

Comparison of Neutron Attenuation in Graphene Hybrid Materials

Danielle Castley

Dartmouth College

Cameron Goodwin, Ph.D

Rhode Island Nuclear Science Center

Ulrike G.K. Wegst, Ph.D

Dartmouth College

Abstract

Graphene is a relatively new and exciting carbon allotrope because of its exceptional property profile. While graphene currently attracts considerable research attention due to its high electron mobility, high strength, and other surprising properties, it has not yet been investigated for its radiation shielding and absorption capabilities [1,2]. Due to the comparable size of carbon atoms and neutrons, graphene-based structures are promising as effective materials for neutron shielding applications in the nuclear industry [3]. Shielding and absorption materials are critical in a variety of nuclear applications for dose reduction during the passive cooling of the nuclear fuel. Advances in the development of these materials may lead to improved characteristics, such as higher absorption and scattering rates and improved thermal performance at low density for weight-limited applications.

The purpose of this study was to explore, evaluate, and compare the neutron attenuation capabilities of graphene oxide to reduced graphene oxide, the neutron attenuation of carbon nanotubes to carbon nanofibers, and different graphene oxide reduction methods. Our hypothesis is that the interfaces that these materials form at several length scales when freeze-cast into porous structures contribute to an improved neutron attenuation performance. Both the low density and high thermal stability of freeze-cast carbon structures are important and advantageous for a range of applications, making these graphene-based materials particularly attractive as possible candidates for advancements in storing and transporting spent nuclear fuel and radioactive waste.

Introduction

After spent nuclear fuel is removed from the reactor, it still has about ninety percent of its energy and various radioactive isotopes that must be contained to avoid harm to nuclear facility employees and the public [4]. To manage the radiation from the fuel it can either be placed into a pool of water, where it relies on an active cooling system to prevent the fuel from overheating, or it can be placed into a passive storage system with materials that can withstand the heat loads while attenuating the radiation. Typically, a combination of active and passive cooling systems is used because existing passive cooling systems are not composed of materials that are thermally stable

enough to contain fresh spent fuel. Ideally, spent fuel would be moved from the reactor and placed directly into passive storage, but new materials must first be developed for suitable storage canisters.

Common thermally-stable neutron-shielding materials, such as concrete or mixed metal matrix composites, are too dense for use in many nuclear fuel transportation applications; they are also expensive to fabricate, transport and install at nuclear grade “Important to Safety” and “Safety Related” standards [5]. Alternative low-density materials, such as borated polyethylene or nylon, are unstable at elevated temperatures [6]. Consequently, these materials deteriorate considerably in properties and performance and are ineffective, when exposed to the high heat loads generated by spent nuclear fuel. Therefore, new carbon allotropes with high phase change temperatures such as graphene oxide, graphene, carbon nanotubes and carbon nanofibers, are explored as potential new neutron scattering materials for the spent fuel cycle.

Graphene has, to date, not reportedly been examined for its neutron shielding abilities but should be more extensively explored, since graphite is used as a neutron moderator in nuclear reactors [7]. Different allotropes of carbon have drastically different shielding and absorption properties and neutrons interact very differently with the various carbon materials [4]. Since neutron attenuation does not depend on the mass density of a material, graphene foams could offer a viable low-density option for neutron shielding. Both graphene and graphite are atomically stable materials and exceed the thermal stability requirements of neutron shielding materials, since neither melt or change phase below several thousand degrees Celsius [8,9]. Graphene, however, has a higher specific surface area, strength, and electrical conductivity than graphite and may also be able to store significant amounts of hydrogen within its structure [10].

The main goal of this study was to fabricate a macroscale graphene oxide structure and begin comparing the neutron attenuation abilities of graphene oxide (GO) to that of reduced graphene oxide (rGO). GO and rGO have two different compositions and structures compared as shown in Figure 1. An additional goal was to compare the neutron attenuation of carbon nanotubes (CNTs) to carbon nanofibers (CNFs). All samples, composed of carbon allotropes in the form of graphene-oxide based macro-assembly materials, were subjected to fast neutrons; clear first attenuation trends could be established.

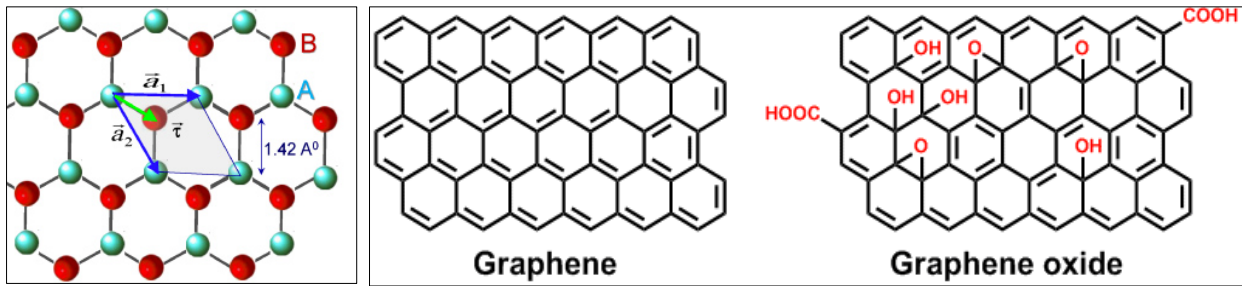


FIGURE 1 – (From left to right) The honeycomb lattice structure of graphene. Each carbon atom has bonds with three other carbon atoms, leaving one valence electron free to travel throughout the structure [1]. Graphene vs. Graphene Oxide: Hydrogen and oxygen rich functional groups attach to the fourth valence electron on the carbon atom in graphene oxide [11].

Methods

Sample Fabrication

An initial challenge to perform irradiation tests on graphene-like materials was to convert graphene from a two dimensional nanosheet into a three dimensional architecture. As previously mentioned, graphene is a single layer of carbon atoms only about 17 Ångstroms thick so freeze-casting, a novel fabrication technique, was employed to create a testable structure [10,11]. To begin, a GO solution was mixed with carbon nanotubes or carbon nanofibers. GO solution is a less pure, defective version of graphene made by chemically oxidizing a piece of graphite and pulling it apart into its individual graphene sheets [11]. During this step, oxygen- and hydrogen-rich functional groups attach to the graphene sheets. After the GO is mixed with either carbon nanotubes or carbon nanofibers, the slurry is poured into molds and directionally frozen to -150°C at a rate of $-10^{\circ}\text{C}/\text{min}$. Once the sample has completely solidified, it is placed in a lyophilizer to remove the ice crystals by sublimation thereby leaving a highly-porous, low-density, scaffold, whose cell walls and struts are composed of GO and carbon nanotubes or carbon nanofibers [12].

Since the goal of this study was to compare GO structures with rGO structures, an additional reduction step was used for the GO structures. Three types of reduction methods were used. The samples were either reduced i) chemically with l-ascorbic acid prior to freezing, or ii) thermally in a furnace after lyophilization, or iii) the slurry was chemically reduced prior to freezing and thermally reduced after lyophilization. Typically, researchers aim to obtain a pure, graphene structure because graphene is a stronger, more electrically conductive material than GO, but rGO is an appropriate first approximation, also because it can be processed more easily by freeze-casting [13].

In the case of some scaffolds, boron carbide nanoparticles were also added to the rGO slurries (the GO samples could not hold the boron carbide within their structure) in an effort to improve the attenuation coefficient of the samples when exposed to thermal neutrons in future experiments; however, we were interested to evaluate their effect when exposed to the fast neutrons used in this study. Ultimately, this study compared twenty-two different types of graphene based

scaffolds with varying amounts of carbon nanotubes or carbon nanofibers, varying reduction methods, and boron carbide additives. The final samples were about 19 mm in diameter and approximately 26 mm in length with densities ranging between $5 \text{ mg/cm}^3 - 20 \text{ mg/cm}^3$. Scanning electron micrographs obtained of a few examples of the highly porous samples are shown in Figure 2 and Figure 3.

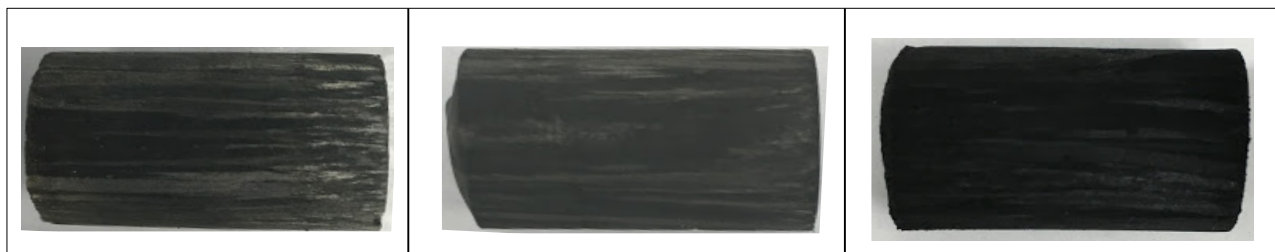


Figure 2: Graphene Oxide scaffolds approximately 19 mm in diameter and 26 mm in length. (From Left to Right) A GO scaffold with 0.50 wt% carbon nanotubes after lyophilization. A rGO Scaffold with 0.50 wt% carbon nanofibers and 0.25 wt% boron carbide, chemically reduced with l-ascorbic acid. A thermally rGO scaffold with 0.50 wt% carbon nanotubes.

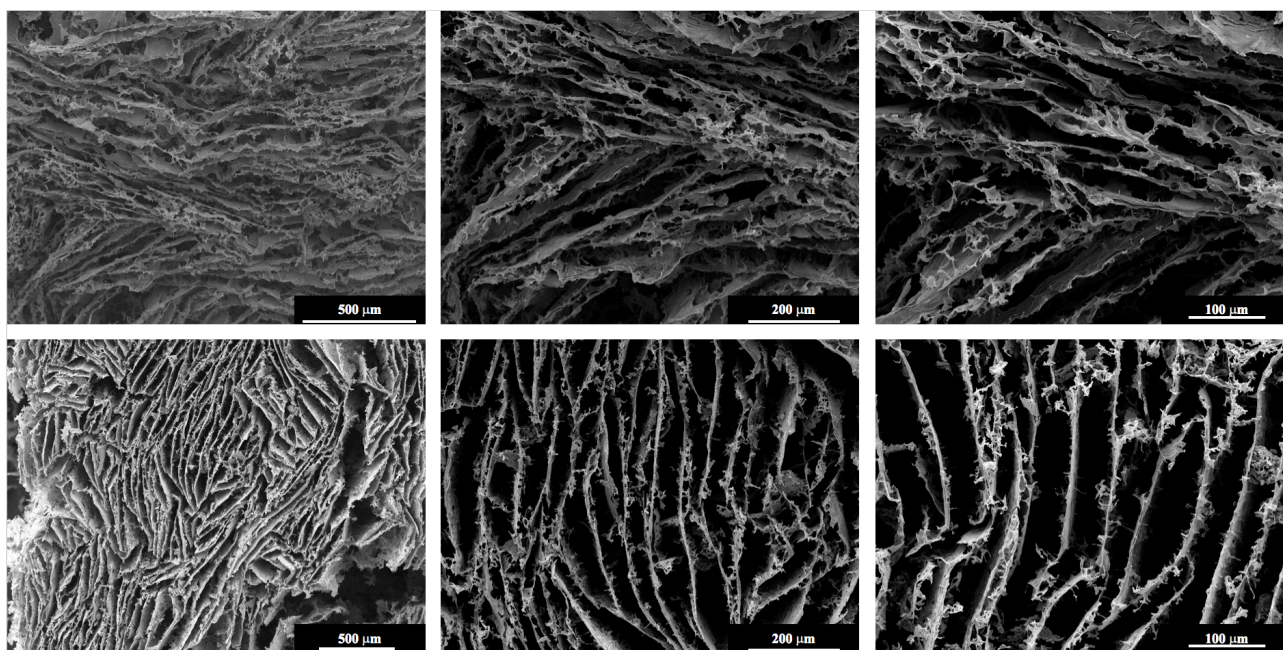


Figure 3: Scanning electron micrographs at three different magnifications of cross-sections cut perpendicular to the freezing direction of (Top Row) a GO scaffold with 0.25 wt% CNT (Bottom Row) a rGO scaffold, chemically reduced with l-ascorbic acid and also containing boron carbide nanoparticles. Scale bars are, from left to right, 500 μm , 200 μm , and 100 μm , respectively.

Neutron Attenuation Testing

The linear attenuation coefficient, μ , describes the fraction of a neutron beam that is absorbed or scattered per unit thickness of the absorber [14]. The value helps compare the neutron absorption capabilities of materials. Neutron attenuation was measured at the Rhode Island Nuclear Science Center using the R3 beam port. The samples were placed in between the neutron beamline and a detector. The total flux was first calculated using a BF_3 detector. The number of neutrons passing through each sample of known thickness, x , was then determined using the same detector. Fast neutrons at 2 MeV were used in a half-inch square beamline; the set-up is shown in Figure 3. The expression $N = N_0 e^{-\mu x}$ that correlates the initial neutron intensity, N_0 , and the intensity, N , of neutrons after passing through a sample of thickness, x , and the samples linear attenuation coefficient, was used to calculate μ for each sample [14,15].

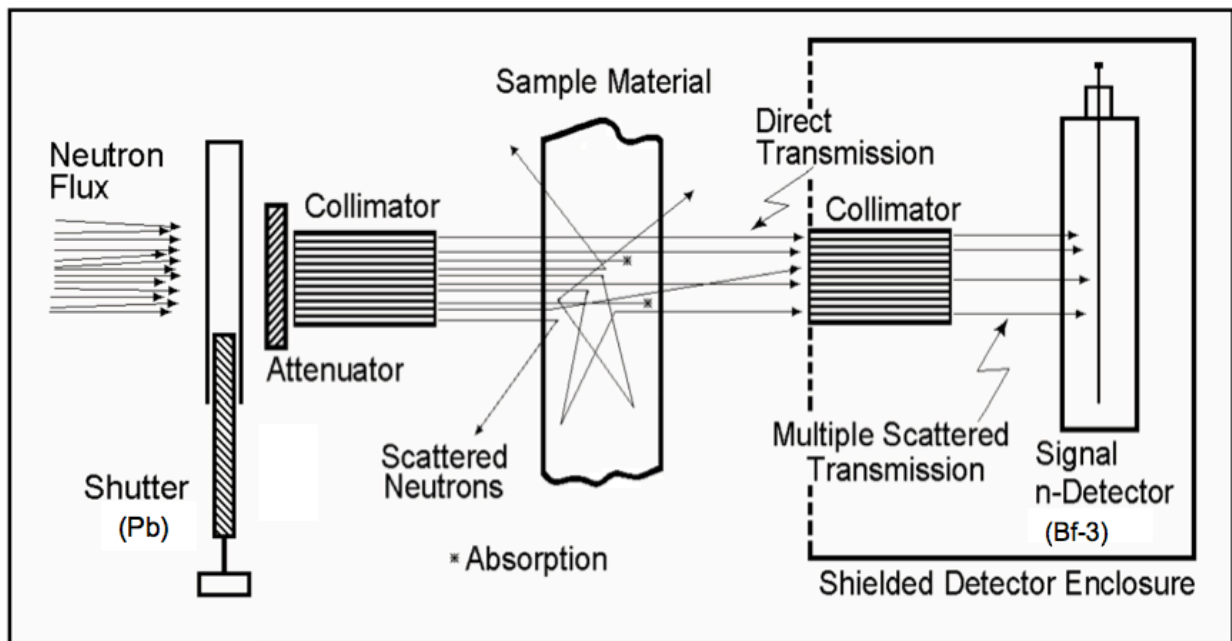


Figure 3: Neutron Attenuation Test Schematic [Adapted from 15]

Results

The results of the attenuation testing of different samples are presented in Figure 4. Figure 5 describes the average linear neutron attenuation coefficient correlation to density of the samples.

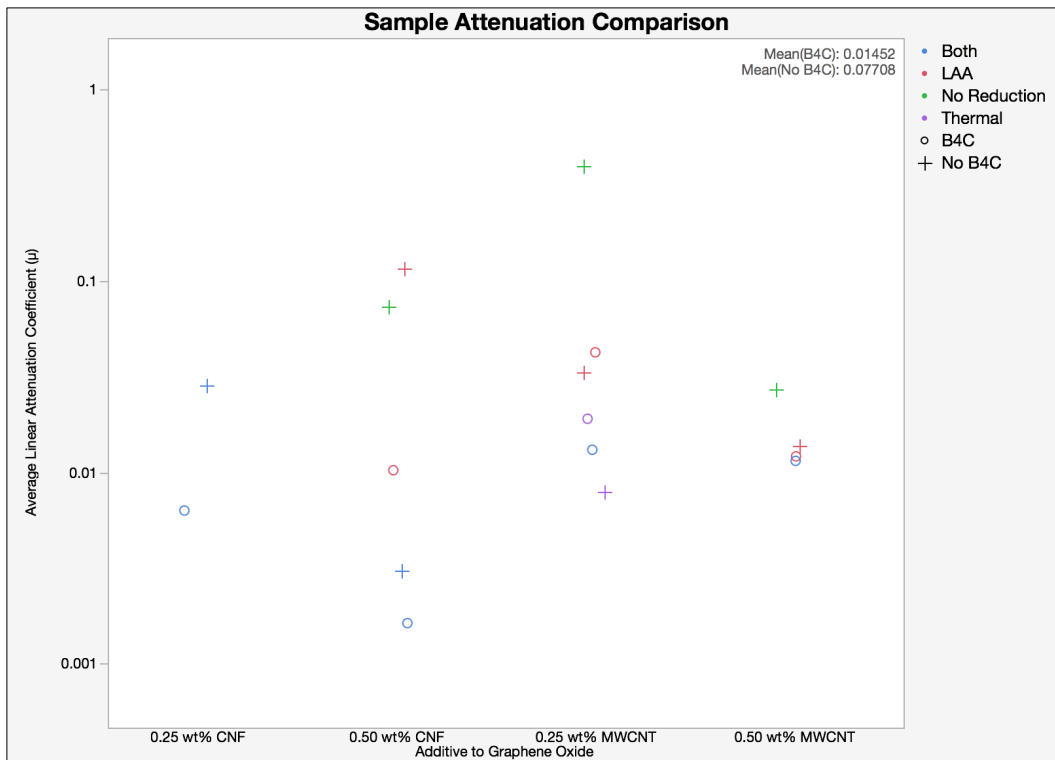


Figure 4: Average Linear Attenuation Coefficient (μ) vs. Additive to Graphene Oxide

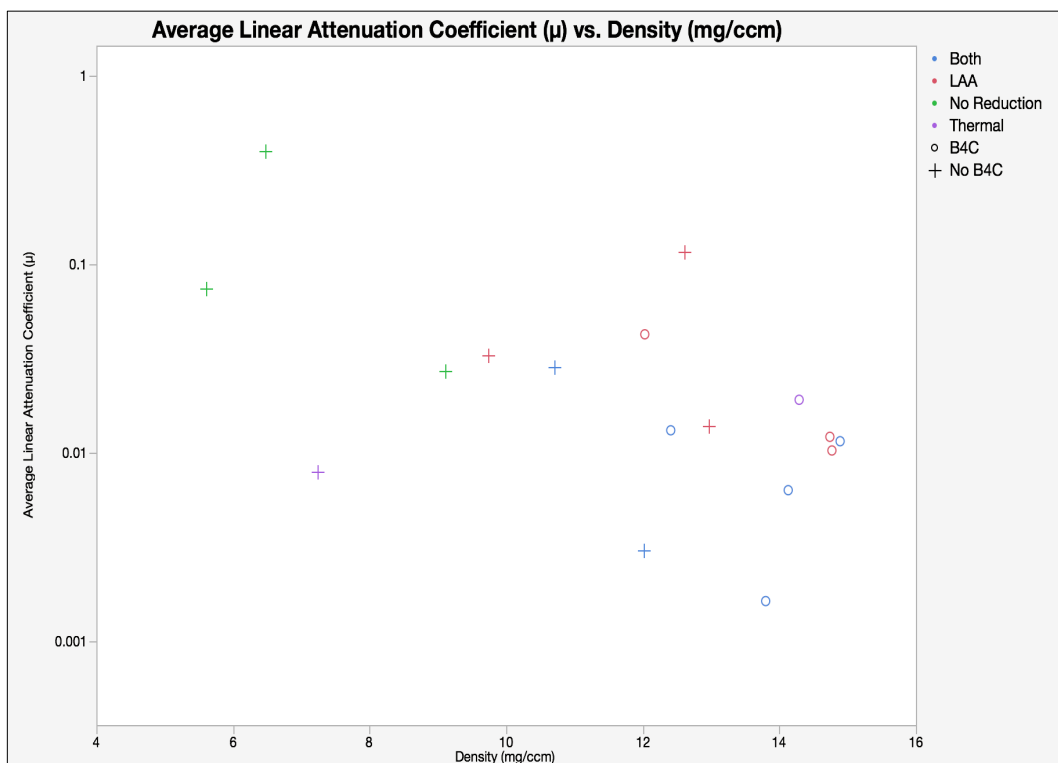


Figure 5: Average Linear Attenuation Coefficient (μ) vs. Volumetric Density

Several GO samples with 0.25 wt% carbon nanotubes were also run in the pneumatic testing system at the Rhode Island Nuclear Science Center to determine the total fluence that the samples could endure prior to failure. This is an air-operated system that sends the samples to a box in the reactor pool next to the core with valves controlled by times in order to have precise control over the amount of total fluence that the samples receive. The samples were irradiated for 30 minutes at a time at flux levels of 1×10^{12} n/cm²-s thermal flux (4×10^{11} n/cm²-s fast flux). The samples were irradiated for a total of 90 minutes (30 minutes at a time) before it was determined that the samples were no longer intact. Due to the comparatively delicate nature of the samples, this could either be a result of the radiation or the samples travel through the pneumatic system.

Discussion

Several trends emerge from the neutron attenuation data presented Figure 4. The GO scaffolds with carbon nanotubes that did not undergo thermal or chemical reduction typically had the higher attenuation coefficient, except in the case of the 0.50 wt% carbon nanofiber sample. The less reduced the sample, the higher the attenuation. On average, the multi-walled carbon nanotubes exhibited higher neutron attenuation than the carbon nanofibers. The addition of boron carbide did not significantly affect attenuation, as expected, because boron carbide has high neutron absorption properties for thermal neutrons rather than the fast neutrons used in this study [2,14]. It should be noted that, since boron carbide cannot be fixed within the graphene oxide structure without first reducing the graphene oxide chemically or thermally, a direct comparison could not be made between reduced and non-reduced samples.

Additionally, the results reveal that samples with lower weight percentages of carbon nanotubes or nanofibers outperformed the higher weight percentages. The samples with the lowest attenuation coefficient contained boron carbide and were reduced twice, first chemically, then thermally. The GO exhibited better attenuation properties than the rGO, likely due to the presence of hydrogen rich functional groups, which remained in the scaffold and aided neutron thermalization. The results indicate that non-reduced materials may behave more desirable also from a commercial perspective, because reducing the material chemically or thermally is time consuming and expensive. However, further testing and analysis of the material is required, whether this trend still dominates, when the materials are exposed to thermal neutrons.

The attenuation capabilities of the samples were not found to correspond to the density of the material. Instead, the results indicated that most of the lower density samples had a higher average attenuation coefficient than those with a higher density. This is likely because most of the samples composed only of carbon were relatively similar in density, whereas the addition of boron carbide increased the density of some of the scaffolds without increased fast neutron attenuation. The 0.50 wt% carbon nanofiber samples reduced with l-ascorbic acid performed slightly better than the non-reduced samples possibly due to the reduced samples density being approximately three times higher than that of the non-reduced samples.

Since our hypothesis is that the interfaces formed by the carbon-based materials at several length scales when freeze-cast into porous structures have an effect on their neutron attenuation and shielding performance, we would also expect differences in shielding performance that, for a given composition, result from different processing conditions. Ice crystal nucleation and growth depend on material composition and freezing rate; the higher the freezing rate, the smaller the pore size that the ice crystals template. Repeating sample preparation with the same material compositions, but with different freezing rates will allow us to determine the effect of pore size, cell wall thickness and amount of interfaces on the attenuation performance.

Conclusions & Future work

The results of this preliminary neutron attenuation study are promising. They indicate that GO appears to be a more effective neutron shielding material than rGO and that structural features such as the type and amount of interfaces at different length scales, introduced through the different carbon allotropes, contribute to the materials neutron attenuation performance. Further, systematic testing of the different compositions with both fast and thermal neutrons will be required to obtain a complete set of fundamental properties of freeze-cast, carbon-based scaffolds. These will help discern compositional (including hydrogen content and storage potential) and structural effects (interface amount and type) on their radiation shielding and attenuation properties, and their prediction and modeling. Future tests on freeze-cast carbon-based structures should be extended to include measurements of their thermal properties such as thermal conductivity, expansion and stability, response to long-term irradiation and high temperatures.

Acknowledgments

The authors are grateful for the support of the project through a Thayer School of Engineering Energy Fellowship (DC) and the Dartmouth NSF Innovation Corps (I-Corps) Grant (1547927).

References

1. Andrei, Eva. Li, Guohong. Du, Xu. "Electronic properties of graphene: a perspective from scanning tunneling microscopy and magnetotransport". Reports on Progress in Physics, Volume 75, Number 5 (April 2012). <<http://iopscience.iop.org/article/10.1088/0034-4885/75/5/056501#citations>>.
2. Neutron Interaction and Activation Calculator. NIST Center for Neutron Research. 03 March 2016. <<https://www.ncnr.nist.gov/resources/activation/>>.
3. Rinard, P. "Neutron Interactions with Matter". Federation of American Scientists. February 8, 2016. <<https://www.fas.org/sgp/othergov/doe/lanl/lib-www/la-pubs/00326407.pdf>>.

4. Klein, Dale E. "Spent Nuclear Fuel is an Abundant Source of Energy". 21st Century Science and Technology. Spring 2011. Pages 33-38. <https://www.21stcenturysciencetech.com/Articles_2011/Spring2011/Spent_Nuclear_Energy.pdf>.
5. Piore, Adam. "In Search for the Black Swan". Scientific America. 17 May 2011. <<http://www.nature.com/scientificamerican/journal/304/n6/full/scientificamerican0611-48.html>>.
6. "Zytel Nylon Resin Data Sheet - Thermal Properties." Dupont. 14 August 2016. <<http://dupont.materialdatacenter.com/profiler/vgMwW/standard/main/ds/17167/4097>>.
7. Graphite-moderated reactor. (2016, May 31). In Wikipedia, The Free Encyclopedia. 5 Mar 2016 <https://en.wikipedia.org/w/index.php?title=Graphite-moderated_reactor&oldid=722968642>.
8. Pei, Songfeng. Cheng, Hui-Ming. "The Reduction of Graphene Oxide". Carbon. Volume 50. Issue 9. August 2012. Pages 3210-3228. <<http://www.sciencedirect.com/science/article/pii/S0008622311008967>>.
9. Zueshen, Wang. Jinjin, Li. Qing, Zhong. Yuan, Zhong. Mengke, Zhao. "Thermal Annealing of Exfoliated Graphene". Journal of Nanomaterials. Volume 2013. 29 March 2013. <<http://www.hindawi.com/journals/jnm/2013/101765/>>.
10. "Graphene and Graphene Oxide (Nanocarbon Materials). TCI America. 02 February 2016. <http://www.tcichemicals.com/eshop/en/us/category_index/03428>.
11. "Dispersion in Water: Single Layer Graphene Oxide (175mL) Data Sheet". Graphene Supermarket. 02 February 2016. <<https://graphene-supermarket.com/Dispersion-in-Water-Single-Layer-Graphene-Oxide-175-ml.html>>.
12. Wegst, U.G.K., Bai, Hao, et al. "Bioinspired Structural Materials". Nature Materials. Volume 14. 14 August 2014. 23-36. <<http://www.nature.com/nmat/journal/v14/n1/full/nmat4089.html>>.
13. Zhu, Cheng T., Han, Yong-Jin et al. "Highly Compressible 3D Periodic Graphene Aerogel Microlattices". Nature Communications, 22 April 2015. doi:10.1038/ncomms7962.
14. MacFarlane, R. "Neutron Slowing Down and Thermalization". Handbook of Nuclear Engineering Springer Science: Business Media LLC 2010.

15. Diacon, B. "Neutron Material Attenuation". Engineering Physics, McMaster University. 16 June 2016. <http://engphys.mcmaster.ca/wp-content/uploads/2013/08/3d3_lab3_n-attenuation.pdf>.