Biopolymeric Nanocarriers for Nutrient Delivery and Crop Biofortification

Saikat Dutta,* Sharmistha Pal, Pankaj Panwar, Rakesh K. Sharma, and Pempa Lamu Bhutia

ABSTRACT: Driven by the possibility of precise transformational change in nutrient-enrichment technology to meet global food demand, advanced nutrient delivery strategies have emerged to pave the path toward success for nutrient enrichment in edible parts of crops through bioderived nanocarriers with increased productivity. Slow and controlled release of nutrient carrier materials influences the nutrient delivery rate in soil and in the edible parts of crops with a sluggish nutrient delivery to enhance their availability in roots by minimizing nutrient loss. With a limited understanding of the nutrient delivery mechanism in soil and the edible parts of crops, it is envisaged to introduce nutrient-enrichment technology for nutrient delivery that minimizes environmental impact due to its biodegradable nature. This article attempts to analyze the possible role of the cellulose matrix for nutrient release and the role of cellulose nanocomposites and nanofibers. We have proposed a few cellulose derived biofortificant materials as nutrient carriers, such as (1) nanofibers, (2) polymer−nanocellulose−clay composites, (3) silk-fibroin derived nanocarriers, and (4) carboxymethyl cellulose. An effort is undertaken to describe the research need by linking a biopolymer derived nanocarrier for crop growth regulation and experimental nitrogen release analysis. We have finally provided a perspective on cellulose nanofibers (CNFs) for microcage based nutrient loading ability. This article aims to explain why biopolymer derived nutrient carriers are the alternative candidate for alleviating nutrient deficiency challenges which are involved in focusing the nutrient delivery profile of biopolymers and promising biofortification of crops.

1. INTRODUCTION

Conventional agricultural practices may no longer be a sustainable option to meet the increasing food demands for a growing population without damaging the environment. Sustainable agricultural techniques need to be adopted in every sector as urgently as possible to mitigate some of the growing hurdles of toxic pesticides, resistant pests, and increasing soil contaminants and more importantly address the challenges of micronutrient deficiency in soil. Modern agriculture is seeking alternatives for the use of agrochemicals through implementation of nanotechnology with bioderived nanomaterials to achieve precision farming that aims at increased productivity with minimal resources. Two major areas where nanotechnology can contribute to agriculture cropping are improving crop yields and increasing resource utilization efficiency. This is an exciting and promising area that contains a scope of rapid expansion by means of improved understanding of fundamental interactions between plants and engineered nanomaterials. Nature derived polymeric nanomaterials can be utilized in varying applications including nanoherbicides, nanodetectors, and nanofertilizers to resolve the conventional challenges of agriculture. For instance, nanocarriers are employed to carry and deliver pesticides in a more controlled and slow release profile to achieve “precision farming”, which targets major crop production with nutrients in edible parts without affecting water and soil resources. Major global health challenges arise within one-third of the population from micronutrient deficiencies such as zinc (Zn), iron (Fe), iodine(I), selenium (Se), and vitamin A which are simply due to the lack of availability. Low dietary diversity and over-reliance on staple crops have led to a situation where we expect nanotechnology to potentially offer micronutrients more directly into the edible part of a crop. Micronutrient deficiencies are generally problems in the region where soil contains low plant available micronutrients such as Zn deficiencies in food products. Staple cereal grains, such as wheat, are, however, inherently low in micronutrient concentration and bioavailability to adequately attain human
nutritional requirements. Molecular and genetic research into Zn uptake, transport, and grain deposition in cereals is critically important for identifying “bottlenecks” in the biofortification of food crops with Zn. Zinc deficiency in soil potentially affects millions of hectares of cropland globally in cereal-growing regions. Therefore, increasing the level of Zn uptake by crops needs further investigation. Transgenic strategies for the biofortification of cereals with Zn are still in their infancy for enhanced root uptake, transport, and grain accretion capacity for Fe or Zn or both in recent work. Providing crop plants with sufficient Zn through the soil and foliar fertilizer strategy under field conditions is essential for biofortification efforts.

As compared to traditional fertilizers, not only can cellulose biopolymer based slow release nanocarriers currently improve the nutrient conversion ratio, but also their degradation by soil microorganisms occurs at a slower rate which creates a controlled release profile. Biofortification of staple foods can be achieved through a sequence of conventional breeding, by selecting genotypes with the highest micronutrient content. For example, in a lignin based slow release system, a lignin coating layer offers hydrophobicity that can slow down dissolution and release of micronutrients in the soil. In the case of slow release fertilizers, various natural, synthetic, or biological coatings act as a barrier to restrict or optimize the translocation of fertilizer nutrients into soil solution.

2. CONTROLLED RELEASE MECHANISM OF NUTRIENTS

The nutrient release rate is controlled by the preparation method and ratio of the coating layer. For example, the hydroxyl and carbonyl groups of lignin may generate insoluble chelates and complexes with Fe and Zn metal ions. However, the slow release mechanism is challenging to visualize. To understand the effects of lignin on retarding the dissolution of urea (i.e., release of urea), the properties of lignin obtained from the pulping spent liquor were investigated to realize the water penetration and dissolution of urea from the impregnated straws. Conventionally, multimicronutrient slow release fertilizers of zinc, iron, manganese, and copper were introduced. The rate curve reveals a multistage process with linear rates at each stage. In recent times, several nanoscale nutrient delivery systems and their interaction mechanisms with active ingredients were found to act through (a) encapsulation, emulsion, entrainment, surface adsorption, (b) crop field application of nanoscale delivery agents, and (c) nutrient release from nanoscale delivery agents, as shown in Figure 1. Generally, micronutrient release from a carrier occurs via water penetration, nutrient dissolution, and nutrient release through porous channels as shown in Figure 2. Toward this pathway, for example, alginate biopolymer rapidly cross-links to divalent cation Ca by forming a rigid shell which entraps small molecules in the core, which enhances the porosity of the granules. This incorporation affects the morphological features, which leads to different combinations of the mechanism of nutrient delivery via polymer relaxation and diffusion through porous architectures.

We try to understand the controlled release of micronutrients via the following steps: (a) controlled release of a fertilizer with a porous surface architecture, (b) penetration of soil water through the surface pores of controlled release fertilizers (CRF), (c) dissolution of nutrients through soil water, and (d) release of dissolved nutrients. It was observed that graphene oxide (GO) sheets are loaded with the micronutrients Cu or Zn metal ions attached to the oxygen functional groups on the surface and edges of the sheets. This significant difference in the release patterns of the micronutrients from the GO based carriers compared to the ZnSO₄ and CuSO₄ salts is partly due to tight coordination of the metal ions and oxygen functional groups on the GO surface. In the cases of Zn²⁺ and Cu²⁺, the Cu²⁺ tends to bind in a syn conformation with oxygen containing functional groups (e.g., carboxylate groups), whereas Zn²⁺ ions are more likely to bind in a direct conformation, while they are sharing two oxygen atoms of the same carboxylic group (Figure 3).

The similar porous surface architecture of biochar based controlled release nitrogen fertilizers (BCRNFs) with water retention was derived via a hydrothermal method and characterized their physicochemical and morphological properties. The N-release profile (biochar nitrogen fertilizer (BNF-2), biobased biochar nitrogen fertilizer (BBNF), and BCRNF) following a parabolic diffusion model indicates that the release involves a combination of dissolution, adsorption, and diffusion processes. As revealed from SEM based microstructure analysis of biochar+urea (B+U), postnutrient release in water results in a smooth and strongly networked surface morphology with microholes (Figure 4a). However, an undulating and coarse surface was evident for BCRNF including nanoscale rough bulges (Figure 4b).

It is proposed that the nutrient release mechanism for BCRNF involves adsorption of biochar and bentonite followed by multistage diffusion as distinct controlled release processes. Initially granules adsorb moisture, resulting in swelling of bentonite at the orifice of pores and channels in the biochar. A subsequent build up of osmotic pressure and irrigation water penetrates the channels of the biochar to condense on the solid fertilizer. This is followed by diffusion based slow release of the nutrient solution under a concentration or pressure gradient. There are a series of chelated micronutrient fertilizers that were employed in the past as conventional fertilizers with a maximum chelation rate of iron (Fe), copper (Cu), and manganese (Mn) under acidic pH and with maximum chelation of zinc (Zn) under alkaline pH. Chelated zinc,
soluble and coated fertilizers for zinc nutrition of maize, i.e., fertilizers containing either Zn-EDTA or Zn-ligno-sulphonate (Zn-LS) which were fixed over pellets of urea and then coated, had the advantage of adding both Zn and N in a single dose with a coating for the slow release feature for the availability of Zn in soil.

3. NEUTRACEUTICAL PROPERTIES OF CROPS

Chitosan nanoparticles may be used as a delivery system for micronutrients to crops, and these chitosan nanoparticles possess antimicrobial activity. Maize waste mainly consists of lignin and cellulose that can be useful and corncob biochar based nanocomposites and can be successfully used as carriers of microelements. On a smaller scale, arabic gum and active carbon composites can be used as carriers for micronutrients. Slow release fertilizers have been reported to increase the yield and vitamin C content in potatoes and were proven to be an effective source of micronutrients and superior over conventional micronutrient sulfates. The good response to the slow release fertilizer was due to the facts that sufficient Mo is released at the initial stages (20–50% over 3 weeks) and the root nodule activity is higher. Slow release Mo fertilizer increased nodulation by 105–161%.

Chillies (Capsicum frutescens) grown on a black soil showed excellent response to slow release Fe–Mn fertilizer. At 2 kg/ha Fe and 1 kg/ha Mn, the yield increased by 179% compared to the control (no Fe–Mn fertilization). The average Fe uptake and vitamin C in chillies were observed to be higher in slow release fertilizer treatments.

Rana et al. reported that the growth attributes and quality parameters of cabbage significantly increased with the application of biofertilizers and micronutrients. Fertilizer release control and soil property improvement are two major issues for which multicomponent and multifunctional sustained release zinc fertilizer was derived from lignosulfonic acid waste.

If we survey the global annual micronutrient production trend in metric tons as per each year of data which were averaged from two previous years from the US Geological Service for the micronutrients (Figure 6), Figure 6 shows that, other than boron, the production of micronutrients has shown a significant increase over the years. Table 1 presents a series of the selected most promising research results of the application of Engineered nanomaterials (ENMs) as nanofertilizers.

4. CONTROLLED RELEASE TIME SCALE OF BIOPOLYMERS

Zn, ZnO, Cu, and CuO nanoparticles were identified as alternatives for seed coating and foiler application based nutrient delivery. Therefore, we got to investigate how
immobilization of ZnO NPs on biopolymers will possibly slow down Zn release. Tensile properties can be modulated in a formulation with a biopolymer from lignin which offers a barrier to phosphorus diffusion through triple phosphate (TSP) fertilizer. Tensile strength can be varied by using PEG, which increases the tensile strength of polysaccharide film composites. In this regard, slow release of dicyandiamide poly(hydroxybutyrate-co-hydroxyvalerate) (DCD-PHBV) pellets was fabricated using a laboratory scale based on the diffusion and biodegradable nature of the PHBV matrix. In another strategy, superhydrophobic biopolymer coated slow release fertilizers (SBSFs) display formidable slow release. Nutrient release is influenced by the slow diffusion of water vapor into the internal urea core of the SBSF, which enhances the slow release feature. A strategy of using urease inhibitor helps in increasing the efficiency of fertilizers, which is further enhanced by an encapsulation process by an appropriate biopolymer to control the nitrogen release behavior on soil of the biopolymer urea fertilizer, in which case chitosan/starch/Allicin/urea cross-linked biopolymers were prepared.

5. CELLULOSE MATRIX FOR NUTRIENT RELEASE

Encapsulation in a chitosan alginate nanocarrier as nano-encapsulation in chitosan nanoparticles to reduce the toxicity of herbicides and chitosan alginate nanocarriers retards the rapid release of the water-soluble insecticide acetamiprid. Chitosan and hydroxyapatite (HA) were two naturally occurring forms used for micro- and macronutrient delivery to soil, respectively. The natural cellulose and other biopolymer pores in wood stems can be used for storing nanofertilizers for N and other element release under different soil samples. The major focus of the early stage investigation was the process of nitrogen release by fertilizer with cellulose nanofibrils which prevents the fertilizer granules from sticking onto each other. It was found that matrix based fertilizer delivery reduced nutrient leaching while maintaining growth of crops. For example, matrix based fertilizer (MBF) helps formulations of both anionic and cationic compounds such as Al(SO$_4$)$_2$·3H$_2$O and/or a Fe$_2$(SO$_4$)$_3$·3H$_2$O–lignin–cellulose matrix. While using these MBFs for addition of pesticides to soil, the ion-exchange matrix will likely bind metochlor and diazinon to the starch–cellulose–lignin matrix, which reduces leaching for both pesticide and nutrients, thereby creating a connection between an effective biofortificant and the cellulose based matrix. The porous architecture spans length scales from the micro- (within particles) to the macro- (within the polymeric matrix) levels, leading to tunable patterns of nitrogen release.

Figure 5. Controlled release mechanism of biochar in soil: (a) granules–moisture interaction, (b) adsorption of moisture and swelling of bentonite, (c) nutrient dissolution and release via diffusion, (d) dehydration of bentonite and stored nutrient solution diffusion into soil, (e) adsorption of moisture under higher osmotic pressure. (Adapted in part with permission from ref 30. Copyright 2019 Springer Nature.)

Figure 6. Global annual micronutrient production trend in metric tons against years. (Adapted in part with permission from ref 43 and 44. Copyright 2015 and 2016 Springer Nature.)

Figure 7. Global annual micronutrient production trend in metric tons against years. (Adapted in part with permission from ref 43 and 44. Copyright 2015 and 2016 Springer Nature.)

Figure 8. Global annual micronutrient production trend in metric tons against years. (Adapted in part with permission from ref 43 and 44. Copyright 2015 and 2016 Springer Nature.)
of nitrogen fertilizer is dependent on a natural cellulose based
known until recently.

6. CELLULOSE NANOCOMPOSITE AND NANOFIBER

In a recent study, it was shown that slow and sustained release
of nitrogen fertilizer is dependent on a natural cellulose based
outer core containing micro-/nanoporous cavities consisting of
two sections: (1) an inner nanocore for micronutrient
nanoparticles and (2) a natural cellulose based outer core
containing micro-/nanoporous cavities. Among these combi-
nations, a ZnO NP/alginite composite offers a steady Zn
delivery in soil pores while avoiding the early stage Zn toxicity
induced by conventional methods of Zn delivery. Evidence
in favor of the mechanistic side of nutrient release is not easily
derivable; however, the limited scope in comparing the
 nutrient release mechanism is described herein. In this process,
the uptake and translocation of nanomaterials or nanocarriers
of nutrients within plants develop nanoenabled biofortifica-
tion. The urea loaded hydroxyapatite nanocarrier delivers
plant nutrients efficiently for rice production therein. Urea
doped hydroxyapatite nanoparticles (Ur@HANP) was also
tested in sand columns and agricultural soil for understanding
the retention capacity of plant nutrients. A combination of
faster and slow release behavior of nutrient release attains an
equilibrium after a well-defined number of days which was
witnessed for mesoporous silica nanoparticles (MeSiNPs) with
a water-soluble N-polymer. The Fe content of ≥37 mg kg⁻¹
in rice plants (on a dry weight basis) at 60 days after sowing
was found to be a guide value for monitoring the Fe-nutrition
status of rice. In a study of the aluminum–organic acids
interaction in the rice rhizosphere in acid soil, the major
organic acids, total weak acid concentration, and monomeric
and polymeric Al were identified and quantified in the
rhizosphere and nonrhizosphere of rice.

6. CELLULOSE NANOCOMPOSITE AND NANOFIBER

The controlled release of micronutrients for biofortification of
soil by cellulose nanocomposite and nanofibers was never
known until recently. Nanocellulose derived hydrogels based
on electostatic interaction result in ionic gelation, molecular
assembly, and chemical cross-linking based hydrogels with
heterogeneity in linking density. Nanocellulose is now used
in fertilizers for precision agriculture by developing super-
adsorbent nanocomposites by using hydrolyzed polyacrylamide
and methylcellulose. In this context, nanocellulose can
promote high water absorption capacity, biodegradability,
and slow release of inputs due to the “obstruction effect” and
imprisonment of the input in the percolation network or
“locking effect”. However, nanocellulose remains an obstacle
for agriculture application due to the cost barrier.

In general, cellulose nanomaterials in the form of cellulose
nanofibers (CNFs) and cellulose nanocomposites (CNCs)
exist high stiffness and specific surface area and low
density. The inorganic nanoparticle encapsulations of Zn,
Cu, Fe, cerium (Ce), and titanium (Ti) are extensively studied
both in laboratory and field conditions. Biopolymeric
nanocarriers of natural polymers, chitosan, and pectin were
developed to provide a sustained and controlled release of
carbendazim with good bioefficacy and inhibition against fungi such as Fusarium oxysporus and Aspergillus parasiticus. Mostly, nanocellulose derived materials as delivery
agents remain within certain morphology types such as films/
nanofibers and nanoparticles which help in nanoencapsulation
in agriculture applications. Drug releasing approaches by
nanocellulose based materials are known of with carboxymethyl cellulose/Cu biocomposite hydrogels with pH sensitive
swelling ratios with promising results from drug release tests
in vitro. In the process of drug release, entanglement of
individual particles in partially fibrillated microcrystalline
cellulose led to formation of an elastic network. First order
and zero order drug release profiles compared to the optimum
filament were achieved by using a hydroxypropyl cellulose
(HPC) blend with ethyl cellulose (EC).

7. CELLULOSE DERIVED BIOFORTIFICANTS

The effects of a combined spray of Zn and Fe on the grain
concentrations of different crops grown on a range of soil types
and under different environmental conditions are not known.
Slow mineralization of N in T1 (cellulose-g-poly(acrylamide))
MC content and higher C contents is known. Similarly, a
recycled cellulose fiber and clay saturated with micronutrient
copper ions and copper nanoparticles transformed into a

Table 1. Series of Different Types of ENMs Exhibiting Nanofertilizer Potential

| Nanomaterial | Concentration | Plant  | Application type | Details                                                                 | Ref  |
|--------------|---------------|-------|-----------------|----------------------------------------------------------------------|-----|
| ZnO          | 6 mg kg⁻¹     | Sorghum | Root and foliar  | Improved plant productivity and stimulated grain nutritional values and N use efficiency, compared with untreated control | 45  |
| 2–16 mg L⁻¹  | Tomato        | Root   |                 | At 8 mg L⁻¹, shoot length (35.8%), root length (28.6%), leaf area (27.9%), antioxidant activities; proline content (65%) and photosynthetic rate increased, compared with control | 46  |
| 25–200 mg L⁻¹ | Cotton        | Root   |                 | Significantly increased growth (131%), total biomass (131%), total chlorophyll (139%), carotenoids (139%), total soluble protein contents (179%), compared with untreated control | 47  |
| Zn–chitosan   | 20 mg g⁻¹     | Wheat  | Foliar          | Enhanced Zn uptake; about 27 and ~42% increase in the two wheat varieties, compared to the control | 48  |
| Fe₂O₃         | 0.25–1 g L⁻¹  | Soybean | Foliar          | Increased grain yield by 48%, compared to control | 49  |
| 100–200 mg L⁻¹| Spinach       | Root   |                 | At 200 mg kg⁻¹, the plant biomass and Fe uptake increased in the plant, compared to control | 50  |
| 50–800 mg L⁻¹ | Tomato        | Root   |                 | Enhanced seed germination, increased plant growth and total biomass, compared to control | 51  |
| FeS           | 2–10 mg L⁻¹   | Mustard| Foliar          | Induced growth and yield of plant and increased antioxidant enzyme activities, compared to control | 52  |
| CuO           | 0.02–8 mg L⁻¹ | Maize  | Root and foliar | Both solution culture and foliar exposure enhanced maize growth (51%) and regulated different enzyme activities, compared to control | 53  |
| 10–500 mg L⁻¹ | Tomato and cauliflower | Root | | Root length (18%), chlorophyll (14%) and sugar (7%) contents increased in tomato plant at 10 mg L⁻¹, compared to control. Concentration dependent increase in antioxidant enzyme activities, and lignin deposition observed. | 54  |
| Cu–chitosan–PVA | 0.02–10 mg kg⁻¹ | Tomato | Root             | At 10 mg kg⁻¹, tomato yield (17%), stem diameter (13%), and dry biomass (30%) increased. At 0.02 mg kg⁻¹, lycopene content, and antioxidant capacity (10%) increased, compared to control | 54  |
| Cu–chitosan   | 0.06 g L⁻¹    | Tomato | Root             | Enhanced plant growth (21–29%) and yield (30%), stomata conductance (7%), and increased the leaf catalase (462%) and fruit lycopene content (12%), compared to control | 55  |

https://doi.org/10.1021/acsomega.2c02494
ACS Omega 2022, 7, 25909–25920
mineral cellulose fiber carrier. Therefore, we propose a number strategies to obtain cellulose and similar biopolymeric composites.

7.1. Cellulose Nanofiber. The tool of heterogeneous amphiphilic interactions between materials of biological and synthetic origin will be implemented for deriving a self-assembled cellulose nanofiber (CNF) composite filled with Zn-EDTA or Zn-lignosulfonate with an extension to cellulose nanofiber (CNF) with ethylene diamine (ED) in the presence of Zn$^{2+}$ salt (Scheme 1).91,92

7.2. Polymer−Nanocellulose−Nanoclay. A uniform bonding of hydrophilic poly(N-isopropylacrylamide) (PNIAm) and CNF occurs through hydrogen bonds, in which PNIAm would undergo conformational change above the lower critical solution temperature (LCST) where the hydrogel film engages with both hydrophobic PNIAm and hydrophilic CNF.93 Poly(N-isopropylamylide) (PNIPAm)/CNF films can be prepared through a photoinitiated radical polymerization with 1.5 wt % photoinitiator (2-hydroxy-2-methylpropiophenone). PNIPAAm chains are fully extended and locked through interchain hydrogen bonding below the LCST (Scheme 2). This strategy can further be modified by a PNIPAAm/CNF-Laponite composite (Scheme 2).

7.3. Silk Fibroin Based pH Responsive Composite. We envisaged construction of a silk fibroin (SF) based self-assembly by using tannic acid (TA), a biocompatible molecular glue to gelation with SF through hydrogen bonding, hydrophobic interactions, and π−π stacking. This process of sol−gel transition of SF under physiological conditions (37 °C, pH 7.4) can generate a supramolecular assembly (Scheme 3).94,95

7.4. Redox Responsive Carboxymethyl Cellulose (CMC). Considering a lower redox potential (equilibrium $E_{\text{th}} \sim 20$ mV) due to the low oxygen content in the soil, a large amount of reductive substances accumulates in the soil. Reductive substances in soil provide “triggers” for redox responsive hydrogels for controlled release of nutrients.96,97 CMC was cross-linked by cystamine dihydrochloride (CYS_2HCl) in the presence of 1-(3-(dimethylamino)-propyl)-3-ethylcarbodiimidehydrochloride (EDC) and N-hydroxysuccinimide (NHS) (Scheme 4).

8. CELLULOSE BASED SLOW RELEASE AGENTS

For the cellulose derived nanofiber class of materials as nanoenabled carriers for nutrient release, previous studies of different kinds of nanostructured materials as nutrient carriers such as nanoclays, hydroxyapatite, nanoparticles, mesoporous silica, carbon nanomaterials, and polymeric nanoparticles are more known.98 Recent developments of superabsorbent nanocomposites use hydrolyzed polyacrylamide and methylcellulose reinforced with montmorillonite for the loading and slow release of agricultural nutrients including macronutrients (urea) and micronutrients (sodium octaborate).99 Such strategies have also offered formation of rigid hydrogels due to formation of a percolation network capable of avoiding the

---

Scheme 1. UA Coating on CNF Assembly upon Loading Nutrients Zn

Scheme 2. Dual-Charged Nanoclay Laponite Scaffold Directed PNIAAM/CNC-Laponite Composite for Fe and Zn Delivery

Scheme 3. Illustration of the Process for Preparing the SF−TA Composite for Loading Zn and Fe

Scheme 4. Gelation Strategy of CMC-Cyst Formation for Nutrient Delivery to Soil and Redox Responsive Behavior of CMC-Cys via Regeneration under $H_2O_2$
conversion of type I CNC into type II, which is more lyophilized. The incorporation of nanocellulose into the hydrogel type of nanocarrier formulation promotes improvements in features and a significant improvement in the mechanical properties as a function of particle–particle and particle–polymer interactions. The cellulose derived carriers for micronutrient delivery will involve controlled release systems through CNC composites (e.g., CNC-alginate microsphere) with consistent swelling patterns, higher encapsulation efficiency, and promising sustained release profiles of micronutrients which would sort of resemble drug delivery. It is claimed that highly ordered mesoporous channels have been created with a pore size of ∼2.9 nm in mesoporous silica nanoparticles (MeSiNPs) and with a source of N-nutrients which involves a water-soluble branched polyethyleneimine (bPEI) attachment. In such a case secondary interactions such as hydrogen bonding and van der Waals forces dominate the release mechanism of pesticides.

9. PERSPECTIVE ON CELLULOSE NANOFIBERS (CNFS) AS NANO CARRIERS

Microcage type tunable porous structures with hydrophilicity, mechanical stability, and pH triggering features can bring required kind of on-demand nutrient loading and release delivery systems. This opens a new avenue for such size based micronutrient delivery based on the polymer network of CNFs. A schematic (Figure 7) shows the formation process of the CNF architecture with microcage for microsized nutrients. Nanoencapsulation involves coating of chitosan, liposome, polylactide, and lipids and protein nanoparticle encapsulation. Therefore, effective translocation of nutrients is carried by a CNF colloidal dispersion to the shoot and root length and chlorophyll by a significant increase of the protein content with effective translocation. To design new generation nanocarriers for the biofortification of nutrients, not only controlled release capabilities for effective nutrient release but also mitigation of harmful effects on the environment and human health is a prerequisite. Either for crop growth regulation of pest control, for efficient utilization of fertilizer, a nanoparticle should satisfy several requirements: (1) biodegradability, (2) higher nutrient or fertilizer loading capacity, (3) flexible response to stimuli in the external environment (pH, light, temperature), and (4) a stable delivery system.

10. RESEARCH NEEDS IN SPECIFIC AREAS

Nanoclays, hydroxyapatite, nanoparticles, mesoporous silica, carbon based nanomaterials, polymeric nanoparticles, and similar other nanomaterials offer their nutrient loading capacities and rapid nutrient release profiles. The choice of nanoenabled carrier to deliver nutrients for biofortification depends on a few factors, which include the following: (1) holding of a large amount of nutrients, (2) a suitable release rate, and (3) minimizing nutrient conversion to non-bioavailable forms.

The set of data in Table 2 suggests various modes of releasing agricultural chemicals. In comparison to urea–HA nanohybrids with slow release behavior with use efficiency of nitrogen ~48% (Table 2, entry 2), a further increase of nitrogen release up to 80% was achieved via a coating strategy (Table 2, entry 3). The future prospect of micronutrient delivery to the edible parts of crops
depends on several factors, as revealed from the results in Table 2. To enhance the effectiveness of fertilizers, core ethyl cellulose (EC) as an inner coating and cellulose based superabsorbent polymer (SAP) with the biochemical inhibitors dicyandiamide (DCD) and thiourea as an outer coating,\textsuperscript{115} bromoacetylated cellulose cross-linked with urea hydrogel,\textsuperscript{116} carboxymethyl cellulose-\textsuperscript{Na}g-\textsuperscript{-d-poly(AAm)} hydrogel,\textsuperscript{117} and superabsorbent polymers SAPWS (grafting wheat straw (WS) to poly(acrylic-co-acrylamide))\textsuperscript{118} are known. In addition, ethyl cellulose (EC) as an inner coating and starch based superabsorbent polymer (starch-SAP) as an outer coating with a stretched 3D network\textsuperscript{119} and carboxymethyl cellulose-g-poly(acrylamide)/montmorillonite superabsorbent composite were reported.\textsuperscript{120} A comparison is shown between the release behavior of urea from superabsorbent composite with 2.7\% montmorillonite at pH 4 and 10 (Figure 8a)\textsuperscript{120} and the release behavior of pure urea particles and coated products in soil at ambient temperature (Figure 8b).\textsuperscript{119} The nutrient release from the fertilizer involves three main stages: (i) water imbibition into the starch-SAP via penetration through the EC layer; (ii) the urea core being gradually dissolved by water; and (iii) nutrient delivery to soil by penetration through the layers of EC and starch-SAP hydrogel.

### 12. SUMMARY AND OUTLOOK

The nanoenabled technology for crop growth regulation includes pesticide detection, mycotoxins' detection, phytopathogen inactivation, and pest control for improving agricultural nanotechnology for biofortification.\textsuperscript{121} The specific agricultural applications include micronutrient delivery for replacement of mesoporous silica with biopolymers for the cargo delivery system. The biopolymeric carrier systems contain the following features: (1) improved utilization efficiency of nutrients from leaves, stems, petioles, and roots and (2) functionalization by gated materials to respond to exogeneous and endogenous stimuli such as pH, light, temperature, and enzymes. In the process of nanocarrier implementation for micronutrient delivery to breeding plants, global agricultural techniques can be integrated which include mutagenesis, genetic modification, engineered nanoparticles can generally enhance plant growth and be effective for suppressing disease, however, effective delivery of critical micronutrients at the early stages of plant growth is further challenging.\textsuperscript{122} The feature of bioaccumulation of metal nanoparticles within the plants and crops is one of the major concerns that involves particle translocation to edible tissues. The particle size and shape dependent phytotoxicity can cause a potential risk to the environment unless pursued under caution. Even when zinc micronutrient plays a significant role, however, Zn phytotoxicity in plants results from Zn interference in chlorophyll biosynthesis and additional biochemical reactions by causing iron deficiency chlorosis as a result of excessive Zn in soil. An adverse modification of protein, lipids, and nucleic acid content by generation of unwanted radical species cannot be ruled out as a result of Zn-NPs accumulation due to the uncontrolled delivery pattern of Zn micronutrients.\textsuperscript{123} Apart from bioaccumulation and phytotoxicity related issues, reversal of photosynthesis parameters as a results of the antioxidant activity level change due to accumulation of nanoparticles as a

---

**Figure 8.** (a) Nitrogen release behavior of urea from superabsorbent composite with 2.7\% montmorillonite at pH 4 and 10. (b) Release behaviors in oil for pure urea particles, urea particles coated with ethyl cellulose (EC) (Reprinted with permission from ref 120. Copyright 2018 Wiley-VCH), and urea particles coated with EC plus starch based superabsorbent polymer (SAP) (Reprinted with permission from ref 119. Copyright 2016 Elsevier).
result of nutrient delivery is a matter of consideration as a coexposure effect.

This review attempts to foresee where the current situation is heading and possible solutions if we rely on natural polymeric nanostructural carriers for the delivery of micro-nutrients. In this context, we revisited the origin of slow release techniques of micronutrients and recollected knowledge of nutrients. In this context, we revisited the origin of slow release carriers for biofortification.

## AUTHOR INFORMATION
Corresponding Author
Saikat Dutta — Electrochemical Energy & Sensor Research Laboratory, Amity Institute of Click Chemistry Research & Studies, Amity University, Noida 201303, India; orcid.org/0000-0003-0868-194X; Email: sdutta2@amity.edu

Authors
Sharmistha Pal — Research Center, ICAR-Indian Institute of Soil & Water Conservation, Chandigarh 160019, India
Pankaj Panwar — Research Center, ICAR-Indian Institute of Soil & Water Conservation, Chandigarh 160019, India
Rakesh K. Sharma — Sustainable Materials and Catalysis Research Laboratory (SMCRL), Department of Chemistry, Indian Institute of Technology Jodhpur, Jodhpur 342037, Rajasthan, India; orcid.org/0000-0002-0984-8281
Pempa Lamu Bhutia — Division of Agroforestry, Indian Council of Agricultural Research (ICAR), Research Complex for NEH Region, Umiam, Nagaland 797106, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c02494

Notes
The authors declare no competing financial interest.

## ACKNOWLEDGMENTS
S.D. acknowledges research funding support by the Department of Biotechnology, Ministry of Science & Technology, Government of India, for grant number BT/RLF/Re-entry/41/2017 under DBT Ramalingaswami Re-entry Fellowship (2019-2024) and a DBT-Public Health Food and Nutrition research grant (2022-2025) BT/PR36226/PFN/20/1478/2020.

## REFERENCES
(1) Jie, C.; Jing-zhang, C.; Man-zhi, T.; Zi-tong, G. Soil degradation: a global problem endangering sustainable development. J. Geograph. Sci. 2002, 12 (2), 243-252.
(2) Sampathkumar, K.; Tan, K. X.; Loo, S. C. J. Developing Nano-Delivery Systems for Agriculture and Food Applications with Nature-Derived Polymers. Sciencemag 2020, 23 (5), 101055.
(3) Chen, J.; Li, S.; Zhang, Z.; Zhao, X.; Li, X.; Ning, P.; Liu, M. Environmentally friendly fertilizers: A review of materials used and their effects on the environment. Sci. Total Environ. 2018, 613-614, 829-839.
(4) Pulizzi, F. Nano in the future of crops. Nat. Nanotechnol. 2019, 14 (6), 507-507.
(5) Valencia, G. A.; Zare, E. N.; Makkandi, P.; Gutierrez, T. J. Self-Assembled Carbohydrate Polymers for Food Applications: A Review. Compr. Rev. Food Sci. Food Saf. 2019, 18 (6), 2009-2024.
(6) Duhan, J. S.; Kumar, R.; Kumar, N.; Kaur, P.; Nehra, K.; Duhan, S. Nanotechnology: The new perspective in precision agriculture. Biotechnol. Rep. 2017, 15, 11-23.
(7) Mullen, A. Expectations from nano in agriculture. Nat. Nanotechnol. 2019, 14 (6), 515-516.
(8) Gödecke, T.; Stein, A. J.; Qaim, M. The global burden of chronic and hidden hunger: Trends and determinants. Global Food Security 2018, 17, 21-29.
(9) Cakmak, I.; McLaughlin, M. J.; White, P. Zinc for better crop production and human health. Plant and Soil 2017, 411 (1), 1-4.
(10) Cakmak, I.; Kutman, U. B. Agronomic biofortification of cereals with zinc: a review. Eur. J. Soil Sci. 2018, 69 (1), 172-180.
(11) Nguyen, T. D.; Cavagnaro, T. R.; Watts-Williams, S. J. The effects of soil phosphorus and zinc availability on plant responses to mycorrhizal fungi: a physiological and molecular assessment. Sci. Rep. 2019, 9 (1), 14880.
(12) Humayan Kabir, A.; Swaraz, A. M.; Stangoulis, J. Zinc-deficiency resistance and biofortification in plants. J. Plant Nutr. Soil Sci. 2014, 177 (3), 311-319.
(13) Kah, M.; Tufeknji, N.; White, J. C. Nano-enabled strategies to enhance crop nutrition and protection. Nat. Nanotechnol. 2019, 14 (6), 532-540.
(14) Trijatmiko, K. R.; Dueñas, C.; Tsakirpaloglou, N.; Torrizo, L.; Arines, F. M.; Adeva, C.; Balindong, J.; Oliva, N.; Sasaapas, M. V.; Borroaro, J.; Rey, J.; Francisco, P.; Nelson, A.; Nakanishi, H.; Lombi, E.; Tako, E.; Glahn, R. P.; Stangoulis, J.; Chada-Mohanty, P.; Johnson, A. A. T.; Tohme, J.; Barry, G.; Slamet-Loedin, I. H. Biofortified indica rice attains iron and zinc nutrition dietary targets in the field. Sci. Rep. 2016, 6, 19792-19792.
(15) Alloway, B. J. Soil factors associated with zinc deficiency in crops and humans. Environ. Geochem Health 2009, 31 (5), 537-48.
(16) Ludwig, Y.; Slamet-Loedin, I. H. Genetic Biofortification to Enrich Rice and Wheat Grain Iron: From Genes to Product. Front. plant Sci. 2019, 10, 833-833.
(17) Bhatnagar, M.; Bhatnagar-Mathur, P.; Dumbala, S.; Anjaiah, V.; Sharma, K. Crop Biofortification Through Genetic Engineering: Present Status and Future Directions. Conference: Genomics and Crop Improvement: Relevance and Reservations, Institute of Biotechnology, Acharya NG Ranga Agricultural University, Hyderabad 500 030 India, 2011.
(18) Kumar, J.; Gupta, D. S.; Kumar, S.; Gupta, S.; Singh, N. P. Current Knowledge on Genetic Biofortification in Lentil. J. Agricul. Food Chem. 2016, 64 (33), 6383-6396.
(19) Hess, S. Y. Zinc: Deficiency Disorders and Prevention Programs. In Encyclopedia of Human Nutrition, 3rd ed.; Caballero, B., Ed.; Academic Press: Waltham, 2013; pp 431-436.
(20) Zhang, H.; Demirer, G. S.; Zhang, H.; Ye, T.; Goh, N. S.; Aditham, A. J.; Cunningham, F. J.; Fan, C.; Landry, M. P. DNA nanostructures coordinate gene silencing in mature plants. Proc. Nat. Acad. Sci. 2019, 116 (15), 7543-7548.
(21) Demirer, G.; Zhang, H.; Goh, N.; Chang, R.; Landry, M. Nanotubes Effectively Deliver siRNA to Intact Plant Cells and Protect siRNA Against Nuclease Degradation. SSRN Electronic Journal 2019, DOI: 10.2139/ssrn.3352632.
(22) Chen, J.; Fan, X.; Zhang, L.; Chen, X.; Sun, S.; Sun, R.-C. Research Progress in Lignin-Based Slow/Controlled Release Fertilizer. ChemSusChem 2020, 13 (17), 4356-4366.
(23) Li, Y.; Sun, Y.; Liao, S.; Zou, G.; Zhao, T.; Chen, Y.; Yang, J.; Zhang, L. Effects of two slow-release nitrogen fertilizers and irrigation on yield, quality, and water-fertilizer productivity of greenhouse tomato. Agric. Water Manag. 2017, 186, 139-146.
(24) Sipponen, M. H.; Rogas, O. J.; Pihlajaniemi, V.; Lintinen, K.; Österberg, M. Calcium Chelation of Lignin from Pulping Spent Hexane with Zinc: A Review. J. ChemSciences 2020, 23 (5), 537-548.
(25) Sipponen, M. H.; Pastinen, O. A.; Strengell, R.; Hyötyläinen, J.; Heiskanen, I. T.; Laakso, S. Increased Water Resistance of CTMP Fibers by Oat (Avena sativa L.) Husk Lignin. Biomacromolecules 2010, 11 (12), 3511-3518.
(26) Bandypadhyay, S.; Ghosh, K.; Varadachari, C. Multi-micronutrient Slow-Release Fertilizer of Zinc, Iron, Manganese, and Copper. *Int. J. Chem. Eng.* 2014, 2014, 327153.

(27) de Matos, M.; Mattos, B. D.; Tardy, B. L.; Rojas, O. J.; Magallães, W. L. E. Use of Biogenic Silica in Porous Alginate Matrices for Sustainable Fertilization with Tailored Nutrient Delivery. *ACS Sustainable Chem. Eng.* 2018, 6 (2), 2716−2723.

(28) Kabiri, S.; Deghyare, F.; Tran, D.; da Silva, R.; McLaughlin, M.; Losic, D. Graphene Oxide: A New Carrier for Slow Release of Plant Micronutrients. *ACS Appl. Mater. Interfaces* 2017, 9, 43325−43335.

(29) Sun, P.; Zhu, M.; Wang, K.; Zhong, M.; Wei, J.; Wu, D.; Xu, Z.; Zhu, H. Selective Ion Penetration of Graphene Oxide Membranes. *ACS Nano* 2013, 17 (1), 428−437.

(30) Liu, X.; Liao, J.; Song, H.; Yang, Y.; Guan, C.; Zhang, Z. A Biochar-Based Route for Environmentally Friendly Controlled Release of Nitrogen: Urea-Loaded Biochar and Bentonite Composite. *Sci. Rep.* 2019, 19 (1), 9548.

(31) Zhou, Z.; Du, C.; Li, T.; Shen, Y.; Zhou, J. Thermal post-treatment alters nutrient release from a controlled-release fertilizer coated with a waterborne polymer. *Sci. Rep.* 2015, 15 (1), 13820.

(32) Jie, M.; Raza, W.; Xu, Y.; Chen, Q.-R. Preparation and Optimization of Amino Acid Chelated Micronutrient Fertilizer by Hydrolyzation of Chicken Waste Feathers and the Effects on Growth of Rice. *J. Plant Nutrition* 2008, 31 (3), 571−582.

(33) Alvarez, J. M.; Obrador, A.; Rico, M. I. Effects of chelated zinc, soluble and coated fertilizers, on soil zinc status and zinc nutrition of maize. *Communications in Soil Sci. and Plant Anal.* 1996, 27 (1−2), 7−19.

(34) Kumar, R.; Kumawat, N.; Kumar, S.; Singh, A. K.; Bohra, J. S. Effect of NPKS and Zn Fertilization on, Growth, Yield and Quality of Rice. *Int. J. Plant Nutr.* 2015−2016, 897−8559.

(35) Bandyopadhyay, S.; Bhattacharya, I.; Ghosh, K.; Varadachari, C. New Slow-Releasing Molybdenum Fertilizer. *J. Agri. Food Chem.* 2008, 56 (4), 1343−1349.

(36) Bhattacharya, I.; Bandyopadhyay, S.; Varadachari, C.; Ghosh, K. Development of a Novel Slow-Releasing Iron-Manganese Fertilizer Compound. *Indust. Eng.Chem. Res.* 2007, 46 (9), 2870−2876.

(37) Rana, S.; Thakur, K. S.; Bhardwaj, R. K.; Kansal, S.; Sharma, R. Effect of biofertilizers and micronutrients on growth and quality attributes of cabbage (Brassica oleracea var. capitata L.). *Int. J. Chem. Studies* 2020, 8 (1), 1656−1660.

(38) Wang, L.; Liu, X. Sustained Release Technology and Its Application in Environmental Remediation: A Review. *Int. J. Environ. Res. Public Health* 2019, 16 (12), 2153.

(39) Bindraban, P. S.; Dimkpa, C.; Nagarajan, L.; Roy, A.; Rabbinge, R. Revisiting fertilizers and fertilization strategies for improved nutrient uptake by plants. *Biolytica* 51 (8), 2019, 897−911.

(40) Dimkpa, C. O.; Bindraban, P. Fortification of micronutrients for efficient agronomic production: a review. *Agron. Sustainable Dev.* 2016, 36, 7.

(41) Dimkpa, C. O.; White, J. C.; Elmer, W. H.; Gardeza-Torresdey, J. Nanoparticle and Ionic Zn Promote Nutrient Loading of Sorghum Grain under Low NPK Fertilization. *J. Agri.Food Chem.* 2017, 65 (39), 8552−8559.

(42) Ding, H.; Liu, D.; Liu, X.; Li, Y.; Kang, J.; Lv, J.; Wang, G. Photosynthetic and stomatal traits of spike and flag leaf of winter wheat (Triticum aestivum L.) under wheat deficit. *Photosynthetica* 2018, 56 (2), 687−697.

(43) Venkatachalap, P.; Priyanka, N.; Manikanad, K.; Ganeshbabu, I.; Indiraarulselvi, P.; Geetha, N.; Muralikrishna, K.; Bhattacharya, R. C.; Tiwari, M.; Sharma, N.; Sahi, S. V. Enhanced plant growth promoting role of phycocyanines coated zinc oxide nanoparticles with P supplementation in cotton (Gossypium hirsutum L.). *Plant Physiol. Biochem.* 2017, 110, 118−127.

(44) Deshpande, P.; Dapkekar, A.; Oak, M. D.; Paknikar, K. M.; Rajwade, J. S. Zinc complexed chitosan/TiO2 nanoparticles: a promising micronutrient nanocarrier suited for foliar application. *Carbohydr. Polym.* 2016, 165, 394−401.

(45) Sheykhbaglou, R.; Sedghi, M.; Shishevan, M. T. H.; Sharifi, R. S. Effects of Nano-Iron Oxide Particles on Agronomic Traits of Soybean. *Notulae Scientiae Biologicae* 2010, 2 (2), 112−113.

(46) Joyesuraman, K.; GopalanRishith Thoppay, U. U.; Hikku, G. S.; Selvakumar, N.; Subramani, A.; Krishnamoorthy, K. Enhancement in growth rate and productivity of spinach grown in hydroponics with iron oxide nanoparticles. *RSC Adv.* 2016, 6 (19), 15451−15459.

(47) Shankramma, K.; Yallappa, S.; Shivanna, M. B.; Manjanna, J. Fe2O3 magnetic nanoparticles to enhance S. lycopersicum (tomato) plant growth and their biomimernalization. *Appl. Nanosci.* 2016, 6 (7), 983−990.

(48) Rawat, M.; Nayan, R.; Negi, B.; Zaidi, M. G. H.; Arora, S. Physio-biochemical basis of iron-sulfide nanoparticle induced growth and seed yield enhancement in B. juncea. *Plant Physiol. Biochem.* 2017, 118, 274−284.

(49) Adhikari, T.; Sarkar, D.; Mashayekhi, H.; Xing, B. Growth and enzymatic activity of maize (Zea mays L.) plant: Solution culture test for copper dioxide nanoparticles. *J. Plant Nutrition* 2016, 39 (1), 99−115.

(50) Singh, A.; Singh, N. B.; Hussain, I.; Singh, H. Effect of biologically synthesized copper oxide nanoparticles on metabolism and antioxidant activity to the crop plants Solanum lycopersicum and Brassica oleracea var. botrytis. *J. Biotechnol.* 2017, 262, 11−27.

(51) Juárez Maldonado, A.; Ortega-Ortiz, H.; Pérez-Labrada, F.; cadenas-pliego, G.; Benavides-Mendoza, A. Cu Nanoparticles absorbed on chitosan hydrogels positively alter morphological, production, and quality characteristics of tomato. *J. Appl. Botany Food Quality* 2016, 89, 183−189.

(52) Gilbertson, L. M.; Pourzahedi, L.; Laughton, S.; Gao, X.; Zimmerman, J. B.; Theis, T. L.; Westerhoff, P.; Lowry, G. V. Guiding the design space for nanotechnology to advance sustainable crop production. *Nat. Nanotechnol.* 2020, 15 (9), 801−810.

(53) Martins, N. C. T.; Avellan, A.; Rodrigues, S.; Salvador, D.; Rodrigues, S. M.; Trindade, T. Composites of Biopolymers and ZnO NPs for Controlled Release of Zinc in Agricultural Soils and Timed Delivery for Maize. *ACS Appl. Nano Mater.* 2020, 3 (3), 2134−2148.

(54) Fertahi, S.; Bertrand, I.; Amjoud, M. B.; Okarroum, A.; Arji, M.; Barakat, A. Properties of Coated Slow-Release Triple Superphosphate (TSP) Fertilizers Based on Lignin and Carrageenan Formulations. *ACS Sustain. Chem. Eng.* 2019, 7 (12), 10371−10382.

(55) Velev, I.; Pratt, S.; Donose, B. C.; Brackin, R.; Pratt, C.; Redding, M.; Laycock, B. Understanding the Mobilization of a Nitrification Inhibitor from Novel Slow Release Pellets, Fabricated through Extrusion Processing with PHBV Biopolymer. *J. Agric. Food Chem.* 2019, 67 (9), 2449−2458.

(56) Xie, J.; Yang, Y.; Gao, B.; Wan, Y.; Li, Y. C.; Cheng, D.; Xiao, T.; Li, K.; Fu, Y.; Xu, J.; Zhao, Q.; Zhang, Y.; Tang, Y.; Yao, Y.; Wang, Z.; Liu, L. Magnetic-Sensitive Nanoparticle Self-Assembled Superhydrophobic Biopolymer-Coated Slow-Release Fertilizer: Fabrication, Enhanced Performance, and Mechanism. *ACS Nano* 2019, 13 (3), 3320−3333.

(57) Ee Huy, C.; Zaureen Nisa Yahya, W.; Mansor, N. Allicin incorporation as urease inhibitor in a chitosan/starch based
(98) Guo, H.; White, J.; Zhenyu, W.; Xing, B. Nano-enabled fertilizers to control the release and use efficiency of nutrients. Curr. Opin. Environ. Sci. Health 2018, 6, 77−83.

(99) Lourdin, D.; Peixinho, J.; Bréard, J.; Cathala, B.; Leroy, E.; Duchemin, B. Concentration driven cocrustallisation and percolation in all-cellulose nanocomposites. Cellulose 2016, 23 (1), 529−543.

(100) Lin, N.; Huang, J.; Chang, P. R.; Feng, L.; Yu, J. Effect of polysaccharide nanocrystals on structure, properties, and drug release kinetics of alginate-based microspheres. Coll. Surf. B Biointerfaces 2011, 85 (2), 270−9.

(101) Kose, O.; Tran, A.; Lewis, L.; Hamad, W. Y.; MacLachlan, M. J. Unwinding a spiral of cellulose nanocrystals for stimuli-responsive stretchable optics. Nat. Commun. 2019, 10 (1), S10.

(102) Zhang, S.; Zhou, S.; Liu, H.; Xing, M.; Ding, B.; Li, B. Pinecone-Inspired Nanomachined Smart Microgels Enable Nano/Microparticle Drug Delivery. Adv. Funct. Mater. 2020, 30 (28), 2002434.

(103) Zhang, S.; Liu, H.; Tang, N.; Ge, J.; Yu, J.; Ding, B. Direct electronetting of high-performance membranes based on self-assembled 2D nanomachined networks. Nat. Commun. 2019, 10, 1458.

(104) Steven, E.; Saleh, W. R.; Lebedev, V.; Acquah, S. F. A.; Laukhin, V.; Alamo, R. G.; Brooks, J. S. Carbon nanotubes on a spider silk scaffold. Nat. Commun. 2013, 4 (1), 2435.

(105) Ariyarthana, I. R.; Nedra Karunaratne, D. Use of chickpea protein for encapsulation of folate to enhance nutritional potency and stability. Food Bioprod. Process. 2015, 95, 76−82.

(106) Ashfaq, M.; Verma, N.; Khan, S. Carbon nanofibers as a micronutrient carrier in plants: efficient translocation and controlled release of Cu nanoparticles. Environmental Science: Nano 2017, 4 (1), 138−148.

(107) Wang, C.-Y.; Yang, J.; Qin, J.-C.; Yang, Y.-W. Eco-Friendly Nanoplatforms for Crop Quality Control, Protection, and Nutrition. Adv. Sci. 2021, 8 (9), 2004525.

(108) Guo, H.; White, J. C.; Wang, Z.; Xing, B. Nano-enabled fertilizers to control the release and use efficiency of nutrients. Curr. Opin. Environ. Sci. & Health 2018, 6, 77−83.

(109) Yi, Z.; Hussain, H. L.; Feng, C.; Sun, D.; She, F.; Rookes, J. E.; Cahill, D. M.; Kong, L. Functionalized Mesoporous Silicon Nanoparticles with Redox-Responsive Short-Chain Gatekeepers for Agrochemical Delivery. ACS Appl. Mater. Interfaces 2015, 7 (18), 9937−9946.

(110) Zhang, S.; Yang, Y.; Gao, B.; Li, Y. C.; Liu, Z. Super-hydrophobic controlled-release fertilizers coated with bio-based polymers with organosilicon and nano-silica modifications. J. Mater. Chem. A 2017, 5 (37), 19943−19953.

(111) Zhang, G.; Zhou, L.; Cai, D.; Wu, Z. Anion-responsive carbon nanosystem for controlling selenium fertilizer release and improving selenium utilization efficiency in vegetables. Carbon 2018, 129, 711−719.

(112) Li, X.; Han, J.; Wang, X.; Zhang, Y.; Jia, C.; Qin, J.; Wang, C.; Wu, J.-R.; Fang, W.; Yang, Y.-W. A triple-stimuli responsive hormone delivery system equipped with pillararene magnetic nanovalves. Mater. Chem. Frontiers 2019, 3 (1), 103−110.

(113) Hou, X.; Pan, Y.; Xiao, H.; Liu, J. Controlled Release of Agrochemicals Using pH and Redox Dual-Responsive Cellulose Nanogels. J. Agric. Food Chem. 2019, 67 (24), 6700−6707.

(114) Ramirez-Rodriguez, G. B.; Dal Sasso, G.; Carmona, F. J.; Miguel-Rojas, C.; Perez-de-Luque, A.; Masiccioni, N.; Guagliardi, A.; Delgado-Lopez, J. M. Engineering Biomimetic Calcium Phosphate Nanoparticles: A Green Synthesis of Slow-Release Multinutrient (NPK) Nanofertilizers. ACS Appl. Bio. Mater. 2020, 3 (3), 1344−1353.

(115) Zhang, M.; Yang, J. Preparation and characterization of multifunctional slow release fertilizer coated with cellulose derivatives. Int. J. Polym. Mater. Polym. Biomater. 2020, 70, 774−781.

(116) Mohammad-Khoo, S.; Moghadam, P. N.; Fareghi, A. R.; Movagharnezhad, N., Synthesis of a cellulose-based hydrogel network: Characterization and study of urea fertilizer slow release. J. Appl. Polym. Sci. 2016, 133 (5), DOI: 10.1002/app.42935

(117) Singh, A.; Sarkar, D. J.; Mittal, S.; Dhaka, R.; Maiti, P.; Singh, A.; Raghav, T.; Solanki, D.; Ahmed, N.; Singh, S. B. Zeolite reinforced carboxymethyl cellulose-Na-g-cl-poly(AAm) hydrogel composites with pH responsive phosphate release behavior. J. Appl. Polym. Sci. 2019, 136 (15), 47332.

(118) Zhao, H.; Song, J.; Zhao, G.; Xiang, Y.; Liu, Y. Novel Semi-IPN Nanocomposites with Functions of both Nutrient Slow-Release and Water Retention. 2. Effects on Soil Fertility and Tomato Quality. J. Agr. Food Chem. 2019, 67 (27), 7598−7608.

(119) Qiao, D.; Liu, H.; Yu, L.; Bao, X.; Simon, G. P.; Petinakis, E.; Chen, L. Preparation and characterization of slow-release fertilizer encapsulated by starch-based superabsorbent polymer. Carbohyd. Polym. 2016, 147, 146−154.

(120) Kenawy, E.-R.; Azaam, M. M.; El-nshar, E. M. Preparation of carboxymethyl cellulose-g-poly (acrylamide)/montmorillonite superabsorbent composite as a slow-release urea fertilizer. Polymers Adv. Technol. 2018, 29 (7), 2072−2079.

(121) Wang, C.-Y.; Yang, J.; Qin, J.-C.; Yang, Y.-W. Eco-Friendly Nanoplatforms for Crop Quality Control, Protection, and Nutrition. Adv. Sci. 2021, 8, 2004525.

(122) Tian, C.; Zhou, X.; Liu, Q.; Peng, J. W.; Wang, W. M.; Zhang, Z. H.; Yang, Y.; Song, H. X.; Guan, C. Y. Effects of a controlled-release fertilizer on yield, nutrient uptake, and fertilizer usage efficiency in early ripening capesed (Brassica napus L.). J. Zhejiang Univ. Sci. B 2016, 17 (10), 775−786.

(123) Ransom, C. J.; Jolley, V. D.; Blair, T. A.; Sutton, L. E.; Hopkins, B. G. Nitrogen release rates from slow- and controlled-release fertilizers influenced by placement and temperature. PLoS One 2020, 15 (6), e0234544.

(124) Xu, Z. P. Material Nanotechnology Is Sustaining Modern Agriculture. ACS Agri. Sci. Technol. 2022, 2 (2), 232−239.

(125) Rajput, V.; Minkina, T.; Mazari, M.; Shende, S.; Sushkova, S.; Mandzhieva, S.; Burachevskaya, M.; Chaplygin, V.; Singh, A.; Jatav, H. Effects on human health. Ann. Agri. Sci. 2020, 65 (2), 137−143.

(126) Sordo, F.; Janecek, E.-R.; Qi, Y.; Michaud, V.; Stellacci, F.; Engmann, J.; Wooster, T. J.; Sorin, F. Microstructured Fibers for the Production of Food. Adv. Mater. 2019, 31 (14), 1807282.