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A Secondary Electron Hyperspectral Imaging characterisation of mechanochemically functionalised carbon black materials

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Background
Carbon blacks find applications in composite materials for energy generation and storage, structural materials, as well as catalysis and as precursor materials. In nanocomposite applications of carbon black, the surface functionalisation of the carbon black is important in determining the structure of the composite and the function of the material [1]. Powders in this form are often characterised as a bulk material, however it is important to understand the local surface chemistry and distribution of chemistries between particles, particularly when the surface of the powder is engineered to achieve certain properties.

Such is the case with carbon black subject to surface oxidation processes. In this case, a one-step ball milling process was used to vary the particle morphology and surface oxidation [2]. X-ray photoelectron spectroscopy (XPS) can tell average oxidation. Transmission electron microscopy (TEM) can tell particle size and surface chemistry – but not for in-situ satellite particles. Therefore, a study which includes local information about particle morphology and functionalisation with process time, may offer insight into the dynamics of the process which includes fracturing, agglomeration, exfoliation and oxidation.

Secondary electron hyperspectral imaging (SEHI) proved to be a valuable technique for characterisation of polymers functionalised by plasma surface treatment [3]. Here we show the technique is applicable to a nano materials characterisation challenge to image the morphology and local surface chemistry of satellite particles in-situ produced during milling on bulk carbon black particles.

Methods
The carbon blacks characterised by SEHI were as-received carbon black and carbon black ball milled without solvent at room temperature for a total of 0h, 1h, 5h, 9h and 11h. Average spectra from 20 µm horizontal field width images were produced for the as-received carbon black and each ball milling process time. A functionalised carbon black model was fitted to spectra to obtain component peak heights using the lmfit python module (Figure 1a). Ratios of peak heights for CH (hydrogenated amorphous carbon) and OH functionalised carbon to sp^2-hybridised graphitic carbon were calculated (Figure 1b). The energy ranges 2.2-2.8 eV, 3.0-3.6 eV, 4.2-4.9 eV and 5.4-6.0 eV were used to create colour maps related to sp^2, CH, OH and CO+sp^3 surface functionalities respectively (Figure 1c). These component images were assigned to channels with hue values equidistantly spaced in the HSV colour space (Figure 1d). The composite map is a sum of these component images (Figure 1e).

Results
The CH:sp^2 ratio decreases from 1.05 to a minimum of 0.5 at 5h milling time, then increases to 1.4 at 11h. The OH:sp^2 ratio decreases from 1.3 to a minimum of 0.8 at 5h milling time then increases to a maximum ratio obtained by processing of 1.3 at 9h. Further milling to 11h decreases the OH:sp^2 ratio to 1.1 (Figure 1b). The results indicate that the sp^2 surface content

is maximum at 5h. Further milling up to 9h oxidises the surface but more milling post 9h produces more amorphous hydrogenated carbon surfaces.
At 5h, the composite colour map indicates a nanoscale 'satellite' particle morphology (see Figure 1d inset for a line profile indicating the particle size) with strongest emissions in the OH component range.

Conclusions
SEHI added to the understanding of the carbon black material by analysing the local chemistry of 'satellite' nano particles which were more oxidised versus the bulk carbon black particle. This is not clear from spatially averaged XPS analyses of the powder.
Meanwhile, a spatially averaged SEHI analysis identified components for carbons and surface carbon compounds. A qualitative comparison of the CH and OH to sp^2 ratios versus ball milling time in oxidative conditions showed a maximum of sp^2 surface chemistry by 5h before this was oxidised to the highest OH:sp^2 ratio at 9h and the highest CH:sp^2 at 11h.
Local characterisation enhances understanding of how the processing influences surface chemistry and morphology resulting from process time.

Graphic:

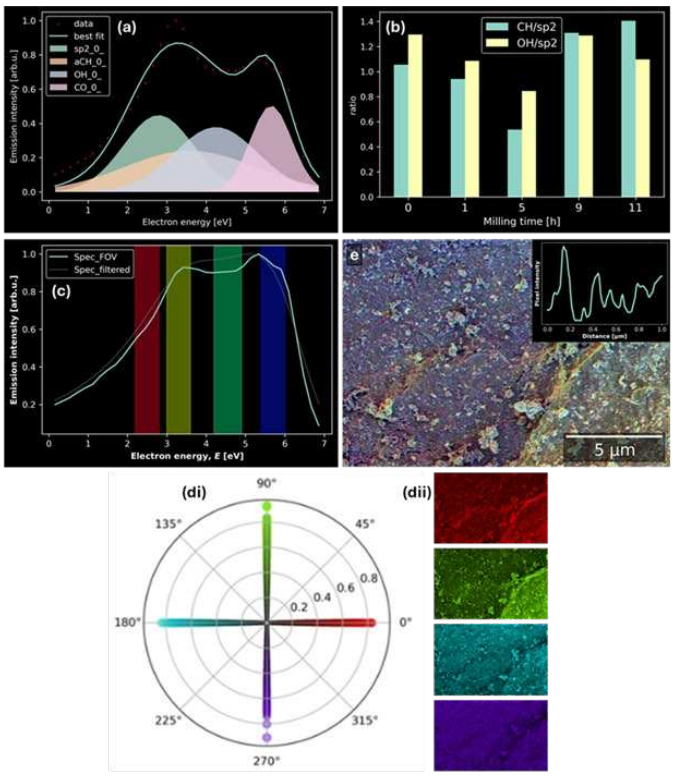

Figure 1 – (a) Component fit to average SE spectra for material produced by 5h ball milling. (b) CH:sp^2 and OH:sp^2 ratio plots for each ball milling time. (c) energy ranges assigned to spaced colour hue channels (fi) to make component images (fii) summed to make the colour image in (e). (e – inset) line profile showing nanoscale satellite particle morphologies.

Keywords:

Carbon black; SEHI; SEM; oxidation

Reference:

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