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# Synthesis of Nano Fertilizers via Physical and Chemical Approaches

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**Abstract**

The widespread utilisation of fertilisers has been encouraged by the growing global population and the corresponding growth in food consumption. Due to a lack of resources and a low fertiliser output, farmer expenditures are increasing dramatically. The creation of customisedfertilisers with the right chemical make-up, higher nutrient use efficiency, and enhanced plant performance is now achievable because of nanotechnology. By properly dispersing and releasing nanoscale active chemicals, the agricultural potential is also boosted. In this work, the synthesis of nanoparticles (NPs) and nanomaterials (NMs), as well as their benefits and drawbacks, are discussed. In order to create nanofertilizers (NFs), which are more effective and efficient than traditional fertilisers, NPs and NMs, which have been shown to be viable alternatives, may be employed. Because NF increases plant stress tolerance and agricultural nutrition, its applications are growing. However, there hasn't been much discussion of the possible negative environmental implications of using NPs and NMs in agriculture. These investigations are essential because NPs and NMs may infiltrate ecosystems via a variety of routes, harming species, reducing their diversity and abundance, and maybe even reaching consumers.

**Keywords:** Nanoparticles (NP), nano fertilizer (NF), fertilizer, agriculture, nanomaterial (NM)

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## 1. Introduction

A potential and novel strategy for raising agricultural output throughout the world is the development of new kinds of fertilisers based on nanotechnology. NF, nano-pesticides, and nano-carriers are a few of the applications of nanotechnology in agriculture that are regularly employed. NF, which increases plants' capacity to absorb nutrients, is one of the most significant applications of nanotechnology [1]. Since they are so small (1-100 nm), molecular aggregates known as NP exhibit physicochemical characteristics distinct from those of bulk materials. NPs have superior physical, chemical, and biological properties, phenomena, and functions because of their enormous surface-to-volume ratio [2]. Physical, chemical, and green (natural) synthesis methods may all be used to create NF. The green process is superior because it uses fewer chemicals, resulting in less chemical pollution, and is safer than physicochemical methods [3]. Figure 1 illustrates how nanotechnology is used in agricultural production. Numerous inhibitory action modalities against different diseases, such as bacterial and fungal species, have given green nanotechnology a significant edge in the modern era. The application of nanotechnology in many production phases, including processing, storage, and transportation of agricultural goods, is crucial [4].

The interdisciplinary branch of study known as nanotechnology has shown promise in biotechnology, engineering, medicine, environmental science, food science, and agriculture. Since they are tiny and have a high surface-to-volume ratio, they exhibit certain qualities that are different from those of the bulk material. Numerous research has examined the cytotoxic effects of NPs on cancer cells for use in the medical sciences. Previous research on using NPs as antibacterial agents has been done similarly. An in-depth analysis has also been done on the possible use of nanotechnology to sanitize water and wastewater. The use of nanotechnology in agriculture has received very little study (Figure 2).

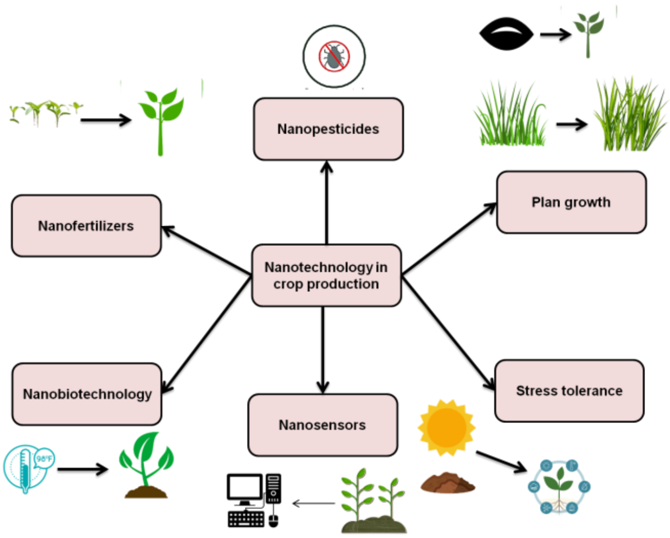


**Figure 1:** Nanotechnology in crop production

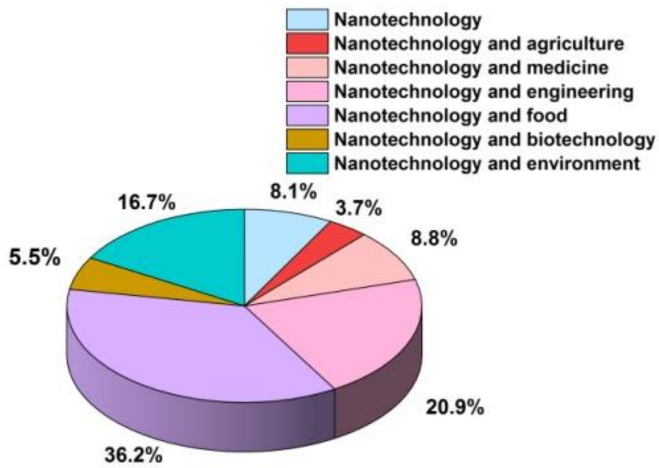


**Figure 2:** Industry employs nanotechnology for ten years

Compared to their bulk counterparts, NP is far more suitable for application due to their more significant surface-to-volume fractions and unique characteristics. The integration of nanotechnologies with agricultural and food research is becoming more and more attractive as a strategy to increase plant growth and production [5]. In addition to increasing fertilizer consumption efficacy, reducing volatilization and leaching, and reducing environmental issues, NF may feed plants gradually and under regulated conditions. Achieving decent sustainability in agriculture continues to be hampered by the ineffective nutrient utilization efficiency and environmental restrictions linked to chemical fertilizers [6]. This research focuses on the physical and chemical methods for synthesizing NF.

For potential nano-fertilizers (NF) uses in agriculture, the study [7] proposed developing integrated risk management systems. The article [8] discussed the many kinds of NP, how they are transmitted via plants, how they affect plants (both physiologically and genetically), and people who consume such plants. The study [9] conducted a novel investigation into the biosynthesis of NPs, their use as nano-fertilizers and nano-pesticides in agriculture, and their influence on the functioning of biofactors. The study [10] discussed concerns with regulation and risk assessment concerning the synthesis of NM and its usage in the food business. The research [11] examined the wide varieties of nano-based fertilizers and their preparation techniques, benefits, and nanotoxicity. The study [12] investigated the effect of the Zn and Cu NPs on the morphological and biochemical characteristics of the basil plant; an experiment was conducted utilizing four levels of Zn NPs and four levels of Cu NPs as a factorial based on a totally randomized design. Increasing the effectiveness of nutrient utilization has been cited [13]. By enhancing soil fertility and other essential aspects of soil quality, the nutrients are employed to support sustainable agricultural production systems and improve crop and cropping systems' general productivity. Different kinds of NF may be created using a top-down or bottom-up strategy, and they are more effective than traditional fertilizers in supplying micronutrients and macronutrients [14]. The effectiveness, affordability, and environmental safety of various NPs may differ from those of conventional fertilizers and insecticides. The article [15] studied the effects of three foliar applications of the nano micronutrient fertilisers zinc, manganese, and iron on the vegetative growth, productivity, physical quality, and nutritional value of the two cultivars of snap beans, Bronco and Flantino, as well as the interactions between these variables.

## 2. Proposed method

Nutrients that have been coated or encapsulated with nanomaterial to allow for regulated release and delayed diffusion into the soil are known as nano fertilizers. The suggested approach covers the mechanical attrition kinds, chemical processes, expansion cooling, and bottom-up and top-down tactics.

### *2.1 Synthesis of aerosols*

NP is produced using five distinct aerosol methods: the physical vapor deposition employing the furnace process, producing particles smaller than 100 nm is exceedingly challenging. With adequate safety measures, the flame process may effectively generate $TiO_2$ NP. Although exact nanoparticle size and shape may be produced using an efficient electro-spray method, the yield is only approximately 1 g per year. Both chemical and physical vapor deposition are efficient processes for generating NP. NPs are created via the aerosol technique by carefully controlling the gas flow rate, heater size, and diffusion dryer size. NP comes in a variety of morphologies, including cube, plate, cage, and wire-shaped particles.

### *2.2 Technique of gas condensation*

The main method used to produce nanocrystalline metals and composites at the moment is gas condensation. A metallic or inorganic substance is vaporised in a setting with a pressure of 1 to 50 m bar using thermal dissipation sources such electron beam evaporate devices and Joule heated refractory crucibles. Because there is a lot of residual gas pressure left over after gas evaporation, ultrafine particles (100 nm) are created by gas stage collision. Ultrafine particles are created when atoms of still-present gas collide with atoms of evaporating gas. The usage of gas pressures more than three mPa (10 torrs) is required. Potential sources of vaporisation include resistive heating, drafting heating, high-energy electron beams, and low-energy electron beams. Atoms that consume gas phase atoms create uniform nucleation clusters close to the source. It comprises a compaction tool, a cold finger scrapper assembly with liquid nitrogen within, and an evaporation source mounted on an ultra-high vacuum (UHV) framework. In the supersaturating zone around the joule heating device, particles heat up and condense.

The NP is released as metallic plates by the scrapper. In refractory metal pots consisting of tungsten (W), tantalum (Ta), or molybdenum (Mo), evaporation has to be done. An electron beam evaporation system will be employed if the metals react with crucibles. The process of gas condensation moves slowly. Temperature variations, source-precursor incompatibility, and changing evaporation rates are some downsides of the amalgamation method.

### *2.3 Method of inert gas condensation*

However, the inert gas condensation approach was also employed to manufacture nanocrystalline powder particles and combine them in situ into a tiny ultra-high vacuum (UHV) state. The process of vapor condensation, which depends on the substrate's temperature and various operating variables, is used to create extremely fine or amorphous alloys. Therefore, this technique produces tiny quantities of pure metal nanostructured. Metal was vaporized within the chamber using various methods, including resistive heating, sputtering, particle sputtering, electron shaft heating, and laser/plasma heating. The area was then evacuated to a high vacuum of nearly 10-7 torr, a tiny amount of low-pressure inert gas helium being added. When vaporized atoms within the chamber experience a loss in kinetic energy, the condensation process produces tiny discrete crystals of free powder. Convection flow is brought on by the evaporation source warming the inert gas. The transmission of small, dense particles to a power tool is also caused by the cold finger, a fluid nitrogen-filled device that is cooled. An annular Teflon ring is then rotated along the length of the cylinder to a compaction mechanism, revealing the powders. They create (Pd) and cobalt(II) oxide nanoparticles by condensing inert gases.

### *2.4 High-energy ball mill*

NP is one of the easiest techniques to create a variety of metals and alloys. It makes use of an energetic ball mill. This procedure uses a variety of mill types, including planetary, tumbler, rod, vibratory, etc. One or more containers are utilised to make small particles. Balls composed of tungsten carbide or hardened steel are kept in containers that also hold the material's powder or flakes (less than 50 mm). The lid generally seals the container tightly. The ideal ratio of balls to substance is often about 2:1. If a container is filled to more than half of its full capacity, milling efficiency is diminished. The grain size will be smaller, and the particle quality will be worse if more giant balls are used for milling. Pollutants from the ball or inert gas and air may be added to the container during the procedure. Temperatures increase during a collision by 100 to 1100 C. Using this technique, nanocrystalline forms of cobalt (Co), chromium (Cr), tungsten (W), and other metals are produced.

### *2.5 Top-down and bottom-up approaches*

The second procedure uses the top-down approach, while the first uses the bottom-up strategy. Top-down and bottom-up methods have both been functionalizing the production of NP. The top-down process is used to split a square of a bulk substance into nanosized particles. The Top-down techniques include lithography, attrition, milling, and other functions. The flaw in the surface structure is the top-down approach's fundamental drawback. Figure 3 displays many techniques for creating nanomaterials.

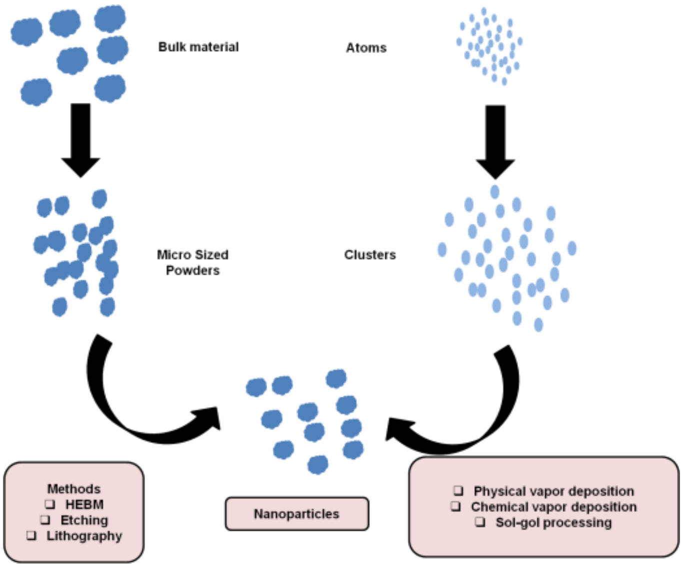


**Figure 3:** Methods for synthesizing nanomaterial

Chemical techniques known as bottom-up methods are used to create nanomaterials, which may be combined into more durable structures. Figure 3 shows how the material is built up cluster by cluster and atom by atom until it reaches the nanoscale. Self-assembly, positional assembly, and the right solvents are used in chemical synthesis to create ultrafine particles from their dissolved molecular state. Some of the methods used in the bottom-up approach include sol-gel, fast solidification, arc discharge, sol-plasma arc, physical vapour deposition, chemical vapour deposition, and inert gas condensation. The ability to construct NM with homogenous size, shape, and distribution is one advantage of the bottom-up approach. Creating NP for use in plant applications is often done via bottom-up techniques. However, the related method is complicated, yields little, and costly equipment is needed; it is only appropriate for highly pure materials and sometimes generates dangerous by-products during the synthesis process.

### *2.6 Mechanical attrition*

The mechanical attrition approach creates nanostructures when the structural breakdown of large-size particles occurs due to plastic deformation rather than cluster aggregation.

- High Energy Ball Mill (HEB)
- Attrition Ball Mill (ABM)
- Planetary Ball Mill (PBM)
- Vibrating Ball Mill (VBM)
- Low Energy Dropping Mill (LETM)

#### *2.6.1 Planetary Ball Mill*

The vial's independent spin and the rotating supporting plate produce radiant energy. On the interior mass of the vial, the charge powder and medium processing spin rapidly (360 rpm) before spilling over the bowl.

#### *2.6.2 Attrition Ball Mill*

Things are dispersed by combining a demonstration with an even set of arms (impellers), a vertical rotator focus shaft, and other components. The spinning speed was raised to 500 rpm. Additionally, the processing temperature was better managed.

#### *2.6.3 Low-Energy Tumbling Mill*

NP has been used to create manually combined powders. They cost little and are simple to operate. Al30Ta70 powder was prepared using S.S. tube rods in a laboratory-scale rod mill to be homogeneous and shapeless. With this technique, AlxTm100-x powders with an inadequate iron concentration may be made in just one procedure with poor gradation.

#### *2.6.4 Vibrating Ball Mill*

A vibrating ball mill is often used while creating amorphous alloys. The discrepancies in milling and powder are unsettling in the vertical trend at a relatively high speed (1200 rpm).

#### *2.6.5 Mechanical Alloying (MA)*

Because of severe plastic deformation, the crucial breakdown of large-grained structures yields nanostructure materials through mechanical alloying (MA). In the wet HEB mill, the powder was continuously welded, fractured, and rewelded throughout the automated alloying process until the rates of specific components in the underlying charge matched the composition of the created powder. This process involves crushing mixtures of pre-alloyed powders using a mechanism that provides high-energy compressive effect powers.

### *2.7 Metal Complexes Thermolyze*

This is the most efficient method for forming NP from organometallic precursors. This breakdown should be able to be brought on by thermolysis, photolysis, and oncolysis. The primary advantage of using organometallic combinations is the ability to separate precursors at shallow temperatures to get the desired end.

### *2.8 Expansion-cooling*

NPs smaller than 5 nm have been created using supersonic-free jets expanding in a vacuum chamber at pressures less than 10-4 bar. A metal vapor-containing inert gas was introduced to several expansions in Bowles' design. Two sonic increases are used to deliver the nuclei. At that moment, NP with mean diameters less than 2.5 nm were produced in a cores development region in a low-weight, subsonic reactor. The size distribution is smaller due to the division of the nucleation and condensation processes than is typically obtained via supersonic expansion.

### *2.9 Chemical methods*

The synthesis or alteration of fertilizer materials at the nanoscale to improve their characteristics and performance is a critical component of chemical approaches for generating nano fertilizers.

#### *2.9.1 Chemical Absorption*

A chemical precipitation process consists of three key stages: chemical reaction, nucleation, and crystal development. Chemical precipitation is often a runaway process in terms of reaction kinetics, solid phase nucleation, and growth mechanisms. Three key requirements must be fulfilled in order to manufacture NPs with a restricted size transport: (i) a high degree of supersaturation; (ii) a constant spatial fixation distribution throughout a reactor; and (iii) a continuous development time for all particles.

#### *2.9.2 Sol-gel methodology*

Aerogels, zeolites, and ordered porous solids are just a few of the materials that may be created using the sol-gel method by combining both inorganic and organic elements. Nanotubes, NP, and tiny rods are among the materials made using the process of sol-gel synthesis. In this procedure, a network is created by creating a liquid called sol and then joining the sol particles. The liquid powders may be dried to produce thin films and massive solids. Metal oxides, nitrides, borides, sulfides, and ceramics are produced as a consequence of this process.

#### *2.9.3 Electrodeposition (ED)*

This technique, which allows composite forms, is relatively inexpensive. The current density and current rates define the layer thickness. This method, which enables composite shapes, is reasonably priced. The current density and current rates represent the layer thickness.

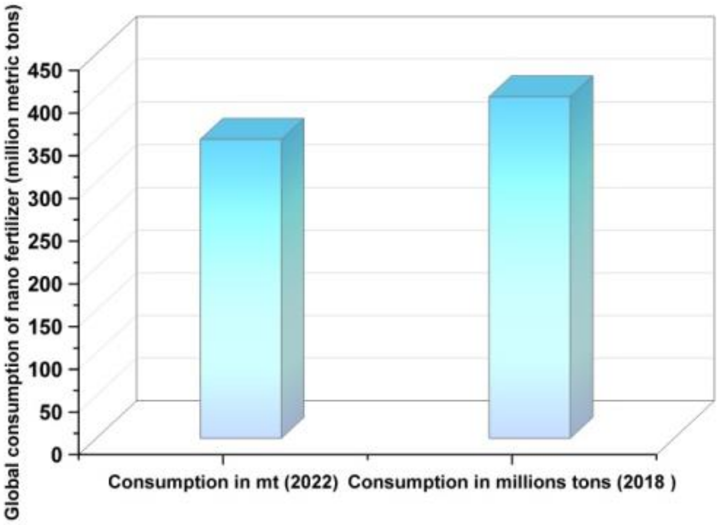


**Figure 4:**Global chemical fertilizer usage by the nutrient in 2018 and 2022

**Table 1:** The challenges of using nano fertilizers

| Global consumption of NF | million metric tons |
|---|---|
| Consumption in mt (2022) | 350 |
| Consumption in millions tons (2018 ) | 400 |

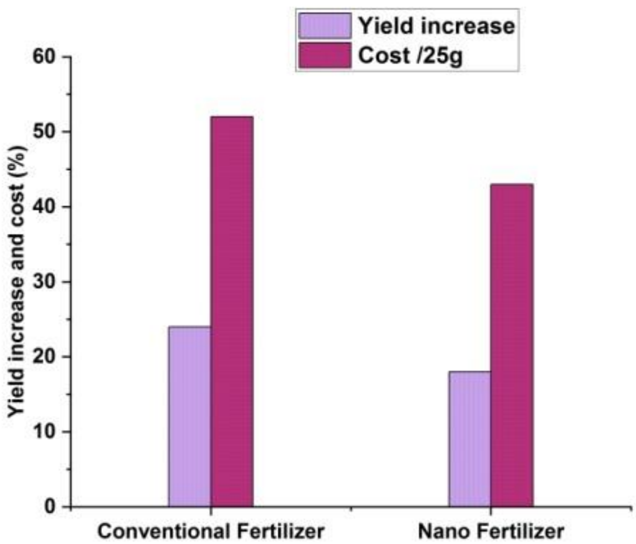


**Figure 5:** A comparison of the cost and yield improvement when using conventional fertilizers versus nano fertilizers

**Table 2:** Economic analysis of nano fertilizers

| | Yield increase and cost (%) | |
|---|---|---|
| | Yield increase | Cost /25g |
| Conventional Fertilizer | 24 | 52 |
| Nano Fertilizer | 18 | 43 |

#### *2.9.4 Chemical vapor deposition (CVD)*

In CVD, reactants are converted into microcrystalline and powder products in the vapor phase, and single crystal films for devices are then created by deposition on a substrate. Vapors are made by heating the volatile starting components; they are combined at an appropriate temperature and transferred to the substrate by the carrier gas. Organometallic is utilized as a precursor in the MetalOrganic Chemical Vapour Deposition(MOCVD) method. Removing them from the substrate transfers the by-products back to the gaseous phase.

#### *2.9.5 Photochemical Synthesis*

The range of photochemical processes triggered by photo energy absorption alters the structures of molecules. Typically, UV light is generated by a low-pressure mercury pillar lamp, whereas visible photo irradiation is carried out using a high-pressure column like an indium lamp.

#### *2.9.6 Method of Gamma-Irradiation*

One of the most advanced and successful methods is the production of nanometer-sized materials using gamma rays. Metals, alloys, oxides, and polymer nanocomposites with nanocrystalline structures have all been produced using this method. More significant among these compounds are semiconductive chalcogenides/polymer nanocomposites. Inorganic/polymer nanocomposites were created with the simultaneous polymerization of monomers and the configuration of inorganic NP by gamma irradiation. In contrast, gamma-irradiation is the well-established approach for creating chalcogenide/polymer nanocomposites.

#### *2.9.7 Spray Pyrolysis*

This technique deposits the source as liquid droplets sprayed onto the substrate to produce the coating. A film forms when the substrate is heated to 350 and 500 C. To make the sprayed liquid, the chemical is diluted in either water, alcohol, or both. The droplets, which contained a precursor solution, disintegrated very fast at low temperatures. This method prevents molecular pressure and advancement while the temperature remains too high to decompose the precursors completely. The completed product, made up of 5 to 10 nm crystallites arranged in a circle and brought together, revealed the kind of original bead and proved that the beads were not separated, sometimes producing NP**.**

## 3. Results and Discussions

Modern agriculture is often chemically concentrated on achieving optimum output, using additional chemical dosages for nutrient management without considering ecosystems and natural resources. The fertilizer accounts for 50% of crop productivity. Shipping prices rose due to the strong demand for chemical fertilizers (Figure 4). In addition to other micronutrients, chemical fertilizers provide essential macronutrients, including nitrogen, phosphate, and potash. However, leaching causes around half of the fertilizer to be lost.

Furthermore, the overuse of chemical fertilizers depletes soil nutrients and creates waste. One of the most excellent methods to deal with this problem is to use macro- and micronutrient sources while enhancing traditional fertilizers. One of the most important factors affecting how efficiently plants absorb minerals is the presence of mineral nutrients in bioavailable form. The difficulties of using NF are outlined in Table 1.

Conventional fertilizers are manufactured or synthetic fertilizers often used in agriculture to give plants the nutrients they need to grow. Compared to traditional fertilizers, nano fertilizers may provide several benefits. Through more focused and regulated nutrient delivery, they may increase nutrient efficiency and lower nutrient losses from leaching or volatilization. Figure 5 shows that using standard fertilizer, which costs $20.00 per 19 g bottle, resulted in an acquiescence increase of 24%, but utilizing nano-fertilizers, which cost US$44.00, resulted in a yield increase of 52%. Table 2 displays the economic analysis of NF.

## 4. Conclusions

In conclusion, physical and chemical methods may be used to create nano fertilizers. Biological processes, including grinding, milling, or attrition methods, entail the size reduction of bulk materials to the nanoscale. These techniques may create NP with increased surface area and reactivity. This technique deposits the source as liquid droplets sprayed onto the substrate to produce the coating. A film forms when the substrate is heated to 350 and 500 C. The substance is diluted in either water, alcohol, or both to create the liquid that is sprayed. The droplets, which contained a precursor solution, disintegrated very fast at low temperatures. This method prevents molecular pressure and advancement while the temperature remains too high to decompose the precursors completely. The outcome was a circle of 5 to 10 nm crystallites that were pushed together, exposing the kind of initial bead and proving that the beads were not split, sometimes resulting in NP. Future research may be done to improve the efficiency, repeatability, and scalability of the synthesis processes for nano fertilizers. This entails experimenting with new methods, enhancing response circumstances, and developing more environmentally friendly and economically viable solutions.

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