas flowing was turned off and the furnace was cooled down to room temperature under argon gas atmosphere. A pure three-dimensional carbon nanotube foam was achieved after etching the nickel away by using 3 wt% HCl aqueous solution and 0.5 M $Fe(NO_3)_3$ aqueous solution at 80 °C, respectively. Then, the obtained CNTF were slightly placed in several baths of DI water, and finally rinsed in isopropanol before drying at 50 °C in ambient condition.

2.2. Fabrication of $Ni(OH)_2$/CNTF

The $Ni(OH)_2$/CNTF composite was fabricated by a hydrothermal reaction as follows: a total of 48 mg of $NiCl_2{\cdot}H_2O$ and 75 mg of urea were added to 30 mL of DI water, and then this homogeneous solution and the as-grown CNTF was transferred into an autoclave reactor. After that, the autoclave reactor was heated to 180 °C for 2 h and then cooled down to room temperature. The resultant $Ni(OH)_2$/CNTF composite was then washed using DI water and isopropyl alcohol several times. Finally, the obtained $Ni(OH)_2$/CNTF specimens were dried at about 60 °C in air oven. As a reference, a pure $Ni(OH)_2$ powder sample was prepared by the same method but without addition of CNTF.

2.3. General characterization

The chemical composition of the product was characterized by X-ray diffraction (XRD, Bruker, D8-Advance X-ray Diffractometer, Cu Kα, $\lambda = 1.5406$ Å). The morphology was examined using field emission scanning electron microscopy (SEM, Hitachi, S4800). Thermogravimetric analysis (TGA) was done using a 5 °C/min heating rate under 100 mL/min flow of air. All the materials were weighted by a high precision electronic balance (Sartorius BSA224S). Raman spectra were recorded on an INVIA Raman microprobe (Renishaw Instruments, England) with a 532 nm laser excitation.

2.4. Electrochemical measurements

Electrochemical measurements were carried out by electrochemical workstation (CHI 660E) using three-electrode configuration in 6 M KOH aqueous solution. The $Ni(OH)_2$/CNTF composite was the working electrode, and the reference and counter electrodes were SCE and platinum foil, respectively. The powder sample was prepared by loading the mixture of 80 wt% active materials, 10 wt% carbon black and 10 wt% Polytetrafluoroethylene (PTFE) on nickel foam ($1 \times 2\,cm^2$). The electrochemical impedance spectroscopy measurements were carried out with a frequency loop from 0.01 Hz to 100 kHz. The specific capacitances were calculated according to the formula of $C = I \times t/(\Delta V \times m)$, where I is the constant discharge current, t is the discharging time, V is the voltage drop upon discharging (excluding the $I\,R$ drop), m is the mass of the active materials on the electrode.

3. Results and discussion

3.1. Morphology and structure characterization

The structure of the CNTF and $Ni(OH)_2$/CNTF composite were investigated by x-ray diffraction, as shown in Fig. 1. For the CNTF, two typical diffraction peaks appear at about 26° and 42.7°, which correspond to the (0 0 2) and (1 0 0) diffraction planes, respectively, as shown in Fig. 1. The sharp (0 0 2) diffraction peak indicates a highly ordered graphitic structure of the CNTFs, which ensures the good electrical conductivity of the samples. The XRD of $Ni(OH)_2$/CNTF composites is also displayed in Fig. 1, and it can be seen that the main diffraction peaks are either due to CNTF or to β-$Ni(OH)_2$. However, some impurity diffraction peaks, which may be from α-$Ni(OH)_2$ (JCPDS: 14-0117), are also detected.

The Raman spectra for the CNTF and the $Ni(OH)_2$/CNTF composite are shown in Fig. 2(a). Both the curves exhibit two prominent peaks at 1342 and 1574 cm^{-1}, corresponding to the D and G bands, respectively. The G-band indicates original graphite features, whereas the D-band is known to depend on disorder features of graphitic structures as well as the presence of small crystalline grains. Commonly, the peak intensity ratio of the D and G band (I_D/I_G) can be used to roughly estimate the disorder degree and average size of the sp^2 domains of the graphite materials. Compared to the CNTF, the I_D/I_G ratio of the $Ni(OH)_2$/CNTF composite is decreased from 1.27 to 0.88, which is perhaps due to the increase in the size of the sp^2 graphitic domains during the preparation process [21]. The 460 cm^{-1} band can be attributed to the Ni-O(H) stretching mode, while the bands at 327 and 532 cm^{-1}

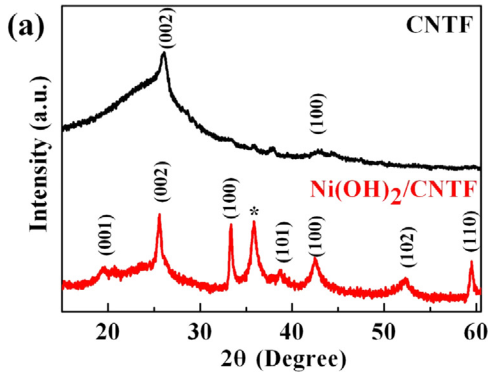

Fig. 1. The XRD patterns for the CNTF and CNTF/$Ni(OH)_2$ composite.