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Synthesis of thin bundled single walled carbon nanotubes and nanohorn hybrids by arc discharge technique in open air atmosphere

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ABSTRACT

Cost-effective synthesis of single walled carbon nanotube (SWCNT) and single walled carbon nanohorn (SWCNH) hybrids, in a single step, by electric arc discharge technique in open air, at lower current densities is reported. The rate of production of the hybrids is 3–5 g/h. The presence of SWCNTs and SWCNHs is confirmed by a transmission electron microscope (TEM). In addition to conventional larger Dahlia-like aggregates of nanohorns, unique nearly-spherical shaped and relatively smaller sized aggregates (mean size ~25 nm) of nanohorns are formed along with thin bundles (mean diameter ~5.7 nm) of SWCNTs.

1. Introduction

Single walled carbon nanotubes [1] and single walled carbon nanohorns [2] are considered as important materials due to their impressive physical, chemical and mechanical properties. The techniques used for the synthesis of SWCNTs are arc discharge [1], chemical vapor deposition (CVD) [3], and laser ablation [4]. Among these techniques, arc discharge is a simple, cost-effective and scalable technique [5] to synthesize SWCNTs. SWCNHs are synthesized by arc discharge [6] and laser ablation [7]. They are classified based on the assembly of the individual nanohorns such as Dahlia-like, bud-like or seed-like aggregates. These aggregates have a mean aggregate size of about 50 nm if synthesized by arc discharge [6] and 80–100 nm if synthesized by laser ablation [2,7]. Nanotube and nanohorn (NTNH) hybrids have received considerable attention in recent years and are being used to fabricate field emission lamps [8] and electrodes for super capacitors [9], due to their high surface area and pore volume. NTNH hybrids are typically prepared by sonication of a suspension of commercial SWCNTs with SWCNHs followed by drying, or by adding catalyst particles to the nanohorn aggregates and growing SWCNTs from the catalyst using CVD technique [8], which involves several steps and is time consuming. In this paper, we report a novel and cost effective method to synthesize NTNH hybrids in a single step using arc discharge technique in open air, resulting in thin bundles of nanotubes and relatively smaller sized nanohorn aggregates.

2. Experimental details

2.1. Synthesis of NTNH hybrids

Graphite rods of 99% purity, 11 mm in diameter, 150 mm in length and with a density of 1720 kg/m^3 were used as anode as well as cathode in an arc discharge setup. A hole of Φ3 mm, and depth of 50 mm, was made at the geometrical center of the cross-sectional surface of the anode. A mixture of graphite (99.98% purity), nickel (99.98% purity) and yttria (99% purity) powders with a weight ratio of 1:1:1 was finely ground with a mortar and pestle for 1 h. The hole in the anode was tightly packed with the above catalyst mixture. An electric arc was established between the electrodes by applying a potential of 36 V with a direct current of 100 A [10] using a SMAW/TIG inverter power source (Fig. 1).

The current density and power density were 105 A/cm^2 and 3.8 kW/cm^2, respectively. The cathode was kept stationary. The anode was manually moved towards the cathode and an arc was established between the electrodes when the separation between the electrodes was at ~1 mm. The anode was consumed continuously and black fumes from the arcing region were collected (as opposed to the soot on the cathode). The whole experiment was carried out in open air and no purging/shielding gases were used during the experiments. The synthesis was carried out for a maximum of 6 min in a single

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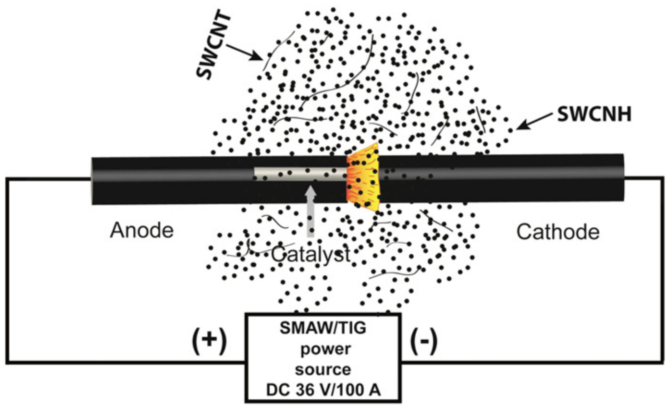

Fig. 1. Illustration of synthesis of NTNH hybrids by arc discharge technique.

run. Other than the heat generated during arcing, no specific effort was made to control the temperature of the chamber.

2.2. Characterization of nano-hybrids

The SWCNTs and SWCNHs were identified using a field emission scanning electron microscope (FE-SEM, FEI Inspect F) with an acceleration voltage of 30 kV. The number of individual SWCNTs in the bundles and the different morphologies of the nanohorn aggregates were characterized using a transmission electron microscope (TEM, Philips CM12) operated at an accelerating voltage of 120 kV. The samples were not purified prior to characterization. The number of SWCNTs present in single nanotube bundle was determined by constructing profile plots using ImageJ software. Raman spectra of the samples were recorded at room temperature using a helium–neon laser (wavelength 632.8 nm, E = 1.92 eV) at a range of 100–4000 cm^{-1}. The acquisition time was 100 s and the spectral resolution was 1.1 cm^{-1}.

3. Results and discussion

Once the arc is established between the electrodes, carbon atoms are discharged from the surface of the anode along with the catalyst (Nickel and Yttria) stuffed in the hole of the anode. The high temperature arc plume contains carbon and catalyst ions. The carbon ions condense together and form the aggregates of nanohorns, at the same time SWCNTs grow from the catalyst particles. Since the availability of the catalyst is lower (2.3 at.% Ni, 1.5 at.% Y), compared to graphite (96.2 at.%), all the carbon ions present in the arc plume are not transformed into SWCNTs. The carbon ions that are not involved in the formation of SWCNTs are converted either into nanohorn aggregates or form the soot on the cathode. The percentage of catalyst with respect to the graphite precursor determines the SWCNT and SWCNH fraction and it can be tuned by varying the catalyst to graphite ratio. The black fumes produced from the arcing region resulted in the deposition of black spongy soot, containing SWCNTs and SWCNHs, in the chamber.

FE-SEM micrograph, with SWCNTs indicated by white arrows and SWCNHs indicated by black arrows, shows the morphology and size of the aggregates present in the soot collected from the chamber walls (Fig. 2a). Since the SWCNT bundles are thin, they are not readily visible in the FE-SEM micrographs even at high magnifications. The well separated SWCNT bundles formed their network throughout the SWCNH aggregates thereby hindering the agglomeration of those aggregates. Spherical and nearly-spherical aggregates of SWCNHs are observed, which are relatively smaller in size compared to the conventional nanohorn aggregates synthesized by arc discharge method in both air and inert atmospheres [11]. D M Gattia et al. observed SWNHs and mutltiwalled carbon nanotube hybrids by arc discharge method in open air as well as Ar atmospheres [12]. They also reported the formation of SWNHs and graphene sheets by same method in air; here they used either AC or DC power sources [13].

Raman spectra, of the NTNH hybrids synthesized with catalyst and SWCNHs without catalyst with similar parameters and by the same instrument, are shown in Fig. 2b. The presence of strong radial breathing mode (RBM) bands at 176 cm^{-1} and 188 cm^{-1} indicates the presence of SWCNTs in the hybrids and the diameter of the nanotubes corresponding to the frequency is 1.3 nm and 1.25 nm respectively. However, an RBM band is not found in the soot containing only nanohorns, synthesized without catalysts. The other two bands that appeared in the hybrids at 1316 cm^{-1} and 1573 cm^{-1} are similar to the bands that appeared in the soot containing only nanohorns known as defect (D) and graphitic (G) bands respectively. This indicates the presence of SWCNH aggregates and it is also similar to the bands obtained during the synthesis of nanohorns using pre-heated graphite rods [6].

TEM micrographs confirmed that the web like features observed in FE-SEM micrographs are SWCNT bundles as shown in Fig. 3a–d. The diameters of the bundles range from 2–15 nm (Fig. 3e). The diameter of the SWCNTs present in the bundles, measured by intensity profile plots on the nanotube bundles (inset Fig. 3a), is found to range from 0.8–2 nm (Fig. 3f). The mean diameter of the SWCNT bundles and the individual SWCNTs is around 5.7 and 1.3 nm respectively. The mean

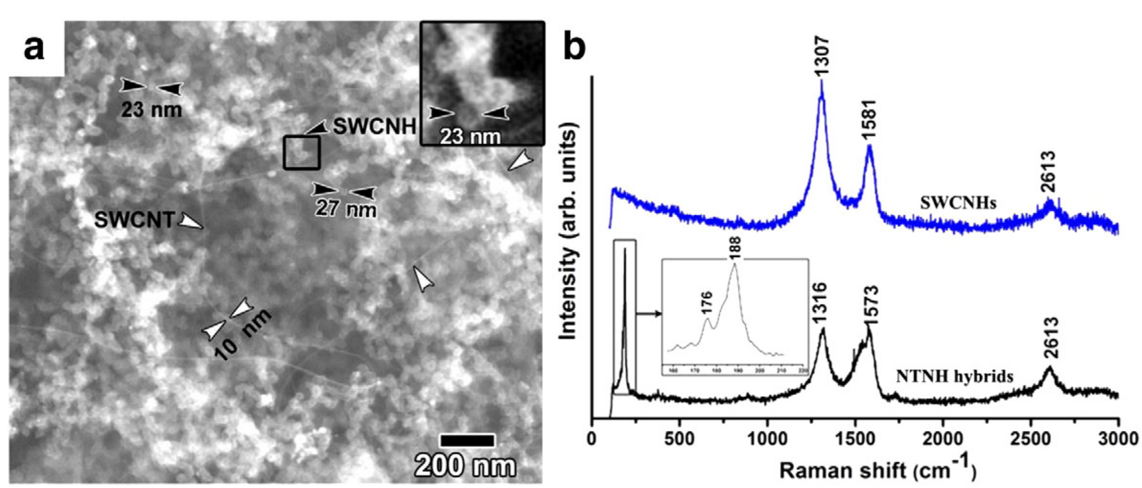

Fig. 2. (a) FE-SEM micrograph of thin SWCNT bundles with smaller aggregates of SWCNHs and (b) comparison of Raman spectra of NTNH hybrids and SWCNHs synthesized in similar conditions. All white and black arrows indicate the SWCNT and SWCNH, respectively.