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Sabine Greßler, André Gazsó*,
Myrtill Simkó, Michael Nentwich,
Ulrich Fiedeler

Nanoparticles and nanostructured materials in the food industry

Summary

Nanotechnology offers interesting manufacturing and processing opportunities for the food production industry and promises a large market potential. On the other hand consumers object to the use of nanoparticles and nanomaterials in food. For this reason, the industry's communications on this sensible subject are only very cautious, and information on current developments and applications is rare. Industry seems to be especially interested in "delivery systems" and nano-capsules for the protection of active food ingredients during manufacturing, distributation and storage. Nanoparticulate colouring agents are in use for beverages and silica nanoparticles serve as flow aid for powdered ingredients in food. Nanoscale vitamins, minerals and herbs in food supplements are on the market. Nanotechnology can also be found in food packaging, in the area of food safety and in sensor techniques.

* Corresponding author

Introduction

Public interest in the subject of nanotechnology in the food industry is growing. Friends of the Earth Germany (BUND), for example, recently published a report entitled "Out of the laboratory and onto our plates" detailing the use of nanotechnology in the food industry. But well-founded information is scarce and many questions, in particular with regard to consumer protection, remain unanswered.

Nanotechnology opens up many new possibilities which are of interest to the food industry. In its study "Nanofood" (2004) the Helmut Kaiser Consultancy predicted its market potential at 20.4 billion US dollars for the year 2010. More than 200 companies worldwide are already believed to be involved in this sector, especially in the USA, Japan and China.[1] In the year 2000 Kraft Foods Inc. (USA), for example, set up the "Nanotek" Consortium, in which 15 universities and research institutions worldwide participate.[1] Mars Inc. (USA) has a patent[2] for ultrathin inorganic coatings for consumables.[3] Nestlé (CH) is investigating encapsulation technology[4] for the delivery of active ingredients in food products (e.g. flavouring agents, vitamins, fatty acids).[5]

Nanotechnology in the food industry is a sensitive subject. Manufacturers fear a blanket rejection of products containing nanomaterials, similar to what has happened with genetic engineering. Their fears are not unjustified, as more recent surveys show that the majority of consumers object to nanoparticles or nanomaterials in food.[6] Food manufacturers hence say little about the use of nanomaterials in their products. As a result the number of such food products currently already on the market remains unknown. Also, there is still a lack of clarity as to which developments can actually be attributed to nanotechnology. There are no clear classifications and definitions – but given the complexity and many different forms of nanotechnology, determining these is no small undertaking.

This dossier begins with an overview of the basis for the application of nanotechnology in the food industry. This is followed by a short description of the various application areas such as food production and packaging, food safety and sensor technology. In the concluding section examples are given of applications and products which are already commercially available.

Basis

Food products naturally contain nano-size ingredients. These are different from synthetically manufactured nanomaterials. Also, for years now our food has been subject to processing and treatments, in the course of which nanostructures are produced which, however, have nothing to do with modern nanotechnology, e.g. coagulation, emulsifying or homogenising. The following two sections give a brief overview of the most important basic principles and definitions.

Natural nanostructures in food

Food proteins are globular particles whose size can vary between 10 and several hundred nanometres. Many polysaccharides and lipids are chain-shaped polymers which are less than one nanometre thick. Coagulation or emulsifying is based on the formation of reticular, two and three-dimension nanostructures. When starch is boiled to make custard, small 3-D crystalline structures only tens of nanometers in thickness are melted[1].

Milk and milk products naturally contain nanostructures, such as milk proteins and casein. When milk is homogenised, fat globules are produced that are about 100 nm in size.[7]

Synthetic nanomaterials in food[8]

Nanotechnology has great potential in the functional food sector in particular ("Functional Food"[9], "Nutraceuticals"[10]). Active agents and substances can be encapsulated in nanostructured materials (encapsulation). The purpose is to

- enhance solubility (e.g. of colouring agents),
- facilitate controlled release (e.g. only in certain parts of the alimentary tract, for instance in order to prevent the bad taste of an ingredient which in itself is beneficial. Example: Omega-3 fatty acids in fish oils),
- improve bioavailability, i.e. the amount of a nutritional ingredient which is actually absorbed by the body (e.g. vitamins, minerals),
- protect micronutrients and bioactive compounds during manufacture, storage and retail.

The most important nanostructured materials are currently nano-capsules (micelles, liposomes) and nanoemulsions.

Micelles

Micelles are spherical structures with a 5-100 nm diameter. They form spontaneously when a surfactant (tenside) is dissolved in water. Micelles are able to encapsulate non-polar molecules such as, for example, lipids, flavouring agents, antimicrobial substances, antioxidants and vitamins. Ingredients which are not normally water-soluble can be solubilised using micelles. Micelles containing solubilised materials are referred to as microemulsions. Micelles have been used in the pharmaceutical industry for a long time but have only recently attracted the attention of the food industry.

Liposomes (lipid vesicles)

Liposomes are spherical, polymolecular aggregates with a bilayer shell configuration. They vary in size from 20 nm to several hundred micrometres.

Liposomes are formed by polar lipids which are frequently found in nature, for example phospholipids from soya and eggs. Like micelles, liposomes can encapsulate a broad spectrum of functional ingredients. The difference however is that liposomes can encapsulate both water-soluble and fat-soluble ingredients. Liposomes are successfully used to encapsulate sensitive proteins so that they retain their function irrespective of external conditions (e.g. chemical influences). The shelf life of milk products, for example, can be extended using liposomes.

Nanoemulsions

Nanoemulsions are very fine, oil-in-water emulsions with a mean droplet size of 50-200 nm. Nanoemulsions do not scatter visible light and are hence transparent. Due to their tiny particles, nanoemulsions remain stable for longer periods, i.e. a separation of oil and water (which leads to a complete breakdown of the emulsion) occurs later than in traditional emulsions. The bioavailability of lipophilic substances can be increased considerably by means of nanoemulsions. Nanoemulsions have been in use for quite some time, for example, in parenteral nutrition. They also demonstrate interesting textural properties – even if the oil droplet concentration is low they have the consistency of a viscous cream, which makes them of interest for the development of reduced fat products.

Application areas

A selection of possible application areas for nanoparticles and nanostructured materials in the food industry is presented below. As well as enhancers and additives, processing technology applications are included.[11]

Food manufacture and food additives

(1) **Functional Food** (or "nutraceuticals"): Micelles and liposomes (lipid vesicles) can act as carriers for ethereal oils, flavouring agents, antioxidants, coenzyme q10, vitamins, minerals, active plant ingredients, proteins, enzymes, and antimicrobial ingredients (example product: Canola Active Oil, made in Israel; micelles with phytosterol). Encapsulating active ingredients (e.g. polyphenol, minerals, micro-nutrients) can also prevent oxidation and their bad taste can be minimised in the end product (example product: Tip-Top Up Bread, made in Australia; bread with nano-capsules for fish oil which contains health-enhancing Omega-3 fatty acids). Nanotubes and nanospheres from milk and/or whey protein can be used as gelling agents and, likewise, for encapsulating active ingredients or as carriers for the controlled delivery of substances (currently being developed).

(2) **Nanoparticulate synthetic lycopene** (a carotenoid; the red pigment of tomatoes) a food supplement and food fortifying agent (e.g. LycoVit, made by BASF). Classified as safe by the US Food and Drug Administration, FDA, ("generally recognized as safe", or GRAS). An application for a licence within the EU has been filed.[12]

(3) **Nanoparticulate beta-carotene** as a colouring agent in beverage manufacturing (example product: Lucarotin 10 CWD, from BASF). A protective colloid made from modified starch encapsulates the nanoparticles and prevents aggregation and agglomeration ("lump formation"). Carotene and modified starch are licensed food additives (E160a and E1450 respectively). Nanoparticulate carotenes are thereby also licensed.[13]

(4) **Nanoparticulate silicon dioxide (SiO_2)**: Silicon dioxide is only licensed for use in certain food products (E551), including among others, dried food in powder form, cheese (in slices or grated), seasoning, food supplements, cooking salt, and cooking salt substitute, and must be declared as a food additive. Its use as a carrier of emulsifiers, colouring agents and aromas is also permitted. The tolerable daily intake is not specified; silicon dioxide is not regarded as posing a health risk.[14] In addition, SiO_2 in gel or colloid form (microscopically dispersed particles) may also be used as a processing aid for plant-based foods.[15] Processing aids are not ingredients but are used in processing technology, and may result in residue in the end product.

Synthetic SiO_2 is also sold as pyrogenic (colloidal) silicon by several companies, for example under the product name Aerosil made by Evonik[16] (applications: food and cosmetics; thickening agent, improved flow of powders, and the prevention of lump formation in powders). For example, "Bad Ischler 7-Kräuter-Salz" (a salt product from Austria) contains Aerosil as a flow aid.[17]

As it is a colloid, the primary particles of pyrogenic silicon are naturally nano-sized. However, the particles tend to form agglomerations bigger than 100 nm. Individual particles only occur occasionally and instead form aggregates which are not regarded as posing a health risk as they are excreted by our bodies unchanged.[18]

Synthetic silicon dioxide is not a product of modern nanotechnology. It has been produced and used in the food industry for many years. Its structure and the fineness of its particles have not been altered.[19]

(5) **Nanoparticulate titanium dioxide (TiO_2)**: in its larger form, TiO_2 is a licensed food colouring agent (E 171). It is used as white pigment in paper and plastic because of its UV-resistant properties. TiO_2 can also be found in food itself, for example in sugar glazing in confectionery or in instant beverages. Mars Inc. (USA) has a patent[20] for inorganic coatings for consumables[21], which, it is claimed, protect confectionery in particular from moisture and oxygen by means of a transparent, ultrathin layer (0.2–500 nm) of inorganic material (SiO_2, SiO, CaO, ZnO, TiO_2 or MnO) thereby extending the product's shelf life. The patent has so far not been applied, it is apparently due to run out in several countries, and is not being renewed.[22] Nanoform TiO2 is not licensed for food. There is no concrete evidence that it is currently being used food.[18]

(6) **Crushing herbs to nano dimensions** (nanopowder, nanoemulsions; in use, for example, in food supplements).

(7) **Water treatment** using nano-membranes (disinfection, removal of pollutants; currently being developed).

(8) Catalytic improvement of frying oil by means of a **nanoceramic insert in commercial deep fat fryers**, which prevents oil polymerisation and the associated bad smells (example product OilFresh, USA).

(9) **Filter paper** with nano-silicon for decaffeinating coffee (currently being developed at the University of Nebraska, Lincoln, USA).[23] Similar filter papers could also be used to remove cholesterol or nicotine.

(10) **Interactive food and drinks with nanocapsules**, which break open at certain microwave frequencies to release the desired aromas and colours ("on-demand-delivery"). In the future this might make it possible to modify a product's flavour or colour in-situ. A well-known example is the so-called "Magic Pizza", which so far however still belongs to the realm of fantasy.

Packaging

Nanocomposites[24] or nanoparticles in packaging materials (e.g. silver, TiO_2, SiO_2, nano-clay) can ensure better protection for food, for example by reducing the permeability of foils, deodorizing, blocking UV light, improving mechanical and heat-resistance properties, and acting against bacteria or fungi.

Nanoform TiO_2 is transparent, it retains its UV resistance, and is sold by several companies as filler particles in foils and plastic containers. Nano-TiO_2 in packaging materials is classified as safe for food, although most of the safety data refers to the larger form of TiO_2. There is no record of any investigations to discover whether packaging materials containing Nano-TiO_2 are just as inert (not generally reactive) as those containing the larger "bulk" form, i.e. it cannot be ruled out that nano-TiO_2 particles migrate from packaging to the food.

Nylon nanocomposites are used for food packaging (e.g. in PET bottles for beer and other alcoholic beverages), because they constitute a barrier to oxygen and CO_2, keeping the product fresh and/or preventing nasty smells.

Safety and sensor technology

(1) Protein-encased **nanocantilevers (measuring gauges)** which vibrate at a specific frequency constitute a new class of ultra-small **sensors** currently being developed. They are supposed to enable viruses, bacteria and other pathogens to be detected quickly. If impurities (for example bacteria) stick to the specified surface, this changes the mass on the cantilever and hence leads to a demonstrable shift in the frequency at which it vibrates.[25]

(2) In the future, **nanowires** with synthetic "dendriform" DNA applied to them could become a kind of **nano-barcode** for detecting pathogens in food.[26]

(3) A portable miniature **microbiodetector** has been developed in the USA using a variety of **nanowires** and specific, fluorescent antibodies to simultaneously detect poisons, pathogens and chemicals. The specific application for the apparatus is the detection of bio-weapons (e.g. anthrax). In the future however it could well prove to be of interest in food safety.[27]

(4) **Coatings with silver nanoparticles** are already used in refrigerators to prevent the spread of bacteria and microbes.

Table 1 gives an overview of the application areas and the nanomaterials used.

Table 1: Nanoparticles and nanostructured materials in the food industry and examples of applications

Category	Nanoparticles, nanostructured materials	Examples of applications
Food manufacturing	Nano-capsules (micelles, liposomes) Nanoemulsions Nanotubes and nanospheres from milk protein	Encapsulation, improved solubility, protection and controlled delivery of ingredients; application for example in "nutraceuticals" and/or "functional food"
	Membranes	Water treatment, filters
	Nanoceramic coatings	Cleaning and preserving deep fat frying oil
	Nanopowders	Herb additives
	Nano-lycopene	Antioxidants for food supplements and food
	Nano-beta-carotene	Colouring agent for beverages
	Nano-silicon dioxide	Food additive and processing aid
	TiO_2, SiO, CaO, ZnO, MnO	Confectionery coatings
Packaging	Nanocomposites, nanoparticles (silver, titanium dioxide, silicon dioxide, nano-clay)	Foils, packaging containers, PET bottles
Safety and sensor technology	Nanocantilevers (metering needles) Nanowires	Sensors to detect pathogens, chemicals, poisons
	Nano-silver	Antibacterial coating in domestic appliances

Nanotech in the retail trade

Nanofood

The Woodrow Wilson Center[28] lists 67 products in the "Food & Beverages" category that the manufacturers explicitly claim are produced using nanotechnology or which contain nanoscale ingredients (as at 29.2.08). Included among these are: antibacterial cutlery, non-stick frying pans, disinfection sprays, cleaning agents, baking tins, airtight PET bottles, storage containers, refrigerators, baby bottles, foil wrapping, as well as forty entries under "food supplements". Only three are foodstuffs:

- Canola Active Oil, Israel: (micelles with phytosterol which prevent cholesterol being absorbed in the intestines).
- Nanoceuticals Slim Shake Chocolate, USA: slimming product with "nanoclusters" (delivery system) to produce the chocolate flavour.
- Nanotea, China: tea with nano-selenium.

The product list at www.nanoproducts.de names ten food industry products (as at 9. 4.08). They comprise two industrial products (nanocapsules), seven food supplements (minerals, zeolite, colloidal silver, and coenzyme q10) and nanotea with selenium.

Other examples are:

- Chewing gum with encapsulated cocoa powder to produce the chocolate flavour, O'lala Foods (USA).[29]
- Tip-Top Up Bread (bread with nano-capsules for fish oil), Nu-Mega and Clover Corp. (Australia):[30] The capsules protect the fish oil from oxidation and prevent the unpleasant fish taste. The consumer derives the health benefits of the Omega-3 fatty acids contained in the fish oil.

Conclusions

An increasing number of products containing nanoparticles and nanomaterials are entering the market. As a result, increased attention was paid to nanotechnology in food production. But many questions remain unanswered due to the lack of communication between the food industry and the public about possible applications and developments. More transparency and dialogue is necessary to discuss potential benefits and risks on a solid base.

Food supplements

Food supplements mostly consist of nanoscale minerals such as silicon, magnesium, calcium, and zeolite, but also nanosilver and nanogold.

The Woodrow Wilson Center lists 40 food supplements, which is the majority of the 67 products listed under the category of "Food & Beverages".[31]

One supplier of food supplements with nanominerals is the company "Neosino" whose products can also be purchased in Austria. Nanoform silicon, magnesium and calcium are supposed to improve bioavailability and strengthen the immune system in particular.[32] Food supplements for bodybuilders are also available, e.g. NaNO Vapor made by the company Margaritella[33], as well as a whole host of products sold by online retailers directly via the internet. These include, for example, NanoPRIME's products which contain nano-zeolite and which, it is claimed, can alleviate a number of illnesses.[34] Colloidal silver and gold water can likewise be bought on the internet and promise not only happiness and harmony but also to cure the most varied of illnesses.[35]

Notes and References

[1] Institute of Food Science & Technology (IFST) (2006): Nanotechnology Information Statement.

[2] US5741505, 25.7.1996.

[3] www.wikipatents.com/ca/2210851.html.

[4] Encapsulation systems protect, transport and deliver active ingredients in form of so-called „nano-capsules" (micelles, liposomes).

[5] Ubbink J. und Krüger J. (2006): Physical approaches for the delivery of active ingredients in foods. Trends in Food Science & Technology 17, 244-254.

[6] Bundesinstitut für Risikobewertung (2007): The majority of consumers view the development of nanotechnology fa-vourably. Press release 19.12.2007, www.bfr.bund.de/cd/10563.

[7] www.milchindustrie.de.

[8] Nach Chen H., Weiss J., Fereodoon S. (2006): Nanotechnology in Nutraceuticals and Functional Food. Emerging technology has shown great potential for delivering bioactive compounds in functional foods to improve human health. foodtechnology 03.06, pp. 30-36.

[9] Functional food is any *food* claimed to have a health-promoting or disease-preventing property beyond the basic function of supplying *nutrients*.

[10] The term „nutraceutical" is a combination of the words *"nutrition"* and *"pharmaceutical"*. Nutraceuticals are food products containing biologicial active ingredients (such as phytonutrients or antioxidants) that provide health and medical benefits (i.e. decreasing the colesterol level).

[11] Nach Chau Ch., Wu S., Yen G. (2007): The development of regulations for food nanotechnology. Trends in Food Science & Technology 18 (2007), pp. 269-280. *Enumeration in the text changed and amended.*

[12] www.media.basf.com/de/presse/mitteilungen/pm.htm?pmid=2961&n=10&id=V00-XxSb3C5RTbcp*e-, 8.4.08.

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[15] Annex updating Annex VI of EU Regulation 2092/91 – modification as of 25.5.2006.

[16] www.aerosil.com/aerosil/de.

[17] www.salinen.at.

[18] Grobe A., Renn O. & Jäger A. (2008): IRGC workshop briefing paper: Appropriate risk governance strategies for nanotechnology applications in food and cosmetics. International Risk Governance Council (IRGC).

[19] On this point verbatim by Evonik nano.evonik.com/sites/nanotechnology/en/responsibility/safe-products/nano-materials-and-consumers/Pages/default.aspx: *„... amorphous silica has been sold to the food industry for many years as a processing aid. Typical applications include powdered spices, tomato powder and powdered egg. Additions are in the lower single-digit percentage range. Synthetic amorphous silica has been tested for use in foodstuffs and has been approved since the 1960s as food additive E551. There has been no change the structure or particle size of the additives used in food since then. Extensive toxicological studies have not shown any signs that it is detrimental to health, nor has there been any indication of negative effects resulting from its use in pharmaceuticals. If new nanomaterials were to be used in food in the future, they would also be subject to stringent safety testing under the applicable food legislation. In Germany, there is a legal requirement to obtain permission before placing such new foods on the market."*

[20] US5741505, 25.7.1996.

[21] www.wikipatents.com/ca/2210851.html.

[22] BUND (Freunde der Erde) (2007): Aus dem Labor auf den Teller.

[23] Goho A. (2004): Hungry for nano: the fruits of nanotechnology could transform the food industry. Science News, 25.9.2004.

[24] A nanocomposite is as material in which nanoparticles are incorporated within the bulk matrix.

[25] ElAmin Ahmed (2006): Nanocantilevers studied for quick pathogen detection, www.nutraingredients.com/news/ng.asp?n=70159-nanotechnology-nanoscale-pathogens.

[26] Color coded pathogens offer safer food formulation (2005), www.foodnavigator.com/news/news-ng.asp?n=60665-colour-coded-pathogens.

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[29] www.olalafoods.com, www.foodprocessing.com/articles/2006/227.html.

[30] www.nu-mega.com; www.foodprocessing.com/articles/2006/227.html.

[31] www.nanotechproject.org, 29.2.08.

[32] www.neosino.at.

[33] www.margaritella.com.

[34] www.nanoprime.at.

[35] www.gela.at.

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Ergänzung zu Dossier Nr. 004, Stand: Dezember 2010

Die im Text genannten Produkte „Canola Active Oil“ (Israel), „Tip-Top Up Bread“ (Australien) und „NanoPRIME“ (Österreich) sind nicht mehr am Markt erhältlich. Das Produkt LycoVit (nanopartikuläres synthetisches Lycopin von BASF) wurde 2009 als Lebensmittelzusatzstoff unter der Novel-Food-Verordnung (258/97) in der EU zugelassen. Das Schlankheitsprodukt „Nanoceuticals Slim Shake Chocolate“ wurde in „Slim Shake Chocolate“ umbenannt. Der Hersteller gibt keine Informationen mehr zu möglichen nanopartikulären Inhaltsstoffen dieses Produkts auf seiner Webseite (www.rbclife.com). Die Firma Margaritella führt laut ihrer Webseite das Nahrungsergänzungsmittel „NaNO Vapor“ nicht mehr. Stattdessen gibt es nunmehr das Produkt naNOX9, das laut Herstellerangaben auf der „Nanomolecular Rapid Explosion Technology™“ beruht (www.margaritella.com). Nano-Membrane werden mittlerweile bei der Wasserreinigung und -aufbereitung eingesetzt.

Die EU-Novel-Food-Verordnung (258/97) befindet sich derzeit in Revision und soll neben der Definition von Nanomaterialien auch ein spezielles Zulassungsverfahren für Lebensmittel mit Nanomaterialien sowie eine Kennzeichnungspflicht vorsehen (siehe dazu auch NanoTrust Dossier Nr. 017, April 2010).

Addendum for Dossier No. 004, Version: December 2010

The following products, mentioned in this paper, are no longer available on the market: „Canola Active Oil“ (Israel), „Tip-Top Up Bread“ (Australia) und „NanoPRIME“ (Austria). In 2009 LycoVit (nanoparticulate synthetic lycopene, BASF) was approved under the Novel Food Regulation (258/97) of the European Union as a novel food ingredient. The slimming product “Nanoceuticals Slim Shake Chocolate” was renamed in “Slim Shake Chocolate”. The company offers no longer information on its website regarding possible nanoparticulate ingredients of this product (www.rbclife.com). According to its website, the company Margaritella no longer offers “NaNo Vapor”, a food supplement for bodybuilders. Instead there is now “naNoX9” available, which bases according to information of the company, on the „Nanomolecular Rapid Explosion Technology™“ (www.margaritella.com). Nano-membranes are already in use for water-purification.

The EU Novel-Food-Regulation (258/97) is currently under revision and shall include a definition of nanomaterials, a specific authorisation procedure as well as labelling of products containing nanomaterials (see NanoTrust Dossier No. 017en, November 2010).