

# Reactor Design for Manufacturing Carbon Hybrid Materials

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This paper addresses the design of a reactor system for manufacturing carbon nanotube (CNT) fabric and carbon hybrid materials (CHM). A web or sock of CNT is formed in a reactor tube in the gas phase pyrolysis method. The sock exits the reactor tube and is wound layer by layer onto a drum to directly form a nonwoven fabric. Metal nanoparticles and continuous microfibers can be integrated into the synthesis process to form CHM. Continuous direct manufacturing of fabric is an advantage of the method. However, the reliability of this manufacturing process in our particular reactor system is affected by several problems. These include occasional breaking of the sock, the need for daily cleaning of the ceramic reactor tube due to carbon deposits on the inside, sagging/bending of the reactor tube, and safety in handling the hydrogen gas produced from the reaction. Possible solutions to the problems are proposed. The importance of this research is that no other bulk material has the combination of properties of CNT hybrid fabric. If the properties can be further improved and customized, and if manufacturing of the material can be scaled-up at reasonable cost, many new commercial applications for nanotube custom materials could open up.

## Introduction to reactor design and CNT fabric manufacturing

The gas phase pyrolysis or floating catalyst method is controlled by process variables such as gas and fuel types and flow rates, temperature and location of the fuel injector, the hot zone temperature in the furnace, wind-up speed of the sock, and deposits on the inside wall of the furnace tube [1,2]. A main problem faced in our process is the sock produced occasionally breaks during the synthesis and must

be reattached to the wind-up drum. The reactor tube must also be cleaned of carbon deposits daily. These problems hinder scale-up of the process and commercialization of CNT materials. Modest properties of the CNT fabric, primarily low strength, have limited commercialization of the material. The reactor design and tuning described in this paper provides improved reliability of our specific process which uses a short, horizontal, small diameter high temperature furnace. Larger diameter tubes and other reactor designs may reduce the problems discussed herein.

The horizontal floating catalyst reactor, **Fig. 1**, produces a CNT sock continuously. After the process runs for several hours, the sock begins sticking to the wall of the ceramic tube causing the sock to break. Using a lower fuel injection rate reduces the deposits on the tube wall and extends the time to when the sock starts breaking. However, pushing the fuel injection rate higher increases the yield of the process. Increasing the yield will reduce the time to manufacture fabric and will reduce the cost. To understand the process and problem, we define three regions of the process tube and speculate on the temperature profiles in the zones: (i) the inlet section with the fuel injector and optionally a particle injector. The tube wall is hotter than the gas, and the gas heats as it leaves the fuel injector and moves through the inlet zone which is thermally insulated and not directly heated; (ii) the hot zone where the temperature is at the set temperature of the reaction, e.g.

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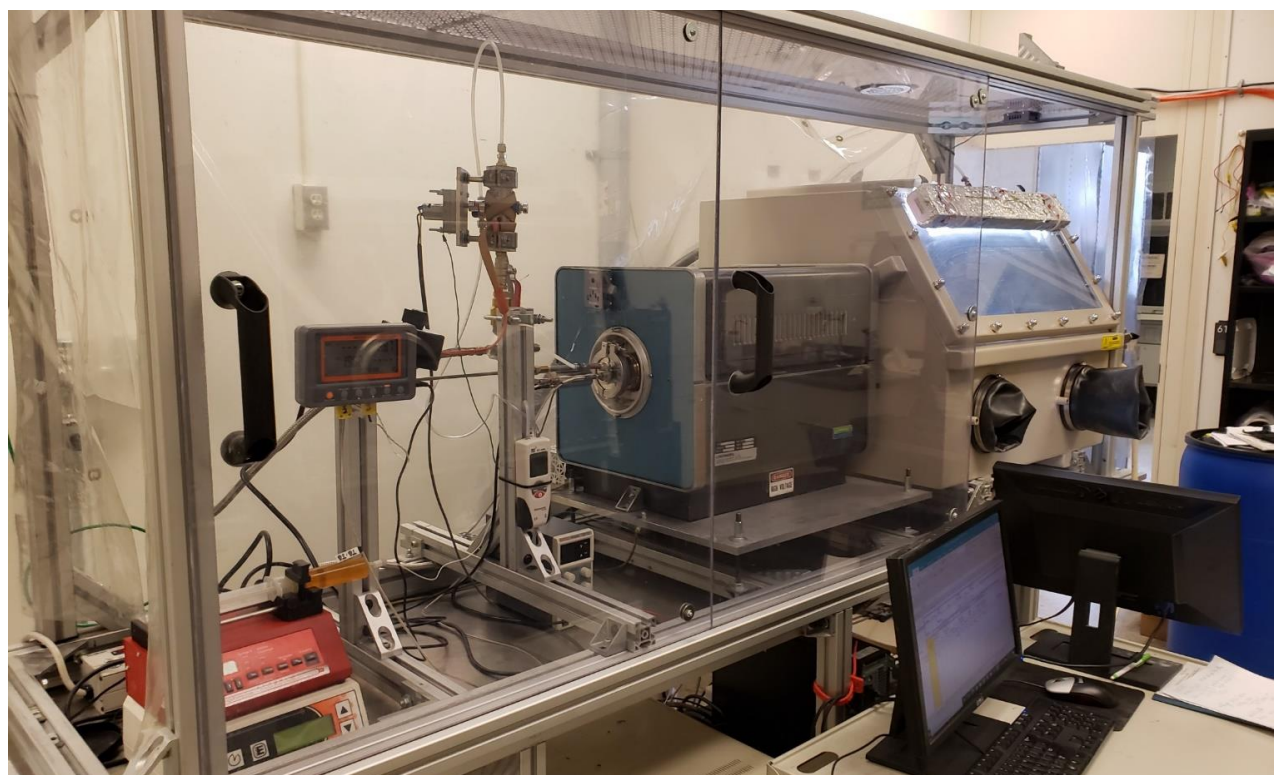
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1420 C, the tube wall is directly heated and is hotter than the process gas moving through the tube, and the gas is rapidly heated; and (iii) the insulated cooling zone where the gas exits the hot zone and cools quickly and exhausts into the harvesting box. The exhausting gas in the cooling zone rises as cooler gas from the glove box enters the bottom of the tube, this causes the sock to rise and rub on the top of the ceramic tube. A partial solution to prevent the sock from rubbing on the wall is to pull the sock downward away from the top of the tube. A vertical reactor may not have this problem, but still gas circulation will occur due to cooling in the tube. Another possible solution is to wind the sock onto a drum closer to the hot zone of the ceramic tube.

From an applications perspective, manufacturing CNT fabric via the floating catalyst method is a step forward in multi-functional materials synthesis. If several of the problems inherent in the process can be mitigated, CNT fabric, tapes, and yarn manufacturing may evolve into a significant new world-wide industry. The CNT fabric produced is non-woven, low density, and has good thermal and electrical conductivity. CNT fabric thus could have unique applications in textiles, personal protective apparel, water and air filtering, electrical conductors, electromagnetic shielding, and potentially many biomedical applications.



**Fig. 1.** CNT custom reactor comprised of an inlet system, a Lindberg furnace, and a MTI glove or harvest box. Fuel and Nanoparticle (NP) injectors (under development) are used. Thermocouples within the injector and in the furnace monitor the process.

## Reactor component parts

The reactor inlet system representative general design is shown in **Fig. 2**. Fuel and particles can be injected. The fuel injection point can be varied to optimize nucleation of the CNT. The particle injection point can be varied depending on the type of particles to be injected [3]. Fuel and Particle Injectors are at the inlet. Fuel is injected, vaporizes in the mixer, chemically cracks in the extender tube, and ferrocene vaporizes, and iron nanoparticles (NPs) melt outside of the extender tube. CNT nucleate outside the extender tube and NPs mix with the fuel in/outside the extender tube. The small diameter dark sock produced is wrapped as a tape on the rotating take-up drum forming a

tape wrapped fabric that is thin, flexible, and mass producible. Temperatures and velocities are controlled to produce the small dense sock that exits the reactor in the center of the tube minimizing touching the walls of the ceramic tube. This reduces carbon build up on the inside of the ceramic tube which increases the efficiency of the process. The sock also does not break as frequently because it is pulled away from the top of the ceramic tube. Gases exiting the ceramic tube produce a high concentration of hydrogen gas in the glove box which is diluted with pre-purified Ar for safety. Gases in the glove box exit through a water bubbler through a filter and into a suction exhaust for the building.

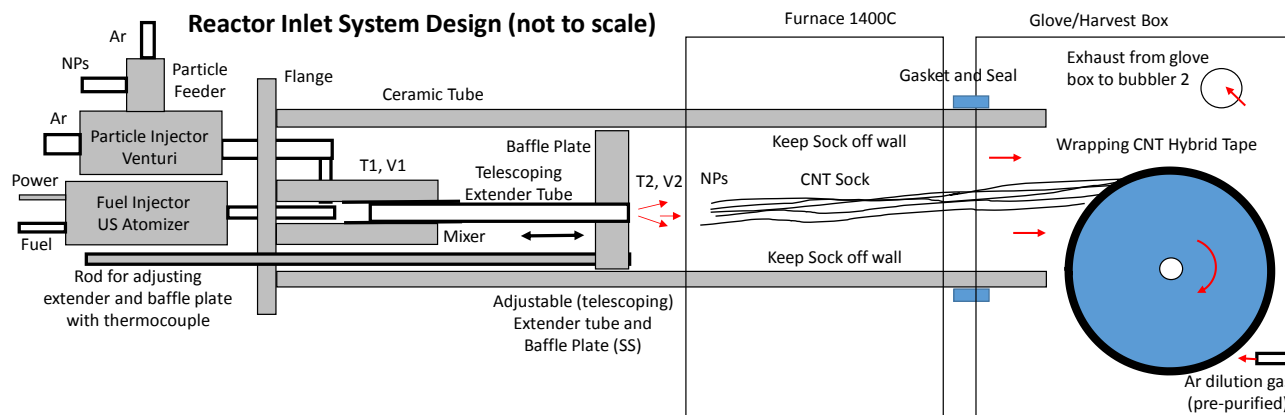


Fig. 2. Schematic of reactor design [3].

The injector hardware is shown in Fig. 3. This is a representative design and there are variations of this.

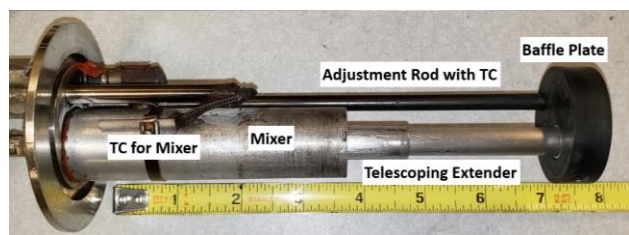


Fig. 3. Telescoping extender. Fuel and NPs are combined in the mixer. Two thermocouples (TC) monitor the process and are used to ensure repeatability and to diagnose problems.

Pulling the sock away from the top of the reactor tube was attempted. This is explained with reference to the three sections (each about 8 inches long) of the reactor: inlet zone with the injectors, hot zone near the heating elements, and the cooling zone with the sock exiting into the glove box. The telescoping extender tube is located toward the bottom of the ceramic tube at the inlet to allow the sock more distance to rise. The temperature of the mixer and outlet of the extender must be correct to form a sock and to have high yield for the reactor. The hot zone must be at a temperature and length to form the sock but not longer than needed to minimize the sock rubbing on the ceramic tube and breaking. The process is described based on our understanding which is incomplete. As the gas exits the extender, it is heated and expands in a circular shape and the sock forms. In the hot zone the ceramic tube is hotter than the gases and the heating is uniform and the heat transfers by convection and radiation from heater elements to the ceramic tube and to the gas mixture inside the ceramic tube. Heat flow from the tube to the gas tends to prevent the sock from rubbing on the wall of the ceramic tube. We think the sock stays about in the center of the reactor tube in the hot zone. Entering the cooling zone, the ceramic tube is cooling toward the outlet, and the gases in the reactor cool. Also, cool Ar gas from the glove box mixes with the exhaust gas. The gas in the cooling zone of the reactor is cooler than the gas trapped in the sock and the

sock rises. The sock may rub on the top inside of the ceramic tube. A small diameter sock has less friction and less tendency to break when slightly rubbing on the top inside of the ceramic tube. In some cases, a small sock may not touch the ceramic tube at all, and the process acts like a linear gas bearing and the sock is produced with minimal breaking if the process tuning is precisely maintained.

The small diameter sock will contain a smaller volume of gas and have less tendency to rise and rub on the top of the ceramic tube and break. A low gas flow rate will help to keep the sock small and from rubbing on the ceramic tube. Ar gas is denser than hydrogen gas and the Ar gas may expand slower. Using all Ar or all hydrogen gas may affect the sock breaking. Small holes in the extender tube might produce multiple small socks. Multiple small diameter socks might be used in one 2-inch reactor. The optimal diameter of the sock has not been determined. The fuel and ferrocene are injected toward the bottom of the reactor tube to reduce the effect of the gas rising and the ferrocene depositing on the top of the ceramic tube as the inlet gas is heated. NP injection involves heating, melting, or vaporization of the NPs. The dry NPs injected can contain catalyst or promoters or metals, ceramics, or carbon materials. The CNTs forming are pushed by the Ar/H<sub>2</sub> gas. If the gas velocity is low, the gas forms a sock or balloon that expands to the diameter of the reactor tube and is pushed out the tube due to the gas pressure difference from the inlet to the outlet of the reactor tube. A small diameter sock can be formed by precisely positioning the extender outlet and using a fast wind-up speed on the drum to pull the sock and keep its diameter small. It is desired to keep the catalyst particles from depositing on the inner wall of the ceramic tube. Also, a larger inner diameter of the ceramic tube seems to favor producing a small diameter rope-like sock that has minimal contact with the ceramic tube. Experiments showed that a 1.75 in ID tube produced a rope-like sock if tuned carefully and for a limited time, whereas a 1.62 in ID tube produced a larger sock about the size of the ID of the tube and this sock was more stable than the rope.



### Description of the reactor

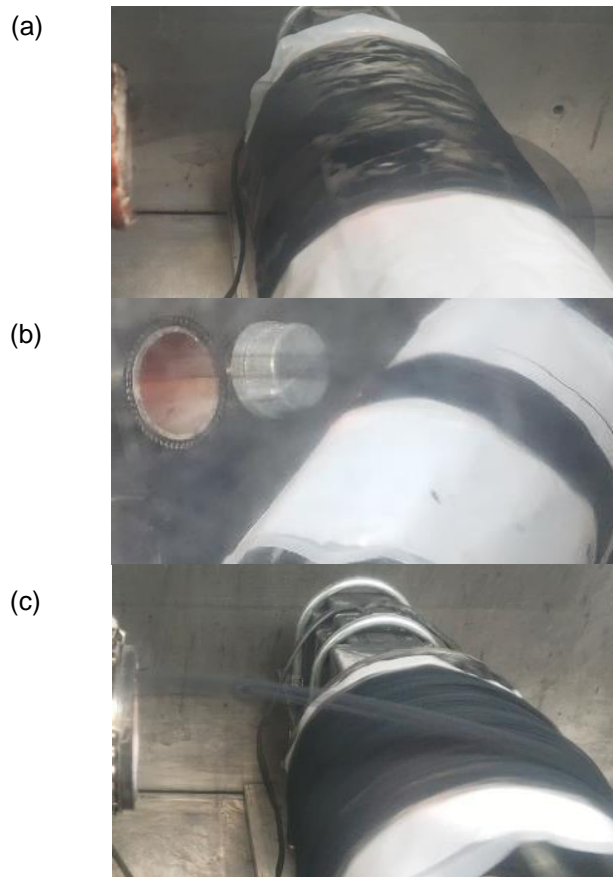
The many applications for CNT materials drive the need for improving the reactor design. Transitioning the technology to industry for commercialization also drives the need for improving the synthesis process. Currently, there is a roadblock in putting assemblages of carbon nanoscale materials such as macroscale sheet, tapes and yarn into applications and everyday use. The roadblock is related to the low throughput and high cost of producing the material, and the need to improve the properties of the macroscale assemblages of carbon nanotubes. Current reactors use long ceramic tubes and resistive heating. Ceramic tubes are susceptible to cracking, especially with larger tubes, and resistive heating is not highly controllable/efficient for large diameter tubes. A breakout technology is needed to increase the yield of nanotube reactors from grams/day in research reactors, to one kg/day for niche applications, and to eventually metric tons (1000kg)/year for large scale industrialization. Also, the properties (strength, conductivity) of CNT macroscale assemblages (fabric and yarn) need to be improved to open up more applications.

The reactor design discussed in this paper is based on Gas Phase Assembly (GPA) where the fuel carrying nanoparticles (NPs) is injected into a tube and forms a small rope of nanotubes that is collected on a drum, **Fig. 4**. This process is contrasting our standard method in which fuel is injected into a ceramic tube and a CNT web or sock is formed and the sock expands and is constrained by the ceramic process tube where some of the CNT deposit on the ceramic tube eventually causing the sock to stick and break. By using our injector system for fuel and NPs, and avoiding the constraint of the tube, the fuel injection rate can temporarily be increased from 30 ml/hr to 80 ml/hr in our test reactor with a 2 in OD process tube until the tube becomes contaminated with C deposits. The reactor design is shown in **Fig. 2**. The reactor uses high velocity fuel and particle injection, a short larger diameter tube that acts as a plenum chamber, and high temperature to produce CHM rope.

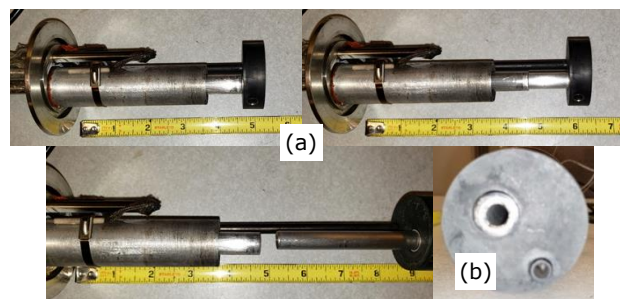
### Process description

The process uses a custom multi-phase fuel and particle injector system, **Fig. 5**. The system ultrasonically atomizes liquid fuel (alcohol precursor, catalyst, promoter), mixes the fuel with Ar and H<sub>2</sub> gas containing NPs delivered into an eductor (venturi) and into the fuel mixer, vaporizes the mixture, dissociates the vapor to form H<sub>2</sub> and CO gas with carbon fragments and atoms, and iron catalyst atoms, and the pressure of the expanding gas principally H<sub>2</sub> from vaporization of the alcohol forces the mixture at higher velocity out of an extender tube and directly into a cold plasma in the beginning of the hot zone of the reactor. A small dense cylindrical sock of nanotubes, **Fig. 4(c)**, is formed and is drawn from the reactor tube at a high rate partially aligning the nanotubes. The sock flattens into a tape as it is laid onto a rotating drum. The fuel and NP components are integrated into one system to reduce the amount of Ar gas needed in the process otherwise stability

of the sock is reduced. The velocity of the gas from the ¼ in extender tube of the injector is 49x the velocity of the gas in the outer ceramic tube. The high velocity of the gas coupled with the deep injection minimize the CNT sock rubbing on the wall of the outer tube. The extender is telescoping, **Fig. 5(a)**.



**Fig. 4.** CNT sock formation by gas phase pyrolysis in our reactor test bed (with 2 in OD short, high temperature furnace with fuel injector). (a) large sock at 60 ml/hr fuel injection winding to form a sheet, but the ceramic tube constrains the sock; (b) a tube sock at 30 ml/hr fuel injection not touching the ceramic tube which is the ideal condition; (c) thick CNT rope exiting the ceramic tube at high wind-up speed barely touching the tube.



**Fig. 5.** Design of injector for fuel and NPs. (a) Extender position controls the temperature where the gases are injected into the ceramic tube. Preliminary testing using two tube diameters indicates that reactor output is proportional to the cross-sectional area of the extender tube and the ceramic tube. Delivering dry powder NPs is a complex problem. (b) The baffle plate minimizes back flow circulation. End of baffle plate showing extender tube and thermocouple.

High temperature short time synthesis achieves high throughput and improves the reliability and reproducibility of the process. Metals, ceramics, or other carbon materials can be integrated into the synthesis process. The multi-phase injector system is unique to the field of CNT synthesis and reduces carbon depositing on the walls of the reactor tube and increases the amount of fuel (from 30ml/hr to about 60ml/hr) that can be input to a reactor tube. CHM synthesis occurs faster than conventional synthesis and tuning the process requires greater precision. The multi-phase material injector must be tuned so the extender tube and baffle plate transfer heat to vaporize the alcohol fuel at the inlet of the tube (boiling point of methanol is 65C). Ferrocene vaporizes near the outlet of the tube (melting point of ferrocene is 173C, boiling point is 249C, iron NP melting point is above 1000C). Two thermocouples in the injector monitor the temperature profile in the inlet. The reactor tube is 24 inches long, 2 inches OD. The hot zone is about 8 inches long. The hot zone length/inner diameter ratio is about  $8/1.75 = 4.6$ .

## Reactor engineering

Design of our custom-built reactor is described. Other reactors may not have the same problems or characteristics as our reactor.

### *Description of the fuel injector*

The fuel injector delivers the fuel and gas mixture to the inlet of the ceramic tube so that the CNT grow quickly in a short travel distance in the reactor tube. The short growth time reduces deposition of CNT on the reactor tube walls. The fast growth enables the sock to be formed for a longer time without breaking which increases the yield of the process because CNT are not being deposited on the reactor wall. Also, with faster growth, the fuel injection rate can be increased without contaminating the reactor. Fuel is contained in a syringe. A syringe pump with low friction injects the fuel into an ultrasonic atomizer. The atomized fuel enters a mixer where Ar gas pushes the fuel into an extender. The fuel is heated and evaporates cooling the inlet area and producing gas. The gas contains carbon species and hydrogen gas. The gas formed increases the pressure and flow of the gas in the small diameter extender. The gas velocity in the  $1/4$  or  $3/8$  ID extender is greater than the average gas velocity in the ceramic process tube. The gas is heated as it moves through the extender and upon exiting the extender the gas expands and decomposes and the CNT sock is formed. If the gas velocity is high, a small diameter sock is formed and is pulled out of the reactor at a higher velocity than the gases exiting the reactor. If tuned precisely, this reduces breaking of the sock thus improving manufacturing of CNT sheet, yarn and tape directly in a continuous reliable process. Temperature is a critical factor in the function of the injector.

If the temperature at the outlet of the extender is too low, we hypothesize that the gas leaving the extender will expand and heat further and then form CNT which will

interact with the wall of the ceramic tube. Some CNT will deposit on the wall and eventually cause the sock to stick to the wall and break. The carbon deposits will require cleaning of the reactor wall. Also, the sock will be large diameter and the velocity of the sock exiting the reactor will be similar to the gas velocity exiting the reactor, which may result in a lower yield process.

If the temperature of the gas exiting the extender is optimal, the gas exiting the extender will immediately coalesce the Fe NPs into appropriate size catalyst particles and form a small diameter dense sock that can be pulled from the reactor at a high rate and that does not contaminate the reactor wall. If the temperature of the gas leaving the extender is too high, C and CNT will form inside the extender and collect on the inner wall of the extender and eventually plug the extender. Also, the Fe NPs will agglomerate into particles too large to nucleate CNTs and the large catalyst particles will be blown out of the extender and out of the ceramic tube and no or few CNT will be formed. Thermocouples are critical to monitor the process. Temperature is the critical factor in the function of the injector. Three thermocouples monitor the total process. In this reactor, the CNT sock (web) forms in about 1-2 seconds based on the gas velocity and length of the hot zone.

### *Description of the particle injector*

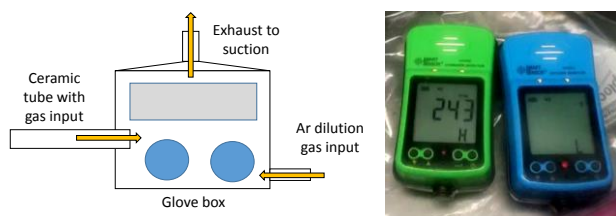
The particle injector is custom designed and delivers dry NPs into a vertical tube. The tube feeds an educator (a venturi designed for dry particle delivery). The venturi is in line with the inlet Ar flow for the mixer. In this way the same Ar/H<sub>2</sub> gas mixture used to deliver the fuel can also deliver the NPs. This ensures good mixing of the NPs with the fuel and reduces the overall flow rate of the reaction which reduces breaking of the sock. It however, mixes the NPs with the nucleating CNTs. This can be detrimental or advantageous depending on the type of NP. The types of NPs used will be the subject of future publications.

Different metallocenes and NPs both catalyst and non-catalyst particles may be used. Ferrocene has also been mixed with granulated activated carbon (GAC) injected and a sock was formed without any ferrocene in the fuel. The route of adding ferrocene in both the fuel and particles may increase the yield of the process and this is part of the science that is to be studied in future research. The conventional floating catalyst process injects fuel into the large reactor tube at one point which is not efficient because back flow [1] and the long tube cause carbon to deposit on the wall of the ceramic tube which reduces the yield and eventually breaks the sock. Conventional synthesis using floating catalyst also uses lower temperature. Our process operates with a higher temperature short dwell time furnace and with a multi-phase material injector. GPA may provide high throughput and chemical integration of NPs into the synthesis reaction to customize CNT fabric.

### *Harvest/Glove box design*

The harvest glove box is used to wind the CNT sock onto a drum to form fabric. The glove box must be safe to use

considering the hydrogen gas produced from the synthesis process enters the glove box. The synthesis process variables typically are: Ar inlet 1400 SCCM; Hydrogen inlet 100 SCCM; Glove box pressure 0.2-0.3 in water; Fuel 90% Methanol, 10% n-hexane, small amount of thiophene, 1% ferrocene; Nanoparticles can be added to the inlet Ar gas. For a nominal condition, the fuel injection rate is 30 ml/hr. H<sub>2</sub> gas is formed by decomposition of the alcohol fuel. The harvest/glove box schematic is shown in **Fig. 6**. The harvest box must safely remove hydrogen gas. Therefore, pre-purified Ar at 20-30 L/min is delivered to the harvest box continuously during the synthesis.



**Fig. 6.** Schematic of harvest-glove box. Hydrogen (showing 243 ppm) and oxygen (showing lower level below resolution below 0.1%) sensors used in the glove box before and during synthesis to tell concentrations and stratification of the gases. Hydrogen is also generated possibly from the alcohol or acetone solvent used to densify the sock in the harvest box.

In some experiments, no hydrogen gas is input to the process. However, a large amount of hydrogen gas is still produced by vaporization of the alcohol fuel used in our synthesis process. The nominal concentrations of gases in the laboratory room housing the reactor are oxygen 21.9%, hydrogen 70 ppm. After purging the glove box (draw suction of 30 kPa (121 in water) and refill with pre-purified or ultra-high purity Ar, repeat six times), the oxygen concentration is 2.2% and the hydrogen concentration is 81 ppm. The sensors used are low cost (about \$280 USD each) and low resolution. Thus, the measurements are approximate. The glove box is further purged with Ar flow for 2.5 hours as the reactor is heating to 1420°C. The concentrations after the long purging during heating and just before the synthesis begins are oxygen 0.2% and hydrogen 167 ppm. After the synthesis process comes to equilibrium, the oxygen concentration is 0.1% or below (this is the lowest reading of the sensor) and the hydrogen concentration is 576 ppm at the bottom of the glove box, which increases to 768 ppm to the top of the glove box. This condition is with no solvent used to densify the sock wrapping on the wind-up drum. The concentrations vary depending on mixing and the measurement location in the glove box. The exact process conditions such as fuel and gas flows, and if acetone solvent is used in the glove box to densify the sock also increase the hydrogen concentration. Also, the hydrogen concentration is higher near the outlet of the reactor tube. The measurements reported represent the average concentrations in the glove box.

The above are important details and results related to safety. Damage could occur to the reactor system in several ways which could allow oxygen to mix with the flammable

gas in the glove box. The types of damage that could occur include the reactor ceramic tube cracking, the glove box glove tearing, or air entering the glove box due to a mistake in operation (e.g., opening the antechamber door before the reactor is cool). Hydrogen is an explosive gas. Thus, the glove box should never be opened until the gas inside is cooled to room temperature. We also use slight suction from the room exhaust system to remove residual gases in the glove box before opening the box to the room air. The glove box is opened after each synthesis run to remove the nanotube fabric produced, and for cleaning the reactor tube and glove box. During the steady-state synthesis process, the oxygen (not air) concentration is below 1000 ppm, and the hydrogen concentration can exceed 1000 ppm in the glove box, for the process conditions listed. The lower explosive limit for hydrogen gas in air at room temperature is 4.1% or 41,000 ppm. At higher than room temperature, the hydrogen gas becomes easier to ignite. The autoignition temperature of hydrogen gas is the temperature of spontaneous ignition in air which is 500 °C. Greater than 2.94 mol% of hydrogen gas in argon is also classified as flammable. The U.S. Environmental Protection Agency recommends evacuation of personnel when the concentration of an explosive gas reaches 10% of the lower explosive limit. Ten percent of the lower explosive limit is 4,100 ppm for hydrogen in air. Explosive limits of hydrogen in a low-oxygen Ar atmosphere at elevated temperature as in the glove box are unknown. At high concentrations in air, hydrogen is a simple asphyxiant gas because of its ability to displace oxygen and cause hypoxia. Hydrogen has no other known toxic activity. This profile considers only hydrogen gas and excludes health effects associated with hydrogen-containing chemicals.

Based on the above discussion, this synthesis process increases safety because the concentration of hydrogen gas in the glove box is low to moderate. Other nanotube synthesis processes may use hydrogen gas as the carrier gas and the concentration of hydrogen in the glove box becomes high. Dilution of the exhaust gas with 20 L/min of Ar is another reason why the hydrogen concentration is reduced in our process. Pre-purified Ar (low purity Ar which is low cost) is used as the dilution gas to lower the cost of the gas. Typically, one cylinder of Ar is used per a few hour experiment. The cost of one cylinder of pre-purified Ar is about \$27 USD. The cost of one cylinder of ultra-high purity Ar is about \$175 USD. There are also other hydrocarbon gases in the glove box that are flammable or explosive. Thus, gases in the glove box should always be treated as explosive.

Safety of the reactor system is the most important aspect of nanotube manufacturing. Safety can be increased by design of the glove box. The glove box has a pressure relief valve to protect the glove box from mechanically failing if the pressure in the box exceeds a set low limit. The gloves would also fail before high pressure is built up. A suction switch will shut off the vacuum pump if the suction is below a set value during purging when the glove



openings are closed. The ceramic tube is heated and cooled at 10°C per minute or slower to reduce the thermal stresses and the chance of cracking. For our particular reactor system, the first step in the synthesis process is to check the suction in the building which should be about -0.65 inches of water. A leak check is then performed before every experiment for the reactor system and leaking should be not greater than 1 inch of water suction per minute measured at 72 inches of water suction in the glove box. This specification was set based on experience with our reactor and could vary for other reactor designs. Hydrogen gas becomes stratified in the glove box and the exhaust for the glove box should be at the top of the box to exhaust more of the hydrogen gas as Ar is heavy and settles to the lower part of the glove box. Efforts to increase safety in the nanotube synthesis process are always being considered.

### Ceramic tubes

Different ceramic tubes can be used for CNT synthesis [4-6]. Our process operates at about 1420 C. Quartz and most metal tubes have lower melting temperature limits and generally cannot be used in the process. Metal tubes also have higher thermal conductivity which makes cooling the seals more difficult. Tubes tested in our process are listed in **Table 1**. Overall, the mullite tube bent too much after long use, **Fig. 7(a)**. But the seals near the ends of the tube (at the inlet flange and at the connection to the glove box at

the outlet) were cooler using the mullite tube. The alumina tube with a thin wall and larger ID was used to produce a rope-like sock that was wound up at high speed and with reduced contact with the wall of the ceramic tube. But the alumina tube also bends a lot, **Fig. 7(b)**. The thicker wall smaller ID alumina tube also bent, **Fig. 7(c)**, but the tube had improved sealing due to the machined ends. The thicker wall alumina tube produced a larger diameter sock wound at lower speed. The smaller ID of the thicker wall tube may have adversely affected forming the small sock. Comprehensive studies of the effect of the tube specifications on forming the sock were not conducted. However, different length tubes and heating zones of the furnace were also used at different times which complicated determining the effect of the tube design alone. The shorter length thicker wall alumina tube and short heating zone are the current best combination. The manufacturers heating rate recommended for these tubes is 5 C/min. The heating and cooling rate used is 10 C/min or slower for the cooling cycle. Heating to 1420 C takes about 140 minutes. The inside of the ceramic tube must be cleaned after every run. A hone is used to remove the carbon deposits, **Fig. 7(d)**. Heating the tube in air can also remove the carbon deposits, but the deposits at the ends of the tube are difficult to remove by heating in air unless the tube is removed from the reactor and heated along the full length of the tube.

**Table 1.** Characteristics of ceramic process tubes, 2 in OD, 24-36 inches long.

Tube Type	Thermal Resistance (C) and Fracture Toughness (MPa m <sup>0.5</sup> )	Shock (C) and Toughness	Thermal Conductivity W/(mK) and Specific Heat J/(Kg K)	Coefficient of Thermal Expansion (micron/C)	Flexural Strength (MPa)	Temperature Limit (C)	Reliability of the 2 in OD tube
Mullite, thin wall (0.125 in) [4,6]	300 and 2		3.5 and 950	5.3	170-180	1500-1700	Large bending after long use, reduced heat conduction along tube. High purity mullite.
Alumina, thin wall (0.125 in) [4,5]	200 and 4.5		30 and 880	8.2	375	1750	Moderate bending after long use, greater heat conduction along tube than mullite. High purity alumina.
Alumina, thick wall (0.165 in) [6]	NA		8.2	8.4	380	1800	Less bending after use. Thicker wall may reduce chance of breakage but slow heating of gas. Machined ends improve sealing.



(a) Mullite tube after use showing bending.



(b) Alumina process tube, 22.5 inches long with a 1.5 inch flange giving a 24 inch effective tube length.



(c) A 24-inch long thick wall alumina tube (OD 2 in, ID 1.62 in) bent ¼ inch after 11 months use. The tube did not crack. Carbon deposits built up on the inside of the tube.



(d) Hone used to clean the inside of the ceramic tube.

**Fig. 7.** Bending of ceramic tubes and cleaning method.

### Reactor tube sealing

The furnace tube must be sealed at the inlet flange and at the junction where the tube enters the glove or harvest box. A short furnace is used in our process. The inlet flange is about 300-400 C when operating. Silicone O ring seals maximum operating temperature is about 320 C. Thus, silicone seals would degrade if used at the inlet. However, the silicone seal would minimize leaking of ceramic tubes that do not have machined ends. Ceramic tubes have a variation in diameter from one end to the other and the tubes are slightly oval, not perfectly round. The outlet flange on the ceramic tube at the glove box is about 600 C when operating. This is too high of temperature for use of silicon o rings. Ar gas cooling of the flange provided only minimal cooling and was not satisfactory for low flow rates of the Ar gas that were practical. Metal o rings were considered but the cost is very high. Water cooling is feasible but adds complication. An alternative was to use rectangular packing seal material and use five packings alternating the gaps. The packing would leak for tubes without machined ends. The tube with machined ends and packing seals at both ends works well. Also, the packing is low cost, especially compared to the alternative of using water cooled flanges. The tightness of the packing seals should be checked regularly. It is critical that no bending moment be produced in the ceramic tube due to the seal at the glove box. The tube is supported at the inlet end and must be carefully aligned to prevent a bending moment that may cause the ceramic tube to crack.

### Reactor tube cleaning

In our process, the reactor tube must be cleaned after every use. During the synthesis, metal rods are used to remove sock caught on the wall of the tube. The ceramic tube is cleaned using a cylindrical hone, **Fig. 7(d)**. The tube can also be cleaned by heating in air, but the ends of the tube are not cleaned as well as the tube in the hot zone.

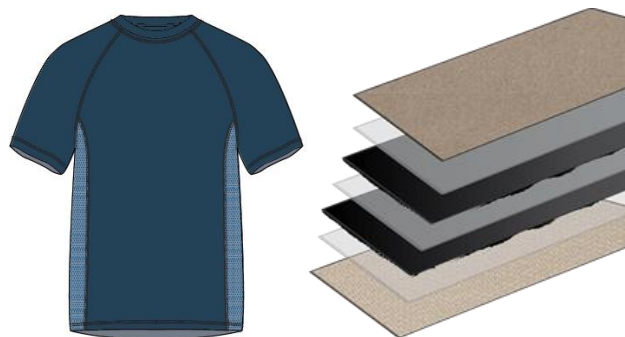
### Uniqueness and importance of the reactor design and manufacturing process

The reactor design described is unique as it operates at high temperature, uses a short reactor tube, a small diameter fuel injector with higher velocity gas, and injects dry powdered nanoparticles, in a controlled way, into the high temperature nanotube synthesis process. If the properties of CNT hybrid fabric can be improved using this process, and if the manufacturing throughput can be increased to lower the cost of the CHM material, new applications may be enabled. As an example, CNT Hybrid fabric can provide heat spreading, flame resistance and electromagnetic shielding for workers in extreme environments. The downside is CNT hybrid fabric at least 30 microns thick is needed to provide certain desired properties. This thickness of fabric is time consuming to manufacture and the cost is currently prohibitive for most textile applications where typically yards of material are needed to from layers in

garments. Compared to other methods of manufacturing CNT fabric [36-41], such as forest grown nanotubes [37,40,41] and buckypaper formed from powdered nanotubes [42], the floating catalyst method offers a combination of tunability of material properties and good manufacturing throughput in a one-step process, but the cost of material must be reduced.

### Possible applications of CNT materials

CNT fabric has a combination of properties unlike any other single fabric [7-35]. The properties include good electrical and thermal conductivity [13,17,19,31,36,37], low density, soft and flexible feel, corrosion resistant, flame resistant [29,32,33], low to modest strength, air and water filtering ability when in thin sheets, and high cost. CNT hybrid materials can improve these properties. Likely applications include electronics cooling, field emission [20,21,24,25,27,28] electrical conductors [17,19] and shielding, composites reinforcement, development of intelligent textiles [22], air filtering [10], and others [11-32]. Safety of the CNT fabric is discussed in [34,35]. CNT pristine strands in fabric pull apart under load and do not fracture in a brittle manner and do not release particles. When nanoparticles are added to the fabric, if metal, they melt and fuse to the CNT and do not release. Non-interacting nanoparticles such as granulated activated carbon and ceramic particles will release from CNT fabric. Textile applications are promising if the manufacturing of CNT fabric can be scaled up. A garment design that uses CNT fabric inside is shown in Fig-8. Recent work is also helping to move CNT fabric synthesis to an industrial level of manufacturing [38,39].



**Fig. 8.** Concept personal protective textile application of CHM fabric. CHM composited fabric shirt with a thermal insulation layer, separator veil layer, CHM layer, veil, CHM layer, veil, and moisture wicking layer.

### Conclusions and future scope

This paper gave recommendations on improving the reliability of the gas phase carbon nanotube hybrid materials manufacturing process. The importance of designing the reactor to improve the safety of the process was also emphasized. The reactor described was carefully designed to minimize rubbing of the CNT sock on the ceramic tube and to reduce breaking of the sock.



Approaches were discussed to minimize several of the practical problems of manufacturing CNT hybrid materials. Areas to study further include other possible approaches to reduce deposition of carbon materials on walls of the ceramic tube, such as injecting Ar along the walls of the ceramic tube, and the long-time goal to increase the length of the individual nanotubes. Hybrid materials design is a new topic and is open for investigation of what nanoparticles to use to modify the conductivity and strength properties of the nanotube fabric produced in the synthesis process. Overall, the reactor described in this paper is still under development. Many changes and improvements to the reactor are still expected. Hence, this paper should be considered as a guide that may be helpful in reactor design, not as a final optimal configuration of the reactor. This paper also predicts CNT materials may become a new player in manufacturing in several areas with economic importance.

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#### Conflicts of interest

There are no conflicts of interest to declare by the authors.

#### Keywords

Carbon nanotube manufacturing, hybrid material, nanoparticles.

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