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Chemical and Biological Technologies in Agriculture

REVIEW

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Recent advances in nitrogen and nano-nitrogen fertilizers for sustainable crop production: a mini-review

Krishan K. Verma[1†], Xiu-Peng Song[1†], Hewan Demissie Degu[2], Dao-Jun Guo[3], Abhishek Joshi[4], Hai-Rong Huang[1], Lin Xu[1], Munna Singh[5], Dong-Liang Huang[1], Vishnu D. Rajput[6] and Yang-Rui Li[1*]

Abstract

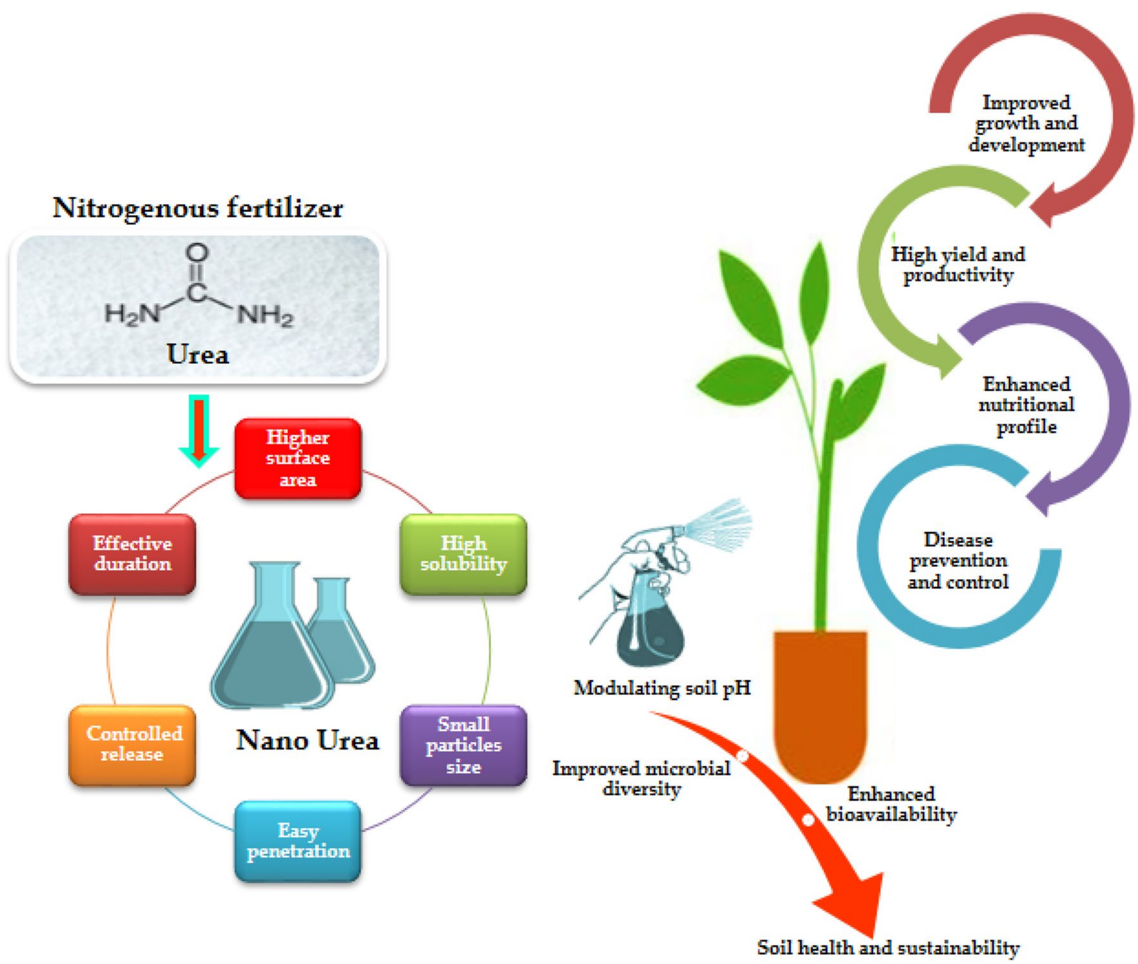
To meet the global food demand while maintaining the minimum possible negative impacts on the soil, air, and water, sustainable and precise agricultural practices are essential. The efficient use of engineered nanomaterials (ENMs) can replace conventional fertilizers and pesticides, subsequently minimizing the environmental impact of agricultural approaches. Slow-release or controlled-release nitrogenous fertilizers may enhance crop productivity while alleviating agro-environmental constraints. Nitrogen is the essential element which limits worldwide agricultural production. Despite numerous efforts, the N-use efficiency (NUE) in agriculture remains around 50%. The ongoing investigation of novel approaches has resulted in the synthesis of innovative nanomaterials (NMs), providing a potent mechanism for the development of unique element characteristics. The most promising engineered materials being explored, whether for soil or foliar applications, is nanofertilizers. Although not much is known about the usage of NFs, significant results have been observed in various plant species. Granular fertilizers are commonly applied to the soil for the nitrogen requirement of plants. These fertilizers may cause more losses due to the surface runoff or leaching with ammonia volatilization and N oxides (N_2O, NO, NOx) emissions. n-NFs are expected to improve NUE by increasing the efficiency of N delivery to plants and minimizing N losses to the environment. A chance to use n-NFs in plants may arise in unique conditions with increasing economic and environmental limitations. This article highlights the possible application of n-NFs as a novel strategy to ensure NUE with the reduction in N losses to the environment, including addressing its potential for sustainable agriculture.

Keywords Biochemical and physiological responses, N-fertilization, N-nanofertilizer, Growth, Productivity, Plant response

[†]Krishan K. Verma and Xiu-Peng Song have equally contributed.

*Correspondence:
Yang-Rui Li
liyr@gxaas.net
Full list of author information is available at the end of the article

Graphical Abstract



Introduction

A remarkable 10 billion people are expected to exist on the planet by 2050 [1]. Due to the rapid growth of the population by 2–3 billion people during the next 80 years, more crop production will be needed, which will also increase the need for fertilizers. To meet the worldwide food needs, crop yields must increase by 56% [2–5]. Agriculture is the main source of food and feed for humans and animals. However, agricultural crop pests and climate change events are significant hindrances to achieving worldwide food security. Achieving and sustaining worldwide food safety is a grand global challenge that will require agricultural approaches to be modified, and perhaps revolutionized, to effectively combat the detrimental stress from climate change, population growth, and reduction in agricultural land [3, 6]. The key challenge for sustainable crop production is the availability of sufficient nitrogen (N) for crops with nitrogen use efficiency (NUE) of about 25–30%. According to statistics, the domestic application of chemical fertilizers accounted for nearly 40% of the world's application in 2011, and has been increasing. From January to May 2022, the output of agricultural N, phosphorus (P), and potassium (K) fertilizers in China reached 23.2 Mt. If the application of chemical fertilizers ceased, the global crop production output would be reduced by about 50% [7–9].

However, since the 1990s, the impact of increasing the amount of fertilizers on improving crop yield has no longer been significant, and the fertilizer utilization efficiency has been relatively low. The problem of high amounts of fertilizer and low utilization efficiency in modern crop production is prominent [10]. Excessive use of chemical fertilizers is also associated with factors, such as declining economic returns and environmental pollution. Therefore, improving chemical fertilizer efficiency and sustaining high yield and quality of crops is one of the main challenges in agricultural development [9].

According to Meena et al. [11], the Haber–Bosch process only produces about 100 Mt of N globally. However, plants are estimated to need 150–200 Mt of mineral N [12], being the most significant macronutrient for plants. N is required in the highest concentration for crop production, because it is the main component of nucleic acids, chlorophyll, adenosine triphosphate (ATP), and amino acids [13]. About 1 tonne of crop biomass production requires 9–11 kg of N [14]. The crop biomass, grain yield, leaf area, and shelling percentage increase with increasing concentration of N [15, 16]. The global N cycle is significant due to its crucial role in addressing environmental challenges. Agricultural activities account for approximately 60% and 10% of the world's anthropogenic N_2O and NO sources, respectively, due to the increased utilization of N fertilizer on crop lands [17].

In Green Revolution, high yielding cultivars were introduced which lead to the excess use of chemical fertilizer. Even if increased chemical fertilizer use benefits society, it has incurred more costs and increased the level of environmental contaminants [18]. Food and agricultural statistics show global annual increase of chemical fertilizer worldwide [19]. A large amount of environmental degradation is majorly caused by intensive fertilizer use [20]. Therefore, there is an urgent need to change the chemical fertilizer pattern and replace it with a more sustainable and less environmentally hazardous nitrogen source. This also contributes to alleviating the dependency of millions of smallholder farmers in developing countries, especially in Africa, on the use of nitrogen fertilizer.

Nitrogen losses from flooded agricultural areas through surface runoff and leaching are significant [21], accounting for about 60% of N lost into the environment during growing seasons in the forms of ammonia, nitrate, and nitrous oxide, which has a significant negative impact on human health [22]. Hence, it is essential to increase NUE to deal with such problems [23]. Numerous N-saving techniques, such as balanced N fertilization, site-specific N management, and controlled-/slow-release fertilizers, have been utilized to increase NUE, but it is unknown how these techniques interact with each other to affect crop productivity and the synthesis of nitrifiers and denitrifiers [24, 25] (Fig. 1).

The nanocomposite releases nearly 78% more N than synthetic fertilizers in sandy soil (pH 7). Compared to traditional fertilizer, this dynamic release pattern could dramatically improve plant production by enhancing N uptake efficiency in supplemented plants [26]. Studies have discussed promising micronutrient formulation

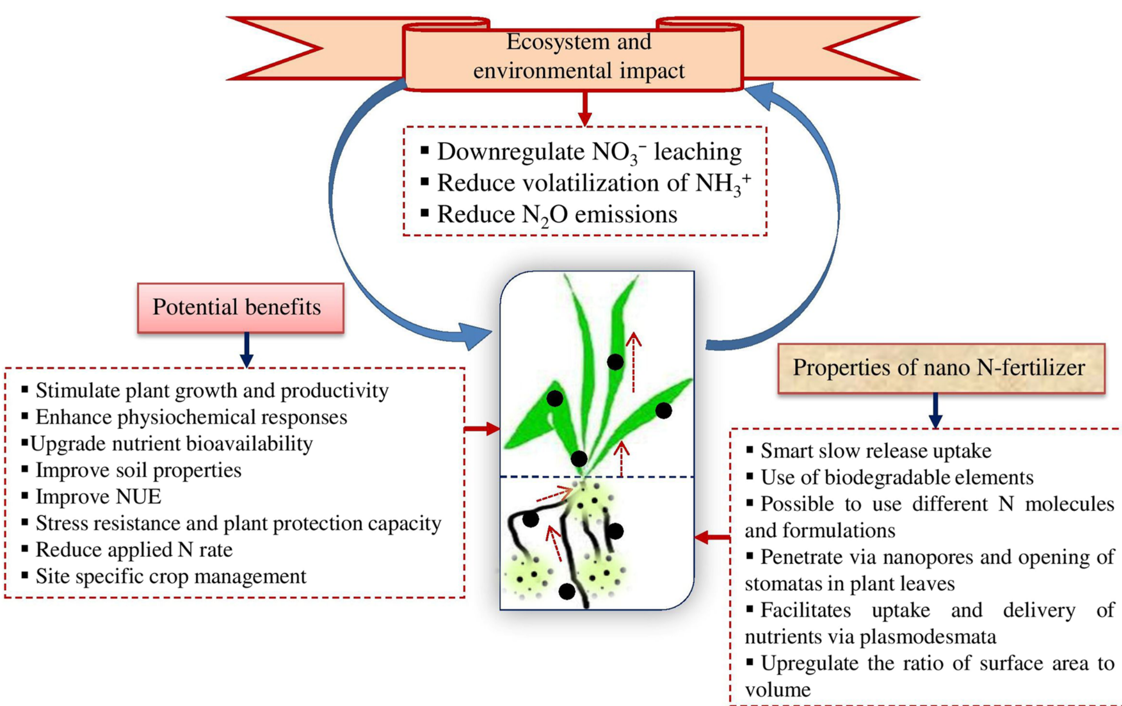


Fig. 1 Potential action mechanism of nano-nitrogen fertilizer-based controlled release fertilizer

based on nanotechnology that improves nutritional dose by releasing N slowly and consistently over time. Notably, in vivo and in vitro conditions [27] indicated the effective progressive release of N, which may be linked to a significant improvement on crop yields, even at 50% lower rate than the traditional use of urea [24]. Urea–hydroxyapatite nanohybrid (6:1) substances, responsible for the efficient slow release of nitrogen are used to produce the nanocomposites. This review discusses the current opportunities for the application of nitrogen and nano-nitrogen fertilizers in sustainable agriculture. A variety of published articles were critically evaluated based on the efficiency of nano-nitrogen fertilizer in their research, the experimental layout, potential environmental impacts, and relative comparison with conventional commercial products.

Influence of nitrogen (N) and nano-nitrogen (nN) on plants

Nitrogen is necessary for plant growth and development, a vital component of the photosynthetic processes. In addition, it is a crucial component of amino acids, which act as building blocks for enzymes and proteins in plants. All living organisms are composed of proteins and enzymes that regulate plants' biochemical processes to attain the optimum crop yield. Furthermore, N found in the roots as proteins and enzymes also assists in water and nutrient intake. In plant cells, some proteins serve as structural components, while other functions as enzymes, enabling various biochemical processes that are the basis of life. Energy substances such as ATP (adenosine triphosphate) allow cells to retain and use the energy released during metabolism. Nitrogen also plays an important role in synthesizing genetic components, such as DNA [28]. Nitrogen nano-fertilizers are the source of rapid plant growth (shoot and root systems) due to increased chlorophyll content in the plant leaves. Nano-fertilizers reduce the length of the agricultural cycle and boost crop productivity by applying NPK (nitrogen, phosphorus, and potassium) [29–31].

Nanoscale nitrogen particles may make up 4% of the liquid form of nano-urea compared to normal urea, due to being smaller in size (20–50 nm), with higher surface area and the higher number of particles per unit area. Consequently, they can easily penetrate through the cell wall or the stomatal pores of leaves and be transferred to other plant organs throughout the plant by plasmodesmata (40 nm in diameter), aquaporin, binding to carrier proteins through ion channels, and endocytosis. The active chemicals in nano-fertilizers are also released in response to biological needs during environmental stresses [32].

Plants uptake N in the form of NO_3^- and NH_4^+ [33, 34]. N-based NFs could be utilized for the continuous uptake of N at slow or controlled release rates to reduce the losses. Manikandan and Subramanian [35] used zero-urea nanofertilizer (n-NF) on *Zea mays* L., and observed higher uptake of nutrients, vigorous plant development and productivity, and observed better food grain quality compared to chemical fertilizers. Mahmoodi et al. [29] applied n-NF to *Borago officinalis* L., and observed significant improvement in plant development, resulting in maximum essential oil production. Similarly, urea-modified zeolites enhanced *Glycine max* L. seed productivity as compared to chemical fertilizers [36]. An n-NF developed by coating urea onto nanofilm was successfully applied in *Brassica napus* L. plants [37]. Nano-N and chelated nano-N were significant in terms of enhancing plant productivity of *Solanum tuberosum* L. and reducing the leaching of nitrate [38]. Ha et al. [39] applied NPK-coated NFs on *Coffea arabica* plants during greenhouse conditions. The authors documented that NPK nanofertilizer enhanced the uptake of nutrients and plant growth by improving the number of leaves, area expansion, and photosynthetic leaf gas exchange. Moreover, the authors observed that NPK was enhanced up to 17%, 16%, and 68%, while the chlorophyll (a + b) content and photosynthetic efficiency were upregulated up to 31% and 72%, respectively, compared to control plants [28].

In contrast to the rapid and spontaneous release of nutrients from conventional fertilizers, nano-fertilizers supplied nutrients progressively. Conventional fertilizers may lose much of their availability and efficiency due to their fast leaching and emission, significantly impairing nutrient absorption and utilization. Contrary to this, n-NF observed to be substantially greater in its uptake due to root exudates and free movement from nanoscale pores via molecular transporters. The crop plants may absorb more nutrients in the form of NPs via different ion channels, as NPs may traverse plasmodesmata effectively to reach the sink sites. Thus, using NFs diminishes environmental contamination, eutrophication, polluted groundwater, and diseases caused by the overuse of conventional fertilizers [40, 41].

The n-NF found as IFFCO nano-urea (India) is available to crops more conveniently due to its small size and higher surface area-to-volume ratio, which ensures higher root biomass and more productive tillers, branches, chlorophyll, and leaf photosynthesis to induce higher agricultural crop production. According to 11,000 field trials conducted throughout India in 2019–2020, production increased by about 8% using nano-urea, lowering agri-input costs. The crops harvested grown with the application of nano-urea were safe for consumption, with better nutritional quality in terms of proteins and nutrient content, and with the benefits of avoiding the harmful usage of chemical fertilizers [42, 43]. The use of nano-urea may promote agricultural sustainability and environmental safety, as it is synthesized in a resource- and energy-efficient manner. It also minimizes runoff, leaching, and volatilization losses. IFFCO nano-urea, used in far smaller amounts than traditional urea, may also significantly reduce transport and storage costs. Practically, farmers prefer nanoscale urea bottles to carrying heavy urea bags.

Why nano-fertilizers is better than conventional fertilizers?

Fertilizer companies face many challenges to increase the efficacy of their products, because properly using these resources is important, to use them strategically to attain higher economic production of crops and reduce nutrient losses to the environment. This can be achieved by boosting elements currently in use or manufacturing novel fertilizers. Among the numerous types of fertilizers, nitrogenous fertilizers are the most sensitive to losses by leaching of nitrate, runoff of different forms of nitrogen, or through gaseous emissions of ammonia, nitric oxide (NO), nitrous oxide (N_2O), or nitrogen (N_2) [44–46]. NO and N_2O gases are produced as reaction intermediates in soil, mainly through nitrification and denitrification. The development of these gases, which is primarily caused by N inputs in agriculture [47, 48], is particularly significant in the detrimental impact on atmospheric chemistry, which directly contributes to the greenhouse effect and stratospheric ozone depletion [45, 46].

As potential plant growth stimulators, nanoparticles (NPs) have unique features, such as high sorption capacity, enhanced surface-to-volume ratio, and controlled-release dynamics at specified locations. These unique factors allowed nano-structured fertilizers (NSFs) to be used as an efficient plant nutrition delivery system. However, because of their poor use efficiency and low availability in the appropriate chemical form, fertilizers—particularly nitrogen (N)—are used excessively [49, 50]. In most agricultural conditions, nitrogen fertilizer (urea) use efficiency is around 30–40% [51]. The major form of nitrogen in aerobic soils is nitrate, but nitrate availability can differ over time and duration depending on microbial activity and leaching. To respond to the fluctuating NO_3^- and NH_4^+ levels in the atmosphere, plants have evolved various acquisition strategies for NO_3^- and NH_4^+, with different affinities [52–54].

Unused fertilizer input is released into the environment, contaminating the soil, air, and water. For instance, urea can volatilize into greenhouse gases, such as nitrous oxide, and release ammonia, contributing to global warming and air pollution [55]. The quality of drinking water influenced by urea leaching into the soil in the form of nitrate. Furthermore, using urea changes the pH of the soil, which impacts how effectively plants absorb essential macro- and micronutrients [56]. For example, unutilized phosphate becomes runoff that leaches into water bodies and causes eutrophication and dead zones [57, 58].

Alternative smart agri-inputs based on principles from advanced chemical engineering, biotechnology, microbiology, and polymer science are being developed for the controlled and slow release of nutrients into the soil to increase the efficiency of nutrient usage [30, 55, 59]. However, due to variable agro-climatic conditions, the diversity of plants, food demands, and soil nutrient profile efficiency are limited. Different advanced approaches are currently being tested, including coated fertilizers for slow release [4, 60], mixtures of macro- and micronutrients [61], crop diversification [62], green manure [63], gradual fertilizer reduction [64], and organic farming practices that use organism-based fertilizer and decomposers.

Synthetic fertilizers boost crop performance while reducing soil fertility and causing an imbalance in the mineral properties of soil. The extensive use of synthetic fertilizers severely damages the soil structure and microbial flora. Researchers are concerned about farmers utilizing a large amount of synthetic fertilizers to meet the rapidly growing agricultural industry demand due to the earth's population's rapid increase [5]. Nanofertilizers are possible alternatives that assure better crop productivity and soil restoration [41]. Macronutrient NFs provide nutrients required by plants in relatively large amounts and include N, P, K, Ca, Mg, and S. According to expectations, the requirement for macronutrient fertilizers will exceed 263 Mt by 2050 [4, 5, 65, 66]. Compared to conventional fertilizers, ENMs can be more effective in terms of nutrient use, due to their high surface area and penetrability [31]. In this context, materials such as nano-enabled urea-coated zeolite chips and urea-modified hydroxyapatite (HA) have been used to achieve controlled or slow release of macronutrients [26, 66]. The efficacy of nanocomposites of urea-modified hydroxyapatite has been observed in response to stress in *Gliricidia sepium* plants [26].

Compared to conventional fertilizers, nano-fertilizers (NFs) release their nutrients gradually. This strategy enhances nutritional management by boosting nutrient-use efficiency (NUE) and reducing nutrient leaching into groundwater. The active chemicals in NFs are supposed to be released in response to physiological and environmental challenges with the boost in photosynthetic activities, seedling growth, germination rate, nitrogen metabolism, and carbohydrate and protein synthesis to increase agricultural productivity.

Fate of nanomaterials in the soil

Natural nano-sized materials found in the rhizosphere soil. The properties of soil control the fate and behavior of any element in the soil. Moreover, the rhizosphere itself can also regulate the movement of the elements. Thus, cultivated plants also might impact the uptake and accumulation of the element in the soil, even when the elements are in nano-form [67, 68], Table 1. The pathways of NPs entry into soil characterize their entry, accumulation and uptake. NPs can enter soil with atmospheric precipitation, sedimentation in the form of dust and aerosols, direct soil absorption of gaseous compounds, and abscission of leaves or as a result of anthropogenic activity [69, 70]. Free NPs possibly could disperse into an environment either through the direct outlet to the environment or during the degradation of NPs. Nanobiotechnology remediation can also be expected to be responsible for discharging a significant portion of NPs into the environment [71, 72]. Specifically, concerning soil and agro-environment, wide applications, i.e., NFs and nanopesticides, seed treatment, and soilless culture are expected to open up advance ways for releasing NPs into the fertile soil [70]. The bioavailability of NPs depends on their transformation in soil. The ionic/dissolved form of NPs indicated higher bioavailability and risk of environmental. In fact, the environmental risk of NPs mostly depends on the bioavailability and chemical composition of NPs in the rhizospheric soil [70, 73]. However, rapid and accurate evaluation of NPs bioavailability in soil is a critical issue that needs to be explored.

Development of effective nano-formulations

In advanced agriculture, NFs are important due to their special formulation properties and delivery function with optimum phytoavailability [3]. Ammonium humate, ammonia, urea, peat, plant wastes, and other synthetic fertilizers are used to produce nano-formulations or nano-sized fertilizers/nano-sized nitrogen fertilizers, which are produced when urea is coated over calcium cyanamide and are considered as an example of a nano-formulation. The nanoscale fertilizers reduce nutritional loss due to leaching, avoid chemical changes, and enhance NUE and environmental variables [74–76]. These are a better substitute for synthetic fertilizers as they promote growth and development while mitigating environmental pollution, because applied excess conventional fertilizers contaminate the agro-ecosystem by leaching synthetic fertilizers. Hence, effective NFs and urea production can be granulated and supplemented with various biofertilizers. The production of NFs comprises mechanical and biochemical techniques. Specifically, materials are mechanically ground to produce nanoscale particles (NSPs), and biochemical approaches may be used to produce efficient nanoscale formulations. NPs frequently contain encapsulated fertilizers, extending improved NUE and absorption efficiency. Possibilities may be explored to encapsulate nutrients with nanomaterials with thin layers of NMs (polymer film) and also nutrients as a nano-emulsion.

Nano-nitrogen fertilizer has been proven to positively impact plant development, especially in terms of plant productivity and quality [3, 5, 6]. The nano-fertilizer led to increased nutrient uptake by plants, better aboveground and belowground biomass, and higher performance in the nutrient-deprived environment. Furthermore, it increased the activity of macro- and microorganisms in the surrounding ecosystem compared to conventional fertilizers, which have helped in upscaling the agricultural output. Hence, in different ways, NFs can benefit modern agriculture (Table 1).

Limitations of nano-fertilizers

In general, smart fertilizers are fertilizers applied in soil that allow for managing the rate, timing, nutrient release duration, and active absorption by the plant roots [101]. Smart fertilizer as "any single or composed nanomaterial, multicomponent, and/or bioformulation containing one or more nutrients that can adapt the timing of nutrient release to the plant nutrient demand via physical, chemical, and/or biological processes, thereby improving crop growth and development and reducing environmental impact when compared to conventional fertilizers." Smart fertilizers are classified as (i) nano-fertilizers, (ii) composite fertilizers, and (iii) bioformulations [102, 103]. Nano-fertilizers, which are based on nanoparticles, as their name suggests, are available as powder or liquid formulations, including manufacturing, design, and application. These fertilizers can help improve nutrient release kinetics and plant uptake efficiency, resulting in benefits, including increased crop productivity, decreased nutrient loss to the environment and enhanced nutritional quality and shelf life [103–106].

Composite fertilizers are composed of various materials containing one or more nutrients that have been developed to take advantage of material synergy and improve essential plant nutrition [103]. Based on material properties, organic and inorganic coating materials (including granules and hydrophobic or hydrophilic materials [matrix or gel]) and inorganic compounds with low solubility are commonly used for coating or mixing fertilizers [102, 107–109]. The precision of fertilizer usage has become a vital point in the agricultural sector worldwide because of the need for increased productivity and reduced over-fertilization with negative impacts on the agricultural ecosystem [103, 110].

Table 1 Impact of nitrogen and nano-nitrogen on crop plants

Crop	Concentration Range	Impact	Source
Oryza sativa L.	25–100% n-NF	Improved plant length, biomass, and number of tillers. The highest crop yield (2.8 t ha^{-1}) was found at 100% n-NF application. Based on the present findings, nano-N fertilizer can reduce negative effects of nitrogen to the environment by minimizing harmful nitrogen inputs	[77]
Zea mays L.	0.32% and 0.76% n-NF	Higher nutrient uptake, improved N-use efficiency, enhanced plant performance, and better fruit/grain quality for nanozeourea application than conventional urea	[35]
Borago officinalis L.	0.002% and 5% n-NF	Nano-urea (n-NF) improved essential oil production and growth responses in terms of plant biomass, both dry and fresh, and also plant length	[29]
Glycine max L. and *Zea mays* L.	25–75% n-NF	Significantly impacted agronomic characteristics, yield and quality. Increases in these traits due to partial replacement of conventional urea with nano-urea might be attributable to nano-fertilization enhancing availability of nutrients to the developing plant and reducing traditional N losses. The application of 25% nN recorded the highest values in both crops as compared to 50% and 75% of nN	[78]
Pennisetum glaucum L.	0.3–0.5% n-NF	The number of productive tillers $plant^{-1}$ was significantly influenced by the application of nano-N fertilizer. When nano-urea was applied twice to the leaves (foliar spray), it increased the nutrient uptake via the stomatal openings and nutrient translocation within the plant. It enhanced the nutrient uptake/accumulation, resulting in increased cell division, meristematic activity, and cell elongation stimulation, producing more productive tillers $plant^{-1}$. The crop productivity was influenced by the use of nano-urea	[79]
Glycine max L.	90 kg N/ha	Shoot, root, nodulation traits, seed yield, and protein were significantly affected. Specifically, seed yield and seed protein were maximum when treated with nN, and number of nodules, biomass of root, and nodule dry weight were enhanced. In addition, the NFs (nano-N) could be a better alternative to the standard N fertilizer (urea)	[80]
Saccharum officinarum L.	80–161 kg N/ha	Increased cane stem length and fresh weight with increasing concentration of fertilizer. The order of NUE for stems and sugar yield changed from high to low. Nano-nitrogen fertilizer had significant effects in reducing nitrate leaching and increasing sugar production. However, when nitrate leaching and its effects on human health and the environment were viewed, nano-fertilizers (nN) awee valuable to urea	[81]
Solanum tuberosum L.	25% n-NF and 46% N	Agronomic traits were significantly enhanced, such as photosynthetic pigments, biomass, soft tubers yield, and the biological yield—proteins and ascorbic acid. NFs had positive impacts on upgrading the quality of potato yield compared to conventional N-fertilizer (urea). Potato plants treated with nN resulted in more soft and dry vegetative yield, potato fresh tuber yield, higher nutrient content. Results were better than the comparison treatment in the presence of better water management and when using drip irrigation technique	[82]

Table 1 (continued)

Crop	Concentration Range	Impact	Source
Triticum aestivum L.	14–41 kg/ha (17% n-NF) and 37–110 kg/ha (46% N)	Improved agronomic and biochemical activities, i.e., biomass, spike weight and length, plant length, number of tillers, stem diameter, seed weight, biological yield, seed yield, harvest index, anthocyanin, flavonoid, proline, soluble carbohydrates, photosynthetic pigments, and carotenoid contents. According to analyzed activities, replacing urea by nano-chelated nitrogen can improve crop production in response to adverse environmental conditions and reduce the amount of required fertilizer	[83]
Zea mays L.	69–161 kg N/ha	Increased growing-season N_2O emissions and enhanced growth and yield traits. The biomass showed an incremental trend with increasing concentration of N application	[84]
Triticum aestivum L.	94–130 kg N/ha	Enhanced plant length, water use efficiency (WUE), dry matter accumulation, crop index, and grain yield. Slow-release N fertilizers had positive and increased effects on crop development and productivity subjected to arid environmental conditions. Various N concentrations showed significant effects on plant development, especially in terms of crop productivity	[61]
Triticum aestivum L., *Pennisetum glaucum* L., *Brassica nigra* L., *Sesamum indicum* L.	2.5 mL/L n-NF	Increased crop yield in wheat (5.35%), sesame (24.24%), pearl millet (4.2%), and mustard (8.4%) by applying n-NFs. The increased yield was observed in agronomic traits, such as wheat tillers, ear head length of pearl millet, capsule number per plant in sesame, and siliquae number per plant in mustard. The results suggested that the field demonstrations with applied organic manure, bio-fertilizer, and NFs in combination resulted in optimum yield and better plant performances when compared to synthetic fertilizer practice	[85]
Brassica napus L.	30–90 kg N/ha	Effectively improved the growth, and physiological and biochemical activities, such as photosynthetic pigments, SOD, CAT, and POD. Reduced MDA content during in vivo and in vitro conditions. The amendment of N-fertilizer could effectively minimize the loss of soil flooding. The application of 60 kg ha^{-1} N after 6 days of stress or 90 kg ha^{-1} N after 9 days of stress had significantly improved the photosynthetic and metabolic responses of rapeseed and contributed to the better recovery of rapeseed. The N-induced increase in soil flooding of rapeseed might be attributed to the strong antioxidant defense system, as well as maintenance of photosynthetic apparatus and nutrient balance	[86]
Punica granatum cv. ardestani	0.25 and 0.50 g nN/L 4.6 and 9.2 g N/L	Increased fruit yield (~ 17–44%) and number of fruits per plant (15–38%). The highest fruit yields and number of fruits per plant were obtained in nN treatment as compared to control plants. On the other hand, fruit diameter, fruit cracking, peel thickness, aril content, weight of 100 arils, juice pH, maturity index, antioxidant responses, and total phenolic compounds were unaffected by N application. Results indicated that the pomegranate fruit yield was improved by the use of nN and application of N (urea). However, quality of fruit was upgraded with the nN as compared to urea. In fact, the application of urea was less efficient than nN	[87]

Table 1 (continued)

Crop	Concentration Range	Impact	Source
Triticum aestivum L.	120–240 kg N/ha	Exhibited higher levels of total chlorophyll content, spike length, 100-grain weight, grain yield in kg/ha, and nitrogen and potassium. Foliar application of nN fertilizer (14 L/ha) combined with mineral fertilizer (240 kg/ha) significantly enhanced the photosynthetic pigments as compared to normal plants. Upregulating the availability of N is an important strategy for enhancing nutrient efficiency, boosting plant nutrition, improving yield traits, and reducing soil contamination	[88]
Lactuca sativa L.	75% nN (drip irrigation) and 25% nN (foliar spray)	Application of nN as a soil and foliar treatment was more efficient. Application of 75% nN via drip irrigation system and 25% of nN in foliar spray significantly affected the agronomic and biochemical activities, i.e., plant biomass, leaf area expansion, relative growth rate, photosynthetic leaf gas exchange, β-carotene, crude protein, and productivity. Similarly, N uptake, N use efficiency, and apparent N recovery were increased as compared to lower N rates. It could minimize the recommended N rate to reduce environmental contamination without any yield loss	[89]
Solanum tuberosum L.	¼, ½, ¾ and 100% of recommended fertilizer	Spraying with NFs showed superiority in plant development in the field, and increased yield and quality	[90]
Triticum aestivum L.	37–110 kg N/ha 14–41 kg nN/ha	Nitrogen (urea) and nano-chelated nitrogen (nN) had significant effects on RWC; ion leakage; protein, phosphorus and potassium content; remobilization; and photosynthetic responses. Application of nN (41 kg/ha), in comparison with urea, led to increased RWC (4%), ion leakage (3%), protein (52%), phosphorus (26%), potassium (6%), remobilization (6%), and photosynthetic rate (21%), as compared to control. Therefore, it was recommended to replace NFs with synthetic fertilizers, especially in sandy soils due to the possibility of more leaching of synthetic urea and groundwater contamination	[91]
Olea europaea L.	2.21 and 2.95 g N 6–8 g nN	Nano-N enhanced the fruit sets. Mineral elements, chlorophyll,and carbohydrate content of plant leaves were affected during summer season and fall by N-treatments. The maximum oil (%) was achieved by nN application. Normally, fertilizing the trees with urea was better than nN	[92]
Zea mays L.	300 kg N/ha 1 and 2 mL/L nN	The interaction between the nN fertilizer and synthetic fertilizer had significant effect on most of the agronomic traits for both seasons	[93]
Triticum aestivum L.	100–200 ppm	Optimum values of macro- and micro-nutrients concentrations in grains except N, Zn, and Mn	[94]
Solanum tuberosum L.	40 L/ha (25% N)	Enhanced the WUE, NUE, PUE, and KUE. It can be concluded that better crop yield can be achieved through the adoption of fertigation and good irrigation strategies, high WUE, AE, and EUE, as well as a consistent distribution of nutrients in the soil	[95]

Table 1 (continued)

Crop	Concentration Range	Impact	Source
Pennisetum americanum L.	80 ppm	The application of 80 ppm of nN on pearl millet plants (15 days) indicated an appreciable improvement in root morphology (539%), root length (159%), root perimeter (46%), number of tips (14%), average root diameter (76%), and total biomass (157%). The result clearly demonstrated the possibility of biosynthesized nN for efficient use as NF	[96]
Pleurotus ostreatus (Jacq. Ex Fr.) P. Kumm	3–5 g kg^{-1} n-NF	Protein (0.64%), total carbohydrates (0.48–3.76%) and fiber contents (0.2%) enhanced as compared to control plants. Essential amino acids improved. Potassium, sodium, calcium, iron, and copper contents reduced with minor changes	[43]
Salvia officinalis L.	40–80 kg N/ fed and 250–500 ppm n-NF	Agronomic traits enhanced with increasing level of nano-N and N application. The highest nitrogen use efficiency (NUE) and nitrogen uptake efficiency (UPE) were achieved by the application of nN	[97]
Camellia sinensis L.	100 kg N $acre^{-1}$	The application of N increased the length of plant height, plant canopy, fresh tea leaves and productivity as compare to control plants	[98]
Camellia sinensis L.	^{15}N-Urea	Foliar application of N significantly increased the N content of the mature leaves and improved the tea quality. The application of N increases the N content of the mature leaves, improved the quality and productivity of spring tea	[99]
Asparagus racemosus L.	100–300 kg N ha^{-1}	The number, length, diameter and biomass of tuberous roots were found higher with application of N and nN. The different concentrations of N noted significant effect on plant length, number of leaves, length, diameter and biomass of tuberous roots as compared to control. Root protein content was found higher at different levels of N, respectively	[100]

n-NF Nano-nitrogen fertilizer, *N* Nitrogen

The nano-size scale, large surface area, and other special properties of ENMs result in significantly increased activity and functionality in biological systems. Various ENMs can be absorbed and biotransformed differently in plant systems relative to their bulk or ionic counterparts [111, 112]. However, the responses of ENMs on plants are also influenced by various stresses [3]. Applying NFs benefits the conventional agriculture system, but some scientific groups are more concerned about their harmful impacts. The excess use of NFs in agriculture systems may result in irreversible and unwanted environmental issues [76, 113]. However, the significant effects of ENMs as stress reliever agents depend on various factors, such as the property of the material (size of particles, morphology/structure, charge, coating), concentration level, variety of plants, and duration/time of application. Careful consideration of dose application and the establishment of an effective and targeted delivery approach are required before utilization [3, 114, 115].

Despite the significant contribution of NFs to sustainable crop production, their availability must also be ensured for marketing as one of the sources of plant nutrients. Some of the approved NFs being used all over the world, and their makers, are as follows: nano-calcium (AC International Network Co., Ltd., Reutlingen, Germany), nano-micronutrients (Shan Maw Myae Trading Co., Ltd., India), nano-green (Nano-Green Sciences, Inc., India), and biozar NFs (Fanavar Nano-Pazhoohesh Markazi Company, Iran). Notably, Prof. Nilwala Kottegoda and her team at the Institute of Nanotechnology (SLINTEC), Sri Lanka, developed NFs, and were also awarded four US patents, even though Sri Lanka imports nano-nitrogen liquid fertilizer from India. Eventually, SLINTEC transferred its technology to an Indian fertilizer firm for large-scale production of NFs, and to generate revenue overseas. Moreover, we need to ensure the application of NFs at no more than an optimum concentration to avoid their excess release into the environment.

Globally, the green revolution enhanced the production of food grains, but at the cost of disproportionate use of synthetic fertilizers, which has gravely harmed the agroecosystem. However, to boost plant productivity in sustainable agriculture, green synthesized NFs, bio-synthesized NFs, or nano-biofertilizers should be investigated [32]. More soil and field-based demonstrations are required to demonstrate the efficacy and, importantly, the reproducibility of ENMs' effects during atmospheric agricultural conditions. Ultimately, economic viability, societal acceptance, and regulatory compliance must be considered to realize the goal of commercialization of NFs for large-scale application.

Conclusions

Implementing nanotechnology in advanced agriculture assists in enhancing the global economy by providing support and advances in various ways. With the advent of NFs, agronomic efficiency and effectiveness are improved compared to traditional resources. Different NFs are under development and consideration; few have already been released. Emerging approaches have been developed to locate and quantify NFs in plant systems to provide the idea of their transformation and safety aspects in a complex system. The nano-urea particles are easily accessible to crops due to their nano-size scale and higher surface area-to-volume ratio, which may favor higher root biomass, as well as more productive tillers, branches, chlorophyll, and photosynthesis, to ultimately enhance agricultural yields. This has been proven through field demonstrations performed throughout India in 2019–2020, which showed improved agriculture production. Interestingly, nano-urea boosts agricultural output while lowering input costs. The crops grown using nano-urea were found to be safe for consumption and have better nutritional quality in terms of protein and nutrient content. Moreover, it minimizes the quantity of chemical fertilizer. The usage of nano-urea may extend agricultural sustainability and environmental safety in the near future by creating a clean and healthy ecosystem.

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Author contributions

Conceptualization, KKV, X-PS, and Y-RL; writing—original draft, KKV and HDD; resources, D-JG and AJ; writing—review and editing, H-RH, LX, MS, D-LH, and VDR; supervision, X-PS and Y-RL; project administration, X-PS and Y-RL; funding acquisition, X-PS, H-RH and Y-RL. All authors have read and agreed to the published version of the manuscript.

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Availability of data and materials

No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Declarations

Ethics approval and consent to participate

Not applicable.

Competing interests

The authors declare no competing interests.

Author details

[1]Key Laboratory of Sugarcane Biotechnology and Genetic Improvement (Guangxi), Ministry of Agriculture and Rural Affairs/Guangxi Key Laboratory of Sugarcane Genetic Improvement/Sugarcane Research Institute, Guangxi Academy of Agricultural Sciences, Nanning 530007, China. [2]School of Plant and Horticulture Science Plant Biotechnology, College of Agriculture, Hawassa University, Hawassa 05, Ethiopia. [3]College of Life Sciences and Engineering, Hexi University, Zhangye 734000, China. [4]Department of Botany, Mohanlal Sukhadia University, Udaipur 313001, Rajasthan, India. [5]Department of Botany, University of Lucknow, Lucknow 226 007, India. [6]Academy of Biology and Biotechnology, Southern Federal University, Rostov-on-Don 344090, Russia.

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