

The synthesis of nitrogen doped carbon spheres and polythiophene/carbon sphere composites

By

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Declaration

I, the undersigned, declare that this MSc. Project is my original work and has not been presented for any degree in any university and all sources of the material used for this MSc. project have been duly acknowledged.

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Signature: _____

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Abstract

This study reports on the synthesis of N-doped carbon spheres (N-CSs) by a simple synthetic procedure. A horizontal CVD type reactor was used to synthesize N-CSs from pyridine. Depending on the dilution of the pyridine with toluene, a nitrogen content of 0.13-5 mol % was obtained. The use of a vertical CVD reactor gave N-CSs with a N-content of 0.19-3 mol % when an ammonium solution and acetylene were used as reactants. The diameters of carbon spheres were found to be in the range of 40 nm to 1000 nm for both CVD reactors. The diameter can be controlled by varying the flow rate, temperature, time, concentration and the reactor type. The samples were characterized by TEM, HRTEM, elemental analysis, Raman spectroscopy, TGA, PXRD and ESR.

We have demonstrated that unsubstituted thiophene can be polymerized by Fe^{3+} -catalyzed oxidative polymerization. The average particle size was about 50 nm, within a narrow particle-size distribution. The undoped carbon spheres (CSs) were reacted with thiophene to give polymer/carbon composites containing polythiophene and carbon nanospheres via chemical oxidative polymerization reaction. Polythiophene molecules were either chemically bonded or physically adsorbed to the surface of carbon spheres. The microstructure and properties of the two types of composites were compared. The thermogravimetric analysis data confirmed that the presence of CSs in the polymer/carbon composites is responsible for the higher thermal stability of the composite material in comparison with pristine polythiophene. The FTIR analysis showed that covalent functionalized nanocomposites exhibit a high intensity of a C-S bond at 695 cm^{-1} , which is not observed in the noncovalent functionalized nanocomposites

Keywords: nanotechnology; chemical vapour deposition; nitrogen doping; electromagnetic spin resonance; polymerization; polythiophenes; functionalized carbon spheres; noncovalent functionalization; covalent functionalization, composites;

Abbreviations

CSs	carbon spheres/undoped carbon spheres
N-CSs	nitrogen-doped carbon spheres
PT	polythiophenes
PT/CSs	polythiophenes/carbon spheres
CVD	chemical vapour deposition
XRD	X-ray diffraction
CNTs	carbon nanotubes
SWCNTs	single-walled carbon nanotubes
MWCNTs	multi-walled carbon nanotubes
f-CSs	functionalized carbon spheres
TEM	transmission electron microscopy
HRTEM	high resolution transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
TGA	thermogravimetric analysis
BET	Brunauer, Emmett and Teller
PXRD	powder X-ray diffractometry
FTIR	Fourier transformation infrared
ESR	electromagnetic spin resonance
T	temperature
t	time

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Chapter 1

Introduction

This chapter commences with the brief history of the nanotechnology and puts more emphasis on the carbon nanotechnology. It then follows with the motivation of the study. The chapter finishes by describing the aim and objectives of the study and the layout of the dissertation.

1.1 Brief history of the Nanotechnology

Nanotechnology is also referred to as the fourth industrial revolution.¹ The concept of nanotechnology was first introduced by Nobel laureate Richard Feynman in 1959.² Owing to the intriguing size-dependent properties of nanophase materials, the development of nanoscale and nanotechnology has opened up novel fundamental and applied frontiers in material science and engineering.³

With the revolutionary discoveries of C₆₀, and carbon nanotubes, carbon nanotechnology has become the building block of the entire field of nanotechnology.⁴ Carbon is the sixth most abundant element in the universe. In addition, carbon is a very special element because it plays a dominant role in the chemistry of life. Carbon was discovered in prehistory and was known to the ancients, who manufactured it by burning organic material making charcoal. There are several allotropes of carbon of which the best known are graphite, diamond, and amorphous carbon.⁵ The physical properties of carbon vary widely with the allotropic form, for example, diamond is highly transparent, while graphite is opaque and black. Diamond is among the hardest materials known, while graphite is soft enough to form a streak on paper. Diamond has a very low electrical conductivity, while graphite is a very good conductor. Under normal conditions, diamond has the highest thermal conductivity of all known materials. All the allotropic forms are solids under normal conditions but graphite is the most thermodynamically stable.⁶

1.2 Motivation

The largest challenge for our global society is to find ways to replace the slowly, but inevitably vanishing fossil fuel supply, and at the same time avoiding negative effects from the current energy system on climate, environment and health. Access to cheap, safe and renewable energy sources is of key importance for sustainable development throughout the world.

Nanoscience and Nanotechnology (the science and manipulation of chemical and biological structures with dimensions in the range from 1-100 nanometers.) can contribute to a positive development in this direction in several ways, for instance by influencing the energy efficiency of industrial production and of household energy use, and by offering schemes to clean up harmful emissions resulting from various energy systems.

Carbon based-materials such carbon spheres, carbon nanotubes, fullerenes with very interesting properties (electrical, mechanical) can be modified by doping them with electron rich nitrogen or electron deficient boron atoms and be used for future electronic devices in nanoscience and nanotechnology. The arrangement of the atoms in nanostructures determines their electronic structures such that their character can be insulating, semiconducting or metallic.⁷ On the other hand, electrical conducting polymers such as polythiophene have received a considerable attention from researchers because of their unique electronic, magnetic and optical properties.⁸ The carbon/polymer nanocomposites are envisaged to overcome the energy crisis we are experiencing. We believe that a composite of carbon material embedded in a polymer can be produce, and will give outstanding performance as an electron emitter material. Also by tailoring the correct choice of polymer and the chemical treatment of the carbon spheres open up the possibility of large area carbon spheres based electronics, including transparent electronics on plastic. However, it must be emphasized that only the materials are produced in this work, applications of the materials are not part of this dissertation.

1.3 Aims and objectives

The project was undertaken to elucidate and optimize a method for the synthesis of N- doped carbon spheres on a laboratory scale. The objectives of the research project are as follows:

- (i) To synthesis N-doped and undoped carbon spheres. Using various nitrogen sources to dope the carbon sphere: these include pyridine, ammonia gas, and ammonia solution.
- (ii) The characterization of the doped and undoped carbon spheres carbon by TEM, XRD, ESR, elemental analysis, Raman spectroscopy and TGA. The doping of the nitrogen heteroatoms into carbon nanospheres is anticipated to modify electronic properties of carbon spheres.
- (iii) Investigate electrical and thermal properties of complexes formed by incorporating carbon nanostructures into polythiophene. Polythiophenes are conjugated polymers with excellent thermal stability.

1.4 The Layout of the dissertation

This chapter serves as a prelude and summarizes the background of the nanotechnology, carbon and the incentive to embark on this study. It outlines the research carried out in this dissertation and future prospects of the work. Chapter 2 deals with theory and highlights the research that has already been done in carbon nanotechnology and it also focuses on the polymerization of thiophenes. In chapter 3, a brief description on the N incorporation in carbon material, the differences and similarities of carbon spheres produced by vertical and horizontal chemical vapour deposition. In chapter 3, the results of the N-doping effect on carbon spheres are discussed. Chapter 4 focuses on the oxidative polymerization of thiophene, the thermal stability, morphology and functional groups present in the polythiophenes. In chapter 5 discusses the organic functionalization of carbon sphere/polythiophene composites. Chapter 6 contains the concluding remarks on the overall study with suggestions on future studies. Lastly, lists of referenced materials and appendices are given.

1.5 Future prospects in solar cells and nanotechnology

Current solar power technology has little chance to compete with fossil fuels or large electric grids.⁹ Today's solar cells are simply not efficient enough and are currently too expensive to manufacture for large-scale electricity generation. However, potential advances in nanotechnology may open the door to the production of cheaper and more efficient solar cells.¹⁰ Conventional solar cells are called photovoltaic cells. These cells are made out of a semiconducting material, usually silicon. When light hits the cells, they absorb energy. This absorbed energy knocks out electrons in the silicon, allowing them to flow. By adding different impurities to the silicon such as phosphorus or boron, an electric field can be established. This electric field acts as a diode, because it only allows electrons to flow in one direction.¹¹ Consequently, the end result is a current of electrons, better known to us as electricity. Conventional solar cells have two main drawbacks: i) they can only achieve efficiencies around ten percent or less and ii) they are expensive to manufacture.¹² The first drawback, inefficiency, is almost unavoidable with silicon cells. This is because the incoming photons, or light, must have the right energy, called the band gap energy, to knock out an electron. If the photon has less energy than the band gap energy then it will pass through the device. If it has more energy than the band gap, then that extra energy will be wasted as heat.

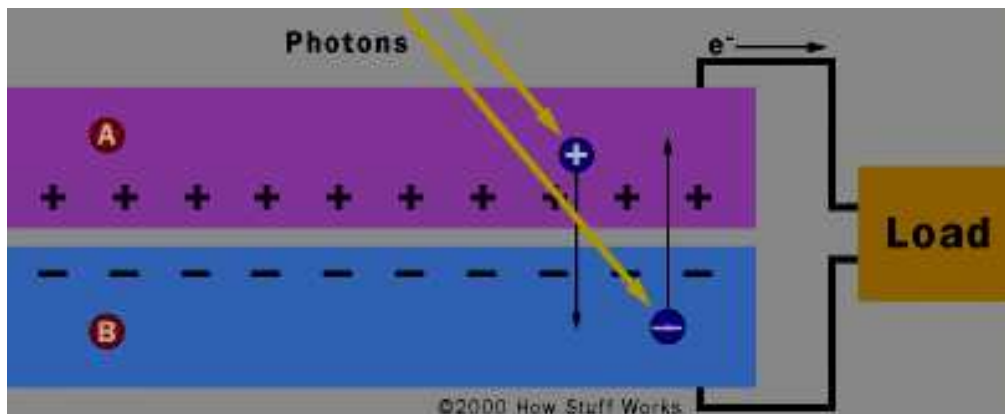


Figure 1.1: Schematic diagram of a photovoltaic solar cell.

Nanotechnology might be able to increase the efficiency of solar cells, but the most promising application of nanotechnology is the reduction of the manufacturing cost. Scientists have discovered a way to make cheap plastic solar cells that could be painted on almost any surface.¹³ These new plastic solar cells utilize tiny nanorods dispersed in a polymer. The nanorods behave as wires because when they absorb light of a specific wavelength they generate electrons. These electrons flow through the nanorods until they reach an aluminum electrode where they are combined with a positive centre. This type of cell is cheaper to manufacture than conventional ones for two main reasons.

First, these plastic cells are not made from silicon, which can be very expensive. Second, manufacturing of these cells does not require expensive equipment such as clean rooms or vacuum chambers like conventional silicon based solar cells. Another potential feature of these solar cells is that the nanorods can be ‘tuned’ to absorb various wavelengths of light. This could significantly increase the efficiency of the solar cell because more of the incident light could be utilized.¹⁴

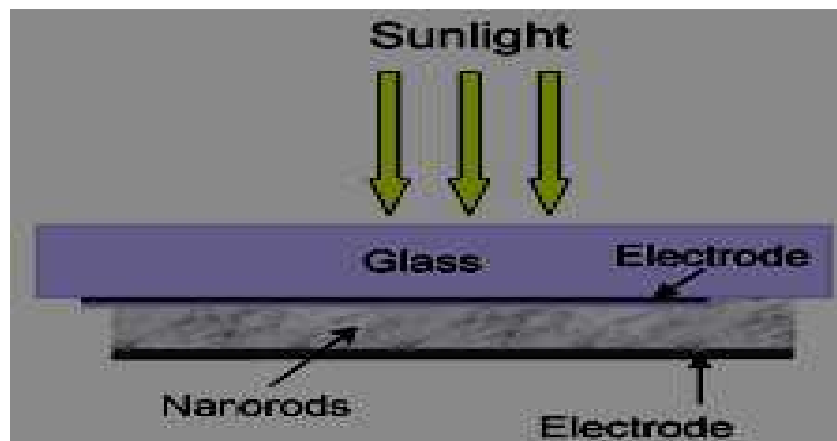


Figure 1.2 Schematic diagram of a nano solar cell.

Since the manufacturing cost of conventional solar cells is one of the biggest drawbacks, nanotechnology could have some impressive effects on our daily lives. Although solar cells are only capable of supplying low power devices with sufficient energy, its implications on society would still be tremendous. It would help preserve the environment, provide electricity for rural areas, and have a wide array of commercial applications due to its wireless capabilities.

References

1. Dai L., *Technology and Engineering*. **260** (2006) 733
2. <http://en.wikipedia.org/wiki/Nanotechnology> 2009 March
3. Goldstein A.N., *Handbook of Nanophase Materials*. Marcel Dekker, Inc., New York (1997)
4. Kang Z.C., Wang Z.L., *J. Mol. Catal: Chem.* **118** (1997) 215
5. Abramson, J., *Carbon*. **11** (1973) 337
6. Mathis, J. S., Rumpl, W., Nordsieck, K. H., *Astrophys. J.* **217** (1977) 425
7. Stephen O., Ajayan P. M., Colliex C., Redlich P., Lambert J. M., Bernier P., Lefin P. *Science*. **266** (1994) 1683
8. Shirakawa H., *Synth Met.* **3** (2002) 125
9. <http://tahan.com/charlie/nanosociety/course201/>
10. <http://www.spacedaily.com/news/nanotech-04zj.html>
11. <http://science.howstuffwork.com/solar-cell.html>
12. Choi Charles. "Nanotech Improving Energy Options." Space Daily. New York:
13. http://www.berkeley.edu/news/media/releases/2002/03/28_solar.html
14. <http://www.wtec.org/> March 2001

Chapter 2

Literature Review

The field of nanoscience and nanotechnology is an interdisciplinary area in the global research arena and activities in this area has been increasing in the past 20 years. While an understanding of the range and nature of functionalities that can be accessed through nanostructuring is just beginning to unfold, the ways in which materials and products are created is already clear.¹ Nanomaterials are of enormous fundamental interest, both from the point of discovering new physical phenomena as well as for their exploitation in novel devices.

The search for synthetic strategies for generating nanostructured carbon or carbon-hybrid materials is an important topic in carbon chemistry, motivated by the natural abundance and therefore the cost effectiveness of carbon precursors and the promising applications of the resulting materials.² Also, new nanomaterials obtained from doping carbon with nitrogen or boron atoms are potential candidates for future electronic devices in nanoscience and nanotechnology.³ The arrangement of the atoms in nanostructures determines their electronic structures such that their character can be insulating, semiconducting or metallic. Carbon structures can also be modified by sulfur atoms (e.g. thiophene) and composites containing polythiophenes have received considerable attention from researchers because of their unique electronic, magnetic and optical properties.⁴

In this project, novel carbon nanostructures and nanocomposites were synthesized and characterized with respect to their chemical and thermal properties. The materials synthesized are envisaged to have potential applications in solar cells and energy storage. The emphasis in this study was however not on the applications. The study in this dissertation comprises a number of aspects: the synthesis of carbon spheres, the N-doping of carbon spheres and the incorporation of the spheres in polythiophenes. To place the study in perspective a brief review of these topics is given below.

Part 1: Carbon nanomaterials

2.1 Shapes of carbon nanomaterials

Carbon is a very versatile material that can form various structures such as diamond, fullerenes (C_{60} and its family) and carbon nanotubes (CNTs).⁵ The variety of the structures produced by carbon is a consequence of its stable bonds arising from sp^2 (graphene) and sp^3 (diamond) orbital hybridization in carbon.⁶ Depending on the growth conditions, the sp^2 carbon atoms can form pentagonal and heptagonal carbon rings that, in combination with the less strained and therefore more thermodynamically favorable hexagonal carbon rings, can produce a large variety of geometrical configurations. These can range from nano- to micron-sized spheres (solid or hollow, amorphous or with onion-like layers) to CNTs having single or multi-walled configurations.⁷ Carbonaceous structures have led to major developments that have impacted on the field of nanoscience and nanotechnology. Figure 2.1 below shows different carbon nanostructures that have been determined .⁸

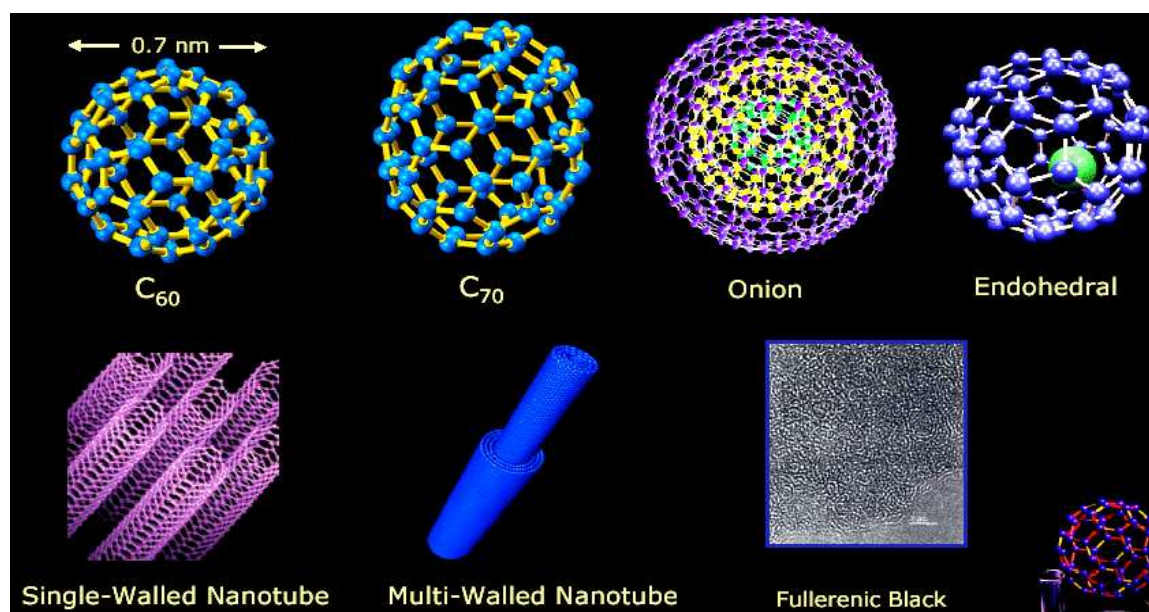


Figure 2.1 Shapes of carbon nanomaterials.

An important feature of the range of carbon nanostructures synthesized is that their properties, such as high tensile strength and physical stability are quite remarkable, making them a potential high-strength lightweight material and reinforcement in composites. Further, their chemical reactions with free radicals and other atoms opens up a chemistry that can be associated with these carbon nanostructures. The observation that atoms and molecules can be placed inside their "cages" e.g. (endohedral fullerenes) has led to the discovery of interesting and novel chemistry. The new carbon structures have shown remarkable superconducting and optical properties.⁹ Among the various forms of carbon known, spherical carbons are a novel material that is increasingly becoming important in research. They can be fabricated by the methods that are normally used to synthesize carbon nanotubes.¹⁰

2.2 Spherical carbon materials

Since the discovery of buckminsterfullerenes, spherical carbon structures have received increased attention from the scientific community. A classification of these spherical carbon structures has been proposed by Inagaki, according to their nanometric texture:¹¹ that is the materials are classified by the concentric, radial or random arrangement of the carbon layers. Serp has also classified carbon into three categories according to their size:¹²

- (i) the C_n family and the well graphitized onion like structures that typically have diameters ranging between 2 and 20 nm;
- (ii) the carbon beads with diameters of one to several microns, and
- (iii) the carbon nanosized spheres that present less graphitized structures and have diameters between 50 nm and 1 μm .

The onion-like graphite structures (type (i) above) are a new allotropic nanophase of carbon materials, which can be potentially be used as single-electron devices,¹³ magnetic refrigerators, nanodiodes,¹⁴ nanotransistors, nanoball bearings and insulator lubricants.¹⁵ The onionlike carbon material was first found by Iijima¹⁶ at the surface of graphite electrodes. Further interest was devoted to the carbon onions in 1992, Ugarte¹⁰ discovered a reproducible technique to obtain their formation that consists of irradiating carbon soot with an intense electron beam. It is well

known that the methods for carbon onion synthesis can be generally divided into two groups.¹⁷ One is based on temperature or irradiation induced transformation of other forms of carbon such as carbon soot¹⁸ or ultra dispersed diamond¹⁹ into concentric spherical cages. The other includes continuous segregation of carbon excess inside bulk materials, which have low carbon solubility. Due to its flexible nature of carbon structures, considerable efforts have been made to fabricate diverse carbon morphologies. Esumi *et al.*²⁰ prepared carbon microbeads from a water-in-oil emulsion using amphiphilic carbonaceous material and urea, followed by heat-treatment at various temperatures. They found that particle sizes between 2 and 15 μm were spherical and the surfaces of the microbeads were very smooth and contained no cracks.

Sharon and Pradham²¹ studied the synthesis of nanobeads by thermal chemical vapor deposition process. They reported that nanobeads were formed at high temperatures (1100 °C) in the presence of nickel and iron catalysts. Solid carbon beads (2–3 μm) have been prepared from a mixture of polyethylene and 10% wt. polyvinylchloride under 30 MPa pressure at 650 °C.²² A method to obtain hollow carbon beads (ca 50 μm) consists of the chemical vapour deposition of carbon from benzene on silica beads and further dissolution of silica with HF.²³ Finally, Wang *et al.*²⁴ have recently reported the production of microbeads (ca 2 μm) from a synthetic naphthalene isotropic pitch by simple heating of the reactants at 420 °C under nitrogen. Potential applications of activated-carbon beads or spheres could be as an adsorbent, as catalyst support or as anode in secondary lithium ion batteries.²⁵ Carbon nanosphere production has been reported *via* mixed valent oxide decomposition of natural gas at 1100 °C and the decomposition of pentane over $\text{Fe}(\text{CO})_5$ at temperatures in excess of 900 °C.^{26,27} Thermal pyrolysis of methane, benzene, styrene, *etc.* has been successfully employed to generate nanospheres at temperatures greater than 1000 °C. The spherical morphology has been reported in the literature to possess a lower crystalline character than filaments, due to imperfections and reactive dangling bonds present on the surface of the spheres.²⁸

Soot was the original source of many of these carbon materials, such as soccer-ball-shaped carbon molecules called fullerenes, as well as carbon nanotubes, both of which are of great interest in the field of nanotechnology.²⁹ Soot plays a role in boilers and furnaces that rely on

flame radiation to transfer heat to the walls to generate steam, but the same mechanism makes these particles harmful for internal-combustion engines, where such heat losses decrease efficiency and require that high-temperature materials be used.

Figure 2.2 shows how soot forms within fires and becomes smoke.²⁹ Combustion requires fuel, which is most often made from long, complex chains of carbon and hydrogen atoms. When a flame is lit, the heat breaks apart these hydrocarbons in a process called pyrolysis. The smaller typically carbon containing fragments that result are often radicals, highly inclined toward chemical reactions, in particular oxidation:

Oxygen combines with the carbon and hydrogen radicals to produce carbon dioxide and water, releasing heat in the process. However, some of the radicals react with one another, rather than with oxygen, forming rings of carbon called polycyclic aromatic hydrocarbons. These newly formed compounds continue to grow into carbon-rich lattices and then into full-fledged particles, which agglomerate into long chains that resemble strings of beads. As these soot masses travel upward inside a flame, they react with oxygen molecules, which can break off pieces and cause the particles to incandesce more brightly, creating the flame's bright yellow glow. Whether or not the soot will be fully burned in this way (completely transformed into carbon dioxide and water) before leaving the flame depends on the type of fire being studied. If not completely burned, the residual soot is released as smoke.

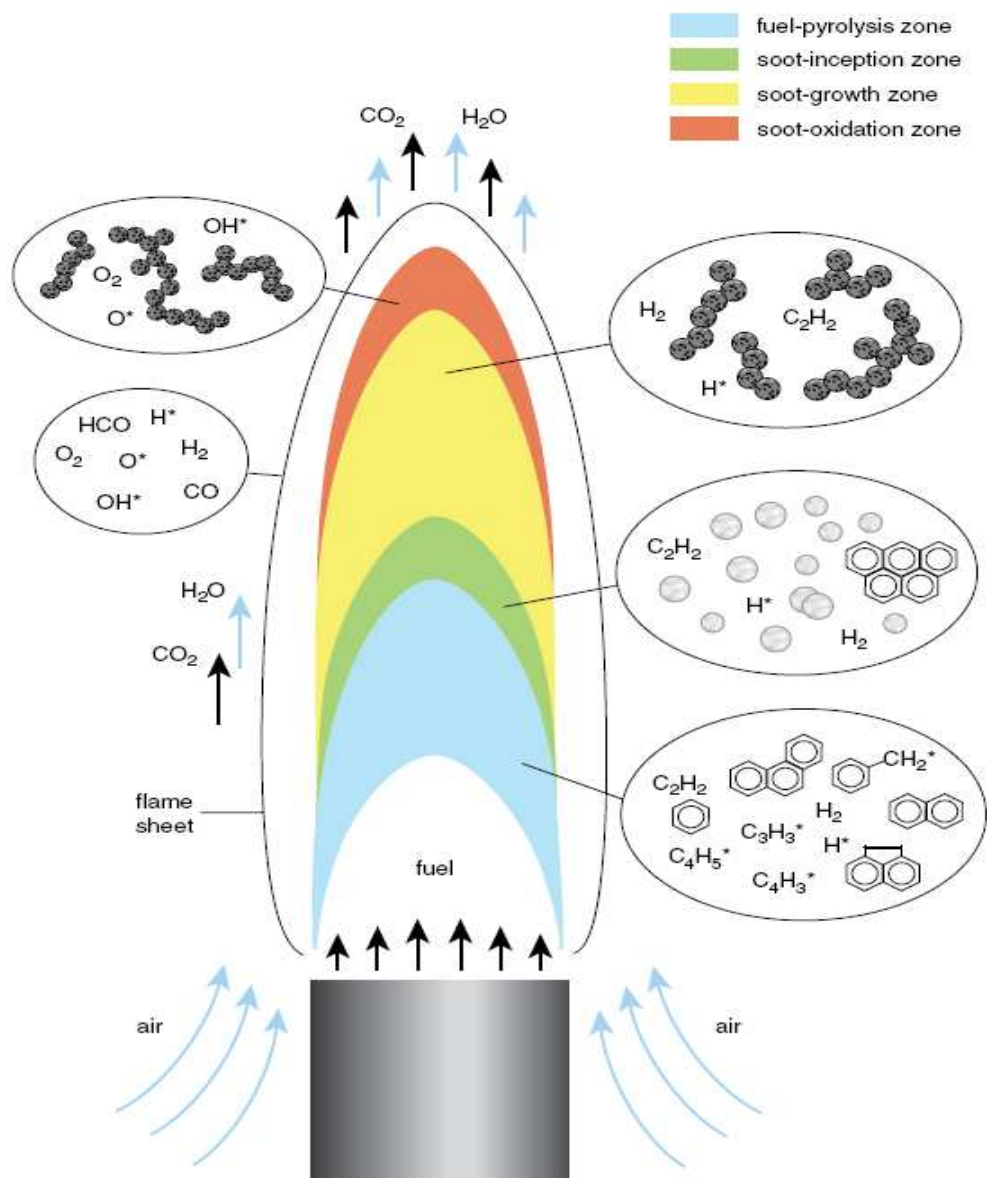


Figure 2.2: Pyrolysis of hydrocarbons.

Another family of colloidal carbons similar to soot but with a much higher surface area to volume ratio is carbon black.³⁰ Carbon black is a material produced by the incomplete combustion of heavy petroleum products such as coal tar, ethylene cracked tar, or small amount from vegetable oil. It was a form of amorphous carbon that has a high surface area to volume ratio, and as such it is one of the first nanomaterials to find commercial use. Its surface area to

volume ratio is low compared to activated carbon. Carbon black is used as a pigment and reinforcement in rubber and plastic products.³¹

2.3 Formation of carbon spheres

Carbon atoms when linked together can form three types of graphitic rings i.e. hexagons with zero curvature, pentagons with positive curvature and heptagons with negative curvature (Figure 2.3).³¹ Pairing of the pentagonal and heptagonal carbon rings with the hexagonal carbon rings can further result in formation of many structures with different geometric configurations.³² A perfectly closed shell structure like C_{60} can be formed if 12 pentagonal carbon rings are introduced in the hexagonal network (Euler's theorem); a pure hexagonal network alone cannot form a closed shell.³¹

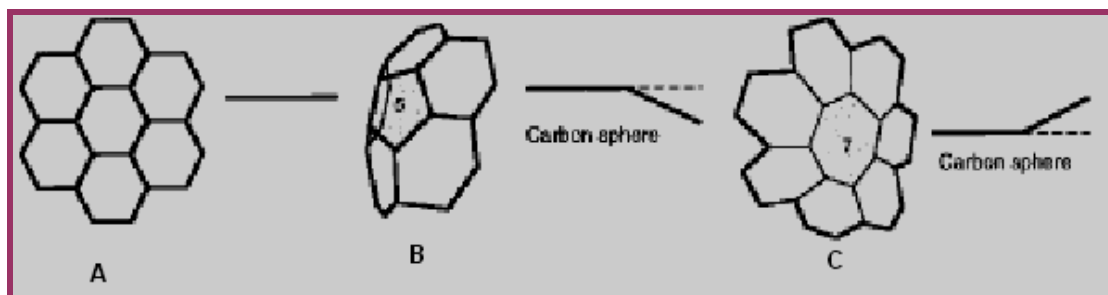


Figure 2.3: Carbon ring structures in graphitic flakes. (a) Hexagonal (zero curvature) (b) pentagonal (positive curvature) and (c) heptagonal (negative curvature).

A carbon sphere is believed to be nucleated from a pentagonal carbon ring which grows to a quasi-icosahedra spiral shell carbon particle (Figure 2.4).³³ Carbon atoms have only four neighbours; therefore the carbon atom located at the edges cannot be shared by three graphitic flakes simultaneously. This results in formation of a gap at the edges of the carbon rings.³¹ It has been shown that the surface of the sphere is composed of unclosed graphitic flakes.³⁴ Usually a sphere with a diameter of less than 40 nm shows a spiral growth. A large graphitic carbon sphere, with the exception of its central core which has a spiral shape, is made up of graphitic flakes containing pentagonal-heptagonal (P-H) pairs.³¹

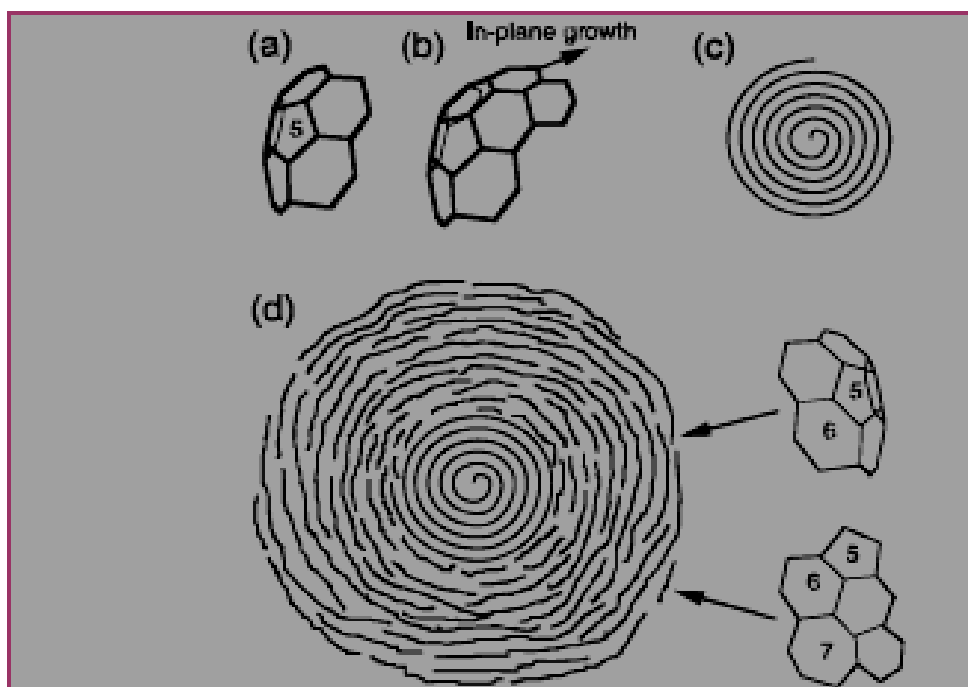


Figure 2.4 Schematic diagrams representing growth of a carbon sphere.

(a) Nucleation of a pentagon (b) formation of a spiral shell carbon particle (c) growth of a large size carbon sphere and (d) graphitic carbon sphere

2.4 Synthetic techniques

The commonly used methods for the synthesis of carbon spheres are described below.

Arc Discharge

In this method, carbon is vaporized from a graphite rod, generating a plasma of carbon which condenses on a second rod of opposite charge in an inert gas environment. A current is passed between two graphite rods, forming a hot, bright electric arc which vaporizes one of the graphitic rods. One of the rods acts as the anode, where vaporization occurs, and the other acts as the cathode, where condensation occurs.³⁵ This method large mainly produces nanotubes, but can also produce some spherical carbon material.³⁶

Laser Ablation

Laser ablation is the process of removing material from a solid (or occasionally liquid) surface by irradiating it with a laser beam. At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimes. At high laser flux, the material is typically converted to a plasma.³⁷ In March 1995 Guo *et al.*³⁸ reported the use of a laser to ablate a block of pure graphite, and later graphite mixed with catalytic metal.³⁹ In the process a graphite target is vapourized at high temperatures using a high power laser, forming 'soot' which is collected using a water cooled collector.

Chemical Vapour Deposition

The chemical vapour deposition (CVD) method can be used to prepare carbon spheres ranging from 60 nm - 1 μm by direct pyrolysis of a diverse range of small hydrocarbons with two to eight carbon atoms in their chains without using a catalyst. The carbon sphere growth is controlled by the reaction time, feed rate and reaction temperature.⁴⁰ Chemical vapour deposition reactors can be either horizontal or vertical in design. The orientation assigned to the reactor refers to the

orientation of the flow within the reactor. The effects of buoyancy and inertial forces flow within the reactor differentiate between these two types of the reactors.⁴¹

Polymerization reactions

Carbonaceous spheres or mesocarbon micro-beads (MCMB) can be prepared from pitch or polymeric materials in large quantities using various methods, such as the direct polymerization from pitch,⁴² an emulsion method,⁴³ and a suspension method.⁴⁴ However, the carbon particles from mesophase pitch are of relatively large size, normally 10–40 μm , and have a wide distribution in size. This method of preparation can produce hollow carbon particles with a narrow size distribution, ranging in a diameter from 3 to 5 μm . Submicrometer-size spherical polymer particles of uniform size are readily prepared by emulsifier-free emulsion polymerization. In addition, it is well known that polyacrylonitrile produces carbonaceous material.⁴⁵

2.5 N- and B-doping of carbon nanostructures

Since the discovery of carbon nanomaterials, there has been an interest in doping of tubes.⁴⁶ Doping of carbon entails the substitution of a carbon atom with another element such as boron and/or nitrogen. Doping of heteroatoms into graphite-like carbon structures is believed to modify the electronic nature and, thereby the electrical conductivity properties of the graphite structure.⁴⁷ For example N-doping may lead to the formation of electron-excess *n*-type semiconducting nanostructures, due to the presence of the lone pairs of electrons on nitrogen, conjugating with the delocalized pi system of the standard graphite sheet. Electron deficiency in graphite can also be achieved by incorporating boron, which acts as an acceptor. B-doping may lead to an electron-deficient *p*-type semiconducting nanostructure.⁴⁶

There have been several reports of N-doping into CNTs.⁴⁷⁻⁴⁹ N-doping into CNTs has mostly been conducted using chemical vapor deposition during CNT growth. Manashi *et al.*⁴⁷ reported N-doped multi-walled CNTs (MWCNTs) by thermal CVD using acetylene over Fe and Co catalysts. The composition of the C-N in the tubes varied between C₁₀N and C₃₃N depending on the catalyst. Yang *et al.*⁴⁸ successfully prepared a double coaxial structure of N-doped MWCNTs by using the template technique with porous anodic alumina oxide as a template. They mentioned that the resulting MWCNTs had not only a double-stack coaxial structure but also dual physicochemical properties.

Liu *et al.*⁴⁹ also demonstrated that N-doped vertically aligned MWCNTs could be synthesized by pyrolysis of pyridine with ferrocene as the catalyst in an NH₃ atmosphere or a mixture of NH₃ and Ar. It is well known that the doping of CNTs with various elements such as nitrogen (N), potassium, and boron is a significant and effective method to tailor both chemical and electronic properties of CNTs. In particular, N-doping in CNTs has been studied intensely because it can induce a transformation of the (C) atomic network of carbon.^{50,51} Also, the N-doping process is an effective way to generate carbon nanostructures. Jang *et al.*⁵² reported on the effects of N-doping on the structure and crystallinity of bamboo-shaped MWCNTs by means of X-ray photoelectron spectroscopy (XPS). In their previous work, they found that the N concentration

was obtained in the range from 0.4 to 2.4% by controlling the $\text{NH}_3/\text{C}_2\text{H}_2$ flow ratio during CNT growth. They also observed that the bamboo-shaped MWCNTs showed a shorter compartment distance at higher N concentrations.⁵³

Recently, Kim *et al.*⁵⁴ reported the synthesis of N-doped double-walled CNTs (DWCNTs) using catalytic CVD. They investigated the electronic structures of N-doped DWCNTs by employing synchrotron XPS. Panchakarla *et al.*⁵⁵ also reported that the diameters of the N-doped DWCNTs appeared to depend on the N source and the reaction conditions. Nevertheless more study on the structural change of N-doped CNTs is still necessary.

Eccles *et al.*⁵⁶ studied the influence of B- and N- doping levels on the quality and morphology of CVD diamonds. They grew diamond films by hot filament and microwave plasma assisted CVD using precursor gas mixture of 1% methane in hydrogen with additional nitrogen and boron dopants. N incorporation in the diamond network induces structural changes that lead to an increase in the sp^2 fraction of the material and therefore enhances the conductivity.

Part 2: Polymerization of thiophene

2.6 Thiophene

Thiophene was discovered by Viktor Meyer in 1883 as a contaminant in benzene.⁵⁷ In the fractional distillation of coal tar and petroleum, it was found in relatively large amounts. Thiophenes are stable to alkali and other nucleophilic agents, and are relatively resistant to disruption by acids.⁵⁸ Thiophene is a colourless liquid at room temperature with a mildly reminiscent smell of benzene. It is considered aromatic, with the degree of aromaticity less than that of benzene. The participation of the lone electron pair on sulfur in the delocalized pi electron system is significant.⁵⁹

Thiophenes are produced in many reactions involving sulfur sources and hydrocarbons, especially unsaturated hydrocarbons. For example; reactions of acetylene and elemental sulfur, were first attempted by Viktor Meyer. They are also classically prepared by the reaction of 1,4-diketones with sulfiding reagents such as P_4S_{10} . Specialized thiophenes can be synthesized via the Gewald reaction, which involves the condensation of two esters in the presence of elemental sulfur.⁶⁰

Thiophenes are used as synthetic intermediates, taking advantage of the susceptibility of the carbon atoms adjacent to S towards electrophilic reactions. They are a recurring building block in organic chemistry with applications in pharmaceuticals. The benzene ring of a biological active compound can be replaced by a thiophene without loss of activity.⁵⁹

2.7 Polythiophene

Polythiophenes (PTs) result from the polymerizations of thiophene. The polymer is formed by linking thiophene through its 2,5 positions.⁶¹ The study of polythiophenes has intensified over the last three decades. The maturation of the field of conducting polymers, including PTs, was confirmed by the award of the 2000 Nobel Prize in Chemistry to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa for the discovery and development of conductive polymers.⁶²

The most notable property of these materials, electrical conductivity, results from the delocalization of electrons along the polymer backbone. The term “synthetic metals” is thus used to describe these conducting non-metallic polymers.⁶³ Conductivity is not the only interesting property resulting from the electron delocalization. The optical properties of these materials respond to environmental stimuli, with dramatic colour shifts in response to changes in temperature, solvent, binding to other molecules and applied potentials. Colour and conductivity changes are induced by the twisting of the polymer backbone leading to the disruption of the conjugation.

Polythiophenes are some of the most studied conducting conjugated polymers. This is as a result of their excellent environmental and thermal stability. They are also commercially available and highly soluble in organic solvents.⁶⁴

2.7.1 Synthesis of polythiophenes

Polythiophenes can be synthesized electrochemically, by applying a potential across a solution of the monomer to be polymerized, or chemically, using oxidants or cross-coupling catalysts.

Electrochemical synthesis

The electrochemical polymerization of thiophene in acetonitrile was reported for the first time by Tourillon in early 1980s. Polythiophene is conveniently prepared in the conducting state by electrochemical oxidation of bithiophene.⁶⁵ A potential is applied across a solution containing thiophene and an electrolyte, producing a conductive polythiophene film on the cathode. As shown in Figure 2.5, the oxidation of a monomer produces a radical cation which can then couple with a second radical cation to form a dication dimer or with another monomer to produce a radical cation dimer.⁶⁶ The method is convenient, since the polymer does not need to be isolated and purified, but the disadvantage is that a crosslinked structure is produced.

The quality of the polythiophene film produced is affected by a number of factors. These include the electrode material, current density, temperature, solvent, monomer concentration, presence of water, and electrolyte.⁶⁷ The potential required to oxidize the monomer depends upon the electron density in the thiophene ring pi-system. Lower oxidation potentials are due to electron-donating groups, and electron-withdrawing groups increase the oxidation potential. Steric hindrance resulting from branching at the alpha carbon of thiophene inhibits the polymerization.

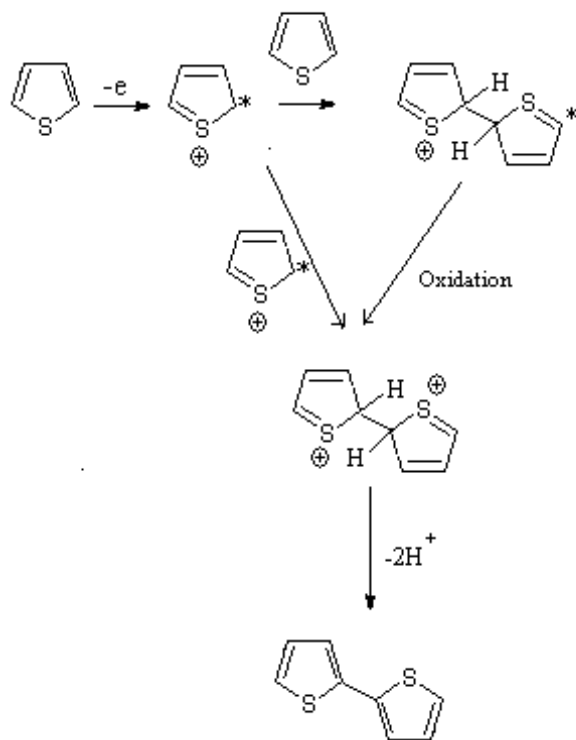


Figure 2.5: Schematic diagram of initial steps in the electropolymerization of thiophene.

Chemical synthesis

Chemical synthesis is the preferred method for the preparation of electrical conducting polythiophenes and other electrical conducting polymers with defined structures. Chemical synthesis offers two advantages compared with the electrochemical synthesis of polythiophenes: a greater selection of monomers, and, if the proper catalyst is used, the ability to synthesize perfectly regioregular substituted polythiophenes. Regioregular PT can be synthesized by catalytic cross-coupling reactions of bromothiophenes, while polymers with varying degrees or regioregularity can simply be synthesized by oxidative polymerization using a FeCl_3 catalyst, Figure 2.6.⁶⁸

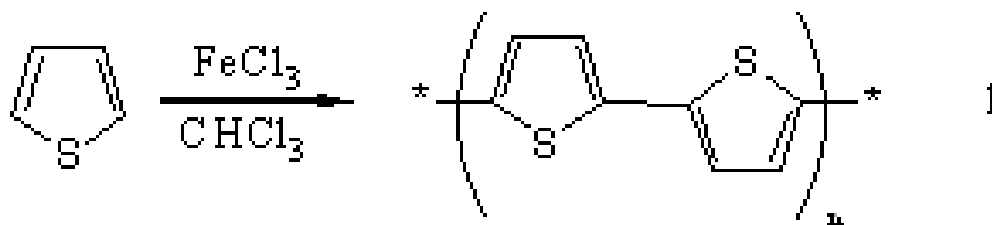


Figure 2.6: Ferric chloride oxidative polymerization of thiophene.

2.7.2 Mechanism of conductivity

In conductive polymers, such as polythiophene, electrons are delocalized along the conjugated backbone through overlap of pi-orbitals, resulting in an extended pi-system with a filled valence band.⁶⁶ The removal of electrons (p-doping) and addition of electrons (n-doping) to the pi-system leads to the formation of a charged unit called a bipolaron. A bipolaron is responsible for the macroscopically observed conductivity of the polymer.

Depending on the level of doping, the polymer can be conducting if the levels are high (20-40%) and semiconducting if level is low (1%). Oxidation of the conducting polymer, via p-doping; can be achieved electrochemically or chemically. Reduction, via n-doping is done electrochemically.⁶⁹ Different reagents have been used to dope polythiophenes. These include iodine and bromine for high conductivities and organic acids such as propionic acids and sulfonic acids for low conductivities.⁷⁰ It has also been found that the latter show higher environmental stabilities when compared to the former. Oxidative polymerization with ferric chloride can result in doping by residual catalyst.

2.7.3 Optical properties of polythiophene

The optical properties of the polythiophene are due to their extended pi-system. The conjugation relies on the aromatic rings, which, in turn requires the thiophene rings to be coplanar. The number of coplanar rings determines the conjugation length; the longer the conjugation length, the lower the separation between adjacent energy levels, and the longer the absorption

wavelength. The twist in the backbone reduces the conjugation length and the separation between energy levels increases, this will result in a shorter absorption wavelength.⁷¹

To determine the maximum effective conjugation length, one requires the synthesis of a regioregular polythiophenes of defined length. The absorption band in the visible region is increasingly red shifted as the conjugation length increases, and the maximum effective conjugation length is calculated as the saturation point of the red-shift.⁷² Reaction conditions, including solvents, temperatures, and dissolved ions, can cause the conjugated back bone to twist, reducing the conjugation length and causing the absorption band to shift.

2.7.4 Uses of polythiophenes

Polythiophenes and some of its derivatives are insoluble and infusible. These features limit considerably their application potential in industry and technology.⁷³ To overcome the disadvantages, several strategies for the modification of polythiophenes have been developed. These include the appropriate modification of the monomer structure prior to polymerization, and the preparation of copolymers, metal composites, and polymer composites.⁷⁴

A number of applications have been proposed for conducting polythiophenes, but none has been commercialized. Applications include field-effect transistors,⁷⁵ solar cells, photochemical resistors, batteries, chemical sensors, diodes and nonlinear optic devices.⁷⁶

In general there are two categories of application viz, static and dynamic⁷⁷

1. **Static applications:** they rely upon the intrinsic conductivity of the materials, combined with their ease of processing and material processing common to polymeric materials.
2. **Dynamic applications:** they utilize changes in the conductive and optical properties, resulting either from application of electric potentials or from environmental stimuli.

The use of polythiophenes as sensors responding to an analyte has also been the subject of intense research. The functionalization of polythiophenes with synthetic receptors helps detect metal ions and chiral molecules in biosensor applications.⁷⁸

Part 3: Carbon/polythiophene composites

2.8 Nanocomposites

Nanocomposites can be defined as multiphase materials where one or more of the phases have a least one dimension of order 100 nm or less. Most nanocomposites that have been developed and that have demonstrated technological importance, have been composed of two phases can that be microscopically classified into three principal types (Figure 2.7) ⁷⁹

- Nanolayered composites: composed of alternating layers of nanoscale dimensions
- Nanofilamentary composites: composed of a matrix with embedded and generally aligned nanoscale diameter filaments
- Nanoparticulate composites: composed of a matrix with embedded nanoscale particles

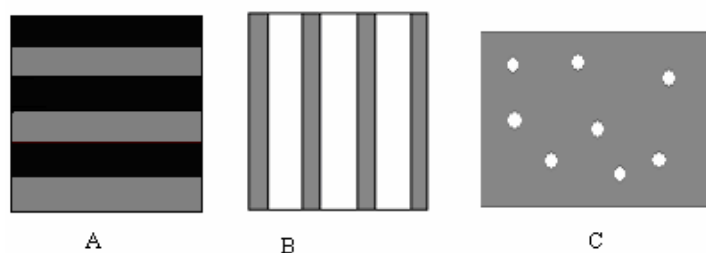


Figure 2.7: Schematic representation of nanocomposite materials: nanolayered (A), nanofilamentary (nanowires) composites (B) and nanoparticulates (C).

As with the conventional composites, the properties of nanocomposites can display synergistic improvements over those of the component phases individually. However by reducing the physical dimensions of the phases down to the nanometer length scale, unusual and often enhanced properties can be realized. An important microstructural feature of nanocomposites is their large interphase surface area to volume ratio. Large surface areas can result in novel and often enhanced properties that can be exploited technologically.⁸⁰

In terms of their engineering applications, nanocomposites can be classified⁷⁹ either as

- **Functional materials** based on their electrical, magnetic, and/or optical behavior
- **Structural materials** based on the mechanical properties.

Many researchers have tried to incorporate carbon materials in polymer matrices to tailor electrical properties suitable for different applications such as electronic devices, semiconductor components, and circuit boards, because different applications normally require specific levels of conductivity.⁸⁰ For instance, a low level of conductivity is enough to give protection against electrostatic discharge, whereas a high level ($\leq 10^4$ ohm/cm) is required to protect against electromagnetic interferences and emission of interfering radiation.

The effective use of carbon materials in composite applications depends on the ability to disperse the material uniformly throughout the matrix without reducing their aspect ratio.⁸¹ To overcome the difficulty of dispersion, mechanical/physical methods such as ultrasonication, high shear mixing, melt blending and surfactant addition have been used.

In 2001, Dupire *et al.*⁸² patented a method for the production of reinforced polymer, in which both a polymer chain and carbon nanotubes were oriented and dispersed by stretching the nanotube-polymer mixture in a molten state using a high shear mixer. However the resulting nanocomposite exhibited limited transparency in the visible range. Harmon *et al.*⁸³ produced conductive and transparent CNT-polymer composites through a combination of sonication, *in-situ* polymerization, dissolution and film casting. Recently, polymer nanocomposites appeared as the subject of mechanical actuation studies. Ounaries *et al.*⁸⁴ developed a technique for making actuating composite materials with polarizable moieties (polyimide) and CNTs using *in-situ* polymerization under sonication and stirring. Kong *et al.*⁸⁵ demonstrated chemical sensor applications based on individual SWNTs. They found that the electrical resistance of a semi-conducting SWNT changed dramatically upon exposure to gas molecules such as NO₂ and NH₃. Sensors based on carbon nanotubes have been preferred because of the fast response and the higher sensitivity they exhibit at room temperatures over existing electrical sensor materials including carbon black-polymer composites operating at high temperatures.

Carbon black is a common polymer additive used for reinforcement and enhancing physical properties, such as conductivity and density.⁸⁶ Properties of CB particles and composites based on this material have been intensively studied in the last 30 years.⁸⁷ There are a lot of reports and

publications about its electrical properties mainly in composites based on polymer-CB in which the electrical charges are carried through “networks” of conductive particles (CB) dispersed into the polymeric matrix.⁸⁸ Choosing the appropriate polymeric matrix, these polymeric composites can have potential application as gas sensors .^{89,90}

San Juan-Farfán *et al.*⁹¹ analyzed the electrical properties of spume polystyrene-carbon black (PSU-CB) composites prepared by a sonication mixing technique using 3-20 %wt of carbon black (CB) as the conductive material. The results showed that the carbon black modified the electrical properties of polystyrene, improving the electrical resistivity from 10^{14} to 10^6 S/cm for pure polystyrene and for composites containing 21 % of carbon black, respectively.

Martinez Salazar *et al.*⁹² studied the morphology and structure of conductive polyethylene-carbon black composites by elongational-flow injection molding. The study of some physical properties of vinylpyridine carbon-black composites was conducted by Soliman and Sayed.⁹³ They prepared samples of a 2-vinylpyridine oligomer and polymer by a chemical method. The polymer and the oligomer were hot-pressed with different weight percentage of CB. It was found that the activation energy for different samples decreased with increasing CB percentage, as did the optical band gap.

2.9 Fabrication of carbon nanocomposites

Nanocomposites have been fabricated to improve material properties such as electrical conductivity, mechanical strength, radiation detection, optical properties, thermal stability, etc. Among these, improving the electrical and mechanical strength properties of composites has been reported to a great extent. In nanocomposites a homogenous dispersion of carbon nanostructures is required.⁹⁴ However, pristine carbon nanostructures are bundled due to van der Waals interactions and are insoluble in organic solvents or water, making their processing difficult. Research shows that simple polymer-nanostructure blends result in a composite with a poor dispersion of nanostructures, which compromises the expected performance. Therefore more work has to be done to develop methods of chemical modification and functionalization techniques to make carbon nanostructures more processable.

The carbon nanostructure surface modification may entail covalent or noncovalent interactions.⁹⁵ In covalent functionalization, the nanostructure surface requires highly reactive species such as azomethine ylides or fluorine. In noncovalent functionalization, the functional molecules interact with the nanostructure surface *via* van der Waals forces, including hydrophobic and π - π interactions. The surface functionalization of carbon may commence from the nanostructure surface defects, which are in the form of carboxylic acid groups due to the oxidative conditions used in purifying the nanostructures. These acidified nanostructures can be functionalized with molecules bearing amino or hydroxylic groups.⁹⁶

The conditions that are used to functionalize carbon spheres are similar, but not identical, to those used for carbon nanotubes. The difference may lie in the surface chemistry of the material. Different ways to functionalize carbon nanostructure are discussed below:

Covalent functionalization

Covalent functionalization occurs through reactions of the p-conjugated skeleton of carbon nanostructures. The procedure has been widely investigated and the methodology⁹⁷ has produced an array of modified nanostructures (e.g. carbon nanotubes) bearing small molecules, polymers and inorganic species. Several covalent functionalization strategies exist to induce functionalization. These include defect site creation and functionalization from the defects, creating carboxylic acids on the endcaps of carbon nanotubes and subsequent derivatization from acids, and also covalent sidewall functionalization.⁹⁶

The sidewall functionalization of carbon nanostructures depends strongly on tube/sphere diameters. For example, single wall carbon nanotubes with a smaller diameter have more reactive sidewalls than those with larger diameters. It is also important to note that covalent functionalization causes changes to properties of the nanostructures. These changes can be dramatic and permanent and are not always controllable. As a result, the desired multifunctionality of carbon nanostructures may be compromised. Moreover, covalent functionalization is not amenable to scale-up for high volume and high rate production.⁹⁶

Noncovalent functionalization

This approach focuses on the non-covalent bonding interactions of molecules, and by doing so it examines the weaker and reversible non-covalent interactions between molecules. These forces include hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π - π interactions and electrostatic effects. These types of studies constitute the field of supramolecular chemistry.⁹⁷

The study of non-covalent interactions is crucial to understand many biological processes from cell structure to vision, that rely on these forces for structure and function. Biological systems are often an inspiration for supramolecular research. Important concepts that have been demonstrated by supramolecular chemistry include molecular self-assembly, molecular

recognition, host-guest chemistry and dynamic covalent chemistry. The emerging science of nanotechnology has also had a strong influence on the subject of non-covalent functionalisation, with building blocks such as fullerenes, nanoparticles, and dendrimers involved in synthetic systems.

Factors that control non-covalent functionalization include thermodynamics and the environment.⁹⁸ Unlike in covalent bond-forming chemistry the rate of bond formation is not increased at higher temperatures. However, low temperatures can be problematic, due to molecule distortion into thermodynamically disfavored conformations. The molecular environment is also of prime importance for the operation and stability of the non-covalent system. The choice of the solvent is crucial, because many solvents have electrostatic, strong hydrogen bonding, and charge transfer capabilities, and are therefore able to become involved in complex equilibria with the system.

References

1. Pradhan D., Sharon M. *Materials Science and Engineering*. **B 96** (2002) 24
2. Smith W. R. *Encyclopaedia of chemical technology*. **3** (1949) 39
3. Saito S., *Science*, **278** (1997) 77
4. Karim M. R., Lee C. J., Lee M. S. *Journal of Polymer Science*. **44** (2006) 5283
5. Iijima S. *Nature*. **354** (1991) 56
6. Jin Y. Z., Gao C., Hsu W. K., Zhu Y., Huczko A., Bystrzejewski M. *Carbon*. **43** (2005) 1944
7. Dresselhaus M. S., Dresselhaus G., Eklund P. C. *Science of fullerenes and carbon nanotubes*. **13** (1996) 1
8. Schwarz J. A., Contescu C. I., Putyera K. *Technology & Engineering*. **125** (2004) 4014
9. Kroto H. W., Heath J. R., O'Brien S. C., Curl R. F., Smalley R. E. *Nature*. **318** (1985) 162
10. Ugarte D. *Nature*. **359** (1992) 707
11. Inagaki M. *Carbon*. **31** (1997) 711
12. Serp Ph., Feurer R., Kalck Ph., Kihn Y., Faria J.L., Figueiredo J. L. *Carbon*. **39** (2001) 615
13. Okotrub A. V., Bulusheva L. G., Kuznesov K. L., Butenko Y. V., Chuvilin A. L., Heggie M. I. *J. Phys. Chem. A* **105** (2001) 9781
14. Joachim C., Gimzewski J. K., Aviram A. *Nature*. **408** (2000) 542
15. Park H., Park J., Lim A.L., Anderson E.H., Alivisatos A.P., McEuen P. L., *Nature*. **408** (2000) 57
16. Iijima S. *J. Cyst. Growth*. **50** (1980) 675
17. Gorelik T., Urban S., Falk F., Kaiser U., Glatzel U. *Chem. Phys. Lett.* **373** (2003) 642
18. Roddatis V. V., Kuznetsov V. L., Butenko Y. V., Su D. S., Schlogl R. *Phys. Chem.* **4** (2002) 1964
19. Troiani H. E., camocho-Bragago A., Armendariz V. *J. Chem. Mater.* **15** (2003) 1029
20. Esumi K., Eshima S., Murakami Y., Honda H., Oda H. *Physicochemical and Engineering Aspects* **108** (1996) 113
21. Pradhan D., Sharon M. *Materials Science and Engineering*. **96** (2002) 24

22. Inagaki M., Washiyama M., Sakai M. *Carbon*. **26** (1988) 169
23. Kamegawa K., Yoshida H. *Carbon*. **35** (1997) 631
24. Wang Y.G., Chang Y.C., Ishida S., Korai Y., Mochida I. *Carbon*. **37** (1999) 969
25. Flandrois S., Simon B. *Carbon*. **37** (1999) 165
26. Kang Z. C., Wang Z. L. *Philos. Mag.* **74** (1996) 59
27. Liu X. Y., Huang B. C., Coville N. J. *Carbon*. **40** (2002) 2791
28. Nieto-Márquez A., Valverde J. L., Keane M. A., *Appl. Catal. A: Gen.* **332** (2007) 237
29. [http://www.americanscientist.org/ IssueTOC/issue/961](http://www.americanscientist.org/IssueTOC/issue/961), 2007 May-June
30. http://carbon-black.org/uer_guide.html.
31. Brady G. S., Henry R. C. *Materials Handbook*. **11** (1979) 134
32. Iijima S., Ichihashi T., Ando Y. *Nature*. **356** (1992) 776
33. Kroto H. W., McKay K. *Nature*. **331** (1988) 328
34. Wang Z. L., Kang Z. C. *J. Phys. Chem.* **100** (1996) 17725
35. Bethune D. S., Kiang C. H., de Vries M., Gorman G., Savoy R., Vazquez J., Beyers R. *Nature*. **363** (1993) 605.
36. Qiao W. M., Song Y., Lim S. Y., Hong S. H., Yoon S. H., Mochida I., Imaoka T. *Carbon* **44** (2006) 187
37. Thess A., Lee R., Nickolaev P., Dai H. J., Petit P., Robert J., Xu C. H., Lee Y. H., Kim S. G., Rinzler A. G., Colbert D. T., Scuseria G. E., Tomanek D., Fisher J. E., Smalley R. E. *Science*. **273** (1996) 483.
38. Guo T., Nikolaev P., Rinzler D., Tomanek D.T., Colbert D.T., Smalley R. E. *J. Phys. Chem.* **99** (1995) 10694
39. Guo T., Nikolaev P., Thess A., Colbert D. T., Smalley R. E. *Chem. Phys. Let.* **243** (1995) 49.
40. Qian H., Han F., Zhang B., Guo Y., Yue J., Peng B. *Carbon*. **42** (2004) 761
41. Totten G. E., Funatani K., Xie L. *Technology & Engineering*. **1** (2004) 966
42. Korai Y., Wang Y. G., Yoon S. H., Ishid S., Mochida I., Nakagawa Y., Matsumura Y. *Carbon*. **34** (1996) 1156
43. Kodama M., Fujiura T., Ikawa E., Esumi K., Meguro K., Honda H. *Carbon*. **29** (1991) 43
44. Yoon S. H., Park Y. D., Mochida I. *Carbon*. **30** (1992) 781

45. Bailey J.E., Clarke A.J. *Nature*. **234** (1971) 529
46. Stephen O., Ajayan P. M., Colliex C., Redlich P., Lambert J. M., Bernier P., Lefin P. *Science*. **266** (1994) 1683
47. Manashi N., Satishkumar B. C., Govindaraj A., Vinod C. P., Rao C. N. R. *Chem Phys Lett*. **322** (2000) 333
48. Yang Q., Xu W., Tomita A., Kyotani T. *J Am Chem Soc*. **127** (2005) 8956
49. Liu J., Webster S., Carroll D. L. *J Phys Chem. B* **109** (2005) 15769
50. Nevidomskyy H., Csányi G., Payne M. C. *Phys Rev Lett*. **91** (2003) 105502
51. Che R. C., Peng L. M., Wang M. S. *Appl Phys Lett* **85** (2004) 4753
52. Jang J. W., Lee C. E., Lyu S. C., Lee T. J., Lee C. J. *Appl Phys Lett*. **84** (2004) 2877
53. Chun K. Y., Lee H. S., Lee C. J. *Carbon*. **47** (2009) 16 9
54. Kim S. Y., Lee J., Na C. W., Park J., Seo K., Kim B. *Chem Phys Lett*. **413** (2005) 300
55. Panchakarla L. S., Govindaraj A., Rao C. N. R. *ACS Nano* **1** (2007) 494
56. Eccles A. J., Steele T. A., Afzal A., Rego C. A., Ahmed W., May P. W., Leeds S. M. *Thin Solid Films*. **333-344** (1999) 637-63
57. Meyer V. *Berichte der Deutschen chemischen Gesellschaft*. **16** (1883) 1465
58. Sumpter W. C. *Chemical Reviews*. **34** (1944) 393
59. Lednicer D. *Wiley Interscience*. **6** (1999) 187
60. Sabnis R. W., Rangnekar D. W., Sonawane N. D. *J. Heterocyclic Chem*. **36** (1999) 333
61. Roncali J. *Chem. Rev*. **92** (1992) 711
62. <http://www.azom.com/SearchResults.asp?MaterialKeyword=Polythiophenes>
63. <http://en.wikipedia.org/wiki/Polythiophenes>
64. Ganapathy H. S., Kim J. S., Jin S. H, Gal Y. S., Lim K. T. *Synthetic Metals*. **156** (2006) 70
65. Tourillon G., Garnier F. *J Electroanal Chem*. **135** (1982) 173.
66. Hoeve W., Wynberg H., Havinga E. E., Meijer E. W. *J. Am. Chem. Soc*. **113** (1991) 5887
67. Ruckenstein E., Park J. S. *Synth. Met*. **44** (1991) 293
68. McCullough R. D., Tristramnagle, S., Williams, S. P., Lowe, R. D., Jayaraman M. *J. Am. Chem. Soc*. **115** (1993) 4910

69. Lopenon M. T., Taka T., Laakso J., Väkiparta K., Suuronen K., Valkeinen P., Österholm J. E. *Synth. Met.* **41** (1991) 479
70. Goto H., Yashima E., Okamoto Y. *Chirality* **12** (2000) 396
71. Izumi T., Kobashi S., Takimiy K., Aso Y., Otsubo T. *J. Am. Chem. Soc.* **125** (2003) 5286
72. Salamone J. C. *Technology & Engineering.* **6** (1996) 4782
73. Garnier F. *Electronic Materials.* Wiley VCH (1998) 559
74. Harrison M. G., Friend R. H. *Electronic Materials.* Wiley VCH (1998) 515
75. Martina V., Pigani L., Terzi F., Ulrici A., Zanardi C., Seeber R. *A&B Chemistry*, **387** (2007) 2101
76. Bäuerle P., Scheib S. *Adv. Mater.* **5** (1993) 848
77. Cammarata R. C. *Chemistry and Material Science.* **8** (2004) 199
78. Usuki A., Kawasumi M., Kojima Y., Okada A., Kurauchi T., Kamigaito O. *Journal of Materials Research.* **8** (1993)1174
79. Ajayan P. M., Schadler L. S., Braun P. V., *Nanocomposite science and technology.* **63** (2003) 331
80. Mylvaganam K., Zhang L. C., *Recent Patents on Nanotechnology* **1** (2007) 59
81. Smalley R. E., Hauge R. H., Kittrell W. C., Sivarajan R., Strano M. S., Bachilo S. M., Weisman R. B. US20067074310 (2006)
82. Dupire M., Michel J. US20016331265 (2001)
83. Harmon J. P., Clayton L. M., Muisener P. US20067094367 (2006)
84. Ounaies Z., Park C., Harrison J. S., Holloway N. M., Draughon G. K., US2006084752 (2006).
85. Kong J., Franklin N. R., Zhou C., Chapline M. G., Peng S., Cho K., Dai H. *Science.* **287** (2000) 622
86. Takada T., Nakahara M., Kumagai H., Sanada Y. *Carbon.* **34** (1996) 1087
87. Donnet J. B., Bansal R. L., Wang M. J. *Carbon Black.* Marcel Dekker, New York 2nd ed (1993) 221
88. Carmona F. *Physica A* **157** (1989) 461
89. Márquez A., Uribe J., Cruz R. *J. Appl. Poly. Sci.* **66** (1997) 2221

90. Mark C., Lonergan Eric J., Severin Brett J., Doleman Sara A., Beaber Robert H., Grubbs Nathan S. *Chem. Mater.* **8** (1996) 2298
91. San Juan-Farfán R., Hernández-López S., Martínez-Barrera G., Camacho-López M. A., Viguera-Santiago E. *Phys. Stat. Sol.* **2** (2005) 3762
92. Martinez S. J., Bayer R. K., Ezquerro T. A., Baltá Calleja F. J., *Colloid Polym Sci.* **267** (1989) 409
93. Soliman L. I., Sayed W. M. *Egypt. J. Sol., Vol.* **25** (2002) 103
94. Kausala M., Zhang L. C. *Recent Patents on Nanotechnology*, **1** (2007) 59
95. Khabashesku V. N., Billups W. E., Margrave J. L. *Acc. Chem. Res.* **35** (2002) 1087
96. Hirsch A. *Angew Chem Int Ed* **41** (2002) 1853
97. Riggs J. E., Guo Z., Carroll D. L., Sun Y. P. *J Am Chem Soc.* **122** (2000) 5879
98. Oshovsky G. V., Reinhoudt D. N., Verboom W., *Angewandte Chemie International Edition.* **46** (2007) 2366

Chapter 3

Nitrogen incorporation in carbon spheres

Nitrogen is the natural choice for doping carbon materials since it differs only by one additional valence electron from a carbon atom. Thus, a relatively easy incorporation into the carbon honeycomb lattice should be achievable. The nitrogen atom, substituted in a graphite-like way was calculated to differ only by 0.01 Å from the equilibrium position of a carbon atom. Although the properties of carbon nanomaterials are nothing short of exceptional, there are nonetheless many areas in nano- and molecular-electronics, optics, electromechanics or chemistry where pristine materials are not the most appropriate. Substitutional doping is expected to provide solutions for such limitations.¹ It has been established that the incorporation of nitrogen in nanotubes results in enhanced conductivity, polarity and basicity, while also modifying surface hydrophilicity.²

Nitrogen doped nanomaterials have been found to be less stable, and oxidize at lower temperatures than their pure carbon counterparts. This is explained by localized defects due to the presence of nitrogen atoms, which generate CNTs that are energetically less stable than a pure carbon lattice.³

Interestingly, it appears that there are no reports on the doping of the spheres by nitrogen. Our group has reported on the doping of the spheres by boron.⁴

In this work, we provide information on the synthesis of undoped and N-doped carbon spheres using vertical and horizontal CVD methods. We examined the morphology, and possible atomic configurations for nitrogen in the nanosphere lattice and discuss their electronic properties.

3.1 Experimental

3.1.1 Technical assembly of vertical and horizontal CVD reactors

A simplified form of the vertical chemical vapour deposition (v-CVD) apparatus is shown diagrammatically in Figure 3.1. This apparatus was designed and fabricated in the nanotechnology laboratory of the school of chemical and metallurgical engineering, university of the Witwatersrand by Iyuke (2005).⁵ It consists of a vertical silica plug flow reactor [1], immersed in a furnace [2] with a sensitive temperature regulator. A system of rotameters, pressure controllers and valves control the flow of gases into the reactor. The upper end of the reactor is connected to a condenser [3], which leads to two delivery cyclones [4,5], where the carbon materials produced is collected. The vaporiser [6] is placed on a heater with a sensitive temperature regulator, which is connected to the swirled mixer [7] and this in turn leads into the reactor.

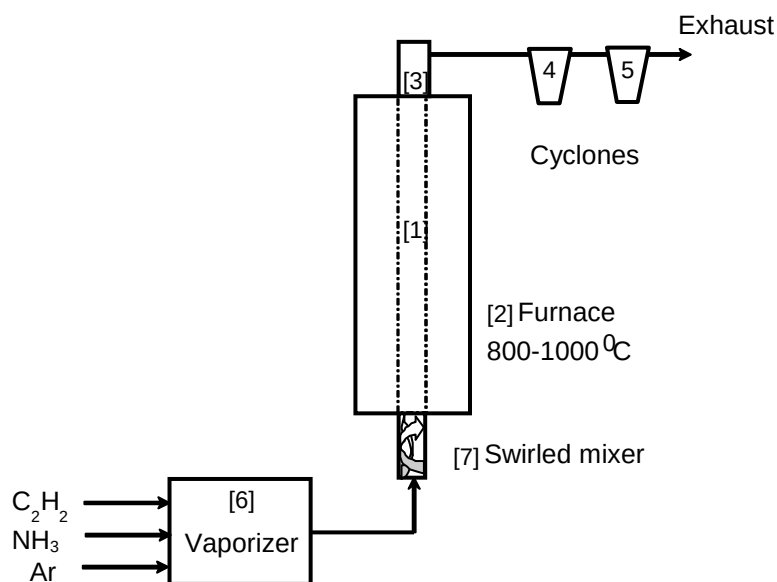


Figure 3.1: Schematic representation of a vertical chemical vapour deposition reactor.

Carbon spheres were also synthesized in a horizontal reactor (Figure 3.2) that has been placed horizontally in a furnace, allowing production of the carbon material. The horizontal reactor is made up of a furnace, temperature gauge, quartz tube, water cooled injector in which a syringe is injected into gas bubbler. The furnace is electronically controlled such that the heating rate, reaction temperature and gas flow rates are maintained accurately as desired.

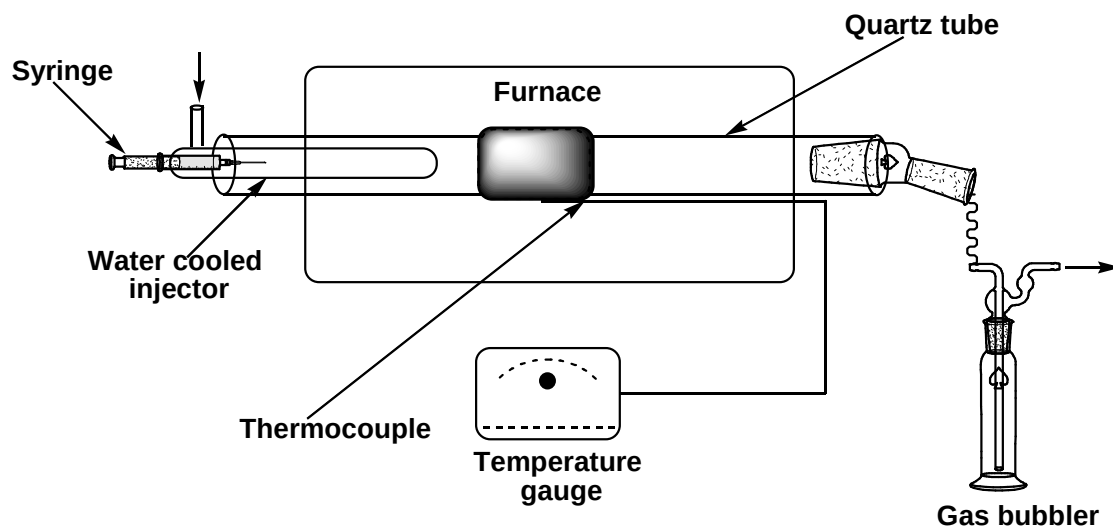


Figure 3.2: Schematic representation of a horizontal chemical vapour deposition reactor

3.1.2 Characterization

The soot was characterized using transmission electron microscopy (TEM) (JEOL 100S Electron Microscope) and thermogravimetric analysis (TGA) (Perkin Elmer Pyris 1 TGA Analyzer), Brunauer, Emmett and Teller (BET) surface area analysis (Micromeritics TriStar Surface Area and Porosity Analyzer) and Powder X-ray diffractometry (PXRD) (Bruker AXS D8 Advance PXRD). No catalyst was required in the synthesis of the CNSs, hence no purification was done. Elemental analysis was done by the institution for soil, climate and water in Pretoria.

All of the ESR measurements were carried out at room temperature using a Bruker ESP300E X-band (microwave) spectrometer operating in the frequency range 9.4 – 9.8 GHz. The samples were placed in standard NMR tubes, and the standard continuous wave (CW) technique was used to obtain all of the derivative spectra.

3.2 Synthesis of carbon spheres using a vertical CVD method

3.2.1 Synthesis of carbon spheres without nitrogen

Nitrogen gas was initially passed through the system in order to flush out contaminants in the reactor. The furnace was set to a desired temperature (1000 °C) and acetylene together with an inert gas (Ar) gas was fed through the reactor. The flow rates of argon and acetylene were kept constant at 100 mL/min and 487 mL/min respectively. A carbon material that evolved from the upper end of the reactor was cooled in a condenser and collected in two cyclones. It took approximately 5 minutes to produce 1.30 g material.

3.2.1 Synthesis of carbon spheres doped with nitrogen

A vertical quartz tube was loaded into the furnace. The temperature of the furnace was operated at 1000 °C, and acetylene together with an inert gas (Ar) was fed through the reactor. The flow rate of argon was kept constant at 100 ml/min; however, the acetylene flow rate was varied between 370-594 mL/min. Nitrogen addition was achieved by bubbling acetylene:argon gas mixture through a concentrated solution containing ammonium ions. The ammonium solution was diluted with water to study the NH_4 dilution effect on formation and morphology of the spheres.

Other nitrogen sources such as pyridine and ammonia gas were also used in the synthesis of N-CSs. NH_3 gas at 100 mL/min was fed together with acetylene (487 mL/min) into the reactor through the swirled mixer at 1000 °C. Due to poor production of the carbon materials, and the low content of nitrogen in the product, no further studies were conducted using pyridine and ammonia

In the case of pyridine, the acetylene:argon mixture was bubbled through pure pyridine at 125 °C. As with NH_3 gas, reaction conditions were not varied.

3.3 Results and discussions

3.3.1 Elemental analysis

Different nitrogen source were used to make the N-CSs. These sources included ammonium hydroxide solution, pyridine, and ammonia gas. This was done to establish the best N-source to use to make high yields of quality N-CSs and to control the nitrogen content. As shown in Table 3.1, ammonium hydroxide gave the highest N content, compared to the results using pyridine and ammonia gas. The dilution of the ammonium hydroxide solution with water played a role in the substitution of C atoms with N atoms. The dilution resulted in decrease in N content of the products. It could be seen that, the carbon spheres can be doped by nitrogen since the elemental analysis detected very low levels of nitrogen (<0.02%) from the spheres prepared using acetylene and no N source.

Table 3.1 Elemental composition of CSs and N-CSs at T= 1000 °C, t = 5 min

N source	Carbon %	Nitrogen %	Yield g
No nitrogen	> 98.00	< 0.02	1.30
NH ₃ gas	98.00	0.19	0.20
Pyridine	98.42	0.15	0.20
25%NH ₄ OH	92.26	3.08	0.75
12.5%NH ₄ OH	92.47	2.70	0.30
5% NH ₄ OH	93.18	2.58	0.20

Due to the high nitrogen content obtained with ammonium hydroxide solution, later synthesis studies to make N-doped carbon spheres were conducted using both acetylene as a carbon source and ammonium hydroxide solution as a nitrogen source. Pyridine and ammonia gas gave low yields of carbon spheres with low content of nitrogen. The effect on the dilution of ammonium solution had negative impact on the yield and nitrogen content of the carbon spheres, they seemed to drop.

3.3.2 The effect of acetylene flow rate on the yield of carbon spheres

Acetylene flow rates were varied to study the effect on the synthesis of carbon spheres. To study the effect of acetylene flow rate on the production rate, size and structural morphology of the carbon spheres, the acetylene flow rate was varied from 370 – 594 mL/min, at 1000 °C. Table 3.2 shows the effect of acetylene flow rate on the yield of spheres obtained.

Table 3.2 Effect of acetylene flow rate on the yield of N-CSs at T= 1000 °C, t = 5 min

C₂H₂ flow-rate (mL/min)	Yield (g)
370	0.50
433	0.55
487	0.75
540	0.80
594	0.95

The increase in acetylene flow rate gave an indication that this process allows for the large scale production of these materials, a maximum production, 0.95 g was obtained at 594 mL/min (Figure 3.3). However, the effect of gas flow rates displayed a larger impact on the size of the carbon spheres. As the flow rate increased, the size of the spheres became smaller. The uniform diameter of 100 nm was produced at 487 mL/min. The size distributions of the carbon spheres products are shown in Figure 3.4.

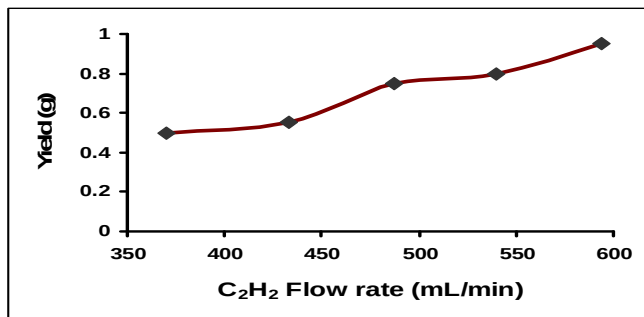
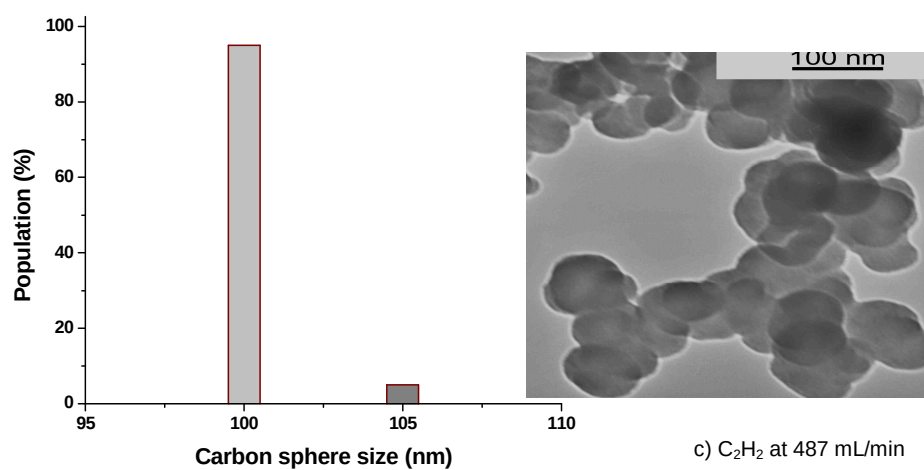
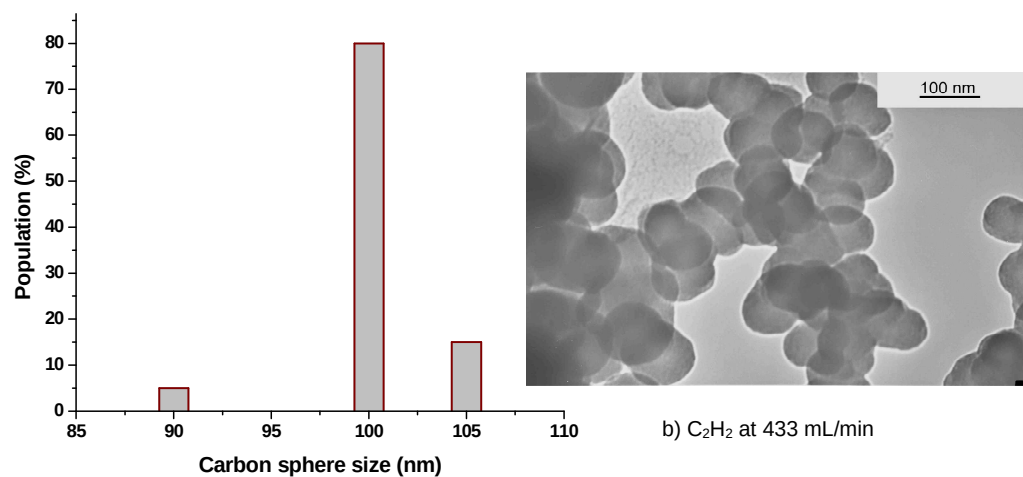
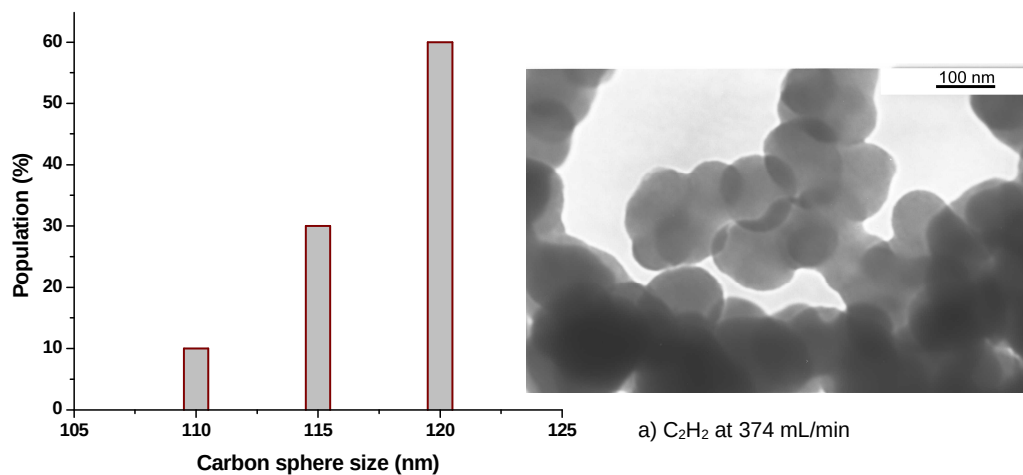


Figure 3.3: Effect of the C₂H₂ flow rate on the yield of N-CSs at 1000 °C



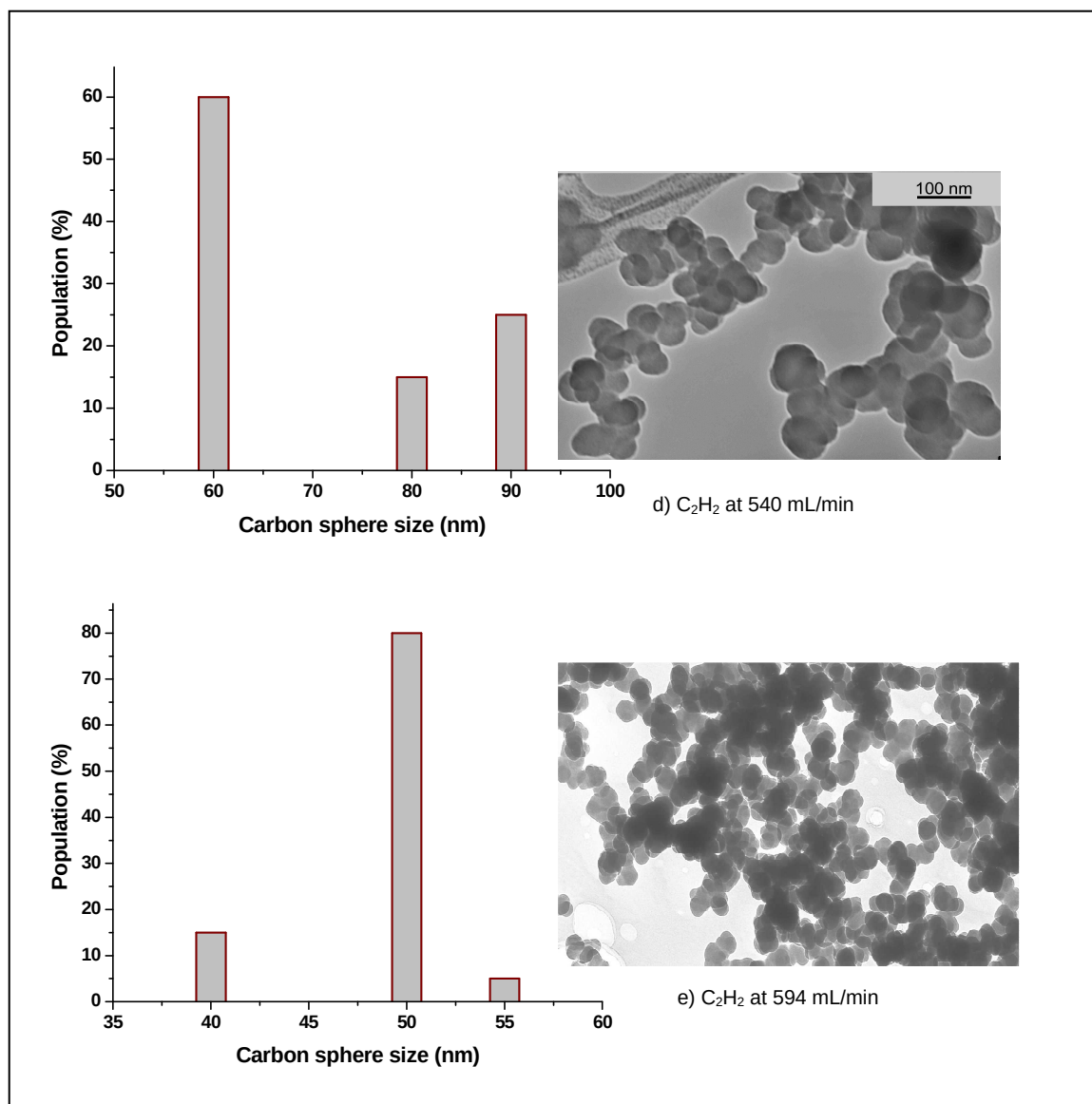


Figure 3.4: Histograms and TEM images of N-CSs synthesized at 1000 °C and at C_2H_2 flow rate of a) 397 mL/min, b) 433 mL/min c) 487 mL/min, d) 540 mL/min and e) 594 mL/min

3.3.3 Morphology investigation

The comparative morphology study of undoped and doped carbon spheres is shown in Figure 3.5. N-CSs and CSs were produced at 1000 °C at flow rate of 487 mL/min. The undoped carbon spheres materials were spongy and very light, the TEM image (Figure 3.5a) and HRTEM image (Figure 3.5b) showed only spheres of an average diameter of 100nm. The TEM image of the N-CSs in Figure 3.5c revealed that spheres have been formed with an average diameter of 100 nm. The HRTEM image in Figure 3.5d showed a poorly graphitic structure with short carbon layers. It can be observed that some of the spheres are linked together (accreted). No distinct difference is observed in the morphology of carbon spheres. No outer core shell was observed with the carbon spheres produced by the vertical CVD.

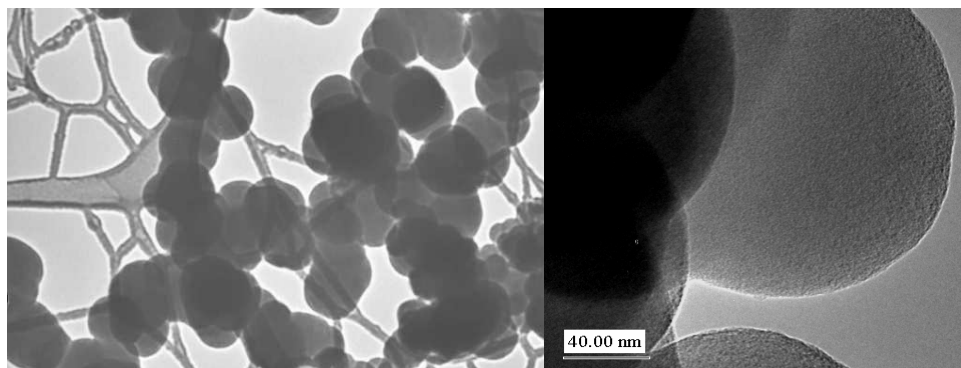


Figure 3.5: TEM (a) and HRTEM (b) images of undoped CSs at 487 mL/min

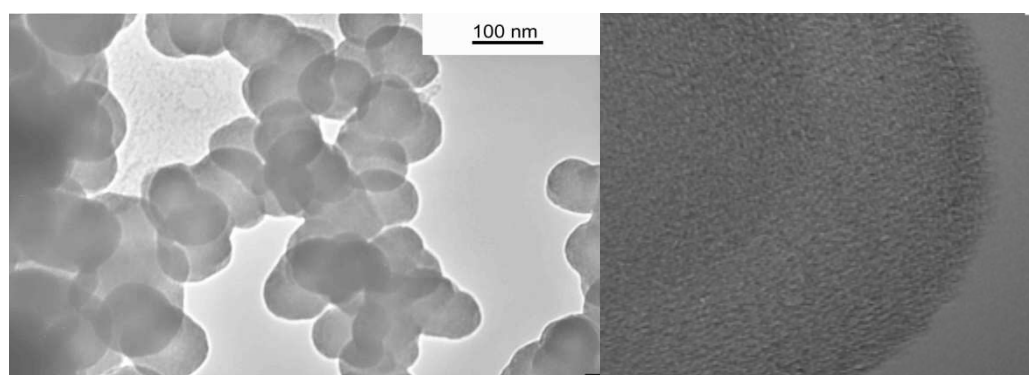


Figure 3.5: TEM (c) and HRTEM (d) images of N-doped CS at 487 mL/min

3.3.4 Thermal and BET analysis

TGA experiments (Figure 3.6(a) and (b)) provide information on the thermal stability of the carbon. Thermal data will be affected by the presence of defect sites because defect sites in graphite planes such as dangling bonds, edges and vacancies decrease the oxidative stability. Basal planes are the most stable towards oxidation and other reactions.⁶ For the undoped CSs (Figure 3.6(a)), TGA data indicated a 23% mass loss between 100 °C and 350 °C. It was observed that 450 °C was the maximum oxidation temperature of the undoped spheres. For the N-CSs (Figure 3.6(b)), TGA data indicated a 15% mass loss between 100 °C and 400 °C. Most of the carbon reacted with oxygen at ca. 510 °C. The steepness of the slope on both graphs is a likely indicator of large numbers of dangling bonds which enable oxygen to readily permeate the spheres facilitating rapid oxidative degradation.

Upon heating the spheres to 300 °C in 1 h under argon, both undoped and N-doped spheres exhibit enhanced oxidative stability, and no mass loss is now observed at lower temperatures. The BET results in Table 3.3 show that the surface area had also increased after heating the spheres. The results suggest that the spheres have species such as polycyclic aromatic hydrocarbons (PAHs) that are physically attached to their surface. The higher % mass loss at lower oxidation temperature for undoped CSs can be attributed to the larger number of hydrogen and carbon radicals which react to form CO₂, H₂O and PAHs.

Table 3.3: BET analysis of carbon spheres

CS type	Surface specific area (m ² /g)	Pore specific volume (cm ³ /g)
Undoped Before	10.019	0.015
After	14.89	0.031
Doped Before	11.01	0.011
After	13.67	0.029

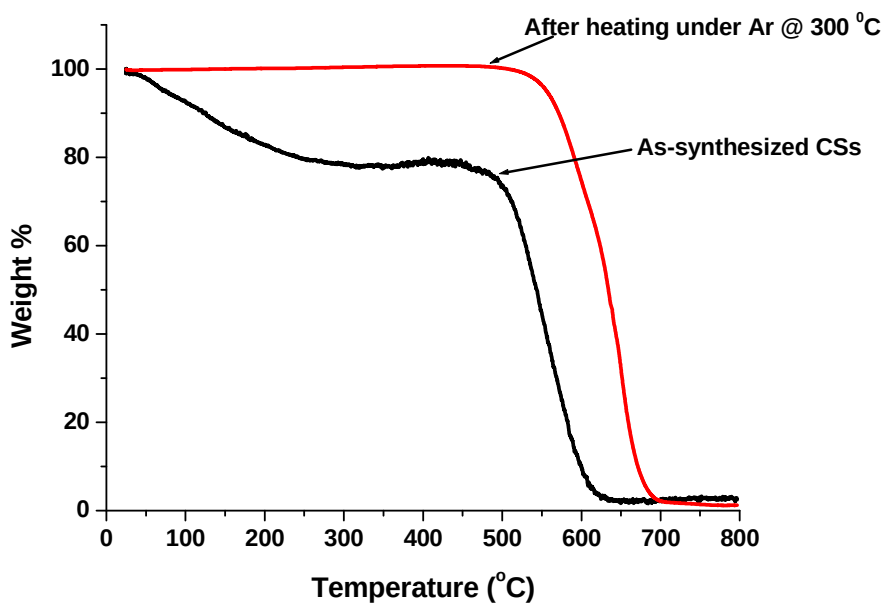


Figure 3.6(a): TGA profile of undoped carbon spheres prepared at 1000 °C in air

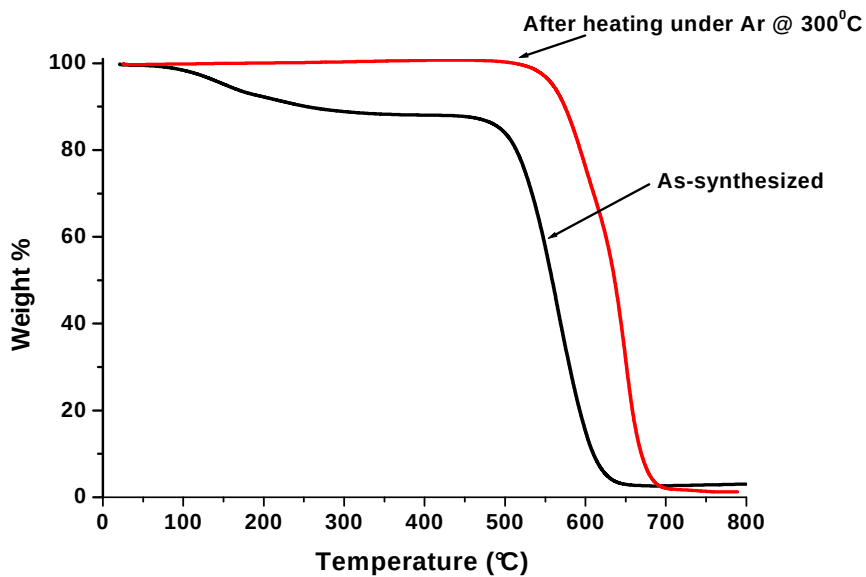


Figure 3.6(b) TGA profile of N-doped carbon nanospheres prepared at 1000 °C in air

The morphology of the post heated spheres is shown in Figure 3.7. The TEM image shows no deformed carbon spheres, and accretion persists. After heating the morphology of the carbon microspheres is almost undestroyed, remaining in perfect sphericity. This can be attributed to the surface chemical activity caused by nitrogen atoms facilitating chemical functionalization. HRTEM shows no alignment in the graphitic sheet of the spheres.

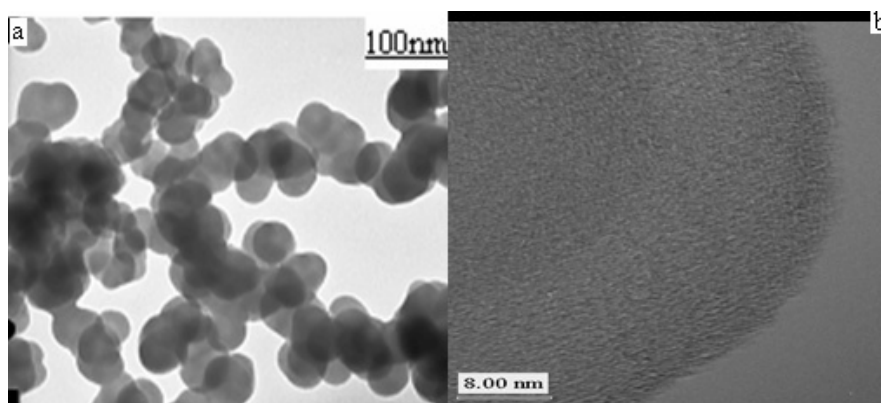


Figure 3.7: Morphological view of post heated spheres under TEM (a) and HRTEM (b).

3.3.5 Powder X-ray diffraction

Nanometre-sized materials are of considerable current interest because of their special size-dependent physical properties. Debye-Scherrer diffraction patterns are often used to characterize samples, as well as to probe the structure of nanoparticle. Unfortunately, the well known Scherrer formula' is unreliable at estimating particle size, because the assumption of an underlying crystal structure (translational symmetry) is often invalid.

Figure 3.8 shows the PXRD pattern of undoped and N-doped carbon spheres. Each profile exhibits a peak at *ca.* 25°, *i.e.* (002) graphite plane.⁷ The broadness of the peak is indicative of only a short range structural order. An ill-defined peak at 43.8° can be assigned to the (100) graphite plane. These results find further support in HRTEM images.

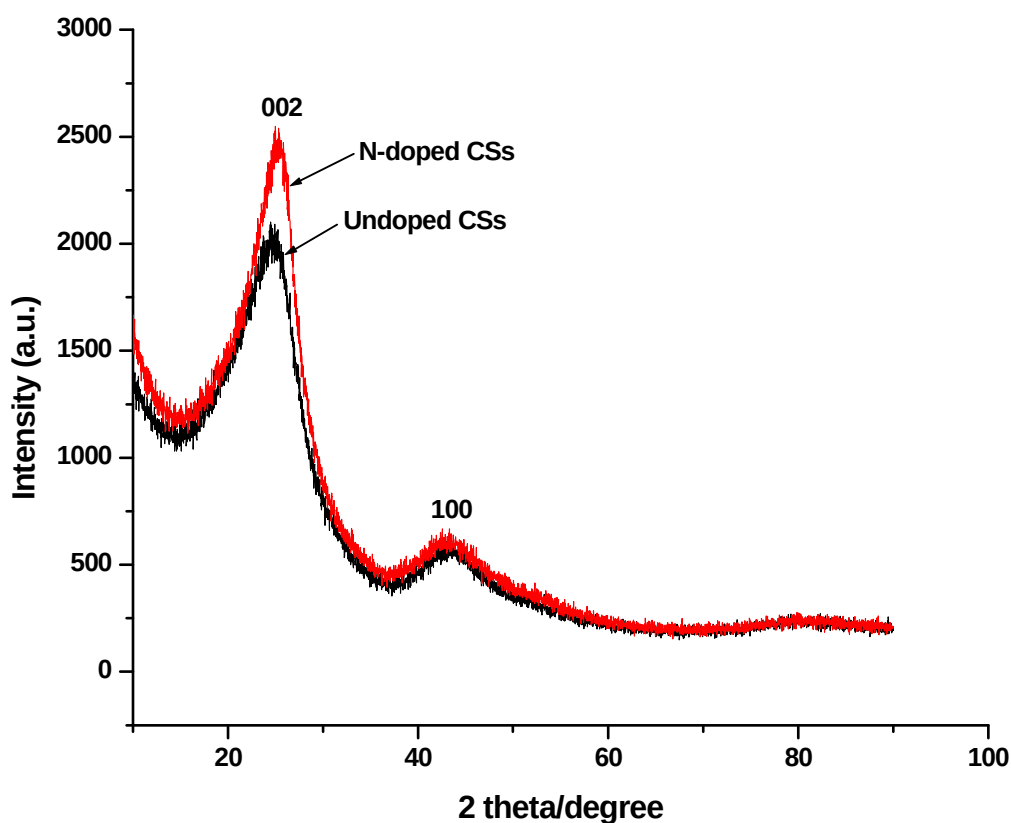


Figure 3.8: PXRD pattern of undoped and N-doped carbon sphere prepared at 1000 °C.

3.3.6 Raman spectral analysis

The Raman spectra of the CSs and N-CSs produced at temperatures of 1000°C show the presence of two broad peaks at about 1348 cm^{-1} and 1591 cm^{-1} corresponding to the D- and G-bands of graphite respectively (Figure 3.9). Usually the ratio I_D/I_G is interpreted as a measure of the degree of order of the material.⁸ Values of I_D/I_G at ~ 0.75 and ~ 0.9 were observed for the CSs and N-CSs respectively. The increase of this ratio indicates that the degree of graphitization of the samples is low with possible presence of disordered carbon. These results help explain and justify the morphology of the N-doped carbon spheres.

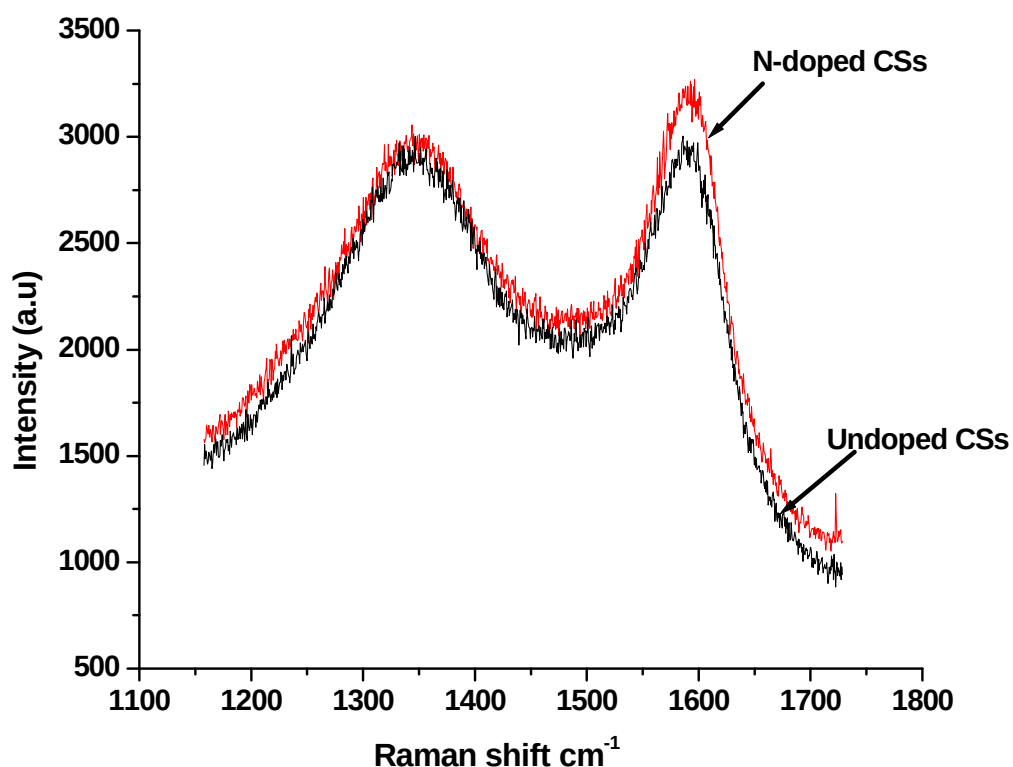


Figure 3.9: Raman spectrum of N-doped carbon spheres.

3.3.7 Electromagnetic spin resonance

Undoped carbon spheres and N-doped carbon spheres were presented for analysis, EMR derivative spectra are shown in Fig. 3.10

Both samples exhibit an ESR response centered at $g \approx 2$. The relatively broad line spectrum obtained for undoped spheres is similar to that obtained in many other carbon nanomaterials studied previously, and may possibly be ascribed to conduction electrons.⁹

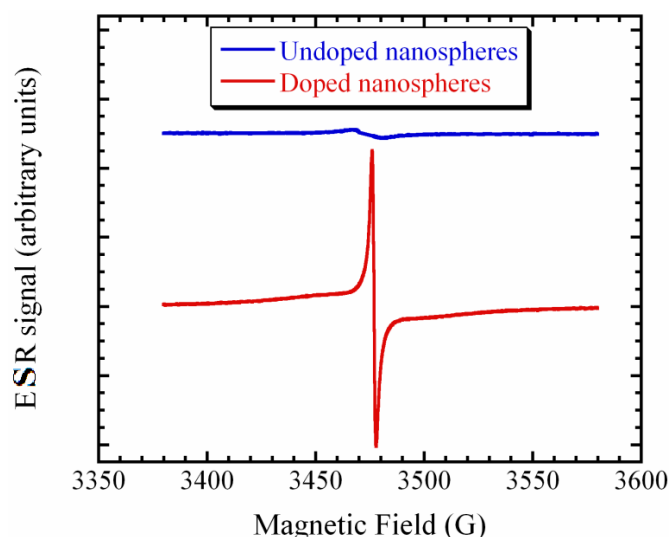


Figure 3.10: ESR derivative curves for CSs and N-CSs. The spectra were obtained using comparable spectrometer settings, and using a similar quantity of sample

N-CSs have a strong paramagnetic peak superimposed on a broad background. The origin of the broad background signal is not known, but as has been pointed out in the previous paragraph, a similar feature appears in the CSs, and so appears to be intrinsic to the nanospheres. The strong central paramagnetic signal is ascribed to substitutional nitrogen, and we may conclude that the nitrogen has indeed been incorporated into the carbon matrix. The increase in concentration of N- source results in a strong paramagnetic signal.

3.4 Synthesis of carbon spheres using a horizontal CVD method

3.4.1 Synthesis of carbon spheres with/without nitrogen

The furnace (Figure 3.2) was set to a temperature of 1000 °C. A carrier gas mixture of 5% H₂:Ar at a flow rate of 100 mL/min which was controlled by the flow meter and the bubbler was injected into the reactor. A volume of 20 ml of toluene at a flow rate of 0.8 mL/min was injected through the water cooled injector into the reactor. Doping was achieved by injecting pyridine (20 mL) at 0.8 mL/min into the reactor. The volume/volume ratio of pyridine:toluene (P:T) was varied (Table 3.4) with all the other parameters kept at constant values. Most of the synthesized hydrocarbon product formed in the middle of the reactor tube.

Table 3.4: Variation of P:T (v/v) ratio at constant temperature and flow rate

P:T Ratio	Flow rate (mL/min)	Temperature (°C)
100:0	0.8	1000
90:10	0.8	1000
10:90	0.8	1000
0:100	0.8	1000

3.5 Results and discussions

3.5.1 Elemental analysis

The incorporation of nitrogen within carbon spheres was confirmed by elemental analysis measurements. The sample produced from P/T precursors containing 100/0 ratio contained 5 at % nitrogen, the nitrogen content decrease to 0.13 at % when P/T ratio was 0/100 (Table 3.5). The increase of the nitrogen source (pyridine) increased the yield of the sample.

Table 3.5 Elemental analysis of carbon spheres

P/T Ratio	Carbon %	Nitrogen %	Yield g
100:0	87	5	0.6
90:10	91.97	3.52	0.55
10:90	94.19	1.48	0.35
0:100	98.94	0.13	0.40

3.5.2 Morphology investigation

Figure 3.11(a) shows the TEM images of the carbon products of the as-synthesized material in the presence and absence of nitrogen. The samples synthesized in the absence of nitrogen source were found to be carbon spheres with a broad size distribution range (200-700 nm). The high resolution transmission microscopy (HRTEM) image of the carbon sphere is shown in Figure 3.11(b). The image shows consecutive light and dark concentric contrast areas on an individual sphere, revealing the core/ shell geometry of the carbon sphere. An electron diffraction pattern taken from a selected area of the shell, displays rings which indicate that the shell is crystalline in nature.

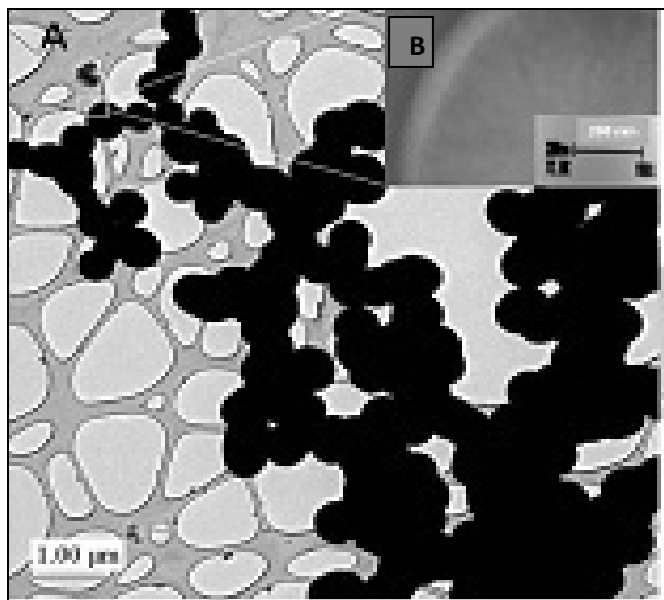


Figure 3.11: TEM (a) and HRTEM (b) images of undoped CSs

However, the diameter of the carbon spheres obtained in the presence of nitrogen in Figure 3.12(a) was in the range of 500-1000 nm. HRTEM analysis of the material in Figure 3.12b shows that the carbon spheres are made up of disordered arrays of graphene sheets of carbon. No outer core shell was observed with N-CSs.

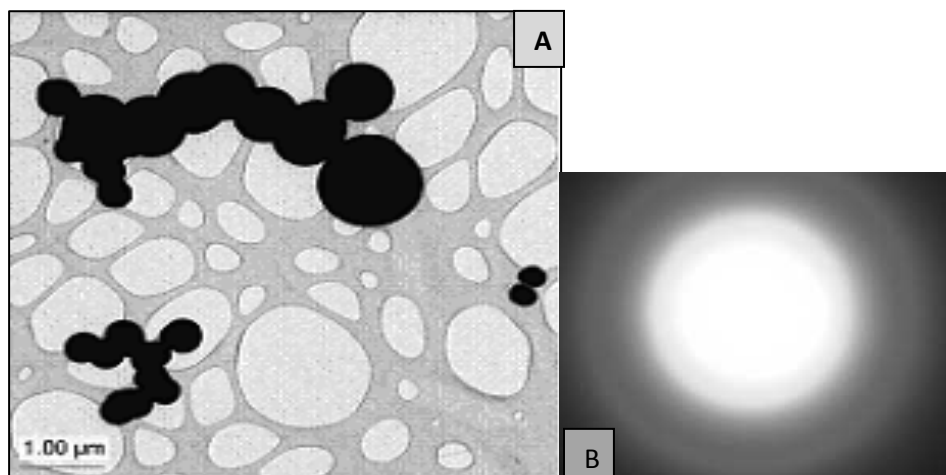


Figure 3.12: TEM (a) and HRTEM (b) of N-CSs

3.5.3 Thermal stability of carbon spheres

Figures 3.13a and 3.13b show the weight loss of the undoped and N-doped carbon spheres respectively. The graphs provide information with regard to the defects when experiments were done in air. The undoped carbon spheres (Figure 3.13a) exhibits a two stage decomposition, at temperatures 590 °C and 680 °C in air. About 5 % mass loss is observed in an inert environment. No reaction of carbon with oxygen is observed at lower oxidation temperatures. The thermal stability of N-CSs in Figure 3.13b shows that the materials were stable below 500 °C, and the weight loss began at 580 °C when heated in air. A three stage decompositions in observed even at higher temperatures.

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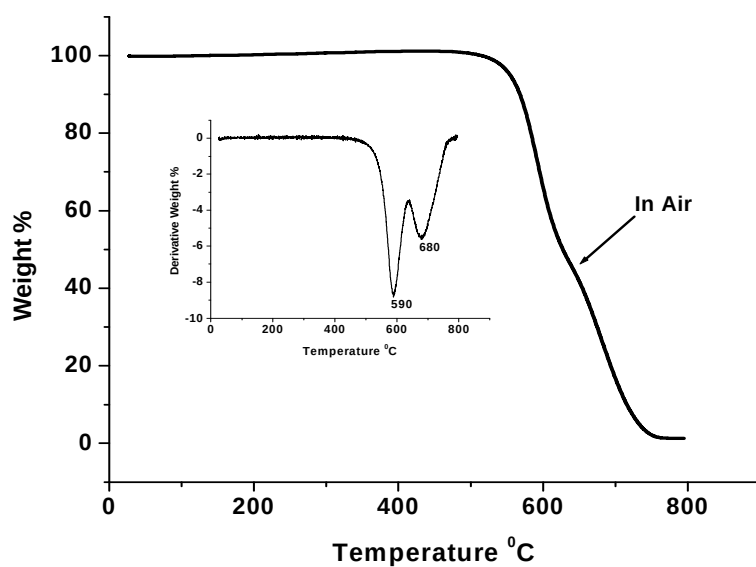


Figure 3.13(a): TGA profile of undoped carbon spheres in an oxidizing (air)

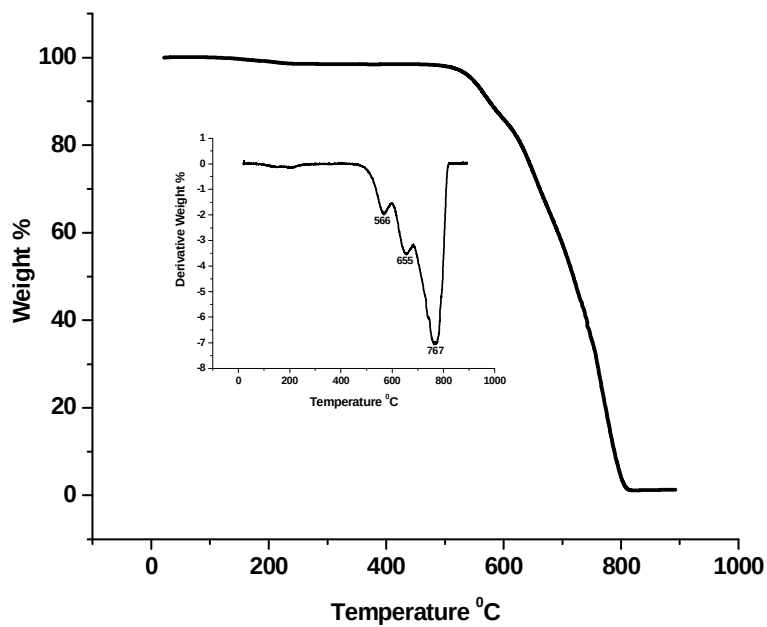


Figure 3.13(b): TGA profile of N-doped carbon spheres in an oxidizing (air) atmosphere.

3.5.4 Raman spectral analysis

The Raman spectroscopy analysis was carried out to investigate the defect degree in the graphite sheets of CSs and N-CSs. In the high frequency region, the G peak at 1580 cm^{-1} and the D peak at 1350 cm^{-1} are clearly detected, corresponding to a C-C stretching (E_{2g}) mode for graphite and the defect degree in the graphite sheets. The I_D/I_G ratios were 0.63 for undoped CSs and about 0.84 for N-doped samples. The value of I_D/I_G at $1000\text{ }^\circ\text{C}$ (~ 0.8) indicates that the degree of graphitization of the samples at this temperature is low with possible presence of disorder carbon. Some research groups reported that the incorporation of N atoms into the graphite sheets also introduces the defects in the hexagonal lattice^{10,11} Using Raman spectroscopy Lim *et al.*¹² noticed a significant down shift of the graphite peak from 1589 to 1580 cm^{-1} upon nitrogen doping. At the same time they observed a significant increase of the ratio of the intensities of the defect and graphitic peaks (I_D/I_G).

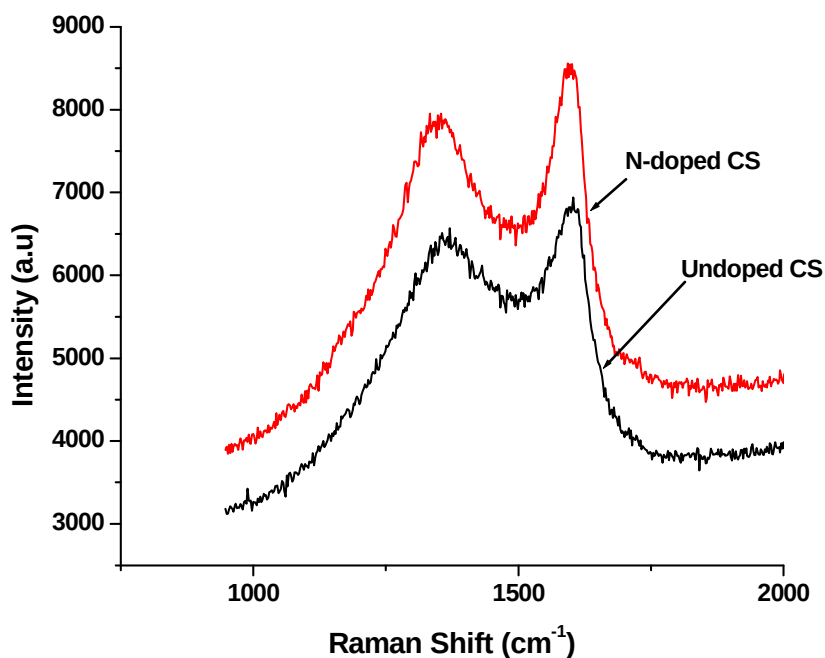


Figure 3.14: Raman spectra of carbon spheres

3.5.5 Electromagnetic spin resonance

Three samples were presented for ESR further analysis. These samples represented an attempt to dope the samples with variable amounts of nitrogen using mixtures of toluene and pyridine as the nitrogen source. ESR derivative curves for N-CSs are shown in Fig. 3.15. The nominal concentrations from the concentration of pyridine (P/T) in the mixture are 10/90, 90/10 and 100/0

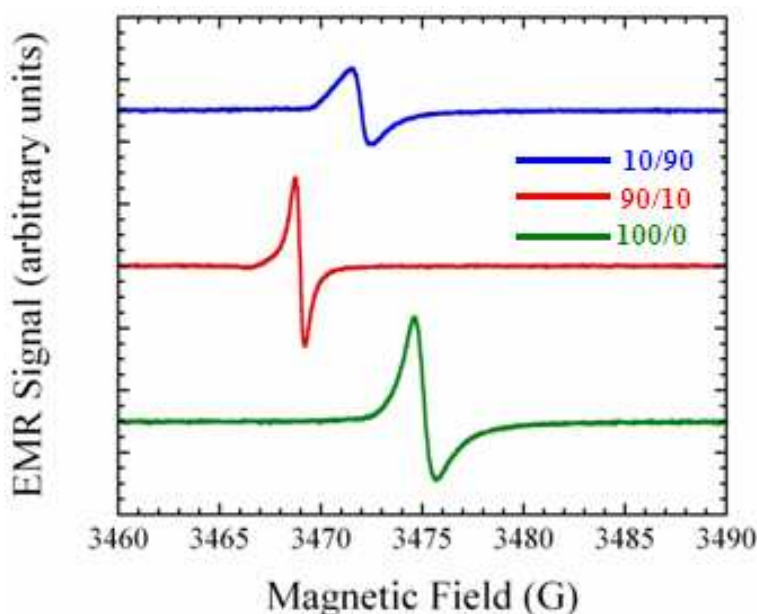


Figure 3.15: ESR derivative curves for 100/0, 90/10, and 10/90 ratios.

The curve for ratio 10/90 may be expected to have a significant proportion of the broad background inherent to the nanospheres, which was discussed previously. The absorption line for 90/10 is significantly narrower than the line for 100/0 pyridine, and is not as asymmetric. Possible reasons for this may include larger spin-spin interaction in 100/0 pyridine due to the larger concentration of paramagnetic ions, and a decrease in the microwave skin-depth for 100/0 pyridine related to an increase in the carrier concentration in this sample.

In an attempt to quantify the paramagnetic ion concentration in each of these three samples, measurements were conducted on carefully weighed amounts of samples. The area under each of the numerically integrated curves of each of the obtained derivative curves was determined, as a first approximation of the paramagnetic ion concentration. The results of these experiments are shown in Figure 3.16, where the normalized area (to mass) is plotted as a function of the nominal concentration obtained from the concentration of pyridine in the toluene-pyridine mixture.

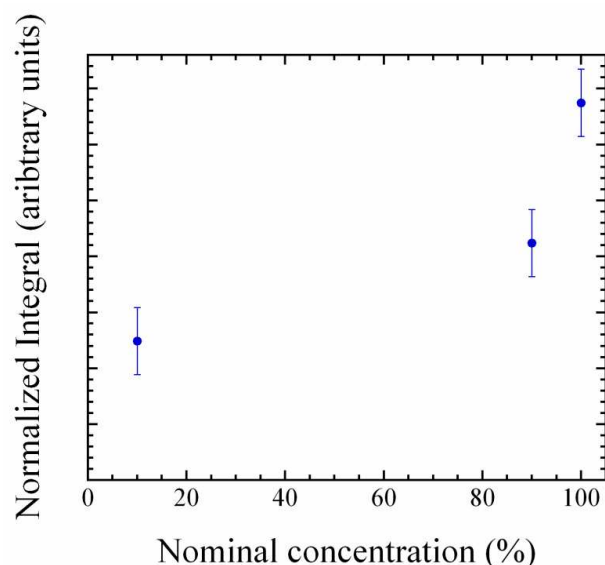


Figure 3.16: Plot of the numerical integral (normalized to the mass) as a function of the nominal nitrogen concentration inferred from the concentration of pyridine in the nitrogen source. .

The results shown should be treated with some caution, as the estimated error in the measured mass is relatively large. In addition, no attempt has been made to separate the background signal and the paramagnetic signal for 100/0 pyridine. Improved measurements may allow for a more accurate determination of the nitrogen concentrations. However, it is clear that the samples have different concentrations of substitutional nitrogen. As expected, the sample produced using toluene (P/T = 0/100) alone is indistinguishable from the undoped sample produced using a vertical reactor.

References

1. Ewels C., Glerup M., Krstić V. *Journal of nanoscience and nanotechnology*. **5** (2005) 1345
2. Roy S.C., Christensen P.A., Hamnett A., Thomas K.M., Trapp V. *J. Electrochem. Soc.* **143** (1996) 3073
3. Lee C. J., Lyu S. C., Kim H.W, Lee J. H., Cho K. I., *Chem. Phys. Lett.* **359** (2002) 115.
4. Mondal K. C., Strydom A. M., Tetana Z., Mhlanga S. D., Witcomb M. J., Havel J., Erasmus R. M., Coville N. J. *Materials Chemistry and Physics*. **114** (2009) 973
5. Iyuke S. E, Danna A. B. M. *Micropo. Mesopo. Mater.* **84** (2005) 338
6. Yao N., Lordi V., Ma S. X. C., Dujardin E., Krishnan A., Treacy M. M. J., Ebbesen T. W. *J. Mater. Res.* **13** (1998) 2432
7. Hall B.D., Zanchet D., Garte D. *Journal of applied crystallography*. **33** (200)1335
8. Maldonado S., Morin S., Stevenson K. J. *Carbon*. **44** (2006) 1429
9. Chipara M., Iacomì F., Zaleski J. M., Bai J. B. *J. Optoelec. Adv. Mat.* **8** (2006) 820.
10. Wu X., Tao Y., Lu Y., Dong L., Hu Z. *Diamond Relat. Mater.* **15** (2006)164
11. Liu J., Webster S., Carroll D. L., *J. Phys. Chem. B* **109** (2005) 15769
12. Lim S. H., Elim H. I., Gao X. Y., Wee A. T. S., Ji W., Lee J. L. *Phys. Rev. B* **73** (2006) 045402.

Chapter 4

Oxidative polymerization of thiophene

Polythiophenes have rapidly become the subject of considerable interest due to their excellent environmental and thermal stability. Since, the first report on the electrochemical synthesis of polythiophene in 1981, polythiophene and its derivatives have been widely studied.¹ Two main routes have been used for the preparation of polythiophene polymers; the chemical and electrochemical synthesis.² The chemical synthesis approach was used in this work due to the advantages it offers compared with electrochemical synthesis of polythiophenes. In particular a greater selection of monomers that can be used if a chemical approach is the synthesis choice.

Although thiophene can be polymerized by exposure to oxidizing agents such as Fe^{3+} , the generated polymer products are insoluble and infusible. These features limit considerably its application potential in industry and technology.³

The potential applications of PT include use in solar cells, nonlinear optical devices, sensors, and electrodes.⁴⁻⁵ Most applications of polythiophene conducting polymers have not been commercialized because of their solubility limitations. To overcome these disadvantages, several strategies for the modification of polythiophene have been developed. Preferentially, applied methods include the appropriate modification of the monomer (thiophene) structure prior to polymerization, and the preparation of copolymers, and polymer composites.⁶

In this work, we report the synthesis of polythiophene using a chemical method. The polymer was characterized and modified to improve both chemical and electrical properties. The work on modifying the polymer is reported in chapter 5.

4.1 Experimental

4.1.1 Materials

Thiophene monomer (99%), the oxidant, anhydrous ferric chloride (FeCl_3 , Aldrich), chloroform (CHCl_3 , Aldrich), methanol (CH_3OH , Aldrich), hydrochloric acid (HCl , Aldrich), and acetone (CH_3COCH_3 , Aldrich), were used as received.

4.1.2 Synthesis of Polythiophene

FeCl_3 (2 g) in 100 mL CHCl_3 was added to a 500 mL, double-necked, round-bottom flask equipped with a magnetic stirrer. The thiophene monomer (1 mL) together with 50 mL of a CHCl_3 solution was placed in a burette and the solution added gradually to the FeCl_3 solution with stirring. The reaction mixture was stirred for 24 h at room temperature. The resultant polythiophene powder was precipitated with methanol, filtered through a Buchner funnel, and then carefully washed in methanol, hydrochloric acid (0.1 M), distilled water, and acetone. The obtained reddish powder was dried under a vacuum at room temperature for 24 h.

4.2 Characterization

The polythiophene chemical composition was determined by elemental analysis and FTIR spectroscopy. Sample morphology was studied by transmission electron microscopy (TEM) using a Joel 100 s electron microscope at 80 kV. Infrared spectra were recorded in the range 400-4000 cm^{-1} using KBr pellets (Bruker Tensor 27 spectrometer). The thermal stability of polythiophene was investigated by heating the samples up to 900 °C under nitrogen and air at 10 mL/min using a Perkin Elmer Pyris TGA 1.

4.3 Results and discussions

4.3.1 Morphology

The samples were prepared by dissolving the polythiophenes in 5 ml of methanol and stirring for 10 minutes. The sample was then transferred to Cu grids coated with a carbon film (using a pipette) for transmission electron microscopy analysis.

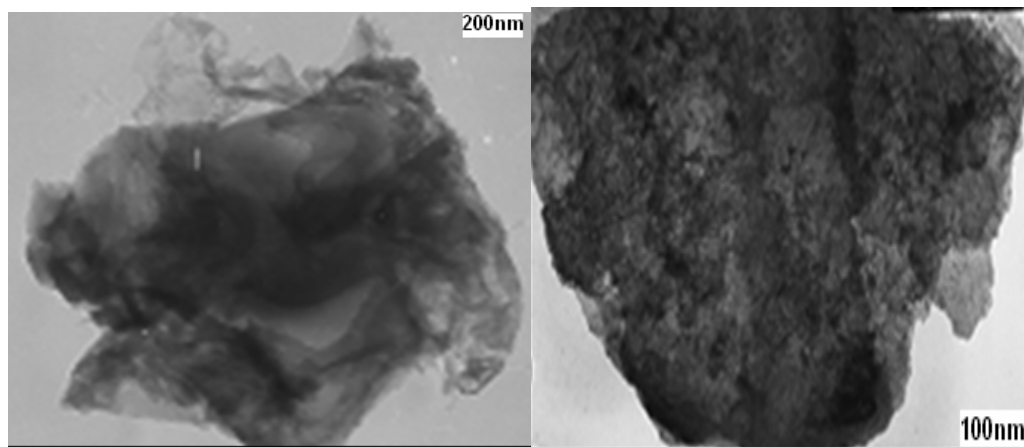


Figure 4.1: TEM images of polythiophene at different magnifications

In Figure 4.1 the transmission electron microscopy images show an amorphous structure of polythiophene with a rough surface. At lower magnification, the polymer exhibits globular structures with particle size about 50 nm and some fibrils. As is known, the morphology and electrical properties are the most important properties of the conductive polymers. For good conductivity, a smooth surface is needed. The oxidative polymerization method employed in this work was anticipated to produce polymers with varying degrees of regioregularity, and thus an amorphous structure.

4.3.2 Elemental analysis

Usually, FeCl_3 is used as the oxidant in polythiophene synthesis; a reaction which can be performed in room temperature. Table 4.1 presents the elemental analysis data of chemically prepared PTs. Due to structural disorder in the polythiophene chains and crosslinking, one positive charge is created per three thiophene rings, which has to be compensated for by bonding of the anion from the oxidant. The expected elemental analysis of polythiophene was calculated assuming a polymer compositions $[(\text{C}_4\text{H}_2\text{S})^{x+} x\text{A}^-]$, where A represents a dopant anion. When FeCl_3 is used in chemical synthesis, Cl^- anions bond to the polythiophene, and $x = 0.33$ is used for the calculation. As shown in Table 4.1 the calculated elemental composition for the polythiophene sample assuming $x = 0.33$ is close to that predicted

Table 4.1 Elemental data for polythiophene

<u>Sample</u>	<u>Carbon %</u>	<u>Sulfur %</u>
Polythiophene	52.28	34.50
Polythiophene ^a	51.13 ^a	34.13 ^a

^a literature value

Ays, eg'ul G'ok *et al.*⁷ reported an elemental composition (wt %) of 53.51 and 36.99 for carbon and sulfur, respectively. The differences between experimental and calculated elemental compositions in the PT sample were very small

4.3.3 Thermal stability

Thermal stability testing was examined using thermogravimetric analysis (TGA). The derivative curve in Figure 4.2b shows a comparison of the mass losses of polythiophene upon heating in air and in a nitrogen atmosphere. Below 100 °C, the mass loss may be attributed to a small amount of water in the samples. At 252 °C, a mass loss was observed in both curves which is due to loss of the polyaromatic hydrocarbons. The next mass loss (ca. 80 %) of the polymer recorded in air is observed at 425 °C. The decomposition of the polymer in nitrogen assumed a two-step decomposition at 325 °C (ca 20 %) and at 507 °C (ca. 70 %).

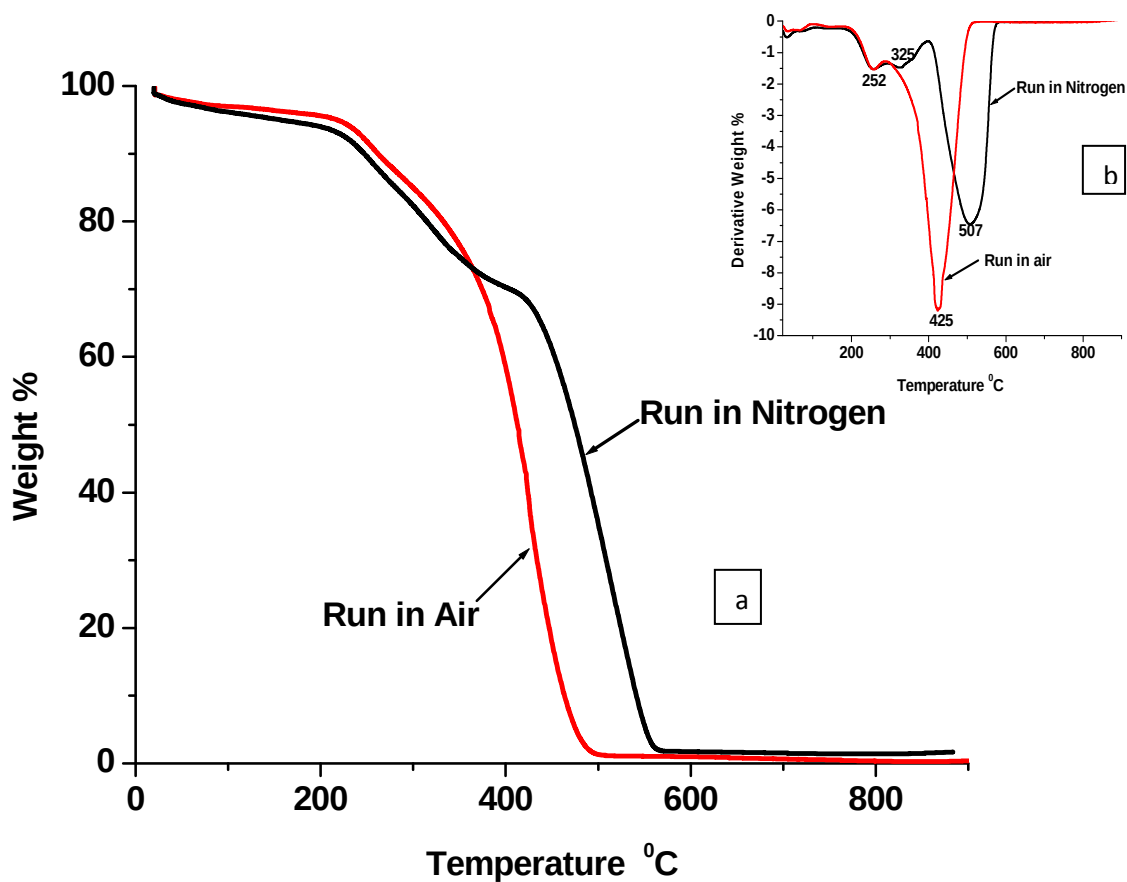


Figure 4.2: Thermogravimetric data for polythiophene under air and nitrogen atmosphere

4.3.4 Infrared spectroscopy

The infrared spectrum of the polythiophene is shown in Figure 4.3. IR spectroscopy was used to determine the functional groups present in the polythiophene polymer. The spectrum of polythiophene shows that there are low-intensity peaks in the range of $2900\text{--}3070\text{ cm}^{-1}$ that can be attributed to the aromatic C-H stretching vibrations. The peaks at 788 cm^{-1} and 1100 cm^{-1} are usually ascribed to the C-H in-plane and C-H out-of-plane deformation modes. The C-S bending mode has been identified to occur at 691 cm^{-1} and indicates the presence of thiophene moieties.

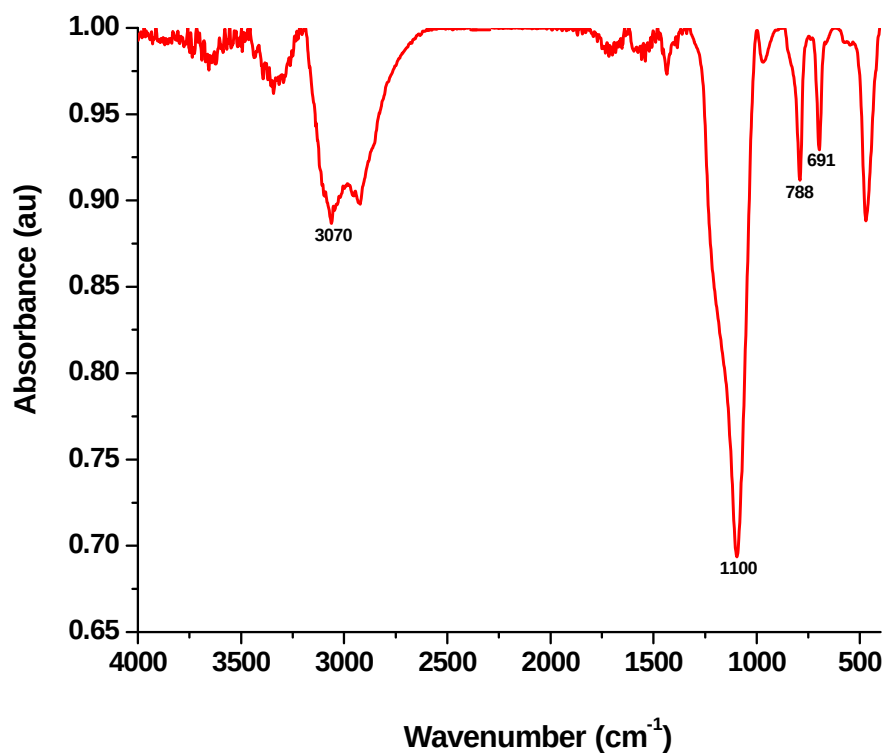


Figure 4.3 Infrared spectra of polythiophene

References

1. Diaz A. F. *Chem. Scripta*. **17** (1981) 145
2. Chiang J. C., MacDiarmid A. G. *Synth. Met.* **13** (1986) 193
3. Garnier F. *Electronic Materials*. Wiley VCH (1998) 559
4. Skotheim T. A. *Handbook of Conducting Polymers*. **1** (1986) 213
5. Skotheim T. A., Elsenbaumer R. L., Reynolds J. R. *Handbook of Conducting Polymers*. **2nd** edition (1998) 823
6. Waugaman M., Sannigrahi B., McGeady P., Khan I.M. *Eur Polym J.* **39** (2003) 1405
7. Harrison M. G., Friend R. H. *Electronic Materials*. Wiley VCH (1998) 515
8. Ays,eg"ul G"ok, M'aria Omastov'a, Ays,e G"ul Yavuz, *Synthetic Metals* **157** (2007) 23

Chapter 5

Organic functionalization of polythiophene/carbon spheres

Functionalization and solubilization are important aspects of the chemistry of carbon nanomaterials, these chemical manipulations being essential for many of the applications of CNTs.¹ Carbon nanotubes have been functionalized by both covalent and non-covalent means.^{1,6–16} The covalent functionalization method typically involves acid treatment of the CNTs followed by reaction with thionyl chloride followed by reaction with a long chain amines. Such amidation gives rise to single walled carbon nanotubes (SWNTs) soluble in non-polar solvents.^{1–4,8,10} Other methods such as fluorination have also been used for the functionalization of SWNTs.^{1,17} Covalent functionalization, however, has the limitation in that it drastically affects the electronic structure of the material hence affects their properties. Non-covalent functionalization of CNTs has been carried out by employing surfactants, aromatics and other reagents.^{12,13,18}

The reaction carried in this study to functionalize carbon spheres is a well known Prato reaction.¹⁹ The Prato reaction in fullerene chemistry describes the functionalization of fullerenes and nanotubes with azomethine ylides in a 1,3-dipolar cyclo-addition. The amino acid sarcosine reacts with a paraformaldehyde when heated to reflux in toluene to an ylide which reacts with a double bond in 6,6 ring position in a fullerene in a 1,3-dipolar cyclo-addition to yield a N-methylpyrrolidine derivative or pyrrolidinofullerene in ~ 80% yield.

This method is also used in the functionalization of single wall nanotubes. When the amino acid is modified with a glycine chain resulting nanotubes are soluble in common solvents such as chloroform and acetone. Another characteristic of the treated nanotubes is their larger aggregate dimensions compared to untreated nanotubes.

5.1 Experimental

5.1.1. Materials

Dimethyl-formaldehyde, N-methyl glycine, thiophene-2-carboxyaldehyde, thiophene monomer (99%), the oxidant, anhydrous ferric chloride (FeCl_3 , Aldrich), chloroform (CHCl_3 , Aldrich), methanol (CH_3OH , Aldrich), hydrochloric acid (HCl , Aldrich), acetone (CH_3COCH_3 , Aldrich), and undoped carbon spheres were prepared by a vertical CVD reactor mentioned in Chapter 3.

5.1.2 Synthesis of Polythiophene/Carbon Spheres nanocomposite

a) Covalent functionalization

The 0.1g carbon spheres were suspended in 50 mL DMF, together with 0.94 mL thiophene-2-carboxyaldehyde and 0.74 mL N-methyl glycine. The heterogeneous reaction mixture was heated at 130 °C for 5 days. The functionalized-carbon spheres (f-CSs) were collected, analyzed and used to synthesize polymer composites.

The routine synthesis of the polythiophene/f-carbon spheres composite was as follows: 100 mL of a CHCl_3 solution containing f-carbon spheres (0.2 g) was added to a double-necked, round-bottom flask equipped with a magnetic stirrer. The mixture was sonicated for 30 min at room temperature to disperse the carbon spheres. FeCl_3 (2 g) in 100 mL of a CHCl_3 solution was added to the solution, which was further sonicated for 30 min at room temperature. The thiophene monomer (1 mL) with 50 mL of a CHCl_3 solution was placed in the small portion line of the double necked flask and added gradually to the suspension solution with constant stirring. The reaction mixture was stirred for an additional 24 h under the same conditions. The resultant polythiophene/carbon spheres composite powder was precipitated in methanol, filtered with a Buchner funnel, and then carefully washed with methanol, hydrochloric acid (0.1 M), distilled water and acetone. The obtained black powder was dried under a vacuum dryer at room temperature for 24 h.

b) Noncovalent functionalization

The routine synthesis of the polythiophene/carbon spheres composite was as follows: 100 mL of a CHCl_3 solution containing carbon spheres (0.2 g) was added to a 500-mL, double-necked, round-bottom flask equipped with a magnetic stirrer. The mixture was sonicated for 30 min at room temperature to disperse the carbon spheres. FeCl_3 (2 g) in 100 mL of a CHCl_3 solution was added to the solution, which was further sonicated for 30 min at room temperature. The thiophene monomer (1 mL) with 50 mL of a CHCl_3 solution was placed in the small portion line of the double necked flask and added gradually to the suspension solution with constant stirring. The reaction mixture was stirred for an additional 24 h under the same conditions. The resultant polythiophene/carbon spheres powder was precipitated in methanol, filtered with a Buchner funnel, and then carefully washed with methanol, hydrochloric acid (0.1 M), distilled water, and acetone. The obtained black powder was dried under vacuum dryer at room temperature for 24 h.

4.2 Characterization

The composites chemical composition was determined by FTIR spectroscopy. Sample morphology was studied by transmission electron microscopy (TEM) using a Joel 100 s electron microscope at 80 kV. Infrared spectra were recorded in the range $400\text{--}4000\text{ cm}^{-1}$ using KBr pellets (Bruker Tensor 27 spectrometer). The thermogravimetric profiles were investigated using a Perkin Elmer Pyris TGA 1. Raman spectral analysis was done study the disruption effect of functionalization in the graphitic structure of carbon spheres

5.3 Results and Discussions

5.3.1 Morphology

Figure 5.1 shows the TEM images of the polymer/carbon spheres composites. The shape of these composites is irregular, close to spherical, although aggregation is found in the image, we still can clearly observe single particle in the images. In comparison with noncovalent functionalized nanocomposites, the covalent functionalized nanocomposites are thick (150 nm in diameter), and their external surfaces were not smooth. The analysis of noncovalent samples under TEM (Figure 5.1c) showed no coupling between the polymer and spheres. It was observed that largely polythiophene and spheres were clustered among themselves. The spheres were in a range of 100-120 nm in diameter.

As mentioned earlier, the 0.1 g carbon spheres were suspended in 50 mL DMF, together with 0.94 mL thiophene-2-carboxaldehyde and 0.74 mL N-methyl glycine. In the experiment, the heterogeneous reaction mixture was heated at 130 °C for 5 days so that there are more oxidized sites available on carbon spheres for attachment with polythiophene. The samples showed interaction between polymer and functionalized spheres. Spheres were mostly covered with polythiophene molecules. This has been clearly shown in Fig. 5.1 (a) – (d). This significant increase in interaction is due to the presence of more possible covalent coupling

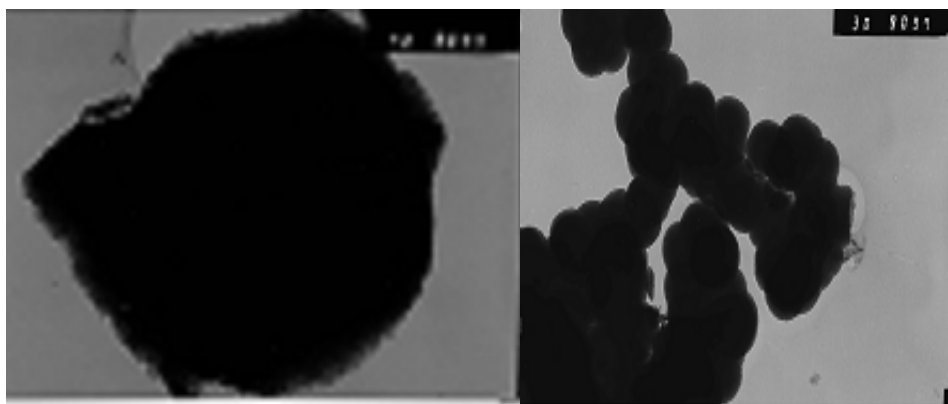


Figure 5.1: TEM images covalent functionalized carbon spheres (a) single carbon sphere
(b) accreted carbon spheres

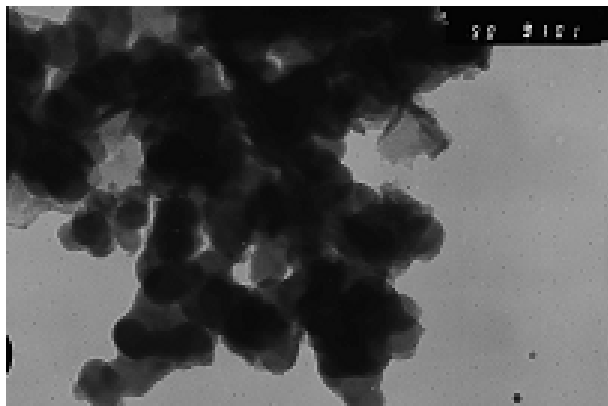


Figure 5.1c: TEM image of covalent functionalized CS/polythiophene composite

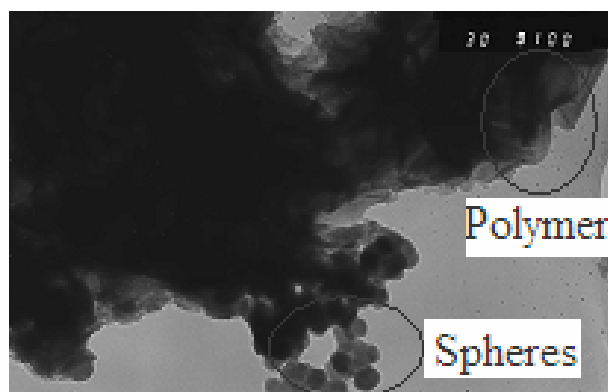


Figure 5.1d: TEM of noncovalent functionalized CS/polythiophene composite

5.3.2 Thermal stability

Polymer materials in pure state are electrical insulators.²⁰ However, carbon nanomaterials are considered to be an ideal inclusion for polymer composites due to their exceptional electrical and mechanical behavior. In order to transfer the properties of nanomaterials to the composite improved compatibility must be achieved.

Thermal stability of the polythiophenes was examined with thermogravimetric analysis (TGA). Figure 5.2a shows a comparison of the mass losses of covalent functionalization and noncovalent functionalization upon heating in a nitrogen atmosphere. The noncovalent are comparatively more stable in the range of 0–400 °C (Figure 5.2b). A speedy decomposition in covalent functionalization is due to the functional groups attached to the carbon spheres as it is indicated by the thermal stability of f-CSs in figure 5.2.

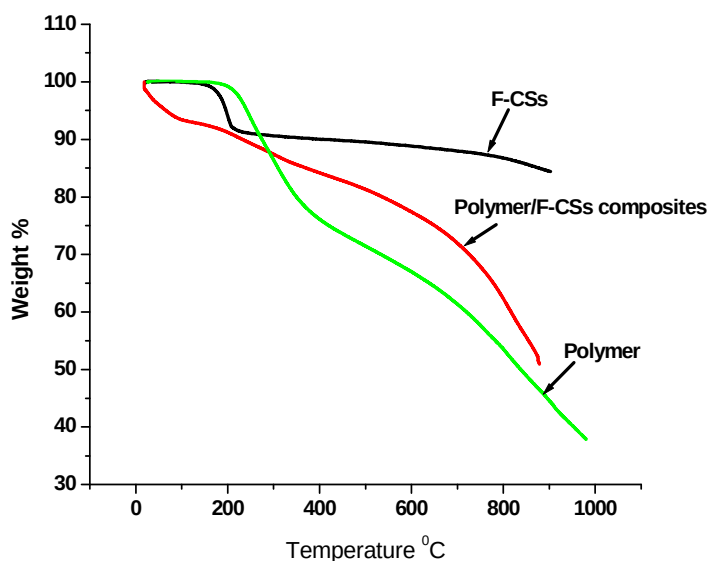


Figure 5.2(a): Thermal stability of the covalent functionalized nanocomposites

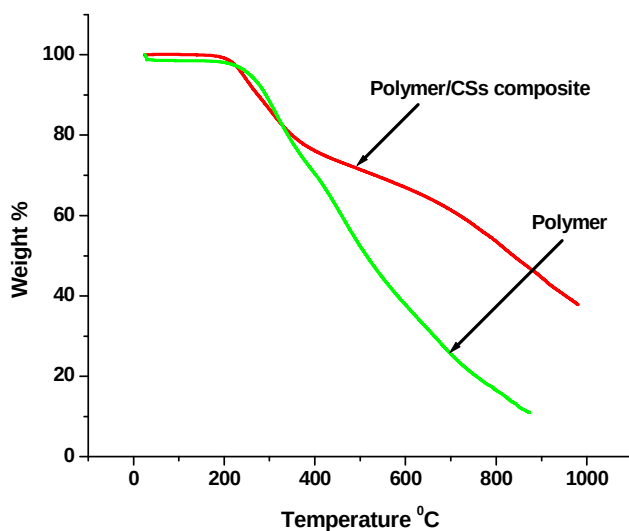


Figure 5.2(b): Thermal stability of noncovalent functionalized nanocomposite

5.3.3 Raman spectroscopy

Raman spectroscopy is a very powerful technique used to get information about the physical and electronic structure of the samples. Therefore it could be envisioned that the technique will be equally efficient for characterizing functionalized carbon spheres.

Raman spectroscopy analysis was carried out to investigate the defect degree in the graphite sheets of noncovalent and covalent functionalized nanocomposites. Figure 5.3a and b show the high frequency region, the G peak at 1590 cm^{-1} and the D peak at 1340 cm^{-1} are clearly detected, corresponding to a C-C stretching (E_{2g}) mode for graphite and the defect degree in the graphite sheets. The I_D/I_G ratios were 0.79 for noncovalent and about 1.5 for covalent samples. The value of I_D/I_G at ~ 1.5 indicates that the degree of graphitization of the sample is low with possible presence of disorder carbon. These results are in agreement with the TEM and the TGA results.

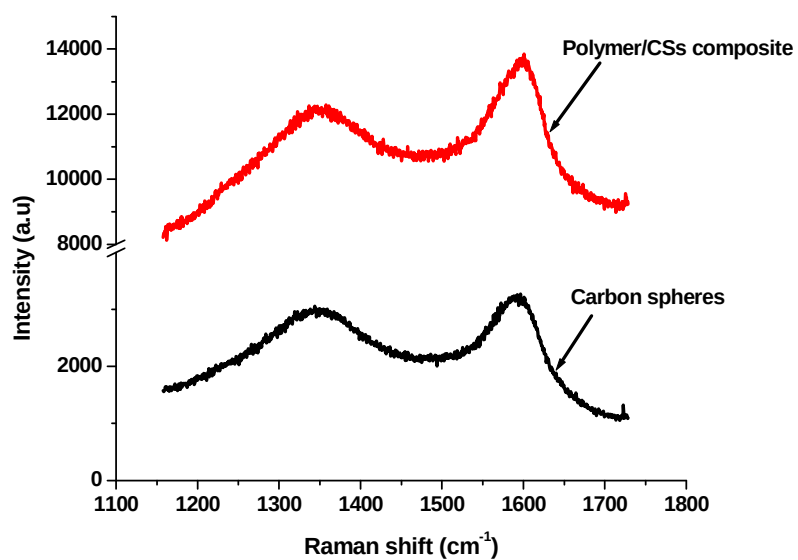


Figure 5.3(a): Raman spectrum of a covalent functionalized nanocomposite

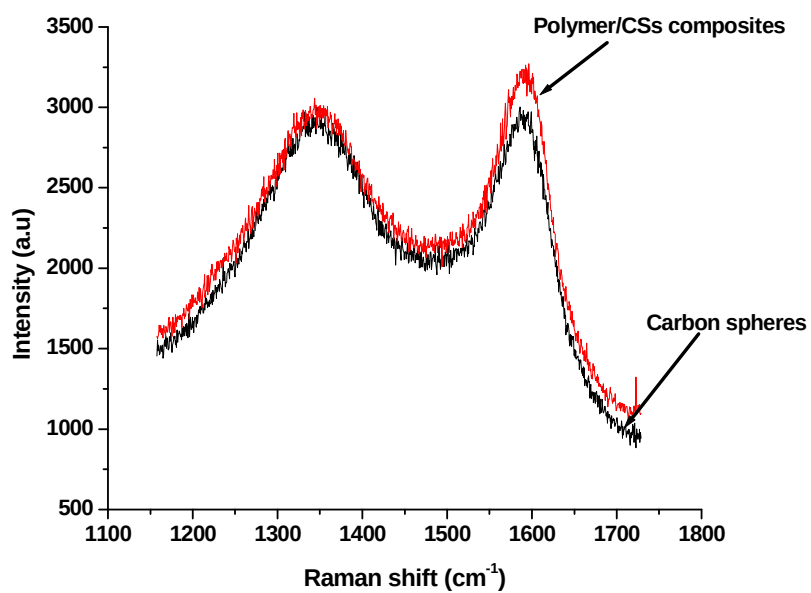


Figure 5.3(b): Raman spectra of a noncovalent functionalized nanocomposite

5.3.4 Infrared spectral analysis

The infrared spectrum of the polythiophene is shown in Figure 5.4. The IR spectroscopy was used to determine the functional groups present in the polymer nanocomposites. In Figure 5.4b, covalent functionalized nanocomposites exhibit a high intensity at 695 cm^{-1} , which is not observed in the noncovalent functionalized nanocomposites (Figure 5.4a). The range $600\text{--}1500\text{ cm}^{-1}$ is the region of polythiophene. The peak at 1100 cm^{-1} is usually ascribed to the C-H out-of-plane deformation modes.

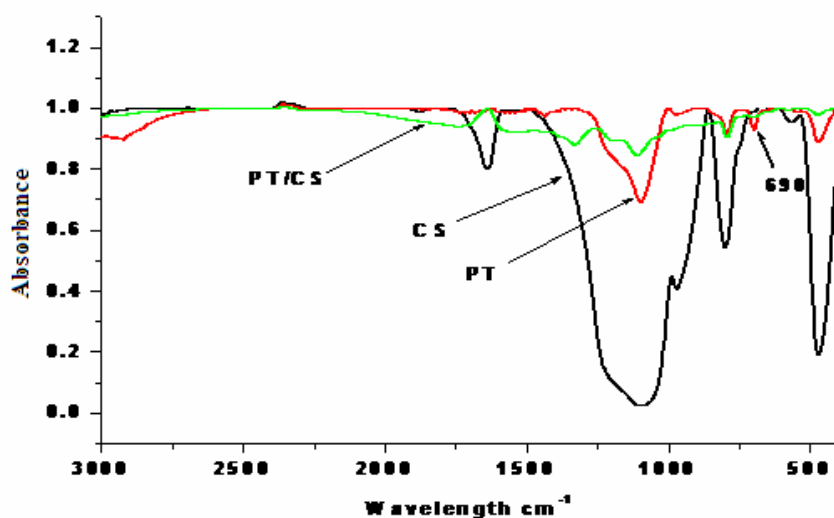


Figure 5.4(a): Infrared spectra of noncovalent functionalized nanocomposites

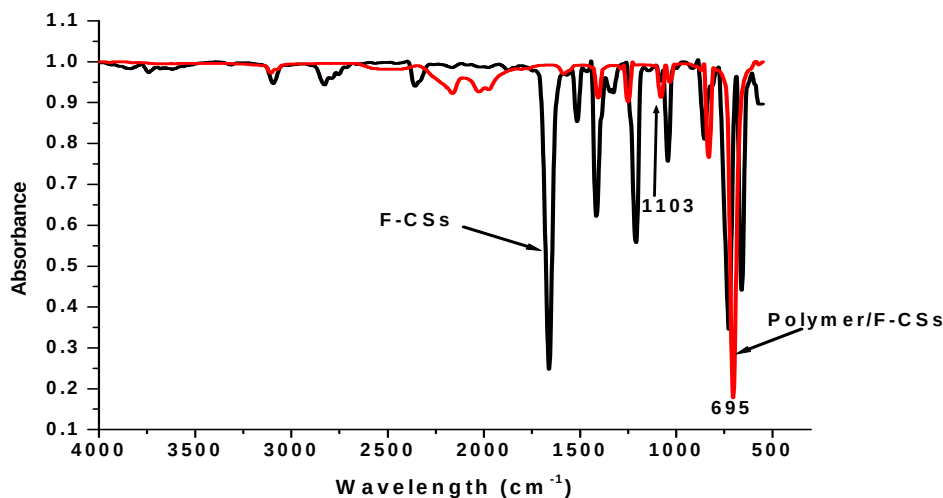


Figure 5.4(b): Infrared spectra of covalent functionalized polymer/F-CSs composites

References

1. Rao C. N. R., Govindaraj A. *RSC Nanoscience and Nanotechnology*. **87** (2005) 211905
2. Dresselhaus M.S., Dresselhaus G., Avouris P. Carbon Nanotubes Synthesis, Structure, Properties and Applications, Springer, Berlin. **80** (2001) 391
3. Niyogi S., Hamon M. A., Hu H., Zhao B., Bhowinik E., Sen R., Itkis M. E., Haddon M. E., *Acc. Chem. Res.* **35** (2002) 1105
4. Feazell R. P., Nakayama-Ratchford N., Dai H., Lippard S.J. *J. Am. Chem. Soc.* **129** (2007) 8438
5. Chen R. J, Zhang Y., Wang D., Dai H. *J. Am. Chem. Soc.* **123** (2001) 3838
6. Liu J., Rinzler A. G., Dai H., Hafner J. H., Bradley R. K., Boul P. J., Lu A., Iverson T., Shelimov K., Huffman C. B., R-Macias F., Shon Y. S., Lee T. R., Colbert D. T., Smalley R. E. *Science* **280** (1998) 1253
7. Boul P. J., Liu J., Mickelson E. T., Huffman C.B., Ericson L. M., Chiang I. W., Smith K. A., Colbert D. T., Hauge R. H., Margrave J. L., Smalley R.E. *Chem. Phys. Lett.* **310** (1999) 367
8. Chen J., Hamon M. A., Hu H., Chen Y., Rao A. M., Eklund P. C., Haddon R. C., *Science*. **282** (1998) 95
9. Grunian J. C., Liu L., Kim Y. S., *Nano Lett.* **6** (2006) 911
10. Hamon M. A., Chen J., Hu H., Chen Y., Itkis M. E., Rao A. M., Eklund P. C., Haddon R. C., *Adv. Mater.* **11** (1999) 834
11. Jeynes J. C. G., Mendoza E., Chow D. C. S., Watts P. C. P., McFadden J., Silva S. R. P. *Adv. Mater.* **18** (2006) 1598
12. Nakayama-Ratchford N., Bangsaruntip S., Sun X., Welsher K., Dai H. *J. Am. Chem.. Soc.* **129** (2007) 2448
13. Star A., Steuerman D. W., Heath J. R., Stoddart J. F. *Angew. Chem. Int. Ed.* **41** (2002) 2508
14. Bhalchandra A. K., Vijayamohanan K. P., *Appl. Surf. Sci.* **254** (2008) 4936
15. Balasubramanian K., Burghard M., *J. Mater. Chem.* **18** (2008) 3071
16. Kakade B. A., Pillai V. K. *J. Phys. Chem. C* **112** (2008) 3183

17. Khabashesku V. N., Billups W. E., Margrave J. L., *Acc. Chem. Res.* **35** (2002) 1087
18. Liu Y., Liang P., Zhang H.Y., Guo D. *Journal of Applied Polymer Science.* **99** (2006) 2874
19. Prato M., Q. Li, Wudl F., Lucchini V. *J. Am. Chem. Soc.* **115** (1993) 1148
20. Soliman L. I., Sayed W. M. *Egypt. J. Sol.* **25** (2002) 103

Chapter 6

Conclusion and Recommendations

This study gives the first reported synthesis of N-CSs by a simply synthetic procedure. Depending on the pyridine:toluene ratio, a nitrogen content of 0.13-5 mol % was obtained from horizontal type reactor. The use of a vertical CVD reactor gave N-CSs with a nitrogen content of 0.19-3 mol %. A comparative study on undoped and doped carbon spheres was also conducted; this was done to elucidate the role of nitrogen in the material. Spheres of diameters in the range 40–1000 nm were obtained, influenced by varying the flow rate, temperature, time, concentration and the reactor type.

Using the Raman spectroscopy, a significant increase of the ratio from 0.75 to 0.9 of the intensities of the defect and graphitic peaks (I_D/I_G) was observed when nitrogen was incorporated into the graphitic sheet of carbon spheres. The ESR results showed a strong central paramagnetic signal for N-CSs which is ascribed to substitutional nitrogen. The results obtained from ESR analysis confirm that the nitrogen has indeed been incorporated into the carbon matrix.

Improved measurements, such as ESR measurements as a function of temperature would also be of great interest. They may allow for a more accurate determination of the nitrogen concentrations. It would be of considerable interest to perform broad-line pulsed Nuclear Magnetic Resonance (NMR) experiments as a function of temperature on all of these samples, as this would allow for quantification of the nuclear spin-lattice interactions with mobile charge carriers, paramagnetic impurities and lattice vibrations.

However, it is worth emphasizing that carbon nanomaterials represent nowadays one of the most active research fields. It is not surprising that a high amount of research is carried out in improving and controlling these properties through different methods. Although some work has been done on different ways of endohedral doping and intercalation, the case of substitutional doping has still some difficulties to overcome.

Secondly, carbon spheres were reacted with thiophene to give polymer/carbon nanocomposites containing polythiophene and carbon spheres. This study is the first direct comparison between covalent and noncovalent nanospheres functionalization. A notable drawback for covalent functionalization is the disruption of the surface of the carbon spheres, which can lead to the reduction of electrical conductivity. For applications requiring electrical conductivity damaging the carbon sphere's ability to transport electrons needs be avoided. It is clear that noncovalent functionalization of carbon spheres can be achieved without disrupting the primary structure of the spheres themselves.

The thermogravimetric analysis data confirms that the presence of CSs in the polymer\carbon composites is responsible for the higher thermal stability of the composite material in comparison with pristine polythiophene. The nanocomposites produced in this study have functional groups which ascribe to the presence of polythiophene. The C-S bending mode has been identified to occur at 691 cm^{-1} and indicates the presence of thiophene moieties.

Future work will be devoted to improve polythiophene and carbon materials/polythiophene nanocomposites morphology by optimizing the chemical synthesis conditions. Further work is needed to understand the influence of nanospheres in the polymer matrix. Surfactants that will interact strongly enough with nanospheres, can be added in noncovalent functionalization. This method is widely accepted to preserve the electrical properties of nanomaterials.

Many studies have been carried out to understand the surface chemistry of nanomaterials and their contribution to the property enhancement of the composite. Despite all of this work, no studies have been done to directly compare the effect of one agent that is covalently and noncovalently combined with nanospheres. This will requires a molecule that can act as a surfactant and can also be covalently attached to the nanomaterials surface in a relatively simple way.

Finally, the changes in nanomaterials microstructure after functionalization may have a dramatic influence on the electrical conductivity of the composites, and due to time constraints these studies could not be done. It is therefore recommended to carry out the electrical conductivity studies.

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