Sonochemistry and sonocatalysis: Harnessing sound for enhanced catalytic-assisted reactions

Abstract The integration of high-frequency ultrasound (HFUS) with heterogeneous catalysis presents a synergistic method for converting renewable sources into valuable chemicals. Utilizing ultrasound-induced cavitation bubbles as microreactors for activating recalcitrant bonds becomes a pivotal initial step in unconventional assisted catalysis. Engineered catalytic materials enable precise control over the location, timing, and nature of cavitation bubbles, offering a promising avenue to reduce the global acoustic energy needed for initiation and selectively manage ultrasound-induced catalytic reactions.

Keywords **Sonocatalysis, cavitation bubble, catalysis, microreactor, radicals, chemical reactions.**

Résumé **Sonochimie et sonocatalyse : exploiter le son pour des réactions catalytiques améliorées**
L'intégration de l'ultrason haute fréquence (HFUS) avec la catalyse hétérogène conduit à une méthode synergique pour convertir des ressources renouvelables en produits chimiques précieux. L'utilisation de bulles de cavitation induites par ultrasons comme microréacteurs pour activer des liaisons « récalcitrantes » devient une étape initiale cruciale pour la catalyse assistée non conventionnelle. Des matériaux catalytiques spécifiquement conçus permettent un contrôle précis de l'emplacement, du timing et du mode de cavitation des bulles, offrant une voie prometteuse pour réduire l'énergie acoustique globale nécessaire à l'initiation et gérer sélectivement les réactions catalytiques induites par ultrasons.

Mots-clés **Sonocatalyse, bulle de cavitation, catalyse, microréacteur, radicaux, réactions chimiques.**

Sonochemistry, a groundbreaking and cost-effective technique, has emerged as a beacon of hope in the field of sustainable chemical syntheses. Its rise is fueled by an ever-mounting concern for environmental impacts. This transformative journey owes much to the pioneering work of Loomis and associates [1], who unearthed the profound physical and chemical effects triggered by ultrasonic frequencies. Initially confined to a specialized domain, sonochemistry has now transcended its boundaries, venturing into the vast landscapes of inter- and multidisciplinary fields. From nanotechnology to drug delivery [2-9], its applications have blossomed, promising innovative solutions to a host of contemporary challenges. The essence of sonochemistry lies in the irradiation of liquids with ultrasound, a process that locally induces pressure fluctuations [10]. When a liquid experience a localized pressure decrease, it plunges below its vapor pressure threshold, birthing a cavitation bubble. This bubble, composed of gas and vaporized liquid, expands in size (as depicted in *figure 1a*) before eventually collapsing with great violence. As it absorbs energy from the surrounding sound waves, it engenders extreme yet confined conditions within its imploded cavity – conditions characterized by astonishingly high temperatures and pressures [11-14]. Simultaneously, this dramatic collapse unleashes shock waves, high-speed jets, and reactive radicals.

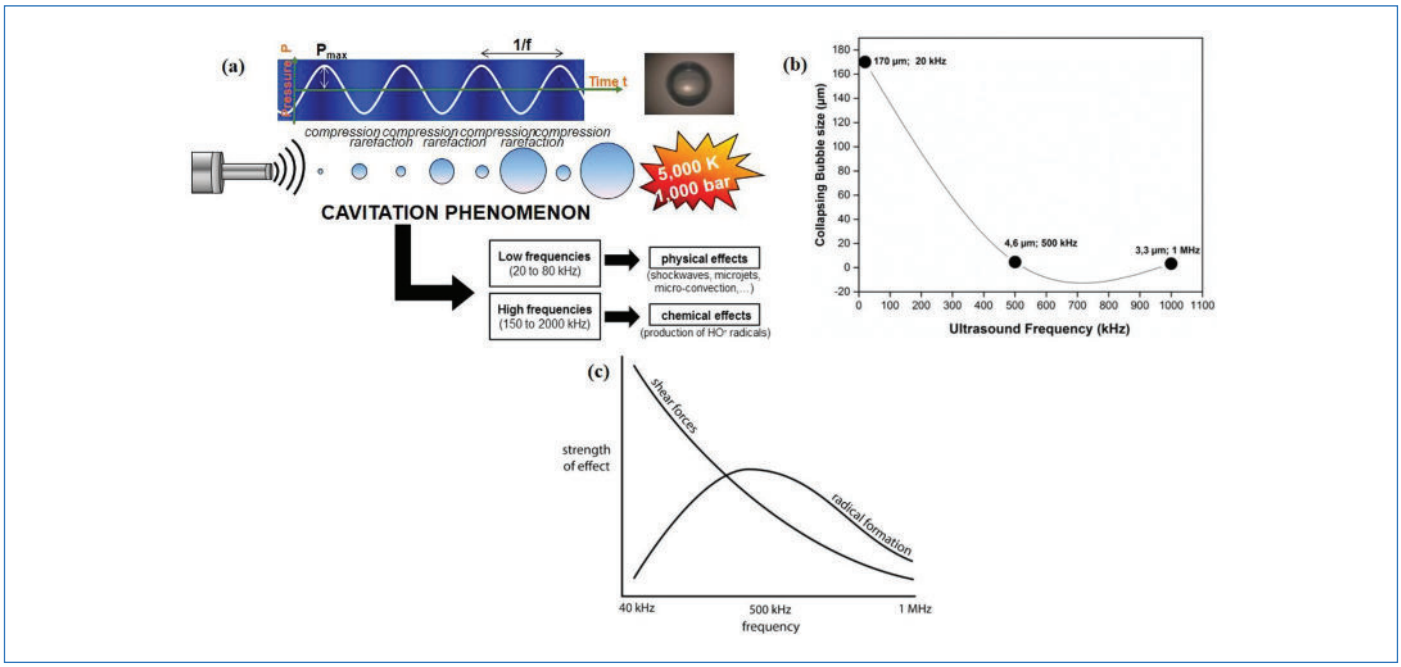

Figure 1 - (a) Cavitation phenomenon, (b) Collapsing bubble size as a function of ultrasound frequency, and (c) Cavitation strength effect as a function of ultrasound frequency.

These extreme conditions stand as the primary catalysts for the chemical and physical transformations brought about by acoustic cavitation in liquids [15-16].

However, it is worth noting that the nature of these effects' hinges on the range of ultrasound frequencies applied. For instance, low-frequency ultrasound (LFUS) in the range of 20-80 kHz engenders the formation of sizable cavitation bubbles (around 170 μm at 20 kHz) [17-18]. Their implosions predominantly induce physical effects, such as the generation of shock waves and high-speed jets. Consequently, LFUS finds applications in particle size attrition, enhanced mass transfer, crystallization, extractions, and more [19].

In stark contrast, high-frequency ultrasound (HFUS), operating in the range of 100-800 kHz, generates an abundance of smaller cavitation bubbles (approximately 4.6 μm at 550 kHz) [17-18]. These smaller bubbles tend to enhance the production of radicals, which can, in turn, initiate chemical reactions (as illustrated in *figure 1b*). The choice of ultrasound frequency allows for a strategic balance between optimizing locally induced shear forces (microstreaming, microjets, shockwaves, and heat) and promoting radical formation (*figure 1c*). Recently, the field of chemical processes has witnessed a resurgence of interest in ultrasound applications, particularly in the fields of organic chemistry and catalysis. This resurgence is driven by the growing societal demand for alternative activation technologies. Within this context, the terms "sonochemistry" and "sonocatalysis" have been coined to encapsulate these transformative concepts [12, 20-21].

This article aims to provide an insightful exploration of the vast potential of ultrasound in activating recalcitrant chemical bonds, leading to the production of high-value-added chemicals. Whether in homogeneous or heterogeneous conditions, ultrasound emerges as a powerful ally in the quest for innovative and sustainable chemical synthesis pathways.

Cavitation induced effects: General concept

Ultrasonic irradiation, a powerful technique, exerts profound physicochemical changes on liquid solutions, encompassing mechanical, chemical, and thermal effects. In this captivating process, the spotlight falls not only on the liquids themselves but also on the cavitation bubbles, which undergo remarkable transformations when subjected to ultrasound, giving rise to a cascade of secondary phenomena. The mechanical impact of ultrasound takes center stage, manifesting in various fascinating forms. Firstly, there's the phenomenon of acoustic microstreaming, a mesmerizing dance orchestrated by cavitating bubbles as they engage in oscillatory radial motions in response to the acoustic field. This microstreaming effect sets the stage for intriguing fluid movements within the liquid environment. Secondly, we encounter the dynamic duo of microjets and shockwaves. These are born from the sheer force of ultrasound, as it propels the cavitation bubbles into intense, directed motions, creating high-speed liquid microjets and propagating shockwaves. These phenomena, akin to nature's own choreography, play a pivotal role in the profound transformations occurring under ultrasound's influence. Moving into the thermal field, we find localized heating brought about by ultrasound's thermal effects. Here, the action unfolds as bubbles deftly convert acoustic energy into mechanical energy. This newfound energy is subsequently transformed into heat, warming the surrounding environment. It's as if ultrasound possesses the power to create miniature furnaces within the liquid, igniting localized temperature increases that can have significant consequences for chemical reactions and processes. Yet, the true magic of ultrasound lies in its chemical wizardry. The chemical effect of ultrasound unfurls a world of possibilities, as it unleashes a host of reactive radical species. These radicals emerge as if conjured by the ultrasound itself, formed in situ during the ultrasonic irradiation process. Once born into this turbulent environment, these radical species possess the power to initiate chemical reactions of great complexity and importance. They are the catalysts of transformation, turning the relatively tranquil liquid milieu into a hotbed of chemical activity. Ultrasonic irradiation is not merely a tool for stirring or heating liquids; it is a symphony of physical and chemical marvels. From the mesmerizing ballet of cavitation bubbles to the dramatic choreography of shockwaves and microjets, and the alchemical creation of reactive radicals, ultrasound's influence on liquid environments is a testament to the astonishing interplay of science and nature. Its potential applications in various fields, from chemistry to medicine, continue to expand as we unravel more of its mysteries and harness its powers for the betterment of our world.

Ultrasound induced chemical reactions: Impactful role of sound

A cavitation bubble, when viewed from a chemical perspective, takes on the role of a miniature chemical reactor [22]. These microscopic bubbles, nestled within their cavities, create an environment where the extreme conditions of pressure (reaching up to 1,000 bar) and temperature (soaring to 5,000 K) give rise to unique chemical reactions [23]. For instance, subjecting water to high-frequency ultrasound generates tiny cavitation bubbles that serve as micro-reactors. Inside these bubbles, water molecules undergo dissociation to form •OH and •H radicals [24]. Upon the bubble's implosion, these radicals are ejected into the surrounding liquid, initiating chemical reactions. This phenomenon is known as homogeneous sonochemistry. The choice of reactant plays a pivotal role in the outcome of organic reactions conducted under ultrasound irradiation. Reactants with high vapor pressure properties tend to diffuse into the cavitation bubbles, leading to their pyrolysis within the bubble interior. Conversely, reactants with low vapor pressure properties typically remain in the bulk phase, where they predominantly interact with shockwaves or react with radicals released during bubble implosion. Thus, one can fine-tune the reactivity of a sonochemical reaction to achieve either pyrolysis-like or radical-like reactions by carefully selecting reactants [22, 24].

In recent research aimed at comprehending and demonstrating the concept of homogeneous sonochemistry and the modulation of reactant behavior, we explored the reactivity of alcoholic aqueous solutions of glucose at varying concentrations under high-frequency ultrasound (550 kHz) (*figure 2*).

At high glucose concentrations (> 40 wt. %), the interaction between the substrate and cavitation bubbles is intensified, leading to glucose "pyrolysis" and the in-situ formation of levoglucosane [22]. Conversely, at low glucose concentrations (< 10 wt. %), glucose reacts with radicals (•OH and •H) in the bulk solution, resulting in the oxidation of glucose to either gluconic or glucuronic acid, depending on the gas atmosphere (*figure 3*) [24].

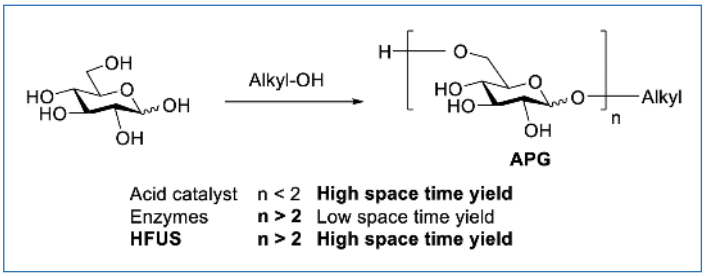

Figure 2 - HFUS induced alkylpolyglycoside formation.

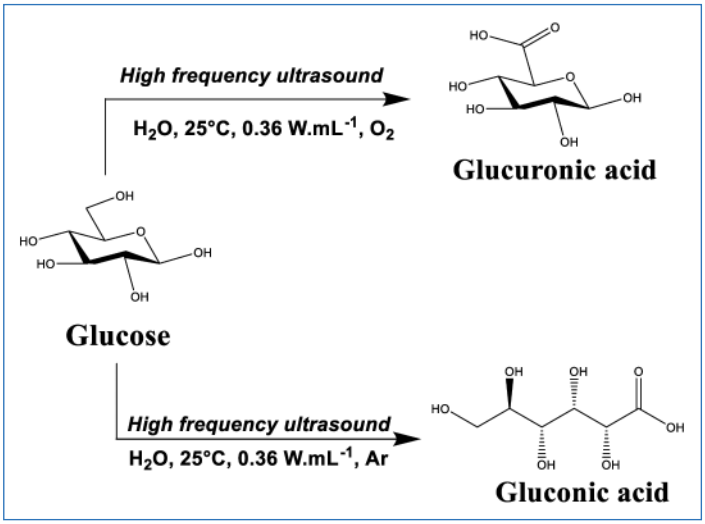

Figure 3 - Sonochemically induced conversion of sugars to value-added products.

These examples vividly illustrate how reactant concentrations can be adjusted to modulate sonochemical reactivity. Thanks to the extreme pressure and temperature conditions within cavitation bubbles, sonoluminescence spectroscopy has demonstrated that gaseous molecules with high bond dissociation energies, such as N_2, O_2, CO_2, and CH_4, can undergo cleavage inside these bubbles [25-27]. This cleavage leads to the formation of radicals and triggers sonochemical reactions. For instance, ultrasonic irradiation (355 kHz) of a mixture containing nitrogen, methane, water, and acetic acid has been shown to yield amino acids such as glycine, ethylglycine, and alanine [28-29]. Such cavitational syntheses open exciting avenues in the study of the origin of life, as evidenced by recent computational simulations showing that cavitational impacts on various gaseous mixtures can lead to the formation of prebiotic monomers like urea, glycolaldehyde, glyceraldehyde, cyanamide, and formamide [29]. A groundbreaking study by Pflieger in 2017, employing sonoluminescence spectroscopy, revealed that NH species can be formed within cavitation bubble interiors when an aqueous solution of NH_3 (0.17 wt. %) is subjected to 359 kHz ultrasound frequency [27].

Inspired by these findings, our research group recently investigated and demonstrated that cavitation bubbles, generated by ultrasonic irradiation of aqueous NH_3 at a high frequency (525 kHz), serve as micro-reactors for activating and converting NH_3 to NH species [30]. This conversion, achieved without the need for any catalyst, yields hydrazine at the bubble-liquid interface. Notably, the segregation of in-situ produced hydrazine in the bulk solution, maintained at approximately 30 °C, effectively prevents its thermal degradation – a challenge commonly encountered in current hydrazine production technologies. In essence, cavitation

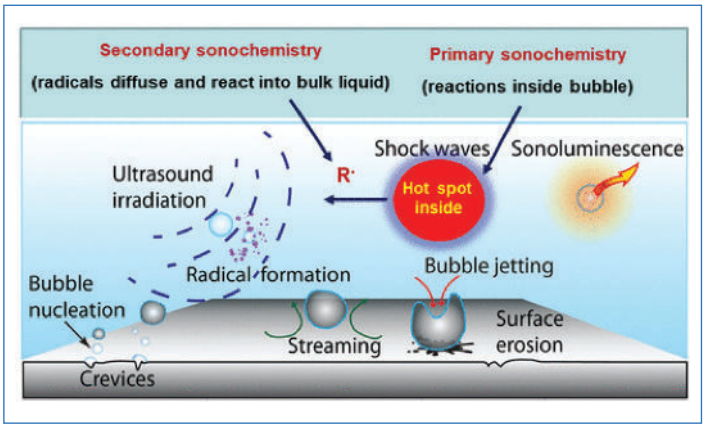

Figure 4 - Cavitation bubble nucleation on solid surfaces.

bubbles, propelled into action by ultrasound, emerge as fascinating micro-reactors with the potential to revolutionize chemical processes, enhance our understanding of the origins of life, and provide innovative solutions to long-standing challenges in chemical synthesis and production.

Sonocatalysis: Sound-assisted catalytic reactions

While homogeneous cavitation holds great promise for intensifying chemical reactions and altering reaction mechanisms, it often demands exceptionally high-peak negative pressure thresholds (- 140 MPa) and acoustic power to initiate bubble nucleation and subsequent cavitation generation. This limitation stems from the need for homogeneous nucleation, which necessitates a substantial amount of energy. To overcome this challenge, an ingenious approach involves the introduction of a solid materials (*figure 4*).

This strategy serves to facilitate bubble nucleation on solid surfaces, reducing the surface energy required to initiate bubble formation and, consequently, allowing for more precise control over the selectivity of radical reactions induced by ultrasound irradiation. In stark contrast to homogeneous solutions, the formation of cavitation bubbles in a heterogeneous solution takes place primarily on the surfaces of solid particles due to heterogeneous bubble nucleation. This physical phenomenon has emerged as a crucial element in sonochemistry, offering the potential for significant enhancements in the selective transfer of in-situ produced radicals to the surface of a solid catalyst. This, in turn, enables superior control over reaction selectivity. Furthermore, the dispersion of the catalyst and reactants, as well as mass transfer, are markedly improved by physical effects such as turbulent flow and shock waves, resulting in enhanced reaction rates. To illustrate the transformative potential of this approach, consider the case of a CuO solid catalyst used for the oxidation of glucose under ultrasound irradiation at 550 kHz in an argon (Ar) gas atmosphere [31].

Here, a remarkable synergy between the non-noble metal oxide catalyst and high-frequency ultrasound was harnessed for glucose oxidation. While both CuO and high-frequency ultrasound individually possess the capability to oxidize glucose into gluconic acid, their combined application resulted in a profound shift in reaction selectivity. Glucuronic acid emerged as the dominant product, thanks to the efficient in-situ interactions between radicals and the CuO catalyst surface. Mechanistically, H• radicals generated through the sonolysis of water were entrapped by the surface lattice

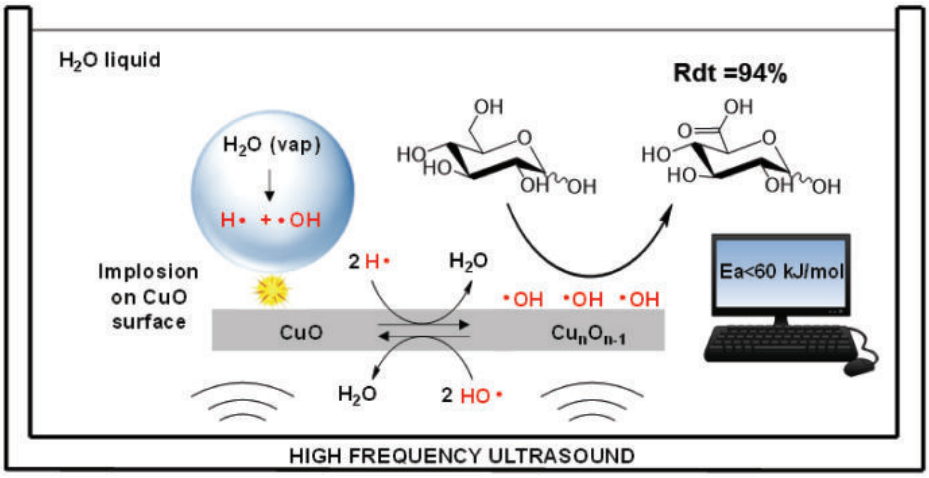

Figure 5 - Sonochemically-induced conversion of glucose to glucuronic acid over CuO catalyst.

oxygen of the CuO catalyst, leaving •OH radicals highly concentrated on the catalyst surface. This concentration rendered the ring-opening of glucose energetically unfavorable, favoring instead the selective oxidation of glucose to glucuronic acid (as depicted in *figure 5*).

In a similar vein, the oxidation of benzyl alcohol in the presence of a CuO catalyst under high-frequency ultrasound irradiation (576 kHz) in an argon atmosphere led to the formation of phenol via a demethylenation mechanism facilitated by the synergistic effect of the CuO catalyst and ultrasound irradiation [32]. Mechanistically, •OH radicals formed in situ through the sonolysis of water were captured on the surface of the CuO catalyst. This surface interaction sequentially activated OH and C-H bonds in benzyl alcohol on the catalyst surface, resulting in the formation of adsorbed benzaldehyde as an intermediate. Subsequently, benzaldehyde underwent C-C cleavage to form the phenyl ring, which was then hydroxylated to yield phenol.

Summarily, the marriage of solid catalysts and ultrasound irradiation brings forth a transformative synergy, enabling the precise control of reaction selectivity and the acceleration of reaction rates. This collaborative approach holds immense promise for advancing the field of sonochemistry and facilitating the design of innovative and efficient chemical processes.

Perspective

These illustrative examples underscore the remarkable potential of ultrasound technology to revolutionize innovative approaches in the fields of chemistry and catalysis, particularly on an industrial scale. However, understanding the underlying principles of ultrasound generation and propagation is crucial to harness its full capabilities. Ultrasound waves are generated by applying an oscillating electrical charge to piezoelectric materials. These materials convert the electrical signal into mechanical vibrations, which are then transmitted through the piezoelectric material into the surrounding medium, propagating the ultrasound wave. The field of sound transmitted from a transducer can be divided into two distinct regions, known as the near field and the far field. The near field refers to the region close to the transducer beam, while the far field extends beyond this point. In the far field, the acoustic intensity gradually diminishes until it eventually reaches zero. The length of the near field in a given transducer setup determines the maximum depth (referred to as "N") of the natural focus of the transducer. This depth is determined by the following equation:

$$N = \frac{D^2}{4\lambda} = \frac{fD^2}{4c}$$

where D is the transducer diameter, f is the transducer frequency, λ is the wavelength and c is the speed of sound in the medium.

According to this equation, the natural focal distance of an unfocused ultrasound transducer is directly proportional to both the transducer's diameter and its frequency. Consequently, it might seem logical that achieving a large focal distance for industrial applications, which ensures effective acoustic intensities at low frequencies, would require the use of large transducers. However, in practice, deploying such large transducers can often be impractical and costly. This limitation is what makes the utilization of high-frequency ultrasound an attractive choice when addressing scalability concerns in industrial ultrasonic applications. High-frequency ultrasound can provide the necessary intensity for various chemical effects while using more compact transducers. However, it's important to strike a delicate balance between the choice of frequency within the range of 100 kHz to 1 MHz for high-frequency ultrasounds and the dimensions of the transducer. This balance is essential to maximize the chemical effects induced during the collapse of cavitation bubbles, ensuring that industrial processes benefit from the advantages of ultrasound technology without compromising practicality and cost-effectiveness.

Even as we delve deeper into the possibilities of harnessing cavitation in chemical reactions, a formidable challenge continues to loom large on the horizon: the substantial energy requirements associated with nucleating cavitation bubbles within pristine reaction media. This issue poses a critical concern, not only in terms of energy efficiency but also in optimizing productivity per unit of input energy. To address this challenge head-on, my recent receipt of an ERC Starting Grant for the "ConCASM" project ("Controlling Cavitation for the Activation of Small Molecules") marks an exciting milestone. The central question driving this scientific endeavor is: How can we effectively bypass the demanding energy thresholds inherent in homogeneous solutions and exert precise control over cavitation, ensuring that it occurs in close proximity to the catalyst? The ultimate goal is to

enhance our ability to dictate the selectivity of chemical reactions. The ConCASM project represents a pioneering effort to pioneer the frontiers of energy-efficient ultrasound-assisted catalytic reactions. By tackling the fundamental question of energy-efficient cavitation control, we aim to pave the way for groundbreaking insights and novel methodologies that will transform the landscape of chemical synthesis and catalysis. The project's vision is not only to illuminate the path toward energy-efficient chemical processes but also to unlock the true potential of ultrasound as a catalyst and catalyst activator. Through innovative research and experimentation, we seek to unravel the mysteries of cavitation and harness its power in ways that were previously inconceivable. Our hope is that the outcomes of this ambitious undertaking will significantly contribute to a more sustainable and efficient future for chemical reactions and industrial processes alike.

Prince Nana Amaniampong is grateful to the CNRS, Research Federation INCREASE, the University of Poitiers, and the Region Nouvelle Aquitaine. The ANR JCJC AminoSound Project ID ANR-20-CE07-0006 is acknowledged for financial support.

[1] K.S. Suslick, The chemical effects of ultrasound, *Scientific American*, **1989**, *260(2)*, p. 80-86.
[2] E.V. Skorb *et al.*, Sonochemical formation of metal sponges, *Nanoscale*, **2011**, *3(3)*, p. 985-993.
[3] E.V. Skorb, D.V. Andreeva, H. Möhwald, Generation of a porous luminescent structure through ultrasonically induced pathways of silicon modification, *Angew. Chem.*, **2012**, *124(21)*, p. 5228-32.
[4] X. Su, R.G. Thomas, L.D. Bharatula, J.J. Kwan, Remote targeted implantation of sound-sensitive biodegradable multi-cavity microparticles with focused ultrasound, *Sci. Rep.*, **2019**, *9(1)*, 9349.
[5] J.J. Kwan *et al.*, Ultrasound-propelled nanocups for drug delivery, *Small*, **2015**, *11(39)*, p. 5305-14.
[6] J. Kwan *et al.*, Ultrahigh-speed dynamics of micrometer-scale inertial cavitation from nanoparticles, *Phys. Rev. Appl.*, **2016**, *6(4)*, 044004.
[7] R.G. Thomas, U.S. Jonnalagadda, J.J. Kwan, Biomedical applications for gas-stabilizing solid cavitation agents, *Langmuir*, **2019**, *35(31)*, p. 10106-115.
[8] T.M. Porter, Tailoring cavitation nuclei for biomedical applications, *J. Acoust. Soc. Am.*, **2018**, *143(3)*, 1861.
[9] C.D. Arvanitis, M. Bazan-Peregrino, B. Rifai, L.W. Seymour, C.C. Coussios, Cavitation-enhanced extravasation for drug delivery, *Ultrasound Med. Biol.*, **2011,** *37(11)*, p. 1838-52.
[10] T. Leighton, *The acoustic bubble*, Academic press, **2012**.
[11] K.S. Suslick, The chemistry of ultrasound, *The yearbook of science and the future*, **1994**, p. 138.
[12] K.S. Suslick, Sonochemistry, *Science*, **1990**, *247(4949)*, p. 1439-45.
[13] K.S. Suslick, N.C. Eddingsaas, D.J. Flannigan, S.D. Hopkins, H. Xu, Extreme conditions during multibubble cavitation: Sonoluminescence as a spectroscopic probe. *Ultrason. Sonochem.*, **2011**, *18(4)*, p. 842-846.
[14] K.S. Suslick, D.A. Hammerton, R.E. Cline, Sonochemical hot spot, *J. Am. Chem. Soc.*, **1986**, *108(18)*, p. 5641-42.
[15] K.S. Suslick, J.W. Goodale, P.F. Schubert, H.H. Wang, Sonochemistry and sonocatalysis of metal carbonyls, *J. Am. Chem. Soc.*, **1983**, *105(18)*, p. 5781-85.
[16] K.S. Suslick, D.J. Flannigan, Inside a collapsing bubble: sonoluminescence and the conditions during cavitation, *Ann.. Rev. Phys. Chem.*, **2008**, *59*, p. 659-683.
[17] M. Ashokkumar, The characterization of acoustic cavitation bubbles - an overview, *Ultrason. Sonochem.*, **2011**, *18(4)*, p. 864-872.
[18] A. Brotchie, F. Grieser, M. Ashokkumar, Effect of power and frequency on bubble-size distributions in acoustic cavitation, *Phys. Rev. Lett.*, **2009**, *102(8)*, 084302.
[19] D. Peters, Ultrasound in materials chemistry, *J. Mater. Chem.*, **1996**, *6(10)*, p. 1605-18.
[20] L.H. Thompson, L. Doraiswamy, Sonochemistry: science and engineering, *Ind. Eng. Chem. Res.*, **1999**, *38(4)*, p. 1215-49.
[21] D.G. Shchukin, E. Skorb, V. Belova, H. Möhwald, Ultrasonic cavitation at solid surfaces, *Adv. Mater.*, **2011**, *23(17)*, p. 1922-34.
[22] P.N. Amaniampong *et al.*, Catalyst-free synthesis of alkylpolyglycosides induced by high-frequency ultrasound, *ChemSusChem*, **2018**, *11(16)*, p. 2673-76.
[23] E.J. Hart, A. Henglein, Sonochemistry of aqueous solutions: hydrogen-oxygen combustion in cavitation bubbles, *J. Phys. Chem.*, **1987**, *91(13)*, p. 3654-56.
[24] P.N. Amaniampong *et al.*, Selective and catalyst-free oxidation of D-glucose to D-glucuronic acid induced by high-frequency ultrasound, *Sci. Rep.*, **2017**, *7*, 40650.
[25] M.P. Brenner, S. Hilgenfeldt, D. Lohse, Single-bubble sonoluminescence, *Rev. Mod. Phys.*, **2002**, *74(2)*, 425.
[26] L.A. Crum, R.A. Roy, Sonoluminescence, *Science*, **1994**, *266(5183)*, p. 233-234.
[27] R. Pflieger, T. Ouerhani, T. Belmonte, S.I. Nikitenko, Use of NH (A 3 Π–X 3 Σ–) sonoluminescence for diagnostics of nonequilibrium plasma produced by multibubble cavitation, *Phys. Chem. Chem. Phys.*, **2017**, *19(38)*, p. 26272-279.
[28] A. Sokolskaya, Glycine and alanine synthesis from formaldehyde and hydroxylamine in the field of ultrasound waves, *Orig. Life*, **1976**, *7(3)*, p. 183-185.
[29] N.-H. Kalson, D. Furman, Y. Zeiri, Cavitation-induced synthesis of biogenic molecules on primordial Earth, *ACS Cent. Sci.*, **2017**, *3(9)*, p. 1041-49.
[30] A. Humblot *et al.*, Conversion of ammonia to hydrazine induced by high-frequency ultrasound, *Angew. Chem.*, **2021,** *133(48)*, p. 25434-438.
[31] P.N. Amaniampong *et al.*, Synergistic effect of high-frequency ultrasound with cupric oxide catalyst resulting in a selectivity switch in glucose oxidation under argon, *J. Am. Chem. Soc.*, **2019**, *141(37)*, p. 14772-779.
[32] T. Bahry *et al.*, Water-assisted sonochemically-induced demethylenation of benzyl alcohol to phenol over a structurally stable cupric oxide catalyst, *Catal. Sci. Technol.*, **2023**, *13(10)*, p. 2982-93.

Prince Nana AMANIAMPONG,
CNRS Researcher, Institut de Chimie des Milieux et Matériaux de Poitiers, Université de Poitiers, CNRS.

Prince N. AMANIAMPONG was awarded with the Young Researcher Award in 2022 by the Catalysis Division (DivCat) of the French Chemical Society.

* prince.nana.amaniampong@univ-poitiers.fr