

Chapter One: Research question and hypothesis

1.1 Introduction

In our present day and age the use of coal in providing power has been escalating due to its abundance, affordability and simplicity of design. Electricity utility companies, industrial processes, the steel industry and exports consume ubiquitous amounts of coal on an on-going basis [1]. Its use ensures that the major economic driving-force industries are ever consistent in providing the needs of our society. However, this type of coal usage creates fly ash in large amounts. In their publication in 2001, Mohapatra and Rao defined fly ash as a solid waste, produced in large amounts during the burning of coal, waste and fossil fuels, that has spherical particles of varying chemical composition and other characteristics depending on its origin [2]. There is a pressing need to recycle or re-use fly ash for industrial purposes because only 10-20 % of the waste is used in the cement, concrete and construction industry [3]. On the other hand the rest is left in holding ponds, lagoons, slag heaps and landfills which proves to be environmentally detrimental and uneconomical considering that these dumpsites occupy the land unproductively and require maintenance [1]-[3]. Fly ash has also been reportedly used in the ceramic industry, as adsorbents for waste management, water stabilisation, materials recovery, agriculture and composite materials synthesis [1]-[3].

In this study the use of fly ash as a catalyst for the synthesis of carbon nanofibres using the chemical vapour deposition (CVD) method was examined. To date, few researchers have studied the possibility of using fly ash to synthesise CNFs using this method [4]-[9]. And none so far, except for Hintsho *et al.* have managed to elucidate a possible mechanism of their growth on the surface of the fly ash particles [10].

Thus in this study the possibility of using fly ash, taken from South African power plants, to synthesise CNFs was assessed. Qualitative techniques were used to explain the possible growth mechanism of these CNFs by looking at their stages of growth along the course of the CVD reaction.

Knowing that pristine CNFs were chemically inert towards polar materials, chemical functionalisation methods were used to introduce active sites to their external surfaces to enable possible covalent bonding with TiO₂ nanoparticles. No one so far has attempted using fly ash synthesised CNFs for this application. These CNFs were

functionalised through an acid treatment which has been commonly employed in the past for the functionalisation of other types of CNFs and CNTs. Once again no one has reported on the functionalisation of CNFs produced from fly ash. It was reasonable to assume that the mere presence of fly ash within the CNFs would have made them behave slightly differently from CNFs synthesised by using conventional catalysts, where these could be washed off using acids and other methods.

Similarly few researchers have tried to modify and use CNFs so-produced for potential industrial use. In this study hybrid materials of CNFs and TiO₂ nanoparticles were made for possible use in photocatalysis.

Many researchers have attempted to coat their carbon nanomaterials (CNMs) with TiO₂ nanoparticles and have either created methods that cannot be easily implemented industrially or these particles did not chemically bind to the surface of these materials [11]-[22]. Even if they did bind they agglomerate or the coating of the anatase nanoparticles onto these CNMs was non-uniform and was easily disturbed by physical methods.

Aim

The aims of the project were as follows:

- 1) To synthesise CNFs from fly ash sourced from the Duvha power station (i.e. Duvha fly ash) using CVD.
- 2) To perform a systematic study of the formation of CNFs on the surface of the Duvha fly ash particles through monitoring of the reaction using electron microscopy.
- 3) To assess the effect of acid functionalisation on CNFs with a HNO₃:H₂SO₄ mixture as a function of time.
- 4) To chemically attach TiO₂ nanoparticles to CNFs by simple, reproducible means.
- 5) To assess the effects of the exposure time to the TiO₂ precursor on the particle size of the TiO₂ nanoparticles formed on the CNFs.

Research questions and hypothesis:

- Can CNFs be synthesised by the CVD method using fly ash obtained from the Dhuva power station as a catalyst?
- Can the growth of the CNFs from the Duvha fly ash particles be assessed qualitatively?
- How does the time of chemical functionalisation of CNFs using $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixtures affect the coating of TiO_2 nanoparticles on their surfaces?
- How does the time of exposure to titanium precursors affect the coating of TiO_2 onto the surface of CNFs?

Objectives

To

- i. Synthesise CNFs from fly ash obtained from the Duvha power station using CVD.
- ii. Deduce the growth mechanism of the CNFs on the surface of the Duvha fly ash particles.
- iii. Functionalise these CNFs and study the effect of time of exposure to acid on their chemical properties and their ability to bind (chemically or physically) TiO_2 (titania) nanoparticles to themselves.
- iv. Investigate the effect of the time of exposure to a titanium precursor on the particle size and establish the characteristics of the CNF- TiO_2 hybrid.

1.2 Outline of Dissertation

Chapter One: introduces the research hypothesis and questions including the aims and objectives of the study.

Chapter Two: gives a detailed literature review on fly ash, CNFs and their proposed growth mechanism, the functionalisation of CNFs, the synthesis of CNF- TiO_2 hybrids and their possible applications in photocatalysis and related reactions.

Chapter Three: indicates the characterisation techniques and experimental procedures used for all the materials that were synthesised in this study.

Chapter Four: discusses the synthesis of CNFs using Duvha fly ash as a catalyst in a CVD reactor and their functionalisation. It also expounds upon the synthesis of the CNF- TiO_2 hybrid.

Chapter Five: provides general conclusions and recommendations for further studies.

References

- [1] 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.
- [2] 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.
- [3] 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*, pp. 217-228, 2001.
- [4] D. C. Nath and V. Sahajwalla, "Application of fly ash as a catalyst for the synthesis of carbon nanotube ribbons," *Journal of Hazardous Materials*, no. 192, pp. 691-697, 2011.
- [5] 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.
- [6] S. Wang, "Application of solid ash based catalyst in heterogeneous catalysis," *Environmental Science & Technology*, vol. 42, pp. 7055-7063, 2008.
- [7] 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," *IEEE Transactions on Electrical and Electronic Engineering*, vol. 4, pp. 787-789, 2009.
- [8] 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, 2012.
- [9] 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.

- [10] N. Hintsho, A. Shaikjee, H. Masenda, D. Naidoo, D. Billing, P. Franklyn and S. Durbach, "Direct synthesis of carbon nanofibers from South African coal fly ash," *Nanoscale Research Letters*, vol. 9, no. 387, pp. 1-11, 2014.
- [11] C. S. Gomes da Silva, "Synthesis, spectroscopy and characterisation of titanium dioxide based photocatalysts for the degenerative oxidation of organic pollutants," Porto, 2008.
- [12] Y. Hu and C. Guo, "Carbon nanotubes and carbon nanotubes/metal oxide heterostructures: synthesis, characterization and electrochemical property," in *Nanotechnology and Nanomaterials; Carbon Nanotubes- Growth and Applications*, M. Naraghi, Ed., Croatia, InTech Open Access Publisher, 2011, pp. 3-35.
- [13] Y. Yan, J. Lu, C. Deng and X. Zhang, "Facile synthesis of titania nanoparticles coated carbon nanotubes for selective enrichment of phosphopeptides for mass spectrometry analysis," *Talanta*, vol. 107, pp. 30-35, 2013.
- [14] 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.
- [15] H. Chen, S. Yang, K. Yu and C. Sun, "Effective photocatalytic degradation of atrazine over titania-coated carbon nanotubes (CNTs) coupled with microwave energy," *The Journal of Physical Chemistry*, vol. 115, pp. 3034-3041, 2011.
- [16] 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.
- [17] 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.
- [18] 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.

- [19] 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*, vol. 345 & 346, pp. 596-600, 2004.
- [20] 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.
- [21] 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.
- [22] B. Liu and H. Zeng Chun, "Carbon nanotubes supported mesoporous mesocrystals of anatase TiO₂," *Chemical Materials*, vol. 20, pp. 2711-2718, 2008.