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Positive pressure assisted-arc discharge synthesis of single-walled carbon nanohorns

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ABSTRACT

Catalyst-free, high-yield (kilogram-scale) and high-purity (> 95%) synthesis of dahlia flower and "bud-like" single-walled carbon nanohorns (SWCNHs) has been achieved via DC arc discharge under high pressures of Ar gas up to 0.35 MPa. In contrast, the mean size (100 nm) of SWCNH particle was twice as large as the counterpart in the literature via arc discharge. A new growth mechanism is proposed rationally to explain the mass production of SWCNHs under positive pressures, the growth mechanisms of SWCNHs rely mainly on the concentration of carbon clusters, rather than the temperature gradient of arc zone.

1. Introduction

Single-walled carbon nanohorns (SWCNHs) have been widely studied in view of their impressive physical, chemical and mechanical properties [1,2]. Potential applications of SWCNHs include as the support of Pt catalysts for fuel cells [3], gas storage [4], and supercapacitor [5]. Compared with numerous methods to obtain carbon nanotubes and graphene, there are very limited ways to efficiently prepare SWCNHs besides laser ablation [6] and arc discharge methods [7,8]. However, high running cost and complex operation retard the popularity of laser instruments by CO_2 laser vaporization. To meet the commercial demands for large-scale, low-cost and facile production of SWCNHs, arc discharge method is considered as a better choice than laser ablation. For example, carbon nanohorns have been synthesized by arcing in different gaseous (air, Ar, He) at atmospheric pressure with catalyst [8,9] or in liquid environments with gas injection [10]. Nevertheless, the obtained arc SWCHNs were not very satisfactory. The mean size was smaller than that of laser-ablated products (80–100 nm), and the yield was poor [7–11]. Investigating the reason, a spherical particle of SWCNH with size of ~100 nm is usually aggregated by about 2000 irregular SWCNTs, which are about 2 nm in diameter and 45 nm in length [12]. We suspect that the main reason and mechanism about forming SWCHNs are not because the temperature gradient of arc zone but because the low diffusion rate of carbon clusters with high concentration. By raising the gas pressure (> 1 atm) to improve the concentration of carbon clusters in our experiment, we successfully synthesized the SWCNHs in positive pressure which were seldom used in the synthesis of nanocarbons by arc method.

2. Experimental

SWCNHs were produced by direct current (110A and 30 V) arc discharge. The purity of graphite electrodes were up to 99.99%. Along with the anode was consumed, the rods were kept at a constant distant from each other of about 1.5 mm by continuously rotating the anode. A 15 mm Φ graphite cathode and a 6 mm Φ graphite anode were set horizontally. SWCNHs were made in positive pressure Ar gas of 0.15, 0.2, 0.3, and 0.35 MPa. The inner wall of vacuum chamber raw soot was collected. All samples were characterized by transmission electron microscopy (TEM, JEOL-200CX) and high-resolution trans-mission electron microscopy (HRTEM, JEM-2010F). Raman spectra were recorded with a HR-800 laser confocal micro-Raman spectrometer using laser excitation wavelength of 633 nm.

3. Results and discussion

3.1. Characterization by TEM and HRTEM

A typical spherical structure with a diameter about 100 nm was observed directly by TEM (in Fig. 1a). The SWCNH aggregates were counted for more than 95% of the soot particles, the rest consisted of amorphous carbon. The largest particle was nearly 140 nm and

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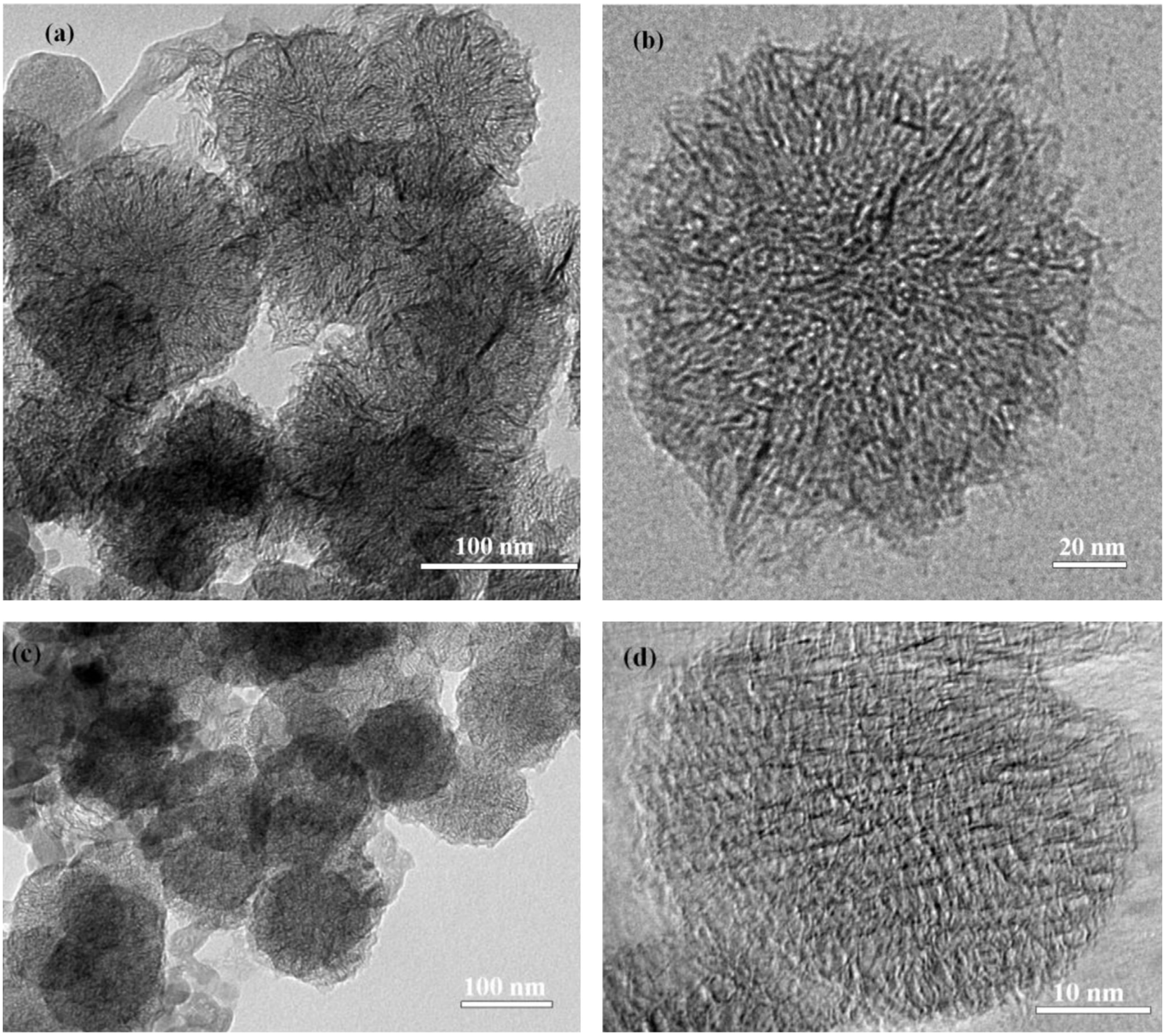

Fig. 1. (a) TEM and (b) HRTEM images of "dahlia-like" SWCNHs; (c) TEM and (d) HRTEM images of "bud-like" SWCNHs.

the best yield was obtained at 0.2 MPa. In Fig. 1b, we can see the aggregates were tubular structures with cone shaped caps and an average cone angle of 20°. With the increased pressure of Ar gas, carbon nanohorns became shorter and fewer in number, then disappeared completely in 0.3 MPa to form the "bud-like" SWCNHs (in Fig. 1c,d).

3.2. Raman spectroscopy analysis

The Raman spectra of the SWCNHs shows two prominent D-(disorder structure), G-band (graphitic structure) at ~1310, and ~1580 cm^{-1} that are characteristics of SWCNHs (in Fig. 2) [5]. The I_D/I_G ratio is frequently used to evaluate the defect density in graphitic nanostructures [13]. The reason that the full-width at half-maximum (FWHM) of D band in 0.15 MPa was much broader and the ratio of I_D/I_G was much higher than other conditions was because there are quantities of amorphous carbon surrounding [14]. When Ar pressure was 0.35 MPa, the FWHM of D band monotonically decreased from 151.71 to 97.56 cm^{-1}, it suggested the amorphous carbon efficiently disappeared. With the increased pressure, the ratio of I_D/I_G decreased from 2.34 to 2.17, indicating explicit improvement of the crystallinity.

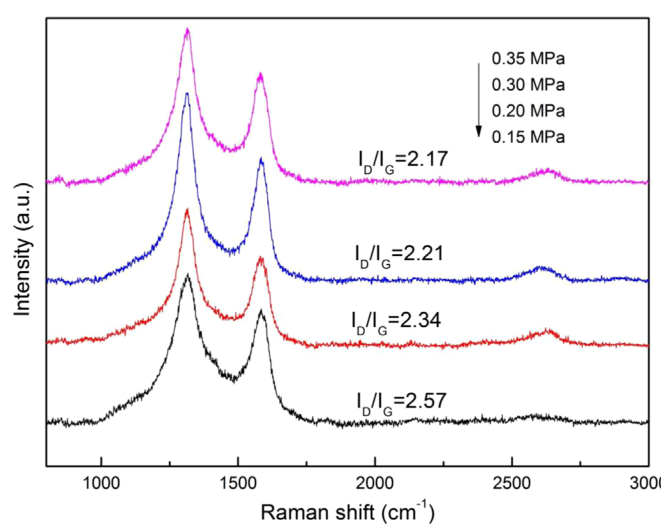

Fig. 2. The Raman spectra of SWCNHs that produced in 0.15, 0.2, 0.3, 0.35 MPa.