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Nanofertilizers: New Products for the Industry?

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ABSTRACT: Mineral fertilizers are key to food production, despite plant low nutrient uptake efficiencies and high losses. However, nanotechnology can both enhance crop productivity and reduce nutrient losses. This has raised interest in nanoscale and nanoenabled bulk fertilizers, hence the concept of nanofertilizers. Nevertheless, large-scale industrial production of nanofertilizers is yet to be realized. Here, we highlight the science-based evidence and outstanding concerns for motivating fertilizer industry production of nanofertilizers, including the notion of toxicity associated with nanoscale materials; scant nanofertilizer research with key crop nutrients; inadequacy of soil- or field-based studies with nanofertilizers; type of nanomaterials to produce as fertilizers; how to efficiently and effectively apply nanofertilizers at the field scale; and the economics of nanofertilizers. It is anticipated that the development and validation of nanofertilizers that are nondisruptive to existing bulk fertilizer production systems will motivate the industry's involvement in nanofertilizers.

KEYWORDS: *nanofertilizer, nanoenabled bulk fertilizer, fertilizer industry, judicious exposure*

INTRODUCTION

The advent of nanotechnology has led to the incorporation of nanomaterials in many consumer products and industrial applications, including agriculture and food. However, nanomaterials are highly reactive due to their small size and enhanced surface area, leading to concerns about unintended environmental impacts upon exposure of biological systems to nanomaterials. To clarify the nature and extent of the bioenvironmental implications of nanomaterials, substantial research is being conducted on their effects in plants and associated microbes.[1] Historically, these studies focused mainly on the toxic aspects of nanomaterials. They were often designed using high doses and short exposure times.[2,3] The studies found mostly negative effects that were either obvious or subtle in nature. In comparison, fewer studies have examined the beneficial effects of nanomaterials in plants, as evidenced from the relatively small number of studies in the mainstream bio-nanoscience literature. These trends, in our opinion, led to the notion that nanomaterials are inherently phytotoxic. Recently, interest has been generated in nutrient element-nanomaterials in the context of fertilizers, hence the term nanofertilizer.[4] Current conventional fertilizers have low nutrient uptake efficiencies and are associated with high losses and attendant negative environmental consequences. The use of nanofertilizers has the potential to reduce loss of nutrients from fertilizers and, perhaps, fertilizer application rates. As will be seen in this Perspective, nutrient losses, particularly of nitrogen and phosphorus, are mitigated when packaged in nano, compared to conventional, forms. Hence, nanotechnology could be used to address the environmental effects of conventional fertilizers.

As illustrated in Figure 1, the idea of nanofertilizer conceptually involves the fertilizer stakeholders (industry, researchers, farmers, and governments) making a leap from bulk-scale mineral nutrient production and use to nanoscale production, input, and practice, with concerns noted regarding nanomaterial particle size, process scaleup, and field application strategies. However, studies evaluating the use of nutrient nanomaterials as fertilizers have skewed disproportionately toward micronutrients—mainly zinc, copper, manganese, and iron. In contrast to their micronutrient requirements, plants require macronutrients (nitrogen, phosphorus, and potassium, and, to a lesser degree, calcium, sulfur, and magnesium) in larger quantities, and the fertilizer industry produces fertilizers containing these nutrients in larger volumes. It is therefore surprising that the rate of nanofertilizer basic research and development (R&D) involving macronutrients has not proceeded in accordance with their importance in crop production.

Figure 1. Conceptual overview of fertilizer advancement from bulk-scale to nanoscale production and application. The question marks represent some of the open questions such as scaling up production and safe and effective nanofertilizer application methods. The blocked (red) arrow indicates that this representation does not advocate for the broadcast application of nanofertilizers.

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Table 1. Nanofertilizer Products Approved for Use in Myanmar[a]

company name	fertilizer name	specification	country of origin
SMTET Eco-technologies Co., Ltd.	Nano Ultra-Fertilizer (500) g	organic matter, 5.5%; T-N, 10%; T-P_2O_5, 9%; T-K_2O, 14%; AC-P_2O_5, 8%; CA-K_2O, 14%; CA-MgO, 3%	Taiwan
Shan Maw Myae Trading Co., Ltd.	Nano Micro Nutrient (Eco Star) (500) g	Zn, 6%; B, 2%; Cu, 1%; Fe, 6%+; EDTA Mo, 0.05%; Mn, 5%+; AMINOS, 5%	India
Green Organic World Co., Ltd.	Plant Nutrition Powder (Green Nano) (25) g	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	Thailand
WAI International Development Co., Ltd.	PPC Nano (120) mL	M protein, 19.6%; Na_2O, 0.3%; K_2O, 2.1%; $(NH_4)_2SO_4$, 1.7%; diluent, 76%	Malaysia
PAC International Network Co., Ltd.	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	Germany
The Best International Network Co., Ltd.	Supplementary Powder (The Best Nano) (25) g	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%	Thailand
Shan Maw Myae Trading Co., Ltd.	Nano Fertilizer (Eco Star) (5) gm	N, 8.2%; K_2O, 2.3%; organic matter, 75.9%; C:N, 5.4	India
World Connet Plus Myanmar Co., Ltd.	Hero Super Nano (25) gm	N, 0.7%; P_2O_5, 2.3%; K_2O, 8.9%; Ca, 0.5%; Mg, 0.2%; S, 0.4%; pH 12.08	Thailand
The Best International Network Co., Ltd.	Nano Capsule (The Best) (60) 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%	Thailand

[a] Information courtesy John Allgood, Global Fertilizer Consultant.

Given the demonstrated benefits of nutrient-based nanomaterials in crop fertilization, the seeming noninvolvement of the major fertilizer producers should be concerning. The objective of this Perspective, therefore, is to assess the science-based evidence for supporting nanofertilizer development and industrial takeoff and to highlight some of the outstanding questions related to the industrial production and use of nanoscale nutrients as fertilizers. In this overview, the terms "nanomaterials", "nanoparticles", and "nanoscale" are used interchangeably, regardless of their nuanced meanings in the nanoscience and nanotechnology literature. These terms refer specifically to nano forms of crop nutrient elements (N, P, K, S, Ca, Mg, Mn, Cu, B, Zn, Fe, Ni, Mo), in contrast to carbon nanotubes, silver (Ag), titanium oxide (TiO_2), cerium oxide (CeO_2), aluminum (Al), and other nanomaterials that are not typically components of conventional crop fertilizers, but that, nonetheless, have been widely evaluated on plants, sometimes with positive results. Also, because the soil is the primary medium for growing most crops, the discussion of the phytotoxicity or benefits of nanomaterials will focus mainly on work done in soil systems, with only brief mentions of work in other growth matrices. Four subjects will be dealt with that could inform how the industry might respond to the idea of nanofertilizers going forward: (i) the "toxic" categorization given to nanomaterials; (ii) evidence of nanofertilizer agronomic benefits; (iii) production of effective nanofertilizers and safer field application strategies; and (iv) the need for cost−benefit analysis of nanofertilizers. Subsequently, ideas and perspectives for triggering industry interest in nanofertilizer investment are provided.

■ WHAT ARE THE NANOFERTILIZER PRODUCTS?

Despite the surge in evidence that nanoscale nutrient elements can be applied as fertilizers when used judiciously, it appears that the large, global fertilizer industry entities have not been excited by the R&D outcomes to the point of investing in nanofertilizers. For clarity, a number of fertilizer products are reportedly claimed to be nanofertilizers; a list of some of these products is provided in recent reviews.[4,5] However, many of the products have been produced by university researchers in small scales for pilot testing in laboratories, greenhouses, or small field plots. Noticeably, most of the nanomaterials reportedly assessed on crops as "nanofertilizers" either are commercial products marketed by chemical companies for purposes other than crop fertilization or were produced in-house, in milligram to gram quantities. As such, any prospect of using them for large-scale agriculture is still improbable. Nonetheless, some countries appear to be moving forward with the idea of nanofertilizers. For example, the government of the Southeast Asian country of Myanmar is presently undertaking a program to include nanofertilizers in their national fertilizer regimen. A list of supposed nanofertilizer products approved to be imported into that country is presented in Table 1. As can be seen from this table, the companies in question are not among the key global fertilizer industry enterprises such as PotashCorp, Mosaic, Uralkali, Belaruskali, Yara International, OCP, CF Industries, ICL, Agrium, K+S, SAFCO, or Koch. Thus, unless such smaller companies are subsidiaries of the larger ones, it is unclear to what extent the current level of their visibility and production scale would influence global nanofertilizer advancement. With regard to product volume, the unit amounts of the listed products are mostly below 1 kg, and as for their being nanofertilizers, except for the "nano" tag in their names, the products appear to be just "concoctions" of different conventional nutrients and other additives, such as the chelating agent, EDTA. There is neither clear information provided on what makes a product "nano" (i.e., size) nor the type of nano product (i.e., whether pristine nano, surface-modified nano, composite nano, or nanoenabled bulk fertilizers). As of November 2016, the Myanmar government is seeking assistance with independent characterization and authentication of the products, perhaps suggesting doubts by them regarding the products' genuineness as nanofertilizers. In fairness, given the very nature of nanomaterials, a specific set of quality assessment criteria has to be developed and used to validate nanofertilizers, in addition to chemical quality (concentration and purity) assessment required for all fertilizers types. Some of the more obvious considerations specifically related to the authentication of nanofertilizers include (i) size, to assess whether they are truly nano (100 nm or less), aggregates of nanos, or bulk (size > 100 nm) materials being passed off as nano; (ii) stability, to evaluate their intactness as nanoscale products or the rate of transformation before and after interaction with soil and/or crop; (iii) shape, which influences the rate of dissolution and, possibly, bioactivity;[6] and (iv) functionalization or composition, which examines whether they are surface-modified or hybrid products. Except for concentration, these parameters require a suite of analytical instrumentation with nanoscale sensitivities that do not typically apply to bulk materials.

■ ARE NANOSCALE MICRONUTRIENTS INHERENTLY PHYTOTOXIC, OR IS IT A MATTER OF HOW AND WHERE THEY ARE USED?

Most of the world's crop production occurs in soil-based production systems, using recommended doses of nutrients that are presumably in agreement with the crop's physiological needs or the soil nutrient levels. Yet, as indicated in selected recent reviews,[3,7,8] the bulk of research in plant nanoscience either consists of experiments conducted in artificial media, such as nutrient solutions, agar, sand, or other nonsoil media; were designed using very high doses of the nanomaterials; are characterized by very short exposure duration, relative to the crop's full growth cycle; or involved nanoscale non-nutrient elements such as Ag, Ti, Ce, Al, and Cd, among others, which are known to be highly toxic. In particular, nonsoil media would influence material behavior differently from agricultural soils, given the variety of chemical, physical, and biological complexities that nanomaterials are faced with in soil. For example, except in the few cases where they have been artificially introduced, the nonsoil media studies have been devoid of the presence of microbes, whereas microbes are a constant biological feature of soil, capable of influencing nanomaterial behavior and activity.[9]

The overwhelming focus of plant nanoscience studies on toxicology involving plant exposure to high doses of the nanomaterials, especially of micronutrients, for short durations in nonsoil media created two impressions: that "nanoscale" implies "toxicity" and that all nanomaterials possess nano-specific toxicity that is always greater than their bulk, or ionic, equivalents. However, is it always a toxicity story for nutrient nanomaterials? Are all nutrient nanomaterials created equal? And, are these materials really more toxic than their conventional counterparts? A look at the evidence indicates that these assumptions have been rather sweeping, considering that most of the nano studies reaching these conclusions were conducted under conditions far detached from actual soil–plant systems and so do not tell the complete story as to how plants would respond to nanomaterial exposure in real agricultural settings. As we now see with increasingly more environmentally relevant data being generated, the toxicity of nanomaterials is context-dependent. The default outcome of nanomaterial–plant interactions is not toxicity. Plants respond to them differently, dependent on the specific nanomaterial, the study matrix (type of environment), the exposure dose and time, and the target plant.[10] In fact, when considered as fertilizers and deployed as such—at the right dose and in soil—the toxic effects are more often than not negated, replaced by either indifference (no effect) or an opposite outcome (beneficial) that may be as inconsistent as effects observed with conventional fertilizers in different soils.

Among the most important soil factors found to be regulating nanoscale micronutrients behavior are pH; the presence and quality of inorganic or organic compounds; and biological factors, including plant root exudates, bacteria, and fungi such as arbuscular mycorrhizae. These factors will modulate nanomaterial dissolution, aggregation, or disaggregation and surface properties (e.g., charge and coating). Accordingly, nanomaterial interaction with these soil factors may result in modified properties to generate different outcomes.[9,11−14] In Table 2, we summarize data,[15−37] by no means exhaustive, from soil-based studies with micronutrient nanomaterials, in which the bioactivity of the nanomaterial is regulated on the basis of soil property, in comparison with their bulk or ionic equivalents. As evident, most of the studies involved Zn, which is not surprising, given its global importance in human nutrition. Notably, the table shows clearly that crop responses are more often than not positive at low doses comparable to doses of conventional micronutrients used in real settings, but negative at high doses, many of which are too high for the crop requirements of the respective nutrients. These studies demonstrate the mitigation or even negation of the toxicity of nanoparticles in soil systems that would not be apparent, or less so, in sterile nonsoil systems and strongly support the assertion that nutrient element nanoparticles are not toxic by default, but act upon crops on the basis of the unique properties of the soil–plant system, as well as on the dose applied. Thus, for all of the prior and ongoing reports that nanoparticles of nutrient elements are phytotoxic, there is contrasting evidence that they are also beneficial. Obviously, whereas the outcome of some of the toxicity-focused studies comparing nanoscale and conventional nutrients have been conflicting, the results collectively suggest that the risks from nanoparticles under soil conditions could be either less potent or no more potent than those from conventional fertilizers at similar application doses.[4,5,7,10] This essentially buttresses our previous argument that in different plant–soil systems, the "nano" (size) nature of the material may be less important in making the "poison" than the exposure dose and environmental condition.[38] Still, it is worth cautioning that the toxicity or benefits of nutrient nanomaterials should be examined on a case-by-case basis, considering type, dose, growth conditions, and plant species. Indeed, for nanoscale heavy metals such as Cu, Fe, and Mn that can accumulate in the plant in particulate forms, the issue of potential residual toxicity should be concerning, because the particles could potentially serve as reservoirs for extended release of ions in planta that could rise to toxic levels, dependent on the application rate, whether foliar or soil applied, and the plant uptake capacity. However, studies such as that of Dimkpa et al.[39] have also shown that ions dissolving from nanoparticles taken up can be sequestered by plant components and, potentially, rendered less bioavailable.

In any case, judicious use of nanoscale materials is critical for maximizing benefits while minimizing risks, and with soil, being cognizant of the influence of specific factors such as pH, inorganic and organic components, and microorganisms would be helpful in optimizing nanofertilizers to realize their benefits. Hopefully, several ongoing micronutrient nanofertilizer research, including those involving the authors' collaborators at the Connecticut Agricultural Experiment Station and the University of Texas at El Paso,[40] as well as others taking place, for example, in the United Kingdom, involving Fe-based nanoparticles with potato[41] will produce positive outcomes that further unravel the promise of nanofertilizers.

■ IS CURRENT RESEARCH CONVINCING ABOUT THE BENEFITS OF MACRONUTRIENTS AS NANOFERTILIZERS?

As indicated by the class of nutrient nanomaterials discussed in the previous section, the published literature on plant nanoscience

Table 2. Effects of Nanoscale Micronutrients on Crops in Soil-Based Systems, without and with Comparisons to Bulk-Scale or Ionic Micronutrients

nanofertilizer	comparison with	concentration (mg/kg or mg/L)	main soil test condition and treatment application	main agronomic findings	effect compared to non-nano equivalent	ref
bare ZnO	N/A	50−500	pH 6.78; sandy-silt soil; applied in soil	stimulation of growth yield and Zn uptake in bean	N/A[a]	15
bare ZnO	N/A	125−500	pH 4.5 vs 7.8; high vs low organic matter and clay; applied in soil	at high pH, Zn uptake less and toxicity negated in wheat at all doses; at low pH, elevated Zn uptake and phytotoxicity	N/A	16
bare ZnO	N/A	45	pH 7.36; loamy-clay soil; applied in soil	reduction in wheat growth	N/A	17
bare ZnO	bulk ZnO, $ZnCl_2$	1000	pH 7.48; applied in soil	initially increased soil pH; some toxicity in radish, vetch, and wheat; enhanced Zn in shoot	same effect as the bulk; Zn salt more toxic and with more Zn uptake	18
bare CuO or ZnO	N/A	10−100−1000	pH 5.8; clay-loam soil; soil application with irrigation	spinach growth inhibited at 1000 mg/L but stimulated at lower rates	N/A	19
bare ZnO	bulk ZnO and Zn salt	100−3200	pH 8.2; loamy soil; soil applied	dose-dependent effect in maize: stimulatory at 100−200 mg/kg, indifferent at 400 mg/kg, toxic at 800−3200 mg/kg	nano slightly more toxic than salt but same as bulk at 800 mg/kg; similar Zn uptake in all	20
bare Fe_2O_3	Fe-EDTA	2−1000	pH 8.1; applied in soil	increased growth, biomass and Zn content of peanut	same effect on growth; less Zn in shoot of nano at comparable treatment	21
bare CuO	N/A	100−300	pH 8.3 vs 4.8; applied in soil	at high pH, Cu uptake less and toxicity negated in wheat at all doses; at low pH and high dose, elevated Cu uptake corresponded with root growth inhibition	N/A	22
ZnO with different surface coatings	uncoated, doped, and bulk ZnO; Zn salt	250−1000	sandy loam soil; applied in soil	increased biomass production	similar effects of all Zn at 250 mg/kg; coated NP increased fresh weight as bulk at 1000 mg/kg	23
ZnO + alginate	ZnO without alginate	100−800	sandy loam soil; pH 7.9; soil applied	alginate mitigated ZnO particle aggregation and corn biomass reduction; and increased Zn uptake	N/A	24
ZnO + arbuscular mycorrhiza (AM)	ZnO without AM	400−800	loam; pH 8.2; AM treatment; soil applied	negated toxicity and increased maize growth at 800 mg/kg	N/A	25
bare ZnO	Zn_2SO_4, ZnO-bulk, $Zn_3(PO_4)_3$, $ZnCO_3$, Zn-PO_4−CO_3	25	pH 6.4; AM treatment; soil applied	not toxic to tomato; no effect on AM colonization of plant root	plant biomass reduced by $ZnCO_3$, relative to Zn nano	26
bare ZnO	bulk ZnO, Zn salt	250−750	loamy soil; pH 7.8; soil application	inhibited alfalfa growth but not germination	less inhibitory than Zn salt; bulk ZnO stimulates growth, but inhibits seed germination as did bulk ZnO	27
bare CuO	bulk CuO	50−200	foliar applied	no reduction in cucumber yield compared to control; compromised fruit quality	nano increased yield at 200 mg/L; bulk increased yield at 50 mg/L; nano reduced photosynthesis and transpiration at 200 mg/L	28
bare Cu, CuO	bulk Cu, bulk CuO, $CuCl_2$	20−80	soil application	reduced cilantro germination, stimulated root and shoot biomass	bulk CuO reduced biomass at 80 mg/kg	29
bare ZnO	bulk ZnO, Zn_2SO4	10−250	suspensions applied in perlite	inhibited rapeseed	less inhibitory to bulk and salt	30
bare ZnO	N/A	100−10000	different soil types: pHs 6, 4.7, 6.7; sandy or silty soil; soil applied	effect on cress highly soil-dependent: stimulation at low dose for all soils; soil-dependent inhibition or stimulation at high dose	N/A	31
bare ZnO	$ZnSO_4$	50−2000	sandy clay loam soil; pH 6.42; foliar applied	promoted germination, growth, yield, and grain Zn content of maize	vegetative, but not reproductive responses greater than $ZnSO_4$ at the comparable rate; Zn uptake greater than $ZnSO_4$	32
fungus-synthesized ZnO	bulk ZnO	10	sandy soil; pH 8.1; ; foliar applied	enhanced growth and biomass of cluster bean	effects greater than bulk ZnO	33
fungus-synthesized ZnO	bulk ZnO	10	sandy soil; pH 8.1; foliar applied	increased root and shoot growth and nodule development; increased P and Zn uptake	effects greater than bulk ZnO	34

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Table 2. continued

nanofertilizer	comparison with	concentration (mg/kg or mg/L)	main soil test condition and treatment application	main agronomic findings	effect compared to non-nano equivalent	ref
nanocomposite: ZnO + CuO + B_2O_3	$ZnSO_4$ + $CuSO_4$ + H_3BO_3	2.8 + 0.6 + 1.3	sandy loam soil; pH 6.87; foliar applied	increased soybean growth, yield; and grain N, K, Zn, and B accumulation under drought	similar effect as salt formulation	35
bare CuO, MnO, or ZnO	bulk CuO, MnO, or ZnO; Cu, Mn or zinc sulfate	100−1000	sandy loam; pH 6.1; soil infested with *Verticillium* wilt fungus; shoot dipping and transplanting	stimulation of plant defense against fungal disease effect; yield stimulation of eggplant and tomato by CuO	effects greater than bulk and salt equivalents for Cu and Mn in eggplant; Zn salt better than nano for tomato	36
bacteria-synthesized Cu	bulk Cu	1−2.5	pH 4.5−5.3; root-rot infestation; foliar application	reduction of disease incidence; enhancement of yield in tea under disease condition	effect better than bulk Cu at 2.5 mg/L	37

[a] N/A, not applicable; comparisons were not made with conventional nutrients.

contains a preponderance of work on micronutrients, in contrast to macronutrients that drive most crop productivity globally. However, studies on nanoscale macronutrients have started to emerge. Particularly with N, its use as "nano-urea" was reported in a recent China-focused review[42] to benefit several crops including rice, radish, celery, cabbage, eggplant, pepper, tomato, and others. In the case of rice, nano-urea significantly increased grain yield and N uptake, leading to reduction in N loss by up to 74%, compared to conventional urea. Yet, compared to micronutrients, less is known regarding the mechanisms of nano-enabled macronutrient fertilizers. Available evidence indicates that the nanoenablement on macronutrient N and P fertilizers either acts in the rhizosphere to regulate the release of the active nutrient or facilitates uptake of the intact nutrients in the fertilizer material.[43−55] This gap, therefore, raises the question of whether the current level of research on nanofertilizers is sufficient to warrant a more than passing interest by the fertilizer industry, whose major products are macronutrients. In this section, studies involving N, P, K, and, where available, S, Mg, and Ca are highlighted (Table 3).[43−49,51−55,58−64] Some of the notable nanoenablings made to N have included the reaction of urea or other N sources with nanoscale hydroxyapatite (urea-HAP), use of nano-clay and other polymers, and reduction of N-salts.[43−50] Collectively, these have led to significant improvement in slowing N release rates and associated N losses and suggest an enhanced use efficiency of N in nanoforms, compared to conventional forms. Thus, they represent both agronomic and environmental stewardship motivations for industry involvement in the production of N nanofertilizers.

Agronomic research specific to nanoscale P was pioneered in 2014, by Liu and Lal.[51] Nanoscale P can be chemically synthesized by a pH-sensitive (i.e., sufficiently alkaline to permit precipitation) stepwise reaction of calcium hydroxide or calcium chloride and phosphoric acid; however, sodium phosphate (Na_2HPO_4) can be used in place of phosphoric acid. A stabilizing agent such as carboxymethyl cellulose (CMC) or hexadecyl(cetyl) trimethylammonium bromide (CTAB) can be added to keep the particles from aggregating in suspension. The resultant product, a nanoscale precipitate, nanohydroxyapatite (nHAP), is a synthetic P- and Ca-rich mineral also found naturally. However, nano-P can also be produced physically by grinding bulk phosphate rock (PR) to nanoscale. Studies describing nHAP or nano-PR effects in crop or environmental systems are presented in Table 3. From the environmental standpoint, P stockpiling in soil is of topical concern in highly intensive agriculture, where P fertilizers are used in large amounts. Generally, the negative effects of excess P in the agricultural environment are not usually reported in terms of phytotoxicity and reduction of productivity of the target crop. Rather, its effect, especially with the more soluble P fertilizers such as triple/single super phosphate (T/SSP), is the pollution of water bodies and resultant eutrophication and loss of aquatic species. Viewed from this negative environmental impact, one major benefit of using nanoscale P fertilizers, whether nHAP or nano-PR, over conventional soluble P fertilizers is the reduction in solubility and mobility of the former and, consequently, the reduced risk of eutrophication,[51] as well as the possibility of plants taking up intact particulate P.[52] These benefits are, of course, in addition to the more tangible effect on crop development and productivity. Although findings related to plant availability, uptake, and agronomic effects of nano-P versus soluble P fertilizers are still inconclusive, and contradictory,[56,57] it still can be argued that the current overall data may be

Table 3. Effects of Nanoscale or Nanoenabled Macronutrients on Crops in Soil-Based Systems without and with Comparisons to Non-nano Macronutrients

nanofertilizer	comparison with	concentration (kg/ha; g/kg; mg/kg or mg/L)	synthesis method and/or main test conditions	main agronomic findings	effect compared to non-nano equivalent	ref
urea-HAP coated with wood powder	conventional urea	N/A	reaction of urea + Ca(OH)$_2$ and H_3PO_4; encapsulation with wood powder from *Gliricidia sepium*	slowed release of N	35% less N release, relative to conventional urea	43
nano-coated urea	conventional urea	N/A	separately, urea + nanophosphate rock (PR), nano-ZnO or pine oleoresin; urea-PR and urea-ZnO were prepared by using oleoresin to facilitate coating of PR or ZnO onto urea	reduction in N_2O emission from urea	relative to conventional urea, N release slowed by pine oleoresin coating by 20%, nano-ZnO coating by 35%, and nano-PR coating by 45%	44
urea-HAP nanohybrid	granular urea	50 or 100	reaction of urea + Ca(OH)$_2$ and H_3PO_4; cro growth in alluvial soil; urea types soil-applied in splits	slowed release of N; enhanced grain yield and leaf N and K content in rice	relative to conventional urea, N release rate reduced 12 times in nano-urea; 50 kg/ha nano-urea more effective than 100 kg of conventional urea in increasing yield and N, K contents in rice	45
NPK-nanochitosan	NPK	10−100	nanochitosan prepared by polymerization of methacrylic acid and chitosan. NPK loading into nanochitosan; crop growth in sandy loam soil; foliar application; nanochitosan control missing; possible surface- adsorbed nanochitosan-NPK not accounted for	rice shoot uptake of intact nano-loaded NPK; enhanced vegetative growth; reduced crop life cycle by 40 days; increased rice grain yield by up to 49%	relative to conventional NPK, 41% increase in yield	46
biosynthesized nano-N	N/A	20−100	reduction of NH_4NO_3 to N by using fungal extract from *Aspergillus tubingenesis*; crop growth in soil, pH 8.76; foliar application; conventional N comparison missing	enhanced N and P-metabolizing soil microbes; increased biomass production in pearl millet	N/A	47
urea-nano-clay composites	urea	N/A	urea + montmorillonite nano-clay (MMT) mixed in water and extruded	slowed N release rate from urea	relative to urea, different urea-MMT ratio slowed N release considerably	48
urea-nano-clay−polymer composites	urea	100	urea + MMT + different polymers: separately ground; mixed in water, and extruded	urea-nano-clay with different polymers significantly slowed N release rate and reduced N_2O emission from urea in a wheat field	relative to urea, between 21 and 25% reduction in N release rate, and between 38 and 86% reduction in N_2O emission, dependent on polymer	49
nHAP	triple super phosphate (TSP)	100	nHAP synthesized by reacting Ca(OH)$_2$, H_3PO_4 and CMC; root applied in peat moss-perlite growth medium	enhanced growth and biomass production, and seed yield in soybean	relative to TSP, growth rate and seed yield enhanced by 33 and 20%, respectively	51
nHAP	N/A	0.5−1.5	nHAP synthesized by reacting Ca(OH)$_2$, H_3PO_4; seed treatment of nHAP suspension; conventional P comparison missing	enhanced germination, seedling growth, and biomass of chickpea	N/A	52
nHAP	N/A	5−30	commercial nHAP; crop growth in Cd-contaminated soil, pH 6.42; soil application; conventional P comparison missing	lowered Cd accumulation; increased biomass; increased antioxidant responses in Chinese cabbage	N/A	53
nHAP	mono- and diammonium phosphate	20	nHAP synthesized by reacting Ca(OH)$_2$, H_3PO_4; crop growth in sandy soil, pH 7.75; foliar application	enhanced growth and biomass production, and increased contents of NPK and beneficial metabolites in baobab	compared to MAP and DAP, vegetative and metabolic parameters enhanced by nHAP	54
nano-PR	SSP	60	sequential milling of rock phosphate; crop growth in clay loam soil, pH 7.9; soil application	increased stover and grain production and NPK contents in maize	effect relative to NPK, crop yield response and NPK uptake less than from SSP	55
nano-K	N/A	not provided	crop growth in silty loam soil, pH 7.7; foliar application; conventional K comparison missing; lack of information on the nano-K	increased dry matter yield in saffron	N/A	58
nano-S	N/A	50−300	synthesized by mixing sodium thiosulfate and plant extract from Chinaberry or Tree of Heaven; acidification and formation of S precipitates; soil application; conventional S comparison missing	root and shoot growth increases, respectively, of 133 and 220% for pumpkin, and 127 and 78% for tomato (at 150 kg/ha application rate)	N/A	59, 60
nano-CaO	bulk CaO and CaNO$_3$	10−1000	synthesized by reacting calcium nitrate and sodium citrate; foliar spray on Ca-deficient plants	increased Ca accumulation; reversal of Ca deficiency; promotion of root development in peanut	effects greater than the conventional Ca sources	61

Table 3. continued

nanofertilizer	comparison with	concentration (kg/ha; g/kg; mg/kg or mg/L)	synthesis method and/or main test conditions	main agronomic findings	effect compared to non-nano equivalent	ref
nano-$CaCO_3$	$CaCl_2$	10 mM	synthesized by reacting $CaCl_2$ in stem bark extract of *Boswellia ovalifoliolata*; seed treatment	improved root and shoot growth, and fresh biomass production in *Vigna mungo*	effects greater than the conventional Ca source	62
nano-Mg	MgO	0.5	commercial nano-Mg; crop growth in soil; foliar application	promotion of photosynthesis, growth and yield in cowpea	effect superior to conventional Mg	63
nano-MgO	N/A	0.1−1.0%	crop grown in vermiculite + perlite infested with *Ralstonia solanacearum* (bacterial wilt pathogen); conventional Mg comparison missing	strong protection of tomato against wilt infestation if plants first exposed to nanofertilizer; less effective if first exposed to pathogen	N/A	64

sufficient grounds to warrant stakeholder reflections concerning all of the ramifications of nano-P fertilizers, in terms of effects on agricultural productivity, improved environmental stewardship, and relative production cost compared to other P fertilizers. Where less than desirable effects of nano-P are due to soil type,[56] further improvements can be made by, for example, using a hybrid product of nHAP and nano-calcium sulfate (nano-CS), which has been shown to further reduce P mobility.[57] This is in addition to the fact that the Ca and S in nano-CS are also supplemental sources of nutrition for the crop.

As indicated in Table 3, compared to N and P, specific studies involving other macronutrients, namely, K, S, Ca, and Mg, are few and far between, but available data[58−64] suggest the potential of K-, S-, Ca-, or Mg-based nanoparticles to serve as fertilizers, although more soil-based studies would be needed to further clarify differences between these nano-nutrients and their conventional equivalents in complex agriculture settings. Among these studies, that of Imada et al.[64] is notable. Although comparison with conventional Mg was lacking in the study, as was the effect on crop productivity, it provided potentially useful information on the importance of early application of Mg as a pesticide, given that plants were either protected, or not, against bacteria wilt, dependent on whether they were first exposed to the nanomaterial or the pathogen.

■ WHAT TYPE OF NANOFERTILIZERS TO PRODUCE AND HOW TO EFFICIENTLY AND SAFELY APPLY THEM?

Nanomaterials derived from mineral nutrients are produced using different chemical synthesis methods, especially wet methods, specific examples of which include sol−gel, hydrothermal, homogeneous precipitation, template synthesis, and reversed micelle methods. Some of these have been briefly alluded to in a previous section. However, there is also production based on green synthesis, involving the use of plant or microbial extracts containing enzymes and reductants to reduce salts into nanoelemental forms. A third method involves the physical grinding or milling of bulk materials to nanosize. Detailed descriptions of these methods are beyond the scope of this study, but nanomaterials can be produced from virtually all of the mineral nutrients using any one or more of these methods. The question, though, is which method is most suitable for industrial scaling up? With respect to green synthesis, crops or microbes would first have to be cultured and processed prior to using their extracts for nanoparticle synthesis, which adds cost and time and, therefore, is an unlikely route for the fertilizer industry. For the physical method, milling to nanoscale of mined bulk minerals such as rock phosphate, K-feldspar, carbonate, and other minerals could yield large amounts of nanofertilizers in a reasonable time, provided the final products are properly characterized to meet the minimum standards for "nano" qualification. However, nano-milling could be very high on energy demand, in addition to its potential to cause human and environmental hazards due to the ease of nanoparticles suspending in air during milling. Hence, grinding bulk products to generate nanomaterials is increasingly less reported in the literature these days. On the other hand, a chemical synthesis approach identified from the large suite of methods currently in use could directly proceed in large reactors, generating large quantities of nanofertilizers in a short period of time. Regardless of the method, proper authentication of nanofertilizers will be challenged by the inherent characteristics of nanomaterials, including their tendency to aggregate, often nonuniformly, dissolve, or become coated on their surface by surrounding materials, to modify their surface charge and intended functionality. These challenges will thus necessitate investment in analytical capabilities to produce stabilized nanofertilizers with specific functionalization.

Upon production of pristine nanomaterials intended to be used for fertilizers, the next hurdle is to decide upon delivery strategies that conform to conventional fertilizer standards. Soil-based trials conducted in pots, greenhouses, or small field plots currently administer nanofertilizers through foliar sprays of nanosuspensions, soil application of dry powder or their suspensions (drench), or via seed coating application. A modified foliar application method[36] involves dipping the leaves of seedling transplants in nanosuspensions prior to replanting. However, dipping the shoot of intact plants in nanofertilizer suspensions, even for stabilized products, is limited to transplant crops and, thus, not operationally feasible with many arable crops that do not require transplanting. In the case of broadcast application of the dry nanoparticles, the relative ease with which nanopowders are suspendable in air would lead to drift losses and potential human inhalation and subsequent health hazards for the handler. For this reason, broadcast application of dry nanofertilizers appears to be unfeasible in large fields. Perhaps, deep placement of the powder may reduce handling hazards, although particle adhesion to equipment surfaces, especially under wet conditions, could be imagined. On the other hand, suspensions of nanoparticles in water, especially of nonstabilized (i.e., bare nanomaterials not surface functionalized) products, for use as soil drench or foliar sprays have at least two potential problems, dependent on the nanoparticle in question: namely, transformation of the particles into ions, or aggregation into submicrometer- or micrometer-sized particles. On the one hand, when dissolution occurs at a high rate, the effect of the nanofertilizer treatment is obfuscated by the dissolved ions. In contrast, aggregation of nanoparticles negates the definition of "nano" and size-specific benefits, whereby the product behaves more like bulk particles. Either way, such transformations counteract the very reason for producing nanofertilizers, which then raises the question of whether it is really worth investing in a (liquid) nanofertilizer that, even before use, ends up transforming into non-nano species. One other issue with the use of nanosuspensions for foliar application is the potential for deposition of nano-aggregates on leaf surface. Not only would this affect uptake of the particles through leaf transport channels (e.g., stomata and pores) that are typically size exclusive,[65] it could also deface the leaves, making them less desirable for consumption, a negative for vegetable crops. A photograph of leaves from lettuce plant treated with a foliar application of composite (ZnO, CuO, MnO, and FeO) nanoparticles shows dark spots resulting from foliar nanodeposition (Figure 2). Published methods for removing nanoparticles adsorbed onto leaf surface[66] were ineffective in eliminating the spots. In contrast, seed coating with nanomaterials may be a more effective strategy to apply nanofertilizers. However, the process would require additional investments in identifying and producing efficient coating materials that would not affect seed germination. Ultimately, the nanomaterial delivery method could influence immediate plant responses, especially at high doses. For example, foliar accumulation of nanoparticles on photosynthetic surface could lead to foliar heating, altering gas exchange due to stomatal obstruction and producing changes in physiological and cellular functions.[65] Soil application would affect root architecture, regulating lateral root formation, the production of plant growth regulators, and metal reduction and uptake dynamics.[12,67,68] These concerns leave us with the critical need to design nanofertilizers that are functionalized to be not only effective for the crop but also responsive to concerns about safe and efficient application methods.

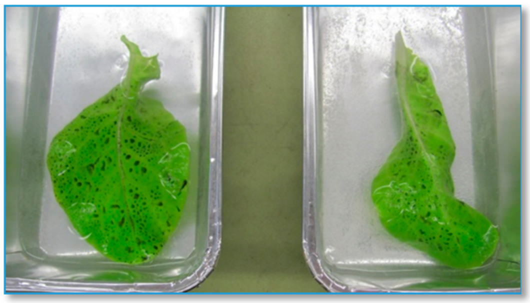

Figure 2. Leaves from lettuce plants sprayed with nanoparticles. The nanodeposition on the leaves has been washed, without success, using published procedures. Image courtesy of Willem de Visser, Wageningen Plant Research, The Netherlands.

■ ECONOMIC ANALYSIS OF NANOFERTILIZERS

Together with agronomic benefits of nanofertilizers, production costs and other associated constraints, as well as availability and affordability to farmers, are important factors likely to come into play in convincing the industry to invest in nanofertilizer production. This is especially true when such costs do not surpass those of existing fertilizers of similar chemistry; when nanofertilizers are so efficient that they cause a lowering of fertilizer application rates or the need for yearly applications; or when the negative environmental effects of conventional fertilizers need to be addressed using regulations. Some of these indications of economic possibilities of nanofertilizers have been raised by nanotechnologists working to improve fertilizers, as reported in both popular and professional news outlets such as *The Economist*[69] and the American Chemical Society's *Chemical and Engineering News*.[70] However, despite the promise of nanofertilizers, one important component still largely lacking is an analysis of their costs and benefits. From the industry perspective, an economic analysis is needed that compares which nanomaterial synthesis method is cheaper and more sustainable for the purpose of nanofertilizers, with high production turnover rate in mind. Also, it is unclear at this point how the cost of producing nanofertilizers in general compares to that of producing conventional fertilizers and whether and to what extent nanofertilizers would disrupt existing fertilizer production systems and the costs associated with such disruption. Yet, to gain traction as nanofertilizers for large field applications and global adoption, these materials would have to be produced industrially in ton amounts per unit time, in contrast to the current gram to kilogram levels often reported in the literature.

The same scenario plays out when viewed from a fundamental standpoint. Virtually all of the basic studies demonstrate agronomic benefits of nanofertilizers without sufficient details of the economic implications of their use. The study of Adhikari et al.[55] noted that maize yield was, overall, lower (1−10% less) with nano-PR (i.e., nanoscale phosphate rock) than with conventional P (SSP), dependent on PR source. However, they also remarked that, for the farmer, the lower cost of producing nano-PR, and its better residual effect in successive cropping, would ultimately counteract the immediate yield benefit obtained with SSP. However, no actual demonstration of any residual effect on successive crops was done to show the cost-saving effects. Similarly, Delfani et al.[63] put the cost of producing 1 kg of nano-Fe at U.S. $800.00, wherein the nano-Fe applied at 0.25 and 0.5 g/kg increased cowpea yield by 63 and 82%, respectively, compared to conventional Fe. Unfortunately, the authors did not provide similar production cost information for the conventional Fe that they used to allow a comparative cost−benefit analysis. In a previous review,[38] we described a yield increase of 24 versus 52%, respectively, when eggplants are treated with conventional versus nano-CuO fertilizers, wherein a 25 g bottle of the conventional CuO costs U.S. $18.50 and the nano-CuO costs U.S. $44.00. This yield difference translated, per acre, to a gain of $4637.00 from the CuO nanofertilizer with an investment of $26.00 ($44.00 − $18.50). That being said, as can be seen from the foregoing, it is not in all cases that nanofertilizers produce better results than conventional fertilizers, or the appropriate comparisons were simply not made. There is, therefore, no gainsaying the fact that a comprehensive economic analysis of nanofertilizers versus conventional fertilizers will contribute useful information for prospective investment in nanofertilizers by the industry and farmers alike.

■ IDEAS AND PERSPECTIVES FOR STIMULATING INDUSTRY INTEREST IN NANOFERTILIZERS

The foregoing narrative shows that nanoscale nutrients are not by default more toxic than their microscale or ionic counterparts and that they can benefit crops when used judiciously. Therefore, fully harnessing the benefits of nanoscale nutrient elements requires attracting the industry's attention to bring nanotechnology into the fertilizer regimen. To this end, nanofertilizer researchers need to evaluate what the fertilizer industry needs and how their current research approaches fit those needs. In doing so, they should treat nanofertilizers as fertilizers, whereby all evaluations of their effects on crops are conducted similarly to regular fertilizers: awareness of application rates in relation to crop and soil needs; judgment of effects based strictly on studies conducted in the growth matrix most appropriate for the crop being evaluated; inclusion of relevant controls (conventional) in experimental designs; researching and adopting appropriate nanofertilizer application strategies; and growing test crops to their full maturity. Furthermore, nanofertilizer assessments should be done using mixtures of nanoscale nutrients to mimic conventional fertilizer application regimens typically involving multiple nutrients applied simultaneously (e.g., NPK). This is in line with the concept of balanced nutrition for crops, which is very relevant for agricultural regions of the world with depleted soils, where crops have become nonresponsive to single nutrient applications, and where multinutrient deficiencies are rife. Most importantly, nanofertilizer R&D should focus more on macronutrients, especially NPK, which are the most important nutrients for the fertilizer industry.

Meanwhile, nanofertilizer R&D scientists should not only produce prototypes of effective nanofertilizers but also develop ideas and concepts toward process scaleup that could be sold to the industry. Having long realized the need to enhance the use efficiency of existing macronutrient fertilizers, R&D efforts led to products with specific properties, such as slow release and triggered release fertilizers, and these have now all been scaled up. Fortunately, nanomaterials possess unique properties that allow them to be functionalized in many ways. These properties are now being exploited to produce effective nanomaterials for other industries. Similar efforts are needed for nanomaterials intended for use as fertilizers, so that nanofertilizers are advanced from the current mostly pristine products easily manipulated by the test environment to more functional products. To this end, improvements so far made to nanoscale nutrients to generate improved nanofertilizers include those already mentioned in previous sections involving surface modifications such as with alginate and chitosan.[24,71] The potential of using other bio- or non-biobased materials, such as lignin, aminopropyltriethoxysilane, or clay, in nanofertilizer design is also noted.[23,48−50,72] Moreover, the demonstrated possibility to produce macronutrient nanofertilizers such as nano-N, nHAP, or urea-nHAP provides a strong premise for producing nanoenabled macronutrient fertilizers and should be attractive to the industry.

Recently, Monreal et al.[73] described ongoing bio-nanoenabled technologies that could improve nutrient use efficiency on the basis of real-time molecular recognition between nanoencapsulated nutrients and root exudates. Similarly, nanocomposites can be envisioned that are responsive to soil type, based, for instance, on pH-sensitive surface properties permitting specific responses in acidic or alkaline soils. Also, the development of NPK fertilizers functionalized with nanoscale Zn, B, Fe, Cu, or other micronutrients could be envisioned not only for improving the use efficiency of some of the macronutrients in the formulations but also to facilitate the uptake of the essential micronutrients into the plant, helping to improve grain or vegetable nutritional quality for human consumption. Conceivably, nanoscale micronutrient-enabled NPK can be produced in-line using aerosol or colloidal spray-coating technologies, wherein the bulk NPK fertilizer is aerosol-sprayed or mixed with nanofertilizers, coating their surface just before the final product exits the production line. Such an in-line procedure occurring downstream of production will be an add-on technology that would not cause any disruption to upstream fertilizer production processes. A simplified schematic representation of this concept is illustrated in Figure 3. The micronutrient nanoenabled NPK is a ready-to-use, all-in-one type product that could be more expensive than its conventional counterpart, but cheaper than separate applications of NPK and micronutrients. However, the yield increase, produce quality improvement, and plant health enhancement expected from the value addition must offset the additional input cost for the farmer.

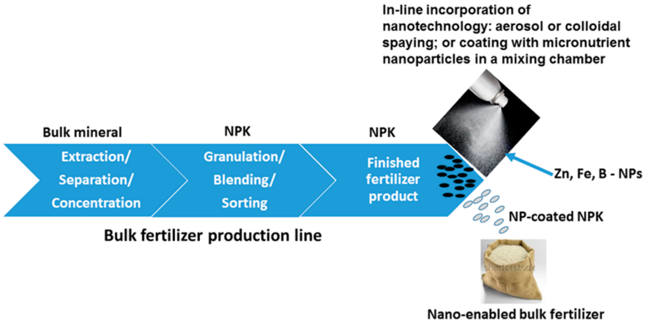

Figure 3. Simplified illustration of the production of nanoenabled bulk fertilizer (in this case NPK). Production of NPK fertilizer occurs upstream, and the finished fertilizer is functionalized with separately produced nanoparticles (NPs) of micronutrients (e.g., Zn, B, Fe) by spraying or mixing the NPK with the nanoparticles in-line, downstream.

The realization of some of these possibilities is not far-fetched. In the case of the type of product envisioned in Figure 3, some research groups are concomitantly involved in micronutrient nanoparticle synthesis, nanoaerosol technology, and crop evaluation of nanoparticles. The International Fertilizer Development Center (IFDC), the authors' institution, has capabilities for coating NPK with micronutrients. Hence, the development of macronutrient fertilizers enabled with micronutrient nanoparticles is achievable, given the right collaborations and industry partnerships. The incorporation of nutrient nanoparticles into bulk fertilizers can allow for resolving some of the concerns associated with nanoparticle stability and how best to apply them in large-scale field operations. For one, the potential for phase separation, premature transformation to non-nano species, and nanodrifting can be significantly reduced by delivering nanofertilizers as physical components of bulk fertilizers.

The use of any agrochemical, whether nano or conventional, is associated with risks for the environment. Noticeably, nanotechnology has started to assume a similar perception as biotechnology, in terms of societal resistance or reluctance to accept the technology, fueled by risk perceptions. Kah[74] discusses how some agrochemical industry players are altogether distancing themselves from the prefix "nano", perhaps explaining why no clear nanoagrochemicals have emerged so far from the big players. Granted, there are legitimate concerns about the negative consequences of nanoscale materials that should be taken seriously. However, in the case of nanofertilizers, concerns not based on context (whether nutrient element or Ag-type nanomaterial, dose applied, matrix used, exposure time, etc.) are unhelpful and could impede genuine progress toward nanofertilizer development and application. In contrast, evidence-based concerns and criticisms and differentiating nutrient nanomaterials from other nanomaterial as we have attempted to do here would help to guide the development and acceptance of nanofertilizers. In this regard, plant nanoscientists should continue to demonstrate and disseminate the benefits of nanofertilizers in crops, based on the use of judicious doses and appropriate growth matrices, comparisons with existing fertilizers, and acceptable application strategies. Other industries are benefiting immensely from nanotechnology advances; there is no reason the fertilizer industry should not.

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