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MINI REVIEW

Overview of Novel and Sustainable Antimicrobial Nanomaterials for Agri-Food Applications

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ABSTRACT

Constant technological advances have inspired the development of new products, processing and methodologies in the entire agri-food chain. As novel products and processing techniques arise, food safety remains a matter of major relevance, since the food industry is continually challenged to avoid the spreading of microbial pathogens along the food chain and to reduce the economic losses caused by spoilage microorganisms. The control of microbial growth in food has been conventionally made by thermal processing or by adding chemical preservatives. However, there is an increasing demand from consumers for more natural food products starting from the field to the shelf and market. Novel technologies have been proposed, and in this context, the use of natural antimicrobial compounds has gained relevance, due to the absence of toxic or undesirable effects to the consumers. Furthermore, nanotechnology can be a powerful tool to provide solutions to the complex set of scientific and technological challenges necessary to improve the safety of the entire agri-food chain. The advances in material science and analytical method logiesled to a rapid development of nanotechnology that has enormous potential to improve food safety, as a powerful tool for delivery and controlled release of natural antimicrobials, allowing a putative increase in food product shelf-life.

Current research trends and some recent results obtained in our laboratories concerning novel and more sustainable strategies and approaches both in agricultural sector, with special focus on plant pathogen control, and in industrial sector, regarding especially food active packaging sector, will be here presented and discussed in order to give an exhaustive overview of the real practical potentiality of the proposed novel materials, also at nanoscale, in agri-food applications.

Introduction

Nanotechnology is a multidisciplinary area or research that involves different sector from engineering and physics to chemistry or biology. The emergence of nanotechnology has reached impressive levels in recent years whereas the development of special nanotools and nanomaterials has found interesting applications in both agriculture and food sectors [1,2]. Nanomaterials exhibit, in fact, physical and chemical properties that differ to a large extent from those exhibited in macroscale materials and thus unprecedented applications and uses may be envisaged for these materials. Most of the investigated nanotechnological approaches initially aimed to solve evolving problems in the agri-food industry in order to impact on the economic potential. Then, after the implementation of new technologies and strategies, that were using nanostructured materials, the worldwide concern was rapidly extended to numerous applications that could be developed by using the science of materials at the nanoscale [3]. Smart materials, biosensors, packaging materials, nutraceuticals, and nanodevices have been designed to address numerous agri-food related issues with direct impact in health, economy, ecology, and industry. As the engineering of nanostructured materials has constantly progressed and extended its applications, there is virtually unlimited potential in this sector. Polymer nanotechnology, for example, involves the design, processing as well as the manufacture, of polymeric materials to produce structures, materials, or devices having at least one dimension at the nanometer scale, that is, with sizes comprised between 1 and 100 nm. For instance, the nanometer dimension is provided by the incorporation of nanometer additives such as nanoparticles [4,5].

However, the widely differing opinions on the applicability and usefulness of nanotechnology between both specialists and the general public, has hampered progress. The main concern manifested by people is related to the potential risk for health and the environmental impact of the recently developed nanoengineered materials and devices. Therefore, current approaches are strictly considering these concerns when designing nanotechnological solutions for agriculture and food sectors. The use of bio-based and/or biodegradable materials in the development, synthesis and process of nanoscale devises and systems, involving also natural sources or wastes, seems to be a promising strategy to overcome safety issues [3].

Lignocellulosic structures, in particular, cellulose and lignin nanoscale materials, have recently attracted much attention due to their renewable nature, wide variety of sources available throughout the world, low cost and density, high surface functionality and reactivity. The high mechanical strength, high aspect ratio and large surface area, allow to these nanomaterials to reinforce a wide variety of polymers even at very low filler loadings. Additionally, nanocomposite approach has developed as an efficient strategy to increase the structural and functional properties of natural and/or synthetic polymers. The combination of biodegradable and/or bio-based polymers with bio-based nanostructures has opened new perspectives for different applications [1,2,6].

This review was argued with the idea to give an overview of our recent reported strategies, novel approaches and recent results on novel and sustainable nanotechnological tools and materials and their applicability in both agriculture, especially in disease control caused by different plant pathogen and, industrial sector especially related to food packaging field (Figure 1).

Plant agricultural production, allows to obtain fundamental products for nutrition as well as industry (food, feed, fiber, and fuels) but, natural resources are limited. Among, modern agricultural practices, it is well documented that excessive and inappropriate use of pesticides has increased chemical residues dangerous for consumers as well as in the environment (from soil to groundwater, till to increase pest resistance). Nanotechnology, similarly for developed and developing countries, has the potential to revolutionize the agriculture and food sector. It can guarantee the delivery of drugs, genes, and pesticides to specific sites at cellular levels in targeted plants and animals, by limiting side effects. Nanotechnology can be used to evaluate gene expression under different stress condition for both plant and animal foods through the development of nanoarray-based gene-technologies. Moreover, it can allow the development of smart nanosensors to detect fertilizers and pesticides by high precision for an adequate management of the natural resources. In addition, numerous industrial-related applications with direct impact on economy have emerged: nano- and micro-structured arrays can detect the early presence of pathogens, contaminants, and food spoilage factors. The broad range of applications in agriculture includes also nanomaterials, possibly bio-based and/or biodegradable, to control plant pathogens. Over the past decade, patents and products incorporating nanomaterials for agricultural practices (e.g., nanopesticides) rapidly increased. In 2011 over 3000 patent applications dealing with nanopesticides were submitted [7], with the collective goal to enhance the efficiency and sustainability of agricultural practices by less input waste than conventional products and approaches [8]. Plant diseases are caused different micro-organisms (i.e.: bacteria, fungi, insects) that are responsible for billions of dollars in agricultural crop loss each year and, only in USA, over $600 million is spent annually on fungicides in an attempt to control pathogens [9]. In this context, it is really simple to understand the need of novel sustainable and cheap solutions.

Smart and active systems for food processing and packaging, as well as nanoemulsion-based decontaminants for food equipment and storage compartments, and nanoparticles that facilitate the bioavailability and delivery of nutrients directly to cells, represent other applications in which the nanotechnologies find large requests. Most plastic packaging is currently petrochemical-based and it is well known that packaging sector represents about the 40 % of annual plastic demand over the world. Many types of commodity and specialty polymers have been used in packaging materials [10], however, conventional plastic packaging also has associated problems of disposal, littering (including ocean pollution), reuse and recycling, because of the very slow rate of environmental degradation and the lack of collection and recycling infrastructure in many countries.

Figure 1: Main goals and focuses of the present overview.

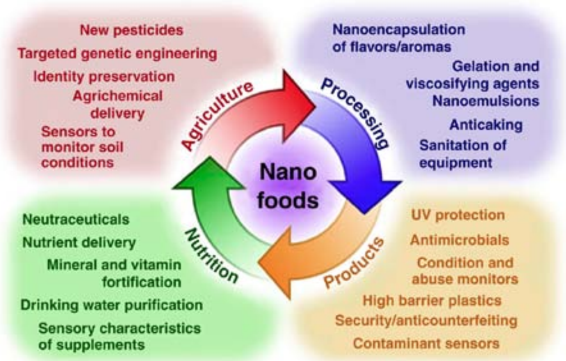

Figure 2: Scheme of the applications of nanotechnology in agri-food science. Nanotechnology has found applications in many different areas ranging from agriculture or food processing to security to packaging to nutrition and neutraceuticals. Reprinted with permission by [18].

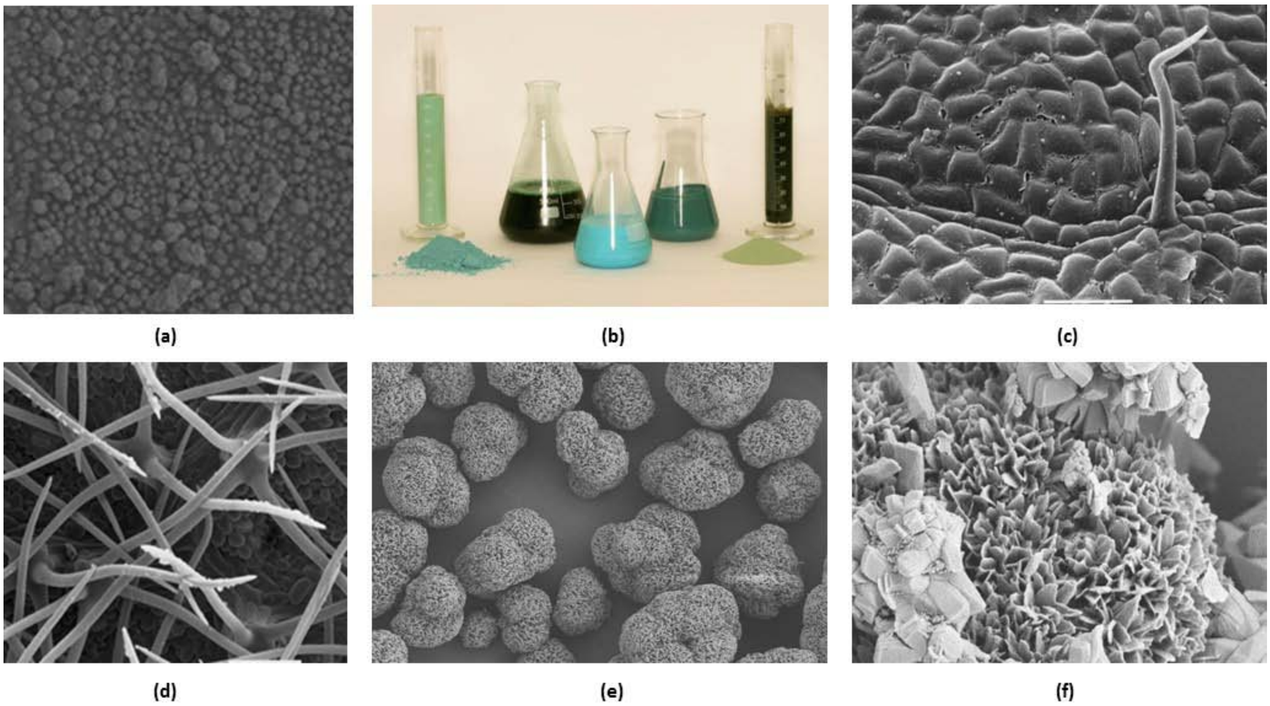

Figure 3: Scanning electronic microscope (SEM) images of traditional and innovative copper formulations for sustainable plant protection strategies: (a) traditional powder cupric salts, 500 X; (b) different copper formulations; (c) cupric salts deposited on upper leaf tissue, 500 X; (d) cupric salts residues on leaf hairs, 200 X; (e) micro-cupric salts, 5000 X; (f) micro-cupric salts linked natural active ingredients, 25.000 X.

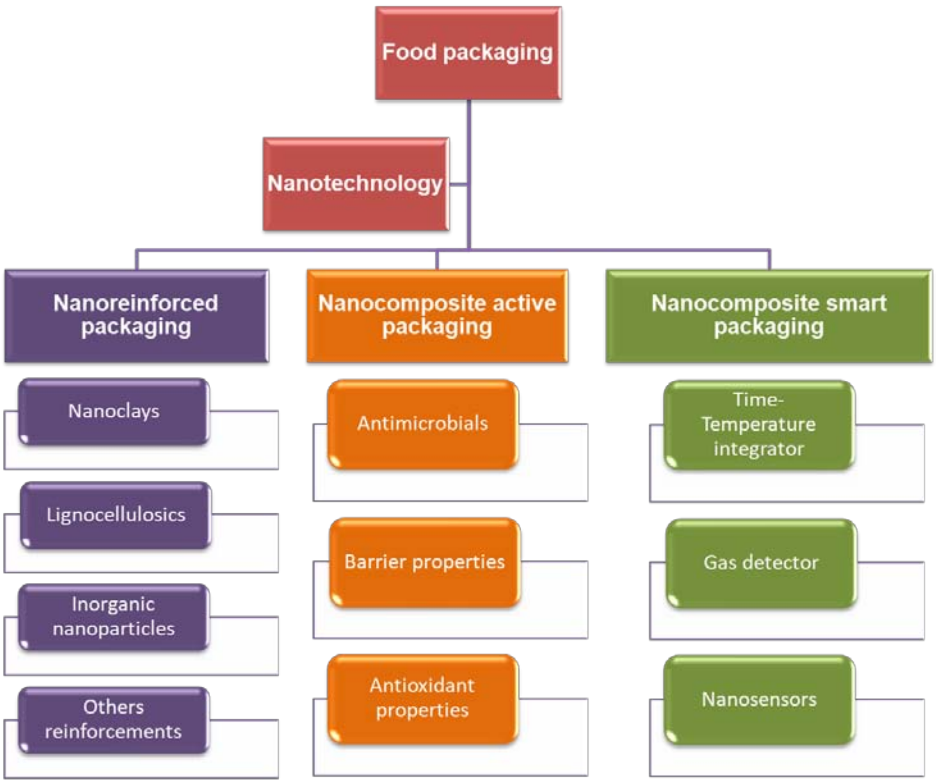

Figure 4: Different types and sub-types of nano-food packaging being used along with their different applications [Reproduced from 42].

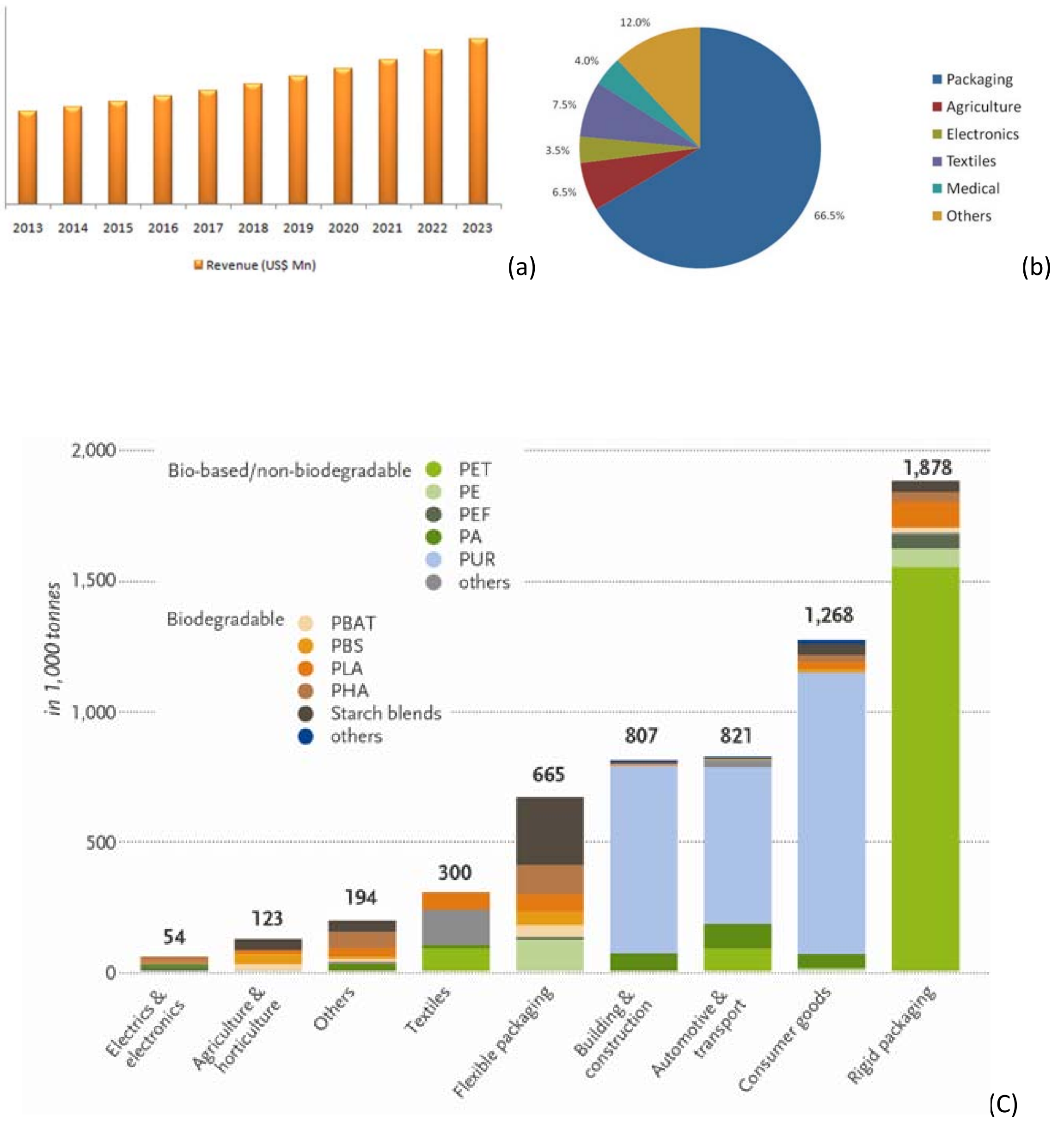

Figure 5: Global Bio-Based Biodegradable Plastics Market trend (a), biodegradable plastics by Applications, 2016 (b) and global production capacities (2021) at European level(c) [43].

Bio-based polymeric materials are currently considered the only alternative in the future to petroleum-derived polymers, as fossil resources become exhausted. Biopolymers from different origins can be used for food packaging applications or food coating purposes, but the functional properties of biopolymer-based materials in terms of their mechanical and barrier properties, need to be adapted to food requirements. To this end, numerous studies have been carried out applying different strategies to reduce the drawbacks of using biopolymers for packaging purposes. The incorporation of antimicrobial or/and antioxidant compounds, also embedded into sustainable micro- and/or nano-carriers, and added to biopolymer-based materials, seems to be a good approach to obtain active films, with more competitive properties, useful to extend the shelf life of foodstuffs. The release kinetics of actives into different food systems need to be evaluated and, in this context, the use of nanocarriers could be useful in the modulation of release and control or maintenance of food organoleptic properties.

In this scenario, this review aims to give a general but comprehensive view and impact of the science of nanometer-sized materials on the field of agriculture and food industry, also discussing some the current inquiries regarding advantages in terms of environment and health, aiming to increase awareness to a wider amount of readers.

Nanotechnology Field and Concepts

Nanotechnology is defined by the US Environmental Protection Agency [11] as the science of understanding and control of matter at dimensions of 1–100 nm. Other challenges to define nanoparticles from the point of view of agriculture include "particulate-based formulations between 10 nm and 1000 nm in size that are simultaneously colloidal particulate".

The burgeoning applications of nanotechnology in agriculture will continue to rely on the problem-solving ability of the material and are unlikely to adhere very rigidly to the upper limit of 100 nm. This is because nanotechnology for the agricultural sector should address the large-scale inherent imperfections and complexities of farm productions (e.g., extremely low input use efficiency) that might require nanomaterials with flexible dimensions, characteristics, and quantities. However, this is in contrast with nanomaterial concept that might be working well in well-knit factory-based production systems. Nanotechnology design and development is, furthermore, usually represented by two different approaches: top-down and bottom-up. Top-down refers to making nanoscale structures from smallest structures by machining, templating, and lithographic techniques, for example, photonics applications in nanoelectronics and nanoengineering, whereas bottom-up approach refers to self-assembly or self-organization at a molecular level, which is applicable in several biological processes. Biologists and chemists are actively engaged in the synthesis of inorganic, organic, hybrid, and metal nanomaterials, including different kinds of nanoparticles that, due to relevant optical, physical, and biological properties, have enormous applications in many fields like electronics, medicine, pharmaceuticals, engineering, and agriculture [12].

Applications of nanotechnology in material science and biomass conversion technologies, applied in agriculture, are the basis of providing food, feed, fiber, fire, and fuels. Through advancement in nanotechnology, a number of state-of-the art techniques are available for the improvement of precision farming practices that will allow precise control at a nanometer scale. Nanotechnology has the potential to change the entire scenario of the current agricultural and food industry with the help of new tools developed for plant diseases control, high sensible and rapid nano-based kits for plant pathogens detection and improvement of plants to nutrients absorption, etc. Nanoscale biosensors, and other smart delivery systems will also help the agricultural industry to better contrast different crop plant pathogens. In the near future, in fact, nanostructure-based catalysts will be available in order to increase the efficacy of commercial pesticides reducing the dose levels required for target crop pests [13]. The current global population is about 7 billion with 50% living in Asia. A large proportion of those living in developing countries face daily food shortages as a result of environmental impacts on agriculture including storms, droughts, and flood [13]. Similarly, agricultural production continues to be constrained by several biotic and abiotic factors. For instance, pests, diseases, and weeds cause are responsible of remarkable damages and losses for agricultural productions. Evidences indicate that plant parasites cause 25% loss in rice, 5–10% in wheat, 30% in pulses, 35% in oilseeds, 20% in sugarcane, and 50% in cotton [2]. In this scenario, nanoscaled carriers can be utilized for an efficient delivery of fertilizers, pesticides, herbicides, plant growth regulators, etc. [14]. These advancements will help increasing the bioavailability of active ingredients to the plant, thereby reducing the amount of effort and waste product. The use of sustainable raw materials for carrier synthesis, by using lignocellulosic materials also derived from residues, as sources for them, could contribute to the "zero waste" and "green circular economy" concepts that are actually of interest in both academic and industrial panorama [1,2]. Finally, current investigations aim to take advantage of polymer nanotechnologyto produce novel food packaging formulations with better mechanical, barrier, antimicrobial properties and to trace the food condition during transport and storage phases. Polymer nanotechnology can, in fact, extend and improve the main functions required for food-packaging, that is, protection and preservation, containment, but also communication and marketing [15-17].

(Figure 2) identifies the potential uses of nanotechnology in the entire agri-food sector [18].

Agricultural Sector and Market: Special Focus on Novel and Sustainable Pesticides

The yield of agriculture is increasing, but the primary concern is safely and sustainable production. Previously, many applied technologies have been innovated in the agriculture sector for improvement of production such as, the usage of synthetic chemicals, but still a gap between the requirement and contentment of a real sustainable agriculture production looking for new technology [2]. Different pests cause huge economic losses and tremendous negative impact on environment respect to the most worldwide cultivated crops (i.e: rice, wheat, cotton) and so it is extremely urgent to develop "green" strategies to contrast them enhancing active ingredients (AIs) from waste agro-food chains [14,19]. Nanotechnology is a prominent technology that in agriculture field is also looking towards this newly growing technology with great hope for future sustainability. Nanoformulations and/or nanoparticles mediate delivery will provide site specific and controlled release of agriculture inputs like pesticides. Their reduction will be helpful in maintaining natural eco-balance of biological cycles, increasingly destroyed or imbalanced using synthetic chemicals and toxic for the next generation so, the need is to move into a sustainable nanotechnology.

In plant protection compounds, those still fundamental are metals but, the use of metal nanoparticles, polymer based nano-formulation and encapsulation of pesticides are in nascent phase [20-22]. Traditional strategies like integrated pest management used in agriculture are insufficient nowadays and excess use of chemical pesticides like DDT has adversative effects on animals and human beings apart from the decline in soil fertility. Nanotechnology promises a breakthrough in improving our presently control of plant diseases, understanding the mechanism of host-parasite interactions at the molecular scale, development of new-generation of pesticides. In the form of nanoformulation, nanoencapsulation and functionalized nanoparticles, this new technology provides lots of new opportunities in the development of new bio-pesticides. For example, about cupric salts used in agriculture for plant protection, the problem is huge. Due to their accumulation in soil and water, disposal issue, phytotoxic effect and accumulation on vegetal tissue, as to induce the development of plant pathogens resistance, the EU wants progressively to ban their use for conventional as well as for organic farms (Figure 3). Removal of copper compounds would have a major impact on disease management of economically relevant crops like potato, tomato, apples and grapes and so, it is extremely urgent to develop alternative and sustainable solutions. In this sense, copper (Cu) nanoparticle is reported effective against disease spread by *Xanthomana* ssp. such as rice bacterial blight disease (Xanthomonasoryzae) and leaf spot of mung by *Xanthomonas* campestris [23]. Other authors reported that Cu nanoparticles have broad spectrum antimicrobial activity against Gram positive and negative bacteria and fungi; at low concentration, it can be used as a fungicide [24]. Similarly, Cioffi and colleagues [25] measured antifungal activity of nanocomposite of copper with polymer against plant pathogens. Copper nanoparticles, due to unique properties, are more efficient than bulk copper particles in activity and functioning and, due to antimicrobial activity, they are finding new applications in agriculture, [26] showing to be able to effectively inhibit growth of many pathogenic bacteria and fungi [27,28]. Various studies have suggested that copper nanoparticles can be used as antimicrobial for disease control in agriculture, where dangerous plant pathogens (fungi and bacteria) cause relevant damages to many crops. Copper based fungicide play an important role in disease prevention and treatment in a variety of plant species [29]. Three different copper based nanoparticles of similar sizes i.e. 11–14 nm and shapes, Cu_2O, CuO and Cu/Cu_2O respectively, were tested in the field against *Phytophthora infestans* on *Lycopersicon esculentum* (tomato) under protected cultivation. The results showed that all the tested copper based nanoparticles were more effective in lower formulated product and active ingredient rate than the four-registered copper based agrochemicals. Along with the promising efficacy, it was also found that copper-based nanoparticles did notinduce any phytotoxic effect to the plants [30]. In this sense, respect to cupric salts, also the use of AIs started to be successfully investigated [2,31-33]. Recently, chitosan hydrochloride (CH)-based coating was proposed to contrast gray mold frequently caused by the two selected plant pathogens (*Botrytis cinerea* and *Pectobacterium carotovorum* subsp. *carotovorum)* during postharvest phases of fruit or vegetable products [34].

Food Protection and Packaging Sector: Bioplastics and Shelf-Life Concept

As discussed in the previous paragraphs, agricultural products influence most aspects of life, including everyday materials, such as fuels, textiles, furniture, feedstock for bio-based products and clearly also food and feed. Technology advancement is needed to achieve the future global needs from agriculture. Material science, and in particular, nanotechnology and nanosciences, have shown great potential in improving food safety, quality, product traceability, nutrient delivery, enhancing packaging performance, and improving agricultural and food processing. During the last decades, polymers have replaced conventional materials (glass, ceramics, metals, paper and board) in food packaging owing to their functionality, light weight, low cost and process ability. However, their mechanical responses are lower if compared to metals and ceramics [35]. As the uses of nanotechnology have progressed, it has been found to be a promising technology for the food packaging industry in the global market: such new packaging materials have excellent barrier properties to prevent the migration of oxygen, carbon dioxide, water vapour, and flavour compounds, higher surface-to-volume ratio than their microscale counterparts, and, therefore, they are able to attach to a vast number of biological molecules, which enhances their efficiency [36]. Unlike some conventional fillers and additives, a very low level of nanoparticles is generally sufficient to improve the properties of packaging materials without any significant changes in density, transparency, and processing characteristics [37]. The addition of certain nanoparticles into shaped objects (e.g. bottles, containers), and other forms of packaging (e.g. films) can render them light, fire resistant, and stronger in terms of mechanical and thermal performance, and may also make them less permeable to gases. It is therefore not surprising that one of the fastest moving sectors to embrace nanotechnology and realise the potential benefits is the food and beverage industry. A number of the world's largest food companies have been reported to be actively exploring the potential of nanotechnologies for use in food or food packaging. It is also clear from a number of reports, reviews, patent applications, and company products that the nanotechnologies have started to make an impact on different aspects of the food and associated industries [38]. Nanotechnology has already opened up a way for a multibillion dollar global industry in recent years. The market impact of nanotechnology reached 1 trillion US$ by 2015, with around 2 million workers [39]. Whilst the majority of manufacturing and use of nanoscaled materials occurs in the United States, the European Union (EU), with its 30% global share of this sector, is not lagging far behind. Within the European Union, the UK accounts for nearly a third of the sector [40,41].

Specifically, recent trends in polymer based-food packaging systems regard nanoreinforcements, nanocomposite active packaging and nanocomposite smart packaging (Figure 4). Nanoreinforcement are mainly used to give extra tensile strength of food packets by different method using nanoclays, lignocellulisics, inorganic partecles, etc. Nanocomposite active packaging is the integration of many useful systems along with the food packets, e.g. antimicrobial, oxygen scavenging and enzyme immobilization system. Similarly, nanocomposite smart packaging mainly involves sensors, e.g. time–temperature integrator (TTI), gas detectors and other nanosensors [42].

Nanoreinforcements are used to increase tensile strength and, in general, the mechanical characteristics of polymer based packaging systems. Polymer nanocomposites usually have a much better polymer/filler interactions than the usual composites. Nanofillers have a vital role to enhance composite performance by improving their properties such as mechanical strength, thermal stability and barrier properties, directly related to the shelf life of food products. The characteristic parameters that contribute greatly in modifying the properties of various composites are the filler loading; their size and shape; and their affinity towards matrix material nanosensors [42]. Nanoclays and/or inorganic nanoparticles as, for example metal nanoparticles, have firstly received significant attention in a nanocomposites approach by the material industry due to their ability to enhance the performances of polymers. However, the growing interest concerning environmental issues and related human health, opened new scenarios to the use of both bio-based and/or biodegradable polymer matrices and nanoreinforcements in food packaging field. Currently, in fact, in packaging industries, the largest part of materials used is non-degradable petroleum. As a result, this non-degradable food packaging materials, represent a serious problem on the global environmental. Therefore, the use of bio-based packaging materials, such as edible and biodegradable films from renewable resources, could at least to solve the waste problem by reducing packaging waste and extend the shelf-life, which in turn, enhance food quality. In this specific framework, nanocomposites based on biopolymers may serve as significant route for the development of new and innovative food packaging material by extending the shelf life and improving the food quality, while minimizing the environmental pollution after usage. Key driving factors identified in the bio-based biodegradable plastics market are regulatory framework for safe waste disposal and management, implementation of environmental conservation initiatives by government and various institutions, and efforts by manufacturers to reduce dependency on crude oil derived products. This market is also mainly driven by the growing conscientious population and government regulations that have started focusing towards the reduction of wastage and usage of biodegradable packaging materials. However, the lack of supply of bioplastics and the higher cost of materials are hindering the growth of this market. According to a new market report published by Credence Research "Biodegradable Food Packaging Market – Growth, Future Prospects, Competitive Analysis, and Forecast 2016 – 2023," the biodegradable food packaging market has been estimated to be valued at US$ 3,403.4 million by the end of 2016, and is expected to reach US$ 7,058.8 million by 2023, expanding at a CAGR of 11.0% from 2016 to 2023 (Figure 5a).

The global biodegradable packaging market by product type and application has witnessed a significant growth in the past few years, and this growth is estimated to persist in the coming years. Europe and North America dominated the biodegradable packaging market in 2013 and accounted for over 65% of the market. Biodegradable plastic packaging market is expected to show the double-digit growth rate by 2019. Packaging application constitutes the largest application segment of bio-based biodegradable plastics market. In terms of volume, it is projected to grow 2-fold by 2020 from 2014. In 2014, the volume share of packaging application was valued at nearly 65% of the total market and is expected to remain the largest application segment over the forecast period (Figure 5b). Looking at the European level, the current market for bio plastics (both bio-based and biodegradable ones) is characterised by a dynamic growth rate and a strong diversification (projection up to 2021), that will help and encourage their use as matrices for nanocomposites in many (Figure 5c) [43].

It is clear from these forecasts of growth for nano-enabled products across all market areas and the specific forecasts for growth in nano-enabled packaging for food and beverage product packaging that this area is leading in terms of having products already in the market place also in terms of expectations of significant growth. Nanotechnology will be an enabler to deliver smart, novel packaging that can benefit not only the product producer, but also the consumer by providing extended shelf life with additional product information and enhanced security at a cost that is acceptable both to the producer and the consumer.

The incorporation of antimicrobial or/and antioxidant compounds into polymer- or biopolymer-based materials is a good approach, for example, to obtain active films, with more competitive properties, and useful to extend the shelf life of foodstuffs contributing to the increase of food quality. The stabilization of bioactive materials encapsulated in nano-carrier systems against deleterious environmental conditions can be achieved by food nanotechnology and thus increase the nutrition and quality of food systems. The release kinetics of actives into different food systems need to be evaluated in order to analyse the effectiveness of these materials for food preservation, adapting them to specific target applications. Of the available natural and non-toxic active compounds, essential oils and their major components have been widely studied, due to their antioxidant and antimicrobial properties together with their Generally Recognized as Safe status.

However, even if concerns have been expressed about the inclusion of nanomaterials and the potential for free nanomaterials getting into the environment, nanotechnology will lead to enhanced performance for lower total packaging weights, there is likely to be less waste for disposal. Nevertheless, the actual use of polymer-nanocomposite in industry is going very slowly, and the main reasons are represented by the cost price of materials and processing, restrictions due to legislation, acceptance by customers in the market, lack of knowledge about the effectiveness and impact of nanoparticles on the environment and on human health, the potential risk due to migration of nanoparticles in food, and balance between the use of biomass for the production of materials or food.

Recent contributions on plant and food protection by using bio-based and/or biodegradable polymers and nano-reinforcement phases, also extracted from natural sources or forest/agricultural wastes, their potentials and possible applicability at a practical point of view with perspectives for agricultural and industrial fields, will be discussed in the following paragraph.

Recent Contributions on Plant and Food Protection

The aim to reduce or substitute chemicals replacing them with organic active principles in plant protection strategies, is a recent main target. From seeds, trough nursery until open field, the negative effects of synthetic pesticide on environment and respect to induce frequent pest resistance are urgent problems to be solved. One of the main objective is to reduce the use of cupric salts (Cu^{++}) to protect plant production respect to different pests and plant pathogens for conventional and in particular for organic farmers. The recent EU guidelines have led to move to a drastic reduction in Cu^{++}use over the next few years and alternative plant protection strategies are so requested. In this sense, recently interesting results were obtained respect to the control of different bacterial plant pathogens on tomato crops. Organic active ingredients (AIs) like botanical extracts and different essential oils, alone and/or in combination with cut amount of copper salts (until less 50% of dosage field doses up to now used) resulted effectiveness to reduce, in vitro, in planta and in open field tests, the multiplication of *Pseudomonas syringae* pv. *tomato* (Pst) and *Xanthomonas axonopodis* pv. vesicatoria (Xav) populations and their damages on tomato plants [44].

To move through traditional pesticides to nanopesticides and/or micro formulation of pesticides resulted helpful to rightly address nanotech approaches. Recent results suggested that AIs as gallic and ellagic acids, especially when formulated together and in microcapsule, ought to be considered for an inclusion in integrated management strategies against bacterial diseases of kiwifruit as alternative to, or in combination, with a reduced amount of copper compounds. Their encapsulation in methacrylate polymeric microparticles showed to improve their usefulness and to prolong remarkably their activity up to 14 days after the treatment, in greenhouse and in field on artificially and naturally infected plants, respectively. These microformulation pointed out their potentiality to future alternative biological control strategies against kiwifruit bacterial diseases caused by *Pseudomonas syringae* pv. *actinidiae, Pseudomonas syringae* pv. *syringae* and by *Pseudomonas viridiflava*, causal agent of bacterial canker, floral bud necrosis and bacterial blight, respectively on kiwifruit plants [22].

As nanopesticide innovative formulation, interesting results have been recently obtained. Novel poly(DL-lactide-co-glycolide acid) (PLGA) copolymer-based bio polymeric nanoparticles (NP) and cellulose nanocrystals (CNC) were evaluated as basic materials for their use as nanocarriers to develop innovative plant protection formulations for tomato crops. PLGA NP were synthesized and tested, and the effect of natural surfactants, such as starch and CNC, on the NP final properties was investigated. In addition, CNC were evaluated as possible nanostructured formulation to be directly applied in plant protection treatments. The effect of both, PLGA NP and CNC, was investigated with respect to their influence on the survival of the causal agent of bacterial speck disease (Pst), on plant development and damages (phytotoxicity effects), on tomato plant. The proposed nanocarriers resulted able to cover, with a uniform distribution, the tomato vegetal surfaces without any damage and allowed a regular development of the tomato-treated plants. Moreover, starch–PLGA NP formulations resulted unsuitable for Pst survival and multiplication along the time on the tomato plants surface. A green and particularly sustainable approach for nanostructured materials useful for biopesticides development comes up by using these nanocarriers; they resulted particularly useful on plants to carry out and to release antimicrobial active ingredients to develop in innovative and sustainable plant protection strategies [14].

New biodegradable multifunctional, antimicrobial and antioxidant systems were rapidly promoted and investigated in some different application fields and in the entire agri-food chain both for plant protection as well as novel food packaging systems in order to have valid eco-friendly strategies to improve the safety and quality of food products. In this scenario, bio-based and/or biodegradable molecules and polymers were considered to be promising solutions to reduce and/or limit the environmental impact respect to the traditional chemicals or plastics [1,45,46].

Concerning the packaging sector, the scientific community and the growing interest of humans promoted the development of new edible and eco-friendly packaging considered as valid alternatives to reduce wastes and residues. In the last decade, researchers focused their attention on the use of lignocellulosic by-products as reinforcing fillers in polymeric matrices. The revalorization of lignocellulosic materials was largely investigated as a valid alternative to extract nano reinforcements completely natural and renewable as cellulose nanofibers, cellulose nanocrystals (CNC) and/or nanolignin [6].

Luzi and co-workers used, for the first time, kiwi Actinidia deliciosa pruning residues as precursors for the extraction of high performing cellulose nanocrystals by applying a bleaching treatment followed by an acid hydrolysis. The resultant cellulosic nanostructures, obtained by an optimize extraction procedure (0.7% wt/v two times of sodium chlorite $NaClO_2$) followed by an hydrolysis step, were then used as reinforcements phases in poly(vinyl alcohol) (PVA) blended with natural chitosan (CH) based films and also combined, for the first time, with carvacrol as active agent. The morphological, optical and colorimetric results underlined that no particular alterations were induced on the transparency and color of PVA and PVA/CH blend by the presence of CNC and carvacrol, while they were able to modulate the mechanical responses, to induce antioxidant activities maintaining the migration levels below the permitted limits and suggesting the possible application as novel packaging strategies of the produced formulations. All the proposed formulations showed, in fact, an important antioxidant activity that was particular evident for carvacrol based systems whereas the barrier effect induced by both carvacrol and CNC, was highlighted by moisture content test stressing the effectiveness of the proposed formulations to improve the shelf-life and quality of perishable food products. Finally, inhibitions on bacterial development were detected for multifunctional systems especially induced by a synergistic effect of chitosan, carvacrol and cellulosic additives, suggesting their protective function against micro organisms contamination [47].

Similarly, we recently successfully extracted CNC from both barley straw and husk by applying two different approaches, a chemical alkaline and more environmental friendly enzymatic pre-treatment, followed by a hydrolysis procedure [48]. The results evidenced the major effectiveness of the enzymatic pre-treatment on the quality of obtained CNC; nevertheless, all the different typologies of nanocrystals were added to the polymers and the morphological, optical, mechanical response, thermal and migration characteristics were investigated, whereas antimicrobial assay were carried out to evaluate the bactericidal effect induced by chitosan presence. Also in this case, poly (vinyl alcohol) (PVA) blended with natural chitosan (CH) was selected as matrix for the production, by solvent casting in water, of nanocomposite films containing cellulose nanocrystals extracted from barley residues. The results indicated that chitosan reduced the optical transparency and the mechanical response of PVA matrix, whereas its combination with CNC (especially when extracted by enzymatic treatment and added at a higher content) could modulate the optical properties, the mechanical and thermal responses. Moreover, inhibitions on fungal and bacterial development were detected for PVA/CH/CNC ternary systems, suggesting their protective function against microorganism contamination.

Binary and ternary polymeric films, also by using PVA and chitosan as matrices, were produced and loaded with lignin nanoparticles (LNP) added at two different amounts (1 and 3 wt%) were produced by solvent casting. Mechanical results revealed that the addition of LNP enhanced the tensile strength and Young's modulus of PVA, producing also a toughness effect in CH matrix. Higher crystallinity values measured in calorimetric characterization confirmed how well dispersed LNP could effectively provide nucleation effects in PVA. Furthermore, LNP notably improved the thermal stability of the binary and ternary nanocomposite systems. Antimicrobial assays revealed a capacity to inhibit the bacterial growth of Gram negative *Erwinia carotovora* subsp. *carotovora* and *Xanthomonas arboricola* pv. pruni over the time, suggesting innovative opportunities against bacterial plant/fruit pathogens in food packaging applications and underlined the possibility to use lignin, a lignocellulosic material extracted from natural sources or wastes, as a potential antimicrobial against different bacteria strains. In addition, the synergic effect of LNP and CH in the antioxidation response of the produced films potentially envisage their use in many different biomedical applications (drug delivery, tissue engineering, wound healing), where innovative antimicrobial strategies are continuously required [49].

Finally, cellulosic material and lignin, at nanoscale, were combined into a polymeric based formulation in order to obtain multifunctional properties with tunable characteristics. The effects on antimicrobial, antioxidant, migration and disintegrability activities of ternary nanocomposite films based on Poly(Lactic Acid) (PLA) incorporating both cellulose nanocrystals and Lignin Nanoparticles (LNP), in two different amounts (1 and 3% wt.), were recently reported [50,51]. Results from antimicrobial tests revealed a capacity to inhibit Gram negative bacterial growths along the time, offering innovative opportunities against dangerous bacterial plant pathogens. LNP proved to be highly efficient in antioxidation activity, based on the disappearance of the absorption band at 517 nm of the free radical, 2,2-Diphenyl-1-Picrylhydrazyl (DPPH) upon reduction by an antiradical compound; moreover, the combination of LNP and CNC generates a synergistic positive effect in the antioxidation response of PLA ternary films. Furthermore, all the studied formulations showed a disintegrability value up to 90% after 15 days of incubation in composting conditions, whereas overall migration test results showed that the films can be considered suitable for application in food packaging field.

Conclusions and Future Trends

This review gave a general overview about nanotechnology that is a rapidly growing field of science and technology with impact on every area of science and technology. About plant protection in agriculture, nanotechnology can offer the opportunity to drastically reduce the amount of chemical inputs to enhance the application of AIs for a sustainable future. It is recognized by the European Commission as one of its six "Key Enabling Technologies" that contribute to sustainable competitiveness and growth in several sectors and, to improve and to support a greener farming it will allow to satisfy all parameters required (from environmental protection to consumers health).

In the promises of sustainable agriculture, nanotechnology can be integrated in an eco-friendly manner to offer great promise for agriculture growth, poverty reduction, food security, environmental services, public welfare, management of natural resource and securing desirable social outcomes.

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