Diesel soot thermal decomposition investigation based on the correlation with nanostructure

Yi Guo[1,2], Svetlana Stevanovic[1,5], Branka Miljevic[1], Neal Fairley[3], Elizabeth Graham[4], Llew Rintoul [4], Peter Hines[4], Puneet Verma[1,2], Mohammad Jafari[2, 1], Richard Brown[2], Zoran Ristovski[1,2]

[1]International Laboratory of Air Quality and Health (ILAQH) – [2]Biofuel Engine Research Facility (BERF) – [4]Central Analytical Research Facility –

Queensland University of Technology, 2 George St, Brisbane City, Queensland 4000, Australia

[3]CasaXPS Software Ltd, Bay House

[5]School of Engineering, Deakin University, 75 Pigdons Road, Waurn Ponds, 3216 Victoria, Australia

Introduction

- Diesel particle matter (DPM) has been a major concern in the environment sector in past decades. Since the application of the diesel particulate filter (DPF) the DPM has been significantly reduced. However, the large amount of soot trapped requires to be burnt off to regenerate the DPF.
- The regeneration of DPF is the thermal decomposition of DPM (diesel soot), which relates to the chemical structure of the diesel soot. To fully understand the diesel soot decomposition process is of great significance for effectively removing soot and for DPF regeneration setup, as well as for controlling the emissions produced in the regeneration potentially. The present study is to investigate the chemical structure of carbon in the diesel soot in order to explore how intrinsic chemical structure of soot impacts on its thermal decomposition, by correlating the two groups of data from diverse 13 soot samples.

Methodology

- The **Differential** Scanning Calorimetry & The thermal Gravimetric Analyser was applied to investigate the parameters of the thermal decomposition of diesel soot. The mass loss during each reaction phase, and the critical temperatures were analysed by NETZSCH Kinetics Neo.
- For the soot structure analysis, Raman Microscope was employed to obtain the soot Raman spectra and the five bands model was applied in peak fitting[1,2]. Therefore, the crystalline graphite (G band), aromatic sp2 carbon (D1 band), polyenic chains (D4 band) and amorphous carbon involving O function groups (D3 band), as well as defects of edge carbon[3] (D2 band) are disclosed in the diesel soot. In addition, in order to strengthen the results, X-ray photoelectron spectroscopy (XPS) and transmission electron Microscope (TEM) were applied to characterise the soot structure in parallel, with providing the elemental composition and nanostructure features respectively.

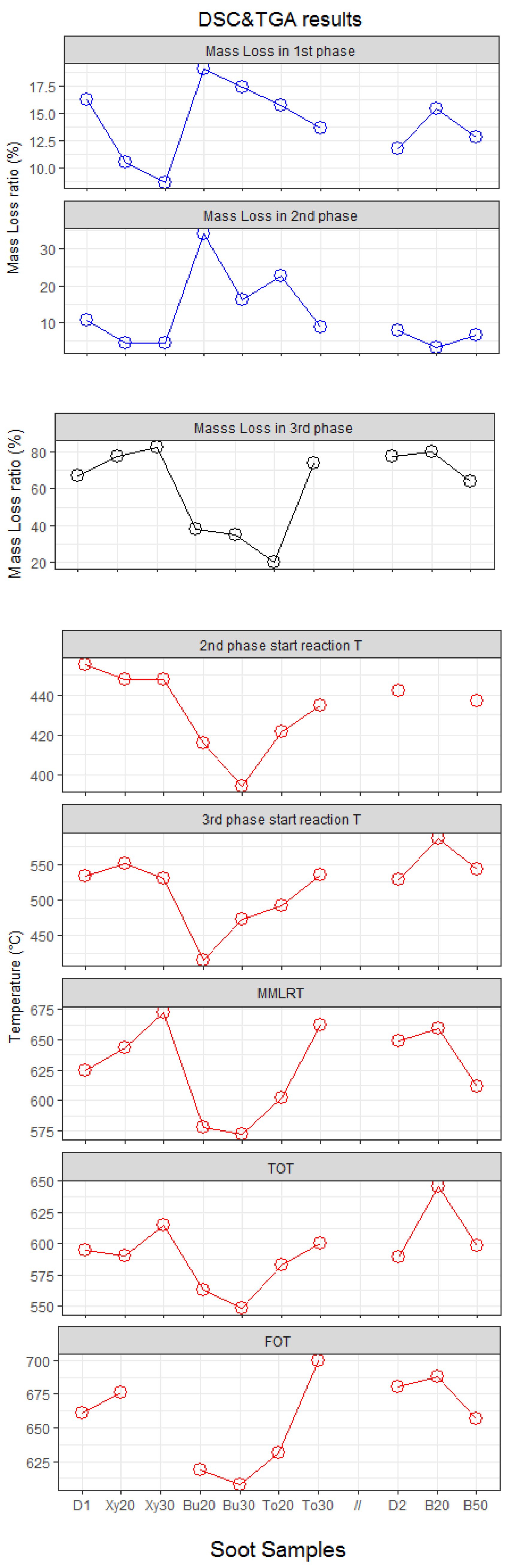
- Regarding soot sample generation, there are 2 groups of soot samples, blended with two different diesels with 4 types of biofuels. Diesel 1 (D1) was bended with Xylene (Xy), Butanol (Bu) and Toluene (To) by 20 % (biofuel20) and 30% (biofuel30) biofuel respectively, so there are 6 bends plus D1 in group 1. In group 2, a different (diesel 2, abbreviated by D2) was blended with coconut biodiesel with 20% (B20), 50%(B50), plus pure coconut biodiesel (B100) and D2. In addition, B96T4 and B90T10 is the blend of the coconut biodiesel and triacetin with 96:4 and 90:10 ratios respectively. To sum up, there are 13 various fuel bends, which generate 13 types of soot under diesel engine combustion.

Results

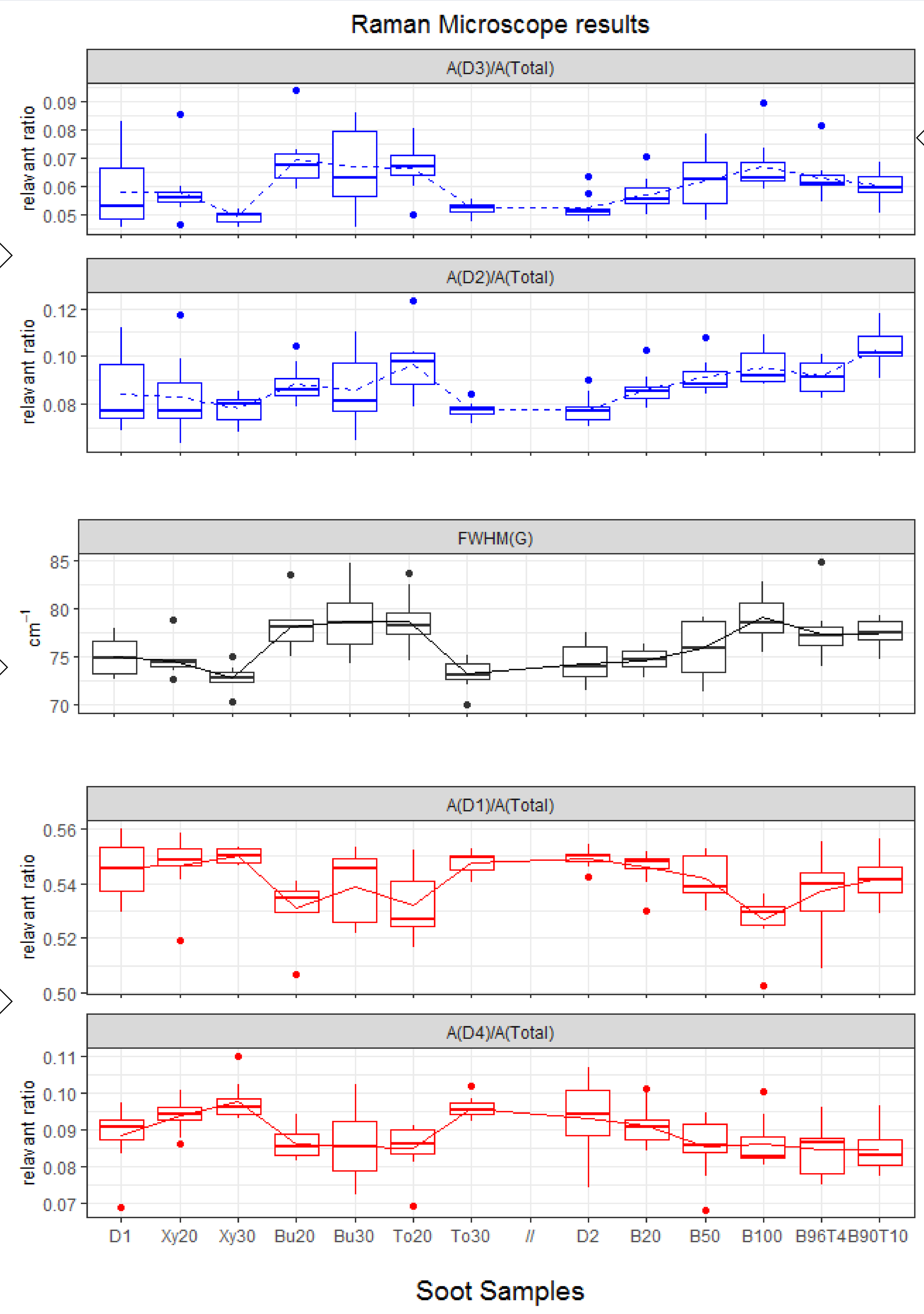
Overviewing all the data curve of the diverse 13 soot samples, the thermal decomposition data curve follows 2 specific trends (blue line and red line) along the soot sample sequence.. Moreover, the thermal decomposition parameters link with Raman bands with high correlation, in statistics way and chemical way.

✓ The soot mass loss ratio in the 1st and 2nd phase have the same trend with D3 band and the D2 band. To be added, the D3 band Raman data are consistent with the Oxygen content provided by XPS, and the D2 band data are supported with fringe tortuosity analysed by TEM. This means that in these 2 stages, for soot with more oxygen and other defects, the loss of mass is higher. More specifically, before 500 °C the soot oxidation is tied to defects removal. Also, it potentially implies that oxygen function groups drives soot reaction initially, which is an interesting point and will be further studied in the following work.

Soot thermal decomposition properties



Soot chemical structure characterisation by Raman Microscope



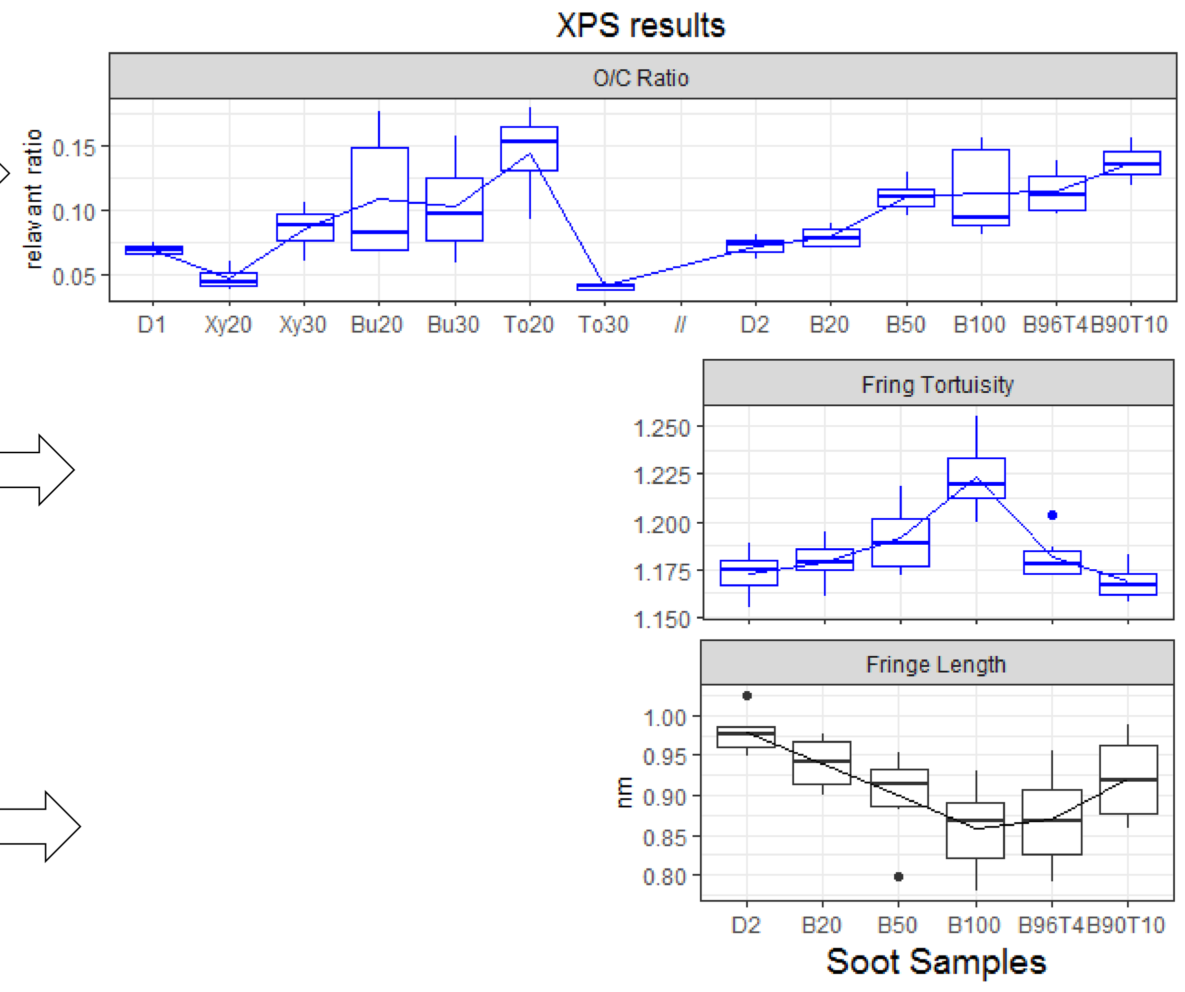
✓ In the 3rd phase, the mass loss ratio correlates with the graphene flake size which is characterised by FWHM (G) inversely in Raman[3] and fringe length in TEM data. It is fairly easy to understand in the 3rd phase which is the main soot burning stage, the graphene bulk is consumed, so the bigger flake area, the more mass consumed.

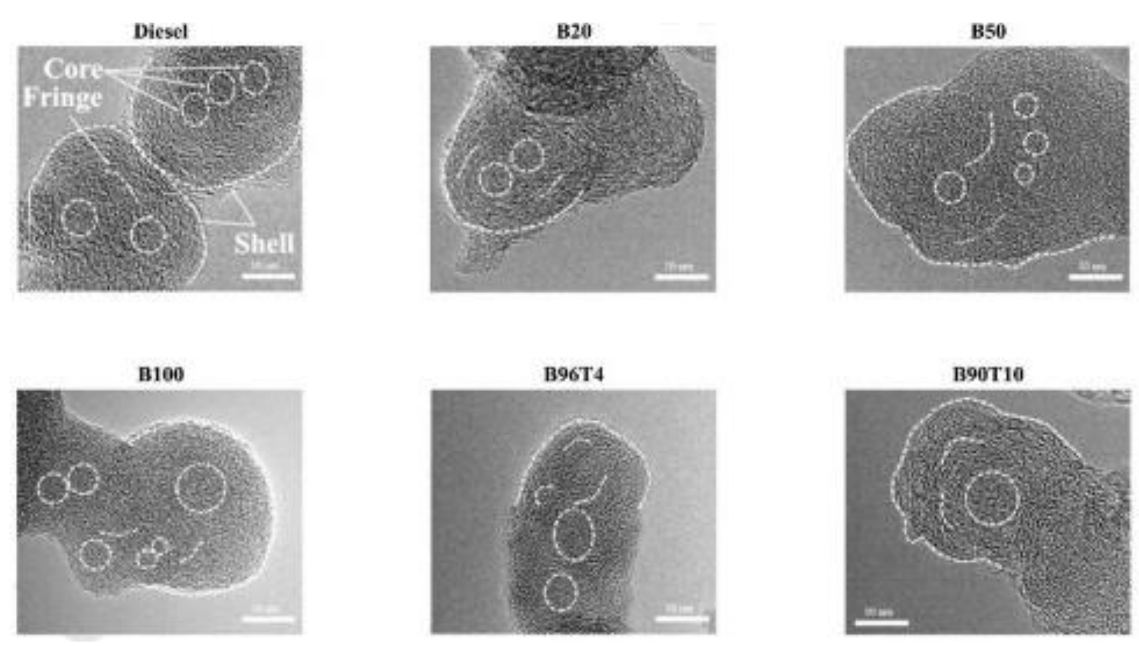
✓ All the reaction temperature during the thermal decomposition highly correlates with Relevant Intensity of D1 band and D4 band, which belong to the double carbon bonds in molecule level. This might be due to the C double bonds that require higher energy to break down in comparison with O function groups and defects.

Conclusion

- Raman microscope is a reliable technique in soot structure characterization, being consistent with XPS and TEM results, which analyse the soot structure from other aspect.

Other supportive results for Raman Microscope





- Soot structure characterised by Raman microscopy ideally explains the soot thermal decomposition parameters. The correlation between these two groups of data gives clue of soot oxidation process, enabling the investigation of oxidation in chemical bond level practically and will direct further research on soot reactivity.

Reference

1. Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niessner, R.; Poschl, U., Raman micro spectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon* **2005,** *43* (8), 1731-1742.
2. Ferrari, A. C.; Basko, D. M., Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nat. Nanotechnol.* **2013,** *8* (4), 235-246.
3. Katagiri, G.; Ishida, H.; Ishitani, A., RAMAN-SPECTRA OF GRAPHITE EDGE PLANES. *Carbon* **1988,** *26* (4), 565-571.

Queensland University of Technology
Brisbane Australia

International Laboratory for Air Quality and Health
WHO Collaborating Centre


Yi Guo
y8.guo@hdr.qut.edu.au