Inorganic Porous Nanoparticles as Pesticide or Nutrient Carriers

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Abstract Nano-enabled agriculture has been gaining interest recently as a pathway to improve crop yield and protection while reducing fertilizer and pesticide application rates compared to traditional agricultural practices. Inorganic, porous nanoparticles can have a pivotal role in the successful deployment of nanotechnology. Inorganic porous nanoparticles can provide a structurally stable framework to encapsulate and transport active ingredients, such as pesticides and fertilizers. Herein, we provide a review of promising features that these porous nanocarriers possess that may be of interest in agriculture. For instance, porous nanocarriers can increase the apparent solubility and mobility of poorly soluble pesticides and control the release of these over time. Commonly studied inorganic nanomaterials include silica, iron oxide, zinc oxide, copper oxide, clays, and hydroxyapatites, each of which has its own attributes and characteristics that can be relevant to crop growth and protection in the field. This chapter also includes explanations of the uptake of these nanocarriers through roots and leaves, and their further translocation within the plants. The important role of particle physicochemical characteristics, e.g., zeta potential and size in uptake and translocation are reviewed along with emerging approaches for rational design of nanoparticles to provide them with stimuli-responsive characteristics that can be triggered by changes in pH, temperature, ionic strength, light, enzymes, and redox agents.

Keywords Inorganic nanocarriers · Nano-enabled agriculture · Nanopesticides · Nanofertilizers · Nanocarrier · Nanoencapsulation · Mesoporous silica nanoparticles

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1 Introduction

Inorganic porous nanoparticles (NPs) are versatile, because of their wide range of mechanical and physicochemical properties. They can be chemically stable over long periods of time and are promising candidates for nanocarriers for pesticide agriculture. As a nanocarrier, they can provide the matrix to carry the active ingredient (AI), which includes a vast spectrum of organic and inorganic molecules (Fernandez-Fernandez et al., 2011; Pérez-De-Luque & Rubiales, 2009), and/or they can be used as an AI itself. Several metallic NPs have been reported to have antimicrobial properties (Rai et al., 2009; Zhang & Chen, 2009; Richter et al., 2015), thus can act as a nanopesticide. Furthermore, some metals are essential micronutrients to plants, such as zinc (Zn) (Tarafdar et al., 2014), and therefore, the respective metallic NPs can be directly used as a nanofertilizer. Inorganic NPs are in general more easily manufactured with consistent properties when it comes to size distribution, shape, and batch-to-batch reproducibility, compared to organic NPs (Mostafa et al., 2021). Furthermore, inorganic NPs are currently easier to analytically track in plant matrices and are more chemically stable in the field with respect to temperature, photo- and biodegradation over time (Lino et al., 2018; Jesus & Grazu, 2012).

A wide range of inorganic porous nanomaterials have potential applications in agriculture, such as those composed of SiO_2 (Rastogi et al., 2019), Zn (Sabir et al., 2014), Fe (Shan et al., 2020), hydroxyapatite (Marchiol et al., 2019), Cu (Kasana et al., 2016), and clay (Manjunatha et al., 2016). These inorganic nanoparticles can be tailored to specific sizes (Lin & Haynes, 2009), porosity (Parra-Nieto et al., 2021), intraparticle pore sizes (Zhang et al., 2011), and functionalized with molecules to manipulate surface charge or functional groups (Mishra et al., 2014; Subbiah et al., 2010). Generally, surface modifications of nanocarriers are made to facilitate uptake and translocation, target the delivery, and to provide controlled stimuli-responsive capabilities to the NPs. Figure 1 summarizes the most commonly studied nanomaterials and their morphologies, potential active ingredients to be encapsulated, and application methods.

2 Nanoparticles as Active Ingredients and Carriers of Active Ingredients

Typically, metal oxide NPs (ZnO, Fe_2O_3, Fe_3O_4, CuO) and nHAP are themselves molecules of interest to be taken up by plants, because they are essential elements for plant development and nutrition. Thus, these NPs are nanocarriers delivering the essential nutrients in their structural matrix, and a different AI is embedded in the matrix. These NPs can be applied bare and as synthesized, without further modifications to the NP surface. This is generally the case when plants have dedicated internalization pathways for the elements delivered by the nanocarrier, e.g., Si, and thus no modifications are required to facilitate the internalization of the NPs.

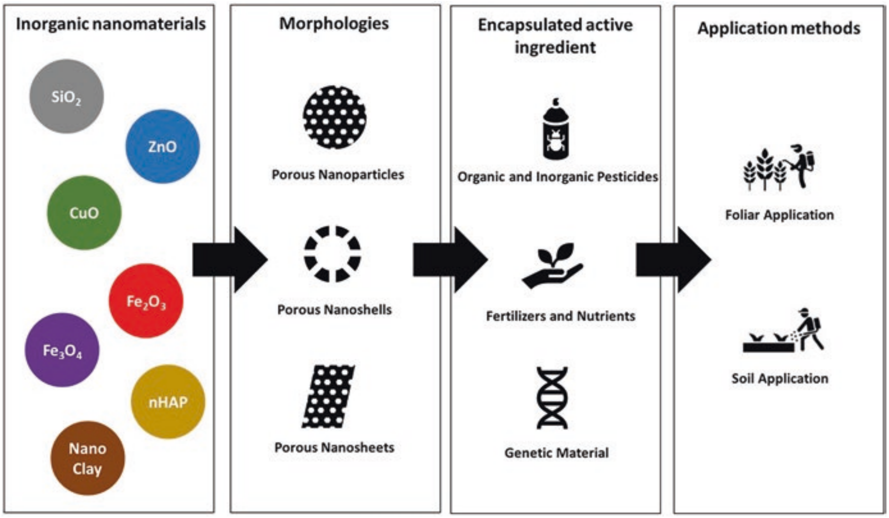

Fig. 1 Commonly studied nanomaterials, morphologies, encapsulated active ingredients, and application methods for nano-enabled agriculture

2.1 Silica Nanoparticles

The use of silica NPs has been proposed for nano-enabled agriculture, primarily for two reasons: (1) Si is considered a *quasi*-essential nutrient for plants (Epstein, 1972) and the use of SiO_2 NPs as a source of Si has been shown to result in beneficial effects on plant health (Luyckx et al., 2017; Abdel-Haliem et al., 2017; Abdelrahman et al., 2021; El-Shetehy et al., 2020). (2) Synthesis and functionalization of SiO_2 NPs of varied forms with a wide range of pore structures and particle characteristics are feasible. Currently, there are established procedures for synthesis of SiO_2 NPs of various structures, such as solid spherical nanoparticles (Stöber et al., 1968), mesoporous nanoparticles (Slowing et al., 2006), and porous hollow nanoparticles (Bueno & Ghoshal, 2020). Furthermore, certain characteristics can be controlled during synthesis, including particle size distribution (Fernandes et al., 2019; Pack et al., 2021), pore size (Nandiyanto et al., 2009; Ren et al., 2021), shell thickness (Tsou et al., 2014), and even functionalization of the surfaces with bioactive molecules (Wang et al., 2015b). Potential applications of SiO_2 NPs in agriculture include acting as nanocarriers for pesticides and fertilizers (Plohl et al., 2021; Gao et al., 2021) as well as the AI itself, delivering Si to plants (Attia & Elhawat, 2021).

Si is considered a *quasi*-essential nutrient, that is Si is not essential for plant development but it is beneficial to plants when present (Siddiqui et al., 2020). For this reason, Si also has dedicated transport pathways for uptake in plants. Si is generally internalized as $Si(OH)_4$ through aquaporin-like channels (Luyckx et al., 2017). Foliar application of SiO_2 NPs has been demonstrated to be beneficial for plant growth (Attia & Elhawat, 2021; Suriyaprabha et al., 2014). Porous hollow

SiO_2 NPs are promising candidates to carry a wide spectrum of organic and inorganic molecules. SiO_2 NP structure is highly malleable during the synthesis, as one can tune characteristics such as the particle size, the size of the pores, the overall porosity, and the presence and size of a hollow core. The facile synthesis of different SiO_2 NP structures and biocompatibility makes them exceptional candidates as nanocarriers. Although most research have been done on solid spherical nanoparticles first synthesized by Stöber et al. (1968), most agricultural applications involve the use of mesoporous nanoparticles, such as the MCM-41, and porous hollow SiO_2 NPs (PHSNs). MCM-41 is a popular choice for medical and agricultural applications because of the enhanced surface area providing the potential for the high-density loading of molecules of interest through sorption. The synthesis procedure is a modification of the Stöber method with the addition of a surfactant called cetrimonium bromide (CTAB), which provides a highly uniform distribution of pores etched in the SiO_2 matrix and an enhanced specific surface area that could reach over 1000 $m^2\ g^{-1}$ (Chen et al., 1993). Several studies have reported having encapsulated pesticides such as prochloraz (Zhao et al., 2018), abamectin (Feng et al., 2021), and herbicides in general (Shan et al., 2019) within mesoporous SiO_2 NPs for targeted delivery. PHSNs have a more complex structure because of the presence of a hollow core within a porous SiO_2 shell. This structure can be achieved either through hard templating using materials such as polystyrene (Vu et al., 2021) or soft-templating using surfactants (Bueno & Ghoshal, 2020; Bueno et al., 2022). While hard-templating methods require the functionalization of the hard template to allow for the anchoring of the soon-to-be nanoshell and the post-synthesis removal of the template by either calcination of solvent extraction, soft-templating methods involve the use of surfactants and/or oil phase as template, which could be part of the final nanoformulation or removed through means of heating or acid wash (Bueno & Ghoshal, 2020; Yang et al., 2021). The hollow core of PHSNs provides a cargo space for the high-density loading of biomolecules or even other nanoparticles. Bueno and Ghoshal (2020) used the hollow core as a nanoreactor to synthesize Fe NPs within the porous SiO_2 shell through the successive addition of Fe ions and sodium borohydride. Some studies reported the encapsulation of biomolecules, such as avermectin (Li et al., 2006), fipronil (Wibowo et al., 2014), and even DNA strands (Hai et al., 2018). The PHSN shell also provides physical protection to the cargo molecules and avoid premature degradation (Li et al., 2007).

2.2 Hydroxyapatite Nanoparticles

Hydroxyapatite (HAP) is one of the most commonly occurring forms of calcium phosphate in nature, with well-defined crystalline structures (Marchiol et al., 2019). Most P-based fertilizers in current use are derived from phosphoric acid, such as triple superphosphate and ammonium dihydrogen phosphate, which rapidly chelate with Al^{3+}, Fe^{2+}/Fe^{3+}, and Ca^{2+} in soil thus becoming unavailable for plants (Szameitat et al., 2021). Therefore, there is increasing interest in HAP as a fertilizer because it is a highly stable, naturally occurring material, which will not chelate with earth-abundant metal ions nor precipitate as easily as phosphoric acid-based fertilizers. Moreover, it is a naturally occurring compound in the environment instead of emerging contaminants from the transformation of phosphoric acid-based fertilizers, which carry in their commercial formulation, particularly triple superphosphate, a certain amount of heavy metals, such as, Cd, Cr, Pb, Hg, Ni, and V that are released into the environment once the phosphorous fertilizer is metabolized (Mortvedt, 1996; Molina et al., 2009). HAP is biocompatible, naturally porous, and can be found in bones and teeth of vertebrates, and for this reason, it has been the target of study for biomedical applications (Sadat-Shojai et al., 2013; Verma et al., 2013; Ansari et al., 2020). Due to the reduced size when compared to the bulk counterpart, nanosized HAP (nHAP) can be internalized through the roots and leaves. To date, although promising, few studies used nHAP as nanofertilizer to provide P to plants. However, Szameitat et al. (2021) recently reported the foliar and root application of nHAP in phosphorous deficient barley restored the plant metabolism and functionalities that were previously limited due to the lack of the element. These promising results may pave the way to more research on nHAP applications in nano-enabled agriculture in the near future.

Conventional phosphorous fertilizers, consisting mostly of soluble phosphates, are estimated to have an overall efficiency of 20% because of their high mobility in soil and susceptibility to being transported with runoff (Taşkin et al., 2018). In this context, nHAP can be a promising candidate to replace conventional phosphorous fertilizers due to its properties of slow but pH-dependent dissolution, and hindered mobility in soil when compared to soluble phosphates (Maghsoodi et al., 2020; Taşkin et al., 2018). Generally, nHAP surfaces are functionalized to maintain their colloidal stability in suspension, and enhance uptake, for instance with carboxymethyl cellulose (CMC) as reported by Liu and Lal (2014) and with urea as reported by Kottegoda et al. (2011).

2.3 Iron Oxide Nanoparticles

Fe is among the essential nutrients for plant health because it participates in several metabolic processes such as photosynthesis, nitrogen cycling, and biomolecules synthesis, as it is involved in the reaction mechanisms of the formation of chlorophyll, chloroplasts, and cytochromes (Tiwari et al., 2016). The lack of Fe in plant nutrition hinders plant chlorophyll production and respiration, thus leading to chlorosis (Jeyasubramanian et al., 2016). In fact, the impacts of Fe deficiency go beyond the agriculture, as over 25% of the human population suffer from anemia (Lopez et al., 2016), a condition directly correlated with the insufficient amount of Fe in the blood. Some studies have reported that increasing the amount of Fe in food crops, particularly rice, has a direct positive impact on human health (WHO, 2009; Meng et al., 2005). Current methods for Fe fertilization have very low efficiencies, because Fe rapidly complexes with organic matter and becomes biologically unavailable to plants and microorganisms (Lucena et al., 2010). The nano-sized forms of Fe minerals, however, are more stable and take longer to release Fe ions compared to the salt-based formulations. The synthesis of porous and hollow-porous Fe NPs can involve different synthesis mechanisms, such as sol-gel (Wang et al., 2015a; Yadav et al., 2015), micelle-assisted (Gavrilović et al., 2014), co-precipitation method (Nikumbh et al., 2014; Safi et al., 2016), radiation-assisted (Li et al., 2015; Raut et al., 2016), and hydrothermal-assisted (Ozel et al., 2015; Tadic et al., 2014). There are conflicting results in the agriculture about the use of Fe NPs in nano-enabled agriculture. Depending on the oxidation state of Fe and concentration of these NPs, they can lead to positive and negative impacts on the plant growth. Rui et al. (2016) reported that ppm levels of Fe_2O_3 NPs had a positive impact in the production of chlorophyll and increased the Fe stock in the *Arachis hypogeae*. Nonetheless, a higher concentration of Fe_2O_3 NPs (50 mg L^{-1}) led to decreased photosynthesis activity in another study (Li et al., 2018). At 30 mg L^{-1}, Fe_3O_4 NPs have been reported to cause oxidative stress to ryegrass and pumpkin grown hydroponically (Wang et al., 2011). However, in another study, at 50 mg L^{-1}, the treatment with Fe_3O_4 NPs resulted in higher chlorophyll activity and attenuated oxidative stress (Li et al., 2021).

There are two pathways for uptake of Fe in plants, particularly rice. The first pathway is through the adsorption of insoluble Fe(III) on the roots, followed by its chelation and reduction to Fe^{2+} ions catalyzed by the ferric-chelate reductase, and lastly the transport of the ions from the cell wall to cytosol mediated by iron-regulated transporters (IRT) (Robinson et al., 1999; Eide et al., 1996). Liu et al. (2021) recently reported that nZVI promoted the formation of an iron plate on rice root surface which resulted in further increase in biomass, chlorophyll content, and grain yield up to 55%, while it simultaneously induced the removal of pentachlorophenol (PCP) from contaminated soil used for rice cultivation. The second pathway consists in excreting mugineic acid (MA) that complexes with insoluble Fe(III), forming MA-Fe(III) that are internalized to the cytosol mediated by YSL transporters (Kobayashi & Nishizawa, 2012). Fe translocation from the cytosol to the other parts of the plants is then mostly mediated by protein members of the YSL family (Curie et al., 2001).

2.4 Zinc Oxide Nanoparticles

Zn is an essential micronutrient for plant health that plays a critical role in maintaining key metabolic activities (Sturikova et al., 2018). It is also a cofactor for several metalloenzymes involved in antioxidant reactions as well as in the synthesis of biomolecules such as nucleic acids, proteins, carbohydrates, and lipids (Palmer & Guerinot, 2009). Furthermore, it participates in the control of cell proliferation, and chloroplast formation, thus being directly involved in the photosynthesis activity (Hänsch & Mendel, 2009). In terms of uptake and translocation within plants, Zn is internalized mostly by the roots in the form of Zn^{2+} or complexed with organic chelators (Palmgren et al., 2008) and is distributed through the xylem by transporters known as zinc regulatory transporters (Milner et al., 2013). Zn uptake could take place through the leaf surface or the roots. The latter is aided by dedicated protein transporters referred to as zinc-regulated, iron-regulated transporter-like proteins, as known as ZIP protein family (Ajeesh Krishna et al., 2020). These proteins are located in the cell wall and mediate the internalization of Zn to the cell plasma and vacuoles (Milner et al., 2013). The internalized Zn is then transferred to the xylem with the aid of another group of transport proteins called heavy metal ATPase, particularly HMA2 and HMA4 (Hussain et al., 2004). Then, from the xylem, the Zn is distributed throughout the plant. There are reports of translocation of Zn through the phloem with the aid of yellow stripe-like (YSL) proteins, but the mechanism is not yet well elucidated (Curie et al., 2009). Foliar uptake of ZnO NPs has been reported to take place through the stomata, which then migrate to the apoplast to be dissolved into Zn^{2+} (Zhu et al., 2020). The cations and some undissolved ZnO NPs are then transferred to mesophyll cells before they finally reach the xylem, leading to the further translocation of Zn inside the plant (Zhu et al., 2020). Porous Zn NPs can be synthesized by a variety of different methodologies, including microemulsion-based synthesis (Zhu et al., 2008), co-precipitation (Akhtar et al., 2017), hydrothermal synthesis (Ramimoghadam et al., 2013), sol-gel (Kim & Tai, 2007), and self-assembly synthesis (Bo et al., 2020).

ZnO NPs have been suggested as a fertilizer alternative to increase the availability of Zn ions to plants. In practice, both positive and negative effects have been reported followed by the application of ZnO NPs to plants. Khan and Siddiqui (2021) reported that ZnO NP application promoted pathogen resistant of beetroot crops against *Pectobacterium betavasculorum*, *Meloidogyne incognita,* and *Rhizoctonia solani*. Semida et al. (2021) reported that ZnO NPs promoted drought stress resistance in eggplants. Dutta et al. (2019) synthesized ZnO NPs functionalized with humic acid and citrate, which promoted smart, sustained release of Zn when photoinduced, and enhanced the growth of wheat. In contrast, other studies listed toxic effects from the application of ZnO NPs such as inhibition of root and shoot growth, cell wall damage, and chlorophyll synthesis impairment (Ma et al., 2015; Torabian et al., 2016; Sturikova et al., 2018). In summary, the factors influencing whether the application will result in positive or negative effects were mostly nanoparticle concentration, method of application, and plant species.

2.5 Copper Oxide Nanoparticles

Cu is not only an essential nutrient for plant health, but also has antimicrobial properties. This allows the use of Cu-based products for both fertilization and pesticidal activity. Cu NPs have been tested to a variety of food crops leading to contrasting results depending on the dose concentration. At low doses (up to 20 mg per plant), CuO NPs have been reported to increase Cu accumulation inside the plant leading to beneficial metabolic activities, such as the oxidative stress tolerance and increased sulfur metabolization, due to the ROS generation from the internalized Cu (Keller et al., 2017; Nair & Chung, 2014). Further increases in dosage, however, leads to increased ROS generation and damaging oxidative stress, which have been reported to impact seed germination (Zafar et al., 2017), promote phytotoxicity (Xiong et al., 2017), and inhibit photosynthesis (Da Costa & Sharma, 2016). The synthesis of porous Cu NPs has been systematically reported in the literature (Ashok et al., 2015; Zhao et al., 2019; Zhang et al., 2014; Jiang et al., 2017; O'Mara et al., 2019).

Both excess Cu and a deficiency in Cu can lead to an increase in the formation of ROS leading to oxidative stress that can harm the plant (Ravet & Pilon, 2013). Therefore, plants have developed a mechanism that closely control the level of Cu inside the cells. Cu uptake takes place mostly through the rhizosphere with the aid of Cu-specific high-affinity protein transporters, as known as the COPT family, which mediate the internalization from the external media to the cell cytoplasm and further facilitate the transfer from the root cells to the xylem (Sanz et al., 2019; Ogunkunle et al., 2018).

2.6 Clay Nanoparticles

Clays are naturally occurring minerals with varying shapes, sizes, and chemical compositions. They are generally referred to as nanoclays when at least one external dimension of these minerals is in the nano-sized range. These nanoclays are usually formed by stratified sheets of aluminosilicates, such as silicon tetrahedra and aluminum octahedra, stacked above one another (Nazir et al., 2016; Uddin, 2008). Due to the porosity, elevated surface area, and ionic charge, nanoclays have been suggested as a promising nanocarrier for the delivery of AIs, such as fertilizers and pesticides (Chen et al., 2018b; Merino et al., 2020). For instance, aluminosilicate nanoclays are generally negatively charged, allowing the complexation with charged or polar organic and inorganic chemicals that are essential for plant nutrition, such as zinc (Shafigh et al., 2019; Songkhum et al., 2018), copper (Yuan, 2014), ammonium (Mazloomi & Jalali, 2019), nitrate (Bhardwaj et al., 2012), urea (Madusanka et al., 2017), and potassium (Said et al., 2018). The elevated surface area and ionic charge of nanoclays facilitates the loading of molecules of interest through sorption and ionic interactions. Some examples include diammonium phosphate (DAP) (Verma et al., 2016), Zn^{2+} (Mandal et al., 2018), urea (Wei et al., 2019), potassium phosphate (Hakim et al., 2019), and potassium nitrate (Ganguly & Das, 2017). The high porosity of nanoclays allows for the loading of these AI through extended surface area of the structure followed by their subsequent slow and/or controlled release, which is one of the advantages of using porous inorganic nanocarriers to deliver AI. Although most studies with nanoclays involved the loading of small molecules and ions, these nanocomposites have also been tested, at a lesser extent, to analyze the sorption efficiency of larger molecule pesticides, such as atrazine, imidacloprid, and thiamethoxam, on nano-montmorillonite and its potential to be used as a delivery system for larger agrochemical molecules (Narayanan et al., 2017). A more sophisticated application involved the topical delivery of RNA interference, loaded on layered double hydroxide clay nanosheets, to *Arabidopsis thaliana*, providing these plants with sustained protection against viruses (Mitter et al., 2017).

Nanoclays, however, are not as tunable and controlled during synthesis as SiO_2 NPs. The size distribution is less uniform, and one can have a population of nanoclay with different size and morphology, and thus unpredictable loading capacity. On the other hand, MCM-41 and PHSN are engineered NPs whereas most nanoclays occur naturally, reducing the energy and materials footprint of chemicals applied in the agriculture and in the environment as a whole.

3 Impact of Size and Surface Properties for Efficient Uptake in Foliar and Root Systems

Nanocarriers must possess very specific properties to overcome several chemical and physical barriers in plants, as shown in Fig. 2. The NPs are primarily taken up through plant tissues in the roots and in the foliar region, particularly through cuticles, stomata, and specialized pores, such as lenticels and hydathodes (Wang et al., 2016). To achieve significant uptake, NPs are required to have the right size and surface properties to cross cellular membranes until they successfully reach the vascular systems and translocate within the plant. The first barriers for foliar entry are the size exclusion limits (SELs) of each pore structure. The stomata are minute orifices on foliar surface to control gas exchange, with sizes ranging from 10 to 100 µm (Eichert et al., 2008; Uzu et al., 2010). However, there is evidence that NPs

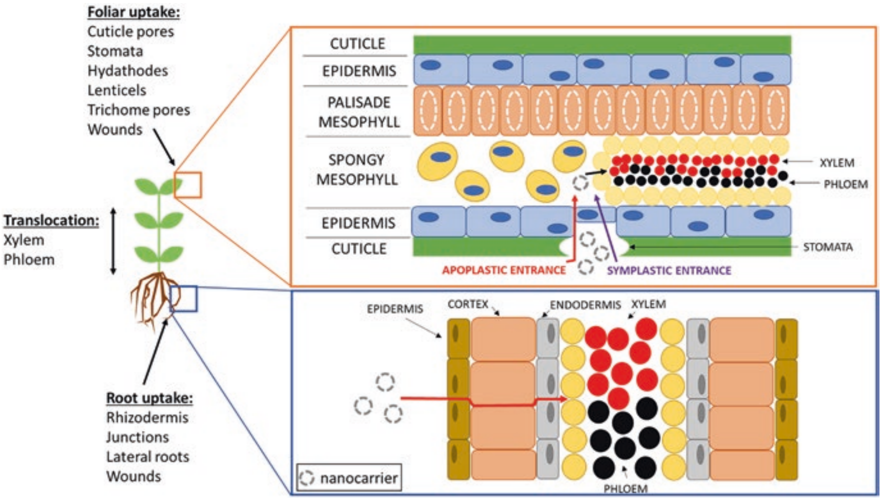

Fig. 2 Schematic representation of possible nanocarrier pathways for uptake through the roots or the leaves followed by translocation through the vascular systems (xylem and phloem)

can be internalized through stomatal uptake for particles up to 50 nm in diameter (Avellan et al., 2019). A second route for foliar uptake would be through the cuticles, which is a protective waxy and porous layer for the leaves and stem. There are significantly more cuticular areas than stomatal areas on leaves; however, the SELs for cuticles are remarkably smaller, ranging from 0.1 to 10 nm (Wang et al., 2016). However, Larue et al. (2014) estimated that NPs up to 100 nm can traverse the cuticle region under certain conditions, such as a temporary disruptions of the waxy layer.

Once the NPs cross the first barrier, they must navigate across cellular membranes and organelles before reaching the vascular systems. One important route to cross from one cell to another is the apoplastic transport, which is a channel where materials can diffuse freely between adjacent cells. The apoplastic pathway is restricted by the opening of the space which can vary from 5 to 20 nm (Eichert et al., 2008; Ma et al., 2010; Dietz & Herth, 2011). The apoplast, however, can be interrupted by Casparian strips which have a SEL below 1 nm limiting the diffusion of compounds (Aubert et al., 2012). Following the apoplastic pathway, the symplastic pathway plays a crucial role in transporting low-density molecules through an interconnected network of protoplast plasmodesmata, which opening size varies from 3 to 50 nm and limits the transport of larger particles (Zhai et al., 2014; Lucas & Lee, 2004).

A priori, one would not expect uptake of NPs exceeding the upper size limit of the SELs. However, some studies reported the uptake and translocation of larger particles, such as gold NPs of 50 nm (Avellan et al., 2019), which clearly exceeds the size barrier for apoplastic and Casparian strip transport. It is speculated that the SEL can be influenced by the particle's surface charge, the presence of some elements such as Ca and Si, (a)biotic stress, which can induce structural changes in these openings (Dietz & Herth, 2011; Schwab et al., 2016; Larue et al., 2014; Larue et al., 2012).

Surface characteristics also play a crucial role in the uptake and translocation of NPs. Surface charge, for instance, can enhance adsorption to rhizodermis, facilitate the chelation process of specialized protein transporters within the cells and vascular systems that further distribute the NPs across the organism, and allow the passage of molecules through cellular ionic channels in plants. It has been reported that positively charged NPs easily attach to the commonly negatively charged rhizodermis of wheat and tomato roots (Spielman-Sun et al., 2017; Li et al., 2019), whereas negatively charged particles have enhanced translocation to aerial parts (Zhu et al., 2012; Li et al., 2016; Spielman-Sun et al., 2019). Both positively and negatively charged NPs are more likely to be internalized when their absolute surface charge surpass 30 mV, while NPs with surface charge close to zero have difficulties in crossing the cellular lipidic bilayer (Lew et al., 2018; Wong et al., 2016). Furthermore, the combination of size and surface properties may facilitate or exclude the uptake of NPs. It has been suggested that smaller-sized NPs require a greater absolute surface charge than larger particles of comparable chemical composition and surface structure (Hu et al., 2020; Lew et al., 2018; Wong et al., 2016).

Overall, it is known that surface charge plays a crucial role in the interaction of the NPs with different biological structures and the subsequent capability to cross the cuticular, stomatal, or rhizodermis barriers, diffuse between adjacent cells, and be carried in the vascular system to distant organelles (Lew et al., 2018; Albanese et al., 2012); therefore, it is important to produce a nanocarrier with specific size and surface properties that has the ability to enter the plant and target the delivery to the specific regions of interest.

4 Surface Functionalization to Facilitate Uptake and to Target Delivery

Surface properties play an important role in the uptake of NPs in plants. Surface charge and charge intensity influence the ability of NP to be internalized and its further translocation (Zhu et al., 2012; Li et al., 2016; Spielman-Sun et al., 2019; Lew et al., 2018). Therefore, although the size is an important factor when designing nanocarriers, surface properties may dictate whether the NP will indeed be internalized and distributed to the organelles of interest. As synthesized NPs might not always fit in all the criteria and thus, surface modifications are a popular pathway to transform bare NPs into a versatile nanocarrier. Santana et al. (2020) functionalized quantum dots (QD) with peptide recognition motifs to target the delivery of these NPs to chloroplasts in *Arabidopsis thaliana*. In this study, the authors used specific guiding peptides on the surface of the QD to mimic chloroplast-biorecognition mechanisms and to target its delivery to the organelle. Although QD are not relevant to plant growth or protection, this approach has the potential to be used for different porous materials as peptide-functionalization has been reported in MSN (Hu et al., 2016).

Future applications might rely on this mechanism to target the delivery of an AI-encapsulated nanocarrier to specific organelles and tissues. Different plant compartments require specific molecules to ensure proper functioning. To obtain these molecules of interest, the cells forming the outer surfaces of these organelles and tissues developed mechanisms to selectively identify the essential biomolecules and facilitate their uptake. In the case of chloroplasts, the redox status controls the diffusion of molecules in and out of the organelle. Santana et al. (2020) took advantage of this mechanism to introduce a chain of polypeptides capable of imitating the redox conditions specific to this organelle and thus being identified by the chloroplast-biorecognition system in the cell membrane leading to the nanocarrier internalization. Another example was the use of citrate to enhance the adhesion of Au NPs to the leaf and the α-1,5-arabinan antibody to target stomata on the leaf surfaces, thus guiding and facilitating the internalization of the NPs (Spielman-Sun et al., 2020). Similar rationale can be used to design nanoformulations to target other organelles and tissues. These rationally designed surface modifications are crucial to further nano-enabled agriculture applications and thus are necessary for the next-generation porous inorganic nanopesticides and nanofertilizers. Nano-enabled agriculture can also benefit from the advances in nanomedicine, where a vast spectrum of molecules have been tested to target the delivery, including antibodies, peptides, aptamers, saccharides, and proteins (Baeza et al., 2015), and porous SiO_2 nanocarriers, in particular, are promising candidates because they can transport and deliver AI in plants and can be easily functionalized their surfaces (Trewyn et al., 2007).

Functionalization can also enhance NP stability and improve the apparent solubility of hydrophobic compounds in aqueous media. For example, it has been reported that functionalizing nHAP with citric acid (Montalvo et al., 2015; Samavini et al., 2018) and CMC (Liu & Lal, 2014) improved overall NP stability in suspension and thus increased P delivery to plants. Carboxylic acid ligands have been reported to enhance the apparent solubility of carbon nanotubes in water by providing a hydrophilic surface coverage (Tripathi et al., 2011; Sonkar et al., 2012). Other advantages of surface modifications include aiding the loading and release of AI in porous nanocarriers and provide different functionalities to the nanoformulation. MSN surfaces were functionalized with nontoxic trimethylammonium to enhance loading and promote the slow-release of 2,4-dichlorophenoxy acetic acid (Cao et al., 2017) and pyraclostrobin (Cao et al., 2016). Functionalizing CuO NPs with biocompatible polymers provided fungicidal properties to the nanoformulation (Cao et al., 2014).

More sophisticated surface modifications can use the surface ligands to trigger a reaction involving a second molecule of interest loaded within the NP. Torney et al. (2007) loaded mesoporous SiO_2 NPs (MSN) with β-oestradiol, capped the pores with small gold NPs to prevent the cargo from leaching out, and functionalized the MSN surface with a double-stranded DNA plasmid containing a green fluorescent protein (GFP) gene. Then, immature maize embryos were bombarded with the transformed MSN to assess whether these NPs could deliver not only the genetic material but also the β-oestradiol, which is responsible to trigger the GFP gene expression. This work successfully reported that the MSN system simultaneously delivered the plasmid as well as β-oestradiol, the chemical responsible to trigger the gene expression to targeted plant cells. Porous nanocarriers are particularly ideal to carry two or more biomolecules that complement each other activities because they can be stored in different areas of the nanoparticle, for example, inside the pores, hollow core, or on the surface of PHSN. Ultimately, these particles can be designed in a way that the multiple molecules of interest loaded in them will only interact with one another at the destination site, usually controlled by gatekeeper molecules, which control the release of AIs after chemical or physical stimuli.

5 Stimuli-Responsive Porous Nanocarriers

Porous nanoparticles are not only able to carry a wide variety of organic and inorganic compounds, protect them from premature degradation, and target their delivery, but they can also provide controlled release of molecules of interest upon triggered on-demand responses. That is, the AIs are loaded into the nanocarrier pores, which are further capped with another type of compound, referred to as gatekeepers, that prevent the AI from leaching out prematurely. These gatekeepers are designed to block the AIs from leaving the pores and unwanted molecules from entering the pores, and to enable the release of the cargo when triggered by a stimulus, as shown in Fig. 3. Triggering factors include pH change (Yang et al., 2010; Liu et al., 2010; Muhammad et al., 2011; Yuan et al., 2011; Gao et al., 2020; Gao et al., 2019; Chen et al., 2019; Baldi et al., 2018), light stimulus (Niu et al., 2014; Li et al., 2014; Zhang et al., 2012; Fomina et al., 2012; Chen et al., 2018a; Xu et al., 2018), ionic strength (Zhang et al., 2018; Bernardo et al., 2018; Cao et al., 2017), redox agents (Koo et al., 2013; Cui et al., 2012; Kim et al., 2010; Hou et al., 2018; Yi et al., 2015), enzymes (Kaziem et al., 2017; Liang et al., 2017; Guo et al., 2015), and temperature (Ye et al., 2011; Wei et al., 2017; Zhang et al., 2019) as summarized in Table 1.

For pH-triggered nanocarriers, the gatekeeper compound capping the pores is sensitive to pH. Compounds containing amines, hydroxyl, and carboxylic acid functional groups are susceptible to protonation and deprotonation depending on the pH of the medium. This can affect the charge of the gatekeeper compound, and thus the interactions with the nanocarrier and AI. Mattos et al. (2018) functionalized thymol-loaded SiO_2 NPs with amino functional group ($-NH_2$), which at neutral pH is protonated ($-NH_3^+$), thus strongly interacting with the electronegative group O^- in thymol and preventing the AI from being released. At acidic pH, however, thymol undergoes protonation, weakening the interaction with the gatekeeper, which then leads to a greater release of the AI. Complex structures, such as polymers (i.e., hydrogels), denature and undergo structural changes depending on the pH of the medium. Sarkar and Singh (2017) reported that at alkaline pH, a hydrogel coating comprised of CMC and citric acid undergo hydrolysis, liberating the release of chlorpyrifos pesticide from a nanoclay matrix.

Photo-responsive gatekeepers can undergo structural change when exposed to the light of a certain wavelength. Some structural changes include oxidation, isomerization, and fragmentation of the interaction with the carrier (Grillo et al., 2021). Chen et al. (2018a) functionalized a glyphosate-loaded porous nano-sized biochar with amino-silicon oil, which undergoes isomerization when exposed to light at 420 nm wavelength. This process, then, releases the loaded glyphosate. Interestingly, when this nanoformulation ceases to be exposed to the specific wavelength of light, the gatekeeper returns to cap the pores of the nanocarrier and block the AI to be released. That is, one can turn on and off the release of the molecule of interest by simply exposing or not the nanoformulation to light.

Ionic strength-responsive gatekeepers generally rely on the electrostatic interactions among the medium, nanocarrier, AI, and the gatekeeper itself. Cao et al. (2017) functionalized 2,4-dichlorophenoxy acetic acid (2,4-D)-loaded MSNs with trimethylammonium (TA) to avoid premature release of the pesticide. Because 2,4-D is extremely soluble in aqueous media, leaching is generally a threat when it is applied in agricultural soils. The TA acts as a binding agent for the 2,4-D, increasing the loading by 21.7% and as a capping agent to avoid leaching. The change in ionic strength, however, can affect the interaction between TA and 2,4-D, leading to either

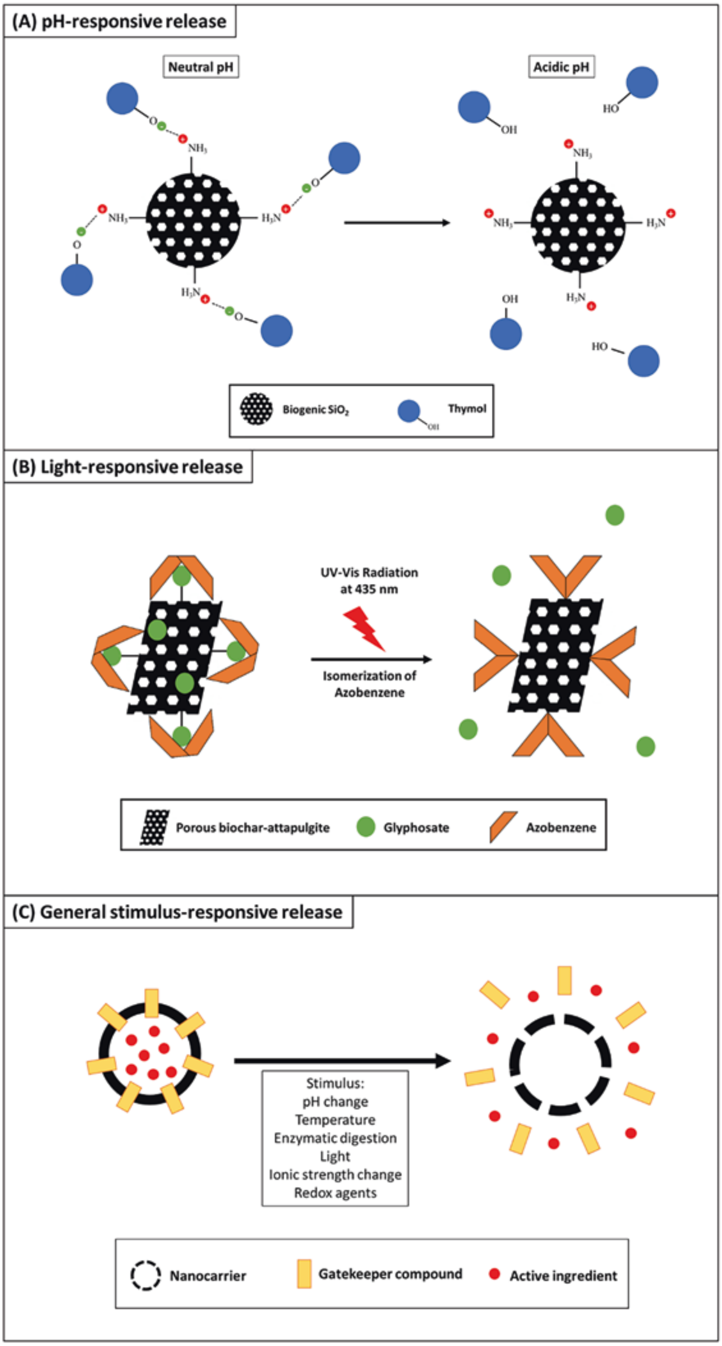

Fig. 3 Conceptual schematic of a (**a**) pH-responsive nanocarrier suggested by Mattos et al. (2018): at neutral pH there is a strong interaction between the negatively charged hydroxyl group in thymol and the positively charged amino group in the functionalized biogenic nano-SiO_2 and when the pH becomes more acidic, this interaction is weakened due to the protonation of the hydroxyl group in thymol; (**b**) light-responsive nanocarrier suggested by Chen et al. (2018a): under UV-Vis light radiation at 435 nm, azobenzene undergoes isomerization releasing the encapsulated glyphosate from the porous biochar-attapulgite framework; (**c**) general stimulus-responsive nanocarrier: the AI is trapped within the nanocarrier until a stimulus disrupts the structure of the gatekeeper compound, thus liberating the pores and allowing the AI to be released

Table 1 List of stimuli-responsive nanocarriers with their respective gatekeepers and active ingredients

Stimulus	Nanocarrier material	Gatekeeper(s)	Active ingredient	Reference
pH	Mesoporous silica	Poly(allylamine hydrochloride)	Doxorubicin	Yang et al. (2010)
	Mesoporous silica	Gold NPs and acid-labile acetal linker	2,2′-bipyridine	Liu et al. (2010)
	Mesoporous silica	ZnO QDs	Doxorubicin	Muhammad et al. (2011)
	Mesoporous silica	Poly(acrylic acid)	Doxorubicin	Yuan et al. (2011)
	Mesoporous silica	Calcium carbonate	Prochloraz	Gao et al. (2020)
	Mesoporous silica	Pluronic F127	Chlorpyrifos	Chen et al. (2019)
	Clay	Hydrogel	Chlorpyrifos	Sarkar and Singh (2017)
	Biogenic silica	Functionalized amino group	Thymol	Mattos et al. (2018)
Light	Mesoporous silica	Gold NPs	Doxorubicin	Niu et al. (2014)
	Mesoporous silica	Sulfonatocalix(4)arene	Gold nanorods	Li et al. (2014)
	Mesoporous silica	Gold NPs	Doxorubicin	Zhang et al. (2012)
	Porous biochar-attapulgite	Azobenzene	Glyphosate	Chen et al. (2018a)
Ionic strength	Porous hollow carbon	Cationic polymer PEI	Selenate	Zhang et al. (2018)
	Hydrotalcite	Mg and Al	Phosphate	Bernardo et al. (2018)
	Mesoporous silica	Trimethylammonium	2,4-dichlorophenoxy acetic acid	Cao et al. (2017)
Redox agents	Mesoporous silica	Glutathione	N-acetyl-L-cysteine	Koo et al. (2013)
	Mesoporous silica	Glutathione	Fluorescein	Cui et al. (2012)
	Mesoporous silica	Glutathione	Cyclodextrin	Kim et al. (2010)
	Mesoporous silica	Glutathione	Salicylic acid	Yi et al. (2015)
Enzymes	Hollow porous silica	α-Cyclodextrin	Chlorantraniliprole	Kaziem et al. (2017)
	Mesoporous silica	Isocyanate and poly(ethylenimine)	Pendimethalin	Liang et al. (2017)
	Mesoporous silica	Carboxymethylcellulose	Emamectin benzoate	Guo et al. (2015)
Temperature	Hollow porous silica	Poly(N-isopropylacrylamide)	Fe_3O_4	Ye et al. (2011)

more release of the AI, or a stronger interaction thus preventing the discharge of the pesticide in the soil.

An example of redox-responsive release is when disulfide bonds between the nanocarriers and the capping agent are undone, liberating the loaded molecules to be released. The most common gatekeepers for redox-sensitive response are β-cyclodextrins, sulfidated polyethylene glycol (S-PEG), and cadmium sulfide. Yi et al. (2015) designed MSN functionalized with decanethiol, through disulfide conjugation. The disulfide bonds between the MSN and decanethiol could be easily cleaved by glutathione (GSH). In this study, the release of salicylic acid was directly controlled by the concentration of GSH in the medium.

Enzyme-triggered response involves using enzymes to degrade the gatekeepers associated with the loaded nanocarrier. Kaziem et al. (2017) synthesized PHSN, loaded these nanocarriers with chlorantraniliprole, and functionalized their surface with α-cyclodextrin. The α-cyclodextrin-PHSN successfully retained the AI under thermal stress and UV radiation; however, the release was triggered when α-amylase was introduced, leading to the degradation of the capping agent, and unblocking the pathway for the AI to be discharged.

AI release can also be triggered by thermal stress. This happens when the gatekeepers are thermosensitive, particularly compounds that are sensitive to temperatures in the environmental range. Because high temperatures can lead to the degradation of the AI and nanocarrier as well, the gatekeeper must be able to undergo transformation with light variations of ambient temperatures. Ye et al. (2011) used a thermosensitive polymer, poly(N-isopropylacrylamide-co-acrylamide), to cover MSN-coated Fe_3O_4 NPs. The subtle difference in temperature from 34 to 42 °C led to changes in structure and magnetic properties of the nanocarrier, that can be used in conjunction with molecules of interest to modulate their release.

In the future, sophisticated applications of nanotechnology in agriculture will take advantage of the ability to functionalize porous nanocarriers, particularly SiO_2 and clay NPs, to target the delivery of the formulation to specific plant organelles and tissues, and to promote stimuli-responsive release of molecules of interest, all at once while carrying several molecules of interest that will only interact with one another at the destination. Two or more compounds will play a role in capping the pores to prevent AI premature release, mimicking biorecognition mechanisms in the different parts of the plants, and in some cases, activating the AI. More research should be focused on the functionalization of porous nanocarriers with biomolecules and how their interaction can modulate the uptake and release of pesticides, fertilizers, and genetic material to plants.

6 Conclusions

Inorganic porous nanoparticles play a pivotal role in nano-enabled agriculture and toward making agricultural practices more sustainable. A variety of methodologies for synthesis and structure modifications of inorganic nanomaterials have been extensively studied, providing us with the expertise to fabricate nanocarriers with specific features to encapsulate, transport, and release agrochemicals in a way that avoids wastage by targeting specific sites in the plant. For instance, the shape, diameter, and porosity can be tuned to optimize the loading of AI but keep it in the range for uptake through roots or leaves, and translocation through the xylem and phloem. Further modifications can be done to improve uptake and translocation as well as target specific organelles, such as changing the zeta potential or functionalizing the nanocarrier surfaces with biomolecules to mimic biorecognition mechanisms.

Given the immense possibilities for inorganic porous nanomaterials to increase crop yields and to offer crop protection many new nanotechnology solutions will be proposed in the near future, with the objective to make agricultural practices more efficient. However, to ensure these developments are sustainable, nanomaterials should be formulated with safe and/or earth-abundant chemicals and using green chemistry principles. However, given that in some instances materials at the nanorange may be toxic compared to their bulk counterparts, the environmental and human health exposures and risks of new nanomaterials used in agriculture need to be evaluated. Although the goal of the use of nanomaterials and nanocarriers is to ensure that AI delivered is utilized efficiently, without wastage, some losses to the environment are expected. For example, the nanomaterials can be washed off leaves and deposit on the ground during precipitation events, and along with nanomaterials applied in soils, may be mobilized in the soil and groundwater. As well nanomaterials dosed in plants may lead to exposures to insects, including those involved in pollination, as well as birds. Thus, their ecological safety needs to be verified. Various silica and other inorganic porous nanomaterials are being used in medicine, which suggest that their safety to human health may already be verified (Mamaeva et al., 2013; Lohse & Murphy, 2012).

It is also important to assess the scalability of production of inorganic porous NPs for field applications, and as well field studies need to perform to verify if the efficacy determined in lab studies are translated adequately to the field. In a recent assessment of technology efficacy and readiness level for commercial applications, nanocarriers for fertilization and pesticide delivery ranked high on both counts, suggesting that their commercial applications are likely to grow rapidly (Hofmann et al., 2020).

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