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Nitrogen-doped carbon nanofibers as anode material for high-capacity and binder-free lithium ion battery

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ABSTRACT

Coral-like nitrogen-doped carbon nanofibers (CNFs) were directly grown onto stainless steel by a thermal CVD with N-rich imidazole and acetylene as precursor gasses. The resultant samples, as anodes without using any conductive additive and binder, were assembled into lithium ion batteries. The representative anode exhibits a high reversible capacity of 862.2 mA h g^{-1} at a current density of 200 mA g^{-1} and a capacity as high as 415.0 mA h g^{-1} at 2000 mA g^{-1} after 150 cycles. Such a superior electrochemical performance can be attributed to the unique coral-like nanostructure of CNFs as a result of nitrogen doping, which could shorten the diffusion distance of Li^+ and largen the contact area between the active materials and electrolyte.

1. Introduction

The rechargeable lithium ion batteries (LIBs) have attracted a great deal of attention for their advantages such as high energy density, high safety and long cycle life. They are welcomed as clean, efficient, low-emission renewable energy sources [1,2]. Extensive researches have been carried out for their anode materials aiming to improving the power and the energy density. Though graphite has been used as anode material for commercial LIBs, its lower capacity (the theoretical capacity is 372 mA h g^{-1}) and limited rate capability cannot meet the growing demands. New carbon-based anode materials need to be developed for LIBs application in high-power devices.

Nitrogen-doped carbon has been regarded as one of promising anode candidates for high-performance LIBs. It was suggested that nitrogen doping can generate extrinsic defects and form disordered carbon structure, leading to an enhanced Li^+ intercalation property [3]. Moreover, nitrogen doping can improve the electrochemical reactivity of the carbon materials and nitrogen functionalities may induce active sites to absorb Li^+ and enhance the capacity [4].

In this work, coral-like N-doped CNFs were directly grown onto the stainless steel (SS) plate by a simple CVD deposition. Nitrogen doping was *in situ* carried out via thermal decomposition of N-rich imidazole, which is an easy-to-operate method for relatively large-scale production. The obtained samples show high charge capacity, excellent cyclability and rate performance as conductive additive- and binder-free anodes of LIBs.

2. Experimental

Materials preparation: The undoped CNFs were deposited by a simple CVD process with a thin Ni film (5 nm thick) covered SS plate as the catalyst and substrate. 50 sccm acetylene was introduced into the quartz reactor of a tubular furnace heated to 800 °C, and maintained for 10 min. For the N-doped CNFs growth, 4 g imidazole was used as dopant and lead to the reactor along with acetylene. The pressure inside the quartz tube was maintained at atmosphere during the deposition.

Materials characterization: The morphologies and structures of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800), high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G^2 F30), and Raman spectrometer (Jobin-Yvon Horiba HR800) with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) analysis was carried on a Kratos Axis Ultra DLD instrument. Nitrogen adsorption–desorption isotherm measurements were performed on a micromeritics ASAP 2020 M volumetric adsorption analyzer at 77 K.

Electrochemical characterization: The electrochemical characterization was performed using CR-2032 coin cells. The cell assemble process has been reported in our previous paper [5]. The as-deposited CNFs on SS plate was directly employed as the working electrode without any conductive additive and binder, and lithium foil was used as the counter and reference electrode. Celgard 2320 was used as the separator membrane. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC)

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and diethyl carbonate (DEC) in a 1:1 volume ratio. The galvanostatic discharge–charge cycling and cyclic voltammetry measurements were carried out at room temperature by using a multichannel battery tester (Neware BTS-610) and an electrochemical workstation (CHI 660C), respectively.

3. Results and discussion

As shown in Fig. 1a, Raman spectrum of the obtained CNFs exhibit two peaks at 1600 (G band) and 1350 cm^{-1} (D band), corresponding to the vibrations of carbon atoms with sp^2 electronic configuration in graphite sheet structure, and the defects and disorder-induced structures in the graphite layers of carbon materials, respectively [6]. Basically, the relative intensity of D-band against G-band (I_D/I_G) represents the degree of disorder in the graphite structure. The Raman spectrum of N-doped CNFs shows a bigger intensity ratio of D-band to G-band, $I_D/I_G=0.95$, while the ratio for undoped CNFs is 0.89, indicating that nitrogen doping promotes the presence of the defects and structural disorder. To get a clear insight to the surface nitrogen functional groups in N-doped CNFs, the XPS spectrum around N1s peak is presented in Fig. 1b. It can be seen that the N1s peak consists of two individual peaks located at 398.4 and 400.7 eV. During the deposition of N-doped CNFs, N atoms from imidazole replace some C atoms, and thus different bonds are formed between carbon and nitrogen atoms with various binding energies (pyridinic N: 398.4 eV

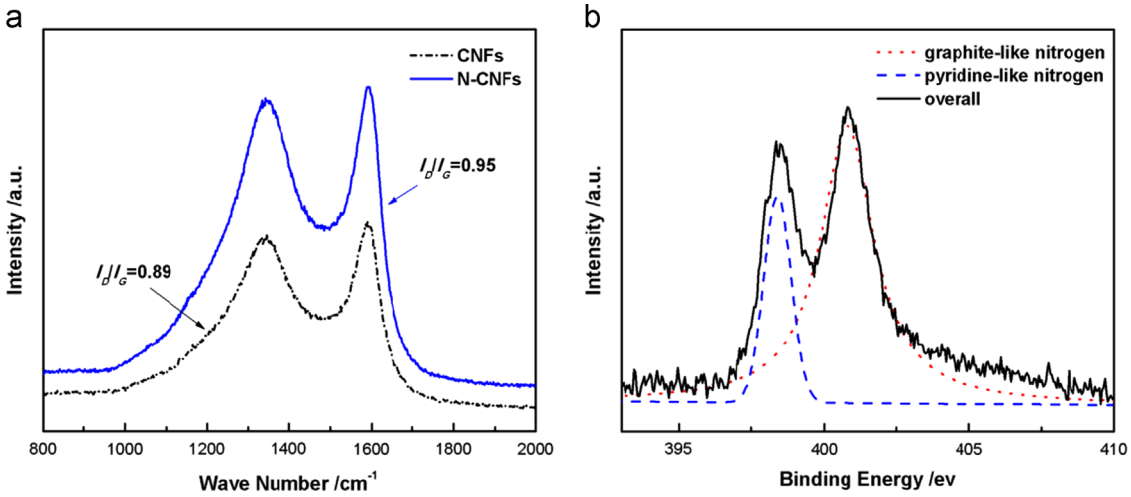

Fig. 1. (a) Raman spectra of undoped and N-doped CNFs; (b) XPS spectrum of N1s in N-doped CNFs.

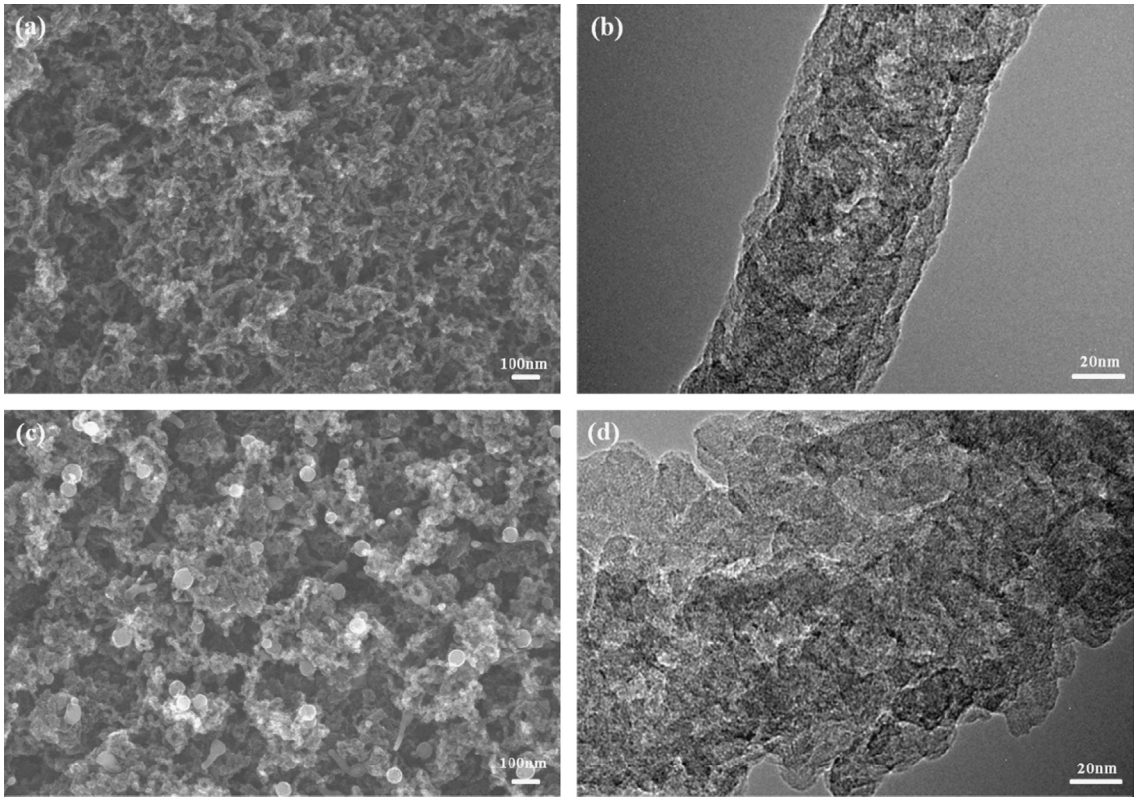

Fig. 2. SEM and TEM images of (a) and (b) undoped and (c) and (d) N-doped CNFs.