Chemical Engineering Science 104 (2013) 389–398

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Counter-current ammonia injection flow during synthesis of single-walled carbon nanotubes by induction thermal plasma

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HIGHLIGHTS

- Effect of reactive gas (ammonia) on the SWCNTs synthesis process was examined.
- Counter-current injection of NH_3 into the SWCNTs synthesis system was performed.
- 10-fold increase in nitrogen content was observed in the SWCNTs material.
- Higher dispersibility was obtained with ammonia-treated SWCNTs sample.

ARTICLE INFO

Article history:
Received 8 April 2013
Received in revised form
18 September 2013
Accepted 20 September 2013
Available online 1 October 2013

Keywords:
Nanostructure
Reaction engineering
Single-walled carbon nanotube
Simulation
Chemical processes
Induction thermal plasma

ABSTRACT

Mass production of single-walled carbon nanotubes (SWCNTs) has been enabled through introduction of solid feedstock into the Ar–He thermal plasma generated by radio-frequency induction torch. The non-reactive nature of Ar–He plasma and solid carbon results in formation of pristine SWCNT final product soot which is insoluble in many solvents and is poorly incorporated in polymers matrix. To better understand the effects of reactive synthesis environment on the SWCNTs material, ammonia (NH_3) was counter-currently injected into the main plasma stream with different nozzles and at different positions in the reactor. Raman analysis showed that the quality of SWCNTs was evidently altered upon the ammonia injection. Elemental analysis of nitrogen on the SWCNT samples revealed a maximum of 10-fold increase after NH_3 injection. TEM imaging showed the presence of onion-like and planar carbon nanostructures in the SWCNT sample obtained after the highest NH_3 injection rate (15 vol%). A long-term dispersibility enhancement was observed for the NH_3-treatd SWCNT sample in dimethylformamide and isopropanol. Finally, to clarify possible reactions and species at equilibrium state and to better understand the importance of nozzle in the NH_3 injection process on the thermo-flow field of the induction thermal plasma reactor, the synthesis system was simulated through a thermodynamic calculation and computational fluid dynamic (CFD) method, respectively.

1. Introduction

Since its discovery by Iijima (Iijima and Ichihashi, 1993), many efforts have been made on the synthesis of single-walled carbon nanotube (SWCNT) owing to its very extraordinary mechanical, thermal, and electrical properties (Popov, 2004). By taking advantage of these unique properties, many applications have been developed for the SWCNTs materials in various fields such as polymers (Ci et al., 2008; Sambarkar et al., 2012), biomedical (Fadel et al., 2010; Zanello et al., 2006), sensors (Cao and Rogers, 2009; Genest et al., 2012), microelectronic devices (Baughman et al., 2002), and catalyst supports (Shen et al., 2008). Since the first SWCNT synthesis method by arc discharge (Iijima and Ichihashi, 1993), many other synthesis methods have been proposed and developed. In general, these methods can be divided into two main categories: low-temperature and high-temperature methods. Low-temperature methods have been mainly developed based on the direct decomposition of hydrocarbons or other carbon containing gases in relatively low-temperature (500–1100 °C) environment. Chemical vapour decomposition (CVD) (Dai et al., 1996; Kumar and Ando, 2010) processes can be placed in this category. On the other hand, high-temperature methods are based on direct vaporization of carbonaceous materials. Since the vaporization temperature of carbon in solid phase (mainly graphite) is very high (i.e., T_{sub}=3600 °C), these synthesis systems need to provide a very high temperature environment followed by a rapid cooling process to bring the generated vapour to supersaturation state for the effective nucleation of SWCNTs on catalysts. To achieve a high production yield, the vaporization rate and yield have

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0009-2509/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2013.09.036

to be very high so that a very demanding source of power is needed to bring the solid materials to the gas phase. Arc discharge, laser-ablation (Thess et al., 1996) and induction thermal plasma (ITP) (Kim et al., 2007) methods can be placed in this category. In these methods, the temperature exceeds several thousand forcing to use an inert environment (inert gases). Since most of the materials at this temperature level will be in their excited form and become highly reactive species so that they could react directly with SWCNT precursors (i.e., C, C_2, C_3, …) suppressing the effective nucleation and growth of SWCNT and producing unwanted by-products. Accordingly, a drastic low-yield synthesis process is expected. Consequently, Ar and He have become the most favourable noble gases for high quality production of SWCNT using high-temperature methods. The non-reactive nature of these noble gases together with intrinsic chemical property of carbon in the solid phase results in formation of pristine SWCNT-containing soot which in first place is insoluble in many solvents and poorly incorporated in polymers matrix (Hirsch, 2002). Therefore, any enhancement in dispersibility and processability of SWCNTs materials is expected to improve their possible use in many applications.

Up to now, no systematic study has been performed to investigate the effect of reactive gas on the synthesis of SWCNTs-containing soot by high-temperature methods, specifically the ITP process. The main goal of this article is to investigate the possible influences that a highly reactive synthesis environment can make on the synthesis process and its SWCNTs product. In this work ammonia (NH_3) was selected as a reactive gas to be studied in the ITP system used for the large-scale production of SWCNTs material. Since NH_3 is a relatively simple molecule constructed only with N and H atoms, the unwanted by-products are expected to be limited. Moreover, the presence of N and H atoms in the CNTs materials has been shown to improve their processability and chemical properties leading to be used in many applications such as polymer composite and nanoelectronic devices (Pantarotto et al., 2004; Ramanathan et al., 2005; Singh et al., 2005). It has been shown that the soft ion bombardment and harsh chemical conditions (e.g., thermal oxidation, HNO_3 reflux) can introduce disorder carbon atoms (defects) on the sidewall of carbon nanotubes. Since such defects are expected to be served as anchor groups for further modification on the surface of SWCNTs, and to be important in the covalent chemistry of SWCNTs, they can be, with a limited tolerance (Chen et al., 2001; Hamon et al., 1999), considered as promising starting points for the further development of SWCNTs chemistry.

For better understanding of the effects of reactive environment on the SWCNT synthesis, NH_3 gas was injected counter-currently into the main SWCNTs synthesis flow at two different positions in the plasma reactor using two different nozzle designs with three different flow rates. Taking into account the formation of reactive species through the decomposition of ammonia, the quantity of species produced during the synthesis process was measured by means of mass spectroscopy (MS). Synthesized SWCNT samples in the presence of NH_3 reactive gas were then characterized by Raman spectroscopy, transmission electron microscopy (TEM), and nitrogen elemental analyzer in order to respectively evaluate the effect of NH_3 on the structural quality, morphology and chemical composition of SWCNT soot. Furthermore, the synthesis reaction system of SWCNT in the presence of NH_3 was first modelled based on the thermodynamic calculations and the results were then compared to the experimental results. Finally, thermo-flow field of ITP synthesis system was numerically modelled after NH_3 counter-current injection with and without nozzle in three-dimension (3D) approach.

2. Thermodynamic calculation

A system consisting of C/Ni/Y_2O_3/S (97.7, 1.2, 0.4, 0.7 at%) and NH_3 gas was considered for thermodynamic calculation. Since the inert gases (He, Ar) do not contribute in the reaction at the temperature window considered for the calculation (500–5000 K), they were not taken into account in the calculation. The primary goal of this calculation was to estimate the effect of NH_3 injection on the final product of SWCNT synthesis and then to predict the formation of reactive species and gaseous by-products in the synthesis system. The FACTSAGE v.6.3 software code was employed for the thermodynamic equilibrium calculations at a constant total pressure of 66.6 kPa. For the calculations, FactPS and FSstel databases were applied. NH_3 gas stream was added to the calculation at a temperature lower than 2000 K. Sulphur (S), the impurity of carbon black, was also considered in the calculation because its effect on the synthesis of SWCNT has been previously observed in another study (Alinejad et al., 2010).

3. Experimental set-up and procedures

SWCNT was synthesized by means of an induction thermal plasma (ITP) system developed for large-scale (kg/day) production (Kim et al., 2009). The unit has been modified as illustrated in Fig. 1 in order to inject the reactive NH_3 gas in the synthesis process. Helium (He) as a sheath gas and Argon (Ar) as central and feedstock carrier gases were injected into radio-frequency (RF) induction torch (TEKNA-PS50) to make plasma with high energy density using a plate power (i.e., the power provided by the generator to the torch) of ~45 kW. The feedstock material was first prepared from a mixture of CB (Monarch-280, 45 nm), Ni (Sigma-Aldrich, 2 μm) and Y_2O_3 (Cerac, 2–4 μm) and then introduced by means of a commercial powder feeder into the plasma torch via an Ar gas line. The injected feedstock is vaporized upon interacting with thermal plasma ($T > 10^4$ K) (Kim et al., 2009). The generated vapour continues its journey along with the plasma into a water cooled cylindrical reactor with an interior wall made of graphite which is used to enhance the thermo-flow field and to increase the temperature profile inside the ITP reactor. A sudden gas expansion along with high cooling water rate circuit around the reactor wall provides a very high gas cooling rate (10^5–10^6 K/s) (Laplaze et al., 2002) which is necessary for rapid supersaturation of vapour. Consequently, such cooling process resulting in a sufficient driving force for the nucleation of the metal nanoparticles is followed by SWCNTs nucleation. A suitable temperature profile along the axis of the reactor allows SWCNTs to continue their growth to several micrometres from the nucleation sites. The final soot product is then separated from the gas phase by means of a filtration system and recovered in form of flexible sheet.

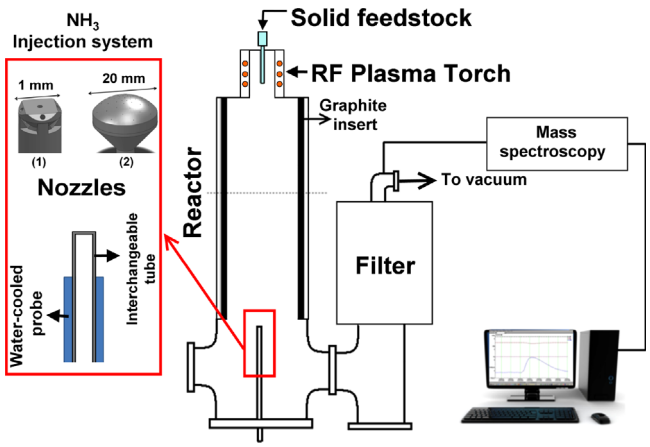

Fig. 1. Schematic of induction thermal plasma unit of SWCNT synthesis developed and modified for an effective continuous NH_3 injection.