Student Prize: In situ electron microscopy studies of carbon particulate matter oxidation and filtration

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Introduction

As the global requirements for energy continue to rise [1], emissions from combustion of fossil fuels have increased as well. When released into the air, carbon particulate matter (PM) is an especially harmful by-product of incomplete combustion as it is harmful to human health and is a major contributor to pollution and climate change [2]. To minimize emissions, and design new filtration technologies, a better understanding of the underlying mechanisms of PM formation and oxidation is required. Apart from emitted carbon, Carbon PM is also a crucial and useful industrial product - with a wide variety of applications in materials science, pharmaceuticals, and electronics. The Combustion Research Lab at the University of Toronto has therefore applied real time imaging of reactions inside an environmental transmission electron microscope (ETEM) to study the underlying mechanisms behind carbon particulate matter formation, oxidation, and reactivity.

Experimental Methodology

The study of nanomaterial presents many challenges; as the microscopes capable of the resolution needed to see the nanoscale reactions traditionally required a vacuum environment around the sample. The vacuum environment limits research to either a reacting bulk sample outside the microscopes, or simply imaging "snapshot" of a non-reacting nanomaterial. Through a partnership with Hitachi Higher Technologies Canada and Norcada Inc. – we have been able to develop and run high temperature in-situ tests on carbon nanomaterials inside of a high-resolution environmental transmission microscope. These experiments have focused on studying how changing combustor designs affects PM reactivity, how we can develop new catalysts, and how we can further apply this technique for synthesizing new nanomaterials.

The ETEM technique relies on a customized transmission electron microscope (Hitachi HF3300) suitable for gas injection into the sample area, a microelectromechanical (MEMS) heating substrate where the sample is deposited, and high sensitivity gas and temperature control systems. The HF3300 was also equipped with secondary electron imaging and energy-dispersive X-ray spectroscopy (EDX). Functioning together, this platform allowed for tests up to 1000ºC and 1Pa of gas surrounding the sample as it was visualized and analysed for morphological and chemical changes in conditions representative of flames or exhaust gases.

In situ nanomaterial experiments are run in 4 stages; material synthesis, sampling, imaging, and post processing. The carbon PM synthesis is accomplished with a diffusion flame with the variation of a specific parameter (e.g. fuel, temperature, or pressures, etc.). By controlling a single variable per study, its effect on the particles generated and their reaction pathways can be studied. The particles are then extracted from the combustor through a rapid injection of a substrate into the flame. The substrates are held in the flame from 20 to 100ms, and the sample deposits on the substrate surface through thermophoresis. The sampling is done directly on a TEM-transparent MEMS microchip, and high-speed imaging ensures minimal flame disruption and proper sampling location. With the samples collected, the MEMS chip is connected to the gas and heating systems and inserted into the ETEM for imaging.

The goal of the imaging in the ETEM is to create an atmosphere as similar as achievable to the real world conditions the particles would undergo in engines, exhaust streams, and reactors. The samples are first heated up to the reaction temperatures, gas mixtures are injected, and any reactions are captured by transmission electron microscopy, secondary electron microscopy, or EDX. The different imaging techniques give us information on the sample's internal nanostructure (TEM), surface properties (SE), and elemental composition (EDX) – all potentially changing as the sample reacts. Combining this real time imaging with other more traditional methods such as thermal gravimetric analysis provides an extra degree of confidence in the new technique that we are not fundamentally changing the reaction pathways with the microscope electron beam and allows us to acquire a complete picture of the nanoparticle evolution during reactions.

Finally, the experimental videos are post processed with video and photo analysis tools such as ImageJ and Photoshop CC. This post processing allows us to measure particle size changes, filter out background generated by the substrate, and more clearly track the reaction mechanism. The conventional post processing follows: conversion to 24bit colour, thresholding, background elimination, and colour blending. The colour blending applies a colour enhancement to the particle, based on the luminance of the base image and the hue and saturation of the blend colour. This preserves the grey levels in the image and is useful for colouring monochrome images and for tinting colour images.

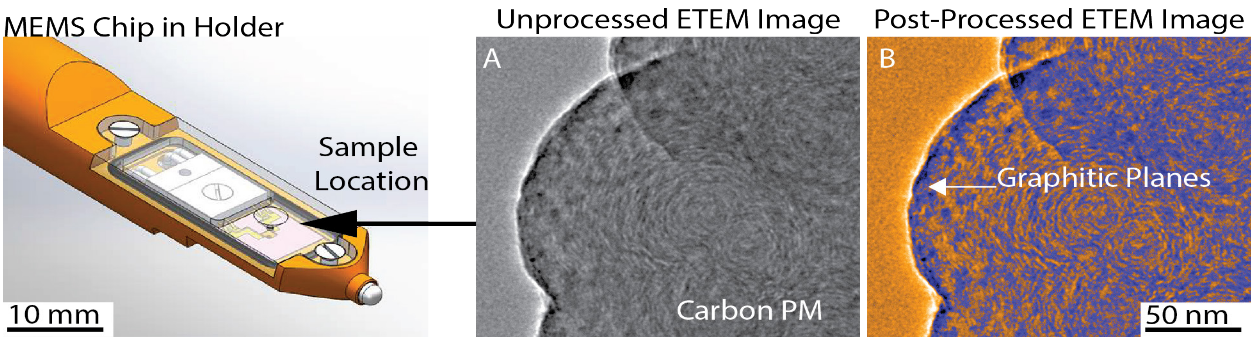

Figure 1. A: Holder Assembly B: Unfiltered sample image C: Filtered Image (purple sample, orange substrate)

Results

Studies have been carried out on the effects of combustor pressures, aftertreatment temperatures, and fuel chemistry on soot reactivity. Real time imaging of carbon particle oxidation was carried out to establish the mechanisms – confirming previously held hypothesis (e.g. how the particles grow protective graphitic "protective shells"[5]), along with discovering new pathways such internal oxidation shown in Figure 2. New nanomaterials and catalysts have also been synthesized and tested in the ETEM - as the techique highlights how active the materials are and how they resond to enviromental changes. These findings allow for cleaner combustor design, as well as fine tuning industrial carbon production to generate carbon PM with specific properties.

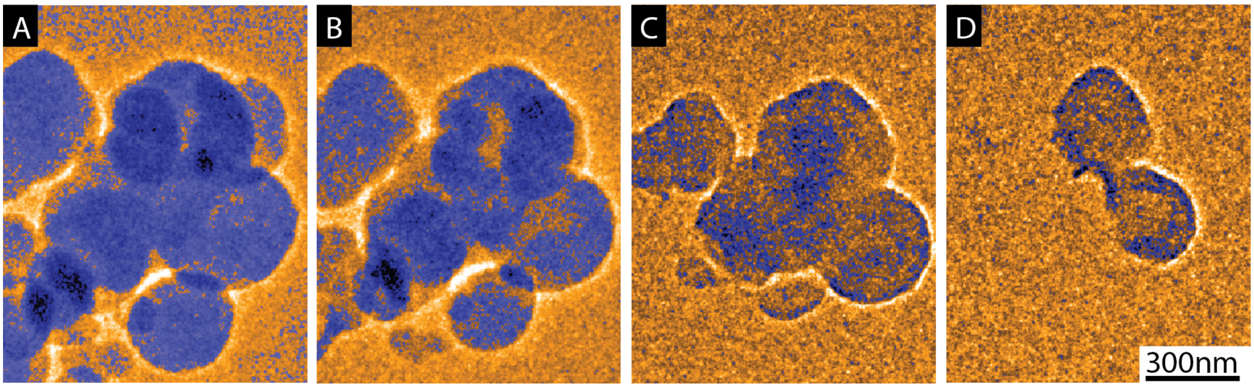

Figure 2. Oxidation pathways shown for a carbon PM particle aggregate

Conclusion

The real time nanoparticle reaction imaging techniques developed provide a powerful workbench for studying carbon particulate matter reactions, restructuring, and chemical changes. The findings allow researchers and our industrial partners to devise novel strategies for controlling emissions or modifying and creating new nanomaterials with specific properties, behaviour, and structure.

Acknowledgment

The authors would like to thank Hitachi Canada and Norcada Inc. for their continued support with the development of this new technique, and NSERC Canada for project funding. We would also like to thank the OCCAM- UofT team, where all the microscopy was performed on the Hitachi HF3300, as well as all our academic collaborators from UofW, KAUST, and PSU.

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