

Synthesis of copper nanoparticles contained in mesoporous hollow carbon spheres as potential catalysts for growing helical carbon nanofibers

By

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A dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfillment for the degree of Master of Science in Chemistry.

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University of the Witwatersrand, Johannesburg. July 2017

DECLARATION

I declare that this Dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

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On this 05 day of July 2017

ABSTRACT

The aim of this study was to synthesize helical carbon nanofibers with controlled diameter by using copper nanoparticles contained inside hollow carbon sphere. In this work, different methods have been explored to synthesize copper nanoparticles contained inside mesoporous hollow carbon spheres in order to minimize the sintering effect of the copper nanoparticles. Mesoporous hollow carbon spheres were used not only as a support for the copper nanoparticles but to stabilize and disperse these nanoparticles to prevent the formation of aggregates. Mesoporous hollow carbon spheres were synthesized using a hard templating method, in which mesoporous silica spheres or polystyrene spheres were used as a sacrificial template. Carbon nanofibers with different morphologies, including straight and helical fibers were obtained by a chemical vapor deposition method where acetylene was decomposed over copper nanoparticles contained inside mesoporous hollow carbon spheres catalyst at 350 °C. The synthesized carbon nanofibers were grown on the surface of the mesoporous hollow carbon spheres as the methods used to synthesize the catalyst failed to incorporate copper nanoparticles inside the spheres. Differences in the diameter of the straight and helical carbon nanofibers were observed from both catalysts. This supports the important effect of particle size on influencing the shape of the synthesized carbon nanofibers.

DEDICATION

This work is dedicated to the following people:

My mom: Sarah Dhlamaga Magubane

My grandparents: Betty N. Mahlangu and the late Benzani Magubane

The rest of Magubane family

My late father NGijana August Kabini

ACKNOWLEDGEMENTS

I would like to extend my warmest gratitude to my supervisor Prof. N.J. Coville for his outstanding contributions to this project.

I would like to thank Tumelo Phahlamohlaaka for guiding me through this project, for showing me around the lab.

To Dr B. Mutuma, thank you for your warm support and guidance through this project.

I would like to thank my family for their love, support, and prayers.

To CATOMAT research group, I'm forever grateful for your positive criticism and for providing an interesting working environment.

I would like to thank MMU unit and XRD unit for their assistance in using the instruments.

I would like to thank Dr J. Wasley-Smith from CSIR for TEM analysis.

I am grateful to NRF Scarce Skills Master's Scholarship for funding.

“The Lord is my shepherd, I shall not want. He makes me lie down in green pastures; he leads me beside still waters; he restores my soul” Psalm 23: 1-3

PRESENTATIONS

Alice Magubane, Tumelo Phaahlamohlake, Neil Coville, *Synthesis of helical carbon nanofibers using hollow carbon sphere coated copper nanoparticles (Poster presentation)*, CATSA annual conference-Capetown, November 2015.

Alice Magubane, Tumelo Phaahlamohlake, Neil Coville, *Synthesis of helical carbon nanofibers using hollow carbon sphere coated copper nanoparticles (Poster presentation)*, NanoAfrica 6th international conference, Unisa-Johannesburg, April 2016.

Alice Magubane, Tumelo Phaahlamohlake, Neil Coville, *Synthesis of helical carbon nanofibers using hollow carbon sphere coated copper nanoparticles (Poster presentation)*, CoE-SM Annual Student Presentations Wits-Johannesburg, May 2016.

Alice Magubane, Tumelo Phaahlamohlake, Neil Coville, *Synthesis of helical carbon nanofibers using hollow carbon sphere coated copper nanoparticles (Poster presentation)*, CATSA annual conference-Kwazulu Natal, November 2016.

Alice Magubane, Neil Coville, *Synthesis of helical carbon nanofibers using copper nanoparticles contained inside mesoporous hollow carbon spheres (Pitch presentation)*, Nanosciences Young Researcher' Symposium Mintek-Johannesburg, November 2016.

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LIST OF ABBREVIATIONS

Abbreviation	Definition
CNF(s)	Carbon nanofiber(s)
HCNF(s)	Helical carbon nanofiber(s)
CNT(s)	Carbon nanotube(s)
mHCS(s)	Mesoporous hollow carbon sphere(s)
HCS(s)	Hollow carbon sphere(s)
PSS(s)	Polystyrene sphere(s)
mSiO₂	Mesoporous silica spheres
C₂H₂	Acetylene
CVD	Chemical vapor deposition
TGA	Thermogravimetric analysis
TEM	Transmission electron microscopy
BET	Brunauer-Emmet and Teller
PXRD	Powder X-ray diffraction
RF	Resorcinol formaldehyde
OA	Oleic acid
OLA	Oleylamine
CTAB	Hexadecyltrimethylammonium bromide
TEOS	Tetraethyl orthosilicate
TOP	Trioctylphosphine
C₁₈TMS	Trimethoxy(octadecyl)silane
HF	Hydrofluoric acid
VLS	Vapor-liquid-solid

Cu/mSiO₂	Copper nanoparticles supported on mesoporous silica
Cu/PSSs	Copper nanoparticles supported on polystyrene spheres
Cu@mHCSs	Copper nanoparticles contained inside mesoporous hollow carbon spheres

Chapter 1: Research question and hypothesis

1.1 Introduction

Carbon can exist in many allotropic forms; the diversity in the morphology of carbon materials provides the flexibility to alter the properties of carbon [1]. Carbon can form various allotropes due to its variable valency [2]. Some of these carbon allotropes include diamond, graphite, carbon fibers, fullerenes, carbon nanotubes (CNTs) etc. Over the past few decades' carbon nanofibers (CNFs) were considered as by-products of catalytic reactions, hence many studies focused on finding ways to eliminate their formation [3, 4]. Researchers showed enthusiasm to make carbon nanofibers after carbon nanotubes were reported by Iijima in 1991 and since then a great deal of research has been conducted on them [3, 5]. This attention was led by the magnificent properties of the CNFs which are similar to those of CNTs. CNFs have high mechanical strength, chemical purity, high surface area, high pore volume, high electric conductivity, and chemical inertness [6, 7]. These are the properties that make CNFs suitable for use as a catalyst support and for use in nanomechanical devices, composite materials, in selective adsorption, and in hydrogen storage [7].

Carbon nanofibers are defined as fibrous carbon materials containing more than 90 % of carbon [8]. They are formed by graphene sheets that stack upon each other which results in both hollow and solid structures [1]. CNFs vary in length from nm to micrometer sizes and range from being amorphous to being highly crystalline [1]. The two most common types of CNFs are the fishbone and the parallel type (Figure 1.1) [2]. The fishbone type consists of graphite planes oriented at an angle to the central axis leaving the graphite edge sites exposed, while the parallel type consists of graphite planes oriented parallel to the central axis [2]. Another type of carbon nanofiber is the helical CNF (HCNF). The unique properties of HCNFs such as high chemical stability, surface area, elasticity, mechanical strength and good thermal and electrical conductivity have led to wide study of these materials [2]. Vapor growth of helical carbon nanomaterials was first

reported by Davis *et al.* in 1953 [1]. Figure 1.2 shows different types of helical carbon nanofibers. In the early studies, the synthesis of HCFs through vapor phase growth was poorly repeatable [9]. After this, extensive research on the synthesis of helical carbon fibers (HCFs) was done by Motojima *et al.* [10-13]. They reported the synthesis of HCFs using catalytic pyrolysis of acetylene with a small amount of sulfur or phosphorus impurity over Ni nanoparticles [10-13]. This method was found to produce micro-coiled fibers in high yield and the method to give HCFs was highly reproducible [10-13]. HCNFs can be classed as a single helix, double helix, triple helix, braid, spiral, coil and spring shaped based on the nature of the helical material [1]. The type and the amount of CNFs formed depends on the variation of variables such as temperature, type of carbon precursor, the particle size of catalyst, gas environment and the type of catalyst [1, 2].

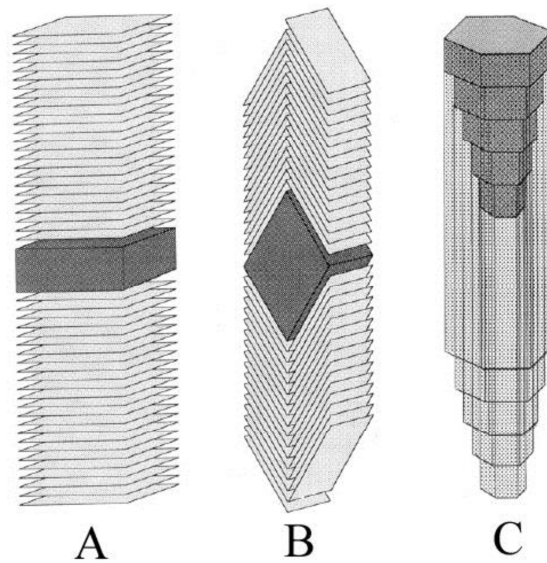


Figure: 1.1: Schema representations of the CNFs: (A) platelet, (B) fishbone and (C) parallel [2].

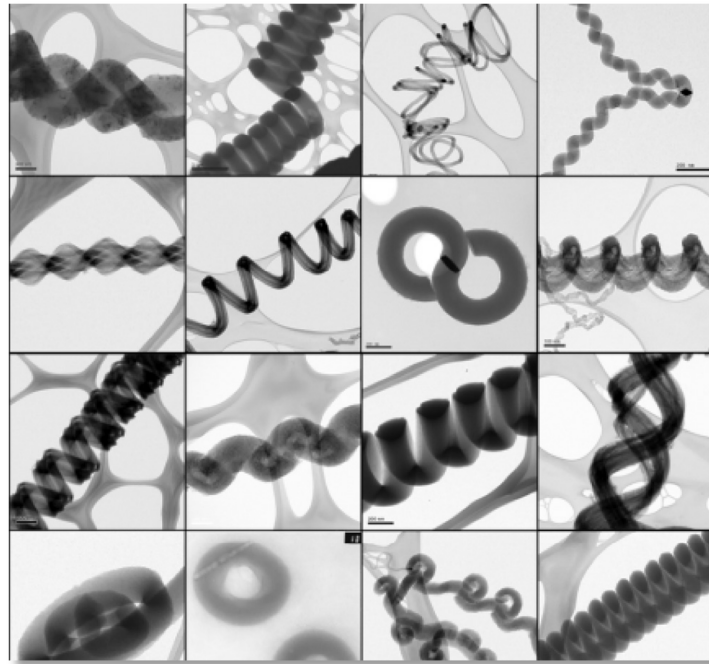


Figure 1.2: TEM images for different types of helical carbon nanomaterials [1].

Different methods such as chemical vapor deposition (CVD), arc discharge and laser vaporization have been used to make HCNFs [2]. Arc discharge and laser vaporization methods use a high temperature ($> 2000\text{ }^{\circ}\text{C}$) hence the carbon atoms are highly mobile resulting to a perfect hexagonal graphite and the formation of straight carbon fibers [2]. For large scale preparation, the CVD process has been noted as the most efficient method for the synthesis of HCNFs [2, 14]. In this process hydrocarbons are decomposed over transition metal nanoparticles such as Cu, Ni, Co and Fe [2]. CVD provides easy control of the experimental parameters; it is cheap and provides a highly reproducible method that can give a high yield of HCNFs compared to other methods [2].

There are two theories as to how the shape of the helical CNF is formed; (i) unequal extrusion of carbon from a catalyst surface giving rise to the curvature and (ii) by the shape of catalyst particles under the influence of van der Waals forces that exist between the fiber and surroundings [1]. The type of metal nanoparticles used to grow CNFs determines the size, morphology, and yield of the obtained CNFs hence the synthesis of CNFs with controlled morphology is a challenge [6]. It has been reported that one of the most important parameters

that affect the morphology and growth of CNFs is the size of the catalyst particle. The same applies to HCNFs.

During the past two decades, many researchers have used copper nanoparticles to make carbon nanofibers [15]. CNFs can be grown catalytically by decomposition of a carbon precursor over metal nanoparticles like Ni, Fe, or Co [5, 16]. Copper nanoparticles have a high surface-to-volume ratio but they are very sensitive to air [15]. Oxidation of copper nanoparticles can be prevented by coating their surface with organic or non-organic protective shells like carbon and silica [15]. These capping agents not only prevent surface oxidation of the nanoparticles but also help stabilize the size of these particles [17]. Surfactants such as oleylamine and oleic acid have been used as a mixture to prevent surface oxidation and agglomeration of numerous types of nanoparticles [18].

Noble metal nanoparticles relative to bulk metals have higher catalytic activity due to the larger fraction of the atoms available for the catalytic process [19, 20]. However, noble metal nanoparticles can form aggregates which results into a loss of catalytic activity as the number of active surface sites decrease [19, 20]. Hollow carbon spheres (HCSs) could act as support for these nanoparticles to stabilize and disperse them, and help prevent the nanoparticles from forming aggregates [19, 20]. Intrinsic properties of HCSs include; structure, large void space, excellent reactivity, porous shell, low density and a controllable surface [21]. Previous studies by Bhoware *et al.*, Shaikjee *et al.* and Li *et al.* have raised a number of questions such as: is there a way that can be used to specifically synthesize CNFs with one morphology [22, 23, 5]? In these studies it has been noted that the effect of gas (N_2/H_2) catalyst particle size, and metal support used during the synthesis of CNFs plays an important role in determining the morphology of CNFs [22, 23]. This study focuses on finding a way to control copper particle size and eliminate formation of aggregation using mHCSs and to synthesize CNFs with helical morphology using Cu@mHCSs catalyst.

1.2 Motivation for the study

Supports such as carbon, SiO₂, Al₂O₃, TiO₂, CaO, and MgO have been used as metal supports to enhance the catalytic activity of a catalyst as they provide good dispersion of the catalyst [5, 22, 23]. Previously helical CNFs have been synthesized using copper nanoparticles supported on mesoporous silica [5, 22]. The problem that was encountered in the previous studies was that copper nanoparticles aggregate at the HCNF formation temperature which resulted in a loss of catalytic activity as the number of active sites decreased [5, 22]. As there was no control of the size of copper nanoparticles both straight and helical CNFs with different diameters were observed.

1.3 Aim and objectives

The purpose of this study was to synthesize helical carbon nanofibers with controlled diameter by using hollow carbon sphere coated copper nanoparticles.

The objectives of this study were:

- ❖ To synthesize (i) mesoporous silica spheres using a modified Stöber method and (ii) polystyrene spheres (PSSs).
- ❖ To load copper nanoparticles onto these supports.
- ❖ To deposit a carbon layer around the Cu/mSiO₂ and Cu/polystyrene composite using CVD and resorcinol-formaldehyde (RF) methods respectively.
- ❖ To remove the template using chemical etching with NaOH/ or hydrofluoric acid (mSiO₂ template) or CVD (PSSs template).
- ❖ To synthesize copper nanoparticles inside the mHCSs.

- ❖ To control the growth of HCNFs using different copper nanoparticles sizes.
- ❖ To ascertain the physical and chemical characteristics of the products by characterizing them through techniques such as TEM, TGA, PXRD, BET and Raman spectroscopy.

1.4 Research questions

- ❖ Can porous hollow carbon spheres containing copper nanoparticles prevent sintering of the copper nanoparticles?
- ❖ How does the size of the metal nanoparticle affect the size of the carbon nanofibers?
- ❖ Will carbon nanofibers grow on metal nanoparticles placed both inside and outside a hollow carbon layer?

1.5 Outline of dissertation

Chapter 1: Gives a short review of CNFs and the aims and objectives of the study.

Chapter 2: Gives a literature review on copper nanoparticles and the mechanism of the formation CNFs using copper as a catalyst.

Chapter 3: Gives the experimental procedures for synthesizing copper nanoparticles inside mesoporous hollow carbon spheres (Cu@mHCSs).

Chapter 4: Reports the results on the synthesis of copper nanoparticles contained inside mesoporous hollow carbon spheres.

Chapter 5: Reports the results on the synthesis of helical carbon nanofibers using copper nanoparticles contained inside mesoporous hollow carbon spheres.

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Chapter 2: Literature review

2.1 Synthesis of carbon materials using copper nanoparticles as a catalyst

2.1.1 Application of copper nanoparticles

The unique properties of metallic copper nanoparticles such as their electrical, physical, chemical and optical properties have led to their use in a wide range of applications in different industries [1]. These applications include nanotechnology, electrocatalysis, and photo-catalysis. Copper and copper-based nanoparticles are based on the earth abundant and cheap copper metal. Copper's range of accessible oxidation states enables it to be used in many different reactions. Copper nanoparticles have been used as an alternative to expensive noble metals such as silver (Ag) and gold (Au) in many conventional commercial chemical processes [2]. However, it is to be noted that the synthesis of copper nanoparticles is difficult due to surface oxidation of this metal [2, 3]. Many researchers have found ways to prevent surface oxidation of copper nanoparticles [4, 5, 6, 7]. Copper nanoparticles are attractive because there are multiple easy ways of preparing them. Copper nanoparticles exhibit properties which are different to bulk copper. This can be attributed to the surface/bulk ratio of copper atoms which varies with the size of a copper particle [2]. The shape of small copper particles can also influence the properties of copper nanoparticles.

Biological properties of copper nanoparticles and its compounds have led to these nanoparticles being used as antibacterials, antivirals and as disinfectants for waste water containing infectious microorganisms [1, 8]. Copper nanoparticles have found a lot of applications in nanotechnology applications [3]. However, this area is dominated by the use of Ag and Au as they usually exhibit superior properties [3]. Due to the remarkable optical properties of copper, it has been found to have a local surface plasmon resonance (LSPR) in the visible region. This effect could be used to

tune chemical reactions occurring on the surface of copper nanoparticles [2, 9, 10]. Copper-based nanoparticles have been used in heterogeneous catalysis such as the Water Gas Shift reaction which produces H₂ and carbon dioxide gas from water vapor and carbon monoxide [2, 3, 11]. Amongst other applications, copper nanoparticles have been used as a catalyst in many organic reactions such as in azide-alkyne cycloaddition, coupling reactions, reduction reactions and oxidation reactions [2, 12]. Also, copper nanoparticles have been used as a catalyst promoter in catalytic reactions such as Fischer-Tropsch synthesis [13, 14].

2.1.2 Synthesis of carbon nanofibers using copper nanoparticles

The size and shape of copper nanoparticles can be controlled by the type of synthesis method used [15]. Copper nanoparticles can be synthesized through different techniques that either utilize a “bottom-up” approach in which atomic precursors are used to synthesize materials in the nano-range or a “top-down” approach in which a bulk solid is broken down into progressively smaller components [16]. The bottom-up approach has often been used due to the flexibility of the method for controlling the shape and size of the resulting nanoparticles [16]. The most important synthetic techniques are chemical methods like chemical reduction, electrochemistry, photochemical reduction and thermal decomposition [15].

2.1.2.1 Unsupported copper nanoparticles

Most studies to make carbon materials using a catalyst have focused on the effect of the catalyst metal particle size and shape on the diameter of CNFs and the morphology of CNF produced. In one paper it has been reported that copper particles with small size (< 100 nm) form helical carbon nanofibers (HCNFs) whereas large particles (> 100 nm) form straight CNFs [17]. However, other studies have shown different results. The size of the metal particle might contribute to the morphology of the fiber formed but the morphology of the metal particle has to be considered, given that the particles of the same size can either form helical or straight fibers [18]. Agglomeration of the metal nanoparticles also plays a role in the formation of straight

CNFs. Before copper nanoparticles are used to make carbon materials in a CVD process they usually have an irregular shape. However, once this catalyst is activated these nanoparticles change to be more regular in appearance. This was demonstrated by Qin *et al.* [17] in their synthesis of HCNFs with a symmetric growth mode using copper nanoparticles as a catalyst (Figure 2.1).

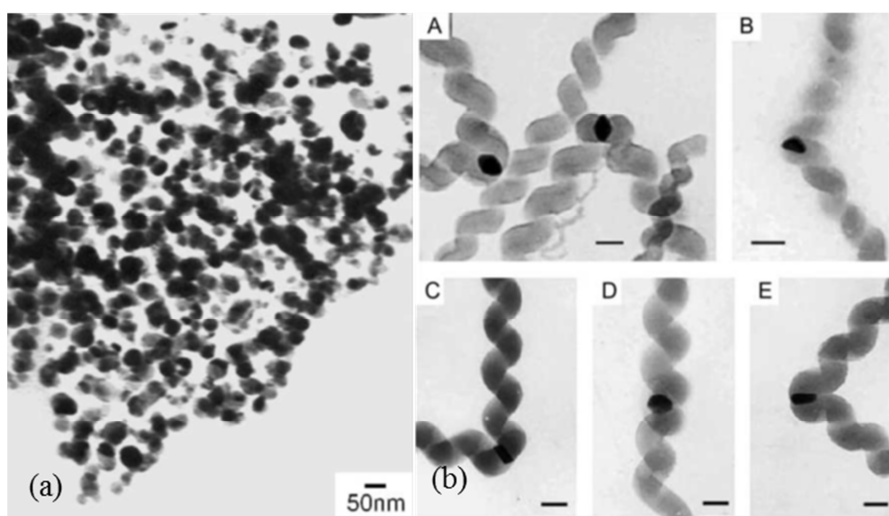


Figure 2.1: TEM images of (a) irregular shaped copper nanoparticles and (b) CNFs synthesized from regular shaped copper nanoparticles (scale bar = 100 nm) [17].

Zhang *et al.* [19] studied the effects of nano-copper catalyst size and reaction temperature on the morphology of CNFs. They reported that the shape of catalyst particle has limited influence on the morphology of CNFs. According to the authors morphology of CNFs is related to the size of catalyst particles. They synthesized three different catalysts (A: 30-60 nm, B: > 120 nm and C: 60-110 nm) in which catalyst formed helical, straight and both CNFs respectively (Figure 2.2).

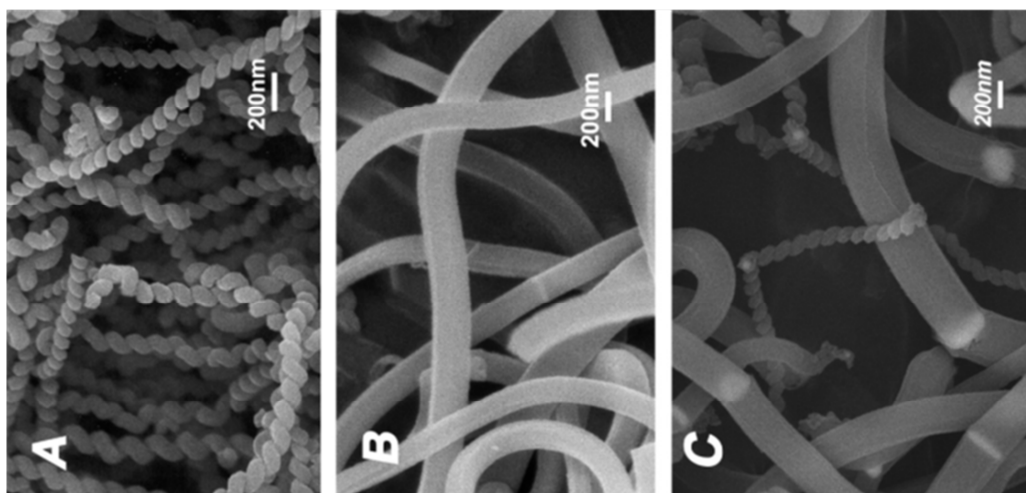


Figure 2.2: TEM images of (a) HCNFs, (b) straight CNFs and (c) straight and helical CNFs synthesized by copper nanoparticles [19].

2.1.2.2 Supported copper nanoparticles

Stöber spheres have been used as a support for copper nanoparticles as they improve the catalytic activity of these nanoparticles through metal-support interactions [20]. The synthesis of CNFs has never yielded 100% pure materials. And many studies have shown that CNFs are formed with diverse morphologies (looped, single helix, straight or double helix). This has led to a study of the effects of the catalyst composition, carbon precursor, impurity elements, pre-treatment conditions and temperature on the formation of helices [21, 22]. Shaikjee *et al.* [21] reported the synthesis of carbon nanostructures over supported copper nanoparticles catalysts at low temperatures. They used different metal oxide supports. The authors reported that the morphology of CNFs depended on the type of catalyst support, copper precursor, and solvent used when preparing the catalyst.

Bhoware *et al.* [20] studied the physical and chemical properties of CNFs produced using copper nanoparticles. They used three different copper supported materials namely: (i) silica coated copper nanoparticles ($\text{Cu}@\text{SiO}_2$), (ii) copper supported on silica spheres (Cu/SiO_2), and (iii) copper nanoparticles. CNFs were produced by passing a mixture of acetylene/ H_2 or acetylene/ N_2 over various copper catalysts at 300 °C for an hour. From the TEM images, it was shown that

over the three copper catalysts only Cu/SiO₂ formed predominantly helical CNFs whereas the other two catalysts formed predominantly straight fibers (Figure 2.3). To account for Cu/SiO₂ forming helical CNFs they concluded that the size of copper nanoparticles on this support is smaller than the size of copper on the other two supports. When the hydrogen gas was replaced by nitrogen it was observed from the TEM images that only straight fibers were formed (Figure 2.4). Also, the yield of carbon was reduced when compared to the yield obtained when using hydrogen gas.

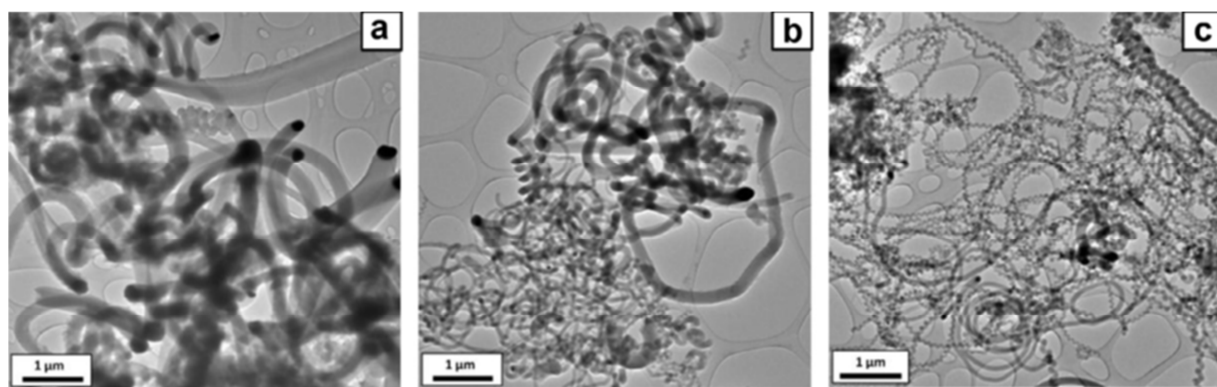


Figure 2.3: TEM images of CNFs grown using (a) copper nanoparticles, (b) Cu@SiO₂ and (c) Cu/mSiO₂ under acetylene/H₂ [20].

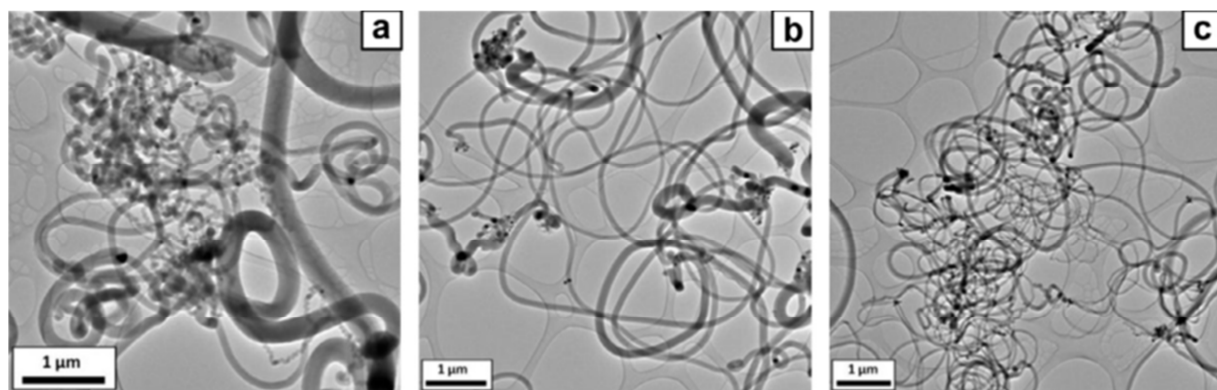


Figure 2.4: TEM images of CNFs grown using (a) copper nanoparticles, (b) Cu@SiO₂ and (c) Cu/mSiO₂ under acetylene/N₂ [20].

Li *et al.* [23] synthesized CNFs using Cu@SiO₂ under acetylene at 340 °C. They reported that during CVD, copper nanoparticles with high catalytic activity migrated out of the silica coating and catalyzed the growth of CNFs. They reported that the thick silica coating prevented copper nanoparticles from catalyzing the growth of CNFs (Figure 2.5 c); hence copper nanoparticles would have to migrate out of silica in order to grow CNFs. After decomposition of acetylene, the copper nanoparticles moved out of the silica coating as indicated by the arrows shown in Figure 2.6 (a). The morphology of these carbon nanofibers was reported to be helical.

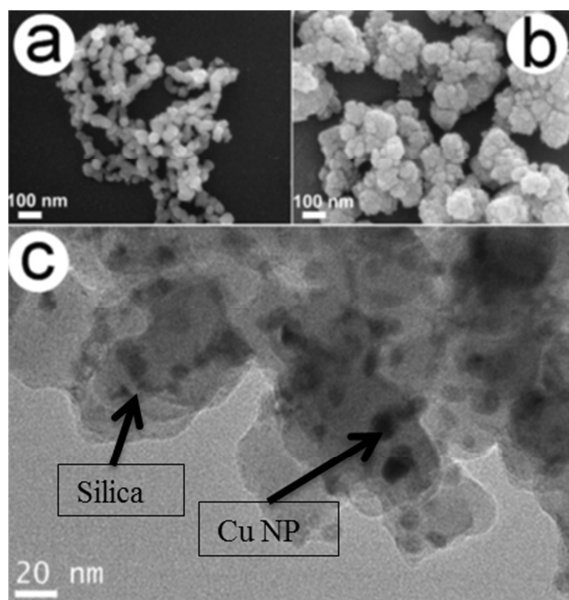


Figure 2.5: SEM images of (a) copper nanoparticles, (b) Cu@SiO₂ and HRTEM image of Cu@SiO₂ [23].

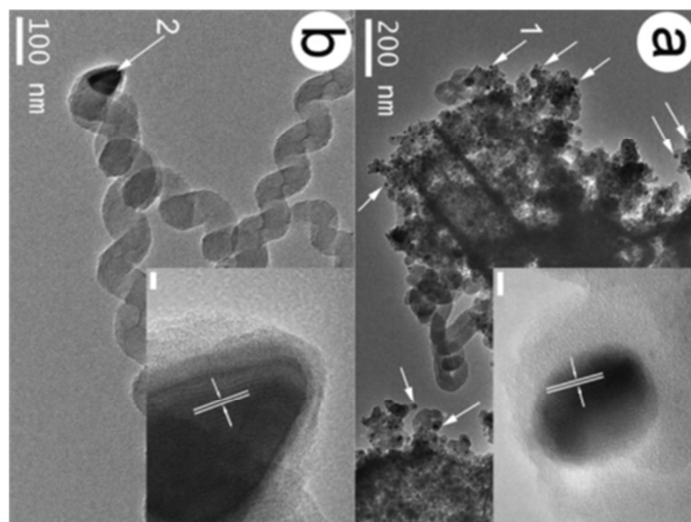


Figure 2.6: HRTEM images of CNFs synthesized using Cu@SiO₂ catalyst [23].

The effect of particle morphology and carbon fiber structure was further studied by Shaikjee *et al.* [18]. The authors used TEM tomography to correlate the morphology of the carbon fiber with the copper catalyst morphology. CNFs were synthesized via catalytic decomposition of acetylene over Cu/TiO₂ for an hour at 250 °C. From 2-D TEM images it was observed that both straight and helical carbon fibers were obtained from the similar shaped (rhombohedral) copper particle (Figure 2.7 (a) and Figure 2.8 (a)). This would suggest that there is no relationship between the morphology or size of the catalyst and the morphology of the carbon fiber.

They went on to do 3-D TEM tilting experiments on the catalyst particles. After doing a series of tilting experiments on the copper particles associated with the growth of a straight fiber, they obtained the TEM images shown in figure 2.7 (b-g). The copper particle was found to be trigonal bipyramidal in shape. A copper particle associated with a HCNF was also studied using tilting procedures and its TEM images are shown in figure 2.8 (b-g). The shape of the copper particle was found to be pentagonal bipyramid. The authors concluded that the difference in the shape of the particle leads to the formation of either straight or helical fibers. HCFs are formed from the five facets which were assumed to be unequal in activity, whereas straight fibers grow from a pyramidal particle with three equal facets on their planes.

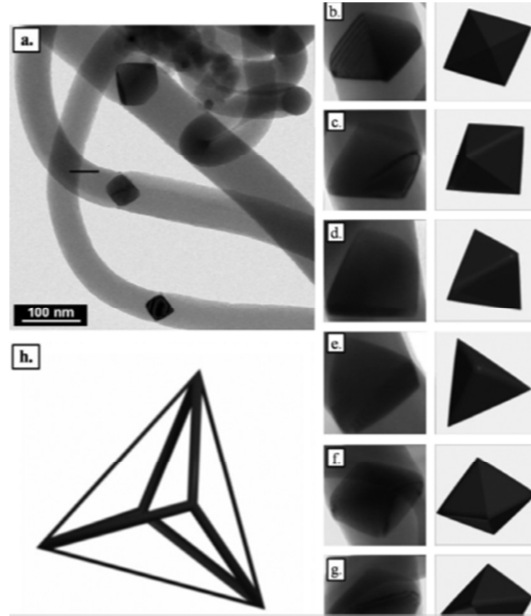


Figure 2.7: TEM images of straight CFs grown from Cu/TiO₂. (a) Straight CFs with symmetrical growth mode; (b-g) TEM images of copper particle tilted at different angles and related computer simulated images; and (h) simulated particle shape (trigonal bi-pyramidal) [18].

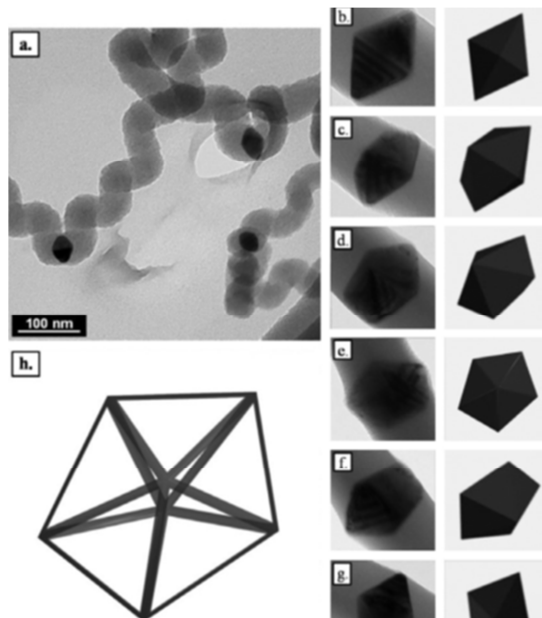


Figure 2.8: TEM images of HCFs grown from Cu/TiO₂. (a) HCFs with symmetrical growth mode; (b-g) TEM images of copper particle tilted at different angles and related computer simulated images; and (h) simulated particle shape (distorted decahedron) [18].

2.1.3 Synthesis of graphene using copper as catalyst

Graphene can be defined as a single atomic layer of carbon atoms arranged in a hexagonal network [24]. Graphene is an attractive material because of its unique high carrier mobility and band structure. The unique electronic, optical, chemical and mechanical properties of graphene have been investigated for potential applications in electronics, optoelectronics, and composites [25]. In 1991 graphite was accidentally observed in the synthesis of diamond by CVD [26]. Graphene was first observed on Ni surfaces that were exposed to carbon sources such as hydrocarbons [26]. On the other hand, graphene was also observed at the same time on single crystal Pt substrates in catalysis experiments [26]. At this stage, it was deduced that graphene formation was due to diffusion and segregation of carbon impurities from the bulk to the surface during the annealing and cooling stages [26].

Graphene can be grown using different methods such as mechanical exfoliation of graphite, sublimation of epitaxial SiC and catalyst assisted chemical vapor deposition [24-28]. Mechanical exfoliation of graphite gives high-quality graphene in low yield; this method is not scalable to high-volume manufacturing [24-28]. Sublimation of epitaxial SiC is scalable but it requires a high temperature ($> 1500^{\circ}\text{C}$) and the SiC substrate is expensive [24-29]. The CVD method has been used as an alternative to synthesizing graphene on transition metals in high yield although this method compromises the quality (carrier mobility) of the graphene product [24]. The CVD method allows for optimization of the growth process which can allow for improvement of the quality of graphene [24] and it allows for exploration of different transition metals as catalysts [27].

CVD has been considered the most promising approach amongst all other methods to make graphene, as it is inexpensive and produces large-area graphene [30]. Synthesis of graphene using CVD over Ni and Cu substrates was first reported in 2008 and 2009, and since then a lot of research using different transition metals (e.g. Fe, Co) has been conducted [24, 30]. The synthesis of graphene using the CVD method involves decomposition of a carbon precursor at high temperatures ($900\text{-}1100^{\circ}\text{C}$) in the presence of metal thin film/foils [27]. Fe, Ni and Co have been used to synthesize multi-layer graphene but use of these catalysts has indicated a lack

of control over the number of layers which can be attributed to the formation of a metal carbide due to the high solubility of carbon on these transition metals (> 0.1 atomic %) at high temperatures when compared to copper (< 0.001 atomic %) [24, 26, 31]. These metals have a small grain size which makes it hard to synthesize large-area graphene whereas annealing of copper can lead to very large grains [32]. Different mechanisms have been proposed for the growth of graphene over Ni and Cu (Figure 2.9) [30]. Copper films/foils are used as they are not expensive and can be easily etched away from the graphene so that transfer on to a desired substrate can easily be achieved [26].

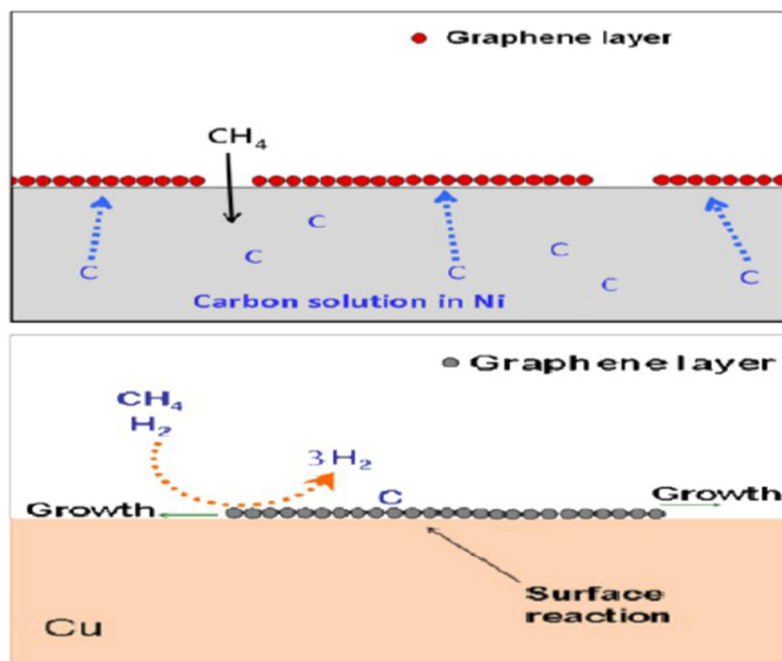


Figure 2.9: Schematic representation illustrating the difference in mechanism of graphene growth on Ni and Cu substrates [30].

Liu *et al.* [24] synthesized high-quality monolayer and bilayer graphene on copper using CVD. They investigated the mechanism determining the growth of graphene. The authors came up with a scheme (Figure 2.10) in which they described the mechanism of graphene growth by low-pressure CVD. Initially, hydrocarbon molecules are absorbed and de-absorbed on the copper surface; after absorption, decomposition of the hydrocarbon on the surface occur leading to the

formation of carbon atoms. The carbon atoms then form aggregates on the copper surface in order to form graphene nucleation centers. This is shown in the top part of Figure 2.10. The carbon atoms then diffuse and attach to nucleation centers to form graphene film (Figure 2.10 (2)). The authors concluded that the purity of the copper film is vital for the controlled synthesis of monolayer or bilayer graphene.

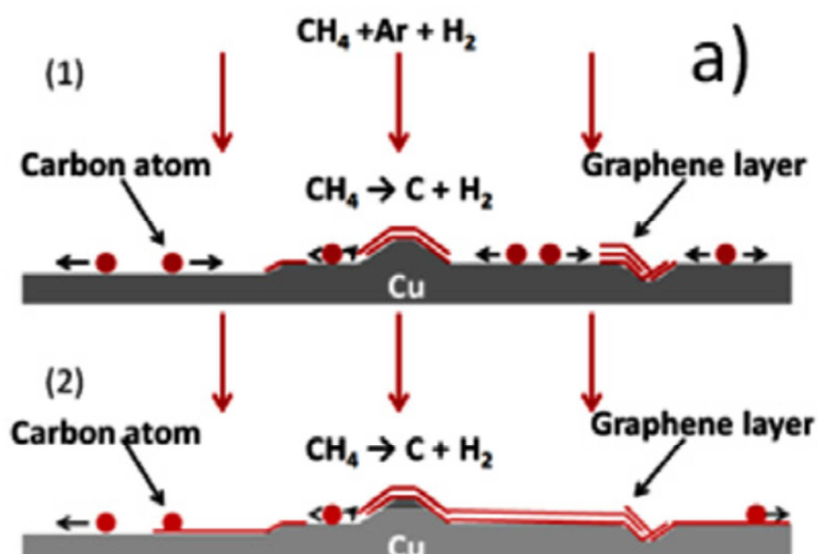


Figure 2.10: Schematic representation of graphene growth mechanism using low-pressure conditions [24].

Losurdo *et al.* [31] studied the role of hydrogen in the CVD graphene growth kinetics of Ni and Cu using CH_4 - H_2 precursors. Prior to this study, only carbon solubility had been reported as a factor contributing to the mechanism of graphene growth on these two transition metals. Their findings were that molecular and atomic hydrogen readily diffused into copper while it recombined on the surface of Ni. Hydrogen diffusion on copper slowed down the deposition kinetics of graphene on copper resulting in blockage of sites on the copper surface which led to the formation of a graphene monolayer. Hydrogen surface combination helped to keep the sites on the Ni surface free for CH_x ($x = 1-4$) dehydrogenation leading to diffusion of carbon which formed multilayer graphene.

Regmi *et al.* [29] studied the effect of the growth parameters on the graphene synthesized by CVD on copper. They varied the temperature from 600 to 1000 °C at a fixed pressure (500 mTorr) to study the temperature dependence on the growth of graphene. Using Raman spectroscopy (Figure 2.11) they determined that no graphene was formed at temperatures below 850 °C. The authors managed to grow single layer graphene at temperatures greater than 900 °C whereas at 850 °C the graphene formed was highly defective suggesting multi-layer graphene.

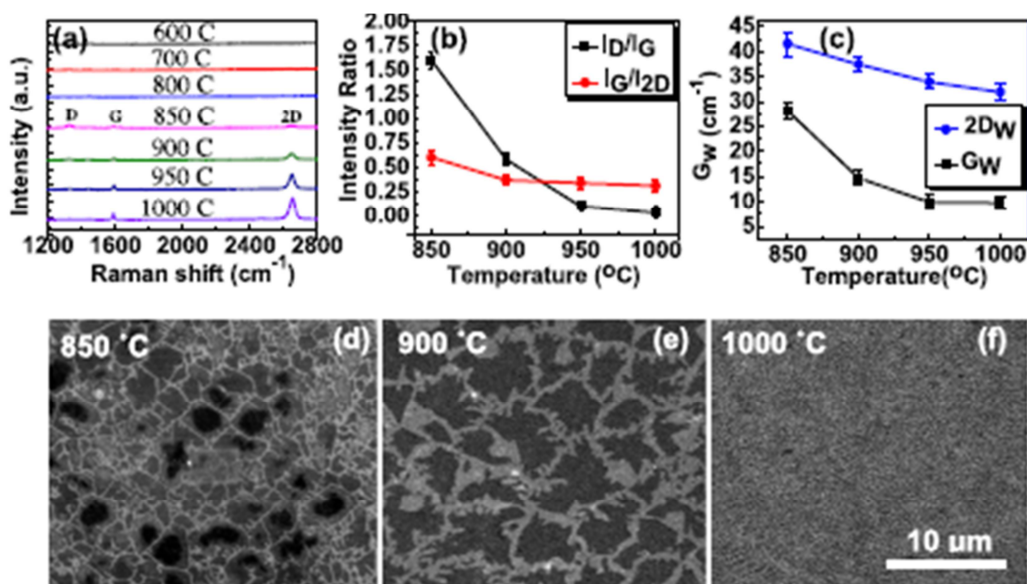


Figure 2.11: (a) Raman spectroscopy of graphene growth as a function of temperature. (b) Average values of I_D/I_G and I_G/I_{2D} from four different measurements. (c) Average values of line widths of G and 2D graphene peaks from four different measurements. (d-f) SEM images of graphene on Cu grown in 30 min [29].

2.1.4 Synthesis of CNTs using copper nanoparticles

Carbon nanotubes (CNTs) are defined as cylinder/s of graphene sheets rolled up to form single walled, double walled and multi-walled entities whereas graphene sheets in CNFs stack up on each other forming solid and hollow carbon structures (Figure 2.12) [33]. CNTs and CNFs can

either take on a straight or helical morphology. Most studies on copper have been based on the synthesis of single walled carbon nanotubes (SWCNTs) [34, 35, 36] and fewer reports have been reported for the synthesis of multi walled carbon nanotubes (MWCNTs) [37].

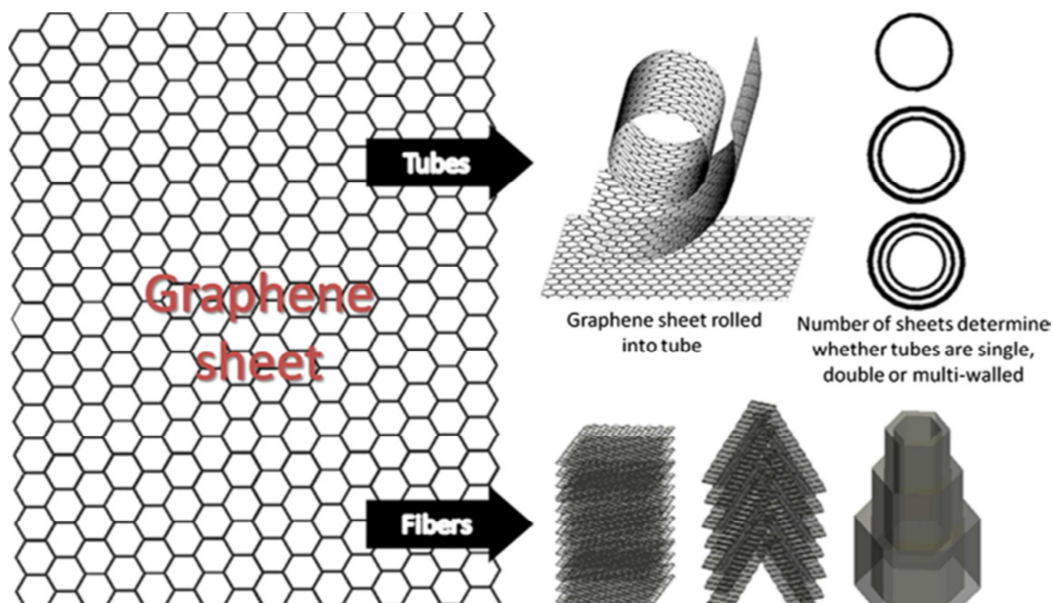


Figure 2.12: Formation of CNTs and CNFs from graphene sheets with different morphologies [33].

Zhu et al. [38] reported the synthesis of bamboo like CNTs grown on a copper foil by CVD. The authors studied the reaction in the temperature range between 600 and 1000 °C and observed that when the temperature was lower than 600 °C there were no CNTs formed. The CNTs started growing when the temperature was above 600 °C (Figure 2.13) and their yield increased with temperature. It was suggested that at higher temperature (> 600 °C) the yield of CNTs might have increased as a result of increased dissolution of carbon inside the catalyst, the enhanced diffusion rate of the dissolved carbon across the catalyst particles and the rate of the growth of CNTs as well as the increased number of copper particles on the CNTs.

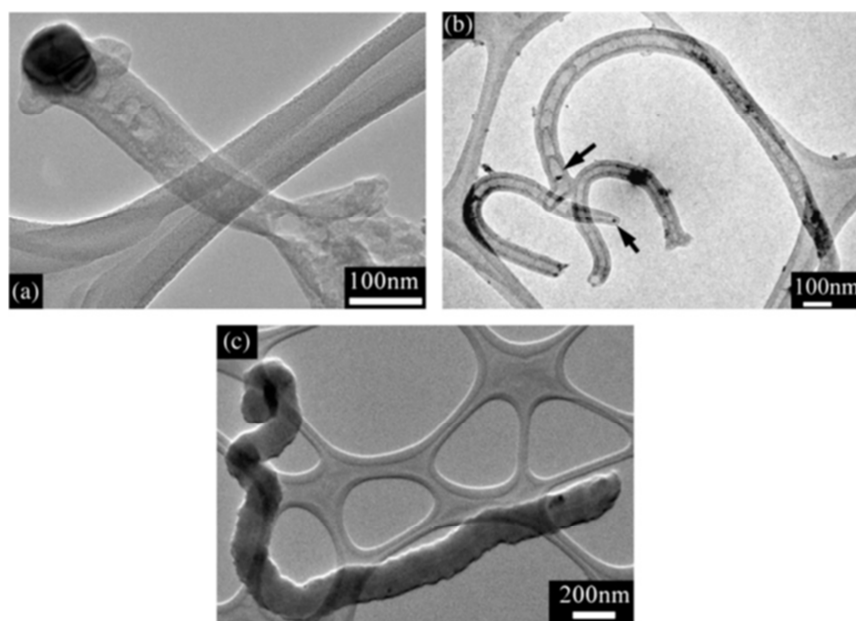


Figure 2.13: TEM images of CNTs prepared for 30 min at (a) 700, (b) 800, and (c) 1000 °C [38].

Previously copper has been considered as a poor catalyst for the synthesis of single walled carbon nanotubes (SWCNTs) [34, 39] but studies have shown that copper can even be better than Fe for the synthesis of SWCNTs [34]. The Fe catalyst is unfavorable for the synthesis of SWCNTs because Fe has higher catalytic activity for the dissociation of alkanes when compared to copper [34].

Zhou *et al.* [35] prepared SWCNTs on the surfaces of silicon wafers and silica microspheres using a copper catalyzed CVD method. The authors found copper had a very high catalytic activity for the growth of both random SWCNT and horizontally aligned SWCNT arrays (Figure 2.14). The presence of high-quality horizontally aligned SWCNT arrays was explained as a result of the weak interaction between copper and silica surface. Takagi *et al.* [36] also demonstrated that copper is an efficient catalyst for the synthesis of SWCNTs, since it was well established that metals such as Fe, Co, and Ni can give high yields of SWCNTs via the CVD method. The authors showed that any metal (Ag, Cu, Au etc.) particle with size of 1-3 nm may produce SWCNTs in the CVD procedure (Figure 2.15).

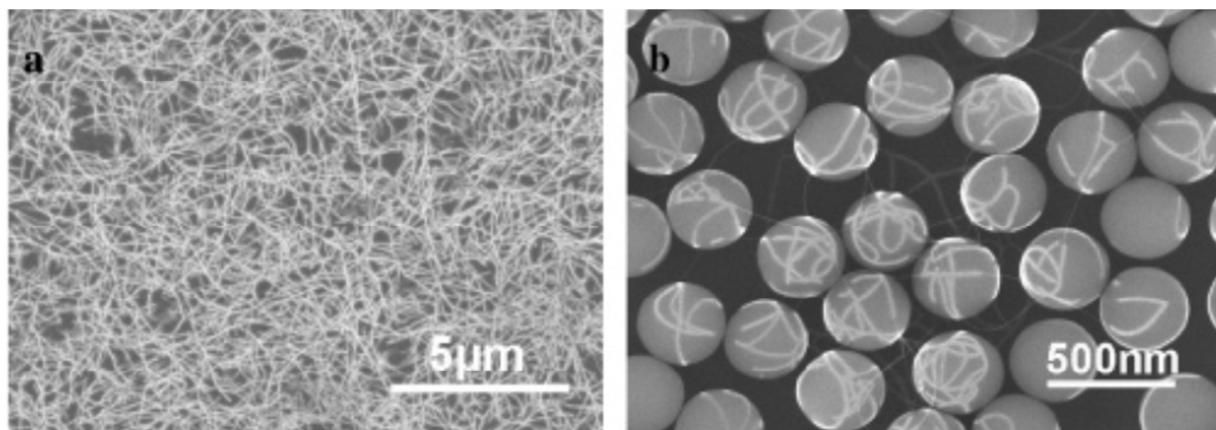


Figure 2.14: SEM images of (a) random networks of SWCNTs grown from the surface of silicon wafer with copper catalyst, (b) SWCNTs grown from the surface of silica microspheres with copper catalyst [35].

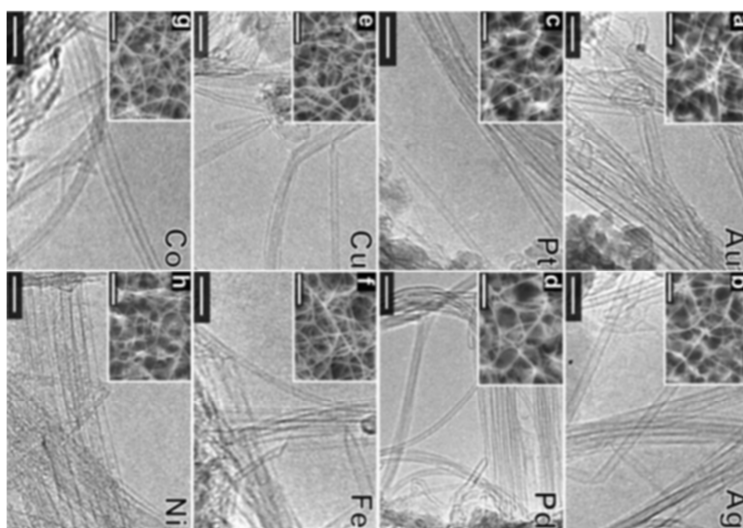


Figure 2.15: TEM and SEM (inserts) images of SWCNTs grown using different metals as catalyst [36].

The synthesis of bamboo-like structures dominated the morphology of the MWCNTs grown over a Cu/Al₂O₃ catalyst by CVD using ethanol as carbon precursor at temperatures between 700 and 850 °C was reported by Xue *et al.* [37]. The percentage yield of the bamboo-like MWCNTs was reported to increase up to 800 °C (40, 85 and 95 %) and decreased at 850 °C (90 %). It was noted

that the reaction temperature plays a key role in the formation of the bamboo-like morphology (Figure 2.16).

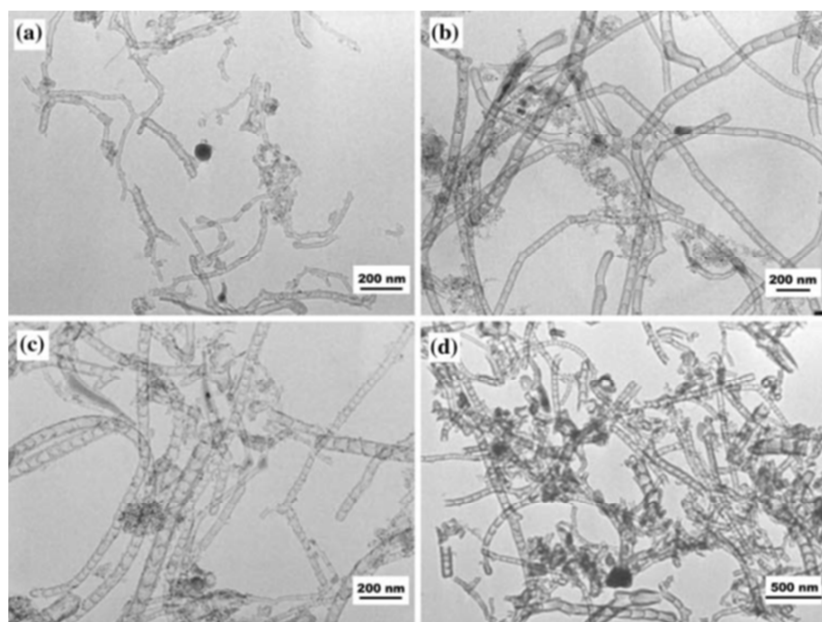


Figure 2.16: TEM images of bamboo-like MWCNTs grown at (a) 700, (b) 750, (c) 800, and (d) 850 °C [37].

2.2 Proposed theories of HCNF growth on a nano-metal catalyst

It has been proposed that the growth of CNFs occurs as a result of adsorption and dissociation of a carbon precursor on the surface of a catalyst particle and dissolution of carbon into the catalyst particle to form a liquid metastable carbide [33, 40, 41]. This latter step is regarded as the rate determining step [33, 42]. Once the catalyst particle has become saturated with carbon, the carbon will crystallize out of the metal particle and be extruded to form a carbon nanofiber [33, 41]. The unequal extrusion of carbon from a catalyst surface, could give rise to the helical nature of the carbon nanofibers (figure 2.17) [33]. This mechanism is known as the vapor-liquid-solid (VLS) method and it was first proposed by Wagner et al. [33, 43-45] for the synthesis of silicon

whiskers. In the early 1970s Baker *et al.* [40] proposed this mechanism can be used to explain the mechanism of filamentous carbon nanomaterials growth. This proposal was based on both kinetic data and observations using controlled-atmosphere electron microscopy (CAEM). To support the proposal that diffusion of carbon through the catalyst particle was the rate determining step the authors recorded the activation energies for the growth of CNFs and compared them to existing activation energies for diffusion of carbon through metals (Fe, Co); data were in agreement.

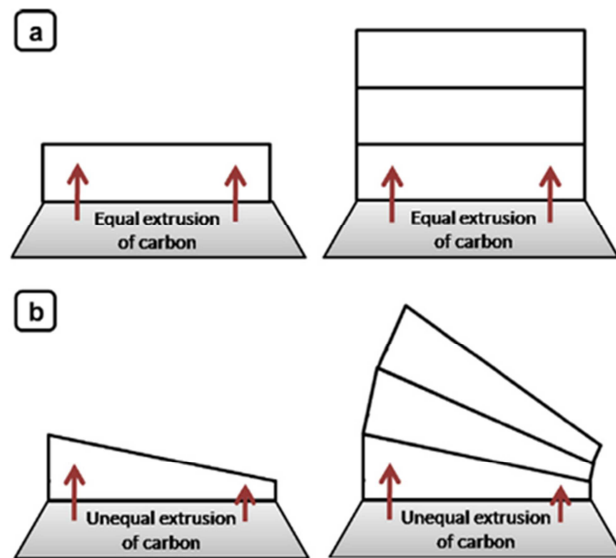


Figure 2.17: (a) Straight fiber formation from the equal extrusion of carbon, (b) Helical fibers formation from unequal extrusion [33].

Baker proposed that the driving force for carbon diffusion through the metal is the temperature gradient created in the particle due to exothermic decomposition of the hydrocarbon and endothermic deposition of carbon [44]. It was noted that this hypothesis did not explain the growth when the dissociation of the carbon precursor is endothermic [40]. Another possible driving force for carbon diffusion through the metal was proposed by Tibbetts *et al.* [46]. In this model, they assumed that molecular decomposition and carbon solution occur at one side of a catalytic particle, which becomes supersaturated. The driving force was found to be the gradient

in chemical potential which causes the carbon to diffuse through the particle. This hypothesis can only account for the growth when the particle is melted but not when it remained solid. Baker *et al.* [47] also reported that a filament growth mechanism is also affected by the interaction between the metal catalyst particle and the support medium. A schematic representation of a growth mechanism of the filaments was developed to account for the growth mechanism of the filamentous carbon (Figure 2.18 a). The growth mode of a carbon filament is also affected by the interaction of metal support and metal catalyst particle. Depending on how strong or weak the interaction between the metal and the support is, the growth mode can either be at the tip or base of the filament (Figure 2.18 b).

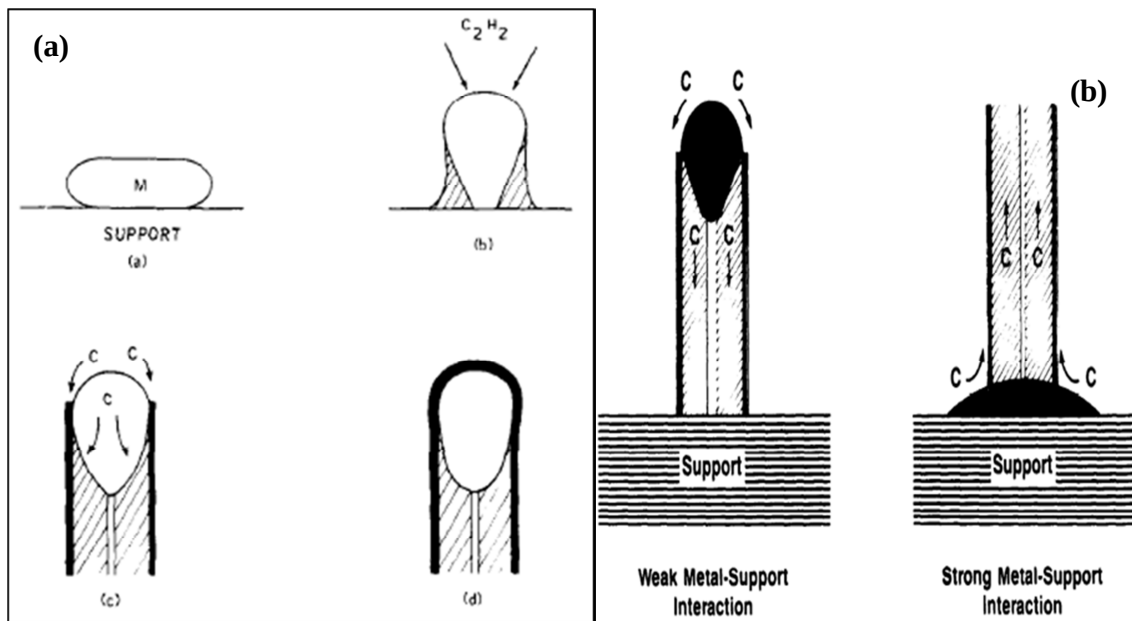


Figure 2.18: (a) Proposed mechanism of a carbon filament growth and (b) Influence of the metal support interaction on the growth mode of filamentous carbon [47].

The VLS mechanism assumes the formation of a metal carbide phase during the CNF/CNT growth [40]. Using XRD and TEM some researchers reported the formation of iron carbide after growth which has also been disputed by most researchers [40]. For example, Oberlin *et al.* [48] identified iron carbide as the phase of the filament growth. However, Tibbetts *et al.* [49] studied the decomposition of methane on a Fe catalyst. Their model assumed that iron which is in an

austenite (Fe-C solid solution) phase becomes supersaturated with carbon atoms and the flux is primarily driven by the concentration gradient. Their argument was that iron carbide does not catalyze the growth of carbon nanofilament and that such carbide particles are formed upon cooling of the supersaturated austenite particles. Baker *et al.* [50] used many in-situ techniques to show that carbon filaments do not grow on iron carbide when iron carbide was reacted with acetylene. Their CAEM studies showed that the iron carbide catalyst is not active during the formation of the carbon filaments. This was in agreement with data from Mossbauer spectroscopy which showed that the iron carbide concentration increased as the catalytic activity decreased.

Kawaguchi *et al.* [51] proposed a quasi-VLS mechanism for the growth of HCFs using a Ni compound seed. This mechanism involves the surface diffusion of the carbon atoms on the Ni compound seed. In the reaction temperature range of 600-800 °C in which the CNFs grow, Ni-C does not form a liquid phase. The authors assumed that the surface of a Ni compound seed should be in a liquid-like state for the carbon atoms to diffuse rapidly on the surface of the seed and maintain the rapid growth of the CNFs. The Ni compound seed was formed by reacting a Ni particle with acetylene and impurity gas (H₂S). It was observed that the exclusive growing point is on the Ni compound seed located at the tip of HCF. The different crystal planes might have different catalytic abilities for the growth of the HCFs as they observed that the opposite planes (X-X, Y-Y) in the Ni compound seed are identical crystallographically, whereas adjacent planes (X-Y) are not identical (Fig. 2.19 a).

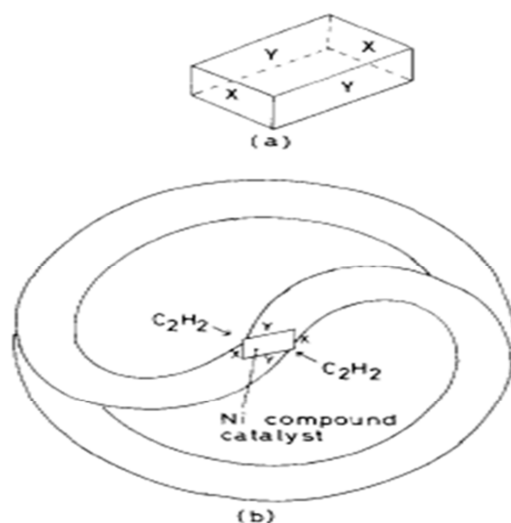


Figure 2.19: (a) Ni compound seed (single crystal) on the tip of a HCNF and (b) growth mechanism of HCNF [51].

Tessonnier *et al.* [40] proposed the most plausible mechanism for the growth of filamentous carbon nanomaterials using a vapor-solid-solid (VSS) mechanism which did not consider bulk diffusion of carbon in the catalyst particle (Fig. 2.20). This mechanism involves the dissociation of the carbon precursor, followed by the surface diffusion of carbon atoms on the catalyst particle, and carbon precipitation in the form of a nanotube growth.

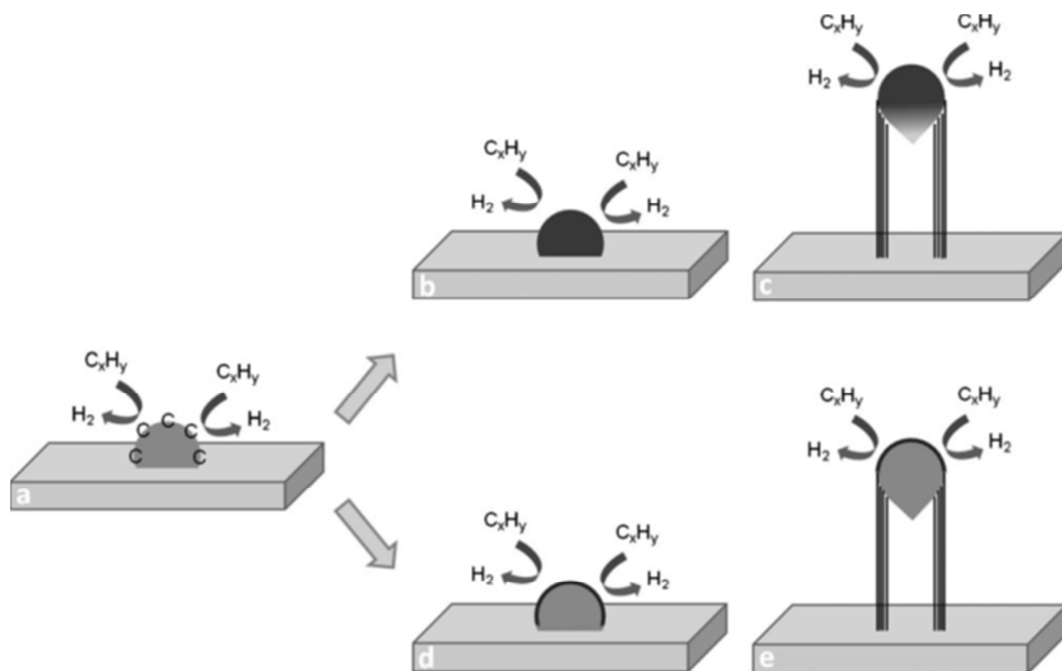


Figure 2.20: Shows the schematic representation of VLS (a,b,c) and VSS (a,d,e) mechanism [40].

The VLS mechanism can only be used to account for the growth of CNFs at high temperatures ($> 900\text{ }^{\circ}\text{C}$). Recently researchers have shown that CNFs and CNTs can be grown at temperatures below 300 and $600\text{ }^{\circ}\text{C}$ respectively. At this stage, there is no metal-C eutectic, assuming that the catalyst is still a solid as opposed to the VLS mechanism [52]. It is now clear that VLS can hardly be applied in the explanation of the growth of CNFs at lower temperatures. It is known that carbon has a low solubility (< 0.001 atomic %) in copper even at high temperatures [53], hence carbon dissociation and diffusion into a copper particle do not occur.

Jian *et al.* [54] studied the growth mechanism of HCNFs grown from copper nanoparticles at $271\text{ }^{\circ}\text{C}$. Using density functional calculations (DFT) they studied the chemisorption of acetylene on the crystal planes of Cu (100), (110), and (111) (Figure 2.21). The Cu (110) plane was found to have the highest surface energy among the 3 low index planes. It was concluded that acetylene is less likely to adsorb on this plane, as the nanoparticles tend to agglomerate and form ellipsoids which do favor formation of HCNFs. The authors proposed a coordination polymerization

mechanism (Figure 2.22). Initially acetylene is adsorbed on the copper surface through interactions between the unoccupied orbital of the copper atom and the π electron of the acetylene molecule. This leads to the formation of a coordination bond. The coordination bond gradually develops into a covalent bond through electron rearrangement, thus regenerating unoccupied orbital for the next process. Acetylene partially decomposes and is adsorbed concurrently on the surface of the copper catalyst. The rate-limiting step for this mechanism is the adsorption of acetylene on copper surfaces whereby they considered adsorption energy as the driving force.

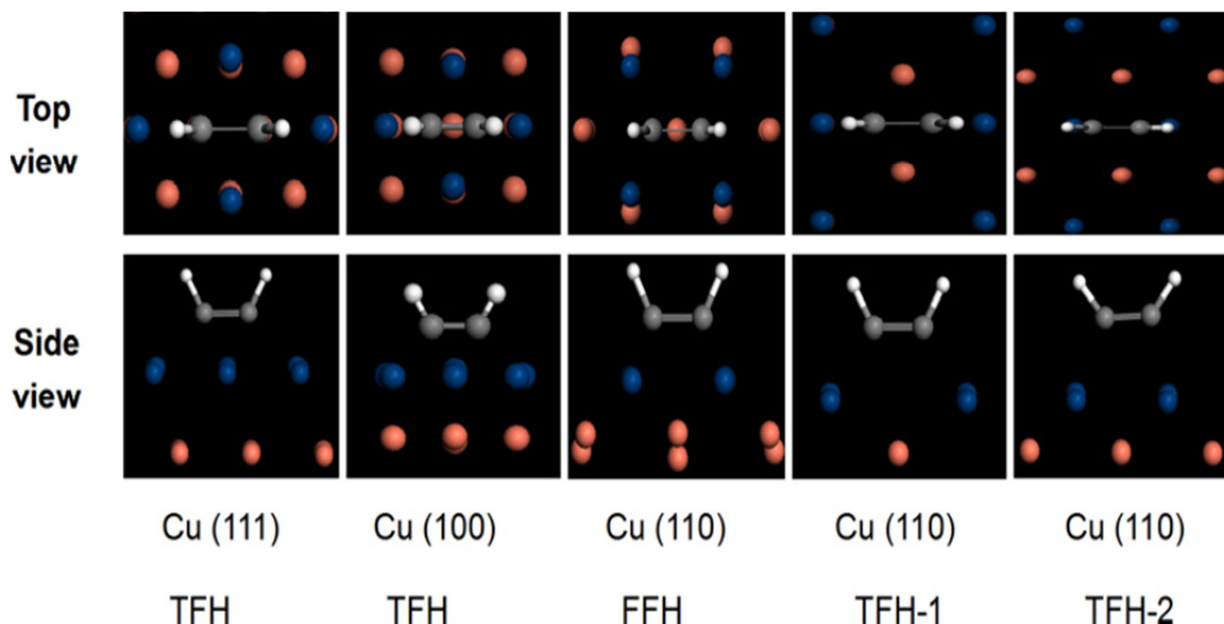


Figure 2.21: Energetically favorable adsorption sites of acetylene on copper catalyst [54].

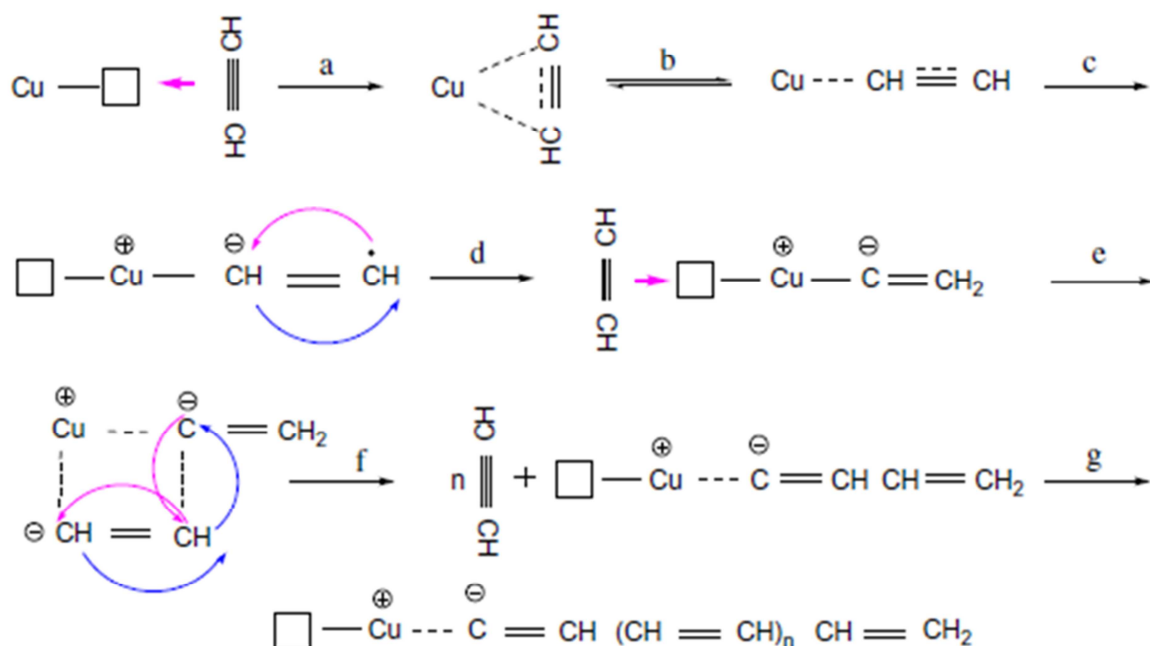


Figure 2.22: The polymerization process of acetylene on the copper catalyst for CNF growth [54].

2.3 Synthesis of Cu@mHCSs

Metal nanoparticles have been used in many applications, including catalysis as they show high catalytic activity [55]. However, it is to be noted that the nanosized particles are not stable hence capping agents are used to stabilize them to prevent them from sintering, which causes a decrease in their catalytic activity [56]. The great interest in catalysis using metal nanoparticles has resulted in the synthesis and investigation of highly functionalized nanoparticles such as the core/shell nanocatalyst, magnetite supported nanocatalyst, nanocarbon catalyst, integrated nanocatalyst, colloidal support etc. [55]. Over the last decades many researchers have developed different methods for the fabrication of hollow nanoparticles [57]. These methods are classified into two categories namely (i) the sacrificial-core-based method which uses a nanoparticle containing a removable core as a template and (ii) self templating method which uses the self-transformation of the solid interior nanoparticle into the hollow structure during chemical reaction [57, 58].

Sacrificial-core-based approach can be further categorized into hard-core templating and soft-core templating. The hard-core templating method has been the most popular method for fabrication of noble metal nanoparticles inside hollow carbon spheres. Figure 2.23 summarizes the general synthetic procedure for the synthesis of metal nanoparticles inside hollow carbon spheres using a decorated core-based approach [57]. The hard-core templating uses a rigid and robust sacrificial core like silica, amorphous carbon or different metal oxides [57, 58, 59].

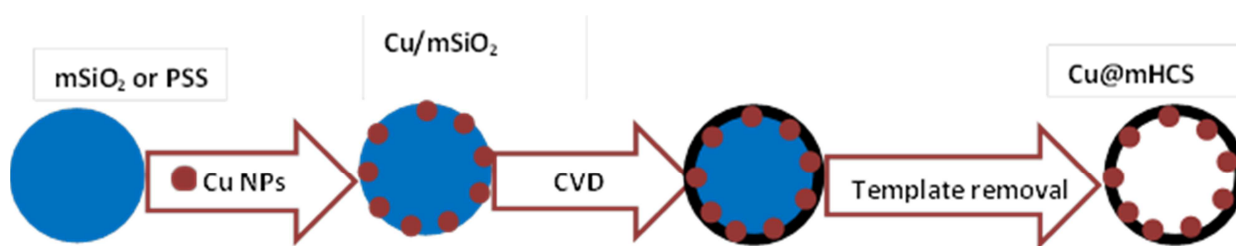


Figure 2.23: Schematic representation of the hard-templating method for the synthesis of Cu@mHCS.

2.4 Synthesis of HCNFs using Cu@mHCSs

HCNFs can be prepared using different methods such as catalytic chemical vapor decomposition (CCVD), arc discharge, and laser vaporization [60]. However, arc discharge and laser vaporization were found to produce mostly straight CNFs as they utilize high synthesis temperature ($> 2000\text{ }^{\circ}\text{C}$) [60]. These two methods give poor yields of HCNFs when compared to the CVD method. The CVD process was found to be the most efficient process for the synthesis of HCNFs and has the most potential for large scale preparation [60, 61]. The CVD method is a chemical process whereby a catalyst and or substrate are exposed to a carbon precursor which is decomposed on the surface of the catalyst/substrate to give solid materials [60]. This method uses a horizontal furnace consisting of quartz tube with quartz boat that is heated to a certain temperature while gases are passed through the tube (Figure 2.24).

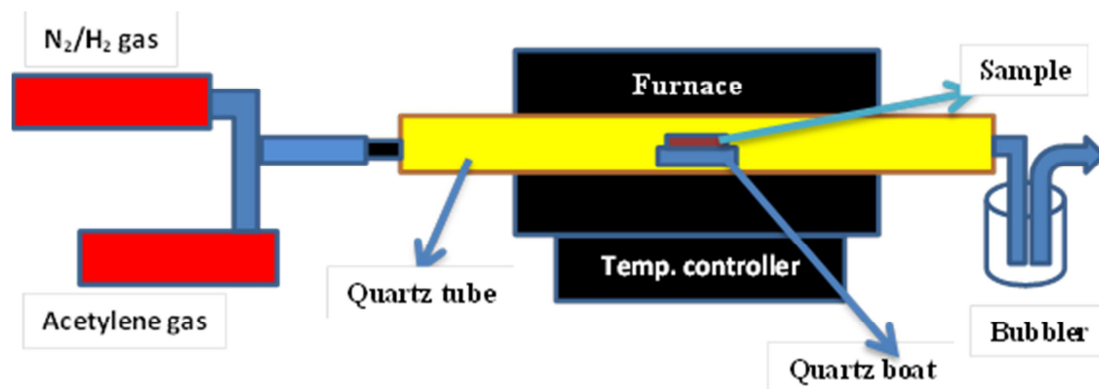


Figure 2.24: Representation of carbonization CVD method.

2.5 Conclusion

It has been demonstrated that copper can be used to grow carbon structures under a range of different conditions, although it was first thought to be an inactive catalyst. The synthesis temperature, particle size, and shape of the metal particle plays a vital role in determining the type of carbon material formed. Different growth mechanisms for the carbon materials have been proposed and they are highly dependent on the metal interaction with the carbon precursors. Copper nanoparticles have the ability to synthesize different carbon materials ranging from amorphous carbon at low temperatures (200-400 °C) to highly graphitic carbon materials at high temperatures (500-1000 °C).

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Chapter 3: Characterization techniques

3.1 Characterization techniques

Different techniques were used to characterize the HCNFs obtained using copper trapped inside the mesoporous hollow carbon sphere catalyst to determine their physical and chemical properties. TEM was used to analyze the morphology, size, and diameter of the obtained products. The pore size and surface area of the samples was obtained using BET. TGA was used to monitor physical and chemical properties (i.e. mass) of the obtained products as a function of increasing temperature. Raman spectroscopy was used to evaluate the degree of graphitization. PXRD was used to analyze the bulk composition of the catalyst.

3.1.1 Transmission electron microscope (TEM)

TEM is an image analysis technique that can be used to obtain information relating to the structure, size, shell thickness, quality, and diameter of the synthesized copper nanoparticles contained inside mesoporous hollow carbon spheres. The images were taken using a FEI Tecnai Spirit G² TEM operating 120 kV. The powder samples were dispersed in methanol and sonicated for 30 minutes. A drop of the prepared sample was then added onto a copper grid and the grid was dried before analysis.

3.1.2 Thermo-gravimetric analysis (TGA)

The thermal stability of the samples was analyzed using a Perkin Elmer TGA 6000 instrument in air or nitrogen gas at a constant rate of 10 °C/min. The sample (10 mg) was heated in the instrument temperature range of 30-900 °C at a flow rate of 20 ml/min (nitrogen) or 50 ml/min (air).

3.1.3 Laser Raman spectroscopy

The crystallinity and disorder of carbon materials was analyzed using a Bruker Senterra Raman spectrophotometer that runs on Opus 7.1 software. The sample preparation involved placing the sample on a glass slide and reading the spectrum in dark field mode.

3.1.4 Brunauer-Emmet and Teller (BET)

A Micromeritics Tristar 3000 instrument was used to analyze the surface area and the porosity of the obtained products. The sample preparations involved pre weighing ~ 2 g of sample which was degassed in nitrogen at 150 °C for 4 hours before the analysis using a Micromeritics Flow Prep 060 sample degasser. Only PSSs were degassed at 70 °C overnight before their analysis.

3.1.5 Powder X-ray diffraction (PXRD)

A D2 phaser equipped with a Lynxene detector was used to determine the crystallinity of the catalysts using Co-K α radiation at 30 kV. The scan ranged from $5^\circ \leq 2\theta \leq 100^\circ$ in 0.026 ° steps. The sample was ground to fine powder, and packed on a sample holder, ensuring a flat surface before analysis.

Chapter 4: Synthesis and characterization of copper nanoparticles contained inside mesoporous hollow carbon spheres

4.1 Synthesis and Characterization of copper nanoparticles

4.1.1 Introduction

Copper is a 3d transition metal with interesting physical and chemical properties [1]. Copper nanoparticles are attractive to use as a catalyst because they display high surface-to-volume ratios compared to bulk catalytic materials [2]. Copper nanoparticles have been used in applications such as electronics, antibacterial agents, and antiviral agents due to their intrinsic optical, catalytic, electrical, and biological properties [1]. Different procedures have been used to synthesize copper nanoparticles such as chemical (e.g. reduction, thermal decomposition etc.), physical (e.g. deposition, pulse wire discharge etc.), and biological (e.g. using bacteria, fungi etc) methods [3]. It is well known that copper is susceptible to surface oxidation, hence in order to produce metallic copper nanoparticles their synthesis has to take place under an inert atmosphere e.g. using N₂ gas [3]. This procedure is not necessarily sufficient to preserve the stability of the copper nanoparticles as these nanoparticles have a high surface energy which makes their surface atoms very active [2]. Surfactants have been introduced not only to prevent oxidation of the copper nanoparticles after exposure to air but to control the size of these nanoparticles [2, 4, 5]. The surfactants prevent agglomeration of the metal nanoparticles by forming a capping layer by adsorption on the particles [4].

Synthesis of the copper nanoparticles with controllable size, shape and surface properties is still a key problem [6]. The difficulty in the synthesis of the copper nanoparticles with a controllable

size arises from their relatively low redox potential and ease of oxidation; hence their synthesis requires a strong reducing agent and a high temperature [2]. This section reports on the synthesis of copper nanoparticles using thermal decomposition of copper (II)-acetate-monohydrate under nitrogen gas. Different surfactants were used to control the particle size of the copper while varying the reaction time from 30 minutes to 6 hours. The chosen reaction times were selected from previous studies on the synthesis of copper nanoparticles.

4.1.2 Synthesis of copper nanoparticles

These methods were modified from the methods reported in the literature that have been used to synthesize cobalt nanoparticles [7, 8, 9].

4.1.2.1 Materials

Some of the chemicals were of technical grade and others were of analytical grade. The oleic acid (90 %) (OA), oleylamine (70 %) (OLA), trioctylphosphine (90 %) (TOP), and absolute ethanol (AR) were purchased from Sigma-Aldrich. The hexane (CP) was purchased from Associated Chemical Enterprise. Copper (II)-acetate-monohydrate, $((\text{CH}_3\text{COO})_2\text{Cu}\cdot\text{H}_2\text{O})$ was purchased from Merck (Pty) Ltd, South Africa.

4.1.2.2 Experimental procedures

(a) Synthesis of copper nanoparticles

A mixture of OLA (10 mL) and 90% OA (0.942 g) contained in a 3 neck round bottom flask was heated up to 210 °C (± 10 °C). A mass of 0.399 g of $((\text{CH}_3\text{COO})_2\text{Cu}\cdot\text{H}_2\text{O})$ was weighed and dissolved in 5 mL of OLA using a small amount of acetone (3 mL). This mixture was then quickly injected into the 3 neck round bottom flask. The mixture was refluxed for 30 minutes or 6 hours at 210 °C. After the reaction mixture had cooled, the resulting product was washed with

hexane and acetone several times. After the copper nanoparticles had settled down they were dispersed in hexane (25 mL) and acetone (10 mL). The copper nanoparticles were not filtered or centrifuged because they were of small size and excess OLA could not be completely removed by washing.

(b) Synthesis of monodispersed copper nanoparticles

A mixture of OLA (5 mL), OA (0.565 g), and TOP (2, 4, 6 mmol) contained in a 3 neck round bottom flask was heated up to 210 °C (± 10 °C). A mass of 0.399 g of $((\text{CH}_3\text{OO})_2\text{Cu} \cdot \text{H}_2\text{O})$ was weighed and dissolved in 5 mL of OLA using a small amount of acetone (3 mL). This mixture was then quickly injected into the 3 neck round bottom flask. The mixture was refluxed for 6 hours at 210 °C. After the reaction mixture had cooled, the resulting product was washed with hexane and acetone several times. After the copper nanoparticles had settled down they were dispersed in hexane (25 mL) and acetone (10 mL). The copper nanoparticles were not filtered or centrifuged because they were of small size and excess OLA could not be completely removed by washing.

For the purpose of the synthesis of the Cu/mSiO₂ (copper nanoparticles supported on mesoporous silica) or Cu/PSS (copper nanoparticles supported on polystyrene spheres); a solution of copper nanoparticles (2 mL) dispersed in hexane and acetone was used. In the synthesis of Cu/PSSs the copper nanoparticles were dispersed in hexane and ethanol.

Characterization techniques

The morphology of the copper nanoparticles was analyzed using TEM. The average particle size was calculated from the TEM images using ImageJ software.

4.1.3 Results and discussion

The synthesis of the copper nanoparticles was accomplished by varying the refluxing time from thirty minutes to six hours using OLA and OA as surfactants. When the copper nanoparticles synthesized for thirty minutes were exposed to air, the color of the solution containing the nanoparticles changed from red-brown to blue. This showed that copper oxide nanoparticles were formed [10, 11, 12]. The TEM image of the oxidized copper nanoparticles showed polydispersed copper nanoparticles with irregular morphology and particle sizes with $d = 85 \pm 31$ nm (Figure 4.1). When the reaction time was raised to six hours a red-brown solution containing the nanoparticles was observed and after exposure to air the color remained the same indicating the formation of metallic copper [10, 11, 12]. Figure 4.2 shows the TEM image of the polydispersed copper nanoparticles with the average particle sizes of 90 ± 24 nm. The morphology of the copper nanoparticles had different shapes (rods, spheres and tetrahedrons). The analysis of the copper nanoparticles showed an increasing trend in the average size with reflux time. This is attributed to the high synthesis temperature used, as the adsorption of capping agents on the copper nanoparticles is less favored at higher temperature (> 150 °C) [6].

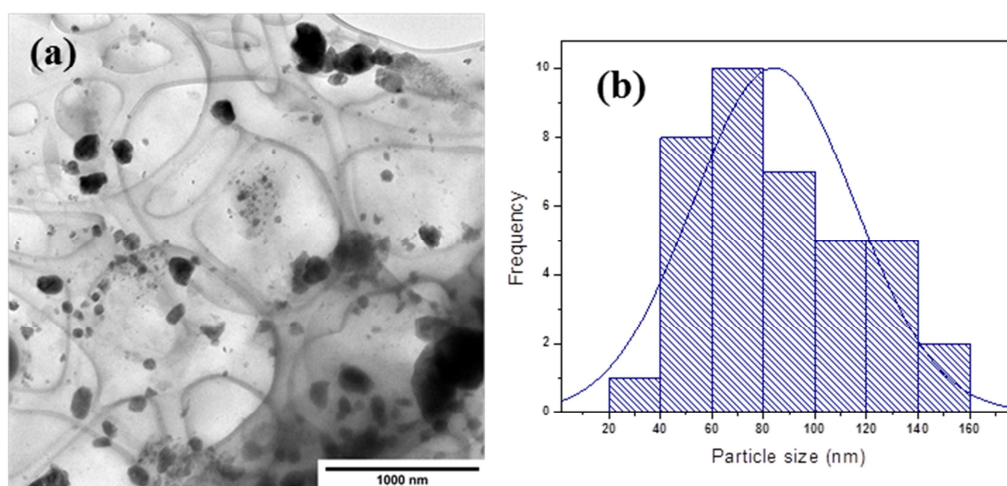


Figure 4.1: (a) TEM image of the copper oxide nanoparticles synthesized at 210 °C for 30 minutes and (b) diameter distribution of the copper oxide nanoparticles.

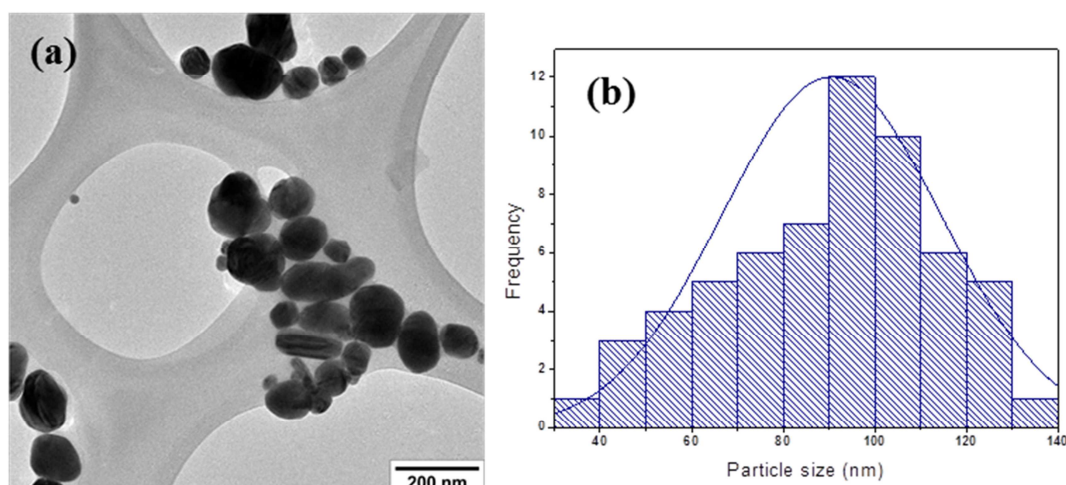


Figure 4.2: (a) TEM image of the copper nanoparticles synthesized at 210 °C for 6 hours and (b) diameter distribution of the copper nanoparticles.

In an attempt to synthesize monodispersed copper nanoparticles with a smaller size, a study using three different capping agents (TOP, OLA, and OA) was conducted. TOP is a strong reducing agent that has a synergistic effect while OA is known to bind tightly to the metal nanoparticle surface [7, 13]. These effects are important for producing highly monodispersed copper nanoparticles as they prevent a fast reduction of the copper ions to metallic copper. Due to copper's low redox potential, it is important to use a strong reducing agent at a high temperature during the synthesis of the copper nanoparticles [13]. Shao et al. synthesized well dispersed Co nanoparticles that showed no agglomeration. The authors noticed that by addition of three different surfactants (TOP, OLA, OA) the average particle size of the Co nanoparticles decreased from 200 nm to 8 nm [7]. The table below indicates the data from studies performed while varying the TOP/Cu molar ratio. The amount of OLA, OA and copper used was kept constant as mentioned in 4.1.2.2 (b).

Table 4.1: Effect of TOP on the particle size of the copper nanoparticles

Amount of TOP (mmol)	Reaction temperature (°C)	Reaction time (h)	Nanoparticles size
2 mmol	210	6	69 nm
4 mmol	210	6	51 nm
6 mmol	210	6	31 nm

A decreasing trend in the nanoparticles size with increasing concentration of TOP was observed as shown from the TEM images (Figure 4.3 a, b, and c). This observation can be explained by the steric effect of TOP and the strong affinity of OA for the metal nanoparticles which slows the copper sintering process during copper particle growth [13]. When 2 and 4 mmol of TOP was added to OLA and OA mixture, a red-brown solution containing the nanoparticles was formed. Over a long period of time the solution containing the nanoparticles synthesized using 4 mmol of TOP partially turned blue indicating formation of copper oxide nanoparticles. When 6 mmol of TOP was used the average particle sizes of the copper nanoparticles had decreased to 31 ± 10 nm, and the solution containing these nanoparticles turned from red-brown to blue immediately after exposure to air. From the literature, it was reported that formation of metallic copper nanoparticles is favored at 210 °C using OLA whereas addition of TOP can only be effective at 250 °C [13].

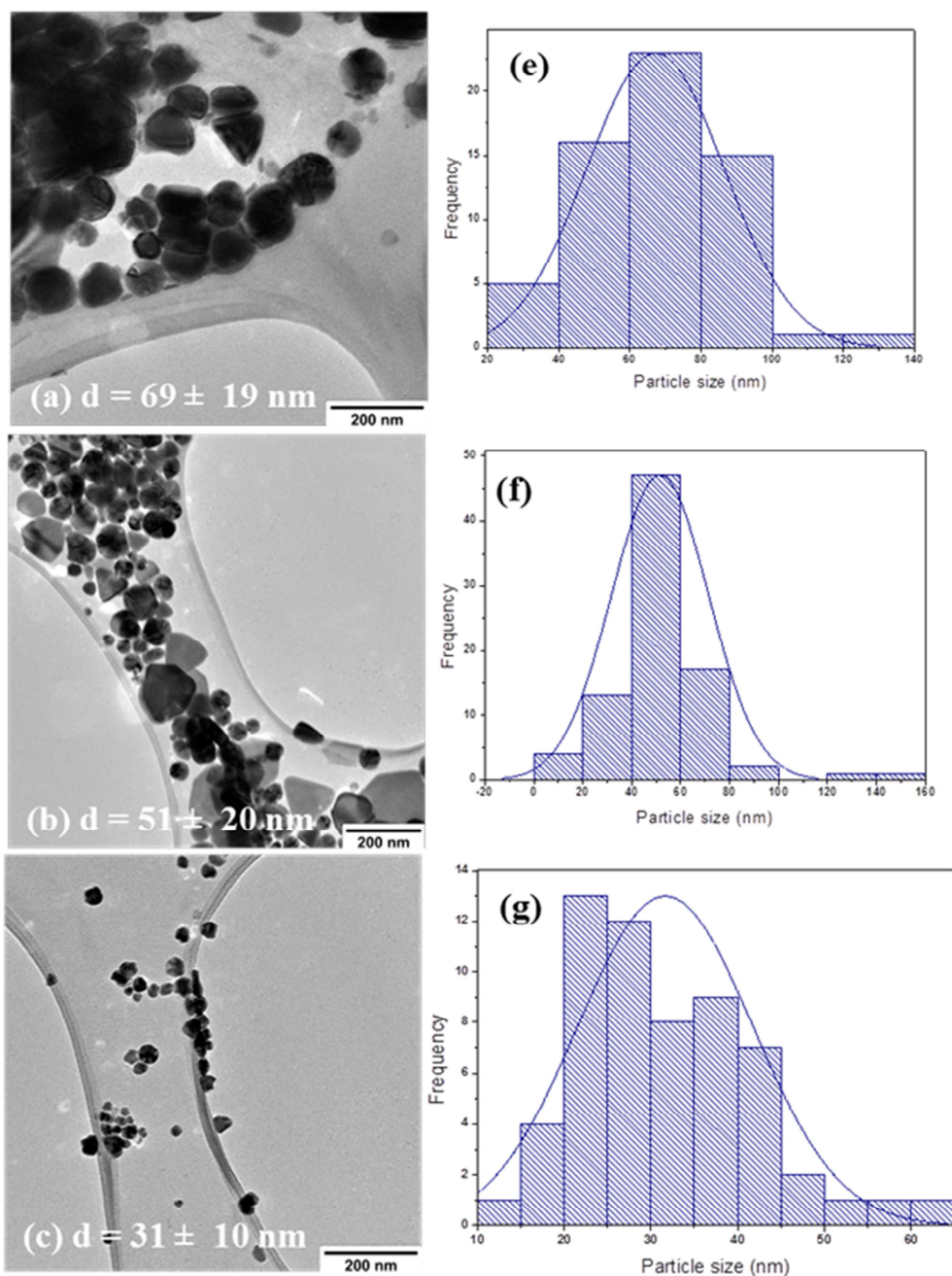


Figure 4.3: TEM images of (a) copper nanoparticles synthesized using 2 mmol TOP, copper oxide nanoparticles synthesized by increasing the amount of TOP (b) 4 mmol, and (c) 6 mmol at 210 °C and (e-g) diameter distributions of the copper nanoparticles.

4.1.4 Conclusion

Copper nanoparticles with particle size ranging from 90-69 nm were successfully synthesized. The effect of the reaction time was shown to be important as it was observed that the nanoparticles synthesized for 30 minutes were immediately oxidized after exposure to air. The addition of TOP to Cu^{2+} ions was shown to decrease the copper nanoparticle size. It was observed that the higher the concentration of TOP; the smaller the copper particle size and the synthesized copper nanoparticles were oxidized upon exposure air. Also the synthesized nanoparticles were not monodispersed as it was intended when using the 3 surfactants method. The capping agents prevented agglomeration of the copper nanoparticles; thus the key role of the surfactant is to enhance the growth of nucleation at the expense of copper ions growing on copper precipitates.

4.2 Synthesis of copper nanoparticles contained in hollow carbon spheres and characterization

4.2.1 Introduction

Hollow nanostructures have attracted a lot of research interest in the past decades. Foremost among these are carbon-based hollow spherical nanostructures [14]. It is possible to use the inside of the hollow carbon spheres (HCSs) as a nanoenclosure to store and use metal nanoparticles. Thus, the interior of the HCS could act as a support for the copper nanoparticles to stabilize, and disperse them and help limit the nanoparticles from forming large aggregates [15]. HCSs have been prepared by various methods such as, pyrolysis, medial-reduction, and solvothermal and chemical vapor deposition procedures [16]. Nanocasting to make a solid core comprising of a mesoporous silica sphere has been intensively used to synthesize carbon capsules with a hollow core and a mesoporous shell by coverage of the silica by carbon and the removal of the silica. In this technique three steps are involved (i) the creation of a spherical SiO_2

template, (ii) coverage of the template with an appropriate carbon precursor and carbonization and (iii) etching of the template core [17, 18, 19].

The templates can either be soft (micelles, micro-emulsion droplets and gas bubbles) or hard (silica, carbon and polymer spheres) [16]. Hollow carbon spheres can be made by the removal of templates, either by dissolution or by calcination at high temperatures [18]. Nanocasting has some disadvantages viz: the procedure is time consuming as it involves multi-steps, uses corrosive media for dissolution of the hard template and uses conditions that are not friendly to the environment. Synthesis using a hard template is more easily controlled, is reproducible and produces HCSs with well-defined shape [20].

In this study the use of a mesoporous SiO_2 (m SiO_2) or polystyrene sphere (PSS) as a template to make Cu/m SiO_2 and Cu/PSSs as a template for the synthesis of Cu@mHCSs using a sacrificial-core-based approach are reported. The experimental procedures will be divided into two sections. The first section (4.2.2) will be on the synthesis of Cu@mHCSs using silica as a template and the second section (4.2.3) will focus on the synthesis of Cu@mHCSs using PSSs as a template.

4.2.2 Preparation of Cu@mHCSs using silica as a template

4.2.2.1 Materials

The hexadecyltrimethylammonium bromide ($\geq 98\%$) (CTAB), ammonia solution (25 %), absolute ethanol (AR), tetraethyl orthosilicate (98 %) (TEOS), trimethoxy(octadecyl)silane (98 %) (C18TMS), and hydrofluoric acid (48 %) (HF) were purchased from Sigma-Aldrich.

4.2.2.2 Experimental procedures

(a) CTAB

A solution of water (20 mL) and absolute ethanol (200 mL) was prepared and 10 mL of ammonia (25 %) was added to the solution. This solution was stirred for 10 minutes at room temperature. A volume of 15 mL of 98% TEOS was then added to the solution which was then stirred for 6 hours to form monodisperse Stöber spheres. CTAB (5 g) and TEOS (2.5 mL) dispersed in ethanol (50 mL) were then added into the solution containing the Stöber spheres. The solution was stirred overnight at room temperature to form a mesoporous silica shell on the pre-formed silica to generate a mSiO₂ composite material. The resulting mSiO₂ spheres were filtered, oven dried at 100 °C for 4 hours and calcined in air at 500 °C for 4 hours.

(b) C₁₈TMS

Instead of using CTAB (5g) and 2.5 mL TEOS, 2 mL of C₁₈TMS and 5 mL TEOS was used and all the other experiment variables were kept the same as in the above method (method a).

(c) Cu/mSiO₂

Copper nanoparticles dispersed in 25 mL of hexane and acetone (5:1 respectively) were sonicated for five minutes. A mass of 1 g of mSiO₂ in 25 mL of acetone was sonicated for five minutes and transferred to the copper nanoparticles solution. This solution was then stirred for 4 hours at room temperature to allow the copper nanoparticles to load onto the mSiO₂. The Cu/mSiO₂ in acetone was centrifuged several times for 10 minutes at 4000 rpm, washing with

acetone to remove the organic content between the procedures. The Cu/mSiO₂ was dried in the oven at 100 °C for 2 hours and calcined in air at 200 °C for 2 hours.

(d) Carbonization of Cu/mSiO₂

The Cu/SiO₂ powder was placed in a horizontal quartz reactor and heated up to 900 °C under a flow of Ar gas at a flow rate of 100 mL/min. The toluene and carrier gas were then bubbled into the reaction for 2 hours to form a carbon shell around a Cu/mSiO₂ core. The silica core was then removed using 5 % HF (48 %) overnight or 2 M NaOH while refluxing at 100 °C for 6 hours.

4.2.3 Preparation of Cu@mHCSs using PSSs as a template

4.2.3.1 Materials

The polyvinylpyrrolidone (Mw 40000) (PVP), styrene (98 %), formaldehyde (37 %), and absolute ethanol (AR) were purchased from Sigma-Aldrich. Sodium carbonate (anhydrous) was purchased from Merck (Pty) Ltd South Africa.

4.2.3.2 Experimental procedures

(a) Preparation of PSSs

An amount of 8 mL styrene and 0.1 g PVP (mw 40000) were dissolved in 200 mL of water and 50 mL ethanol. Potassium persulfate solution (0.15 g in 20 mL water) was added to this solution,

which was then stirred for 15 minutes. The mixture was then refluxed at 80 °C while stirring for 27 hours. The final product was filtered and washed using distilled water and dried at 100 °C for an hour.

(b) Preparation of Cu/PSSs

Copper nanoparticles dispersed in ethanol and hexane (2 mL) were loaded on 2 g of PSSs (50 mL ethanol) and stirred for 4 hours. The mixture was filtered and oven dried at 100 °C for an hour.

(c) Preparation of Cu@mHCSs

Copper nanoparticles loaded on PSSs (2 g) and ammonia solution (25 %; 1.5 mL) were dispersed in ethanol (100 mL). An amount of 1.5 mL formaldehyde solution (37 %), 0.75 g of resorcinol, and 1.0 g CTAB were added into 50 mL ethanol and the mixture was then added to the first solution and stirred for 20 hours to form a resorcinol-formaldehyde polymer around the spheres. PSSs@Cu@RF was transferred into a Teflon lined autoclave and heated at 190 °C for 5 hours. The final product (red) was then filtered while washing with water. PSSs@Cu@RF was first carbonized using CVD under a nitrogen flow (50 mL/min) at 350 °C for an hour to decompose the PSSs which was followed by annealing of mHCSs at 500 °C.

Characterization techniques

TEM, BET, and PXRD were used to characterize the synthesized materials. The average diameter of the spheres and the shell thickness of mSiO₂ were calculated using ImageJ software from multiple TEM images.

4.2.4 Results and discussion

The discussion of results will be divided into two sections. The first section (4.2.4.1) will discuss results on the synthesis of Cu@mHCSs using silica as a template and the second section (4.2.4.2) will focus on the results obtained on the synthesis of Cu@mHCSs using PSSs as a template.

4.2.4.1 Synthesis of Cu@mHCSs using silica template

The silica spheres were synthesized using the Stöber method which can be tailored to give spheres with a desired diameter and narrow particle size distribution. Researchers have improved the original method allowing the synthesis of porous silica particles with desired size and morphology [21]. In this study two surfactants were used to compare the shell of the synthesized silica spheres and to tune the pore size of the silica spheres.

The obtained silica spheres were characterized by TEM (Figure 4.4 and 4.5). The method used to synthesize the silica spheres gave a product with uniform size distribution and high yield. The mesoporous shell from the CTAB-silica spheres was difficult to see by TEM when compared to the C₁₈TMS-silica spheres suggesting a difference in the carbon shell thickness in the two products. The shell thickness of the CTAB-silica spheres was found to 34 nm whereas the one for the C₁₈TMS-silica spheres was 87 nm (Table 4.2). From BET analysis, the CTAB-silica spheres appear to have a slightly high surface area compared to the C₁₈TMS-silica spheres (Table 4.2). This observation can be explained by the small pore size of the CTAB-silica spheres as the silica spheres surface have more pores compared to C₁₈TMS-silica spheres. Table 4.2 summarizes the effects of the two surfactants on the shell morphology of the silica spheres. Based upon the TEM images, the C₁₈TMS-silica spheres (Figure 4.6 b) appear to have a slightly better capacity to support the copper nanoparticles compared to the CTAB-silica spheres (Figure 4.6 a) due to its bigger pores. The mesoporous shell influences the loading of the copper nanoparticles on mSiO₂ spheres.

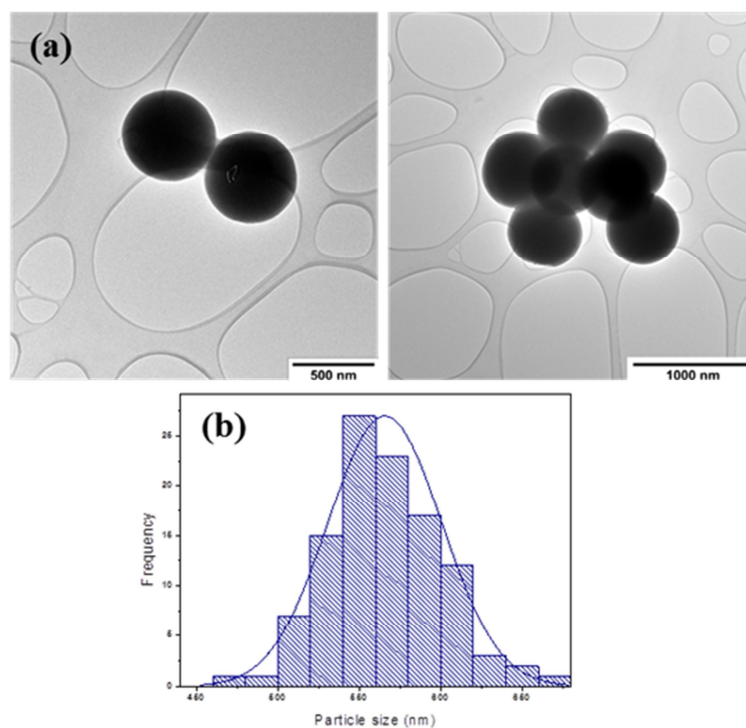


Figure 4.4: TEM images of mSiO₂ synthesized using CTAB with diameter of 566 ± 35 nm (b) diameter distribution of the silica spheres.

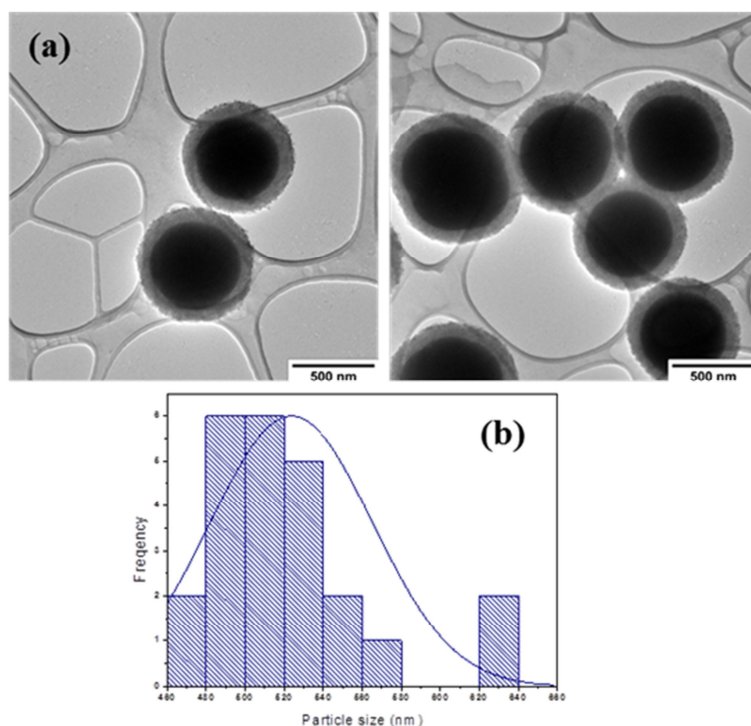


Figure 4.5: (a) TEM images of mSiO₂ synthesized using C₁₈TMS with diameter of 517 ± 41 nm and (b) diameter distribution of the silica spheres.

Table 4.2: Effect of surfactants on the synthesized silica spheres shells

Surfactant	Particle size (nm)	Silica shell thickness (nm)	BET analysis	
			Surface area (m ² /g)	Pore size (nm)
CTAB	566 ± 35	34	159.2	2.8
C ₁₈ TMS	517 ± 41	87	144.0	4.0

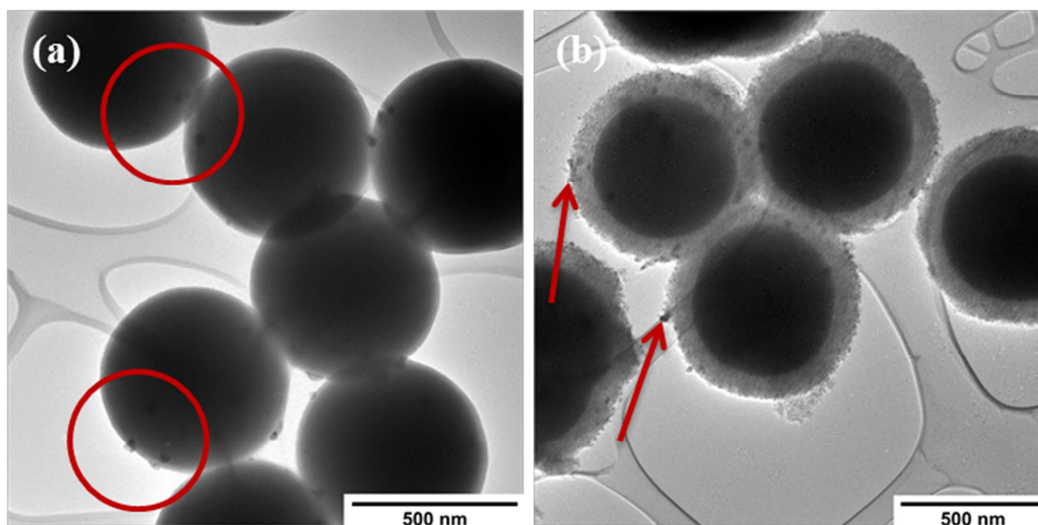


Figure 4.6: TEM images of copper nanoparticles (circles/arrows) supported on (a) CTAB and (b) $C_{18}TMS$ synthesized silica spheres.

After coating the $Cu/mSiO_2$ catalyst with a carbon layer (acetylene) using the CVD method, the silica template was etched out using 5 % HF overnight. Silica etching can be reversible or irreversible depending on the type of solution used. HF etching solution has been reported to be the fastest process that is irreversible [22]. The main etched out product of this process is silicon tetrafluoride (SiF_4) [22]. From the TEM images it was observed that the copper nanoparticles were also removed with the template and only mHCSs remained (Figure 4.7).

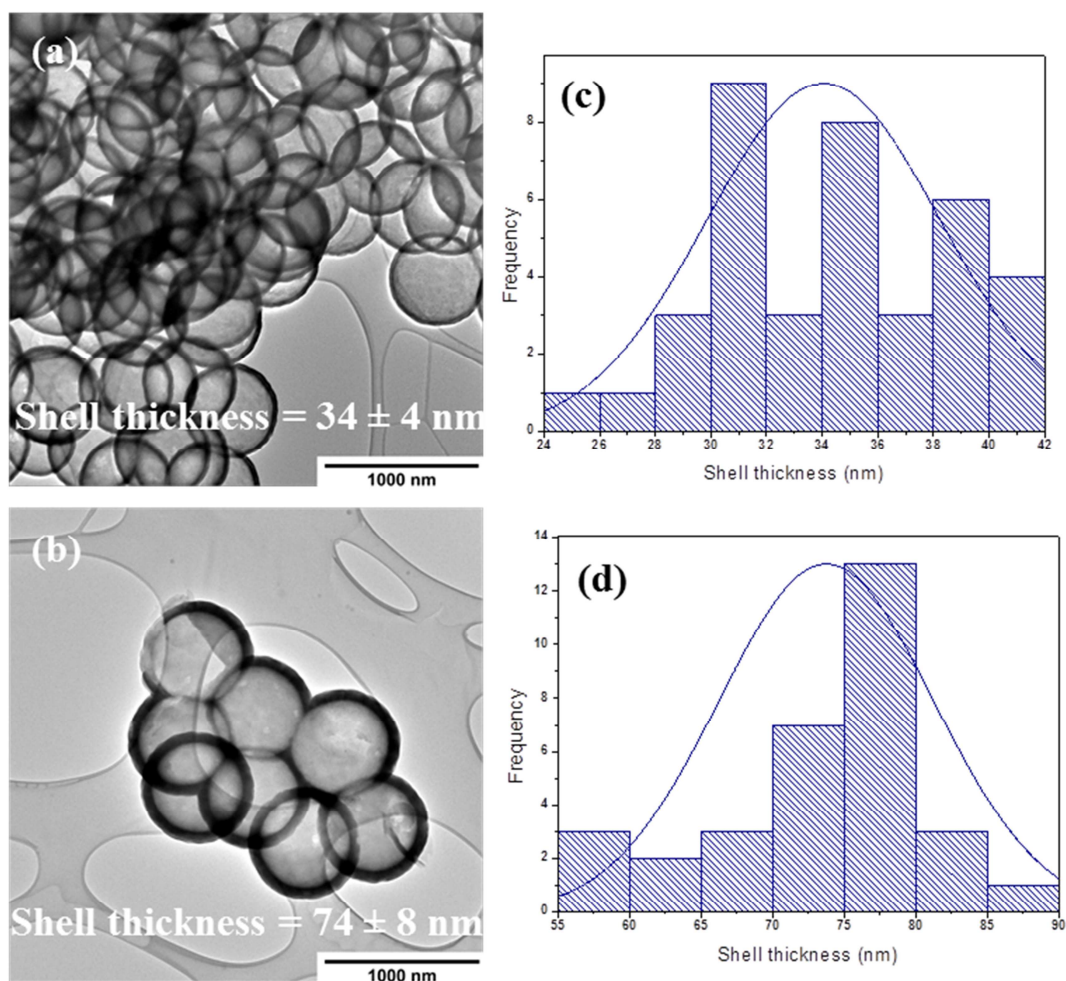


Figure 4.7: TEM images of Cu@mHCSs after etching the (a) CTAB and (b) C₁₈TMS synthesized silica template using 5 % HF and (c-d) shell thickness distributions of the mHCSs.

To confirm that no copper nanoparticles were left, TGA analysis was conducted on the mHCSs. The TGA (Figure 4.8) plot shows the variation of weight as a function of temperature. The TGA data showed that the entire sample decomposed at temperatures around 737 °C and no residue was noted at T = 900 °C, indicating that all the copper nanoparticles were etched out during the template removal.

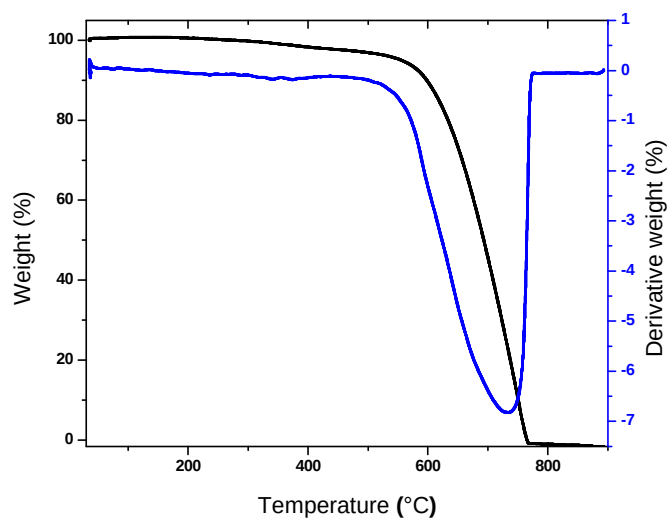


Figure 4.8: TGA and the first derivative of the TGA profile of Cu@mHCSs after template removal.

Another attempt at removing the silica template was made using 2 M NaOH. The OH^- ion can etch the silica framework by coordinating to a Si atom resulting in a breakage of Si-O-Si bonds [22]. Unlike HF, NaOH etching can be reversible as the breakage of Si-O-Si bonds leads to a formation of less condensed oligomers of silica species which can be chemically reversed [22]. From the TEM images, it was observed that some of the mHCSs were broken resulting in the copper nanoparticles being removed from inside the mHCSs and placed on the outer surface of these mHCSs (Figure 4.9).

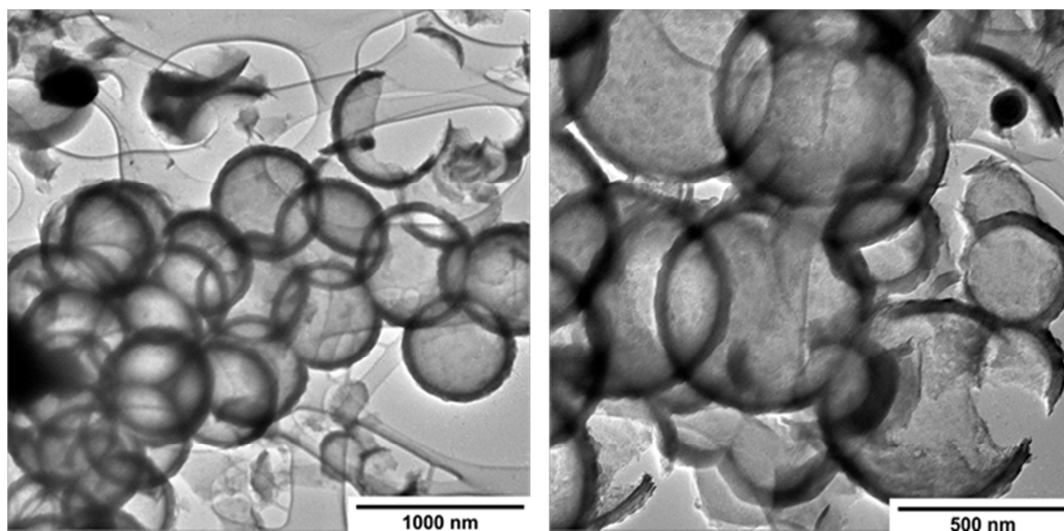


Figure 4.9: TEM images of Cu@mHCSs after etching the silica template with 2 M NaOH.

From the TGA analysis, a 9.2 % residue (presumably due to copper nanoparticles or to residual silica) was observed (Figure 4.10). Only one type of carbon was observed from the TGA profile. The first derivative peak at ~ 512 °C is associated with graphitic carbon. Further analysis of Cu@mHCSs by PXRD was done to confirm the presence of copper nanoparticles. Figure 4.11 shows the XRD pattern of the Cu@mHCSs after the removal of the silica template using 2 M NaOH. The diffraction peaks at 2θ value of 50.58° , 59.32° , and 89.05° correspond to the (111), (200), and (220) planes of face-centered cubic copper (ICSD No. 053246). The pronounced diffraction peak in the range below 40.00° shows a graphitic feature of carbon. The XRD pattern supports that a 9.2 % residue from the TGA profile (Figure 4.10) is due to copper nanoparticles not silica.

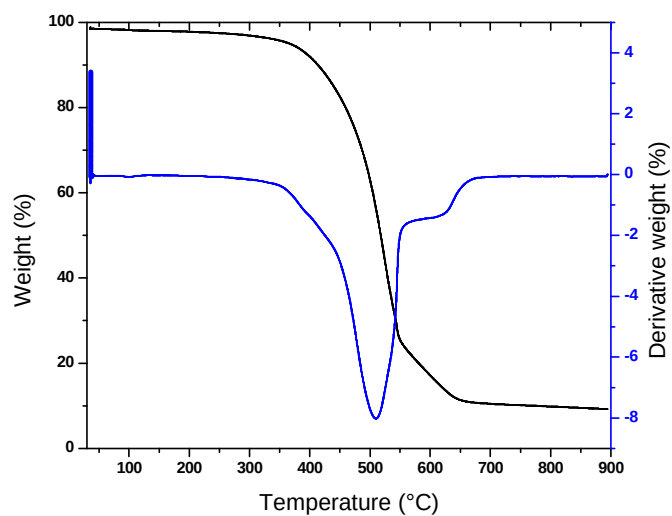


Figure 4.10: TGA plot and the first derivative of the TGA profile of Cu@mHCSs after template removal.

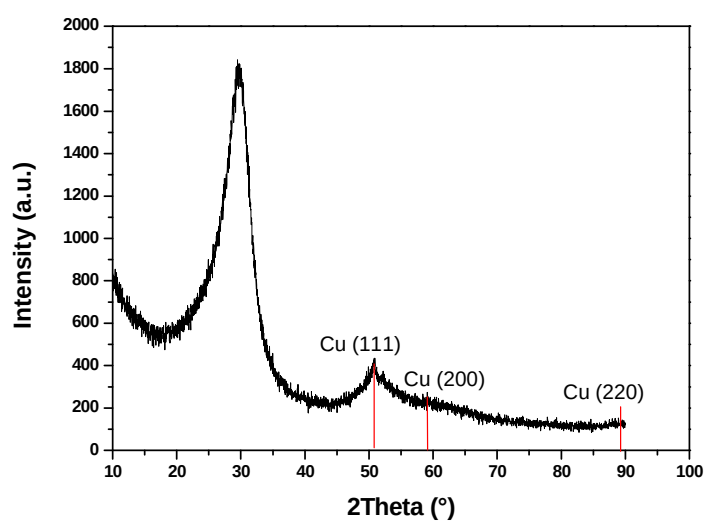


Figure 4.11: Powder X-ray diffraction pattern of Cu@mHCSs after template removal.

4.2.4.2 Synthesis of Cu@mHCSs using PSSs as a template

In order to avoid removal of copper nanoparticles when etching out the silica template, it was decided to make a template that avoided the problem. To achieve this PSSs were chosen as a template. PSSs can be decomposed easily through a CVD method [23]. PSSs with an average diameter of 307 ± 19 nm were successfully synthesized (Figure 4.12a). In a separate TGA experiment it was shown that PSSs decomposed in air from 400 °C (Figure 4.13a). To test the methodology the PSSs were coated with carbon using the resorcinol/formaldehyde methodology. The resorcinol-formaldehyde polymerization process can be catalyzed either by an acid or base [24]. In this reaction ammonia was initially used as catalyst. The removal of the template was thus done at 350 °C by decomposition of the PSSs. The mHCSs/residue was then annealed (500 °C) using a CVD method [23]. The mHCSs were obtained after decomposition of the PSS template from PSS@RF (Figure 4.12 b).

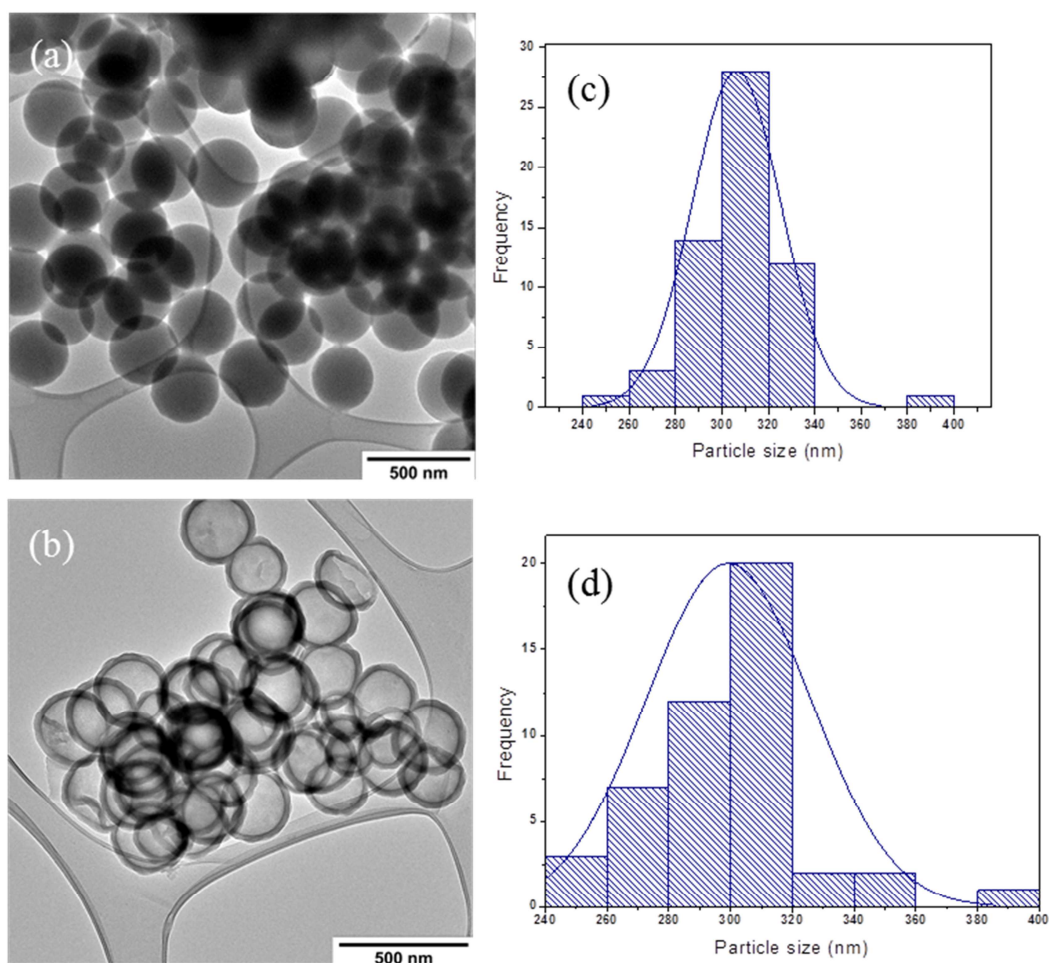


Figure 4.12: TEM images of (a) PSSs spheres with the diameter of 307 ± 19 nm, (b) mHCSs with the diameter of 300 ± 30 nm and (c-d) diameter distributions of PSSs and mHCSs respectively.

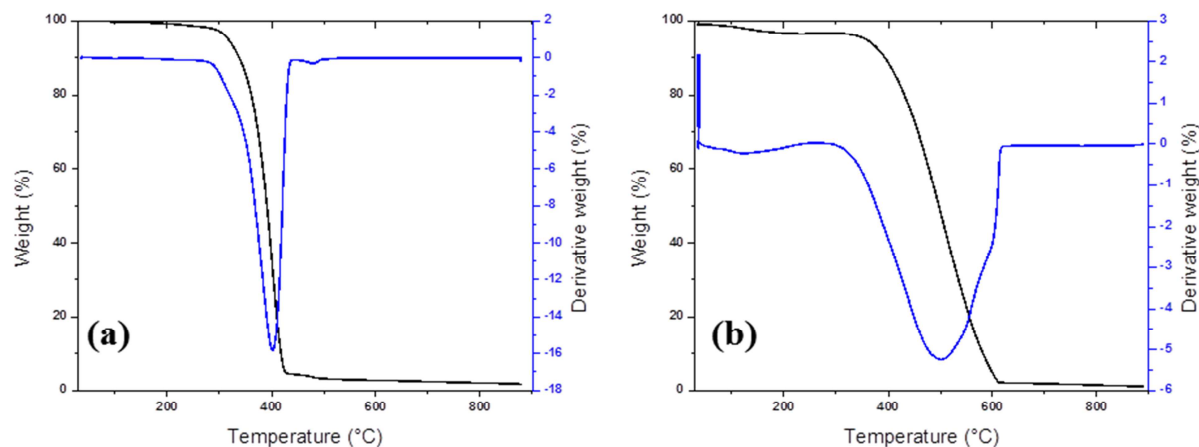


Figure 4.13: TGA and the first derivatives of the TGA profiles of the (a) PSSs and (b) mHCSs.

The PSSs were used as a support for copper nanoparticles. Unlike silica spheres PSSs are not porous. The copper nanoparticles were placed on the outer surface of the PSSs. After this process a carbon layer was added to the Cu/PSSs to test if hollow carbon spheres could be obtained using the resorcinol-formaldehyde polymerization method. When the Cu/PSSs catalyst was coated with RF polymer the formation of Cu/PSSs@RF was expected. Removal of PSSs would then lead to formation of the Cu@mHCSs catalyst. From the TEM images, it was observed that most of the copper nanoparticles were found on the outside surface of the mHCSs (Figure 4.14). The average particle size of the copper nanoparticles from Cu@mHCSs sample was calculated to be 90 ± 21 nm. The TGA and the first derivative of the TGA profile of the Cu/PSSs@C (Figure 4.15) shows weight residues of about 5.4 % which was attributed to the copper nanoparticles. The first decomposition peak at around 380 °C was attributed to the loss of PSSs, while the second decomposition peak at around 445 °C was attributed to the loss of amorphous carbon.

From the literature, it was reported that copper tends to form complex ions in ammonia as copper metal is oxidized to Cu^{2+} [25, 26]. The reaction that takes places in this instance is described in equation (4.1) [27]. Shiomi *et al.* [26] synthesized silica coated copper nanoparticles using a liquid phase method. The authors used 1 M hydrazine to keep the copper nanoparticles from undergoing dissolution/oxidation during silica shell formation that was catalyzed by ammonia. It

was reported that the hydrazine prevented the oxidation of the copper nanoparticles for less 30 minutes, thereafter hydrazine started to decompose. This meant that use of ammonia would be a problem as it will readily dissolve copper nanoparticles. To overcome this problem, we chose to replace ammonia with sodium carbonate as a catalyst for RF polymerization reactions.

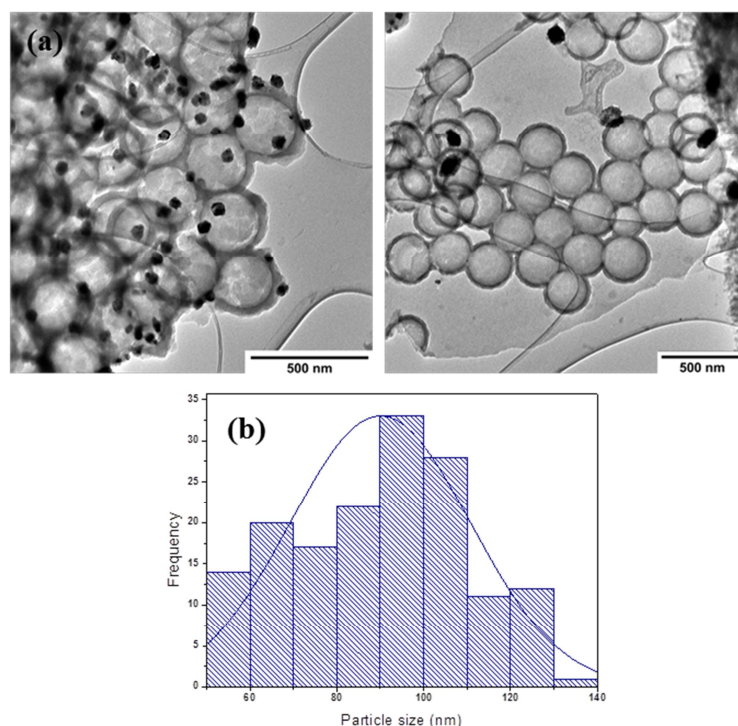
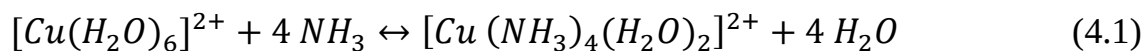


Figure 4.14: (a) TEM images of copper nanoparticles outside the surface of mHCSs (b) diameter distribution of copper nanoparticles.

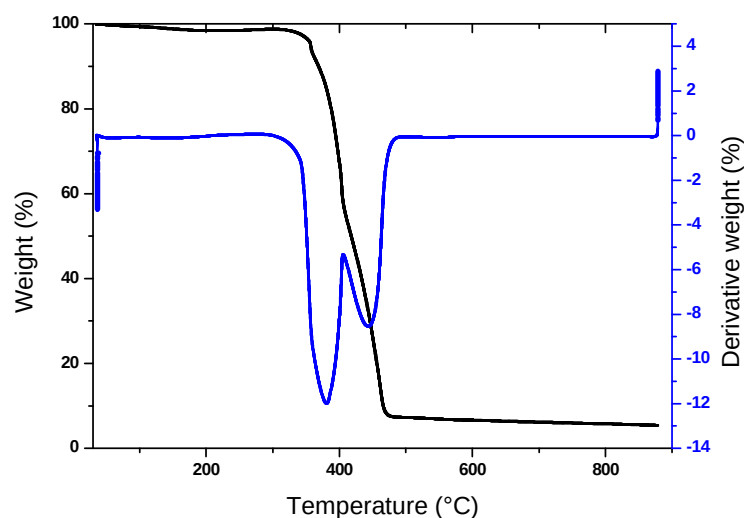


Figure 4.15: Shows the TGA and the first derivative of the TGA profile of Cu/PSSs@C.

Sodium carbonate (Na_2CO_3) is a commonly used base catalyst for the polymerization of resorsinol and formaldehyde [28]. A series of experiments replacing ammonia by Na_2CO_3 to catalyze RF polymerization was conducted to make mHCSs (Table 4.3). The molar ratio of water and ethanol was varied as shown in Table 4.3 due to the poor solubility of anhydrous Na_2CO_3 in ethanol while keeping the molar ratio of the catalyst and formaldehyde constant.

Table 4.3: The effect of reaction time and solvents on the formation of mHCSs

	Na_2CO_3 (g)	Ethanol (mL)	H_2O (mL)	Stirring time (h)	Diameter (nm)
Sample A (HCSs)	1.5898	150	10	72 96 120	275 ± 36
Sample B (HCSs)	1.5898	100	50	72 96 120	266 ± 40 nm

The RF catalyzed coverage of PSSs was achieved to give PSSs@RF catalyst from which the PSSs were decomposed to give mHCSs. Figure 4.16 shows TEM images of mHCSs synthesized by varying the amount of ethanol, water and time. From the TEM images it was shown that HCSs can be formed using a base catalysed RF method. Sample A had less broken mHCSs compared to sample B which was associated with a larger shell thickness. The obtained mHCSs were of diameter 275 ± 36 nm for sample A and 266 ± 40 nm for sample B.

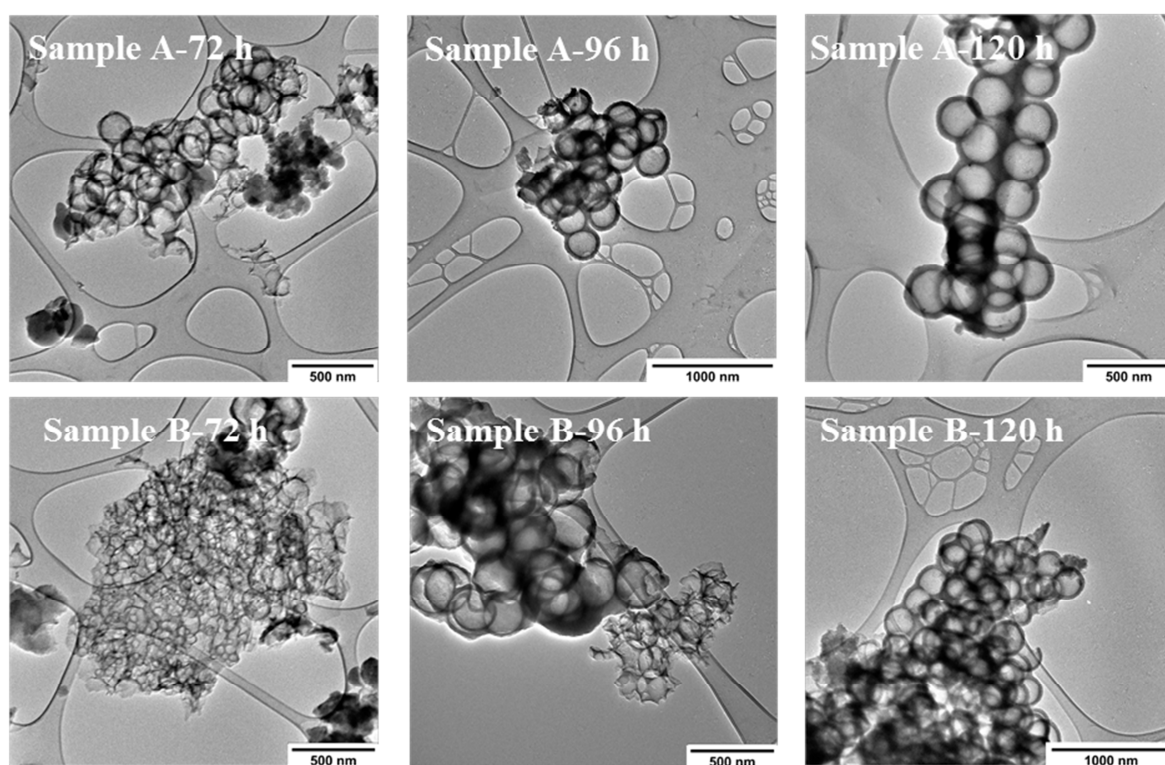


Figure 4.16: TEM images of HCSs synthesized by varying the reaction time and amount of solvents.

Cu@mHCSs were also synthesized using method A and B for 96 and 120 hours (Figure 4.17 a and b respectively). From the TEM images, sample A-96 hours appear to be the optimum method that can be used to synthesize Cu@mHCSs. Copper nanoparticles (enclosed in the overlaid circles) were successfully incorporated inside the mHCSs although some of these nanoparticles were still found on the outer surface of the mHCSs (Figure 4.17). After 120 hours most of the copper nanoparticles had aggregated to form large particles, as shown in the TEM

image (Figure 4.17 b-right) whereas the TEM image shown on the left shows Cu@mHCSs. To confirm the existence of copper in Cu@mHCSs (sample A-96 hours) PXRD analysis was used (Figure 4.18). The PXRD pattern shows that the sample contains copper. Diffraction peaks at 2θ value of 50.53° , 59.13° , and 88.50° represent the (111), (200) (220) planes of face-centered cubic copper (ICSD No. 053246). The particle/crystallite size of the copper nanoparticles was calculated using Scherrer equation (4.1). The two most intense peak of the diffraction pattern corresponding to the (111) and (200) planes were used to calculate the average crystallite size. The calculated crystallite size (23 nm) is close to the average particle size of the copper nanoparticles obtained from the TEM images (24 ± 3.9 nm).

$$D_{hkl} = \frac{K \times \lambda}{\beta \times \cos \theta} \quad (4.2)$$

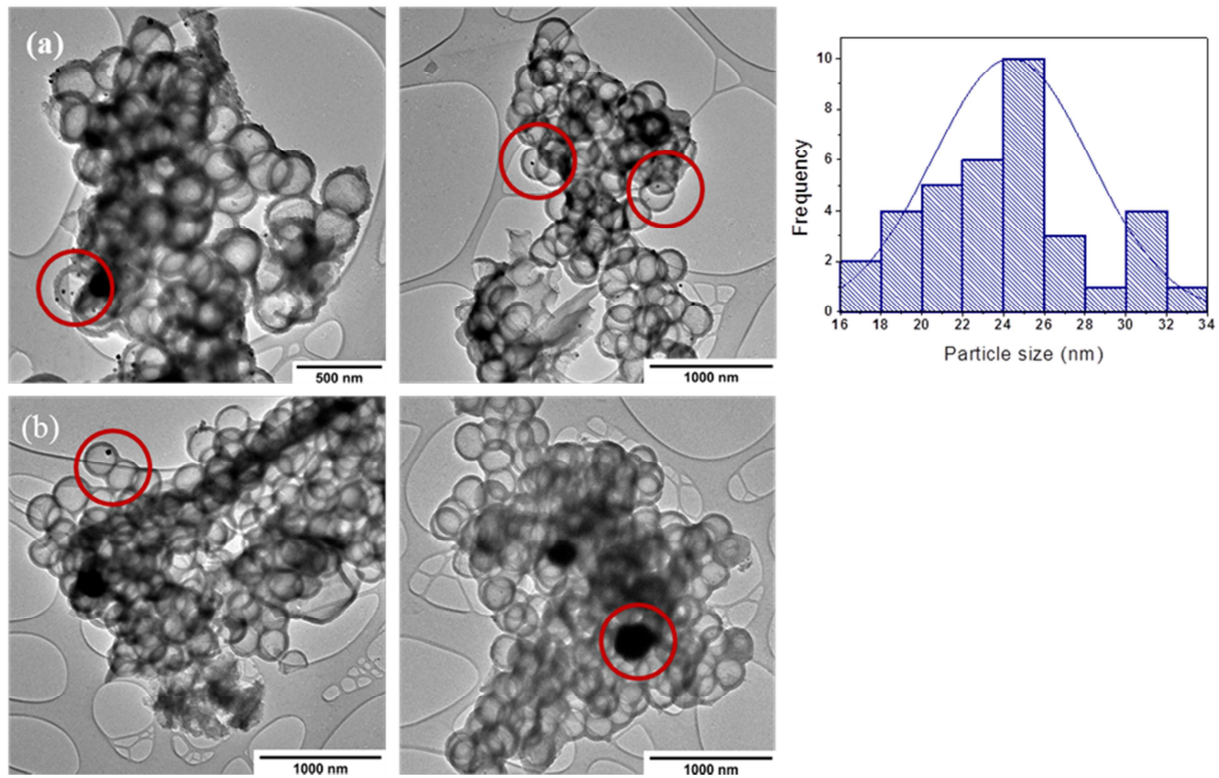


Figure 4.17: TEM images of Cu@mHCSs synthesized using method for sample A at a duration of (a) 96 h and (b) 120 h.

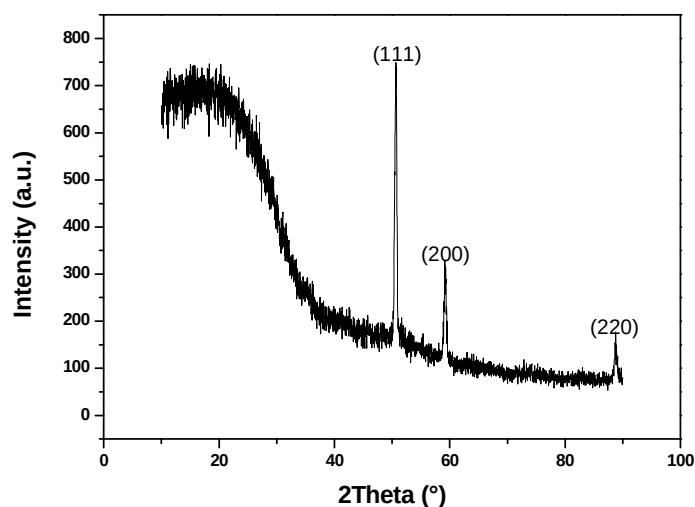


Figure 4.18: Powder X-ray diffraction pattern of Cu@mHCSs after template removal.

4.2.5 Conclusion

Copper nanoparticles supported on mSiO₂ samples were readily prepared. However, coverage by carbon followed by mSiO₂ leaching also led to copper leaching. Thus the methodology used to remove the silica template (most particularly 5 % HF solution) also removed the copper nanoparticles. Attempts to use 2 M NaOH etching also gave copper leaching. Another difficulty that emerged is that insufficient carbon coverage was achieved. Broken mHCSs were observed and it also led to copper loss from the mHCSs. PSSs were used as an alternative template for the synthesis of Cu@mHCSs. The PSSs were covered by carbon using a RF polymerization reaction. The RF polymerization reaction was successfully catalyzed using both ammonia and Na₂CO₃. In the synthesis of Cu@mHCSs it was observed that ammonia did not only polymerize RF but it also oxidized copper. Precipitation of copper nanoparticles occurred on the outer surface of the HCSs as shown in Figure 4.14. TEM and PXRD validated the presence of copper in the Cu@mHCSs whereby the silica spheres were etched out using 2 M NaOH. TEM and PXRD also confirmed the presence of copper in the Cu@mHCSs synthesized using a PSSs template whereby the RF polymerization was catalyzed using Na₂CO₃ catalyst.

4.2.6 References

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Chapter 5: Synthesis and characterization of helical carbon nanofibers

5.1 Introduction

Carbon nanomaterials with helical morphology have been widely studied owing to their unique chemical, mechanical, electrical and field emission properties [1]. These are the properties that make CNFs suitable for use as a catalyst support and for use in nanomechanical devices, composite materials, in selective adsorption, and in hydrogen storage [2]. Researchers have shown that copper nanoparticles can be used as effective catalysts for the synthesis of CNFs. Synthesis of HCNFs using acetylene at low temperatures using supported and unsupported copper catalyst has also been extensively reported [3,4]. Many suggestions have been proposed to rationalize how straight and helical CNFs are formed from the copper nanoparticles as both the morphology and size of the catalyst particles have an influence on the formation of different morphologies of CNFs.

It has been observed that nanoparticles of the same size but with different shape can form either straight or helical CNFs [5]. On the other hand the size of copper nanoparticles has been considered to have an important effect on the morphology of CNFs [6]. However, particle size cannot be considered as the only factor, as this does not explain the synthesis of the wide range of CNF morphologies or how the size relates to a helical morphology [1]. The surface of copper reacts differently in various atmospheres (e.g. C_2H_2 , N_2 , and H_2) and this has been postulated to have an effect on the growth of straight or helical CNFs [7]. Bandaru *et al.* [8] proposed that the helical nature of CNFs can be induced by liquid metals such as Ln , Cu , and Sn because of the large interfacial tension that exists between them and graphite surface angles (wettability). This observation was explained by repulsive interactions which lead to non-linear growth. Metals with small wetting angles such as Ni and Co have been reported to produce predominantly

straight fibers [7]. It is to be noted that these are not the only factors that influence the morphology of CNFs.

The CVD method has been used extensively to make CNFs because of the ease of production of the CNFs on a large scale [3, 9, 10]. The intention of this work was to control the size of copper nanoparticles using mesoporous hollow carbon spheres and to evaluate their effect on CNF growth. From previous studies, the diameter of the catalyst particle used to make the CNF has been observed to be related to the diameter of the CNF [3].

5.2 Experimental procedures

A mass of 0.005 g of Cu@mHCSs powder was placed in a quartz tube in the middle of the furnace and heated to 350 °C in H₂ at a rate of 100 mL/min for 35 minutes to activate the catalyst. Acetylene was introduced, together with H₂ into the reaction chamber at a flow rate of 100 mL/min for 30 minutes. The total flow rate was 200 mL per minute. The system was then allowed to cool to room temperature under a H₂ flow. The reaction time with acetylene of 3 minutes was also studied.

5.3 Results and discussion

The discussion of results will be divided into two sections. The first section (5.3.1) will discuss results on the synthesis of HCNFs using Cu@mHCSs synthesized using silica as a template and the second section (5.3.2) will focus on the results obtained on the synthesis of HCNFs using Cu@mHCSs synthesized using PSSs as a template.

5.3.1 CNFs synthesized using Cu@mHCSs and Cu/mSiO₂

TEM images of CNFs synthesized using the Cu@mHCSs catalyst are shown in Figure 5.1. CNFs with different morphologies (curled, helical, and straight) were observed. Some of the mHCSs are broken (Figure 5.1 a), indicating that the copper nanoparticles could be found on the outside of the mHCSs. In Figure 5.1b the appearance of the CNFs can readily be seen. However, all the CNFs appear to be found on the copper outside of the mHCSs. The CNFs appear to show some coiling. In Figure 5.1c, mHCSs as well as straight CNFs (top right corner) are to be seen. In the bottom part of the picture, broken coiled CNFs can be observed. No evidence for growth of CNFs can be seen inside the mHCSs. From the TEM images it was observed that formation of amorphous HCNFs occurred from small sized copper nanoparticles supported on the mHCSs.

This effect was also observed when a Cu/mSiO₂ catalyst was used to synthesize HCNFs under C₂H₂/H₂ at 350 °C (Figure 5.2). The CNFs grown from Cu/mSiO₂ are more abundant than those grown over Cu@mHCSs. Figure 5.2a would suggest that the CNFs grow from the surface of the silica sphere that contains the surface copper. The majority of the CNFs have a helical shape consistent with literature reports. However, straight CNFs are also seen in abundance (Figure 5.2b). This observation could be explained by small particle size nanoparticles that form on this support [2] and other morphologies were observed from clustered copper nanoparticles that were isolated from the silica spheres and found on the surface of the silica spheres.

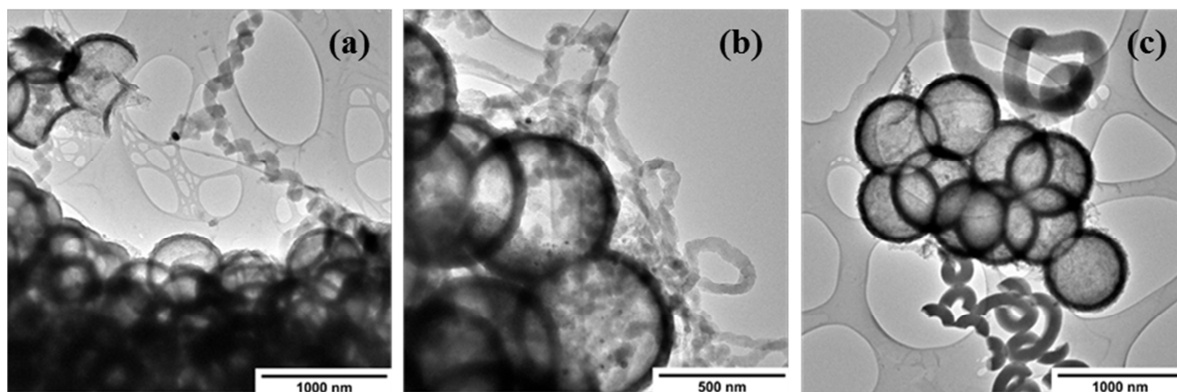


Figure 5.1: TEM images of CNFs synthesized using Cu@mHCSs catalyst at 350 °C under C_2H_2/H_2 for 30 minutes.

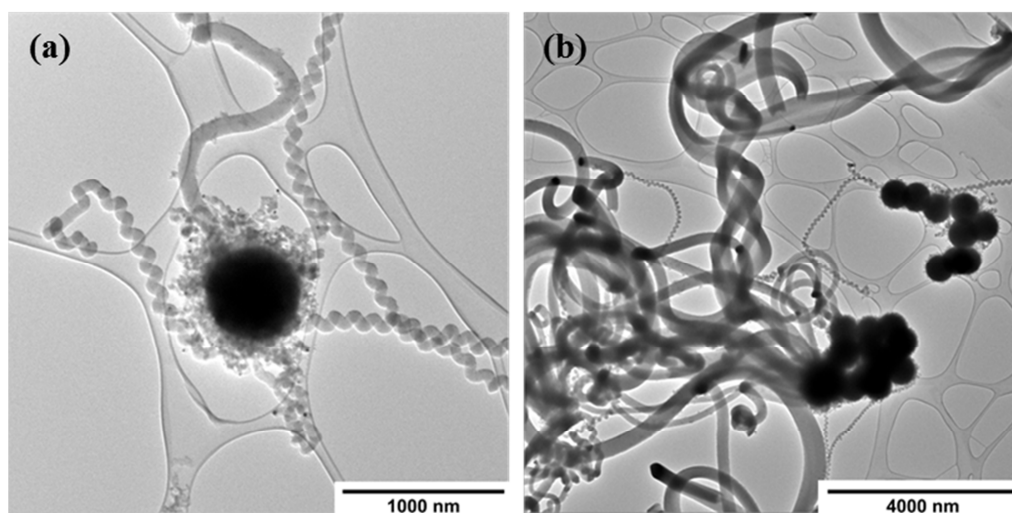


Figure 5.2: TEM images of CNFs grown over Cu/mSiO₂ under C_2H_2/H_2 at 350 °C.

From the TGA analysis (Figure 5.3), two types of carbon peaks were observed. The first decomposition peak was observed at a temperature of 386 °C indicating complete oxidation of amorphous type of carbon and the second and third decomposition peaks occurred at 559 °C and 604 °C indicating decomposition of graphitic type of carbon.

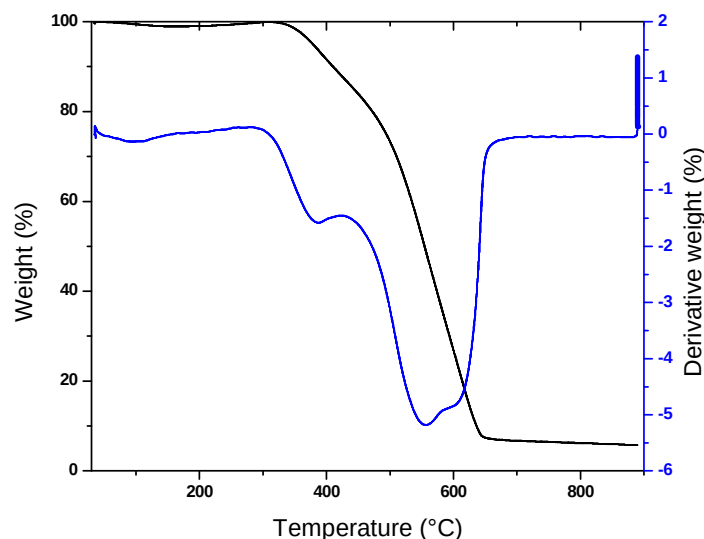


Figure 5.3: Shows the TGA and the first derivative profile of the CNFs synthesized using Cu@mHCSs catalyst.

Raman analysis was used to evaluate the degree of graphitization of the CNFs. Two carbon peaks that are normally observed in the Raman spectra are the D band which occurs around $1280\text{--}1350\text{ cm}^{-1}$ and the G band which occurs around $1580\text{--}1600\text{ cm}^{-1}$ [11]. The D band is associated with the disordered graphite bonds whereas the G band is associated with a vibration of sp^2 carbon atoms [11]. The Raman spectra of the CNFs and Cu@mHCSs catalyst are shown in Figure 5.4. The I_D/I_G ratio for the CNFs synthesized using Cu@mHCSs catalyst was found to be 0.26 whereas the ratio for the Cu@mHCSs catalyst was observed to be 0.68 (Table 5.1). Usually CNFs synthesized at lower temperatures ($< 350\text{ }^\circ\text{C}$) are expected to have more structural defects [3,]; in this case we have a mixture of both mHCSs and CNFs contributing to the observed ratio (0.26). The Cu@mHCSs I_D/I_G ratio indicated that the mHCSs have more disordered carbon while the CNFs formed from C_2H_2 by Cu@mHCSs catalyst have a higher degree of graphitization.

Table 5.1: Summary of the D and G band position and ratio of the intensities of the D and the G bands

Sample	D band position (cm^{-1})	G band position (cm^{-1})	I_D/I_G
Cu@mHCSs	1335	1593	0.68
CNFs	1368	1587	0.26

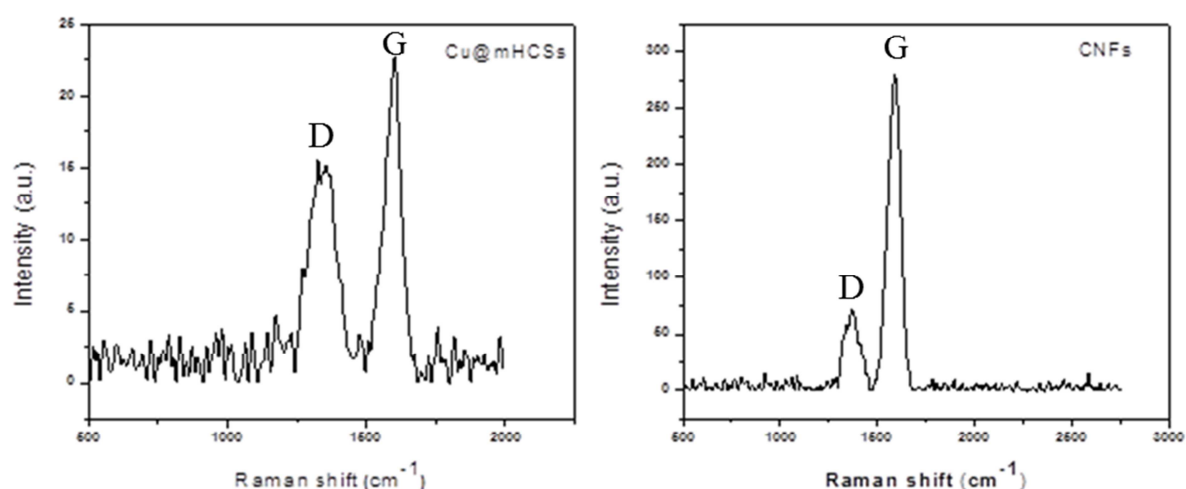


Figure 5.4: Raman spectra of the Cu@mHCSs catalyst and CNFs synthesized using the Cu@mHCSs catalyst.

5.3.2 CNFs synthesized using Cu@mHCSs obtained from Cu/PSSs@C

TEM images of the CNFs synthesized using Cu@mHCSs are shown in Figure 5.5. Broken mHCSs (Figure 5.5a, c, d, e, and f) with diverse morphologies of the CNFs formed from the copper nanoparticles that have escaped from the mHCSs are observed. From these TEM images both straight and helical CNFs can be seen. The straight CNFs appear to have larger diameters than helical CNFs, indicating the difference in the particle size of copper. In Figure 5.5b, the mHCSs without copper nanoparticles can be seen. This shows that the method used to synthesize the Cu@mHCSs did not work.

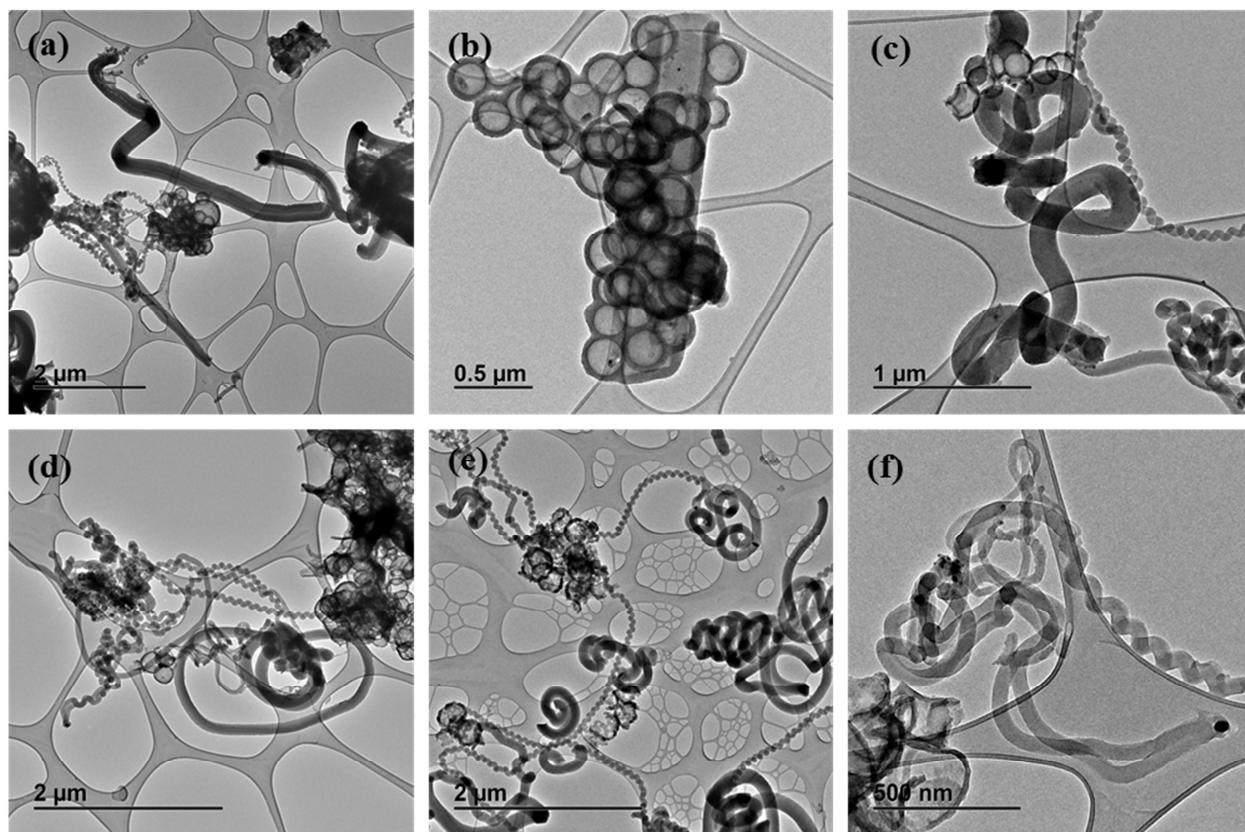


Figure 5.5: TEM images of CNFs synthesized using Cu@mHCSs catalyst at 350 °C under C_2H_2/H_2 for 3 minutes.

From the TGA analysis (Figure 5.6), one type of carbon was observed. The broad decomposition peak was observed at a temperature of 430 °C indicating an amorphous type of carbon. The first small decomposition peak at around 70-100 °C was attributed to the loss of adsorbed moisture in the sample.

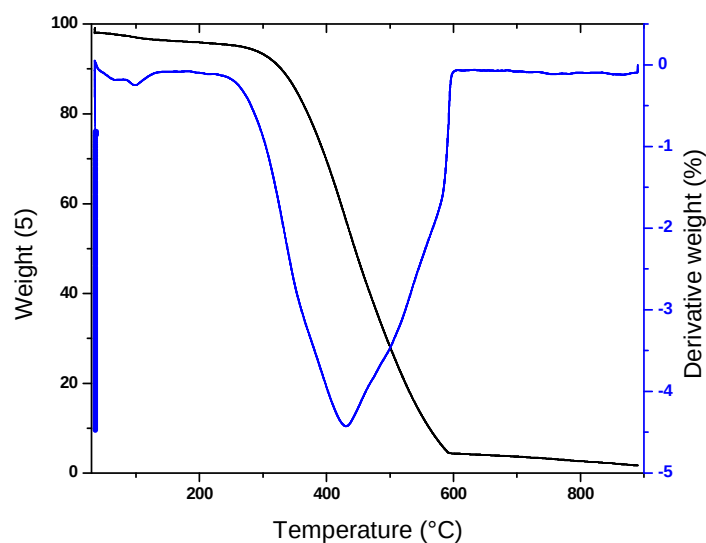


Figure 5.6: Shows the TGA and the first derivative profile of the CNFs synthesized using Cu@mHCSs catalyst.

The Raman spectra of the CNFs and Cu@mHCSs catalyst are shown in Figure 5.7. The I_D/I_G ratio for the CNFs synthesized using Cu@mHCSs catalyst was found to be 0.34 while the ratio for the Cu@mHCSs catalyst was observed to be 0.33 (Table 5.2). The I_D/I_G ratio of both Cu@mHCSs and CNFs indicated that both materials have a higher degree of graphitization. There is no consistency between the Raman and the TGA (Figure 5.6) data. Carbon made from RF polymerization is expected to have structural defects when annealed at lower temperature (500 °C), but the Raman data suggest otherwise. The same applies with CNFs.

Table 5.2: Summary of the D and G band position and ratio of the intensities of the D and the G bands

Sample	D band position (cm^{-1})	G band position (cm^{-1})	I_D/I_G
Cu@mHCSs	1339	1592	0.33
CNFs	1350	1587	0.34

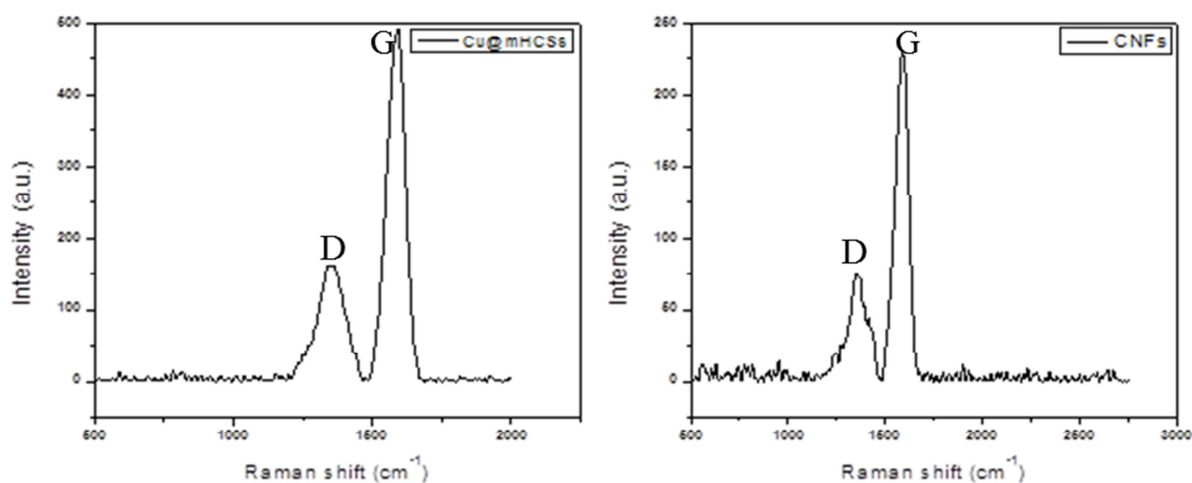


Figure 5.7: Raman spectra of the Cu@mHCSs catalyst and CNFs synthesized using the Cu@mHCSs catalyst.

5.4 Conclusion

Silica template

In summary, it is seen that both the Cu/mSiO₂ and Cu@mHCSs give growth of the CNFs outside the sphere. The range of CNFs shapes is as expected for copper supported on silica spheres. The shapes grown on the copper supported on the carbon is not unusual, but appears to be different to that grown on silica. This would suggest that the copper particles have different sizes or shapes when supported on carbon or silica spheres. However, no evidence is available at this stage to confirm this (expected) statement.

PSS template

The method used to synthesize Cu@mHCSs was not successful, as most of the mHCSs were broken leading to the formation of CNFs outside the mHCSs. From the TEM images there is no evidence that the copper nanoparticles were incorporated inside the mHCSs. Both straight and helical CNFs were observed and the difference in the diameter of both CNFs suggested differences in the size of the copper nanoparticles.

5.5 References

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Chapter 6: Overall conclusions and future recommendations

6.1 Overall conclusions

The main aim of this project was to synthesize HCNFs using copper nanoparticles contained in mHCSs and to correlate the diameter of the HCNF with the copper nanoparticle size. The size of the copper nanoparticles was narrowed from 90 ± 24 nm to 69 ± 19 nm. Both mSiO₂ and PSSs were used as templates for the mHCSs. When silica was used as a template, HF was used to etch out the silica template but in our findings copper nanoparticles dissolved and were etched out together with the silica template. Sodium hydroxide was used as an alternative to HF, but after etching the silica template most of the mHCSs were broken and some of the copper nanoparticles were leached out of the mHCSs. Further, some were found on the outer surface of the mHCSs. When this catalyst was used to synthesize HCNFs using the CVD method, diverse morphologies of CNFs was observed. Most of the CNFs were found on the surface of the mHCSs due to the nanoparticles being present on the outer surface or from the nanoparticles being separated from the surrounding mHCSs (chapter 5). From the TEM images it was not possible to correlate the diameter of the CNF obtained with the particle size of copper.

When PSSs were used as a template, only a few copper nanoparticles were incorporated inside the mHCSs (chapter 4). When this catalyst was used to synthesize the CNFs, it was observed that most of the copper nanoparticles were again found outside of the mHCSs, many of which were seen to be broken. This implies that our goal was not reached. This can be explained by the poor interaction between copper and PSSs, as the nanoparticles do not necessarily attach to the surface of the PSSs.

The catalyst obtained from silica template produced more HCNFs than the catalyst obtained from the PSSs. CNFs were however grown on the copper nanoparticles found on the surface of the mHCSs.

6.2 Future recommendations

This study has shown how challenging working with copper can be, as this metal easily dissolves in HF and ammonia. To synthesize Cu@mHCSs catalyst, solutions such as HF and ammonia have to be avoided. Although NaOH did not seem to have an effect on copper, the structural integrity of the mHCSs was compromised, as it was observed that most of the mHCSs made in this study were broken. More work on the use of PSSs needs to be done, as this material does not compromise the nature of copper because of its ease of removal. The surface of the PSSs can be improved to enhance the surface interaction between copper and PSSs. It may be possible to make one-pot synthesis of Cu@PSSs, during the styrene polymerization to PSSs.

Use of 3-D TEM needs to be explored as this is the easiest technique to show if the copper nanoparticles are indeed inside of the mHCSs. This could help when evaluating the effect of copper particle size on the fiber diameter, as the shape and size of the nanoparticle can easily be observed from the 3-D TEM.