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Full Length Article

Facile flame catalytic growth of carbon nanomaterials on the surface of carbon nanotubes

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ABSTRACT

Hierarchical carbon structures with in-situ growth of small carbon particles on thick CNT (TCNT) were synthesized by a simple flame synthesis method. TEM tomography analysis indicated that flame synthesized CNT (FCNT) with different length and diameter (or carbon sphere particles) were deposited onto both the inner and/or outer tubular wall surface of the TCNT. The nano-confinement effect of the TCNT tubular space on the flame growth of carbon particles was investigated, which led to the formation of shorter and curved FCNT. Electron microscopy studies revealed that the tip growth mechanism dominated the ethanol flame-induced CNT synthesis process and the rate determining step for the flame growth of CNT was the nickel-catalyzed carbon deposit reaction rather than the mass transfer of the carbon source in the confined nano-channels of the TCNT. The influence of the type of metal catalyst on the products was also studied. Substantial improvements of electrochemical properties of TCNT after the decoration with FCNT confirmed the effectiveness and advantages of this method. The FCNT/TCNT anodes delivered a higher reversible lithium ion storage specific capacity than that of the pristine TCNT.

1. Introduction

Carbon materials with various nanostructures have been used and investigated for a very long time and great advances have been made during the last several decades. Many important carbon structures based on carbon nanotubes (CNTs) have been developed and utilized due to their intrinsic features of high theoretical specific surface area, structural tube features, low resistance and high stability in electrochemical reactions, and the existence of macroscopic quantum tunnelling effect, interesting chemical reactions within CNTs, which make them to be ideal electrochemical materials [1,2].

The development of hierarchical multi-scale carbon materials was demonstrated as a valid method to further improve the performance of these carbon materials. For instance, CNFs grafted with CNT [2–5], CNT grown on graphenes [6–8], carbon microtubes coated by carbon skeleton [9], porous carbon nanostructures [10–14], and various assembled-architectures with short CNTs [15] have shown much improved electrical conductivity, surface-to-volume ratio, electrochemical performance, interfacial and mechanical properties, etc. Such nanostructures have been studied as promising materials utilized in catalysis, structure engineering, field emission, sensor devices and electrode materials in batteries and capacitors.

Quite a few techniques have been developed to fabricate these architectures. One of them is to utilize the natural products as the carbon precursors [9–12]. The special construction of the carbon products can provide high energy storage capacity, excellent electrolyte diffusion rate and good rate capabilities. For instance, the capacitance of metaplexis derived activated carbon could be enhanced greatly with a long-term stability after the treatment through the formation of unique structure with carbon microtubes coated by carbon skeleton [10]. Recently, an electrospinning technique has also been employed for the fabrication of CNT/CNF hierarchical nanostructures [3–5]. In such a method, electrospun metal catalyst precursor/polymer nanofibers were carbonized and the CNT were grown on the electrospun carbonized nanofibers forming hierarchical nanostructures. The incorporated CNT on the surface of fibers can bridge adjacent fibers, creating better electrical and thermal conductive networks in the composites and the direct anchorage of CNT on the carbon substrates are in favor of the electric charge transfer between them. The hollow microtubes with micro/meso pores in the tube wall [10] or short CNTs [4,5], endow the

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carbon nano-architectures improved electrochemical energy storage performance.

Among the various methods for CNT deposit *in situ* onto the certain substrates, chemical vapor deposition (CVD) is the most utilized [15–18]. In comparison with the conventional methods by attaching preformed CNTs to the substrate, the technique through *in situ* growth of CNTs have many advantages, including better distribution on the substrate, higher loading density, seamless interface and even control of orientation of CNTs. For example, good interfacial bonding between the flame synthesized CNT and CF substrate was reported recently [19].

Although extensive research work on deposit of CNTs onto various substrate have been reported in literatures, little information on the flame growth of CNTs in confined nano-space is available so far, probably due to the consideration of larger length of deposit CNTs than the small inner diameter of the normal CNTs substrate. The interior nano-space of CNTs provides a nano-reactor and interactions (including electron transfer) between confined nanomaterials and carbon walls could be different from those happened on the nanomaterials on outer tube surface. These benefit the catalysis performance enhancement and extensive attention have been attracted on the effect of confinement inside carbon nanotubes on catalysis and excellent catalytic performance of the particles confined inside CNTs was reported recently [20–22].

In the present work, we utilized a simple flame synthesis method to prepare hierarchical carbon nano-architectures in the ethanol flame and demonstrate that the method readily allows the in situ chemical reduction of metal salt to nano-catalyst and the simultaneously catalytic growth of carbon nanomaterial (nanoparticles or flame synthesized CNTs (FCNTs)) in the confined nanotube space. The issue on the catalyst and nano-confinement effect of the tubular channel of CNT substrate on the flame growth of CNT was addressed in this work, as well as their corresponding growth mechanism. The electrochemical energy storage of the resulted hierarchical carbon materials displayed improved electrochemical energy storage. In consideration of the convenient flame process, low price of the fuel, simple combustion devices, open operation environment, and fast treatment process, the strategy is extremely promising for potential commercial application.

2. Experimental work

2.1. Materials

The thick carbon nanotube (Pyrograf Products Inc., named 'TCNT' here) was used as the substrate and it was first purified with a conventional chemical method using concentrated nitric acid to remove the metal impurities. Carbon nanotubes were in situ deposited onto TCNT by the recently developed flame synthesis method and the technique was provided in detail in our previous studies [23]. Typically, 0.05 mol/L metal chloride in ethanol solution was employed as the catalyst precursor and an ethanol flame with a diameter of ~4 cm was used as the carbon source and deposition environment. Briefly, TCNT with $NiCl_2$ catalyst precursor was put into a homemade stainless steel net and inserted for the flame growth of CNT for given times, where the temperature was controlled at ~500 °C. The samples with the flame growth of FCNT for 3 min and 10 min were noted as TCNT/FCNT3 and TCNT/FCNT10, respectively. The temperature was measured by a Fluke 724 temperature calibrator connected to a thermocouple tip inserted beside the samples in the flame.

2.2. Characterization

Raman spectroscopy of the fabricated samples was performed on an Invia Renishaw Raman using a He-Ne laser at 633 nm wavelength. Scanning electron microscopy (SEM) images were taken on a Zeiss ULTRA Plus and optical images on a Leica microscope. Transmission electron microscopy (TEM) was on the following instruments: routine imaging - Philips CM12 (120 kV), high resolution TEM (HRTEM) – JEOL 2200FS (200 kV); electron tomography-JEOL 1400 (120 kV). The 2D experimental images were recorded in a bright-field mode on a JEOL 1400 (120 kV) using a high-tilt sample holder. The tilt series were acquired with automatic rectification (corrections of focus and horizontal displacement) by using the Serial EM60 software on a 1350 × 1040 pixel Erlangshen CCD camera (Gatan). The tilt range was set from −30° to 30°.

The electrochemical tests were carried out on CR2032 coin cells. The sample slurry was prepared by mixing the active material, carbon black and polyvinylidene fluoride (PVDF) binder in the weight ratio of 80:10:10 using N-methy1–2-pyrrolidone solvent. The slurry was coated onto copper foil, from which pellets of 12 mm in diameter were cut to use as electrodes. The cells were assembled in an Ar-filled glove box with a Li foil as counter electrode, LiPF6 (1 M) in ethyl carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) as electrolyte and a microporous polyethylene film (Celgard 2400) as separator. The coin cells were subjected to cyclic tests at different currents between 0 and 3 V on a battery tester (LAND 2001 CT). The electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 100 kHz to 10 mHz on an electrochemical workstation (CHI660).

3. Results and discussion

3.1. in situ flame growth of carbon particles on TCNT

The formation of hierarchical carbon nanostructures is achieved by decorating TCNT with FCNT via one-step flame growth method. The corresponding fabrication strategy was illustrated as Fig. 1. The pristine TCNT are much thick and their outer diameter is in the range of 50–200 nm and inner diameter is always larger than 20 nm, which can be observed by the open tip highlighted by red arrows in Fig. 2a. Compared to the original clean TCNT (Fig. 2a), the surface of decorated TCNT become rougher due to the flame growth of CNT onto them (Fig. 2b). In contrast to the larger diameter of the pristine TCNT, the deposited FCNT are easy to be defined in the products because of their obviously less outer diameter. As shown in Fig. 2c, some entangled fine FCNT with a diameter up to 20 nm can be seen to be protruding from the open tip of TCNT surface (Fig. 2c) and some can be occasionally seen on the TCNT surface as well (Fig. 2b).

Different from the sparse FCNT found in their SEM images, it is surprising to see that much more FCNT are deposited onto the TCNT substrates by using TEM, as shown in Fig. 2d. Although the growth time is much longer than those deposited on the carbon fibers reported previously with the same flame growth method, the length of most FCNT (< 200 nm) here is much less than those FCNT growing for 3 minon carbon fibers [23], whose length are in micron scale. It is also observed that the outer diameter of the FCNT is in the range of 4–20 nm. As shown in Fig. 2e, the FCNT highlighted by blue arrows

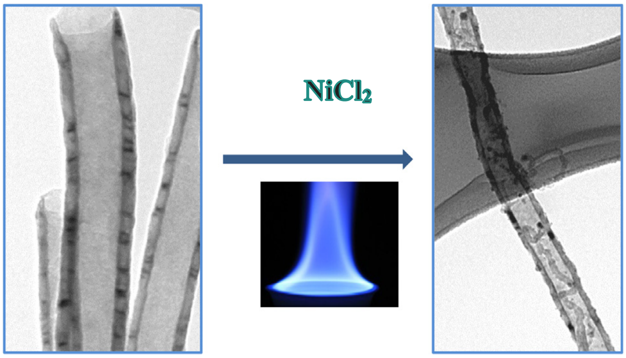

Fig. 1. Schematic of the all-through decoration of TCNT by the in situ flame growth of CNT.