High-Performance and Lightweight Thermal Management Devices by 3D Printing and Assembly of Continuous Carbon Nanotube Sheets

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ABSTRACT: Free-standing carbon nanotube films or buckypaper can provide a significant platform to develop practical applications of nanocarbon materials. For this research, buckypaper with high thermal conductivity (20 W/m K) and large surface area (350 m²/g) was mass produced in-house to investigate for use in lightweight thermal management devices. Floating catalyst chemical vapor deposition carbon nanotube sheets were also studied in this work. We introduced two manufacturing techniques to use the sheets for heat dissipation: (1) printing conductive composite ink on the sheets to make lightweight thermal devices, such as heat sinks and (2) assembling the sheets directly into 3D structures that were mounted on the back of heat-generating devices. These manufacturing techniques resulted in extremely lightweight, high-performance heat dissipation devices compared with other heat sink materials.

KEYWORDS: 3D printing, embedded 3D printing, direct ink writing, buckypaper, carbon nanotube sheet, thermal management

1. INTRODUCTION

Lightweight and highly thermal conductive materials are important in modern electronics, aircrafts, and autonomous devices that require thermal management while minimizing the weight and size.1,2 Several widely studied nanostructured materials, such as silver nanowires, carbon nanotubes (CNTs), and boron nitride nanotubes, have demonstrated the potential to meet various requirements of thermal management devices. Among these materials, CNTs are known to have the potential to provide superior properties, including lightweight, high electrical/thermal conductivity, and excellent mechanical properties.3 Researchers have attempted to transfer the excellent thermal properties of CNTs for heat sinks,4 thermal interfaces,5 oil spill cleaning,6 or fillers to increase the thermal conductivity of composites.7 However, harnessing the properties of individual CNTs into macroscale assemblies for engineering applications is still challenging because of their dispersing issues and fabrication technique constraints.8,9,10 Recently, CNT sheets and fiber materials have been integrated to make macroscale devices and products, such as hybrid composites with multifunctional properties,11 actuators,12 and electromagnetic interference shielding, and so forth.11–13 Results have demonstrated the potential to transfer nanoscale properties of CNTs by using fibers and sheets for potential engineering applications.14 Unfortunately, scalable processing methods to fully implement CNT sheets for thermal management has not been established. This research addresses two approaches to produce lightweight thermal management devices by 3D printing and by an assembly method using in-house-fabricated buckypaper from the continuous infiltration technique14 and using commercial CNT sheets. By using these effective manufacturing methods, we successfully fabricated thermal devices with high performance and extreme lightweight.

2. MATERIALS AND CHARACTERIZATION

Multiwalled CNTs were purchased from General Nano Inc. and dispersed in water with the aid of a surfactant, Triton X-100 (Alfa Aesar) and sonicated to make CNT suspension. This CNT suspension was continuously filtered and dried to form free-standing buckypaper.4,15 Nanocomp Technologies Inc. provided nanotube sheets produced using a floating catalyst chemical vapor deposition (FC-CVD) process. Thin graphite sheets (Panasonic Pyrolytic Graphite Sheet) were purchased from Digikeiy Inc. A hybrid composite ink consisting of epoxy with graphite nanoplatelets and chopped carbon fibers was used for 3D printing. Details regarding the composite ink and printing techniques can be found in a previous paper.16 The microstructures of samples were observed by a scanning electron microscope (SEM, JEOL JSM-7401F). An infrared thermal camera (E40, FLIR) was used to obtain thermal images to investigate temperature distribution. We used an Abaqus 6.13 for finite element analysis (FEA) of the heat transfer. In the heat-transfer simulation, 8-node linear heat-transfer brick (DC3D8) elements were used for meshing the model. Heat transfer was governed by equation 15

\[ k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + q + h\Delta(T - T_{amb}) = \rho c_p \frac{\partial T}{\partial t} \]

where \( k \) is the thermal conductivity (W/m K), \( q \) is the heat generation per unit volume (W/m³), \( h \) is the convective heat-transfer coefficient
measured using the Archimedes method, and the specific rising time of detector temperature reading. The density ($\rho$) was measured using the Archimedes method, and the specific heat ($C_p$) was found in literature. From $\alpha$, $\rho$, and $C_p$, the thermal conductivity ($\kappa$) was determined using $\kappa = \alpha \times \rho \times C_p$. Three tests for each sample type were conducted. A Q50 (TA Instrument Inc.) was used for thermogravimetric analysis (TGA) of nanotube sheets before and after heat treatment at a 10 °C/min rate.

The porosity of the samples was measured using an automated gas adsorption analyzer (Quantachrome Autosorb-iQ3) with nitrogen gas adsorption–desorption isotherms at 77 K. All samples were outgassed at 180 °C for 2 h prior to testing. The Brunauer–Emmett–Teller (BET) specific surface areas were determined from the linear portion of the adsorption isotherm.

3. RESULTS AND DISCUSSION

3.1. Continuous Buckypaper, Heat Treatment, and Thermal Properties. High-quality CNT sheets from scalable manufacturing method could be beneficial for many applications, such as multifunctional composites, flexible heaters, energy related devices, and flexible conductors. Two promising methods for producing the sheets involve a vacuum-assisted filtration and float catalyst chemical vapor deposition. In this work, we used an in-house continuous buckypaper prototype that involves a roll-to-roll manufacturing system. This approach could pave the way for in-line characterization and functionalization of the continuous CNT sheets. Using this process, we produced sheets on a large scale with an average thickness of 20 μm and an aerial density of 10 g/m² of 6–12 in. wide.

Figure 1a–c shows the morphology of the continuous buckypaper. Subsequently, we heated the CNT sheets to 400 °C for 2 h to remove surfactant residues. TGA results show that the residual surfactant in the sheets was removed after heat treatment (Figure 1g). Various post-treatment processes are available to improve their mechanical and electrical properties of CNT sheets, including mechanical stretching, acid treatment, or functionalization.

For this study, we selected heat treatment to enhance the thermal conductivity of the CNT sheets, which is a simple technique and suitable for large sample fabrication. The CNT sheets fabricated by the FC-CVD method (Figure 1d–f) contain more catalyst particles in the sheets (Figure 1f); therefore, heat treatment was not a suitable method to remove the catalyst because of high vapor temperature of the metallic catalyst (Figure 1h).

Materials with large specific surface areas draw great interest in catalyst support, heat exchangers, and electrochemical applications. Single-walled CNTs have large surface areas of up to 1315 m²/g because of their 1D nanostructure. The specific surface area of CNTs is affected by several parameters, such as type of CNT, diameter, impurity, and surface functionalization. Figure 1i shows that the specific surface area of buckypaper increasing from 100 to 350 m²/g after the heat treatment. The increase was attributed to the removal of surfactant residue, and more accessible CNT surfaces were exposed for nitrogen adsorption during BET measurements. The specific surface area of FC-CVD CNT sheets was relatively higher than that of as-prepared continuous buckypaper with surfactant but lower than that of heat-treated buckypaper, which may be due to more iron catalyst residue and amorphous carbon impurities found in the FC-CVD process.

After heat treatment of FC-CVD at 400 °C, the surface area increased only slightly because no significant change in amorphous carbon and catalyst occurred due to the temperature not high enough to remove the amorphous carbon. Although higher temperatures and additional acid treatments could reduce the impurities, we used 400 °C for surfactant removal to avoid oxidation.
We used a laser flash method with an in-plane sample holder (Figure 2a) to measure the thermal properties of CNT sheets. First, we measured aluminum foil as a baseline (Figure 2b) to ensure measurement reliability. The results showed that the thermal conductivity of the aluminum was $\sim 200 \text{ W/m K}$, which is consistent with literature reports. In the thermal conductivity and thermal diffusivity of the continuous buckypaper were 10 mm$^2$/s and 10 W/m K at room temperature, respectively. After heat treatment, the in-plane thermal conductivity of the sheets was 20 W/m K, which was 100% improvement from room temperature (Figure 2c,d). This is largely attributed to the improvement of the dense stacking of CNTs and removal of surfactant residue. For FC-CVD CNT sheets, thermal diffusivity, and thermal conductivity were reduced after heat treatment. A possible reason is the oxidation of metal catalyst in the CNT network, which may introduce thermal resistance in the CNT network. Hence, we decided not to use heat-treated FC-CVD CNT sheets for the following thermal management application study.

3.2. Embedding CNT Sheets into Thermal Devices by 3D Printing. Embedding nanostructures, such as CNT films and yarns, into products should provide the product with novel properties. In the previous section, we reported that the continuous buckypaper has a thermal conductivity of 10–20 W/m K at room temperature with a high specific surface area (100–350 m$^2$/g). This indicates the CNT sheets could be a potential candidate for various thermal management applications. To facilitate transferring the nanotube properties into macroscale devices, we adopted a 3D printing technique for embedding buckypaper into the composite structure to make a lightweight heat sink. In this process, lightweight and thermally conductive composite ink was used to print the 3D structure, and buckypaper was integrated into structure to improve its performance while minimizing the weight (Figure 3a,b). The process is illustrated in Figure 3c–e. We printed the initial layer of the heat sink structure (Figure 3c), and the buckypaper was placed on top of the printed layer (Figure 3d), then an additional layer was printed on the buckypaper (Figure 3e). After curing, the printed composite structure was heated at 120 °C for 2 h. The buckypaper embedded heat sink was made without sacrificing its large surface area. By using the printing technique, we can overcome the difficulty in incorporating CNT sheets into engineering application because of buckypaper’s flexibility.

Figure 4 shows different types of samples fabricated by 3D printing using composite ink and buckypaper. This concept could provide a new way of integrating preproduced nanostructures, such as CNT sheets, for thermal management applications, sensors, or multifunctional composites.

We compared the heat dissipation of 3D printed heat sink with and without embedded heat-treated buckypapers (Figure 5a). Two samples were placed on a hot plate, and the temperature profile was monitored as a function of time. The 3D printed heat sink with buckypaper reached a steady-state temperature faster, as shown in Figure 5b–f. To verify this...
experimental result, we built heat-transfer FEA models using the thermal conductivity value from experimental data ($k = 20$ W/m K for buckypaper and $k = 2$ W/m K for composite ink$^{41}$). Convective heat-transfer coefficient ($h = 20$ W/m$^2$ K) was applied to the sheet area for CNT sheets. Figure 6a shows the temperature profile of the heat sink at steady state, which was similar to the thermal image result (Figure 6b).

The simulation results indicate that the buckypaper area had a high heat flux because of high thermal conductivity and convective coefficient (Figure 6c). The temperature of heat sink as a function of time (marked spot in Figure 6a) also shows that the heat sink with buckypaper reached a steady-state temperature faster than the control sample (Figure 6d). This trend was consistent with experiment results. The experiment and simulation results demonstrated that combining buckypaper using a printing technique effectively improved the performance of heat sink while minimizing weight. These findings indicate potential use for a wide range of applications, including personal thermal management, thermal conductive textiles, or thermoelectric devices.

3.3. Assembly of CNT Sheets into Lightweight Heat Sink. This section introduces another way of using CNT sheets for heat dissipation application. We assembled CNT sheets to make an extremely lightweight and flexible heat sinks harnessing the high thermal conductivity and large surface area of buckypapers (Figure 7c). This approach is advantageous over other works by providing scalability.$^4$

While reported heat sinks at the microscale were fabricated by laser-assisted surface patterning and CVD growth of vertical CNTs, our simple and effective technique can be applied for macroscale products and devices. To the best of our knowledge, this was the first attempt to use large CNT sheets to make heat sinks.

We evaluated the performance of assembled buckypaper heat sinks by monitoring the temperature of a commercial light-emitting diode (LED) (1 W, 3.0−3.6 V, 350 mA, White—Uxcell) with a dc bias. All of the thermal images were captured after LED was on for 2 min. Figure 7a shows a thermal image of the temperature close to the limit of LED without a heat sink. Using a commercial aluminum heat sink to dissipate the heat of LED, the temperature reduced significantly by 13.7 °C (from 44.9 to 31.2 °C), as shown in Figure 7b. Figure 7d−g compares the heat dissipation performance of different types of carbon sheet-based heat sinks that were made of continuous buckypaper, heat-treated buckypaper, FC-CVD CNT sheet, and commercial graphite sheet, respectively. Figure 7d shows that the temperature of LED with the continuous buckypaper heat sink was approximately 4 °C lower than that without a heat sink (Figure 7a). However, no decrease was observed for the temperature of LED with the heat-treated buckypaper heat sink even though it has higher thermal conductivity ($\sim$20 W/m K) and surface area (350 m$^2$/g). We assume that the difference in thermal conductivity was not significant enough to overcome the thermal contact resistance in thermal interface layer used to attach the assembled buckypaper heat sink onto the LED.$^{42}$ As a result, the temperature difference between two samples was not significant. When FC-CVD CNT sheets and graphite sheets were used, the LED temperature decreased by 11.4 °C (from 44.9 to 31.2 °C). These results demonstrated that the performance of FC-CVD CNT and graphite sheet heat sink were equal to 81% of commercial heat sink in terms of heat dissipation. Although the thermal conductivity of FC-CVD CNT sheets was 60 W/m K, which is lower than that of
graphite, 500 W/m K, there was no apparent difference in the heat dissipation performance. Considering the large surface area of CNT sheets, 152 m²/g compared with the graphite surface area up to 5 m²/g, the high surface area of CNT sheets appears to play a critical role in convective heat-transfer coefficient in the heat sink applications.

We further investigated the effects of thermal conductivity and convective heat-transfer coefficient by conducting simulations for different case studies. Figure 8a shows simulation results performed with different thermal conductivities (10, 20, 60, 200, and 500 W/m K) from our case studies, while convective coefficient was kept constant (20 W/m² K). Overall temperature reduction with increased thermal conductivity matched well with experimental results. Slight differences might be originated from the convective coefficient mismatch. Figure 8b shows the simulation to explore the effect of convective coefficient while thermal conductivity was kept constant at 10 W/m K. Interestingly, convective coefficient

Figure 6. Heat-transfer simulation of samples with and without buckypaper layer embedded between fin. (a) Temperature profile from simulation. (b) Temperature profile from experiment. (c) Heat flux contour. (d) Temperature at the end of heat sink fin as a function of time.

Figure 7. Thermal image of lighting LED attached to different type of heat sinks: (a) LED without heat sink, (b) commercial aluminum heat sink, (c) buckypaper heat sink fabricated by assembly of CNT sheets, (d) continuous buckypaper heat sink, (e) heat-treated continuous BP, (f) FC-CVD CNT sheets, (g) graphite sheet.

Figure 8. Heat-transfer simulation of LED temperature with heat sinks for different (a) thermal conductivity and (b) convective heat-transfer coefficients.
also has profound effect on heat dissipation, which explains why the performance of relatively low thermal conductive FC-CVD CNT sheet (60 W/m K) with high surface area was comparable to the high thermal conductive graphite sheet (44–46 (>500 W/m K). Therefore, heat sinks using CNT sheets alone, as shown in Figure 7, is possible and its performance was comparable to the commercial aluminum heat sinks while weighing approximately 50 times less. Additional works on optimization and growing of CNT structure to achieve the large surface area should increase the heat dissipation efficiency further.

4. CONCLUSION

We attempted to harness the high thermal properties of CNT sheets for macroscale thermal management applications. For this purpose, two different techniques were introduced in this work: printing thermally conductive composite inks on CNT sheets and assembling CNT sheets to serve as lightweight effective thermal devices. Results indicate that both techniques are effective ways to transfer the properties of CNT sheets into lightweight thermal devices for thermal management applications. Both experimental and simulation results show that convective coefficient is also important as well as thermal conductivity for heat dissipation. Therefore, CNT sheets appear to be promising materials for high-performance and lightweight thermal management applications.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by NSF Scalable Nanomanufacturing Program (SNM 1344672) and AFOSR FA9550-17-1-0005 project.

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