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Citation for the original published paper (version of record):

Anoshkin, I V., Campion, J., Lioubtchenko, D V., Oberhammer, J. (2018)
Freeze-Dried Carbon Nanotube Aerogels for High-Frequency Absorber Applications
ACS Applied Materials and Interfaces, 10(23): 19806-19811
<https://doi.org/10.1021/acsami.8b03983>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

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Freeze-dried carbon nanotube aerogels for high frequency absorber applications

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KEYWORDS: carbon nanotubes, freeze-drying technique, millimeter wave absorbers, reflectivity, waveguide loads.

ABSTRACT. A novel technique for millimeter wave absorber material embedded in a metal waveguide is proposed. The absorber material is a highly-porous carbon nanotube (CNT) aerogel prepared by freeze-drying technique. CNT aerogel structures are shown to be a good absorber with a low reflection coefficient, less than -12 dB at 95 GHz. Reflection coefficient of the novel absorber is 3-4 times lower than that of commercial absorbers with identical geometry. Samples prepared by freeze-drying at -25 °C demonstrate resonance behavior while those prepared at liquid nitrogen temperature (-196 °C) exhibit a significant decrease in reflection coefficient, with no resonant behavior. CNT absorbers of identical volume based on wet-phase drying preparation show significantly worse performance than the CNT aerogel absorbers prepared by freeze-drying. Treatment of the freeze-dried CNT aerogel with *n*- and *p*-dopants (monoethanolamine and iodine vapors, respectively) shows remarkable improvement in the performance of the waveguide embedded absorbers, reducing the reflection coefficient by 2 dB across the band.

INTRODUCTION

Many millimeter wave and terahertz frequency devices such as circulators, couplers, etc. require termination sections, commonly referred to as loads, to eliminate unwanted signals. Millimeter wave terminations are often realized by back-shortened waveguide sections, which present low reflections

and absorb the incident energy due the presence of an electromagnetic absorbing material inside the waveguide. Load materials are generally magnetic Fe-based absorbers which are easily machined or molded. An ideal waveguide load should simultaneously offer high absorption but also low reflection coefficient, placing contradicting requirements on the absorber material. Therefore, such materials usually are shaped in a tapered geometry in order to improve their reflectivity and operating bandwidth (**Figure S1 a, b**). However, this tapering results in long absorbers of complex geometry, whereas a compact, thin absorber is required for integrated systems. Moreover, integrated waveguide systems, both passive and active, often require absorber materials to be compatible with standard CMOS and/or GaAs processing technology, typically requiring temperature treatment at 200-500 °C and prohibiting the use of epoxy or other polymer-based solutions. These requirements drive the search for new absorber materials, ¹ in particular, carbon nanotubes (CNTs) which can be heated up to 1000 °C without destruction. ²

Over the last decade, developments in CNT technology proved that CNTs can effectively absorb electromagnetic waves due to the presence of sp^2 carbon. In ³ high frequency structure simulations show that pristine CNTs deposited with the dry “press transfer” method of CNT layer formation at the wall of a dielectric waveguide can effectively absorb propagating waves. Alternatively, CNTs can be formed as a bubble-like structure (**Figure S2**) that can provide potentially relevant electromagnetic wave absorption with low reflection coefficient. In ⁴⁻⁶ the bubble-like structure of the CNTs in a polymer matrix was successfully used to form a CNT based absorber, with good performance for the 8–16 GHz ⁶ and 5–40 GHz ⁴ frequency bands. Many different carbon and ferrite-carbon composite based absorbers are widely used in anechoic chambers. ⁷ A significant problem arises during the introduction of CNTs applied via liquid dispersion in a waveguide. Such CNTs align to each other during drying, creating a dense surface. This results in the unwanted reflections and low microwave energy absorption.

In this work, a novel type of compact, non-tapered CNT-based absorber material embedded in a standard metal waveguide is studied at the 75–110 GHz frequency band. The absorber material is

formed by a CNT aerogel and is prepared by freeze-drying, which enables a random orientation of the CNTs. The resulting porous structure offers low surface reflections while maintaining high absorption. The reflection properties of CNT based absorbers are studied in a waveguide-based system prior to subsequent fabrication processes. Standard material characterization techniques based on open Fabry-Pérot resonators⁸ require sample sizes much greater than the aerogels used here. The reflection coefficients of the novel absorbers are compared with commercially available materials to demonstrate their performance.

RESULTS

A schematic drawing of the structure is shown in **Figure 1** and **Figure S3**. The length of the dried aerogel section of 3.5 mm was measured by optical microscopy.

Figure 1. Schematic drawing of the WR-10 waveguide filled with CNT aerogel.

Following the freeze-drying process, the aerogel material was examined using a low voltage (1 kV) Scanning Electron Microscope (SEM). The highly porous nature of the CNT aerogel is clearly visible in the SEM images (**Figure 2 a-d**). The freeze-dried aerogel has 0.1-10 μm scale features, making it electrically small at the frequencies of interest. Transmission electron microscopy (TEM) images (**Figure 2 e, f**) show that the CNT samples mostly contain thin multiwalled (2 – 5 graphene layers) nanotubes with external diameters of approximately 5 nm. Comparison of the SEM images of samples

prepared at $-196\text{ }^{\circ}\text{C}$ (**Figure 2 a, b**) and $-25\text{ }^{\circ}\text{C}$ (**Figure 2 c, d**) reveals no significant differences in the microrelief of the aerogel. However, the liquid nitrogen samples demonstrate a randomized microstructure similar to “cotton pads” (**Figure 2 a, b**), while the samples prepared at $-25\text{ }^{\circ}\text{C}$ are seen to be more “bubble-like” 3D microstructures with 10-20 μm feature sizes (**Figure 2 c, d**). The difference in density of the two samples is clearly visible. Both samples have feature sizes much less than the wavelength.

a)

b)

c)

d)

Figure 2. SEM and TEM images of CNT aerogels obtained with liquid nitrogen at -196 °C (a, b) and with freezing at -25 °C (c, d); TEM images of CNTs (e) and (f).

In **Figure 3** one can see that the freeze-dried CNT aerogel prepared at the liquid nitrogen temperature of -196 °C reflects the electromagnetic wave with a reflection coefficient from -10 to -15 dB at 75 to 110 GHz. Samples prepared at -25 °C (**Figure 4**) demonstrate the similar reflectivity, but strong resonance peaks are observed at ~ 86 GHz. The presence of these peaks can be explained by the reflective behavior of the CNT aerogel surface and the metallic end of the backshort which cause strong resonances and appearance of reflection spikes up to -40 dB at 86 GHz (**Figure 4a**). Mechanical compression of the CNT aerogel inside the waveguide of 20 % and 40 % by volume (**Figure 4b,c**) leads to broadening and decreasing of the resonance peak. This compression results in a change of density of the CNT aerogel which leads to an increase in reflectivity. A similar effect can be seen without fast freezing (**Figure 3b**), where the non-porous sample causes total surface reflection. Compression of the aerogel inside the waveguide (**Figure 4**) leads to a change in the position of the reflective surface and changing the shape of the bubbles to elliptical. Thus, the compression results in flattening of the bubble structure and shifting and decreasing of the peak positions. Similar behavior of reflection peaks was observed in ^{9, 10} for the CNT-Fe₃O₄ composites in the 1 – 18 GHz frequency range.

Figure 3. The reflection coefficient (S_{11}) measurement results: (a) empty waveguide as reference; (b) CNT layer obtained by wet-drying of liquid dispersion; (c), freeze-dried CNT aerogel of 3.5 mm length; (d) freeze-dried CNT aerogel treated with MEA, 3.5 mm; (e) freeze-dried CNT aerogel treated with I_2 , 3.5 mm.

Figure 4. The reflection coefficient (S_{11}) of pristine and compressed CNT aerogels obtained at -25 °C. As prepared (a), mechanically compressed at 20 % (b) and 40 % (c).

By comparison, the same CNT solution wet-dried (not freeze-dried) has a very high return loss of -0.5 dB, close to the untreated back-short (**Figure 3b**). As such, the proposed freeze-drying process is both very effective and useful for making embedded millimeter wave absorbers from CNT dispersion.

To investigate the influence of conductivity on the reflection coefficient, the CNT aerogel was exposed to both *n*- and *p*-dopants in the form of saturated vapor of monoethanolamine (MEA) and iodine (I_2) respectively. The samples were exposed to the vapours at 80 °C for 20 minutes. When exposed to such vapours, the conductivity of the nanotubes changes due to the presence of carboxyl (-COOH), hydroxyl (-OH) and other oxygen containing groups on the nanotube surface and intrinsic adsorption properties. Reaction of amines with acids leads to neutralization and results in *n*-doping. Interaction with I_2 leads to additional electron withdrawal and hence an increase in conductivity.¹¹

Figure 3 shows that such chemical treatment methods can be used to decrease the reflectivity of CNT aerogels. After treatment with MEA the return loss of the CNT aerogel improves by up to 2 dB across the whole frequency band. Treatment with I_2 improves the reflection coefficient up to 0.8 dB at frequencies higher than 95 GHz in comparison to the MEA treated sample.

Several commercial Fe (C-RAM RGD-S-192/PSA 0.040”) and ferrite (C-RAM FF-2 / PSA 0.040”) loaded silicone absorber materials (supplied by Cuming Microwave) were used to benchmark the performance of the CNT aerogel. Samples with geometry identical to that of the CNT aerogel samples were placed into an identical waveguide backshort section. The measured reflection coefficient of these commercial absorbers with 3.5 mm length are shown in **Figure 5**. The lowest measured reflectivity was between -7 and -11 dB for a Fe-loaded absorber C-RAM RGD-S-192/PSA 0.040”.

Figure 5. Comparison of commercial absorbers of identical geometry and length (3.5 mm): (a) measured reflection coefficient (S_{11}) of empty waveguide (reference); (b) ferrite-based absorber; (c) e-based absorber.

The simulated performance of the CNT aerogel model is close to the measured performance of the liquid nitrogen freeze-dried sample, see **Figure 6**. Such a model could be used to optimize the geometry of the absorber, allowing for a further reduction in reflectivity. Electromagnetic modelling also allows for determination of the dielectric properties of the sample. The extracted complex permittivity of the freeze-dried sample is $\epsilon = \epsilon' + j\epsilon'' = 1.3 + j0.78$ at 100 GHz.

Figure 6. Simulated performance of the CNT aerogel (b), based on the model shown in **Figure 1**, with dielectric properties of the aerogel extracted by model parameter fitting to measured data (a).

DISCUSSION

The microstructure of aerogels (porosity and density) depends of the speed of freezing of initial CNT dispersions.¹³ Under low speed freezing, growing water microcrystals force CNTs from the initial solution to the crystal surface and, after evaporation, the resulting aerogel structure has larger cavity sizes, connected by sheet-like CNT surfaces. During fast freezing, the CNTs spread between very small microcrystals, resulting in an aerogel with fewer structured microcavities and a more randomized structure. Aerogel microstructure has a strong effect on the electromagnetic properties of a given aerogel. The bronze mold cooled to -196 °C used for freeze-drying enables the creation of randomized “cotton-pad”-like structures with a bubble size of around 1 μm. If, instead, the initial temperature of the bronze mold was -25 °C the lower freezing speed results in a more structured aerogel with a cavity size up to 10 μm. According to the experimental results shown in (**Figure 2 c, d**) faster freezing (cooling with a significantly higher temperature gradient) leads to randomization

of aerogel structure, which results a broadening the return loss and absence of resonance peaks (**Figure 3, 4**).

The highly porous microstructure of the aerogel surface allows electromagnetic waves to be permeate in to aerogel volume, leading to an overall low level of reflectivity. The primary absorption mechanism of the CNT aerogels is likely multiple internal reflections within the sample (**Figure S5**). There are several potential causes of multiple reflections in the “bubble-like” structured CNT aerogel. Internal reflection inside the CNT structure,^{14, 15} as well as multiple electromagnetic scattering between nanotubes in the aerogel demonstrated in the polymer matrix,^{15, 16} (see **Figure S5**), are the main causes of multiple internal reflections, leading to a significant increase in path-length for signals propagating through the material. Electromagnetic absorption by sp^2 carbon attenuates any propagating signal.

The most attractive feature of the proposed technology is that the CNT aerogel was embedded in the small cavity of a standard metal waveguide (with cross-sectional dimensions of $2.54 \times 1.27 \text{ mm}^2$) without distortions caused by capillary effect by using a freeze-drying technique. The resulting aerogel therefore has vertically orientated CNTs. If the CNTs are considered as simple dipoles, this vertical/partially vertical orientation allows electromagnetic waves to penetrate inside the aerogel, as the dipoles are aligned to the direction of wave propagation. During wet drying, capillary forces align the CNTs to each other and the resulting CNT layer is flat, with a dipole orientation perpendicular to the propagating wave. Strongly connected CNTs after wet drying form a metal-like structure which reflect electromagnetic waves. Standard millimeter wave and/or THz wave absorbers, both in waveguide and free space, either have a special shape (**Figure S1**) or porous morphology (**Figure S2**). Such structures can be formed of multiple different materials, where the resulting shape is then covered with carbon. Absorbers of this kind can be used for microwave frequencies, and perhaps for millimeter wave frequencies. For higher frequencies (i.e. those in the terahertz (THz) region), this process becomes significantly more complicated as the internal dimensions of the waveguides

become less than a millimeter. In contrast, the method proposed here can be scaled to THz frequencies without any additional fabrication complexity.

CONCLUSIONS

A novel method of absorber material preparation, based on the freeze-dried CNT aerogel, for integration in a standard metal waveguide, was developed for the 75-110 GHz frequency band. Despite their compact, non-tapered geometries, the resulting absorbers showed a low level of reflectance and good absorbance across the band due to the highly porous surface and low conductivity. The CNT aerogel-based samples were found to have significantly better absorbing performance than commercially available absorbing materials of the same geometry. Moreover, the reflection coefficient decreases drastically with increasing frequency. Samples prepared at $-25\text{ }^{\circ}\text{C}$ demonstrate resonance behavior, unlike those prepared with liquid nitrogen. Treatment of CNT aerogel with *n*- and *p*-dopants (monoethanolamine and iodine respectively) shows significant improvement in the performance of the freeze-dried CNT aerogel absorbers. This technology opens new opportunities for THz embedded absorbers.

METHODS

Sample preparation. The CNTs were synthesized according to the method described in.¹⁷ “CNT aerogel” with porosity of 96% was prepared similar to the procedure described in,¹³ i.e. the known volume of CNT water dispersion was placed inside a 6 mm long waveguide cavity of a WR-10 metal waveguide (**Figure 7**). After fast freezing inside a precooled heavy bronze mold into which the waveguide is inserted, the waveguide with CNT absorber was placed in vacuum chamber at 10^{-2} mBar for overnight drying.

Figure 7. CNT aerogel sample preparation. A known volume of CNT dispersion is placed inside a metallic waveguide (a), prior to fast-freezing at $-25\text{ }^{\circ}\text{C}/-196\text{ }^{\circ}\text{C}$, which forms the porous aerogel (b). The waveguide absorber is then demolded prior to use.

High frequency characterization. The reflection coefficient (S_{11}) of the absorbers was measured with a Rohde & Schwarz ZVA24 Vector Network Analyzer (VNA) and W-band frequency extension heads. The measured reflection coefficient of the CNT aerogel freeze-dried at $-25\text{ }^{\circ}\text{C}$ and $-196\text{ }^{\circ}\text{C}$ samples is shown in **Figure 3, 4** respectively. The empty backshort waveguide was measured for comparison.

Electro-magnetic modelling of CNT aerogel. A simulation model was constructed in CST Microwave Studio for comparison with the measured performance of the CNT based absorbers and to allow extraction of their electrical parameters (Figure 1). As CNTs and aerogel bubbles are electrically small at W-band frequencies, the CNT aerogel was treated as a homogenous material. Parameter fitting was performed in CST in order to model the dielectric properties of the CNT aerogel. The dielectric constant used in simulations was obtained from experimental and analytical results.

ASSOCIATED CONTENT

Supporting Information

The supporting information material is available at <http://pubs.acs.org>. supporting information includes images examples of industrial microwave absorbers, additional drawings of the experimental setups and some additional information regarding to the manuscript.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

This work was financially supported in part by the European Research Council (ERC) through the Consolidator Grant No. 616846 and by the H2020 Innovative Training Network CELTA under grant number 675683 of Call: H2020-MSCA-ITN-2015.

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