Chapter 1

Introduction

1.1 Plasma

1.1.1 Introduction to plasma

In physics, plasma refers to the state of matter similar to gas, in which a certain portion of the particles are ionized. The charged particles consist of both positive and negative species mixed in almost equal proportions such that the overall medium is electrically neutral. Plasma was first identified by Sir William Crookes in 1879 during his experiments with electrical discharges in vacuum tubes. The word “plasma” for this ionized gas was coined by Irving Langmuir in 1927.

A plasma state is generated when a gas is supplied with sufficient energy in the form of heat, electric field etc. so that electrons are liberated from the neutral molecules/atoms forming ions and free electrons. Therefore, plasma is often called the forth state of matter, in addition to the three states of matter which are familiar to us i.e. solid, liquid and gas. Plasma is all around us in the universe. It is said that more than 99% of our universe is in plasma state. However, plasmas are not routinely encountered on the surface of the earth. But, we do see natural plasmas in the form of lightings and auroras and man-made ones in the form of fluorescent light bulbs and neon signs.

But any ionized gas cannot be called plasma as there is always some degree of ionization in any gas. So, plasma is best defined as a quasineutral gas of charged and
neutral particles, which exhibit “collective behavior”[1]. By quasineutral, we mean that the numbers of positive and negative ions are almost equal to each other so that the overall medium is electrically neutral. The quasineutrality of plasma arises from the fundamental characteristic behavior of plasma of shielding out any electric potential applied to it. They shield out the potential by forming a cloud of ions or electrons around the applied potential. Outside this cloud, the potential is very weak and the density of ions ($n_i$) is almost equal to that of electrons ($n_e$), so that we can take $n_i \approx n_e \approx n$, where $n$ is a common density called the plasma density.

Plasma exhibits collective behavior because it consists of freely roaming clouds of positive and negative charges whose motions generate electromagnetic fields, to which plasma can react in turn. Even though the Coulomb force between two charge regions decreases as $1/r^2$ ($r$ is the distance), but the volume of the space charge that affects other charges at long distances increases as $r^3$. Therefore, the motion of charges in plasma depends not only on local conditions but also on the state of the plasma in remote regions as well, which thus enriches this exotic state of matter with myriads of dynamic processes.

1.1.2 Criteria for plasmas

As discussed above, plasma shields out any externally applied electric potential ‘$\phi$’. For an electron cloud, from Poisson’s equation, we get,

$$\varepsilon_0 \frac{d^2 \phi}{d x^2} = \frac{n_e e^2}{K T_e} \phi \quad \text{........................................1.1}$$

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where \( \varepsilon_0 \) is the permittivity of free space, \( K \) is the Boltzmann’s constant, \( T_e \) is the electron temperature, \( n_\infty \) is the electron density at \( \phi \to 0 \) and \( e \) is the electronic charge.

Now, we define a term,

\[
\lambda_D = \left( \frac{e^2 K T_e}{n e^2} \right)^{1/2}
\]

where \( n = n_\infty \).

We can write the solution of Eq. [1.1] as,

\[
\phi = \phi_0 \exp \left( \frac{-k \lambda_D}{\lambda_D} \right)
\]

where \( \phi_0 \) is the total electric potential.

The term \( \lambda_D \) is called the Debye length and can be defined as the distance over which the potential reduces to \( 1/e \) of the total applied potential. As we see from Eq. 1.2, Debye length decreases with increase in density. One of the criterion for an ionized gas to be a plasma is that it should be dense enough so that Debye length ‘\( \lambda_D \)’ is much smaller than \( L \), the dimension of the system, so that quasineutrality can be maintained in the system.

However, the above picture of Debye shielding is possible only when enough particles are present in the charge cloud called the Debye sphere. The number of particles \( N_D \) in a Debye sphere can be calculated as,

\[
N_D = n \frac{4}{3} \pi \lambda_D^3
\]

Another criteria for an ionized gas to be plasma is that \( N_D \gg 1 \).

The third criterion for an ionized gas to be plasma has to do with collisions. If \( \omega \) is the frequency of typical plasma oscillations and \( \tau \), the mean time between
collisions with neutral atoms, then for the gas to behave like plasma whose motion is controlled by electromagnetic forces rather than ordinary hydrodynamic forces, we require \( \omega \tau > 1 \).

1.1.3 Gas discharges

The phenomenon of electrical current passing through gases is known as Gas discharge. Capacitors were discharged across two electrodes for achieving the same and that is how the term gas discharge was coined. The discharge passage may contain atoms, molecules, positive and negative ions, electrons, exited species, free radicals and photons. The electrode from which the electrons enter the active volume of the discharge is called the cathode and is connected to the negative terminal of a power source. The electrode through which the electrons leave the discharge is called the anode and is generally connected to the positive terminal. Discharges can be classified as self-sustaining and non self-sustaining.

When a voltage is applied between two metal plates immersed in a gas at a certain pressure, a uniform electric field develops between the electrodes. Electrons get accelerated in this field and produce ionization through impact with neutral atoms. If a current flow between the electrodes, but the electrical conduction is due to the external ionizing agents only, it is known as non self-sustaining discharge. The current dies, once the external ionizing agent is removed. An example of a low current non self-sustaining discharge is the Townsend’s discharge.

The transition from non self-sustaining to a self-sustaining discharge is called breakdown and the voltage at which it occurs is known as the breakdown voltage. The self-sustaining discharges are broadly classified into glow discharge and arc.
discharge. At low pressures with high resistance in the external circuit, which prevents the current from reaching high values, a glow discharge develops. The gas is weakly ionized, gas atoms/ions remains almost at room temperature, whereas electrons have a mean energy of around one electron volt. On the other hand, when the pressure is high and the resistance in the external circuit is low, a high current arc discharge develops. The degree of ionization is higher in this case.

As against glow discharge plasmas with much larger voltage drops, arcs usually have a drop of only few volts near the cathode. The low drop is on account of the efficient mechanism of electron emission by the thermionically heated arc cathode. At glow-discharge current level, the cathode hardly heats up in the first case; hence electrons are emitted through secondary processes like by impact of ions, which is facilitated by the build-up of a relatively larger cathode drop.

1.1.4 Thermal plasma

High pressure arc based plasmas are also known as thermal plasma, where because of the higher collisions between species, the neutral part (as well as ions) is thermalized with the electron population (i.e. $T_{\text{gas}} = T_{\text{ion}} = T_{\text{electron}}$). They have very high energy content and often are sources for intense light and sound. Thermal Plasmas are produced in devices called plasma torch; an elaborate description of different verities of plasma torches are presented in the subsequent sections.

Thermal plasmas can reach temperatures as high as few ten thousand Kelvin. However, typical electron temperature of thermal plasma is few eVs only and therefore they are often categorized as low temperature plasmas.
1.1.5 Plasma torches

In laboratory, thermal plasmas are produced by devices called Plasma torch. Plasma torches can be driven with power sources operated at various frequencies. Direct current (DC), radio frequency (RF) or microwave power driven torches are known as DC, RF and Microwave torches respectively. A DC plasma torch consists of a tungsten rod cathode and copper anode. The arc is pushed out into a stable beam by the plasma gas, through a small annular gap between the cathode and the concentric anode. All torch parts, especially the anode, are intensely water cooled.

DC Plasma torches can be operated in transferred and non-transferred mode (figure 1.1). In transferred plasma torch, the arc is electrically transferred from the cathode to the work piece i.e. the work piece acts as anode. The transferred arc mode torch operates at relatively higher voltage and low gas flow rates (compared to the non-transferred one). In case of non-transferred arc, the arc is not electrically transferred to

![Figure 1.1. Simple DC plasma torch showing components (1) Cathode (2) Gas flow (3) Anode (4) Cooling Channel (5) Plasma jet and (6) Substrate operated in (a) transferred and (b) non-transferred mode.](image)
the work piece but is blown out of the torch by the plasma gas. This produces non-current-carrying plasma beyond the anode and is called a plasma jet.

An arc, being a turbulent discharge phenomenon, needs stabilizing mechanisms to maintain it in the steady state i.e. to maintain its motion in a well-defined pattern. Such stabilization process also provides the constriction of the arc column to enable the steady passage of the electric current. Arc stabilization is achieved by different types of external stabilizing mechanisms like gas or water flow, chamber wall and external magnetic fields. A plasma torch therefore is a device that stabilizes the arc by constricting the arc, efficiently cooling the outer layers and defining the path of the arc [2].

In gas flow stabilization technique, a flowing external cold layer of a gas surrounds the arc and constricts it. Depending on the mode of injection of the gas, the

![Figure 1.2. Simple DC plasma torch showing components (1) Cathode (2) Gas flow (3) Anode (4) Cooling Channel and (5) Plasma jet with (a) axial gas flow stabilized and (b) vortex gas flow stabilized.](image-url)
flow can be vortex or axial (figure 1.2). When the gas is injected tangentially, it creates a vortex flow where the centrifugal force drives the cold gas towards the wall of the chamber while the hot core remains at the center. Vortex stabilization is very effective in constricting the arc, thereby increasing the energy density and temperature. Vortex stabilization produces a short, intense plasma jet. The axial flow stabilized arcs have a laminar flow and the cold gas surrounds the hot core. Consequently, the arcs are longer.

In a wall stabilized arc, the arc is constricted by means of cold surfaces like the wall of the confining chamber. It is achieved by allowing the arc to burn through one or several orifices in cooled metal or graphite discs or through a cooled silica tube, thus fixing the position of the arc column. The cold walls effectively cool the plasma and constrict the diameter of the plasma, which then has a higher temperature in the constricted central portion. The plasma will be coaxial within the tube. At high current densities, the magnetic effect of the current may cause a pinch effect resulting in a further constriction of the arc column.

Arcs can also be stabilized by the use of an axial magnetic field. The magnetic field constricts the arc column, preventing it to expand and thereby increasing the density and temperature.

1.1.6 Segmented plasma torch

Segmented arc plasma torch is a wall stabilized configuration, which has the advantage of producing well-constricted and highly stable plasma jet. It usually consists of one [3] or more [4] cathode, a stack of insulated copper plates and an anode. The cathode is usually made from thoriated tungsten in the form of a pointed
rod usually placed at the top of the torch near the gas entrance. The copper plates have holes forming a cylindrical channel at the centre through which the plasma gas flows. The anode is usually in the form of a cylindrical opening at the bottom of the cylindrical channel. This configuration allows another advantage that input power can be enhanced simply by putting more numbers of floating rings in between the electrodes. All these components are intensely water cooled. When a gas is passed in the channel and an arc is initiated between the electrodes, the electric current between the electrodes heats up the gas and ionizes it, pushing it through the anode hole forming a plasma beam. Adding a nozzle after the anode usually increases the exit velocity of the plasma beam. By using proper designs of the nozzle and maintaining appropriate differential pressure across the nozzle, the plasma beams can attain supersonic velocities [3]. The cold water cooled wall along the central hole effectively cools the plasma, thereby constricting the arc and confining the discharge in the center. Any accidental movement towards the wall will cool the arc column which will reduce the conductivity and force the column back to the original position. This configuration constricts the arc column very efficiently and produces a much higher ion density compared to other plasma torch configurations. During plasma processing, the precursor can be injected into the plasma at various axial positions depending on the temperature requirement for proper decomposition which is considered as yet another advantage of this configuration. In this thesis, we have used a segmented plasma torch, exact description of which will be given in the next chapter.

1.2 Nanoparticles

1.2.1 Introduction to nanotechnology
Nanostructure science and technology constitute a wide and interdisciplinary area of research and development that has been growing rapidly over the last few decades. This is evident from the large number of scientific publications and conferences held in this field. It has already made a significant commercial impact which will only increase in future and has the potential for revolutionizing the way in which materials and products are created.

Professor Richard Feynman is often hailed as the earliest proponent of the concept of nanotechnology, who in a talk delivered at CALTECH in 1959, had described a process by which the ability to manipulate individual atoms and molecules might be developed [5]. Nanotechnology had large initial boost in the form of the invention of scanning tunneling microscope in 1981 by Gerd Binnig and Heinrich Rohrer that allowed scientist to see and move individual atoms for the first time, followed by the discovery of fullerenes in 1985 by Harry Kroto, Richard Smalley and Robert Curl [6]. Around the same time, K. Eric Drexler also popularized the concept of nanotechnology and founded the field of molecular nanotechnology.

Originally, nanotechnology was restricted to the control of material structure at molecular level, through atom by atom manipulation. However, with development and increase in interest in this field, the term has been more broadly applied to any technology performed on nanoscale that has applications in the real world. Nanotechnology is most likely to have a huge impact on our economy and society in near future just like the way semiconductor technology had in the past. It has the potential to bring breakthrough in a variety of fields like materials and manufacturing, medicines and healthcare, energy, information technology, biotechnology and electronics [7].
Nanotechnology actually takes advantage of the fact that material properties change abruptly as dimensions are reduced to the nanometer level. The root cause behind this change could be quantum-mechanical effects or other simple phenomenon like enhancement of the specific surface area as the sizes are progressively reduced [8].

1.2.2 Nanoparticles

Nanoparticles are frequently referred as the basic building blocks of nanotechnology. They are actually material particles with sizes in the range of 1-100 nm in at least one dimension and normally in three. The characteristics of nanoparticles are often strongly dependent on their sizes. This opens up the possibility of manipulating the bulk properties of nanostructured materials by changing sizes of the primary nanostructures and creating unique materials with tailored properties for new applications.

Acute size dependence has been observed in terms of physical, chemical, electrical, optical, mechanical and magnetic properties of nanoparticles. For example, the melting point of some nanoparticles is highly dependent on their size, decreasing with decrease in size, as was first observed in the case of gold nanoparticles [9]. Decrease in size may also lead to increase in electrical resistivity and hardness of some metals [10]. One of the most important chemical properties affected by decrease in size is the catalytic activity of specific nanoparticles and this lead to one of the first technological application of nanoparticles [11]. Magnetic properties are also highly dependent on sizes of particles in the nanometer size range. An iron nanoparticle loses its ferromagnetic properties and becomes super-paramagnetic when their size is
reduced below the nanometer level domain sizes [12, 13], while paramagnetic
materials like Rh, Pd, Na and K become ferromagnetic upon reduction to the almost
similar size range [14, 15].

One of the reasons behind why nanoparticles have novel properties is that they
have very high surface to volume ratio compared to bulk materials. As the size of the
nanoparticles decreases, the fraction of atoms on the surface increases drastically. The
increase in the number of atoms on the surface of the nanoparticles increases the
surface energy. In order to reduce the surface energy and hence stabilize the
nanoparticles, reduction in inter-atomic distances, changes in crystal structure from
that of bulk materials and other changes may take place which changes the overall
properties of the nanoparticles from that of bulk materials.

Nanoparticles may also have properties different from that of bulk materials
because of volume effect. Volume effect comes into play when the size of the
nanoparticles becomes comparable to or smaller than the length scale of physical
processes like magnetic domain, mean free path of an electron, wavelength of light
etc. Sometimes, nanoparticles may also exhibit quantum mechanical behavior. When
the size of the nanoparticle are small enough, the energy bands splits into discrete
quantization levels and the band gaps starts opening unlike the bulk materials where
the energy bands are continuous. This is called the size quantization effect.

1.2.3 Applications of nanoparticles

Nanoparticles constitute an important sector of the nanotechnology market and
unlike the many applications of nanotechnology, which are still speculative,
nanoparticles have been in use for quite some time. The earliest use of nanoparticles
dates back as far as the Roman civilization where they used nanoscale gold clusters to make colored glasses [16]. And from the early 1900's, carbon nanoparticles have been regularly used in the tire industry, improving the durability of tires and giving it its characteristic black color [17]. Currently, the use of zinc oxide and titanium dioxide (titania) nanoparticles have made it possible to make transparent sunscreens as these materials are transparent in the nanoscale [18]. Titania nanoparticles have also become a key ingredient in dye-sensitized solar cells where the use of titania in the nanoscale have increased the efficiency of these cells by many folds [19]. Another large scale use of nanoparticles is in the semi-conductor industry in a process known as the chemical mechanical planarization (CMP) where alumina, silica and ceria nanoparticles are used for achieving atomic level polishing [20]. Metal nanoparticle such as iron is used for large scale removal of contaminants from soil/water, while silver nanoparticle is utilized to eliminate bacteria and odor from clothing, food packaging etc. In addition to these large scale applications of nanoparticles, there are also many other emerging applications which make use of their enhanced mechanical, electrical, optical, catalytic, magnetic and other properties [8].

1.2.4 Synthesis of nanoparticles

It is not only sufficient to produce particles having size in the nanometer range but the processing conditions need to be controlled enough so that the product particles have identical shape and morphology with narrow size distribution, which only can have any practical application. It is also equally important to have identical chemical and phase composition and crystal structure. Agglomeration and purity of nanoparticles are other critical issues which need to be addressed during nanoparticle synthesis.
There are different methods for nanoparticle synthesis each having its own advantages and disadvantages. And it is difficult to judge which method is the best since it is not easy to find a method which can produce monodispersed, clean nanoparticles in large quantities. Different metals, oxides, carbides, polymers, core-shell and composite nanoparticles are synthesized by different techniques. But all these processes can be grouped into two main categories, “bottom-up” and “top-down” methods (figure 1.3).

![Figure 1.3. A schematic diagram showing two different approaches for nanostructures synthesis; bottom-up and top-down method.](image)

In top-down methods, a suitable starting material is taken and then broken down physically or chemically to the nanoscale particles. The best example for top-down method for nanoparticle synthesis is ball milling where nanoparticles are produced through controlled, mechanical attrition of the starting bulk material [21]. It is a relatively simple technique but is time consuming and may take up to several days to produce nanoparticles below 20 nm [22]. There are also chances of contamination from the milling media. The top-down approach is also utilized in the semiconductor industry to fabricate electronic devices on silicon substrate through deposition of bulk films, photolithographic patterning and reactive etching [21].
In bottom-up methods, individual atoms or molecules are placed or are self-assembled precisely where they are needed. In these methods, atomic or molecular building blocks are first created and they are fitted together to form particles of desired size and shape. These methods have better chances of producing nanostructures with less defects, more homogeneous chemical composition and better ordering because these methods are driven by the minimization of Gibbs free-energy and so, the nanostructures formed are in a state closer to thermodynamic equilibrium. One fine example in this category is the wet chemical method which has the advantage of excellent control on product size/phases but may be very slow and involve multi step processes. Moreover, the as prepared product may be almost amorphous-like which may require post-treatments for better crystallization, which may further complicate the situation through grain growth and change of phases.

There are several gas phase techniques, which gives high purity nanoparticles in a single step process, but in general has less control on product size and phase structure. In these methods, the material of interest is first evaporated and the vapor is then rapidly cooled down to achieve a state of super saturation. Nanoparticles are formed by homogeneous nucleation of these super saturated vapors, the sizes of which are usually dependent on the quenching rate. Several mediums, such as joule heating [23], Laser [24], arc discharge [6] and thermal plasma [25], can be used for the evaporation of materials. Depending on whether the nanoparticles are formed by physical or chemical methods, gas phase techniques are classified as Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD). In PVD, nanoparticles are formed by atoms evaporated from a solid target and no chemical reaction takes place during the formation of the particles. This process is usually carried out in vacuum or in an inert gas environment. The vacuum approach has the advantage of creating high
purity nanoparticles. But agglomeration of particles is a common problem in PVD which can be reduced by lowering the evaporation temperature or the inert gas pressure in the evaporation chamber. PVD techniques, using thermal sources like an oven can produce large quantities of particles but cannot handle high temperature melting point materials. Synthesis of high temperature melting point material require more powerful heating sources like Laser or arc discharge. CVD is a widely used technique for synthesis of various nanostructures. In this case, nanoparticles are formed by chemical reactions in the gas phase. The chemical reactions may be driven by a number of sources like heat, Laser and electrical discharge. CVD generally creates uniform and pure nanoparticles and have good reproducibility. It also has the advantage of using volatile compounds of high melting point materials like metal chlorides and metal organic compounds.

1.2.6 Thermal plasma synthesis of nanoparticles

Thermal plasmas have emerged as a reliable processing medium for synthesis of nanoparticles over the last few decades. During the thermal plasma aided chemical synthesis of nanoparticles, the reactants, either in the solid, liquid or gaseous state, are introduced into the plasma generally at the point of highest temperature, typically at a temperature range of 6,000-10,000 K. The reactants decompose immediately, which then react chemically forming condensable species as they cool down moving downstream. At the edge of the plasma, the temperature drops drastically and the condensable vapors experiences large super-saturation. Super-saturation can also be brought by external cooling mechanisms like mixing with cold gases. Driven by the super-saturation of the vapors, nanoparticles are formed in the gas phase by homogeneous nucleation, which may also grow further through heterogeneous
condensation or aggregation still at liquid state. The size of the nanoparticles formed is dictated primarily by quenching rate of the precursor vapors. The nanoparticles formed are deposited at downstream locations.

There are some distinct advantages for using thermal plasmas as a medium for nanoparticles synthesis. One of the biggest advantages is that very high temperature can be achieved in a thermal plasma environment, because of which almost any material in the solid, liquid or gaseous state can be used as reactants which will decompose immediately when injected into the plasma. High temperature also enhances reaction kinetics making it a very rapid process, leading to synthesis of materials in large quantities. The bulk production capacity is often considered as the biggest advantage of thermal plasma assisted techniques. Moreover, the high energy density in a thermal plasma beam creates large number of atoms, ions and radicals confined in a small volume which makes it possible to have compact reactor sizes. Another significant advantage is that the high temperature also induces very good crystallinity to the products, which helps in avoiding any post synthesis heat treatment process, thus restricting itself to a single step process.

The very high degree of natural cooling available on the edges of a thermal plasma jet ensures synthesis of very fine particles in the first place, from the precursor vapor embedded in the power beam. High quenching rate also makes possible synthesis of nanomaterials in meta-stable phases which may not be achieved through an equilibrium process. An important feature of the thermal plasma aided technique which is crucial for capacity up-gradation and ultimate commercialization of these processes is that they can be developed as a single step continuous process. In a thermal plasma reactor, the input energy is independent of the chemical reactions
taking place inside the reactor which is in stark contrast with other gas phase techniques like the combustion furnaces where the maximum reaction temperature is limited by the amount of contained feedstock energy [25]. This opens up the possibility of exploring much wider experimental conditions, which may lead to synthesis of novel materials as has happened in the case of carbon, producing a host of new carbon nanostructures like fullerenes, carbon nano-onion, carbon nano-horn, carbon nano-flower, single walled carbon-nanotubes, multi-walled carbon nano-tubes etc. Thermal plasma assisted methods are also considered to be environment friendly as production of green house gases like CO and CO$_2$ can be avoided by eliminating oxygen in the plasma environment. This ability of being able to operate in a controlled low pressure environment also makes it possible to synthesis nanoparticles of nitrides and carbides of metals, which otherwise may get quickly oxidized in a high pressure natural environment.

On the negative side, there are lots of non-uniformities in plasma temperature and velocity, particularly at the plasma edges. This leads to non-uniformities also in the cooling process that translates in the nucleation of nanoparticles with a wide size distribution which is unfavorable. Another problematic issue is the reactant injection. The reactants often fail to penetrate to the point of highest temperature because of high viscosity of the plasma medium. So, bigger solid particles may not fully evaporate during their finite time of transit through the plasma. Also the plasma may get cooled down or extinguished when overloaded with reactants during high rate processing. Imperfect mixing of reactants may also lead to over use of costly gases much more than the stoichiometric amount. Agglomeration and large average size of nanoparticles is another problem associated with thermal plasma aided nanoparticles
synthesis which is because of high temperature and pressure associated with the
process.

1.2.7 Plasma expansion technique

The important issues in the nanoparticles synthesis research are achieving
better control over particle morphology, purity, phase selection and narrow
distribution of particle sizes. Bulk production in a continuous process and efficient
collection of un-coagulated nanoparticles are some other important issues to be
addressed. In conventional thermal plasma assisted process, quenching of the vapor is
achieved usually by mixing the vapor laden plasma jet with a cold gas, which can lead
to very high quenching rate of up to $10^8$ K/second. But this is a fundamentally
turbulent process which usually leads to vast non-uniformity in the processing
conditions. But in order to obtain a product with narrow size distribution, it is
necessary that all the vapor parcels have the similar velocity, temperature, and
concentration history [26]. So, quenching as practiced in conventional plasma reactors
produces particles with wide size distribution. This single problem often offsets the
other distinct advantages as offered by thermal plasma assisted processing of
nanoparticles.

A better technique to achieve uniform as well as high quenching rate ($10^7$
K/sec) [27], is to supersonically expand the plasma jet laden with precursor vapor
through a converging nozzle into a low-pressure environment. During the nozzle
expansion process, the pressure and thermal energy is converted into the kinetic
energy of the plasma beam. The expansion process creates a uniform temperature
profile which ensures homogeneous condensation of particles with a narrower size
distribution. And also during the cooling process, the plasma beam is accelerated in the forward direction which helps in reducing agglomeration of the product particles, as this reduces the probability of collisions among particles seeded in the plasma jet [28]. Another important advantage of the expansion technique is the possible charging of particles after nucleation. Recent observations show that nanoparticles may charge up to several hundreds of electronic charges in such a process [29]. Particles charged to unipolar negative potential in such cases will repel each other and hence can curb unwanted agglomeration among the product particles. Another unique feature of this technique is that here the plasma production zone remains effectively isolated from the particle nucleation/growth zone through a supersonic nozzle. This makes it possible to lower the pressure in the sample collection chamber down to few mbar level, which in a conventional thermal plasma assisted system would have interfered with the plasma production process and destabilized/extinguished the plasma jet.

An experimental plasma chemical reactor with the nozzle expansion configuration has been set up in this laboratory, which was used in the recent past to explore the synthesis of some important high temperature nanomaterials namely, titanium dioxide, titanium nitride, aluminum oxide etc. [28, 30, 31, 32]. It has been demonstrated that the expansion can actually produce a narrow size distribution of the product and the particles are less agglomerated compared to typical plasma synthesized product, which is considered to be a consequence of particle charging in the expanded plasma jet. We have also demonstrated that the pressure in the sample collection chamber can be used as an efficient control parameter, to influence the size distribution as well as the crystallinity of the product, while the former enhances with the reduction of pressure (narrow distribution), the product may get more amorphous under the same trend of variation. This thesis explores synthesis of some other high
temperature nanomaterials by the same plasma expansion technique, where also the ambient pressure in the sample collection chamber was also explored for better control of product properties.

1.3 Carbon nanostructures

Carbon nanostructures occupy a very special place in the world of nanoscience and nanotechnology, both from academic and industry’s point of view. The discoveries of carbon nanostructures like fullerenes [6], carbon nanotubes (CNT) [33] and graphene symbolize bench mark in nanoscience. Fullerene took the noble prize in 1996, graphene in 2010 and carbon nanotube is regularly taking the first spot in a number of published articles and conferences in the field of nanotechnology. The discovery of fullerenes and CNTs cast a completely new light on carbon as an element and the scientific community reacted with such intense interest that their importance was established very rapidly in the world of science. This is shown by the immense number of articles published and conferences held around the world in this field. Other than these nanostructures, carbon has several other nanostructures like carbon nanoparticles [34], carbon nano-fibers [35], carbon nano-wall (CNW) [36], nanonecklace [37], carbon nano-onion [38], and still others which are also drawing a lot of interest from the scientific community and is showing great application potential. Carbon is also regarded as an ideal candidate for coating magnetic nanoparticles to prevent oxidation which otherwise has diverse application potential because of their magnetic properties [39].

1.3.2 Carbon nanoparticles
Carbon nanoparticles, is probably one of the oldest nanomaterials used by men and is also one of the first nanomaterials produced on an industrial scale (in the early 20th century) [25]. Carbon black has been used for thousands of years as pigment in paints and coatings. Currently, they are produced in millions of tons annually [40] and are widely used as fillers in polymers to modify the mechanical, electrical and optical properties, as well as conducting agent in battery electrodes. They may have application potential in energy sector, as a low cost catalyst/catalyst support or as a hydrogen storage material, which will be discussed further in subsequent chapters in this thesis. Conventionally carbon black is produced by the partial combustion or thermal decomposition of hydrocarbons. They can be obtained through different processes and are named as channel blacks, thermal blacks, lamplblacks etc. However, more than 90% of the world’s annual production is achieved with the furnace black process in which a liquid fuel is injected into a flame where its partial dehydrogenation leads to formation of carbon nanoparticles.

Plasma processes provide a better alternative to the conventional flame technique because of their many advantages like independent control of processing temperature and being environmental friendly [25]. In this thesis we report results from experiments on synthesis of carbon nanoparticles by the plasma expansion technique, which introduces some important value addition crucial for development of new applications.

1.3.3 Fullerenes

The first peculiar form of nano-carbon (other than the age-old graphite or diamond) to be discovered was buckminster-fullerene, also called bucky-ball and
fullerene C₆₀ [6]. Bucky-ball is the first spherical carbon molecule with 60 carbon atoms arranged in a soccer ball shape (figure 1.4). The most important technique for fullerene synthesis has been the Huffmann-Kratschmer method[41] which showed for the first time that fullerenes can be produced at milligram quantities and its introduction marked the real beginning of the fullerene science. This method involves arc discharge between high purity carbon rods maintained at small distance and the maximum production was achieved in an atmosphere of 100–200 mbar Helium. Thermal plasma torch aided systems have been used for the production of fullerenes which also provide several advantages over the arc discharge process. The larger plasma volume and lower gas velocities gives longer residence time to the reactive species and powder-like starting material can also be used in thermal plasma systems compared to arc ones[42, 43]. Fullerene synthesis must be followed by procedures to extract and separate the material from the impurities.

1.3.4 Carbon Nanotubes

Since their discovery in 1991 by Iijima [33], the interest in carbon nanotubes (CNT) has been growing throughout the scientific community. Carbon nanotubes are sheets of graphenes, rolled into a cylinder. They can have one or multiple layers and are respectively called single walled carbon nanotube (SWNT) and multi walled carbon nanotube (MWCN). Their large length which can be up to several microns and
small diameter about few to several nanometers result in a large aspect ratio which makes them nearly a one dimensional structure.

They possess many interesting electrical, mechanical, physical and chemical properties. Carbon nanotubes are classified according to their chirality i.e. the twist of the tubes. Nanotubes with different chirality are found to have dissimilar properties like optical activity, mechanical strength and electrical conductivity. Generally, CNTs are produced by three main techniques namely arc discharge, laser ablation and chemical vapor deposition (CVD) [44]. Even though laser ablation produces high quality, clean CNTs, the amount produced by this technique is very small. Arc discharge generally produces large amount of impure materials. The CNTs produced by CVD usually have large diameter range but this technique can be scaled up for mass production. The growth mechanism of CNTs is still a controversial subject. But it is widely seen that a metal catalyst particle is necessary for the growth of CNTs. One of the mechanisms predicts that precursor to the formation of CNTs like C_2 and other active carbon species are formed on the surface of the metal catalyst particle and from this a rod-like carbon is grown rapidly. The graphitization of this rod-like structure leads to the formation of CNTs [45]. Another theory postulates that the carbon precursor deposits only on one half of the spherical or pear-shaped catalyst particles and the carbon diffuses along the concentration gradient and precipitates on the opposite half, around and below the bisecting diameter [46]. CNTs can grow upwards from the metal catalyst particles that remain attached to the substrate which is known as the base growth or the metal particle move at the head of the growing nanotube known as the tip-growth. Depending on the size of the catalyst particles, the CNTs formed may be SWNT or MWNT.
Some of the properties of CNTs which imparts them the potential for novel application include remarkable strength, high elasticity, and large thermal conductivity and current density. The strength of CNTs is reported to be between 50 to 100 times that of steel and the elasticity of SWNT is 11.2 terrapascal (TPa). SWNTs have thermal conductivity almost twice as that of diamond, which is one of the best heat conductors known. Another impressive property of SWNT is its electrical conductivity, which is reported to be $10^9$ Amps/cm$^2$, which is about 100 times that of copper [8]. Because of these novel properties, CNTs have great potential for use in a wide range of applications, including microelectronic devices, as bulk additives in nanocomposite materials, in the field of pharmaceuticals and medicine, as catalyst and biosensors and for hydrogen storage [47, 48]. They have already made their way into commercial applications such as electron field emitters, nano-probes and nano-wires [48]. However, their use in large scale is still restricted due to the unavailability of this material in large quantity. Therefore, the most critical issue faced by nanotubes related research is that of determining the best synthesis method that will provide the most economical large-scale production of SWNT with excellent quality.

1.3.5 Graphene

Graphene is the newest member of the nano-carbon family and is often called the rising star among new materials [49]. Graphene is a honey comb sheet of carbon atoms just one atom thick, forming a perfect two dimensional material. They are the building blocks of graphite which are formed by stacking up graphenes into layers. Graphene exhibits some remarkable properties like highly efficient electrical conductivity combined with an extremely fast charge transport and an extraordinary
strength. They also show some novel electronic properties like the room temperature quantum Hall effect and electrons that behave like mass-less Dirac fermions [50]. These remarkable properties make graphene potentially useful in a wide range of applications like in electronics (high speed transistors, one electron transistors), super-capacitors, batteries, gas sensors, solar cells and in material science. For further studies and future application of graphenes, a controllable and mass producible method for the production of high quality graphene is necessary. Graphene are prepared by various methods like micromechanical cleavage of bulk graphite, chemical vapor deposition, chemical exfoliation and solvo-thermal method [50]. Even though micromechanical cleavage is simple, mass production using this method is limited and the control of the number of layers is difficult. In CVD methods, the layer control is still difficult. Chemical exfoliation can be used for mass production but the method uses chemical processing which are known to degrade graphene. The thermal exfoliation methods produce high quality graphene layers and are also cheap to produce in large quantities but involve very high temperature [51].

1.3.6 Carbon encapsulated magnetic nanoparticles

There is yet another incarnation of carbon in the nano-world; nano-layered carbon has been recognized as the ideal material for coating of magnetic nanoparticles, which otherwise may get quickly oxidized once exposed to environment or get seriously agglomerated. Carbon encapsulated magnetic nanoparticles has huge application potential in large scale purification of water/soil or in the field of targeted drugs delivery. Carbon which is light and highly inert in extreme chemical and physical environments form an excellent coating material for the core magnetic nanoparticle. Moreover, chemical functionalization can modify the
surface properties of carbon coatings, which is yet another advantage of carbon [39]. Carbon encapsulated magnetic nanoparticles have been synthesized by various methods like arc discharge, chemical vapor deposition, laser ablation, explosions and hydrothermal reactions. Thermal plasma aided synthesis process have given best results in terms of the crystallinity of carbon coating and quantity of the product. This is yet another material synthesized by the same plasma expansion technique and reported in this thesis.

1.4 Motivation

The dominant importance of carbon nanostructures in the field of nanotechnology is undisputed. New carbon nanostructures are discovered from time to time, possessing unique novel properties showing large potential in a wide range of applications. But most of these promising applications are yet to be realized in reality or they are still in the laboratory stage and yet to be introduced in the markets for use by common man. One of the main reasons why carbon nanostructures have not yet been commercially exploited is that the amount of such materials produced by contemporary synthesis process is still very small, insufficient to meet the current demands. The only carbon nanostructure produced in industrial scale so far is the carbon nanoparticles, commercially known as carbon black. But such carbon nanoparticles, synthesized by conventional methods are not suitable for use in high end applications.

An answer, at least to the production rate issue, could be thermal plasma assisted synthesis, which has demonstrated impressive capability in industrial scale in terms of titanium dioxide nanoparticles. This laboratory has already established an
expanded thermal plasma jet assisted experimental reactor for synthesis of different high temperature nanomaterials, which in addition has demonstrated some novel controls that may be translated to important value addition of the synthesized material. For example, control may be exercised over the average size as well the size distribution of the material through the ambient pressure in the sample collection chamber. Moreover, the expanded structure of the plasma jet ensures enhanced crystallinity of the embedded material which indeed is an important issue for any carbon nanomaterials. Contrary to conventional plasma assisted reactors, nanoparticles in this special reactor configuration may get similarly charged by collecting a non-equilibrium electron density, which may serve to inhibit particle agglomeration, which again is a unique attribute of this particular technique.

It was apparent that the plasma expansion technique would allow fine tuning of the material properties, tailoring the product nanomaterials for specific applications. This had, indeed, motivated us to synthesize some important carbon nanomaterials by this special technique.

1.5 Overview of the Thesis

This thesis reports studies on experimental synthesis of two relatively less well-known members of the nanocarbon family by the plasma expansion technique, namely carbon nanoparticles and carbon encapsulated magnetic nanoparticles. Chapter 1 gives a broad introduction, while chapter 2 contains detailed description of the experimental system and material characterization techniques used for the present studies. Chapter 2 also contains detail discussion on the principles of optical emission spectroscopy of thermal plasma which was used for plasma characterization.
In chapter 3 of this thesis, we present results on synthesis of carbon nanoparticles by an essentially single step, high-throughput plasma process, where an efficient use of the ambient pressure in the sample collection chamber pressure as a control knob lead to tailored combination of some important properties in the final material product. Low chamber pressure conditions had produced samples with both good specific surface area and crystallinity, which may be ideal for use as catalyst support material as well as in batteries and super capacitors. The hydrogen absorption property of the material was also measured. Further investigation of the nanostructures reveals the physical basis of how the surface area was enhanced in the first place. Techniques of Optical Emission Spectroscopy were used for a better understanding of the actual particle formation process and the possible precursors behind.

Chapter 4 describes studies on synthesis of nano-layered carbon encapsulated magnetic (iron) nanoparticles by the same plasma expansion technique. We here demonstrate that the current technique can actually combine the typical advantages of high-temperature synthesis with efficient pressure dependent particle size control as offered by this special reactor configuration. Both average size and size distribution were seen to get enhanced with reduction in sample collection chamber pressure, which also resulted in smooth variation of the measured magnetic properties with size, which is observed for the first time for iron by a thermal plasma assisted method. The low pressure synthesized samples with smallest individual particle sizes approaches super-paramagnetic behavior, which may be most ideal for biomedical applications.

A general conclusion of the whole thesis is given in chapter 5. Further studies which can be conducted in line with the work presented in this thesis as well as recent developments and future scope of our laboratory is also presented in this chapter.
1.6 Reference


Chapter 1


