Chapter 3
Nanofertilizers: Types, Synthesis, Methods, and Mechanisms

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1 Introduction

The projection of the world's human population reaching 9.6 billion by 2050 poses a significant challenge in terms of food production. To meet the needs of this growing population, a 50% increase in food production is required by 2050 (UNDESA, 2015). The use of conventional fertilizers and pesticides has been on the rise in recent years, resulting in increased yields and poverty reduction. However, the long-term consequences of the Green Revolution have become apparent, as extensive use of chemical fertilizers has disrupted soil mineral content and depleted soil fertility (Mahapatra et al., 2022; Padhan et al., 2021a). This overreliance on chemical fertilizers has also led to environmental degradation and pollution. In order to protect the environment and reduce the excessive use of chemical fertilizers, improving fertilizer absorption efficiency in crop plants is crucial (Liu et al., 2020). The ultimate goal is to minimize the use of plant protection materials, reduce nutrient losses during fertilization, and maximize revenue in the agricultural sector (Servin et al., 2015). Nanofertilizers (NFs) offer a promising solution to achieve these objectives.

Nanofertilizers (NFs), as a groundbreaking innovation, hold immense potential for addressing the growing concerns of global food security and sustainable agriculture. With the world's population on the rise, there is an urgent need to develop efficient and eco-friendly approaches to maximize crop yields while minimizing the

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negative impacts on the environment (Escribà-Gelonch et al., 2023). Traditional fertilizers, although effective in enhancing plant growth, have posed challenges such as nutrient runoff, soil degradation, and contamination of water bodies (Mahapatra et al., 2022). The emergence of nanotechnology has provided a remarkable solution to overcome these hurdles. One of the key advantages of NFs lies in their ability to precisely control the release of nutrients, ensuring that plants receive them when needed the most. This controlled-release mechanism allows for better nutrient absorption, reducing wastage and increasing nutrient use efficiency. By delivering nutrients directly to the root zone, NFs minimize leaching and volatilization, thus preventing nutrient loss and environmental pollution. Moreover, the nanoscale size of these fertilizers facilitates their easy uptake by plant roots, enhancing nutrient availability and uptake rates.

The types of NFs available offer diverse approaches to nutrient delivery and release. Nanostructured fertilizers, composed of nanoparticles or nanocomposites, provide a high surface area for nutrient encapsulation, resulting in slow and sustained release over an extended period. This controlled nutrient release aligns with the crop's growth stages, ensuring that plants receive a continuous supply of essential elements (Nongbet et al., 2022). On the other hand, nanoencapsulated fertilizers protect nutrients from degradation and leaching, allowing for their gradual release and improving their stability in the soil. Nanocomposite fertilizers, formed by combining nanoparticles with traditional fertilizers, offer a synergistic effect by enhancing nutrient availability, reducing losses, and optimizing plant uptake (El-Saadony et al., 2019; Reda et al., 2020). The synthesis of NFs involves various methods, each with its advantages and considerations. Physical methods, such as high-energy ball milling and sol–gel synthesis, enable the production of nanostructured materials by manipulating particle size and morphology. Chemical methods like precipitation and coprecipitation facilitate the formation of nanoparticles and nanoencapsulated fertilizers through controlled chemical reactions. Additionally, biological synthesis methods, employing microorganisms or plant extracts, provide a sustainable and environmentally friendly approach to produce nanoparticles with specific properties (El-Saadony et al., 2020, 2021; Reda et al., 2021).

Understanding the mechanisms of action of NFs is crucial to grasp their impact on plant growth and soil health. The improved solubility of nutrients due to nanosized particles enables better absorption by plant roots, resulting in enhanced nutrient availability and uptake efficiency. The increased diffusion rates of nutrients in the soil matrix ensure a wider distribution, benefiting plant roots beyond their immediate vicinity. Furthermore, NFs can stimulate beneficial microbial activity in the soil, promoting nutrient cycling and improving soil fertility (Tyagi et al., 2022). These multifaceted mechanisms work in tandem to optimize plant nutrition, leading to improved crop growth, increased yield, and, ultimately, food security. The advent of NFs opens up new avenues for sustainable agriculture, offering a promising solution to the challenges faced by conventional fertilizers. The efficient utilization of nutrients, reduced environmental impact, and enhanced crop productivity make NFs a compelling choice for farmers and agricultural practitioners. However, further research is needed to explore the long-term effects, safety considerations, and cost-effectiveness of NFs on a larger scale (Chhipa & Joshi, 2016).

Therefore, NFs commonly termed "smart fertilizers" (Wang et al., 2021) represent a cutting-edge technology that holds immense potential for transforming the agricultural landscape. With their ability to provide controlled release, improved nutrient uptake, and targeted delivery, NFs offer a pathway to sustainable agriculture, ensuring food security while minimizing environmental degradation. Continued advancements in nanotechnology and rigorous scientific research will pave the way for the widespread adoption of NFs as a key tool in global efforts toward a more sustainable and productive future in agriculture.

2 Comparative Analysis of Conventional Fertilizers vs. Nanofertilizers

Fertilizers play a vital role in modern agriculture by providing essential nutrients to plants, enhancing crop productivity, and ensuring food security. However, conventional fertilizers have raised concerns due to their adverse environmental impacts and inefficient nutrient utilization (Kah et al., 2018; Tarafdar et al., 2020). The advent of nanotechnology has introduced a new era in agriculture, offering the potential to revolutionize nutrient management through the development of NFs (Monreal et al., 2016; Feregrino-Pérez et al., 2018). This chapter aims to provide a comprehensive analysis of the differences between conventional fertilizers and NFs, exploring their composition, mode of action, benefits, and environmental implications (Solanki et al., 2015).

2.1 Composition and Structure

Conventional fertilizers typically consist of macronutrients, such as nitrogen (N), phosphorus (P), and potassium (K), in their readily available forms. These fertilizers are often derived from nonrenewable sources and are formulated to release nutrients rapidly upon application (Navarro et al., 2008). In contrast, NFs are nano-sized materials designed to efficiently deliver nutrients to plants. They can be classified into different types based on their composition, namely, nanostructured fertilizers, nanoencapsulated fertilizers, and nanocomposite fertilizers. Nanostructured fertilizers consist of nano-sized materials, such as nanoparticles or nanocomposites, that encapsulate or deliver nutrients to plants. Nanoencapsulated fertilizers involve the encapsulation of nutrients within nanoscale structures, providing controlled release and targeted delivery. Nanocomposite fertilizers combine nanoparticles with conventional fertilizers to enhance nutrient release and improve efficiency.

2.2 Nutrient Release and Uptake Efficiency

Conventional fertilizers often release nutrients rapidly into the soil, leading to inefficient nutrient utilization by plants. This rapid release can result in nutrient leaching, volatilization, and runoff, causing environmental pollution and wastage (Dan et al., 2015; Padhan et al., 2021b). In contrast, NFs offer controlled-release mechanisms, allowing for gradual and sustained nutrient release. This controlled release aligns with the crop's growth stages, ensuring that plants receive a continuous supply of nutrients when needed. By providing steady nutrient availability, NFs enhance nutrient uptake efficiency, minimizing nutrient losses and maximizing plant utilization.

2.3 Targeted Delivery and Nutrient Availability

Conventional fertilizers are typically broadcasted or applied uniformly across the field, resulting in uneven nutrient distribution. This can lead to overfertilization in some areas and underfertilization in others. In contrast, NFs enable targeted delivery of nutrients, ensuring precise placement and efficient utilization. The nanoscale size of these fertilizers allows them to penetrate the root zone more effectively, increasing nutrient availability to plants (Wesołowska et al., 2021). By delivering nutrients directly to the roots, NFs reduce nutrient losses through leaching and improve nutrient uptake by plants.

2.4 Environmental Impacts

Conventional fertilizers have significant environmental implications due to their excessive and inefficient use. Nutrient runoff from fields can contribute to water pollution, leading to eutrophication in lakes and rivers. Moreover, the production and transportation of conventional fertilizers require considerable energy inputs, contributing to greenhouse gas emissions. In contrast, NFs offer the potential to reduce environmental impacts (Pérez-de-Luque A., 2017; Rochette et al., 2018). The controlled-release and targeted delivery mechanisms of NFs minimize nutrient losses, thus reducing the risk of water contamination. Additionally, the enhanced nutrient uptake efficiency of NFs results in lower fertilizer application rates, potentially reducing energy consumption and greenhouse gas emissions (Table 3.1).

The key differences between conventional fertilizers and NFs lie in their composition, nutrient release mechanisms, and environmental implications. NFs offer controlled release, targeted delivery, and improved nutrient uptake efficiency, resulting in reduced nutrient losses and enhanced crop productivity. The potential environmental benefits of NFs include minimized water contamination, reduced energy

Table 3.1 Comparative analysis of conventional fertilizers vs. nanofertilizers

Particulars	Conventional fertilizers	NFs	Explanation
Composition	Macro- and micronutrients	Nano-sized particles or composites	Conventional fertilizers consist of macro- and micronutrients in their original form, whereas NFs are composed of nano-sized particles or composites that enhance nutrient availability and absorption (Navarro et al., 2008)
Nutrient release	Rapid release	Controlled release	Conventional fertilizers release nutrients rapidly upon application, whereas NFs offer controlled release, thus ensuring a steady and prolonged nutrient supply to plants (Slomberg & Schoenfisch, 2012)
Nutrient absorption	Less efficient	Enhanced absorption and utilization by plants	NFs enhance nutrient absorption and utilization by plants, resulting in improved nutrient use efficiency and crop yield. Conventional fertilizers are often less efficient in nutrient absorption (Wesołowska et al., 2021)
Environmental impact	Potential pollution	Reduced leaching and environmental impact	Conventional fertilizers can contribute to pollution and nutrient leaching, leading to environmental concerns. NFs, on the other hand, have reduced leaching and environmental impact due to their controlled-release mechanisms (Rochette et al., 2018)
Efficiency	Variable effectiveness	Improved nutrient use efficiency and crop yield	Conventional fertilizers' effectiveness can vary based on factors such as soil conditions and application rates. NFs have been shown to improve nutrient use efficiency, leading to enhanced crop growth and productivity
Application	Soil application	Multiple application modes (soil, foliar, seed coating)	Conventional fertilizers are typically applied to the soil. In contrast, NFs offer multiple application modes, including soil application, foliar spray, and seed coating, thus providing flexibility in nutrient delivery
Toxicity	Potential toxicity	Proper design minimizes toxicity risks	Conventional fertilizers may have potential toxicity risks if misused or overapplied. Proper design and formulation of NFs minimize toxicity risks while maximizing the nutrient uptake by plants

(continued)

Table 3.1 (continued)

Particulars	Conventional fertilizers	NFs	Explanation
Cost	Relatively low cost	Higher initial cost, but long-term benefits	Conventional fertilizers are generally more affordable compared to NFs, which may have a higher initial cost. However, the long-term benefits of improved nutrient utilization and reduced environmental impact can offset the initial investment
Sustainability	Environmental concerns	Promotes sustainable agricultural practices	Conventional fertilizers raise concerns regarding environmental pollution and sustainability. NFs promote sustainable agricultural practices by reducing nutrient losses, optimizing nutrient absorption, and minimizing environmental impacts

consumption, and lower greenhouse gas emissions (Fleischer et al., 1999; Monreal et al., 2016; Feregrino-Pérez et al., 2018). However, challenges such as safety considerations, cost-effectiveness, and regulatory frameworks need to be addressed. With further research and advancements, NFs hold immense potential for revolutionizing nutrient management in agriculture and contributing to sustainable food production systems.

3 Diverse Types of Nanofertilizers: An Overview

NFs have emerged as a promising solution to address the challenges of conventional fertilizers in modern agriculture. By harnessing the unique properties and functionalities at the nanoscale, NFs offer improved nutrient delivery, controlled-release mechanisms, and enhanced nutrient uptake efficiency (Singh et al., 2020).

3.1 Nanostructured Fertilizers

Nanostructured fertilizers are a type of NF that consist of nano-sized materials, such as nanoparticles, nanocomposites, or nanocoatings, which encapsulate or deliver nutrients to plants (Iravani et al., 2014; Chakraborty et al., 2023). These materials provide a high surface area for nutrient encapsulation and controlled-release mechanisms. Examples of nanostructured fertilizers include:

3.1.1 Nano-Sized Nitrogen Fertilizers

Nitrogen is an essential nutrient for plant growth, and nanoscale nitrogen fertilizers, such as nano-sized urea or ammonium-based fertilizers, offer improved efficiency and reduced losses through leaching and volatilization (Zhang et al., 2015).

3.1.2 Nanocomposite Phosphorus Fertilizers

Phosphorus is another critical nutrient for plant development, and nanocomposite fertilizers, composed of nanoparticles and conventional phosphorus fertilizers, enhance nutrient availability and uptake by improving solubility and reducing phosphorus fixation in the soil.

3.1.3 Nanocoated Potassium Fertilizers

Nanocoatings on potassium-based fertilizers help in controlled release, extending the availability of potassium nutrients to plants over a longer period, thus optimizing plant uptake and minimizing losses.

3.2 Nanoencapsulated Fertilizers

Nanoencapsulated fertilizers involve the encapsulation of nutrients within nanoscale structures, providing controlled-release and targeted delivery mechanisms. This type of NF protects the nutrients from leaching, volatilization, and degradation while enhancing their solubility and availability. Some examples of nanoencapsulated fertilizers include:

3.2.1 Nanoencapsulated Slow-Release Nitrogen Fertilizers

These fertilizers utilize nanostructures, such as polymer coatings or nanocapsules, to encapsulate nitrogen nutrients, ensuring their gradual release and prolonged availability to plants.

3.2.2 Nanoencapsulated Micronutrient Fertilizers

Micronutrients, such as iron, zinc, and copper, are essential for plant growth in small quantities. Nanoencapsulation of micronutrients enhances their stability, solubility, and targeted delivery, ensuring efficient uptake by plants.

3.3 Nanocomposite Fertilizers

Nanocomposite fertilizers combine nanoparticles with conventional fertilizers, resulting in hybrid materials that exhibit enhanced nutrient release properties and improved efficiency. By integrating nanoparticles, these fertilizers offer synergistic effects and improved nutrient utilization (Feng et al., 2019). Examples of nanocomposite fertilizers include:

3.3.1 Nanoparticle-Enhanced Controlled-Release Fertilizers

In this type, nanoparticles are incorporated into controlled-release fertilizers, enhancing their nutrient release properties. For instance, nanoparticles like clay minerals or zeolites can be added to urea-based fertilizers, resulting in improved nitrogen release patterns.

3.3.2 Nanoparticle-Blended Organic Fertilizers

Organic fertilizers, such as compost or manure, can be blended with nanoparticles to improve nutrient availability, release, and plant uptake. Nanoparticles like biochar or clay minerals aid in nutrient retention and slow-release mechanisms.

3.4 Other Types of Nanofertilizers

Apart from the aforementioned types, there are ongoing research and developments exploring additional NFs. These include:

3.4.1 Nanosensors for Nutrient Monitoring

Nanotechnology enables the development of nanosensors that can detect and monitor nutrient levels in soil in real time (Kadhum Alghanimi & Hadi, 2021). These nanosensors provide valuable data on nutrient availability and enable precise nutrient management practices.

3.4.2 Nanoparticles for Seed Coating

Nanoparticles can be applied as seed coatings to enhance seed germination, root development, and nutrient uptake. These coatings can provide controlled release of nutrients, protect seeds from pathogens, and improve the overall plant performance.

Table 3.2 Types of nanofertilizers along with their composition, method of synthesis, and examples

Nanofertilizer type	Composition	Synthesis method	Examples
Nanostructured fertilizers	Nano-sized materials (e.g., nanoparticles, nanocomposites) encapsulating or delivering nutrients to plants	Physical synthesis methods (e.g., high-energy ball milling, sol–gel synthesis)	Nano-sized nitrogen fertilizers, nanocomposite phosphorus fertilizers, nanocoated potassium fertilizers
Nanoencapsulated fertilizers	Nutrients encapsulated within nanoscale structures, facilitating controlled release and targeted delivery	Chemical synthesis methods (e.g., precipitation, coprecipitation)	Nanoencapsulated slow-release nitrogen fertilizers, nanoencapsulated micronutrient fertilizers
Nanocomposite fertilizer	Hybrid materials combining nanoparticles with conventional fertilizers for improved nutrient release and efficiency	Biological synthesis methods (e.g., microbe-mediated synthesis)	Nanoparticle-enhanced controlled-release fertilizers, nanoparticle-blended organic fertilizers
Nanosensors for nutrient monitoring	Nanoscale sensors for real-time detection and monitoring of nutrient levels in soil	Physical and chemical synthesis methods tailored for sensor development	Nanoparticle-based nutrient sensors for nitrogen, phosphorus, and potassium
Nanoparticle seed coatings	Nanoparticles applied as coatings on seeds to enhance germination, root development, and nutrient uptake	Surface modification techniques (e.g., layer-by-layer deposition)	Nano-coated seeds with iron nanoparticles for improved iron uptake
Nano-based soil amendments	Nanoparticles integrated into soil to improve structure, water retention, and nutrient-holding capacity	Physical mixing or application techniques	Nanoclay amendments for enhanced soil structure and water retention

3.4.3 Nano-Based Soil Amendments

Nanoparticles, such as nanoclays or nano-hydrogels, can be used as soil amendments to improve soil structure, water retention, and nutrient-holding capacity. These nano-based amendments enhance nutrient availability to plants and promote healthy root development (Table 3.2).

4 Synthesis Methods of Nanofertilizers

The synthesis of NFs involves various methods, each with its advantages and considerations. These methods are elucidated in the following sections.

Methods of Synthesis of Nanoparticles
The methods of synthesis can be broadly divided into two aspects: synthesis based on raw materials and synthesis based upon the nature of the driving forces.

4.1 Classification of Synthesis Methods Based on Raw Materials

This encompasses two approaches: the bottom-up approach and the top-down approach.

4.1.1 The Bottom-Up Approach

The concept of constructing nanoparticles or nanoclusters atom by atom or molecule by molecule is referred to as bottom-up synthesis. This approach involves the use of chemical or biological methods to gradually build up nanoparticles (Escudero et al., 2021). Wet chemical procedures are the traditional and widely adopted techniques for synthesizing metallic nanoparticles (Baig et al., 2021). The process begins with the formation of nanoscale structures, followed by the incorporation of desired nutrients. The bottom-up approach allows precise control over particle size, morphology, and composition, resulting in tailored NFs with improved nutrient release and plant uptake. These procedures typically involve the growth of nanoparticles in a liquid medium containing specific reactants, including reducing agents like sodium borohydride, potassium bitartrate, methoxy polyethylene glycol, or hydrazine. To prevent nanoparticle agglomeration, a stabilizing agent such as sodium dodecyl benzyl sulfate or polyvinyl pyrrolidone is incorporated into the reaction mixture. Once the synthesis is complete, the nanoparticles undergo physical, chemical, and mechanical characterization to assess their solubility, dispersibility, and stability, among other functionalities (Lin et al., 2014).

The major advantages of the bottom-up approach are as follows:

- *Controlled Nutrient Release*: The bottom-up approach enables the encapsulation of nutrients within nanoscale structures, providing controlled and sustained release. This ensures that nutrients are released gradually, matching the specific requirements of plants during different growth stages (Baig et al., 2021). Controlled nutrient release minimizes nutrient losses and improves nutrient use efficiency, leading to enhanced crop productivity.
- *Tailored Properties*: With the bottom-up approach, NFs can be precisely engineered to possess desired properties, such as size, shape, surface charge, and composition. By manipulating these parameters, researchers can optimize the performance of NFs for specific crops and soil conditions, maximizing nutrient uptake and utilization (Lin et al., 2014).

- *Improved Nutrient Stability*: NFs synthesized using the bottom-up approach exhibit enhanced stability compared to conventional fertilizers. The encapsulation of nutrients within nanoscale structures protects them from leaching, volatilization, and chemical reactions in the soil. This improves nutrient availability to plants and reduces environmental pollution.
- *Synergistic Effects*: The bottom-up approach allows the incorporation of multiple nutrients or additives into a single nanofertilizer formulation. This enables the creation of synergistic effects, where the combined presence of different elements or compounds enhances nutrient uptake, plant growth, and stress tolerance (Chakraborty et al., 2023). Synergistic NFs can provide comprehensive nutrient solutions and address specific nutrient deficiencies.

Demerits of the Bottom-Up Approach

- *Complex Synthesis Procedures*: The bottom-up approach often involves intricate synthesis procedures, requiring specialized equipment and expertise. Chemical synthesis methods may involve multistep reactions, precise control over reaction parameters, and purification steps. These complexities can increase the cost and time associated with nanofertilizer production.
- *Safety Concerns*: The synthesis of NFs using the bottom-up approach may involve the use of hazardous chemicals or high-temperature reactions. Ensuring the safety of researchers and the environment during synthesis and handling of NFs is of utmost importance. Adequate safety protocols and risk assessments are necessary to mitigate potential hazards.
- *Long-Term Effects and Regulation*: As NFs are a relatively new technology, their long-term effects on soil health, ecosystem dynamics, and human health are still being investigated. Additionally, the regulatory frameworks for NFs vary across different regions, posing challenges in terms of standardization, labeling, and commercialization.
- *Cost Considerations*: The bottom-up approach, with its intricate synthesis procedures and specialized equipment, can contribute to higher production costs compared to conventional fertilizers. The cost-effectiveness of NF needs to be explored for its better applicability.

4.1.2 The Top-Down Approach

The process of segmenting large materials into smaller particles using physical or chemical methods is employed in this approach. It involves breaking down a bulk material into its respective nanoparticles. Physical synthesis methods, such as attrition and pyrolysis, are commonly utilized for the production of metallic nanoparticles (Borges et al., 2017; Chen et al., 2017). Attrition involves grinding macro- or microscale particles using a size-reducing mechanism, such as an ordinary or planetary ball mill. The resulting particles are then air classified to separate oxidized nanoparticles. Various factors, including the milling time, material properties, and atmospheric conditions, critically influence the characteristics of the nanoparticles obtained. On the other hand, pyrolysis entails the high-pressure combustion of an organic precursor (liquid or gas) forced through an orifice. The resulting ash is subsequently air classified to recover oxidized nanoparticles. The top-down approach allows for precise control over particle size and shape, leading to the production of NFs with specific properties and controlled-release mechanisms.

Merits of the Top-Down Approach

- *Particle Size Control*: The top-down approach enables precise control over particle size, allowing researchers to tailor NFs to specific requirements. By manipulating the size of nanoparticles, nutrient release rates and plant uptake efficiency can be optimized, resulting in improved nutrient utilization and reduced environmental impact.
- *Rapid Production*: The top-down approach offers a relatively faster production process compared to other synthesis methods. The ability to rapidly reduce bulk materials into nanoparticles allows for efficient production at a larger scale. This scalability makes the top-down approach suitable for commercial applications in agriculture (Chen et al., 2017).
- *Uniformity and Homogeneity*: With the top-down approach, nanoparticles can be produced with a high degree of uniformity and homogeneity. This uniformity ensures consistent nutrient distribution within the NFs, leading to more predictable and reliable nutrient release patterns. Uniform nanoparticles also facilitate their application and interaction with plants and soils.
- *Utilization of Existing Materials*: The top-down approach often involves the transformation of existing bulk materials into nanoparticles. This utilization of available materials can contribute to the sustainable use of resources and reduce waste. It provides an opportunity to repurpose and enhance the properties of conventional fertilizers, making them more efficient and environmentally friendly.

Demerits of the Top-Down Approach

- *Limited Control over Composition*: The top-down approach may have limitations in terms of controlling the chemical composition of NFs. Breaking down bulk materials into smaller particles does not allow for precise manipulation of the internal structure or elemental composition (Chen et al., 2017). This lack of control can restrict the incorporation of specific nutrients or additives, limiting the versatility of nanofertilizer formulations.
- *High Energy Requirements*: The top-down approach often involves energy-intensive processes such as grinding, milling, or fragmentation to reduce the size of particles. These processes require significant energy inputs, which can contribute to higher production costs and environmental impacts. Energy-efficient techniques need to be developed to mitigate these challenges.
- *Risk of Agglomeration and Inhomogeneity*: Nanoparticles produced through the top-down approach may be prone to agglomeration or uneven distribution, which can impact their performance and nutrient release properties. Ensuring the dispersion and stability of nanoparticles throughout the nanofertilizer formulation requires careful attention and appropriate techniques.

- *Environmental Considerations*: The top-down approach may involve the use of chemical processes or high-energy mechanical methods, which can result in the generation of waste products and potentially harmful by-products. Proper waste management and environmental impact assessments are crucial to minimize any adverse effects on ecosystems and human health.

The top-down approach in nanofertilizer synthesis offers distinct merits and demerits that need to be carefully evaluated. While this approach provides control over particle size, rapid production, uniformity, and utilization of existing materials, it also presents challenges such as limited control over composition.

Hybrid Nanofertilizers Hybrid nanofertilizers combine an organic matrix, typically a polymer, with a dispersed inorganic phase consisting of evenly distributed nanoparticles in nano size. A study conducted by Tarafdar et al. (2020) demonstrated the prolonged release of hybrid nanofertilizers for a duration of 14 days in *Abelmoschus esculentus*. In their research, the authors synthesized hydroxyapatite modified with urea, which serves as a nitrogen, calcium, and phosphate source. Additionally, copper, iron, and zinc nanoparticles were incorporated into the modified hydroxyapatite. The inclusion of these nanoparticles resulted in a significant enhancement of the overall absorption of copper, iron, zinc, and other essential nutrients in the fruit.

4.2 *Classification of Synthesis Methods Based on the Nature of the Driving Forces*

The various synthesis methods of nanofertilizers can be summarized into the following categories depending upon the nature of the driving forces.

1. Mechanical methods
2. Physical methods
3. Chemical methods
4. Physicochemical methods
5. Biological methods

4.2.1 Mechanical Methods

NFs have gained significant attention in agriculture due to their unique properties and potential to enhance nutrient management and crop productivity. Among the various methods available for synthesizing NFs, mechanical methods offer a straightforward and effective approach. These methods utilize mechanical forces to break down bulk materials into nanoparticles, allowing for precise control over particle size, morphology, and composition.

Grinding-Based Synthesis

Grinding-based methods involve the application of mechanical forces through abrasion or impact to reduce the particle size of bulk materials. This approach is commonly used for synthesizing metallic and oxide nanoparticles.

(a) *Ball Milling*: This is a widely utilized technique in nanofertilizer synthesis. It involves the use of grinding balls within a rotating cylindrical container to facilitate the breakdown of bulk materials (Barhoum et al., 2017). The collision and grinding action between the balls and the material result in the formation of nanoparticles. Ball milling allows for control over particle size and distribution, making it suitable for producing NFs with specific characteristics.

(b) *High-Energy Milling*: This refers to a specialized form of ball milling where the mechanical forces are intensified through the use of high-speed rotational mills or vibrating mills. This method enables rapid and efficient particle size reduction, leading to the production of nanoscale particles (Jin et al., 2018). High-energy milling is particularly useful for synthesizing NFs with enhanced reactivity and controlled-release properties.

Attrition-Based Synthesis

Attrition-based methods involve the rubbing or friction between particles to break them down into smaller sizes. These methods are suitable for producing oxide nanoparticles and composites.

(a) *Attrition Milling*: This relies on the collision and rubbing between particles to achieve size reduction. It typically involves the use of a rotating impeller or grinding media to create a turbulent environment within a container (Belaiche et al., 2021). The particles are subjected to repeated impacts and shear forces, resulting in the formation of nanoparticles. Attrition milling offers advantages such as simplicity, scalability, and the ability to control the particle size distribution.

(b) *Jet Milling*: This utilizes high-velocity gas streams to propel particles against each other or solid surfaces, leading to particle size reduction. In this method, micron-sized particles are accelerated by supersonic gas jets, causing collisions and fracturing. Jet milling enables the production of fine nanoparticles with narrow size distribution (Angelidis et al., 2015). It is a versatile technique suitable for various materials and can be used for large-scale production.

The mechanical methods of nanofertilizer synthesis offer several advantages and find applications in diverse fields:

(i) *Precise Control*: Mechanical methods allow precise control over particle size, shape, and distribution, facilitating the production of NFs with tailored properties for specific agricultural applications.

(ii) *Scalability*: These methods are generally scalable, enabling the production of NFs on a large scale to meet agricultural demands.

(iii) *Cost-Effectiveness*: Mechanical methods often involve simple equipment and fewer processing steps, resulting in cost-effective nanofertilizer synthesis.

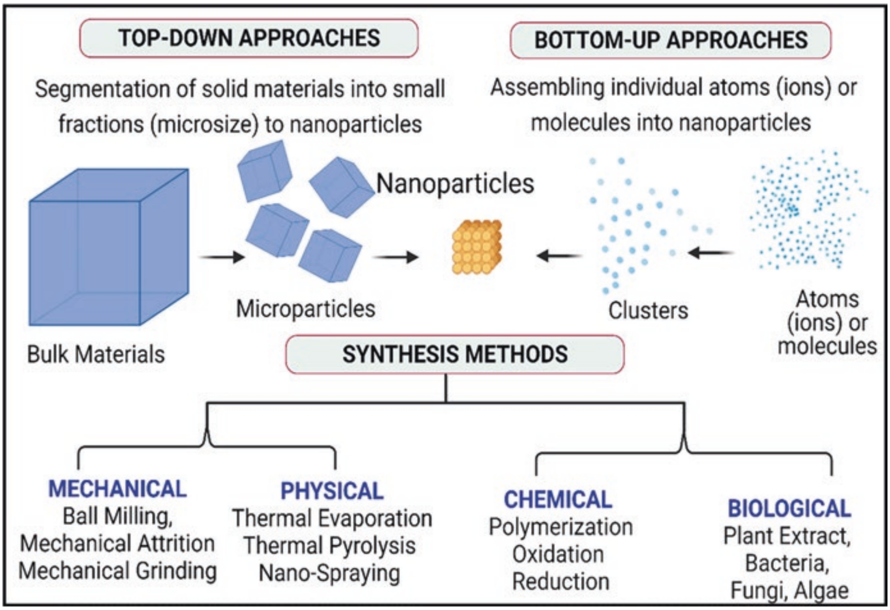

Fig. 3.1 A schematic demonstration illustrating the synthesis of nanoparticles. (Modified from Barhoum et al., 2022)

(iv) *Controlled Release*: NFs synthesized through mechanical methods can exhibit controlled-release properties, allowing for efficient nutrient delivery to plants and reducing nutrient loss.
(v) *Environmental Compatibility*: Mechanical methods are generally environmentally friendly, as they eliminate the need for toxic chemicals and involve fewer energy-intensive processes.

The mechanical methods of nanofertilizer synthesis, such as grinding and attrition-based techniques, provide a versatile and efficient approach to producing nanoparticles with precise control over particle size and morphology. These methods offer advantages in terms of scalability, cost-effectiveness, and controlled-release properties, making them suitable for various agricultural operations (Fig. 3.1).

4.2.2 Physical Methods

Various synthesis methods are employed to produce NFs, including physical methods that harness physical phenomena to generate nanoparticles. Some of the prominent physical methods are described as follows.

Vapor-Phase Condensation

Vapor-phase condensation is a widely used physical method for synthesizing nanoparticles. It involves the vaporization of precursor materials followed by their condensation into nanoparticles. The vapor is created either through thermal evaporation or chemical reactions, and, then, it is rapidly cooled to induce condensation. This method allows for precise control over particle size and composition.

(a) *Chemical Vapor Deposition (CVD)*: CVD is a vapor-phase condensation technique that involves the reaction of gaseous precursor compounds in a reactor chamber to form nanoparticles (Nikam et al., 2018). The precursors decompose or react to generate nanoparticles on a heated substrate. CVD offers excellent control over particle size, composition, and morphology, making it suitable for the production of complex NFs.
(b) *Physical Vapor Deposition (PVD)*: PVD is a vapor-phase condensation technique where materials are evaporated under vacuum conditions and the resulting vapor condenses on a substrate to form nanoparticles. Techniques such as evaporation, sputtering, and laser ablation are commonly employed in PVD. PVD allows for the synthesis of highly pure and well-defined nanoparticles.

Laser Ablation

Laser ablation is a physical method used to generate nanoparticles by irradiating a target material with a laser beam (Barhoum et al., 2017). The high-energy laser pulse vaporizes the target material, creating a plasma plume that rapidly cools and condenses into nanoparticles. Laser ablation offers control over particle size, composition, and surface properties, making it suitable for producing tailored NFs (Janas & Koziol, 2016).

Electrospray and Electrospinning

Electrospray and electrospinning are electrohydrodynamic techniques that generate nanoparticles through the application of an electric field to a liquid precursor solution or melt.

(a) *Electrospray*: This involves the dispersion of a liquid precursor into fine droplets using an electric field. The droplets undergo solvent evaporation, leading to the formation of nanoparticles. Electrospray enables the production of monodisperse nanoparticles with controlled size and morphology.
(b) *Electrospinning*: This is a technique used to produce nanofibers that can be further processed into NFs. It involves the application of a high voltage to a polymer solution, creating a charged jet that elongates and solidifies into nanofibers upon solvent evaporation. Electrospinning offers versatility in controlling fiber diameter, composition, and structure (Panigrahi et al., 2004).

Laser ablation and spinning are commonly utilized physical techniques employed in the synthesis of nanoparticles (Barhoum et al., 2017; Jin et al., 2018). For instance, one approach involves the generation of plasma using radio-frequency heating coils. The process involves placing the metal in a pestle and transferring it into a vacuum chamber surrounded by radio-frequency heating coils. The metal is then heated above its evaporation point using helium, resulting in the formation of plasma (Sánchez-Ahijón et al., 2020). The metal vapor subsequently nucleates on helium gas atoms and diffuses to a cold collector rod, where nanoparticles are collected and passivated by oxygen gas (Belaiche et al., 2021). In the case of laser ablation, the starting material is exposed to the intense energy emitted by a pulsed laser. This causes volatilization of the material particles and formation of plasma, which is then deposited on a support to form thin films (Amendola & Meneghetti, 2009). Laser ablation synthesis in solution involves preparation of colloidal solutions of nanoparticles using various solvents (Janas & Koziol, 2016).

Regarding the spinning method, the bulk material is subjected to low pressure, resulting in its deposition on a cold base. Subsequently, a magnetic field is applied to remove smaller particles that have been deposited on a support, forming a thin film (Pesheck & Lorence, 2009). Another method for the synthesis of nanoparticles in solution involves irradiation-induced synthesis, typically utilizing high-energy (1.5 MeV) electron beam irradiation. Additionally, microwave irradiation, which is a form of electromagnetic irradiation with mobile electric charges, is frequently employed with emulsion systems (Panigrahi et al., 2004).

By employing these physical methods, researchers can manipulate the synthesis process to achieve the desired characteristics and functionalities in the resulting nanoparticles. These methods offer control over particle size, morphology, and composition, allowing for the development of tailored NFs with specific properties for agricultural applications. As research in nanofertilizer synthesis continues to advance, further exploration and optimization of physical methods will contribute to the development of innovative and efficient NFs that can significantly enhance nutrient management and crop productivity in agriculture.

4.2.3 Chemical Methods

Chemical techniques play a significant role in the fabrication of nanomaterials by facilitating nucleation and growth of precursor species. These techniques involve various chemical reactions, including those that occur in the vapor state. In vapor-state reactions, the material vapor is introduced into a chemical vapor deposition (CVD) reactor. Within this reactor, the resulting particles combine with other gases on a base at a specific temperature, leading to the formation of a solid film. This method offers the advantage of preparing quasi-particles that mimic the desired nanostructure. One of the key advantages of chemical methods is their ability to precisely control the size and morphology of the nanomaterials, thereby enabling the production of highly stable nanostructures (Nikam et al., 2018). Various synthesis methods are employed to fabricate NFs, including chemical methods that involve the manipulation of chemical reactions to produce nanoparticles with desired properties.

Precipitation Methods

Precipitation methods are widely employed in the synthesis of NFs, utilizing chemical reactions to precipitate nanoparticles from solution. These methods involve the controlled mixing of reactants to induce the formation of nanoparticles (Tadic et al., 2019). Common precipitation methods include:

(a) *Coprecipitation*: This involves the simultaneous precipitation of multiple elements or compounds to form composite nanoparticles. This method allows for the incorporation of various nutrients or additives into the nanofertilizer matrix, providing a platform for tailored nutrient release.
(b) *Sol–Gel Method*: This involves the conversion of a sol (a stable colloidal suspension) into a gel by a chemical reaction. The gel is subsequently dried and calcined to obtain the desired nanofertilizer (Pesheck & Lorence, 2009). This method offers precise control over the composition and structure of the nanofertilizer.

Hydrothermal and Solvothermal Methods
Hydrothermal and solvothermal methods involve the synthesis of nanoparticles under high-temperature and high-pressure conditions. These methods allow for the controlled growth of nanoparticles through chemical reactions occurring in a solvent. Key methods include:

(a) *Hydrothermal Synthesis*: This involves the reaction of forerunners in an aqueous medium under elevated temperature and pressure. This method enables the formation of well-defined nanoparticles with precise size and morphology.
(b) *Solvothermal Synthesis*: This follows a comparable principle to hydrothermal synthesis but employs organic solvents as the reaction medium. Solvothermal methods offer the advantage of controlling the solvent properties to influence the growth and properties of the resulting nanofertilizer.

Solvent Evaporation
Solvent evaporation is a simple and widely used method for synthesizing nanoparticles. It involves dissolving the precursor materials in a suitable solvent and subsequently evaporating the solvent to induce nanoparticle formation. The rate of solvent evaporation influences the particle size, with slower evaporation leading to larger nanoparticles. This method is advantageous for producing NFs with controlled size and composition.

Electrochemical Methods
Electrochemical methods are based on electrochemical reactions to fabricate NFs. These methods involve the use of electrodes and electrolytes to induce chemical reactions that result in nanoparticle formation. Electrochemical methods offer precise control over the size, shape, and composition of nanoparticles. Key techniques include electrodeposition and electrochemical etching (Panigrahi et al., 2004).

However, it is important to note that chemical methods may require the use of hazardous chemicals during the fabrication process. These chemicals pose potential risks to the environment, and safety considerations must be taken into account. Despite this drawback, the advantages of chemical methods, such as size and morphology control, and the production of stable nanomaterials, make them valuable techniques in nanomaterial synthesis. Chemical methods offer significant benefits in the fabrication of nanomaterials through precise control over size, morphology, and stability. These methods utilize various chemical reactions, including vapor-state reactions and the use of liquid mediums. While the advantages of chemical methods are notable, caution must be exercised due to the involvement of hazardous chemicals. Continued research and development in chemical synthesis techniques will contribute to the advancement of nanomaterials and their applications in various fields.

4.2.4 Physicochemical Methods

Physicochemical approaches are employed in the synthesis of nanomaterials, combining both physical and chemical processes (Tadic et al., 2019; Jhung et al., 2007). An example of a physicochemical method is the electrochemical approach used for fabricating metal nanoparticles, where a metallic anode dissolves in an aprotic solvent. Hydrothermal and solvothermal methods, templating CVD, microwave irradiation, combustion, thermal decomposition, and pulsed laser deposition are also considered physicochemical methods (Tadic et al., 2019). These approaches allow for the modulation of specific nanoparticle properties such as size, shape, crystallinity, and stability. Additionally, the combination of biological and chemical methods can be classified as a physicochemical approach, further expanding the range of techniques available (Komal et al., 2019; Barhoum et al., 2014).

Physicochemical processes offer the advantage of reducing reaction time while enabling control over the desired characteristics of the nanoparticles. Researchers can tailor the size, shape, crystallinity, and stability of the nanoparticles to meet specific requirements. However, the implementation of physicochemical methods often involves the use of sophisticated and costly equipment, and it may also require the use of hazardous chemicals (Komal et al., 2019; Barhoum et al., 2014). Therefore, proper handling and disposal of chemicals are essential to ensure safety and minimize environmental impact.

4.2.5 Biological Methods

Biological methods of nanofertilizer synthesis involve the use of biological entities such as microorganisms, plants, and enzymes to produce nanoparticles. These methods offer several advantages, including their eco-friendly nature, mild reaction conditions, and ability to produce nanoparticles with controlled size and shape.

Microbial Synthesis

Biological methods offer environmentally friendly approaches for the fabrication of nanomaterials by harnessing the unique capabilities of certain microbes and plants (Parsons et al., 2007; Sharma et al., 2023). These methods have distinct advantages, including the elimination of expensive chemicals, reduced energy consumption, and the generation of environmentally benign products and by-products. Plant-based approaches, utilizing plant extracts, are particularly advantageous due to their low-maintenance requirements. The use of plant extracts for the reduction of metal ions to nanoparticles has been known since 1900, whereas the production of nanometals using plant extracts and the synthesis of nanoparticles using living plants have been more extensively studied in the past 30 and 10 years, respectively (Willner et al., 2006). In these biological methods, enzymes and other biomolecules, such as DNA, telomers, and actin filaments, serve as catalysts for nanoparticle growth, whereas various biological organisms, including fungi, bacteria, and cells, act as active units for nanoparticle production.

By leveraging the catalytic properties of enzymes and biomolecules, biological methods enable precise control over the size, shape, and composition of nanoparticles. This control allows for the tailored design of NFs with specific properties that enhance nutrient availability and absorption in plants. Moreover, the utilization of biological organisms as active units for nanoparticle production offers scalability and cost-effectiveness, as they can be easily cultivated and maintained (Chakraborty et al., 2023). Microbes and plants possess inherent mechanisms for the reduction and stabilization of metal ions, which facilitate the synthesis of nanoparticles. Through their metabolic activities, these biological entities mediate the transformation of metal ions into nanoparticles, resulting in the production of NFs. The choice of microbes or plants depends on factors such as their ability to accumulate and convert metal ions, their compatibility with the desired nanoparticle properties, and their ease of cultivation. The biologically mediated methods involved in nanofertilizer synthesis are as follows:

(i) *Plant-Mediated Synthesis*: Plants, including their various parts, such as leaves, stems, and roots, can act as biofactories for the synthesis of nanoparticles. The process involves the uptake of metal ions from the surrounding environment by plants, followed by their reduction and subsequent formation of nanoparticles within plant tissues. Plant-mediated synthesis offers several benefits, such as accessibility, abundance, and the ability to produce nanoparticles using simple reaction conditions (Raliya et al., 2017). Additionally, the resulting nanoparticles tend to be more stable and exhibit enhanced bioactivity, making them suitable for agricultural applications.

(ii) *Enzymatic Synthesis*: Enzymes are highly specific catalysts that can facilitate the synthesis of nanoparticles with precise control over their size, shape, and composition. Enzymatic methods often involve the use of specific enzymes capable of reducing metal ions and facilitating nanoparticle formation. Enzymatic synthesis offers advantages such as high reaction specificity, mild reaction conditions, and the ability to produce nanoparticles with desired characteristics (Parsons et al., 2007). Moreover, enzymes can be easily obtained from natural sources or through recombinant DNA technology, allowing for efficient and sustainable synthesis processes.

(iii) *Alga-Mediated Synthesis*: Algae, including microalgae and macroalgae, have gained attention as potential agents for nanofertilizer synthesis. These organisms possess inherent capabilities to sequester and transform metal ions into nanoparticles through their metabolic activities. Alga-mediated synthesis is environmentally friendly, sustainable, and can be performed in aqueous solutions without the need for high temperatures or toxic chemicals. The resulting nanoparticles exhibit good stability and can be tailored to possess specific properties for agricultural applications.

(iv) *Yeast-Mediated Synthesis*: Yeast, a type of fungus, can be utilized for the synthesis of nanoparticles. Certain strains of yeasts have the ability to reduce metal ions and facilitate the formation of nanoparticles. This method offers advantages such as simplicity, cost-effectiveness, and scalability. Yeast-mediated synthesis can be performed under ambient conditions and does not require elaborate equipment or toxic chemicals, making it a favorable approach for nanofertilizer production.

(v) *Plant Extract-Mediated Synthesis*: Plant extracts containing various biomolecules, such as polyphenols, flavonoids, and proteins, can serve as reducing and stabilizing agents in the synthesis of nanoparticles. These biomolecules present in plant extracts have the capability to convert metal ions into nanoparticles. Plant extract-mediated synthesis is a versatile and environmentally friendly method that allows for the synthesis of nanoparticles with controlled properties. Additionally, plant extracts are readily available and offer a wide range of options for nanoparticle synthesis.

(vi) *Genetic Engineering*: Advancements in genetic engineering techniques have paved the way for the synthesis of nanoparticles using genetically modified organisms (GMOs). By introducing specific genes into microorganisms or plants, researchers can enhance their ability to accumulate and convert metal ions into nanoparticles. Genetic engineering offers precise control over the synthesis process, allowing for the production of nanoparticles with desired characteristics (Sharma et al., 2023; Panigrahi et al., 2021). This method holds great potential for tailoring NFs to meet the specific nutrient requirements of different crops.

(vii) *Microbial Enzyme-Assisted Synthesis*: Microorganisms produce various enzymes that possess the capability to reduce metal ions and participate in nanoparticle synthesis. By utilizing these microbial enzymes, researchers can enhance the efficiency and specificity of nanofertilizer synthesis. Microbial enzyme-assisted synthesis provides advantages such as high catalytic activity, substrate specificity, and the ability to control the size and shape of nanoparticles. This method enables the production of NFs with improved nutrient availability and absorption efficiency.

(viii) *Mycorrhiza-Mediated Synthesis*: Mycorrhizal fungi form a mutualistic association with plant roots, enhancing nutrient uptake and promoting plant growth. Recent studies have explored the potential of mycorrhizal fungi in nanoparticle synthesis. These fungi possess the ability to transform metal ions into nanoparticles, offering a novel approach to produce NFs. Mycorrhiza-mediated synthesis holds promise for developing sustainable and plant-friendly NFs that can improve nutrient utilization and enhance crop productivity.

The biological synthesis of NFs not only offers environmental benefits but also holds potential for improving nutrient management in agriculture. These NFs can enhance nutrient uptake, promote plant growth, and mitigate the adverse effects of nutrient deficiencies. Furthermore, biological methods enable the utilization of natural, renewable resources, reducing the reliance on chemical-based approaches.

They provide sustainable and eco-friendly approaches for the synthesis of NFs (Sharma et al., 2023). Through the activity of microbes and plants, these methods offer precise control over nanoparticle properties and provide opportunities for tailoring NFs to meet specific agricultural requirements. The ongoing advancements in biological nanofertilizer synthesis hold great promise for addressing global food security challenges and promoting sustainable agricultural practices while minimizing environmental impacts (Table 3.3).

Table 3.3 List of important approved and commercially available nanofertilizers

Nanofertilizer	Constituents	Manufacturer country
Nano Ultra	Organic matter, N, P, K, Mg	Taiwan
Nano-calcium (magic green)	Ca, Si, Na, Al	Germany
Nanocapsule	N, P, K, Fe, Mg, Na	Thailand
Nano micronutrient (EcoStar)	Zn, B, Cu, Fe, EDTA-Mo, Mn	India
PPC nano	M protein, Na_2O, K_2O, $(NH_4)_2SO_4$	Malaysia
Nano Max NPK fertilizer	Multiple organic acids chelated with major nutrients, amino acids	India
TAG nanofertilizer	Proteino-lacto-gluconate chelated with micronutrients, vitamins	India
Nano green	Extracts of corn, grain, soybeans, potatoes	India
Biozar nanofertilizer	Organic materials, micro- and macromolecules	Iran
Nano-urea (liquid)	Urea particles	India
Plant nutrition powder (green nano)	N, P, K, Fe, Mg, Na	Thailand
Hero Super Nano	Organic matter, N, P, K, Mg	Thailand
Supplementary powder	Fe, Na	Thailand
Zinc oxide	Zinc	Taiwan
Titanium dioxide	Titanium	Taiwan
Silicon dioxide	Silicon	
Manganese dioxide	Manganese	
Selenium colloid	Selenium colloid	
NanoCS™ of NanoShield®	NPK, Zn	USA
NanoGro®	NPK	
NanoN+™	N	
NanoK®	K	
NanoPhos®	P	
NanoZn®	Zn	
NanoPack®	S, Cu, Mn, Fe	
NanoCalSi®	Ca, Si	
NanoFe™	Fe	
Nano-Ag answer®	NPK, other ingredients 93.4%	USA
Hibong biological-produced fulvic acid	Nanofertilizers, chitosan oligosaccharides	China
Humic acid-embodied granular fertilizer	Humic acid and organic matter	
Seaweed nanofertilizer	NPK, seaweed extract	

5 Mode of Application of Nanofertilizers

NFs offer innovative solutions for efficient nutrient management in agriculture. Their unique properties and enhanced nutrient delivery capabilities make them promising tools to improve crop productivity and reduce environmental impact. The application of NFs can occur through various modes, each with its own advantages and considerations. In this section, we will explore the different modes of NF application and their implications.

5.1 Soil Application

Soil application is the most common mode of NF deployment. NFs can be incorporated into the soil during soil preparation or applied directly to the root zone around the plants. The nanoparticles released in the soil gradually release nutrients, ensuring a sustained nutrient supply to the plants. This mode allows for efficient nutrient absorption by the root system and minimizes nutrient losses through leaching or volatilization.

The uptake of nanoparticles by plants is influenced by plant physiology, with absorption occurring through various structures such as trichomes, stomata, stigma, and hydathodes. Once absorbed, nanoparticles are transported within the plant through the phloem and xylem (Schwab et al., 2016; Wang et al., 2016; Padhan et al., 2021c). Two main routes facilitate the translocation of nanoparticles: the apoplastic pathway and the symplastic pathway. In the apoplastic pathway, macromolecules, including water, move through the apoplast, which consists of cell walls and intercellular spaces. However, the movement of macromolecules in this pathway is constrained by the size exclusion limits (SELs) of the cell walls, typically ranging from 5 to 20 nm (Bernela et al., 2021). In contrast, the symplastic pathway involves the movement of macromolecules from one cell to another through the plasmodesmata, which are small channels connecting the cytoplasm of adjacent cells. This pathway allows for direct transport within the plant's tissues (Šamaj et al., 2004; Etxeberria et al., 2006). The entry of nanoparticles into plant cells can occur through endocytosis from the cell wall, facilitated by the diameter of the stomata (ranging from 5 to 20 nm) or the base of trichomes, and subsequently transferred to other tissues.

The symplastic route relies on the SELs of the plasmodesmata, which typically range from 3 to 50 nm in diameter (Lucas & Lee, 2004; Heinlein & Epel, 2004). The Casparian strip, a specialized cell layer, acts as a barrier to transport into the plant's vascular system (Aubert et al., 2012). Interestingly, there are instances where nanoparticles larger than the SELs of cell walls, plasmodesmata, and the Casparian strip (such as 50 nm nanoparticles) have been internalized, potentially influenced by enzymatic activity. Nanofertilizers can also be combined with nanoparticles to control phytopathogens. When plant pathogens attack, the stress enzymes within plant cells can break the chemical bonds in the nanocapsules of the polymer wall, thus triggering the release of mucilage to prevent infection (Ropitaux et al., 2020). Additionally, the accumulation of nanoparticles on leaf surfaces may lead to foliar heating, which can impact gas exchange due to obstruction of the stomata (Ma et al., 2010).

5.2 Foliar Spray

The size of nanoparticles plays a crucial role in their interaction with plant cells. Nanoparticles ranging from 3 to 8 nm can penetrate the root epidermis and reach the xylem through osmotic pressure, allowing their transport to the aerial parts of the plant (Tripathi et al., 2017; Lin & Xing, 2008; Du et al., 2011; Rajput et al., 2020; Ali et al., 2021). Once they cross the cell walls, nanoparticles are transported apoplastically through extracellular spaces until they reach the central vascular cylinder, enabling their unidirectional upward movement through the xylem. To enter the central vascular cylinder, nanoparticles need to traverse the Casparian strip barrier. This occurs by binding to carrier proteins on the endodermal cell membrane through mechanisms like endocytosis, pore formation, and transport. Subsequently, nanoparticles move from one cell to another via the plasmodesmata, becoming internalized in the cytoplasm (Jha et al., 2011). Aggregated nanoparticles that fail to internalize accumulate on the Casparian strip, while those that reach the xylem are transported to the shoots and then redistributed through the phloem back to the roots (Dimkpa et al., 2012; Josko & Oleszczuk, 2013).

Within plants, nanoparticles can be found in various locations, including the epidermal cell wall, cortical cell cytoplasm, and nuclei (Josko & Oleszczuk, 2013). Nanoparticles that do not enter the root surface of soil aggregates can influence nutrient absorption. Direct absorption of nanoparticles in seeds can occur by entering the coat through parenchymatic intercellular spaces and diffusing into the cotyledon. Nanoparticles can also enter through the root tip meristem or at points of lateral root formation, taking advantage of wounds in the Casparian strip. To enter the epidermal layers of roots, nanoparticles must penetrate cell walls and plasma membranes, with the cell wall pores typically ranging from 3 to 8 nm in size (Carpita & Gibeaut, 1993). Although this size poses a challenge for nanoparticles to enter, it has been observed that nanoparticles can induce the formation of larger pores in cell walls, facilitating their internalization (Navarro et al., 2008).

Conventional fertilizers often result in nutrient leaching and pollution of soil and water, while certain agrochemicals contribute to greenhouse gas emissions and climate change (Rochette et al., 2018; Wesołowska et al., 2021). Controlled release of nanoparticles can address these issues. For example, Torney et al. (2007) demonstrated the controlled intracellular release of desired chemicals in protoplasts using mesoporous silica nanoparticles. To mitigate nitrogen leaching, treatments with polyolefin-coated urea, neem-coated urea, and sulfur-coated urea have been employed to control the release of nitrogen (Preetha & Balakrishnan, 2017). Studies have also explored the use of double-layered hydroxide nanocomposites for controlled nutrient release (Benício et al., 2017) as well as the slow release of integrated superabsorbent fertilizers to enhance soil moisture conservation (Wang et al., 2021). Furthermore, plants can exhibit responses to nanoparticles. For instance, the application of bentonite and titanium dioxide (TiO_2) nanoparticles led to a reduction in the diameter of *Zea mays* seedling root cell wall pores from 6.6 to 3.0 nm (Asli & Neumann, 2009).

5.3 Seed Coating

Another mode of NF application is seed coating, where nanoparticles are coated onto the surface of seeds before planting. This approach ensures that the nutrients are readily available to the germinating seedlings, providing them with a nutrient boost during early growth stages (Chakraborty et al., 2023). Seed coating with NFs improves seedling vigor, enhances root development, and promotes uniform plant establishment.

5.4 Drip Fertigation

NFs can also be applied through drip irrigation systems. By adding NF suspensions to the irrigation water, nutrients are directly delivered to the root zone. This mode enables precise control of nutrient application and minimizes nutrient losses due to runoff or evaporation (Fatima et al., 2020). Drip irrigation with NFs ensures targeted nutrient supply and efficient water usage, making it suitable for both field and greenhouse applications.

5.5 Controlled-Release Systems

Controlled-release systems involve encapsulating NFs within polymer coatings or matrices. These coatings control the release rate of nutrients, providing a sustained and controlled nutrient supply to the plants over an extended period. Controlled-release NFs offer improved nutrient use efficiency, reduce nutrient losses, and minimize the frequency of fertilizer application (Zulfiqar et al., 2019).

5.6 Nano-Hydrogel Application

Nano-hydrogels, which are nanoscale three-dimensional networks of hydrophilic polymers, can be used as carriers for NFs. These hydrogels can absorb and retain water and nutrients, acting as reservoirs that release the nutrients gradually to the plants. The application of nano-hydrogels loaded with NFs improves water retention in the soil, reduces nutrient leaching, and enhances nutrient availability to plants.

5.7 Nanocoating on Substrates

NFs can be coated onto various substrates, such as organic materials or inorganic carriers like zeolites or clay minerals. These coated substrates can be incorporated into the soil or used as top dressings. A nanofertilizer coating provides a controlled nutrient release and protects the nutrients from leaching or immobilization in the soil, ensuring their availability to plants over an extended period.

5.8 Hydroponic Systems

NFs can be used in hydroponic systems, where plants are grown in nutrient-rich water solutions without soil. The nanoparticles can be added directly to the hydroponic nutrient solution, providing a controlled and precise nutrient supply to the plants' root systems (Fatima et al., 2020). Hydroponic systems combined with NF application offer efficient nutrient uptake, water conservation, and optimal nutrient management for soilless agriculture.

5.9 Biodegradable Nanoparticles for Root Coating

Biodegradable nanoparticles can be coated onto the root systems of plants. These nanoparticles gradually release nutrients as they degrade, providing a localized nutrient supply to the plants' roots. Root coating with biodegradable NFs promotes nutrient absorption, enhances root development, and reduces nutrient losses to the surrounding environment.

5.10 Nanoencapsulation

Nanoencapsulation involves enclosing NFs within protective shells or capsules. These encapsulated nanoparticles can be applied through various modes such as soil application, foliar spray, or seed coating. The encapsulation protects the nanoparticles from degradation and enhances their stability, ensuring a controlled release of nutrients over an extended period. Nanoencapsulation enables precise nutrient delivery, reduces nutrient losses, and improves nutrient use efficiency (He et al., 2019; Chakraborty et al., 2023).

5.11 Nanofertilizer Incorporation in Compost

NFs can be incorporated into composting processes to enhance the nutrient content and quality of compost. By adding NFs to the organic waste during composting, the resulting compost becomes enriched with essential nutrients (Raliya et al., 2017). This nutrient-rich compost can then be applied to the soil, providing a slow-release source of nutrients for plants.

5.12 Nanofertilizer Application via Biodegradable Mulches

Biodegradable mulches, such as films or sheets made from biodegradable polymers, can be coated with NFs. These mulches are then laid on the soil surface around plants, slowly releasing nutrients as they degrade. Nanofertilizer-coated mulches offer controlled nutrient release, weed suppression, moisture conservation, and improved soil fertility (Zulfiqar et al., 2019).

It is important to note that the selection of the appropriate mode of NF application should consider factors such as crop type, growth stage, specific nutrient requirements, environmental conditions, and local farming practices. Additionally, proper application techniques, dosages, and timing should be followed to ensure effective nutrient uptake, minimize waste, and mitigate any potential environmental risks (Figs. 3.2 and 3.3).

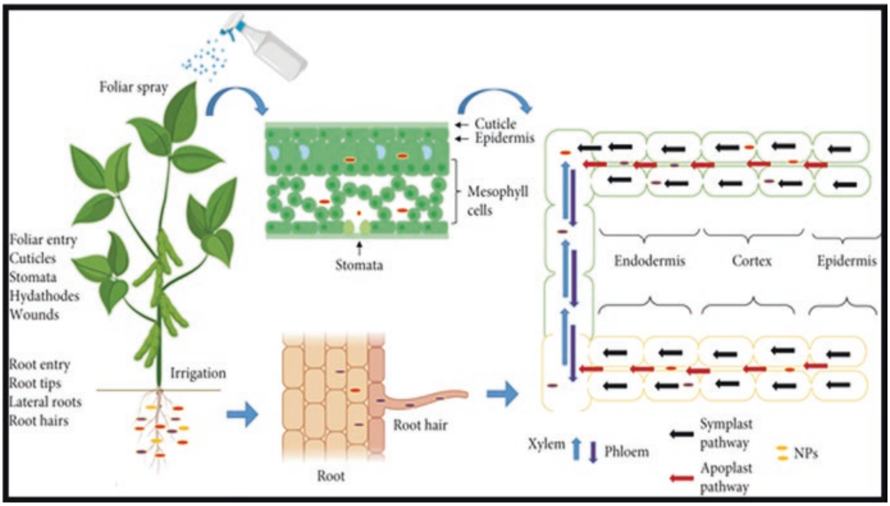

Fig. 3.2 Schematic visualization of the uptake of nanoparticles via various routes and their translocation pathways in various plant sections

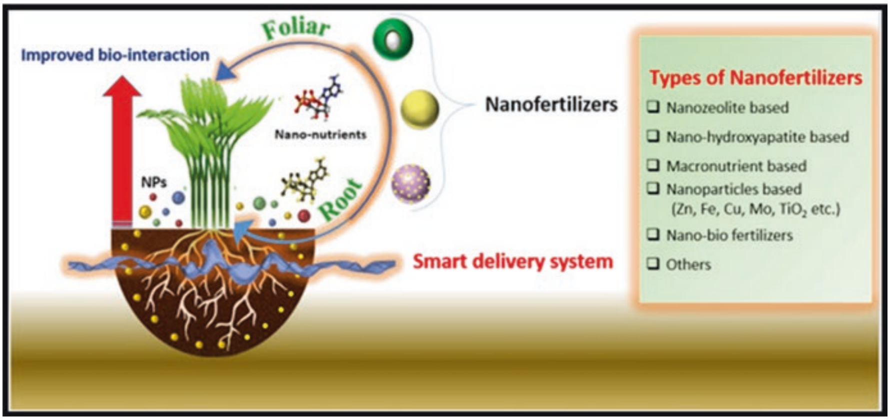

Fig. 3.3 Various approaches of application of NFs (Md. Rashid Al-Mamun et al., 2021)

6 The Mechanisms of Action of Nanofertilizers

Nanofertilizers have gained significant attention in the field of agriculture due to their unique mechanisms of action, which offer potential benefits in nutrient uptake, plant growth, and crop productivity. These mechanisms can be attributed to the physicochemical properties and nanostructured nature of the fertilizers.

The reactivity of nanomaterials facilitates efficient nutrient absorption in plants, leading to greater utilization and minimal losses compared to conventional fertilizers (Prasad et al., 2017; Pérez-de-Luque, 2017). The effectiveness of nanofertilizers in nutrient absorption, distribution, and accumulation depends on various factors, including soil pH, organic matter content, soil texture, and nanoparticle properties such as size and coating (El-Ramady et al., 2018; Ma et al., 2018). Nanofertilizers can be absorbed by plants through roots and leaves, affecting their behavior, bioavailability, and absorption within the plant (El-Ramady et al., 2018). Numerous studies have demonstrated the superior efficacy of nanofertilizers compared to conventional fertilizers. For example, nanofertilizers enriched with macronutrients have shown a 19% increase in plant development compared to conventional fertilizers, whereas those containing micronutrients have exhibited an 18% improvement (Kah et al., 2018). Furthermore, nanofertilizers with carriers for macronutrients have resulted in a remarkable 29% growth enhancement compared to conventional fertilizers. Nanofertilizers based on nano-chitosan, combined with nitrogen (N), phosphorus (P), and potassium (K), have been found to increase the sugar content and improve wheat properties (Abdel-Aziz et al., 2016). In another study focusing on wheat, Salama (2012) observed that the application of silver nanoparticles led to increased shoot and root length, leaf area, and the contents of chlorophyll, carbohydrates, and proteins. Moreover, nanofertilizers have the advantage of slow release, with nutrients being released over a period of 40–50 days, compared to the conventional fertilizers' release duration of 4–10 days (Chen & Wei, 2018).

(i) *Increased Nutrient Availability and Uptake*: Nanofertilizers exhibit a large surface area and high reactivity due to their nanoscale dimensions. This increased surface area allows for better contact and interaction with plant roots. The nanoparticles can release nutrients gradually, ensuring a sustained supply to the plants. The small particle size and high surface energy of nanofertilizers facilitate their penetration into the root tissues, enhancing nutrient uptake efficiency (Sharma et al., 2020). Additionally, the nanoparticles can overcome barriers such as soil pH, nutrient imbalances, and antagonistic reactions, thereby improving nutrient availability to the plants.

(ii) *Enhanced Nutrient Use Efficiency*: Nanofertilizers can improve nutrient use efficiency by reducing nutrient losses through leaching and volatilization. The controlled release of nutrients from nanofertilizers ensures that they are available to plants when needed, minimizing wastage and maximizing utilization (Mahapatra et al., 2022). The nanoparticles can also promote the conversion of nutrients into forms that are readily absorbable by plants, optimizing nutrient utilization and reducing environmental pollution (Shyam et al., 2021).

(iii) *Stimulated Plant Growth and Development*: The unique properties of nanofertilizers can stimulate plant growth and development. The nanoparticles can act as signaling molecules, triggering specific plant responses that promote root growth, shoot development, and overall plant vigor. Nanofertilizers can also enhance photosynthesis, chlorophyll synthesis, and enzymatic activity, leading to improved plant growth, increased biomass production, and enhanced crop yields.

(iv) *Enhanced Stress Tolerance*: Nanofertilizers have shown potential in improving plant tolerance to various abiotic and biotic stresses (Fatima et al., 2020). The nanoparticles can act as antioxidants, scavenging reactive oxygen species and protecting plants from oxidative damage caused by stress factors such as drought, salinity, and heavy metals. Nanofertilizers can also enhance a plant's defense mechanisms, leading to improved resistance against pests, diseases, and pathogenic infections.

(v) *Soil Health Improvement*: The application of nanofertilizers can positively influence soil health and fertility. The nanoparticles can enhance soil aggregation, improve water-holding capacity, and promote the growth of beneficial soil microorganisms (Chakraborty et al., 2023). Nanofertilizers can also mitigate soil degradation and nutrient depletion by replenishing essential nutrients and restoring soil nutrient balance.

(vi) *Nanoparticle Uptake and Translocation*: Nanofertilizers can enter plant cells through various uptake mechanisms. They can be taken up directly by root hairs, penetrating the cell walls and membranes. The small size of nanoparticles enables them to move easily through cell compartments, facilitating their translocation to different plant parts, including shoots, leaves, and reproductive organs (Raliya et al., 2017). This efficient uptake and translocation of nanoparticles ensure a uniform distribution of nutrients within the plant, contributing to balanced growth and development.

(vii) *Controlled-Release and Slow-Release Mechanisms*: One of the advantages of nanofertilizers is their ability to release nutrients gradually and in a controlled manner (Fatima et al., 2020). The nanoparticles can be engineered to have specific coatings or encapsulations that regulate the release of nutrients over an extended period. This slow-release mechanism ensures a steady supply of nutrients to the plants, reducing the frequency of fertilizer applications and minimizing nutrient loss through leaching or runoff.

(viii) *Nano-Enhanced Nutrient Uptake Pathways*: Nanofertilizers can enhance nutrient uptake by promoting the expression of specific transporters and channels in plant roots. The nanoparticles can interact with the cell membranes, modifying their permeability and facilitating the transport of nutrients into the cells. This nano-enhanced uptake pathway enables efficient nutrient absorption and assimilation, leading to improved plant nutrition and growth.

(ix) *Hormonal Regulation*: Nanofertilizers can influence plant hormone signaling pathways, leading to hormonal regulation and physiological responses (Fatima et al., 2020). The nanoparticles can modulate the biosynthesis, metabolism, and distribution of plant hormones such as auxins, cytokinins, and gibberellins, which play crucial roles in plant growth and development. By manipulating hormone levels and their transport, nanofertilizers can stimulate root branching, shoot elongation, flowering, and fruit development.

(x) *Gene Expression and Genetic Regulation*: Nanofertilizers can modulate gene expression patterns in plants, influencing the activation or repression of specific genes involved in nutrient uptake, stress responses, and growth regulation. The nanoparticles can interact with DNA, RNA, and proteins, altering their conformation and activity. This genetic regulation induced by nanofertilizers can enhance nutrient acquisition, stress tolerance, and overall plant performance.

(xi) *Rhizosphere Modification*: Nanofertilizers can modify the rhizosphere, which is the soil region surrounding the plant roots. The nanoparticles can alter the microbial community composition, promoting the growth of beneficial microorganisms that enhance nutrient availability and plant health. Nanofertilizers can also improve the soil structure and water-holding capacity, creating a favorable environment for root growth and nutrient absorption.

(xii) *Synergistic Effects*: Nanofertilizers can exhibit synergistic effects when combined with other agricultural inputs, such as conventional fertilizers, organic amendments, or biostimulants (Kalwani et al., 2022). The nanoparticles can enhance the efficiency and effectiveness of these inputs by improving their absorption, translocation, or utilization by plants. This synergy can lead to enhanced nutrient uptake, growth promotion, and overall crop productivity.

The understanding of the mechanisms involved in the uptake, translocation, and effects of nanoparticles within plants is crucial for optimizing the application of nanofertilizers and ensuring their safe and effective utilization in agriculture. It is important to note that the precise mechanisms of action of nanofertilizers can vary depending on the specific formulation, nanoparticle characteristics, and plant species (Raliya et al., 2017). The interplay between physicochemical properties of nanofertilizers and plant physiological processes is a complex and dynamic interaction that requires further research and understanding.

7 Challenges and Future Prospects

NFs have emerged as a promising technology in the field of agriculture, offering potential benefits such as improved nutrient absorption, controlled release, and reduced environmental impact (Mahapatra et al., 2022; Raliya et al., 2017). However, their widespread adoption and commercialization face several challenges.

7.1 Challenges

- *Safety and Environmental Concerns*: One of the primary challenges associated with NFs is the potential risk to human health and the environment. The nanoscale particles used in NFs may have unknown toxicity effects. It is crucial to conduct comprehensive safety assessments and evaluate the environmental impact before their large-scale deployment.
- *Regulatory Framework*: The regulatory framework for NFs is still evolving, with limited guidelines and standards in place. The development of clear regulations and standards specific to NFs is necessary to ensure their safe and responsible use as well as to facilitate their market acceptance.
- *Scalability and Cost*: The production of NFs on a large scale can be challenging, resulting in higher production costs compared to conventional fertilizers. To promote the widespread adoption of NFs, there is a need for scalable and cost-effective manufacturing processes that can meet the demands of agricultural systems.
- *Integration with Existing Agricultural Practices*: Integrating NFs into existing agricultural practices and supply chains poses logistical challenges. Compatibility with the existing equipment, application methods, and formulation compatibility need to be addressed for seamless adoption of NFs in different farming systems.
- *Knowledge and Awareness*: There is a need to enhance knowledge and awareness among farmers, agronomists, and stakeholders about the benefits and potential risks associated with NFs. Education and training programs can play a crucial role in ensuring the responsible and effective use of NFs.

7.2 Future Prospects

Despite the challenges, NFs hold significant promise for the future of agriculture (Abd El-Azeim et al., 2020). Here are some potential future prospects:

- *Enhanced Nutrient Management*: NFs have the potential to revolutionize nutrient management in agriculture. By fine-tuning the composition, structure, and release mechanisms, NFs can provide targeted and efficient nutrient delivery to plants, reducing nutrient losses and increasing crop productivity (Abdelsalam et al., 2019).
- *Controlled-Release Systems*: Advancements in nanotechnology can lead to the development of advanced controlled-release systems that respond to plant nutrient demands, environmental factors, and soil conditions. These systems can optimize nutrient availability, reduce leaching, and minimize environmental pollution.
- *Precision Agriculture*: The integration of NFs with precision agriculture techniques, such as remote sensing and data analytics, can enable site-specific nutrient management (Raliya et al., 2017; Mahana et al., 2022). This approach can optimize nutrient application based on crop requirements, leading to improved resource-use efficiency and sustainable farming practices.
- *Functional NFs*: Future research may focus on developing functional NFs that go beyond nutrient delivery. These NFs could incorporate additional functionalities such as disease resistance, stress tolerance, and enhanced plant growth promotion, contributing to the overall crop health and resilience.
- *Nanotechnology-Enabled Smart Farming*: The convergence of nanotechnology with other emerging technologies like sensors, robotics, and artificial intelligence can pave the way for smart farming systems (Chakraborty et al., 2023). NFs can play a vital role in such systems by providing precise and timely nutrient delivery, optimizing resource utilization, and enabling real-time monitoring of plant health.

While NFs face challenges in terms of safety, regulations, scalability, and integration, their prospects are promising. Addressing the challenges will require collaborative efforts from researchers, policymakers, industry, and farmers. By overcoming these hurdles and leveraging the potential of nanotechnology, we can harness the benefits of NFs to meet the increasing global demand.

8 Conclusions

From the abovementioned scenarios, it can be concluded that NFs represent a promising approach for enhancing plant nutrient uptake, improving crop productivity, and reducing environmental impacts. They can be synthesized through various methods, including chemical, physical, and biological approaches, with each offering distinct advantages and limitations. Chemical methods allow for precise control over particle size and morphology, while physical methods offer simplicity and scalability. Biological methods, on the other hand, provide environmentally friendly alternatives using plant extracts and microorganisms.

The mechanisms of action of NFs involve their size-dependent entry into plant cells, transport through the vascular system, and interactions with cellular components. Nanoparticles can be absorbed through root and leaf surfaces, where they are translocated via both apoplastic and symplastic pathways. The size and surface properties of nanoparticles influence their uptake and translocation within the plant, affecting nutrient absorption and physiological responses. Furthermore, nanoparticles can induce oxidative stress, alter membrane integrity, and interact with genetic material and cellular organelles. It is important to consider factors such as particle size, shape, surface charge, and interactions with plant cell components when designing and utilizing NFs. Understanding the mechanisms of nanoparticle uptake, distribution, and physiological effects in plants is crucial for maximizing their potential benefits and minimizing any potential risks. Further research is needed to elucidate the specific molecular mechanisms involved and optimize the synthesis and application of NFs for sustainable agriculture.

Overall, NFs hold great promise for revolutionizing agricultural practices, offering targeted nutrient delivery, reduced environmental impact, and enhanced crop productivity. Continued research and development in this field will pave the way for effective and sustainable nanofertilizer strategies, contributing to global food security and environmental sustainability.

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