Aerosol Science Small Research Grant – Successful Submission 2018

Fiona Smail – Teaching & Research Fellow – Awarded £4310

'Optimisation of Continuous Carbon Nanotube Aerogel formation for Scale up - Kinetics of Carbon Nanotube Growth'

1. Aim of the Project

To optimise synthesis of 100% carbon nanotube materials, capable of transforming electrical, thermal and automotive applications, by quantifying the carbon nanotube growth rates in an industrially-scalable production method. Use of tandem DMA and DMA-CPMA techniques to size-select catalyst particles and measure the kinetics CNT growth in an FC-CVD system used for continuous CNT aerogel synthesis, so that industrial exploitation of these materials can be achieved.

The proposed research builds on my work in the field of CNT synthesis identifying the driving forces in the scalable synthesis of 100% macroscopic CNT materials by deconvoluting the reaction. The synthesis is driven by the continuous production of an iron-based catalyst nanoparticle aerosol which reacts with carbon sources at 1000-1200 °C to grow CNTs which bundle together and form a continuously spinnable elastic aerogels.

My recent published work has shown that:

•The bulk aerogel formation is driven by the re-nucleation of the catalyst nanoparticles in the presence of carbon pyrolysis products on the downward slope of the parabolic temperature profile in a tubular reactor.
•A minimum catalyst particle mass concentration is required for spinnable aerogel formation
•Sulphur is essential, ensuring growth of long CNTs by lowering the Fe-particle nucleation energy so that sufficient renucleation occurs at high temperatures optimal for CNT growth.

2. Programme of Work

The kinetics of CNT growth are well characterised for fixed-catalyst bed CVD systems but this is not true in floating catalyst gas phase synthesis as a) in-situ measurement techniques such as TEM are not compatible b) factors such as diffusion-limitations to growth rates, which control carpet growth of CNTs do not apply in the same way. Furthermore, despite its known growth-promotion effects, the scale of influence that S has on the growth rate of CNTs has not been quantified.

I plan to develop a tandem-DMA method, using in house aerosol sampling techniques, to characterise the kinetics of CNT growth in a floating catalyst system suitable for continuous aerogel synthesis to answer the following questions:

1. What is the rate of CNT growth over time for a given set of reaction parameters?
2. How does the rate of CNT growth change in relation to the quantity of S supplied?
3. Does the nature of the S-species (S-precursor) influence the rate of CNT growth?
4. How does Fe catalyst particle size influence the rate of CNT growth?
5. How does H2 concentration (main carrier gas in the reaction) influence the rate of CNT growth?

Fe-particles will be produced by a high-voltage spark generator fitted with pure Fe pins (in-house equipment) or by precursor decomposition in a furnace. These will be size selected using a charge neutraliser and an in-house DMA. The size selected particles will be fed into a 2nd tubular reactor to specific temperature locations where they will react with S and C sources to grow CNTs. Control of all reactants will be achieved using mass flow controllers. Products will be extracted from the reactor using ejection-dilution techniques to allow characterisation.

CNT growth (mass, length) will be quantified using SMPS and CPMA (centrifugal particle mass analyser). By decoupling the Fe catalyst nanoparticle synthesis from the CNT growth step in the synthesis furnace (which we have proved is possible), the CNT reaction can be run in a dilute and controlled manner, preventing full aerogelation, allowing product sampling without blockage of sampling equipment. Then, by changing the distance between the catalyst injection-location and the product-sampling location, the effect of residence time on the reaction can be explored for different reactant ratios. The decoupling also allows the selection of different catalyst nanoparticle sizes so that the effect of particle size on the CNT synthesis can be explored.

To prove that the products are CNTs, material characterisation is required. Sampling of the product stream onto Ag filters or Cu foils provides samples for SEM, TEM and Raman analysis. The microscope techniques will provide information on efficiency of catalyst particle usage for CNT growth, numbers of CNT walls (SWNT, MWNT) and presence of amophous carbon byproducts. Raman (available in house) will provide macroscopic characterisation of the CNT quality and the presence/absence of SWNTs.

3. Potential Applications

Macroscopic 100% CNT materials have low density, high surface area, high toughness and good specific electrical and thermal conductivities and EM shielding properties. Applications will include high-strength lightweight composites (automotive, aeronautic sectors, anti-ballistics), lightning strike protection, component protection (EM shielding) and low-mass wiring requirements (transport systems).

Collaborative partners:

a) Macromolecular Materials Laboratory (Prof. James Elliot, Departmentof Materials Science, University of Cambridge) who synthesise and characterise CNT aerogels. They will provide the electron microscopy necessary for detailed characterisation in the project. Kinetics knowledge gained will be shared so that research in both groups can advance more rapidly.
b) The Advanced Nanotube And Manufacturing project (https://www.anam.eng.cam.ac.uk), running in parallel to this work, which includes both industrial and academic partners looking to convert the promise offered by CNT aerogels into commercial reality. Advice from experts in the CNT field will support this work and results have the potential to deliver scale-up for real world application. (IP agreements within ANAM would cover outcomes from this work, industrial partners have the opportunity to licence any relevant IP outcomes, academic publications are not prevented).

Small pilot scale production by Tortech Nanofibers Ltd requires scaling to meet the potential demand of industrial end users. New reactor designs, informed by the kinetics, will be crucial.
Analysis techniques providing real-time analysis for CNT growth rates are new and will further open up the study of this field and can be applied to other materials (e.g. graphene, BN).

Use of aerosol techniques in CNT reaction characterisation is a new field with many opportunities for further exploitation. To support the aims and objectives of the Aerosol Society, efficient dissemination through publications, and collaborationa and proposed presentations at The Cambridge Particle Meeting 2019, European Aerosol Conference 2019 and the UK Aerosol Society conference in November 2019.

The duration of this project will be 12 months.