NANOTECHNOLOGIES APPLIED TO FOOD: SMALL SIZE FOR GREAT FOOD!

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Food nanotechnology is an area of emerging interest and opens up a whole universe of new possibilities for the food industry. Food related applications of nanotechnologies offer a wide range of benefits to the consumer (Figure 1).

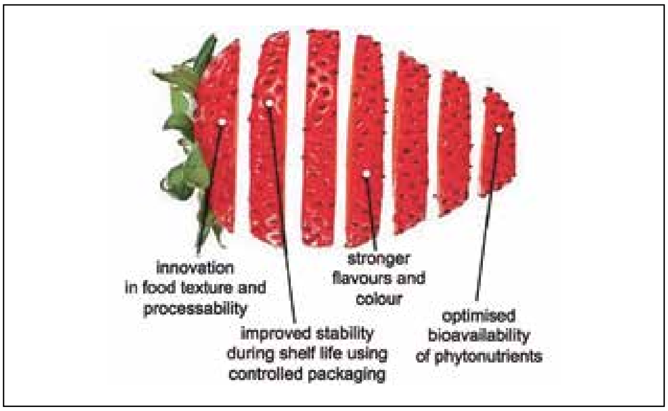

Figure 1: Nanotechnologies applied to food

These include a possible reduction in the use of preservatives, salt, fat and surfactants in food products; development of new or improved tastes, producing stronger flavors and color quality, textures and mouth sensations through nano-scale processing of foodstuffs. Nano-formulations can also improve the uptake, absorption, and bioavailability of phytonutrients in the body compared to bulk equivalents.

A further area is the development of food nano-packaging, which include the improvement of plastic materials barriers, the incorporation of active components that can deliver functional attributes beyond those of conventional active packaging, and the sensing and signaling of relevant information. Nano-packaging materials may extend food life, improve food safety, alert consumers that food is contaminated or spoiled, repair tears in packaging, and even release preservatives to extend life of the food in the package.

How small is “nano”?

The word “nano” comes from the Greek for “dwarf ”. A nanometer is a thousandth of a thousandth of a thousandth of a meter (10^{-9} m). One nanometer is about 60,000 times smaller than a human hair in diameter, a typical sheet of paper is about 100,000 nm thick, a red blood cell is about 2,000 to 6,000 nm in size, and the diameter of DNA is in the range

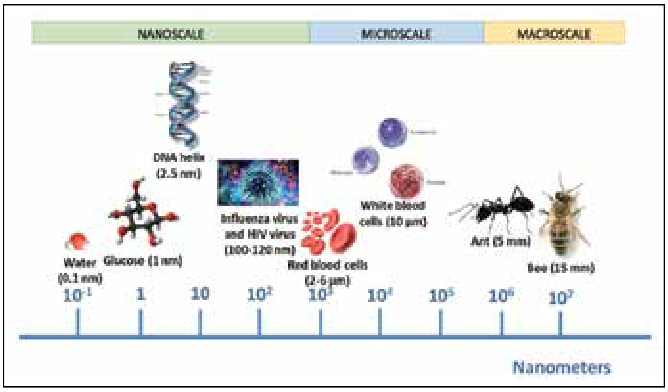

Figure 2: Scale of Nature

of 2.5 nm (Figure 2). Therefore, nanotechnology deals with matter that ranges from one-half the diameter of DNA up to 1/20 the size of a red blood cell. The term ‘nanotechnology’ describes materials, systems and processes that exist or operate at the extremely small scale of a few hundred nanometres or less. Nanoparticles are ‘first generation’ products of nanotechnology, extremely tiny particles used for their novel properties [1]. Manufactured nanoparticles are already in hundreds of products including sunscreens, cosmetics, clothing, agrochemicals, industrial catalysts but also in foods and food packaging.

Does conventional food contains nanomaterials?

Many natural foods contain nanoscale components and their properties are determined by their structure. These have been eaten safely for generations. In fact, some of food’s most important raw materials [proteins, starches, and fats] undergo structural changes at the nanometer and micrometer scales during normal food processing. Food proteins (for example, native beta-lactoglobulin, which is about 3.6 nm in length) can undergo denaturation (via pressure, heat, pH, etc.) and the denatured components reassemble to form larger structures, like fibrils or aggregates, which in turn can be assembled to form even larger gel networks (i.e., yogurt). Caseins, the major milk proteins, occur in the form of large colloidal particles, micelles, presenting an average diameter of 150 nm (Figure 3). Natural protein–polysaccharide mixed solutions can spontaneously separate into a phase with nano- or micro-sized droplets dispersed in a continuous phase. Starch granules expand when heated and hydrated releasing biopolymers that can be

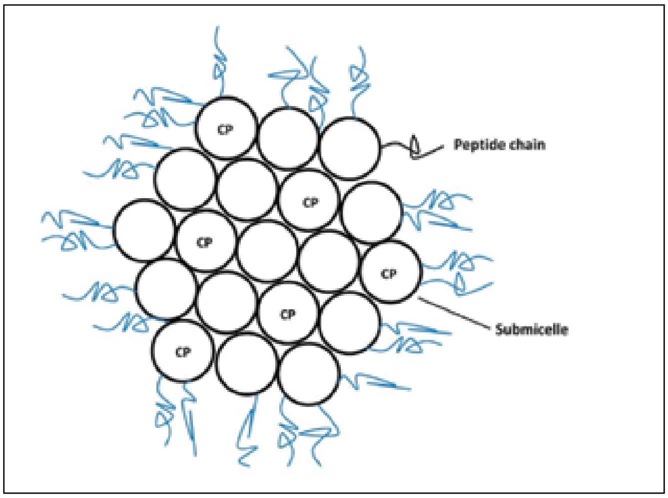

Figure 3: Caseins, the major milk proteins, occur in the form of large colloidal particles, micelles, presenting an average diameter of 150 nm. CP is calcium phosphate.

Figure 4: "Active" and "Smart" packaging. Food freshness indicator

recrystallized into nanosized structures (eg, recrystallized amylose regions may be about 10–20 nm). In the case of fats, monoglycerides, for example, can self-assemble into many morphologies at the nanoscale level, and hierarchically structured into triglycerides can be crystallites (10–100 nm), followed by arrangement into large clusters, then flocs, and finally, fat crystal networks. Dairy technology is not just a microtechnology but also a nanotechnology, and it has existed for a long time. Processes such as homogenization and fine milling cause microstructural changes in food as in the case of homogenized milk has a nanostructure of 100 nm sized droplets in it. The dairy industry utilizes three basic microsized and nanosized structures (casein micelles, fat globules, whey proteins) to build all sorts of emulsions (butter), foams (ice cream and whipped cream), complex liquids (milk), plastic solids (cheese), and gel networks (yogurt) [2,3].

Nanomaterials Changing Food Characteristics

The most interesting areas of food nanotechnologies are the manufacturing of novel food products with improved tastes, flavours, mouth feels (healthy/nutritious/tasteful food products), development of longer shelf-life of food products (contributing to reducing food waste, and a more dependable food supply), creating innovative lightweight, stronger, functional packaging (reducing the cost of transportation and packaging materials in the environment). Additionally, a very interesting growing segment on the market is represented by "Smart" and "Active" labels based on nanotechnologies to ensure food authenticity, safety, and traceability (Figure 4) [4-6].

Nano-structuring of natural food materials can potentially enable the use of less fat but still produce tasteful food products. A typical product of this technology would be a nanostructured ice cream (Figure 5), mayonnaise or spread, which is low-fat but is as "creamy" in texture as the full-fat equivalent. Such products would therefore offer a 'healthy' option to the consumer because the fat content is below 40% and characterized by high content of water. This is possible by using techniques that reduce the dimensions of fat droplets, creating an emulsion that has the same texture, but less fat than the real thing. Researchers are also developing nanometre-sized grains of salt, roughly a thousand times smaller than normal table salt. Carving up a grain of salt into these smaller particles increases its surface area a million-fold, which means that your food needs far less salt to give your taste buds the same savoury kick. The potato chips containing "nanosalt" represent a smart application because salt is plain-old salt crystals, only smaller, and these potatoes can represent a boon for those who, worried about high blood pressure, are trying to reduce their salt intake. Generally, nano-sized or nano-encapsulated food additives and supplements can improve the dispersion of fat-soluble additives in food products, improve food tastes, enable hygienic food storage, reduction in the use of fat, salt, sugar and preservatives. Currently available examples include vitamins, colours, flavours, and preservatives (Fig-

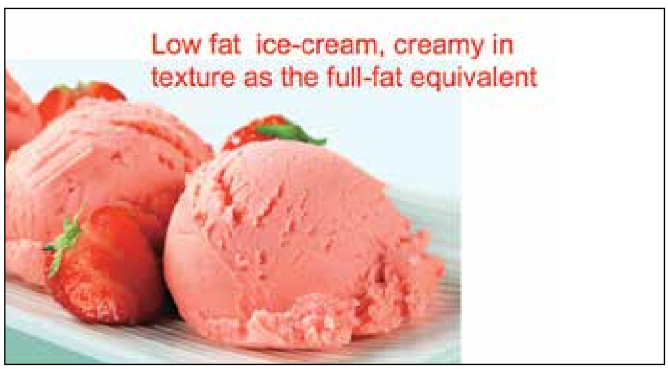

Figure 5: Processed food nanostructures for improved (or new) tastes, textures, and mouth-feels

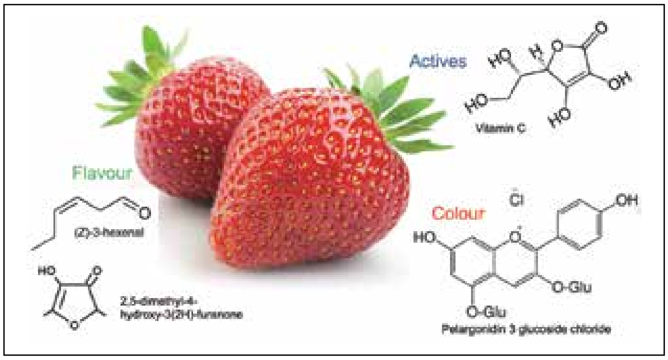

Figure 6: Encapsulation of flavours, colours and actives

ure 6). The nano-carrier systems are also used for taste masking of certain ingredients and additives, or to protect them from degradation during processing.

Furthermore, nanotechnology is enabling the development of nanoscale edible coatings, nanolaminates which consist of 2 or more layers of material with nanometer dimensions as thin as 5 nm that are physically or chemically bonded to each other. Edible nanocoatings could be used on meats, cheese, fruit and vegetables, confectionery, bakery goods, French fries and fast food. These coatings or films could could provide a barrier to moisture and gas exchange. Alternatively, they could improve the textural properties of foods or serve as carriers of functional agents such as colours, flavours, antioxidants, enzymes and anti-browning agents, and could also increase the shelf life of manufactured foods, even after the packaging is opened. The composition, thickness, structure, and properties of the multilayered laminate formed around the object could be controlled in a number of ways, including changing of the type of adsorbing substances in the dipping solutions, the solution and environmental conditions used (pH, ionic strength, dielectric constant, temperature, etc.). The driving force for adsorption of a substance to a surface would depend also on the nature of the surface and the nature of the adsorbing substance and it could be: electrostatic, hydrogen-bonding, hydrophobic interactive, thermodynamically incompatible. The properties of fruit puree edible films can be significantly improved through cellulose nanofibers reinforcement, while an edible antibacterial nanocoating can be applied directly to bakery goods.

Moreover, food packaging is the one sector of the industry where nanotechnology applications are beginning to live up to their promise and nanocomposites is the rapidly growing field. Most food packaging applications developed to date have incorporated metal or oxide particles, or more commonly nanoclays. Nanotechnology-derived polymer composites offer new lightweight but stronger food packaging materials that can keep food products secure during transportation, fresh for longer during storage, and safe from microbial pathogens. Example nanomaterials finding use in packaging include plastic-polymer composites with nanoclay for gas barrier, nano-silver and nano-zinc oxide for antimicrobial action, nano-titanium dioxide for UV protection, nano-titanium nitride for mechanical strength and as a processing aid, nano-silica for hydrophobic surface coating etc. Moreover, the potential for nanotech food seems unlimited. In the food industry, nanotechnology has thrilled manufacturers as its potential uses are explored, including detecting bacteria in packaging, or producing stronger flavors and colorings. A practical application is represented by the use of nanosilver as an antimicrobial and anti-odorant [7].

Encapsulation of phytonutrients and probiotics

Nanoparticles loaded with vitamins, phytonutrients and probiotics can be added to food and beverages performing a number of different roles:

– it serves as a vehicle for carrying the functional ingredient to the desired site of action (i.e. can reach intact the colon)

– it may have to protect the functional ingredient from chemical or biological degradation (for example, oxidation) during processing, storage, and utilization; this maintains the functional ingredient in its active state

– it may have to be capable of controlling the release of the functional ingredient, such as the release rate or the specific environmental conditions that trigger release (for example, pH, ionic strength, or temperature)

– the delivery system has to be compatible with the other components in the system, as well as being compatible with the physicochemical and qualitative attributes (that is, appearance, texture, taste, and shelf-life) of the final product.

A wide variety of delivery systems has been developed to encapsulate functional ingredients, including simple solutions, association colloids, emulsions, biopolymer matrices, and so on. Each type of delivery system has its own specific advantages and disadvantages for encapsulation, protection, and delivery of functional ingredients, as well as cost, ease of use, biodegradability, and biocompatibility (Figure 7) [1, 4-6].

Association colloids

Association colloids range in size from 10 nm to 500 nm and are usually transparent systems. Micelles, reverse micelles, vesicles and related nanocochleates, and liquid crystals such as cubosomes represent the most useful colloids associations. The major advantages of association colloid systems are that they form spontaneously, are thermodynamically favorable, and the formation of association colloids is concentration driven. Diluting the solutions containing the colloids can lead to their spontaneous dissociation.

Micelles are association of surfactants, which may be biopolymers or lipids in a liquid, in the range from 30 nm to 80 nm and can be used in “clear” beverages without phase separation. Their potential applications include lycopene, beta-carotene, CoQ10, omega- 3 fatty acids, phytosterols, and isoflavones. In particular, casein and hydrophobically modified starch formed micelles can be very useful to as nanovehicles for entrapment, protection and delivery of sensitive hydrophobic phytonutrients.

Nanoliposmes are vesicles consisting of a lipid bi-layer with a watery interior and normally include phospholipids, such as phosphatidyl choline. Liposomes enable delivery of both lipid and hydrophilic phytonutrients, and represent a versatile technology with exciting opportunities for food technologists in areas such as encapsulation and controlled release of food materials, as well as the enhanced bioavailability, stability, and shelf-life of sensitive ingredients. The application of nanoliposomes as carrier vehicles of phytonutrients such as coenzyme Q10, but they are very useful for the encapsulation of enzymes, food additives, and food antimicrobials.

Nanocochleates consist of a purified soy based phospholipid that contains at least about 75% by weight of lipid that can be phosphotidyl serine, dioleoylphosphatidylserine, phosphatidic acid, phosphatidylinositol, phosphatidyl glycerol and/or a mixture of one or more of these lipids with other lipids. Additionally or alternatively, the lipid can include phosphatidylcholine, phosphatidylethanolamine, diphosphotidylglycerol, dioleoyl phosphatidic acid, distearoyl phosphatidylserine, dimyristoyl phosphatidylserine, and dipalmitoyl phosphatidylgycerol. Nanocochleates are nanocoiled particles that wrap around micronutrients and have the ability to stabilize and protect an extended range of phytonutrients and flavor.

Cubosomes are discrete, sub-micron, nano structured particles of bi-continuous cubic liquid crystalline phase. It is formed by the self assembly of liquid crystalline particles of certain surface when mixed with water and a micro structure at a certain ratio. Cubosomes offer a large surface area, low viscosity and can exist at almost any dilution level. They have high heat stability and are capable of carrying hydrophilic and hydrophobic molecules.

Nanoemulsions

The use of high-pressure valve homogenizers or microfluidizers often causes emulsions with droplet diameters of less than 100 nm, up to 500 nm, generally denominated nanoemulsions. Phytonutrients can be incorporated within the droplets, the interfacial region, or the continuous phase. Encapsulating functional components within the droplets often enables a slowdown of chemical degradation processes by engineering the properties of the interfacial layer surrounding them. The modern technologies can also create multiple emulsions, oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) emulsions. Phytonutrients could be encapsulated within the inner water phase, the oil phase, or the outer water phase, thereby making it possible to develop a single delivery system that contains multiple functional components. The health benefits of curcumin could be enhanced by encapsulation in nanoemulsions because of the enhanced stability and permeability. Nanoemulsions could improve stability and oral bioavailability of epigallocatechin gallate.

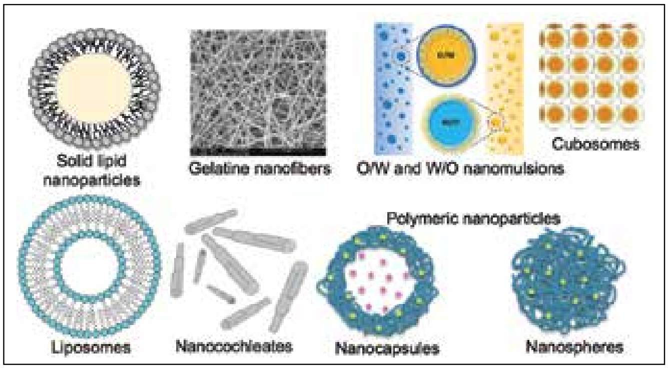

Figure 7: Nanocarriers used for encapsulation of flavours and phytonutrients

Solid lipid nanoparticles

Solid lipid nanoparticles (SLN) are formed by controlled crystallization of food nanoemulsions and have been reported for delivery of bioactives, such as curcumin, lycopene and carotenoids. SLN are either semi-crystalline or crystalline and stabilized by a surfactant coating. These are also made by emulsion technologies, are stable and enable delivery of hydrophobic materials. SLN offer unique properties such as small size, large surface area, high drug loading and the interaction of phases at the interfaces, and are attractive for their potential to improve performance of phytonutrients. The major advantages of solid lipid nanoparticles include large-scale production without the use of organic solvents, high concentration of functional compounds in the system, long term stability, and the ability to be spray dried into powder form.

Polymeric nanoparticles

Polymeric solid nanoparticles for controlled release and targeted delivery of phytonutrients with diameters of 100 nm or less have been largely developed. They are made using food-grade biopolymers such as proteins or polysaccharides or synthetic polymers highly biocompatible and biodegradable such as polylactic acid (PLA) and polylactic-co-glycolic acid (PLGA). The most common polymers are alginic acid, chitosan, sugar beet pectin, milk proteins and Arabic gum. Nanoparticles, including nanocapsules and nanospheres, increase in intestinal cell uptake of diverse phytonutrients such as polyphenols, particulalrly flavonoids, CoQ10, vitamin E, beta-carotene [1, 4-6].

Nanofibers and nanotubes

Two applications of nanotechnology that are in the early stages of having an impact on the food industry are nanofibers and nanotubes. They have small diameters ranging in size from 10 nm to 1000 nm. The main challenge is to produce both from food-grade materials. Self-assembled nanotubes from hydrolyzed milk protein α-lactalbumin, a potential new carrier for nanoencapsulation of nutrients, supplements, and pharmaceuticals, have been reported. Recently, gelatin and gelatin-zein nanofibers have been widely investigated for their use in the phytonutrients encapsulation [8].

Encapsulation of probiotics

Probiotics are generally defined as live mixtures of bacterial species and can be incorporated in foods in the form of yoghurts, yoghurt-type fermented milk, cheese, puddings, and fruit based drinks. Encapsulated forms of ingredients achieve longer shelf life of the product because generally probiotics are very unstable in the acidic gastric medium. Nanoencapsulation is also desirable to develop designer probiotic bacterial preparations that could be delivered to certain parts of the gastro-intestinal tract (i.e. colon). Biopolymer assemblies stabilized by various types of noncovalent forces have recently shown considerable progress (Figure 8). Accordingly, encapsulated probiotic are stored in powders which can be stirred into food but should not be added to food warmer than room temperature, because heat will kill the bacteria, or simply to add to yogurt, kefir (a cultured milk beverage), tempeh (made from soybeans), and kimchi (a Korean fermented cabbage dish) [].

Conclusions and perspectives

Nanotechnology can be applied in all phases of the food cycle – from farm to fork. Nanofood has in fact, been part of food processing for centuries, since many food structures naturally exist at the nanoscale. Although nanofood is still in its infancy, it holds great promise in different sectors of food. Nanotechnology has the potential to improve foods, making them tastier, healthier, and to reduce fat content, or to encapsulate phytonutrients, to generate new food products, new food packaging, and storage and, in many cases cut costs. However, many of the applications are currently at an elementary stage, and most are aimed at high-value products, at least in the short term. Successful applications of nanotechnology to foods are limited but nanotechnology is quickly moving from the laboratory onto supermarket shelves and our kitchen tables and has the potential to revolutionize food systems. Bread containing tuna fish oil loaded in nanocapsules which disaggregate only in stomach to mask the oil taste, canola active oil enriched with encapsulated phytosterol having cholesterol lowering effect, nano forms of selenium used to enrich green tea to enhance antioxidant properties have been already on the market. Additionally, low-fat milkshake by coating microscopic grains of silica, a sand-like mineral, with chocolate, nano-emulsified mayonnaise and ice-creams are also available.

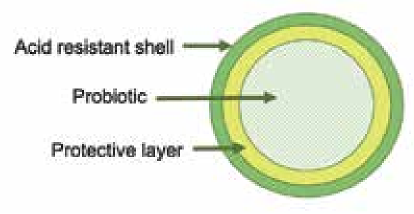

Figure 8: Encapsulation of probiotics

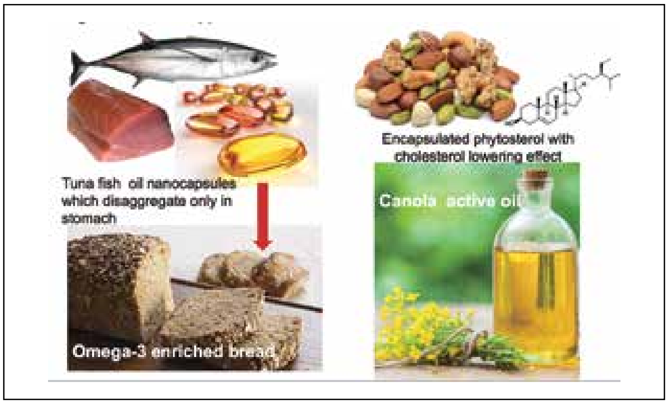

Figure 9: Smart applications of food nanotechnologies

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