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Review

Tools for Nano-Enabled Agriculture: Fertilizers Based on Calcium Phosphate, Silicon, and Chitosan Nanostructures

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Abstract: The Green New Deal requires a profound transformation of the agricultural sector, which will have to become more sustainable and ensure universal access to healthy food. Thus, it will be essential to introduce radical technological innovations. Nanotechnologies have the potential to produce a significant boost to the improvement of the food system. Within this context, in the next years, a strong challenge will need to be faced regarding developing new and more efficient uses of nutrients in agriculture, being the nutrient use efficiency (NUE) paramount in sustaining high crop productivity without depleting biodiversity, and altering both the natural and agricultural systems. Nutrients leaching causes environmental pollution and water eutrophication, while nutrient excess favors pest and weed widespread. Therefore, it will be mandatory to improve plant nutrition efficiency without affecting agricultural productivity and economic sustainability. A promising alternative consists of the introduction of the so-called nanomaterial enhanced fertilizers and plant growth stimulators. Such innovation includes nanotechnological solutions that can improve nutrient delivery for a more finely tuned, accurate, and saving-resources distribution of nutrients. This review provides a critical view of the latest advances in nanofertilizer research, mainly referring to nano-hydroxyapatite, silica nanoparticles, and chitosan-derived nanostructures.

Keywords: sustainable agriculture; nanotechnologies; nano-enabled agriculture; fertilizer delivery; nano-hydroxyapatite; silica nanomaterials; chitosan nanomaterials

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1. Introduction

“The food system is a major driver of climate change, changes in land use, depletion of freshwater resources, and pollution of aquatic and terrestrial ecosystems through excessive nitrogen and phosphorus inputs.” This dramatic statement is contained in a paper published in Nature in 2018 [1]. This scenario must be associated with the demographic issue. The current world population of 7.7 billion is expected to reach 8.5 billion in 2030, 9.7 billion in 2050, and 10.9 billion in 2100 [2].

World agricultural production has to increase by approximately 60–70% to meet future food demand. For this reason, it is estimated that there will be an increase in demand for the main productive factors, such as arable land (+67%), irrigation water use (65%), as well as N and P fertilizers (+51% and +54%, respectively) [3]. Turning the percentages regarding fertilizers into quantitative data, the 2020 forecasted global agrochemical annual use was equal to 120 and 50 million Mt for N-based and P-based fertilizers [4]. In contrast, the requirements are expected to reach 137.4 million Mt and P fertilizers 52.9 million Mt in 2030 [5].

It is enough to look at these few data to understand the concreteness of the initial quote. Therefore, we must acknowledge that the environmental pressure of agriculture, already very high, will only increase further in the coming decades [6]. However, the most severe aspect of that pressure is that the environmental issues are primarily due to the poor efficiency of some agricultural practices: conventional fertilization practices give us a paradigmatic example of that condition.

Nutrient use efficiency (NUE) is a valuable parameter in the evaluation of crop production systems. It can be defined as the maximum crop dry matter produced per unit of that particular nutrient taken up by plants. Therefore, in brief, it measures how well plants use the available nutrients. In a wide-angle view, NUE is a global concept based on (i) nutrient acquisition by plants, (ii) nutrient translocation to shoots and leaves, (iii) element utilization and biomass growth, and (iv) environmental conditions [7]. With current fertilization methods, the NUE comprises 30–55% for N-fertilizers and 18–20% for P-based fertilizers [8]. Therefore, only a fraction of these nutrients enters the composition of plants. In contrast, a relevant amount of fertilizers is released into the environment annually, resulting in eutrophication and groundwater contamination that threaten environmental resources, public health, and economic investments [9,10].

If we analyze this problem with a broader perspective than the field crop management alone, we will verify a dire situation. To do that, we can use the atomic conversion efficiency (ACE), a different metric than NUE, functional to describe the efficiency of fertilization. This approach evaluates the efficiency of N and P fertilization at the atomic scale, starting from (i) industrial synthesis of fertilization (energy, raw materials) to (ii) the delivery and allocation of nutrients into agricultural products. According to an accurate calculation based on ACE, nitrogen and phosphate fertilization efficiency are 8% and 5% [11]. A production cycle having such a low efficiency is simply unsustainable.

The debate on the sustainability of the worldwide food system has recently received a renewed boost due to the report published in early 2019 by the EAT-Lancet Commission [12]. The report stated that “the current global food system requires a new agricultural revolution based on sustainable intensification and driven by sustainability and system innovation”. In addition, we cannot avoid drawing attention to what is happening due to the COVID-19 pandemic. Since the complex global economic, social, and environmental interdependencies, the consequences of this crisis will require enormous investments for structural interventions in health and food systems, education, cities, and sustainable infrastructure, security, and environmental resilience [13].

For all these reasons, there is widespread awareness of the unavoidable need and urgency to design effective interventions to save global food security. The European Union took up this challenge by developing the “Farm to Fork” (F2F) strategy, which constitutes one of the critical components of the European Green Deal [14]. By recognizing the inextricable links between healthy people, healthy societies, and a healthy planet, F2F addresses specifically the challenges of sustainable food systems. Since the excess of nutrients in the environment is a major source of water, soil, and air pollution, negatively impacting biodiversity and climate, the EU Commission by means of the F2F strategy aims to reduce nutrient losses by at least 50%, while ensuring no deterioration on soil fertility. At the same time, a reduction in fertilizer use by at least 20% is expected by 2030 [15]. These goals are certainly ambitious, especially considering that this will have to take place in a scenario where there is also the pressing need to increase food production to cope with the expected demographic increase. This apparent paradox can only be solved through (i) a significant improvement in the efficiency of production processes and (ii) the implementation of technological innovations.

According to OECD/FAO, about 85% of the growth in global agricultural production over the next ten years is expected from the improvement in crop yield resulting from more intensive use of inputs and investments in production technology and best farming practices. The intensification of land use through more crops per year will represent another 10%. At the same time, the expansion of the cultivated area is predicted to represent only 5% playing a marginal role compared to the previous decade, improving the sustainability of agriculture [16].

There is still a long way to go to achieve the ambitious goal of a sustainable agricultural system. However, it has been open for some time with developing the principles of precision agriculture, first mentioned around 1990 [17]. More recently and precisely in response to the future perspectives abovementioned (i.e., growing world population and food security), FAO refined the paradigm by introducing the concept of sustainable crop production intensification (SCPI) [18]. At last was introduced the claim "Agriculture 4.0" to indicate those emergent technologies, such as artificial intelligence, big data, the Internet of Things, gene editing, and drones, to be implemented as solutions to challenges associated with food production maintaining also the profitability of agriculture and environmental protection [19].

2. Nanotechnologies: A Powerful Source of Innovation in Agriculture

The list of technological innovations mentioned earlier is certainly not complete. On the contrary, the one with the most crucial potential is missing. We are referring to the focus of this work. It is widely accepted that nanotechnologies can become the drivers of a new technological revolution in agriculture. In the vision of "nano-enabled agriculture", it becomes concrete to balance growing crop yields, increase agroecosystem resilience, and lower environmental impacts [20–24].

The primary tools of nano-enabled agriculture are the engineered nanomaterials (ENMs) manufactured with particle dimensions in the range 1–100 nm and high surface area to mass ratio giving to ENMs very different properties compared to the corresponding conventional bulk materials [25]. Moreover, however, the manipulation of matter at the nanoscale has opened new frontiers allowing the synthesis of new materials and the assembly of nanohybrid structures, as well [26].

Nature Nanotechnology in 2019 featured a special issue reporting the state-of-the-art on nano-enabled agriculture, which has been defined as "an exciting and challenging area that will develop fast in the near future, especially if the right emphasis is given to understanding the fundamental interactions between engineered nanomaterials and plants" [27]. Although there are many potential applications in nano-enabled agriculture [21], here we will restrict the analysis to the perspective of plant nutrition.

3. Nanofertilizers

The term "nanofertilizer" refers to a structure in the dimension of 1–100 nm designed to deliver nutrients to crops. In addition, this term should also be extended to indicate bulk materials used together with nanoscale structures to construct new products (for example, fertilizing molecules coated with metal nanoparticles). Nanofertilizers, due to their properties, have been shown to increase productivity through target delivery or slow release of nutrients, thereby limiting the rate of fertilizer application. In other words, the expectations of nano-enabled agriculture include a significant increase in the NUE [28].

Currently, the development and utilization of the potential of nanotechnologies in crop fertilization is a high priority in fertilizer research with the target to prevent or minimize nutrient losses [29]. It is expected that adequately designed nanostructures will allow controlled release of nutrients so that this is exactly synchronized with the nutritional needs of the crops [30]. It has been already demonstrated that the size reduction by physical or chemical methods increased the surface mass ratio of fertilizers, which allows a significant increase of nutrient root absorption. In that way, slow, targeted, and more efficient nutrient release becomes possible, allowing: (i) reduction of dosages and application costs, (ii) significant reduction of nutrient losses, and therefore (iii) increase of NUE. It is estimated that the gain in NUE when using nano-agrochemicals instead of conventional products could be 20–30% [31].

Nanomaterials can be classified into different types according to size, morphology, as well as physical and chemical properties. Since several nanomaterials have been proposed for agriculture, a systematic classification is still missing.

Based on their composition and structure—which, of course, must contain at least one element to be released for plant nutrition—we can classify them as

1. *Metal nanomaterials*, metal-based materials commonly regarded as nanosilver, nanogold, quantum dots, and metal oxides [32];

2. *Ceramic nanomaterials*, inorganic, heat-resistant, nonmetallic solids that can be made of both metallic and nonmetallic compounds [33];
3. *Polymeric nanomaterials*, macromolecules composed of many repeating units organized in a chain-like molecular architecture exhibiting a multiplicity of compositions, structures, and properties [34].

Alternatively, considering their application as fertilizers, we can classify such materials according to their specific nutritional role and the expected effects on plants. In this case, we can categorize the nanofertilizers in four classes [35]:

1. *Macronutrient nanofertilizers*: e.g., hydroxyapatite nanoparticles, calcium carbonate nanoparticles, and magnesium oxide nanoparticles;
2. *Micronutrient nanofertilizers*: e.g., iron oxide nanoparticles, manganese oxide nanoparticles, zinc oxide and copper oxide nanoparticles;
3. *Nanomaterial-enhanced fertilizers (NEF)*: according to Liu and Lal [36] NEF are nanomaterials "loaded with plant nutrient(s), aimed at increasing plant-uptake efficiency of the nutrient(s) and/or reducing the adverse impacts of fertilizer application, but the nanomaterials themselves do not contain or supply the targeted nutrient(s)." Some examples of NEF are nanozeolites, silica nanoparticles, and nano chitosan (CHT);
4. *Plant growth stimulating nanomaterials*: e.g., titanium oxide nanoparticles, cerium oxide nanoparticles, single-walled carbon nanotubes (SWCTNs), multiple walled carbon nanotubes (MWCTNs), graphene, and fullerenes. For these nanomaterials, stimulating action on plant growth has been demonstrated. However, in particular, as far as carbon compounds, studies are still ongoing [37].

Although nano-enabled agriculture is still in its infancy [26], most of the scientific literature developed on this topic is focused on the potential of nanofertilizers. However, we must be aware that nanofertilizers—being so different with respect to the bulk counterparts because of their nano-properties—should be supplied to crops with strategies and equipment, which must be adapted to the new materials. Nonetheless, the basic principles of plant nutrition will not change and, with the necessary adaptations, the mineral elements will have to be supplied to plants [38].

The first option is through the bulk ionic form of elements bonded (absorbed/adsorbed) in a nanostructure responsible for the delivery and the release. A second strategy involves the transport of nutrients at the nanoscale by carriers (e.g., nano-hydroxyapatite [39] and nano CHT or hydrogels [40]), to be assimilated through the root system or the leaf tissues. Finally, a suspension of nanoparticles of plant nutrients (e.g., in the form of nano Cu/Fe/Zn or the correspondent nano oxides) can be applied directly to the soil as well as by spraying the plant leaves [25].

The positive prospects related to nanomaterials in agriculture cannot make us underestimate the precautionary principle. The deliberate introduction of nano-sized materials within agricultural activities raises questions and concerns over the possible human and environmental health implications. Nanomaterial residues in soil and crops are expected to increase with exposure routes, including possible bioaccumulation in the environment and food chain. In this perspective, the purpose of achieving sustainable agriculture overlaps the need to balance the benefits provided by nano-products in solving environmental challenges. Thus, the assessment of environmental, health, and safety risks, potentially posed by nanoscale materials in agriculture, will become very soon of paramount importance [41].

The following sections provide state-of-the-art regarding four types of nanofertilizers based on nano-hydroxyapatite, calcium phosphate nanoparticles, silica nanoparticles, and chitosan nanostructures. To give the reader a comprehensive overview of the literature, in Tables 1–6 we report information regarding the experimental conditions, the available details on nanomaterials, and the main findings.

4. Nanoscopic Calcium Phosphate Compounds

Crystalline and nanocrystalline calcium phosphate compounds (CaP) are found (i) in biological system after precipitation in mild conditions of pressure and temperature, and (ii) in the environment as mineral deposits formed in thousands of years under heavier conditions of pressure and temperature [42]. Calcium phosphates are also the most important inorganic constituents of biological hard tissues in living systems. In the form of hydroxyapatite (HA), they are present in bone, teeth, and tendons to give these organs stability, hardness, and function. Owing to their peculiar properties (hosting of a variety of cations, e.g., K, Mg, Zn, anionic substitutions, adsorption of organic molecules, and pH-responsive solubility) CaP, under several crystal forms, has been widely used for a broad range of applications [43]. Among them, the potential of using nano-CaP in precision agriculture for the controlled delivery of plant nutrients is reported in this review.

4.1. Hydroxyapatite Nanoparticles

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH_2)$, and Ca/P molar ratio = 1.67) belongs to the calcium phosphate compounds. Recently, the use of nano-hydroxyapatite (*n*HAP) was proposed as source of phosphorus in crops and carrier of other nutrient elements or other molecules functional for plant nutrition and plant protection [39,44].

Several methods of preparing synthetic HAP are reported in literature including wet chemical deposition, biomimetic deposition, as well as sol-gel and electrodeposition [44,45]. However, HAP can also be extracted from biological sources and wastes such as bovine and horse bones, fish bones and scales and shell sources. Compared to the stoichiometric composition of synthetic HAP, biological HAP contains other ions, such as Na^+, Zn^{2+}, Mg^{2+}, K^+, Si^{2+}, Na^+, and $CO_3{}^{2-}$, which make it similar to the composition of human bones [46–48].

The very low efficiency of plant P supply fertilizers is due to soil P immobilization in Al and Fe-based oxides. On the other hand, the great majority of the P released from soil organic matter is rapidly fixed in insoluble inorganic compounds, and crops can suffer from P-deficiencies even in soils with a high content of total P [49]. Therefore, the challenge is to develop fertilizers able to release P at a slower rate to increase the amount of bioavailable P. However, in connection with this, currently are ongoing studies based on the hypothesis that the release of P from HAP is slower than conventional fertilizers, but at the same time, that the element is mobilized faster than the forms immobilized in the soil.

A literature survey was carried out to verify the progress of scientific research regarding using *n*HAP as crop fertilizer. A summary of the paper's content is reported in Tables 1–3. The papers were distinguished according to their objectives. In particular, Table 1 reports studies in which *n*HAP assumes the role of slow-release P fertilizer. Table 2 summarizes papers in which *n*HAP plays the role of carrier of another macronutrient (and in fact, it is always N as Urea). In contrast, Table 3 refers only to a couple of very recent papers describing the potential of *n*HAP as a carrier of micronutrients.

4.1.1. Nano-Hydroxyapatite as Source of Phosphorus

The most used P fertilizers are (i) ammonium monophosphate (MAP, $NH_3H_2PO_4$), (ii) diammonium phosphate (DAP, $(NH_3)_2H_2PO_4$), and (iii) triple superphosphate (TSP, $Ca(H_2PO_4)$). The fertilizers are applied to soil, and P is released in water-soluble forms, highly mobile, and readily available to crops. However, we have significant P losses by leaching or surface run-off. The use of poorly soluble forms of P, such as phosphate rocks and apatite, on the one hand, reduces P losses, but on the other, it makes more difficult the P supply to plants. Among the critical factors associated with food security and environmental sustainability is P shortage [50].

The possibility of recovering this macronutrient at the nanoscale from waste materials offers an exciting way that will have to be explored in a systematic and in-depth way. Although this has not yet happened, some studies have already been carried out in this direction. Due to its composition, nHAP have been recently advocated as P fertilizer based on the hypothesis that nano-sized particles can potentially move in the soil more efficiently than bulk P fertilizers, and release P more appropriately than the nutritional needs of plants. Table 1 summarizes the state of the art of the studies dedicated to this perspective.

It is clear that these are experiments carried out at different levels of complexity and used as target plant species both worldwide food crops and minor species. In a certain sense, this is the best demonstration of how necessary it is to organize a systematic type of work, which has not been carried out until now. However, we summarize the significant findings of such studies.

Chronologically, the first paper indicating that "application of nano-sized solid P as fertilizer would be a good compromise between agricultural benefits and the environmental hazards" was provided by Liu and Lal (2014) [39] which managed a greenhouse trial to study the fertilizing efficiency of *n*HAP as P source. Growing experiments carried out on soybean (*Glycine max*) demonstrated that root and aerial biomass were significantly enhanced compared to the control. Grain yield increased compared to plant treated conventional P fertilizer, as well. A more recent study was provided by Marchiol et al. [51], which tested the potential of *n*HAP to be used as to be used as both a P supplier and carrier of other elements or molecules in a germination trial carried out on *Lycopersicum esculentum* (Table 1).

The fate of P in soil is strongly influenced by the properties of the soil itself, such as temperature, moisture, aeration, and pH [52]. For this reason, studies on the behavior of nHAP in soil columns were conducted [53]. In this case, the potential of *n*HAP was evaluated at two levels. At first, bulk HAP and *n*HAP were compared in saturated soil column experiments using two Andisols (from Chile and New Zealand, respectively) and two Oxisols (from Australia). Subsequently, the P availability to *Triticum aestivum* fertilized with bulk HAP, TSP, and *n*HAP was evaluated. The results showed that in the experimental conditions, the P uptake and the percentage of P in the plant that was derived from the fertilizer followed the order: TSP > *n*HAP > bulk HAP (Table 1). A second experiment dedicated to studying the behavior of nHAP in soil was carried out by Xiong et al. [54]. In this case, three forms of *n*HAP having different surface charges (positive, neutral, and negative) were administered to *Helianthus annuus* grown in P deficient Ultisol and Vertisol, respectively. Conventional P fertilizers (TSP and rock phosphate) were tested, as well. In the acid Ultisol (pH 4.7), the addition of TSP or any of the *n*HAPs increased plant biomass, whereas, in basic Vertisol (pH 8.2), none of the *n*HAPs significantly increased the plant growth. Both studies confirmed the potential of *n*HAP, but the fertilizing effect was lower than conventional TSP. On the other hand, likely, the nanofertilizers that will be used on a large scale in the future will be different from the nano-forms studied at this time. New design criteria for nanofertilizers will be developed based on the results of the studies conducted in this still exploratory phase.

Studies are also conducted on cultivated species of regional interest. That is the case of a work carried out on *Adansonia digitata* (baobab) where the effectiveness of the foliar application of MAP, DAP, and *n*HAP was investigated [55]. Baobab plants sprayed with *n*HAP showed a significant increase in several growth traits (plant height, stem diameter, number of leaves per plant, leaf area, root length, total dry weight) compared to conventional P fertilizers. A conceptually similar study was conducted on *Camelia sinensis* [56]. Different P fertilization strategies were tested, which included comparing conventional fertilizers and *n*HAP, and a different fractionation of doses. However, the most relevant aspect of this study is that it was carried out for three years in different locations in Sri Lanka characterized by different climatic and pedological conditions, thus also introducing environmental variables. Overall, the results demonstrated that the application of slow-release fertilizer significantly increased soil P, leaf N, and P concentration, particularly in unfavorable climatic conditions.

To conclude this section, we cite a recent study concerning the synthesis of hybrid nanostructures [57]. In this case, the possibility of associating natural or synthetic humic substances with *n*HAP, exploiting the interaction between the polyphenolic groups of humic substances (HA) and the surface charge of *n*HAP. *Zea mays* were grown in a pot trial and fertilized with commercial P fertilizer, bare *n*HAP, and *n*HAP-HA. The synergistic co-release of P ions and humic substances resulted in a significant increase in plant growth, corn yield, and resistance to salt stress (Table 1).

4.1.2. Nano-Hydroxyapatite as Nitrogen Carrier

Urea (CH_4N_2O) is the most common source of nitrogen for field crops. Therefore, it was reasonable to expect that the first studies concerning nitrogen nanofertilizers would be carried out on this molecule, and this is indeed what happened. The perspectives for the use of *n*HAP in fertilizer applications have been revealed by Kottegoda et al. [58], which opened the way to using N-carrying nanomaterials. A nanohybrid structure based on urea molecules encapsulated inside *n*HAP was synthesized and characterized. By comparing the N-release from the nanohybrid to conventional urea, it was demonstrated that the nanostructure had a significantly slower release of N. This study observed the release kinetics of a urea molecule from the nanostructured, but without using plants as targets for N-release. A while after, in a study by Subbaiya et al. [59], the effects of conventional urea and a nanostructure of urea-*n*HAP on germination and early growth of plantlets of *Vigna radiata* were assayed. The nanostructure proved to be stable over time, and the N-release was slower than that of urea, determining positive effects on both germination and the growth of the seedlings (Table 2).

Thanks to these first encouraging results, interest in synthesizing new nanostructures designed for crop N-delivery has developed in different directions. Gunaratne et al. [60] carried out a pot study to test the potential of the nanocomposites Urea-Hydroxyapatite-Montmorillonite (U-*n*HAP-MMT) and Urea-Hydroxyapatite encapsulated wood chips (U-*n*HAP-wood) on *Festuca arundinacea*. The results showed that both nanocomposites decreased N leaching compared to conventional fertilizers. Overall, the slower N release compared to conventional fertilizers was synchronized with the physiological needs of the plants (Table 2). Furthermore, on this specific aspect, significant improvements are expected thanks to the properties of nanofertilizers.

Very similar work was devoted to some methodological aspects of the nanohybrid synthesis process. In particular, Madusanka et al. [61] worked on the low-cost preparation of U-*n*HAP-MMT involving lower water use, which implies a reduced need for energy for drying the material. Subsequently, the fertilizer potential of the nanohybrid was tested on plants of *Oryza sativa* grown in a pot experiment. The comparison with conventional fertilization confirmed the better efficiency of the nanofertilizer in terms of rice yield and a significant decrease of soil N leaching (Table 2). The study by Kottegoda et al. [62] is particularly interesting because it was carried out in a first phase under controlled conditions and subsequently in a field trial. Nitrogen fertilization was provided to *Oryza sativa* with three applications of classic granular urea and urea-*n*HAP. The N-release from urea and urea-*n*HAP were evaluated, and leaf nutrient content and nitrogen agronomic use efficiency (NAE) were measured. The study demonstrated that the expected slower N release by *n*HAP resulted in a better NAE than conventional fertilizer (Table 2).

The most recent study in this field was provided by Pradhan et al. [63] who compared the effects of different N and P fertilization strategies on germination of *Oryza sativa*. Beyond conventional urea and P salt, *n*HAP and urea-*n*HAP were tested. Physiological and biochemical activities of germinating seeds responded positively to the treatments; in particular, plantlet growth and dry matter accumulation were enhanced in urea-*n*HAP treatment if compared to control and conventional fertilizers. In addition, both *n*HAP and urea-*n*HAP were also tested in sand columns and agricultural soil to understand the retention capacity of plant nutrients in the sand and their interaction with soil colloids. The response was very promising as both the materials showed greater N and P retention capacity with respect to the conventional materials (Table 2).

4.1.3. Nano-Hydroxyapatite as Micronutrients Carrier

Recently the perspectives of the use of *n*HAP are growing. The use of *n*HAP to deliver micronutrients could open huge perspectives in viticulture, fruit farming, and horticulture.

In these fields of agriculture, the microelement deficiencies are particularly formidable both from a phytosanitary point of view and from an even more important point of view: the organoleptic and nutritional features of the fruits.

Table 3 reports two studies in which different nanostructures were tested after loading with metal nanoparticles. The first study was carried out using *Asparagus officinalis* as a target species. The nanofertilizer was conceived and designed as a "micronutrient nanosystem" consisting of *n*HAP loaded with nano element (Fe, Cu, and B) or nano oxides (ZnO). Then, short-chain alginate was used to obtain the final structure of the nano system. In order to evaluate the better formulation, different ratios of alginate and *n*HAP were investigated. A 10 days long germination test and subsequent plant growth demonstrated a positive response of treated plants in comparison to the control ones [63].

Conceptually similar work was carried out by Tarafder et al. [64], who synthesized a nanostructure constructed by assembling nano urea and *n*HAP, subsequently loaded with *n*Cu, *n*Fe, and *n*Zn. This nanofertilizer was used in a field experiment where the growth of the tropical plant *Abelmoschus esculentus* was studied. In plants treated with the nanofertilizer, a significant increase in total uptake of Cu, Fe, Zn, and other nutrients was observed when compared to the control due to a slower release of micronutrients from the nanofertilizer (Table 3).

Table 1. Nano-hydroxyapatite as source of P.

Material	Species	Treatment	Experimental Conditions	Results	Reference
*n*HAP, 16 nm	*Glycine max*	21.8 mg L^{-1} as P	Perlite-peat moss (1:1), nutrient solution, greenhouse.	Increased growth rate (+32.6%), aerial biomass (+18.2%) and seed yield (+20.4%) than control.	[39]
*n*HAP, 94–163 nm	*Solanum lycopersicum*	0, 2, 20, 200, 500, 1000, 2000 mg L^{-1}	Germination, hydroponics.	Stimulation of root elongation; no plant toxicity.	[51]
*n*HAP, primary size 22 nm	*Triticum aestivum*	0–150 mg kg^{-1} P *n*HAP, bulk-HA, triple superphosphate (TSP)	Soil columns; glasshouse pot experiment; Andisol and Oxisol.	Increased shoot dry matter and P uptake than bulk-HA but less than the conventional P fertilizer.	[53]
*n*HAP $^{(+)}$, *n*HAP $^{(0)}$, *n*HAP $^{(-)}$, average size 25.7 nm	*Helianthus annuus*	150 kg ha^{-1} *n*HAP $^{(+)}$; *n*HAP $^{(0)}$; *n*HAP $^{(-)}$; (iv) triple superphosphate (TSP); rock phosphate (RS)	Glasshouse pot experiment; P-deficient Ultisol (pH 4.2) and Vertisol (pH 8.2).	In Ultisol *n*HA $^{(-)}$ more effective in supplying than TSP; in Vertisol nHAP did not increase plant growth.	[54]
*n*HAP, rod shaped 59.5 × 10.6 nm	*Adansonia digitata*	Control (unfertilized); MAP; DAP; *n*HAP	Pot experiment; sandy soil. Foliar application of 20 mL of different P sources weekly.	Increased plant growth (plant height, leaf area, plant fractions dry matter) compared to other P sources.	[55]
Urea–*n*HAP nanohybrid, <100 nm	*Camellia sinensis*	50% NPK 4 Splits; 50% NPK 2 Splits; 100% N (HA-urea nanohybrid) + 100% K MOP (2 Splits); 100% N (Urea-*n*HAP) + 100% K MOP (4 Splits); 50% N (Urea-*n*HAP) + 100% K MOP (4 Splits); 50% N (Urea-*n*HAP) + 100% K MOP (2 Splits); 100% conventional NPK fertilizer (4 Splits).	Field experiments in three different locations; Urea-*n*HAP nanohybrid provided as ground fertilizer.	Enhancement of NUE; increased quality parameters of tea leaves (e.g., total polyphenols and total amino acids).	[56]
*n*HAP with natural and synthetic humic substances (HA)	*Zea mays*	*n*HAP-natural HA; *n*HAP-synthetic HA; Superphosphate; *n*HA	Growth chamber; pot experiment.	Early growth, better salt stress tolerance and yield.	[57]

Table 2. Nano-hydroxyapatite as N-carrier.

Material	Species	Treatment	Experimental Conditions	Results	Reference
Urea-Hydroxyapatite Montmorillonite (U-*n*HAP-MMT); Urea-Hydroxyapatite encapsulated wood chips (U-*n*HAP-wood)	*Festuca arundinacea*	Nutrients (g pot^{-1}): 1.8 N, 1.2 P_2O_5, 1.2 K_2O; 1.8 N, 1.2 P_2O_5, 1.2 K_2O	Pot experiment; Ceylon tea soil.	Decreased N leaching; improvement NUE.	[58]
Nano Urea (*n*U); *n*HAP composite	*Vigna radiata*	Conventional U; chemically synthesized *n*U + *n*HAP; biologically synthesized *n*U + *n*HAP	Pot experiment.	Promoted seed germination; increased seedling growth.	[59]
Urea-Hydroxyapatite Montmorillonite nanohybrid composite (U-*n*HAP-MMT)	*Festuca arundinacea*	Conventional fertilizer: 120 kg ha^{-1} N; 40 kg ha^{-1} P_2O_5, 40 kg ha^{-1} K_2O	Soil columns, pot experiment; Ceylon tea soil.	Slower N release; significant yield enhancement compared to control.	[60]
Urea-modified Hydroxyapatite nanohybrid composite (U-*n*HAP).	*Oryza sativa*	Granular urea compared to U-*n*HAP	Field experiment.	Slower N release relative to conventional urea.	[61]
*n*HAP and Urea-*n*HAP	*Oryza sativa*	10 mg kg^{-1}, 50 mg kg^{-1}, and 100 mg kg^{-1}. Control (untreated), Urea; conventional P salt; *n*HAP; Urea-*n*HAP	Germination; Petri dishes. Soil columns.	Enhancement germination; increased α-amylase activity and starch content.	[62]
Hydroxyapatite nanoparticles (*n*HAP, 40–60 nm), Urea doped hydroxyapatite nanoparticles (Ur@*n*HAP)	*Oryza sativa*	Water (Control); conventional Urea; Ca dihydrogen phosphate conventional P salt (Ca dihydrogen phosphate), *n*HAP, Ur@*n*HAP	Germination; Petri dishes.	Ur@*n*HAP more efficient than conventional N-P fertilizers.	[63]

Table 3. Nano-hydroxyapatite as micronutrients carrier.

Material	Species	Treatment	Experimental Conditions	Results	Reference
*n*HAP + micronutrients; rod shaped 20–25 nm × 86 nm	*Asparagus officinalis*	Micronutrients nano system: Alginate-*n*HAP loaded with Ag, Co, Cu, Fe, and Zn	Germination experiment; 90 d plant growth.	Slower micronutrients release; faster germination rate than control.	[64]
Hybrid nanofertilizer (HNF) *n*Urea + *n*HAP + micronutrient nanoparticles	*Abelmoschus esculentus*	*n*Urea-*n*HAP-*n*Cu-*n*Fe-*n*Zn; 50 mg per week of nanohybrid; 5 g of conventional fertilizer	N/A	Enhancement of NUE and crop yield. Increase of Cu^{2+}, Fe^{2+}, and Zn^{2+} uptake in treated plants.	[65]

4.2. Amorphous Calcium Phosphate Nanoparticles

Amorphous calcium phosphate (ACP) is the first phase precipitated from a supersaturated solution containing calcium cations and phosphate anions. The compound has an apatitic short-range structure, but with a crystal size so small that it appears amorphous in X-ray diffraction experiments [42].

Recent studies explored the fertilizing potential of ACP nanoparticles (*n*ACP), reporting encouraging results. Compared to hydroxyapatite, these compounds are more soluble and more reactive, have a higher capability to adsorb small molecules (e.g., urea) on their surface, enabling higher payloads of macronutrients. Although the number of studies is not high, the most critical result concerns the improvement of the NUE obtained thanks to the promising properties of *n*ACP. This evidence was obtained on different crops and using different fertilization methods (Table 4).

One of the most important goals of nano-enabled agriculture is to increase the efficiency of agricultural systems. Ramirez-Rodriguez et al. [66] provided an encouraging example in this direction demonstrating the capability of urea-doped ACP nanoparticles (U-*n*ACP) to maintain both crop yields and quality at reduced N dosages. The synthesis was carried out through a simple batch method, which does not require hazardous reagents. U-*n*ACP nanoparticles present similar morphology, structure, and composition to the amorphous precursor of bone mineral, but contain a considerable amount of nitrogen as adsorbed urea (about 6 wt.% urea). Preliminary experiments with stained *n*ACP were also carried out to gain insights into nanoparticle uptake routes and their translocation in plant tissues. It was evidenced that nanoparticles could penetrate through the epidermis of the roots or the stomata of the leaves. However, the root uptake occurs only in 1 h, while the entry through the leaf stomata was much slower (two days). After U-*n*ACP characterization, a plant growth trial was carried out in tests performed on durum wheat (*Triticum durum*) under controlled conditions (growth chamber). During the stem elongation, plants were treated with (i) leaf sprayed suspension of U-*n*ACP (15 kg N ha^{-1}) + DAP (60 kg N ha^{-1}) and (ii) DAP (150 kg N ha^{-1}). The total N dosage with the nano-treatment was reduced by ca. 40% in comparison to the positive control. Main yield parameters (i.e., shoot number, kernel numbers, and weights) and seed protein content were evaluated at harvest. It was verified that grain yield and quality in plants treated with U-*n*ACP were not different if compared to control plants that received much higher N dosages (Table 4).

A simple green protocol to obtain multinutrient nanofertilizers doping both ACP and apatite nanoparticles (Ap) with two N forms (nitrate and urea) and K ions was developed by the same research group [67]. After the characterization carried out by transmission electron microscopy (TEM) imaging, Fourier transform infrared (FTIR) and Raman spectroscopies, inductively coupled plasma optical emission spectrometry (ICP-OES), and elemental analysis, it was found that *n*ACP, incorporates both N forms to a larger extent than Ap (2.6 vs. 1.1 wt%, respectively). The Ca, K, and P release was measured in water at room temperature by ICP-OES. In contrast, vertical columns filled with synthetic soil were used to evaluate the urea release kinetics. The nutrient release kinetics from *n*ACP doped with potassium, nitrate, and urea (nano U-NPK) and its efficiency as a N supplier have been preliminarily evaluated on *Triticum durum*. Durum wheat plants were grown in controlled conditions in the framework of a completely randomized duplicated block design with three nitrogen-fertilizing groups. The experimental setup applied an initial amount of conventional fertilizer (36 kg N ha^{-1}) to all the treatments at seeding. During the stem elongation phase, plants respectively received DAP (150 kg N ha^{-1}) and nano U-NPK (15 kg N ha^{-1}) supplied as sprayed aqueous suspension combined with 60 kg N ha^{-1} of granular DAP. It was shown that the application of nano U-NPK allows reducing the amount of N supplied to the plants by 40% when compared to conventional treatment without affecting the final kernel weight per plant (Table 4).

A significant field of studies still in the initial phase concerns the methods of synthesis of nanofertilizers. A new chemical approach towards a highly efficient post-synthetic modification (PSM) of *n*ACP was recently proposed [68]. The protocol, not particularly complex and expensive, leads to the production of *n*ACP doped with urea (nano U-ACP). Compared to one-pot synthesis where urea and nitrate are jointly added during the ACP synthesis, the PSM method offers higher N-payloads (up to 8.1 wt%, from the initial 2.8 wt% level). The fertilization tests carried out on hydroponically grown *Cucumis sativus* demonstrated the higher NUE showed by nano-U-ACP (69%) than its conventional fertilizer counterpart (urea, 49%). Although cucumber plants treated with nano U-ACP received a 50% reduced N content of urea than those supplied with conventional urea, the root and shoot biomass yield was similar (Table 5). The high NUE and a cost-effective preparation method support the usage of N-doped *n*ACP as a nanofertilizer. As for the synthesis process of nano-U-ACP, it is believed that a further coating with biocompatible, slowly dissolving polymers can be envisaged toward a more sustainable release of urea (Table 4).

Sustainability is particularly relevant also in viticulture. A part of the emerging challenges related to the expected consequences of climate change, adequate and efficient fertilization and plant protection practices are decisive to achieve adequate yield levels and the expected composition of grapes [69]. Nano-enabled viticulture is still a largely unexplored research field. However, positive signals in this direction are represented by some recent studies regarding the use of nanocarriers for Cu delivery against the grape parasite *Plasmopara viticola* [70,71]. As regards fertilization, we can report two interesting recent studies concerning the use of *n*ACP as N carrier to vine plants.

The first study has assessed the efficiency of a vineyard fertilizer treatment involving the foliar application of urea doped *n*ACP (U-*n*ACP) to improve grape quality [72]. Foliar urea application to grapevines is still known to increase the concentration of nitrogen, as well as phenolic and aromatic compounds in grape berries [73]. The novelty is represented by the use of U-*n*ACP instead of an aqueous solution of urea. In field experiments carried out on *Tempranillo* grapevines, the effects of foliar-applied two urea solutions (3 and 6 kg N ha^{-1}, respectively U3 and U6) and U-*n*ACP (0.4 kg N ha^{-1}). The treatments (200 mL $plant^{-1}$) were applied at grapevine veraison and one week later. The results indicated that plants treated with U-*n*ACP and U6 provided similar levels of yeast assimilable N, despite the considerable reduction of nitrogen dosage. In addition, aminoacids content was more significant in U-*n*ACP-treated plants than U3 treatment and comparable with those observed in U6 treatment. Therefore, the main target of nano-enabled agriculture, i.e., increase NUE, was demonstrated (Table 4).

A conceptually similar experiment was reported in the paper by Gaiotti et al. [74]. In this case, a two-year trial was carried out in semi-controlled conditions on adult potted vine plants (cv. *Pinot gris*). Nitrogen was supplied to plants in the following ways: (i) granular soil fertilization (NH_4NO_3, 45 kg N ha^{-1}) after budding, (ii) U-*n*ACP applied in fertigation (three applications of aqueous suspensions, 36 kg N ha^{-1}), and (iii) granular fertilization + foliar application of U-*n*ACP (36 kg N ha^{-1}). Experimental results showed the capability of vine plants to use the N supplied by U-*n*ACP similarly to that applied to the canopy or to the soil. All of the parameters observed in plants fed with U-*n*ACP were comparable to those of plants grown in conventional conditions. Therefore, these results provide clear evidence of U-*n*ACP nanoparticles' efficacy to optimize the dose/benefit ratio towards more sustainable viticulture (Table 4).

Table 4. Amorphous calcium phosphate nanoparticles as nanofertilizers.

Material	Species	Treatment	Experimental Conditions	Results	Reference
U-*n*ACP	*Triticum durum*	Control (no fertilizer); U-ACP, 15 kg N ha^{-1} sprayed suspension + 60 kg N ha^{-1} granular DAP; 150 kg N ha^{-1} granular DAP.	Pot trial, growth chamber. 1:1 clay-loam soil/sand mixture (12:12 h light/dark cycle).	Crop yield parameters and grain quality parameters unaltered in comparison to positive control plants.	[66]
nano U-NPK	*Triticum durum*	Control (only water); 150 kg N ha^{-1} granular DAP; nano U-NPK 15 kg N ha^{-1} sprayed aqueous suspension + 60 kg N ha^{-1} DAP.	Pot trial, growth chamber. 1:1 clay-loam soil/sand mixture (12:12 h light/dark cycle).	Same grain yield from conventional fertilization and nano U-NPK (−40% N).	[67]
U-*n*ACP	*Cucumis sativus*	Control (N-starvation), U-*n*ACP (1 mM U), U-*n*ACP 0.5 (0.5 mM U), Urea (1 mM).	Hydroponics. 7 d full nutrient solution; 7 d N-starvation followed by treatments	U-ACP with a 50% reduced N content resulted in similar root and shoot biomass than conventional U.	[68]
U-*n*ACP	*Vitis vinifera* cv. Tempranillo	Control, solution Urea 3 kg N ha^{-1}, solution Urea 6 kg N ha^{-1}, suspension U-*n*ACP 0.4 kg N ha^{-1}.	Field trial	U-ACP treated plants have similar levels of yeast assimilable N and aminoacids than other treatments.	[72]

Table 4. *Cont.*

Material	Species	Treatment	Experimental Conditions	Results	Reference
U-*n*ACP	*Vitis vinifera* cv. Pinot Gris	Control (unfertilized), N1 (granular NH_4NO_3 27%, 45 kg N ha^{-1}), N2 (fertigation U-*n*ACP 36 kg N ha^{-1}), N3 (granular fertilization + foliar U-*n*ACP, 36 kg N ha^{-1}).	Pot trial, outdoor conditions, sand–peat–clay (50–35–15% by volume)	Despite the restrained dosage of N applied with the nanoparticles quanti-qualitative parameters were comparable to those of plants managed with conventional strategies.	[74]

5. Silica Nanoparticles

Silicon (Si) is the second most abundant element on earth surface [75]. Despite this, its availability is usually found in small concentrations in the soil [76]. Its role in the plant metabolism is proven by the several benefits and effects that its administration provides. With the advancements of the genetic and biomolecular studies, science has been able to unveil many (but not all) of the biological mechanisms that involve Si, from the uptake to the final effects. The latter being circumscribable within defense mechanisms versus both biotic and abiotic stresses. According to Epstein [77], Si performs its functions in two ways: by polymerization of silicic acid which induces the formation of solid amorphous, hydrated silica, and by being instrumental in the formation of organic defense compounds.

Several papers in literature deal with the role of Si in plants and its importance as a nutrient. For instance, the absorption of Si has been studied and characterized as having a Michaelis–Menten kinetics of uptake in wheat [78], and the presence of Si dedicated transport genes was also proved in rice genome [79] as well as in other species such as soybean [80]. In the latter work, the authors revealed the presence of proteins belonging to the major intrinsic protein (MIP) family whose proteins are involved in forming channels with high selectivity to control transport of water and different solutes (Si in that case). Soybean was proven to be genetically capable of absorbing the element, more precisely, as silicic acid $Si(OH)_4$.

Inside the plan, after precipitating as SiO_2 and being incorporated into biological structures (e.g., the cell-wall), Si exerts its protective action forming a physical barrier [81] as component in the lignin-carbohydrate complex in leaf epidermal cell walls and inducer of lignification in these structures which confer resistance to pests and pathogens [82]. However, this passive role is too simplistic and does not explain why plants supplemented with Si are better suited to face exogenous stresses. Si in the nano form can be instrumental to agriculture as both as a carrier of nutrients and other substances that play an important role in the crop development and yield, as well as alternative form of Si as plant nutrient. In this section, examples of recent research papers within these contexts are briefly reported.

The experiments reported in this review on plant treatment using nanosilica show that amorphous nanosilica is usually not applied as a source of nutrient other than Si, which means that it is not used as nutrient carrier. This is likely because mesoporous nanoparticles are more suitable to be loaded with nutrients making them a better choice, compared to the amorphous counterpart, when it comes to fertilization. Mesoporous nanoparticles loading mechanism is double: physical and chemical. The first refers to the trapping of nutrients inside their structure; the second refers to the electrostatic interaction with the nutrients by means of superficial charges and functional groups.

The majority of the works found in literature are focused on the plant resistance to both abiotic and biotic stresses while not a big amount of papers deal with the crop yield and crop fertilization. When it is about plant resistance, Si nanoparticles are usually compared with other treatments (i.e., pesticides), and the nanoparticles are not doped with any substance; therefore, the nanoparticles are not seen as carriers of active molecules but they are rather seen as Si in a form that is different from the bulk. The fact that most of literature is focused on defense mechanism, in turns, it can be seen as an opportunity to deepen the research over the use of silica nanoparticles with the double aim of increasing the natural resistance and carrying nutrients with a slower release kinetics when compared to the traditional fertilization. Moreover, most of the experiments regard confined conditions and lab trials while only few are performed in field conditions. This is because the application of Si nanoparticles, and nanoparticles in general, is still under observation and its scalability is yet to be verified. This explains the high number of the germination tests that are meant to determine the toxicity of Si nanoparticle to seeds and plantlets.

Si Nanoparticles as Plant Nutrient Carrier

Table 5a lists recent articles in literature about the application of silica nanoparticles as nanofertilizers on different plant species. Nutrient release from conventional fertilizers is usually very rapid and gives plants a short time laps for uptaking nutrients. As previously stated, the outcomes are negative being the impact on the ecosystem and on the economy of the farmers rather high. Loading nanoparticles with nutrients may represent a solution to this issue if the nutrients rate release is reduced and the Nutrient Use efficiency (NUE) increased.

Several works are focused on studying the release kinetics of nanofertilizers versus commercial/traditional fertilizers. Results are so far encouraging. For instance, Naseem et al. [83] studied the response of *Oryza sativa* in a pot experiment when fertilized with commercial urea or Si mesoporous nanoparticles ($ZnAl_2Si_{10}O_{24}$; 64 nm) functionalized with urea; both fertilizers were applied to the soil at the same doses. The authors observed that the release of urea from the nanocomposite was maximum and faster in the first three days and it lasted up to 336 h (14 days). The yield resulting from the treatment with nanofertilizer was significantly higher when compared to the conventional fertilizer (Table 5a).

Another interesting work by Li et al. [84] considered maize and micro-nanostructured silica spheres (solid silica spheres (S-Si), hollow silica spheres (H-Si) and sea urchin-like micro–nanostructured hollow silica spheres (SUH-Si, ~500 nm) with different surface roughness and morphologies as carrier for N to improve the adhesion capacity on plant leaves when applied as foliar fertilizers. Results indicated that SUH-Si–N provide nitrogen nutrition for maize seedlings and promote their growth and development. Furthermore, the authors gave an explanation in terms of contact angles of the SUH-Si–N on maize leaves demonstrating the superior wettability of SUH-Si–N on the crop surface. This highlights the importance of the morphological aspect of the nanocarriers in determining their persistence on the plant surface, hence the permanence of the nutrient they carry. Such aspect is crucial and is one of the key factor and research issue that should be addressed to prove the applicability and efficacy of nanofertilizers (Table 5a).

An interesting work by Suriyaprabha et al. [85] compared Si foliar application with two different forms of Si. The authors studied the effects of 20–40 nm nano SiO_2 versus bulk silica pre-dissolved in distilled water at a concentration of 15 g L^{-1} and sprayed on *Zea mays* in a pot experiment. Not only SiO_2 content was found to be significantly higher with nano SiO_2 than bulk (9.3% and 6.2%, respectively) but such increased SiO_2 deposition favored the K and P contents, too. Therefore, the nutrient status of the leaves was improved indirectly, that is without loading the Si nanoparticles with nutrients. The authors, citing some of their previous studies, concluded that the Si foliar application was not as performing as the application to soil, although confirming most of the findings despite to a lesser extent. The indirect influence of nano Si on plant nutrition was not confirmed on rice [86].

Lima de Oliveira et al. [87] studied the effect of nano Si foliar application from a different point of view. In their work they studied the physiological effects of nano Si on plants of *Sorghum bicolor* in terms of gas exchange according to the hypothesis that there was a differential response to different sources (sodium silicate, two forms of potassium silicate, silicic acid and nanosilica) and concentrations of Si. What they reported is that all silicon sources increased photosynthesis but the magnitude of increase was higher in nanosilica and stabilized silicic acid although the induced higher transpiration and stomatal conductance negatively interfered with the biomass allocation in case of water deficiency or drought conditions. The authors concluded that the role of Si is confirmed to be crucial in promoting water savings and the element increases the dry weight in sorghum plants, with Si-alkali and Si-potassium being the best sources of Si for foliar fertilization of sorghum (Table 5a).

Several works deal with the effects of nano forms of Si on germination and/or on the first stages of agronomic plants development (maize [88,89], tomato [90], wheat and lupin [91], *Lens culinaris* [92], and sugarcane [93]) (Table 5b). On the one hand, this testifies the precautionary approach of research about this topic and on the other hand, the current level of readiness of this new technology which is still quite low. There is a general agreement on the positive effect of nanosilica on seed germination that resulted to be higher than the other forms of Si for all the papers listed above, and no toxicity effects were recorded with the exception of the observations on the genotoxicity by Khan and Ansari [92] that reported clastogenic effect on root tip cells of lentil at the highest concentrations. This must be taken into account considering that the experiments described in the works were different in terms of type of nanoparticles, species, and doses as well as the growth conditions (Table 5b).

Table 5. Silica nanoparticles and other nanostructures.

(a)

Material	**Species**	**Treatment**	**Experimental Conditions**	**Results**	**Reference**
Urea loaded zinc aluminosilicate (UZAS) mesoporous nanocomposite, 55.2 nm (pore size: 13 nm)	*Oryza sativa*	0 mL UZAS (0 g N pot^{-1}); 20 mL UZAS (0.45 g N pot^{-1}); 40 mL UZAS (0.90 g N pot^{-1}); 60 mL UZAS (1.35 g N pot^{-1}); 0 mL UZAS (1.80 g N pot^{-1}); 100 mL UZAS (2.25 g N pot^{-1})	Pot experiment.	Increased yield and higher nitrogen recovery efficiency compared to commercial urea.	[83]
Micro–nanostructured silica spheres (solid silica spheres (S-Si), hollow silica spheres (H-Si) and sea urchin-like micro–nanostructured hollow silica spheres (SUH-Si); particle diameters ~500 nm	*Zea mays Arachis hypogaea*	Foliar application (50 mL) of: deionized water, NH_4Cl solution (5 g L^{-1}), S-Si–N (1.5 g L^{-1}), HSi–N (1.5 g L^{-1}) and SUH-Si–N (1.5 g L^{-1}). 50 mL of deionized water simulated rainwater scouring.	Pot experiment in growth chamber (26 °C/21 °C; 14 h/10 h light–dark; light intensity 300 mol photons per m^2 s^{-1}).	Leaf adhesion of SUH-Si–N higher than S-Si–N and H-Si–N at 1.5 g L^{-1}; SUH-Si–N enhanced root length, chlorophyll content and plant height in maize.	[84]
Amorphous silica nanoparticles (20–40 nm)	*Zea mays*	Silica nanoparticles and bulk Si 15 g L^{-1}	Pot experiment (sandy loam soil; pH 7.0 ± 0.5). In vitro cytotoxicity experiment.	Augmented Si accumulation and regulated expression of defense compounds.	[85]
Highly soluble silicate and amorphous nanosilica (<200 nm)	*Oryza sativa*	Nanosilica (Si = 106 g L^{-1}) and soluble silicate (Si = 115 g L^{-1}) at 0, 605, 1210, and 2420 g ha^{-1}.	Pot experiment.	Increase of lignin content in leaves. Enhanced Si uptake.	[86]
Amorphous nanosilica (4.0 nm), silicic acid, stabilized sodium, potassium silicate, and potassium silicate	*Sorghum bicolor*	Foliar application of 0, 0.5, 1.0, and 1.5 g L^{-1} of Si.	Pot experiment.	*n*Si spraying at V4, V8, R1 increased plant growth; Si concentration enhanced photosynthesis.	[87]

Table 5. *Cont.*

(b)

Material	**Species**	**Treatment**	**Experimental Conditions**	**Results**	**Reference**
Sodium silicate (Na_2SiO_3), micron silica (SiO_2), silicic acid (H_4SiO_4), tetraethyl orthosilicate [$Si(OC_2H_5)4$], nanoSi from rice husk (50 nm; pore size 1.52 nm)	*Zea mays*	10 mg L^{-1} Si from Na_2SiO_3, SiO_2, H_4SiO_4, $Si(OC_2H_5)_4$ and nanoSi	Germination trial in soil (pots).	Enhanced seed germination.	[88]
Amorphous *n*SiO_2 (12 nm, SSA 200 m^2 g^{-1})	*Lycopersicum esculentum*	*n*SiO_2 0, 2, 4, 6, 8, 10 and 12 g L^{-1}	Germination trial in Petri dishes.	Enhanced % germination and seedling dry weight.	[89]
SiO_2 microparticles, *n*SiO_2 (25 nm, SSA 274 m^2/g, pore size 1.46 nm)	*Zea mays*	micro SiO_2 and *n*SiO_2 1000 mg kg^{-1}	Germination trial in Petri dishes, cotton method and Soil method.	Enhanced root elongation.	[90]
Mesoporous silica nanoparticles MSN (20 nm, pore size 2.78 nm)	*Triticum aestivumLupinus albus*	MSN 0, 200, 500, 1000, 2000 mg L^{-1}	Germination trial in Petri dishes and seedling growth in hydroponics.	Enhancement of seed germination, increased plant biomass, total protein and chlorophyll content and photosynthesis (500–1000 mg kg^{-1}). No oxidative stress or cell membrane damage even at 2000 mg kg^{-1}.	[91]
Amorphous *n*SiO_2 (5–50 nm; SSA 50–500 m^2 g^{-1})	*Lens culinaris*	0, 25, 50, 75, 100, 200, 300 µg mL^{-1}	Germination trial in Petri dishes.	Increased seed germination, seed vigour index and seedling biomass at lower concentrations. Dose-dependent decrease in mitotic index at higher concentrations.	[92]
Amorphous *n*SiO_2 (4 nm, SSA 750 m^2 g^{-1}), monosilicic acid + PEG-400 (Si-acid), Na-K silicate stabilized + sorbitol (Sialkali); Si-K	Sugarcane	Si sources at 0, 0.25, 0.5, 0.75, 1.0 mmol L^{-1}	Pot trials. (i) foliar treatment (0.16 ml per plant) 18, 25, 32, 39 and 46 DAE; (ii) foliar treatment (1.92 ml $plant^{-1}$) 101, 114, 128 and 144 DAE.	Si beneficial effects on plant growth more evident for Si soluble sources with stabilizers than Si-K and *n*Si.	[93]

6. Chitosan Nanoparticles

The chitosan (CHT) is the deacetylated form of chitin, which is linear copolymer of 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose. Chitin as biological source plays a relevant ecological role since it is the second most represented biopolymer after cellulose in earth biomes and it is retrievable in the exoskeleton of crustaceans and insects, as well as in the cell walls of fungi [94].

Albeit several synthesis methodologies have been proposed since Ouya and coworkers in 1994 initially implemented the emulsion cross-linking synthesis, the most affordable, reproducible, and scale-up protocol to be applied for agronomic applications is by far the ionotropic gelation. This synthesis takes place at room temperature, is simple, and lacks side effects at the biochemical level; furthermore, it has been tested in both foliar treatments and seed priming. Physico-chemical features such as size, stability, shape, and rate of polymerization of nanoparticles are strictly related to the degree of de-acetylation of the CHT used as reaction substrate. In more detail, the nanomaterials synthesis is obtained by a cross-linking between the cationic ammino groups of CHT with the anionic tripolyphosphate (TPP+). Such a cross-linker denotes the appreciable characteristic to be ineffective towards cell metabolism and the strength of CHT effects [95]. From a theoretical point of view CHT nanoparticles (*n*CHT) exhibit high surface charge and thus should be enabled to easily interact with biological membranes, even though cutinized integument tissues largely impeded them to pass through. Indeed, field experiments on large scale have led to controversial results about permeability characteristics of CHT nanomaterials, so that their use in agriculture has been restricted to plant protection or growth enhancement [95]. Such defense inducing activity relies in a boosting effect on plant immune response against several diseases caused by fungi, bacteria, and viruses. For a more extensive explanation of this issue and of chitosan signal perception, please refer to the review paper of Chandra and coworkers [96]. The most updated description of the pathways stimulated by metallic *n*CHT underlying their antimicrobial activity and defense mechanism has been revised by the Chouhan and Mandal [97].

The distribution of bulk CHIT on plants has long been associated with beneficial effects generally described as bio-fortification. Such definition involves the already cited strengthening of plant defense against pathogen, the development of ROS scavenging activities and secondary metabolite synthesis, the increase of drought tolerance, the enhancement of plant growth and seed germination together with an improvement on quality and shelf life of fruits [98]. In agreement with the proposed bio-stimulant activity of CHT, its application at different doses in maize during seed priming under low temperature, induces an increase of the germination index and growth in both shoot and root portion. In parallel, several physiological traits such as membrane permeability, sugar concentration, and ROS scavenging enzymes are ameliorated in comparison to control. In particular, the observed seed priming is explainable by the enforcement of osmotic potential due to the enhancement of proline and soluble sugars concentration [99].

The application of *n*CHT as plant bio-stimulant could further improve the mode of action (efficiency) in comparison to raw material, since it allows bypassing the most undesirable peculiarity of bulk CHT, which is soluble only in acidic solutions. Indeed, the nanomaterials based on CHT polymers would be particularly interesting regarding applications in a modern sustainable agriculture, since they possess several remarkable properties, such as bio-stimulation and protective effects, together with the ability to enhance them by appropriate functionalizing agents.

The treatment with functionalized *n*CHT increases plant vigor and resistance to pathogens [100] and it prompts a beneficial effect on seed germination due to the induction of amylase and protease activity [101]. This is one of the suggested physiological mechanisms underlying the favorable effect exerted by *n*CHT on plant metabolism. The activation of rapid degradation process of seed reservoirs is probably a drive for fast development and growth during the first phenological stages.

A number of papers attest the positive impact of *n*CHT on morphological and physiological traits in the case of both germinating seed and foliar treatments. Studies undertaken on chickpea, maize, and tomato seedlings have demonstrated that *n*CHT increase their growth, fresh and dry weight, germination rate, and seed vigor index [101–103], and in some cases exert even stronger effect than bulk CHT. It has to be stressed that these growth-promoting effects have been observed after seed treatment by Cu-functionalized *n*CHT. At least in two cases the main goal of the nanomaterial application was to verify its anti-fungal activity, so in these papers the observed bio-fortifying outcomes are presented somehow as side effects.

In the case of fully developed plant, *n*CHT treatments show similar beneficial results on leaf area and growth together with enhanced photosynthetic pigments and activity, stomatal conductance and nutrient uptake in coffee [104]. Also in maize, a growth promoting activity is retrievable due to the application of *n*CHT in both potted-grown plants and field grown ones. The former exhibit also a high chlorophyll content, while the latter show better productivity performance in comparison to untreated plants [105]. In tomato, foliar distribution of *n*CHT obtained by ionotropic gelation provokes similar beneficial effect on yield, enhancing at the same time several reproductive indicators [106].

However, a diffuse analysis concerning the application of *n*CHT in fertilization on a large scale is still lacking. The specific experimentation at field level needs to be promoted;

in particular, tests regarding the utilization of this nanomaterial as fertilizer shuttle in different pedoclimatic environments are poorly widespread, probably because a precise and specific regulation (at legislative level) is still missing. The proven biodegradability and extremely low toxicity of chitosan could dissipate doubts and concerns that accompany the use of these innovative materials. CHT nanomaterials meet the major obstacles affecting the nutrient use efficiency in modern agriculture, since they could deliver nutrients to plant at a nanoscale size, facilitating uptake. In addition, *n*CHT functionalization by fertilizing agents ensure a slow and long-lasting release of entrapped nutrients [95], with a significant decrease in environmental dispersal.

6.1. Nutrient Delivery by Chitosan Nanoparticles

The use of *n*CHT as fertilizer carrier is particularly appreciated thanks to their biodegradability that ensures controlled and slow release of macro- and micronutrients [107]. This feature is relevant in the case of micronutrients, whose over-dosage may cause toxicity. For this reason, field experiments regarding micronutrient fertilization has received more attention in comparison to macronutrient application.

Micronutrient deficiencies are a serious matter of concern, especially for agriculture in emerging countries. In particular, concerning the cultivation of cereals, the problem has consequences for the diet and health of a large part of the population [108]. Application of *n*CHT is particularly attractive in the case of micronutrients, whose concentration could be often inadequate because of pedoclimatic conditions or massive exploitation of nutrient reserves. This is just the case investigated in tomato, where Zn-functionalization of *n*CHT is able to ameliorate the micronutrient content in starved plants of wheat by foliar nanoparticles application during five weeks after the anthesis. The treatment increases zinc concentration in a value ranging from 27% to 42% and furthermore induces its translocation inside both leaf and seed tissues [109].

Further experiments allow to demonstrate in wheat grown under field conditions an increase in grain quality, again due to foliar treatments with chitosan nanomaterials functionalized by zinc. Anyway, the Zn supply induces a switch on of genes related to metal transport and homeostasis, even though the zinc intake with nanoformulation is ten times less than that provided by conventional techniques [110]. Accordingly, the same research group demonstrates the efficacy of nanofertilization by *n*CHT complexed with Zn, since the delivery of the metal in a 10% amount in respect to $ZnSO_4$ treatment still ensures biofortification and zinc-enrichment of seeds, but avoids environmental pollution [110] (Table 6a).

Choudary and coworkers obtained comparable results by the application to maize seed *n*CHT functionalized with Zn. Besides the already observed yield increase and protection against pathogen, they confirm the positive effect exerted on grain quality due to high Zn content [111]. On the other hand, a more strictly methodological approach is used to determine the loading efficiency of *n*CHT in the case of doping with Zn [112]. According to the provided evidence, the treatment on single cotton plant with 50 ppm of *n*CHT loaded with zinc and synthetized in the presence of zein induced an increase in root length, plant height, and leaf number. These morphological traits were significantly higher in comparison to those observed in the case of conventional fertilization (Table 6a).

The pioneering work of Corradini and coworkers demonstrates the possibility to obtain functionalized CHT nanomaterials able to encapsulate NPK plant macronutrient, using calcium phosphate, urea, and potassium chloride as nutrient sources. At the same time, researchers provide a detailed characterization of the obtained *n*CHT-polymethacrylic acid-NPK NPs using TEM, FT-IR, and light scattering analysis, demonstrating also adequate dimension and stability of the functionalized nanoparticles [113] (Table 6a).

The macronutrients distribution by means of CHT-nanomaterials has been applied as an innovative and smart technique able to improve use efficiency of the so called NPK fertilizers, thanks to a more accurate delivery and to a prolonged release [114] (Table 6b). Fertilization by *n*CHT ensures a relevant additional benefit regarding macronutrient supply.

Actually, it should be taken in account the further contribution of 9–10% nitrogen present in the raw material [115], together to phosphorus provided by TPP, which is the catalyst used in ionotropic gelation for polymer synthesis and exhibits a 24% P content [116] (Table 6b). Another methodological expedient has been developed by Dhlamini and coworkers who has applied a nanoformulation of CHT characterized amorphous nature and loaded by NPK fertilizers together with S. Greenhouse experiments conducted on maize reveal that CHT nanofertilizer encapsulating four macronutrient improves plant height and stem diameter, chlorophyll content, and leaf number in respect to conventional fertilization treatments [117] (Table 6b).

6.2. Hybrid Functionalization and Multiple Distribution by Chitosan Nanomaterials

An innovative technique for the synthesis of hybrid nanomaterials has been refined. Starting from a mixture of CHT and sodium alginate as raw materials, the hybrid complex is synthesized by polyelectrolyte catalysis. Such procedure is environmentally friendly and leads to formation of a biodegradable nanocomposite where doping molecules are embedded. The hybrid nanostructure has been tested for CuO delivery and demonstrates the appreciated ability to prolong the release of the Cu at a significant extent even in comparison to CuO-NPs [65,118] (Tables 3 and 6b).

Concerning distribution, a new intriguing modality is offered by multiple delivery of nutrients coupled with metabolism regulator that has been obtained by co-encapsulation of Cu and salicylate [116]. Similarly, an innovative solution is the simultaneous functionalization with different metals as micronutrients (e.g., Zn and Cu) allows a slow release of these elements and enhances the bio-fortification and plant defense response due to double metal application [100].

Table 6. Chitosan nanoparticles loaded with macro/micronutrients.

(a)

Material	**Species**	**Treatment**	**Experimental Conditions**	**Evidences**	**Reference**
Zinc loaded chitosan nanoparticles (Zn-CNP), bulk Zn ($ZnSO_4$)	*Triticum durum*	Foliar spray (i) Water; (ii) $ZnSO_4$. (400 mg L^{-1} Zn); (iii) Zn-CNP (40 mg L^{-1} Zn).	Field trial.	Foliar application influences expression of genes implicated in Zn transport. Zn enrichment on grain storage proteins.	[109]
Zn loaded chitosan nanoparticles Zn-CNP1 (40 mg L^{-1} Zn) Zn-CNP2 (4 mg L^{-1} Zn)	*Triticum durum*	Leaf spray (i) Water; (ii) Urea; (iii) Urea + $ZnSO_4$ (400 mg L^{-1} Zn); (iv) Urea + $ZnSO_4$ (40 mg L^{-1} Zn); (v) Urea + Zn-CNP1; (vi) Urea + Zn-CNP2.	Field trials	Increased grain Zn content without affecting grain yield, protein content, spikelets per spike and kernel weight.	[110]
Zn loaded chitosan nanoparticles (200–300 nm)	*Zea mays*	Foliar spray Zn-chitosan NPs 0.01–0.16%.	Petri dishes; pot trial and field experiment	Strengthening of plant immunity by elevating antioxidant and defense enzymes; in field better control on *Curvularia* leaf spot disease; increased grain yield and enriched Zn content.	[111]
Zn loaded chitosan/TPP (Tripolyphosphate)–Zein coated nanoparticles	*Gossypium hirsutum*	(i) Control; foliar spray 50 mg L^{-1} of (ii) ZnSO4; (iii) Zn loaded chitosan;, (iv) Zn loaded chitosan/TPP–Zein coated 0.1%; (v) Zn loaded chitosan/TPP–Zein coated 0.2%; (vi) Zn loaded chitosan/TPP–Zein coated 0.3%.	Pot trial	Particles coated with Zein (0.1%) increased plant height, number of leaves and root length.	[112]
Chitosan-polymethacrylic acid-NPK nanoparticles	Proof of concept	500 mg/mL of N, 60 mg/mL of P and 400 mg/mL of K in the most concentrated nanoformulation.	Laboratory conditions.	NP mean diameter (in the dry state) ≈ 78 ± 1.5 nm; ζ potential varies depending on the amount of nutrient encapsulated.	[113]

Table 6. *Cont.*

(b)

Material	Species	Treatment	Experimental conditions	Evidences	Reference
Chitosan-polymethacrylic acid-NPK NPs	*Triticum aestivum*	500 mg/mL of N, 60 mg/mL of P and 400 mg/mL of K in the most concentrated nanoformulation.	Pot filled with sandy soil, foliar distribution of nutrient solution, outdoor conditions.	Enhanced plant height, main spike weight, crop yield, and harvest index.	[114]
Cu and salicylic acid (SA) co-encapsulated chitosan	*Zea mays*	Nanofertilizer (0.01, 0.04, 0.08, 0.12, 0.16%, *w/v*), water (Ctrl), bulk chitosan (0.01%, *w/v*), SA (0.01%, *w/v*) and CuSO4 (0.01%) used to treat seeds and as foliar spray on adult plants.	Germination trial; pot trial.	Increased activities of antioxidant enzymes, and enhanced chlorophyll contents in leaves.	[116]
Chitosan-TPP-NPKS nanoparticles (220–530 nm)	*Zea mays*	(i) Control; (ii) conventional NPK; (iii) conventional NPKS; (iv) chitosan-TPP; (v) chitosan-TPP-NPKS. 0.125, 0.25, 0.5 and 1% chitosan.	Pot trial.	Increased plant height, number of leaves, and chlorophyll content.	[117]
*n*CuO–PEC [Chitosan/Alginate] (300 nm)	*Fortunella margarita*	(i) *n*CuO 10 ppm; (ii) *n*CuO 50 ppm; (iii) *n*CuO 100 ppm; (iv) *n*CuO–PEC 10 ppm; (v) *n*CuO–PEC 50 ppm; (vi) *n*CuO–PEC 100 ppm.	Petri dishes	Increased seed germination.	[118]

7. Conclusions

There is a consensus on the need to introduce significant innovations into the global agricultural system for sustainable intensification to ensure food security and protect natural capital. In this perspective, nano-enabled agriculture is expected to significantly enhance the efficiency of agrochemicals (fertilizers, pesticides, fungicides, and herbicides), reducing their environmental impact while increasing crop yields. For this very reason, there is a growing expectation of overcoming some inefficiencies of the global agricultural system. This consideration alone places this field of study in a vanguard position concerning the expectations expressed by the EU Green Deal.

The physico-chemical characteristics of the nanostructures influence their behavior (e.g., solubility, stability, nutrient release rate). For this reason, the design and development of nanofertilizers requires close collaboration between researchers in the field of nanochemistry, crop nutrition and agronomy. In the studies cited in this review, it is shown how much this interaction is necessary.

Knowledge in this field is developing very rapidly. The literature highlights the high potential of nanomaterials in crop fertilization in terms of more accurate delivery of nutrients. Likewise, this will also occur for plant protection products (e.g., pesticides, fungicides, herbicides). This favorable evidence supports the prospects for further research development. On the other hand, the evolution of materials rapidly opens up new perspectives. In a few years we have moved from nanoparticles to nanostructures doped with other elements in a few years, while more recently, nanohybrids materials have been introduced. New perspectives in the direction of the circular economy look at the valorization of waste biomasses to produce smart nanostructures.

Many efforts have yet to be undertaken for optimization of nanoparticles delivery, aiming to minimize risks from over-dosage and accumulation. For these reasons, the use of highly biodegradable biopolymers that reduce the persistence of nanostructures in the soil and on the plants is promising (e.g., cellulose, lignin, zein, chitins) [119]. The risk of undesired effects must therefore lead to find technological solutions able to optimize the interaction between nanomaterials and plant, thus enabling agronomical treatments with a low environmental impact, which is exactly what nanotechnologies are applied for in agriculture. These considerations imply an accurate design and customization of the nanoparticles concerning their charge, as well as morphology for a specific interaction with different plant species. The choice of spherical particles might not be the best technological solution in the case of foliar distribution, where rod- and platelet-like carriers provide a more efficient adhesion due to their high contact surface area. Therefore, the aspect ratio and morphology of nanoparticles has to be considered in the future for the best assessment of field applications [119].

However, the fact remains that most of the literature data come from studies carried out in artificial conditions (laboratory and hydroponic experiments, or pot experiments with commercial potting soil or other artificial substrates). Since they do not predict the results under natural soil conditions, more experiments with natural soil and field conditions are strongly requested. Field trials are also necessary to develop more applicative knowledge relating to the open field handling of nano-agrochemicals, the use of specific operating machines, and precautions for operators and consumers. Such information is also essential to provide the elements necessary to structure the rules, standards, prescriptions, and precautions to develop nano-enabled agriculture and reap the expected benefits fully.

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