RESEARCH ARTICLE

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Synthesis Tuning for Manufacturing Carbon Hybrid Materials

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The overall hypothesis for this paper is that accurately tuning the gas phase pyrolysis synthesis process and using appropriate raw materials will enable manufacturing different types of carbon hybrid materials (CHM). Optimizing multiple variables including particle melting and vaporization temperatures, fuel flow rate, gas flow rates, gas velocity, and sock wind-up speed is needed to achieve reliability of the synthesis process. Results from our specific reactor are presented to show how the process variables interact and how they affect CNT sock yield and stability. Metal nanoparticle (NP) injection enables the formation of hybrid materials. Several types of CHM materials created by incorporating different types of NPs into the carbon nanotube (CNT) synthesis process and CNT sock are discussed. Many possible combinations of metal NPs can be used in the process to customize the properties of CHM. However, it is a complex problem to determine what metal compounds can chemically join with CNT. Some of the first results testing the new CHM process are presented in this paper.

Vision for developing CHM

Creating new materials and better materials historically enables technological leaps. In *Engines of Creation: The Coming Era of Nanotechnology* (1986), "K. Eric Drexler laid the theoretical foundation for the field of nanotechnology and described the possibilities for engineering at the molecular scale [**1**]. It was predicted the new age of nanotechnology would give us thorough and inexpensive control of the structure of matter." In *Made to Measure: New Materials for the 21st Century* (1997), "Philip Ball describes how scientists are inventing thousands of new materials, ranging from synthetic skin, blood, and bone to substances that repair themselves and adapt to their environment, that swell and flex like muscles, that repel any ink or paint, and that capture and store the energy of the Sun." He explains this is being accomplished precisely because, for the first time in history, materials are being "made to measure" or designed for particular applications, rather than being discovered in nature or by haphazard experimentation [**2**]. The National Academies of Sciences, Engineering, and Medicine, in its *Review of the National Nanotechnology Initiative* (2006), argues that it is difficult to predict the future capabilities of nanotechnology [**3**]. "Although theoretical calculations can be made today, the eventually attainable range of chemical reaction cycles, error rates, speed of operation, and thermodynamic efficiencies of such bottom-up manufacturing systems cannot be reliably predicted at this time. Thus, the eventually attainable perfection and complexity of manufactured products, while they can be calculated in theory, cannot be predicted with confidence. Finally, the optimum research paths that might lead to systems which greatly exceed the thermodynamic efficiencies and other capabilities of biological systems cannot be reliably predicted at this time. Research funding that is based on the ability of investigators to produce experimental demonstrations that link to abstract models and guide long-term vision is most appropriate to achieve this goal."

In the thirty-six years since Eric Drexler proposed molecular assembly, many advances in materials modeling, design, and synthesis have occurred [**4-30**]. Carbon Hybrid

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Materials (CHM) synthesis based on gas phase pyrolysis is one method being developed [**9,20**] that can experimentally create (demonstrate) many variations of CNT materials. The CHM process assembles CNT molecules with metal or other nanoparticles or micro-fibers to form hybrid fabric with properties that can be customized based on the constituent materials used. Dry nanoparticles are injected into the inlet of the high temperature nanotube synthesis process and may melt and chemically react with the nanotubes. Also, short or continuous microfibers can be added to the nanotube matrix at the outlet stage of the process. The CHM process is thus flexible and scalable to large rate manufacturing at justifiable cost. The science behind developing CHM has not had much attention in the literature. This paper discusses the synthesis approach and problems of creating CHM materials. Phase diagrams are used to indicate the interaction of different metals with carbon. Microfiber integration at the outlet of the reactor is studied based on fibers mechanically interlocking within the nanotube matrix and being held with van der Waals forces. CHM is a method to create new materials that are designed or “made to measure” for specific applications.

The research described is helping to provide understanding of the basic chemical and physical processes (per engines of creation) used to design multi-element CHM. Scientific subareas of this research include; Studying fundamental materials science and chemistry to enable assembly and integration of CNT with nanoparticles and microfibers; Using gas phase pyrolysis to produce multiple functionalities in CHM and understanding the range and limits for each functionality; Finite element modeling of the reactor to understand flow and temperature effects; and Designing new CHM materials for multiple applications. Many types of hierarchical CHM can be envisioned to be constructed using nano/micro scale additive materials [**4,6,12-16,18-20,24,30**] including using coal powder as a carbon source [**28,29**].

Overview of synthesis tuning

Tuning the synthesis process involves adjusting many parameters. Key is the position and temperature for injection of the fuel. The alcohol fuel contains a carbon precursor, sulphur promoter and iron catalyst. The position of the fuel injector in the inlet of the reactor determines the quality, quantity and stability of the sock produced. See [**32**] for details of the fuel injector and reactor design. The fuel injection position must be adjusted by trial and error. Our hypothesis is that the alcohol will evaporate first (about 65 ^{o}C), the ferrocene will vaporize (about 273 ^{o}C), the alcohol will decompose (about 500 ^{o}C) and the ferrocene will decompose (about 900 ^{o}C). After the ferrocene decomposes, the iron atoms released will melt and agglomerate and form catalyst particles. The carbon atoms and fragments produced by cracking of the alcohol fuel will dissolve into the catalyst particles and nucleate a nanotube. A depiction of the hypothesized process is shown in **Fig. 1(a)**.

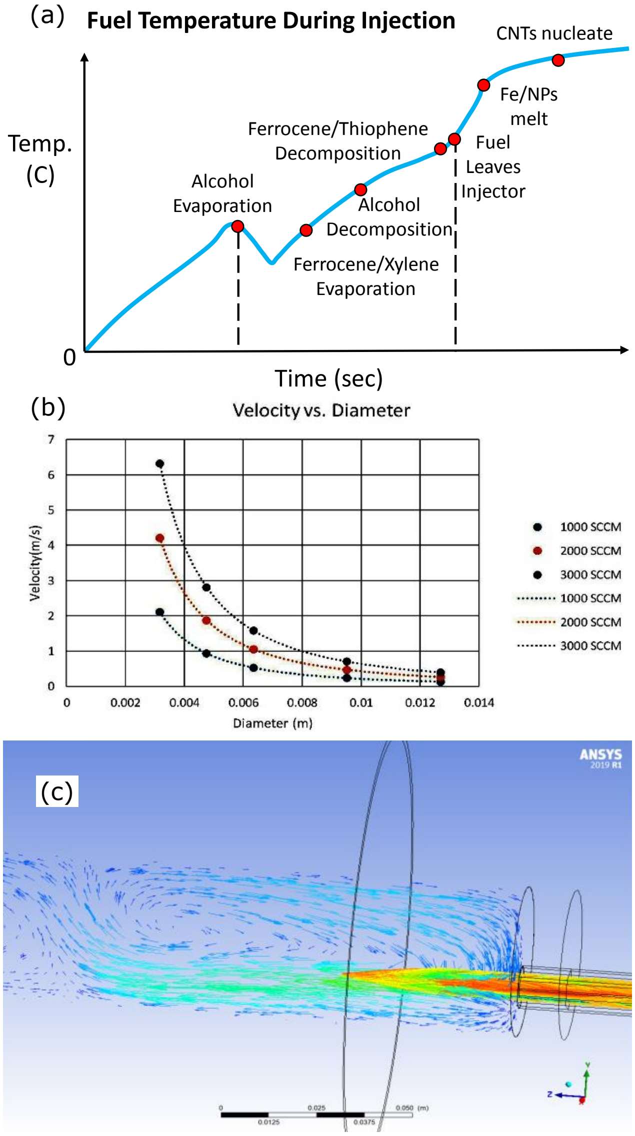


Fig. 1. Parameter studies for tuning the process: (a) Hypothesized temperature profile of the fuel during injection. (b) Gas (Ar and H_2) flow velocity for different diameter and flow rates in the extender tube at the right of the figure. (c) Simulation of flow and heat transfer in the tube. Cool gas flow leaves the extender tube from the fuel injector on the right and enters the larger ceramic tube. Circulating longitudinal flow and backflow occurs due to the entering gas being heated and rising [9]. Modelling will help guide the design of the fuel and particle injectors.

When operating the synthesis process with fuel injection only (particle injection off), two problems that are not fully understood may occur: (i) If the fuel injection point is too far away (too low of temp) from the hot zone and the velocity of the gas and fuel mixture is low, the fuel mist will spread out and carbon and ferrocene may deposit on the walls of the reactor. Also, the agglomeration of iron atoms to form the appropriate size catalyst particles may be reduced as the iron atoms are too dispersed to combine to form catalyst particles after the ferrocene is decomposed and the iron atoms melt. (ii) If the fuel injection point is too close (too high of temp) to the hot zone and the velocity of the gas and fuel mixture is low, amorphous carbon may deposit on the wall of the extender tube, or the ferrocene may decompose and form nanotubes inside the extender tube which may plug the extender tube. The catalyst may also become too large and reduce nucleation of CNTs. If the gas velocity is high, a light wispy sock will form. Orange glowing iron particles can also be carried out of the reactor tube. The ideal case is where the alcohol vaporizes and decomposes near the outlet end of the extender tube, and the gas velocity is high enough to prevent the carbon from depositing onto the wall of the extender, and the ferrocene and sulphur vaporize and decompose as they leave the extender tube. The velocity should also be appropriate for agglomeration of the catalyst to nucleate small nanotubes in a short distance from the outlet of the extender tube, before the carbon can move to the walls of the reactor and before the catalyst disperses. The velocity of the gas for different diameter extender tubes and gas flow rates is shown in **Fig. 1(b)**. Temperatures from three thermocouples are compared to simulation values to anchor or partly verify the modelling, **Fig.1(c)**. The simulation model provides the temperatures, flow velocities, and argon and hydrogen gas concentrations. Decomposition of the fuel injected is not specifically modelled yet.

Ideally, a small diameter dense sock is formed in the synthesis process. The sock would be pulled along the center of the reactor tube and rise toward the outlet of the tube and exit the tube without touching the wall of the reactor. The sock would then be wound at high speed onto the translating drum in the harvest box, **Fig. 2(a)**. If the sock does not contact the wall of the reactor tube, the process will be more reliable and industrial. The extender tube will keep the carbon and catalyst together until at the right moment and at the optimal temperature where the fuel leaves the extender tube and nucleates a sock. Gas in the center of the sock will escape through the walls of the sock.

The sock is wound at higher speed than the gas exiting the reactor tube. This process described may increase nucleation efficiency and increase the yield of the synthesis process. A thermocouple is used to monitor the temperature at the tip of the extender where the gas exits. Since the process takes time for the reactor temperature to stabilize, and this equilibrium temperature changes once the fuel is turned on, the process must be allowed to come to equilibrium temperature before synthesis occurs. Imprecise tuning causes the sock to stick to the reactor wall and requires frequent cleaning of the reactor tube.

Several engineering problems in the tuning process can be difficult to troubleshoot when developing a reactor system. The temperature profile in **Fig. 1(a)** is the most critical factor in tuning the synthesis process to provide the correct catalyst size and to maximize the nucleation and yield of the CNT material. Another consideration is that the nanoparticles injected are sensitive to temperature and restrictions in the flow system. A right angle turn in the flow system does not affect the gas flow but particles such as ferrocene which agglomerates easily will build up on the walls of a flow turn in the tubing and eventually restrict or block the flow. As another example, passages in the fuel atomizer must be large enough to prevent being blocked. Additives to the fuel or ferrocene in the fuel can deposit on the inside of flow passages such as a metering needle and can block the needle. The temperature of the atomizer affects the deposition of additives on the tubing. A solution to both problems is to avoid sharp bends in the flow system, and do not use micro-tubing.

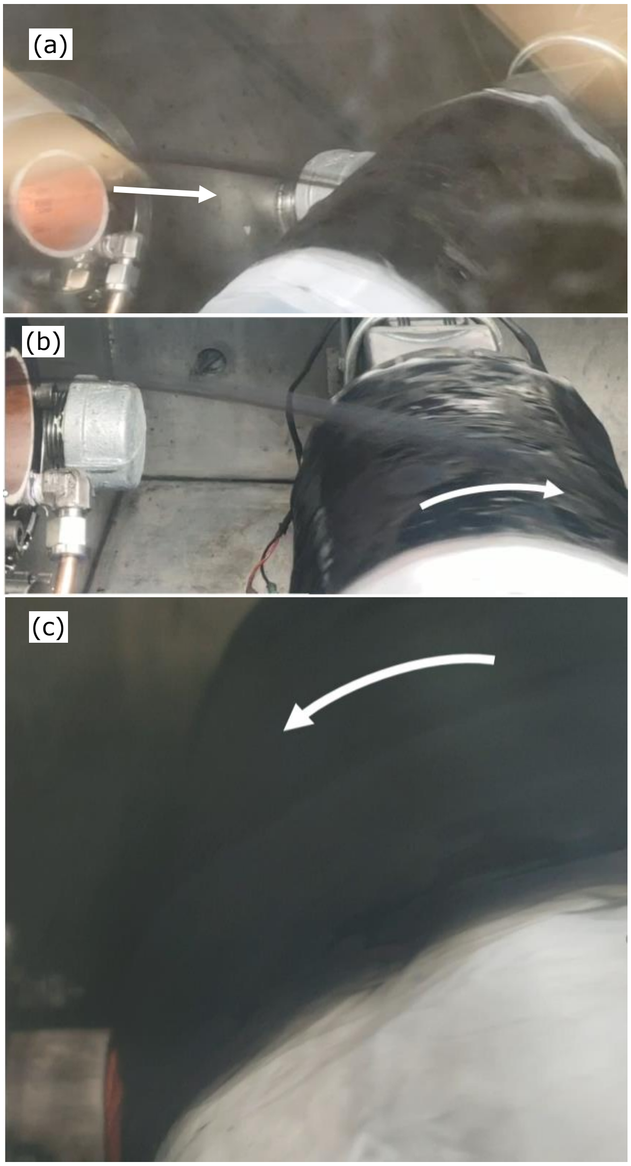


Fig. 2. Winding the sock onto the drum. (a) Small diameter CNT rope like sock wound fast on the wind-up drum to minimize the sock rubbing on the top of the ceramic tube. Here the drum is below the outlet of the ceramic tube to pull the sock downward. (b) The CW rotation direction of the drum is shown. A 1.75 in ID ceramic process tube is used in a,b. (c) A 1.62 in ID ceramic process tube is used in this case and the drum is above the tube outlet. A large diameter sock is wound onto the drum with CCW rotation. Here the drum is above the outlet of the ceramic tube to collect the large sock exiting the tube. Placing the drum above the outlet reduces breaking of the sock.

Cooling temperature study

The reactor operating at normal conditions producing pristine sheet was changed to a cooling function while all other conditions for the normal synthesis were maintained. As the reactor cooled, the sock became lighter and eventually broke. The continuous cooling at 10 ºC/min allowed the dependence of sock condition on temperature to be studied quickly in one experiment. One limitation of this approach is the inlet baffle plate did not change temperature much as the reactor was cooling. Thus, a steady-state temperature condition was not achieved. This will affect determining the optimal temperature for synthesis. However, the baffle plate [32] can be adjusted to a position that is hotter even though the maximum temperature of the furnace is lower than the nominal set temperature of 1420 ºC. Thus, the experiment shows the effect of the furnace temperature on the sock condition keeping the baffle plate about at a constant temperature. **Fig. 3** is a graph of the furnace and baffle plate temperatures versus time.

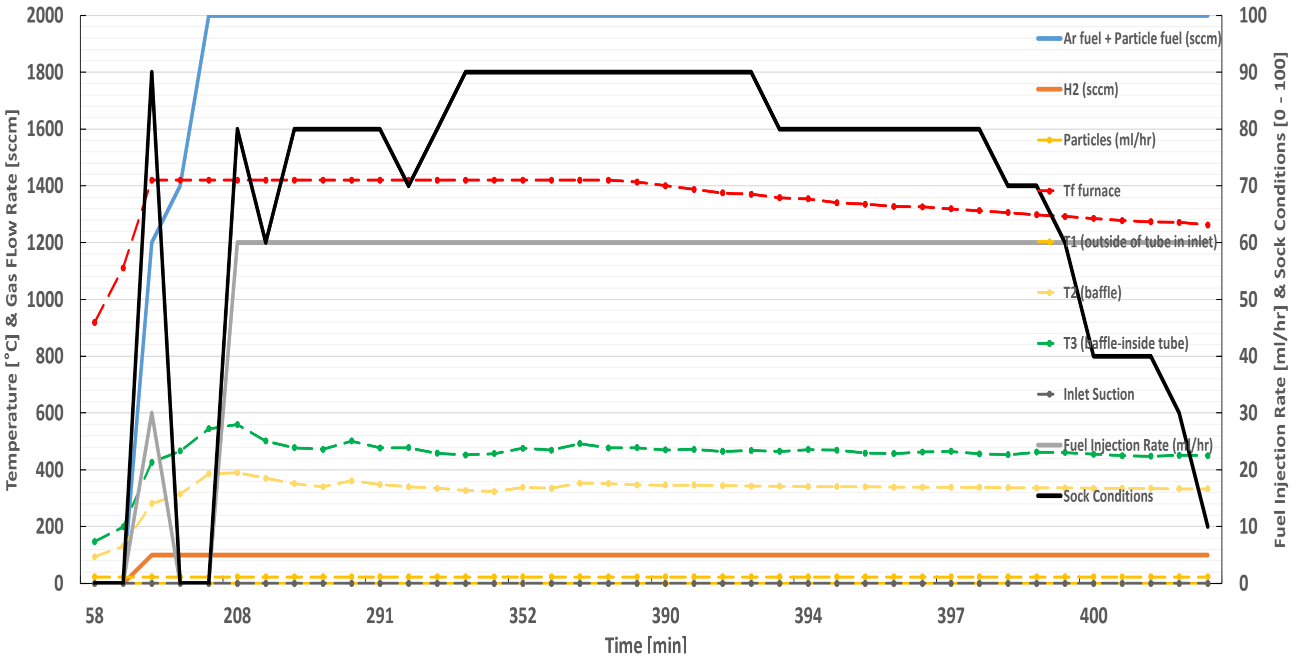


Fig. 3. Temperatures of the reactor while the furnace is cooling and producing a sock. The black line is the sock condition (0-100) where 100 represents stable continuous sock production. As the furnace cools the sock condition deteriorates. Especially below about 1300 ºC (red line) the sock condition deteriorates quickly. Note the T3 baffle temperature (green line) changes slowly upon cooling. Note the time axis is not linear. The plot helps to understand interactions between process variables and their effect on the sock condition.

Process tuning

Variables that are tuned in the process are reactor temperature, fuel injection rate, particle injection rate, gas flow rates for Ar H_2, the baffle plate position, wind-up drum speed, the fuel composition, the particle type and size, and the glove box pressure. Ferrocene (a catalyst) can also be used in the particle injector typically mixed with other particles such as granulated activated carbon (GAC) and many types of metal particles. A tuning run may start with the baffle plate almost fully extended at 1.5 inches. At the start of the run, the sock for example could be light and break. The baffle plate can then be moved in steps to its retracted position. The sock condition may improve as the temperature of the baffle plate increases to an equilibrium condition. Every process variable affects every other variable. Generally, the highest Ar flow rate is desired when using particle injection. The Ar flow rate affects the dwell time that the CNT grows in the reactor. The CNT sock forms in about 1-2 seconds based on a gas flow rate of about 8 inches/second. Increasing the fuel injection rate cools the reactor. Once the fuel injection is turned off, the temperature on the hot side of the baffle plate [see 32 for injector geometry] increases.

Sock design

A goal of the synthesis is to design the sock, which means controlling the position of the sock in the reactor so the sock does not rub and deposit on the wall of the ceramic tube. The sock rubbing on the wall of the tube reduces the amount of CNT produced. Further goals are to grow the longest CNT possible, produce high quality CNT as characterized by a high Raman G/D ratio, and to inject NPs that are uniformly distributed within the sock. A schematic of the sock formation process based on our hypothesis is shown in **Fig. 4**. The schematic is a possible explanation of how the sock rubs on the reactor wall and breaks.

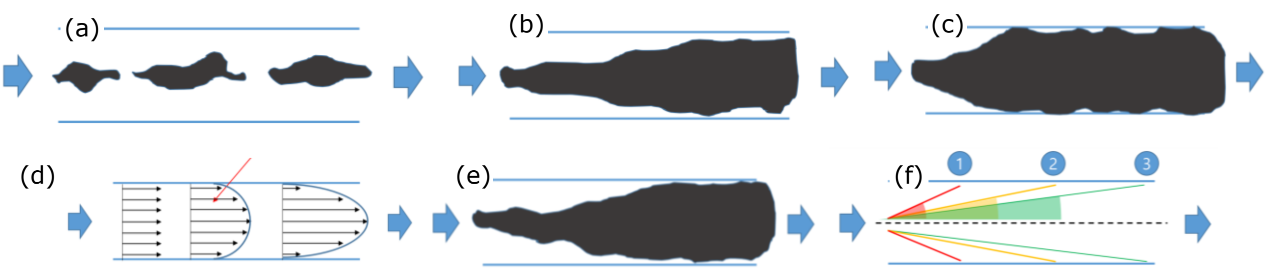
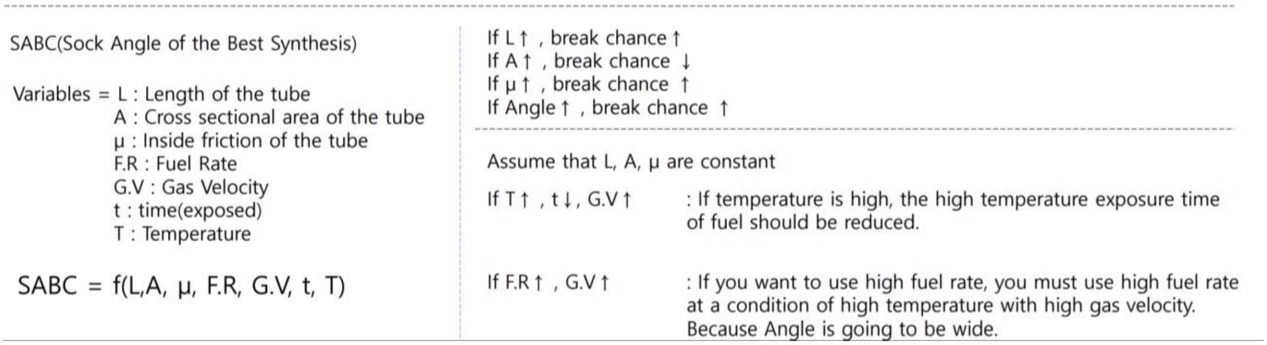


Fig. 4. Sock formation and breaking as a function of synthesis temperature and gas flow rate. (a) synthesis temperature is low, only sock fragments are formed, breaking frequently occurs; (b) with increased temperature the fuel reaction is continuously occurring, the sock is larger and more stable and continuous, some webs form on the wall of the reactor tube, particles can attach to the wall of the ceramic process tube; (c) as the temperature increases further, the size of the sock increases, the area where the sock rubs against the inside of the ceramic tube increases, the sock is continuously generated and breaking occurs randomly as the larger sock has greater friction and sticks to the tube wall; (d) as the velocity of the gas increases, in the general case the drag against the wall of the tube increases and the laminar flow transitions to turbulent flow at the boundary, as the gas flow rate further increases, the point where turbulence occurs in the tube rapidly increases. As the velocity of the gas increases, the sock must break more often; (e) However, the size of the sock is also determined according to the time the fuel is exposed to the high temperature. The faster the gas velocity, the shorter the time the fuel is exposed to high temperature. Therefore, the point at which the sock growth is optimal is pushed back, so a continuous stable sock is achieved. The fuel flow rate also affects the sock formation. Increasing the fuel flow rate increases the amount of nanotubes nucleated, reduces the gas temperature due to the cooling effect of vaporization of the fuel, and increases the gas velocity due to the hydrogen gas generated by vaporization of the alcohol fuel.; (f) So, the temperature, dwell time, and fuel flow rate determine an angle of the sock formation as seen from the left of the figure. If the inside of the ceramic tube had no friction, ideally angle 1 is the optimal. Otherwise, angle 2 or angle 3 may be optimal (optimal in the sense of increasing CNT throughput while minimizing breaking of the sock) depending on the coefficient of friction of the wall of the ceramic tube. As the process runs longer, carbon deposits on the wall of the tube increase which increases friction.

Trends for tuning the synthesis process to reduce breaking are given in **Fig. 5**. The sock formation can be modelled qualitatively to predict the sock angle for best synthesis (SABS).



SABC(Sock Angle of the Best Synthesis)

Variables = L : Length of the tube
A : Cross sectional area of the tube
μ : Inside friction of the tube
F.R : Fuel Rate
G.V : Gas Velocity
t : time(exposed)
T : Temperature

SABC = f(L,A, μ, F.R, G.V, t, T)

If L↑ , break chance↑
If A↑ , break chance ↓
If μ↑ , break chance ↑
If Angle↑ , break chance ↑

Assume that L, A, μ are constant

If T↑ , t↓, G.V↑ : If temperature is high, the high temperature exposure time of fuel should be reduced.

If F.R↑ , G.V↑ : If you want to use high fuel rate, you must use high fuel rate at a condition of high temperature with high gas velocity. Because Angle is going to be wide.

Fig. 5. Qualitative guidelines to predict the sock angle for best synthesis.

The sock tends to drag at the outlet end of the ceramic tube. This is likely due to the gas rising as it leaves the hot zone of the reactor and enters the insulated cooling zone. Cool gas in the sock will reduce the sock from rising in the hot zone. Making the ceramic tube larger at the outlet might reduce the deposits on the tube. The yield depends on the injector and extender design. Injecting metal NPs may strengthen the sock.

Nanoparticle injection

An example of nanoparticle injection is described. A particle distributor delivers NPs to a venturi eductor [**32**].

In **Fig. 6**, the particle injector distributor (top part of the injector) delivered about 20 ml of Zn NPs in about 40 minutes. The delivery rate is slow and uniform using a 1.3 RPM motor. The particle injector distributor is attached to an eductor (optionally) and connected to the reactor to provide gas and particles to the mixer [**32**]. The NPs are integrated into a CNT sheet, minus the loss of some particles collecting on the walls of the injector and depositing on the inside wall of the ceramic tube. Zn NPs (60 nm diameter) melt and vaporize and deposit within the CNT sheet or CNT. Characterization using SEM, TEM and EDAX is needed to understand how the NPs integrate into the CNT fabric and to determine what applications may benefit from the new CNT-Zn material. Zn particles injected at a low-rate melt/vaporize and maintain the stability of the sock.

Plugging of the eductor can occur if the injection parameters are not optimal. Some NPs are better behaved than others, and some NPs are extremely cohesive and will build up on eductor internals. The diameter, shape, and material of the NP all affect how it injects. A cohesive or sticky material can plug up a mini-eductor quickly due to the very small internals. A larger eductor would drag out the required cleaning interval, but it would use more motive air/gas. Heating the eductor may also help in some conditions. The motive flow rate and the suction flow rate are controlled by separate mass flow controllers. Design and tuning of the particle injector will be the subject of a future paper. Material delivered by particle injection is shown in **Fig. 6(c)**. Zn has a low boiling point and can be integrated into the growing CNTs. Zn is also biocompatible and non-toxic in the body in low concentrations which may open medical applications of CNT hybrid materials.

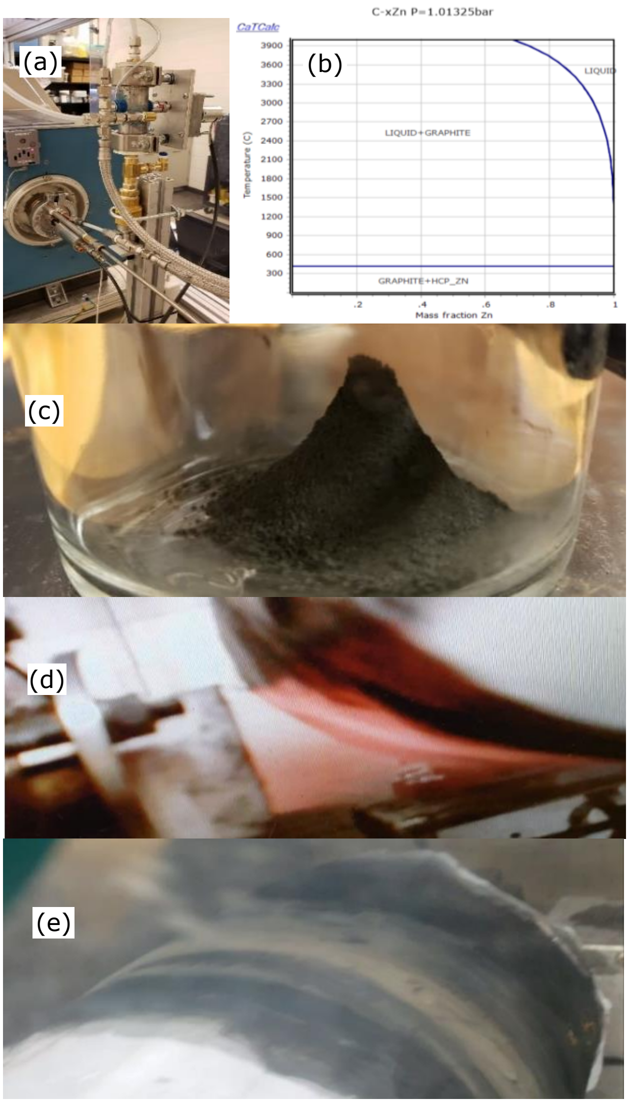


Fig. 6. CNT hybrid material produced with NP injection. (a) The particle injector. (b) Phase diagrams are used to predict the outcome of mixing different metals with carbon. The simple phase diagram is from [31]. (c) Zn NPs delivered in testing the delivery rate of the injector. (d) CNT sock exiting the ceramic tube and winding onto the take-up drum to form CNT sheet. (e) Zn particles produce the grey colored strip shown.

Forming CHM

Various types of CHM can be formed starting with the sock material as shown in **Fig. 7(a)** where in this case the sock is not densified using a solvent spray in the glove box. Pristine CNT sheet (width 6 in, length 20 in, thickness 17 microns) can be formed in one hour using a fuel feed rate of 60 ml/hr. The reactor tube ID=1.65 inch. Scaling up the synthesis process to increase the throughput and reduce the cost is needed to put CNT sheet into commercial applications. CHM can be combined with carbon fiber (CF) tape using a custom tape winder located in the glove box as shown in **Fig. 7(b)**. Chopped carbon fiber and GAC can also be integrated into the CNT sheet, in this case from the glove box, **Fig. 7(c)**.

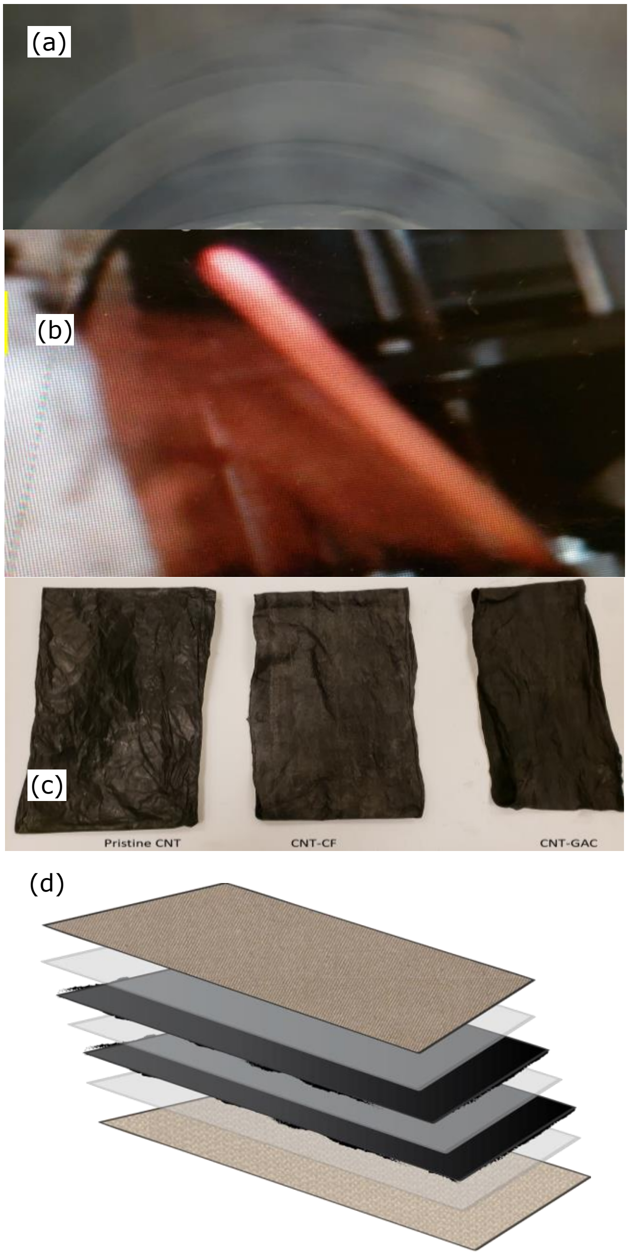


Fig. 7. CHM being formed starting with the CNT sock. (a) Carbon nanotube sock being layered onto a drum without densification. (b) CNT sock deposited on carbon fiber (CF) tape to improve the properties of the tape. (c) Pristine CNT sheet, CNT-CF where CF mesh is integrated into the CNT sheet to increase strength in the harvest box, and CNT-GAC sheet to increase porosity and breathability of the fabric in the harvest box. (d) CHM used to form symmetric composited textiles. Black layers are CHM.

NPs can be compounded to use in the reactor to form composite fabric. NP combinations may provide wetting and improved conductivity: e.g. (i) Ag-56%, Cu-42%, Ni-2%, and (ii) Ag-65%, Cu-28%, Mn-5%, Ni-2%. A textile example of CHM composited (layered) with other fabric is shown in **Fig. 7(d)**. As CHM is thin to reduce cost, composited fabric can be formed with improved properties from the CHM. The CHM adds almost no mass or stiffness to the textile, but provides modest improvements in flame resistance, static electricity discharge, electromagnetic shielding, and heat spreading.

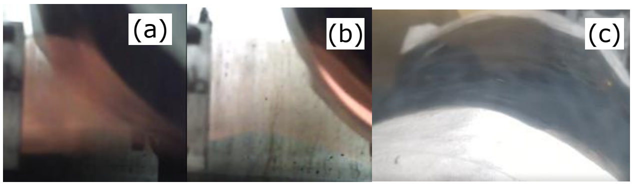


Fig. 8. Synthesizing CNT-Fe-Zn fabric. Tuning the NP injection to be uniform is a challenge. (a) high density sock exiting the reactor tube. (b) low density sock exiting the reactor tube. (c) CHM fabric.

CNT-Fe-Zn CHM

CNT metals can be formed in different ways [**33-36**]. Here we inject NPs into the CNT synthesis process. In this example, a mixture of Fe (ferrocene) and Zn NPs (50/50 powder mixture) is injected into the inlet area of the reactor tube. The NPs are injected 2.5 inches beyond the exit of the extender tube to be closer to the hot zone of the reactor. The Fe-Zn NPs are injected (in an adjustable tube) separately from the fuel in this case. Fe is a catalyst and increases the yield of the process. Fe also acts to increase the flame resistance of the CHM fabric. Zn vaporizes and distributes throughout the CNT sock. Zn is anti-microbial and possibly anti-virus which makes the material possibly suitable for air filtering applications. The NPs added may also increase the electrical and thermal conductivity and strength of the fabric. The density of the CHM will increase also. The CHM fabric bring produced is shown in **Fig. 8**. The material has not been characterized yet. The injector design is also still in development to provide a more uniform rate of injecting the NPs. **Fig. 8(a)** shows a high-density sock while **Fig. 8(b)** shows a low-density sock. Improved injection tuning could provide a continuous high-density sock. Our hypothesis is CHM fabric, **Fig. 8(c)**, can be manufactured at a higher rate and with customized properties using particle injection. Besides showing the need to improve the stability of the particle injection, which is mainly a mechanical design problem, this experiment also indicated that mixing ferrocene with the NPs and injecting them separately from the fuel seems to make the sock formation more uniform as compared to injecting Zn NPs with the fuel in the mixer. A higher percentage of NPs can be injected when they are mixed with ferrocene. The optimal ratio of NPs to ferrocene, and the possibilities to compound NP mixtures using different metals need to be investigated. Overall, the CHM process is an emerging technology and some of the first results evaluating this new process are presented in this paper.

Summary and conclusions

This paper gave recommendations on tuning the synthesis process to manufacture carbon nanotube hybrid materials. New materials that are combinations of CNT and metals are being formed. Families of carbon hybrid materials can be produced by choosing different elements of the periodic table. Further research will uncover what benefits these materials that are “made to measure” will have.

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Conflicts of interest

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

Keywords

Carbon nanotube synthesis, hybrid materials, nanoparticles, fabric.

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