

REVIEW ARTICLE

Nanotechnology and the application in the food industry

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ABSTRACT

The application of nanotechnology in the food industry enables prioritization of consumers' needs. Nanotechnology has the ability to provide new forms of control on food structure; therefore, this technology has higher industrial value. This paper briefly introduces the main concepts of nanotechnology and its correlation with size reduction performance. This paper also introduces the main nanobjects and their potential applications in food, and summarizes various studies and their applications in food industry.

Keywords: Nanomaterials; Nanocomposites; Nanoemulsion; Packaging; Composition

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1. Introduction

Nanoscience and nanotechnology is expected to become one of the most innovative fields. Nanotechnology allows the control and modification of substances and systems at the nano scale, which enables significant change to their properties relative to those observed at the macro scale.

The nano size ranges from about 1 to 100 nm^[1], and size is a key parameter for identifying nanomaterials (NMs). The prefix “nano” originated from Greek, meaning “short” and “small.” It is used to represent the coefficient of 10⁻⁹ (1 nm = 1 × 10⁻⁹ m) in the international system of units.

The European Commission recommends that nanomaterials should be categorized as natural, incidental or man-made substances, with 50% or more of the particle sizes between 1 and 100 nm^[2]. ISO defines it as a material with nanoscale external dimensions (nanobject or nanoscale internal or surface structures (nanostructured materials)^[1]. Therefore, NMS is different from reference materials in physical, chemical or biological aspects. These changes are due to its small volume, combined with the surface energy, which gives the number of atoms on the outer surface and the number of atoms inside the material. On the other hand, the electrons in materials are distributed at different energy levels, resulting in different electronic structures, quantum phenomena and different electrical, optical and magnetic properties of the system.

Nanoparticles (NPs) are nanobjects in only external nano sizes, with which the lengths of the long axis and the short axis are not significantly different from each other. They can self-assemble and have different reaction activity, hardness, conductivity, solubility, absorption rate and bioavailability compared with large particles. These characte-

ristics of NPs produce new ingredients and other methods to produce foods with different structures and characteristics, which increase or improve their functions, thereby elevating their commercial values.

Nanotechnology provides important opportunities for the development of innovative products and is applied in food production, processing, pre-processing and packaging. The availability of nanotechnology-derived food has increased significantly. According to Food and Agricultural Organization^[3], 183 “nano” and “food” patents were published from 2009 to 2011, including 47 related to packaging or coating, 19 related to nano additives, and 10 related to nanotechnology detection methods. In addition, developing countries are particularly interested in nanotechnology because it is a productive and economic activity with low requirements for its implementation (e.g., land, maintenance, energy and material availability). Aguilera suggests that there are two interrelated basic dimensions or axes in the current and future food industry^[4]:

- 1) The center of the “food chain” starts from the production of raw materials to the packaging and distribution of products.
- 2) The axis of “consumers” must be considered comprehensively.

At present, consumers are interested not only in

the contribution and bioavailability of nutrients, but also in the positive effects of diet (satiety, weight control, gastronomical experience, health, etc.). These requirements are the result of social changes in recent years. In this society, consumers have more opportunities to obtain information and are on a constant pursuit for better quality of life.

NMs used in food are divided into three different groups^[5] (**Table 1**):

- 1) Organic NMs include lipids, proteins and polysaccharides, which are used to wrap vitamins, antioxidants, dyes, condiments and preservatives to form micelles, liposomes or nanospheres. They have the advantages of increasing intake, absorption, biocompatibility and stability.
- 2) Organic/inorganic bound NMs are called surface functionalized NMs and are added to the matrix through specific functions (antibacterial agents, antioxidants, permeability and stiffness regulators).
- 3) Inorganic NMs are metals and metal oxides, NPs of silver, iron, selenium and TiO₂, which are used as additives, food additives or packaging materials.

Table 1. Classification of NMS in food
Nanomaterials for food and food contact

Organic	Organic/inorganic combination		Inorganic
Micelle and release system	Polymers, compounds and emulsions	Clay surface modification	Surface modification of metal or metalloid Clay Metals and metal-loids Fullerenes and carbon nanotubes

Source: Authors' elaboration, adapted from Peters R^[5].

Nanocomposites are formed by adding a low percentage (<5%) of NPs into the polymer matrix, which is reinforced by these nanofillers with higher rigidity and strength. In addition, the addition of NPs will lead to the circuitous flow of gas in nanocompounds, so as to regulate the gas exchange between packaging materials and the environment. The main polymers used can be natural or synthetic, chitosan, cellulose, carrageenan, polyvinyl alcohol, polylactic acid, polyglycolic acid, polyethylene, polyamide, polyvinyl chloride, etc. As fillers, inorganic or organic NPs, clay, silicate, Cu, Ti, cellulose, carbon, etc. with different geometries

(spheres, flakes, nanotubes, fibers, etc.) are used. These fillers can be bonded to the matrix in the form of inter-layer or delamination^[6] and extrusion or coating methods. In the process of adding materials, the quantity and dispersion of NPs, their interaction with matrix and possible aggregate should be controlled.

Nanoemulsion is a dispersion of two incompatible liquids, such as oil and water. It is stabilized by surfactant molecules that form an interfacial layer. The average diameter of each drop is between 20 and 200 nm. If the drop diameter is less than 40 nm, it is suitable for transparent food. They have a large surface area and

slow release of bioactive substances, which avoid the deposition or precipitation of cream caused by Brownian motion. In addition, they will improve the texture, flavor and color of food and act as an appropriate system to release less water-soluble compounds by increasing the dispersion and stability of drops^[7]. The composition and structure of nanoemulsion can be properly designed to protect the compound and achieve the expected performance in vivo. In addition, the ability of nanoemulsion to form gel allows the design of foods with different textures.

Oil/water nanoemulsion can be used to encapsulate hydrophobic compounds (vitamins, minerals, saponin components, antioxidants, carotenoids), while water/oil/water nanoemulsion can be used to encapsulate water-soluble bioactive substances embedded in aqueous heart. The bioavailability of compounds contained in droplets is inversely proportional to the size of droplets, which may be due to increased enzyme activity, prolonged contact with mucosa, direct transport through epithelium, and increased water solubility of hydrophobic components.

In order to be used in industry, nanoemulsion must be prepared with generally recognized as safe (GRAS)¹ ingredients and allow industrial production in operation and economy. In addition, because nanodroplets can increase their bioavailability, in vivo evaluation must be carried out.

Nanoencapsulation may also improve the solubility, stability and bioavailability of food and prevent adverse interactions between components. Nanoliposomes and nanochelates are the main carriers of bioactive substances, which help to control and release nutrients, enzymes, vitamins, antimicrobial drugs and additives. Nanochelates stabilize micronutrients and improve the nutritional value of processed foods^[8].

2. Food improvement and innovation

Nanotechnology can be used to prepare innovative foods and add new ingredients and additives with specific functions, such as antibacterial agents, antioxidants, texture enhancers and flavor enhancers. In

addition, it can also be used to design foods with specific nutritional characteristics to meet individual nutritional and health needs (e.g. allergies, chronic diseases) or preferences, or to produce interactive foods that release color and taste according to consumer needs.

At present, the formula of dietary supplements used in nutrition, sports and health food market contains mineral NPs (SiO₂, Mg, CA, etc.). In Australia, Nanocapsular provides omega-3 oil, which is only released into the stomach to avoid unpleasant taste. In Argentina, liposomes are made of lecithin with stable structure and resistance to gastric digestion. Nanoencapsulated iron and omega-3 can increase the absorption of minerals and avoid intestinal discomfort caused by intake (<https://www.fan.org.ar/potfolios/nutranova-la-linea-de-suplementosdietaarios-de-lipomize>). Unilever has developed ice cream, mayonnaise, and low-fat, low-calorie cream that tastes like cream, while Nestle has developed a quick thawing nanoemulsion. Aquanova has developed micelles to improve the stability, effectiveness and bioavailability of components (vitamins C, E and fatty acids). Novasolare provides nanocapsules of bioactive compounds (DL- α -tocopherol; coenzyme Q10, ω -3 fatty acids and vitamins A, D, D3, E and K) and natural dyes (apocaro Tenal, β -carotene, turmeric, chlorophyll, lutein). Nutralease also provides bioactive compounds (lutein, lycopene, vitamin A, D3, E, Q10, phytosterols and isoflavones) for use in a variety of foods and beverages, or nanoemulsions to protect flavor components^[9].

At the same time, many scientific papers related to this subject have been published, which are still subject to further evaluation and validation because of their effectiveness. Ha *et al.* showed that by preparing lycopene nanoemulsion added to tomato extract, the in vitro bioavailability of bioactive substances was enhanced, stable in aqueous medium, and poor in oxidation^[10]. Ban *et al.* achieved similar results in the oral bioavailability of oil/water nanoemulsified flavonoids^[11]. On the other hand, Akbas *et al.* prepared a transparent capsaicin nanoemulsion with inhibitory activity against *Staphylococcus aureus* and *Escherichia coli*^[12], which is suitable for functional food, edible coatings or

¹Generally recognized as safe (GRAS) refers to a rule that requires a chemical designated by the U.S. Food and Drug Administration (FDA) or a substance added to food, which is considered safe by experts and is

therefore not subject to the tolerance requirements of food additives under the Federal Food, Drug and Cosmetic Act (FFDCA).

packaging. Meanwhile, Lane *et al.* developed omega-3 linseed oil and seaweed nanoemulsion to make fortified food^[13]. Silva *et al.* prepared a stable double emulsion composed of olive oil, flax oil and fish oil^[14]. Quercetin and gallic acid were added to the internal and external aqueous phases as a substitute for fat in food formula.

On the other hand, by adding nanoencapsulated quercetin prepared from a mixture of soybean oil and water to chicken legs, the lipid oxidation of the product was prevented, and a sensory acceptable product was obtained^[15]. The treatment of rainbow trout with nanoemulsion of sunflower seed oil/water and *Eupatorium multiflorum* essential oil has similar results^[16]. Gani and Benjakul pointed out that adding coconut oil/sodium caseinate nanoemulsion to surimi gel not only improved the whiteness of the gel, but also improved the texture and appearance of the gel^[17].

For isotonic beverages, Bovi *et al.* developed Buriti (*Mauritia flexuosa* L.) oil nanoemulsion^[18], which contains high content of steroids and provides stable natural colorants for these drinks. Wang *et al.* prepared a functional dehydrated beverage including salt, lipophilic and hydrophilic vitamins through peppermint oil nanoemulsification process and pectinas nanoencapsulated sodium caseinate^[19]. Meanwhile, Ghosh *et al.* obtained a eugenol nanoemulsion containing sesame oil/tween 80-20/water^[20], which extended the shelf life of orange juice by inhibiting the growth of *S. aureus* and controlling the local flora during storage at 4 °C.

3. Food packaging

The main purpose of packaging is to ensure the protection and preservation of food quality from production to consumers. Container is a kind of goods container, which is convenient for transportation and handling. Similarly, a well-designed package must be attractive and easy to use to the consumers, and is able to promote the products (marketing) and provide information about products.

At present, the application of nanodevices in packaging aims to improve its function by using nanocomposites as packaging materials or coatings. In this way, gas exchange, temperature, humidity, flexibility, mechanical strength and thermal strength can be controlled. Generally speaking, nanocomposites will not

change the density or fluidity of the film, nor change its transparency, and have the advantages of recyclability, thus reducing environmental pollution. They allow the synergy of antibacterial compounds, antioxidants, oxygen absorbers and water vapor, and detect and provide information about food (freshness, temperature abuse, etc.).

Montmorillonite layer ($M_x(A_{14-x}Mg_x)Si_8O_{20}(OH)_4$) is the most commonly used clay filler. It can improve the mechanical and physicochemical properties of polymer composites by improving the gas barrier performance. Some companies have developed nanocomposites based on montmorillonite-added nylon polymer matrix and provided them as particles, and used Durethan RKU2-2601, (Nanocor TM)^[21] for packaging flavored alcoholic beverages (Honeywell International) or PET bottles, and multilayer nanocomposites for beer and carbonated beverages^[22].

Picouet *et al.* studied the addition of nanoclay to polyamide 6 (PA6) matrix of vacuum-packed beef loin, and verified the increased rigidity of the packaging and the barrier performance against oxygen and ultraviolet light^[23]. At the same time, montmorillonite nano antifungal column was prepared by simple intercalation method with pomegranate residue extract (*Punica granatum*), and the efficacy of apple gray mold was tested *in vitro* and *in vivo*^[24].

On the other hand, metal/metal oxide NPs can also be effectively used as antibacterial agents because they produce reactive oxygen species that can destroy cells and change their structure or function through interaction with metal ions. It must be remembered that one of the most critical aspects of the food chain is the deterioration caused by microbes.

NPs and nanocomposites of silver are widely used in industry because of their antibacterial properties in fruit, herbal medicine, bread, cheese, soup and meat packaging, and are offered under the name of Fresher Longer™, Bags Fresher Longer™ (USA). They are also added to food trays and sold as nanosilver food containers (Korea), zeomic (Japan), nanosilver food (China)^[20]. To date, some studies have shown that nanocomposites do not or begin to migrate from containers or model systems in contact with food^[25,26].

When packaging meat, cheese, lettuce, apples and eggs with ethyl vinyl alcohol (EVOH) and AgNPs,

Martinez Abad *et al.* found a decrease in *Salmonella* and monocytic *E. coli*^[27]. On the other hand, when Lorette *et al.* put cellulose AgNPs adsorption pads in chopped meat, kiwi fruit and melon sample containers to determine that the antibacterial activity depends on the food matrix^[28]. Montmorillonite AgNPs was also prepared by replacing Na⁺ ions in clay and applying it to fruit salad. By inhibiting changed microorganisms, products with good sensory quality and long shelf life were obtained^[29]. In addition, films were made from a mixture of binary agar and banana powder and enhanced with AgNPs, which proved to have a strong effect on pathogens and Gram-negative bacteria^[30]. Other films based on agar and NPs Ag-Cu have strong inhibitory activity against monocytic proliferative *E. coli* and *Salmonella* Typhimurium, and can be used as packaging materials^[31].

In order to preserve freshly cut apples, Li *et al.* prepared polyvinyl chloride bags containing ZnO NPs (200–400 nm) and determined their effectiveness in controlling product degradation, reducing respiratory activity and browning^[32]. Luo *et al.* found similar results in freshly cut sweet potato packaged with nano CaCO₃ low density polyethylene (LDPE), and discovered that the browning rate decreased due to the decrease of oxidase activity^[33]. Marra *et al.* found that the mechanical properties of the colorless NPs of ZnO-a biodegradable polylactic acid film were improved and the gas permeability was low^[34], while Zhang *et al.* found that the mechanical properties of the film were improved, and were effective against *E. coli* and *S. aureus*^[35]. Other authors added NPs of CuO (1%) to LDPE film and applied it to cheese ultrafiltration to verify the control of coliform during storage^[36]. In addition, benzoic acid and vanillin nico NPs in polylactic acid, ethanol polylactic acid and polyethylene glycol biopolymers also inhibit the growth of *Salmonella* Typhimurium, *E. coli* O157:H7 and mononucleosis in raw and cooked chicken^[37].

TiO₂ has the effect of light and enhanced antibacterial properties. It is used to increase the bleaching capability and luster of toothpaste, candy and mayonnaise, and prevent product agglomeration. By adding TiO₂ NPs into polyethylene, Xing *et al.* observed the inhibitory effect on *S. aureus* and *E. coli*, which increased after ultraviolet irradiation^[38]. At the same time, Cozmuta

et al. prepared a nanocomposite with Ag-TiO₂ and polyethylene for packaging fresh bread, thus extending the shelf life of the product^[39].

On the other hand, Dias *et al.* applied carbon nanotube (CNT) - allyl isothiocyanate film to chicken chop to verify their safety and antioxidant capacity^[40]. Similar results were observed by Zimoch Korzycka and Jarmoluk^[41] and Dehnad *et al.*^[42] who used chitosan coating on meat or formed nanocomposites with cellulose. The application of chitosan together with cellulose nanocrystals to whole pears (*Pyrus communis* L.) resulted in delayed ripening and the appearance of post-harvest deterioration symptoms^[43]. On the other hand, Kim *et al.* applied carnauba wax/montgras nanoemulsified oil on grapes (*Vitis labruscana* Bailey) and observed the inhibition of pathogens while avoiding mass loss^[44]. Similarly, fresh strawberries coated with alginate and limonene liposomes can also prolong their shelf life after harvest^[45].

Pectin/turmeric/cinnamon oil nanoemulsion coatings were also tested on chicken slices, which were effective for microbial control and slow degradation^[46]. In low-fat cheese, nanoemulsion was prepared with sodium alginate orange fiber and oregano oil, Artiga-Artigas *et al.* determined its effectiveness and appearance retention against *S. aureus* and native flora^[47]. In meat, Amna *et al.* found that packaging materials containing ZnO olive oil nanofibers were effective against *S. aureus* and *Salmonella* Typhimurium^[48], and Khan *et al.* found the same situation was in CNTs-containing nisin^[49].

4. Nanosensor

Nanosensor can be an electrode or active layer of nanostructure, as well as an electronic data processor, which is used to convert the detected signal (the presence of light, gas or organic matter) into electronic signal. It has the advantage of being a non-destructive method, with high sensitivity, fast response and recovery. Nanosensors can be used as indicators, labels or coatings to add intelligent functions to containers to detect changes in pH, gas composition, components released due to deterioration, container integrity, temperature, time, or microbial safety. In addition, they can be integrated with equipment during processing or storage in gondola or refrigerator to avoid NPs from direct

contact with food. They are widely used in the field of food safety to detect pathogens, mycotoxins or allergens. They can also be used for environmental monitoring and agriculture to detect pesticides in fruits and water.

Kraft Foods has developed an electronic language, which is included in the package. The language consists of a series of nanosensors that are very sensitive to the gas released by spoiled food. These sensors produce a sensitive freshness signal showing color changes^[21]. The application of electronic nose and electronic tongue in beer fermentation and the detection of fungal pollution in grain were introduced through examples.

Biosensors use various nanotargets, nanofibers, NPs and quantum dots to fix antibodies, DNA, enzymes, etc. Portable devices using nanowires and antibodies are also provided, which can quickly detect, identify and quantify pathogens, interfering substances and allergens. Some nanosensors can detect gold NPs containing antibodies and can detect and recognize pathogens in milk, apple juice and meat^[50], or have immobilized xanthine oxidase, which can be used as an indicator of the freshness of canned tuna^[51]. Abargues *et al.* designed a chip containing gold NPs to monitor changes in chicken^[52], and Liu *et al.* developed a chemically resistant CNT detector modified by Co and medium arylmorpholine complex to detect biogenic amines and monitor changes in meat and fish^[53]. Sensors with NPs quantum dots were also used to detect *Salmonella* Typhi^[54] or *E. coli* O157:H7 in various meats^[55].

Due to its photosensitivity, TiO₂ NPs are used to prepare oxygen sensors, as is SnO₂ NPs^[56]. Biodegradable nanosensors are also being developed to monitor temperature and humidity and to monitor these parameters during transportation and storage of packaged food.

Recently, a large number of sensors have been designed for different purposes, particularly in line with consumers' demand for safer and more natural food, which has spawned a series of scientific progress and industrial development.

5. Final considerations

Nanotechnology has a tremendous potential in the food sector, which enables the prioritization of

consumers' needs. At present, many products containing NMs in the market, especially additives and food contact materials, are usually consumed and ignored.

A major safety concern is the ignorance of the effects of NMs entry and accumulation in the body. NPs can be ingested directly and intentionally released into food as additives, supplements, pesticide residues or put in contact with packaging materials. Although NPs have special characteristics of affecting microbial cells or improving the bioavailability of bioactive substances, they may be cytotoxic to human cells or cause inflammatory processes due to oxidative stress. Therefore, it is necessary to conduct a comprehensive assessment of the toxicity risk of the NMs to be used and develop a specific legislative framework to manage this technology.

Finally, nanotechnology can control food structure, thereby elevating food functionality and value. The application and proper regulation of this technology in the food industry can continue to expand in a very promising way.

Conflict of interest

The authors declared no conflict of interest.

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