A role for ultrasound in the fabrication of carbohydrate-supported nanomaterials

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Abstract

Nowadays, sonication is a well-known technique for the fabrication and surface modification of nanomaterials with various sizes, shapes, and chemical and physical properties. In addition to conducting catalyst-mediated chemical reactions and enhancing medicinal properties, such as antibacterial and antifungal activities, nanoparticles made from biodegradable and biocompatible carbohydrate coatings and glycosidic frameworks offer exciting opportunities for the development of biomaterials, optical sensors, packaging materials, agricultural products, and food. This review article discusses the synthesis of carbohydrate-coated nanoparticles by ultrasound radiation as well as the many applications of these nanoparticles.

Graphical abstract

Keywords Carbohydrate · Metal · Nanoparticles · Ultrasound · Biodegradable · Fabrication

Introduction

In 1927, Loomis was the first to apply ultrasound (100–500 kHz) [1] for the hydrolysis of dimethyl sulfate (iodine clock reaction). Since then, ultrasound has been used to accelerate the reaction rates of a wide variety of chemical reactions, resulting in the blossoming of a new subdiscipline called ‘sonochemistry’. In addition to being applied in sonochemical reactions, ultrasound energy has been used for homogenization (dispersing and de-agglomeration,

emulsifying, wet-milling, and grinding), disintegration (cell extraction and hot water disinfection), welding of thermoplastics, degradation of used plastics, degassing or cleaning of unwanted materials, medical imaging (2–10 MHz), physiotherapy, dentistry, and sound navigation and ranging (SONAR) techniques. Generally, sonochemistry operates in the region of 20 kHz–1 MHz. This high-energy-based technology disperses the reagents and initiates as well as accelerates chemical reactions through collisions. Ultrasound-mediated chemistry is governed by different parameters, including the amplitude and frequency of the applied sound field, temperature, surface tension, vapor pressure, gas content and nuclei density of the solution, and vessel and probe geometry. However, sonochemical reactions are independent of acidity, basicity, and dipole moment. Ultrasound low energies (20 kHz–500 MHz) are not capable of

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directly altering electronic, vibrational, or rotational molecular states; however, they can indirectly affect chemical reactions via a phenomenon called cavitation, which produces enough energy to alter vibrational and rotational molecular states. The formation of acoustic cavitations or microbubbles, which grow and collapse continuously, results in the generation of temperatures of 5000–8000 K and pressures greater than 10,000 atm on a nanosecond timescale within the vapor phase of the bubble, followed by rapid cooling at a rate of 109 K/s (Fig. 1) [2, 3]. Due to the generation of local heating combined with extraordinarily rapid cooling, this method provides a unique means of controlling chemical reactions, such as increasing the rate and yield of reactions, improving the reactivity of reagents or catalysts, switching off reaction pathways, improving the activity of phase-transfer catalysts, blocking phase-transfer catalysts, activating metals and solids, and initiating radical polymerization. Thus, this unique energy-saving and temperature-efficient mechanism offers a means of providing compounds, even in an aqueous solution, with higher rates, shortening reaction times and improved selectivity of reactions.

Overview of sonication in the nanoworld

For the fabrication of nanomaterials [4–7], sonochemistry is a highly useful and promising technique, involving sonic waves, their properties, and their effects on chemical, physical, and biological systems. Generally, the solution of the bulk material contains large aggregates of molecules, and those aggregates are broken into smaller structures by the ultrasonic radiation. To modulate and equip a hybrid functional metal oxide, such as silver, ferrite, iron oxide, and gold, with various properties, sonochemistry plays an important role [8–10]. Sonication techniques are user-friendly and induce the ultrahigh surface area to form monodisperse organic/inorganic hybrid materials containing particles of nanometer size [11]. It is an excellent method for coating the surfaces of various particles and for forming a smooth layer of the coated materials, such as LiMn_2O_4 spinel, which

is coated sonochemically with MgO [12]. In addition, ultrasound helps to synthesize nanostructured noble metals, e.g., Au, Ag, Pt, and Pd. Metal nanoparticles are used for magnetic, optical, electrical, and catalytic applications in a variety of fields [13–18], and the functionalities of nanoparticles differ significantly from the corresponding bulk materials [19–22].

Application of nanotechnology in the development of new drug delivery techniques [23] might overcome many difficulties in drug delivery because of the unique and well-defined physicochemical properties of nanoparticles compared with their bulk counterparts, such as ultra-small and controllable quantum-size effects, shape characteristics, surface to volume ratio [24], functionalizable structure, surface charge, and unique electrodynamical interactions [25–28]. Organic or organic–inorganic hybrid nanoparticles [29] offer significant advantages as these particles are biodegradable, biocompatible, bioavailable, and easily modifiable [30–32]. Ultrasound-mediated fabrication of nanomaterials also helps to modify surface properties, to control the size and dispersion of nanoparticles, and to decrease the agglomeration tendency of nanoparticles while improving the catalytic, optical, electrical, and magnetic properties. High-intensity ultrasound is a simple and versatile tool for synthesizing nanostructured materials and offers possibilities that are unavailable in conventional methods.

Role of carbohydrates in biology, medicine, and organic synthesis

Carbohydrates are the most abundant organic molecules in all forms of life and are essential for biological recognition processes and the structural framework of cells and tissues. For example, the carbohydrates on the cell surface can serve as receptors for other cells, pathogens, toxins, or other molecules. They are also implicated in the development of several diseases, such as aberrant glycosylation in the cell membranes of tumor cells [33]. In addition, oligosaccharides, glycoproteins, glycolipids, and other glycoconjugates

Fig. 1 The acoustic cavitation phenomenon that occurs under ultrasonic radiation

are often key elements in signaling processes, cell–cell communication, pathogen defense, and molecular and cellular targeting [34]. Carbohydrate-based materials have a notable role in the development of different therapeutic agents, including anticoagulants such as low-molecular-weight heparins and fondaparinux [35, 36], and α -glycosidase inhibitors [37, 38]. Monosaccharides acting as chiral pools for the asymmetric synthesis of natural products, pharmaceutically active ingredients, and building blocks [39, 40] are well known in pharmacy, industry, and academics [41].

The structural complexity of large and densely functionalized carbohydrates, such as oligosaccharides and polysaccharides, renders their chemical syntheses difficult due to the stereoselective glycosylation of two or more sugars. In addition, the construction of orthogonally protected monosaccharides and the control of chemistry at the anomeric center of monosaccharides for different oligosaccharide syntheses need special consideration and attention [42–45].

Many nanoparticle-based strategies, including the formation of liposomes, niosomes, dendrimers, bio-polymers with carbohydrate coatings, and glycosidic frameworks, are reported to offer exciting opportunities not only for synthetic organic chemistry but also for the development of biomaterials and new drug delivery methods [46]. For biomedical applications, lactose-coated gold nanoparticles have been shown to be potential anti-adhesive tools in *in vivo* tumoral metastasis progression [47]. The poly(*c*-benzyl L-glutamate) or poly(lactic acid) nanoparticles containing carbohydrate-carrying polystyrene amphiphilic polymers serve as both an emulsifier and a surface coating for delivering liver-specific targeting drugs [48]. Nanoparticles coated with carbohydrate-carrying polymers, [49], e.g., chitosan/poly- γ -glutamic acid (γ -PGA) nanoparticles, and incorporated in the alginate–gelatin hydrogels are an efficient carrier for antibiotic drugs (amoxicillin) [50].

Effects of ultrasound on carbohydrates

It is noteworthy that like pH, enzymes, and temperature, ultrasound is an external stimulus in the preparation of nanoparticles [51, 52]. The most challenging synthesis is the fabrication of nanoparticles using environmentally benign approaches [53–55]. The literature shows that the application of ultrasound for the synthesis and surface modification of carbohydrate and non-carbohydrate nanomaterials is classified as an external-stimulus-triggered and ‘green’ chemical reaction. In our previous review articles, the chemical synthesis based on carbohydrates using ultrasound irradiation has been thoroughly discussed [56]. In carbohydrate chemistry, much effort is required to develop effective strategies for inter-conversion and oligomerization of monosaccharide building blocks, whose assembly is challenging due

to severe difficulties caused by orthogonal protection and deprotection. In addition, the use of monosaccharides in the complete synthesis of a wide range of complex natural products, biologically important molecules, building blocks, and glycoconjugates requires multiple steps with efficient and proper methods. Dissatisfaction with long reaction times, use of expensive catalysts, formation of by-products, sensitivity to reactants and products, less stereoselectivity, and a limited scope for different substrates in classical methods have all inspired the development of sonication-mediated carbohydrate chemistry, which is a highly promising and nonconventional form of chemistry. It is well known that ultrasound-induced energy provides better yields, shortening of reaction times, improved chemo-, regio-, and stereoselectivities for glycoside and oligosaccharide synthesis, and compatibility with different protection–deprotection and modification reactions of functional groups. Several oligosaccharides such as chitosan, pullulan, and starch are crucial in the formation of coated nanoparticles.

Ultrasound irradiation for the synthesis and application of carbohydrate-coated nanoparticles

Chitosan is a polymer of poly(*D*-glucosamine) derived from chitin deacetylation (poly [*N*-acetyl-*D*-glucosamine]), with antimicrobial, anti-inflammatory, antioxidant, antitumor, tissue regeneration (especially skin and bones), non-toxic, inexpensive, biocompatible, and biodegradable properties.

Generally, the synthesis of chitosan-based magnetite results in two types of structures: a single magnetite core surrounded by a chitosan layer, and/or magnetite ‘multi-cores dispersed in a chitosan matrix [57, 58]. Chitosan contains both primary and secondary hydroxy groups and amino groups. Therefore, it can activate the electrophilic and nucleophilic compounds by hydrogen bonding and lone pairs of O- and N-atoms.

Recently, Safari and Javadian [59] have synthesized Fe₃O₄–chitosan nanoparticles by a co-precipitation method under ultrasound irradiation in two different steps. First, the magnetic nanoparticles were primed by chemical co-precipitation, followed by functionalization with chitosan under ultrasonic irradiation.

In this procedure, FeCl₃·6H₂O and FeCl₂·4H₂O were dissolved in deionized water, followed by addition of NH₄OH solution at 80 °C under N₂ atmosphere. The black magnetic Fe₃O₄ nanoparticles were isolated in the magnetic field and washed three times with distilled water. Subsequently, the Fe₃O₄ nanoparticles were dispersed in distilled water under ultrasound irradiation, and chitosan in 2.0 wt % acetic acid solution was slowly added under vigorous stirring at 50 °C for 1 h. The modified Fe₃O₄–chitosan nanoparticles were

Scheme 1 Preparation of Fe_3O_4 -chitosan nanoparticles

Fig. 2 SEM images of (a) pure Fe_3O_4 and (b) chitosan-coated Fe_3O_4

recovered by magnetic decantation and washed with CH_2Cl_2 . Finally, Fe_3O_4 -chitosan nanoparticles were dried at 60°C (Scheme 1).

The particles were characterized by scanning electron microscope (SEM) images, which revealed that the diameter of Fe_3O_4 -chitosan nanoparticles became 20 nm bigger than that of pure Fe_3O_4 nanoparticles (Fig. 2a, b). Thus, the characterization data show that the coating process changes the size of particles.

Scheme 2 Application of Fe_3O_4 -chitosan-coated nanoparticles

Table 1 Selection of catalyst for the synthesis of 2-amino-4H-chromenes

Entry	Catalyst	Time (min)	Yield (%)
1	None	30	82
2	Fe_3O_4	24	98
3	Chitosan	21	97
4	Fe_3O_4 -chitosan	20	99

Table 2 Effect of ultrasound for the synthesis of 2-amino-4H-chromenes using Fe_3O_4 -chitosan

Entry	Catalyst (g)	Without sonication (reflux)/yield (%) time (min)	With sonication (50°C), yield (%) /time (min)
1	0	71/65	82/30
2	0.05	78/47	87/25
3	0.10	85/49	88/23
4	0.15	90/31	99/20
5	0.20	90/31	99/20

After the coated Fe_3O_4 -chitosan nanoparticles were synthesized, they were used as a catalyst for the one-pot multicomponent reaction of aldehyde, malononitrile, and resorcinol in water under reflux conditions to obtain 2-amino-4H-chromene derivatives. In ultrasound chemistry (Scheme 2), compared with traditional chemistry, the presence of Fe_3O_4 -chitosan afforded a higher yield in products and shorter reaction times; and even chitosan-coated nanoparticles provided better results than other catalysts (Tables 1 and 2).

To create chitosan-based nanoparticles, Freire et al. used the ultrasound-assisted production of chitosan-magnetite nanocomposites as a modified electrode sensor [60]. The authors also discussed a rapid ultrasonic-assisted in situ route to crop magnetic Fe_3O_4 -chitosan nanocomposites, in which the chemical co-precipitation and functionalization occur together. This technique curtails the oxidation of magnetite and drastically decreases the synthesis time from several minutes or hours for the conventional co-precipitation method down to a few minutes (~ 2 min) under sonication. The process of sonication also minimizes the probable oxidation of magnetite. The sensor of hybrid materials based on chitosan and Fe_3O_4 was made for the detection of glucose and urea as well as for the diagnosis of diseases.

The procedure for the synthesis of chitosan/ Fe_3O_4 nanoparticles involves sonication of a mixture of chitosan, dissolved in acetic acid 1% (v/v) and Fe solution 0.33 mol ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ($\text{Fe}^{3+}:\text{Fe}^{2+}$, 2:1 molar ratio) creating the chitosan/ Fe_3O_4 nanoparticles. The cross-linker was glutaraldehyde, which is useful for stabilization purposes, forming Schiff base linkages and so providing stability to the final nanocomposites chitosan/ Fe_3O_4 nanoparticles (Scheme 3). The sonication waves cause a homogeneous dispersion with an ultrahigh surface area between chitosan and the iron ions. Transmission electron microscopy (TEM) images confirm that ChM-NPs possess an average diameter in the range of 10–25 nm, in agreement with XRPD data (crystallite size, 8–13 nm)

Scheme 3 Preparation of chitosan/ Fe_3O_4 nanoparticles

Fig. 3 TEM images of ChMNs

and magnetic measurements (11.3–11.9 nm) (Fig. 3). The magnetization study describes that the absence of hysteresis loops (the coercivity and remanence values were zero) can be attributed to superparamagnetic behavior. The saturation magnetization (M_s) for samples of Fe_3O_4 , ChM 0.01, ChM 0.05, or ChM 0.1, where the numbers 0.1, 0.05 and 0.01 represent the different amounts of chitosan in g, is found to be 56.78, 54.35, 49.48, and 36.0 emu g^{-1} , respectively. The diamagnetic effect of chitosan coating decreases the M_s values of chitosan/ Fe_3O_4 nanocomposite.

Sonochemical synthesis of silver nanoparticles coated with starch was reported by Brajesh et al. [61]. The optimal reaction conditions include sonication of a mixture of 10 mL of 1 mM AgNO_3 , 25 mg starch, at pH 11, for 20 min at room temperature. The solution of colloidal silver nanoparticles exhibited an increase in absorption from 420 to 440 nm,

Table 3 Average size of sonochemical starched AgNPs at different pH for 20-min sonication

$\text{AgNO}_3/\text{starch}$ (1 mM)	pH	UV–Vis	Average particle size
10 mL/25 mg	5.5	560	0.1811
10 mL/25 mg	7.0	500	0.1424
10 mL/25 mg	8.0	440	0.2757
10 mL/25 mg	8.5	480	0.2585
10 mL/25 mg	9.0	460	0.2192
10 mL/25 mg	10.0	440	0.1876
10 mL/25 mg	11.0	420	0.0857
10 mL/30 mg	11.0	440	0.0978

with an increase in starch quantity. TEM and DLS indicated the building of spherical, polydispersed, and amorphous silver nanoparticles of diameters ranging from 23 to 97 nm, with a mean particle size of 45.6 nm (Table 3). Selected area electron diffraction pattern (SAED) analysis suggests a partially crystalline and amorphous nature of the silver nanoparticles. Figure 4 shows DLS and Fig. 5 shows TEM

Fig. 4 DLS image of AgNPs synthesized under ultrasonic irradiation

Scheme 4 Synthesis of 2-(2-chlorophenyl)-1H-benzimidazole

and SAED images of AgNPs: (1) 25 mg starch and (2) 30 mg starch under ultrasonic irradiation for 20 min, after 4 days.

These colloidal nanoparticles were used as a catalyst for the synthesis of 2-(2-chlorophenyl)-1H-benzimidazole (Scheme 4).

It was also observed that polyurethane-functionalized starch nanoparticles produced good results in the purification of biodiesel with enhanced adsorption properties [62].

Hospital-acquired (nosocomial) infections and multidrug-resistant bacteria are a major concern for healthcare systems worldwide. Because no doses of antibacterial drugs are high enough against these bacteria, the only solution is to transform hospitals into pathogen-free and patient-safe environments through highly effective and durable antibacterial textiles. In this respect, Marc Salat reported the production of antimicrobial cotton textile coated with ZnO nanoparticles, which were, under ultrasound, embedded in an in situ enzymatically generated bioadhesive [63]. To produce biocompatible fabrics with durable antibacterial properties, the author developed a single-step sono-enzymatic process for the coating of cotton medical textiles with antibacterial ZnO nanoparticles (NPs) and a bio-based adhesive generated by the enzymatic cross-linking of GA gallic acid (GA).

Fig. 5 TEM and SAED images of AgNPs: (a) 25 mg starch and (b) 30 mg starch

The mixture containing an aqueous solution of ZnO NPs (1 mM), GA (0.3% w/v), 150 μ L laccase product, and the cotton sample (5×10 cm, 0.7 ± 0.05 g) was subjected to ultrasound for 30 min. Under hospital laundry regimes, the ZnO NP–GA-coated fabrics maintained an antibacterial efficacy of above 60% after 60 washing cycles at 75 °C.

Figure 6 shows the HRSEM micrographs of cotton fabrics coated with ZnO NPs and GA in the presence of active laccase (1) before and (2) after ten washing cycles and in the presence of denatured laccase (3) before and (4) after ten washing cycles. These results confirmed that the sono-enzymatic process equipped the fabrics with durable antibacterial properties.

Saha et al. [64] synthesized carbohydrate polymer–silver nanoparticles (AgNPs) through an ultrasound-assisted, green process using a unique combination of a biomolecule (tyrosine) and starch. The synthesis of starch-stabilized silver nanoparticle was carried out using different amounts of starch in hot Millipore water, followed by the addition, under sonication, of a AgNO_3 (different concentrations) solution to the starch solution. After 5 min, different amounts of 10^{-3} M alkaline tyrosine were added to this mixture and subjected to sonication for 30 min to obtain nanoparticles.

The size distributions and stability of AgNPs were determined by dynamic light scattering DLS, which revealed a narrow hydrodynamic size distribution and a negative zeta potential (9–16 mV), indicating moderate stability and

negligible toxicity of biopolymer-generated AgNPs. The HRTEM images (Fig. 7) show that the nanoparticles were spherical in shape and had uniform sizes. The SAED pattern (111, 200, 220, and 311 planes) suggested face-centered cubic structures, and the weight percentage and atom percentage from EDX spectra (carbon: 9.56% and 42.14%; oxygen: 0.46% and 1.52%; and silver: 54.40% and 26.70%) revealed that AgNPs were capped by starch. These carbohydrate-polymer-coated AgNPs (AgNP2–13) operate through reactive oxygen species (ROS) and show filaricidal (against *Setaria cervi*) and mosquitocidal (against second and fourth instar larvae of *Culex quinquefasciatus*) activities, with the AgNP10 showing the most effective larvicidal properties.

Another interesting example is the synthesis, by Jung et al., of antimicrobial packaging paper coated by chitosan–starch–silver nanoparticles (Chet–St–AgNPs) [65]. Chitosan was mixed in the St–AgNP solution with different ratios of 9:1, 8:2, 7:3, and 5:5 by weight. The authors observed that the properties of the coated papers were strongly dependent on the ratio of Cht to St–AgNPs. The Cht:St–AgNP-coated paper prepared with a ratio of 9:1 had excellent mechanical properties and a good resistance against water and oil.

The procedure involves the sonication of starch and AgNO_3 in deionized water for 60 min at 90 °C. The UV–Vis spectrum of the synthesized St–AgNP solution showed an absorption peak at 420 nm, which is due to the surface

Fig. 6 HRSEM micrographs of cotton fabrics coated with ZnO NPs and GA

Fig. 7 HRTEM images of (a) AgNP10, (b) AgNP11 (b), and (c) AgNP12

Fig. 8 (a) UV-Vis spectrum and (b) TEM image of synthesized St-AgNPs

Table 4 The rate constants of HEC degradation with various nanoparticles

Process	$k \times 1010$ ($\text{mol}^{1.8} \text{L}^{-1.8} \text{min}^{-1}$)
US	1.44
US + Fe_3O_4	3.90
US + Rutile	2.63
US + ZnO	2.27
US + Anatase	2.17
US + MMT	1.63

plasmon resonance of AgNPs (Fig. 8a). TEM analysis showed a spherical morphology, with a particle size ranging from 5 to 20 nm and an average value of 7 nm (Fig. 8b). The Cht:St-AgNP-coated papers showed a remarkable enhancement in mechanical strength, oil and water resistance, and antibacterial and antifungal activities, which can make these papers a potential candidate for antimicrobial packaging material.

The degradation of 2-hydroxyethyl cellulose (HEC) by means of ultrasound irradiation and its combination with heterogeneous catalysts such as TiO_2 (rutile and anatase), montmorillonite clay (MMT), ZnO, and Fe_3O_4 nanoparticles were investigated by Taghizadeh and co-workers [66]. Degradation of HEC was studied through FTIR, XRD, and SEM techniques; the kinetics of degradation was studied by viscometry; and the reduction in molecular weight (Mw) of the polymer was investigated by gel permeation chromatography (GPC) analysis. It was found that the sonocatalytic degradation of HEC was remarkably higher than that of sonolytic degradation (Table 4). The different nanoparticles were mixed with HEC solution and stirred for 20 min to make a good dispersion of catalyst, after which the solution was subjected to ultrasound irradiation. The best HEC

degradation was obtained when the Fe_3O_4 amount added was 0.4 g/L. HEC is useful as a thickening agent, protective colloid, binder, and stabilizer, as well as a suspending agent in pharmaceuticals, textiles, paper, coatings, adhesives, and emulsion polymerization.

SEM images of HEC–nanocatalysts after and before degradation (Fig. 9a) revealed that before ultrasonic radiation the polymer surface was almost smooth and without cavities, with nanoparticles well dispersed on the surface of the polymer. After degradation, cavities and cracks appeared on the surface of the polymer, depending on the catalyst used. MMT nanoparticles resulted in small cavities and cracks on

the surface of the polymer, as shown in Fig. 9e, whereas, the deeper cavities and cracks are produced in the presence of Fe_3O_4 (Fig. 9b). However, the presence of TiO_2 nanoparticles formed the cavities on the surface, which became coarser with time (Fig. 9c, d), whereas, ZnO nanoparticles show less compatibility with the polymer matrix (Fig. 9f).

Farris and co-workers [67] proposed that bio-nano-composite coating, based on natural montmorillonite ($\text{Na}^+ - \text{MMT}$) and pullulan (an exopolysaccharide of microbial origin), might be a good candidate for substituting synthetic polymers in oxygen barrier coatings with highly wettable surfaces. Ultrasound helps to fully exfoliate the platelets

Fig. 9 SEM of Rutile-HEC (a) before and after degradation, (b) Fe_3O_4 , (c) Anatase, (d) rutile, (e) MMT, (f) ZnO

during the water dispersion phase of the coating process; exfoliation is a pivotal factor in the performance of the oxygen barrier of the final material even at high relative humidity (RH) [oxygen permeability coefficients $\sim 1.43 \pm 0.39$ and $258.05 \pm 13.78 \text{ mL} \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot (24 \text{ h})^{-1} \cdot \text{atm}^{-1}$ at 23°C and 0% RH and 70% RH, respectively]. The morphology of the coatings revealed that clay lamellae were stacked on top of one another, and the electron microscopic analyses disclosed a peculiar cell-like arrangement of the platelets. The stacking of the clay lamellae and the cell-like array are responsible for the excellent oxygen barrier properties of the coating. The FESEM images (Fig. 10) show (a) the surface image of the coating at $5000\times$ magnification; (b) the cross-sectional overview at $2000\times$ magnification; (c) the exfoliated platelets “‘wrapped’ by pullulan at $50,000\times$ magnification, with four stacked layers within the frame; and (d) the cell-like

morphology at $25,000\times$ magnification, as highlighted by the circle.

Native starch (NS) extracted from the seeds of *pinhão* (*Araucaria angustifolia*) was modified by two methods: acid hydrolysis (AH) and ultrasound (US) [68]. In this study, three starch samples were subjected to spray drying and then characterized. Chemical composition and rheological characteristics were evaluated, and morphology was analyzed by scanning electron microscopy. The starch modified by US and AH attained nanometric size, with mean particle sizes of about 453 and 22 nm, respectively (Fig. 11). Aside from the modified starch reaching nanometric size, the three starch preparations were significantly different in four characteristics: starch and amylose contents, the percentage of syneresis, and colorimetric properties. The AH sample differed from the others in terms of solubility (more soluble), hygroscopicity (more hygroscopic), and paste clarity (more

Fig. 10 FE-SEM micrographs of the optimized pullulan nanocomposite coating

Fig. 11 SEM images of (a, b) native *pinhão* starch, and starch subjected to (c, d) acid hydrolysis or (e, f) ultrasound

translucent). Modified starch nanoparticles obtained by AH and US can be useful for the development of novel biocomposites with improved properties, and these biocomposites could be employed as coating materials or films.

A green sonochemical method was developed to create kappa carrageenan (κ -carrageenan)-capped silver [69] nanoparticles (AgNPs). κ -carrageenan is used as a gelling agent and texture improver for, among others, cottage cheese, toothpaste, air freshener gels, cosmetic creams, and shoe polish. It is a natural eco-friendly stabilizer and a reducing agent. Suspensions of 0.1 M AgNO_3 and κ -carrageenan (0.1, 0.15, 0.20, 0.25, and 0.3 wt %) were stirred for 1 h to obtain AgNO_3/κ -carrageenan and then exposed to intense ultrasonic irradiation (400 W, 24 kHz) for 90 min at room

temperature. The number of AgNPs increased with increasing κ -carrageenan concentration. The TEM image for the highest concentration of κ -carrageenan showed a distribution of AgNPs with an average particle size of approximately 4.21 nm, while the SEM image revealed the spherical shape of the AgNPs. UV–Vis spectroscopy visualized the formation of AgNPs by measuring surface plasmon resonance (SPR) bands. The SPR band characteristic of AgNPs was identified to be around 402–420 nm (Fig. 12a).

Vega-Baudrit and co-workers [70] described the sonochemical synthesis of silver nanoparticles coated with chitosan. In their approach, chitosan was treated with sodium hydroxide to neutralize chitosan's charge and to facilitate binding and reduction of silver ions. UV–Vis and

Fig. 12 Photograph of Ag⁺/κ-carrageenan and Ag/κ-carrageenan, and synthesis of AgNPs capped with κ-carrageenan

Fig. 13 3D image of silver nanoparticles by AFM

characterization by atomic force microscopy (AFM) showed that spherical nanoparticles were obtained of approximately 10 nm in diameter. The DLS results show that $(98 \pm 1) \%$ of the nanoparticles have a diameter ≤ 20 nm and that these particles represent $(87 \pm 5) \%$ of the total volume of particles in the solution with a polydispersity index of 0.532 (Fig. 13).

Rocktotpal et al. [71] used starch as a macromolecular matrix in the domain of green bio-nanotechnology for the biomimetically generation of starch-assisted spherical silver nanoparticles (av. diam., 5.4 nm), using sonication and the reductive potential of *M. ferrea* aqueous leaf extract. Ultrasonication was carried out with a standard sonotrode (tip diameter 3 mm) in a high-intensity ultrasonic processor (UP200S, 24 kHz, and an acoustic power density of 460 W/cm²). The complex of starch and *M. ferrea* aqueous leaf extract, which affects the morphology of nanoparticles, generated branched silver nanostructures upon aging for 24 days (~440 nm, along with the long axis with an average branch diameter of 11.5 nm). As shown in Fig. 14, the nanoparticles were characterized by TEM images (a) upon aging for 72 h (the inset shows the histogram of the particle size distribution), (b) upon aging for 24 days (branched silver nanostructure), and (c) under statistically optimized sonication parameters (the inset shows the histogram of the particle size distribution). The antimicrobial activity, as well as the anti-candidal activity, was more pronounced against Gram-positive bacteria (*S. aureus* and *B. subtilis*) than

against Gram-negative bacteria (*P. aeruginosa*). The MIC of the sonicated samples (6.32, 6.32, 25.3, and 12.65 μg/mL) was less effective compared with the MIC of the unsonicated sample (12.65, 25.3, 37.95, and 32.5 μg/mL) against *S. aureus*, *B. subtilis*, *P. aeruginosa*, and *C. albicans*, respectively.

Wei and co-workers [72] created starch-coated zinc oxide nanoparticles (ZnO NPs) to be used as antifungal agents. The zinc oxide nanoparticles are synthesized using starch as a stabilizing agent under ultrasound to make ZnO NPs-based starch paste. Transmission electron microscopy reveals that ZnO NPs (Fig. 15) synthesized under an optimal condition are highly dispersed and well-defined crystals with diameters of ca. 5 nm. The antifungal performance of ZnO NPs-based starch paste is evaluated in an environment with a high temperature and humidity, and is compared with traditional fungicides, alum, and pure terephthalic acid. Compared with paper mounted with pristine starch paste, the paper mounted with ZnO NP-based starch paste has superior antifungal properties, which are essential for protecting paper documents from mold growth.

Hee-Young et al. [73] described a synthesis of starch-based nanoparticles in which waxy maize starch was dispersed (14.7% solids) in aqueous sulfuric acid (3.16 M) and hydrolyzed up to 7 days at 40 °C with ultrasonic treatments at different vibration amplitudes (20 and 40%) and durations (30 and 60 min/day). The DLS indicates that ultrasonic treatment (20% amplitude, 30 min) increases the number of nanoparticles from 20 to 70%. For an ultrasonic treatment at 60% vibration amplitude for 3 min, all microparticles were completely transformed into nanoparticles. As shown in Fig. 16, the nanoparticles were characterized by FESEM: (a) with acid hydrolysis for 7 days and an ultrasonic treatment during the hydrolysis at 20% amplitude for 30 min; and (b) for 2 days and an ultrasonic treatment at 60% amplitude for 3.0 min with the re-dispersed suspension of precipitated hydrolyzates.

The effect of ultrasonic treatments at 40–90% amplitude (A) and for 2.0–3.0 min (T), as shown in Fig. 17 for light transmittance of re-dispersed suspensions of precipitated starch hydrolyzates (14.7% solids, 2 days of hydrolysis), was determined.

Later, the same group [74] published ultrasound-mediated starch hydrolyzates after the aqueous dispersion of starch hydrolyzates (750 W, 20 kHz) at approximately 4 °C. The recovery yield of starch hydrolyzates after acid hydrolysis was higher at low temperature and resistant to ultrasonic compared with that from high-temperature hydrolysis at 40 °C. As shown in Fig. 18, for the determination of particle size distribution, ultrasound (60% amplitude, 3 min duration) was employed on the starch hydrolyzates after various hydrolysis temperatures for 6 days.

Fig. 14 TEM image of starch-templated silver nanoparticles

Hasanvand [75] described the synthesis of vitamin D3-loaded nanoparticles using two types of starches with different amylose to amylopectin ratios (high-amylose corn and potato starches) and under sonication for different durations and at different temperatures (Fig. 19). VD3-loaded starch nanoparticles were visualized by FESEM (Fig. 20). Both high-amylose corn and potato starch nanocarriers (CSN and PSN) had a granular structure with particle sizes ranging from 32.04 to 99.2 nm and an encapsulation

efficiency ranging from 22.34 to 94.8%. The experiments showed that PNS had a larger size, a higher zeta potential, a higher encapsulation efficiency, a higher encapsulation load, and lower polydispersity index values in comparison with high-amylose corn starch nanoparticles.

Tukhani et al. [76] developed a heterogeneous Pd-catalyst system (Pd-MNPSS) using immobilization of Pd species (Pd^{II} and Pd^0) on starch-functionalized magnetic nanoparticles. The magnetic nanoparticles (MNPs) are coated with

Fig. 15 TEM photographs showing: (a) morphology of ZnO NPs and (b) morphology of ZnO NPs-based starch paste

Fig. 16 FE-SEM images of the optimally prepared starch nanoparticles

a silica layer ($\text{Fe}_3\text{O}_4@\text{SiO}_2$) as a stabilizer and functionalized with thionyl chloride (SOCl_2) to generate chlorosilyl groups on the surface of MNPs. The reaction of starch with chloro-functionalized MNPs leads to a magnetic reusable polyhydroxy-functionalized supported palladium on a magnetic nanoparticle–starch substrate (Pd–MNPSS) (Fig. 21).

The supported catalyst was used for C–C coupling in water for the Sonogashira and Heck reaction as shown in Scheme 5, with a 78–93% yield depending on substitution.

The general Heck reaction comprises the addition of a catalyst, phenylacetylene (1.2 mmol), and aryl halide (1.0 mmol), in H_2O (5.0 mL), in the presence of K_2CO_3 (2.0 mmol) under reflux.

Resistant starch (RS) is defined as starch and starch degradation products that are not absorbed in the small intestine of healthy individuals. RS is classified into subgroups, RS1–RS5, in which the RS plays a role as dietary fiber because the non-digestible starch may have health benefits

Fig. 17 Effect of ultrasonic treatments on light transmittance of re-dispersed suspensions of precipitated starch hydrolyzates

in humans. To develop resistant starch nanoparticles, Onbit [77] hydrolyzed waxy rice starch with acid for 10 days, and acid-hydrolyzed waxy rice starch (AHW) was cross linked with sodium trimetaphosphate. The RS nanoparticles were

Fig. 19 Mean values of three replications of turbidity of 0.16% (w/v) of different VD3-loaded nanoparticles and a pure nanoparticle solution

collected by freeze-drying (FD), freeze-drying after sonication (SFD), and ethanol dehydration after sonication (SE). The hydrolysis rate ranged from 44.62 to 49.43%, and AHW particle size decreased as hydrolysis time increased. The size of maximum peak particles, ~200 nm, was obtained from

Fig. 18 Effect of ultrasonication (60% amplitude, 3 min duration) on particle size distribution

Fig. 20 FE-SEM images of VD3-loaded nanoparticles: (a) CSN-0-10, (b) PSN-0-10, and (c) V-type amylose structure in VD-loaded high-amylose corn starch nanoparticle

a 10-day acid hydrolysis, but the particle size had a broad distribution. Cross-linking improved RS level and nanoparticle size distribution, and prevented water absorption in a colloid system with zeta potential (-40 mV). Sonication prevented the aggregation of starch particles, and freeze-drying helped to grind the particles finely. Figure 22 shows the starch that was acid hydrolyzed for 7–10 days (AHW-7, AHW-8, AHW-9, and AHW-10) and the cross-linked RS4 created with different drying methods (FD, SFD, and SE) from AHW-10 particles.

Ding and Yongbo [78] reported the properties of resistant starch type IV (chemically modified starch, RS4) prepared

after ultrasonication with the water-in-oil mini-emulsion cross-linking technique (214.57 W; sonication time, 114.73 min; and oil/water ratio, 10.54:1), applying three-factor Box–Behnken design and an optimization method. The nanoparticles reached a size of about 600 nm, and SEM images showed that ultrasonication induced notches and grooves on the surface of the nanoparticles. X-ray diffraction results revealed that the crystalline structure was disrupted, but anti-digestibility remained after ultrasonication, so the nanoparticles may be used in biomedical applications and implemented in new medical materials (Fig. 23).

Fig. 21 Different magnifications of SEM images of the Pd–MNPSS catalyst

Scheme 5 Use of a catalyst for the Sonogashira and Heck reaction

Yongbo et al. [79] applied the high-intensity ultrasonic method for nanoscale retrograded starch (RS III) in combination with the water-in-oil (w/o) mini-emulsion cross-linking technique. Starch in an aqueous solution of KOH was stirred by a magnetic stirrer (200 rpm) at 50 °C for 2 h, and then MBAA (*N,N'*-Methylenebis (acrylamide) $\text{K}_2\text{S}_2\text{O}_8$, and NaHSO_3 were added to the solution as a cross-linking agent. The solution was quickly mixed and immediately emulsified in cyclohexane containing Tween-80 and Span-80 to produce a w/o emulsion, which was stirred for 30 min. Subsequently, the emulsion with submicron drops was prepared by ultrasonication at 232 W for 85 min, and the final RS

III submicron particles were obtained after 12 h of cross-linking and solidification. The particle sizes of nanoscale RS-III became smaller after ultrasonication, decreasing from several micrometers for the original samples toward approximately 600–700 nm after 85 min of ultrasonication. SEM images showed that ultrasonic treatment produced notches and grooves on the surface of nanoscale RS III particles. The synthesized nanoscale RS III particles exhibited a low in vitro starch digestibility rate and high adsorption capacities. Nanoscale RS III particles were broken down and eroded (Fig. 24a and a). Nanoscale RS III particles had a rough and uniform shape, as well as a cohesive porous network structure. In contrast, the native RS III particles, which had a sponge structure, had smooth surfaces. No signs of damage on the surface of the particles were observed, and the average size was within a range of 5–15 μm (Fig. 24b and b). According to the DSC data, the native RS III particles had endothermic peaks between 99.471 and 121.92 °C, whereas the nanoscale RS III particles had peaks between 114.15 and 166.26 °C (Fig. 25).

Mohammad [80] carried out an ultrasonic-assisted synthesis of well-dispersed and uniform starch-stabilized silver nanoparticles (AgNPs) with a relatively narrow size distribution. The size of the AgNPs decreases with the ultrasonic time. In water, the silver ions and starch produced starch-capped AgNPs, which were integrated into antibacterial wound dressings. Five aqueous solutions containing AgNO_3 (0.1 M) and starch (1.0% wt.) were irradiated at an

Fig. 22 Particle size distribution patterns of starch nanoparticles

Fig. 23 SEM images of RS4 (**b** and **b**) and RS4 nanoparticles (**c** and **c**)

Fig. 24 Scanning electron micrographs of nanoscale RS III (**a** and **a**) and native RS III particles (**b** and **b**)

amplitude of 50 nm for 5, 15, 30, 45, or 60 min. Depending on the irradiation times, the solutions display a spectrum of colors, from light yellow to dark yellow. The elemental contents of the AgNPs, exposed to 60 min of sonication, were measured using EDX analysis. The dark yellow color indicates high AgNP concentration, which was confirmed by the UV–Vis absorption spectra. The weak characteristic

UV–Vis absorption of AgNPs after 5 min sonic irradiation, with an increased intensity at the surface plasmon resonance (SPR) peak at 431 nm, also indicates the formation of AgNPs. Gradually increasing the irradiation times, from 5 to 60 min, increases the corresponding peak intensities, with concomitant blue shifts from 431 to 416 nm (Figs. 26, 27, 28).

Fig. 25 DSC curves of (a) RS III and (b) nanoscale RS III particles

Fig. 26 Change in colour with irradiation times of starch-capped AgNPs in solution

Fig. 27 Full scale 2421 cts Cursor:–0.043 (802 cts) keV

According to Mie's theory, nanoparticles with different sizes have different optical properties due to differences in SPR bands. When the diameter of starch-stabilized AgNPs decreased from 14.1 ± 4.31 to 8.5 ± 2.31 nm, the λ_{max} of SPR blue shifted from about 431–416 nm. The SPR study discloses that under shorter ultrasonic irradiation, larger AgNPs are formed, with AgNPs disintegrating due to further sonication. The sharp SPR band of starch-stabilized AgNPs indicates the formation of uniform spherical nanoparticles. The TEM images showed the formation of AgNPs due to

Fig. 28 UV–Vis spectra of synthesized AgNPs in starch solutions at different sonic irradiation times

sonic irradiation after 5 and 60 min, and the corresponding particle size distribution of the synthesized AgNPs at different sonic irradiation times. The TEM results confirmed the UV–Vis spectra and indicated that the samples obtained over a longer period of time (Fig. 29c, d; 60 min) retained a narrower particle size distribution with a mean particle diameter of 8.5 ± 2.31 nm.

Haaj [81] prepared nano-sized starch particles (NSP) from starch granules using high-intensity ultrasonication without any additional chemical treatments and a low temperature of $8\text{--}10^\circ$, to prevent plasticization with water and to obtain maximal reduction in particle size. The starch suspension, with a solid content of 1.5% and kept in a glass cell, was immersed in a water bath at a constant temperature of $8 \pm 1^\circ\text{C}$ and sonicated at 80% power output for more than 75 min. The outcome of the experiment was the production of starch nanoparticles between 30 and 100 nm in size. FESEM confirmed the presence of particle clusters ranging in size from 80 to 200 nm and showed that the size of the individual nanoparticles in the clusters ranges from 20 to 80 nm. An FESEM image of starch particles at different ultrasonication intervals is shown in Fig. 30. Raman analysis confirmed the decrease in crystallinity with sonication and

Fig. 29 TEM images and particle size distributions of synthesized Ag- NPs at different sonic irradiation times: (a, b) 5 min and (c, d) 60 min

suggested the occurrence of breakage along the branching point formed by the α -1,6 glycosidic linkage (Fig. 31).

Chang et al. [82] described starch-based composites reinforced with chitin nanoparticles (CNP). Rather than producing the familiar whiskers of slender parallelepiped rods, successive acid hydrolysis and mechanical ultrasonic treatments created unique chitin nanoparticles of about 50–100 nm (Fig. 32). CNP exhibits lower crystallinity than conventional chitin whiskers. Glycerol–plasticized potato starch (GPS) was combined with CNP to prepare nanocomposites by casting and evaporation. Chitin flakes were initially treated with 3 N hydrochloric acid with vigorous stirring at 105 °C for 3 h, and the residue was collected after centrifugation and treated with two identical acidic solutions. Finally, the centrifuged residue was further mechanically disrupted/dispersed in distilled water using ultrasound for 10 min. The suspension was collected, and the process was repeated

six times in total or until the suspension became clear; the residual precipitate was discarded. The collected suspension was subsequently centrifuged at 12,000g for 20 min, dried and ground to obtain a light yellow CNP powder.

Cholesterol-modified pullulan (CHSP) conjugate with succinyl linkages was synthesized by Wen-Zhi et al. [83] through probe sonication in an aqueous medium. The degree of substitution (DS) of cholesterol moiety was determined by ^1H NMR ranging from 3.87 to 5.70 cholesterol groups per hundred glucose units. First, CHSP conjugates were suspended and swollen in distilled water at 37 °C for 24 h to give a milky suspension, followed by sonication using a probe-type sonifier at 100 W for 2 min; this sonication process was repeated three times. The solution of self-aggregated nanoparticles was passed through a membrane filter (pore size: 0.45 μm , Millipore) and stored at 4 °C. MTO-loaded CHSP self-aggregated nanoparticles were prepared

Fig. 30 FE-SEM images of starch particles at different ultrasonication intervals

(a) native waxy maize, (b) waxy maize after 30 min sonication

(c) 45 min sonication,

(d) 75 min sonication

(e) native standard maize, (f) standard maize 30 min sonication,

standard maize after 75 min sonication

Fig. 31 Raman spectra of (a) standard starch and (b) waxy maize before and after 75-min ultrasound treatment

by dissolving MTO in dimethyl sulfoxide and added to the CHSP self-aggregated nanoparticles and dimethyl sulfoxide, followed by removal of free MTO through dialysis (Fig. 33).

Insulin-bearing aquasomes were constructed by Jain and co-workers [84] to obtain nanocrystalline calcium phosphate dihydrate ceramic cores, which self-assembled during the reaction process by colloidal precipitation and by sonication at a low temperature of a disodium hydrogen phosphate solution and a calcium chloride solution. The sonication helps the self-assembling of crystalline calcium phosphate particles by increasing the surface free energy. These nanoparticles were further coated with a thin film of polyhydroxy oligomer by sonicating with polyhydroxy oligomers (trehalose, cellobiose, or pyridoxal-5-phosphate coating materials). The polyhydroxy oligomer stabilized the core through ionic, non-covalent, and entropic forces. The self-assembled carbohydrate-stabilized ceramic nanoparticles (aquasomes) may be used for the parenteral delivery of insulin. The size, shape, and size distribution and the drug loading efficiency were characterized, and the *in vivo* performance of the aquasome was compared with standard porcine insulin solution, showing better results compared with insulin solution (Table 5).

Conclusions and future prospects

Applications of ultrasound include not only cell extraction, hot water disinfection, welding of thermoplastics, degradation of plastics, degassing or cleaning of unwanted materials, medical imaging, physiotherapy, dentistry, and SONAR but also the control of chemical reactions, production of sensors, improvement of optical properties, development of

Fig. 32 TEM of CNP

Fig. 33 **a** TEM image and size distribution of CHSP self-aggregated nanoparticles and **(b)** MTO-loaded CHSP self-aggregated nanoparticles with a drug loading content of 8.14% measured using DLS. Scale bar below each image represents 100 nm **(a)** or 200 nm **(b)**

Table 5 Percentage blood glucose reduction after subcutaneous administration of plain insulin and various aquasome formulations to albino rabbits

Time (hour)	Blood glucose reduction (%)			
	PL	Aqueous Ce	Aqueous Py	Aqueous Tr
0	0	0	0	0
1	74.92 ± 0.88	40.75 ± 0.36	75.57 ± 0.20	70.19 ± 1.40
2	61.85 ± 0.48	44.48 ± 0.43	90.6 ± 0.88	80.70 ± 1.95
3	50.98 ± 0.77	30.18 ± 0.35	91.40 ± 0.90	68.98 ± 1.96
4	26.56 ± 0.33	23.88 ± 0.09	84.10 ± 0.58	59.09 ± 2.23
5	11.76 ± 0.24	5.65 ± 0.40	72.49 ± 0.58	50.73 ± 2.14
6	3.06 ± 0.88	2.54 ± 0.27	64.60 ± 0.58	42.24 ± 3.58
24	–	–	13.93 ± 0.56	–

packaging materials, and development of new techniques in the agricultural and food industries. The carbohydrates used for the modifications include starch, chitosan, pullulan, and

different metal nanoparticles. The high-intensity ultrasound promotes surface modification, enhances nanoparticle size, prevents agglomeration, and reduces reaction times. Therefore, these biodegradable and biocompatible carbohydrate-based nanomaterials are expected to have many applications in academics, industry, and pharmacy.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical Approval This article does not contain any studies with human participants and animals performed by any of the authors

Informed Consent No informed consent was necessary for the studies

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