CHAPTER 5

Nanostructured Materials in the Food Industry

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Contents

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Abstract Nanotechnology involves the application, production, and processing of materials at the nanometer scale. Biological- and physical-inspired approaches, using both conventional and innovative food processing technologies to manipulate matter at this scale, provide the food industry with materials with new functionalities. Understanding the assembly behavior of native and modified food components is essential in developing nanostructured materials. Functionalized nanostructured materials are finding applications in many sectors of the food industry, including novel nanosensors, new packaging materials with improved mechanical and barrier properties, and efficient and targeted nutrient delivery systems. An improved understanding of the benefits and the risks of the technology based on sound scientific data will help gain the acceptance of nanotechnology by the food industry. New horizons for nanotechnology in food science may be achieved by further research on nanoscale structures and methods to control interactions between single molecules.

I. INTRODUCTION

Nanotechnology involves the application, production, and processing of materials at the nanometer scale. It is an enabling technology that can be used to create novel materials, devices, and systems based on manipulation of matter at the nanometer scale. Thus, while the strict definition of nanoparticles refers to entities of less than 100 nm, it is the manipulation of matter at this scale that leads to the development of new materials which may have the same gross composition but widely varying properties. New exciting materials created at the atomic, molecular, and supramolecular scale are proving that nanotechnology will continue to have a significant impact on society. Nanotechnology enables the development of a radically new generation of existing products and processes for diverse industries including manufacturing, electronics, engineering, telecommunications, medicine, agriculture, cosmetics, and food (Chaudhry *et al.*, 2008; Farhang, 2007; Roco, 2003; Sanguansri and Augustin, 2006).

In the food industry, the benefits of nanotechnology hold promise for the development of new functional materials, micro- and nanoscale processing, new product development, and design of methods and instrumentation for food safety and biosecurity. Examples of some developments include packaging materials with improved barrier properties and increased resistance to high temperature and mechanical stresses; nutrient delivery systems that enable targeted delivery; nanosensors for detection of pathogens, chemicals, and contaminants; and nanotubes and functionalized membranes for efficient processing and delivery (Moraru *et al.*, 2003; Morrison and Robinson, 2009; Sozer and Kokini, 2009). These applications exemplify the use of nanotechnology to achieve products with improved control, selectivity, security, functionality, bioavailability, and product targeting.

II. APPROACHES FOR NANOSCALE MANIPULATION OF MATERIALS

Principles and techniques in nanotechnology using biological- and physical-inspired approaches are applied to create and modify materials at the nanoscale level. In the bottom-up approach, materials are constructed by self-assembly. Molecular recognition is a defining feature in developing nanostructures. By self-organization, individual molecules are built-up and integrated into larger units and hierarchical structures with unique functionalities. This process and control of nanostructures requires having compatible building blocks and an understanding of how to control the self-assembly processes (Forster and Konrad, 2003; Seeman and Belcher, 2002). The forces of attraction and repulsion that govern the self-assembly of molecules is influenced by many factors including pH, temperature, concentration, and ionic strength. In addition, the conformation of molecules may be altered by various stresses including mechanical forces (e.g., pressure, extension, ultrasound, shear), electric and magnetic fields. All these factors can change the way molecules assemble, resulting in a variety of structures that can be formed from the same molecular building blocks.

The top-down approach looks at shaping the structure of the material to the desired specification and generally involves size reduction. The top-down approach is a process that has been conventionally used by the food industry, but nanotechnological developments have introduced more precise tools that allow better control and finer dispersions to be made. A smaller size leads to a bigger surface area and this alters the functionality of materials. Food nanotechnology exploits both the top-down and bottom-up approaches for the development of new materials. The challenge for the food scientist of the future is to harness the natural self-assembling character of a food ingredient (protein, lipid, or polysaccharide) and design nanostructures for particular applications (Dickinson, 2003).

III. PROCESSES FOR STRUCTURING OF FOOD MATERIALS

Various processes may be used to alter the size and structure of food materials at various length scales and this has the potential to modulate the self-assembly behavior of food components and alter functionality.

Selected technologies that have established use or the potential for structuring food materials in the food industry are discussed briefly.

A. Milling

Milling results in particle size reduction. Milling techniques have long been used for size reduction of pharmaceutical powders to improve body absorption (Bentham *et al.*, 2004). An increased surface area of food materials will increase the rate of water absorption of materials, improve solubility of dry products, and increase accessibility of sites for chemical reactions (e.g., oxidation, digestion, flavor release, catalyst, and enzyme activity). The structure of food is also important as it dictates how, when, and where food nutrients and flavors may be released. The effectiveness of nutrient bioavailability in food is in part related to its size although other factors such as interactions of the component with a matrix also influence how the component is released.

Ball milling was a more efficient method for extracting arabinoxylan from psyllium seed husk, compared to jet milling when particles were milled to the same size. Ball milling reduced the molecular weight of the arabinoxylan and its viscosity was lowered whereas jet milling did not reduce its molecular weight (van Craeyveld *et al.*, 2003). Examples of other effects of milling on functionality of materials are given in Table 5.1.

B. Homogenization

In homogenization, a liquid product or slurry is subjected to a high shear stress. Homogenizers have traditionally been used for reducing the size of fat globules to improve the stability of emulsions. High-pressure homogenizers are capable of producing finer milk emulsions than conventional homogenizers (Thiebaud *et al.*, 2003). Membrane emulsification is an alternative process that may be used to form emulsions with narrow particle size distribution and it requires relatively less surfactant than other high-energy processes (Joscelyne and Trägårdh, 1999). Monodisperse emulsions are formed using cross-flow emulsification when the dispersed phase volume is low but the method is not ready for large-scale production of emulsions (Kim and Schroën, 2008).

High-pressure homogenization/micronization have been exploited to improve the functionality of a variety of plant materials. High-pressure-micronized particles from starfruit pomace, carrot, and orange (insoluble fiber-rich fraction) had the highest oil- and water-holding capacity, swelling capacity, cation-exchange capacity, glucose adsorption capacity, alpha-amylase inhibitory activity, and pancreatic lipase inhibitory activity compared to that obtained by ball milling or jet milling

TABLE 5.1 Modification of plant-based material properties and functionalities by milling

Process	Product	Functionality	References
Ball milling	Various starches	Fragmented starch particles had improved cold water binding properties and freeze–thaw stability	Niemann and Meuser (1996)
	Green tea	Microfine particles (300–1000 nm) were produced which had enhanced antioxidant activity compared to middle grade tea (>1000 nm)	Shibata (2002)
	Konjac flour	Native particles (657 μm) were reduced to 24 μm. Micronized particles had reduced crystallinity and antiobesity effects *in vivo* when tested in rat models	Bin *et al.* (2005)
Vacuum ball milling	Cassava starch	Micronized starch particles (8–24 μm) had reduced gelatinization temperature	Che *et al.* (2007)
High-energy ball milling	Jicama starch and cassava starch	Starch granules were partially fragmented; water absorption index and water solubility was improved; crystallinity was destroyed; moisture content during milling had an influence on functional properties of the milled starch	Martinez-Bustos *et al.* (2007)

(Chau *et al.*, 2006a,b, 2007a). Huang *et al.* (2008) found that high-pressure-homogenized-micronized fibers (9.7–14.3 μm) of starfruit (insoluble fiber and cellulose) improved bowel health, as demonstrated by decreased caecal ammonia concentration, increased fecal output and lowered colonic bacterial enzyme activity in feces of hamsters. Jet milling of the same material was not as effective. The beneficial effects of size reduction were dependent on the process and on the reduction in particle size achieved (Huang *et al.*, 2008).

High-pressure homogenization is also capable of disrupting macromolecules. The structure of biopolymers such as proteins and polysaccharides can be altered, protein/polysaccharide complexes may be formed and in addition aggregates of protein or protein/polysaccharide complexes can be microparticulated by high-pressure homogenizers (Paquin, 1999). Examples of the effects of high-pressure homogenization on macromolecules are given in Table 5.2. Recent work has shown that ultra-high-pressure homogenization can alter the structure of proteins adsorbed at the interface. This will influence the interaction between protein-coated oil globules and consequently its stability (Lee *et al.*, 2009).

C. Microfluidization

Microfluidization is a form of homogenization that uses interaction and auxiliary chambers with microchannel architecture designed to provide optimum cavitations (formation and collapse of vapor cavities in flowing liquid), shear (pulling apart), and impact (shattering effect) forces for either size reduction, dispersion, or emulsion formation (Kasaai *et al.*, 2003). One of the benefits of microfluidization over conventional homogenization is the formation of a narrower size distribution of oil droplets when microfluidization is used to prepare emulsions. However, at very high pressures (>40–60 MPa), there is the risk of reagglomeration of droplets (Jafari *et al.*, 2007). Microfluidization can also disrupt aggregates (Table 5.3) and depolymerize macromolecules with subsequent alterations to their functionality (Table 5.4).

D. Ultrasound

High-power ultrasound has been used to disrupt cells, disperse aggregates, and modify food texture and crystallization (Knorr *et al.*, 2004). The ultrasonic wave causes intense localized heating and this generates gas bubbles which cavitate and result in intense pressure and shear (Povey and Mason, 1998). It is the high pressure and shear which cause physical disruption of food components and materials and can change the rate of chemical reactions. Kentish *et al.* (2008) used a flow-through power ultrasound systems at 20–24 kHz to produce an oil-in-water emulsion with

TABLE 5.2 Effects of high-pressure homogenization technologies on macromolecules

Process	Material	Functionality	References
Ultra-high-pressure homogenization	Methylcellulose	Ultra-high-pressure homogenization (>100 MPa) degraded methylcellulose; a decrease in intrinsic viscosity was obtained which was correlated to the decrease in molecular weight	Floury *et al.* (2002)
Dynamic pulsed pressure	Modified corn starch	Processing of modified corn starch at 414 or 620 MPa at 70 °C decreased melting temperature but viscosity was not affected	Onwulata and Elchediak (2000)
High-pressure valve homogenization	High methoxy pectin	Molecular weight of pectin was reduced by homogenization at 124 MPa; of the three pectins that had been depolymerized, only one of these had altered flow behavior	Corredig and Wicker (2001)

TABLE 5.3 Microfluidization for disruption of aggregates

Product	Comments	References
Low-protein rice starch	Microfluidization disrupted protein–starch aggregates enabling improved separation by subsequent density-based separation	Guraya and James (2002)
Denatured whey protein	Microfluidization disintegrated aggregated denatured whey proteins formed as a result of heating; the disrupted aggregates were stable to sedimentation but not to reheating	Iordache and Jelen (2003)

TABLE 5.4 Effects of microfluidization on macromolecular properties

Material	Properties and functionality	References
Xanthan gum	Microfluidization caused depolymerization with molecular weight being lowered from 25×10^6 to 4×10^6; the microfluidized product had reduced thickening and stabilizing properties	Lagoueyte and Paquin (1998)
Chitosan	Chitosan was depolymerized but degree of acetylation was not changed	Kasaai *et al.* (2003)
Resistant starch	Microfluidization of heated starch suspensions reduced molecular weight and increased viscosity	Augustin *et al.* (2008)

particle size of 135 nm. Tsai *et al.* (2008) manipulated the particle size of ionotropically gelled chitosan-tripolyphosphate nanoparticles by the use of ultrasound in combination with mechanical shearing. The degradation by ultrasound is due to cavitation effects while degradation by mechanical action is by tearing and stretching effects.

E. Electrospraying

Electrospraying is a method to electrostatically manipulate droplet formation. The mechanism involves applying an electric field to pull at the surface of the liquid to form droplets by reducing the surface tension force. Nanometer size droplets containing electric charge may be formed using this technique. The introduction of electrical charge to each droplet during its formation allows electrostatic stabilization to take place and prevents coalescence of droplets. Electrostatic manipulation enables control the formation of structures and how they may be deposited or released. An electrified coaxial liquid jet was used to encapsulate inner liquid with an outer liquid surround (Loscertales *et al.*, 2002). The action of the electrohydrodynamic (EHD) forces surrounding the compound jet enable the continuous formation of this core shell structure with a diameter range of tens of nanometers to tens of micrometers. The control of deposition and release is also possible by means of charge control, where liquid can be charged to be attracted to oppositely charged surfaces. The release may be also controlled by selecting a shell material that will disintegrate to release the core when a trigger point is reached. The electrospray process has been successfully applied to produce cocoa butter microcapsules through nano-micrometric coaxial jets caused by EHD forces (Bocanegra *et al.*, 2005). A variation of this method is to spray a conducting liquid inside insulator baths. In this case, the spray dynamic is also dependent on the conducting liquid. This may be advantageous in some controlled applications where liquid–liquid emulsion uniformity is important (Barrero *et al.*, 2004). Electrospraying application in micro/nanoencapsulation and electroemulsification has been reviewed by Jaworek (2008).

F. Rapid expansion of supercritical solution process

The rapid expansion of supercritical solution (RESS) process consists of dissolving the product in a supercritical fluid (usually carbon dioxide) and then rapidly depressurizing the solution through a spray nozzle thus causing extremely rapid nucleation of the product into a highly dispersed material. Various technologies based on supercritical fluids are given in Table 5.5.

The most important limitation of RESS is the low solubility of compounds in supercritical fluids and the use of co-solvent to improve solubility is usually costly and not economically feasible. As an alternative a supercritical fluid anti-solvent (SAS) process was introduced where a supercritical fluid is used to cause substrate precipitation or recrystallization from a polar liquid solvent (Subramaniam *et al.*, 1999). Zhong *et al.* (2008) successfully used SAS to produce alcohol soluble zein micro- and nanoparticles. A number of other technologies based on manipulating supercritical fluids have been successfully used to produce nanoparticles (Della Porta and Reverchon, 2008; Matsuyama *et al.*, 2003; Meziani and Sun, 2003; Shariati and Peters, 2003; Subramaniam *et al.*, 1999).

TABLE 5.5 Rapid expansion supercritical fluid-based technologies[a]

Acronym	Description
RESS	Rapid expansion of supercritical solutions through a nozzle causing rapid nucleation of product into highly dispersed nanoparticles
RESOLVE	Rapid expansion of supercritical solutions into a liquid solvent chamber that can contain surfactant that act to impede particle growth
GAS/SAS	Gas or supercritical fluid antisolvent introduces gas or supercritical fluid to decrease the solvent power of a polar liquid solvent in which a substrate is dissolved causing substrate precipitation or recrystallization
ASES	Aerosol solvent extraction system involves spraying of a polar liquid with a substrate as fine droplets into an atmosphere of compressed carbon dioxide causing precipitation of fine nanoparticles
SEDS	Solution-enhanced dispersion by supercritical fluid to achieve small droplet size and intense mixing of supercritical fluid and solution for increased transfer rates
PGSS	Particles from gas-saturated solutions or suspensions achieved by dissolving a supercritical fluid into a liquid substrate, or a solution of the substrates in a solvent, or a suspension of the substrate(s) in a solvent followed by rapid depressurization of this mixture through a nozzle causing the formation of solid particles or liquid droplets

[a] Based on Jung and Perrut (2001) and Meziani *et al.* (2004).

IV. NANOSTRUCTURED MATERIALS

The processes described in Section III have been used to influence the assembly of food components into nano- and micron-sized structures, which are the basis for the hierarchical architectures of food materials on a macroscopic scale. The processing treatments and the order in which they are applied can give rise to food materials with the same gross composition but varying functional properties. The aggregation of materials can be driven by self-assembly of molecules to achieve a state of minimum free energy via noncovalent interactions (hydrophobic interactions, hydrogen bonding, electrostatic interactions, and Van der Waals interactions). An example of self-assembly involving noncovalent interactions is the spontaneous formation of monoglycerides dispersed in water. In certain types of aggregation (e.g., heat-induced aggregation of whey proteins), covalent as well as noncovalent interactions can be involved. For the purpose of this chapter, nanostructured materials are divided into biopolymeric nanostructured particles, lipid nanoparticles, emulsions, and composites. In this section, the principles underlying the process for manufacturing these nanoparticles are discussed with limited examples. Further examples of the potential use of nanostructured particles are given in Section V.

A. Biopolymeric nanostructured particles

These particles can form as a result of the self-assembly of like biomolecules or complexes of different biomolecules (e.g., proteins, polysaccharides).

1. Whole proteins

Self-assembly of proteins under different conditions can lead to the development of different structures depending on the pH of the system and the type of protein.

The casein micelle is an example of a naturally occurring nanoparticle formed when the different types of caseins (α_{s1}, α_{s2}, β, and κ) self-assemble around amorphous calcium phosphate. This allows it to be a natural carrier for calcium. The casein micelle also serves as a carrier for hydrophobic bioactives (Livney and Dalgleish, 2007). Treatments such as ultrahigh pressure have been reported to alter the structural characteristics of the casein micelle by partially removing parts of the surface of the casein (Sandra and Dalgleish, 2005). Altering the surface properties of these nanoparticles is expected to alter their functional properties.

Proteins (e.g., β-lactoglobulin, bovine serum, albumin, hen egg white ovalbumin, egg white) form particulate gels at their isoelectric point (pI). At a pH that is greater than or less than that of the pI of the protein, fine-stranded gels are formed from denatured globular proteins as a result of aggregation of protein strands. The conditions for formation of protein gels can be manipulated to obtain gels of different textures (Foegeding, 2006).

In contrast to the formation of gels with single proteins, gels can be prepared by self-assembly of oppositely charged globular proteins. Nanogels (hydrodynamic radius 100 nm) are formed from mixtures of ovalbumin (pI 4.8) and lysozyme (pI 11). These proteins are mixed at pH 5.3, adjusted to pH 10.3, stirred, and heated. The pH of formation of the gels is between the pI of the two proteins and in this pH region the proteins carry opposite charge and are electrostatically attracted to each other. The gels have a core and shell structure (Yu *et al.*, 2006).

2. Hydrolyzed protein

A unique protein nanotube has been obtained by the self-assembly of partially hydrolyzed α-lactalbumin (a milk protein). This is the only nanotube that is derived from food proteins to date (Graveland-Bikker and de Kruif, 2006). Hydrolysis is carried out using a protease from *Bacillus licheniformis* under specific conditions. The products of hydrolysis are the building blocks for the formation of the protein-based nanotubes but the hydrolyzates need to be in the presence of a suitable ion for the formation of tubular structures. The α-lactalbumin nanotubes have potential for use in a range of applications. The high aspect ratio and stiffness of the tubes make them effective viscosity modifying agents. The protein nanotubes produce stronger gels than other proteins at equivalent concentrations. The 8 nm cavity of the nanotubes and the ability to control their disassembly make it possible for the tubes to carry and deliver valuable nutrients in food vehicles (Graveland-Bikker and de Kruif, 2006).

3. Polysaccharides

Starch and gums are commonly used texturing agents in food. The way in which they assemble dictates their functional properties on a macroscopic scale. Traditionally, the conditions of solutions (e.g., pH, presence of ions) have been altered to obtain various functionalities of these macromolecules. For example, altering the potassium ion concentration of κ-carrageenan solution influences the temperature at which this polymer gels. Low methoxy pectins and alginates form gels in the presence of calcium ions.

Some examples of high shear processes that can be used to alter the nanostructure of polysaccharides have been provided before, with different shear processes having different effects (Tables 5.2–5.4). In addition, the mode of heating can also influence the nanostructure of these components. Starch gels are traditionally formed by cooling convection-heated aqueous dispersions of starch. Starch gels are also formed using microwave-assisted heating but the gels formed in this way undergo incomplete gelatinization, as evidenced using atomic force microscopy. The extent of changes to the starch nanostructure by microwave heating was dependent on the type of starch used (An *et al.*, 2008). Understanding the changes in the structure of starch at the nanometer scale can guide the selection of suitable starches for microwave processing.

4. Protein–polysaccharide mixtures

When proteins and polysaccharides carry an opposite charge, complex formation is driven by the attractive electrostatic interactions between the two biopolymers. Soluble and insoluble complexes may be formed depending on the strength of the interactions, the balance of negative and positive charges, and their distribution on the biopolymers, molecular weight, and biopolymer flexibility under the conditions used (e.g., pH, ionic strength, concentrations of biopolymers). At or near charge neutrality, the complexes usually aggregate and dense phases predominate. When the overall charges of the biopolymers are not neutralized, the complexes are soluble. The strongest attraction between proteins and anionic polysaccharides (e.g., carrageenens, pectins) occurs at a pH below the pI of the protein when the protein carries a positive charge. Complexes can also be formed between anionic polysaccharides (e.g., chitosan) and proteins (e.g., whey protein isolate). In the latter case, the interactions are strongest at pH above the pI of the protein where the protein possesses a net negative charge. Recent reviews on protein–polysaccharide interactions discuss the principles and applications of these systems (de Kruif *et al.*, 2004; Turgeon *et al.*, 2007).

Interactions between proteins and polysaccharides give rise to various textures in food. Protein-stabilized emulsions can be made more stable by the addition of a polysaccharide. A complex of whey protein isolate and carboxymethylcellulose was found to possess superior emulsifying properties compared to those of the protein alone (Girard *et al.*, 2002). The structure of emulsion interfaces formed by complexes of proteins and carbohydrates can be manipulated by the conditions of the preparation. The sequence of the addition of the biopolymers can alter the interfacial composition of emulsions. The ability to alter interfacial structure of emulsions is a lever which can be used to tailor the delivery of food components and nutrients (Dickinson, 2008). Polysaccharides can be used to control protein adsorption at an air–water interface (Ganzevles *et al.*, 2006). The interface of simultaneously adsorbed films (from mixtures of proteins and polysaccharides) and sequentially adsorbed films (where the protein layer is adsorbed prior to addition of the polysaccharide) are different. The presence of the polysaccharide at the start of the adsorption process hinders the formation of a dense primary interfacial layer (Ganzelves *et al.*, 2008). These observations demonstrate how the order of addition of components can influence interfacial structure. This has implications for foaming and emulsifying applications.

B. Lipid nanoparticles

Lipid nanoparticles are comprised a lipid core that is surrounded and stabilized by a surface-active material. A single surfactant or a mixture of surfactants such as lecithins and polysorbates may be used to stabilize the lipid. Co-surfactants (e.g., bile salts, butanol) may be incorporated into the formulation. The formulation is homogenized and then cooled, resulting in the formation of the lipid nanoparticle (Weiss *et al.*, 2008). When choosing a fat, it should be recognized that the melting point of triglycerides within lipid nanoparticles is lower than that of the bulk fat and, furthermore, that the rate of polymorphic transformations in emulsion is increased compared to that in the bulk lipid phase (Higami *et al.*, 2003).

The emulsified lipid carriers are destabilized when recrystallization of the lipids occurs. The nature of the lipid influences the stability of the nanoparticle and their carrier properties. The type of emulsifier used has also an important role in influencing the crystallization process (Westesen *et al.*, 1997).

Solid lipid nanoparticles have received attention in the food industries. An advantage of the solid lipid particle over liquid lipids is their improved stability and finer control over the release of components entrapped within the lipid matrix. However, a potential limitation with solid lipid nanoparticles is their susceptibility to aggregation, due to the polymorphic transitions which occur during processing and storage. Strategies that could be used to alleviate this aggregation include an increase in the level of surfactant, choosing a surfactant that can modify polymorphic transitions, or selecting a lipid in which α to β polymorphic transformation is slow (Helgason *et al.*, 2008). Solid lipid nanoparticles have found their place as carriers of a range of lipophilic bioactive compounds (Weiss *et al.*, 2008).

C. Nanostructured emulsions

There are many types of emulsions—simple oil-in-water emulsions, double emulsions, multilayered emulsions (formed by layer-by-layer deposition of oppositely charged surfactants), and microemulsions. Various types of oils and surfactants including low-molecular-weight surfactants (e.g., monoglycerides, diglycerides, polysorbates, Tweens) and high-molecular-weight surface-active components (e.g., proteins, gum arabic) may be used in the formulation. Emulsion-based systems of various structures have been developed and except for microemulsions, which are formed spontaneously, most emulsions are formed by homogenization of a dispersion of the oil, water, and surface-active components. The oil–water interface of an emulsion has to be stabilized by a surface-active agent. The formulation and the conditions used for preparation of the emulsion system influence the structure of the emulsion and the architecture of the interface. Proteins form thicker layers at an interface compared to low-molecular-weight surfactants. However, protein-based films are prone to displacement by the more surface-active low-molecular-weight emulsifiers depending on the nature of the interactions between surfactant and protein at the interface and in the continuous phase (Dickinson and Tanai, 1992; Diftis and Kiosseoglou, 2004). In addition, there can be migration of oil between droplets in a mixed oil emulsion. This occurs over time in the absence of re-homogenization. If there is re-homogenization, there is instantaneous exchange of oil (Elwell *et al.*, 2004). These results demonstrate the potential for redistribution of the components of the emulsion. However, the challenge is to structure the emulsions so that they have improved kinetic stability and interfaces that display novel functionality (Leal-Calderon *et al.*, 2007).

1. Simple oil-in-water emulsions

Most of the conventional triglyceride-based simple emulsions are in the >100 nm to μm range. These emulsions are opaque because at dimensions >100 nm, light is scattered. Recently, Wooster *et al.* (2008) used the microfluidizer to form transparent long chain triglyceride oil nanoemulsions with average particle size <40 nm that do not undergo Oswald ripening for up to 3 months.

2. Double emulsions

Double emulsions (water-in-oil-in-water, W/O/W or oil-in-water-in-oil, O/W/O) have the advantage that they can carry both water and oil-soluble components. These emulsions are normally made using a two-stage process. For W/O/W emulsions, a primary water-in-oil emulsion is made and this is followed by emulsification of the primary emulsion in water. One of the drawbacks of double emulsions is that they are prone to destabilization. Increasing the viscosity of the phases is a strategy which may be used to stabilize these emulsions. The use of biopolymer hybrids or conjugates of a protein and polysaccharide as the external emulsifier also helps stabilize double emulsions (Benichou *et al.*, 2004).

Most double emulsions are in the micron range and use a mix of surfactants in their formulations. However, recent work has shown that it is possible to form stable double emulsions with droplets under 100 nm (Hanson *et al.*, 2008). These authors proposed the use of racemic, disordered, hydrophobic polypeptide segments which interact via hydrogen bonding to stabilize nanoscale double emulsions.

3. Microemulsions

These are transparent isotropic structured fluids composed of two immiscible phases that are stabilized by surfactants. Often a co-surfactant and a co-solvent are present in the formulation. Microemulsions form spontaneously and are thermodynamically stable. Their transparency is due to the small droplet size (<100 nm) in microemulsions (Flanagan and Singh, 2006; Garti and Aserin, 2007).

4. Structuring emulsions for functionality

A growing use of nanostructured emulsions is the delivery of bioactive lyophilized components (McClements *et al.*, 2007). The size of the emulsion droplets and the nature of the interface have a significant impact on the properties of the emulsions. For example, one would expect the rate of reactions that occur at an interface such as oxidation and lipolysis to increase with decreasing droplet size. However, there are conflicting reports in the literature on the effects of droplet size on these reactions. For example, there was no effect of droplet size on oxidation of structured lipid emulsions (Osborn and Akoh, 2004), no clear effects of heat treatment and droplet size on oxidation (Kiokias *et al.*, 2007), and a slower oxidation rate in methyl linoleate emulsions with smaller droplet size (Imai *et al.*, 2008). This shows that the effects of droplet size on the properties of emulsions cannot be considered in isolation from the nature of the interface.

There are similar issues when considering lipolysis of emulsions. Armand *et al.* (1992) found that pancreatic lipase activity was increased with decreasing emulsion size. However, modification of the interface of emulsions by heat treatment of the encapsulant (a mixture of caseinate and modified starch) prior to emulsion formation altered the rate of lipolysis of emulsions in model systems (Chung *et al.*, 2008). The structuring of interfaces for the target delivery of oils and oil-soluble bioactives is currently an active field of research (Singh *et al.*, 2009).

D. Nanocomposites

Nanocomposites are typically hybrids of materials. Traditional nanocomposites are made with synthetic polymers and inorganic solids. Nanocomposites may be formed by assembling biopolymers with inorganic nanometer-sized solids. These are known as bio-nanocomposites. Bio-nanocomposites can be engineered to form materials with enhanced mechanical, thermal, and barrier properties. Often the development of bio-nanomaterials is based on bio-inspired approaches and an understanding of bio-mineralization processes (Darder *et al.*, 2007). Compared to conventional nanocomposites, these bio-nanocomposites have the advantage of being more biocompatible and biodegradable.

An example of a bio-nanocomposites is the hybrid formed between gelatine and silicates. The formation of this hybrid organic–inorganic composition is due to the strong interaction between the two components. This results in gelatine–silicate composite gels which are weaker than the protein gel under the conditions of the experiment (Coradin *et al.*, 2004). However, these authors suggest that it is possible to manage the self-assembly of the particles by controlling the conditions of the reaction.

An interesting nanocomposite was formed from natural cellulose fibers incorporated with sucrose (Fahmy *et al.*, 2006). These authors used cotton linters and a key finding was that sucrose could be incorporated into the micropores of mercerized fibers that had not been previously dried. This allowed stronger fibers to be prepared. Although this example is not from the food industry, the finding that sucrose incorporation in nondried fiber preserves the nanostructure may have implications for improving the properties of cellulose used in food applications.

V. FUNCTIONALITY AND APPLICATIONS OF NANOSTRUCUTURED MATERIALS

Selected applications of nanotechnology in the food industry are discussed below. These include advances in (a) nanosensors and nanotracers, (b) food packaging and edible coatings, and (c) encapsulated food components. There are also other applications and further information is available in a number of reviews (Chaudhry *et al.*, 2008; Moraru *et al.*, 2003; Sanguansri and Augustin, 2006; Weiss *et al.*, 2006).

A. Nanosensors and nanotracers

The introduction of nanotechnology has given sensor specialists the tools required to design and manufacture nanosensors that are capable of rapid measurements on a very small scale. New nanostructures such as carbon nanotubes are used as a component in the construction of nanosensors while processes like lithography and inkjet printing may be used to directly construct tiny electronic circuits and sample delivery channels for nanosensors. The understanding of how biological systems work in the real world is important in identifying how to detect target organic molecules or even microorganisms. A typical nano-biosensor device normally consists of a molecular recognition element which is derived from an understanding of biological systems and a transducer which can be made up using nanotechnological processes or new nanostructures (Vo-Dinh *et al.*, 2001). Nakamura and Karube (2003) have recently reviewed research in biosensors.

Table 5.6 shows a number of molecular recognition elements which can be monitored using detectors in transducers to measure specific parameters. The electrical signal may be displayed in a number of different ways, depending on the application requirement.

Nanosensors may be used as rapid detectors to quickly identify threats in the case of suspected food poisoning, or integrated into packaging. Rapid detection of toxins and microorganisms is critical for the survival of

TABLE 5.6 Nanosensor devices based on molecular recognition[a]

Molecular recognition	Transducer parameters	Detector	Result display
Antibodies	Weight	Thermistor	Color changes
Receptors	Light	Photomultiplier	Light
Enzyme	Chemical substance	Semiconductor electrodes	Buzzer
Animal and plant cells	Electrical signals	Quartz crystal microbalance	Liquid crystal display
Animal and plant tissues	Sound	Photodiode	
Organelles and microorganism	Heat	Sound detector	

[a] Based on Nakamura and Karube (2003).

sufferers in such outbreaks. The use of nanosensors in food packaging to detect growth of microorganisms and change of color when a threshold level is reached is useful for preventing food poisoning. Micromechanical oscillators were developed for rapid detection of active growth of *Escherichia coli* (Gfeller *et al.*, 2005). The sensor design is based on a nanomechanical cantilever (springboard) microfabricated using standard silicon technology. Its basic principle is to use tiny plates or leaf springs as cantilevers that may be as small as 20 μm wide × 100 μm long × 0.2 μm thick and attaching a molecular recognition element at the end (Fritz, 2008; Frómeta, 2006; Ziegler, 2004). The presence of a specific toxin or microbial organism will cause changes in the cantilever which may be measured in resonance frequency and converted to an electrical signal that can be interpreted. Other changes that can be detected by the cantilever include superficial tension, temperature, and mass.

Due to its small size this type of sensor can also be designed to detect multiple toxins and microorganisms by putting a series of cantilevers with different molecular recognition elements together in an array mounted on a single chip (Lange *et al.*, 2002; Mabeck and Malliaras, 2006). The use of molecular recognition is based on understanding biological systems and micromechanical devices. This type of sensor is sometimes referred to as bio-micromechanical systems or BioMEMS (Bhattacharya *et al.*, 2007). In some cases, molecular recognition elements such as protein antibodies have stability issues that limit signal transduction. Synthetic materials that can mimic the function of bioreceptors are sometimes used as molecular recognition elements to overcome this problem. These synthetic materials are created using molecularly imprinted polymer (MIP) techniques. The synthetic polymer gives high sensitivity and selectivity while maintaining excellent stability (Jenkins *et al.*, 2001). There are a number of nanosensors being developed that have applications in food, either for rapid detection or as nanotracers to show the history of the food product and whether it is of acceptable quality at any given time. More examples of nanosensor development for food applications are shown in Table 5.7.

B. Food packaging and edible coatings

Nanomaterial developments are influencing how food is packaged. Bio-nanocomposites with improved thermal, barrier, and mechanical properties are becoming available.

Examples of the use of nanostructured materials for packaging applications have been given in Chaudhry *et al.* (2008) and references therein. One of the first market entries into the food packaging arena was polymer composites containing clay nanoparticles (montmorillonite). The natural nanolayer structure of the clay particles impart improved barrier properties to the clay–polymer composite material. Some of the polymers which have been used in these composites for production of packaging bottles and films include polyamides, polyethylene vinyl acetate, epoxy resins, nylons, and polyethylene terephthalate.

Edible coatings have been used in the food industry for extending the shelf-life of food products. Traditionally, the food to be coated is dipped in a polysaccharide or protein-based solution or emulsion and a thin layer of the coating material is formed around the surface of the food product. Developments in nanotechnology with the potential to impact on the edible coating industry have been discussed (Vargas *et al.*, 2008). Multilayered coatings may be obtained using layer-by-layer electrodeposition (Weiss *et al.*, 2006). Sequenced immersion of the product in solutions of oppositely charged polyelectrolytes produces the multilayered coating. This allows the assembly of oppositely charged polyelectrolytes in succession and may, in principle, be applied to the edible coating of fruits. Coatings may be used as carriers of functional ingredients (e.g., antimicrobial agents) by using microencapsulation or nanoencapsulation techniques (Vargas *et al.*, 2008). Edible films based on chitosan, with improved barrier and mechanical properties, may be obtained by incorporating nanoparticles made from unmodified or organically modified montmorillonites, nanosilver, or silver zeolite. The rate of improvement depended on the type of nanoparticle incorporated (Rhim *et al.*, 2006).

TABLE 5.7 Nanosensors for food application

Application	Description	References
Pesticide and insecticide in water	MIPs for sequestering of nonhydrolyzed organophosphate coated on optical fiber	Jenkins *et al.* (2001)
	Detection of seven different pesticides in water using multiwalled carbon nanotube-based sensor	Asensio-Ramos *et al.* (2008)
Glucose and other saccharides	Copper nanoparticle and carbon nanotube-based sensor	Male *et al.* (2004)
	Multiwalled carbon nanotube-based biosensor with high stability of 86.7% after 4 months	Wang *et al.* (2003)
Trypsin	MIPs using amorphous, crystalline, and solubilized trypsin as template with 100 ng/ml detection limit	Hayden *et al.* (2006)
Catechol	A chip-based nanofluidic device that amplifies catechol electrochemical signal; capable of detection of a few hundred molecules	Wolfrum *et al.* (2008)
Ascorbic acid	Nanoparticle printed onto carbon-paste electrode capable of 8.3 µM detection limit	Ambrosi *et al.* (2008)
Electronic nose	Metal oxide semiconductor thin-film sensors for red wine characterization	García *et al.* (2006)
Electronic tongue	Multicomponent carbon nanotube composite sensor array for bitter, sweet, salty, umami, and sour detection	Pioggia *et al.* (2008)

C. Encapsulated food components

Nanostructured biopolymers and emulsions lend themselves to encapsulation of food ingredients that need to be protected from their environment until they are released at a specific time or site. Controlled breakdown of the matrix material and release of the encapsulated core can be achieved by selection of appropriate encapsulant materials and processing techniques. A recent review of nanostructured assemblies for the delivery of food ingredients provides more detail (Augustin and Hemar, 2009). Selected examples of encapsulated food components are given in Table 5.8.

The ability of proteins to form gels and stable emulsions makes them suitable encapsulant materials for delivery of a range of food components. By controlling the microstructure of the gel network, the release of the entrapped food component (e.g., bioactive) can be manipulated (Chen *et al.*, 2006).

The nanocomplexes formed between proteins and polysaccharides, and emulsion-based systems have been examined for their ability to protect and deliver a variety of food components. Cross-linking biopolymers has been used to improve microcapsule stability. Glutaraldehyde is an effective cross-linking agent but is not allowed in food. An alternative to glutaraldehyde that has been examined is tannin.

An interesting example which capitalizes on the ability of the hydrophobic cavity of β-lactoglobulin to carry a hydrophobic molecules and complexation has been recently reported (Zimet and Livney, 2009). It was found that β-lactoglobulin binds docosahexaenoic acid (DHA) and further that DHA-loaded β-lactoglobulin can form nanocomplexes ($\sim$ 100 nm) with low methoxy pectin at a pH $<$pI of the protein. These complexes have good colloidal stability and protected DHA against oxidation.

Liposomes have been used by the pharmaceutical industry to deliver a range of drugs. Liposomes are made of phospholipid bilayers with one of more aqueous compartments depending on whether they are unilamellar, multilamellar, or multivesicular vehicles. Because of the bilayer structures they can adopt, they are versatile vehicles as carriers of water-soluble, oil-soluble as well as amphiphilic components. Hence, they can be used to encapsulate a wide range of food components including flavors, oils, amino acids, vitamins, minerals antimicrobials, and enzymes. Their potential applications in the food industry have been discussed by Mozafari *et al.* (2008)). Examples of the potential applications of liposomes in food include the delivery of cheese ripening enzymes and natural antioxidants (e.g., vitamin E).

Hatanaka *et al.* (2008) examined a number of different types of encapsulation systems for coenzyme Q_{10}. Systems examined included a novel liquid nanoemulsion and water-soluble powder formulations, acyclodextrin inclusion complex, and a dry emulsion. Of the delivery systems examined the novel nanoemulsion delivery system, which had the smallest particle size (60 nm) compared to the other delivery systems examined (770–2400 nm), had the highest bioavailability when tested in rat models (Hatanaka *et al.*, 2008).

TABLE 5.8 Nanostructured microencapsulated food components

Encapsulant system	Core	Comments	References
Biopolymeric nanoparticles			
Gelatin-based simple coacervate	Capsaicin	Coacervate cross-linked by glutaraldehdye; thermal stability was enhanced	Wang *et al.* (2008)
Gelatin–gum acacia complex coacervate	Capsicin	Coacervate cross-linked with tannins	Xing *et al.* (2004)
Carboxymethylated (CM) chitosan–alginate	Bovine serum albumin (BSA)	BSA-loaded microspheres prepared from carboxy methylated chitosan and alginate with emulsion phase separation and cross-linked with Ca ions	Zhang *et al.* (2004)
Whey protein isolate–low methoxy pectin	Thiamine	Thiamine entrapped in whey protein isolate–pectin complex; entrapment efficiency was highest at pH 3–3.5	Bédié *et al.* (2008)
Whey protein isolate–alginate	Riboflavin	Riboflavin-loaded microspheres formed; riboflavin release slowed in simulated gastric fluid with complete release of the bioactive in simulated intestinal fluid	Chen and Subirade (2006)

Emulsions			
Sunflower oil and surfactants	β-Carotene	Particles (400 nm) were formed; the colloidal particles were stable and water-dispersible; carotene was protected against degradation	Hentschel *et al.* (2008)
Nonionic food grade emuslifiers/water/limonene/ethanol/propyleneglycol	Lycopene	Enhanced solubilization of lycopene; water dilutable food grade microemulsions	Spernath *et al.* (2002)
Molecular inclusion complexes			
Starch	Stearic acid	V-type starch inclusion complex formed using continuous dual feed homogenization; potential use as delivery vehicle	Lesmes *et al.* (2008)

VI. NANOTECHNOLOGY AND SOCIETY

Although there are many potential benefits of nanotechnology, the public perception of the technology will determine how rapidly it will be adopted in the market place. Regulations for the use of nanotechnology need to be developed. Among some of the issues that need to be considered include definition of the particle size range and how it can be measured, the physicochemical properties of the particles and the processes used to produce them and overcoming safety concerns (Chau *et al.*, 2007b). There has to be transparent processes to deal with the safety aspects of the technology (Powell and Colin, 2008).

As with any new technology, the potential risks need to be evaluated in a balanced fashion. Stern and McNeil (2008) have recently reviewed the published data on safety concerns surrounding the exposure of humans and the environment to nanomaterials. These authors considered the design of experiments and methodologies used to assess the risks in their analysis of the literature. Taking into consideration where there is agreement or points of difference between the published studies, these authors' opinion was that published data suggest that the human organs (i.e., lung, gastrointestinal tract, and skin) can serve as significant barriers to many nanomaterials. However, they also advocate a cautious approach to application of nanotechnology until unknown facts such as degree of and hazards of exposure and life cycle analysis of these materials are better defined and understood.

VII. THE FUTURE

The ramifications of nanotechnology in the food arena have yet to be fully realized. This requires further research into biopolymer assembly behavior and applications of nanomaterials in the food industry. Researchers should keep abreast of the development of research tools and what is being done to push resolution limits for techniques such as atomic force spectroscopy or the synchrotron coupled to various spectroscopic techniques and higher resolution microscopy. New techniques should be exploited and the knowledge gained used to understand the dynamics and interactions of food materials at the single-molecule level and to describe assembly behavior in quantitative thermodynamic terms. There are questions about the interactions of nanoparticles with the food matrix and within the human body. These questions need to be addressed by future research (Simon and Joner, 2008; Sletmoen *et al.*, 2008).

Further research is required on nanoscale structures and methods that can be used to control the interactions between molecules to enable nanotechnology to have an impact on food and health. The future challenge would be to decide on what application of nanotechnology in food would be of most benefit to the consumer, environment, and industry. It is important to educate the consumer about the implications of applying nanotechnology in food and for regulatory bodies to take an active role in approvals of new products made as a result of nanotechnology. This would include evidence that food product made as a result of nanotechnology is safe and have benefits that would otherwise not be possible using current practices.

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