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# Synthesis of high quality single-walled carbon nanotubes with purity enhancement and diameter control by liquid precursor Ar–$H_2$ plasma spraying

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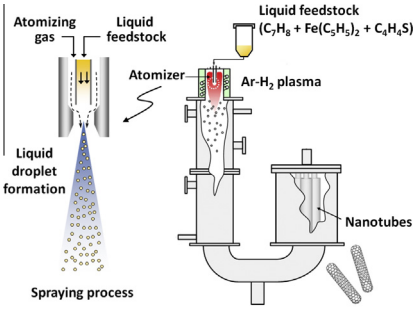
## HIGHLIGHTS

- A new plasma process is proposed for the synthesis of SWCNTs at a large-scale.
- High-quality SWCNTs were produced due to the high temperature of the plasma.
- Hydrogen plasma contributes to the purity enhancement by selective etching of amorphous carbon.
- The in situ diameter control is demonstrated by adjusting the sulfur content in the feedstock.

## GRAPHICAL ABSTRACT

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## ABSTRACT

As usage of carbon nanotubes continues to increase in both scientific research and practical applications, there has been a growing interest in the large-scale synthesis of those materials with high quality and high purity. Here we report a new plasma process developed for the large-scale synthesis of high quality single-walled carbon nanotubes (SWCNTs). An induction thermal plasma with a liquid precursor spraying technique was employed for an effective synthesis of SWCNTs from a mixture of toluene and ferrocene. It has been successfully demonstrated in this new process that high quality SWCNTs can be synthesized continuously with a reasonably high-purity, the structural quality of the materials produced being comparable to those of SWCNTs produced from the laser vaporization process. The high temperature of the plasma, over 4000 K, seems to be responsible for the production of high quality SWCNTs and the rapid treatment of a large amount of feedstock, whereas the hydrogen plasma contributes to the purity enhancement by selective etching of amorphous carbon. It is also found that the diameter distribution of SWCNTs can be controlled effectively by varying the sulfur content in the feedstock mixture, which is very promising for many advanced applications of SWCNTs such as SWCNT-based electronics.



## 1. Introduction

Carbon nanotubes (CNTs) are considered as the ultimate materials for advanced energy, composites, biomaterials, electronics, and optical applications due to their extraordinary physico-chemical properties [1–6]. Thus, there have been tremendous efforts to develop economical production methods for CNTs, the main issues being structural quality and purity enhancement, scalability, selectivity to single-walled carbon nanotubes (SWCNTs), and diameter or chirality control.

The production methods developed so far can be classified broadly into two groups: high-temperature and low-temperature

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methods. In the high-temperature methods, such as arc discharges [7], laser vaporizations [8], and solar beams [9], elevated temperatures over 4000 K (i.e., the sublimation temperature of solid carbon) are essential for the effective generation of CNT precursors from vaporization of solid carbon feedstock, followed by rapid condensation of the carbon vapors into CNTs in the cooler zones. Thanks to the high-temperature environment, the degree of the crystallization of the CNTs produced is very high through in situ thermal annealing. Moreover, CNTs are produced mostly under inert atmospheres (Ar or He) so the sidewalls of CNTs are free from the damage of etching agents such as hydrogen or oxygen. Therefore, the high-temperature methods have been able to produce CNTs with very high structural quality [10]. However the yield rates (i.e., the amount of CNT produced for a given time duration) in these methods are limited by the lifetime of consumable electrodes or solid targets: they are intrinsically batch mode processes. The as-produced materials from these high-temperature routes can also contain significant amounts of non-CNT carbon impurities such as amorphous carbon and incompletely processed feedstock fragments.

The low-temperature methods include catalytic thermal chemical vapor decomposition (TCVD) [11], plasma enhanced chemical vapor decomposition (PECVD) [12], combustion [13], spray pyrolysis [14] and fluidized bed or floating catalyst methods [15]. In these approaches, the process temperatures are much lower than the sublimation temperature of solid carbon so the CNT precursors are mostly provided from decomposition of hydrocarbons by pyrolysis, combustion, or collision with highly energetic electrons. The CVD methods have been able to produce nicely aligned or patterned CNTs on the substrate surface with purity exceeding over 90 wt.% but the yield rate is very low due to the slow reaction kinetics and the deactivation of catalysts. To overcome the low yield rate, floating bed or floating catalyst designs have been introduced with good scalabilities and it seems that they are making good headway into the large-scale production of CNTs [16,17]. The main challenge in the low-temperature routes is that the structural quality of the CNTs produced is typically not as high as those of the vaporization methods due to the low process temperatures [11,12]: the thermal energy is not enough to induce the re-organization of defects for healing. Even though several low-temperature processes can produce CNTs with high structural quality at relatively large-scales or induce healing of structural defects [18], they still need to be optimized further.

To bridge the gap between the two distinct approaches, continuous high-temperature processes based on the thermal plasma jet technology have been developed. In this approach, high enthalpy directional flows (i.e., plasma jets) generated from plasma torches are employed for the continuous treatment of feedstock at high temperatures. The thermal plasma jet technology is extraordinarily well suited for the CNT nucleation and growth owing to its high temperature (1000–15,000 K), high energy density, abundance of reactive species (ions and neutrals), and strong temperature gradients ($\sim 10^6$ K/s), which are not readily achievable by other methods [19]. The process time is also as rapid as a few ms due to the short residence time of feedstock in plasma jets. These exceptional features allow for fast treatment of large quantities of feedstock materials for the production of high quality CNTs in a continuous manner.

Smiljanic et al. reported a gas-phase synthesis of SWCNTs by a microwave plasma torch [20]. This process was able to produce SWCNTs with a reasonable structural quality but accompanied production of a fair amount of amorphous carbon. Several studies have investigated synthesis methods utilizing direct current (DC) plasma torches. Harbec et al. reported a production of multi-walled carbon nanotubes (MWCNTs) and onion-like structures from the decomposition of gas-phase tetrachloroethylene ($C_2Cl_4$) [21]. Choi et al. exploited a DC plasma process for a high purity synthesis of MWCNTs from methane decomposition [22,23]. Although this method is a high-temperature process, the crystallization degree of the CNTs produced was unexpectedly low. This is mainly attributable to the short residence time of CNTs in the hot zone due to the high speed and small volume of the DC plasma jet. Hahn et al. reported a synthesis of high purity CNTs from catalytic decomposition of carbon monoxide over iron particles [24–26]. They successfully produced single, double and multi-walled CNTs selectively by changing the injection position or hydrogen content in the working gas. Despite the low content of less-ordered carbon impurities in the samples, the D-band intensities in the Raman spectra of the as-produced materials were slightly high, suggesting the structural quality is not as high as those of other materials produced from the conventional high-temperature routes. Bystrzejewski et al. reported a synthesis of CNTs from continuous feeding of a graphite rod to a DC plasma jet [27]. An alternating current (AC) method has been also studied by Okuno et al. for a high-yield synthesis of peculiar CNTs and carbon necklaces from solid carbon [28].

Radio frequency (RF) plasma processes have been developed and seem to be one the most promising methods for the large-scale synthesis CNTs from various solid carbon feedstock [29–32]. In contrast to DC plasma torches, RF plasma torches generate plasma jets with large hot volumes and low speeds which would extend the interaction time between plasma and feedstock or CNTs produced [19]. Recently, Kim et al. reported a RF plasma synthesis of high quality SWCNTs at a large scale from solid carbons [30]. Due to its good scalability [30,32], it has already been commercialized.[1] However it turned out that the purity of the samples produced in this process is typically in a range of 20–30 wt.% [31]. The low purity of the RF induction plasma process seems to be mainly attributable to the incomplete treatment of solid feedstock in the plasma jet and to the formation of amorphous carbon as a by-product, which are typical drawbacks of the vaporization methods [31]. Although there has been a significant purity enhancement recently up to 40 wt.%, further improvement in purity would be beneficial to this RF plasma process.

In this regard, we have further advanced the RF induction plasma process to achieve higher purities, by employing liquid feedstock rather than solid feedstock. In this new process, solution mixtures of liquid hydrocarbons and metallic catalysts are fed continuously into a RF induction plasma torch through an atomizer. In the plasma jet synthesis of CNTs, liquid feedstock has many advantages over solid or gaseous feedstock in terms of the purity enhancement: (i) due to the lower evaporation energy of the liquid compared to the solid, higher evaporation rate or treatment efficiency is guaranteed, (ii) untreated liquid feedstock will not contaminate the product as it will eventually dry up during the process due to their high vapor pressures, (iii) hydrogen freed from the decomposition of liquid hydrocarbon sources would be able to etch out amorphous carbon in the course of the CNT synthesis [33], (iv) some metallic catalysts or promoters can be directly dissolved into liquid carbon sources ensuring their homogenous mixing, and (v) the liquid has a higher initial injection momentum compared to gas allowing better penetration into the plasma jet core. Despite these advantages, very little study has been carried out on the plasma jet synthesis of CNTs from liquid-phase carbon sources.

In this paper, we report a large-scale synthesis of high quality SWCNTs with a reasonably high-purity from a liquid carbon source by an Ar–$H_2$ induction thermal plasma (Fig. 1). A computational fluid dynamics (CFD) simulation has been performed first to investigate the thermal flow characteristics inside the reaction chamber

[1] http://www.raymor.com.