Introduction

The technology advancement and quality life of mankind have constantly been closely related with the development in material science and technology of material processing. There have been remarkable developments in the ground of nanotechnology in the recent past years, with several methodologies developed to explore and exercise single atom and molecule for manifold applications in diverse field of scientific world such as physical, chemical, biological, material, pharmaceutical and engineering sciences. In modern science, the field of nanotechnology is one of the most dynamic research areas. Recent progress and findings in nanotechnology and the expression based on a variety of quantum size effects in nanoparticles (NPs), disclose that the majority of the novel work and devices of the future will be based on characteristics of nanomaterials (NMs).

In nanotechnology, a nanoparticle (NP) is described as a small object that acts as a whole unit in terms of its transport and properties. NPs exhibit new or improved properties based on specific characteristics such as size, crystallinity, composition, distribution and morphology (Mody et al., 2010). The prefix nano is derived from the Greek word nanos meaning “dwarf” that describes to things of one-billionth (10^{-9} \text{ m}) in size. Although Richard Feynman a physicist and Nobel laureate, is regarded as the father of nanotechnology, it was Norio Taniguchi who first defined the term in 1974. Since then the definition of NMs is evolving and it currently assumes that NPs are insoluble or bio-persistent materials that are produced intentionally and that have one or more external dimensions or an internal structure on a scale from 1 to 100 nanometer (nm).

The basis of the 100 nm limit is the fact that the novel properties which differentiate particles from bulk material typically develop at a critical length scale
of under 100 nm (Mody et al., 2010). However, it must be taken into account that according to the researchers the earlier limit, which was the basis for the dimensions of NPs, is now out of date. Creating any new regulations should be based on the newer, advanced systematics. This is because sometimes additives have almost identical characteristics, such as reducing “normally” produced chemicals to the nanoscale whereas synthesized NPs of the same material have entirely different properties depending on the size of particles.

In a more generalized term, nanotechnology is the manipulation of matter with at least one dimension sized from 1 to 100 nm. It is an enormously potent technology which offers a lot of new developments in the fields of catalysis, photonics, optoelectronics, biological tagging, pharmaceutical applications, environmental pollution control, drug delivery systems, material chemistry, bio-nanotechnology, biosensors, nanodevices in molecular nanotechnology, biomedicine for diagnosis, therapeutic drug delivery and treatment development of many diseases and disorders (Wise and Brasuel, 2011). With the reduced particle size (below 100 nm), the solid particles begin to demonstrate unusual properties from the bulk material based on quantum mechanics. These surface related and quantum properties play a fundamental role in differentiating the properties of bulk material with that of the NPs (Roduner, 2006). The critical particle size of the crystal structure and the size effect differ with the materials. NPs exhibit various effects depending on the material used to produce NPs and properties like solubility, transparency, colour, absorption or emission wavelength, conductivity, melting point and catalytic behaviour are changed only by varying the particle size. Properties like dispersability, conductivity, catalytic behaviour and optical properties alter with different surface properties of the particle. If the surface properties are not controlled, NPs quickly turn into larger particles due to agglomeration and most of the size dependent effects are then lost. The optical properties of NPs depend on kind of metal and particle size of NPs. They absorb the light with a specific wavelength and due to surface plasmon resonance i.e., the interaction of electromagnetic radiation and the electrons in the conduction band
around the NPs they transmit different colours (Parka and Kim, 2008). The large specific surface area of the NPs is an important property related to reactivity, solubility, sintering performance, etc. This is also related with the mass and heat transfer between the particles and their surroundings. Furthermore, the crystal structure of the particles may change with the particle size in the nanosized range in many cases. This is attributed to the compressive force exerted on the particles as a result of the surface tension of the particle itself. Thermal properties of NMs differ from their corresponding bulk materials due to their free surface and size. As the atoms and molecules located at the particle surface become significant in the nm order, the melting point of the material decreases from that of the bulk material. This is because they tend to move swiftly at lower temperature. The reduction of the melting point of ultrafine particles is regarded as one of the unique features of the NPs related with aggregation and grain growth of the NPs or improvement of sintering performance of ceramic materials.

The hardness of crystalline materials increases with the decreasing crystalline size, and the mechanical strength of the materials considerably increase by micronizing the structure of the metal and ceramic material or composing them in the nano-range (Niihara, 1991). When materials are reduced to nano level, electromagnetic forces become predominant in NPs. The mass of the nanoscale object is so small, that the gravity becomes negligible and electromagnetic forces surpass the gravitational force. The minimum particles size in order to keep the ferroelectric properties different depends on the kind and composition of the materials. NPs are broadly classified by Hett (2004) on the basis of dimensional structures (Fig. 1).

I. One dimension NPs: One dimensional system (thin film or manufactured surface) has been used for decades. Thin film (size 1–100 nm) or monolayer is now common place in the field of solar cells offering, different technological applications, such as chemical and biological sensors, information storage systems, magneto-optic and optical device, fiber-optic systems.
II. Two dimension NPs: Carbon nanotubes (CNTs)

III. Three dimension NPs: Dendrimers, quantum dots (QDs), fullerenes (carbon 60)

The schematic presentation of classification of nanomaterials

Classification of non-polymer nanoparticles

- Carbon based NMs
- Quantum dots
- Metal based NMs
- Metal oxide based NMs

Among the NPs, carbons NMs have acquired a significant place due to their unique mechanical, electrical, thermal and chemical properties. These NMs are mostly composed of carbon, where predominantly they acquire forms of hollow spheres, ellipsoids or tubes. These particles have many potential applications, including improved films and coatings, stronger and lighter materials, and applications in electronics. Carbon-based NMs are produced and used in many industrial sectors. These materials include CNTs, fullerenes, carbon nanofibers,
carbon black and carbon-anions. The properties of carbon-based NMs can be changed. Recently, chemical doping of nano diamonds has been studied extensively aiming to control their physical properties and enable the design of nanoscale diamond-based semiconductors and fluorescent biomarkers with the desired physical properties (Kumar and Kumbhat, 2016). A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, whose size vary from few nm to few hundred nm. Changing the size of quantum dots, changes their optical properties. These have the potential to dramatically improve the clinical diagnostic tests for an early detection of cancer. These tiny glowing particles, when conjugated with antibodies, peptides, proteins, or DNA, form bio-conjugated dots that can act as markers on cells and genes, giving scientists the ability to rapidly and differentially mark pathologic tissues (Bhatia, 2016).

Metal based NPs have fascinated scientist for over a century. These materials can be synthesized and modified with various chemical functional groups which allow them to be conjugated with antibodies, ligands, and drugs of interest and thus open a wide range of potential applications in biotechnology, magnetic separation, targeted drug delivery and vehicles for gene and drug delivery and diagnostic imaging. These NMs include gold (Au) NPs, silver (Ag) NPs, etc. Au NPs also known as colloidal Au is a suspension of nm sized particles of Au. The history of these colloidal solutions dates back to Roman times when they were used to stain glass for decorative purposes. However, the modern scientific evaluation of colloidal Au began with Michael Faraday’s work in the 1850s, when he observed that the colloidal Au solutions had properties that differ from the bulk Au hence the colloidal solution is either an intense red colour for particles less than 100 nm or a dirty yellowish colour for larger particles (Tong et al., 2009). The interesting optical properties of Au NPs are due to their unique interaction with light, the free electrons of the metal NPs undergo an oscillation in
electromagnetic field of light with respect to the metal lattice (Jain et al., 2006). Another most reported metal NP is Ag NPs with particle size between 1 and 100 nm. Like Au NPs, ionic Ag has a long history, currently; there is also an effort to incorporate Ag NPs into a wide range of medical devices, including bone cement, surgical instruments, surgical masks, etc. Additionally, Samsung has created and marketed a material called silver nano, which includes Ag NPs on the surfaces of household appliances. The surface plasmon resonance and large effective scattering cross-section of individual Ag NPs make them ideal candidates for molecular labelling (Schultz et al., 2000).

Metal oxides play a very important role in many areas of chemistry, physics and material science. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion and as catalysts. Metal oxide NPs can exhibit unique physical and chemical properties due to their limited size and a high density of edge surface sites. Particle size influences the structural characteristics, namely the lattice symmetry and cell parameters. Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the increasing importance of surface free energy and stress with decreasing particle size must be considered. In order to display mechanical or structural stability, NPs must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. Among various oxide NPs, copper oxide NPs (CuO NPs), zinc oxide NPs (ZnO NPs) and ruthenium oxide NPs (RuO$_2$ NPs) have been described in detail.

Copper is a chemical element with symbol Cu (Latin: cuprum) and have atomic number 29. It is a malleable and ductile metal with very
high thermal and electrical conductivity. Copper oxide (CuO) is a compound composed of two elements copper and oxygen. CuO is a semiconductor metal which has many unique properties like optical, electrical, magnetic, biocide and antimicrobial properties. CuO NPs appear as a brownish-black powder. They can be reduced to metallic copper when exposed to hydrogen or carbon monoxide under high temperature. The biomedical applications of CuO NPs focuses mainly on disease recognition and many other areas, for example, in the detection of viruses in the human body (Ahamed et al., 2014). Apart from this, various researches have been concentrated on the effects of CuO NPs in plants. Copper is an important micronutrient, which is required for the plant growth and reproduction. It is involved in physiological process of plants in oxidative forms (Cu$^{2+}$, Cu$^+$. Although at cellular level Cu plays a significant role in photosynthetic electron transport chain, cell wall metabolism, hormone signaling, transcriptional signaling, protein transport, secondary messenger and oxidative phosphorylation, etc. (Marschner, 1995; Solymosi and Bertrand, 2012). The cheap price, high surface reactivity and the specific high surface area of this material qualify CuO NPs as cost-effective catalyst for various chemical reactions. CuO NPs are used in a wide range of applications such as in electronics, air and liquid filtration, ceramics, wood preservation, textiles, bioactive coatings, skin products, films, lubricant oils and inks. The action of CuO NPs on plant cells has not been studied satisfactorily, and the existing results are indistinct. However, it is known that nanopowders are successfully used as microfertilizers and pesticides (Nekrasova et al., 2011). Plants need only traces of copper, therefore increased concentration of CuO NPs exerts noxious effect by penetrating directly into the cell, apparently by causing oxidative impairment to cell structures and molecules. Hence, the release of CuO NPs from different products to the environment has raised alarms over their prospective toxic effects on ecosystem, human and plant health.
Zinc oxide is an inorganic compound with the molecular formula ZnO. It appears as a white powder and is nearly insoluble in water. The powder ZnO is widely used as an additive in numerous materials and products including ceramics, glass, cement, rubber (mainly car tires), lubricants, paints, ointments, adhesives, plastics, sealants, pigments, foods (source of zinc nutrient), batteries, ferrite and fire retardants (Singh et al., 2016). In the earth crust, ZnO is present as zincite mineral but mostly ZnO used for commercial purposes is produced synthetically. ZnO is often called II-VI semiconductor in material science because zinc (Zn) and oxygen belong to the 2\textsuperscript{nd} and 6\textsuperscript{th} groups of the periodic table. ZnO semiconductor has several unique properties such as good transparency, high electron mobility, wide band gap and strong room temperature luminescence. These properties account for its applications in transparent electrodes in liquid crystal display (LCD) and in energy-saving or heat-protecting windows and other electronic applications. Among several metal oxide NPs, ZnO is considered to be one of the best exploited at nano dimensions. The wide band gap and large excitonic binding energy have made ZnO significant for both scientific and industrial applications (Wang et al., 2004). ZnO NPs have attracted intensive research efforts for their unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors, spin electronics, gas sensor, biosensor, cosmetics, storage, optical devices, solar cells, drug delivery and window materials for displays (Sawai et al., 1996; Song et al., 2006). ZnO nanostructures display high catalytic efficiency, as well as strong adsorption ability, and are more frequently used in the manufacture of sunscreens. ZnO is nontoxic; it can be used as photocatalytic degradation materials of environmental pollutants, bulk and thin films of ZnO have demonstrated high sensitivity for many toxic gases (Ryu et al., 2003). ZnO is currently listed as a “generally recognized as safe (GRAS)” material by the Food and Drug Administration and also used as food additive.
Ruthenium is a chemical element with symbol Ru and atomic number 44. It is a rare inert transition metal and is the last of 4d transition metals that can adopt the group oxidation state +8. It is the 74th most plentiful element in Earth's crust and is relatively rare, found in about 100 parts per trillion. Ru is produced commercially as a by-product from nickel, copper and platinum metal ore processing. Ru can be oxidized to ruthenium (IV) oxide (RuO₂) and further oxidized to tetrahedral ruthenium tetroxide (RuO₄). RuO₄ is a strong oxidizing agent, effective fixative and stain for electron microscopy of organic materials, used specially to disclose the organization of polymer samples. Applications in various sectors enable Ru to be used in electrical contacts because it hardens platinum and palladium alloys. RuO₂ with lead and bismuth are used in thick-film chip resistors. Increased corrosion resistance in titanium alloys led to the development of a special alloy (with 0.1% ruthenium) and some more advanced high-temperature single-crystal super alloys, with an application in the turbines of jet engines. Ru-centered complexes are being researched for potential anticancer properties. With an aqueous suspension of CdS particles loaded with RuO₂, the energy of visible light can split hydrogen sulfide and is used to remove H₂S in oil refineries and other industrial handling services. Ru stimulated cobalt catalysts are used in Fischer-Tropsch synthesis and also in ammonia decomposition. Ru-complexes have been used for light absorption in dye-sensitized low-cost solar cells, data storage for use in microprocessors and as an enormous magneto-resistive read element for hard disk drives.

Synthesis of NPs refers to methods for creating nanostructures. Synthesis of NPs can be broadly categorized into two approaches i.e. top-down and bottom up approaches. Top-down approach for synthesis of NMs involves the traditional workshop or nanofabrication method where tools are used to cut, mill and shape materials into the desired shape and order, for example solid-phase synthesis.
Bottom-up approach refers to methods where devices 'create themselves' by self-assembly. It utilizes physical or chemical forces operating at the nanoscale to assemble basic units into larger structures, for example liquid-phase and gas phase synthesis. Several methods are used for synthesis of NPs such as physical, chemical, enzymatic and biological. Physical methods include plasma arcing, ball milling, thermal evaporate; spray pyrolysis, diffusion flame synthesis, etc. Similarly, the chemical methods are used to synthesize NPs by electro-deposition, sol–gel process, Langmuir Blodgett method, hydrolysis and wet chemical method, etc. Physical and chemical methods used high radiation and highly concentrated reductant and stabilizing agents that are harmful to environment and to human health. Hence, biological synthesis of NPs is a single step bioreduction method and less energy is used to synthesize eco-friendly NPs (Sathish et al., 2009). Apart from that, the biological methods use eco-friendly resources such as plant extracts, bacteria, fungi, micro algae such as cyanobacteria, diatoms, seaweeds (macroalgae) and enzymes (Iravani, 2011).

Characterizations of NPs are primarily evaluated by the particle size distribution and morphology. Properties such as size distribution, average particle diameter, charge affect the physical stability and the in vivo distribution of the NPs surface morphology, size and overall shapes are determined by electron microscopy techniques. Features like physical stability and redispersibility of the polymer dispersion as well as their in vivo performance are affected by the surface charge of the NPs.

The rapidly-growing world population is projected to reach 9.6 billion by the year 2050 (UN, 2013), a 30% increase with reference to that in 2010s. Moreover, preferences towards meat-based diet and increasing demands for bio-energy crops are also driving an ever increasing demand for global agricultural production. In the context of sustainable agriculture, applying innovative
nanotechnology in agriculture including fertilizer development is regarded as one of the promising approaches to significantly increase crop production to feed the world's rapidly-growing population. Concerned by the low efficiency (merely 30–50%) of the conventional fertilizers and few management options to enhance the rates, many researchers also urged application of nanotechnology to fertilizer research and development (Singh et al., 2016).

Currently, positive and negative effects of NPs on plants have been reported, and researchers have studied the effects of NPs on plant germination and growth with the goal to promote their use for agricultural applications. However, certain reports have confirmed that NPs can induce phytotoxicity and have a negative effect on seed germination and growth, but simultaneously, the exclusive properties of NPs can be used to improve seed germination and crop performance (Singh et al., 2015). Concerning the nanotoxicity, many scientists have commented that there are no conclusive studies and these studies involving NPs and plant toxicity are only beginning. It is also clear that this aspect requires additional research. In this context, we believe that research related to the use, application and elucidation of the action mechanism of the NPs in plants is essential, whether developed in the environmental area or in physiology and crop production.

The objective of the present study was undertaken to explicate a basic part of an exclusive plan of investigation and understanding in the field of plant NPs interaction. The effect of selected metal oxide NPs on the important commercial crop plants viz., Solanum lycopersicum and Brassica oleracea var. botrytis either positive effects on germination, physiology, biophysical and biochemical parameters, or the toxic effect were well examined. Factors that enhance the uptake of these NPs are also well documented. Copper and zinc are important micronutrients, which are required for the plant growth and reproduction. In a
study conducted by the Indian Institute of Soil Sciences (IISS), a key research body of Indian Council of Agricultural Research (ICAR), establishes that soils of 13 states including Uttar Pradesh are deficient in secondary nutrients like Zn (40%) and Cu (4.3%). The present work may help broaden our understanding of positive and negative aspects of these NPs in structured way, may prove promising to enhance the crop production via natural and low-cost additives. The present thesis entitled “Effect of nanoparticles on growth and metabolism of some crop plants” represents a description of the research conducted in the plant physiology laboratory in the Department of Botany, University of Allahabad, Allahabad during the years 2014-2017. The effect of green synthesized and chemically synthesized NPs were comparatively assessed. One of the objectives of this thesis is to analyze the role of ZnO NPs in mitigation of salt stress in tomato plant. In this thesis, we have also discussed the role of CuO NPs in plant growth and development and evaluated the comparative study between two exposure media i.e., sand medium and foliar spray exposure. We conducted an experiment to evaluate the best exposure medium of NPs which can affect the plant growth and development. The comparative effects of ZnO NPs and zinc sulphate (ZnSO₄) ionic medium were also recorded for germination and growth of Solanum lycopersicum L. in filter paper and sand culture respectively.

The climatic condition of India along with the present soil texture of Gangetic plain has been taken into account to conduct this work with following aims:

- Green synthesis of nanoparticles using flower extract of Thymus serpyllum L.
- Effects of green and chemically synthesized nanoparticles on Solanum lycopersicum L.
- Comparative evaluation of application of copper oxide nanoparticles on...
Brassica oleracea var. botrytis L. by foliar and root exposure methods

- Effects of zinc oxide nanoparticles in mitigation of salt stress in Solanum lycopersicum L.
- Effects of zinc oxide nanoparticles and zinc sulphate on germination and metabolic activity of Solanum lycopersicum L.
- Effects of ruthenium oxide nanoparticles on germination and metabolic activity of Solanum lycopersicum L.
- Effects of copper oxide nanoparticles on metabolic and antioxidant enzyme activity of Solanum lycopersicum L. and Brassica oleracea var. botrytis L.

This thesis comprises of five chapters:

- Introduction as the first chapter which deals with the subject and scope of study
- Review of literature deals with the work done in the related fields.
- Materials and methods, how the work has been conducted
- Results deal with interpretation of data obtained.
- Discussion includes interpretations of results in light of recent researches in related fields.
- Cited references are formatted in Vancouver style and appended at the end under the head “Bibliography”. 