

Nanomaterial's applications in agriculture

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ABSTRACT

Technical innovation in agriculture is of extreme importance, in particular to address global challenges such as population growth, climate change and the limited availability of important plant nutrients such as phosphorus and potassium. Nanotechnology applied to agricultural production could play a fundamental role for this purpose and research on agricultural applications is ongoing for largely a decade by now. The application of nanomaterials in agriculture aims in particular to reduce applications of plant protection products, minimize nutrient losses in fertilization, and increase yields through optimized nutrient management. Despite these potential advantages, the agricultural sector is still comparably marginal and has not yet made it to the market to any larger extent in comparison with other sectors of nanotechnology application.

New devices and tools, like nanocapsules, nanoparticles and even viral capsids, are examples of uses for the detection and treatment of diseases, the enhancement of nutrients absorption by plants, the delivery of active ingredients to specific sites and water treatment processes. The use of target-specific nanoparticles can reduce the damage to non-target plant tissues and the amount of chemicals released into the environment. Nanotechnology derived devices are also explored in the field of plant breeding and genetic transformation. The potential of nanotechnology in agriculture is large, but a few issues are still to be addressed, such as increasing the scale of production processes and lowering costs, as well as risk assessment issues. In this respect, particularly attractive are nanoparticles derived from biopolymers such as proteins and carbohydrates with low impact on human health and the environment. For instance, the potential of starch-based nanoparticles as nontoxic and sustainable delivery systems for agrochemicals and biostimulants is being extensively investigated.

Nanomaterials and nanostructures with unique chemical, physical, and mechanical properties (e.g. electrochemically active carbon nanotubes, nanofibers and fullerenes) have been recently developed and applied for highly sensitive bio-chemical sensors. These nanosensors have also relevant implications for application in agriculture, in particular for soil analysis, easy bio-chemical sensing and control, water management and delivery, pesticide and nutrient delivery. In recent years, agricultural waste products have attracted attention as source of renewable raw materials to be processed in substitution of fossil resources for several different applications. Nanocomposites based on biomaterials have beneficial properties compared to traditional micro and macro composite materials and, additionally, their production is more sustainable. Many production processes are being developed nowadays to obtain useful nanocomposites from traditionally harvested materials. For example, it is possible to use chemical-mechanical processes to obtain nanofibers with enhanced thermal properties for the production of thermoplastic composites, starting from wheat straw and soy hulls.

KEY WORDS: Nanocomposite, Nanofibres, Nanocapsules.

1. INTRODUCTION

Nanomaterials as smart delivery systems for disease and pest control in plants: The most relevant nanodevices for plant protection are nanocapsules and nanoparticles, both at a scale ranging from 0.1 to 1,000 nm. A nanocapsule is composed by a shell that contains an active compound, like an agrochemical product for the protection of the plant against pests or diseases. The shell can be constituted by different elements, such as polymers, lipids, viral capsids or nanoclays. Its main function is to protect the active compound until it is released, but it can also improve the solubility and the penetration of the compound into the plant tissues. Depending on the specific characteristics of the shell, the active compound can be released slowly and gradually, or completely after the shell opening is triggered by certain circumstances (e.g. pH changes or enzymatic degradation).

Nanoparticles have a solid core or a matrix that can be composed by different materials (such as metals or polymers) and is surrounded by linkers and biomolecules. Due to the small size, the ratio between surface area and volume is increased in the nanomaterials (compared with bulk forms), improving the biochemical reactivity and conferring unusual and valuable physical properties (e.g. superparamagnetism). An example of application of nanocapsules for plant protection is the use of nanodisks for delivering amphotericin B, an important antimicrobial. The nanodisk is a matrix composed by a bilayer of phospholipids containing the molecules of amphotericin inside. This structure protects amphotericin molecules against the degradation by external agents (e.g. pH or light) while improving its solubilisation. While medical applications are intended to protect or cure one individual at a time, plant protection in agriculture is a massive treatment for thousands of plants. Therefore, it is important that the active compound is applied in relatively small doses to cover large plant surfaces. The characteristics of the product must thus be designed taking into account these wide treatments, and also if the mechanism of action is systemic or by contact.

An important aspect concerning plant protection products involves the way in which they are absorbed by the plant and their translocation within the plant tissues and organs. The formulation of the product varies if the absorption of the active ingredient takes place through the leaves or the roots. Absorption through the roots could be easier due to their biological role for nutrient assimilation, but the advantage of getting absorption through leaf tissues is that they are more easily available for field treatments. However, the knowledge about how these mechanisms work with nanomaterials is still to be improved. Magnetic carbon-coated nanoparticles can be tracked and used to analyse nanomaterials behaviour moving all along the plant structure. They are easily detectable and their magnetic properties allow their accumulation in tissues by way of using magnetic fields.

The use of nanocapsules and nanoparticles for plant protection products offers important advantages. Since active compounds are protected in capsules, they are not degraded by external agents or the crop plant itself, and are not involuntarily dispersed into the soil, allowing the use of a reduced amount of active compounds for plant treatments and consequently causing a lower environmental impact. Other environmental benefits of using nanodevices, e.g. nanoclays, derive from the potential reduction of leaching and further water contamination. Additionally, thanks to the protective capsule, it is possible to use also labile chemical products for plant protection, which can be less harmful to the environment and are currently not employed in agriculture because of their quick degradation. Finally, nanoparticles linked with biomolecules with specific affinity (e.g. antibodies or aptamers) guarantee the selectivity and specificity of targets.

Another valuable potential application of nanotechnology related to agriculture is plant genetic transformation. Nanoparticles carrying nucleic acid constructs and with specific ligands to penetrate the cell wall can increase the delivery of nucleic acid vectors into the plant cells, enhancing the development of new genetically modified (GM) plant varieties. The genetic manipulation through nanoparticles has potential advantages with respect to the transgenesis methods currently used. It is a system applicable to any plant species, while the more conventional *Agrobacterium*-mediated transformation can be applied only to selected species. Additionally, plant transformation through nanotechnology can lead to an increased efficiency in transformation rate with respect to biolistic methods. Moreover, with nanodevices it is possible to aim for both permanent and temporal genetic transformation, including gene silencing. In addition, genetic transformation could also be performed *in vivo* and not only *in vitro* like the other methods, allowing for specific transformation of individual plant organs or parts (fruits, branches, etc.). As illustrated with its application in disease and pest control, nanotechnology for plant genetic transformation offer very attractive advantages, but commercial applications are not yet mature, and further assessments of the safety of its use have to be conducted.

Starch-based nanoparticles in sustainable agriculture: Agricultural nanotechnology can be applied to sustainable production methods such as organic agriculture. The clear advantage of this approach is that starch is biocompatible, biodegradable and non-toxic for plants, animals and the environment. The first step to develop starch nanocontainers for sustainable and organic agriculture is to produce starch with improved content of amylose, which is the linear fraction composing starch and determines its functional properties, and therefore easily obtain starch particles with reduced size. This is possible through improved wheat varieties with higher amylose content obtained by molecular mutagenesis techniques.

The second step is the sustainable preparation, functionalization and characterization of starch nanoparticles suitable to be used as nanocontainers. The main approach adopted to produce nanoparticles from starch is based on the acid hydrolysis of starch granules, but these methods have several drawbacks that include long duration, low yield and environmental concerns about the production of toxic waste. To overcome these problems, it is possible to successfully apply ultrasounds as an eco-friendly approach for the production of wheat starch nanoparticles, without the need of any additional chemical reagent. Once nanoparticles are produced, their surface has to be functionalized: their physical-chemical and biological properties must be chemically or enzymatically modulated to obtain the entrapment of molecules to be delivered and released in a controlled way.

Different kind of molecules can be delivered through starch nanocontainers. They can be employed to deliver nutrients into plants tissues at slow release rates for the long-term feeding of plants, and to protect phosphorus and micronutrients (e.g. iron, manganese, zinc) in alkaline soils. Biostimulant compounds can also be slowly released through nanocontainers according to the plant needs, while being protected from microbial degradation before plant uptake. Moreover, starch nanocontainers can be developed for the delivery of plant protection products, e.g. antibacterial active principles, which can also be suitable for organic agriculture (e.g. vegetal extracts, copper) and thereby used in smaller amounts. On horticultural as on stone fruit plants, recent successful experiences (in greenhouse as well as in open field) revealed the great potentiality of these nanocontainers to protect the plants along the time against harmful pathogens.

Overall, the advantages of starch nanoparticles application in agriculture are the following:

- Absence of phytotoxicity;
- Reduction of harmful residues in soils;

- Reduction of chemical compounds use for nutrition/ protection of crops;
- High selectivity towards the crops treated;
- High quality and no harmful residues in the final products;
- Low production costs.

Sensors and diagnostic devices to monitor environmental conditions: Nanostructures as transducers in biosensors: Nanotechnology consists in the creation of novel functional materials, devices and systems through the control and utilization of nano-scale matter which presents unique properties (i.e. physical, chemical, electrical, mechanical, optical and magnetic characteristics) due to its scale. Some of the peculiar properties of nanomaterials represent specific advantages in the production of sensors and diagnostic devices. The quantum size effects of the nanomaterials result in unique mechanical, electronic, photonic, and magnetic properties. The chemical reactivity of nano-scale materials is different and much greater with respect to macroscopic state, mainly because of the increased surface area per unit mass. The lower scale allows new chemical forms of common chemical elements, such as fullerenes, nanotubes of carbon, titanium oxide, and zinc oxide. These properties enhance a great variety of nanostructures, all of them with different properties for different applications.

The most important nanostructures for sensors and diagnostic devices are fullerenes, nanotubes, nanofibers, nanoparticles, nanocolumns, nanocavities, graphene and carbon quantum dots. An important field of research concerning sensors and diagnostic devices is the analysis of soils, which can have relevant implications also for application in agriculture. The extreme miniaturization of the devices permits the analysis of planets soils, overcoming the typical problems of remote sensing, such as large sensors and sample size, the need of maintenance and calibration, the stability and reproducibility of the analyses and the power consumption. Nanomaterials and nanotechnology can provide solutions to these problems by decreasing the sensor and sample size, maximizing the number of sensors and reducing the power consumption. In some cases it is possible also to perform direct soil analysis using chemical microscopes, without sampling, solvents, and reagent delivery. Bio-silica nanostructures are particularly suited for building diagnostic and sensor devices based on proteins. Biosilica is produced by marine species (e.g. diatom and sponges) in order to support and protect the unicellular organisms. Such nanostructured material can be used for protein immobilization and stabilization, developing robust biosensors.

Nanomaterial-based nanodevices provide a new horizon for applications. They have already shown their efficiency in some cutting edge technologies, and they will have a very profound effect in emerging technologies in the near future. In particular, agricultural technologies will benefit from direct and easy bio-chemical sensing and control, water management and delivery, pesticide and nutrient delivery and monitoring and food safety for consumer protection.

Bio-nanocomposites from agricultural residues: Natural fibres from plant and wood are used as reinforcement materials for bio-composite production since the beginning of the 20th century. With their relative high strength, high stiffness, low density and being renewable, these biocomposites are of interest as a replacement for synthetic fibre reinforced composites in an increasing number of industrial sectors, including the automotive industry, packaging, construction and consumer product industries.

There are an estimated 500 million tonnes of agricultural residues such as corn, soybean and wheat, available in North America each year. Only a small percentage is being used in applications such as feedstock and energy production¹⁸. Most get burned on the field. Cellulose is a fibrous, semicrystalline and the most abundant biopolymer on Earth. It is the main constituent of plant structures. Plant cell walls consist of rigid cellulosic microfibrils embedded in a soft hemicelluloses and lignin matrix. Cellulose chains are packed in an ordered manner to form compact microfibrils, which are stabilized by both inter-molecular and intra-molecular hydrogen bonds. These microfibrils are formed by elementary fibrils (nanofibres) that are 8-50 nm in diameter and length of a few microns. Because of their crystal structure, nanofibres give strength to the plant stem. The main challenge in adopting this new technology is constituted by increasing the production scale of the nanofibres and their applications in industrial scale. In order to obtain this, one option is to create synergies between the industries that benefit from using natural fibres, such as packaging, automotive, textile and medical, and the potential producers of the natural nanofibres.

Potential Benefits of Nanomaterials Applications in Agriculture: Currently the research and development pipeline has the potential to make agriculture more efficient, increase yields and product quality, and thereby increasing nutritional benefits. Developed countries are using or testing nanosensors and nanoagricultural chemicals, nanoparticles for soil cleaning and nanopore filters, nanoceramic devices, and nanoparticles. An increasing number of applications are expected for food and agriculture uses, including nanosensors, potentially capable of detecting chemical contaminants, viruses, and bacteria; nano delivery systems, which could precisely deliver drugs or micronutrients at the right time and to the right part of the body; as well as nanocoatings and films, nanoparticles, and quantum dots. There are several reports on the great potential of agricultural and food nanotechnology in developing countries. Promising nanotechnology applications address low use efficiency of agricultural production inputs and stress of drought and high soil temperature. Nanoscale agrichemical formulations can increase efficiency

use and decrease environmental losses. Nanoporous materials capable of storing water and slowly releasing it during times of water scarcity could also increase yields and save water. Researchers have shown that applying nanotechnology to reduce the effects of aflatoxin (a fungal toxin) increases the weight of food animals. The potential for nanotechnology in agriculture continues to grow that more ambitious uses of nanoparticles are bio-remediation of contaminated environments, biocides and antifungals on textiles. Photocatalysis in agriculture is another direction in which nanomaterials can play an important role. Different nanostructures of titanium dioxide (TiO₂) and zinc oxide (ZnO) have been widely studied as photocatalysts. Chemicals presented in pesticides are transformed in relatively harmless molecules such as CO₂, N₂ and H₂O. Under progress is also the removal of pesticides and herbicides on plants and the soil through photocatalysis. Carbamate pesticides used in a variety of field crops are completely mineralized in the presence of ZnO and TiO₂, dichloropyrifos being an example of an often used pesticide. Apart from nanoparticles, there are reports on the use of nanotubes and nanostructures thin films for degrading pesticides.

2. CONCLUSION

Nanotechnology applications have the potential to change agricultural production by allowing better management and conservation of inputs to plant production. Researchers in nanotechnology can do a lot to benefit society through applications in agriculture and food systems. Introduction of any new technology always has an ethical responsibility associated with it to be apprehensive to the unforeseen risks that may come along with the tremendous positive potential. Public awareness about the advantages and challenges of nanotechnology will lead to better acceptance of this emerging technology. Rapid testing technologies and biosensors related to the control of pests and cross contamination of agriculture and food products will lead to applications of nanotechnology in the near future. Nanotechnology application in agriculture and food systems is still at the nascent stage and a lot more applications can be expected in the years to come. Nanoparticles present an extremely gorgeous platform for a diverse range of biological applications. As it provides the single step process for biosynthesis of nanoparticles, it attracts more researchers to go for future developments in the area of electrochemical sensor, biosensors, medicine, healthcare and agriculture. New research also aims to make plants use water, pesticides and fertilizers more efficiently, to reduce pollution and to make agriculture more environmental friendly.

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