Review Article

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Strategic applications of nano-fertilizers for sustainable agriculture: Benefits and bottlenecks#

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Abstract: The application of nano-fertilizers (NFs) is an emerging research field in agriculture. These are materials in the size range of 1–100 nm that support the nutrition of the plants. It is a novel way to optimize the nutrient supply, either alone or in combination. NFs are an economical alternative to ordinary chemical fertilizers that can increase global food production in a sustainable way. NFs are made up of nutrients and micronutrients and may act as carriers for nutrients. The nanocarriers deliver the nutrients to the right place, reducing the additional amount of active chemicals deposited in the plant, besides a slow release. Although nano-coated materials manage to penetrate through the stomata with a size exclusion limit greater than 10 nm, the nanoparticles appear to be able to make holes and enter the vascular system. This review addresses the potential benefits of NFs to agriculture, synthesis, mode of entry, mechanisms of action, and the fate of nanomaterials in soil. Finally, policy makers will have the bases to regulate the dose, frequency, and time period of NF applications for food production. We suggest formulating the integrated risk management frameworks for the possible applications of NFs in agriculture.

Keywords: soil and foliar nano-fertilizers, nanostructures, bionanofertilizers, slow release

This paper is dedicated to the memory of Mr. Sushant Bhusari.

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1 Introduction

Several challenges are faced by farmers in traditional agriculture, including chemical toxicity owing to the excessive use of fungicides/pesticides, development of resistance to the existing fungicides/pesticides, and sometimes their high cost, which is beyond the reach of marginal farmers, particularly in developing countries. In today's agriculture, despite improvements in understanding the mechanisms behind nutrient assimilation by plants, there are no fertilizers that successfully provide optimal plant nutrients. The essential nutrients required for crop growth are nitrogen (N), phosphorous (P), and potassium (K). However, it was reported that these key macronutrient elements (N, P, and K) applied to the soil are lost by 40–70, 80–90, and 50–90%, respectively, causing a considerable loss of resources. Therefore, their usage in agriculture is extensively increased. Wang *et al.* [1] and Zulfiqar *et al.* [2] proposed that NPK consumption for crops can increase to 265 million tons by 2020; however, recent data is not available on this aspect. Considering the various concerns associated with excessive usage of chemical fertilizers, the declaration of the European Commission to reduce 50% of pesticides by 2030 is highly appreciable.

Nitrogen required by the plants is usually supplied in the form of nitric acid, ammonium nitrate, synthetic ammonia, urea, or sodium nitrate [2–4]. Unfortunately, large quantities of urea are applied to fertilize the soils, 100–782 kg per 100 m^2 [3,5]. Phosphate is supplied in the form of ammonium phosphates, calcium metaphosphates, defluorinated phosphates, diammonium phosphates, phosphoric acid, or superphosphates [3,6,7], which come from phosphate rocks [4]. To supply crops with potassium commonly kainite, sulfate potash magnesia, potassium chloride, and potassium carbonate are used, which are derived from potash [4,8].

Although fertilizers are essential for agriculture to feed the growing population, the excessive use of large amounts of chemical fertilizers leads to environmental pollution [9,10]. Besides, as discussed above, only 20–50% of the applied fertilizers are used efficiently; the other 50–80% are lost through leaching, emissions, or incorporation into the soil by microorganisms in the long term, generating ecological problems such as reduced soil fertility and economic losses [11]. The soil is a system full of life, particularly symbiotic relationships with plants. Plant–microbe interactions are mutually beneficial, where rhizosphere microorganisms such as rhizobacteria solubilize minerals and mycorrhizal fungi transport these nutrients to the plant [12].

Many efforts are being made to ensure world food production in a sustainable way. The UN has proclaimed the 17 sustainable development goals as an effective method of global mobilization to achieve social priorities around the world, such as zero hunger. Sustainability includes agricultural practices without adverse environmental impacts, ensuring the production and quality of fruits and vegetables. Faced with this situation, it is urgent to formulate new fertilizers to release the nutrients in smaller quantities and in a slow and sustainable way, so that the crops can absorb them. Recent research on the application of nanotechnology in crop production has received attention as it seeks to streamline resources with agrochemical supply systems or sensors. The controlled release of agricultural inputs reduces the quantity and cost of fertilizers [13].

Nanofertilizers (NFs) are designed to be more efficient than conventional fertilizers by providing available elements with little bioavailability, such as phosphorus and zinc, and reducing the loss of mobile nutrients to the soil, such as nitrate [14,15]. NFs can be divided into nanomaterials (NMs) that act as nutrients themselves made of macronutrients or micronutrients and NMs that act as carriers of macronutrients loaded with nutrients or enhanced fertilizers [16]. Crops can absorb nutrients slowly and sustainably because the nanostructure of NFs provides a high surface-to-volume ratio [17,18], leading to a greater number of active sites for biological activity. There are high expectations about the applications of nanotechnologies in the agricultural sector. Apparently, the nano-tools perform an efficient and controlled delivery of agricultural inputs, which will offer sustainable solutions to climate change and environmental pollution [19].

In this review, we have attempted to discuss the role of NMs in agriculture, synthesis, modes of entry, and mechanisms of action. Moreover, the fate of NMs in soil and legislation to regulate the application of NFs in food production have also been examined.

2 Smart NMs for sustainable agriculture

Nanotechnology has been defined as the understanding and control of matter at dimensions ranging from 1 to 100 nm, possessing unique properties where phenomena enable novel applications. In agriculture, nano-technological applications are well reported earlier [20–24]. It has been suggested that there is a smart release of fertilizer particles following some specific signals. Nanobiosensors are suspended in a biopolymer that coats fertilizer particles. Signals are emanated according to plant needs as a biogenic trigger through which the communication is carried out by ions released by the root system [25]. Several studies with nitrogenous NFs have demonstrated to be effective. One of them is the NF of hydroxyapatite modified by urea and encapsulated in softwood cavities of *Gliricidia sepium*, supplying N slowly and steadily to the soil [26]. In another study, Ramírez-Rodríguez *et al.* [27] studied calcium phosphate nanoparticles doped with urea to fertilize *Triticum durum* plants. These nanoparticles contained a considerable amount of nitrogen as adsorbed urea. They found a high yield and quality of the durum wheat. Also, phosphorus (P)-NPs are used successfully; for example, chemically synthesized hydroxylapatite ($Ca_5(PO_4)_3OH$) NPs were evaluated in soybean (*Glycine max*). Interestingly, it was found that hydroxyl apatite NPs increased growth by 33% and seed yield by 20% when compared to conventional chemical phosphate fertilizers due to the supply of Ca and P [28].

Recently, due to noteworthy applications of nanotechnology in various sectors associated with agriculture, scientists around the globe are focusing on these fields. Moreover, it can be clearly seen from the currently published large number of scientific publications and patents on the application of NMs in agriculture and, particularly, as NFs for plant growth promotion and protection [10,29–31]. Technology developers in agriculture always look for the products or technologies that help to raise agricultural crop yields while reducing environmental damage. Since NFs minimize the use of chemical fertilizer inputs, they are becoming very popular. The bioactivity and biomodification of some metallic nanoparticles in soil that can influence plant growth have been studied, such as silver nanoparticles (AgNPs), titanium oxide nanoparticles (TiO_2), nickel nanoparticles, (NiNPs), silica nanoparticles (SNPs), carbon nanotubes (CNTs), and others, with relevance to plant yield [2,32–37].

NFs offer a number of benefits compared to conventional fertilizers for sustainable and eco-friendly crop production. Some of these mainly include the following: (i) the enhanced absorption and efficient utilization of nutrients without higher losses, (ii) significant reduction of the risk of environmental pollution due to the decrease in the losses of nutrients, (iii) the considerably higher diffusion rate and solubility of NFs compared to the conventional synthetic fertilizers, (iv) controlled release of nutrients in NFs compared to chemical fertilizers in which it is very spontaneous and rapid in case of chemical fertilizers, (v) requirement in low amounts of NFs than synthetic fertilizers due to reduced loss and higher absorption, and (vi) improvement of soil fertility and also development of a feasible environment for microorganisms [38,39]. Table 1 shows the difference between conventional fertilizers and NFs [38].

3 Harnessing the potential of NFs

Large amounts of fertilizers are currently used to produce food, as they are essential for crop productivity. However, the efficiency of conventional fertilizers is very low. For example, of the total nitrogen applied to the soil, 50–70% is lost through leaching as water-soluble nitrates and by emission of gaseous ammonia and nitrogen oxides [40,41]. The efficiency of phosphate fertilizers is from 10 to 25%, and that of potassium is from 35 to 40% [41]. For example, the consumption of NPK in India in 2014 was 23 Mt to produce grains to feed the population, and by the year 2025, taking into account the growing population, the country will require 45 Mt of these fertilizers [42].

In this context, nanotechnology can solve some of these problems. The main benefit of the use of NFs in agriculture is the greater efficiency of plants to absorb them, minimizing the amount of fertilizers and consequently reducing the toxicity to the soil environment [43] (Figure 1).

NFs in agriculture have drawn attention for their unique features, such as ultra-high absorption, increased production, and increased photosynthesis due to leaf surface coverage. The uptake and penetration of zinc oxide nanoparticles in tomato plant leaves is an example of nanoparticles with potential of NFs, because when sprinkled on leaves, growth and biomass production of the plants improved as compared to control plants [44,45]. In another study, Shinde *et al.* [46] studied the efficacy of green synthesized magnesium hydroxide nanoparticles [$Mg(OH)_2$NPs] in seed germination and *in vitro* and *in vivo* plant growth promotion on *Zea mays* at different concentrations. The results obtained showed that $Mg(OH)_2$NPs at 500 ppm showed enhanced seed germination (100%) and growth. Moreover, the effect of $Mg(OH)_2$NPs on plant growth was analysed using plant efficiency analyser by measuring the plants' height and chlorophyll a fluorescence. Chlorophyll a fluorescence measurements revealed that plants treated with $Mg(OH)_2$NPs showed a high rate of photosynthesis which was confirmed by the maximum performance index and minimum dissipation as compared to control and plants treated with bulk Mg. All the findings strongly suggested that $Mg(OH)_2$NPs can be promisingly used for the enhancement of seed germination and growth promotion in *Z. mays*. The application of different NFs in various crops was reported to have a considerable increase in crop yield. Table 2 shows the impact of NFs on the productivity of different crop plants [47].

The application of a nanocomposite that consists of the nutrients necessary for plants such as N–P–K and

Table 1: The difference between conventional fertilizers and nanofertilizers

Properties	Nanofertilizer	Conventional fertilizer
Rate of nutrient loss	Low loss of fertilizer nutrients	High loss rate *via* drifting, leaching, run-off
Controlled release	Rate of release and release pattern precisely controlled	Excess release of nutrients lead to high toxicity and soil imbalance
Solubility	High	Low
Bioavailability	High	Low
Dispersion of mineral micronutrients	Improved dispersion of insoluble nutrients	Lower solubility due to large size particle
Effective duration of release	Effective and extended duration	Used by the plant at the site and time of application; the rest is converted into an insoluble form
The efficiency of nutrients uptake	Enhanced uptake ratio and saves fertilizer resource	It is not available to roots and the efficiency of nutrients uptake is low
Soil adsorption and fixation	Reduced	High

Aadapted and modified from Thavaseelan and Priyadarshana [38]; an open access article.

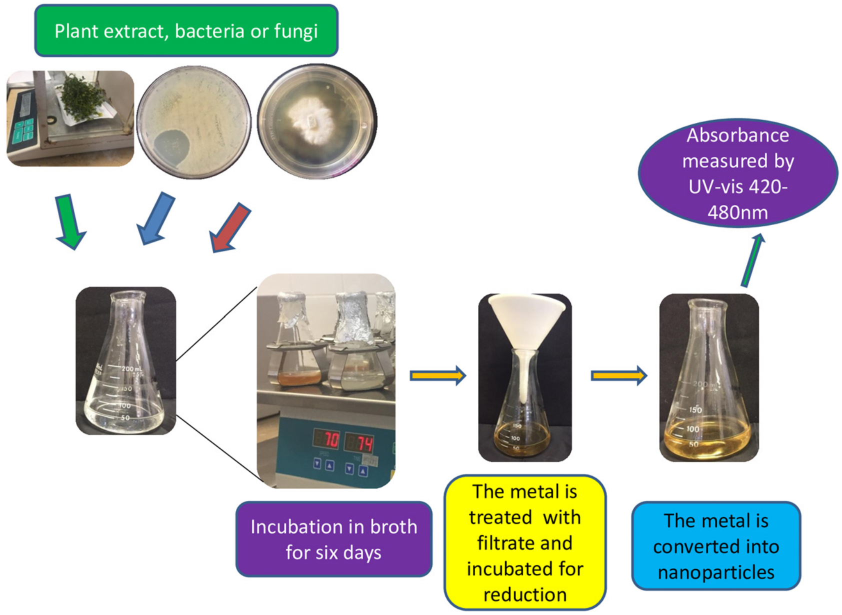

Figure 1: Biosynthesis of nanofertilizers.

Table 2: Impact of NFs on productivity of different crops plants

Nanofertilizers	Crops	Yield increment (%)
Nanofertilizer + urea	Rice	10.2
Nanofertilizer + urea	Rice	8.5
Nanofertilizer + urea	Wheat	6.5
Nanofertilizer + urea	Wheat	7.3
Nano-encapsulated phosphorous	Maize	10.9
Nano-encapsulated phosphorous	Soybean	16.7
Nano-encapsulated phosphorous	Wheat	28.8
Nano-encapsulated phosphorous	Vegetables	12.0–19.7
Nano chitosan-NPK fertilizers	Wheat	14.6
Nano chitosan	Tomato	20.0
Nano chitosan	Cucumber	9.3
Nano chitosan	Capsicum	11.5
Nano chitosan	Beet-root	8.4
Nano chitosan	Pea	20.0
Nanopowder of cotton seed and ammonium fertilizer	Nanopowder of cotton seed and ammonium fertilizer	16.0
Aqueous solution on nanoiron	Cereals	8–17
Nanoparticles of ZnO	Cucumber	6.3
Nanoparticles of ZnO	Peanut	4.8
Nanoparticles of ZnO	Cabbage	9.1
Nanoparticles of ZnO	Cauliflower	8.3
Nanoparticles of ZnO	Chickpea	14.9
Rare earth oxides nanoparticles	Vegetables	7–45
Nanosilver + allicin	Cereals	4–8.5
Iron oxide nanoparticles + calcium carbonate nanoparticles + peat	Cereals	14.8–23.1
Sulfur nanoparticles + silicon dioxide nanoparticles + synthetic fertilizer	Cereals	3.4–45

Adapted from Iqbal [47]; an open access article.

micronutrients improves the absorption and use of nutrients by crops [48]. Moreover, as compared to the chemical fertilizers, NFs have the potential to release nutrients gradually into the soil under a controlled system; hence, they are called smart fertilizers. We have reviewed two mode of applications of NFs, *i.e.*, aerosol foliar spray and direct mixing in soil (Table 3) [28,33,45,49–81].

4 Synthesis/production of NFs

4.1 Top-down methods

Synthesis of NFs involves either the top-down approach (physical methods) or the bottom-up approach (chemical methods). The top-down approach usually involves the breaking down of the bulk material into their respective nanosized structures or particles. These techniques are the extension of those that have been used for producing micron-sized particles. This approach uses substrates such as zeolites or other materials, which are ball-ground for several hours to obtain the nanodimension. Other minerals, in addition to zeolites, which have high cation exchange capacities, include clays, smectites, typically montmorillonites, and caulinites [82–85]. For example, natural zeolite measures between 1,000 and 3,000 nm [42]; by means of grinding with a high energy ball mill reduced to the desired size. The physical method to synthesize nanoparticles is simple; however, the product is heterogeneous nanoparticles that generally agglomerate; thus, stabilizing agents such as polymers or surfactants must be used to reduce agglomeration [86].

Besides, NMs must have an affinity for anions so that the anionic nutrients can be loaded efficiently for use as slow-release fertilizers. Zeolite-based slow-release fertilizers are limited to nutrients that can be loaded in cations such as NH_4^+ and K^+; however, if they are loaded in anions such SO_4^{2-}, NO_3^- and PO_4^{3-}, the charge is negligible in the unmodified zeolites. To achieve anionic properties on the surface of the zeolite, it can be modified with a surfactant such as surfactant modified zeolite and hexadecyltrimethylammonium bromide (HDTMABr).

Surfactant-modified zeolites have high oxyanion sorption and retention capacity, and HDTMABr is a cationic surfactant used to obtain a zeolite surface with positively charged surfactant head groups. Thus, the surface-modified zeolite retains important nutrients such as phosphate [87], sulphate [88], and nitrate [89].

4.2 Bottom-up methods

Similarly, the bottom-up approach refers to the build-up of material from the bottom, *i.e.*, atom-by-atom, molecule-by-molecule, or cluster-by-cluster. It means it starts with molecules in the solution and moves *via* molecule association to form NPs through certain chemical reactions. Since it is a chemically controlled process, the particle size can be controlled [90–93].

This approach begins at the atomic or molecular scale involving chemical reactions [91]. These controlled synthetis processes for producing NPs include emulsion, co-precipitation, micelle formation, and reverse micelle formation, focusing on minimal coagulation or aggregation and generating homogeneous NPs. Once synthesized, they must be characterized physicochemically and mechanically to know their functionality such as solubility, dispersibility and stability [94]. To achieve an adequate physiological interaction of NP with the plant, it is essential to know what characteristics will be effective depending on the type of nutrition of each crop. These characteristics are chemical properties, surface functionality, thermal stability and composition in addition to physicochemical characteristics such as shape, size, surface composition and charge, boiling point, melting point, pH variation, moisture, solubility, purity, soil type, stability, thermal and isoelectric properties, and heat and diffusion-controlled release [5,91,95]. Besides, NFs can be stabilized or encapsulated using synthetic polymers. Additionally, nutrients can be coated with a light NP film or encapsulated with NFs [42].

4.3 Hybrid NFs

Hybrid NFs are formed by an organic matrix (usually a polymer) and a dispersed inorganic phase in the form of homogeneously distributed nano-sized particles. Tarafdar *et al.* [38] demonstrated the slow release of hybrid NFs for up to 14 days in *Abelmoschus esculentus*. The authors synthesized hydroxyapatite modified with urea, as it is a source of nitrogen, calcium and phosphate. They could also be added to the modified hydroxyapatite, copper, iron, and zinc nanoparticles. As a result, they obtained a significant increase in the total absorption of copper, iron, zinc, and other nutrients in the fruit.

4.4 Biogenic synthesis: A greener way

Green synthesis is carried out with simple, cost-effective, less toxic, environmentally friendly, and efficient methods

Table 3: Tested plants for the effects of NPs through a particular mode of application

Mode of application	Nanoparticles tested	Tested plants/system	Reference
Aerosol foliar spray	CeO_2-NPs	Tomato (*Solanum lycopersicum*)	Adisa *et al.* [49]
	CeO_2 NPs	Bean crop (*Phaseolus vulgaris*)	Salehi *et al.* [50]
	Nano calcite	Rice (*Oryza sativa*)	Kumara *et al.* [51]
	CuO-NPs	Lettuce and cabbage (*Lactuca sativa* and *Brassica oleracea*)	Xiong *et al.* [52]
	Ag-NPs	Lettuce (*Lactuca sativa*)	Larue *et al.* [53]
	TiO_2 and ZnONPs	Tomato (*Solanum lycopersicum*)	Raliya *et al.* [54]
	TiO_2NPs	Barley (*Hordeum vulgare*)	Janmohammadi *et al.* [55]
	TiO-NPs	Lettuce (*Lactuca sativa*)	Larue *et al.* [56]
	Fe-NPs	Peace Lily (*Spathiphyllum illusion*)	Rasht [57]
	Different NPs	Watermelon (*Citrullus lanatus*)	Wang *et al.* [58]
	Fe-NPs	Wheat (*Triticum* sp.)	Reazaei *et al.* [59]
	Chitosan-silicon nanofertilizer (CS–Si NF)	Maize (*Zea mays*)	Kumaraswamy *et al.* [60]
	Salicylic acid-chitosan nanoparticles (SA-CS NPs)	Wheat seedlings (*Triticum* sp.)	Kadam *et al.* [61]
	Nano chitosan NPK	Wheat (*Triticum* sp.)	Abdel-Aziz *et al.* [62]
	Zn, Fe, NPK nanofertilizers	Chickpea (*Cicer arietinum*)	Drostkar *et al.* [63]
	Nitrogen, phosphorus and potassium nano-fertilizers	Egyptian cotton (*Gossyppium Barbadense*)	Sohair *et al.* [64]
	Nano micronutrient (Mn, Fe, and Zn)	Snap bean (*Phaseolus vulgaris*)	Marzouk *et al.* [65]
	Oxide nanoparticles of zinc, iron, and manganese	Squash cv. Eskandarani F1 (*Cucurbita* sp.)	Shebl *et al.* [66]
	Silica-NPs	Corn (*Zea mays*)	Suriyaprabha *et al.* [67]
	Zinc nano oxide	Rice (*Oryza sativa*)	Ghasemi *et al.* [68]
	Zinc oxide nanoparticles	Foxtail Millet (*Setaria italica*)	Kolencík *et al.* [69]
	ZnONPs	Tomato (*Solanum lycopersicum*)	Khanm *et al.* [70]
Direct soil mixing	Fe-NPs	Peace Lily (*Spathiphyllum illusion*)	Rasht [57]
	CeO2-NPs	Tomato (*Solanum lycopersicum*)	Adisa *et al.* [49]
	Ag-NPs	Soil, root-zone in soil	Colman *et al.* [71]
	Fe_3O_4, TiO_2, CuO, ZnO	Soil, root-zone in soil	Ben-Moshe *et al.* [72]
	ZnONP	Alfalfa (*Medicago sativa*), Tomato (*Solanum lycopersicum*), Cucumber (*Cucumis sativus*)	De la Rosa *et al.* [45]
	ZnONP	Maize (*Zea mays*)	Adhikari *et al.* [73]
	Ti-NPs	Soil, root-zone in soil	Fang *et al.* [74]
	ZnO, TiO_2 and Ni	Soil, root-zone in soil	Josko and Oleszczuk [33]
	Nanometrials	Soyabean (*Glycine max*)	Priester [75]
	FeO NPs	*Arabidopsis thaliana*; root-zone in soil	Kim *et al.* [76]
	CuNPs	Pigeon pea (*Cajanus cajan*)	Shende *et al.* [77]
	CuNPs	Kidney bean (*Phaseolus vulgaris*)	Apodaca *et al.* [78]
	TiO_2 and ZnONPs	Tomato (*Solanum lycopersicum*)	Raliya *et al.* [54]
	Hydroxyapatite nanoparticles as a phosphorus fertilizer	Soybean (*Glycine max*)	Liu and Lal [28]
	Layered double hydroxides interspersed with phosphate ions based on nanostructured materials.	Maize (*Zea mays*)	Benício *et al.* [79]
Hydroponic system mixing	CuO NPs	Rice (*Oryza sativa*)	Da Costa *et al.* [80]
	CuO and TiO2 NPs	Chinese mustard (*Brassica juncea*)	Rao and Shekhawat [81]

to synthesize NPs. Metal and metal oxide NPs can be synthesized biologically by using natural sources such as plant extracts, fungi, yeasts, bacteria, actinobacteria, and algae [41] (Figure 2).

The green synthesis methods are eco-friendly because they can be implemented at room temperature without the use of high temperature, pressure, and toxic chemicals. The size of nanoparticles can be controlled by altering the synthesis conditions [41,96]. Bio-based molecules such as proteins, enzymes, alkaloids, phenolic compounds, pigments and amines of plants and microorganisms by the reduction reaction can synthesize NPs [41]. These NPs have a higher specific surface area and higher catalytic reactivity [97].

In the case of microbial synthesis of nanoparticles, the desired microbes are cultivated in the growth medium and the microbial biomass is separated by filtration [98]. This cell-free filtrate is used for the synthesis of NPs. In the biosynthesis technique, the nanoparticles are usually capped and stabilized by enzymes and proteins. However, in the case of biosynthesis of nanoparticles by plants, the phytochemicals such as phenolics, cofactors, terpenoids, and flavonoids, among other are used for biosynthesis and capping of nanoparticles.

5 Classification of NFs

NFs are usually classified into three types, which mainly include nanoscale fertilizers, nanoscale additives, and nanoscale coatings [99]. Among these, nanoscale fertilizers are composed of nanoparticles that contain nutrients. However, nanoscale additive fertilizers are referred to as traditional fertilizers containing nanoscale additives and nanoscale coating fertilizers are traditional fertilizers coated or loaded with nanoparticles [31]. It is well known that the application of nano-scale fertilizers has attracted considerable attention and hence, several nano-based fertilizers have been developed and their industrial-scale production has also been started. However, still, this field is in the early stages of development, and hence, considerable time and effort will be required in order to commercialize newly developed NFs. Currently, developed large-scale production methods are only for few NMs. Therefore, successful large-scale production up of different nanomaterial-based fertilizers will require a great deal of technological and scientific investigation, followed by the set-up of pilot plants before any full-scale production. Moreover, quality control can be one of the most crucial issues that need to be considered. Similarly,

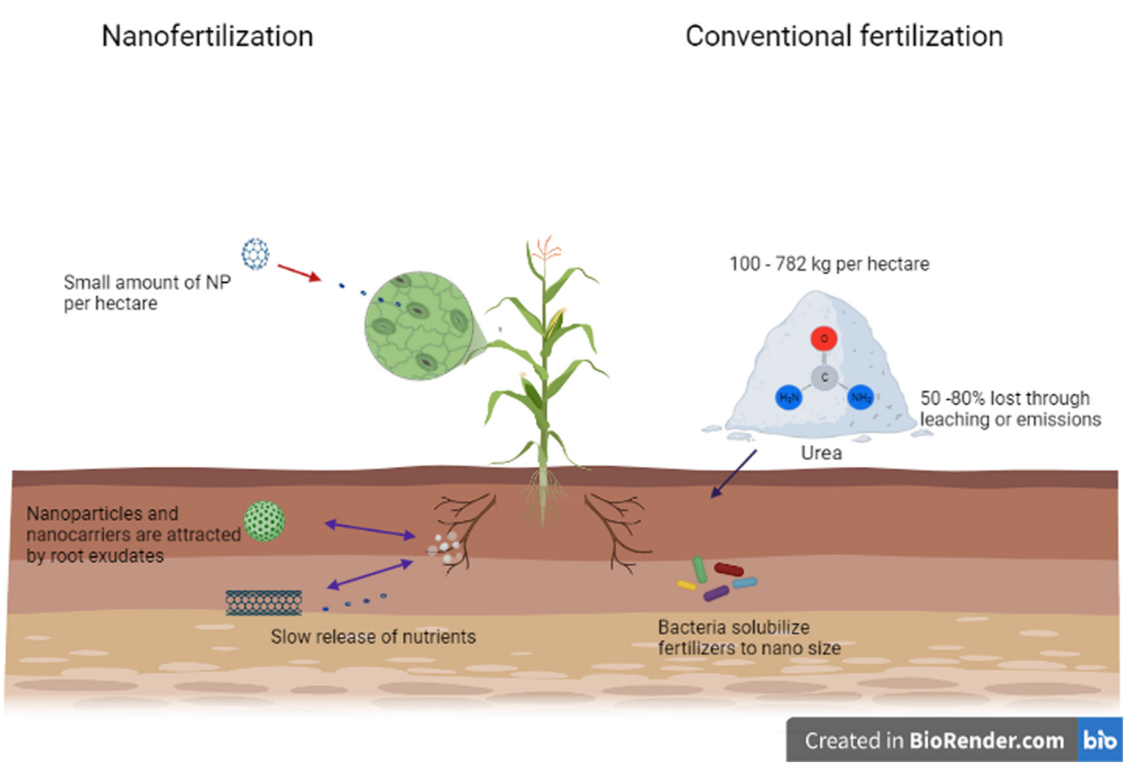

Figure 2: Nanofertilizers *versus* conventional fertilizers.

production cost would be another important factor because the application of NMs should not lead to a huge increase in the price of the final product. It is believed that, if all these problems are overcome, it will definitely help in accelerating the large-scale production of NFs. Moreover, to date several NFs have been approved and commercially available in the market. Some of the important NFs available in the market with their constituents and manufacturer are shown in Table 4 [100–106].

6 Mode of application of NFs

6.1 Foliar

The uptake of nanoparticles depends on the physiology of the plants [107]. Usually, NPs are absorbed by trichomes, stomata, stigma, and hydathodes and transported within the plant through the phloem and xylem [108]. The translocation of NPs takes place by two routes: apoplastic and symplastic pathways. In the apoplastic pathway, the movement of macromolecules (*e.g.*, NPs, water, *etc.*) occurs through the apoplast, *i.e.*, cell wall and other intercellular spaces. However, in this transport, the movement of such macromolecules is limited by the size exclusion limits (SELs) of cell walls (5–20 nm) [109]. However, in the case of the symplastic pathway, the movement of macromolecules (NPs) from one cell to another cell occurs by plasmodesmata which is an inner side of the plasma membrane.

The NPs can enter the cells from the cell wall by endocytosis [110,111]. The entry of the nanoparticles through the plant cell wall is determined by the diameter of the stomata, which varies from 5 to 20 nm [112], or by the base of the trichrome, and then they are transferred to the tissues.

Transport *via* the symplast route depends on the SELs of the plasmodesmata, which are 3–50 nm in diameter [113,114]. The Casparian strip is a barrier to transport into the vascular system [115]. In fact, NPs' entry and translocation depend on SEL; however, there are studies that 50 nm NPs larger than SELs of cell walls, plasmodesmata, and the Casparian strip have been internalized, perhaps influenced by enzymes.

Some studies reported that CeO_2 NPs were absorbed by cucumber leaves and distributed to plant tissues [116]. Similarly, Ag NPs sprayed on leaves can be absorbed and transported by all plant tissues of lettuce [53]. In another study, Abd El-Azeim *et al.* [117] recommended foliar application of NPK NFs to increase potato production when compared to edaphic applications of NPK conventional fertilizers. NPK NFs have been proved to be an environmental, economic, and ecological alternative.

NFs can also be combined with nanoparticles to control phytopathogens. Plant cell stress enzymes can break chemical bonds in the nanocapsule of the polymer wall. When the plant detects the attack of plant pathogens, it releases mucilage to prevent infection [118]. Moreover, the accumulation of nanoparticles on the surface of the leaflets may cause foliar heating that can generate alterations in gas exchange due to the obstruction of the stomata [119].

6.2 Roots

NPs penetrate through epidermis of the root crosses endodermis reaches the xylem, where they are transported to the aerial part of the plant. NPs enter the cell wall through pores, when they are between 3 and 8 nm [2,120,121].

NPs can also enter through the root tip meristem, or at the points of lateral root formation, since there are wounds in the Casparian strip. To enter the epidermal layers of the roots, NPs must penetrate cell walls and plasma membranes. From there they enter the vascular tissues (xylem). The sizes of the pores of the cell walls are 3 to 8 nm [122] which is a very small size for NPs to enter, however, it has been proved that NPs induce the formation of large pores in cell walls where they can be internalized [123].

For example, tomato roots can absorb AuNP of 3.5 nm, although they could not absorb these nanoparticles of size 18 nm [2]. Roots of *Arabidopsis thaliana* can uptake spherical silica NPs of 14–200 nm [124]. Besides, in *Solanum lycopersicum*, sphere AuNPs of 40 nm, were translocated from roots into shoots [125]. The microelements enter the plant through the hairs of the feeder roots. Thus, Ca, Mg, Fe, S or Zn encapsulated microspheres, are dissolved by the organic acids or phenols of the root exudates [126]. After the application of fertilizers in soil, much of the nutrients are lost due to leaching as a consequence of which soil and water are polluted. Not only this, certain agro chemicals are responsible for greenhouse gases and climate change [127,128]. As far as the controlled release of NPs is concerned, Torney *et al.* [129] reported the controlled intracellular release of desired chemicals in protoplasts using mesoporous silica nanoparticles. To overcome nitrogen leaching problems in the soil, treatments with

Table 4: Some important approved and commercially available nanofertilizers [100–106]

Nanofertilizers	Constituents	Name of manufacturer
Nano ultra-fertilizer (500) g	Organic matter, 5.5%; nitrogen, 10%; P_2O_5, 9%; K_2O, 14%; P_2O_5, 8%; K_2O, 14%; MgO, 3%	SMTET Eco-technologies Co., Ltd., Taiwan
Nano calcium (magic green) (1) kg	$CaCO_3$, 77.9%; $MgCO_3$, 7.4%; SiO_2, 7.47%; K, 0.2%; Na, 0.03%; P., 0.02%; Fe-7.4 ppm; Al_2O_3, 6.3 ppm; Sr, 804 ppm; sulfate, 278 ppm; Ba, 174 ppm; Mn, 172 ppm; Zn, 10 ppm	AC International Network Co., Ltd., Germany
Nano capsule	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.8%; Fe, 2.0%; Mn, 0.004%; Cu, 0.007%; Zn, 0.004%	The Best International Network Co., Ltd., Thailand
Nano micro nutrient (EcoStar) (500) g	Zn, 6%; B, 2%; Cu, 1%; Fe, 6%+; EDTA Mo, 0.05%; Mn, 5%+; AMINOS, 5%	Shan Maw Myae Trading Co., Ltd., India
PPC nano (120) mL	M protein, 19.6%; Na_2O, 0.3%; K2O, 2.1%; (NH4)2SO_4, 1.7%; diluent, 76%	WAI International Development Co., Ltd., Malaysia
Nano max NPK fertilizer	Multiple organic acids chelated with major nutrients, amino acids, organic carbon, organic micro nutrients/trace elements, vitamins, and probiotic	JU Agri Sciences Pvt. Ltd., Janakpuri, New Delhi, India
TAG nano (NPK, PhoS, Zinc, Cal, *etc.*) fertilizers	Proteino-lacto-gluconate chelated with micronutrients, vitamins, probiotics, seaweed extracts, and humic acid	Tropical Agrosystem India (P) Ltd., India
Nano green	Extracts of corn, grain, soybeans, potatoes, coconut, and palm	Nano Green Sciences, Inc., India
Biozar nano-fertilizer	Combination of organic materials, micronutrients, and macromolecules	Fanavar Nano-Pazhoohesh Markazi Company, Iran
Nano urea liquid	30 nm urea particles (4.0% total nitrogen (w/v))	Indian Farmers Fertiliser Cooperative Ltd, India
Plant nutrition powder (green nano)	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.8%; Fe, 1.0%; Mn, 49 ppm; Cu, 17 ppm; Zn, 12 ppm	Green Organic World Co., Ltd., Thailand
Hero super nano	N, 0.7%; P_2O5, 2.3%; K_2O, 8.9%; Ca, 0.5%; Mg, 0.2%; S, 0.4%;	World Connet Plus Myanmar Co., Ltd., Thailand
Supplementary powder (the best nano)	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.75%; Fe, 0.03%; Mn, 0.004%; Cu, 0.007%; Zn, 0.004%	The Best International Network Co., Ltd., Thailand
Zinc oxide [ZnO] – universal additive agent 1–50 nm	zinc oxide 99.9%	Land Green & Technology Co., Ltd., Taiwan
Titanium dioxide [TiO_2] – universal pigment [20 nm]	Titanium dioxide 99%	Land Green & Technology Co., Ltd., Taiwan
Silicon dioxide [SiO_2] – universal stabilizer agent [20–60 nm]	Silicon dioxide 99%	
Manganese dioxide [MnO_2] – universal purifier [1–50 nm]	Manganese dioxide 99.9%	
Selenium colloid [Se] – universal antioxidant [1–20 nm]	Selenium colloid 99.9%	
NanoCS™ of NanoShield® products 1–100 nm	NPK, zinc	Aqua-Yield®, USA
NanoGro® 1–100 nm	NPK	
NanoN+™	Nitrogen	
NanoK®	Potassium	
NanoPhos®	Phosphorus	
NanoZn®	Zinc	
NanoPack®	Sulphur, copper, iron, manganese, and zinc	
NanoCalSi®	Calcium and silicate molecules	
NanoFe™	Iron	
Nano-Ag Answer®	NPK = 1.0–0.1–5.5. Total nitrogen 1.0%. Available phosphate 0.1%. Soluble potash 5.5%. Other ingredients 93.4%	Urth Agriculture, USA
Hibong biological fulvic acid	Nano fertilizer, humic acid. Chitosan oligosacchairides ≥ 30 g/L, N ≥ 46 g/L, P_2O_5 ≥ 21 g/L, K_2O ≥ 62 g/L, organic matter: 130 g/L,	Qingdao Hibong Fertilizer Co., Ltd., China
Humic acid granular fertilizer	Humic acid: 55%, organic matter: 70%,	
Seaweed nano organic carbon fertilizer	NPK: 2–3–3, seaweed extract ≥5%, organic matter: 35%, humic acid ≥5%, amino acid ≥5%	

polyolefin-coated urea, neem-coated urea, and sulphur-coated urea was given to control the release of N [130].

In a study, double layered hydroxide nanocomposites were used for the controlled release of nutrients [79]. Wang *et al.* [131] studied the slow release of integrated superabsorbent fertilizer and the water retention capacity of soils with this fertilizer. They found that the surface cross-linked product had good slow release property and also very good soil moisture conservation. Interestingly plants can also react to NPs. The diameter of *Z. mays* seedlings root cell wall pores were reduced from 6.6 to 3.0 nm after bentonite and TiO_2 nanoparticles were applied [132].

7 Mechanism of action of NFs

The high reactivity of NMs ensures high and effective absorption of nutrients for plants [133] and greater utilization efficacy, thus having minimum losses compared to conventional fertilizers [4,134]. The efficiency in the absorption, distribution, and accumulation of NFs depends on the exposure to many factors such as the pH of the soil, organic matter content, and soil texture (Figure 3) in addition to factors inherent to the nanoparticle such as size and coating [135,136].

Indeed, as NFs can be absorbed through roots and leaves, this influences the behaviour, bioavailability, and absorption in the plant [135]. Several studies have shown that NFs are more effective than ordinary fertilizers. For instance, NFs of macronutrients increase plant development by 19% compared to conventional fertilizers. NFs of micronutrients are better by 18%, and NFs of carriers for macronutrients increase growth by 29% compared to ordinary fertilizers [14].

Similarly, NFs based on nanochitosan with nitrogen (N), phosphorus (P), and potassium (K) increased the sugar content and improved the properties of wheat [137]. In another study on wheat, Salama [138] reported that when silver nanoparticles were applied, the length of the shoots and roots, the leaf area, and the contents of chlorophyll, carbohydrates, and proteins increased. Besides, nutrients can be released over 40–50 days in a slow release rather than 4–10 days by the conventional fertilizers [139].

8 Fate of NFs in soil

The fate of NFs is the same as conventional fertilizers, albeit in a small amount. The fate of NFs in soil appears to be controlled by their mobility and stability. The NFs when entering the soil can be modified depending on their nature and interaction with the organic and inorganic soil components [140]. Aggregation is the first physical process that occurs when NFs are applied to the soil, reducing the area of action. Increasing the size of aggregates will decrease their mobility in porous media [141]. Movement of nanoparticles in the soil is guided by the Brownian motion towards the soil pores [142]. Hence, the fate of NFs in the soil is influenced by soil composition.

Soils are composed of micro-pores and macro-pores. During transport through these pores, single NPs are absorbed into mobile colloids, and their mobility through micropores is improved, maintaining mega complexes of NPs in the macropores. However, the mobility of single NPs is inhibited when absorbed on non-mobile particles. Humic acids or organic matter in the soil and the ionic strength of water influence NP mobility [143].

Once released into the environment, engineered NFs are aggregated to some extent [144]. This suggests an association of NFs with suspended solids and sediments accumulated by organisms. The interaction of NF and soil molecules can be favoured by the traits of the particles and the surrounding environment. Therefore, the organic content of the soil, the environmental conditions, and the chemical characteristics of NFs can improve or inhibit NP mobility [74,145].

On the contrary, there is always a huge debate on the toxicological effects of different NPs used in different formulations like NFs on the environment, soil microflora, aquatic organisms, and human beings. It is well known that, soil microbes play a key role in maintaining the balance in the biosphere because soil microorganisms are closely in contact with plants [146]. However, the diversity, abundance, and activity of such soil microbes may be affected by NMs applied in the form of NFs or released into the soil from other sources. NMs can influence the performances of soil microbes in various manners [147]. It was demonstrated that metallic NPs such as silver NPs affect the dehydrogenase activity of bacteria and suppress growth when present in the range of 0.1–0.5 mg kg^{-1} in soil [148]. Moreover, Throbäck *et al.* [149] reported that denitrifying bacteria present in the soil are more susceptible, which disturbs the nitrogen cycle through blocking the denitrification of nitrates to nitrogen. Similarly, other metallic NPs, like copper NPs, iron NPs, *etc.*, and CNTs are also reported to have some adverse effects on beneficial soil microflora.

In addition to soil microflora, NMs are also found to have toxic effects on aquatic life or the ecosystem, which mainly includes aquatic plants, aquatic microbes, and

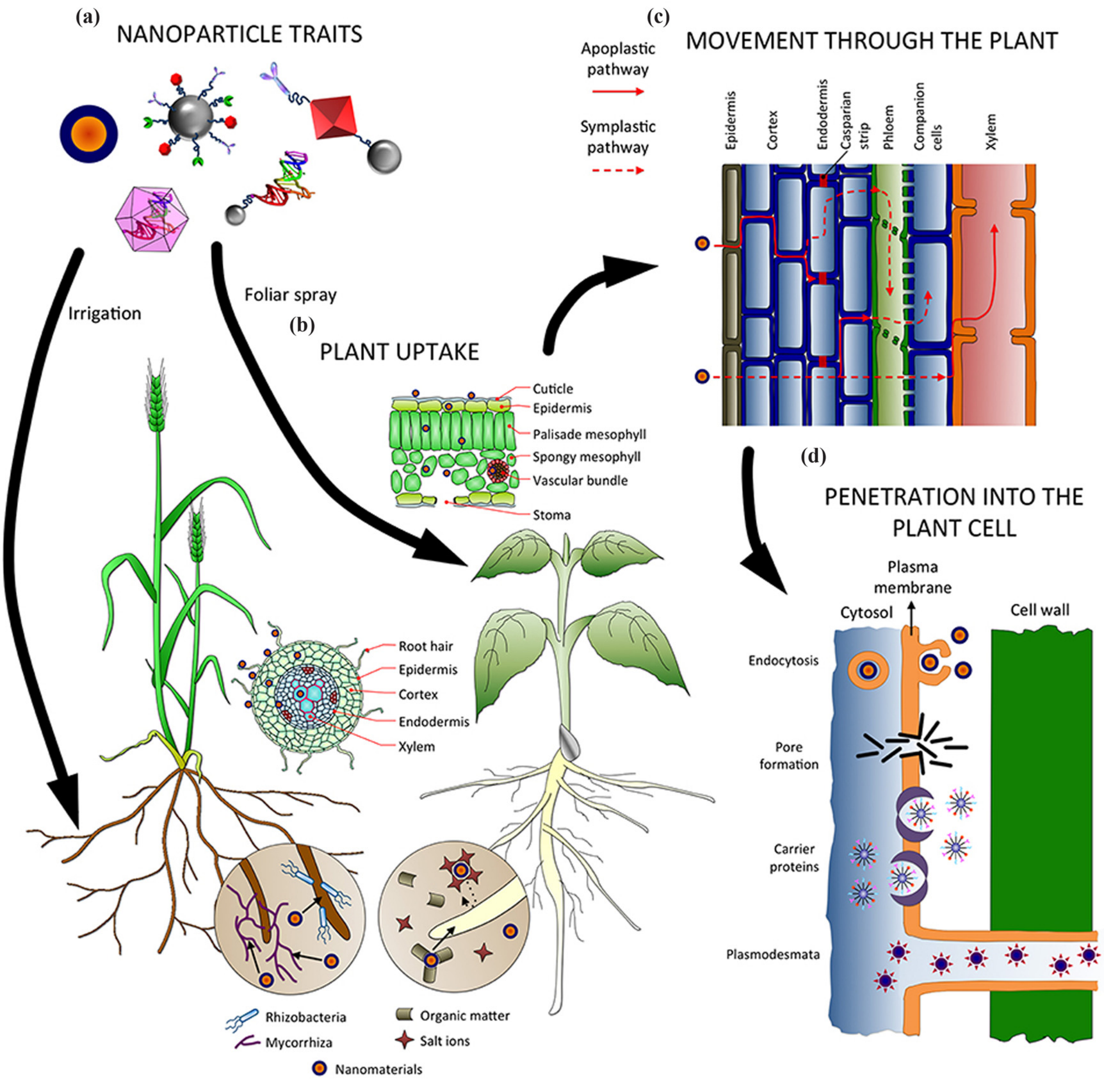

Figure 3: Effect of different factors on absorption, uptake, transport and penetration of nanoparticles in plants. (a) Nanoparticle traits affect how they are uptaken and translocated in the plant, as well as the application method. (b) In the soil, nanoparticles can interact with microorganisms and compounds, which might facilitate or hamper their absorption. Several tissues (epidermis, endodermis…) and barriers (Casparian strip, cuticle…) must be crossed before reaching the vascular tissues, depending on the entry point (roots or leaves). (c) Nanomaterials can follow the apoplastic and/or the symplastic pathways for moving up and down the plant, and radial movement for changing from one pathway to the other. (d) Several mechanisms have been proposed for the internalization of nanoparticles inside the cells, such as endocytosis, pore formation, mediated by carrier proteins, and through plasmodesmata. Reproduced from Pérez-de-Luque [126] under the Creative Commons Attribution 4 International Licence.

vertebrates [150]. Some of the studies on zinc NPs showed the accumulation of Zn^{2+} ions in aquatic vertebrates, microbes, and plants which is directly related to the toxicity of zinc NPs [151]. Moreover, from the study of Zhao *et al.* [152], it was revealed that graphene oxide NPs showed toxic effects on freshwater algae; they observed the penetration of these NPs inside the algal cell, which led to the generation of oxidative stress and ultimately caused membrane damage and nutrient depletion. Apart from all these, such NMs can directly or directly the human health because human beings are mostly dependent on agriculture and aquatic animals (fish) for their food. Consumption of food items contaminated with NMs can also have harmful effects on human health [153].

9 Legislation

Since it is important to validate extrinsic properties of NMs such as biological interactions, physiological effects, biokinetics, uptake and distribution, and biological effects in different scenarios of exposition, the European Chemicals Legislation revised the Annexes to Chemical Legislation (REACH) for NMs and specify the technical data requirements for these [154]. The new provisions, entered into force on January 1, 2020, list requirements for manufacturers, importers, and users for the registration and evaluation of the safety of NMs. It further recommends that protocols be developed to determine NMs' adsorption/desorption, degradation, exposure scenarios, and ability to cross biological membranes [155].

In addition, the OECD has organized expert meetings to define concepts for NMs' hazard assessment in different regulatory frameworks and to understand the application and extrapolate potential NM regulatory hazards [156,157]. Currently, the NPs' legislative frameworks of many countries do not cover agriculture. Therefore, regulatory frameworks on the application of NFs in agriculture are an issue that must be addressed. The evaluation of the possible risks and the advantages of NFs and conventional fertilizers in the ecology of the soil and the environment should be considered to achieve sustainable agriculture.

10 Future research perspectives for the application of nano-fertilizers

Research to measure concentrations of NFs and conventional fertilizers accumulated in soil and evaluation of efficacy warrants further investigations since these are not quantified in experiments. Information underlying would help elucidate environmental fate, behaviour, transport pathways, eco-toxicology and sustenance of NFs in soil.

With regard to soil applications of NF, through metagenomics, the possible effects that the use of NF implies on the soil microbiota can be explored. Another interesting topic to investigate is the evaluation of the microbial signalling mechanisms of plants when interacting with NFs. The modelling of the biological and biochemical interactions of the NF in the soil should also be explored, and the degradation of the NFs are areas of research for a sustainable agriculture.

11 Conclusion and opinion

The efficiency of conventional fertilizers is very low; nitrogenous ones range from 20 to 50%, phosphates range from 10 to 25% and potassium range from 35 to 40%, thus, NFs have a positive impact on the agricultural sector by reducing the volume of conventional fertilizers currently applied, in addition to achieving higher crop yields. Moreover, the economic benefit of reducing the leaching and volatilization of conventional fertilizers is very attractive for producers in addition to being clean technologies for the environment. There is uncertainty related to the fate of NMs with the environment; however, they have the same fate as the thousands of tons of conventional fertilizers that are used today. In fact, the policies related to major NFs are made in developed countries (*e.g.*, USA, Europe, *etc.*); whereas, developing countries (which are higher food supplier in the world) are far behind in forming the policies and implementations in this sector.

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