

Chapter Two: Literature review

2.1 Fly ash

Population growth and socio-economic development are closely related, if not proportional, to the growth of energy demand. Emerging economies that have greater populations have the greatest energy demand and consumption. The British Petroleum (BP) statistical review of world energy, June 2013, states that 90% of the world's net increase in global energy consumption is accounted for by China and India, which are countries with the largest populations in the world [1]. Approximately 82% of the world's energy demands are met by fossil fuels and of that percentage 40% is accounted for by coal because of its wide geographic distribution as well as stable and predictable costs.

The average coal consumption rate is currently over 7 billion tons per annum in the world and it is projected that by the year 2020 it will be over 10 billion tons per annum [2]. The major drawbacks caused by the use of coal have to do with their high emission of CO₂ and other by-products produced after burning. In 2013 coal burning power stations produced over 750 million tons of waste of which 80% was fly ash; this means that 600 million tons of fly ash on average are produced yearly with an expected growth trend.

Fly ash can be described as one of the by-products of coal combustion that is grey in colour, abrasive, alkaline and refractory in nature [3]. It consists of fine powdery cenospheres (hollow spheres) and plenospheres (solid spheres) that are vitric [3]-[7] along with an additional composition of angular carbonaceous material [3], [4] (**Fig 2.1.1**).

The morphology of the fly ash particles depends upon two factors: the combustion temperature and the cooling rate of the boiler. The coal is converted into char which burns at high temperatures and the finer minerals entrapped within the char get released. The fine minerals decompose and get gasified and eventually upon homogeneous condensation they form spherical ash particles which have diameters between 0.02 – 0.2 µm. The excluded minerals undergo complex transformations that form spherical particles that have a size range between 10 – 90 µm; included minerals which are fragmented form particles of within the 0.2 – 10 µm range [8], [9].

From their study, Fischer *et al.* were able to correlate the nature of the spheres to the composition of the melts [10].

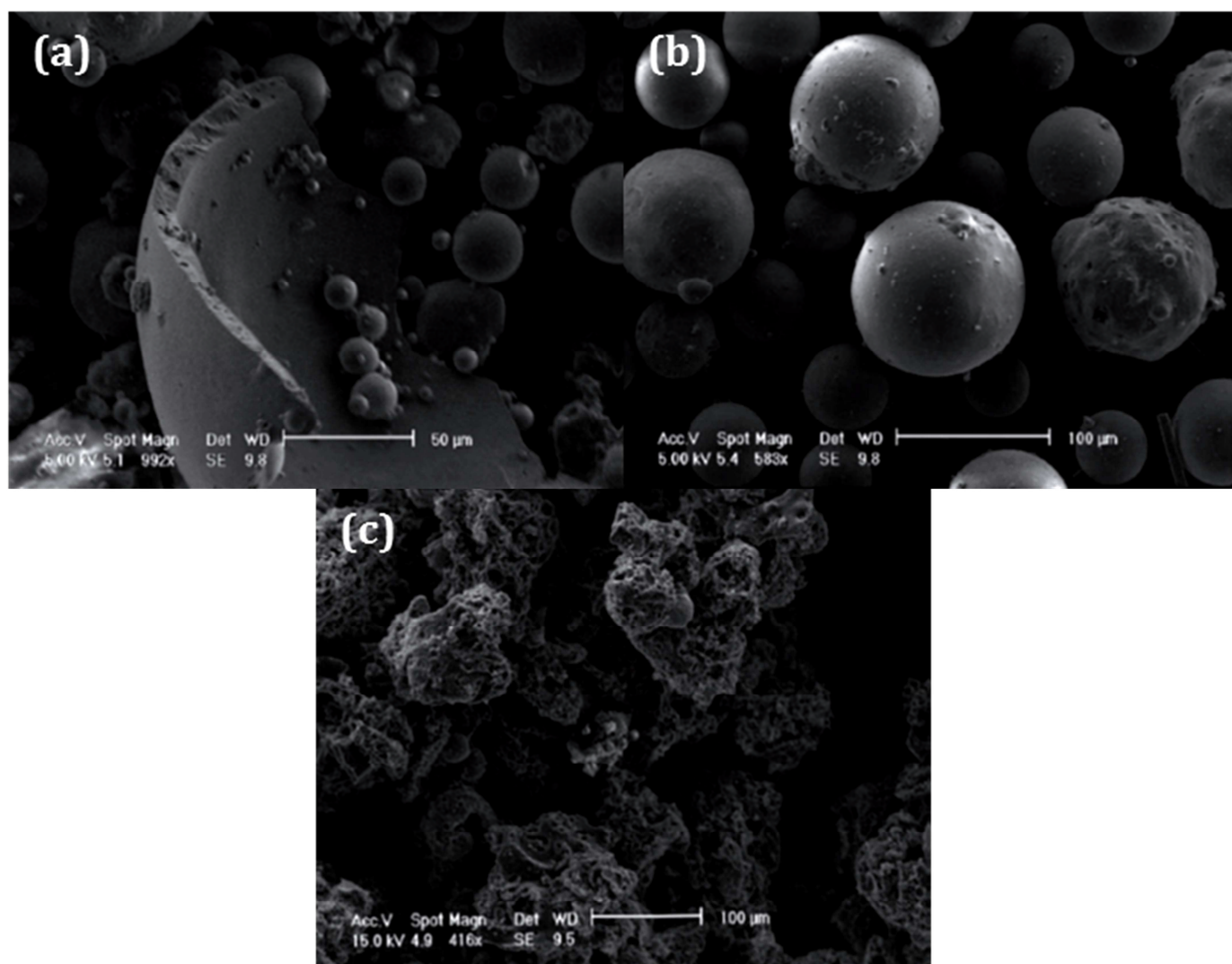


Figure 2.1.1: SEM images of a broken plerosphere (a), a cenosphere (b) and angular carbonaceous material (c) ^[4]

Their study stated that cenospheres and ‘stereospheres’ resulted from pure silicate melts. Plerospheres came from a melt of iron oxides in a silica matrix. Ferro-carbonaceous spheres resulted from the coal and or iron oxides which were mixed together during heating (see the schematic diagram of the morphogenesis of these particles (**Fig 2.1.2**, below)) ^[10].

Plerospheres contain generally smaller particles of iron oxide and other silicates while ferro-carbonaceous spheres have the Fe_2O_3 mixed with carbonaceous materials. Since iron is known to be an excellent catalyst in carbon nanomaterial (CNM) synthesis ^[11], both ferro-carbonaceous spheres and plerospheres were of prime interest in this study.

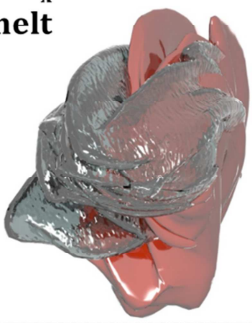
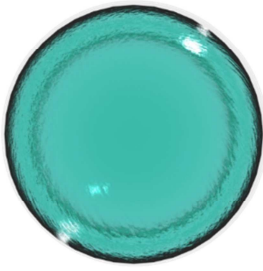
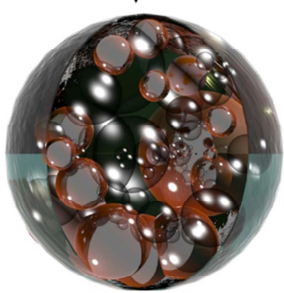
Silica melt 		FeO_x in silica matrix melt 	Carbonaceous material & FeO_x melt 
<i>Materials exposed to higher temperatures for long durations become spherical</i>			
Presence of volatiles lead to hollow spheres	Absence of volatiles results in solid silica spheres	Volatiles trapped within the mixture result in smaller FeO and Al-SiO₂ cenospheres being trapped in bigger Al-SiO₂ spheres	Unburnt coal minerals mix with Fe_xO_y particles to become spheres on cooling
			
Cenosphere	Stereasphere	Plerosphere	Carbon/Fe_xO_y sphere

Figure 2.1.2: Different melts and the types of spherical fly ash particles they form [10]

The primary minerals in fly ash are: SiO₂, Al₂O₃, Fe₂O₃, FeO, CaO, MgO and SO₃ [12] where the unburnt carbon content is determined using the loss on ignition (LOI) analysis (Table 2.1.1). It is known that these compositions vary depending on the type of coal and the geographical location of the coal [4].

According to the American Society for Testing Materials (ASTMs) fly ash is categorized into two classes: class-C and class-F [3]. Class F fly ash has a total calcium content ranging from 1-12% mostly in the form of calcium hydroxides and sulphates while class-C fly ash has 30-40% calcium hydroxide and has a greater amount of alkalis (sodium+potassium) [3], [13]- [17].

Table 2.1.1: General chemical composition estimations of low to medium grade coal used in power stations [3]

Component (wt.%)	Bituminous	Sub-bituminous	Lignite
SiO ₂	20–60	40–60	15–45
Al ₂ O ₃	5–35	20–30	10–25
Fe ₂ O ₃	10–40	4–10	4–15
CaO	1–12	5–30	15–40
MgO	0–5	1–6	3–10
SO ₃	0–4	0–2	0–10
Na ₂ O	0–4	0–2	0–6
K ₂ O	0–3	0–4	0–4
LOI	0–15	0–3	0–5

From the above facts it is evident that there is a need to recycle or re-use the fly ash for industrial purposes that will be beneficial. It is estimated that only 16% of the fly ash we have worldwide is used [12]. The rest is left in holding ponds, lagoons, slag heaps and landfills and this is environmentally detrimental as well as uneconomical [12], [18], [19].

Since fly ash is a multicomponent system, containing a range of trace element nanoparticles of hazardous metals, these can be distributed into the rest of the body as well as cause chronic and acute diseases (**Fig 2.1.3**) [20].

Thus for people working in coal power stations and peripheral neighbourhoods, there is a high chance of being affected by these metals not only because of pre-concentration, but also because of the possibility of the particles becoming airborne [6].

Although so much is being left in dumpsites, scientists are going into great depths of finding alternative, sustainable and economic ways of using fly ash. A major quantity of the ash is being used in the construction and building industry as a replacement for cement because of its pozzolanic nature. This means that its alumina and silica cenospheres can react with Ca(OH)₂ to become cementitious [3], thus it is also used as a filler for the prevention of land subsidence when a mine reaches the end of its life. It is estimated that when a ton of cement is replaced with fly ash about 119 litres of oil are saved [21]. It is also estimated that by using a ton of ash in concrete \$ USD 129.10, 376.3 litres of water, 310 litres of gasoline and 1.7 barrels of oil are saved. Likewise, the carbon footprint is reduced by roughly 800 kg per ton of ash used [22].

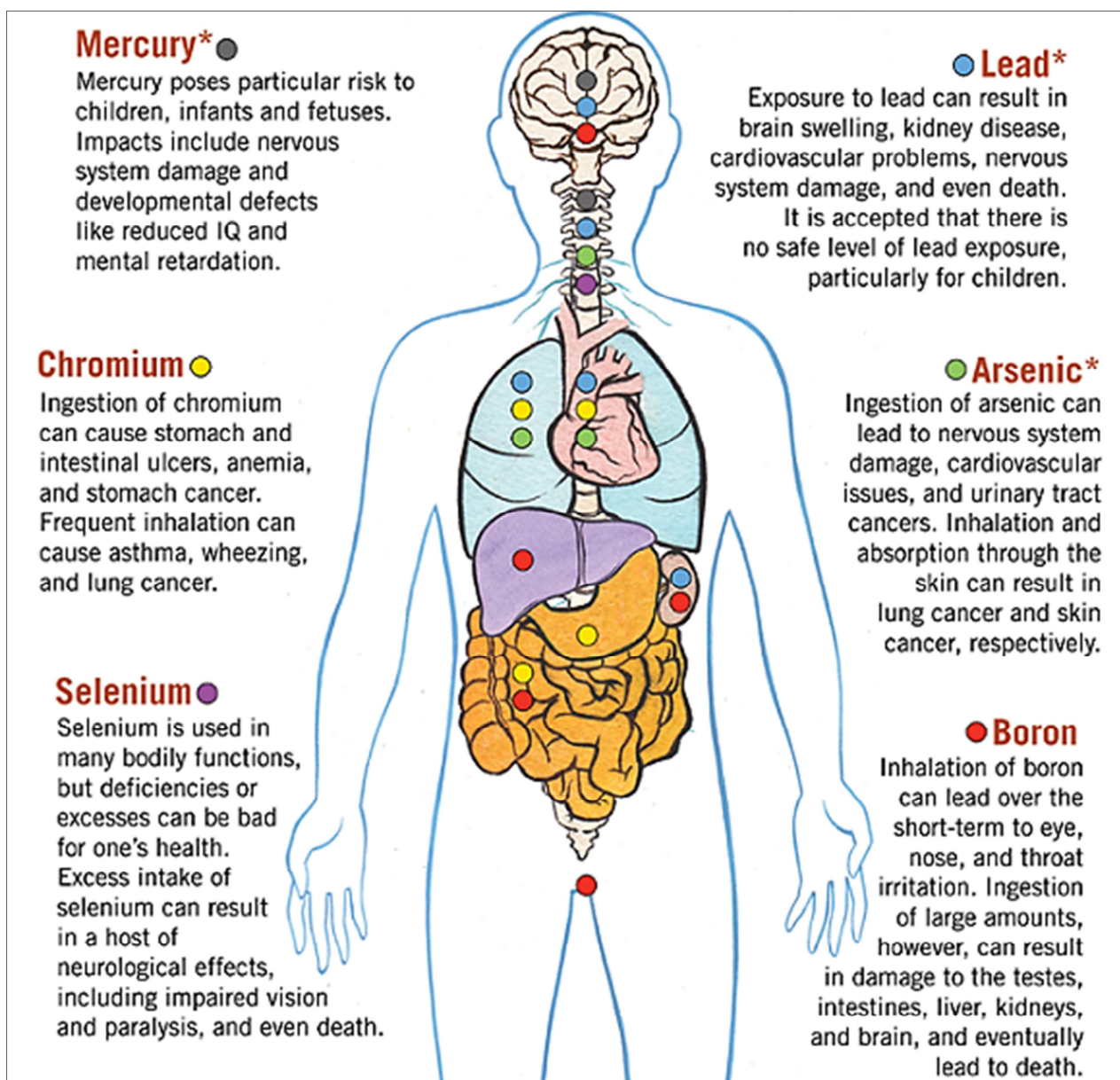


Figure 2.1.3: Schematic diagram that shows areas of the body that are susceptible to toxic trace elements found in coal fly ash [6].

Since fly ash is also refractory in nature and lightweight it is useful for ceramics, light weight aggregates and brickmaking [3], [21], [23]. Because fly ash also contains different essential elements, including both macronutrients: P, K, Ca, Mg as well as micronutrients: Zn, Fe, Cu, Mn, B, and Mo, it has been used for the enrichment of infertile soils [3], [4], [17], [21], [24]. The high percentage of silica (60–65%), alumina (25–30%), magnetite and haematite (6–15%) enables its use for the synthesis of: (i) high cation exchange capacity zeolites (for heavy metal sequestration and water purification) [21], [23], [25]–[27], (ii) alumina, and (iii) precipitated silica. Some valuable metals like: Al, Si, Fe, Ge, Ga, V and Ni have been extracted from fly ash [21], [28]. Research has also been

done to establish the possible distribution of the elements in fly ash particles. Data obtained so far suggests that there is a heterogeneous distribution of metals in the matrix and on the surface of the ash particles where the concentration of the metals appears to depend on the size of the ash particle [29]. For instance, the smaller the ash particles the more concentrated some elements become [29]. Based upon various methods including leaching studies, the elemental distributions discussed have been suggested below.

The surface of fly ash particle has been associated with elements such as: As, Zn, Cd, Pb. The glassy interior matrix of these particles has been found to consist predominantly of strongly bound elements of Si, Al, Na, La, rare earth elements (REE). On the other hand minerals composed of: Mn, Be and Cu appear to have been distributed between the inner matrix and the surface of these particles (**Fig 2.1.4**) [29]-[32].

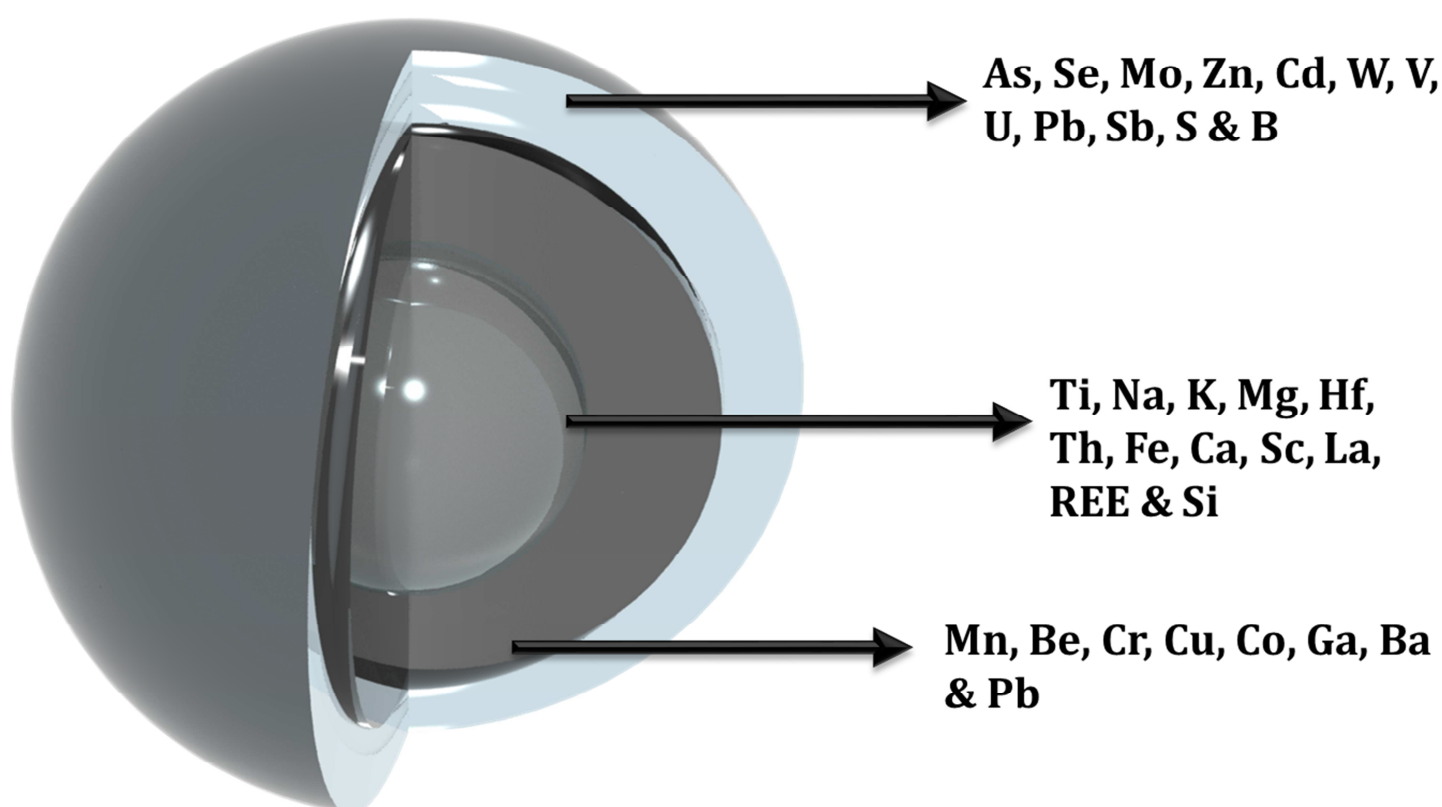


Figure 2.1.4: A simplified diagram indicating the possible elemental distribution of elements in fly ash particles, as obtained from leaching studies [29]- [32].

The presence of the following metals in the fly ash make it a potential catalyst/support in the chemical vapour deposition (CVD) synthesis of CNFs: Fe, Ni, Co, Mn, Cu, V, Cr, Mo and Pd [33], [34] because they have been commonly used for their synthesis.

A few researchers have used fly ash as a support or a catalyst for the synthesis of CNMs [5], [35]- [39] through the CVD method. Among the researchers, one is from South Africa, and thus this study focused on the testing of untreated South African fly ash as a possible catalyst for this use.

2.2 Carbon nanofibres

Carbon forms a range of allotropes, from standard to exotic. These allotropes are able to form different nanostructures that can be categorized according to their shape, size and morphology. These forms range from the main types which are: diamond-like, sphere-like, tube-like and sheet-like (**Fig 2.2.1**) into the more exotic shapes like: spirals, onions, helices and cones [40]. Carbon materials can have different sizes depending on their use. Carbon materials whose sizes are in the nanometer scale are classified into three groups according to their preparation method: (a) Through the vaporisation of carbon clusters or fragments (b) By use of nanosized catalyst particles or (c) By use of templates, substrates and other methods [41]. These can be further classified by designed and controlled structure and texture through control of their [41]:

- (i) nanosize pores
- (ii) molecular structures
- (iii) precursors and
- (iv) interfaces.

Extensive research has been conducted into the synthesis of tubular nanomaterials, namely: carbon nanofibres (CNFs) and carbon nanotubes (CNTs) in their different variations [40]-[46]. CNFs and CNTs are very versatile because they can be used for many applications including: electronic components, as additives to polymers, in gas storage and as supports for catalysts [47], [48]. CNFs are normally used for energy related applications like hydrogen storage, batteries and as a material for supercapacitors [49].

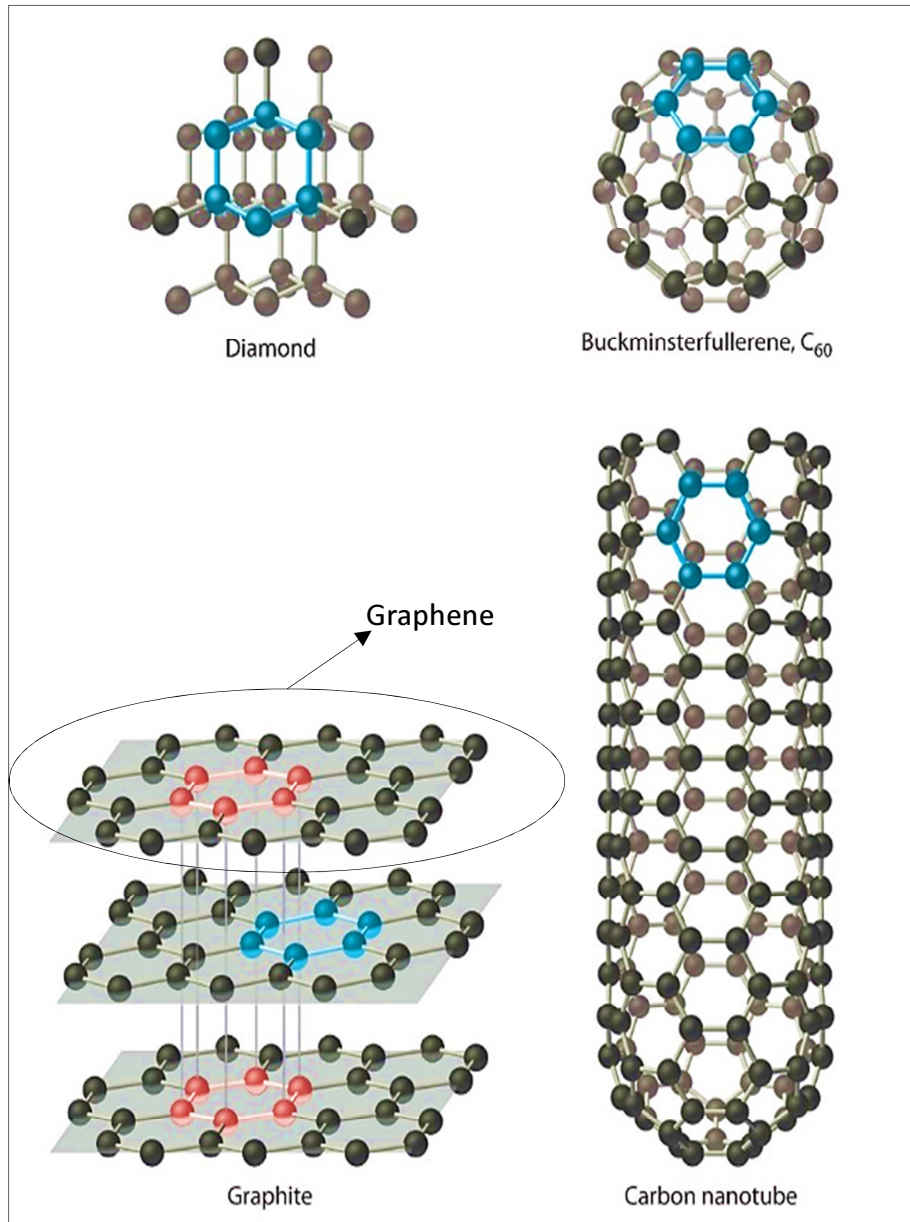


Figure 2.2.1: The five main allotropes of carbon (modified from [50])

CNFs are carbon filaments that have diameters ranging from 0.4-200 nm and they can be classified into four types: amorphous, stacked, and herringbone/fish-bone [51], [52]. For stacked CNFs it is known that the graphite platelets are parallel to each other along the axis of the fibre, while the herringbone structure type has platelets at an angle to each other. By contrast the amorphous CNFs have a random, disordered orientation relative to each other along the axis of the fibres and platelet CNFs have a concentric arrangement of tubes [52] (**Fig 2.2.2**).

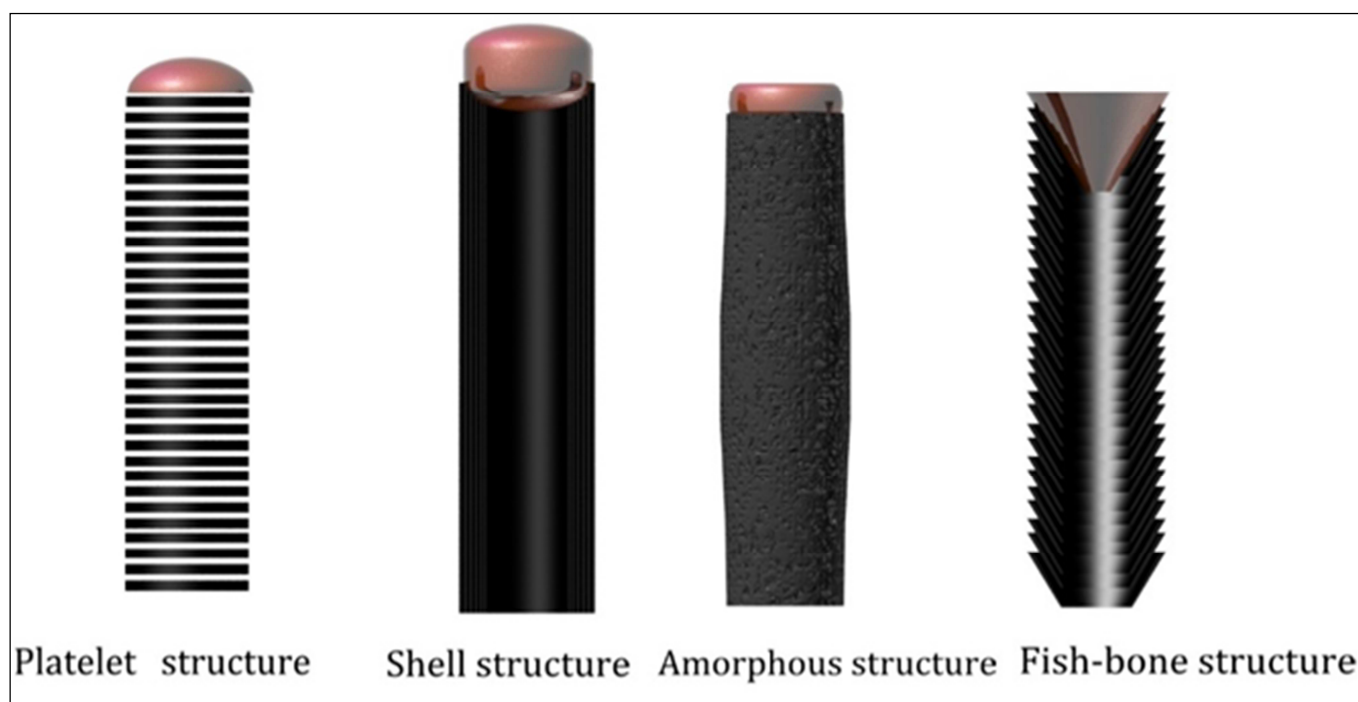


Figure 2.2.2: Cross sections of straight, low temperature synthesis CNFs, in their different structures [52].

These are a number of common methods employed to synthesise CNFs and/or CNTs including: arc-discharge, laser ablation and chemical vapour deposition (CVD). A brief description of these will now follow to provide a substantiation for the method chosen (i.e. CVD) in this study.

Arc-discharge

A typical setup of this method of synthesising carbon nanomaterials involves applying a direct-current (80-100 A) at fixed voltage across two graphite electrodes with an average diameter of 6-10 mm separated by a gap of 1-2 mm in a chamber filled with one or more of the following: $H_2(g)$, aqueous salt solutions [53] or methane at low pressure [47], [54]- [56]. One of the electrodes serves as a cathode (negative electrode) and the other as an anode (positive electrode). During the arcing process, which can reach up to 3000K, a deposit forms at low rates predominantly on the cathode, but also throughout the chamber while the anode is being consumed. The distance between the electrodes is maintained by adjusting the position of the anode either manually or mechanically [57] (Fig 2.2.3).

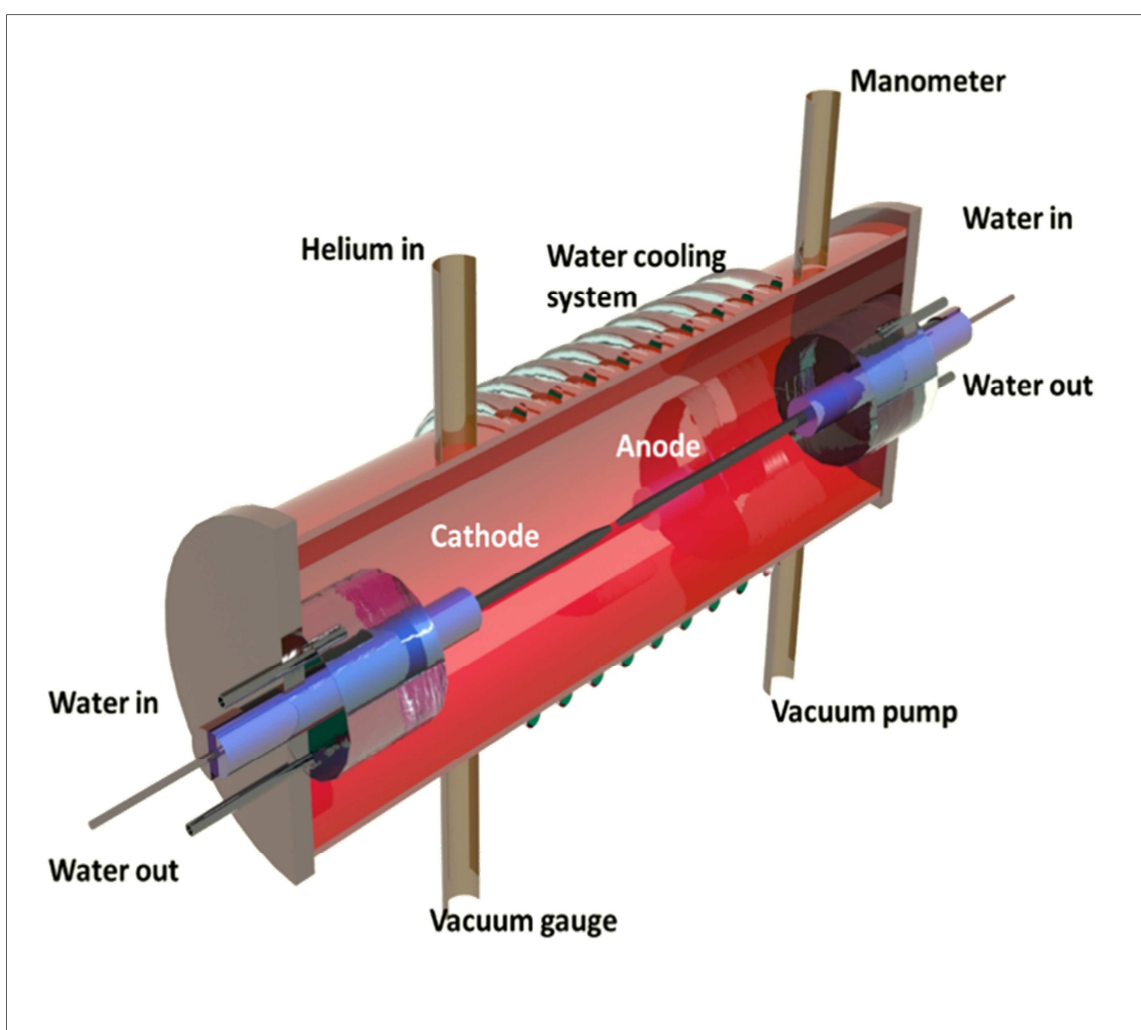


Figure 2.2.3: A schematic diagram showing a typical arc-discharge setup (modified from [54]).

When high purity graphite rods are used, fullerenes are deposited as soot inside the chamber and multi-walled carbon nanotubes are deposited on the cathode. When a graphite anode containing metal catalysts like: Ni-Y, Co-Ru, Co-Pt, Co-Ni-Fe-Ce and Rh-Pt mixes is used in conjunction with a pure graphite cathode, carbon nanofibres and/or tubes are formed predominantly on the cathode [47], [53].

Because high currents are required in the arc-discharge method, equipment costs can be high. Equally the requirement of graphite rods and reaction gases makes this technique expensive. Although this method can produce high quantities of carbonaceous products that have fewer structural defects in comparison to other techniques, one of its main disadvantages is the formation of by-products such as polyhedral graphitic particles, amorphous carbon and encapsulated metal particles, which can substantially lower the yield of CNFs or CNTs [47].

Laser ablation

The pulsed laser ablation technique was developed by Guo *et al.* in 1995 ^[58]. This method involves the use of a laser beam and a target surface composed of a metal-graphite mixture (**Fig 2.2.4**). The targets are made in a three step process involving moulding, heating under constant pressure and curing. They are made from mixing high-purity metal oxide with graphite powder and carbon cement. The metals that are typically used are: Cu, Co, Nb, Ni, Pt, Y and their mixtures. The lasers that are used are typically neodymium-doped yttrium aluminium garnet (Nd:YAG) lasers but occasionally CO₂ lasers can be used for the same purpose. They can be operated under pulsed or continuous-wave settings.

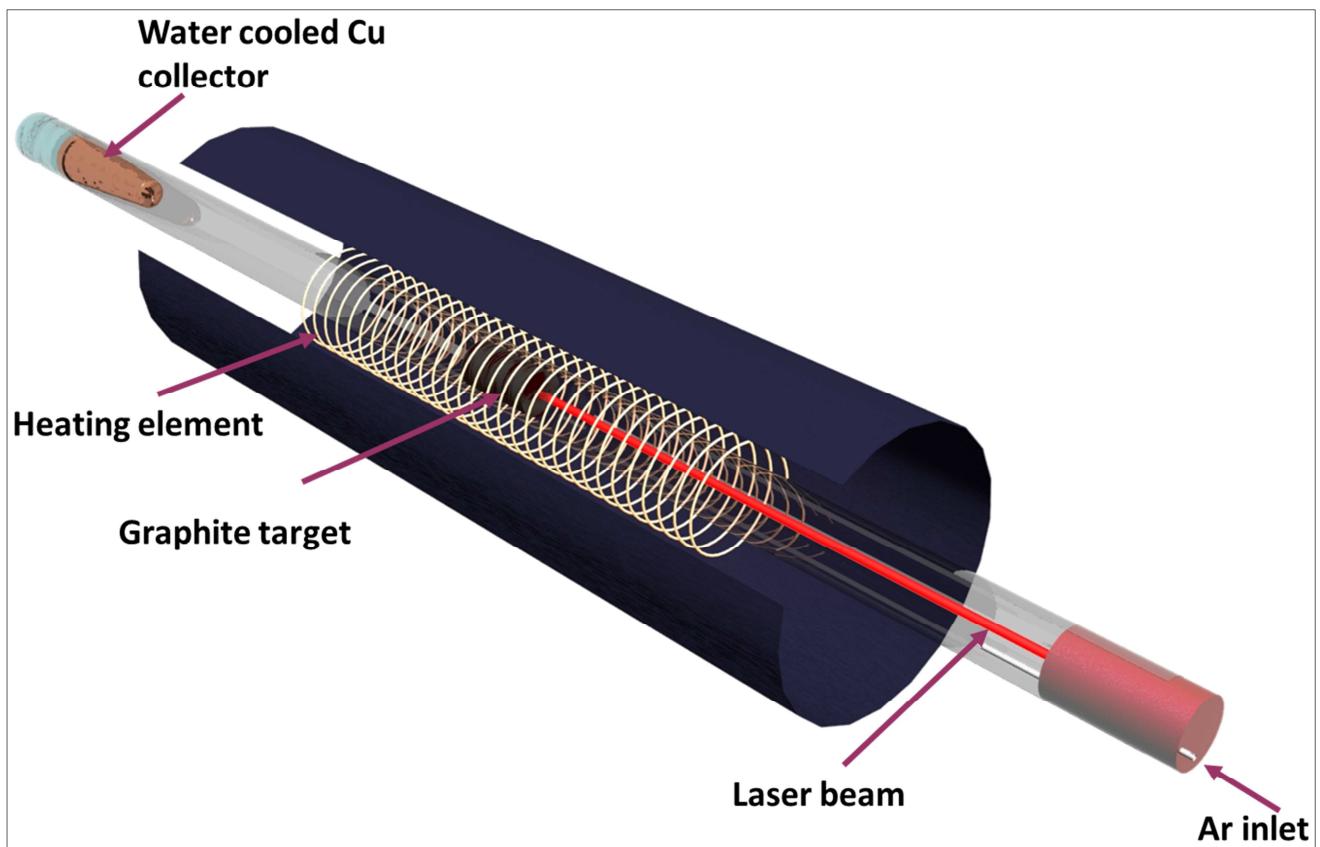


Figure 2.2.4: A laser ablation setup (modified from ^[55]).

Here the laser beam is scanned uniformly across the target which is placed in a high temperature furnace and a soot deposit is produced. The soot is blown using Ar gas towards a water-cooled copper collector which is positioned in the opposite direction of the gas flow, outside the furnace.

This method has been developed and varied since its initial use, but it has been shown that the nature of the materials that can be formed can be tailored. For a large yield one has to use a continuous-wave mode combined with a longer wavelength. As it is currently understood, this method has its own disadvantages: it results in a number of impurities including: graphite particles, amorphous carbon, hydrocarbons and fullerenes [55], [59].

It is clear that both arc-discharge and laser ablation produce superior nanotubes and fibres, but they require a large amount of energy, pure materials and their general design and setup is difficult and expensive [59].

Chemical vapour deposition

Chemical vapour deposition-plasma or thermal enhanced, as defined by Dunens *et al.* is a chemical synthesis technique where a gaseous carbon source is catalytically decomposed at moderate temperatures in a furnace, in the presence of a metal catalyst [36].

This method is extensively used for commercial production of CNFs of high purity because it is easy to control. There are mainly four types of furnaces that are used in CVD: horizontal (**Fig 2.2.5**), vertical, fluidised bed reactor and plasma enhanced furnaces [52]. These furnaces have a temperature range from the lower hundreds to 1200 °C. The carbon sources in this process are typically hydrocarbons (acetylene, methane, xylene, ethane, isobutene, ethanol and their mixtures [56]) because they decompose in the temperature range of the furnace. Some researchers have used CO gas too [60]. These carbon sources are advantageous because they accommodate a variety of substrates [60] that can be used for templating the growth of CNFs [56].

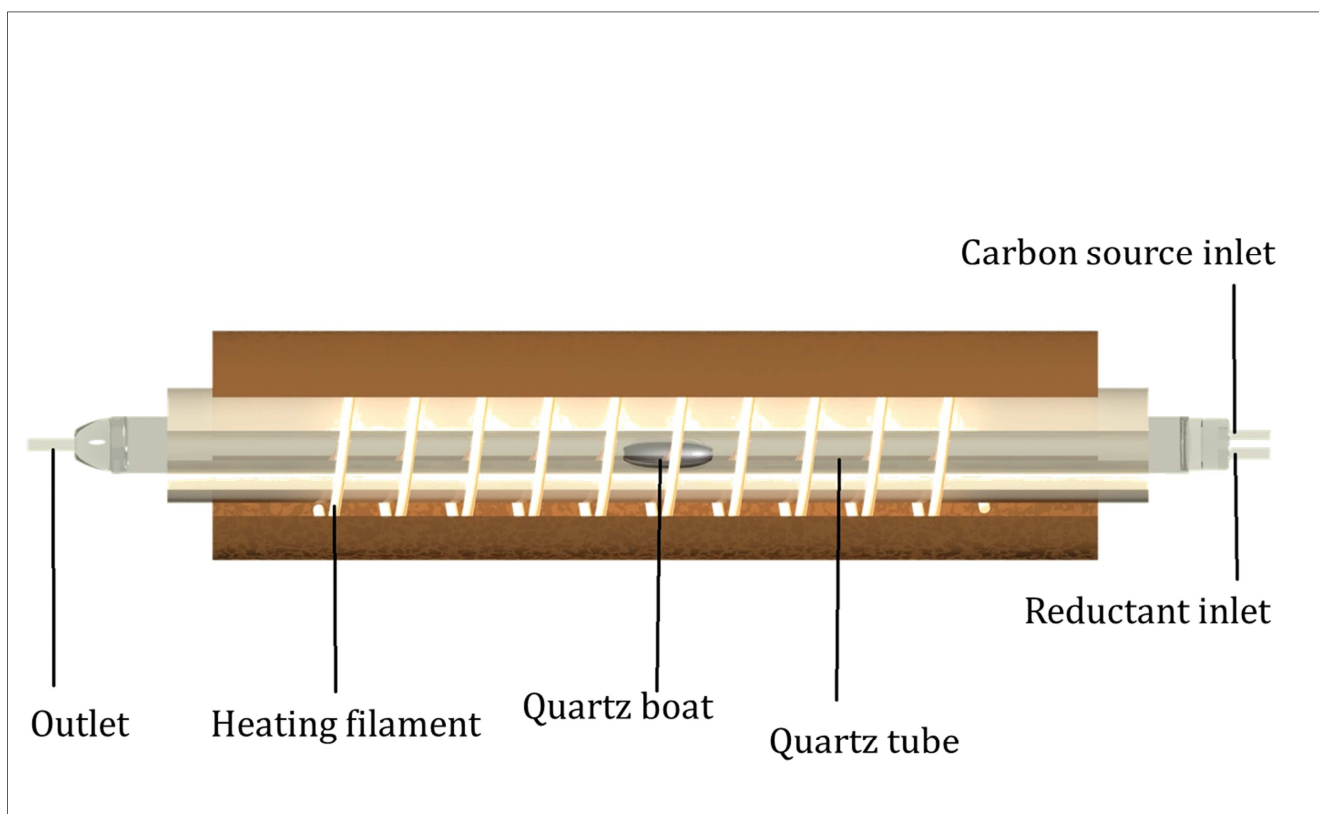


Figure 2.2.5: A typical horizontal furnace used for CVD synthesis (modified from [36])

Catalyst particles typically used for the synthesis of CNFs are: Fe, Ni, Co, Mn, Cu, V, Cr, Mo and Pd, although others have been demonstrated [33], [34]. Many researchers agree that CVD seems to be the method with great potential for industrial applications [61]. It can be operated at lower to moderate temperatures as well as used to make aligned arrays of nanomaterials with controlled diameter and length [60]. It has the simplest experimental setup of all the techniques mentioned previously [62]. Products formed in CVD are easy to purify. Likewise, many of the reaction variables can be changed for controlling products. Although control of these products is not completely customisable, the extent of manipulation to get the desired materials is reasonable.

Chao-Wei *et al.* in their research have suggested that the morphology of CNFs depended on the shape of the catalyst particles [63]. If the catalyst particles had flat or polygonal surfaces they resulted in the formation of herring-bone type CNFs and CNFs with inclined graphene layers, respectively. The size of the fibres was found to be dependent on the size of the catalyst particles. It was also noted that varying reaction temperature

resulted in CNFs with different structures. CNFs without a tube structure were usually formed at low temperatures [64]. Temperature, catalyst particle size, morphology of catalyst particle surface and composition of reactant gases among others could all be altered to produce desired types of CNFs [63].

It has been shown that CNFs grow through tip and root growth mechanisms in the CVD method (**Fig 2.2.6**) [64], [65]. In this process it has been suggested that a hydrocarbon gas adsorbs, decomposes, dissolves and then the resulting carbon species diffuses through the catalyst to precipitate carbon onto the opposite surface of the catalyst particle to form nanofibres [51].

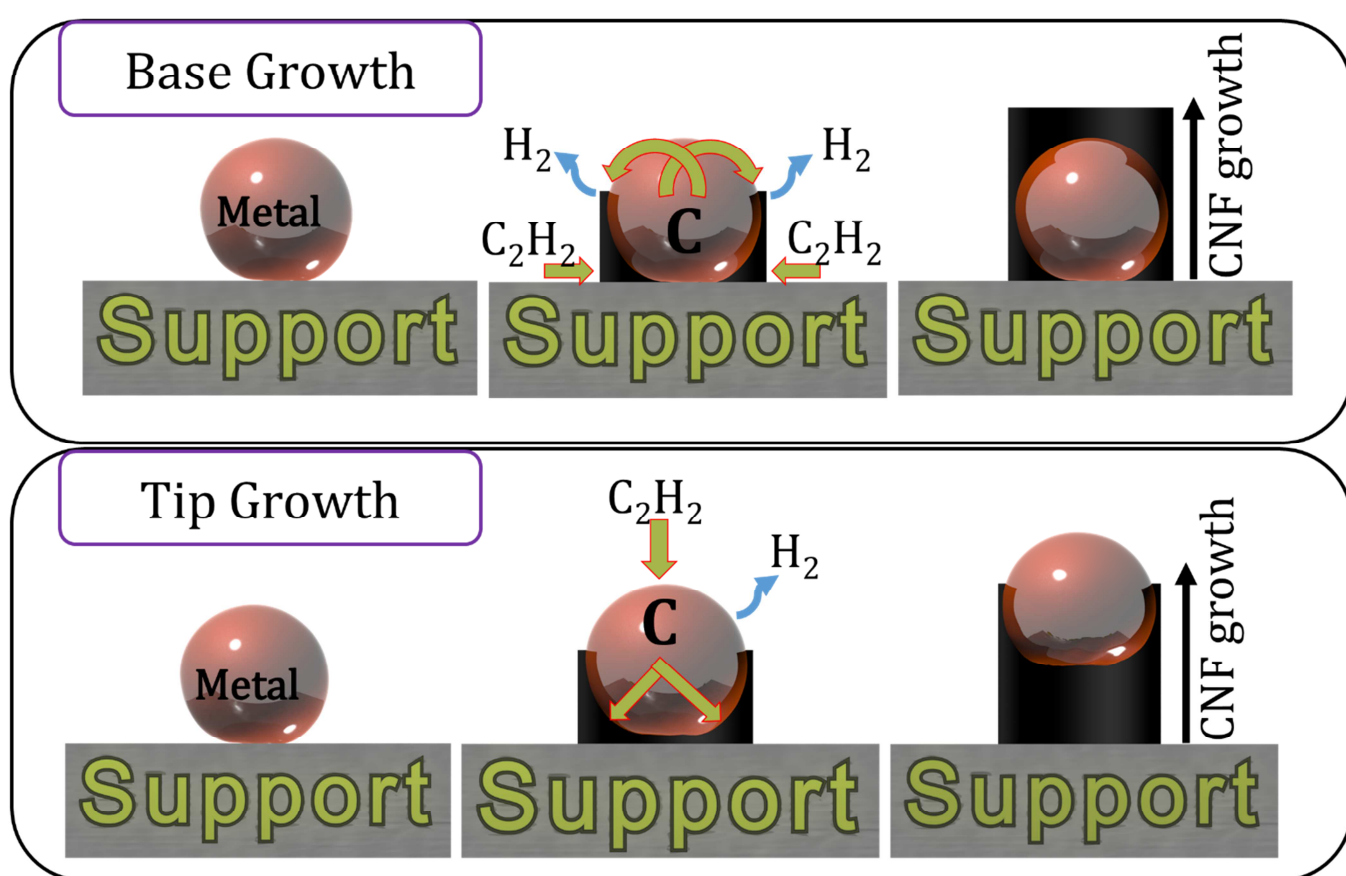


Figure 2.2.6: Shows the accepted base (root) and tip growth mechanism of carbon

It should be noted that some scientists propose that at low temperatures (<500 °C) the carbon species don't diffuse into the catalyst (as accepted for high temperature synthesis) [67], but remain on its surface [51].

These growth models explain the formation of straight CNFs, but do not explain other vast types of CNFs that have been synthesised. Likewise they also do not account for any additional (non-metallic) entities and bimetallic catalysts that are responsible for many exotic forms of CNFs [65]. These types include: bidirectional growth of CNFs that form from diamond shaped bimetallic catalysts (**Fig 2.2.7 (a)**) [68], or rotary type catalysts that result in the formation of spirals (**Fig 2.2.7 (b)**) [69] and helices (**Fig 2.2.7 (c)**).

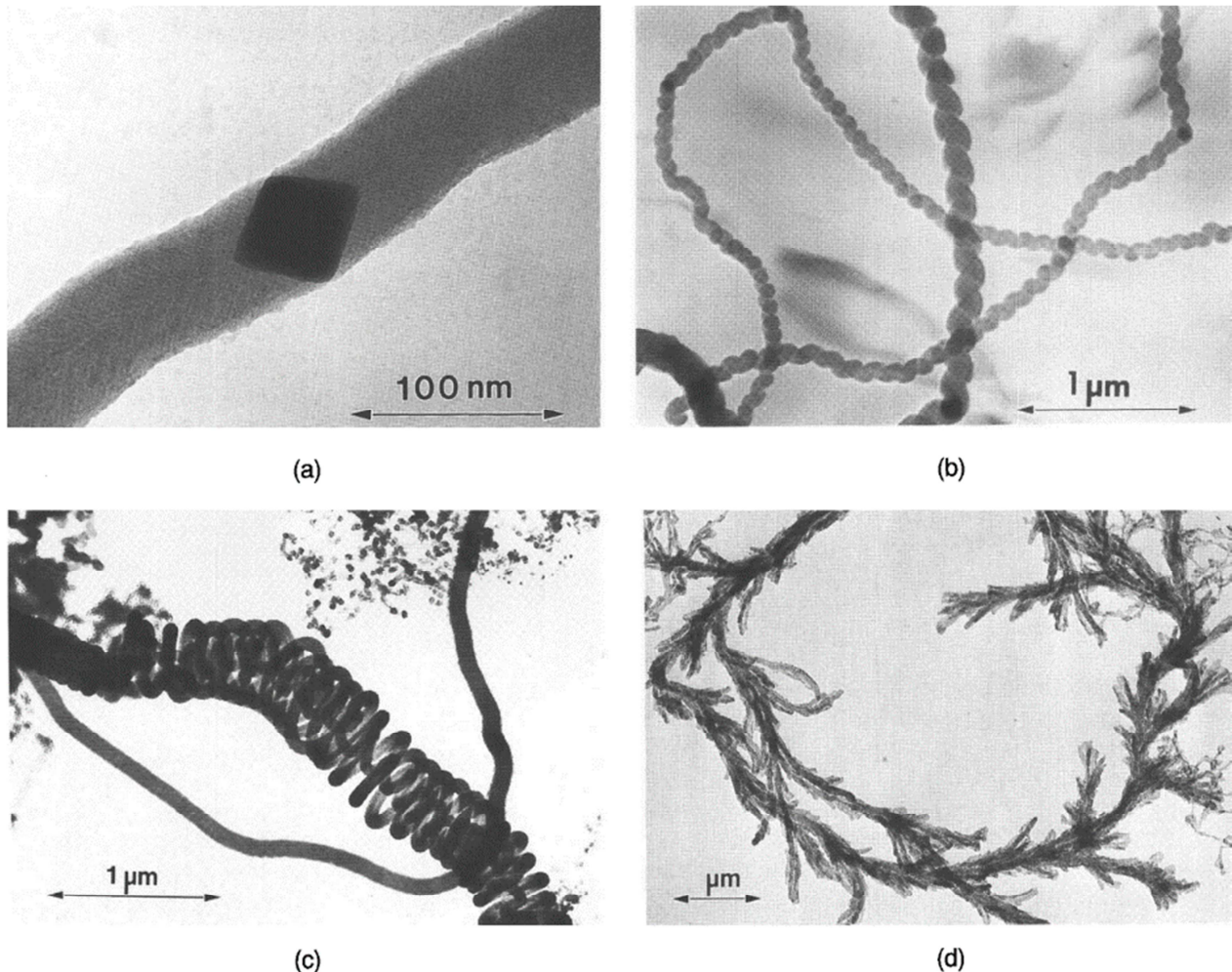


Figure 2.2.7: Other CNFs growth mechanisms: (a) a bi-directional/multi-directional growth mechanism for a fibre (b) a rotary catalyst growth mechanism that forms spirals (c) and helices; (d) a branched growth mechanism from a catalyst particle that “exploded” [65], [69].

There is another type of CNF that forms multiple branches resulting from particles that propagate the growth of CNFs in a particular direction and then explode to form other smaller fibres that resemble branches (**Fig 2.2.7 (d)**) [65].

An important factor that determines the degree of the crystallinity of carbonaceous materials made using CVD, is the spreading capability of the catalyst on the support during their interaction. The spreading capability of a catalyst can be quantified by its contact angle (θ) on the surface of the support (**Fig 2.2.8**). Typical supports for the synthesis of CNFs are aluminosilicates and silica particles [36].

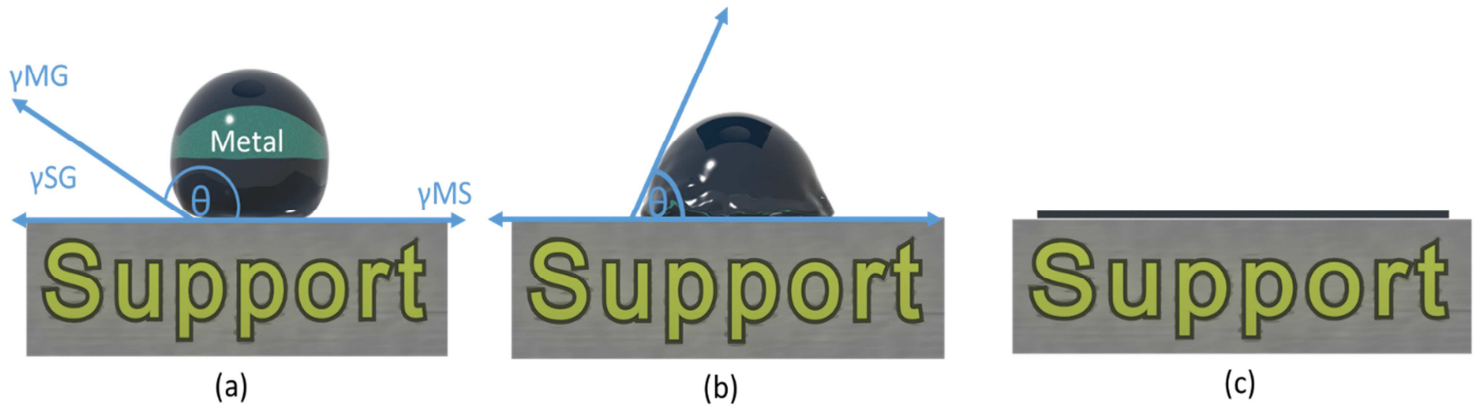


Figure 2.2.8: A schematic diagram showing the relationship of the contact angle (θ) with the surface energy of the support (γ_{SG}), the surface energy of the metal (γ_{MG}), and the metal-graphite interfacial energy (γ_{MS}) for (a) $\gamma_{MG} > \gamma_{SG}$ (non-wetting), (b) $\gamma_{MG} < \gamma_{SG}$ (wetting) and (c) $\gamma_{SG} + \gamma_{MG} > \gamma_{MS}$ (spreading) (modified from [65])

The contact angle (θ) is determined by the surface energy of the support (γ_{SG}), the surface energy of the metal (γ_{MG}) and the metal-graphite interfacial energy (γ_{MS}) and is expressed as follows:

$$\gamma_{SG} = \gamma_{MS} + \gamma_{MG} \cos\theta$$

If $\gamma_{MG} > \gamma_{SG}$, the contact angle (θ) is above 90° (**Fig 2.2.8 (a)**) then wetting doesn't occur. However, when $\gamma_{MG} < \gamma_{SG}$, then wetting will occur and the contact angle (θ) will be less than 90° (**Fig 2.2.8 (b)**). Finally when $\gamma_{SG} + \gamma_{MG} > \gamma_{MS}$, then the metal will spread as a thin film over the support (**Fig 2.2.8 (c)**). Hence Rodriguez suggested that Fe particles form amorphous carbon nanomaterials at temperatures below 1000°C , which is iron's spreading temperature, in the presence of a hydrocarbon gas [65].

As far as it is possible to know from literature no one, certainly not in South Africa, has done a systematic study of the formation of CNFs on the surface of the fly ash particles. The reaction progress between $\text{C}_2\text{H}_2/\text{H}_2$ and fly ash was studied using electron microscopy.

Functionalisation of CNFs

Pristine fibres are known to be chemically unreactive towards any polar substances [70] [71]. Thus it is difficult to disperse them in aqueous media [72]. Two problems arise on as-synthesised CNFs: (i) they agglomerate and (ii) they are inert. These two factors limit the theoretically predicted mechanical and electrical properties of individual CNFs [73]. It is therefore necessary to modify their surface characteristics to enable the formation of hybrid materials [73]. Surface treatments of CNFs can lead to either physical or chemical functionalisation [74] [75].

Physical functionalisation

The interfacial properties of CNFs can be improved by non-covalent functionalisation. For instance CNFs can be suspended in the presence of a polymer such as polystyrene or poly(phenylene vinylene) leading to the formation of supermolecular CNFs complexes. Here the polymers wrap around the CNFs through van der Waals and π - π stacking interactions due to their aromatic rings (**Fig 2.2.9 (a)**) [76].

Surfactants which are non-ionic, anionic or cationic can be used to functionalise CNFs. Here physical adsorption of the surfactant lowers the surface tension of the CNFs, helping to overcome Van der Waal's forces by repulsive forces (steric or electrostatic) and thereby prevent agglomeration. Non-ionic surfactants work on hydrophobic attractions with CNF surfaces and self-assemble into micelles above a critical concentration (**Fig 2.2.9 (b)**) [77].

Alternatively when CNFs are hollow they can be functionalised endohedrally. This method of physical functionalisation of CNFs involves the storage of guest molecules into their inner cavities. The insertion of these moieties often takes place at defect sites, which are concentrated at the ends or sides of the CNFs (**Fig 2.2.9 (c)**) [78].

In general physical functionalisation methods cost less, are non-invasive, the fibres remain intact while their chemical, electronic and physical properties do not change [73], [76]. CNFs functionalised this way can be practical for further use, however, they fail when load transfer applications are desired [76].

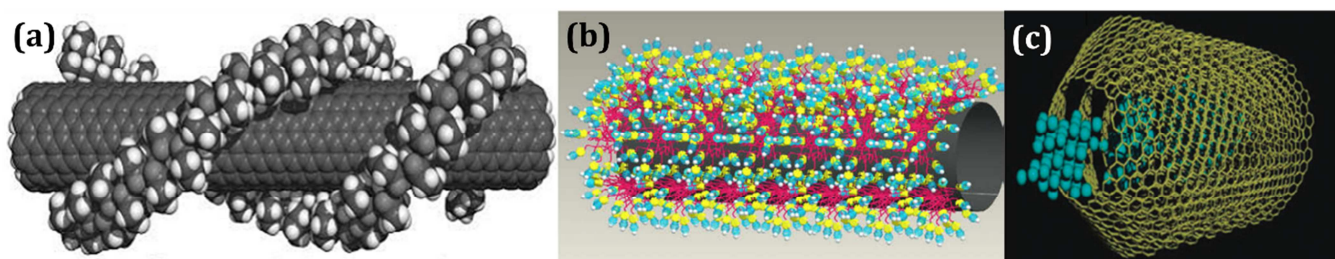


Figure 2.2.9: The different types of physical functionalisation; (a) Polymer functionalisation ^[76], (b) Surfactant functionalisation ^[77] and (c) Endohedral functionalisation ^[78].

Chemical functionalisation

Chemical functionalisation on the other hand leads to the formation of covalent bonds between the covalent linkage entities and the framework of the CNFs. There are many ways of chemically functionalising CNFs on the wall or even on their edges. The CNFs can be fluorinated using HF and then the weak C-F bond can be substituted with amino, alkyl or hydroxyl groups through subsequent treatments ^[79]. Besides halogenation, chemical treatments such as Diels-Alder ^[80], hydrogenation ^[81] and azomethine ylide reactions have been successfully used for the functionalisation of CNFs ^[75].

CNFs have been functionalised under different conditions using various reagents. For example, the conventional way of treating CNFs, particularly CNTs/CNFs, is by acid treatment with acids like: nitric ^[82] and/or sulphuric acid ^[83] to introduce carboxylic and hydroxyl groups on the surface or even using linking agents like benzyl alcohol ^[84].

The functionalisation of CNFs works because of many reasons: (i) the presence of defects, (ii) sp^3 hybridised centres with OH and H functional groups attached to the surface, (iii) oxidation induced carboxylic groups ^[85]. Oxidation using $HNO_3:H_2SO_4$ acid mixtures results in the highest amount of defect sites and functional groups like: quinones, lactones, phenol, carbonyl, nitro, hydroxyl and sulphonic groups ^[45], ^[86], ^[87]. These defects provide anchors for other functional groups to bind to and this is the same way CNFs react when they have defects ^[85] (**Fig 2.2.10**).

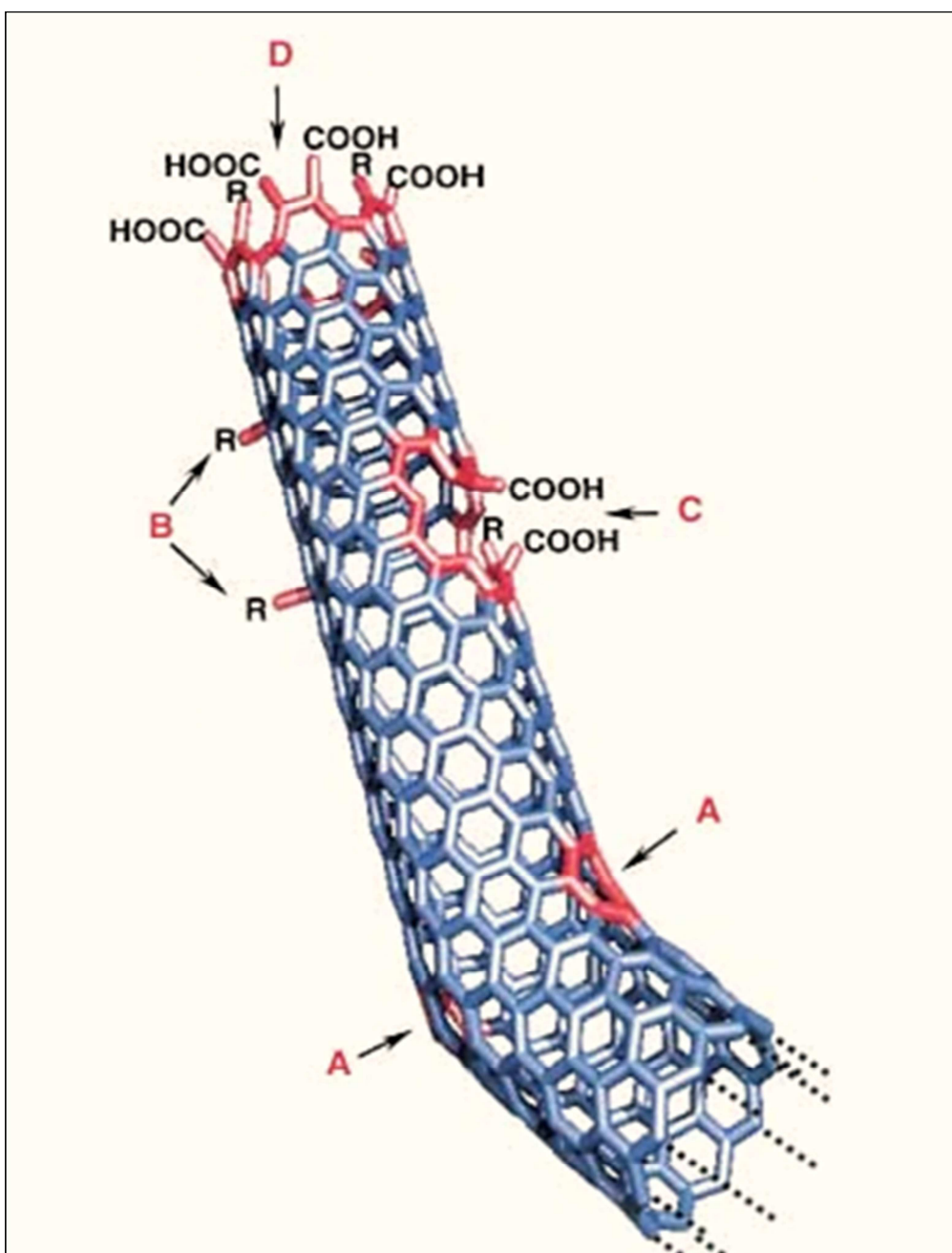


Figure 2.2.10: Typical defects in a single walled nanotube (SWNT): (A) 5 or 7 membered rings in the frame work (bending) (B) sp^3 hybridised defects (R= OH or H) (C) Carbon framework destroyed by oxidative conditions (like acid functionalisation) leaving carboxylic groups on the carbon framework along with other functional groups [85].

No one has thus far reported on the systematic treatment of CNFs made from South African fly ash, with a concentrated $HNO_3:H_2SO_4$ mixture. This study aimed to assess the effect of acid functionalisation on such CNFs with a $HNO_3:H_2SO_4$ mixture as a function of time. The surface of the functionalised CNFs (fCNFs) were then bound with titania

(anatase) nanoparticles in order to produce a possible CNF-TiO₂ hybrid as a catalyst for photosensitive reactions.

Although, Yasui *et al.* have suggested the possible use of their materials for optical applications [5], to date none of the researchers who have used coal fly ash for CNF synthesis has benefitted their carbonaceous materials for this type of application. The benefits of the approach taken in this study is that these CNFs were not synthesised from a commercially produced catalyst, but from fly ash (an abundant waste material), which if fully successful will minimise the potential costs of commercialising the whole process.

2.3 CNF-TiO₂ hybrid

Titanium is a lustrous and strong, low density metal that derives its name from Greek mythology. It was discovered by a British clergy man, William Gregor in 1791, and named by Martin Heinrich Klaproth after the titans. These titans were powerful 'deities' that were born of the 'gods' Gaia (earth) and Uranus (heaven) [88]. This primeval race was said to have incredible strength and because titanium is strong and resistant to commonly corrosive processes it was obvious to Klaproth to name it after these mythical characters. Its metal oxide form is called titania (TiO₂).

TiO₂ has been researched intensively after the demonstration of photocatalytic water splitting on a titanium dioxide electrode by Fujishima and Honda [83], [89], [90]. Photocatalysis is a catalytic reaction involving light absorption by a catalyst or substrate. Electrons from the valence band are excited into the empty conduction band, leaving a hole in the valence band. Electrons in the conduction band are good reductants and the holes in the valence band are powerful oxidants. The electron-hole pairs have an oxidising potential of 2.9 V vs the normal hydrogen electrode (NHE), which is enough to oxidise most pollutants [91]. Water can interact with the holes generated in the valence band to form H⁺ ions and OH• while O₂ gas interacts with the electron in the conduction band to form an oxygen radical. This owes to the fact that anatase has a broad bandgap of 3.2 eV [83] and thus it can absorb photons with a wavelength equal to or lower than 388 nm (UV light) (**Fig 2.3.1**). These ions and radicals can convert most organic pollutants into H₂O and CO₂.

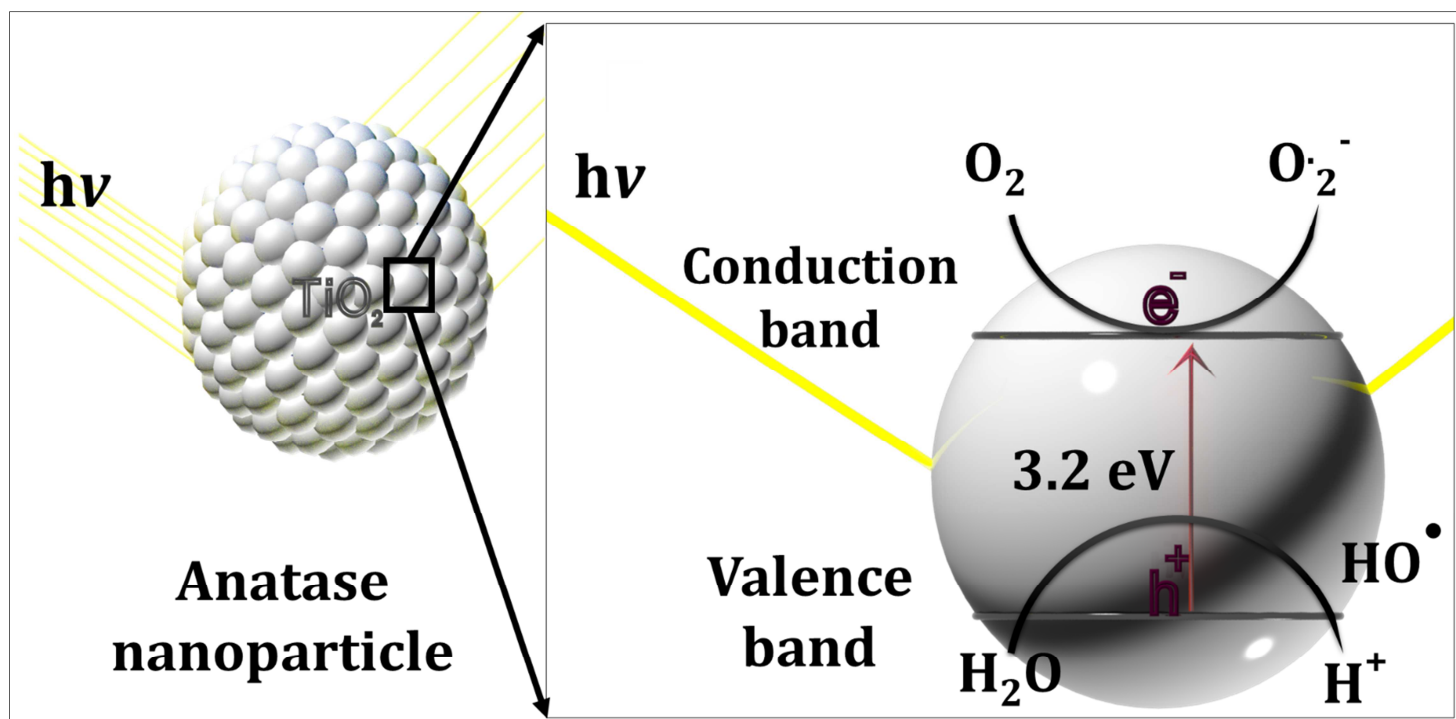


Figure 2.3.1: An image of a TiO_2 nanoparticle absorbing light (a) and (b) a titania nanoparticle suggesting how electron/hole pairs are generated [83].

TiO_2 has three natural polymorphs: anatase is tetragonal (**Fig 2.3.2(a)**) brookite is orthorhombic (**Fig 2.3.2(b)**) and rutile is tetragonal as well (**Fig 2.3.2(c)**) and they all have different space group symmetries [92]. For photocatalytic reactions only rutile and anatase are considered here because brookite is not chemically stable enough to be efficiently photocatalytic [91]. It is said that the mobility of electrons in anatase is 89 times higher than in rutile which also has little electron diffusivity [93]. This suggests that anatase is better for photocatalytic applications [94].

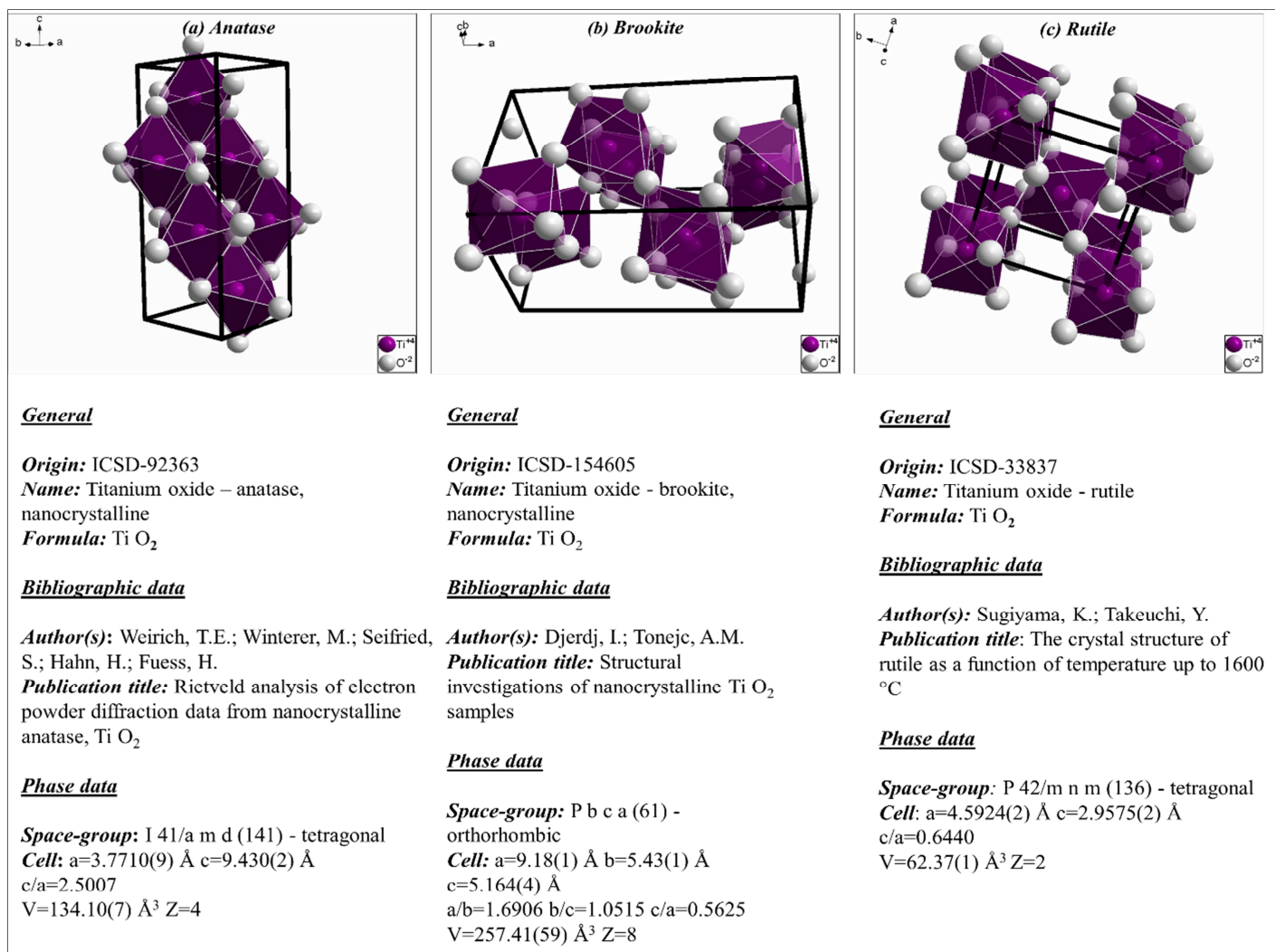


Figure 2.3.2: TiO₆ polyhedra and a summary of the crystallographic data [as obtained from the ICSD and generated using Diamond version 3-2k] below for (a) anatase nanocrystals (b) brookite nanocrystals and (c) rutile.

Nano-sized titania particles have a high surface area which is good for catalytic reactions, but this has its own disadvantages. Recovering nanoparticles from reactors is cumbersome and there is a possibility of particle aggregation. Another major hurdle for the use of titania as a photocatalyst, is that it has a high recombination rate of photogenerated electron-hole pairs [95]. All of the above-mentioned disadvantages make the photocatalytic activity of pristine TiO₂ nanoparticles too low for any feasible industrial application. Yet, several ways have been attempted to increase their activity namely: (i) reducing the particle size, (ii) generating defect structures to induce space-charge separation and (iii) doping or co-crystallising TiO₂ with other metal or metal oxides nanoparticles [95]. Another method of increasing the activity of TiO₂ nanoparticles is to anchor them on an appropriate support.

2.3.1 Methods of synthesising the CNF-TiO₂ hybrid

There are many methods that have been developed for attaching metal oxide nanoparticles to carbon nanomaterials (CNMs) both in situ and ex situ. Ex situ methods require that nanoparticles be attached to CNMs via linking agents that use pi-pi stacking, covalent or electrostatic interactions [43]. While in situ methods involve the formation of nanoparticles directly on the surface of pristine or modified CNMs. In situ techniques can be done in various ways: (i) in solution through sol-gel [96]-[102], (ii) solvothermal and (iii) electrochemical techniques [103]-[105] or in the gas phase through: CVD [106] or through physical thermal treatments like sputtering and laser ablation [43].

Sol-gel [96]-[102], [107], [108] and hydrothermal [83], [109], [110] techniques have been ubiquitously applied in CNF-TiO₂ composite formation. Thus, the synthetic focus was narrowed down to these two methods and, in particular, more emphasis was given to the solvothermal/ hydrothermal technique because it was used in this study.

A major part of the current research has been to coat carbon nanofibres with TiO₂ nanoparticles. Many scientists have managed to fully or partially coat carbon nanomaterials with TiO₂, particularly on single-walled and multi-walled carbon nanotubes [43], [83], [96]- [101], [107], [110]-[112]. In many instances the binding of the TiO₂ was poor and this could be easily discerned visually.

The sol-gel synthesis technique

The synthesis of metal oxide nanoparticles has been routinely and preferably been performed in the past through the sol-gel technique, because it has allowed for the control of the morphology of the final products. An advantage of the sol-gel technique is that it can be performed in aqueous and non-aqueous media. In aqueous media there are a few hurdles to overcome: (i) metal oxide precursors are very reactive towards water, (ii) water acts as a ligand and a solvent, (iii) there are many parameters that need to be strictly controlled for the process to be reproducible e.g. hydrolysis, condensation rates of the precursors, pH, temperature, method of mixing, rate of oxidation, concentrations of anions, etc. Another factor that needs consideration is that the as-synthesised precipitates are generally amorphous, so post-synthetic annealing steps are needed to induce crystallisation. However, this means that the shape and size cannot be easily controlled.

The sol-gel method includes the use of alkoxides (titanium butoxide) or metal chlorides (titanium tetrachloride) as metal sources. The solvents used are either organic solvents or water which are capable of complexing the metal atoms. The solution is converted into a sol by treatment using water/organic solvents with or without a base or acid (hydrolysis and condensation). A sol is a dispersion of solid particles (colloidal particles) with diameters of 1-100 nm. It is aged, shaped and thermally treated/sintered by condensing it by removing colloidal particles in the liquid until it becomes a gel. A gel can be described as an interconnected, rigid network with pores of sub-micrometre dimensions and polymeric chains whose average length is greater than a micrometre [113]. To form different morphologies of materials there are several processes that can be followed.

For instance to form tubes the sol can be spun, otherwise a uniform powder can be formed by precipitation. On the other hand if a sol is allowed to gel and evaporate it can form a xerogel. Alternatively if the wet gel is supercritically dried, an aerogel can be formed. Finally, if a dense thin film is desired a xerogel can be coated onto a surface and then heated (**Fig 2.3.3**) [114].

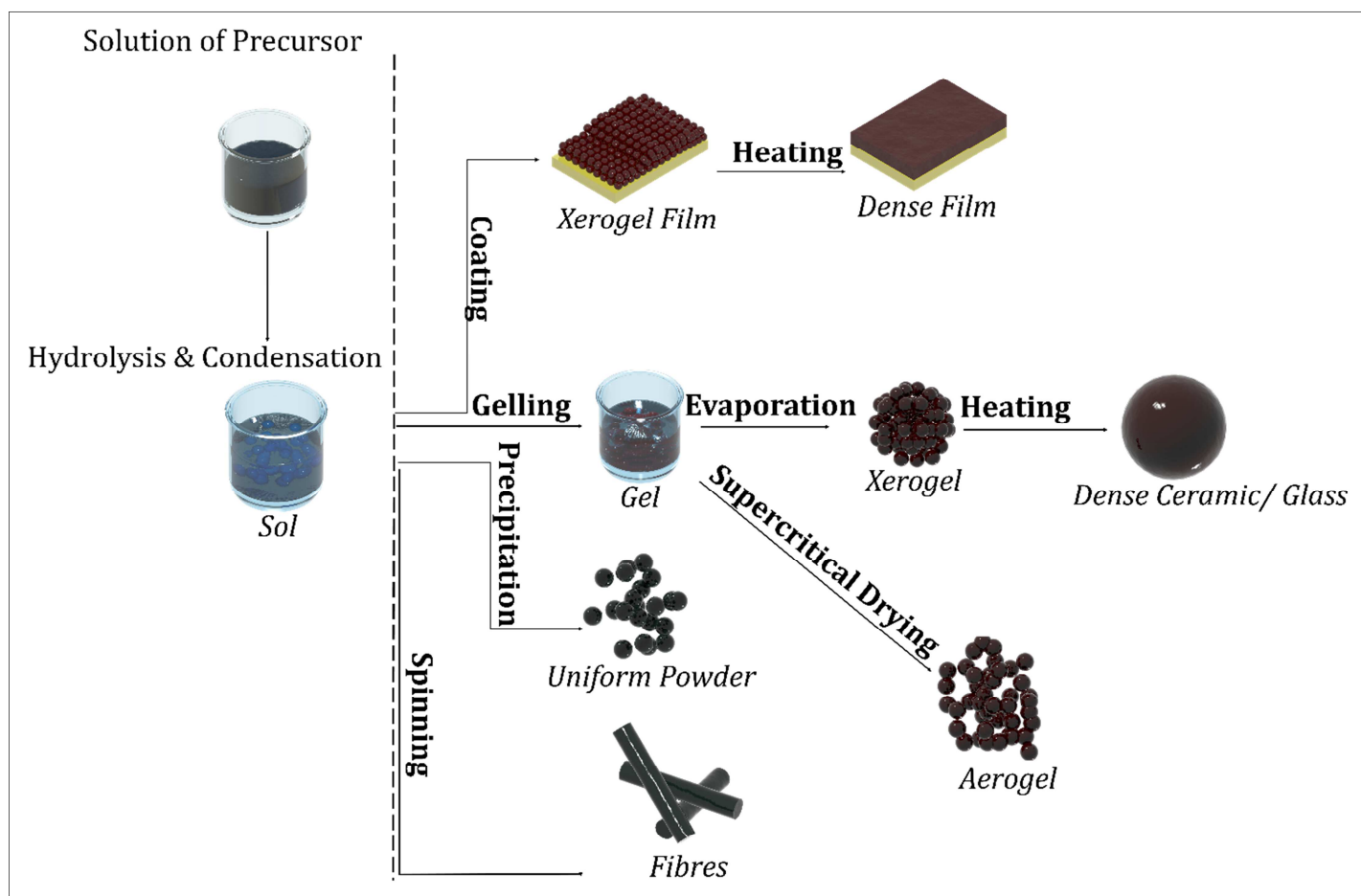


Figure 2.3.3: A scheme of the different types of manipulations that are possible when using the sol-gel technique in order to produce different morphologies (modified from [114]).

In the sol-gel technique it has been found that the properties of the nanoparticles like the: size, morphology and phase are strongly affected by the ageing time of the gel, the pH of the mixture and the choice of the metal atom source as well as the presence of a surfactant [99], [115].

The hydrothermal/solvothermal synthesis technique

The hydrothermal/solvothermal method involves the same principles that are used in the sol-gel method, where there is a metal source (chlorides or alkoxides) that is heat treated in solution. The reaction temperature is normally kept at or slightly below the boiling point of the solvent (water or organic solvents), which is sufficient to produce nanoparticles.

Hydrothermal techniques have been studied in depth and so are better explored than sol-gel methods. They provide means to synthesise nanoparticles at low temperatures

using a direct route to nano-sized metal oxide nanoparticles, while avoiding the calcination step required in the sol-gel method [116]. Srivastava *et al.* have shown that the hydrothermal technique produced smaller nanoparticles at lower temperatures in comparison with the sol-gel technique [117]. Yoshimura *et al.* reviewed methods for the synthesis of materials and noted that there were many advantages of using the hydrothermal technique as compared to others, including that they: are energy saving, simple, cost-effective, have better nucleation control, higher dispersion, higher rate of reaction, better shape control and have lower operation temperatures in the presence of an appropriate solvent [118]. In this study a simplified hydrothermal method for the synthesis of the CNF-TiO₂ hybrid was used.

The mixing of TiO₂ and carbon in some instances has resulted in the enhancement of photocatalytic activity. Although there is still a dispute as to how this happens per se. Some researchers have implied that simple powder mixing, intimate contact or even wet chemical binding is required to have such an effect [83]. On the other hand other researchers have insisted that the Ti-O-C bond is needed because it extends the light absorption of TiO₂ to longer wavelengths [83]. Furthermore it is believed that the Ti-O-C bond can serve as an electron transfer pathway to accelerate the excited electrons from CNFs to TiO₂ and vice versa to significantly improve the photocatalytic efficiency of the nanohybrid [119]. Most of the work that has been performed thus far has used FTIR minimally, if at all, to monitor the Ti-O-C vibrational characteristics [71], [95], [118]-[132]. Unfortunately even among these, little agreement has been reached.

Abbasi *et al.* (**Fig 2.3.4 (a)**) have noted that using sol-gel and other methods to modify the CNT surface results in heterogeneous, non-uniform decoration and aggregation of the TiO₂ on the surface of the CNTs. Another disadvantage noted was that the methods themselves required special equipment [133]. Similarly, Woan *et al.* (**Fig 2.3.4 (b, c)**) used a hydrothermal method and found that the surfaces of their CNTs were randomly covered with TiO₂ agglomerates [108]. It should be noted that agglomeration does not occur only because of the amount of TiO₂ precursor used. Other factors which affect this will be discussed in detail in the sections which follow [108].

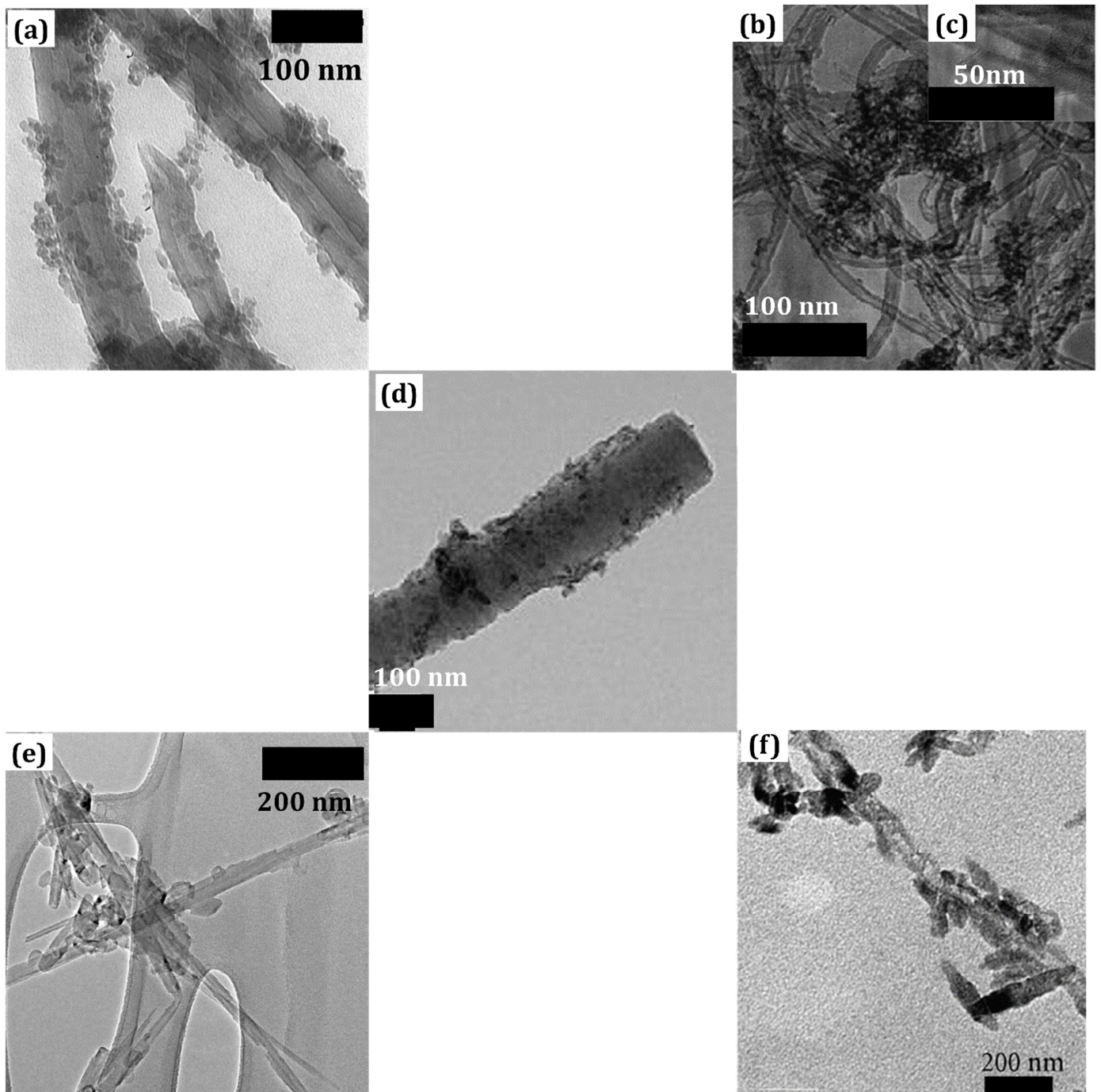


Figure 2.3.4: (a) CNFs coated with TiO_2 using a modified hydrothermal method ^[133], (b, c) TEM images of CNTs coated with TiO_2 by hydrothermal method with an insert with a 10 nm scale bar ^[108], (d) CNFs sparsely coated with TiO_2 nanoparticles using sol-gel ^[134], (e) CNT- TiO_2 hybrid made using sol-gel ^[91], (f) a random distribution of rice grain shaped TiO_2 nanoparticles coating MWNTs ^[120].

Likewise, Ouzzine *et al.* and Lee have also noted that their CNFs were unevenly coated when they tried to coat them with TiO₂ nanoparticles using the sol-gel method (**Fig 2.3.4 (d and e)**) and that the coating was not complete even after they acid treated their fibres ^{[91], [134]}. Xia *et al.* were able to synthesise rice-grain shaped TiO₂ particles next to fibres using an autoclave-type of hydrothermal reaction, however, they too were not able to control the coverage or the particle size (**Fig 2.3.4 (f)**) ^[120]. The above authors generally all acknowledged that the coating was not as consistent as desired (**Fig 2.3.4**).

In this study a simplified one-pot hydrothermal method to synthesise a CNF-TiO₂ hybrid is presented. Likewise, the effects of the duration of the functionalisation of these CNFs on the size of the TiO₂ nanoparticles as well as the reaction time on the extent of TiO₂ coverage are systematically presented. To our knowledge this is the first time that a systematic study on either of these variables in relation to CNFs synthesised from coal fly ash is presented.

References

- [1] BP Statistical Review of World Energy 2013, "BP statistical review of world energy," BP Statistical Review of World Energy, London, 2013.
- [2] World Energy Council, "World Energy Resources 2013 Survey," World Energy Council, London, 2013.
- [3] M. Ahmaruzzaman, "A review on the utilization of fly ash," *Progress in Energy and Combustion Science*, vol. 36, pp. 327-363, 2010.
- [4] R. Blissett and N. Rowson, "A review of the multi-component utilisation of coal fly ash," *Fuel*, vol. 97, pp. 1-23, 2012.
- [5] A. Yasui, Y. Kamiya, S. Sugiyama, S. Ono, H. Noda and Y. Ichikawa, "Synthesis of carbon nanotubes on fly ashes by chemical vapour deposition processing," *IEEJ Transactions on Electrical and Electronic Engineering*, vol. 4, pp. 787-789, 2009.
- [6] B. Gottlieb, S. Gilbert and L. Evans Gollin, "Coal ash the toxic threat to our health and environment; A report from physicians for social responsibility and earth justice," Massachusetts, 2010.

- [7] C. Khatri and A. Rani, "Synthesis of a nano-crystalline solid acid catalyst from fly ash and its catalytic performance," *Fuel*, vol. 87, pp. 2886-2892, 2008.
- [8] A. Sarkar, R. Rano, K. Mishra and I. Sinha, "Particle size distribution profile of some Indian fly ash- a comparative study to assess their possible uses," *Fuel Processing Technology*, vol. 86, no. 11, pp. 1221 - 1238, 2005.
- [9] A. Bhattacharjee, H. Mandal, M. Roy, J. Kusz and W. Hofmiester, "Physical characteristics of fly ashes from three thermal power plants in West Bengal, India: A comparative study," *International Journal of ChemTech Research*, vol. 5, no. 2, pp. 836- 843, April- June 2013.
- [10] L. G. Fisher, A. B. Prentice, D. Silberman, J. M. Ondov, A. H. Biermann, R. C. Ragaini and A. R. McFarland, "Physical and morphological studies of size-classified coal fly ash," *Environmental Science & Technology*, vol. 12, no. 4, pp. 447- 451, April 1978.
- [11] A. Tanaka, S.-H. Yoon and I. Mochida, "Preparation of highly crystalline nanofibers on Fe and Fe-Ni catalysts with a variety of graphene plane alignments," *Carbon*, vol. 42, no. 3, pp. 591-597, 2004.
- [12] R. S. Iyer and J. Scott, "Power station fly ash- a review of the value-added utilization outside of the construction industry," *Resources, Conservation and Recycling*, vol. 31, no. 3, pp. 217-228, 2001.
- [13] V. Hequer, P. Ricou, I. Lecuyer and P. Le Cloirec, "Removal of Cu^{2+} and Zn^{2+} in aqueous solutions by sorption onto mixed fly ash," *Fuel*, vol. 80, pp. 851- 856, 2001.
- [14] J. C. Hower, "Petrographic examination of coal-combustion fly ash," *International Journal of Coal Geology*, vol. 92, pp. 90-97, 2012.
- [15] H. Cho, D. Oh and K. Kim, "A study on removal characteristics of heavy metals from aqueous solution by fly ash," *Journal of Hazardous Materials B*, vol. 127, pp. 187-195, 2005.
- [16] S. Wang and H. Wu, "Environmental-benign utilisation of fly ash as low-cost sorbents," *Journal of Hazardous Materials B*, vol. 136, pp. 482-501, 2006.

- [17] S. Jala and D. Goyal, "Fly ash as a soil ameliorant for improving crop production- a review," *Bioresource Technology*, vol. 97, pp. 1136- 1147, 2006.
- [18] I. Queralt, X. Querol, A. Lopez Soler and F. Plana, "Use of coal fly ash for ceramics: a case study for a large Spanish power station," *Fuel*, vol. 76, no. 8, pp. 787-791, 1997.
- [19] R. Mohapatra and J. Rao, "Review some aspects of characterisation, utilisation and environmental effects of fly ash," *Journal of Chemical Technology and Biotechnology*, vol. 76, pp. 9-26, 2001.
- [20] L. O. Silva, K. DaBoit, C. H. Sampiao, A. Jasper, M. L. Andrade, I. J. Kostova, F. B. Waanders, K. R. Henke and J. C. Hower, "The occurrence of hazardous volatile elements and nanoparticles in Bulgarian coal fly ashes and the effect on human health exposure," *Science of the Total Environment*, vol. 416, pp. 513-526, 2012.
- [21] X. Querol, N. Moreno, J. Umana, A. Alastuey, E. Hernandez, Lopez-Soler and F. Plana, "Synthesis of zeolites from coal fly ash: an overview," *International Journal of Coal Geology*, vol. 50, pp. 413-423, 30 January 2002.
- [22] "Coal Ash Facts," American coal association educational foundation, 17 March 2009. [Online]. Available: <http://www.coalashfacts.org>. [Accessed 9 June 2014].
- [23] W. Chunfeng, L. Jiansheng, S. Xia, W. Lianjun and S. Xiuyun, "Evaluation of zeolites synthesised from fly ash as potential adsorbents for wastewater containing heavy metals," *Journal of Environmental Sciences*, vol. 21, pp. 127- 136, 2009.
- [24] V. Pandey and N. Singh, "Impact of fly ash incorporation in soil systems," *Agriculture, Ecosystems and Environment*, vol. 136, pp. 16-27, 2010.
- [25] C. XiaoYan, K. Wendell, J. Zhu, L. JiangLi, Y. Xianxian and Z. Zhijian, "Synthesis of nano-zeolite from coal fly ash and its potential for nutrient sequestration from anaerobically digested swine wastewater," *Bioresource Technology*, vol. 110, pp. 79-85, 2012.
- [26] J. Chen, H. Kong, D. Wu, X. Chen, D. Zhang and Z. Sun, "Phosphate immobilisation from aqueous solution by fly ashes in relation to their composition," *Journal of Hazardous Materials B*, vol. 139, pp. 293-300, 2007.

- [27] K. K. Panday, G. Prasad and V. N. Singh, "Copper (II) removal from aqueous solutions by fly ash," *Water Resources*, vol. 19, no. 7, pp. 869-873, 1985.
- [28] R. H. Matjie, J. R. Bunt and J. H. P. van Heerden, "Extraction of alumina from coal fly ash generated from a selected low rank bituminous South African coal," *Minerals Engineering*, vol. 18, pp. 299-310, 2005.
- [29] D. Hansen and G. L. Fisher, "Elemental distribution in coal fly ash particles," *Environmental Science & Technology*, vol. 14, no. 9, p. 1111-1117, 1980.
- [30] M. Izquierdo and X. Querol, "Leaching behaviour of elements from coal combustion fly ash: an overview," *International Journal of Coal Geology*, vol. 94, pp. 54-66, 2012.
- [31] H. Chen, V. H. Grassian, L. Saraf and A. Laskin, "Chemical imaging analysis of environmental particles using the focused ion beam/ scanning electron microscopy technique: microanalysis insights into atmospheric chemistry of fly ash," *Analyst*, vol. 138, no. 2, pp. 451-460, 2013.
- [32] S. Dai, L. Zhao, J. Hower, M. Johnston, W. Song, P. Wang and S. Zhang, "Petrology, mineralogy, and chemistry of size-fractioned fly ash from the Jungar power plant, inner Mongolia, China, with emphasis on the distribution of rare earth elements," *Energy and Fuels*, vol. 28, pp. 1502-1514, 2014.
- [33] Morgan, P, *Carbon fibers and their composites*, 1st ed., T. & Francis, Ed., Boca Raton, Florida: CRC Press, 2005, pp. 1-1200.
- [34] K. DeJong, D. Ferrington and J. Geus, "Carbon nanofibres; catalytic synthesis and applications," *Catalysis Reviews*, vol. 42, no. 4, pp. 481-510, 2000.
- [35] D. C. Nath and V. Sahajwalla, "Application of fly ash as a catalyst for the synthesis of carbon nanotube ribbons," *Journal of Hazardous Materials*, vol. 192, pp. 691-697, 2011.
- [36] O. M. Dunens, K. Mackenzie and A. T. Harris, "Synthesis of multi-walled carbon nanotubes on fly ash derived catalysis," *Environmental Science & Technology*, vol. 43, pp. 7889-7894, 2009.

- [37] S. Wang, "Application of solid ash based catalyst in heterogeneous catalysis," *Environmental Science & Technology*, vol. 42, pp. 7055-7063, 2008.
- [38] N. Salah, S. S. Habib, Z. H. Khan, A. Memic and M. N. Nahas, "Growth of carbon nanotubes on catalysts obtained from carbon rich fly ash," *Digest Journal of Nanomaterials and Biostructures*, vol. 7, no. 3, pp. 1279-1288, September 2012.
- [39] N. Salah, A. A. Alghamdi, A. Memic, S. S. Habib and Z. H. Khan, "Formation of carbon nanotubes from carbon rich fly ash: growth parameters and mechanism," *Materials and Manufacturing Processes*, pp. 1-19, 2015.
- [40] A. Shaikjee and N. Coville, "The synthesis, properties and uses of carbon materials with helical morphology," *Journal of Advanced Research*, vol. 3, no. 3, pp. 195-223, 2012.
- [41] M. Inagaki, K. Kaneko and T. Nishizawa, "Nanocarbons- recent research in Japan," *Carbon*, vol. 42, pp. 1401-1407, 2004.
- [42] N. Keller, G. Rebmann, E. Barraud, O. Zahraa and V. Keller, "Macroscopic carbon nanofibres for use as photocatalyst support," *Catalysis Today*, vol. 101, pp. 323-329, 2005.
- [43] Y. Hu and C. Guo, "Carbon nanotubes and carbon nanotubes/metal oxide heterostructures: synthesis, characterization and electrochemical properties," in *Nanotechnology and nanomaterials; carbon nanotubes- growth and applications*, M. Naraghi, Ed., Croatia, InTech Open Access Publisher, 2011, pp. 3-35.
- [44] P. Zarabadi Poor and A. Badiei, "Synthesis of carbon nanotubes using metal-modified nanoporous silicas," in *Carbon Nanotubes- Growth and Applications*, M. Naraghi, Ed., Croatia, Intech, 2011, pp. 59-74.
- [45] I. Capek, "Dispersions based on carbon nanotubes- biomolecules conjugate," in *Carbon nanotubes- Growth and Applications*, M. Naraghi, Ed., Rijeka, InTech, 2011, pp. 74-96.

- [46] S. E. Iyuke and G. S. S. Simate, "Synthesis of carbon nanomaterials in a swirled floating catalytic chemical vapour deposition reactor for continuous and large scale production," in *Carbon Nanotubes- Growth and Applications*, M. Naraghi, Ed., Rijeka, InTech, 2011, pp. 35-58.
- [47] M. Terrones, "Science and technology of the twenty-first century: synthesis, properties, and applications of carbon nanotubes," *Annual Review of Materials Research*, vol. 33, pp. 419-501, June 2003.
- [48] K. Jong De and J. W. Geus, "Carbon nanofibers: catalytic synthesis and applications," *Catalysis Reviews: Science and Engineering*, vol. 42, pp. 481-510, 2000.
- [49] M. Kunowsky, J. P. Marco Lozar, A. Oya and A. Linares Solano, "Hydrogen storage in CO₂-activated amorphous nanofibers and their monoliths," *Carbon*, vol. 50, pp. 1407-1416, 2012.
- [50] B. Averill and P. Eldredge, *General chemistry: principles, patterns and applications*, 1st ed., San Fransisco: Prentice Hall, 2007, pp. 1-1250.
- [51] S. Mori and M. Suzuki, "Non-catalytic, low-temperature synthesis of carbon nanofibers by plasms-enhanced chemical vapour deposition," in *Nanofibers*, A. Kumar, Ed., Intech, 2010, pp. 295-308.
- [52] K. B. K. Teo, C. Singh, M. Chhowalla and W. I. Milne, "Catalytic synthesis of carbon nanotubes and nanofibers," in *Encyclopaedia of Nanoscience and Nanotechnology*, vol. 10, H. S. Nalwa, Ed., American Scientific Publishers, 2003, pp. 1-22.
- [53] A. Hosseini, M. Allahyari and D. S. Besheli, "Synthesis of carbon nanotubes, nanofibres and nano onions by electrical arc discharge method using NaCl accuse as solution and Fe and Ni particles and catalysts," *International Journal of Science, Environment and Technology*, vol. 1, no. 3, pp. 217-229, 2012.
- [54] H. Terrones and M. Terrones, "Curved nanostructured materials," *New Journal of Physics*, vol. 5, no. 126, pp. 1-34, 2003.

- [55] A. Szabo, C. Perri, A. Csato, G. Giordano, D. Vuono and B. J. Nagy, "Synthesis methods for carbon nanotubes and related materials," *Materials*, vol. 3, pp. 3092-3140, 2010.
- [56] J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adam and R. Kizek, "Methods for carbon nanotubes synthesis- review," *Journal of Materials Chemistry*, vol. 21, pp. 15872-15884, 2011.
- [57] E. T. Thostenson, Z. Ren and T.-W. Chou, "Advances in the science and technology of carbon nanotubes and their composites; a review," *Composites Sciences and Technology*, vol. 61, pp. 1899-1912, 2001.
- [58] T. Guo, P. Nikolaev, A. G. Rinzler, D. Tomanek, D. T. Colbert and R. Smalley, "Self-assembly of tubular fullerenes," *Physical Chemistry*, vol. 99, pp. 10694-10697, 1995.
- [59] A. M. M. Rafique and J. Iqbal, "Production of carbon nanotubes by different routes- a review," *Journal of Encapsulation and Adsorption Sciences*, vol. 1, pp. 29-34, 2011.
- [60] A. Chatterjee and B. L. Deopura, "Carbon nanotubes and nanofibre: an overview," *Fibers and Polymers*, vol. 3, no. 4, pp. 134-139, 2002.
- [61] S. D. Su, S. Peranthoner and G. Centi, "Nanocarbons for the development of advanced catalysts," *Chemical Reviews*, vol. 113, pp. 5782-5817, 2013.
- [62] H. y. Pacheco, J. Pacheco and R. Valdivia, "The synthesis of carbon nanofibers by glow arc-discharge," in *Nanotechnology and Nanomaterials*, K. Ashok, Ed., InTechOpen, 2010.
- [63] C. W. Huang, H. C. Wu, W. H. Lin and Y. Y. Li, "Temperature effect on the formation of catalysts for growth of carbon nanofibers," *Carbon*, vol. 47, pp. 795-803, 2009.
- [64] R. T. K. Baker, "Catalytic growth of carbon filaments," *Carbon*, vol. 3, no. 27, pp. 315- 323, 1989.
- [65] N. M. Rodriguez, "A review of the catalytically grown carbon nanofibers," *The Journal of Materials Research*, vol. 8, no. 12, pp. 3233-3250, 1993.

- [66] K. J. MacKenzie, O. M. Dunens and A. T. Harris, "An updated review of synthesis parameters and growth mechanisms for carbon nanotubes in fluidized beds," *Industrial and Engineering Chemistry Research*, vol. 49, no. 11, pp. 5323-5338, 2010.
- [67] A. Melochko, V. Merkulov, T. McKnight, M. Guillorn, K. Klein, D. Lowndes and M. Simpson, "Vertically aligned carbon nanofibers and related structures; controlled synthesis and directed assembly," *Journal of Applied Physics*, vol. 97, pp. 1-39, 2005.
- [68] M. S. Kim, N. Rodriguez and R. Baker, "The interaction of hydrocarbons with copper-nickel and nickel in the formation of carbon filaments," *Journal of Catalysis*, vol. 131, pp. 60-73, 1991.
- [69] M. Kim, N. Rodriguez and R. Baker, "The role of interfacial phenomena in the structure of carbon deposits," *Journal of Catalysis*, vol. 134, pp. 253-268, 1992.
- [70] E. Rokhina, M. Lahtinen, K. Makarov, V. Jegatheesan and Virkutyte, "Theoretical and practical aspects of chemical functionalization of carbon nanofibers (CNFs); DFT calculations and adsorption studies," *Bioresource Technology*, vol. 113, pp. 127-131, 2012.
- [71] J. Sun, M. Iwasa, L. Gao and Q. Zhang, "Single-walled carbon nanotubes coated with titania nanoparticles," *Carbon*, vol. 42, pp. 885-901, 2004.
- [72] R. Yudianti, H. Onggo, Sudirman, Y. Saito, T. Iwata and J. Azuma, "Analysis of functional group sited on multi-wall carbon nanotube surface," *The Open Material Science Journal*, vol. 5, pp. 242-247, 2011.
- [73] P. Ma, N. A. Siddiqui, G. Marom and J. Kim, "Dispersion and functionalisation of carbon nanotubes for polymer-based nanocomposites: a review," *Composites: Part A*, vol. 41, pp. 1345-1367, 2010.
- [74] A. Micoli, "Functionalization of carbon nanotubes for construction of supramolecular nanostructured materials," Trieste, 2012.

- [75] F. B. Bonalume. C, W. G. Lebrao and L. J. Rossi, "Functionalized carbon nanotubes for nanocomposites," in ICCS16 (16th *International Conference on Composite Structures*), Porto, 2011.
- [76] V. Mittal, "Carbon nanotubes surface modifications: an overview," in *Surface Modification of Nanotube Fillers*, V. Mittal, Ed., Weinheim, Wiley-VHC Verlag GmbH& Co. KGaA, 2011, pp. 1-24.
- [77] Y. Geng, M. L. Yang, J. Li, X. Mei and K. J. Kim, "Effects of surfactant treatment on the mechanical and electrical properties of CNT/Epoxy nanocomposites," *Composites: Part A*, vol. 39, pp. 1876-1883, 2008.
- [78] J. R. White, R. Luque, V. L. Budarin, H. J. Clark and J. D. Macquarrie, "Supported metal nanoparticles on porous materials. Methods and applications," *Chemical Society Reviews*, vol. 38, pp. 481-494, 2009.
- [79] J. Stevens, A. Y. Huang, H. Peng, I. W. Chiang, V. N. Khabashesku and J. L. Margrave, "Sidewall amino-functionalization of single-wall carbon nanotubes through fluorination and subsequent reactions with terminal diamines," *Nanoletters*, vol. 3, no. 3, pp. 331-336, 2003.
- [80] M. Holzinger, J. Steinmetz, D. Samaille, M. Glerup, M. Paillet, P. Bernier, L. Ley and R. Graupner, "[1+2] Cycloaddition for cross-linking SWCNTs," *Carbon*, vol. 42, pp. 941-947, 2004.
- [81] S. K. Kim, D. J. Bae, R. J. Kim, K. A. Park, S. Chu, C. Lim, J.-J. Kim, W. B. Choi, C. Y. Park and Y. H. Lee, "Modification of electronic structures of a carbon nanotube by hydrogen functionalization," *Advanced Materials*, vol. 14, no. 24, pp. 1818-1821, 2002.
- [82] S. Aryal, K. C. Kim, K. k. Kim, S. M. Khil and H. Y. Kim, "Multiwalled carbon nanotubes/TiO₂ composite nanofibre by electrospinning," *Materials Science and Engineering C*, vol. 28, pp. 75-79, 2008.
- [83] H. Chen, S. Yang, K. Yu, Y. Ju and C. Sun, "Effective photocatalytic degradation of atrazine over titania-coated carbon nanotubes (CNTs) coupled with microwave energy," *The Journal of Physical Chemistry A*, vol. 115, pp. 3034-3041, 2011.

- [84] N. Bouazza, O. M, M. Lillo Rodenas, D. Eder and A. Linares Solano, "TiO₂ nanotubes and CNT-TiO₂ hybrid materials for the photocatalytic oxidation of propene at low concentration," *Applied Catalysis; Environmental*, vol. 92, pp. 377-383, 2009.
- [85] A. Hirsch, "Functionalization of single-walled carbon nanotubes," *Angewandte Chemie, International Edition*, vol. 41, no. 11, pp. 1853-1859, 2002.
- [86] S. Santangelo, G. Messina, G. Faggio, S. Abdul Rahim and C. Milone, "Effect of sulphuric-nitric acid mixture composition on the surface chemistry and structural evolution of liquid-phase oxidised carbon nanotubes," *Journal of Raman Spectroscopy*, vol. 43, pp. 1432-1442, 2012.
- [87] A. Rasheed, J. Howe, M. Dadmun and P. Britt, "The efficiency of the oxidation of carbon nanofibres with various oxidising agents," *Carbon*, vol. 45, pp. 1072-1080, 2007.
- [88] J. Emsley, *Nature's building blocks: An A-Z guide to the elements*, 1st ed., Oxford: Oxford University Press, 2002.
- [89] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, pp. 8-37, 1972.
- [90] R. Leary and A. Westwood, "Carbonaceous nanomaterials for the enhancement of TiO₂ photocatalysis," *Carbon*, vol. 49, pp. 741- 772, 2011.
- [91] S. Lee, "Photocatalytic nanocomposites based on TiO₂ and carbon nanotubes," Florida, 2004.
- [92] M. Landmann, E. Rauls and W. Schmidt, "The electronic structure and optical response of rutile, anatase and brookite TiO₂," *Journal of Physics: Condensed Matter*, vol. 24, pp. 1-6, 2012.
- [93] H. Tang, K. Prasad, R. Sanjines, P. Schmid and F. Levy, "Electrical and optical properties of TiO₂ anatase thin films," *Journal of Applied Physics*, vol. 75, pp. 2042-2047, 1994.
- [94] G. Lu and X. Zhao, "Nanoporous materials - an overview," *Nanoporous Materials- Science and Engineering*, pp. 1-12, 2004.

- [95] Y. Yu, C. J. Yu, J. G. Yu, Y. C. Kwok, Y. K. Che, J. C. D. L. Zhao, W. K. Ge and P. K. Wong, "Enhancement of photocatalytic activity of mesoporous TiO₂ by using carbon nanotubes," *Applied Catalysis A: General*, vol. 289, pp. 186-196, 2005.
- [96] C. S. Gomes da Silva, "synthesis, spectroscopy and characterisation of titanium dioxide based photocatalysts for the degenerative oxidation of organic pollutants," Porto, 2008.
- [97] A. Brioude, P. Vincent, C. Journet, J. Plenet and S. Purcell, "Synthesis of sheathed carbon nanotube tips by sol-gel technique," *Applied Surface Science*, vol. 221, pp. 4-9, 2004.
- [98] A. Jitianu, T. Cacciaguerra, R. Benoit, S. Delpeux, F. Beguin and S. Bonnamy, "Synthesis and characterisation of carbon nanotubes-TiO₂ nanocomposites," *Carbon*, vol. 42, pp. 1147-1151, 2004.
- [99] A. Jitianu, T. Cacciaguerra, M. Berger, R. Benoit, F. Beguin and S. Bonnamy, "New carbon multiwall nanotubes—TiO₂ nanocomposites obtained by the sol-gel method." *Journal of Non-Crystalline Solids*, Vols. 345-346, p. 596–600, 2004.
- [100] P. Vincent, A. Brioude, C. Journet, S. Rabaste, S. Purcell, J. Le Brusq and J. Plenet, "Inclusion of carbon nanotubes in a TiO₂ sol-gel matrix," *Journal of Non-Crystalline Solids*, vol. 311, pp. 130-137, 2002.
- [101] B. Gao, G. Z. Chen and G. Puma Li, "Carbon nanotubes/titanium dioxide (CNTs/TiO₂) nanocomposites prepared by conventional and novel surfactant wrapping sol-gel methods exhibiting enhanced photocatalytic activity," *Applied Catalysis B; Environmental*, vol. 89, pp. 503-509, 2009.
- [102] T. Sugimoto, X. Zhou and A. Muramatsu, "Synthesis of uniform anatase TiO₂ nanoparticles by sol-gel method: 4. Shape control," *Journal of Colloid and Interface Science*, vol. 259, pp. 53-61, 2003.
- [103] D. J. Guo and H. L. Li, "High dispersion and electrocatalytic properties of Pt nanoparticles on SWNT bundles," *Journal of Electroanalytical Chemistry*, vol. 573, no. 1, pp. 197-202, 2004.

- [104] Z. He, J. Chen, D. Liu, H. Zhou and Y. Kuang, "Electrodeposition of Pt–Ru nanoparticles on carbon nanotubes and their electrocatalytic properties for methanol electrooxidation," *Diamond and Related Materials*, vol. 13, no. 10, pp. 1764-1770, 2004.
- [105] H. Tang, J. Chen, Z. Huang, D. Wang, Z. Ren, L. Nie, Y. Kuang and S. Yao, "High dispersion and electrocatalytic properties of platinum on well-aligned carbon nanotube arrays," *Carbon*, vol. 42, no. 1, pp. 191-197, 2004.
- [106] H. Yu, X. Quan, S. Chen and H. Zhao, "TiO₂-multiwalled carbon nanotube heterojunction arrays and their charge separation," *Journal of Physical Chemistry C*, vol. 111, pp. 12987-12991, 2007.
- [107] W. Wang, P. Serp, P. Kalck and J. L. Faria, "Visible light photodegradation of phenol on MWNT-TiO₂ composite catalysts prepared by a modified sol-gel method," *Journal of Molecular Catalysis A; Chemical*, vol. 235, pp. 194-199, 2005.
- [108] K. Woan, G. Pyrgiotakis and W. Sigmund, "Photocatalytic carbon nanotube- TiO₂ composites," *Advanced Materials*, vol. 21, pp. 2233-2239, 2009.
- [109] K. Byrappa, A. Dayananda, Sajjan, C.P, B. Bavasalingu, M. Shayan and M. Yoshimura, "Hydrothermal preparation of ZnO:CNT and TiO₂:CNT composites and their photocatalytic applications," *Journal of Material Sciences*, vol. 43, pp. 2348-2355, 2008.
- [110] Y. Yan, J. Lu, C. Deng, Zhang and Xiangmin, "Facile synthesis of titania nanoparticles coated carbon nanotubes for selective enrichment of phosphopeptides for mass spectrometry analysis," *Talanta*, vol. 107, pp. 30-35, 2013.
- [111] Q. Wang, D. Yang, D. Chen, Y. Wang and Z. Jiang, "Synthesis of anatase titania-carbon nanotubes nanocomposites with enhanced photocatalytic activity through a nanocoating-hydrothermal process," *Journal of Nanoparticle Research*, vol. 9, pp. 1087-1096, 2007.
- [112] B. Liu and H. Zeng Chun, "Carbon nanotubes supported mesoporous mesocrystals of anatase TiO₂," *Chemical Materials*, vol. 20, pp. 2711-2718, 2008.

- [113] L. L. Hench and J. K. West, "The sol-gel process," *Chemical Reviews*, vol. 90, no. 1, pp. 33-72, 1990.
- [114] M. Niedeberger and P. Nicola, "Aqueous and Nonaqueous Sol-Gel Chemistry," in *Metal Oxide Nanoparticles in Organic Solvents; Synthesis, Formation, Assembly and Application*, B. Derby, Ed., London, Springer London, 2009, pp. 7-18.
- [115] P. Ha, H. Youn, H. Jung, K. Hong, Y. Park and K. Ko, "Anatase-rutile transition of precipitated titanium oxide with alcohol rinsing," *Journal of Colloid and Interface Science*, vol. 223, pp. 16-20, 2000.
- [116] D. Segal, "Chemical synthesis of ceramic materials," *Journal of Materials Chemistry*, vol. 7, no. 8, pp. 1297-1305, 1997.
- [117] M. Srivastava, S. Chaubey and A. Ojha, "Investigation on size dependent structural and magnetic behavior of nickel ferrite nanoparticles prepared by sol-gel and hydrothermal methods," *Materials Chemistry and Physics*, vol. 118, pp. 174-180, 2009.
- [118] M. Yoshimura and K. Byrappa, "Hydrothermal processing of materials: past, present and future," *Journal of Materials Science*, vol. 43, pp. 2085-2103, 2008.
- [119] P. Lei, F. Wang, S. Zhang, Y. Ding, J. Zhao and M. Yang, "Conjugation-grafted-TiO₂ nanohybrid for high photocatalytic efficiency under visible light," *Applied Materials and Interfaces*, vol. 6, pp. 2370-2378, 2014.
- [120] X. H. Xia, Z. J. Jia, Y. Yu, Y. Liang, Z. Wang and L. L. Ma, "Preparation of multi-walled carbon nanotube supported TiO₂ and its photocatalytic activity in the reduction of CO₂ with H₂O," *Carbon*, vol. 45, pp. 717-721, 2007.
- [121] W. Fan, L. Gao and J. Sun, "Anatase TiO₂- coated multi-wall carbon nanotubes with the vapour phase method," *Journal of the American Ceramic Society*, vol. 2, no. 89, pp. 731-733, 2006.
- [122] S. Shanmugam and A. Gedanken, "Carbon- Coated Anatase TiO₂ Nanocomposite as a High-Performance Electrocatalyst Support," *Small*, vol. 3, no. 7, pp. 1189-1193, 2007.

- [123] S. Yu, J. H. Yun, Y. H. Kim and J. Yi, "Carbon-doped TiO₂ nanoparticles wrapped with nanographene as a high performance photocatalyst for phenol degradation under visible light irradiation," *Applied Catalysis B: Environmental*, vol. 144, pp. 893-899, 2014.
- [124] G. Hu, X. Meng, X. Feng, Y. Ding, s. Zhang and M. Yang, "Anatase TiO₂ nanoparticles/carbon nanotubes nanofibers: preparation, characterization and photocatalytic properties," *Journal of Material Sciences*, vol. 42, pp. 7162-7170, 2007.
- [125] S. Kedem, J. Schmidt, Y. Paz and Y. Cohen, "Composite polymer nanofibers with carbon nanotubes and titanium dioxide particles," *Langmuir*, vol. 21, pp. 5600-5604, 2005.
- [126] B. Ahmmad, Y. Kusumoto, S. Somekawa and M. Ikeda, "Carbon nanotubes synergistically enhance photocatalytic activity of TiO₂," *Catalysis Communications*, vol. 9, pp. 1410-1413, 2008.
- [127] H. Omidvar, F. Mirzaei, M. Rahimi and Z. Sadeghian, "A method for coating carbon nanotubes with titanium," *New Carbon Materials*, vol. 27, no. 6, pp. 401-408, 2012.
- [128] P. Zhang, C. Shao, Z. Zhang, M. Zhang, J. Mu, Z. Guo and Y. Lui, "TiO₂@carbon core/shell nanofibers: controllable preparation and enhanced visible photocatalytic properties," *Nanoscale*, vol. 3, pp. 2934-2949, 2011.
- [129] H. Y. Ng, I. V. Lightcap, K. Goodwin, M. Matsumura and P. V. Kamat, "To what extent do graphene scaffolds Improve the photovoltaic and photocatalytic response of TiO₂ nanostructured films?," *Journal of Physical Chemistry Letters*, vol. 1, pp. 2222-2227, 2010.
- [130] W. Zhang, B. Xu and L. Jaing, "Functional hybrid materials based on carbon nanotubes and metal oxides," *Journal of Materials Sciences*, vol. 20, pp. 6383-6391, 2010.

- [131] A. Kuvarenga, R. M. Krause and B. B. Mamba, "Multi-walled carbon nanotubes decorated with nitrogen, palladium co-doped TiO₂ (MWCNT/N, Pd co-doped TiO₂) for visible light photocatalytic degradation of eosin yellow in water," *Journal of Nanoparticle Research*, vol. 14, no. 776, pp. 1-16, 2012.
- [132] K. Byrappa, "Novel hydrothermal solution routes of advanced high melting nanomaterials processing," *Journal of the Ceramic Society of Japan*, vol. 117, no. 3, pp. 236-244, 2009.
- [133] S. Abbasi, S. M. Zebarjad and S. H. N. Baghban, "Decorating and filling of multi-walled carbon nanotubes with TiO₂ nanoparticles via wet chemical method," *Engineering*, vol. 5, pp. 207- 212, 2013.
- [134] M. Ouzzine, M. Lillo Rodenas and A. Linares Solano, "Carbon nanofibres as substrates for the preparation of TiO₂ nanostructured photocatalysts," *Applied Catalysis B: Environmental*, vol. 127, pp. 291-299, 2012.