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Physical and chemical techniques to produce nano fertilizers

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Abstract

The increasing food demand due to the rising global population has encouraged the large-scale use of fertilizers. Due to resource constraints and low use productivity of fertilizers, the cost to the farmer is increasing dramatically. Nanotechnology offers a great potential to adapted fertilizer production with the desired chemical composition, improve the nutrient use efficiency that may reduce environmental impact and enhance the plant efficiency. Additionally, controlled release and targeted delivery of nanoscale active ingredients make the agricultural potential more sustainable and accurate. The purpose of this paper is to provide an overview of the synthesis of nanomaterials (NMs) and nanoparticles (NPs), highlighting their advantages and disadvantages. NPs and NMs have been demonstrated to be an attractive alternative for the manufacture of nanofertilizers (NFs), which are more effective and efficient than conventional fertilizers. The utilization of NFs is expanding, because of their impact on crop nutritional quality and stress resistance in plants. However, there are practically no studies on the potential environmental effect of NPs and NMs when utilized in agriculture. These investigations are necessary because NPs and NMs can be transferred to ecosystems by various pathways where they can cause toxicity to organisms, influencing the biodiversity and abundance of these environments, and may ultimately even be transferred to consumers.

Key words: Nanofertilizer, Nanomaterial, Fertilizer, Agriculture, Nanoparticles

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1. Introduction

Plant growth and yield improved by adding fertilizers. Vital compounds of modern synthetic fertilizers are nitrogen, phosphorous, and potassium with secondary nutrients. Synthetic fertilizers extensively improved the quality and quantity of food, but their excess use is debated by environmentalists. Growing plants take chemical components from earth for growth that can replace by fertilizers and fertilizer also enhanced the earth growing potential, and by this way beneficial growing environment achieves better than natural soil in last few decades. Outburst of world population has moved towards higher production of agricultural so that population of billion people could meet their needs, especially in advanced countries. Due to widespread occurrence of nutrient deficiency in soil, there occur huge economic losses for farmer, remarkable nutritional quality decrease and also overall grain quality for human beings and livestock. Fertilizer can increase crop productivity remarkably. Usually, half of the applied chemical fertilizer being used by the crop plants, but the left over minerals percolate down, and causes air pollution due to getting fixed in soil [1]. But extensive chemical fertilizer use is not best option to increase productivity of crop for extended time, because on the other hand soil fertility decreases and soil mineral balance also disturbed [2]. Not only incurable damage occurs to soil structure, due to excess use of fertilizers but also disturb mineral cycles, damage microbial flora plants and moreover food chain across ecosystem moved to heritable mutations of consumers in future generation [3]. There is need to develop smart materials to programmable release of chemicals to specific sites that are targeted in plants, in viewing to above discussed points, it is urges necessity to control insufficiency of nutrition in agricultural field. Here “Smart delivery system” stands for a mixture of particularly targeted highly controllable lightly regulated and high efficient attribute can be said smart delivery system to overcome biological restrictions for efficient targeting. Treatment of materials at atomic molecular level and macromolecules scales performed by Nanotechnology whose function is at 100nm, their properties highly vary at large scale. The surface area to volume ratio enhances catalytical properties of material as well as mechanical also enhanced. Changing thermal mechanical as well as catalytical properties of materials enhance by surface area to volume ratio.

Nanotechnology can develop slow release efficient fertilizers [4]. Development in technology has enhanced different ways for significant fabrication of nanoparticles of physiologically essential metals, which are these days known as “smart delivery systems” that are being used for advance fertilizer formulation, it helps in controlling nutrient loss also increase plant cells uptake. Because of larger surface area, nanofertlizers sorption capacity, and controlled release kinetics to target sites, proves them as a smart delivery system. Energy economy and environment are highly impacted by nanofertlizers because it minimizes nitrogen loss due to leading also decreases emission and long-term absorption that occurs by microorganisms of soil. Nanofertilizers are less costly to manufacture that use natural material for granules coating and cementing of soluble fertilizers than artificially type fertilizers. The soil may also improve by decreasing poisonous effects associated with over application of fertilizer by utilization of slow, controlled released fertilizers [5]. Before adopting the use of nanofertilizer it is necessary to evaluate it carefully, because the safety and ethical issues due to the nanoparticles use for efficiency of plants are limitless [6]. Various type of nano materials can synthesizes by different techniques, that include cluster, colloids, thin films, tubes, wires etc. For synthesize of different type of nanomaterials few basic conventional techniques are optimized. That’s why multiple methods used to produced nanomaterials like chemical, physical, biological and hybrid.

2. Physical methods

2.1. Gas condensation method

The main strategy is used to synthesize nanocrystalline metals and composite was the gas condensation. By utilizing thermal dissipation sources for example a Joule heated refractory crucibles, electron beam evaporation gadgets, in an atmosphere of 1-50 m bar a metallic or inorganic material is vaporized in this method. In gas evaporation, by gas stage collision a high residual gas pressure causes the arrangement of ultrafine particles (100 nm). By collision of evaporated atoms with residual gas atoms the ultrafine particles are formed. Gas pressures more notewoethy than 3 mPa (10 torr) are required. High energy electron beams, low energy electron beam, resistive heating and drafting heating might be vaporization sources. In the gas phase by homogenous nucleation bunches created in the region of the source developed by ingestion of atoms in the gas phase. It contains an ultra-high vacuum (UHV) framework fitted evaporation source, a cluster gathering apparatus of liquid nitrogen filled cold finger scrapper get together and compaction device. In the supersaturating zone near joule heating device particles condense during heating. The nanoparticles are expelled as metallic plate by scrapper. Evaporation is to be done from tungsten (W), tantalum (Ta) or molybdenum (Mo) refractory metal pots [7]. Electron beam evaporation system is to be utilized, if the metals react with crucibles. Gas condensation method is tremendously slow. The strategy numerous limitations in an amalgam, such as a temperature ranges, source-precursor incompatibility, and dissimilar evaporation rates [8].

2.2. Inert gas condensation method

For synthesis of nanocrystalline powder particles and also to consolidate in situ into small ultra-high vacuum (UHV) condition, however, inert gas condensation method was also used. Vapor condensation method used to produce very fine-grained or amorphous alloys, which depend on the substrate temperature, also many operating conditions. Thus, this technique is used to synthesize the small quantities of nanostrucrured pure metals. Metal evaporated within chamber by different techniques, radio recurrence warming, resistive warming, sputtering, particle sputtering electron shaft warming, or laser/plasma warming, which evacuated to largely high vacuum of almost 10^{-7} torr, by utilizing few hundred pascals of low pressure inert gas helium after that inlayed. By condensation method, small discrete crystals of free powder are synthesized, when inside the chamber evaporated atoms and lose their kinetic energy. Convection flow produces by warming of the dormant gas by the evaporation source. Moreover, the cooled by the fluid nitrogen-filled gadget (cold finger), leads to conveying of dense fine powders to power tool, after that they are uncovered by shifting an annular Teflon ring down the length of cylinder to a compaction device. Inert gas condensation method used to produce (Pd) and Cobalt(II) Oxide (CoO) nanoparticles [9].

2.3. Aerosol synthesis method

To synthesize nanoparticles five multiple aerosol methods are used, that include (i) furnace method (ii) electro spray (iii) flame method (iv) physical vapor deposition and (v) chemical vapor deposition method.It is quite difficult to produce the size of particles less than 100 nm by using furnace method. To successfully produce TiO_2 nanoparticles flame method can be used with efficient precautions. Exact size and shape of nanoparticles can be formed with efficient Electro-spray method but with very low yield of about (1 g per year). For nanoparticles production physical vapor deposition and chemical vapor deposition are efficient methods. Aerosol technique is used for production of nanoparticles by accurately controlling das flow rate, heater size and also the diffusion drier size. Nanoparticles can be categorized into various shapes; cube-shape, plate-shape, cage-shape and wire-shape [1].

2.4. High energy ball mill

One of easiest method to generate nanoparticles of some metals and alloys High energy ball mill is used. In this method, various categories of mill are used including planetry, tumbler, rod, vibratory etc. For fine particles production one or more containers are used. In containers hardened steel or tungsten carbide balls along with powder or flakes (< 50 μm) of a material are kept. To close the container normally tight lid is used. Balls to material ratio 2:1 are normally suitable. Efficiency of milling get reduced if container is more than half occupied. Smaller grain size and larger defects in in particles occurs if larger balls used for milling. During the procedure ball may add impurities or container could be filled with inert gas and air. Temperature increases in range of 100 to 1100 ^{o} C during collision. By this technique cobalt (Co), chromium (Cr), and tungsten (W) etc. are made nanocrystalline [10].

2.5. Bottom up and top down approaches

Moreover by combining atoms/molecules/clusters or breaking down the bulk material into smaller and smaller size nanocrystalline synthesizes. The primary method is known as bottom up approach and the second is known as the top down approach. Both of approaches top-down and bottom-up have been functionalizing for the synthesis of nanoparticles. The nanosized particles synthesize by breaking a square of a mass material in the top-down methodology. Milling or attrition, lithography etc integrated in the Top-down approaches. The main disadvantage of the top-down method is the defect of the surface structure. Then again, in the bottom-up methodology where required the every atoms and molecules are found or self-assembled especially. To create nanoparticle the particles or nuclear fit together in bottom-up methodology. Bottom-up approaches are more significant and admired for the generation of nanoparticles [11].

2.6. Mechanical attrition

The structural break down of large size particles as a result of plastic deformation not by cluster accumulation produces nanostructures by mechanical attrition method. High energy ball mill were used for the preparation of elemental powders of Aluminium (Al) and Silicon carbide (β-SiC). Ceramic nanocomposite Tungsten (IV) Carbide (WC-14%) Magnesium oxide (MgO) material has been formed more recently. Mechanical alloying is a distinguishing method which can be carried out at room temperature. This method occurs on high energy mills, vibratory type, low energy tumbling mill centrifugal type mill, and vibratory type mill,

High energy mills include [8-12]

- Attrition Ball Mill
- Planetary Ball Mill
- Vibrating Ball Mill
- Low Energy Tumbling Mill
- High Energy Ball Mill

2.7. Attrition Ball Mill

The dealing out methodology happens by a mixing activity of a demonstrator which has a vertical rotator focal shaft with even arms (impellers). The rotation speed expanded to 500 rpm. Similarly the processing temperature was in more major control.

2.8. Planetary Ball Mill

Radiating powers be brought about through revolution of the sustaining plate and self-sufficient rotating of the vial. The processing media and charge powder move on the internal mass of the vial and be lost over the bowl by fast (360 rpm).

2.9. Vibrating Ball Mill

Amorphous alloys produced generally by vibrating ball mill. At very high velocity (1200rpm) the changes of powder and milling tools are disconcerted in the vertical trend.

2.10. Low Energy Tumbling Mill

For the preparation of mechanically alloyed powder they have been utilized. They are easy to use and cheap. A laboratory scale rod mill was utilized to get ready homogenous shapeless Al30Ta70 powder by utilizing S.S. tube rods. By using this method single-stage indistinct powder of AlxTm100-x with low iron focus can be formed.

2.11. Mechanical alloying

The critical breakdown of large-grained structure produces nanostructure materials by mechanical alloying because of brutal plastic deformation. During mechanical alloying process in a dry high energy ball mill continued welding, breaking and rewelding of powder happened until the rates of particular component in the underlying charge relates to the composition of the resulting powder. During this procedure blends of pre alloyed powders are exposed to crushing under a defensive environment in mechanism prepared to do high-energy compressive effect powers, for example, attrition mills, vibrating ball mills and shaker mills. Mostly extremely energetic small shaker mills utilized for the work on nanocrystalline materials. This method produced nanocrystalline structures in pure metals, inter metallic compounds and immiscible alloy systems. After sufficient processing time nanometer-sized grains have been achieved [13].

2.12. Molecular Beam Epitaxy (MBE)

To store elemental or compound quantum dots, quantum wells, quantum wires in a proscribed way this method can be utilized. High level of perfection in materials is achieved by utilizing ultra-high vacuum (superior to 10 -10 torr). Particular sources of deposition known as Knudsen cell (K-cell) or emission cell are utilized to get atomic light emissions constituent components. The deposition rate is reserved exceptionally low and substrate temperature is somewhat high so as to attain adequate mobility of components on substrate and layer by layer development to acquire nanostrcturures [14].

2.13. Thermolysis of Metal Complexes

This is the effective strategy to frame nanoparticles by breakdown of organometallic precursors. This disintegration should be possible by warmth (thermolysis), light (photolysis), or sound (sonolysis). The primary advantage of using organometallic mixes is that precursors can be separate at similarly low temperatures to get the product of interest. Much of time, polymers, organic topping agents, or basic hosts are used to control the nanoparticles size advancement [15].

2.14. Vacuum arc deposition method

This is the settled method to form of thin films and nanoparticles. In this process arc is produced by contacting a cathode which is made of a material of interest. An anode is used to generate a low voltage, high current self-sustaining arc by connecting with igniter. A small area on cathode from arc ejects ions and materials droplet. The particles are moving towards a substrate although any large droplets are filtered out before deposition [16].

2.15. Expansion-cooling

Condensable gas expansion by a spout prompts gas cooling and a resulting homogeneous condensation and nucleation. It was appeared by numerical recreations that the particles of about 100nm with relative narrow size allocation are created by expanding an organometallic precursor N_2 in a subsonic nozzle. The pressure decline from 2 bar to 0.75 bar because of development. Supersonic free jets expanding in a vacuum chamber with pressures littler than 10^{-4}mbar have been utilized to produce nanoparticles smaller than 5 nm. An inert gas containing a metal vapor was presented to various expansions in the crafted of Bowles. Because of two sonic expansions nuclei are delivered. At that point a cores development district in a subsonic, low-weight reactor created nanoparticles with mean sizes beneath 2.5 nm. The partition of nucleation and condensation processes results in a smaller size distribution than usually achieved by supersonic expansion. By expansion in a vacuum further development is stopped. Nanoparticles have additionally been produce by utilizing Converging nozzles which make an adiabatic expansion in a low-pressure flow. Boundary layer impacts minimize by special nozzle design and approaches a one-dimensional temperature gradient in the flow direction. This prompts a very uniform extinguish rate and therefore to nanoparticles with a narrow size distribution [17].

3. Chemical methods

3.1. Chemical vapor deposition (CVD)

In CVD in the vapor phase microcrystalline and powders products are prepared from reactants, and after that single crystal films for device is produced by deposition on a substrate. By heating volatile starting materials vapors are produced, after that mixed at a suitable temperature and transported to the substrate by carrier gas. The compounds which have tendency to be volatile like hydrides, halides, and organometallic compounds are included in typical starting material. MOCVD (Metal Organic Chemical Vapor Deposition) is a process in which organometallic is used as a precursor. The by-products transported back to gaseous phase by removing from the substrate. [18].

3.2. Chemical Precipitation

Chemical reaction, nucleation and crystal growth are the three main steps of a chemical precipitation process. In conditions of reaction kinetics, solid phase nucleation and growth processes chemical precipitation is usually not a controlled process. In this manner, wide molecule size distributions, uncontrolled particles morphology alongside agglomeration solids are gotten by chemical precipitation. To produced nanoparticles with a narrow size conveyance, the essential prerequisites are (i) a high level of supersaturation, (ii) a uniform spatial fixation dissemination inside a reactor and (iii) a uniform development time for all particles [19].

3.3. Sol-gel technique

This process is generally a low temperature process. Different materials such as aerogels, zeolites, ordered porous solids by organic-inorganic hybridization are getting by sol-gel process. Nanotubes, nanoparticles, and nanorods etc. synthesize by using sol-gel technique. In this process network is formed by the formation of ‘sol’ is a liquid and then connecting the sol particles. By drying the liquid powders, thin film, and even massive solid can be obtained. Ceramics, metal oxides, sulphides, borides and nitrides are produced by this method [20].

3.4. Electrodeposition

To produce nanocrystalline materials electrodeposition is a conventional process and easily handled. Electrodeposition of multilayered metals either can be achieved by using two unique electrolytes or all the more appropriately by legitimate control of fomentation and the electrical condition from one electrolyte. 3D nanostructure crystallites can be formed by utilizing the interference of one ion with the deposition of the other. On the conducting surface metal layer can be deposited by this method. Current in the external circuit is the carrying charge rate of the ions in solution that are deposited onto the negatively charged cathode. This method is comparatively contemptible, permits composite shapes. The current density and current rates specify the layer thickness [17].

3.5. Photochemical Synthesis

The absorption of the photo energy induces the variety of photochemical reactions and change molecule structures. Usually for ultraviolet irradiation a low-pressure mercury pillar lamp and for visible photo irradiation a high-pressure column like indium lamp are widely utilized. The advantage of this method is that mild reaction conditions used and the apparatus concerned are simple and economical [21].

3.6. Gamma-Irradiation Method

Nanometer materials synthesis by gamma-irradiation, it is one of the latest and efficient methods. Nanocrystalline metals, alloys, oxides and polymer nanocomposites extensively prepared by this method.

Presently, in various application and research inorganic and organic composites are of major concern. Semiconductive chalcogenides/polymer nanocomposites are more important among these compounds. Polymerization of monomers and configuration of inorganic nanoparticles by gamma-irradiation obtained concurrently which lead to the fabrication of inorganic/polymer nanocomposites. Conversely, the gamma-irradiation is the well-established method to the synthesis of chalcogenide/polymer nanocomposites. Efficient nanoparticles are developed by this method with the inspection of their structure property association [21].

Table 1. Comparison between physical and chemical methods

Sr. No	Physical methods	Advantages	Disadvantages
1.	Gas Condensation method	By gas phase collision very fine particles are produced (100nm). Gas condensation was the first method which is utilized to produce nanocrystalline metals and alloys	The method is particularly slow. A source-precursor incompatibility
2.	Inert gas Condensation	By using ultra-high vacuum nanocrystalline powder particles are produced into small disk. Nanoparticles of Mn, AuPd and CoO were achieved.	Inert gas pressure specify the crystal size The rate of evaporation and the composition of gas
3.	Aerosols synthesis method	Exact size and shape of nanoparticles can be produced Highly pure nanoparticles obtained Low temperature needed Less cost parameters	To produce nanoparticles by aerosol technique one has to accurately control the gas flow rate, Heater size Diffusion drier size. Yield is very low (1 g per year)
4.	High energy ball mill	Nanoparticles of some metals and alloys in the form of powder is formed by this simplest method Some of the materials such as Co, Cr, and WETC are produced nanocrystalline by this method.	A temperature rise is maximum (100 to 1100°C) The gases like O_2 , N_2 etc. can be the source of impurities
5.	Bottom up	Ultra-fine nanoparticles, nanoshells, nanotubes can be organized Deposition parameters can be proscribed fine size delivery is possible (1-20 nm) economical technique	Huge level manufacture is not easy Chemical distillation of nanoparticlesis required
6.	Top down	Large scale production deposition over a large substrateis possible Chemical purification is not required	Broad size distribution (10-1000 nm) varied particle shapes or configuration deposition parameters is complicated to attain Impurities, stresses, defects and imperfections get introduced costly method
7.	Mechanical alloying	Nanometer-sized grains can be obtained by controlling	Risk of contaminating powders by elements from the atmosphere, the

		milling parameters.	balls, the container walls, or even from milling agents, occasionally added to promote the synthesis
8	Molecular beam epitaxy	Elemental or compound quantum dots, wells, wires etc deposited in a very controlled manner in this technique.	The rate of deposition is kept very low and substrate temperature is rather high to achieved nanostructures
9	Thermolysis method	Decomposition of organometallic prcursors to formed nanoparticles. Additional reducing agent does not required.	The size of the nanoparticle growth controlled by using polymers, organic capping agents or structural hosts.
10	Vaccum arc deposition	Vacuum arc deposition is conventional process for the formation of thin films and nanoparticles.	Low-voltage, high-current self-sustaining arc is produced by connecting igniter to an anode
11	Expansions cooling method	Very fine size particles 100 nm gained with a maximum production rate extremely consistent Pressure decrease from 2 bar to0.75 bar by expansion.	Converging nozzles have to produce nanoparticles
	Chemical methods		
12	Chemical vapor deposition	High purity Low temperature process Controlled synthesis Efficient productivity CVD method also used to form nano composite powders	The reaction is activated in thermal CVD by a high temperature above 900 °C. The reaction is activated by plasma at temperatures between 300 and 700 °C in plasma CVD
13	Chemical precipitation method	Precursors not expensive All the chemical reactions safely takes place Less time required Less place required	In conditions of reaction kinetics does not controlled Solids obtained by chemical have large range of size and uncontrolled shapes of precipitation
14	Sol-gel technique	Low temperature process. It has the ability to control the microstructure of final product by controlling chemical reaction parameters Less energy utilization and less pollution too. Precursors are not very exclusive.	High experience compulsory Hydrolysis of precursors occurs
15	Electrodeposition	Produce nanocrystalline materials 3D nanostructure crystallites obtained This technique can yield porosity-free finished products formed that do not needed successive consolidation dispensation	Grain sizes in nanometer range obtained.

16	Photochemical method	Mild reaction conditions and suitable to operations Equipments involved are simple and cheap	High-pressure indium lamp as the visible photo irradiation source have to apply Sometimes some precipitating agents are used
17	Gamma –radiation method	New and efficient methods for production of nanometer material. preparation of nanocrystalline metals, alloys, oxides and polymer/metal nanocomposites can be made	The simplicity, reproductivity and adaptability of this synthetic approach is less inorganic/polymer nanocomposites mainly obtained
18	Spray pyrolysis	Multicomponent particles: easily prepared Various types of morphology Spherical particles	Material which is to be sprayed should be dissolvable

3.7. Spray Pyrolysis

In this method, to form the coating on substrate the source is deposited in droplets of liquid sprayed. The film formation formed when the substrate is heated to about 350-500ºC. The sprayed liquid is made of the material diluted in either water or alcohol, or both. The droplets were decomposed comparatively at low temperature which containing a precursor solution. At the point when temperature is still high to totally decay the precursors, this technique keeps away from molecule advancement and pressure. The item comprised of 5 to 10 nm crystallites pressed together in circles, demonstrating the type of the beginning bead and showing that the beads were not divided, so at times nanoparticles were gotten [17].

4. Conclusion

Nanotechnology is act as a next revolutionary technology in agriculture in which nanofertilizer and nano-pesticicide can provide sustainable tools to conventional farming practice. Nanoform of advanced technology provides target delivery and controlled release of active component that can decrease the excessive drain-off and prevent eutrophication and residual contamination. The use of encapsulated and metal nanofertilizer and nanopesticide has been evidenced their promising approach in agriculture. Calcium and Phosphorous hydroxyapatite, Iron, zinc oxide, Titanium oxide, Silver nanoparticles and carbon nano tubes can be used as an alternate of conventional agricultural. Further, more research is necessary in environment impact evaluation of nanotools before commercialization.

REFRENCE

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