Chapter I

CHAPTER - I

INTRODUCTION

1.1 Introduction

Nanotechnology is a well known area of exploration since previous century. This technology had made a revolutionized development since after the Nobel laureate Richard P. Feynman's, famous lecture in 1959 "There's plenty of room at the bottom" [1]. Nanotechnology produces various types of particles at nanoscale range. Nanotechnology has the capability to consider atoms individually. Nanoparticles are generally mentioned as molecules among 1-100 nm dimensions. Nanoparticles are of great technical curiosity among disquisition community because they make an efficient link between substances and subatomic configuration [2].

A substance will possess a steady physiological property regardless in despite of its magnitude, however for particles at nanoscale is contrary. The features of many conventional materials change, because a nanoparticle had a greater surface to volume ratio than the bulk particles that cause a nanoparticle to be more reactive. Many properties which are size dependent like, quantum confinement as seen in semiconductor particles, surface plasmon resonance as seen in metal nanoparticles and super magnetism as seen in magnetic materials are observed [3].

Nanoparticle exhibit many unique features in relation to its bulk counterpart. When the substance approaches the nanoscale their properties change, and the total amount of atoms present at the surface of the substance becomes important [4]. The nanoparticles show unpredicted observable characteristics because, these nanoparticles are fairly compact to capture their electrons and generate quantum effects. Silver at its bulk form is white metal but the nano-scale silver is black in colour. All the three interrelated significant physical properties of nanoparticles are i) highly movable in their free state ii) having enormous specific surface area and iii) they show quantum effects [5].

Metal nanoparticles are of much concern in both research and technology by virtue of specific properties not available in bulk metals. These metal nanoparticles are made up of pure metal precursors. The peculiar properties of these nanoparticles are used in the field of catalysis, sensing and imaging [6]. Metal nanoparticles posses' large surface energy and hence have the ability to absorb small molecules. Metallic nanoparticles were utilized to build framework that hold specific electric, photonic and catalytic properties like local surface plasmon resonance, surface enhanced Raman scattering and surface enhanced fluorescence [7].

Metallic nanoparticles could be synthesized by two various techniques: the bottom-up approach (synthesizing the material from atomic or molecular species through chemical reaction) [8] and the top-down approach (approach initiate with the bulk materials and then break it into smaller pieces by mechanical, chemical or other form of energy) [9]. The Bottom-up technique creates a large scale synthesis of the nanoparticle, but the particles are usually of non-uniform size and shape comparable with those generated by top-down method. The top-down approach includes extracting material from the bulk substrate to pursue the desirable nanostructures [10].

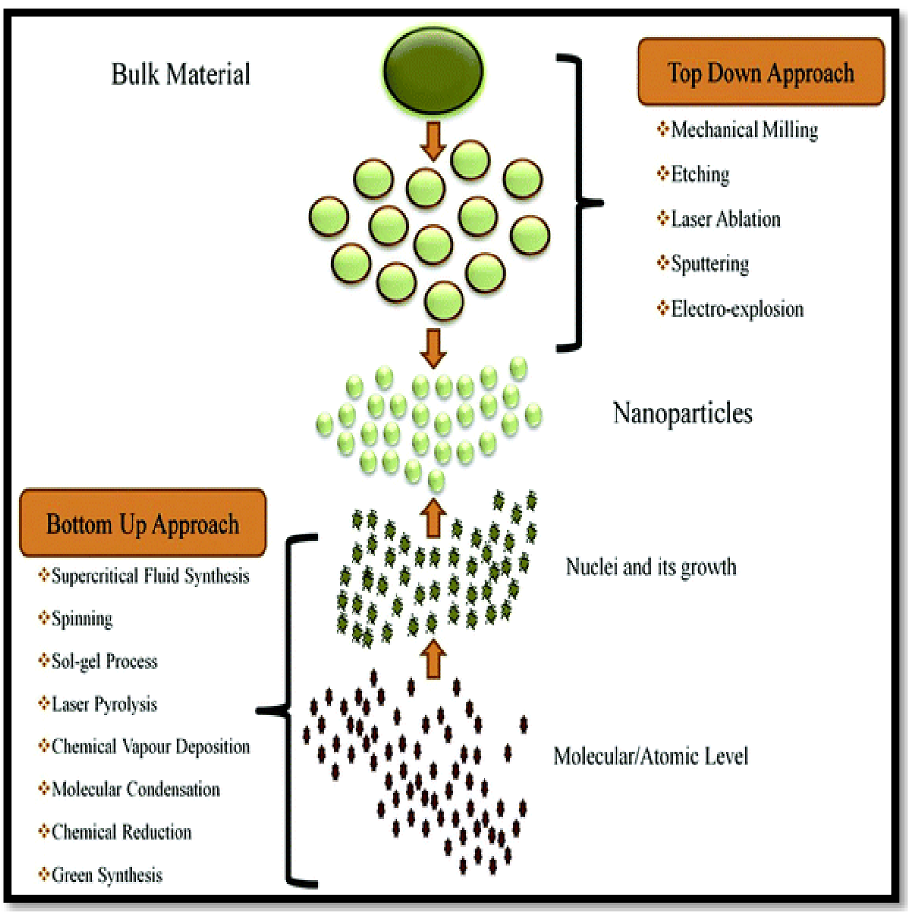

Figure 1.1: The synthesis of nanomaterials via top-down and bottom-up approaches [11].

Nanoparticles with high and low aspect ratio are classified separately. High aspect ratio morphologies include nano-tubes and nano-wires with various shapes, such as helical shape and zigzag shape. Small aspect ratio morphologies include sphere shape, oval shape, and cubic shape [12].

1.2 Classification of Nanoparticles

Nanoparticles are categorized on the basis of dimensionality and morphology [13]. Based on the dimensionality the classification of nanoparticles is a generalized concept of aspect ratio. They are as follows,

1.2.1. Zero dimension nanomaterial

These are materials whose growth is confined along all the directions. The utmost general illustration of zero dimensional materials is quantum dots. These particles have interesting electronic properties because of their energy band gaps [14].

1.2.2. One dimension nanomaterials

The materials with one dimension are in range of nanoscale. Nanowires, nanorods and nanotubes are examples of one dimensional nanomaterial. The application of one dimensional materials have been used in various fields like electronics, storage systems, sensors, fiber-optic communication system, magneto-optic device and optic device etc., [15].

1.2.3. Two dimension nanomaterials

The two dimension nanomaterials are free particles having large aspect ratio. They are materials within high degree of anisotropy and chemical functionality. Nanofilms, nanolayers and nanocoatings are examples of two dimensional materials. The properties of these materials are less understood and there is less advanced capability in the manufacturing process [16].

1.2.4. Three dimension nanomaterials

The materials of equiaxed nanometer sized grains are three dimensional nanomaterials. Some examples of these materials include nano-crystals, particles, precipitates, colloids, and fullerenes. Natural three dimension materials like metallic oxides, combustion products etc., are well known, whereas the understanding properties of fullerenes, dendimers are the greatest challenges [17].

Additionally, nanoparticles could be divided as hard particles and soft particles. Titania, silica and fullerenes are some of the examples of hard nanoparticles. Liposomes, vesicles and nano droplets are examples of soft nanoparticles. Thus, nanoparticles have a vast scope of combination rely upon the application of particles [18].

1.3 Application of nanoparticles

Nanoparticles possess various structures and they are labelled and distinguished by their distinct shapes eg., nano-spheres, nano-tubes, nano-boxes and nano-clusters etc. By utilizing the properties of nanoparticles through modifying their shapes can take advantage for various upcoming technologies [19]. These different morphologies are used for different applications. Carbon nano-tubes are used to bridge an electrical junction, porous nano-spheres are used in sensors, nano-spheres and nano-clusters are used in targeted drug delivery etc. Based on the unique properties of nanoparticles they might be exploited for various applications.

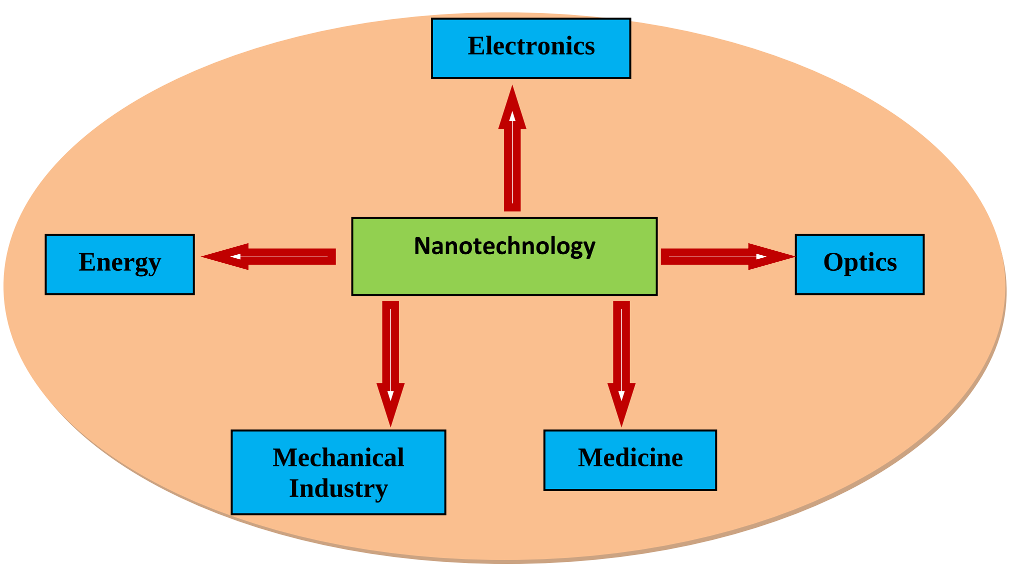

Figure 1.1A: Schematic diagram of Application of nanoparticles

1.3.1. Applications in Optics

Most of the metal nanoparticles combined within bio-molecule systems consist of many use in catalysis, delivery, therapy, imaging and sensing. Immobilisation of bio-molecule on the surface of noble metal nanoparticle serves a platform to build biosensors that regulate using properties such as localized surface plasmon resonance (LSPR), surface enhanced raman scattering (SERS) and surfaced enhanced fluorescence (SEF) [20].

1.3.2. Application in Electronics

Printed electronics is considered to be one of the developing areas in the realm of electronics. These printed electronics offers attraction to established silicon methods and the potency for affordable flexible displays & sensors. The functional inks in printed electronics comprise of metallic nanoparticles which has been predicted to flow quickly as a bulk production procedure for advanced types of electronic equipment [21]. Specific structural and optical properties of one dimensional nanoparticles made the key structural block for recent era of electronic, sensors & photonic materials [22].

1.3.3. Application in Mechanical Industry

The nanoparticles accustomed for multipurposes in mechanical industry especially for coating, lubricants and adhesive application for their efficient Young's modulus, stress and strain properties. Nanoparticles offers enhanced sliding and delamination property which leads in low friction with high lubricant effect. On the basis of alumina, titania and carbon nanoparticles had shown mechanically strong characteristics which increases the toughness and wear resistance of the materials [23].

1.3.4. Application in Energy

Nanoparticles have large surface area, optical behavior & catalytic nature. Limitation and scarcity of fossil fuel has warned us in the recent years, therefore, scientist community has shifted their investigation methods to create renewable energy among well accessable resources. Nanoparticles are one of the key areas which have contributed to this purpose. These particles are used in photo catalytic application. The nanoparticles are generally utilized to produce energy from photo electrochemical & electrochemical water splitting [24]. Nano generators can convert mechanical energy to electricity by the use of piezoelectric effect that is an unconventional way to induce energy [25].

1.3.5. Applications in Medicine

Nanoparticles have drawn interest in the field of medicine for the capability to transmit drugs and to increase its therapeutic efficiency of the drugs [26]. To use nanoparticles for biomedical application, the particles should possess eminent magnetization value, smaller dimension ie., less than 100 nm & fine particle size distribution [27]. Some medical uses of nanoparticles include bio-imaging, nano-biosensors, and anticancer agents [28].

1.4 Importance of Metal Oxide Semiconducting Gas Sensor

The most commonly accepted definition for sensor is quoted by Jacob Fraden in his *Handbook of modern sensors* [29], which states that "a sensor is a device that receives a signal or stimulus and responds with an electrical signal". Sensor device gives response in the form of signal after detection or measurement of a physical form of energy. It converts any kind of measurands into the measurable form of energy. The metal oxide semiconductors are widely explored gas sensing materials due to their efficient physical and chemical properties. According to their electronic configuration d^n of the oxides, metal oxides has been divided as transition and non-transition metal oxides. Only metal oxides from d^0 & d^{10} found its application in gas sensing as they are sensitive to the environment.

Gas sensor showed an important part in environmental observation by the era of industrialization in discovering harmful gases [30]. The environment we live it consists of various types of chemicals instinctive & manmade, few are crucial to human activities while some are destructive to a higher or minor extension. At the current time, factory-made mechanisms inflation associated the use and produces exceedingly deadly substances, especially noxious and ignition gases. Sometimes gas ejects in some areas, which generates a probable threat to the plants, employees and those people living near to that industries.

Metal oxide semiconductors are one among the necessary substances which should be utilized for gas sensing. These substances have been first found a long time in the past that molecules combining with semiconductor surfaces may have an effect on the surface properties of semiconductors, like conductivity & surface potential. The chemo resistive semiconductor fuel sensors had been initially produced with the aid of Seiyama in 1962 [31]. Then onwards, MOS had been extensively examined as gas sensors due to the fact of their affordable & its liability. Metal oxides have a wide range of electronic, chemical & physical characteristics that are regularly sensitive to the variations in their chemical surrounding. Because of these features, metallic oxides had emerged as a famous commercial sensor. Various substances had been proved to be utilized as metal oxide sensors which include singular & multi-component oxides [32].

On the basis of electronic configuration, metal oxide semiconductors such as ZnO, Co_3O_4, NiO, CuO, Fe_2O_3, etc. are apt for examining reducing or oxidizing gases by conductive computations [33,34]. Due to the broad electronic structures; they are classified as transition & non transition metal oxides [35]. Again, the non-transition metal oxide can be categorized into two sub-divisions: pre-transition and post transition metal oxide [36]. The pre-transition metal oxides were seemed to be inert, for their broad band gap that reduces the probabilities of electrons/holes formation. Because of the complications in electrical conductivity computations, they are not often chosen as gas sensor materials. But, the post transition-metal oxides are determined to be highly sensitive than pre - transition metal oxides to surroundings [37]. Anyway, structural instability & non-optimality of different parameter vital for conductometric gas sensors restrict their area of application. A number of semiconducting metal oxides had been broadly utilized for determination of harmful gases. However, a huge amount of other materials were examined to produce good & efficient gas sensing main focus was on metal oxide sensors. Metal oxides show an efficient gas sensing performances but they have lots of drawbacks like higher operating temperature, lower selectivity and many more [38-40].

The semiconductor gasoline sensors provide cheap, excessive sensitivity and simplicity in work; benefits that need to do in their desire as innovative purposes develop. Furthermore, the opportunity of effortlessly joining in the similar system the features of a sensitive factor & signal converter and manipulate electronics noticably clarifies the structure of a sensor and consider the predominant benefit of chemiresistive kind sensors over biochemical, optical, acoustic, and various gas sensing gadgets [41,42]. Reactions including gas molecules can do at the semiconductor surface to change the density of charge carriers available.

Ammonia is a colorless gas with an aromatic smell and in its natural form is called as anhydrous ammonia. It is extensively used in production field or industries as manure, food, medicine and synthetic chemical. Hence, in order to control workplace abuses and disaster a gas, identifying system is an imperative to avoid risks and accidents. Ammonia does appear naturally in the environment all be it in fragment quantities. Ammonia interacts vigorously with H_2O, is treated destructive and noxious as it will result in a casualty to skin, eyes and respiratory system. If the person exposed to high concentration levels of ammonia possibly causes death. For over a century, ammonia gas has been used a refrigerant gas and as such has no universal warming possibility or ramification on the ozone level. The main imperfection of ammonia gas is the toxicity, pungent odor and in high concentrations its flammability [43].

Highly toxic ammonia (NH_3) and trimethylamine (TMA - ($N-(CH_3)_3$)) are few of the many constituents of the atmospheric particulate matter that affects the biodiversity which is harmful to the environment as well as a human habitat. As agriculture is the backbone of Indian economy and the major gases that are released from the livestock and fertilizers are CH_4, NH_3 and TMA. It is highly alarming for the need of an efficient detection system of these toxic and hazardous elements in our regime. According to the standards of occupational health and safety administration, over a period of 8 h, only 25 ppm of NH_3 and 10 ppm of ($(CH_3)_3N$) is the exposure limit above which it has a severe effect on human health [44]. Hence, the detection of these harmful gases was closely related to human habitat.

1.5. Importance of Nanomedicine

Nowadays, use of nanomaterials in various fields like agriculture, food, environmental remediation, medicine, and cosmetics are increasing and as a consequence, the exposure of nanomaterials to the environment increases. This lays emphasis to consider the toxicity associated with nanomaterials that interact with the living organism [45]. The toxicity of the nanomaterials is largely based on their physical and chemical characteristics that influence the possible interaction with the biological cells [46]. Hence, to understand the toxic effects of nanoparticles, their physico-chemical properties have to be evaluated precisely. The physico-chemical properties of nanomaterials like crystalline structure, particle size, particle shape, agglomerated and the dispersed state, surface charge, chemical composition, hydrophilicity and hydrophobicity can influence the toxic effects on the living system and hence they have to be studied in detail using various characterization techniques [47]. Some of the biomedical applications of nanotechnology are:

Biological assessment evaluates the participation of specific components emerge as rapidly, delicate and highly adjustable while certain nanoparticles establish labor as tags [48].

Nanotechnology provides current possiblities in drug delivery systems. It is an engineered technology which utilized nanoparticles for the targeted delivery and maintained discharge of therapeutic agents [49].

Nanotechnology may assist to recreate or to rebuild injured tissue. It is known as 'tissue engineering' exploits man-made triggered cell proliferation through utilizing appropriate nonmaterial on the basis of scaffolds and developed elements [50].

1.6. Present study

The aim of this work is to synthesize Co_3O_4 nanoparticles using low-cost chemical route method. The composition of Co_3O_4 nanoparticles were confirmed using different characterization techniques. The gas sensing efficiency of Co_3O_4 nanoparticles were improved by introducing dopants (Zn, Fe, Cu, Ni) of various concentrations such as 3%, 5% and 10%. This study deals with the detection of Ammonia [NH_3] gas at room temperature for nanosensor applications. Finally, it is also utilized for the application of nanomedicine using trypan blue exclusion method for evaluating the cytotoxicity analysis.

1.7. Conclusion

Nanotechnology is an adaptable topic that offers with science & engineering. Twenty first century is the era of computerization that demands rapid, simple, reliable & controlled calculation technology of physical measurements. Hence an essential sophisticated robust digital devices to improve the ability and capability of instruments. Protection of environment from pollution is the matter of greatest concern in the current scenario. In this regard, the detection of toxic gases is very important. Nanosensors exhibit very prominent part in gas detection in view of their high sensitivity. The application of nanoparticles in cancer therapy is also gaining momentum, taking into consideration their effectiveness in drug delivery and targeted therapeutic approaches. This research was done to study the possibility of the application of Co_3O_4 nanoparticles (both pure and doped) synthesized by the hydrothermal method, in nanosensors and in cancer treatment. The cobalt oxide nanoparticles were doped with the dopants Zn, Fe, Cu and Ni. Three different concentrations (3%, 5% and 10%) of the dopants were studied.

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