Improved Performance of Ultra-Fast Carbon Nanotube Film Heaters

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Abstract—With current level of development, mankind is about to face many energy-related problems unless we find ways for more efficient power generation and transmission. In this paper, we depicted the operation of highperformance carbon nanotube film heaters, which show a clear advantage over traditionally employed materials. The material was synthesized by a facile one-step method and used as resistive heating element. The results have shown very effective conversion of electric power into heat. To improve the homogeneity of the heaters electrical resistance, we explored a selection of volatile solvents. Such a pretreatment step prior to heaters use caused densification of the material and favorable changes to the electrothermal behavior.

Index Terms—carbon nanotubes, heating elements, electrical properties

I. INTRODUCTION

Carbon nanotubes (CNTs) can be imagined as seamlessly rolled-up graphene sheet(s) using a single (single-wall CNTs), two (double-wall CNTs) or many lavers (multi-wall CNTs). Ever since their discovery in 1991 [1], the material has shown unparalleled properties particularly in terms of electrical and thermal conductivities. In theory, these features are fully tunable and the scientific community has committed efforts to tailor them to specific applications. On the one hand, CNTs outperform copper by orders of magnitude, the material known for extremely high electrical [2] and thermal [3] properties. On the other hand, proper selection of synthesis conditions yields CNTs of the opposite nature [4]. These are highly resistive to the transport of electricity and thermal energy and so they are good candidates for heating elements.

There is a growing interest in the development of nanocarbon-based heaters. Reports from other scientific groups showed successful production of CNT- or graphene-derived heating layers. They are isotropic, deposited on a substrate and can reach up to $200 \,^{\circ}$ C in a few seconds [5]-[7]. We have recently created free-standing CNT film heaters [4] by a facile one step method [8], [9]. Because they are made of an aerogel, they are extremely flexible and light (consist of 99% of air). Moreover, they have a spectrum of features such as lag-less heating-up or cooling-down (in less than 10 ms),

resistance to corrosion [10], stable operation at 400 $^{\circ}$ C in air and 100% efficiency. It is important to mention that we produce them using natural gas as a carbon source what makes the whole process environmentally friendly.

We compared the CNT films performance with that of their main contender *i.e.* nichrome (an alloy of nickel and chromium) present in most of the electrical heating appliances of the modern world. The material we produced is much more resistive and because of its anisotropy, we are not limited by the wire geometry. In addition to changing wire's length and diameter, we can readily meet application's expectations and shape the heater towards a particular use. Finally, when we normalized the heating performance by weight, our CNT film heaters showed a 120,000x advantage over nichrome.

This work attempts to find a strategy to even out slight irregularities in electrical resistance among the samples of the CNT films. As mentioned above, the CNT film heaters come from aerogel, and thus one may expect voids within the material. We aimed to find a way to minimize the fluctuation in the content of these macroscopic cavities by solvent evaporation-induced densification of the material. There are reports which indicate that the use of a volatile solvent such as acetone or low molecular weight alcohols improve packing density of CNT macrostructures [11], [12]. To our humble knowledge however, it has not been tested so far whether such a treatment would result in improved reproducibility of heat generation from electric power. We employed a spectrum of appropriate solvents to examine such a possibility.

II. MATERIALS AND METHODS

A. Synthesis of Cnt Films

Methane (carbon source), ferrocene (catalyst) and thiophene (promoter) were combined under H₂ at 1200 $^{\circ}$ C in a vertical reactor. Catalytic Vapor Deposition (CVD) caused formation of aerogel, which was continuously collected on a winding roll as previously reported [8], [9]. Fig. 1 shows a roll of CNT films, which is subsequently cut open to yield A4 sheet. 15 mm x 40 mm specimens were subsequently cut, peeled off and transferred onto custom designed sample holders equipped with Al tape electrical terminals. Ag conductive paint was used to eliminate the issue of contact resistance.

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Figure 1. CNT film collected on a paper roll. It is then cut along the dashed line to give a CNT film sheet of approximate A4 size with the alignment showed by the small white arrows.

B. Condensation

A droplet of acetone, ethanol or isopropanol was placed on the surface of the CNT films, which caused slight shrinking of the material (successful improvement to the packing density). Literature indicates that application of a flash gun may cause condensation of the material as well [13], hence it was also explored here. CNT films were subjected to a single flash from a 500 W light bulb from a distance of 50 mm, which was fired normal to the surface.

C. Experimental Setup

Fig. 2 shows the experimental setup we used in the study. CNT film was placed on a sample holder, to which we connected a DC power supply (TTi QL-564P). The power source was wired to a computer and dedicated LabVIEW application controlled and recorded bias voltage and current in-situ. For these measurements we used two digital multimeters (Precision Gold N56FU) also connected to the computer. Surface temperature was probed by a non-contact mode *i.e.* pyrometer (Impac IPE140). The temperature values were registered by the same application.



Figure 2. Experimental setup

III. RESULTS AND DISCUSSION

As the magnitude of electric power was increased in steps, we observed a rapid increase in surface temperature of CNT films (Fig. 3a) due to the Joule heating. The material used in this study was found to be remarkably resistant reaching values in the order of $10^{-4} \Omega$ m, what is

two orders of magnitude higher than that of nichrome used in resistive wires [14] and thus responsible for the observed effect.

The as-made sample (black curve) has eventually reached 545 $\$ before a rapid scission-like cut across the sample was observed and the electrical circuit was broken. It is important to note that, according to our performance tests [4], 400 $\$ is the limit for the long-term stability. Here however, our aim was to compare as-made and densified material up to their breaking points to see possible discrepancies within the whole operational range of temperatures.



Figure 3. Measurement of (a) Electric power input vs. surface temperature; (b) The variation of relative resistance as a function of surface temperature (b) of as-made batch, acetone, ethanol, isopropanol and flash condensed CNT film heaters. Shaded area represents standard deviation.

Flash gun application (yellow curve) resulted in a mild increase in P vs. T slope, what translates into a slightly elevated electrical resistance of the CNT heaters. When they are subjected to a flash from a short distance, the temperature of the nanotube assembly can reach up to a thousand degrees. That in turn causes heat-assisted evaporation of side products of the CNT synthesis, which commonly contaminate the material. Some of them, such as polyaromatic residues are electrically conductive, so their removal contributes to the increase of resistance. Nevertheless, the standard deviation was not altered. Next, two different volatile alcohols *i.e.* ethanol and isopropanol (blue and green curves, respectively) were used. Removal of voids within the material resulted in a profound reduction to the standard deviation, but the material became much less thermally stable. Too high packing density does not allow for facile heat exchange with the surroundings and local overheating becomes much more probable. As a consequence, we observe thermal failure of the material in lower temperature range. Finally, acetone (red curve) was employed and its densifying action showed a tradeoff between temperature stability and reduction in standard deviation (as a measure of varying content of voids among samples). The CNT film heaters pretreated this way became uniform and their ability to convert electric power to heat was much more predictable.

In parallel, we examined whether the treatments influence the temperature coefficient of resistance (TCR) as it is important in a heater case. Such a parameter shows how electrical properties of a device react to the change in temperature. It can be calculated by applying linear regression to Fig. 3 and using Eq. 1. TCR is then a slope of relative resistance (resistance at a temperature of choice divided by room temperature resistance) as shown in the plot. The measured values are: 0.000296 (as-made), 0.000269 (flash), 0.000480 (ethyl alcohol), 0.000446 (isopropyl alcohol) and 0.000297 (acetone) K⁻¹. With the exception of alcohol treated samples which are prone to local overheating as mentioned above, CNT heaters follow TCR of nichrome equal to 0.000225 K⁻¹ [15].



Figure 4. Individual measurements of electric power input vs. surface temperature of as-made (top) and acetone pretreated CNT film heaters (bottom).

$$\alpha = \frac{1}{T - T_0} \left(\frac{R_T}{R_{T_0}} - 1 \right) \tag{1}$$

where: α (temperature coefficient of resistance), T (temperature), RT (electrical resistance at temperature T)

Fig. 4 takes a closer look at how acetone condensation of the CNT heaters improves the uniformity of the material and thus the electrothermal performance. The top part of the plot shows the behavior of ten as-made samples each of which was driven by current up to its thermal breaking point. One can see that there is a lack of coherence and samples' behavior is similar, but not exactly the same. On the other hand, the bottom part of the plot depicts how removal of voids from within the material by the action of acetone gives improved results. Every CNT film heater follows the same path and generation of heat from electric power is more predictable.

To make a justification of the underlying reason of improved electrothermal performance, we acquired Electron Microscopy images (Fig. 5). As we can see, significant changes to the microstructure of the CNT heaters took place. As-made reference (Fig. 5a) appears as feather-like material with plethora of voids within the CNT bundles.



Figure 5. Scanning electron micrographs of as-made (top) and acetone pretreated CNT film heaters (bottom).

In contrast, acetone droplet application (Fig. 5b) resulted in significant densification and apparent removal of cavities which are the main reason for inferior uniformity of the structure and electrothermal performance of the CNT film heaters.

IV. CONCLUSIONS

We have successfully created CNT film electrothermal heaters that can convert electric power into heat with very high efficiency. They are made from an aerogel and as a consequence one may find voids within the material filled with air. We employed a spectrum of liquid chemicals so as to cause solvent-evaporation induced densification of the material. Out of acetone, ethanol and isopropanol (as well as a flash gun application reference), the first choice worked best. A single droplet of acetone deposited on asmade CNT film heater gave a significant improvement to the electrothermal behavior of the material upon evaporation. We believe that the use of such a rapid, light-weight and corrosion-free heater with improved performance could be of benefit to the scientific community.

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REFERENCES

- S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, pp. 56-58, 1993.
- [2] S. Hong and S. Myung, "Nanotube electronics: A flexible approach to mobility," *Nature Nanotechnol.*, vol. 2, pp. 207-208, 2007.
- [3] E. Pop, D. Mann, Q. Wang, K. Goodson, and H. Dai, "Thermal conductance of an individual single-wall carbon nanotube above room temperature," *Nano Lett.*, vol. 6, pp. 96-100, 2005.
- [4] D. Janas and K. Koziol, "Rapid electrothermal response of hightemperature carbon nanotube film heaters," *Carbon*, vol. 59, pp. 457-463, 2013.
- [5] Z. Wu and J. Wang, "Preparation of large-area double-walled carbon nanotube films and application as film heater," *Physica E*, vol. 42, pp. 77-81, 2009.
- [6] H. Jang, S. Joon, and S. Nahm, "The manufacture of a transparent film heater by spinning multi-walled carbon nanotubes," *Carbon*, vol. 49, pp. 111-116, 2011.
- [7] D. Sui and Y. Huang, "Flexible and transparent electrothermal film heaters based on graphene materials," *Small*, vol. 7, pp. 3186-3192, 2011.
- [8] Y. Li, I. Kinloch, and A. Windle, "Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis," *Science*, vol. 304, pp. 276-278, 2011.
- [9] K. Koziol, J. Vilatela, A. Moisala, M. Motta, P. Cunniff, M. Sennett, *et al.*, "High-performance carbon nanotube fiber," *Science*, vol. 318, pp. 1892-1895, 2007.
- [10] D. Janas, A. Vilatela, and K. Koziol, "Performance of carbon nanotube wires in extreme conditions," *Carbon*, vol. 62, pp. 438-446, 2013.
- [11] M. De Volder, S. Tawfick, R. Baughman, and A. Hart, "Carbon nanotubes: Present and future commercial applications," *Science*, vol. 339, pp. 535-539, 2013.

- [12] S. Tawfick, Z. Zhao, M. Maschmann, A. Brieland-Shoultz, M. De Volder, J. Baur, *et al.*, "Mechanics of capillary forming of Aligned carbon nanotube assemblies," *Langmuir*, vol. 29, pp. 5190-5198, 2013.
- [13] P. Ajayan, M. Terrones, A. Guardia, V. Huc, N. Grobert, B. Wei, et al., "Nanotubes in a flash- ignition and reconstruction," *Science*, vol. 296, pp. 72-75, 2002.
- [14] M. Sinha, S. Mukherjee, B. Pathak, R. Paul, and P. Barhai, "Effect of deposition process parameters on resistivity of metal and alloy films deposited using anodic vacuum arc technique," *Thin Solid Films*, vol. 515, pp. 1753-1757, 2006.
- [15] C. Au, M. Jackson, and W. Anderson, "Structural and electrical properties of stable Ni/Cr thin films," *J. Electron. Mater.*, vol. 16, pp. 301-306, 1987.



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