

CARBON NANOTUBE COMPOSITE FOR EMI SHIELDING AND THERMAL SIGNATURE REDUCTION

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1. Introduction

Multifunctional materials, capable of EMI shielding and cooling that are also lightweight, chemical stable and mechanical strong, are desired in many defense and civilian applications. If possible, a spectral band selective transmission and blocking would also be desirable.

Our current research on carbon nanotube (CNT) composites is set up to explore the feasibilities of incorporating some or all these desired functionalities into one or more such composites, with the emphasis on understanding the mechanisms and the parameters affecting the electrical and thermal conductivities, optical transparency, and EMI shielding of CNT/polymer composite films with CNT content far above the percolation threshold.

In this undertaking, one approach has been to increase electrical conductivity for both EMI shielding and heat dissipation without overly sacrificing optical transparency. A success in such an effort would extend the use of such composite to applications that require transparent electrodes such as solar cells. It would be tempting to entertain the notion of displacing the predominant indium-tin oxide (ITO) in thin film display technology with a cheaper but comparably transparent and conductive composite electrode, especially when indium has become increasingly expensive due to shortage of supply. However, ITO has set such a tall bar in conductivity-transparency product that the nanotube-polymer composite alternatives under development in this project has been unable to cross over

One strategy for strengthening the nanotube-polymer composites and for increasing conductivity, differentiating from prior efforts, is the cross-linking of the nanotube matrix by e-beam irradiation prior to polymer infiltration. This cross-linking strategy has been shown to be effective in microscopic samples of nanotubes in an SEM chamber in the literature [1]. It has not been deployed in macroscopic nanotube films. To assess its prospect for deployment in large area films, we first study and optimize the e-beam cross-linking conditions, followed by developing a

method for the formation of homogeneously dispersed cross-linked nanotube matrices. While the closed graphitic shell structure of nanotubes gives rise to the extraordinarily greater Young's modulus compared with that of carbon fibers, it is also the reason behind the observed fact that the free nanotubes tend to bundle together. The bundles are bound by van der Waals forces, and can therefore slide on each other much like the layers in graphite and with shear strength weaker than that of graphite. From our own earlier discovery of "fusion" of nanotubes under prolonged exposure to the e-beam in an SEM imaging process and the later quantitative analysis reported by a Swiss group [1], it is found that stable cross-linking, resulting from e-beam irradiation, can form between nanotubes in contact with each other and give rise to a 30-fold increase in the bending modulus

It is known that a nanomesh structure of semiconducting material allows to some extent decoupling of its thermal conductivity from its electrical conductivity. [2] This decoupling could be made greater in our CNT thin film system for the benefit of IR sensing. Adding polymer to the system gives one more degree of engineering freedom for further enhancing one effect and reducing another. It is known that in the pursuit of composites with extended functionality and lighter weight, many polymers were examined. One polymer, poly(N-isopropylacrylamide) (PNIPAM) stood out as most interesting. PNIPAM is a three-dimensional porous hydrogel. It manifests a phase transition from a swollen hydrated state at lower temperature to a shrunken dehydrated state at higher temperature at 32 °C, losing about 90% of its mass. [3] PNIPAM has several additional merits for our purpose including a porous structure, beneficial for incorporating a cooling mechanism and reducing weight. PNIPAM is also environmentally safe and biocompatible. This polymer is incorporated into some of our experiments, one of which relates the EMI shielding efficacy to PNIPAM concentration.

2. Experiment Setup

Water-soluble single-walled CNTs can be obtained from both within our lab and commercial supplies such as Nanointegris, Inc. In cases where diameter, length and their uniformity are not critical, we prefer to use commercially supplied CNTs. Thin films of CNTs were prepared by membrane filtration method and the nanocomposites of CNT/PNIPAM were fabricated by drop casting. A projection e-beam system was employed for crosslinking of CNT films. In some cases, nanoporous anodized aluminum oxide (AAO) membranes of 50 nm pore diameter using oxalic acid solution[4] and metal micromesh (SPI) were used to create nano-/micro-patterns on CNT films by reactive ion etching (RIE), respectively. A UV/Vis spectrophotometer (Cary 500) was used for optical transparency, scanning electron microscope (SEM, LEO 1530-VP), an atomic force microscope (AFM, Veeco), a home-built network analyzer for EMI shielding efficiency, and a four point probe electrical resistivity measurement setup are employed for sample characterization.

3. Results and Discussion

E-beam crosslinking of CNT films was carried out with fixtures shown in Figure 1. Figure 2 and 3 shows a photograph after e-beam crosslinking and sheet resistance change with e-beam dosage for 20 nm-thick CNT film, respectively. The amount of electron beam irradiation was apparently sufficient to have changed the color of CNT film [Figure 2 (a)], which suggests that the e-beam irradiation modifies CNTs themselves either chemically or physically. As shown in Figure 2 (b), at low e-beam dosage till 10000 $\mu\text{C}/\text{cm}^2$ the sheet resistance decreases significantly by a factor of four, then levels off at higher dosages, finally increases again. This result demonstrates that e-beam crosslinking method could indeed help the development of transparent and conducting CNT films.

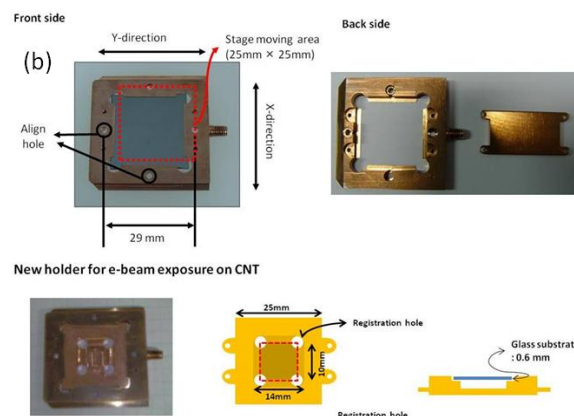
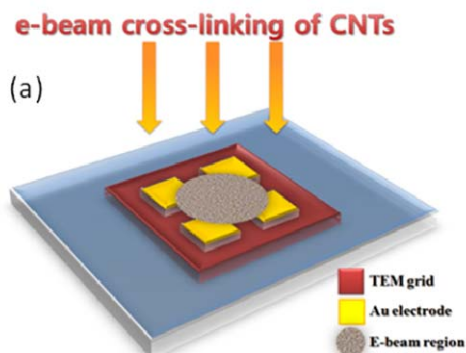


Fig. 1. Apparatus for e-beam cross-linking. (a) A schematic and (b) detailed descriptions of actual parts.

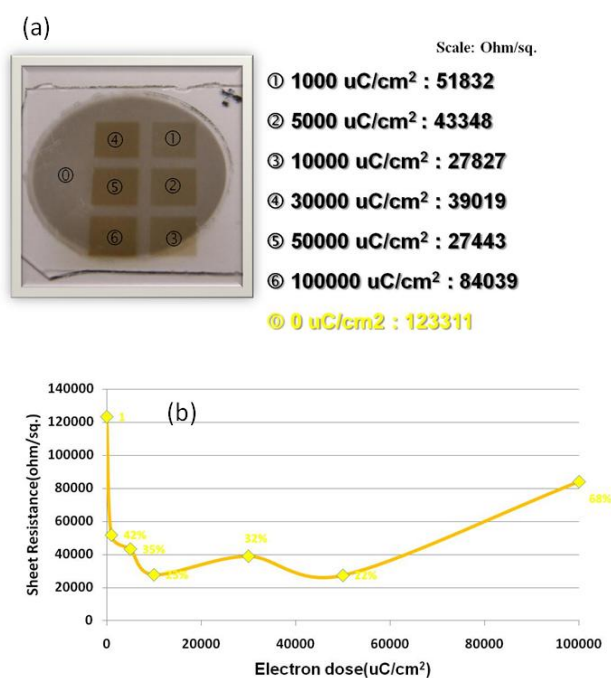


Fig. 2. (a) Photograph after e-beam exposure and (b) sheet resistance of CNT film of 20 nm thickness with electron dosage.

Figure 3 (a) and (b) shows SEM images of nano- and micro-patterned CNT thin film of 20 nm thickness using AAO nanopore array template and nickel micromesh as etching mask, respectively. We have characterized the optical transparency (Figure 4) and sheet resistance of these films (Table 1). The optical transparency (Figure 4) has significantly increased by 34% in the nanomesh patterned CNT film and 26% in the micromesh patterned film, but

an unexpectedly large increase of sheet resistance was measured. This large increase can not be accounted for by the conductive areal reduction. It also counters the effect of any crosslinking induced in the RIE bombardment. This is not necessarily a bad news as it reveals the complexity of the electron conduction in such a random network of resistors that operate in both the quantum regime (within the nanotube and tunneling between the tubes) and the classical regime (boundary scattering limited mean-free lengths). It also suggests that current RIE conditions may have damaged the CNTs or chemically modified CNT films, or simply accumulated charged particles resulting in volume expansion and increased gaps in the junctions between CNTs. Further study on the unintended increase of the sheet resistance is called for.

The patterning of the nanotube network happens to be in the interesting regime of the length scale that is smaller than the intrinsic electron mean free length and the phonon mean free length in a high quality nanotube but larger than the inter tube electron and phonon scattering lengths. What effect on phonon transport does patterning at this length scale in such a random network of phonon waveguides? This turns out to be an open question not yet being dealt with in the literature. Motivated by the need to gain insight into this question, lateral thermal conductivity across the network was performed.

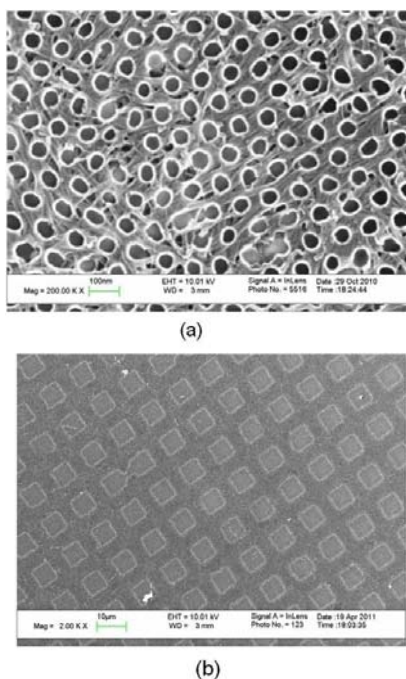


Fig. 3. (a) Nanopatterned CNT film created by AAO masking and (b) micropatterned CNT film of 20 nm thickness created by nickel mesh masking.

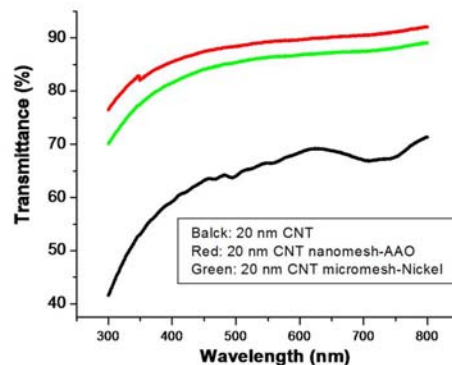


Fig. 4. UV/Vis transmittance of nano- and micro-patterned CNT films.

Table 1. Sheet resistances of nano-/micro-patterned CNT film of 20 nm thickness. Values in Ω/Sq .

	Sheet Resistance	Ratio
Original: 20 nm	995	1
Nanomesh-1	20000	20
Nanomesh-2	109000	110
Micromesh-3	2.07x 10^8	208000
Micromesh-4	5.36x 10^8	539000

It is intriguing that a substantial thermopower is measured in both patterned and unpatterned network films. Moreover, a substantial increase in thermopower is measured in the nanopatterned sample relative to the unpatterned one, as will be discussed later on.

In samples prepared for experiments on effects other than transparent electrodes, such as EMI and cooling for example, the nanotubes are dispersed with a particular polymer -PNIPAM. The CNT/PNIPAM nanocomposites were prepared by drop casting. For effective mixing without bundling of CNTs, both CNT and PNIPAM solutions were prepared in 1% SDS and then mixed to the given ratio of CNT and PNIPAM. A scanning electron microscope image of the CNT/PNIPAM nanocomposite shows well dispersed CNTs within the nanoporous PNIPAM structure (Figure 5).

We summarize in figure 6 the relationship between the DC electrical conductivity, EMI shielding efficiency, and optical transparency with changing ratio of CNT to polymer.

Figure 7 shows a good correlation between these properties, suggesting the possibility of a theoretical model could emerge from further analysis and lead to quantitatively guidance to future designs.

One result is particularly pertinent to a goal central to a functionality we set out to incorporate into the composite – EMI shielding. With this CNT/PNIPAM composite, Films of only a few micrometers yield an EMI shielding efficiency of 20-30 dB, which is comparable to that obtained in current EMI shield films of thickness ~10 times larger, and is also superior to previously reported CNT/polymer composites ~100 times thicker. [5]

Based on the known hydrophobicity phase-transition of PNIPAM and the accompanying large volume change, one can speculate that there could be an effect of cooling to be had in the CNT/PNIPAM composite. Measurements of the time evolution of temperature in samples do indicate that a cooling function could also be built into these nanocomposite thin films.

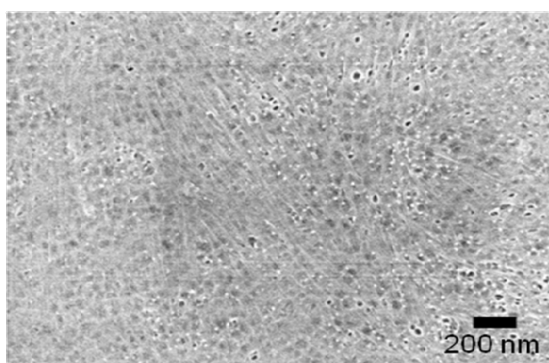


Fig. 5. SEM image of CNT/PNIPAM nanocomposite that shows homogeneous areal and local (~10 nm) dispersions.

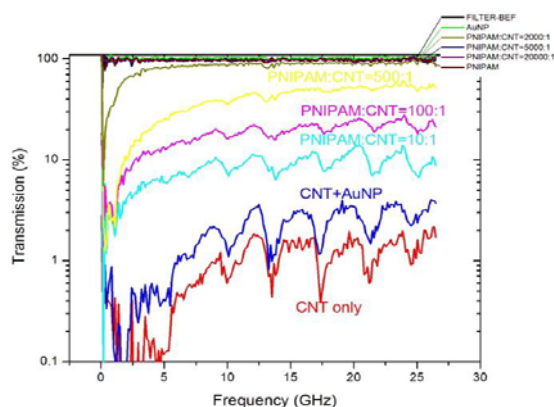


Fig. 6. EMI shielding spectra of nanocomposites with changing ratio of CNT to polymer.

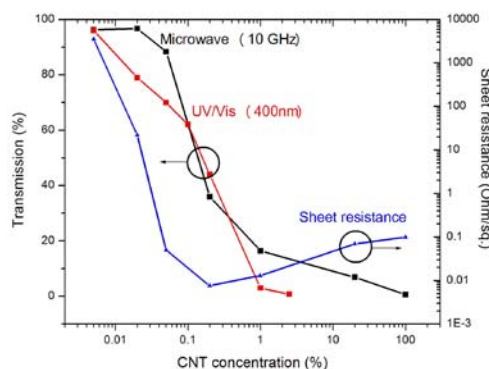


Fig. 7. Correlation between EMI shielding efficiency, electrical conductivity and optical transparency.

Since CNT/PNIPAM nanocomposites are nanoporous and have a high thermal conductivity, the cooling of this nanocomposite could occur even faster than that of the PNIPAM alone. At this stage, we are more interested in the relative difference the introduction of the PNIPAM could bring to the composite. For comparison, various types of samples were measured: nanoporous alumina membrane (AAO), AAO with a CNT film on top, AAO with a PNIPAM film on top, and AAO with a CNT/PNIPAM composite film on top. FLIR Silver SC5000 IR Camera was employed to see the temperature change of each film, which is floated on water wells. Figure 7 shows the evolution of IR images of these films with time. AAO with CNT/PNIPAM composite indeed showed highest cooling efficiency of 40% temperature decrease in given time, compared to 34%, 36%, and 36% of AAO, AAO/CNT, and AAO/PNIPAM, respectively. These results are preliminary but already indicative of the potential of the CNT/PNIPAM for thermal signature reduction, and possibility of optimization by changing the ratio of polymer to CNT and employing alternative film preparation methods.

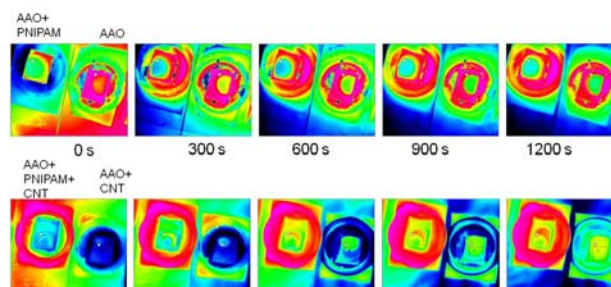


Fig. 7. Images of IR camera for AAO, AAO/PNIPAM, AAO/CNT, and AAO/PNIPAM/CNT with time. Initially samples were heated to 60 °C.

Next, we return to the topic of the effect of nanopatterning on the thermal properties of CNT films, that was previously shown in Figure 3 (a). In connection to the prospect of high cooling efficiency exhibited by the CNT/PNIPAM composite, it is important to assess both the new possibilities opened by nanopatterning on the control of the thermal properties and the limitations that could be brought with it. For the time being, we will focus on the potential benefits, in particular, the thermopower, or Seebeck coefficient, which has direct applications in thermal energy harvesting.

One strategy for increasing the thermopower could be by increasing boundary scatterings via nanopatterning and thereby suppressing the phonon contribution to the system's thermal conductivity. Previous studies on nanopatterned silicon and rough silicon nanowires have indicated suppression of the phonon transport in these structures compared with their pristine counterparts. Figure 8 shows the thermo-voltage plotted as a function of the temperature gradient between the hot and cold sides for a nanopatterned CNT film and a pristine CNT film. The Seebeck coefficient is given by the slope of the data, and labeled next to each curve. Comparison of the two otherwise similar systems indicates an increase of almost 30% in the Seebeck coefficient due to nanopatterning. Similar enhancement of the thermopower has also been in bismuth films. Nanopatterned bismuth films showed enhancement of the thermopower in excess of 25%. One advantage of this AAO based nano-patterning strategy is that it is low cost and parallel process, and scalable to arbitrary sample size. It has been demonstrated in full 8-inch wafers and could be easily extended to accommodate even larger samples. This represents a considerable advantage over other strategies that require extensive use of optical or electron beam lithography to achieve nanostructures.

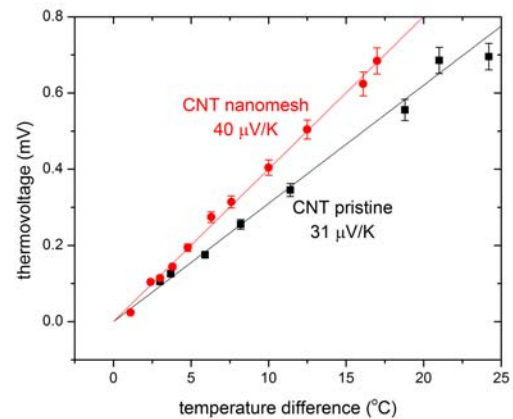


Fig. 8. Thermopower of nanopatterned CNT film (red) and pristine CNT film (black).

4. Summary

We have developed a new method of e-beam crosslinking to improve electrical conductivity without deteriorating optical transparency of CNT thin films. After e-beam crosslinking the electrical resistivity decreased four times. Nano- and micro-patterning on CNT thin films are found to be effective in improving optical transparency, but comes at a cost of reducing electrical conductivity. It is also found that thermal conductivity of the nanotube films can be significantly reduced by nanopatterning, which however may have more to do with increased phonon scatterings by increased boundaries associated with the nanopatterning as they are at the length scales smaller than inherently long phonon mean free length in high quality nanotubes. A decreased thermal conductivity may not all negative, as it could help thermal energy harvesting through increasing Seebeck coefficient and ZT. A number of parameters are identified in the process that can be explored and optimized to controllably alter the composite thermal properties including thermoelectric power and thermal conductivity. As an example, multifunctional nanocomposites of CNT and PNIPAM were prepared and they showed high EMI shielding efficiencies and thermal signature reduction while remain optically transparent.

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