CHAPTER ONE

Introduction

According to many anthropologists, the great expansion of agricultural yield is the singular achievement of modern human civilization. This was achieved by increasing reliance on mechanical labor and by the use of petrochemical based fertilizers and pesticides to enhance production (Rifkin 2002). However from the thermodynamic point of view, modern agriculture is the least productive form of agriculture in history. It uses far more energy inputs to power the machinery and provide the synthetic fertilizers and pesticides per unit of every output than in any previous period (Farb 1978).

In spite of this huge energy investment, food security continues to remain the biggest concern of mankind. The challenge is how to feed the growing human population by producing more on a stagnant or a shrinking landscape, with lower input costs and with fewer hazards to the ecosystem. If we were to consider India, here the future scenario, with regard to agriculture appears grave. Indian agriculture reached its pinnacle as far as the food production is concerned, in the 1960s. The model ‘green revolution’ increased potential yields and farm incomes substantially by adopting micro or farm economics. But ‘green revolution’ placed less emphasis on judicious use of soil, water, nutrients and pesticides. Also the globalization of agriculture trade in 1990s led to changes in some macro economic policies that supported agriculture and subjected the Indian farmers to potential market risks. All of these have led to a steady decline in farm incomes and consequent distress in rural India. The problems are compounded by degradation of natural resource base – soil, water and climate. The complex situation in Indian agriculture can increasingly be ascribed to ‘technology fatigue’.

Thus, an urgent need is being felt for more scientific and targeted management of the agriculture sector. Nanotechnology has the answers to many of these challenges. Strategic
application of nano science can do wonders in the agriculture scenario. Applications of nanotechnology have the potential to change the entire agriculture sector and food industry chain from production to conservation, food processing and food packaging. Nanotechnology promises to reduce pesticide use, improve plant and animal breeding and create new nano-bioindustrial products. It promises higher yields and lower input costs by streamlining agricultural management thereby reducing waste and labor costs. Nanoscience is leading to the development of a range of inexpensive nanotech applications to increase soil fertility and crop production. Nanotech materials are being developed for slow release of efficient dosage of fertilizers and pesticides (Liu et al. 2008) for plants and nutrients and medicine for livestock. Nanosensors are being used to monitor the health of crops and magnetic nanoparticles (NPs) are being used to remove environmental contaminants (Stucky et al. 2012).

1.1 NANOTECHNOLOGY: SMALL SCIENCE WITH A BIG FUTURE

The word ‘nano’ is derived from the Greek word for dwarf. Though, dwarfness alone does not account for all the interest in nanoscale. According to The United States’ National Nanotechnology Initiative (NNI) ‘nanotechnology’ is “the ability to understand, control and manipulate matter at the level of individual atoms and molecules (in the range of about 0.1 to 100 nm), in order to create materials, devices and systems with fundamentally new properties and functions because of their small structure”. It is about creating new chemicals and biological nanostructures, uncovering and understanding their novel properties and ultimately about learning how to organize them into more complex and more efficient functional structures and devices.

Though the term nanotechnology was defined by Norio Taniguchi (Taniguchi 1974) in 1974 and the idea was first vividly explored by K. Eric Drexler (Drexler 1986) in the 1980s, the concept of manipulating materials at nanoscale regime was first envisioned by the
Nobel laureate physicist Richard Feynman. On 29th December 1959, in his famous talk “There is plenty of room at the bottom” (Feynman 1959) at the annual meeting of the American Physical Society at California Institute of Technology, he imagined the whole of the Encyclopaedia Britannica written on the head of a pin and anticipated the increasing ability to examine and control matter at the nanoscale. According to him the biological phenomena in which chemical forces are used in repetitious fashion to produce all kinds of ‘weird effects’ inspired him to anticipate manipulation of individual atoms and molecules. Though the term ‘nanoparticle’ is a coinage of modern science, NPs have been used for a very long time. Probably the earliest use was in the early Chinese porcelain for glazes. Medieval European church painters used gold and silver colloids to obtain different colors for their stained glass paintings that adorned church walls. Carbon black is the most popular NP being produced in millions of tons for decades. If we consider modern era scenario, human civilization was destined to look at miniaturization, to rearrange atoms to get the desired products. Moore’s law is no longer applicable in downsizing microelectronics at an exponential rate and it made the use of nanotechnology imminent in silicon industry. Over the past decade there has been an explosion in academic and industrial interest in nanomaterials not only in electronics, but also in every field of basic science and technology.

Nanotech building blocks may consist of anywhere from a few hundred atoms to millions of atoms. On this scale, different forces dominate and different models are required to explain their novel phenomena. There are at least four ways in which nanoscale materials differ from macroscale materials.

i) Gravitational forces become negligible because gravity is a function of mass and distance and is weak between nanoscale objects having very low mass. Instead electromagnetic force, a function of charge and distance unaffected by mass, can be
very strong for nanosized particles. Moreover, at nano scale van der Walls force becomes important.

ii) Quantum mechanics is required to describe motion and energy of NPs instead of classical mechanics.

iii) NPs have greater surface area to volume ratio. This increase in surface area per unit mass makes NPs more reactive. As particles decrease in size, a greater proportion of atoms are found at the surface compared to those inside. So less energy is required to move these surface atoms.

iv) In nano domain random molecular motion becomes highly significant.

For these reasons optical, electrical, physico-chemical properties of materials change radically at nano scale. For example, bulk gold is yellow, but nano gold is red in color and its melting temperature is only 300°C, whereas bulk gold has melting temperature of 1064°C. Carbon nanotubes are the strongest material yet to be discovered (Yu et al. 2000) and they function as conductors or semi conductors depending on the diameter, arrangement of atoms or number of walls present. Suspensions of NPs are possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences, which otherwise usually result in a material either sinking or floating in a liquid.

Nanotechnology got a start in the 1980s with the enhancement in resolution of electron microscope and invention of newer microscopic tools which helped researchers to visualize and manipulate particles at nano domain. Atomic force microscope (AFM), scanning tunneling microscope (STM), magnetic resonance force microscope (MRFM) and high resolution electron microscopes, having resolution of 0.1 nm to 0.2 nm, enabled researchers to characterize materials at nanoscale, allowing individual atoms to be observed and analyzed. Other common techniques used for characterization of NPs are dynamic light
scattering [DLS], x-ray photoelectron spectroscopy [XPS], powder x-ray diffractometry [XRD], Fourier transform infrared spectroscopy [FTIR] etc.

There are two broad approaches to synthesis and fabrication of NPs: top down and bottom up. Top down approach refers to grinding or successive cutting of a bulk material to get nano sized particle. Attrition or milling is a typical top down method for NP synthesis. Bottom up approach refers to the buildup of a material from the bottom i.e. atom by atom, molecule by molecule or cluster by cluster. Carbon nanotubes, silicon nanowires and nanodots, self assembled polymer monolayers etc. are synthesized by this process.

1.2 NANOPARTICLES – NATURAL AND MAN MADE

There are plenty of nanoscale objects in nature. Fossil fuel exhaust, volcanic ash, sea foam, products of photoionization is some of the sources of atmospheric nano particulate matter. Living organisms possess millions of nano sized devices which perform various biological functions. DNA, RNA are nothing but biological NPs. Ribosomes, various enzymes like, ion pumps, the photosynthetic machinery in plants and bacteria are complex nano devices functioning inside the biological world.

Nowadays different types of engineered NPs are being used in industrial and biomedical application. The most popular of them is probably carbon nanotubes and buckyballs, which are members of fullerene structural class. They can be used in various nanoelectromechanical systems and even in biomedical applications like scaffold material for bone formation (Haddon et al. 2006). Buckyballs can be used as drug-delivery agents (Jiang et al. 2007). Graphene, one-atom-thick planar sheets of carbon atoms, hold the key to almost everything from super small computers to high-capacity batteries. Recently Wenbing et al. (2010) discovered its anti bacterial potential. Lipid based liquid crystals or liposomes are being extensively used in pharmaceutical industries for their ability to encapsulate molecules
and then breaking down inside cells once their payload has been released (Park 2002). Gold NPs are being used for killing cancer cells (Chen et al. 2007), intravenous contrast enhancers in medical imaging (McMahon et al. 2008) and also as delivery vehicles of drug (Han et al. 2007). Silver NP, as an antibacterial component, has been used in the formulation of dental resin composites (Herrera et al. 2001) and in coatings of medical devices (Hillyer et al. 2001; Bosetti et al. 2002). There are many oxide NPs available in the market, like titanium, zinc, aluminium, iron, silicon oxides to name a prominent few. Titanium dioxide NPs cause photocatalytic degradation of water contaminants; hence it can be used in water purification system (Abdel-Mottaleb 2009). Nano Zinc oxide has superior UV blocking capacity compared to bulk zinc oxide. So nano zinc oxide is often used in sunscreens (Mitchnick et al. 1999). Moreover, it has excellent bactericidal properties (Yuvaraj et al. 2010). NPs of iron oxide are biocompatible, non toxic and can be used as contrast agents in magnetic resonance imaging (Cheong et al. 2011), in labeling cancerous tissues and localized thermotherapy (Huber 2005). NPs made of semi conductor materials are called quantum dots. These nanostructures confine conduction band electrons, valance band holes or excitons in all three spatial directions. Quantum dots can be used as fluorescent biological labels (Wang et al. 2002; Jamieson et al. 2007). Several core shell NPs are also being used in bioimaging, cell labeling and drug delivery (Huang et al. 2006; Lee et al. 2007). Polymer NPs have potential applications in controlled drug release (Soppimath et al. 2001), targeted nucleic acid delivery (Davis 2009), and biological and antibody receptor mimics (Allender et al. 2000). Calcium phosphate NPs present a unique class of non-viral vectors, which can serve as efficient and alternative DNA carriers for targeted delivery of genes (Roy et al. 2003a).

1.3 NANO TECHNOLOGY IN THE FOOD MARKET AND IN AGRICULTURE

Over the past few years nanotechnology has become a significant part of the food industry and agriculture sector. The USA is investing billions of dollars in agri-nanotech through NNI.
Other countries like Japan, the European Union, China and India have initiated programs in nanotechnology for agricultural and food industry.

Many multinational companies are investing in the arena of agri-nanotech. Kraft is clearly the leader in nano-food development. It took the first steps in bringing nanotech to the industry when it established the Nanotek Consortium, a collaboration of 15 universities and national research labs, in 2000. Kraft is developing "interactive" foods and beverages that can be personalized to fit the tastes and needs of individual consumers, from fun stuff like drinks that change colors to innovative foods that can adjust to a consumer's allergies or nutritional requirements. Nanotechnology based precision farming using carbon nanotube or dendrimer based nanosensors can maximize agricultural output while minimizing input like pesticides, fertilizers etc. by monitoring environmental variables and applying targeted actions. Encapsulation and controlled release technology have revolutionized pesticide and herbicide sectors. Many companies are making formulations which contain nanosized particles that are able to dissolve in water more effectively than existing ones. Syngenta, one of the world’s largest agrochemical companies has marketed a quick release micro-encapsulated product under the name ‘Karate’ which has the active ingredient lambda-cyhalothrin which breaks open on contact with leaves. Another Syngenta encapsulated product ‘gutbuster’ only breaks open to release its contents when it comes in contact with alkaline environments, such as stomach of certain insect pests. Nestle is exploring ‘nutraceuticals’- nano-capsules that deliver nutrients and antioxidants to specific parts of the body at specific times. The technology turns previously insoluble nutrients into nano-sized particles that can be released into the body and properly absorbed, with big potential benefits for a whole new kind of health food. Nanocor, a subsidiary of Illinois-based AMCOL International, is the leading producer of nano-composite plastics. These plastics not only serve as superior barriers to the flow of oxygen and carbon dioxide, keeping all kinds of products fresher longer, but also
block out smells and prevent the packaging from absorbing any of the flavors or vitamin content of the food.

1.4 SILICA NANOPARTICLE AND ITS VERSATILE APPLICATION

Silica or silicon dioxide (SiO$_2$) can be crystalline and amorphous and can be natural or synthetic in origin. Crystalline silica exists in multiple forms like quartz, porosil etc. In nature, amorphous silica can have different origins. It can be condensed from vapors emitted in volcanic eruptions, can be deposited from supersaturated natural water or can be found from skeletal structures of different living organisms (Iler 1979). Diatomaceous earth (DE) which is fossilized deposit of cell walls of diatoms (a type of algae) is widely being used as natural insecticide to protect crops from insect pest infestation (Athanassiou et al. 2004; Iatrou et al. 2010). United States Department of Agriculture (USDA) has declared the commercial use of amorphous silica as safe (Stathers et al. 2004).

The application of synthetic and engineered amorphous nanosilica or silica NPs (SNPs) has wide ranging applications both in scientific research and industries because of their easy preparation and their potential uses in various fields. SNPs are used as catalysts (Banerjee et al. 2009), electronic and thin film substrates (Jeong et al. 2010), electronic and thermal insulators (Kim et al. 2011), humidity sensors (Wang et al. 2005). These are produced on an industrial scale as additives to cosmetics, drugs, printer toners, varnishes and food. Recently SNPs have shown promising potential in the field of biotechnology. These inert optically transparent materials can be conjugated with a variety of fluorophores, leading to development of robust, fluorescent nanoprobes (Zhao et al. 2004; Ow et al. 2005). Fluorescent SNPs are being experimented for imaging and diagnosis of cancer (Santra et al. 2005; Tsuji et al. 2006; Kumar et al. 2008). These NPs can be tagged with a peptide for targeting specific cell type or tissues (Sharma et al. 2004; Qian et al. 2008). Most importantly, the chemistry of silica provides the opportunity for a variety of surface
functionalization with hydroxyl/amine/thiol/carboxyl groups (Han et al. 2006; Walcarius et al. 2006), which can be used to attach a number of biotargeting molecules. Tan et al. (2004) developed SNPs, functionalized with both streptavidin and antibody and they can be used in fluoroimmunoassay for the detection of carcinoembryonic antigens and hepatitis B surface antigens. Zhao et al. (2004) developed a SNP-based method for the detection of single bacterium. Bioactive molecules like enzymes, genetic materials and chemotherapeutic drugs can also be incorporated within porous SNPs. So these NPs have great potential as DNA (Bharali et al. 2005; Gemeinhart et al. 2005) or drug delivery agent (Slowing et al. 2008; Climent et al. 2010; Escoto et al. 2010; Manzano et al. 2010; He et al. 2011a, b; Stark 2011; Wang et al. 2012). Zhou et al. (2004) developed dye-doped core-shell SNPs for microarray-based analysis.

These NPs have also been tested for potential use in photodynamic therapy (Roy et al. 2003b; Kim et al. 2007). Moreover, they can be used as biosensors for assaying glucose (Zhang et al. 2001) and enzyme immobilization (Qhobosheane et al. 2001).

In spite of the versatile application of SNPs, the potential of these NPs in agriculture remains unexplored. Specifically, pest management researchers are impelled to find out newer insecticides because of human health hazard, growing problem of environmental pollution and increasing insect resistance associated with the conventional insecticides. Though DE based amorphous micron sized silica has become very popular as an insecticidal agent, application of synthetic amorphous SNPs as insecticide was unknown till date.

In this study surface functionalized SNPs were synthesized, their physico-chemical characterization was carried out and their entomotoxicity was tested on a variety of insects followed by assessment of the mode of action. Lastly toxicity of SNPs was evaluated both in vitro and in vivo.