Chapter 1

General Introduction

In this chapter, a general introduction pertaining to the research work has been described. An overview on nanomaterials, different types of nanomaterials - carbon nanomaterials, metal based nanomaterials, the synthetic strategies and the diverse applications were presented. In particular, discussion on carbon nanomaterial, carbon nanocomposites and other metal based nanomaterial from bio-resources have been stressed upon. Drawing reference from contemporary literature, the objectives of the proposed research has been set.

1.1. Nanomaterials: definition and importance

Conventionally, the nanomaterials are defined as materials having a characteristic length scale less than about a hundred nanometer at least in one direction. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of immense interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These exotic properties have the huge potential for application in electronics, medicine, and other fields.

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular, and macromolecular scales, where properties differ significantly from those at a larger scale. Nanotechnology is the design, characterization, production, and application of structures, devices, and systems by controlling shape and size on a nanometer scale. The size range that provides the greatest potential and hence the greatest interest is that below 100 nm, and larger particles may also some application potentials. The materials can be prepared at such a small scale that gives them the potential to possess very interesting properties. Copper becomes transparent at nanoscale but opaque at macroscale [1,2]. Platinum acts as effective catalyst at nanoscale [3, 4]. The properties of gold at nanoscale are quite significant depending on the size of the nanoparticles [5, 6]. This significant difference in properties in nanoscale regime is attributed to the increased relative surface area and quantum confinement effect. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Such properties opened the door to a broad range of applications including energy conversion and storage, catalysis, electronic and optoelectronic as well as biomedical applications.

1.1.1. Nanomaterials in nature

Nature furnishes adequate evidence of nanomaterials and nanotechnology, based on its ability to work at the atomic, molecular and supramolecular levels. The history of nanomaterials began immediately after the big bang when nanostructures were formed in the early meteorites. The wall gecko lizard is able to hang upside down using millions of nano hairs on each toe which grips the ceiling with a miniscule force. The antiglare and antireflective eye lens of moth lessens easy predation on them. The butterfly wings pigments causes light to bounce off nanoscale layers in the structure of the wings [7]. These reflect how macromolecules govern self-assembly of biominerals or the action of antifreeze proteins [8]. Nature inspired design and fabrication of man-made nanostructures that may mimic the functions of natural systems are fast capturing the attention of researchers. For instance, biomolecules such as proteins, peptides, DNA, lipids and carbohydrates can act as templates - their shapes and chemical properties can be employed - to arrange inorganic substances such as metals on nanoscale [9]. Current research seeks to explore approaches to fabricate objects at nanoscale and to incorporate nanostructures into macrostructures.

1.2. Classification of nanomaterials

Nanomaterials are classified as 0, 1, and 2D according to their dimensions in three, two and one directions in space. Dimension in the nanometer range can be considered as dimensionless or zero dimensional. Thus a material with all three dimensions in nanometer range is known as zero dimensional material. When the dimension of these materials is comparable to those of their corresponding excitonic Bohr radius, they show the quantum confinement effect i.e. the system behaves as particle in a three dimensional box. The excitonic energy depends on the size of the materials and such materials are termed as quantum dots [10-13]. The zero dimensional particles may have spherical morphology [14, 15]. The morphology of the particles is responsible for changes in optical properties [16, 17]. Due to quantum confinement effect, nanomaterials behave quite differently from their bulk counter parts [18]. The energy quantization alters the band structure in turn their optical [11, 19], magnetic [20], and electronic [21 properties significantly. One dimensional nanostructured material is string like, in accordance with their structure these are termed as nanorods [22], nanowires [23], nanotubes [24, 25], and nano-ribbons [26]. The ratio of the diameter to the length is called the aspect ratio. Nanostructured materials having minimum dimension in the Z-axis and dimensionless in X and Y axes are termed as nanorods. The aspect ratio of nanorods is in the range 10 to 100 nm. When the aspect ratio of the nanorods exceeds 100, these are called nanowires. Thus nanowires are essentially long nanorods. The nanowires have a crucial role in futuristic electrical connectors for nanodevices. The nanotubes are nanowires with hollow interior. Because of the very thin wall of a few nanometers, nanotubes are very important in technological fields. Depending on the structure of wall of the carbon nanotubes [24, 27], these could behave as insulator, semiconductor or conductor. Nanoribbons have thickness and width in the nanometer range and length in the micrometer. When the dimension of the material is in nanometer range only in one direction with usual dimensions in other two directions the materials are known as two dimensional nanomaterials [28]. Thin paper like substances with nanometer thickness in Z direction and spread over XY plane in micrometer scale are considered to the typical example of 2D nanomaterials. As the charge carriers always remain confined in one plane, these materials also exhibit some important and useful properties.

1.3. Approaches to synthesis of nanomaterials

There are basically two approaches for the synthesis of nanostructures: '**Bottom-Up**' approach and **'Top-Down'** approach **(Fig.1.1)**. In top-down approach, the bulk materials are gradually broken down to nanosized materials. In the bottom-up approach; the nanostructures is built by growing or assembling of atoms or molecules. The building blocks may be manipulated through controlled chemical reactions to self assemble producing nanostructures.

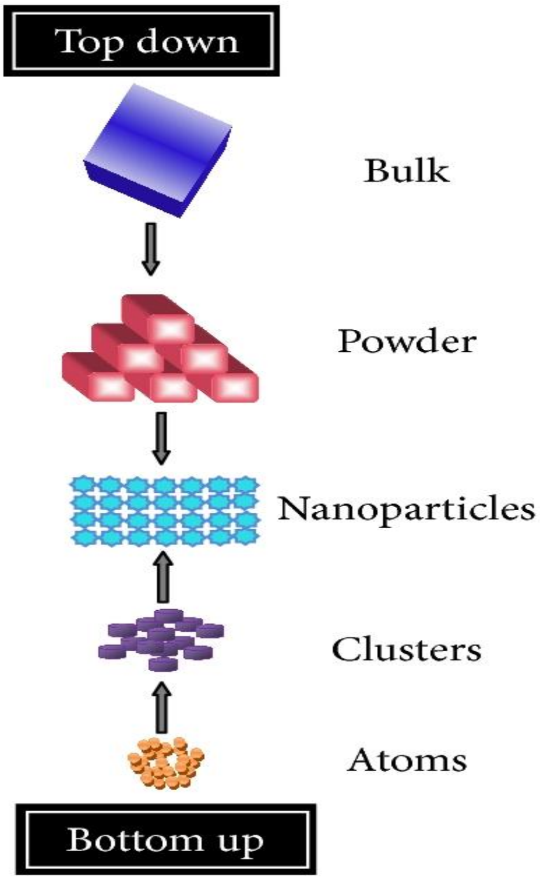

Fig.1.1. Schematic representation of top down and bottom up approach [29]
(Source: Madhumitha, G., & Roopan, S. M. *J. Nanomater.*, 2013, **2013**)

Manufacturing nanoparticles can be achieved through a wide variety of different routes: some have been around for many years; others are far more recent. Most popular among them include mechanical grinding, wet chemical synthesis, electric arc discharge method, laser ablation and chemical vapour deposition(CVD) method. In the following section we briefly touch upon these preparative techniques.

1.3.1. Mechanical grinding

Mechanical grinding is a typical top down method. Nanomaterials are prepared by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This is a popular method because of its simplicity, relatively inexpensive equipment need, and applicability to the synthesis of all classes of materials. The major advantage is the possibility of industrial scale production of materials for various applications.

1.3.2. Wet chemical synthesis

Wet chemical synthesis includes colloidal chemistry, hydrothermal methods, sol-gel method, precipitation etc. where materials containing the desired precursors are mixed in well-defined quantities and under controlled conditions of heat, temperature and pressure to promote the formation of insoluble materials. These materials so formed are then collected through filtering and/or spray drying to produce a dry powder. The advantages of the method are that a large variety of materials can be fabricated, including inorganic, organic and also some metals, in essentially cheap equipment and significant quantities. The important factor of the wet chemical route is the ability to control particle size closely and to produce highly monodispersed materials [30]. Development of facile synthesis strategies for high-quality nanoparticles with controlled composition, crystalline phase, shape, and size is crucial in tuning their chemical and optical properties and exploring their potential applications in diverse fields. To this extent, a variety of methods have been established to synthesize different kinds of upconversion nanoparticles with controlled crystalline phases, sizes, and shapes, including coprecipitation [31-33], thermal decomposition [34-35], hydrothermal synthesis [36-38], sol-gel process [39-40], and combustion synthesis[41], which have been reviewed in many papers [42- 47]. Gold nanorods with aspect ratios of 4.6, 13, and 18 with 16 nm short axis have been prepared by a seeding growth approach in the presence of an aqueous miceller template [48].

1.3.3. Electric arc discharge method

Arc discharge technique is one of the earlier technique used to make CNTs. Kratchmer et al. (1990) developed mass production method of fullerenes by resistive heating[49]. Iijima observed CNTs in 1991 in the carbon soot of graphite electrodes during an arc discharge process [24]. This technique led to the discovery of multiwalled carbon nanotubes (MWCNT). During the arc discharge, two graphite rods are placed in an enclosure that is filled with inert gas (helium or argon) at low pressure (between 50 and 700 mbar). The carbon rods act as electrodes which are kept at different potentials. The anode is moved close to the cathode until an arc appears and the electrodes are kept at the distance of 1 mm for the whole duration of the process that takes about one minute. After the de-pressurisation and cooling of the chamber the nanotubes together with the by-products, can be collected. This method is being used for the synthesis of fullerenes, MWCNTs and SWCNTs and binary metal catalysts [30, 50, 51].

Arc discharge method is a promising technique for production of bulk quantity graphene, as it is environmentally friendly and yields high purity graphene flakes compared to chemical exfoliation. Plasmas of the arc discharge can also provide a convenient way to add functional groups in situ during synthesis [52 -54].

1.3.4. Laser Ablation

In Laser Ablation, a high power laser is irradiated on a carbon target. Smalley and his group in 1995 used laser ablation to grow high quality nanotubes [55]. Intense laser pulses ablate a carbon target which is placed in a tube-furnace heated to 1200°C. During the process some inert gas like helium or argon flows through the chamber to carry the grown nanotubes to the copper collector [56].

Pulsed laser ablation technique allows the production of high quality nanoparticles and their functionalisation with biomolecules and polymers which offers versatile scope for application in the arena of medicine and engineering. Thus besides, physical and chemical routes, use of lasers in generating nanoparticles in liquid dispersions have attracted the attention of scientists[57-59].The laser method is specially suitable for producing nanomaterials that can be integrated into different material, new and unexplored material, high purity metal and alloys etc.

1.3.5. Chemical vapor deposition (CVD) method

CVD is a process in which a mixture of gases passing over a hot surface undergoes chemical reactions which lead to solid deposit on the surface. This is the most popular technique for preparation of nanoforms of carbon in terms of product purity and large scale production. This method is simple and economic for synthesizing CNTs at low temperature and ambient pressure. CVD allows the experimenter to avoid the process of separating nanotubes from the carbonaceous particulate. CVD reactions are strongly affected by the experimental parameters, such as reactor temperature, pressure, precursor composition catalyst and concentration. A minor modification in the experimental parameters causes a drastic change in the results. A little change in temperature and catalyst leads to different morphologies of CNT derived from the same precursor. General experience is that low temperature CVD (600-900^{0}C) yields MWNTs, whereas higher temperature (900-1200^{0}C) reaction favours SWNT growth [60, 61]. The CVD method allows CNT growth at much lower temperatures compared to the arc discharge and laser ablation methods. The CVD method is a controllable process for the selective synthesis of CNTs either individually or in bulk. The hydrocarbons (C_2H_2, CH_4, C_2H_4, etc.) or CO are usually used as carbon source. Hydrocarbon decomposition has the drawback of forming an amorphous carbon coating, due to the self-pyrolysis of the reactant at high temperatures, which generally requires additional purification steps prior to CNT utilization. The CVD synthesis can be carried out either in the gas phase or on substrate materials.

Sonication and oxidative purification are usually not needed for the SWCNT samples grown directly on the device substrate, significantly reducing the possibility of defect formation and altering of the CNT properties. Patterns can be introduced by various lithography methods, which is useful for many applications such as field emission, sensors, transistors, memory devices etc. The substrate materials used for the synthesis can be divided into particles and flat substrates. For growth on particles, SiO_2, MgO and Al_2O_3 are the most commonly used substrate materials with both hydrocarbons [62,63] and CO [64, 65]. Zeolites [66] and CaCO3 [67] are also known to provide good substrates for the CNT growth. Kong et al. [68] synthesized SWCNTs from patterned iron catalytic islands on a SiO_2 substrate using methane as a carbon. Huang et al. [69] prepared millimetre long SWCNTs with iron catalyst on a SiO_2 wafer using CO. Zheng et al. [70] reported that the addition of H_2 greatly enhanced the SWCNT growth using iron catalyst on a silica substrate by CO disproportionation. Peng et al. [71] and Kasumov et al. [72] synthesized SWCNTs from iron catalyst on Si_3N_4 membranes using CH_4 and C_2H_2, respectively. CNT syntheses on Al_2O_3 substrates have been extensively described using hydrocarbons [73, 74] and CO [70] as carbon sources. Other materials, including quartz [75], sapphire [76], diamond [77] and mica [78] were also efficiently used as supports for CNT growth.

Scrutiny of literature reveals that synthesis of carbon nanomaterials (CNMs) are carried out using petroleum derived materials as precursors. Being expensive and at the verge of depletion, alternate renewable sources of precursors to synthesize CNMs are warranted. This is also in keeping with tenets of Green Chemistry. Hence, to explore renewable materials for CNM synthesis with high efficiency is a significant option. Exploring environment-friendly sources for production of CNMs and optimise the conditions for growing multiwalled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs) and vertically aligned MWCNTs on the suitable catalytic support by a simple and inexpensive chemical vapour deposition (CVD) technique is fast getting popular [79,80]. CNMs have been synthesized by catalytic decomposition of camphor and its analogues, turpentine oil, eucalyptus oil, neem oil and many more such renewable sources [81-88].

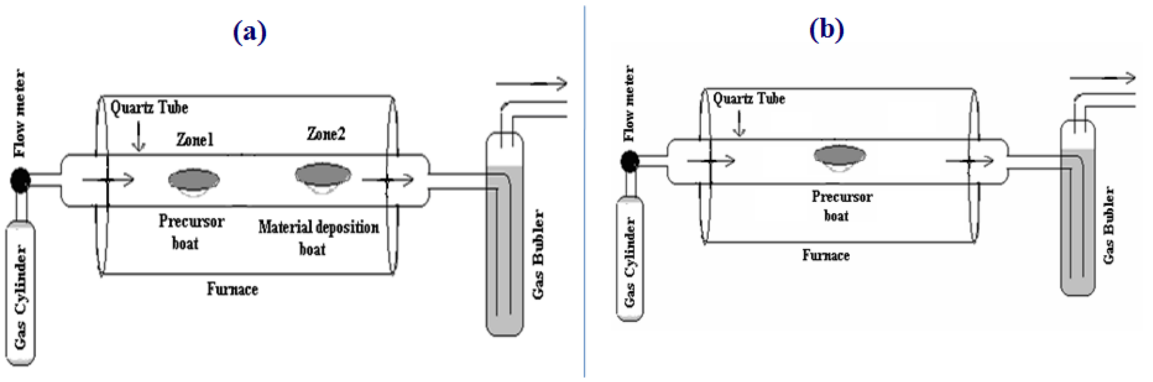

Fig.1.2. Experimental setup of (a) chemical vapour deposition unit (b) pyrolysing unit

1.4. Carbon nanomaterials

Carbon nanomaterials as a class of low-dimensional materials have drawn significant attention among material and biological researchers since the discovery of fullerene in 1985 [89] followed by the discoveries of carbon nanotubes (CNTs) and graphene in 1991[24] and 2004[90]. These carbon nanomaterials are basically a seamless network of conjugated π- electrons. With little contrast, carbon dots comprises of mixed sp^2 and sp^3 carbon atoms with defects and hetero atoms, alongside nano diamonds consisting of mostly sp^3 carbon atoms. Allotropic forms of carbon nanomaterials are depicted in **Fig.1.3.** [91]

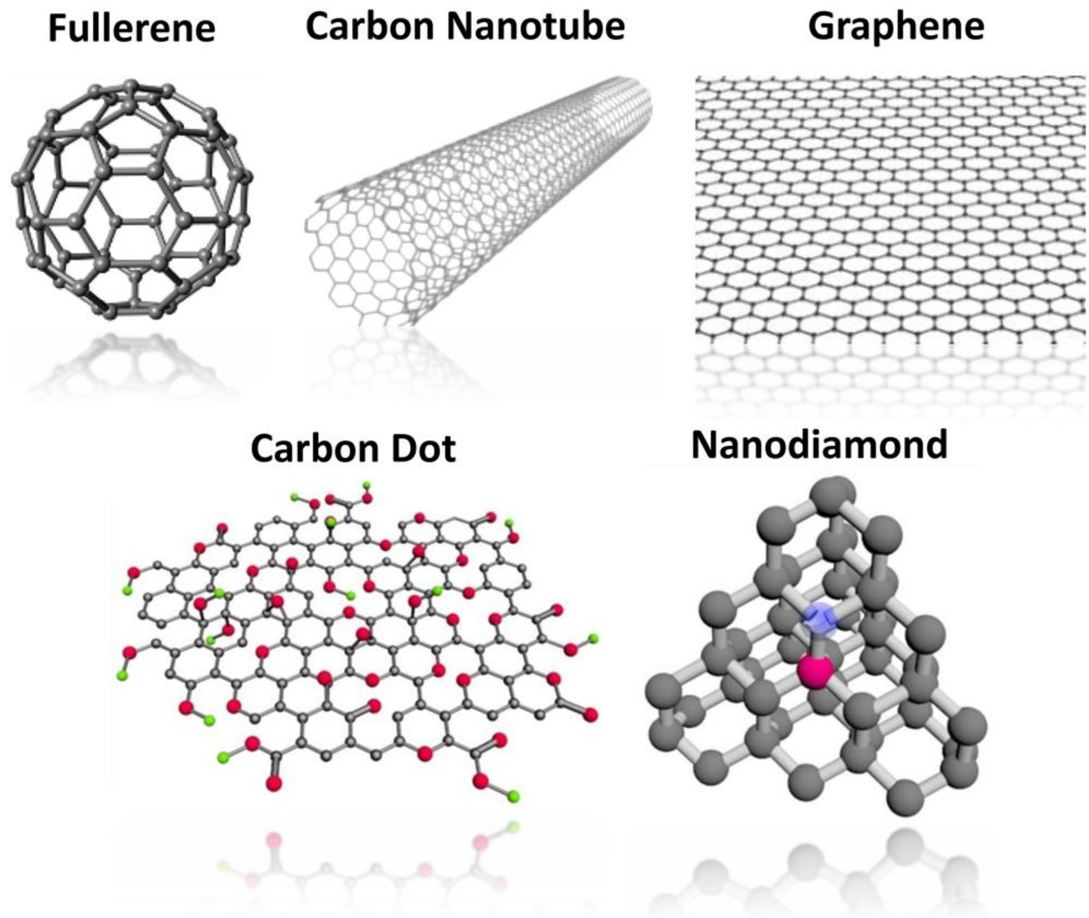

Fig.1.3. Different types of carbon nanomaterials

[Source: Hong, G., Diao, S., Antaris, A. L., & Dai, H. *Chem. Rev.*, 2015, **115**, 10816.]

In the context of present research it is deemed appropriate to highlight the different aspects of CNTs in particular. The diverse range of CNT electronic properties as a function of their chiral vector coupled with their quasi-one dimensional structure presents a number of attractive opportunities for electronic applications. Semiconducting CNTs are promising channel materials in field-effect transistors (FETs), whereas metallic CNT thin films are potentially useful as transparent conductors. A CNT FET is a three-terminal switch where current is passed through the CNT connected to two electrodes (**Fig.1.4**). Switching is achieved by modulating the carrier density in the CNT by a third electrically isolated electrode (gate) [92, 93].

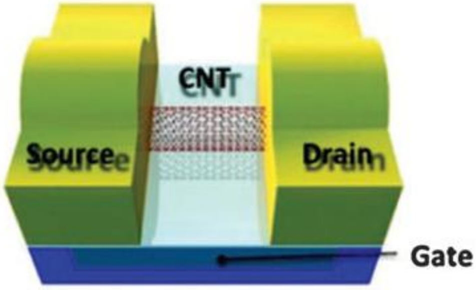

Fig.1.4. Schematic of a bottom-gate CNT FET [92]

[Source: Franklin, A. D., Luisier, M., Han, S. J., Tulevski, G., Breslin, C. M., Gignac, L. Lundstrom, M. S. & Haensch, W. *Nano Lett.*, 2012, **12**, 758]

The one-dimensionality of CNTs is particularly interesting in electronic applications. Electroluminescence has been observed in unipolar CNT FETs by impact excitation processes which are at least 3 orders of magnitude more efficient than in conventional bulk semiconductors [94].

While the explosion in graphene research was triggered by the seminal paper on single layer graphene by Geim and Novoselov in 2004,[90] the unique electronic properties of graphene were known from theoretical predictions for more than half a century. The first calculations of the electronic structure of graphene were reported in 1947 [95]. The unique electronic structure of graphene stems from its honeycomb lattice in which a carbon atom is bonded to its neighboring three carbon atoms through sp^2 hybridized bonds [96]. The high field-effect mobility of graphene has inspired significant efforts to explore its utility for digital electronics. The high mobility allows faster switching circuits, and the ideal two-dimensional structure enables ultimate scaling of the device channel [97]. An upsurge in biomedical research has been witnessed using carbon nanomaterials which are advantageous primarily owing to small size, unique optical properties, and large surface area. The similar dimensions between nanomaterials and many fundamental biomolecules are crucial to maintaining the basic functions of life. Carbon nanomaterials typically range from 1 nm to 1 μm in size. This is comparable to the sizes of proteins (1-100 nm) and DNA (2-3 nm in width) in biological environments making them ideal nanocapsules and nanocarriers to load and deliver drugs and genes to specific targets in vivo. Moreover, the optical properties unique to some carbon nanomaterials have also attracted a lot of interest for a variety of biomedical applications.Recent progress in biological imaging and nanomedicinal therapy using carbonaceous nanomaterials has been reviewed [91].

1.5. Metal based nanomaterials

Metal based nanomaterials have attracted great interest in both fundamental as well as applied research domains owing to their interesting physical and chemical properties and also promising applications in many fields including catalysis, coatings, membranes and electronics. In the arena of metal based nano materials several distinct types are also possible such as noble metal nanoparicles (Au, Ag etc.), nano metal oxides (Co_3O_4, SnO_2, and MnO_2 etc.), sulphides (CdS), carbonates ($CaCO_3$), bimetallic nano composites (CdSe), metal-carbon nano composites (SiC) etc. Ag and Au nano particles exhibit interesting optical, electronic, and molecular-recognition properties. Gold nanoparticles have great applications not only in bio sensing drugs but also in drug, gene and protein delivery. Nanometal oxides (Co_3O_4, CoO) are being intensely investigated for their applications in heterogeneous catalysis, sensors, anode materials in lithium ion rechargeable batteries, energy storage, magnetic materials and so on [98-101]. Semi conducting nanoparticles such as CdS, CdSe, SnO_2 etc. finds application as gas sensors, nanocapacitors, as high capacity anode materials for lithium ion batteries and other opto-electronic devices [101].

1.6. Nanocomposite

A nanocomposite is a matrix to which nanoparticles have been added to improve a specific property of the material. The properties of nanocomposites have enticed researchers to consider using this material in several fields.These materials have received great attention due to properties such as low density, high specific surface area and uniform pore size, and thermal and mechanical stability [102]. The applications of such nanomaterial are linked to, magnetic, catalytic, energy and absorptive, among others [102, 103]. Nanocomposite [104-109] are beginning to be commercially available and finding applications in several industries, including automotive, military, food, electronics and leisure, due to their enhanced mechanical, electrical and thermal properties. Ceramic and metallic nanocomposites are at an early stage of development. Passive electronic components based on nanocomposite materials are under development [110]. Another type of nanomaterial and their composite that has attracted tremendous attention in the last decade or so are graphene [111-118]. Nanocomposite that incorporates carbon is also no exception in this regard [109].

1.7. Scope and Objective

Nanoscale materials have stimulated great interest due their importance in basic scientific research and potential technological applications. Synthesis of nanomaterials with controllable morphologies has opened up newer opportunities for systematic exploration on the relationship between structures and functions of such materials. Developing controlled synthetic methods for nanomaterials of different shapes and sizes is the most important goal in the field of nanoscience and nanotechnology.

However, growing environmental concerns have motivated researchers to look for innovative alternative synthesis strategies that avoid toxic and expensive chemicals which pose an ecological threat. Shape control of inorganic materials found in biological systems is often achieved either by growth in constrained environments such as membrane vesicles [119] or through functional molecules such as polypeptides that bind specifically to inorganic surfaces [120-122].

Several attempts were made to prepare inorganic nanomaterials using phyto molecules of plant extract. Preparation of triangular gold nanoprisms using lemongrass (*Cymbopogon flexuosus*) plant extract [123]. Use of phytochemicals such as proteins, amino acids, vitamins, polysaccharides, polyphenols, terpenoids, and organic acids such as citric acid, as environmentally viable natural products constitute a green approach. Chemicals, such as sodium borohydride, thiols and amines, used in the synthesis of metal nanoparticles are not considered green reagents owing to their adverse environment effect.

This challenge has led to the development of green nanoparticle synthesis methods based on mild and environmentally friendly bio-reductants and capping agents derived from natural products. A straightforward approach toward green synthesis of nanomaterials is the use of plant-derived reagents, e.g. phytochemicals as reducing agents for metal salts. Considerable research has been carried out in this direction and extracts have been obtained from different parts of plants, such as leaves, stems, bark, pods, flowers, and fruits. Although numerous reports describe the use of plant extracts for the synthesis of nanoparticles, this perspective is restricted to the synthesis of noble metal nanoparticles, specifically silver, gold, palladium, and platinum. Silver nanoparticles are particularly attractive because of their plasmonic response properties [124]. Their bactericidal and fungicidal activity has been exploited in a range of consumer and pharmaceutical products such as soaps, pastes, food, textiles, water filtration systems, antimicrobial paints, ointments and gels for topical use, packaging paper for food preservation, fabrics for clinical clothing, bandages, cotton swabs, and anticancer drugs[122]. Realising such applications require the implementation of large scale synthesis methods and greener techniques. The use of different plant extracts led to nanoparticles of diverse perspective. Of particular relevance here to mention about synthesis of carbon nanomaterials which hold great promises. Considering that non renewable precursors like fossil fuels etc. are fast depleting, the production of carbon nanomaterials from renewable sources using inexpensive methodologies appears to be a prudent option. In light of this, exploring suitable renewable plant based precursors for synthesis of carbon nanomaterials has been an engaging theme of the present research work. Rich carbonaceous matter and micro quantity of minerals present render such precursors an ideal staring material for accessing variety of carbon nanostructures including carbon nanocomposites.

Accordingly in keeping with this motive, the primary objectives of the present Ph. D. research programme are set as-

1) To devise strategies for accessing novel nanomaterials using cheap and easily available natural substances.
2) To characterize as-synthesized nanomaterials using SEM-EDAX, TEM, XRD, UV-visible, FT-IR, Raman studies etc.
3) To study electrical properties such as capacitance behavior of few select materials.
4) To investigate antimicrobial properties of few select materials
5) To investigate antioxidant properties of few select materials.

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