

Heat treatment of carbon nanotube hybrid material for textile applications

Abstract

The paper describes the synthesis of carbon nanotube hybrid material and its post-processing treatment such as heat treatment of carbon nanotube (CNT) sheet to improve its properties for in textile applications. The CNT sheet is synthesized using the floating catalyst chemical vapor deposition (FCCVD) method. The floating catalyst method is a continuous process and can produce industrial scale nanotubes in a single step. The lightweight of the CNT material and its flexibility makes it a suitable candidate for textile and wearable applications. The synthesis process and applications of the new hybrid material are discussed along with the customization of the material.

Keywords: hybrid CNT material, smart textiles, flexible CNT sheet

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Introduction

Carbon nanotube (CNT) material has attracted considerable attention since its discovery. This wonderful material possesses excellent electrical, mechanical, and thermal properties, which provide it a wide range of potential applications.¹⁻³ But the scale-up to macroscale material forms and translating the electrical and mechanical properties to macroscale material forms has proved to be challenging despite extensive efforts throughout the past two decades. The electrical and mechanical properties of the macroscale materials have been limited by defects, impurities, and discontinuity of the CNT strands.⁴⁻⁶ The strongest macroscale CNT material (long nanotube) has been reported to show a tensile strength of 80 GPa to date.⁷ However, this material is a long CNT, not a handleable or scalable material form. Besides structural defects and impurities, the main problem associated with the macro-assembly has been identified as these short CNT components, which overlap with each other and are assembled only by the weak van der Waals force. Macroscale material properties are far below the properties of individual CNT.

The as-synthesized CNT sheet from the floating catalyst chemical vapor deposition (FCCVD) method contains residual metal catalysts encapsulated inside or on the outside of the nanotubes. To remove the impurities and improve the CNT properties, a post processing method such as heat treatment is usually performed.⁸⁻¹⁰ The post-processed material can be used in textile applications. The concept of nanoengineered textiles is under extensive research.¹¹⁻¹³ An example is to use the anisotropic heat conduction of CNT fabric for firefighting applications. A smart garment was simulated to direct heat from the garment to an external cold sink, which lowered the temperature of the body.¹⁴ CNT materials are being integrated into textiles in personal protective equipment for firefighters¹⁵ and for energy storage applications for wearable electronic textiles.^{16,17}

In this paper, we will discuss the synthesis process for the CNT and carbon nanotube hybrid (CNTH) materials. The physical properties of these materials are also investigated. A short overview on the use of CNTs for textile applications is also provided.

Material and methods

Carbon nanotube sheets were synthesized using the floating catalyst chemical deposition method. A fuel consisting of a carbon precursor, metal catalyst, and sulfur additive was injected using a syringe into the atomizer into the one end of the ceramic tube. At the other end of the reactor tube, a CNT sock was collected onto the rotating drum to form a sheet. The temperature of the furnace was ~1420°C. Further details of the synthesis process can be found in our previous work.¹⁸⁻²⁰ The surface morphology of the synthesized material was characterized using Scanning electron microscopy (SEM) (FEI SCIOS, Waltham, MA, USA) and transmission electron microscopy (TEM) (CM-20, Philips, Andover, MA, USA). Tensile testing was performed using an Instron 5948 machine. A laser micromachining system (Oxford Laser A-Series, Didcot, UK) was used to cut the CNT sheet samples. The electrical conductivity of the sheet was measured using a four-probe technique.

Carbon hybrid material

For hybrid material, a customized particle injector was used to integrate metal, ceramic, and other nanoparticles inside the CNT sheets during synthesis process. The type and size of the nanoparticles is application specific but the integration of the nanoparticles with CNTs mainly depends upon the nanoparticle wetting properties. A detailed study on wetting properties is done in our previous work.¹⁹ The floating catalyst method is a continuous method and is capable of large-scale synthesis. Various factors such as carrier flow gas, synthesis temperature, and type of metal catalyst can be varied to customize the CNT hybrid material.

Post-processing treatments

The most common method for metal catalysts impurities removal is heat treatment. Here, CNT sheets were annealed at 200°C, 300°C, 600°C, and 900°C using a rapid thermal annealing furnace. Heat treatment was performed in the AG Associates Heatpulse 410 Rapid Thermal Processor (RTP). The heatpulse 410 uses high intensity visible radiation to heat a single substrate for a short period at

precisely controlled temperatures. The temperature was monitored by a thermocouple and the system was purged with nitrogen gas to maintain the inert environment. The heating rate was kept at 220°C/sec, when the temperature was steady, each sample was held for 2mins.

Microscopy characterization

In Figure 1(A), the sock collection process is shown. A CNT sock is coming out of the reactor end and is collecting on the rotating drum. The final as-synthesized CNT sheet consists of hundreds of thin layers of CNT web or sock about 1 inch wide that is wrapped on the drum. The thickness of the sheet can be customized by varying the collection time of the sock. According to the requirements of specific applications, CNT sheets can be customized. For filtering

applications, the collection time can be reduced to make the sheet permeable and for other application where strength is needed these sheets can be collected for hours to provide a strong mechanical support. Figure 1(B) shows the scanning electron microscope (SEM) image at the micrometer scale and Figure 1(C) shows the transmission electron microscope (TEM) image at the nanometer scale. As we can see in the SEM image, there are lots of vacancies in the CNT sheets and its loosely packed fiber structure which makes it porous and can be used for filtering applications.²¹ From Figure 1(C), we can see that the nanotubes are ~7nm in diameter and have metal catalyst impurities trapped inside. Before heat treatment, we can see a lot of agglomeration on the CNT sheet in Figure 1(D). The CNT material after heat treatment is shown in Figure 1(E) and Figure 1(F). With the increase in temperature and the removal of the impurities and the amorphous carbon and the agglomerations started to disappear.

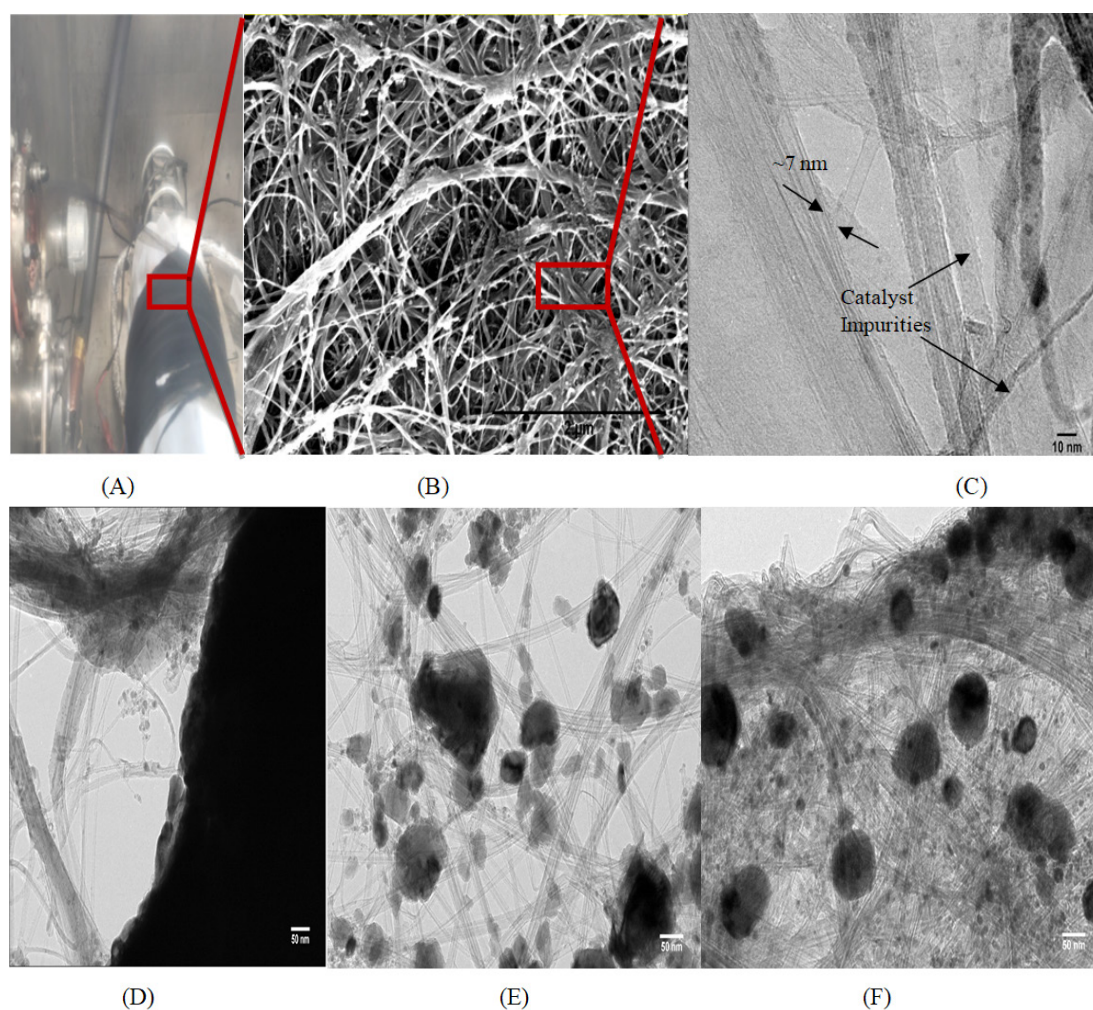


Figure 1 (A) CNT sock collection; (B) SEM image at 2 μm ; (C) TEM image at 10nm; (D) CNT-Cu hybrid material before heat treatment (at 50nm scale); (E) CNT-CU annealed at 600°C (at 50 nm scale); (F) CNT-Cu annealed at 900°C (at 50 nm scale).²²

Mechanical and electrical characterization

For mechanical testing, each sample was cut into a rectangular shape with a dimension of 25mm x 2mm using a laser. The laser cut samples then was pasted onto a paper strip, which was clamped by two pneumatic clips with a gauge length of 10 mm. The clips in the testing underwent vertical movement with a strain rate of 1mm/min until the sample was broken. Electrical measurements were performed

using a four-point probe method, the four heads were gently placed on the surface of the CNT sheet. The resistivity was calculated using $\rho = \pi t / \ln 2 \cdot V/I$, where V is the voltage, I is the current and t is the thickness of the film. For each sample, 5 values of resistance were measured at different points, because the anisotropic nature of CNT materials, another 5 values was measured after turning the sample 90° (Figure 2).

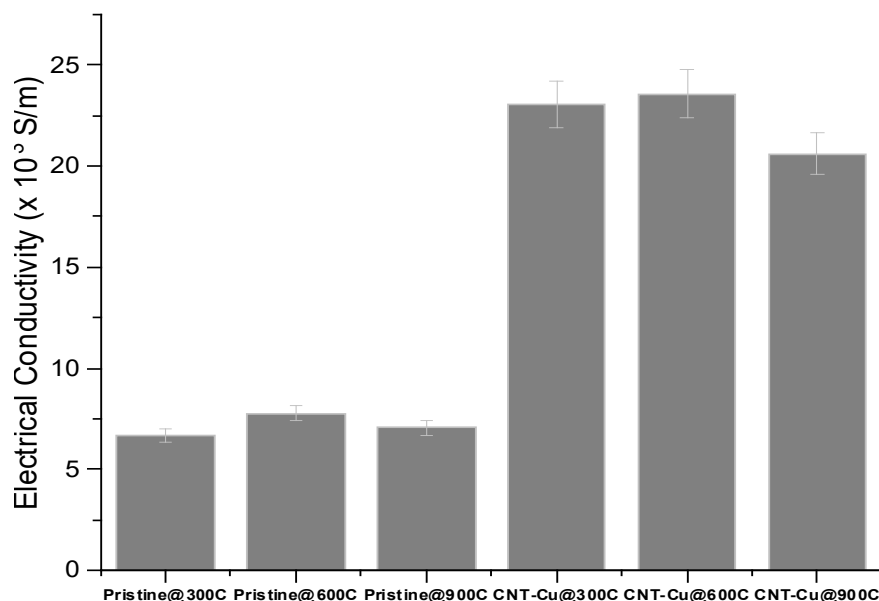


Figure 2 Electrical conductivity in-plane of Pristine CNT and CNT-Cu hybrid sheet.²²

The electrical conductivity of the hybrid material showed better performance than pristine. The conductivity of the material is highly dependent on the annealing temperature. The conductivity of the both pristine and hybrid CNT-Cu increased with an increase in annealing temperature which showed a semiconducting behavior. The conductivity increased due to the decrease in contact resistance between CNTs below the transition temperature. The conductivity of the samples reached its maximum value at 600°C and started decreasing with an increase in temperature and showed metallic behavior.²³ After the transition temperature conductivity started to decrease due to the increase in resistance in individual CNT tube. The other reason for lower conductivity is due to the barrier potential which can interrupt the electrons flow hence reduce the conductivity.²⁴

More than ten samples were used for the tensile test. Figure 3 shows the normalized tensile strength for pristine sample, which is CNT alone with no nanoparticles, and hybrid CNT-Cu samples annealed at different temperatures. Heat treatment improved the mechanical properties of material by removing impurities from CNTs. The tensile strength reaches a maximum value after performing the heat treatment at 600°C, which is 1.8 times more in strength as compared to pristine. At higher temperature (>600°C) defects are increasing in CNTs which can lead to disorder which deteriorates the performance of the material. The oxidation of raw multi-walled CNTs started at 420°C and finished at 630°C whereas the oxidation of the graphitic multi-walled CNTs started at 640°C and finished at 780°C.²⁵

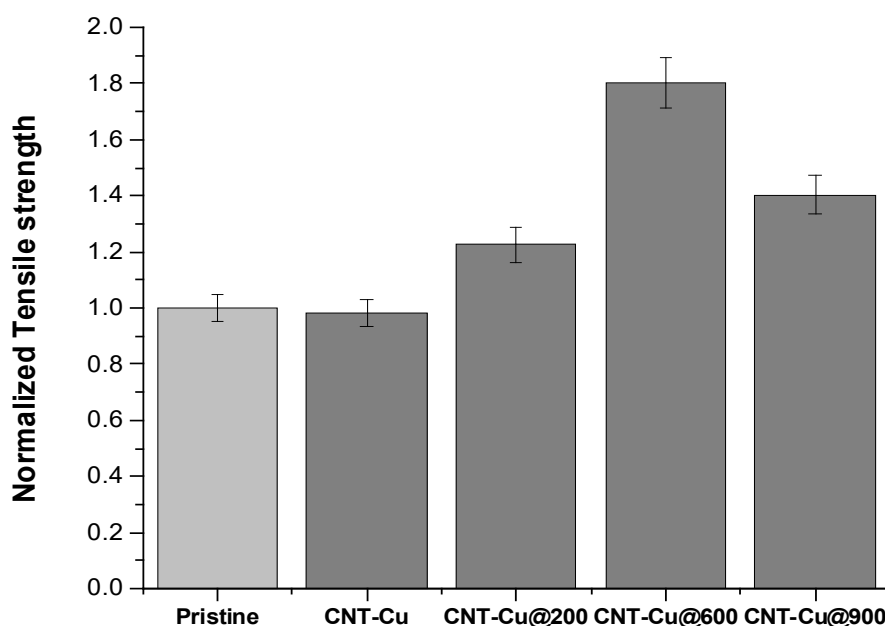


Figure 3 Normalized Tensile strength for pristine and annealed hybrid CNT-Cu samples.

CNT smart textile applications

The integration of CNT and CNT hybrid materials into textiles has many possibilities in the fashion industry, and in personal protective equipment, smart, flexible, and wearable textiles. CNT and its composites have been used to improve strength and make it lightweight,^{26,27} to improve electrical conductivity and use as a conductive textile,^{28,29} and in wearable electronics textiles.³⁰ A flexible textile of carbon nanotube/graphene was used as an electrode for a flexible supercapacitor to use its high surface area and flexibility.³¹ CNT materials can be integrated in garments to make invisible antenna patches.³² The antenna arrays integrated in garments can communicate with sensors and devices in and on the body. A detailed discussion about the integration of the CNTH fabric with textiles and its potential applications in fire fighter garments, flame retardant, and in fashion apparel has been discussed in Chapter 12.³³

Conclusion

The paper described the synthesis process for CNT and CNTH material. The CNTH material is a multifunctional material and showed improved electrical and mechanical properties compared to pristine material. The synthesis process is a single-step continuous process and can produce large-scale material. Heat treatment was performed on the material to further improve its properties. The customization of this CNTH material makes it suitable for applications such as filtering, sensors, energy storage, and others. Successful commercialization of the smart and flexible textiles needs an innovative approach, interdisciplinary collaboration, and an understanding of material science and nanotechnology.

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Conflicts of interest

The authors have no conflict of interest regarding this paper.

References

- Baughman RH, Zakhidov AA, De Heer WA. Carbon nanotubes - The route toward applications. *Science*. 2002.
- Appenzeller J, Martel R, Derycke V, et al. Carbon nanotubes as potential building blocks for future nanoelectronics. *Microelectron Eng*. 2002;64(1–4):391–397.
- Chen DR, Adusei PK, Chitranshi M, et al. Electrochemical activation to enhance the volumetric performance of carbon nanotube electrodes. *Appl Surf Sci*. 2021.
- Koziol K, Vilatela J, Moisala A, et al. High-performance carbon nanotube fiber. *Science*. 2007.
- Beese AM, Wei X, Sarkar S, et al. Key factors limiting carbon nanotube yarn strength: Exploring processing-structure-property relationships. *ACS Nano*. 2014.
- Ericson LM, Fan H, Peng H, et al. Macroscopic, neat, single-walled carbon nanotube fibers. *Science*. 2004.
- Bai Y, Zhang R, Ye X, et al. Carbon nanotube bundles with tensile strength over 80 GPa. *Nat Nanotechnol*. 2018.
- Han L, Song Q, Sun J, et al. The role of CNT in improving the mechanical strength retention rate of C/C composites during heat treatment. *Compos Part B Eng*. 2020.
- Dini Y, Rouchon D, Faure-Vincent J, et al. Large improvement of CNT yarn electrical conductivity by varying chemical doping and annealing treatment. *Carbon*. 2020.
- Niven JF, Johnson MB, Juckes SM, et al. Influence of annealing on thermal and electrical properties of carbon nanotube yarns. *Carbon*. 2016.
- Brown PJ, Stevens K. Nanofibers and nanotechnology in textiles. 2007.
- Tarafder N. Applications of nanotechnology for textile products: a review. *Nanoscale Reports*. 2018.
- Yetisen AK, Qu H, Manbachi A, et al. Nanotechnology in textiles. *ACS Nano*. 2016.
- Sullivan J, Schulz M, Vemaganti K, et al. Carbon nanotube fabric cooling system for firefighters and first responders: Modeling and simulation. *J Fiber Bioeng Informatics*. 2015.
- Janas D, Rdest M, Koziol KKK. Flame-retardant carbon nanotube films. *Appl Surf Sci*. 2017.
- Hu L, Pasta M, La Mantia F, et al. Stretchable, porous, and conductive energy textiles. *Nano Lett*. 2010.
- Kubley A, Chauhan D, Kanakaraj SN, et al. Smart textiles and wearable technology innovation with carbon nanotube technology. *Nanotub Superfiber Mater Sci Manuf Commer*. 2019.
- Schulz MJ, Chitranshi M, Chauhan D, et al. Pioneering carbon nanotube textile engineering & fashion technology. *J Text Eng Fash Technol*. 2019.
- Chitranshi M, Pujari A, Ng V, et al. Carbon nanotube sheet-synthesis and applications. *Nanomaterials*. 2020.
- Chen DR, Chitranshi M, Schulz M, et al. A review of three major factors controlling carbon nanotubes synthesis from the floating catalyst chemical vapor deposition. *Nano Life*. 2019.
- Li P, Wang C, Zhang Y, et al. Air filtration in the free molecular flow regime: A review of high-efficiency particulate air filters based on Carbon Nanotubes. *Small*. 2014.
- Chitranshi M, Grinspun M, Kubley S, et al. Carbon nanotube hybrid material for air filtering applications. *Video Proc Adv Mater*. 2021.
- Zhang X, Liu H, Temperature dependence of electrical conductivity of carbon nanotube films from 300 to 1100 K. *Springer Proc Phys*. 2019.
- Ravi S, Kaiser AB, Bumby CW. Charge transport in surfactant-free single walled carbon nanotube networks. *Phys Status Solidi Basic Res*. 2013.
- Bom D, Andrews R, Jacques D, et al. Thermogravimetric analysis of the oxidation of multiwalled carbon nanotubes: evidence for the role of defect sites in carbon nanotube chemistry. *Nano Lett*. 2002.
- Kumar S, Doshi H, Srinivasarao M, et al. Fibers from polypropylene/nano carbon fiber composites. *Polymer (Guildf)*. 2002.
- Bhanushali H, Bradford PD. Woven glass fiber composites with aligned carbon nanotube sheet interlayers. *J Nanomater*. 2016.
- Behabtu N, Young CC, Tsentalovich DE, et al. Strong, light, multifunctional fibers of carbon nanotubes with ultrahigh conductivity. *Science*. 2013.
- M in het Panhuis, Wu J, Ashraf SA, et al. Conducting textiles from single-walled carbon nanotubes. *Synth Met*. 2007.
- Lima RMAP, Alcaraz-Espinoza JJ, Da Silva FAG, et al. Multifunctional wearable electronic textiles using cotton fibers with polypyrrole and carbon nanotubes. *ACS Appl Mater Interfaces*. 2018.

31. Cheng H, Dong Z, Hu C, et al. Textile electrodes woven by carbon nanotube-graphene hybrid fibers for flexible electrochemical capacitors. *Nanoscale*. 2013.
32. Foroughi J, Mitew T, Ogunbona P, et al. Smart fabrics and networked clothing: recent developments in CNT-based fibers and their continual refinement. *IEEE Consum Electron Mag*. 2016.
33. Schulz MJ, Shanov V, Yin Z, et al. Nanotube superfiber materials: Science, manufacturing, commercialization. 2019.