Synthesis of carbon dot from various precursors and study of its different properties

A thesis submitted towards partial fulfilment

of the requirements for the degree of

Master of Technology in Nanoscience and Technology

Submitted by

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CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled “Synthesis of carbon dot from various precursor and study of its different properties” is a bonafide work carried out by DEBNATH DEBSINGHA under our supervision and guidance for partial fulfilment of the requirement of Master of Technology in Nanoscience and Technology in School of Materials Science and Nanotechnology during the academic session 2017-2019.

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This foregoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner satisfactorily to warranty its acceptance as a prerequisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not endorse or approve any statement made or opinion expressed or conclusion drawn therein but approve the thesis only for purpose for which it has been submitted.

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DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Technology (Nano Science and Technology) studies during academic session 2017-2019.

All information in this document has been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by this rules and conduct, I have fully cited and referred all material and results that are not original to this work.

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Dedicated to my

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For their support and encouragement

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Abstract

The thesis entitled “Synthesis of Carbon Dots from various Precursors and Study of Its Different Properties” is a detailed report of the works done on the synthesis and characterizations of zero dimensional carbon nanostructures (carbon quantum dots). Recently one and zero dimensional carbon nanostructure like carbon nanotubes and carbon quantum dots have attracted the attention of the researchers for different size dependent properties. Here the focus was on to synthesize carbon quantum dots from different natural precursors by different synthesis processes and also to explore the variation in dimensions and properties of the synthesized carbon quantum dots.

Quantum dots (QDs) are defined as nanoparticles with a dimension between 1 to 10 nm. QDs are characterized by quantum confinement and size dependent properties. Different organic and inorganic materials have been used for the synthesis of QDs. Cadmium Selenide quantum dots (CdSe QDs) were among the first quantum dots (QDs) ever synthesized. Carbon quantum dots (CQDs) show a wide range of applications, such as, bio imaging, chemical sensing, photo-catalysis and electro-catalysis, which are attributed to singular features including excellent photoluminescence, biocompatibility, low toxicity, photo-induced electron transfer properties and so on.

In this work, Carbon quantum dots (CQD) have been synthesized from different natural precursors by simple chemical processes. Different synthesis techniques were also used to synthesize CQDs from different precursors to study the effect of the synthesis conditions on the characteristics of the as prepared CQDs. The samples were characterized by field emission scanning and transmission electron microscopy, Fourier transformed infrared spectroscopy, Raman and UV–Vis spectroscopy. The photoluminescence (PL) properties of the as prepared CQDs were also studied in details. It is noticed that with the increase of excitation wavelength, there was a visible variation in PL emissions for the different samples. The results have been explained in terms of the excitation dependent emission, variations in size of the CQD and presence of different functional groups on the surface of CQDs.

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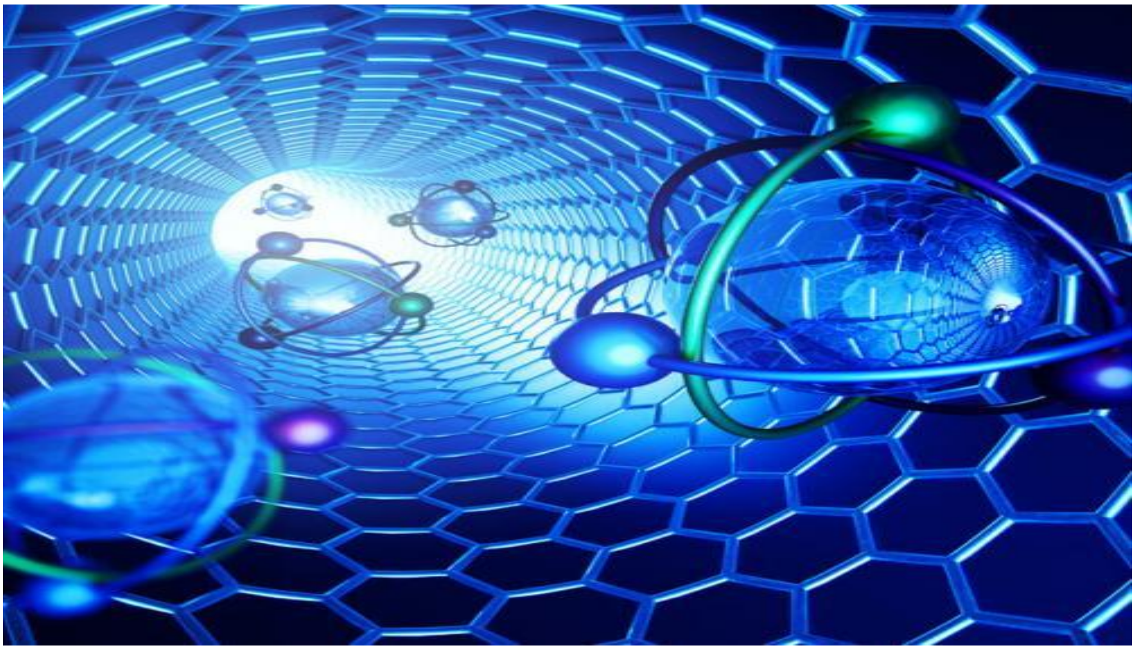

1.1 Introduction to Nanoscience & Nano technology :

Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nano meters. One nano meter is a billionth of a meter, or 10-9 of a meter. Nanotechnology is manipulation of matter on an atomic, molecular, and supramolecular scale. Nanotechnology as defined by size is naturally very broad, including fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, energy storage, microfabrication, molecular engineering, etc. The associated research and applications are equally diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale.

1.1.1 What is nanotechnology?

Most definitions revolve around the study and control of phenomena and materials at length scales below 100 nm and quite often they make a comparison with a human hair, which is about 80,000 nm wide.

It seems that a size limitation to the 1-100 nm range, the area where size-dependant quantum effects come to bear, would exclude numerous materials and devices, especially in the pharmaceutical area, and some experts caution against a rigid definition based on a sub-100 nm size. This definition reflects the fact that quantum mechanical effects are important at this quantum-realm, and so the definition shifted from a particular technological goal to a research category inclusive of all types of research and technologies that deal with the special properties of matter which occur below the given size threshold. It is therefore common to see the plural form "nanotechnologies" as well as "nanoscale technologies" to refer to the broad range of research and applications whose common trait is size.

Another important criteria for the definition is the requirement that the nano-structure is man-made, i.e. a synthetically produced nanoparticle or nanomaterial. Otherwise we would have to include every naturally formed biomolecule and material particle, in effect redefining much of chemistry and molecular biology as 'nanotechnology‘.

1.1.2 How it started?

The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled ―There‗s Plenty of Room at the Bottom‖ by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology on December 29, 1959; long before the term nanotechnology was used. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Thus, physicist Richard Feynman is called the father of nanotechnology.

1.1.3 Who coined the term Nanotechnology?

The term was coined in 1974 by Norio Taniguchi of Tokyo Science University to describe semiconductor processes such as thin-film deposition that deal with control on the order of nano meters. It wasn't until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms, with which modern nanotechnology began.

Inspired by Feynman's concepts, K. Eric Drexler used the term "nanotechnology" in his 1986 book Engines of Creation: The Coming Era of Nanotechnology, which proposed the idea of a nanoscale "assembler" which would be able to build a copy of itself and of other items of arbitrary complexity with atomic control.

Today, scientists and engineers are finding a wide variety of ways to deliberately make materials at the nanoscale to take advantage of their enhanced properties such as higher strength, lighter weight, increased control

of light spectrum, and greater chemical reactivity than their larger-scale or bulk counterparts.

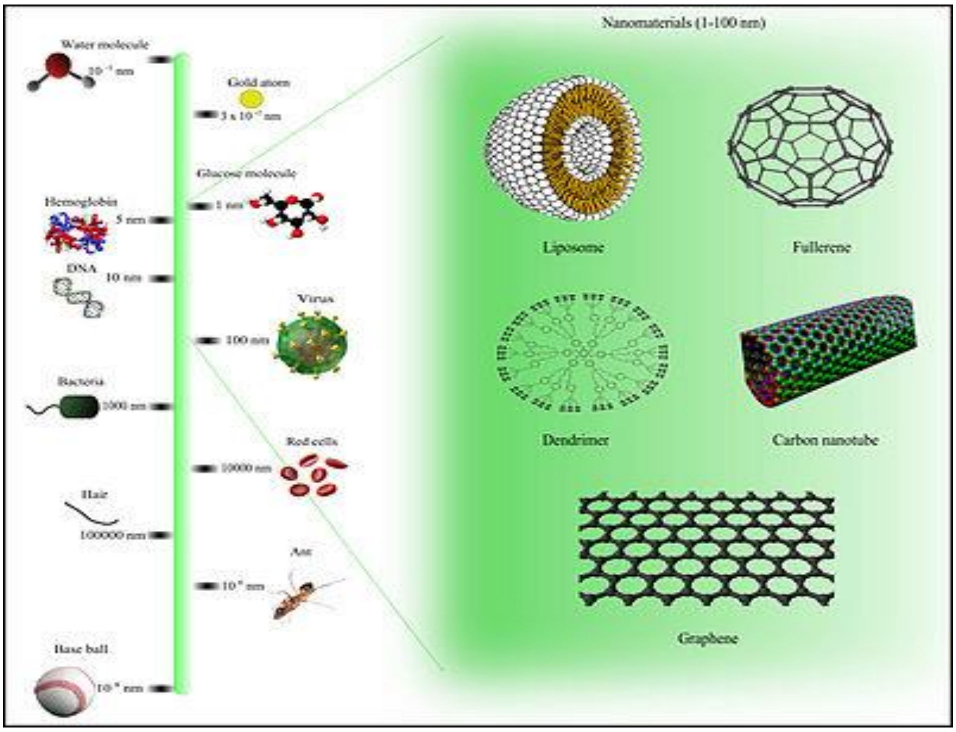

Fig.1.1: Schematic diagram of nanotechnology and its size comparison

1.1.4 A brief history of nanotechnology:

- 2000 years ago: Sulphide Nano crystals used by Greeks and Romans to dye hair.
- 1000 years ago (middle ages): Gold nanoparticles of different sizes used to produce different colours in stained glass windows.
- 1959: Physicist Richard Feynman gave a radical lecture at an American Physical
- Society meeting at Caltech titled —‖There is plenty of room at the bottom‖.
- 1974: _Nanotechnology_- Professor Norio Taniguchi for the first time uses the term nanotechnology [4].
- 1981: IBM develops Scanning Tunnelling Microscope [5].
- 1985: _Buckyball_- Scientists at Rice University and University of Sussex discover Fullerene (C60) [6].
- 1986: _Engines of Creation_- First book on nanotechnology by K. Eric Drexler [7]. Atomic Force Microscope invented by Binnig, Quate, and Gerbe.
- 1989: IBM logo made with individual atoms.
- 1991: Carbon Nanotubes discovered by S. Ijima.
- 1999: _Nano medicine_- First Nano medicine book by R. Freitas.
- 2000: _National Nanotechnology Initiative was launched.

1.1.5 What distinguishes nanomaterial from bulk?

While most micro structured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometre dimensions are significantly different from those of atoms and bulk materials. Among the characteristics of nanomaterial that distinguish them from bulk materials, it is important to note the following:

- Large fraction of surface atoms;
- High surface energy;
- Spatial confinement
- Reduced numbers of imperfections that do not exist in the corresponding bulk materials .

The use of nanomaterial provides the following advantages :

First, all nanomaterial consist of very small particles. This is the first advantage of nanomaterial and nanotechnologies, promoting attainment of super miniaturization. Because they are small, nanostructures can be packed very closely together. As a result, on a given unit of area one can locate more functional nano devices, which is very important for Nano-electronics. Their high packing density has the potential to bring higher area and volume capacity to information storage and higher speed to information processing (because electrons require much less time to move between components). Thus, new electronic device concepts, smaller and faster circuits, more sophisticated functions, and greatly reduced power consumption can all be achieved simultaneously by controlling nanostructure interactions and complexity.

Second, because of their small dimensions, nanomaterials have large specific surface areas, accelerating interactions between them and the environment in which they are located. Nanoparticles have a much larger surface area per unit of mass compared with larger particles. Because growth and catalytic chemical reactions occur at surfaces, this means that materials in nanoparticle form will be much more reactive than the same mass of material made up of larger particles. A strong increase in the participation of surface atoms in the physical and chemical properties of nanomaterials is another consequence of a decrease in particle size.

It is known that the volume of an object decreases as the third power of its linear dimensions, but the surface area decreases only as its second power. In case of nanoparticles, the surface area-to-volume ratio (the ratio between surface and bulk atoms) increases than that of bulk.The variation of surface or volume ratio as a function of particle size is given in Fig.1.3.

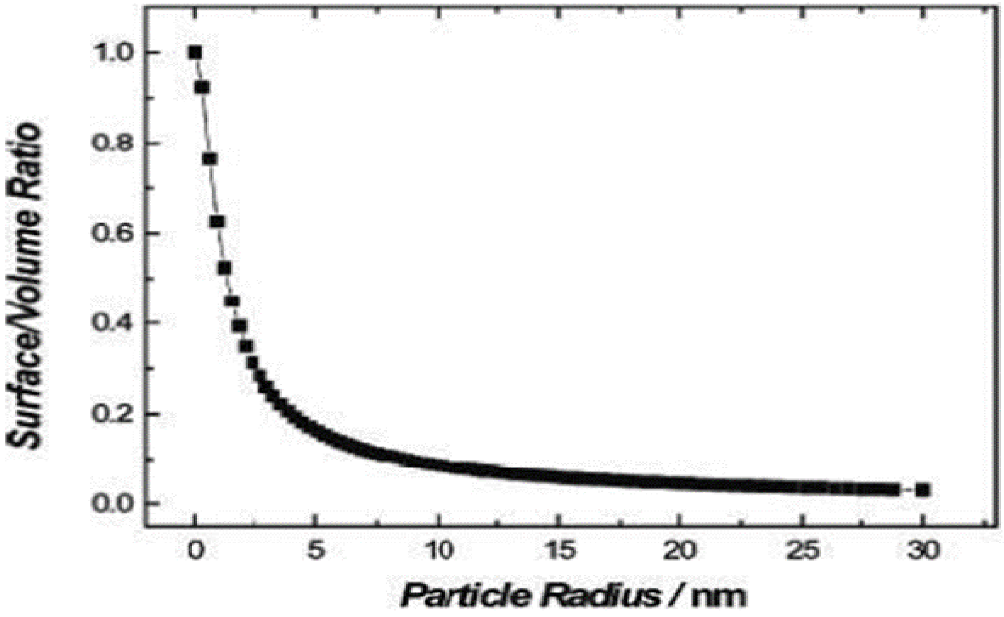

Fig.1.2: Surface/volume ratio as a function of particle size

It is known that atoms on the surface of nanoparticles have unusual properties. These surface atoms make nanoparticles very different from just small particles, because not all bonds of surface atoms with neighbouring atoms are enabled. For atoms on uneven surfaces, no saturation of the bonds is even higher. For this reason, corner atoms normally have the highest affinity to form bonds to adsorbate molecules, followed by edge and in-plane surface atoms, a fact that is of great importance for catalytic activity. Alternatively, because of their low stabilization due to low coordination, edge and in particular corner atoms are often missing on single crystals, even in thermodynamic equilibrium Recently, size-dependent variation in oxidation state and lattice parameter has been reported for cerium oxide nanoparticles .

As a result of the changes that occur in particles with a decrease of particle size, nanomaterials can have extremely high biological and chemical reactivity. For example, catalytically active nanomaterials allow accelerating either chemical or biochemical reactions by tens of thousands, and even a million times. This attribute explains even 1 g of nanomaterial can be more effective than 1 ton of a similar but macro substance.

Another aspect we must consider is that the free surface is a place of accumulation (sink) of crystallographic defects. At small particles sizes, the surface concentration of such defects increases considerably. Hardeveld and Hartog in 1969 calculated classically and showed that the largest changes of proportions between facets, edges, corners, and micro defects at the surface occur between 1 and 5 nm . As a result, strong lattice distortion and even a change of lattice type can take place on the surface layer. In fact, due to accumulation of structural defects and chemical impurities on the surface, we can observe purification of the bulk area of the nanoparticles.

An important specific characteristic of nanomaterial properties (we mean here polycrystalline materials with grain size less than 40 nm) is an increase of the role of interfaces with decrease of the size of grains or crystallites in nanomaterials. Experimental research has shown that the state of grain boundaries has a non-equilibrium character, conditioned by the presence of the high concentration of grain boundary defects. This non-equilibrium is characterized by extra energy of the grain boundaries and by the presence of long-range elastic stress. At the same time, the grains have ordered crystallographic structure, while the grain boundary defects act as a source of elastic strains. Non-equilibrium of the grain boundaries initiates the occurrence of the lattice distortion, the change of interatomic distances, and the appearance of sufficient displacement of atoms, right up to loss of an ordered state.

Another important factor peculiar to nanoparticles is their tendency to aggregation. The possibility of migration (diffusion) of either atoms or groups of atoms along the surface and the boundaries, as well as the presence of attractive forces between them, often leads to processes of self-organization into various cluster structures. This effect has already been used for creation of ordered nanostructures in optics and electronics.

One more important aspect of nanomaterial properties is connected with the fact that, during transport processes (diffusion, electro- and thermal conductivity, etc.), there are certain effective lengths of free path of a carrier of this transport (Le), such as phonon and electron mean free paths, the Debye length, and the exciton diffusion length for certain polymers.

While proceeding to sizes smaller than Le , transport speed starts to depend on both the size and the shape of the nanomaterial; generally, the transport speed increases sharply .

The principal characteristics of nanomaterials are conditioned by not only by their small the size, but also by the appearance of new quantum mechanical effects in a dominating role at the interface (Esaki 1991 ; Serena and Garcia 1997). Those quantum size effects occur at a critical size, which is proportionate with the so-called correlative radius of one or another physical phenomena, for example, with the length of the free path of electrons or photons, the length of coherence in a superconductor, sizes of magnetic domains, and so on. As a rule, quantum size effects appear in materials with crystallite sizes in the nano range D <10 nm. As a result, in nanomaterials with characteristic size, one can expect the appearance of effects which cannot be observed in bulk materials.

1.1.6 Classification of Nanomaterials:

Nanomaterials can be classified dimension wise into following categories shown in Table 1.

Classification	**size**	**Example**
Zero dimension	Less than 100 nm	Particles, quantum dots, hollow spheres etc.
One dimension	Less than 100 nm	Nano-rods, nano-wires etc .
Two dimension	Less than 100 nm	Tubes, fibres, platelets etc.

On the basis of phase composition, nanomaterials in different phases can be classified as,

- Single phase solids include crystalline, amorphous particles and layers, etc.
- Multi-phase solids include matrix composites, coated particles, etc.
- Multi-phase systems include colloids, aero gels, Ferro fluids, etc.

1.1.7 Synthesis of Nanomaterials:

In order to explore the unique physical properties & phenomena and also to realize the useful applications of nanostructures and nanomaterial, the ability to fabricate and process nanomaterial and nanostructures is the first hurdle in nanotechnology. The following schematic diagram in Fig. 1.4 shows the two significant approaches in the synthesis of nanomaterial.

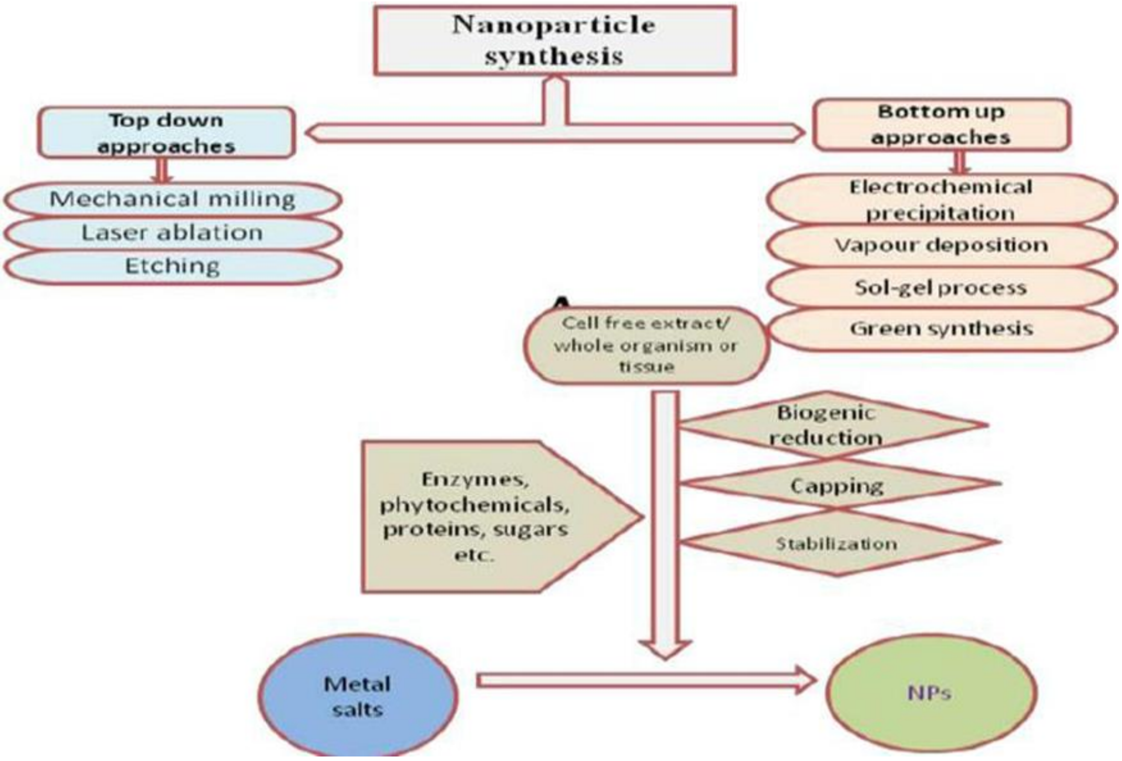

Fig.1.3: Schematic diagram of different synthesis approaches of nanometer

For the fabrication and processing of nanomaterial and nanostructures, the following challenges must be taken care of :

- Overcome the huge surface energy, a result of enormous surface area or large surface-to- volume ratio.
- Ensure all nanomaterial with desired size, uniform size distribution, morphology, crystallinity, chemical composition, and microstructure which result in desired physical properties.
- Prevent nanomaterial and nanostructures from coarsening through either Ostwald ripening or agglomeration.
- Many technologies have been explored to fabricate nanostructures and nanomaterial. These technical approaches can be grouped in several ways like growth media or the form of products.

(1) According to growth media:

- Vapour phase growth, including laser reaction pyrolysis for nanoparticle synthesis and atomic layer deposition (ALD) for thin film deposition.
- Liquid phase growth, including colloidal processing for the formation of nanoparticles and self-assembly of monolayers.
- Solid phase formation, including phase segregation to make metallic particles in glass matrix.

(2) According to the form of products:

- Nanoparticles by means of colloidal processing, flame combustion and phase segregation.
- Nano rods or nanowires by template-based electroplating, solution liquid- solid growth (SLS), and spontaneous anisotropic growth.
- Thin films by molecular beam epitaxy (MBE) and atomic layer deposition (ALD).

(3) ‘Top Down’ and ‘Bottom Up Approach’:

The top down approach uses traditional methods to guide the synthesis of Nano scale materials [1, 15]. The paradigm proper of its definition generally dictates that in the top down approach it all begins from a bulk piece of material, which is then gradually or step by step removed to form objects in the nanometre-size regime. Well known techniques such as photo lithography and electron beam lithography, anodization, ion and plasma etching all belong to this type of approach. The bottom up approach is exactly the opposite of top down approach.

In this case instead of starting with large materials and chipping it away to reveal small bits of it, it all begins from atoms and molecules that get rearranged and assembled to large nanostructures. It is the new paradigm for synthesis in the nanotechnology world as the bottom up approach allows a creation of diverse types of nanomaterial, and it is likely to revolutionize the way of material fabrication. Schematic representation of Bottom up and Top down approach is shown in Fig.1.5.

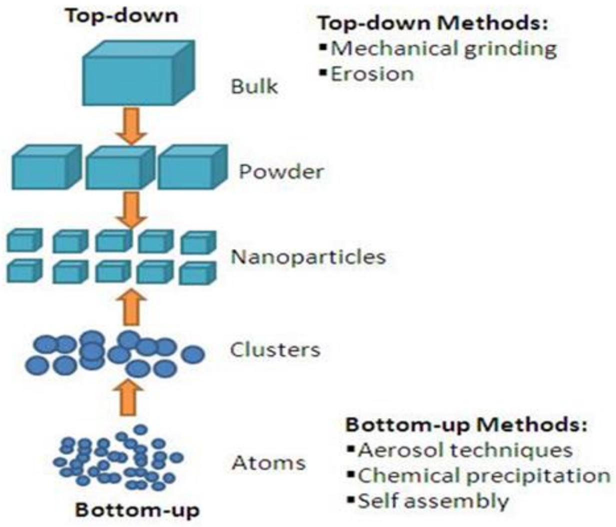

Fig.1.4: Schematic diagram of Top Down and Bottom Up Approach

Attrition or Milling is a typical top down method in making nano particles, whereas the colloidal dispersion is a good example of bottom up approach in the synthesis of nano particles.

(4) Self-assembly:

One bottom-up method is nature's way; ***—self-assembly”***. Self-organizing processes are common throughout nature and involve components from the molecular (e.g. protein folding) to the planetary scale (e.g. weather systems) and even beyond (e.g. galaxies). The key to using self-assembly as a controlled and directed fabrication process lies in designing the components that are required to self-assemble into desired patterns and functions. Self assembly reflects information coded- as shape, surface properties, charge, polarizability magnetic dipole, mass etc. in individual components; these characteristics determine the interactions among them

1.1.8 Applications of Nanotechnology

Nano technological application is extended in different field of research with various unique applications. When a particle is shrunk to nano-scale, several properties of the material change in accordance with size. So it gives new applications in several fields. As due to the size the surface to volume ratio increases, it gives more surface area to react. Several optical as well as mechanical properties are also dependent on the diameter or the size of particles. The following diagram of **Fig.1.6** shows some few such applications.

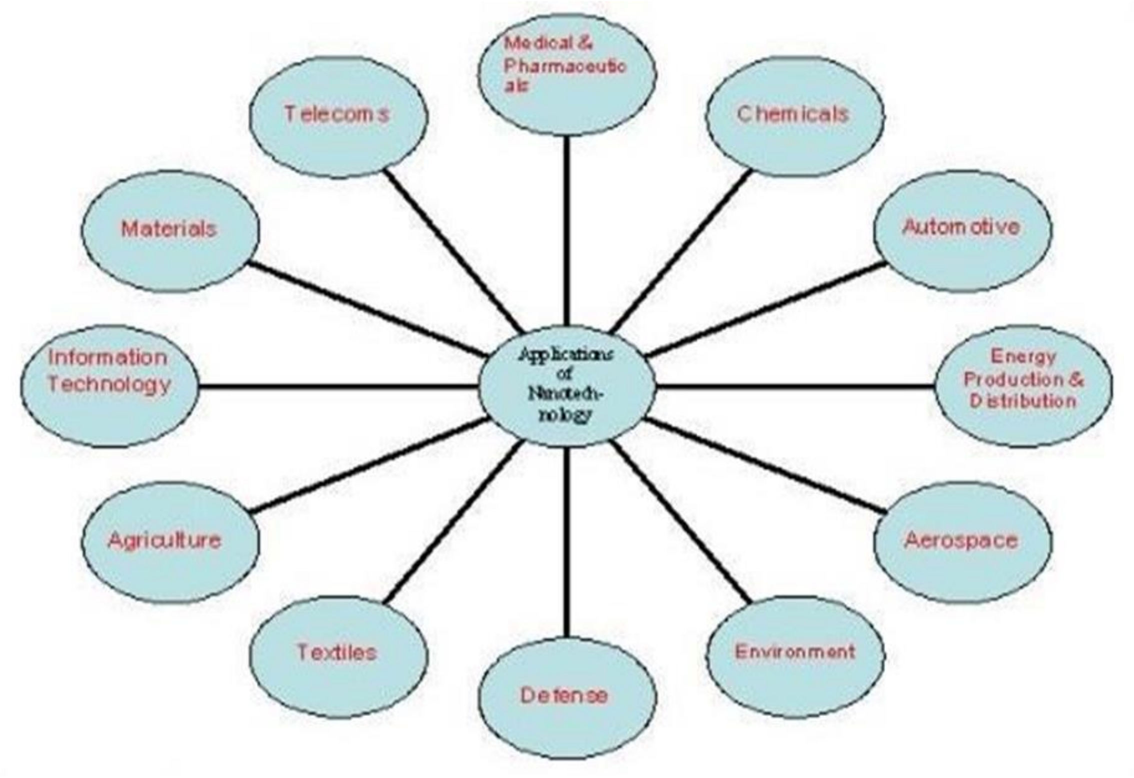

Fig.1.5: Applications of Nanotechnology

Nanotechnology has innumerable applications in variety of diverse fields all of which are interconnected with each other. The modern world has burgeoned in a consequential extent with the advent of newer technologies based on Nano science . The applications include nanoscale pattering of electronic circuits, high density data storage, quantum computers, fuel cell catalysts, environmental catalysts, industrial catalysts, waste water treatment, functional nanocomposites, food packaging, food processing catalysts, hydrogen production photocatalysts , automotive catalysts, fuel additive catalysts, lithium ion battery electrodes, natural or synthetic polymer hybrid fibres, reinforced plastics, controlled drug release, cancer therapy, drug delivery, bio imaging, bio markers, hyperthermic treatment, MRI contrast agents, IR contrast agents, ultra violet protection like sunscreens, antioxidants, ultra violet blocking coatings, water resistant coatings, gas barrier coatings, anti-microbial coatings, self-cleaning building surface, food quality and safety analysis sensors, chemical sensors, gas sensors, high sensitive sensors, pollution monitoring sensors, functional nanocomposites, nano pigments, super thermal-conductive liquid, nano phosphors for display, super plastic ceramics, transparent conductive polymer films, chemical mechanical planarization, nano inks, single electron transistors, quantum lasers, high power magnets, pollutant scavengers, interactive food, neutraceutical, fungicides and pesticides, medical textiles, technical textiles, heat retaining textiles, self-cleaning textiles, anti-stain textiles, electro-conducting textiles, ultra violet blocking textiles, wound dressing, dental ceramics, bone growth, tissue cells engineering, molecular tagging, dye sensitized solar cells, paint-on solar cells, hydrogen storage materials, bio-composites, Ferro-fluids, refractive index engineering, aerospace engineering and many others. Detail applications in some important fields are given below:

Nanotechnology in Energy and Environment:

Energy crisis and environmental pollution in present days have severe negative impact in human life. To provide sufficient energy to the developing world, nanotechnology is the key factor because less expensive improved energy can be produced through suitable nanomaterial. Recent nanotechnology projects to diminish the energy crisis is related to the parameters like storage, conversion, sufficient super capacitance and recyclability production with the help of small amount of nanomaterial, thermal insulation increment etc. Energy application with the help of nanomaterial:

1. Fuel cell (e.g. CNT) for hydrogen storage and related automobile applications.
2. Cheap, light weight and more efficient metal oxide nanomaterial photovoltaic application for the purpose of water splitting and efficient dye sensitized solar cell.
3. Nanotechnology can be used to the further reduction of combustion engine pollutants by nano-porous filters; this can clean the exhaust mechanically.
4. Nanotechnology in water disinfection with the help of nanostructured photosensitized catalyst and further step towards environmental safe and green technologies.

5. Solid state lightening is a powerful tool to reduce total electricity consumption by 10% and cut carbon emission by the equivalent of 28 million tons/year.

Nanotechnology in Flexible Electronics:

Nanotechnology in electronic industry is gradually becoming popular because smaller size and compact design of electronic devices can ensure faster processing, reduction of delay in circuitry and processing power consumption. Nanotechnology in electronics industry introduces microprocessors less than 100 nanometres (nm) in size. However, Nano electronics is basically the extension of microelectronics and research in Nano electronics will develop CNT, Graphene based flexible independent electronic devices in future.

1. CNT based field emission display is highly efficient because light weight CNT can be used as field emitters with extremely high efficiency for field emission displays (FED) with very low power consumption.
2. Nanotechnology is employed to increase the density of memory chips. Researchers are developing a type of memory chip with a projected density of one terabyte of memory per square inch or greater. Integrated nano-sensors are used for collecting, processing and communicating massive amounts of data with minimal size, weight, and power consumption.
3. Research in nanotechnology introduces transistors with Graphene and CNT as active materials and CNT transistor based processor for computer application is about to commercialize in future market. Due to their smaller size and lower power consumption CNT and Graphene based transistors are easy to integrate in the integrated circuits.
4. Large magnetic moment and adequate coercivity nanomaterial can help to produce magneto caloric effect on a particular scale so that refrigeration could be possible without need of refrigeration fluids.

Nanotechnology in Health and Medicine:

Nanotechnology has a high impact on the research and applications related to biology and medicine. Nano-drug delivery is the safest procedure for medication because small quantity of nanomaterial can help to recover with reducing side effects. Nano medicine has also the potential to enable early detection and prevention, and to essentially improve diagnosis, treatment and follow-up of diseases with the help of bio-sensors.

1. Carbon nanotubes have promising application for the development of advanced biosensors with novel features.

2. CNT, though inert, can be functionalized at the tip with a probe molecule. Their study uses AFM as an experimental platform. i. Leukaemia cells identification ii. Catheter development.
3. Nano devices can make gene sequencing more efficient.
4. Tissue engineering makes use of artificially stimulated cell which can help in transplantation of organs or artificial implants.
5. The technology is also being used to develop sensors for cancer diagnostics.

Nanotechnology in Transportation:

Nanomaterial is used as faster and cost effective new fuel source. The main advantage of using nanomaterial is light weight so that easy to carry in fuel chamber of cars and aeroplanes.

1. Suitable Nanomaterials can effectively reduce the emission of pollutants in the process of incomplete combustion in engine. Nano Twin Technologies has recently released an air filter to remove hazardous chemicals from the air in car cabins.
2. Nanoparticles of inorganic clays and polymers are an effective alternative for carbon black tires results in environmental friendly, wear resistant tires. Frictional resistant tires are also made possible through Nano science.
3. Nano coating of metallic surfaces such as steel to achieve super-hardening, low friction, and enhanced corrosion protection.

Nanotechnology in Defence and Security:

Nanotechnology will lead to higher protection, more lethality, longer endurance and better self-supporting capacities of future combat soldiers. Substantial advantages are expected to be gained which include threat detection, novel electronic display and interface systems, as well as a pivotal role for the development of miniaturised unmanned combat vehicles and robotics. Nanotechnology will also enable small portable sensor systems capable of identifying chemical, biological and nuclear, radiation, or explosive threats.

Nanotechnology in Information & Communication:

Electronic memory designs in the past have largely relied on the formation of transistors. The miniaturization of electronic industry has been the driving force behind the rapid research and development of Nano science and technology. Continuing to shrink silicon chips is getting expensive and difficult. Chips built using the molecular transistors are the industry's best hope for building faster, cheaper computers well into this century. "With the electronics we're talking about, we're going to make a computer that doesn't just fit in your wristwatch, not just in a button on your shirt, but in one of the fibres of your shirt," says Philip Kuekes , a computer architect at Hewlett-Packard Laboratories. According to the manufacturers, NRAM (Nanotube-based/Non-volatile random access memory) is a universal memory chip suitable for countless existing and new applications in the field of electronics. In the modern communication technology traditional analog electrical devices are increasingly replaced by optical or optoelectronic devices due to their enormous bandwidth and capacity. Two promising examples are photonic crystals and quantum dots. Quantum dots are nanoscale objects, which can be used for the construction of lasers. The advantage of a quantum dot laser over the traditional semiconductor laser is that their emitted wavelength depends on the diameter of the dot. Quantum dot lasers are cheaper and offer a higher beam quality than conventional laser diodes.

Nanotechnology in Filtration:

Nano-porous membranes are suitable for filtration with extremely small pores like 10nm. It is mainly used for separation of ions or different fluids which find application in renal dialysis. Nanoscale particles increase the efficiency of absorbing contaminants and it is relatively inexpensive compared to traditional filtration metho

1.2 Introduction of carbon quantum dots :

Carbon quantum dots were first discovered by Xu et al. in 2004 accidentally during the purification of single-walled carbon nanotubes [1]. This discovery triggered extensive studies to explore the fluorescence properties of carbon quantum dots. Much progress has been achieved in the synthesis, properties and applications of carbon quantum dots .

As a new class of fluorescent carbon nanomaterials, carbon quantum dots possess the attractive properties of high stability, good conductivity, low toxicity, environmental friendliness, simple synthetic routes as well as comparable optical properties to quantum dots [2]. Carbon quantum dots have been extensively investigated especially due to their strong and tunable fluorescence emission properties [3] which enable their applications in biomedicine, optronics , catalysis, and sensing [4].

The fundamental mechanisms responsible of the fluorescence capability of carbon quantum dots are very debated. Some authors have provided evidence of size-dependent fluorescence properties, suggesting that the emission arises from electronic transitions with the core of the dots, influenced by quantum confinement effects[5] ,whereas other works have rather attributed the fluorescence to recombination of surface-trapped charges [6], or proposed a form of coupling between core and surface electronic states [7]. The excitation-dependent fluorescence of CQDs, leading to their characteristic emission tenability has been mostly linked to the inhomogeneous distribution of their emission characteristics [8], due to polydispersity, although some works have explained it as a violation of Kasha's rule arising from an unusually slow solvent relaxation [9].

To achieve uniform properties for particular applications and mechanic study, it is of great importance of control the size of CQDs during preparing process or via post-treatment. A majority of the reports demonstrated the processes of purifying the as-synthesized CQDs fragments via post-treatment such as filtration, centrifugation, column chromatography and gel-electrophoresis . In addition to post-treatment, controlling the size of CQDs during the preparing process is also widely used. For instance, Zhu et al. reported hydrophilic CQDs through impregnation of citric acid precursor. After pyrolyzing CQDs at 300 oC for 2 hours in air, then removing silica, followed by dialysis, they prepared CQDs with a uniform size of 1.5-2.5 nm which showed low toxicity, excellent luminescence, good photostability, and up-conversion properties.

Properties of CQDs

The structures and components of CQDs determine their diverse properties. Many carboxyl moieties on the CQD surface impart excellent solubility in water and biocompatibility [10] .CQDs are also suitable for chemical modification and surface passivation with various organic, polymeric, inorganic or biological materials. By surface passivation, the fluorescence properties as well as physical properties of CQDs are enhanced. Recently, it has been discovered that amine and hydoxamic acid functionalized CD can produce tricolor (green, yellow and red) emission when introduced with different pH environment and this tricolor emission can be preserved in ORMOSIL film matrix [11].

Based on carbon, CQDs possess such properties as good conductivity, benign chemical composition, and photochemical stability [12].

Synthesis of CQDs

Synthetic methods for CQDs are roughly divided into two categories, "top-down" and "bottom-up" routes. These can be achieved via chemical, electrochemical or physical techniques [13]. The CQDs obtained could be optimized during preparation or post-treatment [14]. Modification of CQDs is also very important to get good surface properties which are essential for solubility and selected applications.

Synthetic methods

"Top-down" synthetic route refers to breaking down larger carbon structures such as graphite, carbon nanotubes, and nanodiamonds into CQDs using laser ablation, arc discharge, and electrochemical techniques [15]. For example, Zhou et al. first applied electrochemical method into synthesis of CQDs [16]. They grew multi-walled carbon nanotubes on a carbon paper, then they inserted the carbon paper into an electrochemical cell containing supporting electrolyte including degassed acetonitrile and 0.1 M tetrabutyl ammonium perchlorate.

"Bottom-up" synthetic route involves synthesizing CQDs from small precursors such as carbohydrates, citrate, and polymer-silica nanocomposites through hydrothermal/solvothermal treatment, supported synthetic, and microwave synthetic routes. Recently, green synthetic approaches have also been employed for fabrication of CQDs.

Size control

To achieve uniform properties for particular applications and mechanic study, it is of great importance of control the size of CQDs during preparing process or via post-treatment [17].

A majority of the reports demonstrated the processes of purifying the as-synthesized CQDs fragments via post-treatment such as filtration, centrifugation, column chromatography and gel-electrophoresis [18].

In addition to post-treatment, controlling the size of CQDs during the preparing process is also widely used. For instance, Zhu et al. reported hydrophilic CQDs through impregnation of citric acid precursor.

APPLICATION

Possessing such superior properties as low toxicity and good biocompatibility renders CQDs favorable materials for applications in bioimaging, biosensor and drug delivery [19]. Based on the excellent optical and electronic properties, CQDs can also find applications in catalysis, sensors, and optronics [20].

1.3.LITERATURE REVIEW

Carbon dots (denoted as CQD) acknowledged as discrete, quasispherical and fluorescent carbon material with the diameter below 10 nm. CQD are generally composed of sp2 conjugated core. It is reported that CQDs contain suitable oxygen content in the forms of multiple oxygen-containing species represented by carboxyl, hydroxyl, and aldehyde groups . The CQDs were reportedly discovered during electrophoretic fractionation of arc-discharge soot with a dimension of 1 nm. Nearly two years after its discovery, research work from Sun’s group ignited a lot of research interest on this carbon nanomaterials known as carbon dots, or carbon nanodots , or carbogenic quantum dots. Since its discovery CQDs have received tremendous interest among the researchers for its composition and biocompatibility. CQDs have been explored for its application in LEDs , solar cell drug carriers biomedicine and bioimaging due to their excellent fluorescence properties, good biocompatibility and low toxicity. CQDs are mainly explored their excellent photoluminescence (PL) properties. CQDs are characterised by excitation wavelength-dependent , excitation wavelength-independent and size dependent PL properties . Since 2006 the research interest on the CQDs increased tremendously due to mainly simple synthesis, low cost, and excellent biocompatibility. Infect CQDs are considered as replacement of semiconductor quantum dots (QDs) like CdSe or CdS QDs due to the colourful photoluminescence, high photostability, and low toxicity. The important events related with the discovery and application of CQDs is shown in Fig. . The CQDs have been widely explored mainly in sensing, bioimaging, nanomedicine, catalysis, optoelectronics, and energy conversion/storage mainly cantered around its excellent PL properties.

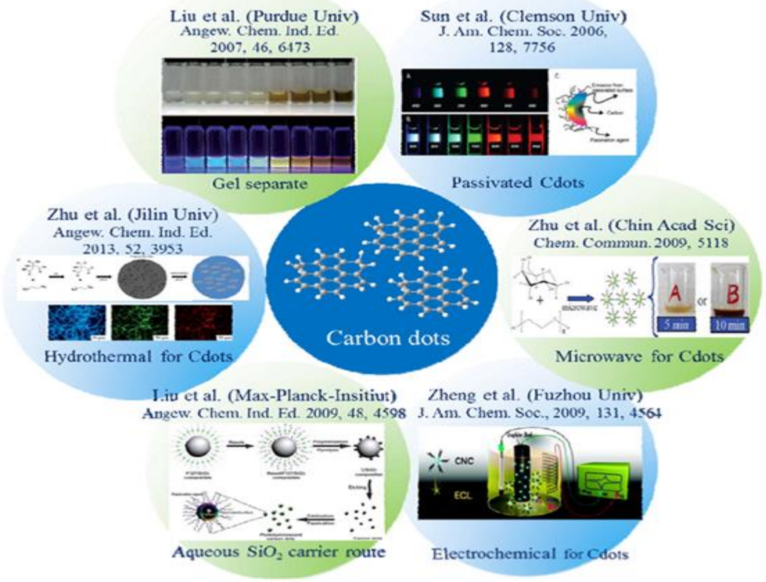

Fig.1.6:name of different reseachers working on carbon quantum dots across the world

Many top down and bottom up approaches have been reported for the synthesis of CQDs. Basically most of the current synthetic methods can be used for the synthesis carbon CQDs in large mass regardless of the intrinsic nature of raw materials, while in practice, only a few works carried out the mass production. Deng et al. reported the preparation of CQDs through the electrochemical carbonization of low-molecular-weight alcohols. The as prepared CQD had amorphous core and it demonstrated excellent excitation and size dependent PL characteristics without complicated purification and passivation procedures. Hu et al. reported the fabrication of fluorescent CQDs by laser irradiation of a suspension of carbon materials in an organic solvent Microwave irradiation of organic compounds can also be used as a fast and cheap technique for synthesizing CQDs. Hydrothermal carbonization (HTC) or solvothermal carbonization is another popular method used for the synthesis of CQDs. Hydrothermal method is considered to be low temperature, environmentally friendly cheap, and nontoxic technique to fabricate novel carbon-based materials from several starting materials. In this process solution of organic precursor is placed and sealed in a hydrothermal reactor and heated at elevated temperature. Sahu et al. have synthesized CQD by hydrothermal synthesis from orange juice [98]. CQDs have been prepared from protein, citric acid , glucos chitosan, and banana juice precursors by hydrothermal process. Solvothermal carbonization followed by organic solvent extraction by different methods is a common technique to synthesize CQDs. In our case we have synthesized CQDs by hydrothermal treatment of solution containing glucose and ethanol followed by centrifugation.

CQDs are mainly investigated for its optical especially excellent PL properties. CQDs have reportedly demonstrated special excitation-dependent fluorescence emission property. Sun's group have reported that the acid treated nanoscale carbon particles did not show noticeable PL until surface passivation by amine derivative polymers. So it can be estimated that from here that PL from CQDs might be attributed to surface energy traps that became emissive upon stabilization as a consequence of surface passivation. But the exact reason for the exciting PL properties is still not well explained due to unpredictable experimental clarifications caused by the large heterogeneity of individual particles from the same synthesis together with less- precisely defined properties of CQDs obtained from different processes.

To get a better understanding of the synthesis condition and effect of the size of the CQDs on the PL properties the synthesis conditions were varied during the preparation of CQDs from sucrose. The response of PL also was studied under different excitation wavelength in our case.

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Chapter-2

Instruments & Apparatus

2.1 Experimental set up:

2.1.1 Box furnace

Box furnaces are commonly used for solid state heating. Starting materials are stoichiometrically mixed and annealed in the furnace within the temperature range of 1000 – 1200 0C for 15 – 20 h. Thorough intermediate grinding is an important step for phase uniformity. The temperature controller usually controls the rate of heating and maintains the temperature with an accuracy of ±0.5 0C. Fig.1 (a) shows the digital image of the furnace used. A low temperature oven was used for drying the samples and also for certain hydrothermal reactions. The digital image of a typical oven is shown in Fig.1 (b).

Fig.1: Digital images of (a) Furnace and (b) Oven

2.1.2. Magnetic Stirrer

The magnetic stirrer can stir the magnetic bit within the solution of the beaker through a revolving magnetic arrangement attached with it. A heater arrangement associated with the stirrer can heat the solution at a desired temperature and the temperature is controlled by a knob as shown in **Fig.2**.

Fig.2: Digital image of a magnetic stirrer

2.2 Characterization tools:

2.2.1 X–Ray diffractometer (XRD):

In 1895, x-ray is discovered by Röentgen. From the year 1912, the application of x– ray has started when the wave nature of x–ray was recognized from the x–ray diffraction by any crystals. X–ray diffraction by the different set of planes has been applied to identify crystal structures. The structural characterization of synthesized samples is carried out by recording the X–Ray Diffraction pattern of the samples. XRD pattern was taken using Cu K_α radiation (λ = 1.5406˚A) (Rigaku–Ultima–III). The photograph is shown in the figure 3.3 below. The basic law involved in the crystal structure analysis is the Brag's law of diffraction. When monochromatic X–rays incident upon the atoms in a crystal lattice, each atom acts as a source of scattering. The crystal lattice acts as series of parallel reflecting planes and the reflected beams at certain angles form constructive interference which is an integral multiple of λ. This condition called Bragg's law is given by the relation,

Where n is the order of diffraction and d is the spacing between two consecutive planes *and* λ is the wavelength of the x–rays, and Θ is the glancing angle. XRD studies of any sample give a whole range of information about the crystal structure, average crystallite size and various stresses in the thin film. Generally, the obtained experimental data of the sample are compared with the standard inorganic crystal structure database (ICSD) to confirm the phase purity of our synthesized samples.

From the shift in peak position, one can calculate the change of d–spacing, which signify the change of lattice constant under inhomogeneous or homogeneous strain. Inhomogeneous strain differs from crystallite to crystallite or within a single crystallite.

This causes the peak broadening which increases with sin θ. This broadening also occurs from the crystalline size effect, but here the broadening is independent of sin θ. If there is no inhomogeneous strain, the crystallite size, D can be calculated from the Scherrer's formula:

Where, β is the full width of height maximum (FWHM) of a diffraction peak, k is the Scherrer constant and θ is the diffraction angle

Fig. 3. the X-ray diffractometer

2.2.2 Field emission scanning electron microscope (FESEM):

In standard electron microscopes, electrons are mostly generated by heating a tungsten filament (electron gun). They are also produced from a crystal of LaB6. The use of LaB6 results in a higher electron density in the beam and a better resolution than that with the conventional used device. In a field emission (FE) electron microscope, no heating but a so– called "cold" source is used. Field emission microscope is a type of electron microscope that is usually employed to investigate the surface of a sample by scanning it with a high energy beam of electrons. Here, the wave properties of electrons (λ = h/p, λ associated with a beam of electrons of momentum p) are used to obtain resolution. If the electrons are accelerated through a potential difference V, they acquire energy, having wavelength of √

So V = 100,000 V leads to λ = 3.9 × 10-12 m, which is about a hundredth of the separation of the atoms in molecules (~0.25 nm) or crystals [1].

In FESEM, the electron beam passes through objective lens deflect horizontally and vertically so that the beam scans the surface of the sample [Figure 3.6 (right)]. As the electrons penetrate the surface of the sample, a number of interactions occur that can result in the emission of electrons or photons from or through the surface. The generated secondary electrons are collected by the detector and converted into voltage. The amplified voltage is applied to the grid of the CRT which changes the intensity of the spot light. In this way an image is produced on the CRT; every point that the beam strikes on the sample is mapped directly onto a corresponding point on the screen [1, 6–7]. The schematic diagram of FESEM is presented in figure 3.6 (right). When an electron beam interacts with the atoms of a nano structures sample, each incident electron undergoes two types of scattering elastic and inelastic. In elastic scattering, only the trajectory changes and the kinetic energy and velocity remain constant. In the case of inelastic scattering, the incident electrons displace electrons from the sample orbits around nuclei of atoms [1]. The electron interacts with the sample produces signal about the sample’s morphology, composition and other properties. The morphologies of the synthesized nanomaterials are characterized with the help of field emission scanning electron microscopy (FESEM, S–4800). The photograph of the instrument is shown in figure 3.6 (left).

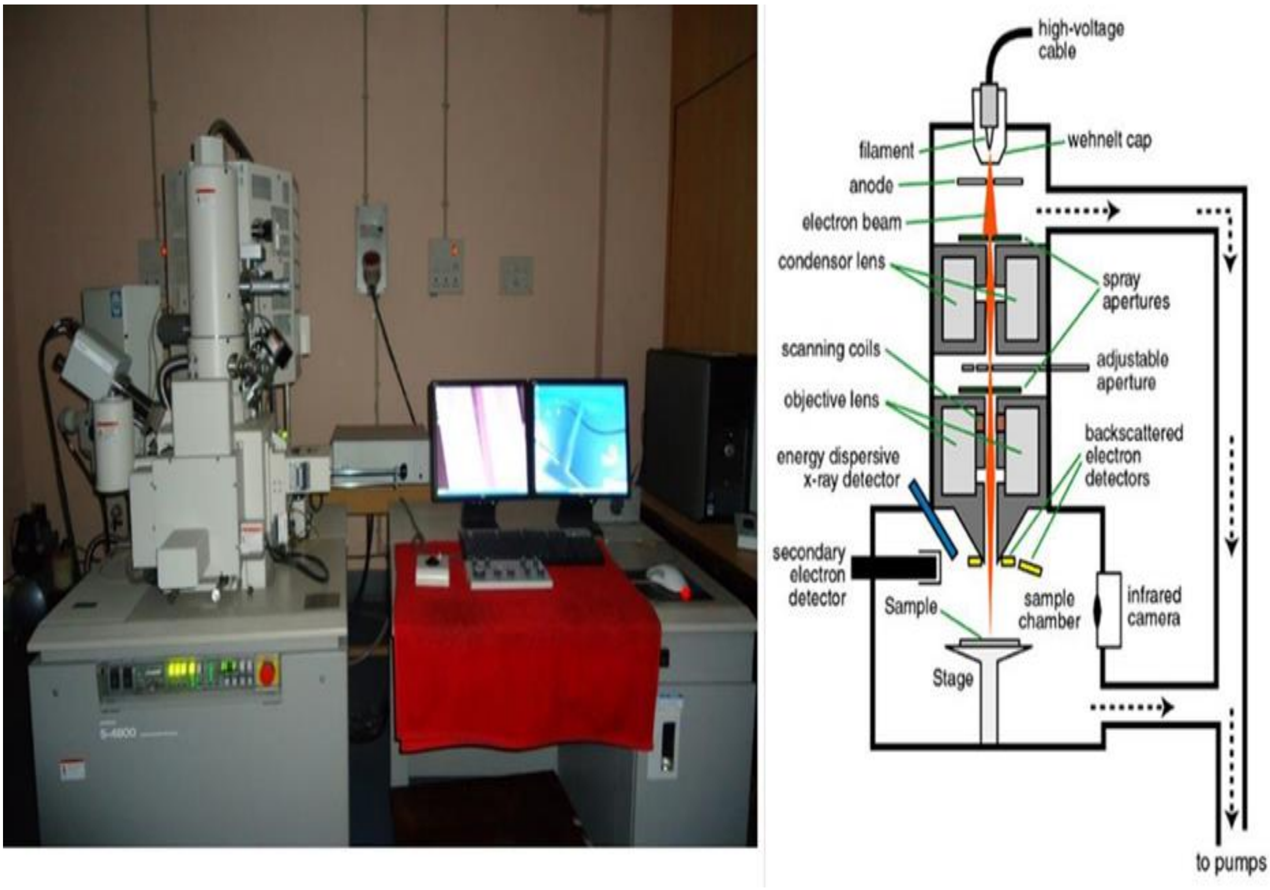

Fig. 4 . Left: Hitachi S4800 FESEM with EDX attachment

Right: Simple schematic of FESEM instrument

Energy Dispersive X–Ray (EDX) is one of the most versatile tools for analyzing the compositions of the synthesized samples. It is sometimes referred to also EDS or EDAX analysis. EDX is the integrated feature of both SEM and TEM. During EDX analysis, the specimen is bombarded with an electron beam inside electron microscope. The bombarding electrons collide with the specimen atom and knock some of them off in the process. The electrons vacated from the inner shell are eventually filled with the higher energy outer shell electrons and emit X–ray in this method. In this run, X–rays emitted from atoms represent the characteristics of the elements, and their intensity distribution represents the thickness–projected atom densities in the specimen. EDAX is a very important tool for identifying the chemical composition of a specimen .

2.2.3 Transmission electron microscope (TEM):

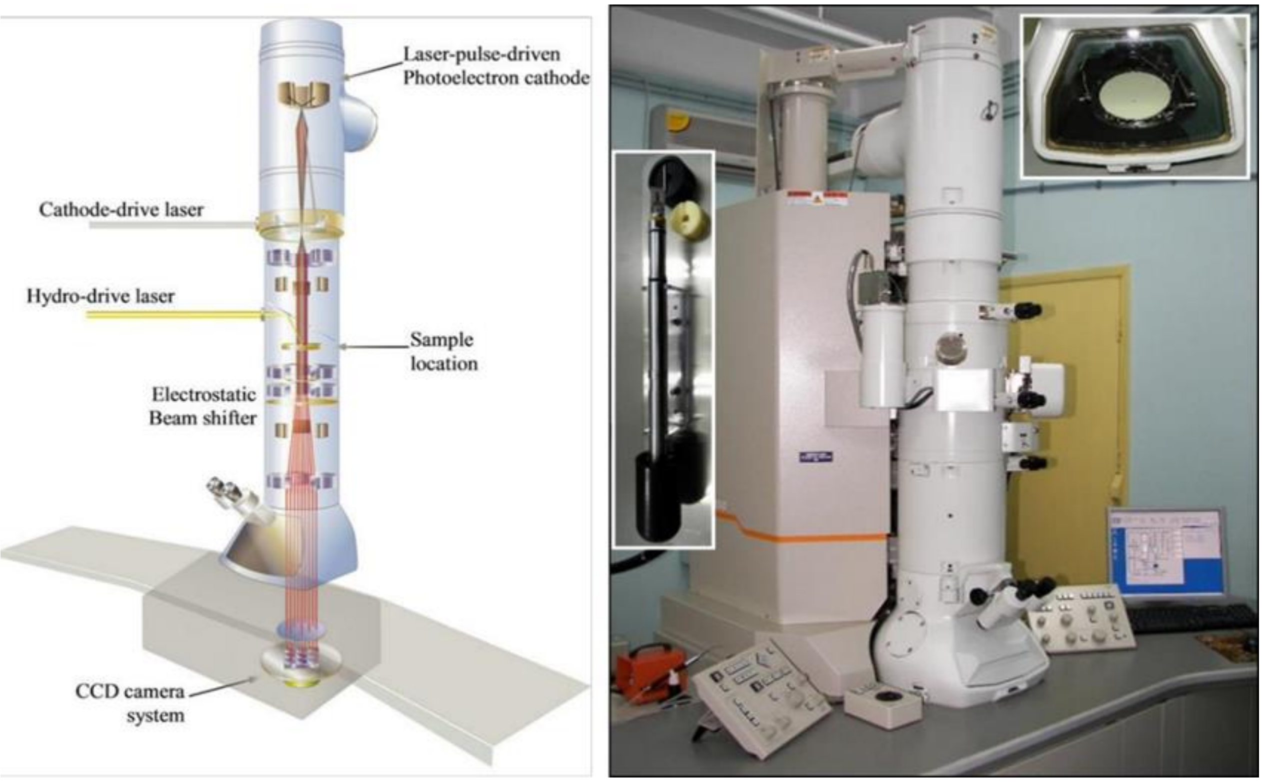

Fig.5 Left: Layout of optical components of basic TEM instrument.
Right: JEOL JEM-2100 HRTEM

Transmission electron microscope (TEM) is a unique tool in characterization ofmaterials crystal structure and microstructure simultaneously by electron diffraction and imaging techniques. The basic TEM instrumentation is summarized in Figure 3.7 (left). The accelerating voltage is considerably higher than in an FESEM and is typically 100–300 kV. The benefits of high voltage improve imaging resolution and also penetration depth which facilitates the ability to study thicker samples. The specimen thickness must be no more than a few hundred nanometers and is usually in the Carbon coated copper grid of 3 mm diameter. The sample specimen is located between the pole pieces of the objective lens. The combination of the objective lens and the projector lens system provides an overall magnification of around 106. Along with that high resolution transmission electron microscopy (HRTEM) is used to visualize the lattice images of the crystalline material which allow the direct characterization of the sample's atomic structures. The resolution of HRTEM is ~1 nm or less.

The contrast in high magnification image shows the periodic fringes. These fringes represent direct resolution of the Bragg diffraction plane that possesses inter-planar spacing greater than the lateral spatial resolution. The selected area electron diffraction (SAED) of a small area of 0.1 µm diameter helps to determine the crystal structure of different parts of the sample. Basically diffraction patterns are distinguishable as sport pattern from single crystal diffraction zones or ring patterns are obtained from the randomly oriented crystal aggregates (polycrystalline). The d spacing of the planes corresponding to the rings can be determined by the following equation: $Dd = L\lambda$, where D is the ring diameter of the electron diffraction pattern, L is the effective camera length, λ is the de Broglie wavelength of the accelerating electrons and d is the interplanar spacing. The morphologies of the as synthesized nanomaterials were characterized with high resolution transmission electron microscopy (JEOL JEM-2100).

2.2.4 Raman spectrometer:

Vibrational properties of material as well as further information about phonon confinement, structure, phase, grain size etc. can be extracted using Raman spectroscopy. When a monochromatic radiation is scattered by molecules, a small fraction of the scattered radiation is detected to have a different frequency from the incident one due to the inelastic scattering. This down converted frequency shift is known as Strokes shifted scattering. Whereas Anti–strokes shift scattering results when the incident radiation absorbs a phonon and emerges with higher energy. In a Raman Spectroscopy, an intense monochromatic radiation, i.e., a laser source is incident on the sample. The weak scattered light is passed through the mono-chromator to discard the Raleigh scattering and photo detectors detect the Raman shifted wavelength. The phonon confinement in a material can be found as the shift in the Raman line frequencies from the bulk material. Acoustic modes of bulk materials are not observable because of their low frequencies but in case of nanostructured material it appears in the measurable range. The frequency of the acoustic mode is inversely proportional to the size of the particles. Confinement of optical phonon results in the frequency shift and asymmetrical broadening of transverse and longitudinal optical mode line shape.

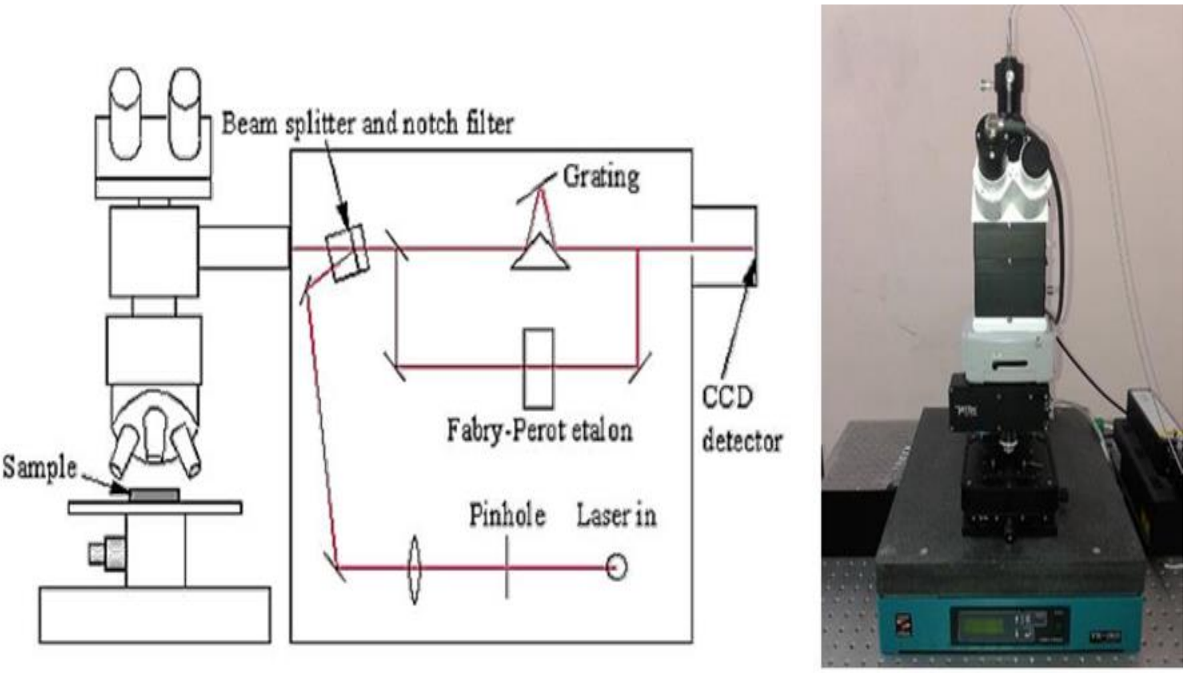

Fig.6. Left: Block diagram of the optical system of a spectrophotometer. Right: WITec alpha 300RS RAMAN spectrometer.

In the dissertation, all Raman spectra were obtained with the excitation (λexc) of 532 nm laser source (WITec). The picture of the instrument and block diagram of the optical instrument is shown in figure 2.8 (left) and (right).

2.2.5 Fourier transform infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a technique which is used to analyze the chemical composition of many organic compounds, polymers, paints, coatings, adhesives, lubricants, semiconductor materials, coolants, gases, biological samples, inorganics and minerals. FTIR can be used to analyze a wide range of materials in bulk or thin films, liquids, solids, pastes, powders, fibers, and other forms. FTIR analysis can give not only qualitative (identification) analysis of materials, but with relevant standards, can be used for quantitative (amount) analysis. An FTIR (Fourier Transform Infra-Red) is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform (FT) on the interferogram to obtain the spectrum. An FTIR Spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum. An FTIR is typically based on a Michelson Interferometer the interferometer consists of a beam splitter, a fixed mirror, and a mirror that translates back and forth, very precisely. The beam splitter is made of a special material that transmits half of the radiation striking it and reflects the other half. Radiation from the source strikes the beam splitter and separates into two beams. One beam is transmitted through the beam splitter to the fixed mirror and the second is reflected off the beam splitter to the moving mirror. The fixed and moving mirrors reflect the radiation back to the beam splitter. Again, half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting in one beam passing to the detector and the second back to the source.

Principle

A beam of infrared light (wavelength ~ 0.7-500 μm) is focused on the sample using all reflective optics. Depending on the sample composition, differing amounts of light are absorbed at different wavelengths. This pattern of light absorption is unique for almost every organic compound (except optical isomers) and many inorganic materials. From the pattern of light absorbed, identification of the composition (qualitative analysis) can be made. With additional control over the sample thickness or sampling depth, the intensity of the individual absorbing components can be used to perform quantitative analysis (amount of each compound present). User-provided reference samples aid in positive substance identification and compositional verification. FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. A Shimadzu IR Prestige-21 FTIR spectrometer was used to record the spectra in the mid IR region, (i.e. 400 – 4000 cm−1).

FTIR Spectra

The primary event in infrared absorption is the transition of a molecule from a ground state (M) to a vibrationally excited state (M*) by absorption of an infrared photon with energy equal to the difference between the energies of the ground and the excited states. The reverse process, infrared emission, occurs when a molecule in the excited state (M*) emits a photon during the transition to a ground state (M). In infrared spectroscopy, one derives information by measuring the frequencies of infrared photons that a molecule absorbs and interpreting these frequencies in terms of the characteristic vibrational motions of the molecule. In complex molecules, some of the frequencies are associated with functional groups that have characteristic localized modes of vibration. A plot of signal intensity against wavenumber constitutes FTIR spectrum.

Fig. 7. FTIR spectrometer

2.2.6 UV-VIS spectroscopy

It is used in analysis of detection of impurities, structure elucidation of organic compounds, quantitative analysis, qualitative analysis, dissociation constants of acids and bases, chemical kinetics, quantitative analysis of pharmaceutical substances, molecular weight determination and band gap analysis etc.

Principle

Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher antibonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state. A beam of light of selected wavelength is passed through the sample. The light is gets absorbed by the sample at certain wave length depending upon the band gap of the material. The absorption is associated with change in electronic structure of ions and molecules through the excitation of bonded and non-bonded electrons. Visible, near-infrared or ultraviolet light from the lamp enters the monochromators, which disperse the light (spread it into a spectrum) and select the particular wavelength chosen by the operator for the measurement.

Light of selected wavelength strikes a rotating mirror, which directs the light beam alternately through the sample and along a reference path. The two light beams converge on the detector. The relative intensities of the two beams, which strike the detector, provide a measure of the amount of light absorbed or transmitted by the sample. Absorbance or transmittance spectrum of the sample is obtained by automatic recording with a scan-drive system, which changes the wavelength setting of the monochromators and drives the recorder chart. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I0. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm. If the sample compound does not absorb light of a given wavelength, I = I0. However, if the sample compound absorbs light then I is less than I0, and this difference may be plotted on a graph as intensity versus wavelength, that will gives the absorption/transmission spectra. Absorption may be presented as transmittance (T = I/I0) or absorbance (A= log I0/I). If no absorption has occurred, T = 1.0 and A= 0. Most spectrometers display absorbance on the vertical axis, and the If the sample compound does not absorb light of a given wavelength, I = I0. However, if the sample compound absorbs light then I is less than I0, and this difference may be plotted on a graphs intensity versus wavelength, that will gives the absorption/transmission spectra. Absorption may be presented as transmittance (T = I/I0) or absorbance (A= log I0/I). If no absorption has occurred, T = 1.0 and A= 0. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λmax. Different compounds may have very different absorption maxima and absorbances. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector, and this requires the use of completely transparent (nonabsorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane. The UVVIS spectroscopy is carried out by Shimadzu UV 1700 spectrophotometer.

Fig. 8. The UV – Vis spectrometer

2.2.7 Photoluminescence (PL) spectrophotometer

Photoluminescence (abbreviated as PL) is light emission from any form of matter after the absorption of photons (electromagnetic radiation). It is one of many forms of luminescence (light emission) and is initiated by photoexcitation (i.e. photons that excite electrons to a higher energy level in an atom), hence the prefix photo- Following excitation various relaxation processes typically occur in which other photons are re-radiated. Time periods between absorption and emission may vary: ranging from short femtosecond-regime for emission involving free-carrier plasma in inorganic semiconductors up to milliseconds for Phosphorescence processes in molecular systems; and under special circumstances delay of emission may even span to minutes or hours.

Observation of photoluminescence at a certain energy can be viewed as an indication that an electron populated an excited state associated with this transition energy.

While this is generally true in atoms and similar systems, correlations and other more complex phenomena also act as sources for photoluminescence in many-body systems such as semiconductors. A theoretical approach to handle this is given by the semiconductor luminescence equations.

Experimental Methods

Photoluminescence spectroscopy is a widely used technique for characterisation of the optical and electronic properties of semiconductors and molecules. In chemistry, it is more often referred to as fluorescence spectroscopy, but the instrumentation is the same. The relaxation processes can be studied using Time-resolved fluorescence spectroscopy to find the decay lifetime of the photoluminescence. These techniques can be combined with microscopy, to map the intensity (Confocal microscopy) or the lifetime (Fluorescence-lifetime imaging microscopy) of the photoluminescence across a sample (e.g. a semiconducting wafer, or a biological sample that has been marked with fluorescent molecules).

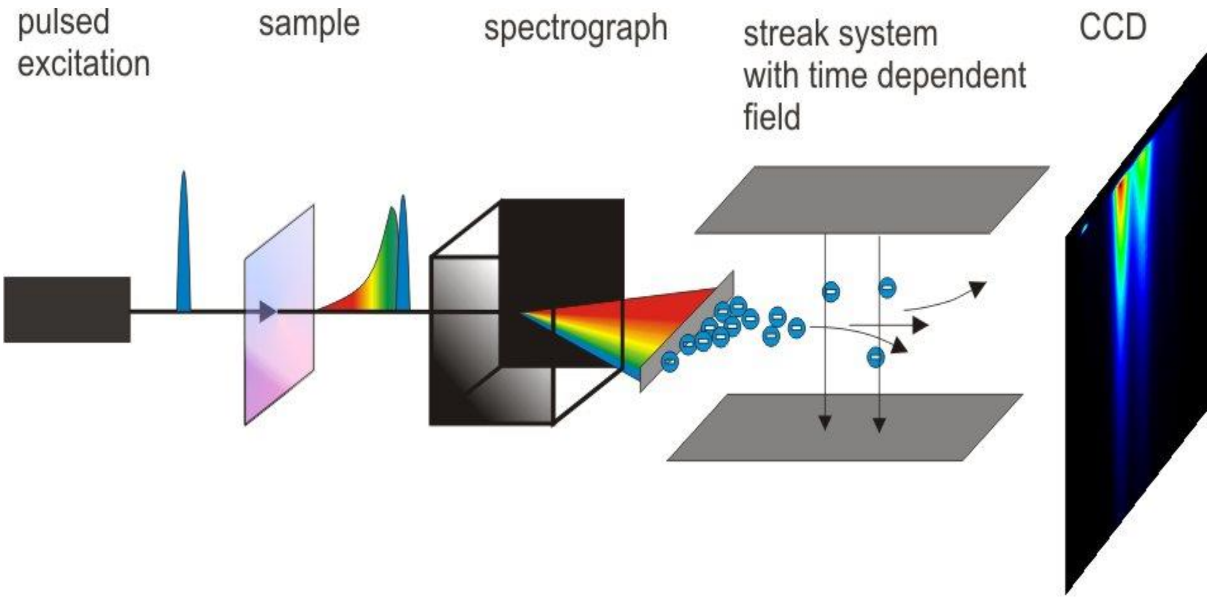

Fig.9.Working principle of PL spectroscopy

Fig.10. PL spectroscopy

Chapter 3

Synthesis of carbon dots from tea leaves by chemical synthesis process and study of its optical properties

Introduction:

Carbon based nanomaterials have recently attracted the attention of the scientific community and researchers worldwide .The different carbon nanostructures include one dimensional carbon nanotube ,nanofibers , two dimensional graphene, three dimensional diamond ,fullerene or zero dimensional carbon dots .carbon dots have a size of less than 10 nm ,consist of mainly sp^3 hybridized carbon unlike graphene The main advantages of carbon dots are that they shows good photoluminescence properties ,chemical stability, and environmental friendly etc . Carbon dots have potential applicability in various fields like chemistry, biology, medicine as pl sensor, in bio-imaging [1-4], in drug delivery vehicles, in catalysis and in various optoelectronic devices.

There are a number of reports present regarding the synthesis of carbon dots from different organic compounds, plants leaves etc. CQDs can be synthesized by different top down or bottom up techniques [5, 6, 7]. However most of the synthesis techniques [8, 9] often requires use of toxic materials, multiple complex steps and they have low quantum yield .Carbon dots have advantages over existing semiconductor quantum dots for their environment friendly, cost effective and high yield.

Keeping all these in mind, we have done the synthesis of the water soluble carbon quantum dots from tea leaves because of its low cost, can be used for large scale synthesis with no need to use high pressure, energy, temperature [10] and without any special preparation .The carbon dots prepared in this way are stable even after several months of preparation.

3.2 Materials used:

Green tea leaves were collected from tea garden at Siliguri. Acetic acid were obtained from Sigma-Aldrich and Ethanol (absolute) were obtained from Analytical Reagent.

3.3 Experimental and Characterization

3.3.1 Synthesis Process:

Tea leaves (in the crush tear curl (CTC) form) was first heated at 100 °C for about 2 h, followed by grinding to powder form. This tea powder was again heated at 200 °C for about 8 h. Then formed black carbonized powder of tea was cooled to room temperature and stored in a glass vial. A quantity of 300 mg of the carbonized tea powder was dispersed in 10 mL of 0.1 M acetic acid and kept for 40 h.

The dispersed medium was then centrifuged at 10 000 rpm for 0.5 h, and the supernatant liquid containing tea carbon dots (TCDs) were collected and preserved.

3.3.2 Characterization:

The TCDs were characterized using photoluminescent (PL) spectroscopy [11], High resolution transmission electron microcopy (HRTEM),Field emission electron scanning microscope (FESEM) ,Fourier transmission infrared spectrophotometer (FTIR) ,UV and dynamic light scattering (DLS) techniques .Photoluminence (PL) spectra show the fluorescence [12] behaviour of the TCDs. With the increase in the excitation wavelength, emission wavelength also increases which is a characteristic behaviour of TCDs in some cases. From the HRTEM images the size of the TCDs were estimated in the range of 10 nm.

3.4 Results and Discussion

Microscopic study

3.4.1 Morphological Analysis by FESEM:

FESEM images of the sample with high magnitude are shown in below. From FESEM images, it is seen that the synthesized confirmed the quantum size of the prepared carbon dots are so small in size that they are almost out of the resolution of the instruments. Still it is seen that spherical [13] particles of dimension of around 10-60 nm are well dispersed throughout the field of view. a

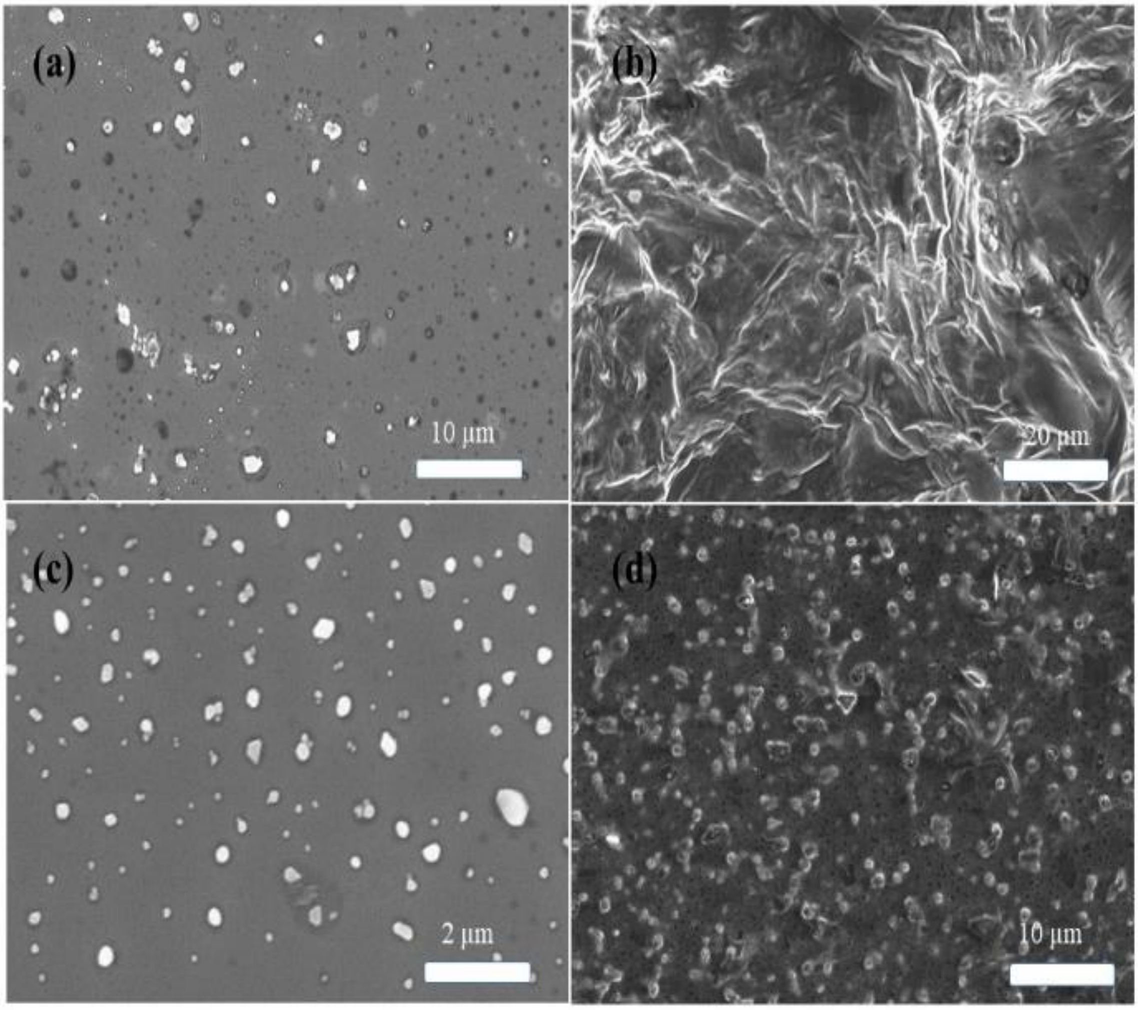

Fig.1 (a), (b), (c), (d), FESEM image of TQD Samples

3.4.2 Morphological Analysis by HRTEM:

HRTEM images **Fig. 2.** (a, b, c & d) are given below along with corresponding higher magnitude images. From FESEM images we were not able to estimate the exact dimensions of the carbon dots. Due to this reason we have characterised the as prepared samples by HRTEM. From HRTEM images it is seen that the dimension with the dimension in the range of 10 nm are well dispersed in the sample. The morphology [14] of the carbon dots were also studied with high resolution transmission electron microscopy (HR-TEM). It can be seen **Fig. 2.** (c & d) that the particles are almost circular in nature with an average diameter in the range of than 10 nm.

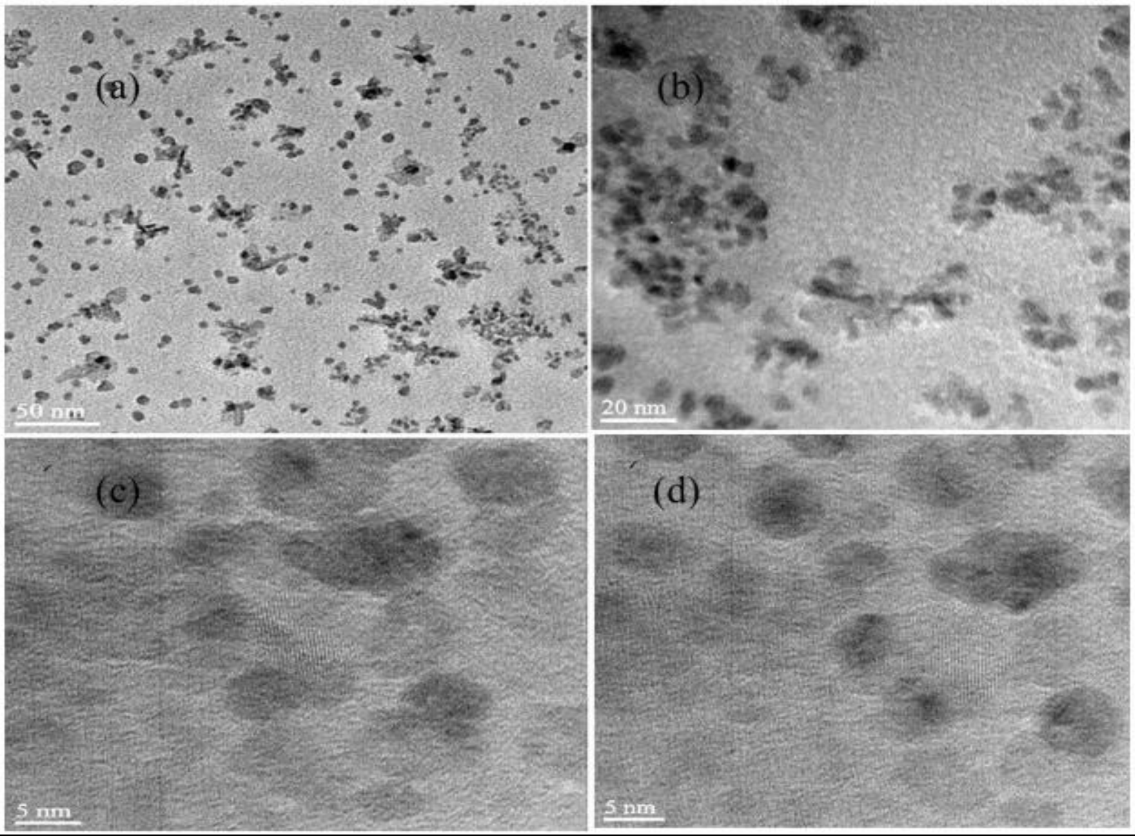

Fig.2. (a), (b), (c), (d), HRTEM image of TQD Samples

3.4.3 Study of Photoluminescence (PL) Property:

The size and excitation energy dependent photoluminescence (PL) property of all the samples have been studied. The PL spectra obtained after excitation of the carbon dots at wavelength ranging from 350 nm to 800 nm as shown in **Fig.3.**

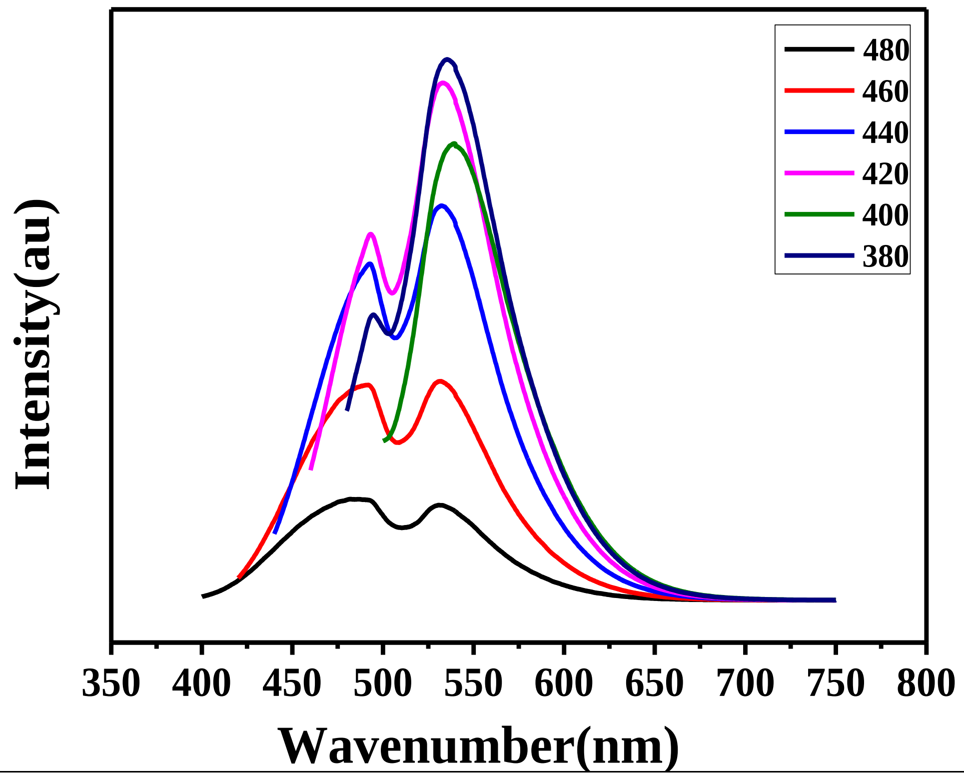

Fig.3. Variation of PL spectra with excitation wavelength

From figure, it is interesting to note that with an increase in excitation of the carbon dots at wavelengths ranging from 380 nm to 480 nm, first the emission gradually increased and shifted and emission maxima at a certain wavelength [15].Then the intensity [16] of the emission gradually decreased .The emission maxima are at wavelength of 535.8 nm, 532.4 nm, 531.6 nm, 530.8 nm, 530.8 nm. It is seen that when the excitation wavelength was increased from 500 nm to 535.8 nm, PL spectra is increased with a gradual increment .When the excitation wavelength further increased from 535.8 nm to 650 nm, the PL spectra decreased gradually and also peak of the PL spectra shifted when excitation wavelength [17] is increased.

3.4.4 FTIR Analysis:

The chemical structure of the prepared carbon dots is also characterized with FTIR .Tea leaves are a source of different types of polyphenolic compounds [18] with high aromatic structures along with extensive carboxylate, hydroxyl, amine groups [19] etc. The FTIR spectra in absorption mode is taken in the wavenumber range 500-4500 cm^{-1}. The samples were prepared by drop casting on Si wafer s describe in the previous section .The FTIR spectra shows several distinct peaks cantering around 603 ,750 ,825 ,867,1004 ,1103 ,1556 ,1654 ,1701 ,3547,3738 cm^{-1}. 3500 cm^{-1} band is the characterization of the OH bond .The band between 1400 and 1850 cm^{-1} is the signature of presence of different C-H,C-C and C=O [20] bond .The peak around 600 cm^{-1} forms from the Si-O-Si bond of silicon substrate due to formation of SiO_2 layer [21] .The peak around 900 cm^{-1} forms is due to presence of Si-H bending vibration .The peak at 1103 cm^{-1} is due to presence of C-O-C bond .For clear observation of all the peaks distinctly the ftir spectra of the sample has been separately shown in **Fig**.4.

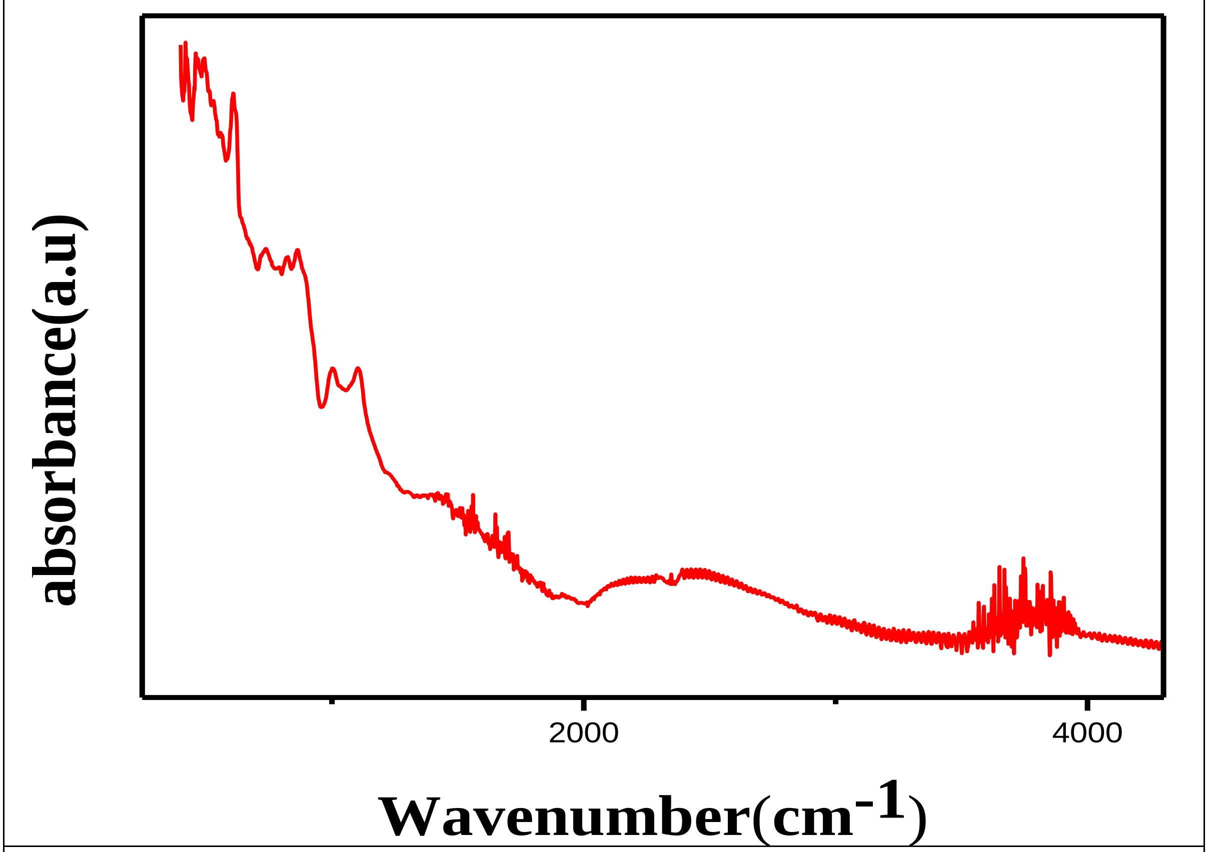

Fig.4.FTIR spectra of the sample

The various peaks between 1530–1050 cm^{-1} are due to mixed vibrations of various groups of atoms, including the hydrogen atom, HCH, OCH, COH, and CCH groups .The prominent peaks are observed at 3021 cm^{-1}, 2841 cm^{-1}, 1602 cm^{-1}, 1400 cm^{-1}, 1200 cm^{-1} and 750–600 cm^{-1}. The peak at 3021 cm^{-1} is due to the N–H stretching bond, 2841 cm^{-1} is due to the C–H stretching vibration, and the 1602 cm^{-1} peak is due to the C=O stretching vibration [22]. The peaks between 1400 cm^{-1} and 1200 cm^{-1} are due to the OH-in plane deformation, and the peaks from 750 cm^{-1} to 600 cm^{-1} are due to C–S–C asymmetric stretching and C–S symmetric stretching vibration.

3.4.5 UV-vis Absorption study:

The UV-Vis absorption spectra is shown below .It can be seen from the figure that the carbon dots have two absorption peaks which are located at 238 nm, 234 nm. This absorption is the main characteristic of π-π* electron transfer in C=C bonds [23]. Also UV-spectra shows that there is another weak band present in the spectra around 234 nm which the signature of different polyaromatic chromophores [24] is appearing during the synthesis of the sample of carbon quantum dots.

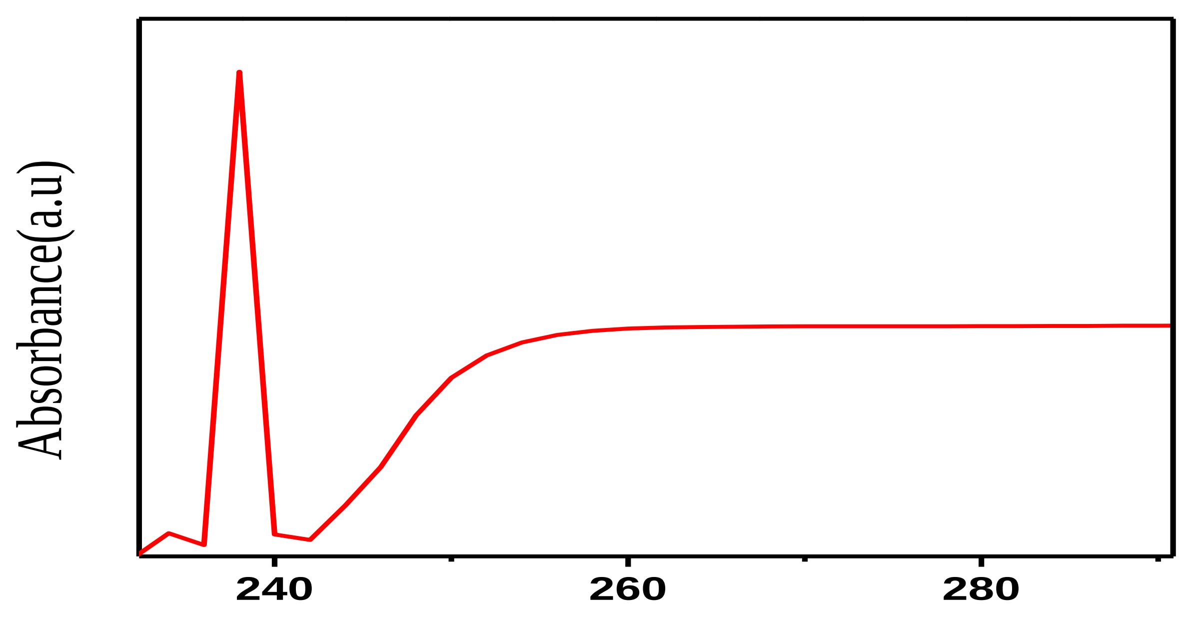

Fig.5. UV-vis absorption spectra of the sample

3.4.6 XRD study:

The XRD spectra [25] is shown below. It can be seen from the spectra that there are two peak and the value of this two peak are at 69 degrees, 60 deg. The first peak is due to presence of Si and the second peak is due to presence of carbon.

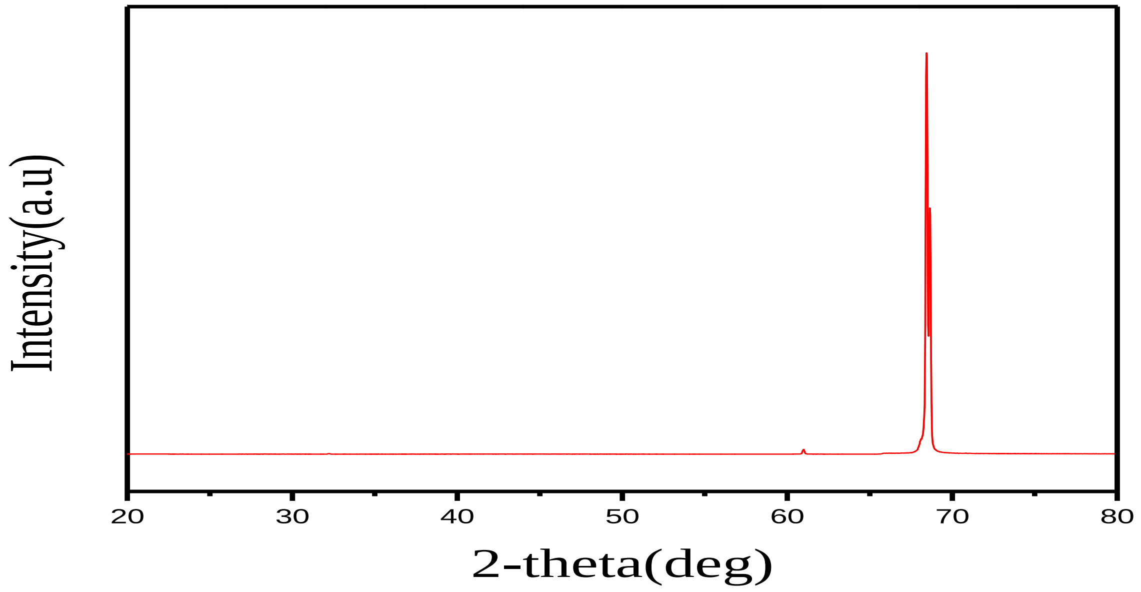

Fig.4.XRD of the sample

Conclusion:

Carbon quantum dots have been synthesized via very simple process .The synthesis process is cheap and does not pose any threat to the nature. HRTEM study confirmed the size of the carbon dots .FTIR spectroscopic studies revealed the different bonds and attachments of different functional groups on the surface of the carbon dots. As carbon dots shows excellent PL property that shows profound effect on synthesis condition and particle size as well as excitation wavelength. The variation in PL property is explained in terms of the structure and different bonds of the carbon dots.

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Chapter 4

Synthesis of carbon dots from tea leaves by Hydrothermal Method and investigation of its optical properties

4.1 Introduction:

Carbon-based quantum dots consisting of graphene quantum dots (QGDs) and carbon quantum dots (CQDs, C-dots or CDs) are a new generation of carbon nanomaterials with dimension below 10 nm. Nanostructured carbon quantum dots with fascinating properties have progressively become a popular among the researchers as a new nanocarbon member due to their benign, abundant and inexpensive nature. When stimulated by light, the CQDs fluoresce strongly, which makes them useful for medical imaging. Such particles could latch on to cancer cells and then be lit up, helping physicians to detect tumours at an earlier stage. CQDs could also act as catalysts for the clean-up of industrial waste, in which light is used to create unstable compounds called free radicals that degrade pollutants. And their ability to be tuned to different wavelengths of light means that CQDs could be used to improve the efficiency of solar cells.

Carbon dots have a size of less than 10 nm, consist of mainly sp3 hybridized carbon unlike graphene. The main advantages of carbon dots are that they shows good photoluminescence properties, chemical stability, and environmental friendly etc. Due to the aforementioned specific structures, CQDs unfold distinct properties such as effective absorbance of solar light, tunable photoluminescence (PL), infrared-responsive up-converted photoluminescence (UCPL) and unique photoinduced electron transfer. By selecting a particular synthesis routes, the surface states of the CQDs could be modified to achieve tunable light emission, which renders them efficient for different purposes in optical science research. Carbon dots have potential applicability in various fields like chemistry, biology, medicine as pl sensor, in bioimgaing [1-4], in drug delivery vehicles,in catalysis and in various optoelectronic devices.

CQDs can be synthesized by different top down or bottom up techniques [7,8,9].However most of the synthesis techniques [10,11] often requires use of toxic materials , multiple complex steps and they have low quantum yield. Three problems facing CQDs preparation need to be noticed: (i) carbonaceous aggregation during carbonization, which can be avoided by using electrochemical synthesis or solution chemistry methods, (ii) size control and uniformity, which is important for uniform properties and mechanistic study, and can be optimized via post-treatment, such as gel electrophoresis, centrifugation, and dialysis and (iii) surface properties that are critical for solubility and selected application.

Among all the synthesis techniques, hydrothermal carbonization (HTC) or solvothermal carbonization is a low cost, environmentally friendly, and nontoxic route to produce novel carbon-based materials from various precursors. In a hydrothermal reactor generally, a solution of organic precursor is sealed and reacted in a hydrothermal reactor at high temperature. CQDs have been prepared from different natural precursors like glucose, citric acid, chitosan and banana juice. Particles produced using such natural products also seem to be less harmful to the environment. Keeping all these in mind, we have synthesized of water soluble carbon quantum dots from tea leaves collected from the Dooars in Jalpaiguri district, West Bengal, India. However, studies of tea-based synthesis so far have been small and sparse. There is no certainty that industry will be attracted by the concept of using plants or fungi in nanomaterials synthesis. The carbon quantum dots prepared from tea leaves using hydrothermal synthesis technique have many advantages in the form of easy synthesis process, no need to use high pressure and temperature. Moreover the CQDs prepared in this way remain stable in after several months of preparation.

4.2 Materials used:

Green tea leaves were collected from tea garden Dooars in Jalpaiguri district, West Bengal, India. Acetic acid were obtained from Sigma-Aldrich . and absolute Ethanol were obtained from Analytical Reagent.

4.3 Synthesis Process:

Carbon of different sizes have been prepared by a simple low-temperature hydrothermal process as described by Sahu.et.al. In a typical experiment certain amount of water and ethanol was taken in a 100 ml Teflon lined autoclave reactor with stainless steel jacket.1.5625 g tea leaves was added to the solution and stirred for 30 min .The PH of the solution has been set to be 5.

Then the autoclave was heated in an air oven for different temperature and different time and subsequently the samples were left to cool normally.

The solutions were centrifuged at 15000 rpm for 45 min to prepare the water soluble carbon quantum dots .Course particles dissolved in the solution can be separated through filtration.

Sample one was prepared by heating the autoclave at 180 ℃ for 150 min and sample two was prepared by heating the autoclave at 150 ℃ for 150 min.

4.4 Results and Discussion:

The prepared samples were characterized by Field emission scanning electron microscope (FESEM,Hitachi,S-4800),High resolution transmission electron microscopy (HRTEM,JEOL-JEM2100),Fourier transformed infrared spectrophotometer (FTIR-8400S) , X-ray diffraction(XRD), and UV-vis spectrometer(Shimadzu UV-3600).Also the steady state photoluminescence measurement was carried out by Shimadzu RF5301 spectrofluorometer.

4.5 Microscopic study

4.5.1 Morphological Analysis by FESEM:

FESEM images of the sample with high magnitude are shown in **Fig. 1 and Fig. 2.** The FESEM images are numbering with a ,b ,c ,d respectively. It is seen that the as synthesized CQDs are so small in size that they are almost out of the resolution of the instrument. Still it is seen that spherical particles of dimension of around 10–50 nm are well dispersed throughout the field of view.

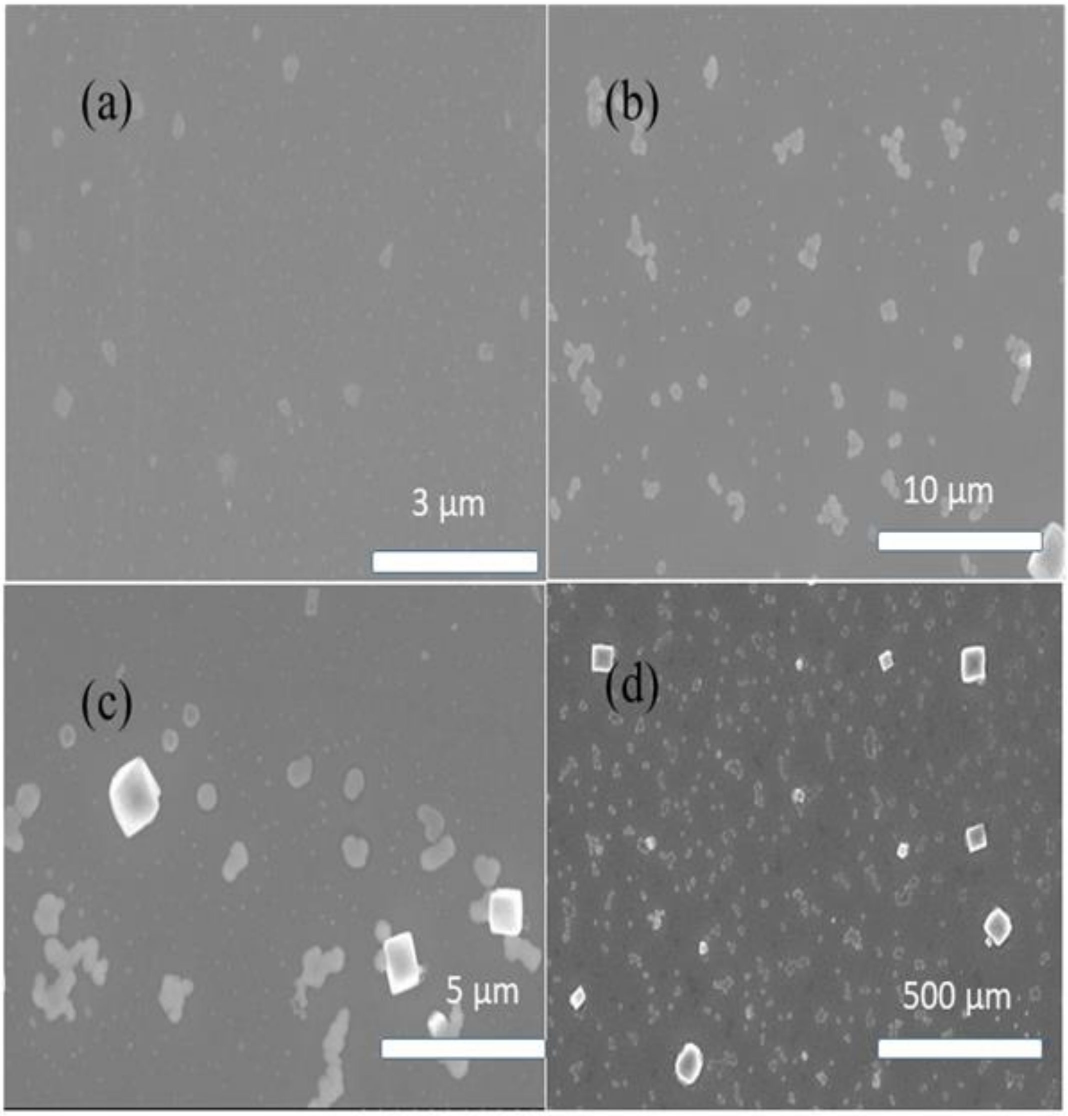

Fig.1.(a)FESEM image of the CQD samples prepared from tea leaves by hydrothermal synthesis process.

4.5.2 Study of PL property:

The intensity of PL spectra obtained after excitation of the carbon dots at wavelength ranging from 200 nm to 600 nm and the PL spectra graph are shown below in **Fig.2.**

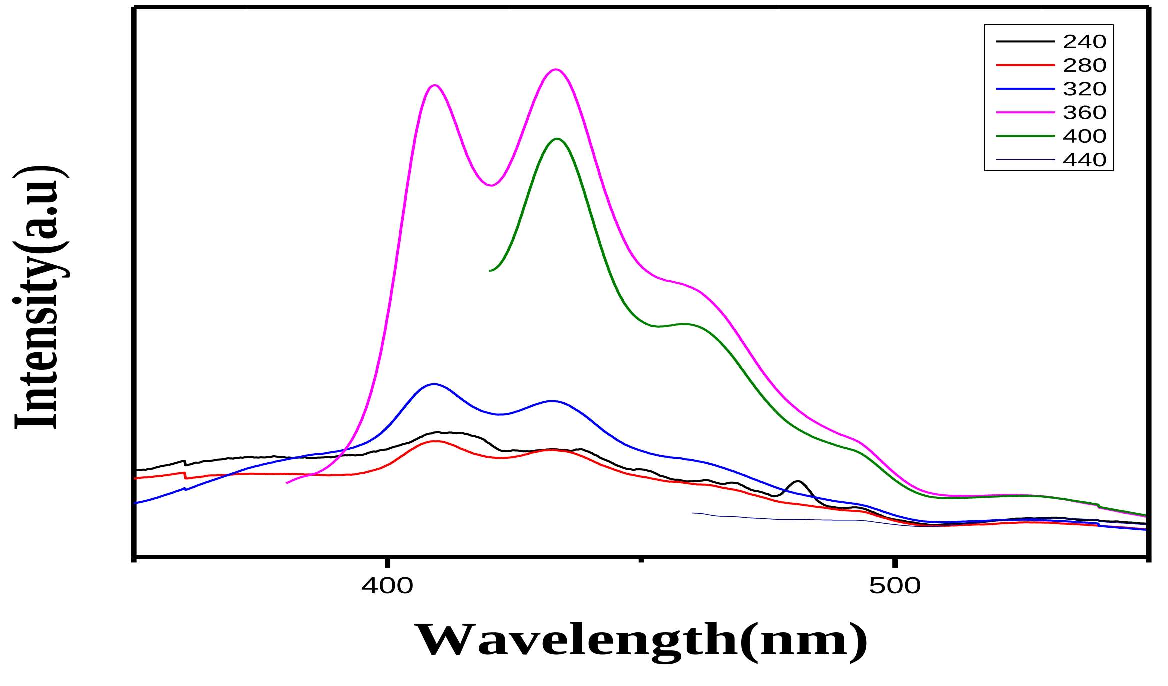

Fig.2. Variation of PL spectra with excitation wavelength

From **Fig.2.**, it is interesting to note that with an increase in excitation of the carbon dots at wavelengths ranging from 418 nm to 434 nm, first the emission gradually increased and shifted and emission maxima at a certain wavelength [14].Then the intensity of the emission gradually increased .The emission maxima are at wavelength of 434 nm, 432.8 nm,431 nm,433.8 nm ,530.8 nm. It is seen that when the excitation wavelength was increased from 434 nm to 451.8 nm , Intensity of PL spectra is decreased. When the excitation wavelength [15] further increased then the intensity of PL spectra decreased gradually and also peak of the intensity of PL spectra shifted when excitation wavelength is increased.

It is to be noted that CQDs can have different chromophoric center of CQD skeleton and different energy trap centers on the surface of the CQD which along with the size are believed to be the major parameters for PL properties [16]. It is also known that the optical propertie in solids take place due to activities of hole and electron [17]. It is reported that the emission in the range of 430-446 nm (blue emission) is due to the electron hole recombination or quantum size effect and emission in the range of 510 nm (green emission) is due the presence of surface defect states. Moreover presence of different functional groups like C=O, C-H on the surface of CQD create different emissive traps. Certain trap states become active with the change in excitation wavelength resulting in a change of emission as evident in the PL property all the four samples [12]. For most of the samples the emission was in visible range only (400-700 nm). So the CQD samples can be used for bio-imaging and optoelectronic applications. Hence, the exciting photoluminescence (PL) property of the CQDs can be attributed to the presence of sp^2 and sp^3 carbon core, quantum confinement and presence of different trap states on the surface of the quantum dots as reported by others [18]. PL centers in our case also are yet to be investigated. It is to be noted that for samples, double peaks in PL spectra can be observed which is mainly associated with the double size distribution of the CQDs as reported in our previous work [12].

4.5.3 FTIR analysis:

The chemical structure of the prepared carbon dots is also characterized with FTIR .Tea leaves are a source of different types of polyphenolic compounds with high aromatic structures along with extensive carboxylate, hydroxyl, amine groups, etc. The FTIR spectra in absorption mode is taken in the wavenumber range 0-5000 cm-1.The samples were prepared by drop casting on Si wafer s describe in the previous section .The FTIR spectra shows several distinct peaks centering around 617 ,736,852,1018,1365,1460,1554,1649,1701,1840,2000,2389,3589,3670 cm-1. 3500 cm-1 band is the characterization of the OH bond .The band between 1400 and 1850 cm-1 is the signature of presence of different C-H,C-C and C=O [16] bond .The peak around 617 cm-1 forms from the Si-O-Si bond of silicon substrate due to formation of SiO_2 layer [17].The peak around 852 cm-1 forms is due to presence of Si-H bending vibration [18].The peak at 1018 cm-1 is due to presence of C-O-C bond [19] .For clear observation of all the peaks distinctly the FTIR spectra of the sample has been separately shown in **Fig**.3.

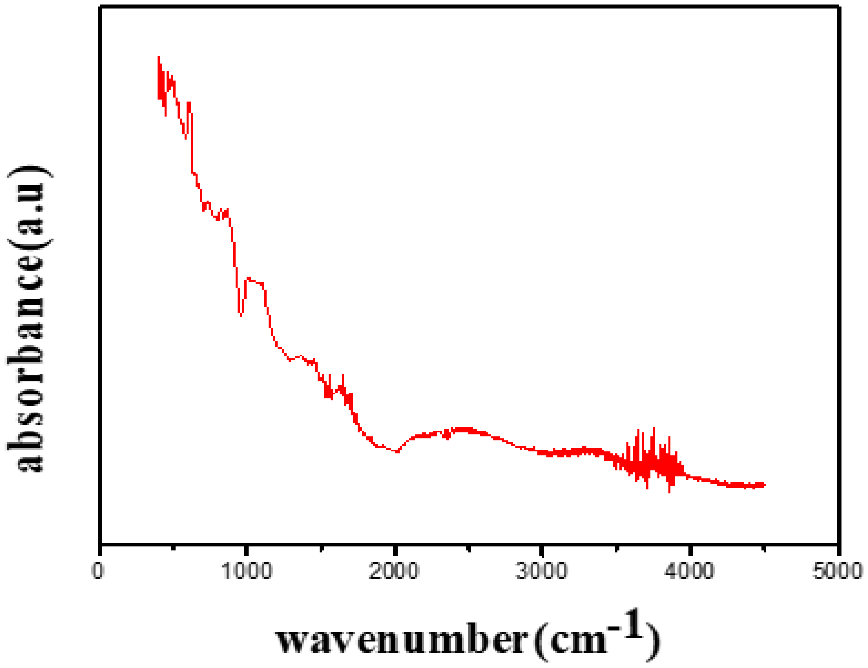

Fig.3. FTIR spectra of the sample

The various peaks between 1530–1050 cm-1 are due to mixed vibrations of various groups of atoms, including the hydrogen atom, HCH, OCH, COH, and CCH groups [20] .The prominent peaks are observed at 3021 cm-1, 2841 cm-1, 1602 cm-1, 1400 cm-1, 1200 cm-1 and 750–600 cm-1. The peak at 3021 cm-1 is due to the N–H stretching bond, 2841 cm-1 is due to the C–H stretching vibration, and the 1602 cm-1 peak is due to the C=O stretching vibration. The peaks between 1400 cm-1 and 1200 cm-1 are due to the OH-in plane deformation, and the peaks from 750 cm-1 to 600 cm-1 are due to C–S–C asymmetric stretching and C–S symmetric stretching vibration [21].

4.5.4 UV-vis Absorption study:

The UV-vis absorption spectra is shown below .It can be seen from the figure that the carbon dots have two absorption peaks which are located at 472 nm, 476 nm. This absorption is the main characteristic of π-π* electron transfer in C=C bonds .Also UV-spectra shows that there is another weak band present in the spectra which is the signature of different poly-aromatic chromophores [22] appearing during the synthesis of the sample of carbon quantum dots.

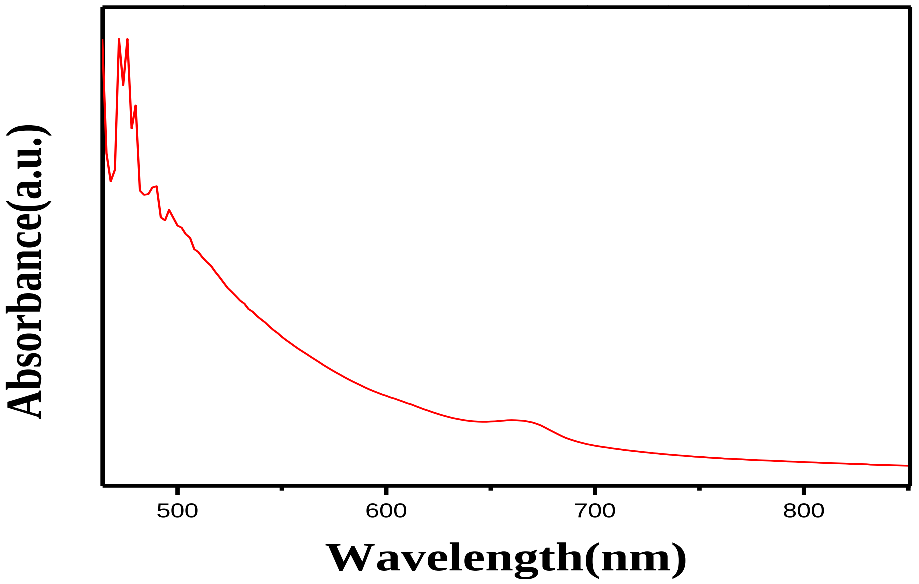

Fig.4. UV-vis absorption spectra of the sample

4.5.5 XRD study:

The XRD spectra is shown below .It can be seen from the spectra that there are two peak and the value of this two peak are at 69 deg , 60 deg . The first peak signifies the presence of silicon (Si) as the prepared solution is spring-coated on silicon wafer for characterization. The second peak signifies the presence of carbon in the prepared solution.

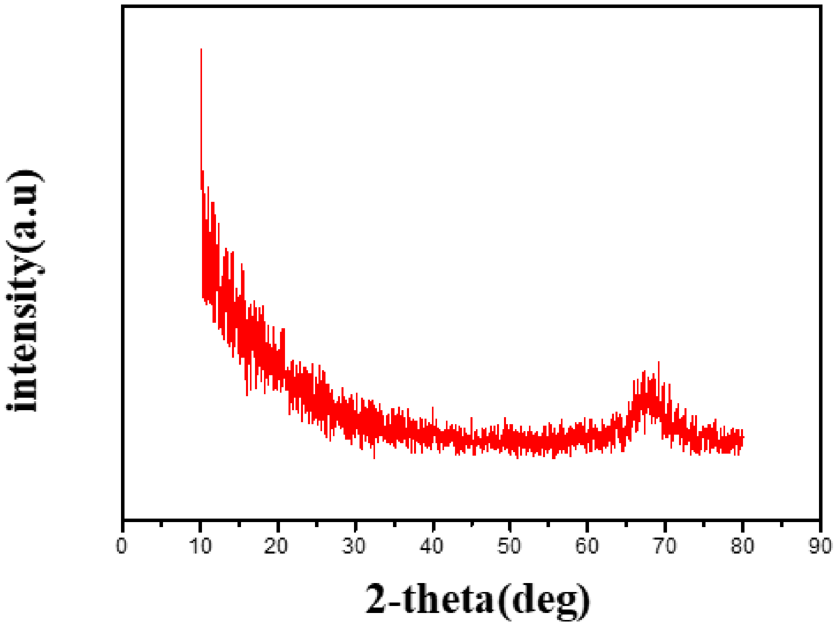

Fig.5. XRD of the sample

Conclusion:

Carbon quantum dots have been synthesized via very simple process .The synthesis process is cheap and does not pose any threat to the nature. FESEM study confirmed the well dispersed natureof the carbon dots. FTIR spectroscopic studies revealed the different bonds and attachments of different functional groups on the surface of the carbon dots. As carbon dots excellent PL property that shows profound effect on synthesis condition and particle size as well as excitation wavelength. The variation in PL property is explained in terms of the structure and different bonds of the carbon dots.

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Chapter 5

Synthesis of carbon dots from L-Methionine and study of its optical properties

5.1 Indroduction

Carbon dots [1] the new fluorophore member of the carbon hybrid nanomaterials family, have recently attracted the attention of the scientific community and researchers worldwide. Carbon dots have a size less than 10 nm, consist of mainly sp3 hybridized carbon unlike graphene [2,3] and GQDs [4] and show bright [5] fluorescence. The main advantages of carbon dots are that they possess good photoluminescence properties, chemical stability, and biocompatibility, are easy to prepare, have low cytotoxicity, are environmentally friendly etc [6]. Due to these exceptional properties, carbon quantum dots have distinguishable differences from other metal quantum dot systems. Carbon dots have potential applicability in various fields like chemistry, biology or medicine as PL sensors [7] in bio-imaging [8] in drug delivery vehicles [9] in catalysis [10] and in various optoelectronic [11] devices. Until now, various strategies for the synthesis of carbon dots have been explored, like hydrothermal, microwave assisted, electrochemical carbonization, chemical ablation, [12] etc.

The synthesis of optical [13] nanoparticles is a great challenge nowadays as the conformation and molecular reorganization play a vital role in various fields, such as negative refractive materials chiro plasmonic high-sensitivity bioanalysis, stereoselective reactions, chiral memory applications, hyperbolic meta-surfaces [14] catalysis [15] chiral sensors etc. There have been only a few reports on the synthesis of chiral quantum dots. The generation of chirality on graphene quantum dots (GQDs) by covalent attachment of L/D cysteine moieties to the edges was first reported by N. Suzuki et al.20 J. K. Choi and his co-workers first demonstrated that the chirality of quantum dots could be inverted and tuned, without changing the absolute configuration of the ligand but by only modifying the structure of the chiral capping ligands. M. V. Mukhina et al. have demonstrated a new route of enantiomeric biomolecular recognition using chiral CdSe quantum dots assays [16]. M. V. Nakagawa and his coworkers synthesized chiral graphene quantum dots using a simple esterification reaction and they successfully transferred the chirality to pyrene molecules. Recently, Yalin Zhang et al. synthesized chiral carbon dots by the hydrothermal treatment of citric acid and simultaneously capping with L and D-cysteine to introduce chirality in the system. But in all these reports the chirality of the nanomaterials is introduced mainly by capping or by covalent modification with other chiral moieties. It is a new challenge to synthesize chiral carbon dots without functionalization, doping or capping with other chiral molecules. The main advantage of our synthesized carbon dots is that they are intrinsically chiral and need no capping or doping with other chiral moieties to induce chirality.

In this work, we have for the first time successfully synthesized fluorescent carbon dots (CDs) from different precursor molecules by incomplete carbonization [17] of precursor molecules without attaching, doping, capping or covalently modifying with other moieties. The CDs were prepared from D-methionine, L-methionine by an easy synthesis process. Furthermore, it was observed that D- and L-carbon dots interacted differently with azobenzene-type photo-switchable molecules. The azobenzene molecule is regarded as the ideal photosensitizer, because when irradiated with UV light it transforms from stable to metastable cis form [18].

5.2 Materials used:

L-methionine (C5H11NO2S) were purchased from Sigma Aldrich . All the chemicals were used as obtained without further purification. The water used throughout the experiments was from a Milli-Q water purification system.

5.3 Synthesis Process:

For the synthesis of carbon dots (CDs), we employed a simple pyrolysis procedure for the precursor molecules. 1 g of the precursor molecule is put into a glass beaker and heated to just above its melting point for 10 minutes. On heating, solid precursors are gradually changed to liquid, and the color turns from a color-less liquid to orange, implying the incomplete carbonization of the precursor molecules. These orange colored liquids are transferred dropwise to 30 ml of sodium hydroxide solution (10 mg ml^{-1}) under vigorous stirring for 5 minutes. Then the dispersion is ultrasonicated for 10 minutes and centrifuged at 5000 rpm for 5 min. Then the supernatant part of the dispersion is collected, which contains the carbon dots.

Thus we have successfully prepared a stable aqueous dispersion of fluorescent CDs. This dispersion of CDs is used for further characterization.

5.4 Results and Discussion:

The characterization of the synthesized CDs was carried out with a UV-visible absorption spectrophotometer (Shimadzu, UV-2600), Fourier Transform Infrared Spectrophotometer (Nicolet 6700), Transmission Electron Microscope (JEM 2100), and a Scanning Electron Microscope (Carl Zeiss Psigma-VP). A Powder XRD spectrum of the CDs was recorded on a Bruker D8 Advance diffractometer.

Microscopic study:

5.4.1 Morphological Analysis by FESEM

The FESEM images are given below as in Fig. 1. (a , b ,c ,d) respectively. Scanning electron microscopy images confirmed the well dispersed nature of the prepared carbon dots as shown in **Fig. 1**. (a, b ,c. d). From FESEM images we can say that the average size of the prepared carbon dots was very small and the size is uniformly distributed.

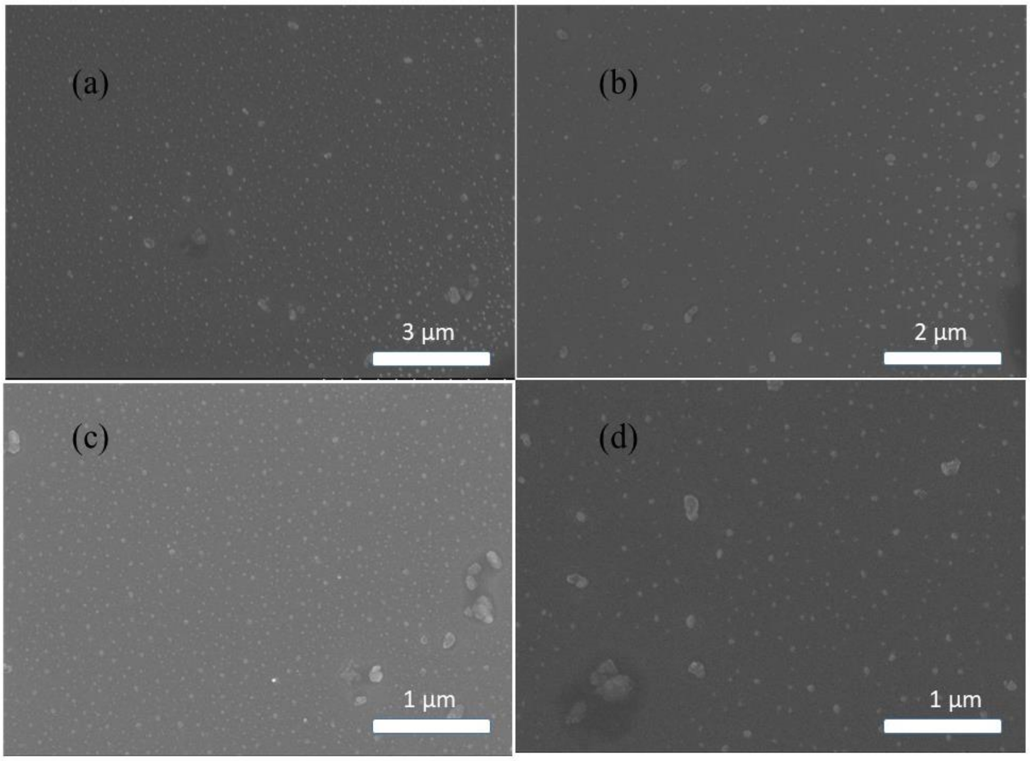

Fig.1. (a)FESEM image of CQD samples prepared from L-Methionine

5.4.2 Study of PL property :

The PL properties of the synthesized CDs was studied in detail . The stacked PL spectra obtained after excitation of the CDs at wavelengths ranging from 300 nm to 450 nm are shown in Fig.2 . From Fig.2, it is interesting to note that with an increase in the excitation wavelength from 300 nm to 450 nm for L-CD-Meth first the emission from the CDs increased and shifted and showed emission maxima at a certain wavelength, then the intensity of the emission gradually decreased. As-prepared L-CD-Meth show excitation-dependent PL properties, as shown by other carbon dots and GQDs reported earlier. The origin of excitation-dependent or excitation-independent PL properties has led to many hypotheses, from particle size distribution to the presence of different emissive states and solvent relaxation around CDs, and the participation of discrete multiple electronic states in the carbon dot system. The emission maxima for L-CD-Meth is at wavelengths of 300 nm. Our synthesized CDs have a size less than 10 nm and are dispersed in the same solvent (water), so there is no effect of size and solvents on the PL behavior of CDs. From the investigation of the PL spectra, it is confirmed that chirality also has no role in the fluorescence properties of carbon dots. The exact mechanism is not well known or understandable, but for our case all the CDs mainly differ in

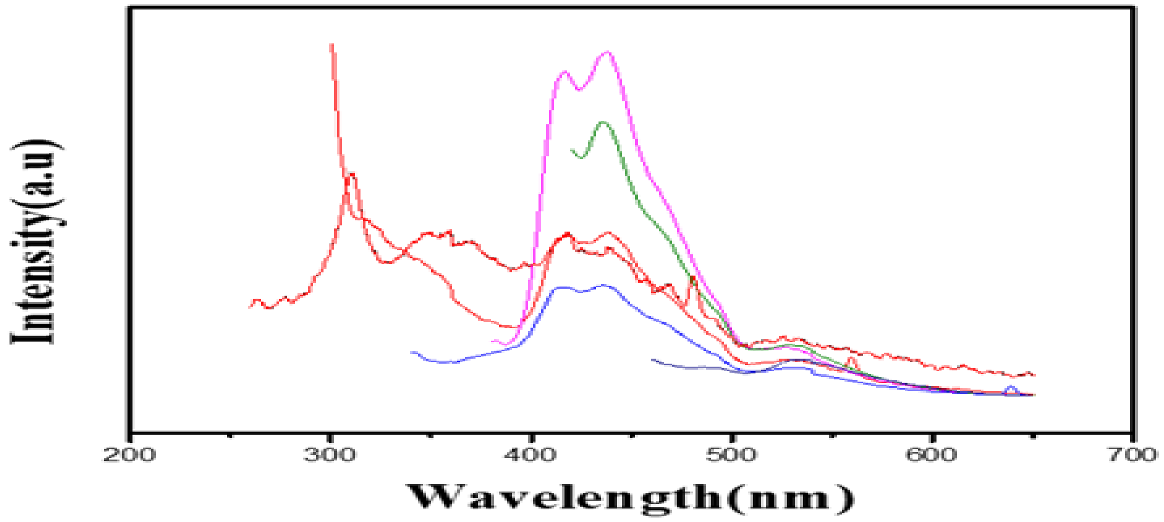

Fig.2. Variation of PL spectra with excitation wavelength

their functional groups . There is a report that surface functionalities also affect the PL properties of carbon nanomaterials.

5.4.3 FTIR study :

The chemical structure of the prepared fluorescent carbon dots is also characterized with FT-IR in Fig.3 .The prominent peaks of L-CD-Meth are observed at 3021 cm^{-1}, 2841 cm^{-1}, 1602 cm^{-1}, 1400 cm^{-1}, 1200 cm^{-1} and 750.600 cm^{-1}. The peak at 3021 cm^{-1} is due to the N.H stretching bond, 2841 cm-1 is due to the C.H stretching vibration, and the 1602 cm-1 peak is due to the C=O stretching vibration. The peaks between 1400 cm-1 and 1200 cm-1 are due to the OH-in plane deformation, and the peaks from 750 cm-1 to 600 cm-1 are due to C-S-C asymmetric stretching and C-S symmetric stretching vibration [19].

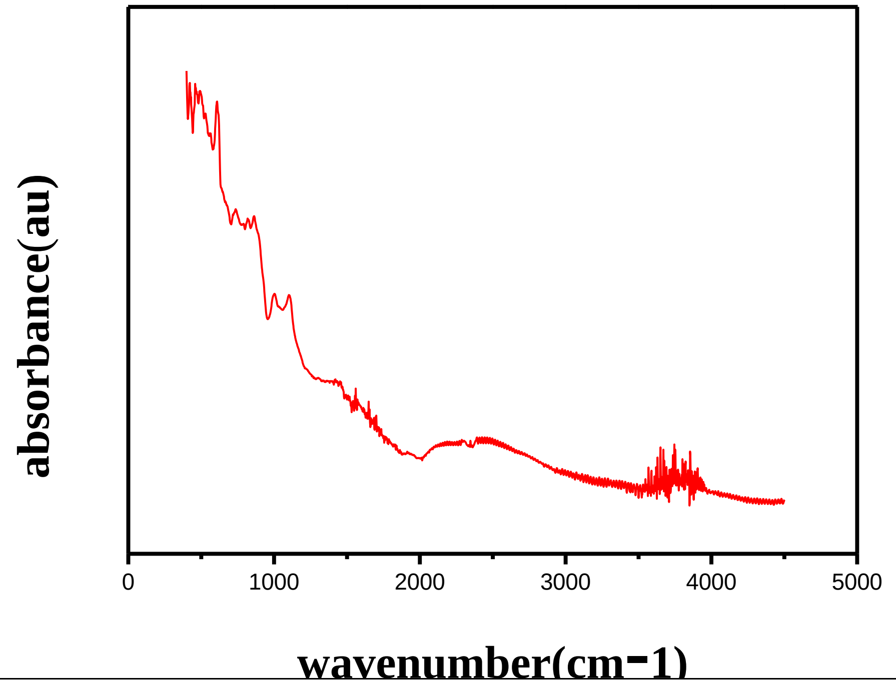

Fig.3.FTIR spectra of the sample

5.4.4 UV-vis Absorption study:

The synthesized carbon dots are characterized using UV-visible spectroscopy. It is evident from Fig.4 that all carbon dots show a prominent peak between 270 and 280 nm. These peaks are due to the n–p* transition of OH, NH2, and carboxylic acid (COOH) [20] groups present on the surfaces of the CDs. Again there is no prominent difference in the UV-visible spectra of the synthesized CDs and precursors. The UV-visible spectra of all the precursor molecules [21] are depicted in Fig.4.

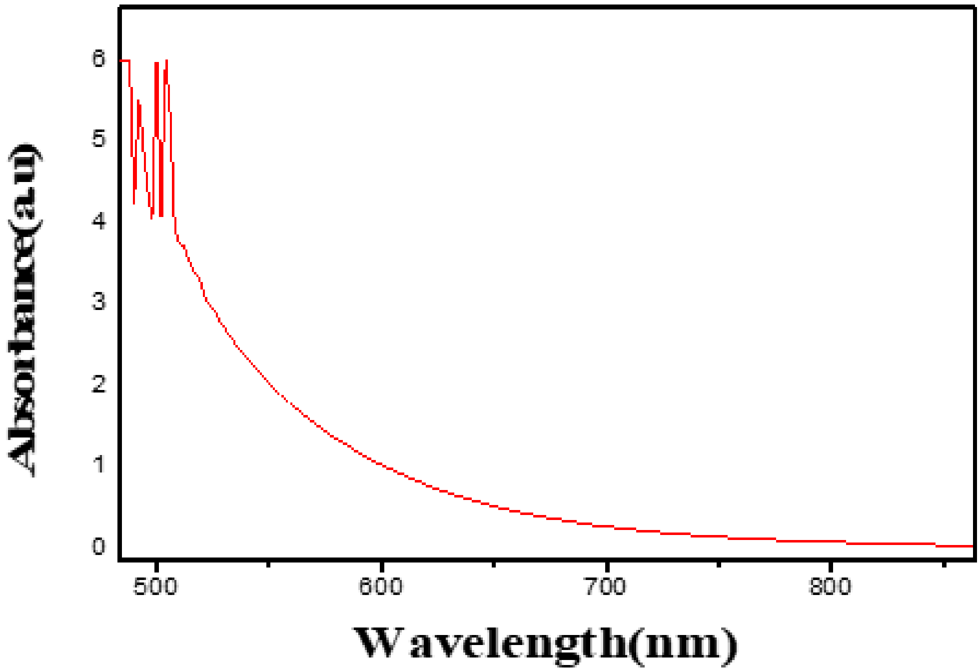

Fig.4. UV-vis absorption spectra of the sample

5.4.5 XRD study :

We have also investigated the crystallinity of the prepared CDs using XRD analysis. From **Fig.5** , it is clear that all the carbon dots show a broad band between 2theta= 20 deg and 30 deg ,which confirms the amorphous nature of all the prepared CDs. It is interesting to note that the precursors of all the synthesized CDs are crystalline, and this is confirmed from the powder XRD data.

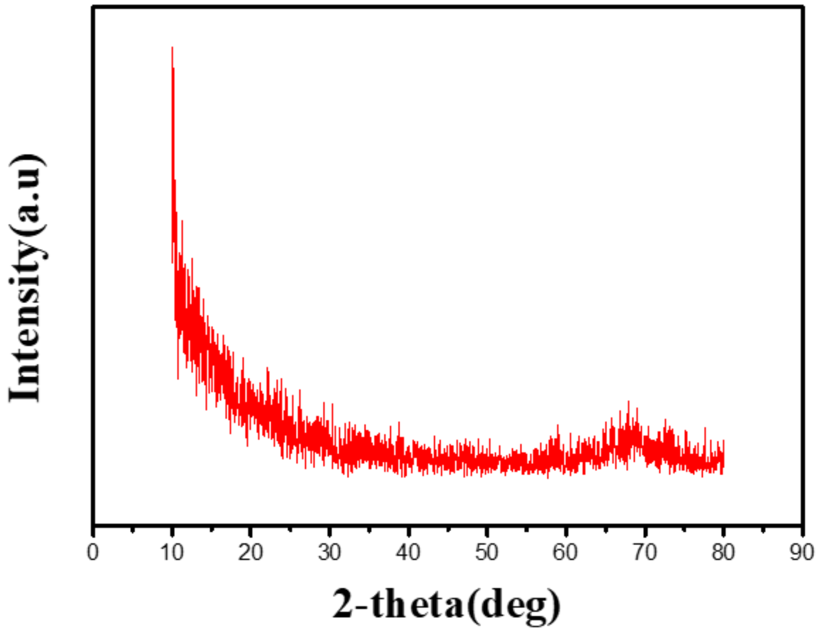

Fig.5.XRD of the sample

Conclusions

In summary, we have successfully synthesized carbon dots from precursor molecules. We successfully prepared L-CDs L-methionine . These L-carbon dots interacted differently with azobenzene photosensitizer molecules when they transformed from the transformed from the trans to the cis isomeric form. In this work, we synthesized carbon dots by incomplete carbonization of precursor molecules without capping or functionalization with other chiral moieties. We think that this type of understanding of this type of properties of carbon quantum dots will pave the way for a new direction of research on carbon hybrid nanomaterials and that it deserves further investigation.

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