

Part One
Basic Elements of Nanofunctional Agriculture
and Food Science

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Nanotechnologies for Agriculture and Foods: Past and Future

Cecilia Bartolucci

National Research Council of Italy, Foresight Group, Department of Chemical Sciences and Technology of Materials, Institute of Crystallography, Via Salaria km 29.300, Rome 00015, Italy

Nanomaterials and nanoparticles are not an invention of the twentieth century. Examples of nanostructured materials can be found throughout the fourth to the seventeenth century. Important examples are vividly colored stained glass windows in European cathedrals obtained through the use of gold nanoparticles; silver or copper nanoparticles used in the Islamic world to give luster to their ceramics; and finally carbon nanotubes and cementite nanowires present in the famous Damascus saber blades. These materials, showing unusual characteristics, were generally produced empirically by talented craftsmen, often through the use of high temperature.

The intentional manipulation at atomic level or molecular scale to manufacture nanoparticles or nanostructured materials, however, requires the understanding and the control of matter at dimensions between 1 and 100 nm, approximately, and was possible only after the advent of high-powered microscopes, in particular the scanning tunneling microscope by Gerd Binnig and Heinrich Rohrer in 1981, which for many marked the birth of nanotechnologies. From that moment, tools were developed that allowed imaging, measuring, modeling, and manipulating matter at nanoscale to achieve altered characteristics that could differ greatly from those on the macroscale. One should talk about nanotechnologies only if the correlation between the nanostructure of the novel materials and the resulting highly unique properties is recognized and deliberately applied. This criterion excludes naturally occurring nanoparticles and hence naturally formed biomolecules and material particles, and separates these from the particles resulting from nanotechnological applications. It is also clear from the above description of nanotechnologies that these encompass a whole group of different technologies and involve many different disciplines. Soon, several countries recognized the applicability of nanotechnologies in several different sectors such as medicine, biotechnology, electronics, materials science, energy, and more. In 2000, the US National Nanotechnology Initiative

(NNI) was created to support this highly interdisciplinary technological development, while in 2009, the European Commission recognized nanotechnology as one of the six key enabling technologies [1]. Several developing countries such as India, Brazil, South Africa, Thailand, the Philippines, Chile, Argentina, and Mexico invested millions in pursuing nanotechnologies during the first decade of the twenty-first century, while in 2005, the number of nanotechnology patent applications from China ranked third, behind the United States and Japan [2].

While consumer products making use of nanotechnologies and engineered nanomaterials began appearing on the marketplace in everyday products such as cosmetics, clothing, sporting goods, and computer processors, the applications in the agriculture and food sector lagged behind. The main reason for this different development is probably due to different levels of risk/benefit factors attributed to distinct applications. In fact, while the benefits due to the use of nanotechnologies in medicine are, despite possible risks, recognized as being very important by most stakeholders, including consumers, the applications of engineered nanomaterials or nanoparticles in, or around food cause alarm. In 2004, Britain's Royal Society and the Royal Academy of Engineering published a report [3] in which they illustrated not only the opportunities provided by nanotechnologies but also the necessity for an open debate and the need to address uncertainties about the health and environmental effects of nanoparticles. They also recommended the evaluation of nanospecific regulations. In 2011, the European Commission published a "Recommendation on the definition of nanomaterials," which uses size as the only defining property of the material (i.e., size range 1–100 nm) [4]. Regulations on food information followed soon afterwards [5], requiring indication of nanomaterials in the list of ingredients. Specifically, the ingredients to be labeled "XX (nano)" are "engineered nanomaterials," further characterized as "any intentionally produced material," with size on the order of 100 nm, or above, retaining "properties that are characteristics of the nanoscale." These characteristics are related to the large specific surface area, and/or physicochemical properties different from those of the nonnanoform of the same material [5]. The discrepancies between the recommendation and the regulation underline the regulatory uncertainties regarding nanolabelling, uncertainties which still exist also outside the European Union.

In the past years, there have been great national and international efforts in developing risk assessment and risk management approaches that propose and implement strategies to identify potential hazards. Today, the need for a differentiated debate involving all actors is becoming increasingly necessary. For years, the word "nano" has been used as an advertising tool by both supporters and detractors of nanotechnologies. The former used it to underline unprecedented, possibly all-resolving characteristics; the latter as an overall warning sign. In particular, in the public perception, anything "nano" applied to agriculture and food runs counter-current to the trends on "organic," "natural," and "environment-friendly." A study conducted in 2012 [6] showed that while there was an increased effort in addressing the complexity of the "nano issue" among the experts community (both scientists, policy makers, and regulatory bodies), the

results were communicated insufficiently, the processes were less transparent, and the industries remained, or became silent. As a consequence, the knowledge among consumers regarding nanotechnologies and the benefits of their applications decreased, while uncertainty and expectation of the risks to health and environment increased significantly. It has been shown [7] that communication of scientific uncertainty for a given risk will give rise to a disproportionate increase in the seriousness of risk perception. The type of risk is less important; the uncertainty itself and the trust in the source of information are critical to risk acceptability.

In their first axiom about communication, Paul Watzlawick *et al.* [8] said: “One cannot not communicate.” Even if communication is being avoided, this is a form of communication and leaves room to the development of one’s own frames and patterns, and often nourishes mistrust in those who fail to communicate. The success of technological innovation, particularly in a field as close to the consumer, both literally as well as emotionally, as food, is tightly linked to consumer acceptance. Therefore, it is mandatory to reinforce communication and transparency, as well as every form of knowledge acquisition and education. Inventions need to provide real benefits and they become innovations only if they can be adopted effectively by users or other parties to improve what they are doing [8]. The needs of society are the most important drivers for responsible development and innovation. Whenever addressing technological advances, technologies should never be the starting point. The key question should be how their applications can benefit a broad community and which societal needs they can address.

Considering the projected increase in the world’s population in the next decades, some of the greatest challenges to mankind will be to sustainably and equitably provide better living conditions, to deliver vital goods and services, and to support human health and well-being. Few studies consider the interaction between all these challenges. However, in the future, it will be imperative to address them in a concerted way and design strategies that will support a more holistic approach. In particular, there is a need to provide global food security.

Food is a necessity for all, making each of us a stakeholder in this important sector. It is such a critical need that the implications connected to food security are enormous, and extend from physical and mental health and well-being to development, economy, migration, and conflict. While the demand for food may increase 70% by 2050, the production of food worldwide has a high impact on natural resources on which it is fundamentally dependent. In a very recent report on “Food Systems and Natural Resources” [9] the UNEP provides evidence of unsustainable and/or inefficient practices used globally by current food systems. According to this report, 33% of the world’s soil is moderately to highly degraded; at least 20% of the world’s aquifers are overexploited; 60% of global terrestrial biodiversity loss is related to food production; over 80% of the input of minerals does not reach consumers’ plates, implying very large nutrient losses to the environment. It is clear that one of the greatest challenges of our time is to address both food security and sustainability. If we want to ensure food

security while maintaining healthy ecosystems, we also need to consider climate change, weather variability, and possible increase in the number of extreme events, habitat loss, constraints in available water and energy resources, competition for arable land and urbanization, as well as the use of fertilizers and other inputs, which constitute huge challenges on the resilience of the food system. Furthermore, a changing population, not just a growing one, also poses a challenge to meeting the growing global demand for food and nutrition, thus further complicating the system. Higher average incomes, urbanization, a more aged and more educated population are all factors that will contribute to increased food consumption and dietary changes, with a greater proportion of resource-intensive food such as meat and dairy products [10]. In fact, according to the World Resource Institute one-third of the expected growth on food demand will be attributed to the increased purchasing power [11].

Meeting food security requires addressing availability, access, and utilization over time. The World Food Summit of 1996 defined food security as existing, “when all people at all times have access to sufficient, safe, nutritious food to maintain a healthy and active life.” Currently, the global food production, which has almost tripled during the past 50 years [12], is enough to feed the entire world population (2700 kcal/person/day produced vs 1800 to 2200 kcal/person/day required) as estimated by the World Health Organization. Yet, more than 800 million people face hunger daily, and over 2 billion still suffer from vitamin and mineral deficiencies, in particular iron, vitamin A, iodine, followed by zinc, folate, and calcium [13]. An estimated 162 million children experience stunted growth, reflecting chronic undernutrition during the early stages of life. This phenomenon, which occurs predominantly during the first 2 years of life, causes mental and physical growth failures. Simultaneously, 42 million children under 5 years of age are overweight, and two-thirds of these children reside in low- and middle-income countries. Globally, more than 2 billion people are overweight or obese [14], conditions that are linked to an increase in chronic diseases such as diabetes, cardiovascular disease, and cancer.

Clearly, there is something seriously wrong with our current food systems. Recent Foresight studies [9,15–17] agree that there is an urgent need to address critically the failures of the present agriculture and food sector and that substantial changes throughout the whole system will be required. The concept of a food system approach is recurrent among experts involved in the great challenge of a sustainable food production, able to ensure food security. There is also consensus in the demand to acknowledge that without mitigation of climate change and maintaining biodiversity and ecosystems services, there is no chance to achieve sustainability.

Rather more complicated is the evaluation of supply and demand projected to 2050. While the numbers regarding population growth recurrently point to an increase from nearly 7.2 billion today to 8 billion by 2030, and more than 9 billion by 2050 under a medium growth scenario [18], numbers regarding the quantification of potential demand and necessary supply are often divergent, even though all point to the need to increase production. These variations are

due to applying different measures and premises and considering different drivers of demand and supply such as population growth, income growth, socio-economic development, climate change, and bioenergy expansion. In a recent study [19], it was shown that while results depend largely on the chosen scenarios, variations in food demand are more sensitive to socioeconomic assumptions than other factors such as climate change. The most frequently found number, however, is a required increase in food production of 70%, based on a paper written in 2009 by FAO [20]. Since then, there have been papers reporting the required increase in the production of specific agricultural products, ranging from 45% for cereals to 89% for oil crops [21]. Murray, from the Institute for Health Metrics and Evaluation, went even further and showed, while examining current global diets and human requirements, that the current production of certain food items is higher than what is required for a healthy diet [22]. In particular, the production of whole grains and fish is currently 50% higher, while the production of red meat is 568% higher. Hence, according to Murray, an increase in food production is currently necessary only for certain items, for example, vegetables by 11%, seeds and nuts by 58%, fruits by 34%. This aspect is very important, because it directly links supply to nutrition and health and introduces the factor quality where usually only the factor quantity is taken into consideration.

Quantity is, in fact, the leading aspect in most considerations about food security, and increase in crop yields is one of the main targets. Agricultural productivity is usually evaluated using the standard definition of yield, which is in tonnes per hectare (or similar units). Cassidy *et al.* in their paper proposed to calculate agricultural productivity by determining the actual food delivery, expressing yield in calories of human-consumable product per hectare, or people nourished per hectare [23]. This is one way to stress food availability, considering that crops are allocated to different uses besides just food. Currently, 36% of the calories produced by crops are being used for animal feed, and eventually only 12% of these feed calories contribute to animal product calories [23]. To further complicate the picture, human-edible crops are used to produce biofuel, for example, in 2010 United States and Brazil combinedly used 6% of global crop production (by mass) for this purpose [24]. Cassidy *et al.* argued that by growing crops exclusively for human consumption, global calories availability could be increased by as much as 70%, enough to feed additional 4 billion people.

The focus on food quality can be pushed even further by considering the real nutritional value of food in addition to merely calculating the calories. The scientific world is becoming increasingly aware of the link existing between health and diet, and of the importance of a nutritious, diversified diet. The providing of sufficient calories does not protect from malnutrition, which is often caused by micronutrients deficiencies. Further proof of a diet rich in “empty calories” is the constant increase in obesity rates in poor communities and underdeveloped countries [25]. The food quality, defined as the nutritional value of the food, is essential in providing a healthy diet.

While there is a greater awareness of the complexity of the food system(s) and the necessity to address all processes starting even before the production of raw materials and running through the whole food chain to food loss and food waste, there is still a need to bridge the gap between theory and implementation in this crucial sector. No single technology should be advertised as a panacea. However, nanotechnologies can have a disruptive impact at every step of the food chain, provided that other technologies, such as biotechnology, system biology, and information and communication technology, converge toward its development and application. It is imperative however to analyze the opportunities offered by the introduction of such technologies with a forward looking approach, and to define a medium and a long-term vision, in order to elaborate coherent research strategies. Four main areas of application for nanotechnologies in the agricultural and food sector had been originally identified, namely, agriculture, food processing, food packaging, and supplements; but the most exciting innovation in nanoscience should be investigated at the intersection of these areas. This kind of research requires a highly interdisciplinary system approach and encourages the transfer of knowledge from one sector to another. Nanotechnologies are *per se* inter- and transdisciplinary and therefore best suited for this endeavor.

The new food system will have to be driven by the necessity to create a balance at many different levels. It will be mandatory to find a balance between demand and supply, quality and quantity, and the needs of the developed and the developing world, just to mention a few. The spread and implementation of existing knowledge and technologies can already contribute to addressing these challenges, however, investments in research and development will be essential.

A key role for addressing food demand is often assigned to input intensification. According to preliminary results from the GFWS platform [16], a continued increase in crop yield productivity by at least 0.5% per year should be sufficient to meet food requirements of a crop-based food supply by 2050. This goal can be reached only with an increased use of fertilizers and water, which would put an unsustainable stress on our planet [26]. In fact, the production of nitrogen fertilizers is not only highly energy-intensive but also contributes considerably to greenhouse gas emissions. Fertilizer technology is 100 years old. Still, the fertilizer – nitrogen – use efficiency by crops is not more than 30–50%. The remainder is lost via volatilization, denitrification, leaching, and stabilization into soil organic matter. It will therefore be necessary to find new ways to deliver the nitrogen, essential to food production. In the past years, there has been a remarkable development in nanoagrochemicals, which include nanofertilizers and nanopesticides, and there have been increasing incentives in the scientific community to develop nanoproducts that are more efficient and less harmful to the environment compared to conventional agrochemicals. Nanotechnology could support the development of new products offering benefits such as increased efficiency, durability, and reduction in the amount needed. While researchers were originally interested in inorganic nanoagrochemicals, organic-based nanomaterials such as nanodelivery systems used in medical applications are now being investigated intensively. Equally interesting are nano-enabled

formulations, for example, emulsions or microcapsules showing a well-defined nanopore network. Eventually, these new particles and formulations should allow the introduction of an essential functionality: the synchronization between crop demand and release of required inputs.

Multifunctional nanomaterials could provide this intelligent feature of synchronizing demand and response, a characteristic which is also of great advantage in addressing other problems, for example, water supply. Agriculture, including irrigation, livestock and aquaculture, is responsible for 70% of water withdrawal [27]. It also contributes to the pollution of groundwater through the use of pesticides, fertilizers, and other chemicals. Nanotechnological applications could offer new and affordable solutions for the remediation and purification of water: ligodynamic metallic nanoparticles, nanoporous fibers, and nanoporous foams are being developed to be used in microbial disinfection; nanocomposite membranes offer a low energy alternative for desalination; functionalized ligand-based nanocoatings will soon be available for the removal of heavy metals. In the future nanodevices, delivery systems and nanocapsules could play an important role in the controlled release of water in response to different signals, and, linked through a network of nanosensors, they could eventually support the diffusion of precision agriculture, which combines accurate data collection with a controlled response.

A wireless monitoring system developed through nanosensors is also a tool that can be used to address environmental stresses and crop conditions, allowing for responses that are optimized for the needs of specific plants, soil, and climate conditions. The result would be a more tailored and on-demand supply of inputs and a more controlled decision-making process, which could greatly contribute to a sustainable use of resources.

Also starting at the field level is the improvement of the quality of the food that we consume. Within the food chain, the protection or the introduction of nutrients should start as early as possible. Taking the whole system into consideration, all possible points of improvement should be identified. Technologies that until now have been used mainly to enhance productivity in terms of quantity should be used and developed to enhance quality. The quality of soil can be improved through the application of intelligent nanoagrochemicals, which would avoid temporal overdose and reduce the amount of input needed, minimizing impact on environment and reducing waste. The quality of the crops could be enhanced by using nutrient delivery systems, allowing for a targeted uptake from roots and leaves.

Nutrient fortification, for example, through micro- and nanoencapsulation is yet another way to enhance the quality of the raw materials, protecting the targeted compounds and increasing their bioavailability. Processing technologies using nanodelivery systems or nanoemulsions could intervene at a later stage in the production of food products. In fact, smaller particle size confers improved bioavailability of bioactive agents, while nanoemulsions offer a preferred means of fortifying aqueous products with functional ingredients. Nanotechnologies not only provide the means to add active ingredients to food, they also allow the

production of foods with reduced fat or salt content or the creation of new foods with novel textures, flavors, and tastes. While all these attributes are part of food itself, it is important to keep in mind that in the creation of new nanoproducts there should be a real benefit, a real added value. It is the responsibility of the scientific community and regulatory bodies to show the benefits and the safety of products for the consumer. Validation procedures and safety tests will need to be introduced at each step of the chain, in particular when new technologies or new materials will be used. There is still a need to acquire a basic knowledge of food structures on the micro- and nanoscale, and of the existing link between raw material, food processing, and food structures. One should also consider a reverse approach “from fork to farm,” starting with the analysis of food absorption, particularly at gut level, and back to the structure dynamics, checking the efficiency and safety of the proposed solution.

Dietary requirements are varied and in order to have adequate nutrition, we will need to be able to monitor changes in metabolism, and to evaluate nutrient needs in a dynamic way that takes into consideration the complexity of the whole system. The tools used to achieve that should eventually reach the consumer and deliver the necessary information to allow knowledge-based decisions. Here too intelligent, responsive nanosensors could play an important role and support the development of a preventive, personalized nutrition in combination with a preventive and personalized medicine. The stress lies on prevention and it is mandatory that scientific-based knowledge and new communication strategies support a change in attitude that also recognizes a scale of action. Acknowledging the current longer life expectancy, it is important to realize that investing in healthy nutrition today will result in a better quality of life tomorrow.

Highly nutritious, healthy food should be strictly connected to safe food. Along the whole food chain there are points of intervention where nanotechnologies can not only help in identifying contaminated or spoiled food, they can also provide tools to prevent contamination and spoilage. Nano- and biosensors, connected or not to a remote sensing system, can monitor soil conditions (moisture, soil fertility, nutrients, etc.) as well as pathogens, insects, and weeds. They can provide information about when and how much pesticide or herbicide needs to be administered, eventually triggering an *in situ* response only when and where those substances are really needed, thereby avoiding overuse and unnecessary exposure of nontarget organisms. Applications of nanotechnology-enabled gene sequencing could also contribute to the effective identification and utilization of plant trait resources, improving their capability to react against environmental stresses and diseases.

Nanomaterials can also play a fundamental role in maximizing food safety both during processing and during packaging. Coatings for food production machinery (e.g., biofilm formation), nanostructured sieves, filters and membranes (e.g., enabling cold sterilization), nanostructured as well as nanoscale adsorbents and catalysts are only few of the applications providing benefits in food processing. In particular, nanofood contact materials can add novel

self-cleaning and antiseptic properties, useful in the production of safe food. In addition to surface biocides, nanotechnology in plastics and bioplastics in packaging can provide improvement in barrier properties and greater protection and preservation of food, and facilitate new and more efficient active functionalities. One property necessary for promoting food safety is traceability, which allows, for example, the removal of all tainted products from the market and the system during a recall process. It also ensures authenticity, adding value to the product. One could envisage, in the future, the placing of nanodevices not only on the packaging, but embedded inside the food, or even inside the raw materials allowing consumers to trace back the origin of all ingredients and providing information about the processes used to produce the products.

Food packaging applications currently form the largest share of nano-enabled products in the food sector on the market. They provide an opportunity “to do things right” at all levels, scientific, regulatory, and social, as well as at the economic and market level. Consumers are more open to accepting nanotechnologies applied outside the food, for example, packaging, rather than in the food, for example, nanoemulsions or nanoencapsulation. It is the responsibility of all stakeholders to implement methods to measure exposure and toxicity, and to develop risk-benefit assessment procedures, including impact on humans and environment. Developed countries should also adapt the innovation to the specific requirements of the food market in developing countries.

In fact, the needs and practices in developed and developing countries are quite different and often divergent. Potentially, successful technological innovation should be adaptable to different realities. A meaningful example is given by food waste, which plays a fundamental role in sustainability. It has been estimated that about 30% of all food grown worldwide is lost or wasted. Loss occurs mainly at the farm end in developing countries, while waste is produced at the fork end in developed countries. In the Foresight report of the British Government the importance of reducing food loss and waste is quantified in this statement: “Halving the total amount of food waste by 2050 is considered to be a realistic target . . . If the current global estimate of 30% waste is assumed, then halving the total could reduce the food required by 2050 by an amount approximately equal to 25% of today’s production.” [15] There is waste, and consequently potential for improvement at every stage, adding value to waste by enabling its usage. Through the new acquisition of knowledge, the application of innovative technologies, and especially through a better-developed system approach, we should be able to substantially minimize waste. In high-income communities, the introduction of sensor technologies described for quality testing and traceability should persuade consumers to rely on more specific information rather than the “best before” label, responsible for a great amount of wasted food. Waste is generally associated with quantity not quality. However, emphasizing nutritious, quality food is an essential component in the reduction of waste. Innovation and education should be combined and used to induce a permanent cultural change in behavior. This might take

generations, but would have a great impact both on society's health and on sustainability. What is essential in developing, low-income countries is to reduce post-harvest loss. Technologies, including nanotechnologies, developed for precision agriculture apt to avoid spoilage and waste of inputs can contribute to reaching this goal. Furthermore, food-contact nanomaterials for more efficient, safer processing and storage, and all technologies that support agricultural practices more adaptable to environmental and climate changes, could contribute to reducing food loss.

Developing countries face larger barriers regarding the applications of nanotechnologies than the developed countries for several reasons, including lack of funding and human capacity. Prioritization is hence particularly important and funding programs should focus on those applications that could provide maximum benefit-risk ratio for the poor [28]. Nanotechnology has the advantage that it often does not require technological expertise to be adopted. The final users, who eventually determine the acceptability of any new technology, need to know it exists and what its purpose is. However, the implementation of safety regulations could put an additional strain to poorer societies. Efforts should be put into communicating and knowledge sharing between developed and developing countries, in order to avoid a "nano divide," shifting the focus of nanotechnologies applications even further away from the necessities of the poor.

One of the pillars of food security is availability. Producing more food, particularly more nutritious food, minimizing waste, and changing dietary habits are measures that all need to be tackled at the same time. Still, it would not be enough to ensure food security unless one ensures that food reaches everyone. In recent decades, and in many countries, food production has evolved into an ever more centralized model. While this has generated notable advances in productivity, enabling us to produce enough calories globally, it has failed to distribute adequately the food produced and hence to meet the nutritional needs of our societies. There is now a need to decentralize food production and give greater priority to rural development. A decentralized production, able to use local resources would also be more easily adaptable to specific requirements posed by environment, health, and diverse economic, cultural, and social challenges. This should allow for greater availability and affordability of different nutrient sources, which supports both the concept of a food supply tailored to specific needs and an on-demand production. Ideally, food should be produced where needed and in the quantity needed. In the food system a responsible, evidence-driven adoption of nanotechnologies integrated with other converging technologies can greatly contribute to a distributed and networked food production supply. However, to increase public acceptance, it is imperative to evaluate carefully the use of new technologies, particularly of nanotechnologies, and to assess the risk of new nanomaterials. The assessment of food value chain sustainability should integrate natural, social, and political sciences and also consider "nontraditional" sustainability dimensions such as health and ethics.

It is urgent that we address food safety and sustainability problems. In doing so, we have a chance to review how we produce and consume food and radically

change our approach. A more holistic view will be necessary, requiring a highly inter- and transdisciplinary food system approach. Knowledge sharing and knowledge transfer are prerequisites for such a change, and communication among different sectors will be necessary in order to integrate innovative technologies into social change. This is what this book is about.

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