Chapter Three: Experimental and analysis

3.1 Introduction

As previously mentioned, there are a number of methods that are used in the synthesis of carbon nanofibres including: arc-discharge [1]-[4] laser ablation [5] and chemical vapour deposition (CVD) [6]. CVD is believed to be more industrially applicable than the other methods because it has a simple setup, uses less energy and can be easily scaled up [6]. There are several types of CVD synthesis techniques including: hot thermal wall and plasma assisted. Even then, there are sub categories according to: pressure, physical characteristics of the vapour conditions in the reactor and by their means of generating vapour. Practically the one that is employed for batch or industrial use is the hot-thermal wall, which is also known as catalytic chemical vapour deposition (CCVD) [7]. Likewise, there are four types of CVD furnaces namely: horizontal, vertical, fluidised bed reactor and plasma enhanced [7] (**Fig 3.1.1**).

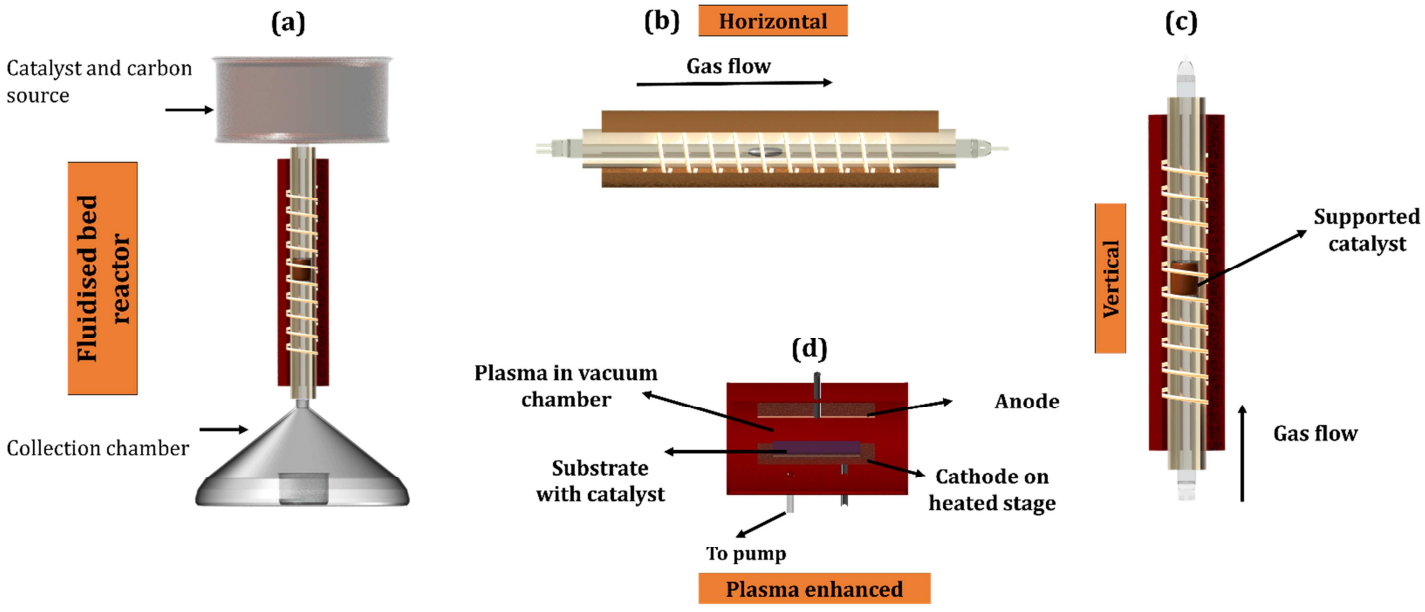

Figure 3.1.1: The four types of CVD reactors (a) fluidised bed, (b) horizontal, (c) vertical, reactor and (d) plasma enhanced CVD around a vacuum (modified from [7])

The one that was used throughout this study was a horizontal furnace (**Fig 3.1.2 (b)**) and its dimensions are summarised in **Table 3.1.1**.

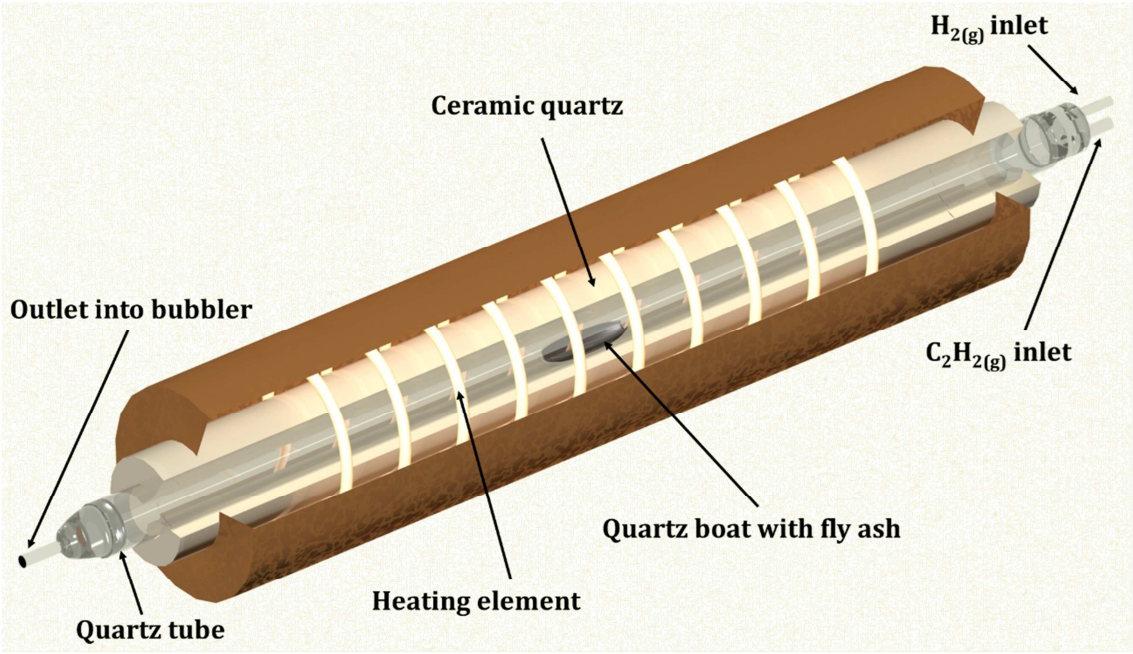

Figure 3.1.2: The typical CVD setup that was used in the experiments

Table 3.1.1 summarises the dimensions of the horizontal furnace used for the CVD setup.

Component	Dimensions (cm)
Ceramic Quartz	
Internal Diameter	4.0
External Diameter	5.0
Length	100.0
Quartz tube	
Internal Diameter	3.0
External Diameter	3.5
Length	130.0
Heating element	
Heating length	30.0
Thermocouple type	K type
Quartz boat	
Depth	0.6
Length	7.0
Width	1.3

One of the main aims of this study was to synthesise CNFs from waste coal fly ash and then coat them with TiO_2 nanoparticles. In order to achieve this, these CNFs had to undergo functionalisation. As previously indicated such functionalisation could either be achieved by chemical or physical methods. Chemical functionalisation was the preferred method for this study because it allowed for the possibility of the formation of the Ti-O-C bond which was necessary for the desired applications, previously indicated in Chapter 2.3. Chemical functionalisation involves methods such as: fluorination, hydrogenation, Diels-Alder and acid treatment. In this study acid treatment was preferred because the desired anchors i.e. carboxylic/carbonyl groups for the formation of the Ti-O-C bond would have formed under these conditions [8].

CNF-TiO_2 hybrids have many potential applications, hence controlling the coating of the TiO_2 on the surface of carbonaceous materials is a requirement [9]. For instance, in the environmental sector these hybrids can be used to remove organic contaminants and in catalysis they could be used as supports or even catalysts for reactions like energy generation through water splitting. In the literature so far, there has been no systematic study on how this hybrid could be tailor-made for specific applications. However, studies that have been conducted have only served to point out the unpredictability of the reaction, the formation of TiO_2 aggregates as well as the uneven and uncontrollable coating of TiO_2 that can occur [10]-[12].

As formerly stated, no literature exists where such hybrids have been studied on fly ash synthesised CNFs. Two methods that could be used to synthesise this hybrid include: sol-gel [10], [13]-[20] and hydrothermal techniques [21]-[25]. From the literature it is seen that neither of these methods allows complete versatility. However, hydrothermal methods are better, as they have less processing steps and in most cases don't require the "as-is" product to be further calcined to form particles (preferably nanoparticles) on the surface of the CNFs. The hydrothermal method used in this study involved the use of a Ti precursor and water. Here the water served as the source of the O^{2-} ions that eventually lead to the formation of TiO_2 nanoparticles. For the potential photocatalytic application required in this study, anatase nanoparticles were preferred over rutile nanoparticles due to their previously mentioned superior properties [21], [26], [27].

3.2 The synthesis of CNFs and their functionalisation

Synthesis of CNFs from fly ash

The main ingredients in CNF synthesis are a carbon source, a reducing gas/ inert gas and a catalyst with or without a support. In the experiments conducted in this study 2.5 g of fly ash (obtained from Duvha, an Eskom power station in South Africa) were used as the catalyst and loaded into a quartz boat. Acetylene and hydrogen gas were allowed to flow into the reactor at 200 ml/min for two hours. The reaction temperature was set at 650 °C. The furnace was ramped at 10 °C/min to reach the desired temperature and held there for an hour. After two hours the acetylene was switched off and the hydrogen ran till the reaction had cooled down to room temperature. These conditions are a modified version of what was used by Hintsho et al. [28].

Study of the growth mechanism of CNFs on fly ash

The reaction conditions during the growth mechanism study were the same as above, but the reactions were run for shorter intervals. The first reaction was allowed to run for 15 min and it was cooled down to room temperature from 150 °C. The product was collected in a sample vial and characterised thereafter. The proceeding reactions were performed, using new batches of CFA, in 10 min incremental intervals from the former reaction time of 15 min up to 125 min. From 65 min to 125 min the reaction was held at 650 °C.

Functionalisation of CNFs

The as-synthesised CNFs were functionalised using an acid mixture of HNO_3 (ACE, 67%) and H_2SO_4 (Fluka, 98%) at a ratio of 3:1 v/v. The total amount of the acid mixture used was 60 ml for every 4 g of CNFs to be functionalised. 4 g of CNFs were placed in a 100 ml round bottom flask (RB) equipped with a stirrer bar. The acid mixture was added into the RB flask and the contents were heated under reflux for functionalisation over different times: 2, 6, and 12 h. The refluxing temperature was set to 110 °C. The products were then placed in 3 L beakers filled with deionised water for 24 h to allow for settling and dilution. After the first 24 h the pH of the water was measured and if it was below 3, the above step was repeated until the pH went above 3. Generally, after three days the suspension of CNFs would be at pH values above 3. These functionalised CNFs (fCNFs) were gravity filtered and rinsed with deionised water until the pH went between 6 and neutrality. The fCNFs were then oven dried at 100 °C for 8 – 12 h.

3.3 The synthesis of the CNF-TiO_2 hybrid

The CNF-TiO_2 hybrid was synthesised using a simple hydrothermal method. A mass of 1 g of fCNFs (2, 6 and 12 h functionalisation time) were added into a RB flask equipped with a magnetic stirrer bar. A volume of 200 ml of ice water was then added into the RB flask which was also placed in an ice bath. A volume of 0.3 ml of $TiCl_4$ (Sigma Aldrich, 99%) was then added drop wise into the mixture while stirring. This mixture was heated under reflux at 115 °C for 2, 6 or 12 h and then allowed to cool to room temperature. The CNF-TiO_2 hybrid was gravity filtered and washed with water to a neutral pH. The product was then oven dried for 8-12 h at 100 °C.

All of the above-synthesised materials were collected for characterisation using the variously listed techniques below:

- Transmission electron microscopy (TEM) with energy dispersive x-ray spectrometer (EDS)
- Scanning electron microscopy(SEM) with an EDS spectrometer
- Thermogravimetric analysis (TGA)
- Fourier transform infrared spectroscopy (FTIR)
- Laser Raman spectroscopy
- Powder X-ray diffraction (PXRD)
- X-ray fluorescence spectrometry (XRF)
- Brunauer-Emmett-Teller surface area analysis (BET)

3.4 Characterisation techniques

TEM with EDS

A FEI Tecnai T12 transmission electron microscope (120 kV, tungsten) was used for the characterisation of all the synthesised materials. It was used to deduce the shape and size of the nanomaterials. The Oxford Inca windowed detector was used for determining the elemental composition of the synthesised materials by using EDS.

<u>Sample preparation:</u>

A small amount of sample was dispersed in an appropriate solvent (ethanol, methanol, water or acetone) in a sample vial. The samples were sonicated in sonicating bath for 5-10 min and then added drop-wise onto a copper grid coated with holey carbon. The copper grid was then placed in a sample holder and inserted into the microscope.

SEM with EDS

The FEI Nova Nanolab 600 focused ion beam (FIB) scanning electron microscope (30 kV) was used to obtain all the SEM images. It gave a morphological view of the synthesised materials and their surface features too. It had the same EDS component as the FEI Tecnai T12 TEM and so it was also used to determine the chemical composition of the nanoparticles.

Sample preparation:

A thin layer of the sample was spread on a piece of filter paper and a sample holder where sticky carbon tape was dabbed onto the surface of this and then the sample was loaded into the stage of microscope.

TGA

A Perkin-Elmer Simultaneous Thermal Analyser (STA 6000) was used for the thermogravimetric analysis. TGA provided information on the decomposition temperature of the carbonaceous materials as well as the residual ash. If a mixture of components with different decomposition temperatures was present, TGA also provided that information.

Sample preparation

A mass of 10 mg of each sample was weighed out and loaded on a small ceramic crucible. This was then put into the STA 6000 and heated from room temperature to 900 °C at 10 °C/min under air.

ATR-FTIR spectroscopy

A Bruker Tensor 27 was used for all of the ATR-FTIR spectra that were obtained. This provided information about the functional groups that were present in the synthesised materials. In the case of carbon nanomaterials it was noted from literature that these materials absorbed most of the light and so the transmittance was very poor. Accordingly the literature also indicated that when the transmittance peaks were low these spectra could be affected or even inverted [29]. This technique was used for fly ash, CNFs, fCNFs and the CNF-TiO_2 hybrid to deduce the presence of functional groups as well as the changes that took place with functionalisation of the CNFs and with TiO_2 coating.

Sample preparation

A spatula of each of these samples were placed on the ZnSe window of the FTIR. Each sample was set in place using a suspended clamp. Then measurements were made on a spectral range of 500 to 4000 cm^{-1}.

Laser Raman spectroscopy

The Bruker Senterra dispersive micro-Raman, with a 532 nm line, was mainly used for the laser Raman analyses. When the growth mechanism was being studied the Horiba, Jobin-Yvon LabRAM Raman spectrometer equipped with a 514.5 nm line was also used. This technique was used for fly ash, CNFs, fCNFs and the CNF-TiO_2 hybrid because each material had unique vibrational modes. Laser Raman was used to determine the graphitic nature of the carbonaceous products that were produced via CVD as well as to confirm the phase of the TiO_2 nanoparticles attached to their surface.

Sample preparation

A sample was placed on a glass slide and then flattened using another glass slide. The sample was placed under the objective lenses and readings were taken.

PXRD

The Bruker D2 PHASER with a LYNXEYE detector, was used for all the powder diffraction patterns. This technique allowed us to determine the crystalline phases of the compounds in our products. The scans were done for 600 sec at 0.026° steps from $10 \leq 2\theta \leq 90°$, unless if stated otherwise. The fly ash, CNFs, fCNFs and the CNF-TiO_2 hybrid were all characterised by PXRD. The X-ray source that was used was the Co-K_α radiation at 30 kV.

Sample preparation

A sample was placed on a sample holder and flattened using a glass slide thereafter the sample was packed on the holder by shaking it with the slide above. Then the sample was placed into the XRD instrument and analysed.

XRF

The presence of trace and major elements in all the products of the study were obtained using the Bruker, S2 ranger X-ray fluorescence spectrometer (XRF). The bioavailability

of the potentially dangerous elements was monitored using this technique as well as their enrichment and depletion.

Sample preparation

A mass of 2 g of sample was pressed into a pellet using a boric acid binder. Thereafter these pellets were melted in a mould and then cooled. The sample binder mix came out as a glassy pellet that was simply loaded into the equipment and then analysed for elements [30].

BET surface area analysis

Surface area analysis measurements were performed using the Micromeritics Tristar 3000 surface area analyser. This technique was used to determine the surface area of the materials and their porosity types. Adsorption and desorption isotherms were obtained to monitor the change of the surface area for the fly ash, CNFs, fCNFs and the CNF-TiO_2 hybrid.

Sample preparation

A mass of 0.2 g of each sample was placed in BET sample tubes and degassed for 4 hours. The samples were then loaded into the BET instrument and N_2 adsorption isotherms were obtained for both multipoint and five point analysis conditions.

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