



Ni(OH)₂ nanosheets grown on graphene-coated nickel foam for high-performance pseudocapacitors

T. Xiao^a, X. Hu^a, B. Heng^a, X. Chen^a, W. Huang^a, W. Tao^a, H. Wang^a, Y. Tang^{a,*}, X. Tan^b, X. Huang^b

^a Institute of Nano-Science and Technology, College of Physical Science and Technology, Central China Normal University, Wuhan 430079, PR China

^b Research Institute for New Energy, China Three Gorges University, Yichang 443002, PR China

ARTICLE INFO

Article history:

Received 29 May 2012

Received in revised form 6 September 2012

Accepted 7 September 2012

Available online 16 September 2012

Keywords:

Graphene

Ni(OH)₂

Nanosheets

Pseudocapacitors

ABSTRACT

This paper reports a new two-step approach for growing hybrid Ni(OH)₂/graphene structure on nickel foam for the first time. Firstly, graphene was synthesized on nickel foam, which was used both as catalyst and template, by a CVD method. Then the three-dimensional network structured Ni(OH)₂ nanosheets were deposited on the graphene-coated nickel foam by a hydrothermal method. Electrochemical tests of this kind of electrode show a high specific capacitance (1440 F/g) and excellent cycling performance of ~100% capacitance retention over 2000 cycles in a 1 M NaOH electrolyte. The presence of the graphene is critical to the high-performance of the electrode, and the experiment using the Ni(OH)₂ on bare nickel foam exhibited a much worse cycling performance.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Pseudocapacitors, storing energy via reversible faradaic redox reaction at the electrode surface, are considered as a promising candidate for energy storage systems due to much higher specific capacitances and energy density compared with supercapacitors [1]. Up-to-date, the most attractive materials for pseudocapacitors are cheap transition metal oxides or hydroxides and conducting polymers [2–6]. However, they often result in compromises of rate capability and reversibility because redox kinetics is limited by the rates of ion diffusion and electron transfer [7,8]. To deal with the problems, attempts at novel electrode design have been extensively made, that is anchoring nanostructured active materials onto highly conductive substrates (e.g. carbon aerogels [9], conducting polymers [10], and graphene [11,12]) with large specific surface areas.

Among these substrates, graphene, a two-dimensional monolayer of carbon atoms packed into a honeycomb lattice, is an ideal single-atom-layered conductive substrate for growth of other functional materials to render them electrochemically active and electrically conductive to the outside current collectors. Besides the single-layer-atom thickness, they have aroused increasing attention owing to their large specific surface area, high flexibility, mechanical strength, extremely high thermal and electrical conductivity and lightweight [13–17]. Recent works have shown significant role of graphene in graphene-based functional

composites for energy storage application. For instance, MnO₂ grown on graphene coated three-dimensional, porous textiles exhibit promising characteristics with a maximum power density of 110 kW/kg, an energy density of 12.5 Wh/kg, and excellent cycling performance of ~95% capacitance retention over 5000 cycles [11]. One of the most common methods for fabricating graphene-based functional composites electrodes can be described as the following three steps: (1) preparing of graphene oxide (GO) by Hummers method or modified Hummers method followed by a reduction of GO to reduced graphene oxide (RGO); (2) combining RGO with a second component [12,18–21]; and (3) mixing the active materials with a conductive agent and a binder to make a paste and then apply it to current collectors. This method, however, suffers some drawbacks, as follows: (1) graphene obtained from “Hummer” method is usually in low quality; (2) the combining process of graphene with second components usually suffers from the aggregation of graphene or the second components; (3) it is difficult to make a homogeneous paste in the electrode preparation process. Recently, Chen et al. fabricated three-dimensional flexible and conductive interconnected graphene network on nickel foam by template-directed chemical vapor deposition. Even with a loading as low as ~0.5 wt.%, graphene can significantly enhance the electrical conductivity of the graphene-based composites. And the electrical conductivity is ~6 orders of magnitude higher than chemically derived graphene-based composites [22]. In these regards, we explore a new two-step approach for growing hybrid Ni(OH)₂/graphene structure on nickel foam. The first step is to grow graphene directly on nickel foam using CVD technique, which is considered as the most effective way for fabrication of large-area

* Corresponding author. Tel.: +86 27 67867947; fax: +86 27 67861185.

E-mail address: ywtang@phy.cnu.edu.cn (Y. Tang).

and high-quality graphene films. The second is the deposition of $\text{Ni}(\text{OH})_2$ on the as-prepared graphene-coated nickel foam. Here, nickel foam has been used as unique substrate because the following: nickel is one of the most commonly used catalysts in CVD technique for high-quality graphene growth and also an ideal current collector. Furthermore, nickel foam with three dimensional (3D) network structure also working as template for the growth of graphene and subsequent $\text{Ni}(\text{OH})_2$ results in the 3D structure for the whole electrode, thus facilitating easy access of electrolyte ions to electrode surface. In addition, the final nickel foam can be directly used as electrode without further treatment. In general, this new two-step strategy takes advantages including in simple and cost-effective preparation process, high-quality of graphene, and uniform mixture of graphene and $\text{Ni}(\text{OH})_2$. This method may be helpful for developing novel design for graphene-based composite electrode materials.

2. Experimental details

2.1. Synthesis

All of the reagents used in the experiments were of analytical grade and used without further purification. The $\text{Ni}(\text{OH})_2$ /graphene structured nickel foam was fabricated by a two-step approach. Firstly, the graphene was synthesized on nickel foam by a CVD method, as follows: a piece of nickel foam was placed at the center of a horizontal quartz tube mounted inside a high-temperature furnace. Before heating, 100 sccm N_2 was introduced for 20 min to remove the air. Then the nickel foam was rapidly heated to 1000 °C under N_2 (50 sccm) and H_2 (50 sccm) and annealed for 5 min to clean their surfaces and eliminate a thin surface oxide layer. A small amount of C_2H_2 (8 sccm) was then introduced into the reaction tube as carbon source at ambient pressure. Four minutes later, both the C_2H_2 and H_2 were turned off and the furnace was cooling under ambient N_2 . Secondly, the $\text{Ni}(\text{OH})_2$ were deposited on the graphene-coated nickel foam by a simple hydrothermal method: 0.291 g $\text{Ni}(\text{NO}_3)_2$ and 0.72 g hexamethylenetetramine were dissolved in 50 mL deionized water and then were transferred into a Teflon-lined stainless steel autoclave. Then the graphene-coated nickel foam was placed in the reaction solution and the autoclave was sealed and kept at 80 °C for 10 h. After natural cooling to room temperature, the sample was washed with deionized water and then dried at 60 °C for 60 min.

2.2. Characterizations

The products were characterized using powder X-ray diffraction (XRD, Bruker D8 Advance, Cu-K α radiation; $\lambda = 1.5418 \text{ \AA}$), scanning electron microscopy (SEM, JEOL JSM-6700F, 8.0 kV), transmission electron microscopy (TEM, JEOL JSM-2010, 200 kV) and Raman spectroscopy (LabRAM HR 800 UV with laser excitation at 514 nm). The electrochemical properties were examined with a dual channel electrochemical workstation using a conventional three-electrode system. For electrochemical tests, the electrode with a geometrical surface area of $\sim 1 \text{ cm}^2$ (the active material is about 1 mg) was used directly as the working electrode, a saturated calomel electrode (SCE) was used as the reference, and a platinum wire was used as the counter electrode. The electrolyte was 1 M NaOH solution.

3. Results and discussion

Fig. 1a shows the Raman spectrum from nickel foam after the growth of graphene, revealing the presence of D, G, and 2D peaks.

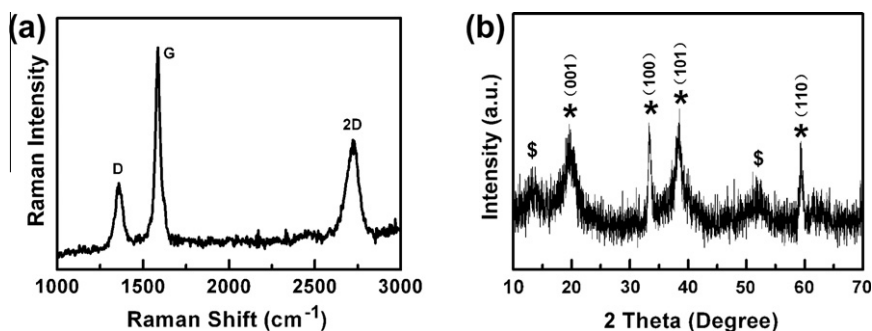


Fig. 1. (a) Raman spectrum of the graphene coated nickel foam, (b) XRD pattern of the nickel foam after hydrothermal process (*: $\text{Ni}(\text{OH})_2$; \$: $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$).

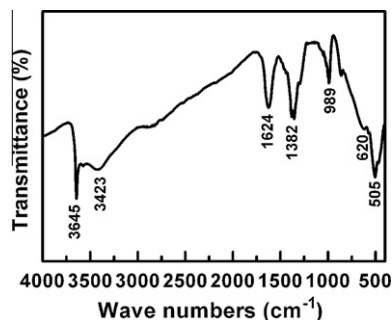


Fig. 2. FTIR spectrum of the sample after the hydrothermal process.

The D peak would originate from the edges and the subdomain boundaries of graphene layers. The G peak is located at $\sim 1585 \text{ cm}^{-1}$, coinciding with the G peak for planar graphene. The position and shape of this G peak along with the symmetric 2D peak at $\sim 2720 \text{ cm}^{-1}$ provide evidence that graphene was indeed formed [23]. In order to detect the phase of the final films after the hydrothermal reaction, we used XRD characterization, and the result (Fig. 1b) shows that the main peaks can be well indexed to $\text{Ni}(\text{OH})_2$ (JCPDS no. 03-0177). Besides the main peaks, two weak peaks from the $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ (JCPDS no. 22-0752) can also be detected, suggesting that some NO_3^- intercalate in the interlayer.

Fourier transforms IR (FTIR) spectrum (Fig. 2) provides evidence for the presence of intercalated NO_3^- . It has been reported that $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ possesses a layered structure (even larger interlayer distance than $\text{Ni}(\text{OH})_2$) can potentially facilitate ion diffusion [8]. Two strong peaks observed at 989 and 1382 cm^{-1} prove the presence of interlayer nitrate anion. Three peaks at 505, 620, and 3645 cm^{-1} are associated with the ν -Ni-O vibration, σ -OH vibrations and ν -OH stretching, respectively. Two peaks at 1624 and 3423 cm^{-1} are associated with the vibrations of H_2O .

The representative SEM images shown in Fig. 3a and b reveal the surface morphology of the Ni foam before and after the graphene growth. Abundant ripples and wrinkles are formed on the graphene films, due to the different thermal expansion coefficients between nickel and graphene [24]. These ripples and wrinkles probably result in better adhesion when integrated with other components to form composite materials [22]. SEM images in Fig. 3c and insert demonstrate the $\text{Ni}(\text{OH})_2$ nanosheets are uniformly coated onto the graphene-wrapped nickel foam and forms to a 3D network structures. A close examination of the exposed profile (Fig. 3d) reveals that thickness of the nanosheets is about 10 nm.

The TEM image (Fig. 4) of an individual nanosheet shows the sheet has a very faint and homogeneous contrast, reflecting its thin nature and uniform thickness. The corresponding ring-like SAED patterns from the inside to the outside can be indexed to the

Download English Version:

<https://daneshyari.com/en/article/1615157>

Download Persian Version:

<https://daneshyari.com/article/1615157>

[Daneshyari.com](https://daneshyari.com)