Microwave Absorption by Carbon-Based Materials and Structures

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The microwave range, *i.e.*, from 0.3 GHz to 300 GHz, is one of the most developed parts of the electromagnetic spectrum, both in terms of devices and material basis. However, the design and practical realization of efficient microwave absorbers for resonant or broadband use that are simultaneously lightweight and/or thin, optically transparent, mechanically rigid or on the contrary flexible, thermally stable, heat conductive or insulating, and respectful of ‘green chemistry’, remain a challenge.

Carbon is one of the main focuses for the development of “on-demand” materials and components. Indeed, carbon materials offer a wide range of electromagnetic properties, from dielectric diamond to conductive carbon black, through semiconductor and metallic carbon nanotubes [Iijima, Sumio (1991), Nature, **354** (6348): *56–58;* Chang Liu, Hui-Ming Cheng, J. Am. Chem. Soc. 2016, 138, 21, 6690–6698] and graphene [Novoselov, K. S. et al. Two-dimensional atomic crystals. Proc. Natl Acad. Sci. USA 102, 10451-10453 (2005)] which, depending on their level and nature of doping, can be either 0-bandgap semiconductors or metals [Slonczewski, J.C., Weiss, P.R. Band structure of graphite. Phys. Rev. 109, 272-279 (1958)].

Our Editorial provides an overview of the most efficient strategies for the design and fabrication of carbon-based absorbers, targeting ‘green chemistry’ pathways, multifunctionality and electromagnetic robustness.

There are a number of well-known strategies for approaching perfect or broadband microwave absorption. Broadly speaking, the two most common methods are to play with the dielectric and magnetic constitutive parameters of the material, or to focus on the geometric characteristics of the components.

The first strategy typically involves a solid material, which a thickness greater than the skin depth, and whose electromagnetic response is then determined by the material’s constitutive properties. The dielectric and/or magnetic losses indicate the physical absorption mechanism of these materials.

There is a large collection of micro- and nanocomposite materials, whose electromagnetic response is governed by the microstructure and electromagnetism of the individual, aggregated or lattice inclusions [Lulu Zhong, et al, Review of carbon-based electromagnetic shielding materials: film, composite, foam, textile, 2020, Textile Research Journal 91(2):004051752096828, DOI: 10.1177/0040517520968282; Jia Jia, et al, A review on one-dimensional carbon-based composites as electromagnetic wave absorbers, 2022, Journal of Materials Science: Materials in Electronics 33(45) DOI: 10.1007/s10854-021-07363-7]. Percolation phenomena play an important role in their electromagnetic behavior. Clustering, aggregation and dispersion of functional particles can significantly alter the expected response compared to size-dependent percolation models of individual particles [Wolfgang Bauhofer, et al, A review and analysis of electrical percolation in carbon nanotube polymer composites,

Composites Science and Technology, Volume 69, Issue 10, August 2009, Pages 1486-1498, https://doi.org/10.1016/j.compscitech.2008.06.018].

Extra functionality comes from the combination of two or more functional fillers in composite materials, *e.g.* the combination of nanocarbon with magnetic particles inclusions [J. Vejpravova, et al, Magnetic impurities in single-walled carbon nanotubes and graphene: a review, (Tutorial Review) *Analyst*, 2016, **141**, 2639-2656, DOI: 10.1039/C6AN00248J]. Today, many research papers focus on a synergistic use of various additives along with carbon-based ones.

A composite absorber that uses carbon nanoparticles in a polymer matrix offers great flexibility for design and properties control, as the composite can be tuned and optimized by modifying both the filler particles (carbon black, carbon nanotubes, carbon fibers, graphene nano-platelets and reduced graphene oxide) and the embedding matrix (rubber, thermoplastic, etc.).

At the same time, resonant effects in the composite material may occur, originating from the specific electromagnetic response of the individual inclusions, *e.g.* carbon nanotubes having antenna-like resonances related to their ‘finite’ length [Hanson, G. Fundamental transmitting properties of carbon nanotube antennas. *IEEE Trans. Antenn. Propagat.* **53**, 3426–3435 (2005); Slepyan, G. Y. *et al*. Theory of optical scattering by achiral carbon nanotubes and their potential as optical nanoantennas. *Phys. Rev. B* **73**, 195416 (2006)].

Instead of using solid materials, materials with various porous architectures may be preferred, as they can preserve the simplicity of the bulk material, while being much lighter, and more absorptive. Carbon monoliths with open porosity and a skeleton thickness compatible with the skin depth could be resonantly absorptive in microwaves, when their pore size is compatible with the wavelength [M. Letellier, et al, Electromagnetic properties of model vitreous carbon foams, *CARBON*, 122 (2017) 217-227 https://doi.org/10.1016/j.carbon.2017.06.080].

Another interesting route to approaching high absorption is to explore the thin carbon film concept. A free-standing conductive carbon film, including nm-thick pyrolytic carbon or properly doped graphene, could absorb up to 50% of microwave radiation, when its thickness is much smaller than the skin depth [K. Batrakov, et al, Enhanced microwave shielding effectiveness of ultrathin pyrolytic carbon films, Applied Physics Letters, 103, 073117 (2013); doi: 10.1063/1.48186802013]. By playing with the properties and thickness of the substrate, also adding back reflector to support constructive interference, even perfect absorptivity can be achieved [Anna C. Tasolamprou, et al, Experimental Demonstration of Ultrafast THz Modulation in a Graphene-Based Thin Film Absorber through Negative Photoinduced Conductivity, *ACS Photonics*, 2019, *6* (3), pp 720–727 DOI: 10.1021/acsphotonics.8b01595].

A more efficient way to achieve high broadband or perfect resonant absorption, is to use layered structures, comprising alternating conductive carbon-based and dielectric layers, each of which can be electrically thin [A. Paddubskaya, et al, Electromagnetic and Thermal properties of 3D Printed Multilayered Nano-carbon / Poly(lactic) Acid Structures, Journal of Applied Physics **119**, 135102 (2016); doi: 10.1063/1.4945576]. Constructive interference in such a layered structure could lead to the suppression of reflection and thus to near-perfect absorption achieved under resonant conditions, *e.g.* at ¼ wavelength (Salisbury screen).

While microwave “absorption” is commonly adopted for coatings to shield microwave, the apparent thickness-dependent shift of the “absorption” peaks ponders the appropriateness of the continuing usage of the “absorption” instead of “shielding” in some cases. The peak position of true absorption should largely stay constant regardless of the thickness of the coating or the concentration of the active absorbing materials, which is indeed frequently observed oppositely. The good correlation between quarter-wavelength thickness of the coating and effective “absorption” peak position also cautions us that new mechanisms may be needed to achieve broad-band microwave “absorption” instead of thickness-dependent narrow-band “absorption”.

The metamaterial approach, which belongs to the second strategy, refers to the geometry and electromagnetic properties of the subwavelength metaatoms array to achieve the desired electromagnetic pattern. Physically, this can result from surface plasmon polariton excitation, the effect of enhanced transmission / induced transparency by specific cavity modes, anapole excitation [Alexey A. Basharin, et al, Extremely high Q-factor metamaterials due to anapole excitation, Phys. Rev. B 95, 035104, 2017], and many others.

Along with fundamental electromagnetics, *i.e.*, effective medium and homogenization theories and percolation modeling for composites, optical processes simulations through diffraction, scattering, interference for structured surfaces and metamaterials, and plasmonics of metasurfaces, one more important ingredient for making a successful absorber is materials science.

Depending on the targeted frequency window and the chosen strategy for the fabrication of carbon-based absorbers, one can consider using:

- Nanocarbon or hybrid composites, including another functional additive to extend the material functionality;
- 3D-printed meshes composed of carbon-filled polymer;
- 3D architectures made of carbon or graphene scaffolds;
- Metasurfaces made of structured carbon (carbon nanotubes, graphene);
- Non-carbon metasurfaces enhanced with graphene;

and many other approaches.

All the above technological routes could be used to add an extra dimension, multi-functionality, to the electromagnetic absorber. For instance, highly absorptive graphene/polymer microwave shields are flexible and optically transparent [K. Batrakov, et al, Enhanced microwave-to-terahertz absorption in Graphene, Appl.Phys. Lett. 108, 123101 (2016) http://dx .doi.org/10.1063/ 1.4944531]. PLA composites filled with nanocarbon inclusions could be used not only for electromagnetic, but also for thermal and mechanical management, being 3D-printable [Rumiana Kotsilkova, et al, Exploring thermal annealing and graphene-carbon nanotube additives to enhance crystallinity, thermal, electrical and tensile properties of aged poly(lactic) acid-based filament for 3D printing, July 2019, Composites Science and Technology 181:107712, DOI: 10.1016/j.compscitech.2019.107712].

In addition to multifunctionality, the tunability of the electromagnetic response is a very important property needed for the design and fabrication of state-of-the-art electromagnetic devices. Graphene, which is highly tunable by the application of external forces (mechanical deformation, biasing, laser irradiation), is a material of choice for tunable electromagnetic components [Long Ju, et al, Graphene plasmonics for tunable terahertz metamaterials, *Nature Nanotechnology* volume 6, pages630–634 (2011)].

In line with UN sustainable development goals, it is important to think also about ways to synthesize / manufacture carbon-based materials and components as environmentally friendly as possible. Researchers are paying increasing attention to the greener character that the materials they develop should have, and the niche of materials for electromagnetic applications is no exception to this trend. This is especially true since the carbonaceous materials discussed here have organic precursors, many of which can be conveniently replaced by naturally occurring counterparts. This is particularly true of phenolic resins, which can be easily replaced by plant polyphenols that are abundant, non-toxic, cheap and chemically reactive, for example, to be doped with heteroelements or metal particles [A. Celzard, V. Fierro. “Green”, innovative, versatile and efficient carbon materials from polyphenolic plant extracts. Carbon **167** (2020) 792 – 815]. Simple sugars (sucrose, glucose, ...) or complex sugars (cellulose, starch, ...) are also precursors of choice, whose final carbon structure can be easily oriented by the preparation method used: foaming, gelation, polymerization, emulsification, templating, etc. [D. Bychanok, et al. Hollow carbon spheres in microwaves: a bioinspired absorbing coating. Applied Physics Letters **108** (2016) 013701-1 – 013701-5; D. Bychanok, et al. Fully carbon metasurface: absorbing coating in microwaves. Journal of Applied Physics **121** (2017) 165103-1 – 165103-9]. Some methods use almost only water and little or no other chemicals, such as hydrothermal synthesis and mechanosynthesis [A. Sanchez-Sanchez, et al. Synthesis and properties of carbon microspheres based on tannin-sucrose mixtures treated in hydrothermal conditions. Industrial Crops and Products 154 (2020) 112564-1 – 112564-12; J. Castro-Gutiérrez, et al. Synthesis of Perfectly Ordered Mesoporous Carbons by Liquid-assisted Mechanochemical Self-assembly of Tannin. Green Chemistry **20** (2018) 5123-5132], and even some previously polluting methods such as chemical synthesis of graphene are now possible with much more environmentally friendly methods and naturally occurring chemical reductants [Z. Ismail. Green reduction of graphene oxide by plant extracts: A short review. Ceramics International (2019) 23857-23868]. Material savings can also be achieved through the development of carbon 3D printing, where the use of natural and non-toxic precursors is increasing [P. Blyweert, et al. 3D printing of carbon-based materials: a review. Carbon **183** (2021) 449 – 485].

Finally, an important problem to be addressed for efficient use of theoretical predictions and advances in materials science, is the durability of electromagnetic performance of engineered composite materials, 3D architectures, metamaterials and device component with respect to material defects, fabrication imperfections, and other problems coming from ‘irregularity’ and randomly deviations in materials properties and device configurations. Due to the electromagnetic coupling of graphene flakes, graphene grain boundaries and hole-like defects slightly influence on the electromagnetic response of the graphene-based absorber [Michaël Lobet *et a,* Robust electromagnetic absorption by graphene/polymer heterostructures, 2015 *Nanotechnology* 26, 285702], and the microwave efficiency of nanocarbon and graphene-based components appears to be substantially robust.

The Special Topic *“Microwave Absorption by Carbon-Based Materials and Structures”* offers a perspective on the experimental efforts to develop microwave absorbers composed of carbon nano- and microstructures addressing all of the above strategies and issues. Carbon-based materials are of great relevance to a wide range of potential applications that cover radar absorption, electromagnetic protection against natural phenomena (lightning), nuclear electromagnetic pulse protection, electromagnetic compatibility for electronic devices, anechoic chambers, and human exposure mitigation.

In particular, special topic proposes a number of elegant solutions for synergetic nanomaterials comprising different functional components to approach a perfect and / or broadband microwave absorption [Journal of Applied Physics **131**, 035103 (2022); https://doi.org/10.1063/5.0070633; Journal of Applied Physics **131**, 055110 (2022); https://doi.org/10.1063/5.0071157; Journal of Applied Physics **130**, 224301 (2021); https://doi.org/10.1063/5.0073714], including tunable options [Journal of Applied Physics **130**, 175101 (2021); https://doi.org/10.1063/5.0068768].

It also explores size dependent percolation in nanocarbon based composites [Journal of Applied Physics **131**, 044101 (2022); https://doi.org/10.1063/5.0071517], that might be important for multifunctional materials fabrication, as electrical, mechanical and rheological percolation thresholds might be substantially different.

The ultralight porous structures [Journal of Applied Physics **130**, 230902 (2021); https://doi.org/10.1063/5.0068122; Journal of Applied Physics **130**, 163102 (2021); https://doi.org/10.1063/5.0063171] as well as thin layered carbon membranes [Journal of Applied Physics **130**, 175302 (2021); https://doi.org/10.1063/5.0068192] as efficient microwave absorbers are also presented.

Finally, very interesting solution for high-performance absorptive metasurface through additional diffusion mechanism [Journal of Applied Physics **130**, 023106 (2021); https://doi.org/10.1063/5.0056252] and randomness of chaotic patterning [Journal of Applied Physics **130**, 165101 (2021); https://doi.org/10.1063/5.0065004] are investigated likewise.

In addition, THz range as the high frequency edge of microwave band is covered [Journal of Applied Physics **131**, 025110 (2022); https://doi.org/10.1063/5.0075497; Journal of Applied Physics **131**, 064103 (2022); https://doi.org/10.1063/5.0075242]. Adjustable graphene absorptance in THz frequencies gives extra dimension to terahertz imaging [Journal of Applied Physics **131**, 033101 (2022); https://doi.org/10.1063/5.0074772].

In particular, special topic proposes a number of elegant solutions for synergetic nanomaterials comprising different functional components to approach a perfect and / or broadband microwave absorption [Journal of Applied Physics **131**, 035103 (2022); https://doi.org/10.1063/5.0070633; Journal of Applied Physics **131**, 055110 (2022); https://doi.org/10.1063/5.0071157; Journal of Applied Physics **130**, 224301 (2021); https://doi.org/10.1063/5.0073714], including tunable options [Journal of Applied Physics **130**, 175101 (2021); https://doi.org/10.1063/5.0068768]. It also explores size dependent percolation in nanocarbon based composites [Journal of Applied Physics **131**, 044101 (2022); https://doi.org/10.1063/5.0071517], that might be important for multifunctional materials fabrication, as electrical, mechanical and rheological percolation thresholds might be substantially different. Ultralight porous structures [Journal of Applied Physics **130**, 230902 (2021); https://doi.org/10.1063/5.0068122; Journal of Applied Physics **130**, 163102 (2021); https://doi.org/10.1063/5.0063171] as well as thin layered carbon membranes [Journal of Applied Physics **130**, 175302 (2021); https://doi.org/10.1063/5.0068192] as efficient microwave absorbers are also presented. In addition, very interesting solution for high-performance absorptive metasurface through additional diffusion mechanism [Journal of Applied Physics **130**, 023106 (2021); https://doi.org/10.1063/5.0056252] and randomness of chaotic surface patterning [Journal of Applied Physics **130**, 165101 (2021); https://doi.org/10.1063/5.0065004] are investigated likewise. Finally THz range as the high frequency edge of microwave band is covered [Journal of Applied Physics **131**, 025110 (2022); https://doi.org/10.1063/5.0075497; Journal of Applied Physics **131**, 064103

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