Chapter 1 General Introduction of Nanomaterial

1.1 Introduction of Nanomaterial

In 1959, Physics Nobel Laureate Richard Feynman gave a talk at Caltech on the American Physical Society meeting[1]. The talk was entitled[2], "There's Plenty of Room at the Bottom." In this lecture, Feynman said:

> "What I want to talk about is the problem of manipulating and controlling things on a small-scale … What are the limitations as to how small a thing has to be before you can no longer mold it? How many times when you are working on something frustratingly tiny like your wife's wrist watch have you said to yourself, "If I could only train an ant to do this!" What I would like to suggest is the possibility of training an ant to train a mite to do this … A friend of mine (Albert R. Hibbs) suggests a very interesting possibility for relatively small machines. He says that, although it is a very wild idea, it would be interesting in surgery if you could swallow the surgeon. You put the mechanical surgeon inside the blood vessel and it goes into the heart and "looks" around. It finds out which valve is the faulty one and takes a little knife and slices it out."

Feynman's vision was amazing. Although Feynman could not predict it, this lecture was to become a Central Point in nanotechnology, long before anything related to the word 'Nano' had emerged. During the 1970-80s, when the first through fundamental studies with "nanoparticles" were underway in the USA (by Granqvist and Buhrman)[3] and Japan, (within an ERATO Project) they were called "ultrafine particles" (UFP).

However, during the 1990s before the National Nanotechnology Initiative was launched in the USA, the new name, "nanoparticle," had become fashionable[4]. At that time nanoparticles may or may not exhibit size-related properties but differ significantly from those observed in fine particles or bulk materials[5].

1.1.1 Nano

The term 'Nano' derives from the Greek word for 'dwarf'. It is used as a prefix for any unit such as a second (nanosecond) or a meter (nanometer), and it means a billionth of that unit. Hence, a nanometer (nm) is a billionth of a meter or 10^{-9} meters.

1.1.2 Nanomaterial

"A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm." by The European Commission[6].

"Material with any external dimension in the nanoscale or having the internal structure in nanoscale is Nanomaterial." Definition from International Organization for Standardization (ISO)[7].

1.1.3 Nanoscience and Nanotechnology

Nanoscience deals with the study of structures that have at least one physical dimension in the nanoscale (i.e., between 1–100 nm). Nanotechnology is the application of nanoscience to solve challenges in the real world[8].

Nano is now a popular label for much of modern science, and many nano words have recently appeared in dictionaries, including nanometer, nanoscale, nanoscience, nanotechnology, nanostructure, nanotube, nanowire, and nanorobot. Many words that are not yet widely recognized are used in respected publications, such as Science and Nature. These include nanoelectronics, nanocrystal, nanovalve, nanoantenna, nanocavity, nanoscaffolds, nanofibers, nanomagnet, nanoporous, nanoarrays, nanolithography, nanopatterning, nanoencapsulation, etc.

The first known application of nanotechnology was in stained glass windows used in churches in medieval Europe[9]. Glass artisans mixed gold chloride into the molten glass, unknowingly reducing the gold complexes to form small gold nanoparticles.

In the last 35 years, the growth of nanotechnology has opened several novel views in medical sciences, especially in the field of drug delivery[10]. New and new moieties are coming handy for treating diseases. The biotechnology has also produced several potent drugs, but many of these drugs encounter problems delivering them in biological systems. Their therapeutic efficacy is significantly marred owing to their incompatibilities and specific chemical structure. The input of today's nanotechnology is that it allows real progress to achieve temporal and spatial site-specific delivery. The market of nanotechnology and drug delivery systems based on this technology is being widely used by the pharmaceutical industry.

In recent years, the number of patents and products in this field is increasing significantly. The most straightforward application is in cancer treatment; with several products in the market are Doxil®, Transdrugr®, Abraxane®, etc.

1.2 Causes of Interest in Nanomaterials

These materials have created a high interest during recent years by their applications in the vast field, from medicines to electrical and from physics to ceramics.

Some examples are given below:

- Nanostructured metal clusters and colloids of mono- or multimetallic composition have a special impact in **catalytic** applications. They may serve as precursors for a new type of heterogeneous catalysts (Cortex-catalysts[11]) and have been shown to offer substantial advantages concerning activity, selectivity and electrocatalysis (fuel cells[12]). Enantioselective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles.
- **Polymer-based composites** with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap[11] structure.
- In **electronics & optoelectronics** 'nanophosphors' for affordable high-definition television and flat panel displays. electroluminescent nanocrystalline silicon, opening the way for optoelectronic chips and possibly the new type of color displays. Efficient light-emitting diodes based on quantum dots with a voltage-controlled, tunable output color. Powder or plastic layers using nanoparticles as an active scattering medium.

- **Gas sensors** for NO_x, SO_x, CO, CO_2, CH_4 and aromatic hydrocarbons. Ultraviolet (UV) sensors and robust optical sensors based on nanostructured silicon carbide (SiC).Smoke detectors etc.
- **Medicinal applications** like, longer-lasting medical implants of biocompatible nanostructured ceramic and carbides. biocompatible coating for medical applications[13]. Magnetic nanoparticles for hyperthermia[14]. Also for controlled drug release and drug delivery, etc.
- Nanoparticles with **Dispersions and Coatings** property give applications like, thermal barriers, optical (UV) barriers, imaging enhancement, ink-jet materials and storage devices, etc.

There are many applications, which made Nanomaterials so popular now days. Based on types of nanomaterial several applications were illustrated in below table.

Table 1 Fields of applications by type of nanomaterials[15]

Nanomaterials	Application
Nanoceramics	Structural composite materials - components anti - UV - polishing substrates (wafers) in microelectronics Chemical - photocatalytic applications
Nanometallics	Antimicrobial activity, catalysis, conductive layers of screens, sensors and energetic materials
Nanotubes	Electrical conductive nanocomposites - structural materials - single-walled nanotubes for applications in the field of electronics and screens
Dendrimers	Medical field (administration of drugs, rapid detection) - domain cosmetic
Quantum Dots	Optoelectronics (screens) - photovoltaic cells - inks and paints for applications of type marking anti - counterfeiting
Fullerenes	Sport (nanocomposites) and cosmetics sectors
Nanowires	Applications in the conductive layers of screens or even solar cells and electronic devices
Nanoporous	Aerogels for thermal insulation in the areas of electronics, optics and catalysis - biomedical field for tracing or even implants type applications

1.3 Classification of Nanomaterials

Depending on the dimension the Nanomaterials it can be classified as 1) Zero-dimensional (0D), e.g. quantum dots, 2) One-dimensional (1D) e.g. Nanowires, 3) two-dimensional (2D) e.g. Nano Films, 4) Three-dimensional (3D) e.g. Bulk or polycrystalline materials.

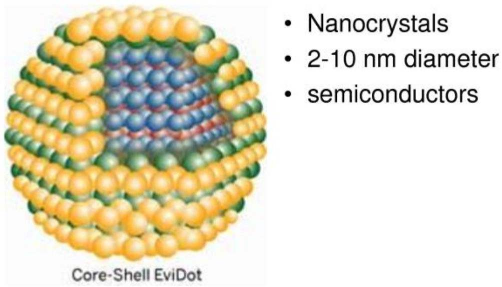

Figure 1 Quantum Dot[16]

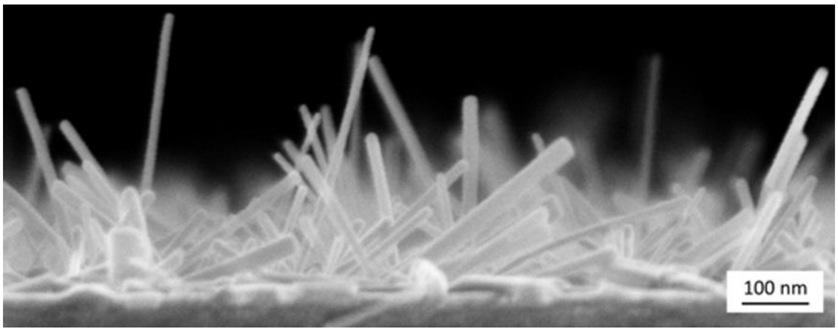

Figure 2 Nanowires (1D) of Tungsten oxide[17]

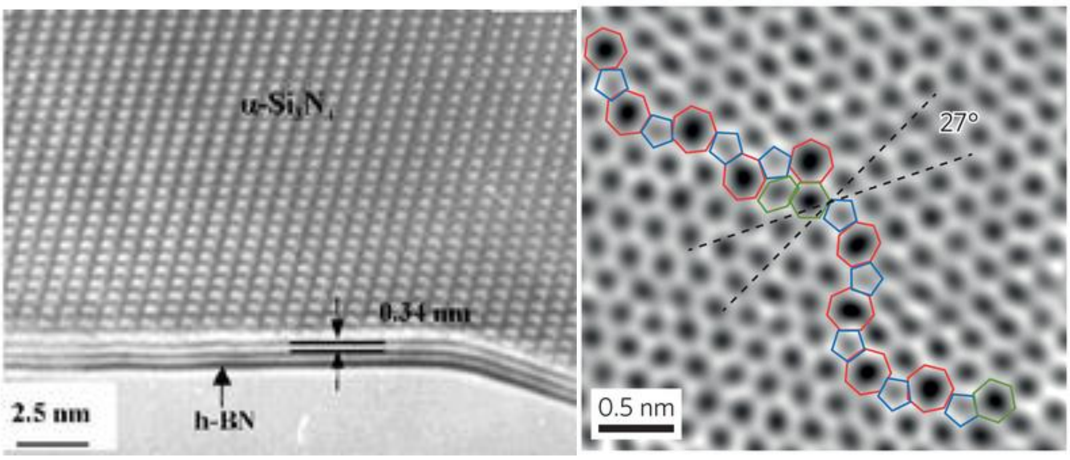

Figure 3 Nano-Film[18] (2D) of Si_3N_4 (Left), Polycrystalline (3D) graphene grains with two lattice orientations[19] (Right)

1.4 Synthetic Paths of Nanomaterials

Basic approaches for the synthesis of Nanomaterials are Bottom-up and Top-down (shown in figure). In Bottom-up approach, atoms or molecules assemble in such a way that it makes Nanomaterials. While in Top-down approach, disassemble or dissociation of bulk material into smaller Nanomaterials.

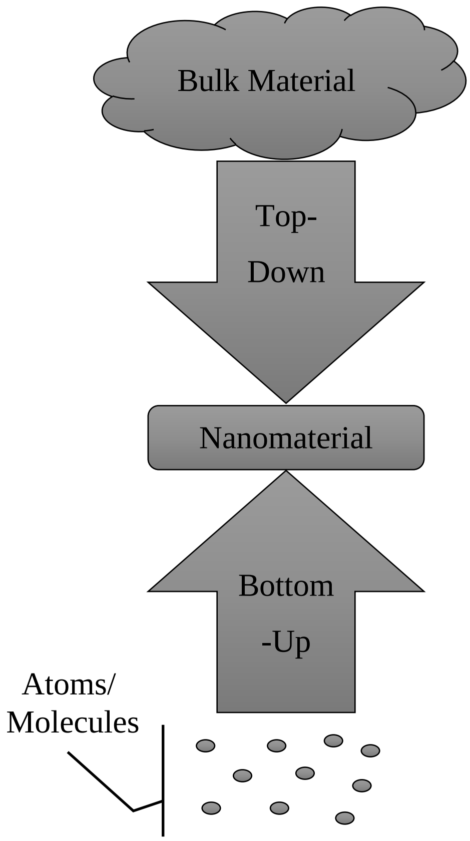

Figure 4 Basic Synthetic Approaches of Nanomaterials

There are many methods to synthesize Nanomaterials, but most common methods are described below are (1) Mechanical grinding (Solid Phase synthesis), (2) Wet synthesis (Liquid Phase synthesis), (3) Gas phase synthesis, (4) Microwave processing (Plasma Phase synthesis).

1.4.1 Mechanical Grinding

Mechanical grinding is a typical example of 'top-down' method of synthesis of Nanomaterials, where the material is prepared by the structural decomposition of bristlier-grained structures[20]. It is a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment needed, and the applicability to synthesize all classes of Nanomaterials. The major advantage often quoted is the possibility for scaling up to tonnage quantities of material for various applications. The drawback with this method is contamination by the atmosphere or milling media. Another drawback of this method is inadequate for metal oxides.

1.4.2 Wet Chemical Synthesis of Nanomaterials

In this method, top-down and bottom-up approaches have been used to synthesize Nanomaterials. For example, the synthesis of porous silicon by electrochemical etching is a top-down method[21]. While the sol-gel method and precipitation methods are bottom-up methods. There are many wet chemical synthesis methods other than described above, but the most popular amongst all is the sol-gel method. In which precursor is dissolved in alkoxides solvent and by dehydration gelation forms, which is furthermore polycondensed, so viscosity of solution increases and a viscous Gel is formed. Then aging of Gel is done, so, Gel is transformed into solid mass. Then solid mass is calcined at high temperature in the furnace to obtain Nanomaterials.

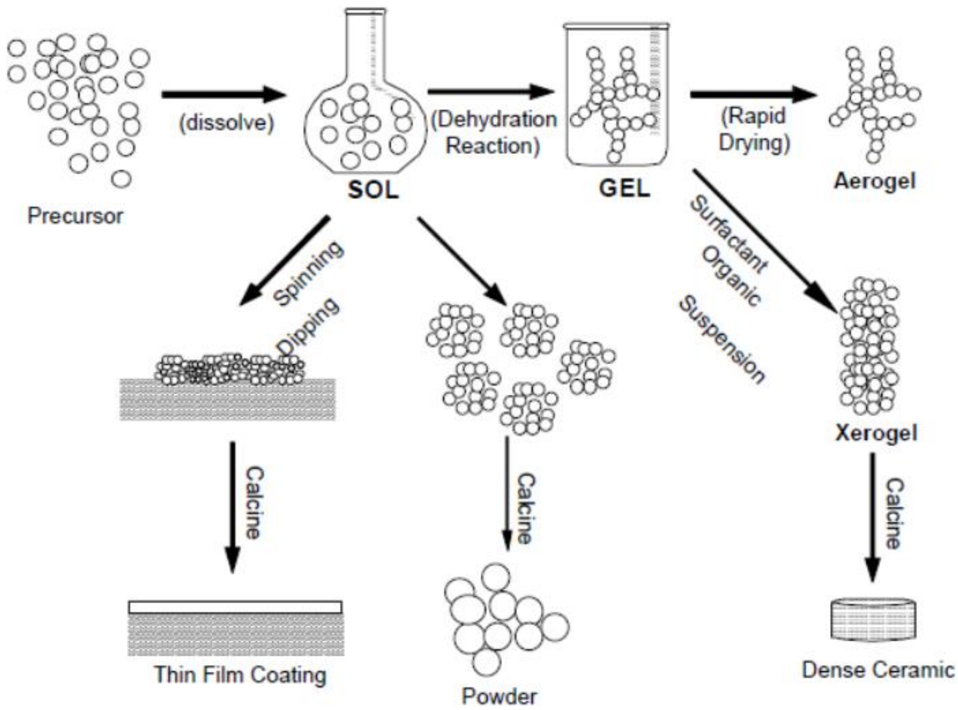

Figure 5 schematic representation of Sol-Gel Method[21]

1.4.3 Gas Phase Synthesis of Nanomaterials

The Gas phase synthesis methods are of increasing interest because they allow an elegant way to control process parameters in order to be able to produce size, shape and chemical composition controlled nanostructures. General conventional Chemical

Vapour Deposition[22] (CVD) is a Gas Phase synthesis method of Nanomaterials. Several modified CVD methods have been also developed. Gas phase processes have inherent advantages, which are, an excellent control of size, shape, crystallinity and chemical composition. Also highly pure materials can be obtained and easy control of the reaction mechanisms. Other Gas phase methods are flame assisted ultrasonic spray pyrolysis[23], Gas Condensation Processing[24], etc.

1.4.4 Microwave Processing

This technique is similar to the previously discussed chemical vapor condensation (CVC) method but employs plasma instead of high temperature for decomposition of the metal organic precursors. The method uses microwave plasma in a small reaction vessel made of quartz placed in a cavity connected to a microwave generator. A precursor such as a chloride compound is introduced into the front end of the reactor. The major advantage of the plasma-assisted pyrolysis in contrast to the thermal activation is the low temperature reaction, which reduces the tendency for agglomeration of the primary particles.

There are many other popular methods for synthesizing Nanomaterials.. Some of them left to mention above are sonochemical method[25], hydrothermal and solvothermal method[26], etc.

1.5 Aim and Scope

PLA has become a versatile polymer due to its excellent biocompatibility and biodegradability. Consequently, PLA based materials have received attention for application in many areas, such as environmentally safe products[27], drug delivery[28], tissue engineering [29], antimicrobial[30], packaging[31] applications, etc.

In the present investigation, inorganic Nano Zirconium dioxide (Zirconia) and Nano Zinc oxides have been selected as nanofillers because of their antimicrobial behavior as well as filler effect.

Moreover, the catalytic effect of activated Nano Zirconia and Nano sulfated Zirconia (SZ) has been selected to synthesize some organic moieties and for studying reusability.

The second chapter divided into two sections each with two stages. In the first stage, it is proposed to undertake synthesis via the solvent casting method and In the second stage, characterization of the nanocomposite would be carried out.

While In the third chapter followed in three sections. In the first sections, proposed to undertake synthesis and characterization of Nano Zirconia and Nano SZ, In the second sections, synthesis and characterization of Benzimidazole derivatives and in the third sections synthesis and characterization of Benzodiazepines with the help of Nano Zirconia and Nano SZ.

1.6 Objectives

The present investigation focuses on the following objectives

- To synthesis of PLA and ZrO_2 nanocomposite by the solvent casting method with diverse loading ratio
- Characterizing the PLA/ZrO_2 Nanocomposites by different analytical techniques
- To Synthesis of PLA/ZrO_2/ZnO nanocomposite with varied loading ratio
- Characterizing the PLA/ZrO_2/ZnO nanocomposite by different analytical techniques such as spectroscopy, thermal analysis and electron microscopy
- To Synthesis of organic moieties with the Nano Zirconia and Nano SZ
- Study reusability and applicability of Nano Zirconia and Nano SZ as Nanocatalyst