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Facile synthesis and electrochemical performance of nitrogen-doped porous hollow coaxial carbon fiber/Co_3O_4 composite

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ABSTRACT

Economy and efficiency are two important indexes of lithium-ion batteries (LIBs) materials. In this work, nitrogen doped hollow porous coaxial carbon fiber/Co_3O_4 composite (N-PHCCF/Co_3O_4) is fabricated using the fibers of waste bamboo leaves as the template and carbon resource by soaking and thermal treatment, respectively. The N-PHCCF/Co_3O_4 exhibits an outstanding electrochemical performance as anode material for lithium ion batteries, due to the nitrogen doping, coaxial configuration and porous structure. Specifically, it delivers a high discharge reversible specific capacity of 887 mA h g^{-1} after 100 cycles at the current density of 100 mA g^{-1}. Furthermore a high capability of 415 mA h g^{-1} even at 1 A g^{-1} is exhibited. Most impressively, the whole process is facile and scalable , exhibiting recycling of resource and turning waste into treasure in an eco-friendly way.

1. Introduction

With the development of the society, the use of traditional energies especially the fossil fuels has brought great harm to the environment, such as greenhouse effect, acid rain and haze, etc. Lithium ion batteries, as a kind of clean energy have attracted the extensive interests of researchers for its high specific capacity [1,2], long cycle life [3,4] and excellent rate performance [5], and have been widely used in mobile phone, notebook, and hybrid-electric or all-electric vehicles. However, commercial graphite, the main anode material of LIBs, possesses low theoretical specific capacity (372 mA h g^{-1}) and poor cycle performance, which are far below the needs of high performance electric appliances and limit the development of LIBs. Therefore, it is urgent to replace the graphite by advanced anode materials.

Cobalt oxide (Co_3O_4) has long been the focus of scientific workers for LIBs due to its large theoretical specific capacity (890 mAh g^{-1}), resources abundant and low cost [6]. However, Co_3O_4 suffered from a low electric conductivity and the large volume change in the process of lithium ion (Li^+) insertion/extraction, which bring to the declined cycling performance, poor rate capability and restrict its commercial application in LIBs. In order to solve these problems, Co_3O_4/C especially nitrogen doped carbon (N-C) /Co_3O_4 with various structures were prepared [7,8]. Sun et al. [8] synthesized a hierarchically structured Co_3O_4/C by assembling layered double hydroxide (LDH) nanosheets to improve the cycling performance and rate capability. Park et al. [9] prepared Co_3O_4/C nanocapsules with onion-like carbon shells as anode material for LIBs, improving electrical conductivity, structural stability and electrochemical performance. And Han et al. [10] fabricated porous fish-scale structures Co_3O_4/N-C derived from a well-designed N-rich Co-MOF template for building LIBs. Furthermore, dodecahedrons structure Co_3O_4/N-doped porous carbon hybrid was prepared by Hou et al. by a two-step thermal transformation of a Co-ZIF [11]. As far as we know, the nitrogen doped hollow porous coaxial carbon fiber (N-PHCCF/Co_3O_4) composite has not been prepared and used for anode material of LIBs.

In this work, porous hollow coaxial N-PHCCF/Co_3O_4 composite was successfully prepared by a simple, low-cost and eco-friendly route, using waste bamboo leaves as the template and carbon resource. The doping of N element in C material not only enhanced the conductivity of the product, but also provided more active sites for lithium storage by inducing plenty of defects to form disordered structure, which is benefit for improving the electrochemical performance. As an anode material for LIBs, the N-PHCCF/Co_3O_4 composite shows a high reversible specific capacity, excellent rate performance and good cycling stability.

2. Experimental section

2.1. Materials

The waste bamboo leaves were collected from Hefei qingyuan market (P. R. China). $Co(NO_3)_2{\cdot}6H_2O$, NH_3H_2O, H_2SO_4 and Absolute

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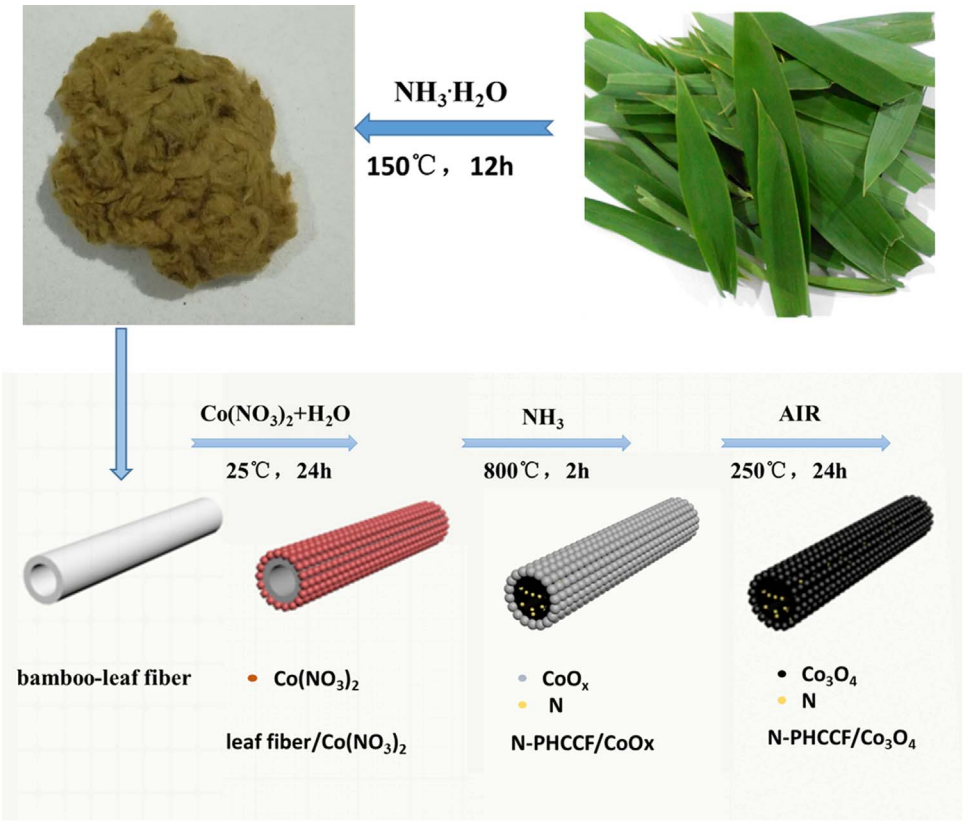

Scheme 1. The Synthesis of N-PHCCF/Co_3O_4 nano particles.

ethanol were obtained from Shanghai Chemical Reagent Co. Degussa (P. R. China) and of analytical grade. Milli-Q water (Millipore Corp., with resistivity of 18.2 MΩ cm) was employed for all experiments.

2.2. Synthesis of porous N-PHCCF/Co_3O_4 composite

The synthesis process of N-doped hollow coaxial carbon fiber/Co_3O_4 nanocomposites is shown in Scheme 1. Typically, the waste bamboo leaves were rinsed with Milli-Q water and absolute ethanol, followed by fragmented with a high-speed blender. Then, 2 g of these fragments were put into Teflon-lined stainless steel autoclave containing 100 mL of 70 mL $NH_3{\cdot}H_2O$. Next the autoclave was sealed and placed still in an electric oven at a temperature of 150 °C for 12 h. When cooled down to room temperature naturally, the obtained precursors were collected by vacuum filtration with common filter paper, washed by distilled water for three times and dried at 80 °C in an electric oven. Subsequently, the precursors were immersed into $Co(NO_3)_2$ solution (0.4 mol L^{-1}, 50 mL) at room temperature for 24 h, making the Co^{2+} thoroughly infiltrated into the fragments of bamboo leaves to form the adsorption products. Then the products were freeze-dried for 2 days, and annealed at 800 °C in the NH_3 atmosphere for 2 h (ramp: 5 °C min^{-1}). After this, the products were kept at 250 °C in air for 12 h at a rate of 1 °C min^{-1}. After cooling down to room temperature, the N-PHCCF/Co_3O_4 composite was obtained.

For comparison, the N-PHCCF was obtained from dispersing N-PHCCF/Co_3O_4 into 2 M H_2SO_4 solution and stirred for 48 h while the Co_3O_4 was gotten from keeping N-PHCCF/Co_3O_4 at 600 °C in air for 2 h at a rate of 3 °C min^{-1} for removing N-PHCCF.

2.3. Characterization

The phases of the samples were ascertained by X-ray diffraction (XRD) using an X-ray diffractometer instrument (DX-2700, Dandong Haoyuan instrument Co., Ltd., P. R. China) with Cu-Kα radiation (λ = 1.5406 Å), and the accelerating voltage and applied current were 35 kV and 25 mA. The scanning electron microscopy (SEM) measurements of the as-synthesized products were conducted by scanning electron microscopy (JEOL S-4800). Transmission electron microscopy (TEM) images were obtained using JEM-100SX electron microscope (Japan Electron Co. Ltd.). The Raman spectra of products were performed by Raman spectrometer (Renishaw inVia-Reflex, frequency range between 100 and 2000 cm^{-1}, with excitation wavelength of 532 nm). Thermogravimetric analysis (TGA) was analyzed using a TGA-50 instrument. X-ray photoelectron spectra (XPS) were carried out using an ESCALAB 250 spectrometer (Perkin-Elmer).

2.4. Electrochemical measurement

The electrochemical performances of samples were measured by using CR2016 type coin cells. The working electrodes were fabricated with 75 wt% active materials, 15 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP) to form uniform slurry. Then the slurry was coated on copper foil and dried in vacuum at 120 °C for 10 h. The coin cells were assembled in an argon-filled glove box using metallic lithium as the counter electrode, polypropylene film (Celgard, 2400) as the separator and $LiPF_6$ (1 M) dissolved in the mixed solution of dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 in volume ratio) as the electrolyte, respectively. The galvanostatic charge and discharge were performed in the voltage range of 0.01V-3.0 V (vs. Li^+/Li) using a battery test system (Neware CT-3800W, P. R. China). Cyclic voltammetry (CV) measurements were carried out on a CHI660D electrochemical workstation (Shanghai Chenhua instruments Co. Ltd. P. R. China) over the range from 3 V to 0.01 V at a scanning rate of 0.2 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was also conducted on the electrochemical workstation with amplitude of 5 mV in the frequency range between 0.01 Hz and 100 kHz.