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Flowing nitrogen assisted-arc discharge synthesis of nitrogen-doped single-walled carbon nanohorns

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ABSTRACT

Nitrogen-doped single-walled carbon nanohorns (N-SWCNHs) have been synthesized by a flowing nitrogen assisted arc discharge method at atmospheric pressure in a tubular reactor. X-ray diffraction and thermogravimetric analysis have revealed their high quality. Scanning electron microscopy and transmission electron microscopy examinations have shown that N-SWCNHs have typical spherical structure with a diameter of 40–80 nm. Oxidation treatment suggests the opening of cone-shaped caps of N-SWCNHs. The FT-IR and X-ray photoelectron spectroscopy analysis indicate that most of the nitrogen atoms are in N-6, N-5, and triple-bonded —CN bonding configuration present at the defect sites or the edges of graphene layers.

1. Introduction

Single-walled carbon nanohorns (SWCNHs) are cone-shaped single-layered graphitic aggregates with a typical diameter of 50–100 nm, which have drawn great attention due to their scientific importance and potential applications including: magnetic resonance imaging [1], immunosensor [2], methane storage [3], catalyst supports [4,5], supercapacitors [6,7], drug delivery system [8,9], electrochemical detection and fluorescent detection [10–12]. Some techniques for making SWCNHs have been reported, including CO_2 laser ablation [13–15], flash-ignition of SWCNTs [16], the arc discharge in liquid [17,18], the torch arc in air [19], direct current arc discharge [20], the pulsed or alternating current arc-discharge method [21,22]. Of these available methods, the direct current arc discharge method is most widely used because of its simplicity and cost-effective technology compare to expensive laser equipments [20,23].

Kawai et al. have revealed that the formation of SWCNHs depends on not only the initial reaction condition (including the power density, the type of buffer gas or its pressure), but also the temperature gradient (controlled by arc in liquid, gas injection or gas composition) [24]. For example, the SWCNHs can be formed by the pulse or AC arc discharge though changing the power density [21,22]. Sano have demonstrated that the N_2 injection is necessary for the formation of SWCNHs using the arc discharge in water method. The key condition is that reactive carbon species must be immediately excluded from the arc zone, maintaining a rapid quenching rate of ablated carbon to form SWCNHs, but the SWCNHs have no nitrogen doping due to the existence of water hinder the ionization of nitrogen gas, and the production rate is also much lower due to the reaction of water and graphite anode in the hot arc zone [17]. Even for the CO_2 laser ablation method, the Ar gas flow moves the products immediately from the reaction chamber that is very important for the formation of SWCNHs [13].

The properties of nanocarbons are intrinsically associated with the type of hybridization, defects, and the doping of heteroatom. Heteroatom doping is an effective and promising way to tailor the electronic, mechanical, surface properties of nanocarbons that are of great potential in a number of fields such as fuel cells, sensors, field emission devices, lithium ion batteries, and catalyst supports [25,26]. It is well know that arc discharge is one of the most effective ways to ionize nitrogen rich precursors or nitrogen gas and deliver active nitrogen ions which is important to form nitrogen-doped (N-doped) carbon materials. Glenis et al. prepared N-doped carbons by arc vaporization of carbon rods in the presence of pyrrole and obtained an amount of 2.3 at.% of nitrogen doping [27]. Carbon nitride, N-doped carbon films, carbon-nitride heterofullerenes and N-doped carbon nanotubes had also been prepared by arc discharge in nitrogen or nitrogen/helium atmosphere [28–31].

In this paper, we report on the large scale synthesis of nitrogen-doped single-walled carbon nanohorns (N-SWCNHs) by a flowing nitrogen assisted direct current arc discharge method at atmospheric pressure.

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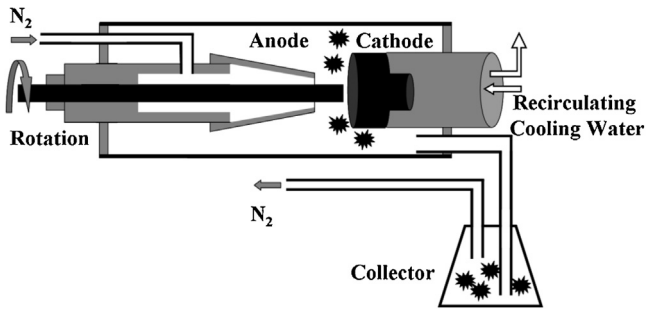

Fig. 1. A schematic of the continuous flow tubular reactor for making N-SWCNHs.

2. Experimental

The experiment was carried out in the nitrogen flow at atmospheric pressure. Fig. 1 is a schematic of the continuous flow tubular reactor (400 mm in length and 50 mm in diameter) used for making N-SWCNHs. The anode and cathode were made of high purity graphite rod (8 mm diameter, 300 mm in length for anode and 15 mm in diameter, 25 mm in height for cathode). The cathode was not destroyed after the arc discharge. The direct current arc-discharge was conducted at a current of 120 A in a flowing nitrogen of 6 L min^{-1} and the gap between the electrodes was kept at *ca.* 1 mm by rotating the anode. For each run, when pure graphite anode with length of 30–40 mm was consumed in *ca.* 3 min, about 2 g of N-SWCNHs can be obtained in the collector. As-made N-SWCNHs were purified by a gravitational sedimentation method. Typically, 1 g of as-made N-SWCNHs was dispersed in 500 ml ethanol using an ultrasonicator, and then the dispersion was left to stand for 48 h. Most giant graphite-balls were settled down, while N-SWCNHs remained in the supernatant [32].

X-ray diffraction (XRD) pattern was collected on a Rigaku D/Max2400 diffractometer with Cu Kα radiation (40 kV, 100 mA). Thermogravimetric analysis (TGA) was performed on a Netzsch 449C STA system from room temperature to 850 °C at a rate of 10 °C min^{-1} under an air flow of 50 sccm. The structures of the samples were observed by scanning electron microscopy (SEM, JSM-6301F, 20 kV) and transmission electron microscopy (TEM, Philips Tecnai G^2 20, 200 kV). Nitrogen sorption measurements were performed at −196 °C with a Micromeritics ASAP 2020 instrument. Prior to the sorption measurement, the samples were degassed at 200 °C for 5 h. Specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) equation in a relative pressure range from 0.06 to 0.30. The micropore volumes were obtained by *t*-plot method. The total pore volumes were the adsorbed amount at a P/P_0 of 0.99. The pore size distributions of the samples were obtained using the DFT approach. Fourier transform infrared (FT-IR) spectroscopy was carried out on a Nicolet-20 DXB spectrometer. X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo VG Corporation, USA) was used in the surface analyses of the samples. Al Kα line (15 kV, 10 mA, 150 W) was used as a radiation source, and the C1s peak position was set at 284.6 eV as an internal standard. The peak separations of the N1s and O1s core level peaks were estimated by least squares with Gaussian–Lorentzian functions after subtraction of background noise. The concentration of each element was calculated from the area of the corresponding peak calibrated with the atomic sensitivity factor using C as reference.

3. Results and discussion

The typical XRD profile of N-SWCNHs is shown in Fig. 2. The as-made N-SWCNHs show a sharp (0 0 2) diffraction peak due to the presence of the graphite balls formed in the preparation step

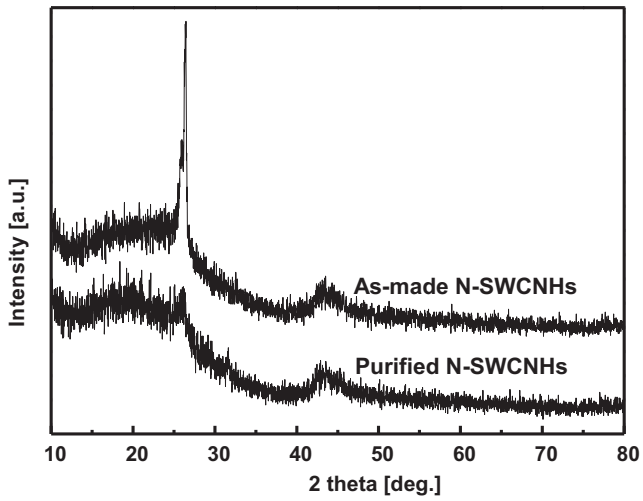

Fig. 2. XRD patterns of the N-SWCNHs.

of the N-SWCNHs. After the purification treatment, high quality N-SWCNHs were obtained evidenced by the fact that no such sharp (0 0 2) diffraction peak is present [33].

TGA has been widely used to evaluate the purity of the SWCNHs. According to the reports in literature, amorphous carbons, SWCNHs and giant graphite-balls can be burned at temperatures of *ca.* 350 °C, 570 °C and 700 °C, respectively [34]. The TGA results (see Fig. 3(a)) suggest that *ca.* 10 wt.% of graphite-balls with a weight loss at 700 °C is presented in the as-made N-SWCNHs, while in the purified N-SWCNHs, a single peak at 550 °C is observed in Fig. 3(b), indicating

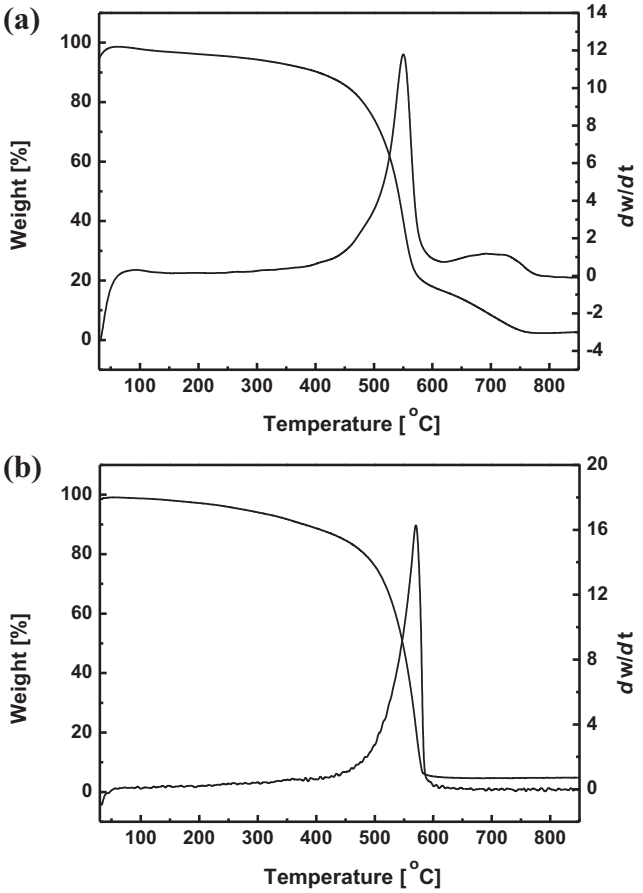

Fig. 3. TGA curves of (a) the as-made N-SWCNHs and (b) the purified N-SWCNHs.