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Special Collection: Microwave Absorption by Carbon-Based Materials and Structures

Polina Kuzhir 🕶 🔟 ; Alain Celzard 🕶 🗓 ; Xiaobo Chen 🗓



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Polina Kuzhir, 1,a) D Alain Celzard, 2,a) D and Xiaobo Chen D

AFFILIATIONS

- Department of Physics and Mathematics, Institute of Photonics, University of Eastern Finland, Yliopistokatu 7, Fl-80101 Joensuu, Finland
- ²Université de Lorraine, CNRS, IJL, F-88000 Epinal, France
- ³University of Missouri-Kansas City, Kansas City, Missouri 64110, USA

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^{a)}Authors to whom correspondence should be addressed: polina.kuzhir@uef.fi and alain.celzard@univ-lorraine.fr

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The microwave range, 0.3-300 GHz, is one of the most developed parts of the electromagnetic spectrum, both in terms of devices and materials. However, challenges remain in 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; heatconductive or insulating; and respectful of "green chemistry."

Carbon is one of the main areas of development for "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 nanotubes¹ and graphene,² which, depending on their level and nature of doping, can be either 0-bandgap semiconductors or metals.³

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, with 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 responses are governed by the microstructure and electromagnetism of the individual, aggregated, or lattice inclusions.4,5 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 indi- & vidual particles.6

Extra functionality comes from the combination of two or 80 more functional fillers in composite materials, e.g., the combination of nanocarbon with magnetic particles inclusions. 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 antennalike resonances related to their finite length.85

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.

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. 11 By playing with the properties and thickness of the substrate, also

adding back reflector to support constructive interference, even perfect absorptivity can be achieved.1

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.¹³ 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 1/4 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 meta-atoms 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, 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 the following:

- · 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.¹⁵ PLA composites filled with nanocarbon inclusions could be used not only for electromagnetic, but also for thermal and mechanical management, being 3D-printable.16

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.

In line with UN sustainable development goals, it is important to think also about ways to synthesize and manufacture carbonbased materials and components as environmentally responsibly 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.¹⁸ Simple sugars (sucrose, glucose, etc.,) or complex sugars (cellulose, starch, etc.,) are also precursors of choice, whose final carbon structure can be easily oriented by the preparation method used: foaming, gelation, polymerization, emulsification, templating, etc., 19,20 Some methods use almost only water and few or no other chemicals, such as hydrothermal synthesis and mechanosynthesis, 21,22 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.²³ Material savings can also be achieved through the development of carbon 3D printing, where the use of natural and non-toxic precursors is increasing.

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 N other problems coming from "irregularity" and random deviations in materials properties and device configurations. Due to the electromagnetic coupling of graphene flakes, graphene grain boundaries and hole-like defects slightly influence the electromagnetic response of the graphene-based absorber,²⁵ 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 [J. Appl. Phys. 131, 035103 (2022); https://doi.org/10.1063/5.0070633; J. Appl. Phys. 131, 055110 (2022); https://doi.org/10.1063/5.0071157; J. Appl. Phys. 130, 224301 (2021); https://doi.org/10.1063/5.0073714], including tunable options [J. Appl. Phys. 130, 175101 (2021); https://doi.org/10.1063/5.0068768]. It also explores size dependent

percolation in nanocarbon based composites [J. Appl. Phys. 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 [J. Appl. Phys. 130, 230902 (2021); https://doi.org/10.1063/5.0068122; J. Appl. Phys. 130, 163102 (2021); https://doi.org/10.1063/5.0063171] as well as thin layered carbon membranes [J. Appl. Phys. 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 [J. Appl. Phys. 130, 023106 (2021); https://doi.org/10.1063/5.0056252] and randomness of chaotic surface patterning [J. Appl. Phys. 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 [J. Appl. Phys. 131, 025110 (2022); https://doi.org/10.1063/5.0075497; J. Appl. Phys. 131, 064103 (2022); https://doi.org/10.1063/5.0075242]. Adjustable graphene absorptance in THz frequencies gives extra dimension to terahertz imaging [J. Appl. Phys. 131, 033101 (2022); https://doi.org/10.1063/5.0074772].

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