Chapter 5: General conclusions and recommendations

The aims of this study were to: (i) synthesise CNFs from Duvha coal fly ash, (ii) determine the growth mechanism of these CNFs, (iii) functionalise these CNFs using acid treatment and (iv) use the functionalised fibres for the synthesis of a CNF-TiO_2 hybrid. Essentially this involved the synthesis of CNFs from fly ash using the CVD method, where acetylene and hydrogen were used as the carbon source and carrier gas, respectively. Based upon the data obtained, the following observations and hence conclusions were made:

1) Waste coal fly ash was able to be used as a catalyst in the synthesis of CNFs at 650°C using CVD of acetylene. Furthermore, fly ash was found to be present in these CNFs. This was confirmed by PXRD, XRF and ATR-FTIR spectroscopy where various components of fly ash including: mullite, quartz and haematite, etc. were found to be present in the CNFs. TGA and laser Raman spectroscopy corroborated the presence of carbonaceous materials (i.e. CNFs) as well as residual fly ash amongst other products, which had not combusted after analysis. Electron microscopy (both TEM and SEM) fully confirmed that tubular CNFs had formed from the fly ash.
2) When the growth mechanism of the CNFs was monitored using laser Raman spectroscopy, silica and haematite peaks which were initially present during the reaction between coal fly ash and C_2H_2 in H_2, were quenched by the presence of D and G peaks which were assigned to carbon. This indicated that carbonaceous material, in particular CNFs began to form at temperatures as low as 350°C. TEM analyses revealed that the CNFs grew predominantly from two different particle types in the fly ash: irregular-shaped metallic oxide particles and spherical particles. These particles predominantly gave rise to different types of growth for the CNFs. Irregular-shaped metal oxide particles resulted in CNFs by tip growth and spherical particles resulted in CNFs from root growth. EDS verified that the Fe in the fly ash particles was responsible for the most of the growth of the CNFs, in conjunction with minor contributions from Ca.
3) The surfaces of the CNFs were successfully functionalised. This was confirmed by a number of techniques. Firstly the surfaces of the CNFs were shown by TEM to have

increased in roughness with increased functionalisation time. Thereafter laser Raman spectroscopy of these fCNFs showed that disorder in the CNF structure had increased as functionalisation time increased. Here the G-band decreased with increased functionalisation time while the intensity of the D band increased. Hence a drop in the I_G/I_D ratio was consistent with the surface roughening and the introduction of disorder in the surface of the CNFs. Then ATR-FTIR spectroscopy confirmed the presence of C=O moieties on the surface of the CNFs after functionalisation. As further confirmation of these functional groups, ATR-FTIR spectroscopy revealed that the CNFs were able to absorb water after functionalisation. This indicated that the fCNFs had increased in hydrophilicity by comparison with pristine CNFs. Finally, BET surface area analyses showed that a systematic decrease in the surface area of the CNFs had occurred as functionalisation time was increased. It was suggested, based on literature, that this decrease had occurred by the blockage of CNF pores due to the presence of C=O functional groups.

4) A CNF-TiO_2 hybrid was successfully synthesised. This was once again shown by PXRD, TGA, laser Raman spectroscopy and ATR-FTIR spectroscopy to contain fly ash. Significantly, TiO_2 in the form of anatase, was found to be in association with the CNFs by PXRD and laser Raman spectroscopy. Peaks found by ATR-FTIR spectroscopy, were tentatively assigned to the presence of Ti-O-C bands, despite the lack of conclusive literature on carbon-TiO_2 composites. It further showed that though both functionalisation and $TiCl_4$ exposure duration increased the intensity of the Ti-O-C peak in ATR-FTIR, it was significantly affected by the latter. Significantly the assigned peak was in agreement with peaks found in organic polymer-TiO_2 composites. TEM analyses showed that the TiO_2 particle size and dispersion in the CNF-TiO_2 hybrid varied with the duration of exposure to $TiCl_4$ and functionalisation time. In general it was concluded that the increased duration of exposure to $TiCl_4$, at fixed functionalisation times, caused the TiO_2 nanoparticle size to increase and the particles to agglomerate on the surface of the CNFs. Here, minor variations in the BET surface areas of these hybrids were observed, despite the increase in nanoparticle size or their agglomeration. Similarly the nanoparticle size of the TiO_2

nanoparticles increased as the functionalisation time increased, at fixed duration of exposure to $TiCl_4$. However, here the surface coverage increased with increased functionalisation time, with little to no agglomeration observed. Again these variations were concluded to have played a minor effect on the surface areas of the resultant hybrids. TGA analyses revealed that CNF-TiO_2 hybrids which had the largest residual weight %s after combustion, had the lowest BET surface areas. Since all samples were prepared to deposit 10% (m/m) of TiO_2, it was concluded that the increased residual weight %s were fly ash and that this had influenced the surface area the most.

In summary it could be concluded that: (i) waste coal fly ash could be used as catalysts to synthesise CNFs by the CVD method, (ii) these CNFs were formed by either tip or root growth depending on the shape of the catalysts in the fly ash, (iii) Fe-rich particles in the fly ash were responsible for CNFs growth, (iv) CNFs synthesised this way could be functionalised, (v) these functionalised CNFs could be used to make CNF-TiO_2 hybrids.

The formation of the Ti-O-C bond between fCNFs and TiO_2 nanoparticles is significant because it allows the nanoparticles to be recovered easily from reactors. It also creates a pathway for electrons from the graphitic carbon into the TiO_2 nanoparticles and vice versa. This phenomenon lowers the band gap of anatase nanoparticles from the UV to the UV-vis range of radiation by reducing e-/h recombination time. Potentially, this work would allow better absorption of sunlight for photocatalytic reactions.

Future work

Although the aims and objectives of this study were successfully achieved there are still some aspects of this work that need to be explored further. Firstly, the kinetics of the growth of the CNFs on the fly ash particles could be studied in further detail. This could be achieved using a series of techniques such as timed in situ variable temperature powder X-ray diffraction (VTPXRD) as well as with HRTEM, to assess when crystalline anatase nanoparticles begin to form while closely examining their morphology and size using the latter technique.

Secondly, simple and environmentally-friendly methods could be developed to remove the fly ash from the CNFs after synthesis if the need arose. Removing ash could improve the surface area of the CNF-TiO_2 hybrids, although in most optics processes having silica would be advantageous.

Thirdly, in depth studies could be performed to further assess the effects the remnant of fly ash on the functioning of the CNF-TiO_2 hybrids. This would be accomplished by using the composite in photocatalysis after the removal of silica and before. This would be done to assess if the fly ash had any substantial effect on the activity of the composites.

Fourthly, these CNF-TiO_2 hybrids could be tested in various photocatalytic processes (e.g. water purification or splitting) to establish their efficiency. The experiments would have to be modelled using solutions of known concentration before assessing their effectiveness on real waste water samples. Solar simulators could be used to see and study the effects of flux and amount light shone on the experiments as a function of time.

Fifthly, some scanning probe microscopic (SPM) techniques such as atomic force microscopy (AFM) along with ultra high resolution scanning transmission electron microscopy (UHR-STEM) could be used. These methods are extremely sensitive to the strains and chemical environments of the atoms. They could assist in determining any differences in chemical environments near the carbon bonded titania with the one 'free' or away from such a chemical environment.

Finally, the CNF-TiO_2 hybrid could also be doped or even decorated with other metal nanoparticles so that it could be used as a support for other photocatalytic or catalytic reactions. Reactions such as photocatalysis, water gas shift reactions or even Fischer-Tropsch could use the CNF-TiO_2 hybrid 'as is' or doped with metals such as Fe, Co and Ni to improve their catalytic behaviour.