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Review

Foliage adhesion and interactions with particulate delivery systems for plant nanobionics and intelligent agriculture

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A B S T R A C T

The constantly increasing global food demand galvanizes innovative agricultural actions aimed to transcend current production levels. The predicted near-future food security scenario is alarming, requiring actions beyond traditional agricultural practices. Following the success of nanotechnologies in pharma and health sciences, nano-enabled agriculture is expected to increase crop yields and limit losses to pathogens, pests and other threats. Associated efforts are enabled by real-time sensing and controlled delivery, the latter of which considers cargos designed for controlled and targeted release, especially if triggered on demand. In this review, we introduce recent breakthroughs in these areas, including pesticide delivery as well as genetic modification and the engineering of nanoparticles for application in living materials. We offer a critical discussion on the physico-chemistry of adhesion of nanoparticles to vegetal tissue, their uptake and translocation in and within plants.

Contents

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Introduction

Population growth translates into an ever-increased food and feed needs, thus placing a heavy pressure on the traditional agriculture practices. Expansion of croplands is limited and will not match the projected expectations for crop production [1]. Hence, it is critical to improve crop productivity, which can be strategically approached by decreasing losses to environmental (e.g. drought and flooding) and biological (e.g., microbes or weeds) stresses as well as increasing plant fitness. Traditional agriculture practices are becoming obsolete and will not keep the food supply over demand for long; meanwhile, agricultural traits increase the waste of resources and create environmental burdens via agrochemicals that may induce problems related to pathogen resistance, bioaccumulation in the food chain, and loss of biodiversity. While a recent study shows that only about 0.1–10% of agrochemicals serve their final purpose, their bioaccumulation in soil and groundwater have a deleterious impact on the water quality, flora and fauna [2].

Nanotechnology has brought a step forward in research aimed to efficiently use agrochemicals [3–7]. The first wave of research within nano-enabled agriculture focused mostly on the development of delivery platforms to promote, control, or slowdown the release of pesticides [8], fertilizers [9], and phytohormones [10], as well as improving the delivery of acid nucleic across the plant cell walls [11]. The platforms have included engineered nanoscaled hydrogels, pellicles, fibers, and particles based on biodegradable polymers, lipids, proteins, minerals, among others. They often use an active ingredient (cargo) encapsulated or physically entrapped in a carrier. Primarily, such platforms allow control on the dissolution profiles of the cargo, preventing its early physicochemical degradation [12] and improving its pest-control efficiency [12–14]. The advantages of delivery platforms over traditional ones (e.g. dissolved or emulsified agents) have been thoroughly discussed in the recent literature [2,15–22]. They include, the possibility to disperse hydrophobic pesticides in water, higher stabilization against environmental degradation, lower dosage levels, and prevention of evaporation and leaching, all of which leading to higher efficiency and lower contamination. Moreover, given the projected needs for enhanced crop production (ca. 50% more by 2030), agriculture nanotechnologies align with other more advanced agriculture practices such as indoor, vertical and hydroponic farming as well as the development of genetic modified organisms (GMO). In fact, the utilization of nanocarriers is sought to completely change the GMO landscape, making it more efficient and specific [23]. On the other hand, even as very efficient and clean systems, indoor farming cannot substitute the open field cultivation, but they should complement, given the massive volume of crops needed to feed approximately 9 billion people. Therefore, agriculture nanotechnologies should be seen as allies of GMOs and indoor farming.

Inspired from an extensive body of biomedical research [24,25], particulate delivery systems for agricultural (botanical) applications have been designed to target specific tissues or organisms or to act upon a given stimuli. Adhesion and uptake of particles (Fig. 1a) are tethered to the particle properties (size, chemistry, geometry, etc.) (Fig. 1b), which also impact heavily the translocation and accumulation of particulate inside plants (Fig. 1c). Such systems aim to further improve control over agrochemical release to the environment by acting on-demand (Fig. 1d), thus achieving considerably higher crop productivity with much less contamination. Engineered particles are targeted to specific plant tissues and cells by controlling interfacial interactions at the nanoscale [26,27], and have allowed augmentation of plant's performance and the preparation of living, plant-based materials that can act as sensors, actuators and other devices (Fig. 1e). In turn, they provide real-time diagnosis of the health of plants and crops [28,29]. Herein we discuss the recent breakthroughs in targeted and stimuli-responsive engineered particulate delivery systems for intelligent agriculture. The review covers not only aspects related to delivery of pesticides, but that of molecules used for genetic modification as well as engineered particles for the preparation of living materials. We first introduce some fundamental aspects related to the role of interfacial interactions and particle morphology on particle adhesion to vegetal tissues, as well as their uptake and translocation into and within plants. Such aspects are then factored in the performance of targeted and stimuli-responsive systems. Finally, we critically discuss technical and scientific advances needed to bring forward engineered particulate systems to achieve improved food productivity.

Adhesion of engineered particulate on foliar tissues

Foliar adhesion is of primary importance for an efficient use of particulate delivery platforms, aimed to either protect or modify plant function. A strong interaction between carriers and foliage minimize biocidal leaching and, therefore, prevent bioaccumulation in non-targeted organisms. Moreover, controlled adhesion allows localization of the cargo and bioactives in the target tissue (targeted delivery).

Foliar tissues, especially their outer layers (cuticle and epidermis) display rich morphological and chemical features that varies according to plant diversity and environmental conditions [30]. For instance, there is stomata differentiation between botanical families (e.g. amphistomatic, hypostomatic and epistomatic lamina) which may depend on temperature and humidity. In the context of colloidal adhesion, the commonly found multiscale hierarchical structures of the leaf cuticle limits adhesion. Additionally, the leaf cuticle typically comprises wax layers that endows low surface energy – high water contact angle – and prevents wetting (e.g., via spraying). However, adhesion between the surface of a plant and a carrier could be manipulated if one considers the shape, size and composition of the latter (Fig. 2a). In this context, carriers should be designed keeping in mind the target plant and its surface (leaf, root or stem) since there are morphology and composition-centered variations arising from the plant population and planting conditions. From a simplified morphological perspective, rod- and platelet-like carriers may be preferred for foliar applications given their higher contact area compared to that of spherical counterparts. However, for practical reasons, most carriers are prepared and used as spherical.

Although the biggest share of carrier design for delivery systems considers only the mechanisms for control the release kinetics, increasing attention is being placed on plant adhesion considerations. For instance, aiming at improving the adhesion to cucumber foliage, the surface of carriers (ca. 450 nm) based on poly(lactic acid) (PLA) loaded with an insecticide (abamectin) were tailored to endow hydrophobicity, positive surface groups and other properties [31]. By grafting acetyl, amine or carboxylic acid groups on the particle's surface, it was possible to adjust its adhesion to cucumber leaves,

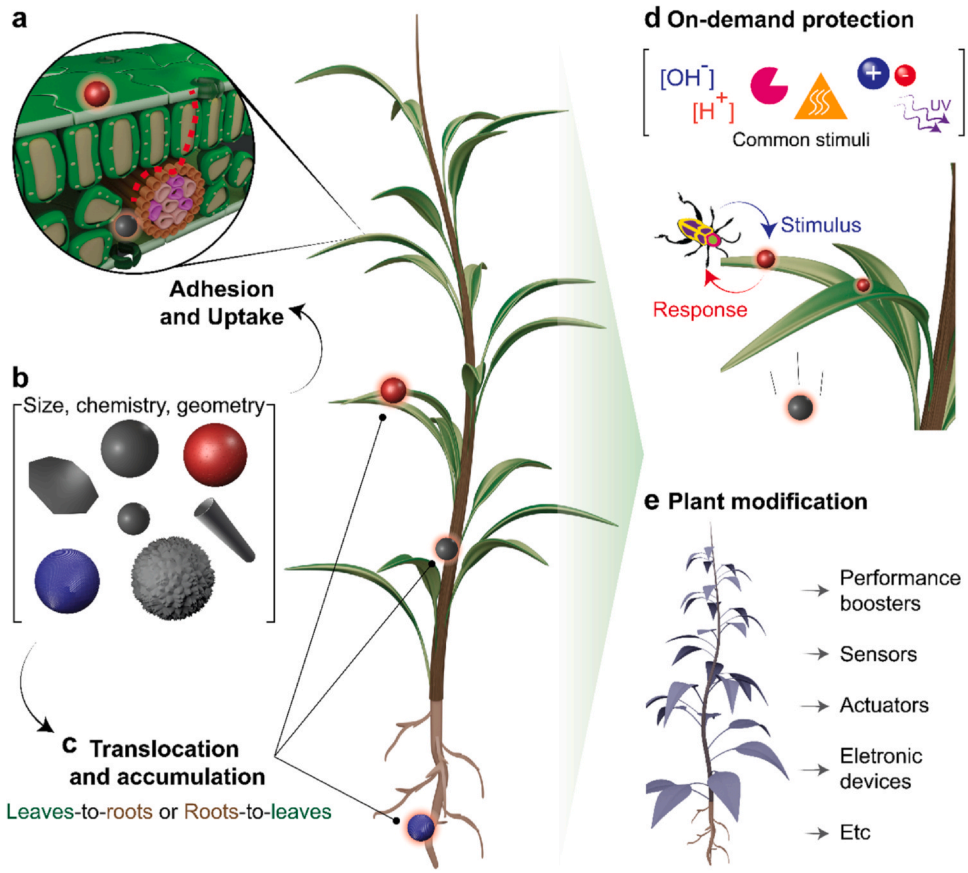

Fig. 1. Nano-enabled agriculture to promote more efficient plant protection and production, to introduce new functions and to modify plants through specific interactions. (a) Particle adhesion to plant tissues and uptake is tethered to the (b) particulate properties, which also impacts the (c) their translocation to and accumulation in a given plant tissue. (d) Targeting is key for smart delivery systems that can be designed to respond to specific stimuli, such as pH, light, enzymes, ionic strength and temperature. (e) Plant modification, towards several end-goals, is achieved through targeting particles designed to accumulate in specific sites of the plant tissues thus functioning accordingly.

which was ranked according to the order amine > acetyl > carboxylic acid (Fig. 2b). Amine-functionalized PLA carriers persisted strongly attached to the leaves, even after multiple washing steps (Fig. 2c) [31]. By tuning the type of interface interactions it was possible to modulate adhesion and therefore to optimize biocidal performance.

The strong binding capacity of tannins, especially tannic acid [32], has been harnessed to improve carrier adhesion to vegetal tissues and delivery of abamectin (insecticide) or azoxystrobin (fungicide) [33]. The retention rate of carriers coated with tannic acid on cucumber foliage was remarkably enhanced, by more than 50%, compared with the unmodified systems (Fig. 2d). The adhesion is promoted by multiple H-bonding, involving phenolic OH and the leaf surface, which also induce high persistence (Fig. 2e). Additionally, the presence of a polyphenolic molecule on the carrier lead to an increase in the pesticide photostability, with no negative effects on the release profiles [33]. Other carrier functionalization strategies have considered carboxymethylcellulose (CMC) with ethanediamine to encapsulate fipronil (insecticide) [34], coating of hymexazol-containing graphene oxide nanosheets with polydopamine [35], and coating of styrene-methacrylic acid/avermectin carriers with polycatechol [36]. We end noting that while most of the studies have measured foliar retention on cucumber leaves, a simple, non-hierarchical surface, other superhydrophobic leaves comprising hairy morphologies, may be considered since in such cases adhesion is greatly hindered. Studies on the effect of carrier morphology and surface chemistry are needed to better understand the role of interfacial phenomena and adhesion, an effort that can use the already existing experience in the area of drug delivery in biomedical research [37].

Plant uptake of engineered particulate

The uptake of particles by plants may take place through the roots and leaves [38–40], which is important in the context of modification, protection and bioaccumulation [40–42]. Herein, we describe uptake mechanisms as far as internalization and allocation strategies, which aim at protecting or modifying vegetal organisms. Translocation, the ability of particles to move within and across plant tissues, of internalized particulate occurs in root-to-leaves and leaves-to-roots direction (Fig. 3a), which is a subject that is poorly understood. Internalization via roots is an important in hydroponic cultures, while uptake by leaves is relevant for particulate delivery via spraying or casting on the foliage. Foliar uptake, for instance, has been shown to be required primarily when seeking delivery of genes to plant cells [26,27].

Similar to what has been discussed for foliar adhesion of carriers, uptake by roots or leaves is closely linked to the physical-chemical properties of the carriers. Systematic studies addressing mechanisms and dimensional thresholds for particle uptake by plants have focused on metallic particles. Such studies provide the basis for understanding the effect of size, shape and surface chemistry, e.g., to promote carrier uptake by plants and to track their biological fate, after internalization.

The correlation between particle surface charge and root uptake dynamics, via hydroponic culturing, was recently investigated using cerium oxide (CeO_2) nanoparticles (ca. 4 nm) functionalized with positively-charged, negatively-charged and neutral dextran [43]. Monitoring the Ce distribution along the plant, from roots to the leaves, for over 34 h of exposure to the particle suspensions, it was

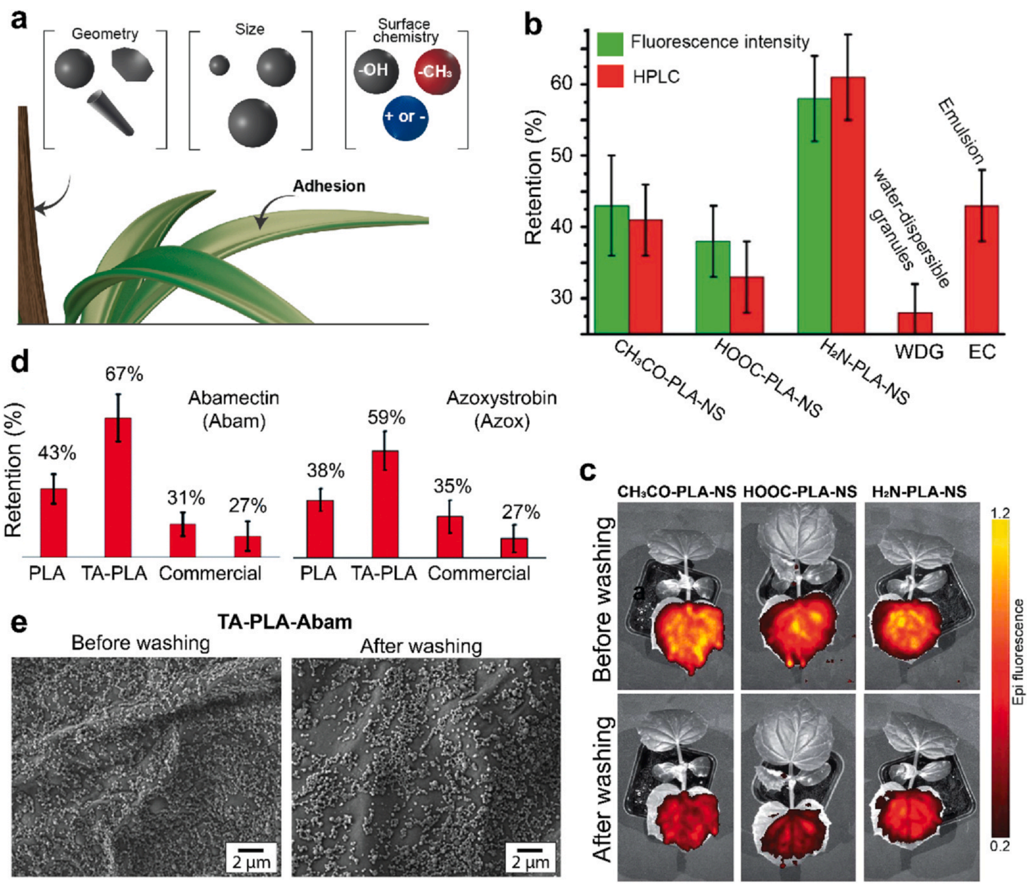

Fig. 2. (a) Carrier adhesion on plant surfaces may depend on its shape, size and surface chemistry. (b) Functionalization of submicron PLA particles with acetyl, amine and carboxylic acid groups has showed improved adhesion to cucumber leaves, when compared to commercial and emulsified biocide formulations. The content of biocide was quantified using fluorescence intensity and HPLC. Reproduced with permission from Ref. [31] Copyright (2017) The Royal Society of Chemistry. (c) The modified particles have also shown high resistance against leaching, reproduced with permission from Ref. [31] Copyright (2017) The Royal Society of Chemistry. (d) Carrier coating with tannic acid leads to enhanced attachment of PLA carriers on plant leaves, which was independent of the biocide loaded. Reproduced with permission from Ref. [33] Copyright (2019) The Royal Society of Chemistry. (e) High persistence, against washing was observed in systems where adhesion was enhanced by the use of tannic acid, reproduced with permission from Ref. [33] Copyright (2019) The Royal Society of Chemistry.

found that positively-charged CeO_2 particles adhered very strongly to the roots (Fig. 3b), displaying negligible translocation to the leaves. Over time, the negatively charged CeO_2 nanoparticles were incorporated by the roots and translocated more efficiently to the leaves. Additionally, a 15–20% of reduction from Ce(IV) to Ce(III) was verified for both roots and leaves [43]. An additional example of surface charge effects on root uptake includes the exposure of three forms of silver nanoparticles (Ag_0, Ag_2S and $AgNO_3$), measuring up to 20 nm in diameter, to the roots of duckweed (*Landoltia punctate*). It was observed that all the three forms of silver accumulated on the surface of the roots, and partially penetrated their tissues [44]. In such transport processes, the vascular anatomy of the plant is fundamental to the pattern of particle accumulation. For instance, the uptake of CeO_2 NPs (ca. 4 nm) by roots and leaves of dicots was higher than monocots, likely due to the higher transpiration rates and more considerable water uptake of the roots as the larger airspace volume in dicot leaves compared to monocot [45]. However, this is not a rule, once the root absorption driven by transpiration stream can be modified with a hydrophobic barrier imposed by Casparian strips in some botanical species [46].

Particle uptake by the leaves can take place by four different routes. Particles can enter the leave either by a cuticular or stomatal pathways, via symplastic or apoplastic transport (Fig. 3c). The stomata openings in most of the leaves display apertures in the range of micrometers and is a spontaneous route for particle uptake and allocation into or transportation through the leaf mesophyll. However, small nanomaterials are expected to also penetrate significantly through the joints of the cuticular tissues. In order to understand how the physico-chemical properties of the carriers influence their interactions and translocation through the plant tissues, a thorough study was carried out by exposing wheat leaves to gold (Au) nanoparticles of different sizes and surface chemistries [47]. The particles recovery and their distribution inside the plant varied significantly with the size (3, 10 or 50 nm) and surface chemistry (polyvinylpyrrolidone, PVP and citrate coatings) (Fig. 3d), which was highly connected to the initial adhesion to the leaves (Fig. 3e). The persistence of small Au nanoparticles on the leaves was remarkably higher when compared to the 50 nm particles. PVP-coated particles adhered better to the leaves when compared to the citrate-coated counterparts, which failed to penetrate the cuticle, even after two weeks. In contrast, for the same given size, all the PVP-coated Au nanoparticles were internalized and translocated mostly up to the mesophyll cells. Interestingly, a great fraction of the larger particles was transported to the roots [47].

Translocation from leaves to roots was observed when liposomes composed of plant-derived lipids (hydrogenated soybean L-α-phosphatidylcholine) were drop cast onto tomato leaves. Liposomes (100 nm diameter) containing Fe and Mg ions penetrated the leaf and translocated in a bidirectional fashion to deliver the ions directly to the plant cells, overcoming acute nutrient deficiency that otherwise could not be achieved through common spraying. In fact, up to a third of the applied liposome penetrated the leaf, compared to

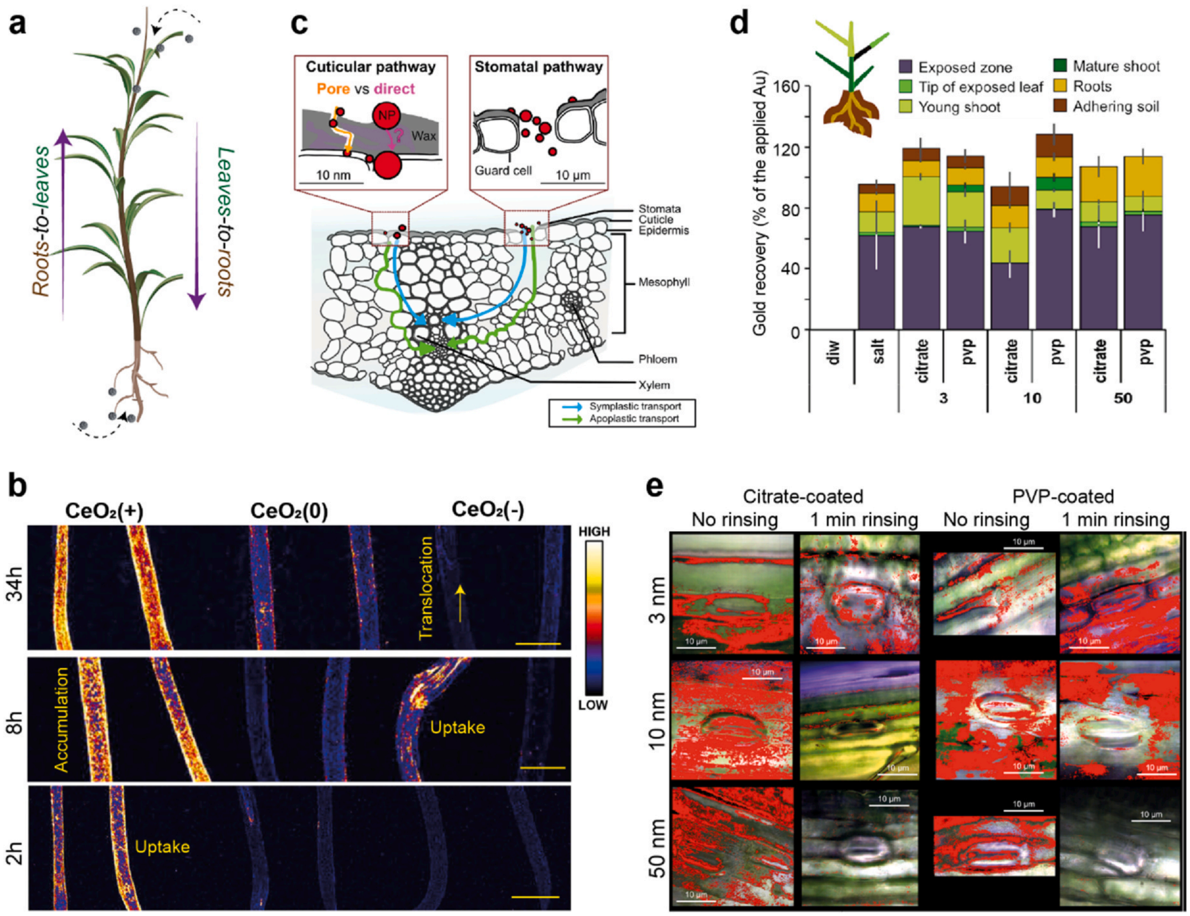

Fig. 3. (a) Particulate uptake takes place by either roots or leaves, via transport in the root-to-leaves or leaves-to-roots direction. (b) Root uptake, and further translocation in the root-to-leaves direction, of cerium dioxide nanoparticles (CeO_2) by wheat plants depends on the surface charge of the particle. Reproduced with permission from Ref. [43] Copyright (2017) American Chemical Society. (c) Uptake of nanomaterials by the leaves can take place by cuticular and stomatal opening, via either symplastic (through the cells) or apoplastic (in between the cells). Reproduced with permission from Ref. [47] Copyright (2019) American Chemical Society. (d) Translocation of nanomaterials from the leaves to the roots, as well as (e) their distribution along the plant, depend heavily on the particle size and surface chemistry. Persistence on the leaves, which is driven by the surface chemistry and size, is primary to allow uptake, i.e. no uptake takes place without adhesion. Reproduced with permission from Ref. [47] Copyright (2019) American Chemical Society.

nearly 1% of penetration when free molecules were applied in the same manner. Liposomes were found in the roots of the plant already after 24 h of exposure to the leaves [48].

More specifically in the context of particulate carriers for pesticide delivery, the leaf uptake of atrazine (herbicide)-containing poly (ε-caprolactone) capsules of ca. 300 nm in diameter, was investigated using mustard leaves [49]. The capsules remained mostly on the surface 24 h after spray deposition. However, after 48 and 96 h, the capsules were found in the vessel elements and in the spaces between the mesophyll cells, respectively. Consequently, the encapsulated atrazine showed remarkable herbicide activity when delivered to the site of action even after 10-fold dilution [14,49].

Recent examples demonstrating the uptake of carriers include zein nanoparticles applied to sugarcane through the root [50]; metolachlor-loaded polyethylene glycol (PEG)–PLGA particles (ca. 100 nm) delivered to the roots of model plants (*Oryza sativa*, *Digitaria sanguinalis*, and *Arabidopsis thaliana*) [51]; solid lipid nanoparticles (SLN), nanostructured lipid carriers (CLN), and lipid-based nanoemulsions (ca. 150 nm) in plants via the apoplastic route (transport on the surface between the cell membrane and plasma membrane) or by the means of plasmodesmata, called the symplastic pathway [52–54]. The several physiological barriers that a given carrier must pass until its uptake and translocation should be better understood, particularly as far as the interfacial interactions between the vegetal tissue and the carrier. To our knowledge, the effect of particle shape on its uptake and translocation within the plant has not been systematically investigated. Studies in the area have confirmed the successful internalization of carbon nanotubes (high aspect ratio particle) in plant's chloroplasts [26,27], but the effects of geometry and dimension have not been considered.

Natural and engineered particle formation in plants

As discussed earlier, uptake and translocation of substances by and within plants is only possible due to their vascular anatomy and their inherent capillary-driven mechanisms of fluid transport. The latter is tethered, to some extent, by the size of the plant's anatomical elements [55]. Such nature-given abilities enable the formation of particulate inside plants by (controlled) precipitation of dissolved entities, which can derive from a natural uptake from the environment (e.g. mineral enriched soils) or from man-made solutions (e.g. metallic salt solutions). The ability of plants to accumulate substances, through their roots, has been harnessed in the past decades for bioremediation of contaminated areas, e.g. by phytoextraction or phytomining [56–59], and more recently in bioaugmentation efforts [60,61]. Herein we briefly exemplify both natural and artificial formation of particles inside plants in order to correlate what is naturally done in Nature with the emerging field of bioaugmentation.

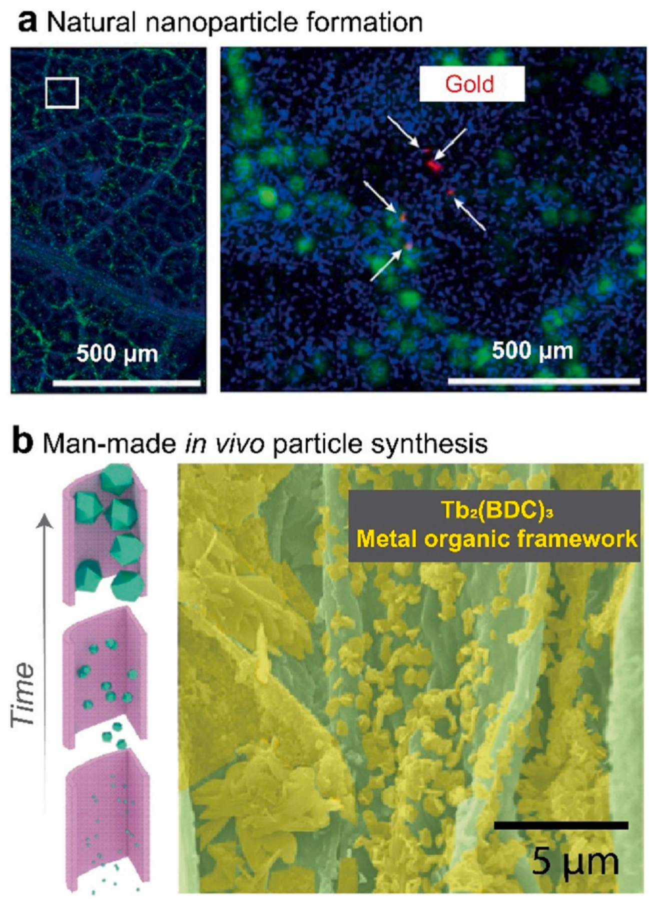

Fig. 4. Natural and engineered formation of nanoparticles inside living plants. (a) Observation of gold nanoparticles in Eucalyptus leaves due to the root uptake and translocation to leaves of gold metal soluble entities extracted the environment. The presence of gold in the leaves led to the discovery of gold deposits in deep soil layers. Reproduced with permission from Ref. [63] Copyright (2018), Springer Nature. (b) Engineered metal organic framework (MOF) inside plant tissues, which were later used as biosensors for dissolved volatile organic compounds (in this case acetone). Reproduced with permission from Ref. [60] Copyright (2018) John Wiley & Sons.

Phytoextraction has arisen as a viable passive bioremediation strategy that takes advantage of the ability of some plants (over 700 species listed so far) to hyperaccumulate substances, to remove metals from contaminated areas by accumulating them within their above-ground tissues [58]. Hyperaccumulating plants, given their high metal tolerance and specific biosynthetic pathways, can uptake over 100 times more metals than regular plants [58]. Phytomining is a concept that follows closely phytoextraction; however, it is qualitatively different as the main goal is to harvest the metal from the plant for further use, being primarily focused on to build a profitable market, even if in parallel it promotes bioremediation. Remarkable examples of phytoextraction have been showcased by the isolation of high amounts of nickel accumulated in flourishing plants (e.g. *Alyssum murale*, mustard) [59,62], gold nanoparticles in the leaves of *Eucalypts* trees (Fig. 4a) [63], cadmium and zinc in the stems of maize and other species from the Brassicaceae family (e.g. *Noccaea caerulescens*) [56,57], and iron from perennial grass (*Imperata cylindrica*) [64]. The accumulation can be extremely high, up to 40,000 mg of metal (Ni and Zn) per kg of dried biomass, which leads to extraction values of 400 kg metal by hectare yearly. Mineral micro (e.g. Fe, Cu, Zn, Mn, B, Si) and macro (e.g. N, Ca, K, P, Mg) nutrients usually impose no (or much less) toxicity against most of the plants, and therefore they could be also phytoextracted, although not in a bioremediation perspective. For instance, silica nanostructures formed inside the tissues of Si-accumulating plants, e.g. rice and plants of the genus *Equisetum*, have been extracted [65,66] and further used in agricultural nanotechnologies such as biocide delivery systems [67,68].

The potential for metal-accumulation of some plants has incentivized efforts on the utilization of plant extracts (e.g. carbohydrates, polyphenols, flavonoids, among others) as reducing and stabilizing agents in the synthesis of nanoparticles [69]. Although the synthesis is typically performed after extracting the plant-based compound [70,71], some studies have shown the possibility to synthesize the particles in vivo. In vivo synthesis of nanoparticles is highly relevant in the context of nano-enabled agriculture as it allows the functionalization of the plant to function in real-time and serve a given purpose. For instance, alfalfa plants were grown in the presence of gold precursor ($AuCl_4$ rich environment) [61]. After 2 weeks growing in optimal pH conditions, several Au nanoparticles, with diameter averaging at 10 nm, were found inside the alfalfa plants, which were later confirmed to be in crystalline state [61]. The process enabled biolabeling and bioimaging, both highly relevant in phytoprotection and plant modification strategies. More recently, metal-organic frameworks (MOFs) were formed inside a plant of the genus *Lilium* [60] (Fig. 4b). Zinc(2-methylimidazole)$_2$ and lanthanide$_2$(terephthalate)$_3$ – metal(organic ligand) – particles were synthesized following either a single or two-step process. MOFs from Europium (Eu) and Terbium (Tb) were used as bioimaging based sensors given their luminescent features. The sequence of infiltration for the MOF's precursor (organic ligands and metal ions) was found to be key for the in vivo formation [60], in which the infiltration of the organic ligand prior the metal ion has favored the MOF assembly.

Therefore, although the bioremediation and bioaugmentation fields target highly distinct outcomes, both efforts are fundamentally tethered by the inherent uptake and accumulation abilities displayed by plants. Combining the natural ability of some plants to hyperaccumulate metals with man-made strategies for in vivo particulate formation is sought to leverage several opportunities in nano-enabled agriculture, but also towards smart bio-based sustainable materials.

Targeting in intelligent agriculture

Targeting may refer to the localization of (nano)materials in specific plant tissues to serve a given purpose, or it may be associated with the programmed design of carriers to protect the plant against specific phytopathogens. The latter is often achieved through the development of stimuli-responsive carriers, as certain pathogens, for instance, secrete given molecules that trigger delivery mechanisms. The subject of stimuli-responsive systems is discussed later in this review. Targeting is extremely correlated with adhesion and uptake, as they are primary factors affecting the interactions of particles with plant tissues. Controlling adhesion, uptake or translocation of cargo-containing carriers to specific plant tissues, e.g., stomata, could be as well considered targeted delivery. Herein, we discuss targeting of carriers for plant protection, performance enhancement and to introduce new functions in plants.

Targeting for protection

Considering that the mechanism by which pathogens attack plants involve entrance in the natural (e.g. stomata and trichomes) or artificial (e.g. cracks) openings on the plant leaves, targeting delivery systems to these areas may be an intelligent approach to control more efficiently plant diseases. In such context, a recent study revealed a correlation between the surface chemistry of materials and targeted adhesion (Fig. 5a) [72]. Model Au nanoparticles (13–24 nm) were coated with citrate and an anti-pectic polysaccharide (α-1,5-arabinan) antibody (LM6M), a protein that has

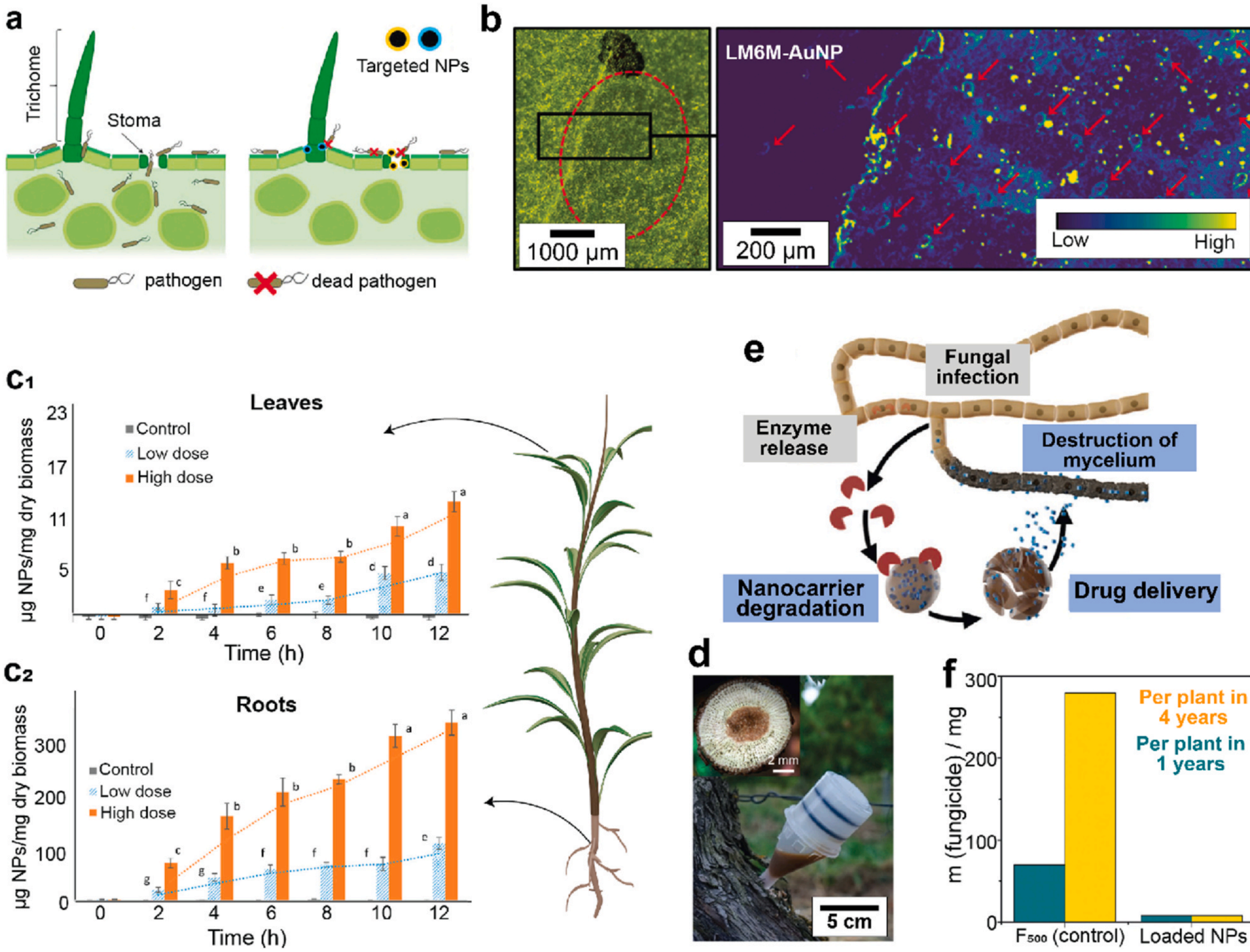

Fig. 5. Targeted delivery towards plant protection. (a) Surface coating of the nanocarriers aiming at their allocation on the stomata and trichome leaf tissues. Reproduced with permission from Ref. [72] Copyright (2020) The Royal Society of Chemistry. (b) Coating with antibody (LM6M) specially targeted stomata, as demonstrated in gold model nanoparticles. Reproduced with permission from Ref. [72] Copyright (2020) The Royal Society of Chemistry. Positively charged zein nanocarriers targeted specifically roots of sugarcane when grown hydroponically. Targeted accumulation was experimentally showed by quantifying the zein particles in both (c1) leaves and (c2) roots. Reproduced with permission from Ref. [50] Copyright (2018) American Chemical Society. (d) Lignin-based fungicide-loaded nanocarrier to target a specific grape tree disease (Esca) being applied in field. Reproduced with permission from Ref. [73] Copyright (2019) John Wiley and Sons. (e) The system is designed to respond only to the enzymes secreted by the fungi, which allows a (f) very efficient use of the fungicide over many years. Reproduced with permission from Ref. [73] Copyright (2019) John Wiley and Sons.

chemical affinity with functional groups of the stomata on the leaf surfaces. Bovine serum albumin (BSA) was used to coat the Au nanoparticles as a protein control. Suspensions of citrate-, LM6M- and BSA-coated particles were drop cast on leaves of broad bean (*Vicia faba* cv. Windsor), and their accumulation after drying was monitored by X-ray fluorescence mapping. It was shown that while the citrate surface promoted non-specific coverage of the plant leaf, LM6M-coated Au nanoparticles strongly attached to the stomata guard-cells (Fig. 5b), displaying high adhesion and persistence after rinsing with basal salt solution. Also, BSA-coated Au nanoparticles specifically targeted the trichome tissues on the plant leaf [72].

In another effort, positively charged zein nanoparticles were synthesized to deliver active ingredients specifically to the roots of sugarcane grown hydroponically [50]. The positively charged zein nanoparticles displayed high affinity to sugarcane roots because such tissues exudate a mucilage that is rich on amino- and organic-acids thus providing an overall negative net charge on the roots surface. One can expect several alternative molecules that could be used for the same purpose, such as chitosan, either as coatings [170] or as a carrier [171] . The polydisperse zein nanoparticles, sizes from 50 to 230 nm, were quantified in the roots and found to be at least one order of magnitude higher (300 μg nanoparticles by mg of biomass) when compared to the leaves (up to 15 μg nanoparticles by mg of biomass) (Fig. 5c1–2) [50]. In this case, size may have synergized with surface chemistry to prevent extensive uptake and translocation to the leaves. However, particles in this size range have been demonstrated to be passively uptaken by plants, as discussed earlier in this review.

Cross-linked lignin nanoparticles were designed to carry a hydrophobic fungicide (pyraclostrobin) targeting a specific, very economically important, grapevine trunk disease, named Esca [73]. First, kraft lignin was methacrylated and then cross-linked with 2,2′(ethylenedioxy)bis(ethylamine) in the presence of the fungicide. The fungicide loading efficiency was over 90%. The cross-linking step was performed in a microemulsion using surfactants to stabilize the oil-water interface. Using a microfluidizer, the system was upscaled to liter volumes that allowed investigations in the field (Fig. 5d) and over many years, which is rare in experimental validations of such delivery systems. The cross-linked lignin-based carriers (with size adjusted from 200 to 700 nm) responded only to the specific enzyme secreted by the Esca-causing fungus creating a *negative feedback* type of control (Fig. 5e). Targeted action of the engineered materials allowed control over Esca much more efficiently when compared to the unloaded fungicide (Fig. 5f) [73].

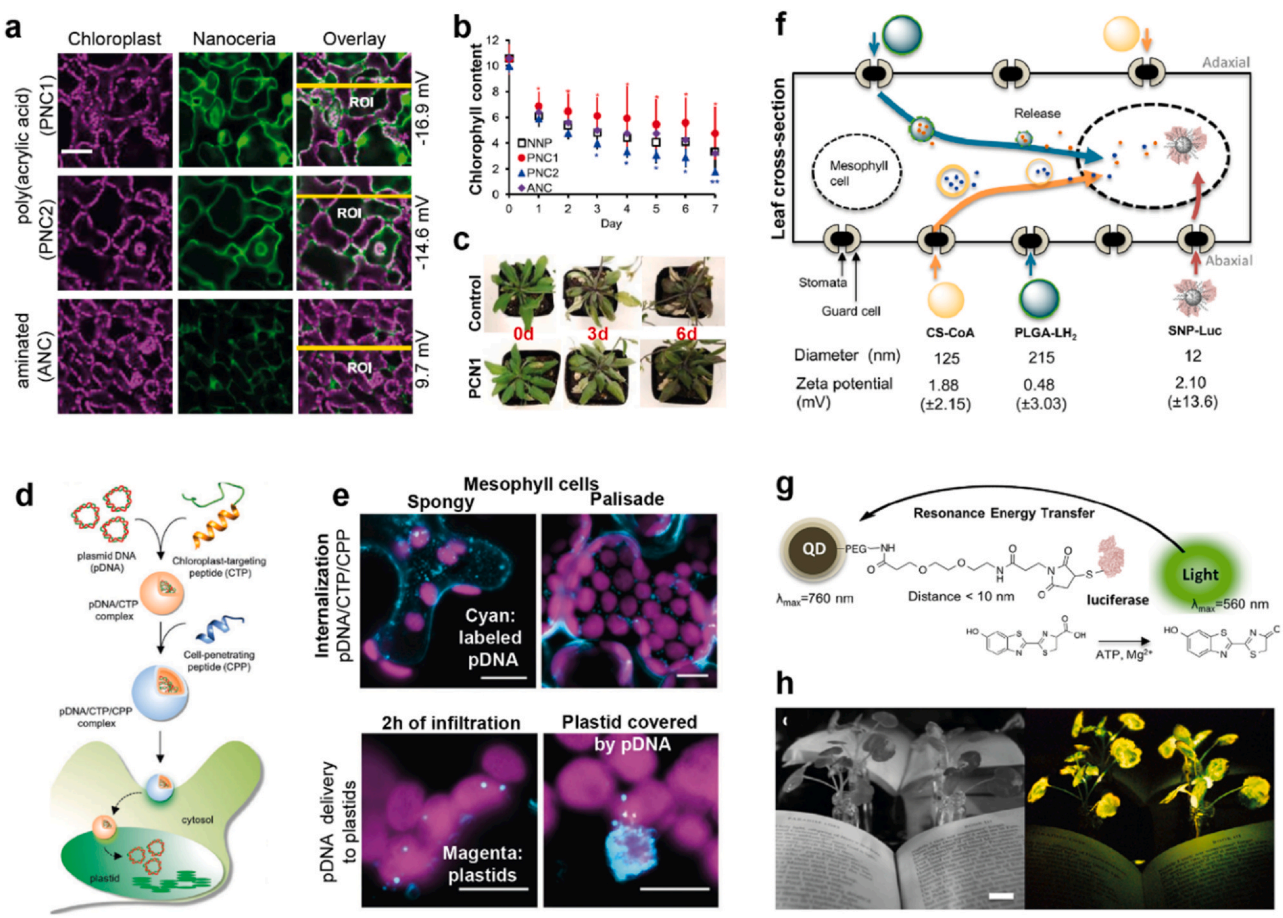

Fig. 6. Targeting nanomaterials to enhance plant's performance or to introduce new functions. Use of cerium oxide nanoparticles to (a) target chloroplast to promote radical scavenging of reactive oxygen species, to consequently (b) improve the photosynthesis performance over abiotic stressful conditions (excess of sunlight demonstrated in (c)). Reproduced with permission from Ref. [79] Copyright (2017) American Chemical Society. (d) Lipid-based nanocarrier for plasmid DNA (pDNA) delivery in the plastid, prepared via ionic complexation, that can (e) efficiently target cells in the mesophyll to deliver pDNA. Reproduced with permission from Ref. [82] Copyright (2019) John Wiley and Sons. (f) Use of a variety of nanocarriers, of given size and surface chemistry, to target different tissues within the leaf, to deliver an enzyme and a molecule to different, targeted sites. Reproduced with permission from Ref. [83] Copyright (2017) American Chemical Society. The co-delivered aimed at a specific (g) bioluminescence reaction in order to create (h) light emitting plants. Reproduced with permission from Ref. [83] Copyright (2017) American Chemical Society.

Targeting for enhanced performance and functions

Additionally to targeting particles to specific plant surfaces (stems, leaves or roots) for their protection against phytopathogens, there is a growing interest in the development of engineered systems to target specific plant cells, aiming at the delivery of a great variety of molecules to enhance the plant's performance, or to introduce new functions [74]. The enhancement of the plant performance is commonly approached by delivering DNA molecules to specific organelles, as an attempt to genetically modify the plant, thus developing evolved – e.g. more productive or resistant – new lines [23,75]. The introduction of new functions in living plants through nanotechnology, recently termed *plant nanobionics*, is a powerful and versatile tool for achieving, for instance, real time sensing of the soil conditions in a crop field and to monitor the plant's health [28,29]. Related issues are discussed herein, putting in perspective the importance of specific targeting and the associated nanotechnology-centered strategies.

The photosynthetic machinery in the chloroplast cannot convert all received sunlight into sugars (less than 10% of full sunlight saturates the capacity of the photosynthetic system). It was found that owing to its unique optical and electronic properties, single-walled carbon nanotubes (SWCNTs) embedded within the chloroplasts can enhance the light-centered reactions of photosynthesis. The mechanism relies on the conversion of absorbed light energy – in a wider spectrum than the chloroplast itself – by the SWCNTs into excitons that can transfer electrons to the photosynthetic plant machinery. However, targeting nanomaterials to allocate inside the chloroplasts cells requires their transport through the lipid bilayer of the outer chloroplast envelope. In such context, surface functionalization of the SWCNTs with $ss(AT)_{15}$ (a DNA fragment) or chitosan proved to promote efficiently the imbibition of the nanotubes within the chloroplasts, whereas polyvinyl alcohol (PVA)- and lipid-coated SWCNTs did not interact with the lipid bilayer [76]. Remarkably, SWCNTs with either highly negative or positive electrostatic potential favored the nanotube to adsorb on the chloroplast lipid membrane, and subsequently, to be internalized by passive uptake. With the allocation of the SWCNT within the cells, it was possible to enhance the photosynthesis and chloroplast reactive oxygen species (ROS) scavenging, as well as to detect the presence of nitric oxide, a plant biomarker to determine oxidative stresses [76]. In a similar context, the enhancement of light energy usage by specific and well-allocated nanoparticles has been demonstrated in biochemical synthesis related to the metabolism of yeast cells [77].

The internalization mechanism through the chloroplasts lipid membrane, named lipid exchange envelope penetration (LEEP), has been further investigated in detail and modeled to determine whether a given pre-designed nanoparticle would spontaneously and kinetically be trapped within the organelles [26,78]. Understanding, and validating the LEEP mechanism prior to the synthesis of the engineered nanoparticle has been instrumental to efficiently target nanoparticles to given plant cells [26]. In another example, chitosan-complexed with SWCNTs were used as nanocarriers for plasmid DNA (pDNA) for delivery inside the chloroplasts, aiming at genetic modification of the plant [27]. Interestingly, due to strong ionic interactions at the pDNA-chitosan interfaces, at the relatively acid pH characteristic of the leaf mesophyll, the pDNA-chitosan-SWCNT complex protected the pDNA very well until the penetration into the weakly basic pH (ca. 8) inside the chloroplast. At basic pH, the delivery of the pDNA occurred due to its weaker interface with chitosan, thus disassembling the ionic complex [27]. This platform for transgene delivery has demonstrated to be simple and cost effective. As a bioengineering platform for line development, there would be no concerns related to persistence of nanoparticles in the plants (especially in the case of edible plants) due to the multiple rounds of selection and breeding usually associated with modified crop organisms.

Nanoparticles such as CeO_2, have been also investigated in bioaugmentation efforts, through targeted localization within plant tissues [79–81]. Nanoceria acts as a hydroxyl radical scavenging of ROS that decrease the photosynthetic performance of the plant. Typically, ROS accumulate from plant abiotic stresses, such as the excess or completely absence of light. Recently, it was shown that targeting negatively charged, small CeO_2 (ca. 10 nm) to allocate inside the chloroplast (Fig. 6a) could improve the photosynthesis performance of the plant beyond typical boundaries, when submitted to stressing conditions (excess of light, heat or dark chilling) [79]. Surface functionalization and size (must be below the cell wall porosity) of the CeO_2 played crucial roles for its successful internalization inside the chloroplast. For instance, whereas poly(acrylic acid)-CeO_2, displaying $\zeta = -16.9$ mV allocated efficiently in the chloroplasts (46%), aminated-nanoceria of similar size but positively charged ($\zeta = 9.7$ mV) corresponded to much lower internalization success (27%). Transportation of the nanoparticles took place by non-endocytic pathways, which is heavily driven by the electrochemical gradient of the plasma membrane potential. The ratio between the ionized states of Ce in the nanoparticle (Ce^{3+}/Ce^{4+}) influenced the bioaugmentation performance. CeO_2 nanoparticles with lower Ce^{3+}/Ce^{4+} ratio (35%) performed better than the ones with higher ratio (60.8%), as far as reducing ROS levels, and protecting the plant photosynthesis from simulated harsh abiotic stresses (Fig. 6b and c).

In another example, a peptide-DNA complex was designed to target specific plant cells (plastids) aiming at genome engineering [82]. Two peptides were used; one for targeting specifically the chloroplast cells (i.e. chloroplast-targeting peptide, CTP, KH9-OEP34); and the other to promote cell penetration (i.e. cell-penetrating peptide, CPP, BP100). The negatively charged pDNA was first electrostatically complexed with the positively charged CTP peptide to form spherical nano-scaled particles, which were further coated by the CPP peptide (Fig. 6d). Such design allowed the clustered CTP-pDNA-CPP particles, ca. 150 nm in size, to move toward and translocate through the plant cell membrane and deliver the DNA to the plastid efficiently (Fig. 6e). Uptake occurred via vesicle formation and intracellular trafficking. This gene modification strategy has been shown to work not only in model plant specimens such as *Arabidopsis thaliana*, but also for tobacco and tomato plants, among others [82].

Nanomaterials can be designed, through surface functionalization and by controlling size, to specifically allocate in targeted leaf tissues aiming at inserting new functions in the living plant. This has been successfully demonstrated during the development of plants emitting light in the visible range [83]. The system comprised the firefly luciferase enzyme loaded in silica nanoparticles and luciferin encapsulated in poly(lactic-co-glycolic acid) (PLGA). Such nanomaterials were engineered to enable trafficking and localization in specific organelles within the living plants (watercress), where the conditions were favorable for the reactions to happen (Fig. 6f). Briefly, as the stomata opening is bigger than 10 µm, all nanoparticles designed could enter the leaf mesophyll. However, by size exclusion, each nanoparticle could be targeted to a given tissue. The 12 nm silica-containing luciferase localized near the organelles, chloroplasts and mitochondria. Whereas, the larger ~ 200 nm luciferin-containing PLGA particles were allocated within the intracellular spaces in the mesophyll, thus releasing the luciferin to encounter the enzyme that was released deeper in the leaf tissues. In the presence of adenosine triphosphate (ATP), oxygen (O_2), and magnesium ions (Mg^{2+}), the firefly luciferase catalyzed the oxidation of the released luciferin, thus, creating bioluminescence (Fig. 6g and h). Such approach is a concept that can be used for sensing purposes in agriculture [28,84].

Stimuli-responsive delivery systems

Traditional agrochemical applications, either for protection or fertilization, tend to display uncontrollable and fast (burst) release of the pesticides to the surrounding environment. Consequently, aligned to resource usage efficiency, several health-centered issues arise from the volatilization of the toxic molecules, its leaching into the soil and groundwater as well as its bioaccumulation in non-targeted fauna and flora. The preparation of engineered release systems gave a degree of control over the delivery dynamics of agrochemicals; however, more specific systems, that can respond to specific stimuli are desirable to bring an extra and more precise control over the release dynamics. For applications in agriculture, however, the carriers must be biocompatible, biodegradable and essentially be inert to other chemicals (e.g. other agrochemicals for fertilization) and non-targeted organisms. Such features restrict significantly the options for precursors to build feasible stimuli-responsive systems, especially because the carrier-cargo interface plays a key role in determining the release mechanisms and response to a given stimulus [85–88].

In the context of agriculture, the primary stimuli responsible for triggering cargo release derive from the environment surrounding the individual to be protected or modified. Depending in the interplay between the carrier design and the type of stimulus, the delivery systems can display an intermittent (Fig. 7a) or progressive release profile (Fig. 7b). The most common stimuli in botanical applications relate to the presence of enzymes (Fig. 7c), changes in temperature (Fig. 7d), light, humidity, pH (Fig. 7e) and ionic strength, as well as variations in biomarker levels and excretion of natural exudates from harmful organisms. Briefly, a progressive profile could be characterized by an infestation of harmful microorganisms that secrete specific molecules while growing and multiplying; thus, the stimulus would be present until the complete elimination of the colony. An intermittent profile is often a result of repetitive cycles such as day and night. Surprisingly, although there is a vast spectrum of possibilities, in stimuli-driven delivery systems for agriculture are still in their infancy. Here, we discuss the most recent outcomes of delivery systems triggered by or in response to stimuli (biotic or abiotic) which are widely present in natural environments.

Temperature

Temperature fluctuations directly affect the emergence, prevalence, and development of agricultural pests. It is well known that most of the insects, weeds, bacteria, and fungi become more active with the increase of temperature. For instance, *Xanthomonas oryzae* (one of the most important bacterial diseases in rice) prevails in daytime when the temperatures are ca. 35 °C [89]. Additionally, it has been shown that the defense mechanism of plants may be compromised at elevated temperatures [90], thus making the plant more

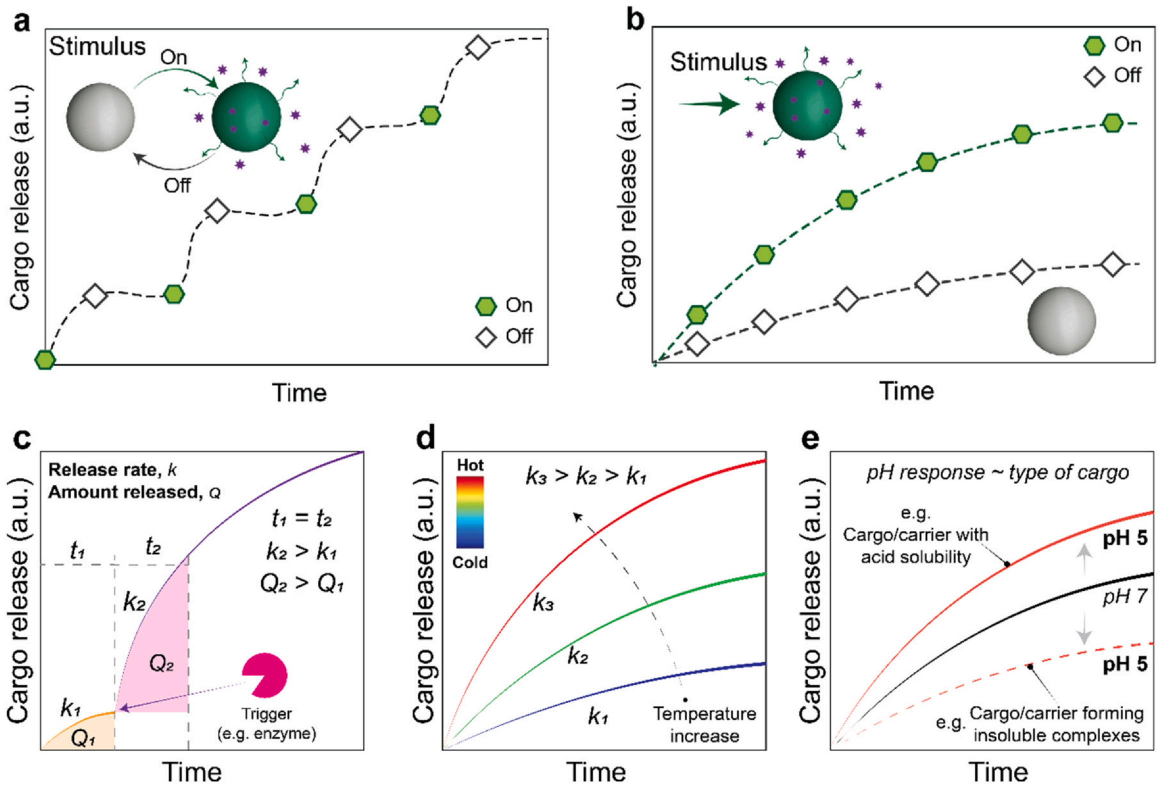

Fig. 7. Main two types of release profiles achievable when designing stimuli-responsive delivery systems: (a) Intermittent release, characterized by cyclic stimulus, e.g., sunlight. (b) Progressive release, which takes place under a continuous stimulus, e.g., microbial colonization. Few examples of typical alterations in the kinetics of release upon stimuli include (c) the presence of enzymes that usually triggers carrier modification and results in faster release kinetics, (d) temperature typically has a positive correlation with the release kinetics, and (e) pH response is fully tethered to the cargo/carrier properties.

vulnerable to the attack of pests. However, this is not a general rule since some organisms are also adapted to cold or warm climates. Therefore, through specific thermal-responsive release systems, engineered to target a given disease, a pesticide can be preserved at non-optimum temperature but released at a temperature that approaches the microorganism's optimum growth range. Thermal responsiveness has been mainly achieved by using materials that change with temperature, such as those with a lower critical solution temperature (LCST). The latter include thermosensitive synthetic polymers such as poly(N-isopropylacrylamide) (PNIPAm), poly (N, N-diethylacrylamide) and poly (N, N dimethylamino)ethylmethacrylate as well as biopolymer counterparts such as chitosan and chondroitin sulfate [91]. Generally, a thermo-responsive polymer is used to assemble the carrier, as a shell or part of the bulk, for a given active agent. However, some of these polymers have LCST above environmental capacity (< 40 °C), requiring man-made triggering to be efficiently used (e.g. temperature control in greenhouses).

For example, a temperature-responsive delivery system was proposed by using a nanocomposite consisting of a clay compound (attapulgite, ATP), ammonium carbonate (NH_4HCO_3), amino silicone oil and PVA to create a carrier to delivery glyphosate – a known herbicide. Thus, the temperature responsiveness of the delivery system was achieved by the temperature-dependent water dissolution profiles of PVA, which increased at higher temperatures. Also, the herbicide-loaded thermo-responsive carriers clearly showed better efficiency over weed control when treated at 40 °C (Fig. 8a). Such result arises from a faster release kinetic at high temperature when compared to the respective controls [92]. Similar effects have been observed for other thermosensitive controlled release systems for fertilizers (copper, potassium, and phosphorus) [93] or a wide range of commercial biocides such as emamectin [94], avermectin [95,96], pyrethrins [97], diazinon, trifluralin and alachlor [98]. In such efforts, it was shown that the temperature to which the cargo display faster release dynamics is mainly tethered to the carrier material.

The cargo-carrier interfacial interactions may also play a role in the temperature-centered dissolution kinetics of the cargo from the carrier. For instance, the release dynamics of thymol from functionalized silica carriers (functionalities –OH, $–NH_2$, and –COOH) in general displayed faster release rate as the temperature increased from 25 °C to 45 °C. Interestingly, the stronger interface between thymol the $–NH_2$ functionalized carrier was shown to require more thermal energy in order to promote dissolution of the carrier, which was later attributed to the higher activation energy of the system [88].

Additionally, some systems may be triggered not only by temperature shift but by light or magnetic fields that can induce hot and localized spots within the carrier. In these systems, materials with photothermal (e.g. gold or polydopamine nanoparticles) or magnetic (e.g. Fe_3O_4 or Ni nanoparticles) properties can be excited by a light stimulus or magnetic field, thus to convert the photon/magnetic energy into thermal energy that alters the structure of the carrier, and therefore promote the delivery of the cargo [99]. Although such systems have been mostly exploited in biomedical applications [100], they could offer a powerful set of tools to improve the management of agrochemicals by conditioning and optimizing the practical aspects to provide the stimulus in large scale and open field applications. A few examples within agriculture include the preparation of a near-infrared (NIR)-responsive system for controlled release of pesticides. The latter system comprised polydopamine microspheres (photothermal agent) capped with a PNIPAm shell (thermosensitive agent) for the encapsulation of imidacloprid (an insecticide) (Fig. 8b). The core-shell hybrid displayed a positive response to NIR-light sensitivity when exposed to NIR-light (808 nm with 2 W/cm^2). Thus, the temperature of the release media increased

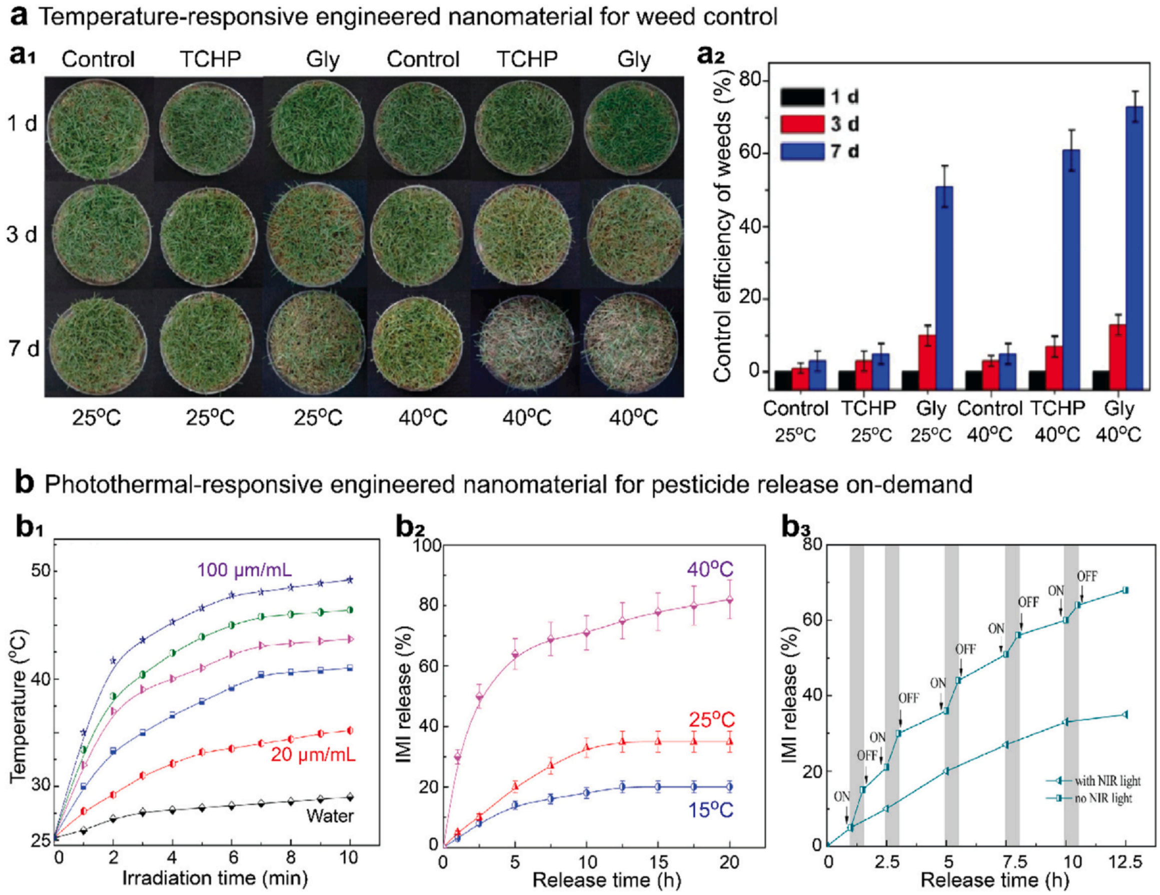

Fig. 8. Temperature (a) and light (b) responsive systems for the delivery of agrochemicals. (a1) Pictures of weed (*Zoysia matrella*) samples treated with encapsulated glyphosate in a thermo-responsive carrier (TCHP), pure herbicide (GLY) and control, at different temperature over 7 days. The pictures emphasize the temperature effect on the control of the weed, as demonstrated quantitatively in (a2). Reproduced with permission from Ref. [92] Copyright (2017) American Chemical Society. A photothermal-responsive system built from polydopamine and poly(N-isopropylacrylamide) (PNIPAm) to deliver a pesticide. The systems use near-infrared light to increase the temperature of the carrier material (b1) to then promote the relaxation of the polymeric chains of the PNIPAm to allow the release of the pesticide (b2). Therefore, the system can react in an intermittent fashion to quickly increase the release rate of the pesticide (b3) Reproduced with permission from Ref. [101] Copyright (2017) American Chemical Society.

directly with the concentration of the suspended delivery system (Fig. 8b1), which consequently resulted in faster release due to the increase in temperature in the media (Fig. 8b2). Moreover, the release profile was intermittent (Fig. 8b3), similar to that suggested in Fig. 7a [101]. In another study, a NIR-responsive system for the controlled release of hymexazol was proposed by using graphene oxide and polydopamine, also with significant NIR-laser response [35].

Light

Delivery systems that respond to incident light have shown satisfactory results for the management of agrochemicals. They can be regulated by parameters such as light intensity, wavelength and exposure time, which is especially attractive for applications in greenhouses where light can be dosed. However, when preparing light-responsive systems, one should consider the size and materials of the carriers. For instance, it was shown that visible light penetrates significantly only in the outer surface of the silica-based carriers, while UV light is completely blocked [67]. Such observations may not be as significant for nanoscaled carriers, but one should consider light scattering and diffraction effects for the selection of the materials to be used as carrier. Also, photocages – molecules activated by light – when associated with nanocarriers, are expected to trigger the release of the loaded-cargo as a response of exposure to light of a specific wavelength (e.g. UV, visible or NIR). The triggering mechanism may involve *i)* photo driven isomerization and oxidation, *ii)* surface plasmon absorption and photothermal effects or *iii)* photo driven hydrophobicity changes, thus causing fragmentation or de-crosslinking of the carrier [102]. Examples of photocages include 2-nitrobenzyl, coumarin, p-hydroxyphenacyl, nitroindoline, azobenzene or their derivatives.

More specifically for agriculture applications, an example of light-responsive delivery system was built from the combination of biochar, clay (attapulgite), silicone oil and azobenzene, e.g., in the design of a carrier to deliver the herbicide glyphosate. In such effort, azobenzene acted as the light-triggering component that could specifically react when receiving irradiation at 365 and 435 nm [103]. Additionally, in another molecularly engineered system that used coumarin-caged spirotetramat-enol, the insecticide was only released when exposed to blue light (420 nm), and could respond intermittently (switching on and off) by light [104]. Also, coumarin was demonstrated to be very versatile as light-triggering component. In another study, an acrylate and PEG carrier, containing coumarin, was designed to be a photo-responsive system for the delivery of 2,4-dichlorophenoxyacetic acid (herbicide) that showed controlled release of the loaded-herbicide only in the presence of UV light (310 and 350 nm) [105].

pH

Changes in pH of the sorrounding microenvironment are strongly connected to the infestation of pathogens since the acidic condition may be related to the capacity of the harmful organism to successfully colonize, invade, and kill the targeted host. For instance, certain fungi such as *Fusarium oxysporum*, *Sclerotinia sclerotiorum*, *Aspergillus* sp. and *Penicillium* sp. [106], secrete significant amounts of organic acids to damage host tissues. It is suggested that acid conditions are the best microenvironment for the growth and multiplication of these phytopathogens. Relevant for foliage diseases [107], for example, is the fact that the pH of the phloem is moderately alkaline (7.3–8.5) and differs significantly from other regions of the plant that are usually acidic (pH 5–6). Engineered carriers with pH-responsiveness have attracted significant attention, thus resulting in the biggest share among all stimuli-responsive delivery systems for agriculture. Promising delivery systems have been developed to act from stimulus arising from pH shifts either for pesticide [108–113] or fertilizer [114–116] applications.

For example, an amphiphilic polysuccinimide star copolymer was developed to encapsulate naphthaleneacetic acid (a model pesticide molecule) and to display pH responsiveness, especially at neutral to basic conditions. By tracking the model molecule inside the vegetal tissues, it was showed that it was mostly released in the phloem, where the pH is ca. 8 [117].

Manipulation of cargo-carrier interface interactions is also of interest to regulate the response of the system to pH changes (Fig. 9a). pH-dependent protonation/deprotonation of amine, hydroxyl or carboxylic acid groups can affect the dissolution/release profiles. This was demonstrated by loading thymol, a phenolic biocide, into –NH_2 modified silica carriers. For instance, at pH 7 the NH_2 group protonates to NH_3^+, while at this pH thymol displays O^-, thus making a strong interface that decreases the release of the biocide. On the other hand, at acid pH the carrier (with NH_3^+) and the biocide (with OH) do not interact as strongly, thus displaying faster release (Fig. 9b) [88].

Macro-scaled delivery systems such as hydrogels, i.e. not intended for internalization in plants, but can be manipulated to react to the physiological conditions of the surrounding soil. In this context, plants such as rapeseed (*Brassica napus* L.), that secrete malic and citric acids from the roots during phosphorus deficiency [118], decrease the pH of the microenvironment. Such pH change can be harnessed to trigger nutrient delivery from a given engineered delivery system, especially fertilizers. Several materials with ionizable groups capable of changing their conformation or solubility in response to pH have been developed. Examples include polyacid or polybasic polymers, such as poly (methacrylic acid), poly(N, N-dimethylaminoethyl methacrylate), poly(succinimide), chitosan, poly (acrylic acid), poly(ethyleneimine), among others. Porous loaded-nanoparticles could also be infused in the polymeric hydrogels to be released accordingly to structural changes in their microstructure [119,120].

Hydrogel-based delivery systems have been developed by crosslinking CMC with citric acid in the presence of bentonite (clay) to release thiamethoxam insecticide faster at alkaline conditions due to hydrolysis of ester crosslinking [121], and polydopamine/calcium alginate/attapulgite (clay) hydrogel to release chlorpyrifos (organophosphate pesticide) when exposed to more alkaline pH [122] (Fig. 9 d). In the later, a more significant swelling and water dissolution of the calcium alginate at alkaline conditions drove the pH responsiveness. Additionally, hydrogels are attractive candidates for a wide range of agriculture applications because they can be multifunctional as a delivery system and as a soil conditioner, to

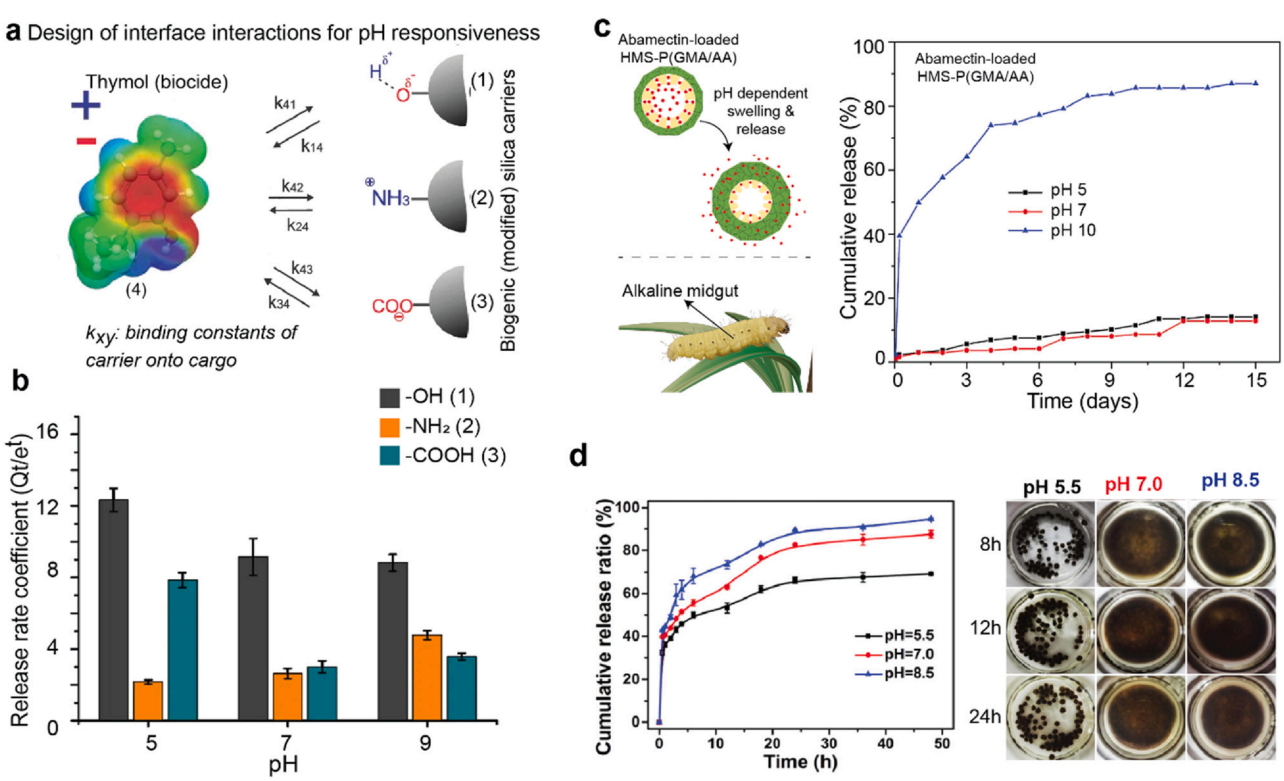

Fig. 9. (a) Carrier-cargo interfacial interactions can be designed to be responsive to changes in pH in the release media, in this case by taking advantage of protonation/deprotonation effects. Reproduced with permission from Ref. [88] Copyright (2018) Springer Nature. (b) The release rate of each modified systems relates to their (de)protonated state and interactions with the biocide (thymol, a phenolic compound). Reproduced with permission from Ref. [88] Copyright (2018) Springer Nature. (c) pH-responsive delivery system based on silica mesoporous particles coated with polymer designed to swell at alkaline pH and therefore release the pesticide in the alkaline environment of the pest midgut. Reproduced with permission from Ref. [124] Copyright (2019) Elsevier. (d) Nanostructured hydrogel beads based on polydopamine, attapulgite and calcium alginate carrying chlorpyrifos that is effective in controlling grubs without non-targeted toxicity due to the pH responsiveness. Reproduced with permission from Ref. [122] Copyright (2018) American Chemical Society.

improve the water retention thus reducing the water scarcity in growing plants [123].

Responsive polymers can be used to coat or to form composites with porous particles and to induce responsiveness at the nanoscale. A few examples have been demonstrated, such as mesoporous silica nanoparticles, which were coated with carboxymethyl chitosan, toward gate-keeping functions, for release of a fungicide, Azoxystrobin [110], salicylaldehyde-modified mesoporous silica for a controlled release of the insecticide chlorpyrifos [108], and poly(glycidyl methacrylate-co-acrylic acid) grafted hollow mesoporous silica for the controlled release of the insecticide abamectin [124] (Fig. 9 c). Silica nanostructures have been heavily exploited in such strategies due to their high degree of manipulation as far as surface chemistry, porosity and size.

A great variety of strategies have been taken for the development of pH-stimuli responsive carriers for botanical applications. They include the phytic acid-modified wheat straw platform for the release of the insecticide imidacloprid [109]; magnetic polysaccharides for the release of quaternary ammonium herbicides [125]; poly(dopamine)-graft-poly(acrylic acid) brushes for the release of Cu, K, P and N [114]; Fe-EDDHSA/$CaCO_3$ hybrid crystals [116] and microcrystalline and clay microfibers [115] for the controlled release of iron as a micronutrient. Nowadays, however, the development of pH-responsive systems should not only focus on biocidal performance, but also on non-targeted toxicity, which is an essential factor to consider when launching a new technology [126,159].

Ionic strength

Not many efforts have focused on the development of delivery system that respond to changes in the ionic strength of the surrounding media. However, such systems could play an important role in the management of agrochemicals, especially under stress conditions. For instance, plants may secrete exudates that change the ionic strength of the soil microregion under a given external stimulus, such as plant competition, nutrient deficiency, or water limitation [127]. Another interesting approach would be to design ion-responsive biocide systems to respond to the presence of specific ions such as those found in insect tracts. In the latter, the system would be activated only if ingested by the targeted insect, and nothing or very minimal would be released to non-targeted organisms.

An anion-responsive system for fertilizer release was recently reported [128]. Hollow/mesoporous carbon was modified with polyethyleneimine to associate with selenate via electrostatic attraction. The delivery of Se ions from the nanocarrier was sensitive to the presence of PO_4^{3-}, CO_3^{2-} and OH^-, which occurred by ion exchange. The study showed that such system decreased losses, from leaching, of Se ions in the soil, as well as regulated the absorption of selenite by vegetables [128]. Engineered fertilizers based on layered double hydroxides (LDH) can display ion-responsiveness due to the great capacity of LDHs to carry ion-exchange with charged species found in the soil [129]. Additionally, in another effort, positively charged mesoporous silica nanoparticles (functionalized with trimethylammonium) were loaded with 2,4-dichlorophenoxyacetic acid (2,4-D), using its anionic form (sodium salt). The ionic complex at the cargo-carrier interface was responsive to the ionic strength of the media, at which ion exchange mechanism was the driven factor leading to responsiveness [130].

Microorganisms

The delivery rate of a given cargo can be modified by interactions of microorganisms with its carrier material. This is especially relevant for carriers built from biopolymers or biomolecules, such as lipids, polysaccharides and proteins since they are easily broken down by enzymes. The extent of the modifications, as far as release performance, depend on the diversity, type and activity of the microorganisms, which are usually complex in natural environments such as soils. Although not displaying a triggering effect but rather a stimulant for the delivery, kasugamycin-pectin conjugate carriers released aminoglycoside antibiotic when in the presence of *Pseudomonas syringae pv. lachrymans* – a pathogenic bacteria [131]. On the other hand, soil microbiota – type and volume – has shown to cause marginal effects on the release profiles of nitrogen from slow-release fertilizers based on urea-formaldehyde, isobutylidene diurea, and crotonylidene diurea [132]. Due to the natural complexity of soil microbiota, and associated synergism of multiple organisms taking place in a single pathogenic colonization, the development of microbe-triggered delivery systems for agriculture are rare. Some successful developments in the biomedical area, however, have incentivized efforts in botanical applications. A timely example is the use of hyaluronic acid (HA)/poly-L-lysine (PLL) LbL nanofilms for the treatment of wounds that display faster release in contact with virulent bacteria, such as *Pseudomonas aeruginosa* [133]. On the other hand, microorganisms are being associated with carriers to increase the efficiency of slow release biofertilizer formulations, mostly to reduce the cost of the engineered system. This has come to attention when *Raoultella planticola* (Rs-2 strain) was encapsulated in composite matrix composed by clay (bentonite) and alginate. Such strain increases the germination of the seeds and promote growth in saline conditions; however, its encapsulation was key to improve colonization, mostly because these cells are susceptible to natural competitors in the soil [134].

Redox

A variety of redox molecules have been studied aiming to function as gatekeepers in controlled release systems, e.g. cadmium sulfide (CdS), β-cyclodextrins, thiol-terminated PEG(-SH). These molecules can alternate between its reduced and oxidized forms, which can manipulate interactions at the molecular scale. For instance, when mounted at the entrance of templated pores in carrier, such redox-responsive interactions can open and obstruct the access to the pores in an intermittent manner, on demand. This system allows any loaded molecules to go out (released to the environment) in a very controlled manner. Glutathione (GSH) and 1,4-dithiothreitol (DTT) are the mainly "bond-breaking" from these redox molecules. Glutathione is one of the major component in the natural antioxidant defense system of the plants [135,136], therefore, under infestation, the plant would naturally excrete such molecules that trigger the delivery of the entrapped/encapsulated biocide. Few examples related to the redox-responsive gate-keeping strategy include the fabrication of decanethiol gatekeeper grafted onto mesoporous silica nanoparticles (Fig. 10a1) for the stimulus-responsive release of salicylic acid used as a phytohormone. Here, the release rate of the plant hormone was significantly higher in the presence of relatively small amounts of glutathione (Fig. 10a2) [137]. In another study, a redox-responsive hydrogel based on disulfide-crosslinked CMC was developed for the controlled-release of other plant hormones (naphthyl acetic acid and 6-benzyladenine), when exposed to 1,4-dithiothreitol. The CMC-based responsive hydrogel was also capable of sequestering undesirable metal ions, such as Cu^{2+} and Hg^{2+} [138].

Enzymes

Several enzyme-responsive materials have been developed over the last 80 years of research on drug delivery and for biomedical applications [139]. However, most of these systems never make it to the market, in clinical applications, due to high restrictive regulations as far as testing, practical validation and technology transfer.

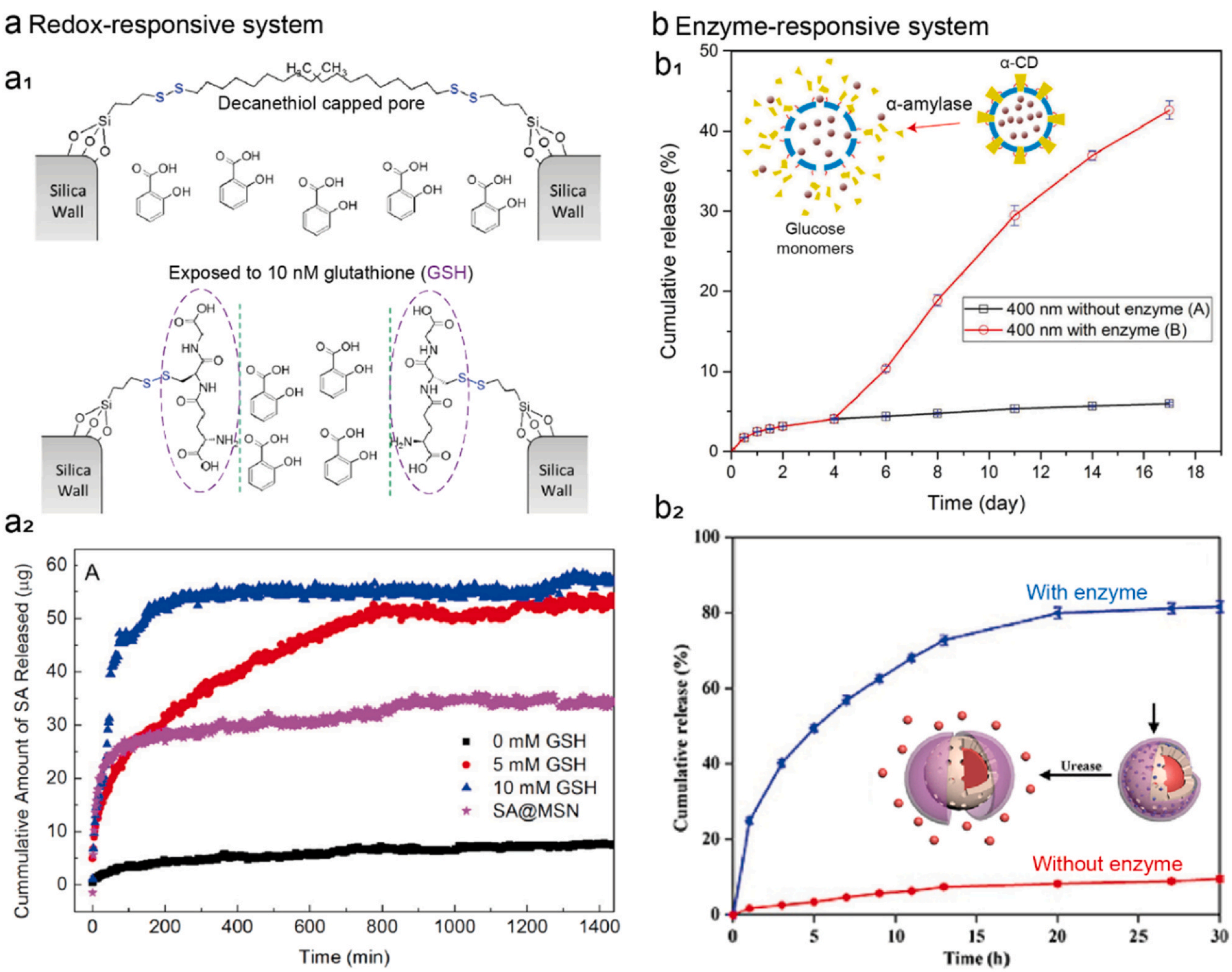

Fig. 10. Redox (a) and enzyme-responsive (b) systems designed for applications in agriculture. Mesoporous silica can be capped with decanethiol to act as a redox-responsive system that is triggered by the presence of glutathione (GSH) (a1). (a2) The release profiles respond very well to different concentrations of GSH. Reproduced with permission from Ref. [137] Copyright (2015) American Chemical Society. The carrier material can be designed to be enzyme-responsive, for instance using (b1) α-cyclodextrin (CD) that are degraded by α-amylase into monomeric sugars. Reproduced with permission from Ref. [142] Copyright (2017) American Chemical Society. or (b2) using isocyanate-modified silica cross-linked with polyethylenimine via urea bonds, which are break in the presence of urease to therefore release the cargo. Reproduced with permission from Ref. [143] Copyright (2017) American Chemical Society.

Such knowledge is being adapted to the development of smart carriers for agriculture. However, the use of nanomaterials in botanical application also have led to concerns related to persistence in edible plants [140,141].

Enzymes are ubiquitously found in soil, plants and insects. For instance, amylases, chitinases, glucosidases, lipases and proteases are widely distributed in nature. Therefore, carrier materials that can respond, interact or be degraded by such enzymes could be used to design promising enzyme-responsive delivery systems for agriculture. For instance, mesoporous silica was functionalized, at the pore rims, with α-cyclodextrin for later use to carry an insecticide (chlorantraniliprole). The release rate of the insecticide was accelerated in the presence of α-amylase (Fig. 10b1), which was tested in vivo using *Plutella xylostella* larvae, a moth-containing α-amylase body [142]. Other examples relevant to agriculture includes the use of isocyanate-functionalized silica cross-linked with polyethylenimine via urea bonds to encapsulate the herbicide pendimethalin. Due to the designed urea bonds, the system reacts to urease activity thus tethering the release of the herbicide to the presence of the enzyme (Fig. 10b2) [143]. Other works using similar approaches include the use of metal-organic frameworks– porous porphyrinic, PCN-224 – microcapsules encapsulating tebuconazole (fungicide) that are responsive to pectinase [144], zein nanoparticles loaded with a mixture of botanical insecticides that are reponsive to trypsin [172], and a composite matrix of silica-epichlorohydrin-CMC that encapsulates emamectin benzoate (insecticide). In the latter effort, the capsule shell breaks when in contact with cellulase, thus releasing the active [145].

Multi-stimuli

Carriers that possess a multiple, higher degree of sensitivity are often beneficial for the development of delivery systems with fine-tuned release profiles. Therefore, multi-stimuli triggered systems have been developed by taking advantage of multi-responsive ligands, well-controlled multiphase systems built from mixed monolayers comprising different ligands, each responding to different stimuli, or by using the stimuli-responsive nature of the carrier material by itself [146]. A great share of the dual and multi-stimuli triggered systems already developed for agrochemical release are listed in Table 1. It is observed that pH/thermo and enzymatic/pH systems are the most common strategies, which have been used mostly to delivery pesticides.

Table 1
Summary of recent efforts to develop multi-stimuli responsive delivery systems in agriculture.

Stimuli	Type of carrier	Cargo	Ref.
NIR-light and pH	Graphene oxide and polydopamine	Hymexazol	[35]
pH and temperature	Chitosan hydrogel with multi-walled carbon nanotubes	1,3,5-triazine-2,4,6-tribenzaldehyde	[147]
	Polymer brushes of poly(N,N-dimethylaminoethyl methacrylate) grafting from polydopamine-coated ammonium zinc phosphate	PO_4^{3-}, Zn^{2-} and NH_4^+	[148]
	Poly(2-dimethylamino-ethylmethacrylate)-grafted chitosan microcapsule	Pyraclostrobin	[149]
	3-glycidoxypropyl-trimethoxysilane with silica nanospheres	Indole-3-butyric acid	[150]
	Graphene oxide (GO) with N-isopropylacrylamide (NIPAM) and acrylic acid (AA) hydrogel	Imidacloprid	[151]
	Poly(oligoethylene glycol methacrylate) hydrogel	Avermectin	[96]
Enzymatic, pH and ultrasound	Hollow mesoporous silica nanoparticles associated with carboxylatopillar[5]arene ammonium salts functionalized Fe_3O_4 nanoparticles	Gibberellic acid	[152]
pH, ionic strength and temperature	Mesoporous silica nanoparticles functionalized with trimethylammonium	2,4-dichlorophenoxyacetic acid	[130]
Enzymatic and redox	Pectin-conjugated silica microcapsules	Kasugamycin	[153]
pH and redox	Palmitic chloride-grafted nanogels cross-linked with glyoxal-modified carboxymethyl cellulose and 3,3′-dithiobis(propionohydrazide).	Salicylic acid	[154]
Enzymatic and pH	Carboxymethyl cellulose grafting dimethyldiallylammonium microcapsules	Avermectin	[152]
	Mesoporous silica nanoparticles linked with chitosan	Prochloraz	[155]
	Porous porphyrinic metal-organic frameworks	Tebuconazole	[144]

Key. List of indicated compounds; Insecticides: Imidacloprid and Avermectin. Herbicides: 1,3,5-triazine-2,4,6-tribenzaldehyde and 2,4-dichlorophenoxyacetic acid. Fungicide: Hymexazol, Pyraclostrobin, Prochloraz and Tebuconazole. Hormone: Indole-3-butyric acid and Gibberellic acid. Others: Kasugamycin and Salicylic acid.

The near future scenario of intelligent agriculture

Technologies born in the last century have enabled a massive increase in crop production without need of added lands. Mechanization from the seedling to harvesting, new irrigation concepts, development of new agrochemicals and processes for their production in mass, as well as better resistance and productive plant traits have helped to achieve higher crop yield. However, such efforts brought in parallel a gigantic cost to the environment [156]. With mechanization (and fertilization) came higher emissions of greenhouse gases, irrigation brought excessive and uncontrolled use of water, more resilient plants opened the doors for a more intensive use of agrochemicals. Although the food security is guaranteed by the current agriculture practices, this scenario will not be sustained in the near future. The uncontrolled use of agrochemicals as well as natural resources are already been seen to degrade soils (becoming unfertile) and bring resistant pests, and polluted water (unsuitable for reuse in irrigation).

Nanotechnology emerges within agriculture to revolutionize the way we currently manage and use resources [3]. As we thoroughly discussed in this review, many factors affect the performance of engineered nanomaterials to control the delivery of pesticides and fertilizers. Such systems, currently, can be designed and produced to display slow and sustainable delivery rate, and to target given tissues or to act upon stimuli at certain extent. Plant performance can be boosted by transporting the right nanomaterials to the right location, leading to the enhancement of the photosynthetic machinery or to induce self-defense mechanisms. New functions have been introduced in plants via nanobiotechnology [28]. There is an increased interest in nano-enabled agriculture [157]; however, the transference of such precise, well-controlled, and often complicated technologies into large scale technical applications is still far from reality. A successful, technical use of delivery systems in agriculture, for instance, will depend on production costs and energy trade-off. For implementation, synthesis needs to consider simple approaches and inexpensive carrier materials, preferably sourced from agricultural side streams. On the other hand, although it is natural that new nano formulations are planned for large scale markets, one must consider applications in niche markets such as ornamental flowers, wood protection, where higher costs may be affordable due to their lower required volume. Also, industrial-scale plant tissue culturing such as micropropagation of plants [158] and genetic modification of organisms – GMOs – may also be a good adopters of nano-enabled technologies [23]. Major challenges exist. For instance, there is no consensus on the method for field application of a given engineered nanomaterial. Used either in suspension, emulsion or in dried forms, during application and harvesting there is a risk of having colloidal particles in the soil and in air (which is aggravated by drifting). For this reason, the fate, behavior and ecotoxicological aspects of such nanomaterials should be thoroughly evaluated [159], as well as studies that provide insight into such interaction mechanisms [160]. However, to properly address such points, there should be more studies on the interfacial interactions of nanomaterials and vegetal tissues as well as with organic matter in the soil [161]. Thus, to avoid persistence in soil, where the fauna is rich and very active, the designs of the carriers should rely on biocolloids and biopolymers that display high biodegradability, such as cellulose, lignin, zein, chitins and related. However, most of the stimuli-responsive carriers designed are synthetic, non-biodegradable materials. This is understandable as biopolymers and biocolloids are perhaps not as easy to engineer as the synthetic counterparts. Nevertheless, there has been a remarkable effort to build eco-friendly smart nanocarriers using biodegradable materials through greener synthesis routes (e.g. pH-responsive lignin-based nanocapsules for controlled release of coumarin-6) [162]. Also, computational approaches, such as modeling and simulation, may be utilized to improve the fabrication of new safe-by-design nanocarriers [163], as well as to assist risk assessment studies [164].

The scientific community has been addressing the toxicity of nanoparticles – mostly metals – along the past decade, but studies more focused on the phytotoxicity of organic engineered nanomaterials are expected in the upcoming years. Moreover, studies on persistence of nanomaterials in plants and their transference within the food chain are needed in order validate the technologies before the regulatory bodies [159,165,166]. Additionally, dosages below the minimum inhibitory concentration of active molecules could increase the pathogen resistance against them as well as to induce stimulatory effects on biota, within a hormetic context [167]. While pathogen resistance is quite problematic, this has been overlooked as far as delivery systems for pesticides. As far as nanotoxicity, macro-scaled but nanostructured materials perform similar to nanoparticles in terms of delivery dynamics but they may be safer to non-targeted fauna and flora. Robust superstructured granules, i.e. particle of particles, are suitable routes to achieve high performance with reduced non-targeted action as they mirror the functionalities of nanoparticles into the macroscale. Cohesion in such granules is of extreme importance, and it can be achieved universally by forming a composition of the given particle (carrier) with inexpensive plant biocolloids, cellulose fibrils [168].

For fertilizers, for instance, a macro-scaled system is preferable to avoid high mobility in soil; however, for foliar applications this may not hold true as usually the adhesion of nanoparticles (onto leaves) is much higher than the macroscale. Therefore, one must consider the advantages and disadvantages of each length scale before developing particulate systems for a given application within agriculture. More studies of the effects of the engineered delivery system geometry and size on their interactions with foliage and soil are timely needed in order to create proper guidelines for further developments, as well as creating carriers that can be better handled in the environment [173]. Only from such information we will be able to propose safe-by-design delivery strategies for agrochemical management.

Lastly, introducing new agricultural nanotechnologies into the market may suffer from the limited consumer knowledge about their benefits and possible risks. It has been recently shown that the public perception of nanotechnology is still modest, with a negative receptivity that is driven mostly by lack of information [169]. Specifically, in the case of agrochemicals, we believe that the major concern is still linked to the residual pesticides in food and the environment, rather than the materials incorporated in their formulations. Additionally, there is consumer apprehension in relation to "nanoproducts" as being expensive. Therefore, concerns related to cost and risk can be reduced from the introduction of comprehensive discussion about the topic and scientific dissemination initiatives to inform about the effect of "nano" to society. Thus, public can understand the real risks and benefits of such technologies, demystifying common perceptions and avoiding future prejudice. These actions will have direct implications in the development of future agriculture policies and technologies.

CRediT authorship contribution statement

Renato Grillo: Conceptualization, Resources, Supervision, Writing - original draft, Writing - review & editing. **Bruno D. Mattos**: Conceptualization, Writing - original draft, Writing - review & editing. **Debora R. Antunes**: Writing - original draft. **Mariana M.L. Forini**: Writing - original draft. **Fazel A. Monikh**: Writing - review & editing. **Orlando J. Rojas**: Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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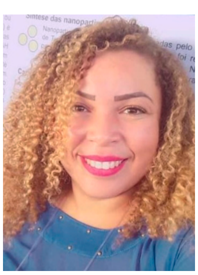

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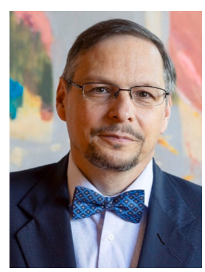

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