Dose limited TEM and STEM characterisation of electron beam sensitive inorganic nanomaterials

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Calcium carbonate is of widespread interest as a structural biomaterial and for its environmental and industrial importance, which has led to extensive research into its formation and properties. Furthermore, calcium carbonate is an important model system for fundamental studies of nucleation, growth and polymorphism in inorganic crystals. Industrially, calcium carbonate is found as both a filler and as an active ingredient in formulated products, for example, nanoscale calcium carbonate particles stabilised by a surfactant are used to neutralise acid build-up in combustion engines. The physical properties of the calcium carbonate core have significant implications for the stability and performance of the final product. Transmission Electron Microscopy (TEM), both conventional and scanning, can be used to investigate the physical and chemical properties of these materials at multiple scales, and with high specificity. However, calcium carbonate is known to degrade into polycrystalline calcium oxide (CaO) under electron irradiation. To ensure confidence in measurements made using TEM/STEM, it is necessary to consider the impact of beam induced degradation and to operate under conditions where electron beam damage is minimised.

Calcite nanoparticles, of size ~55nm were used as a model system to set thresholds for acceptable levels of electron beam damage, and to evaluate microscope operating conditions. A marker of degradation was chosen to be the breakdown of lattice images, indicating disruption to the crystal structure (Figure-1). Operating at 300 kV extended the lifetime of the particles, compared to 80 kV due to the increase in inelastic mean free path length. 300 kV STEM allowed for lattice imaging at fluences higher than was possible using 300 kV TEM only when hydrocarbon contamination was present. Under these conditions critical electron fluences for STEM and TEM were $1.8 \times 10^{8} e^{-} nm^{-2}$ and $5.6 \times 10^{7} e^{-} nm^{-2}$ respectively. Contamination build-up in STEM apparently inhibits the formation of CaO (Figure 1F$_{vs}$1C). When heated to 75ºC in-situ, contamination is desorbed and the 300 kV STEM degradation threshold is reduced to $1.35 \times 10^{7} e^{-} nm^{-2}$.

These fluence thresholds were applied to the characterisation of commercial calcium carbonate fuel detergent particles. Low-dose Bright-Field (BF) TEM and Annular Dark-Field (ADF) STEM show particles of size ~2-6nm, with an indication of the presence of crystalline cores in some of the larger particles (Figure-2). These findings will be correlated to bulk studies using Infrared, and X-Ray Absorption Spectroscopies, to confirm and investigate the impact of potential crystallinity in the particle cores, and identify crystalline polymorphs present.

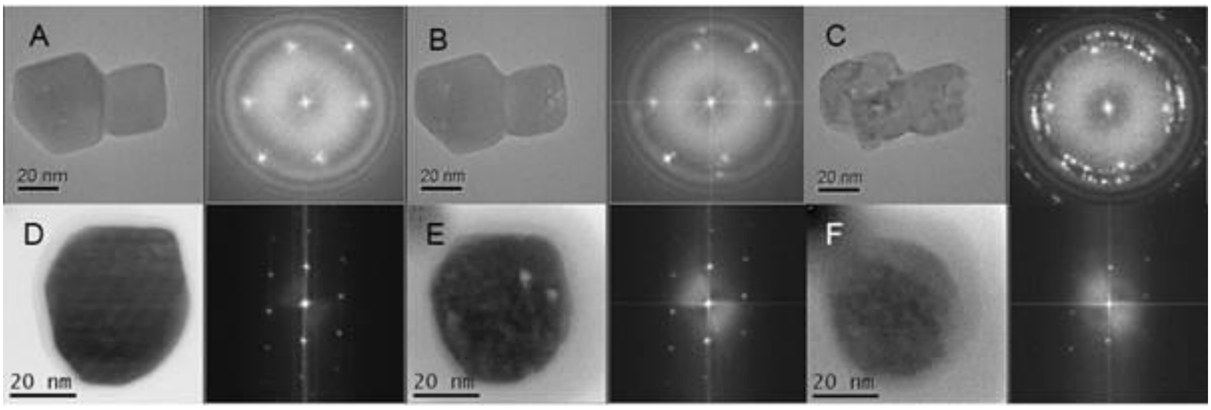

Figure 1 - Comparison of the extent of electron beam damage in calcite nanoparticles under 300 kV irradiation.

Top row- BF-TEM images and FFTs (indicating calcite $[4\bar{4}1]$ direction) at different accumulated fluences: A) $1.3x10^7e^-nm^{-2}$; B) $5.6x10^7e^-nm^{-2}$ and C) $1.35x10^8e^-nm^{-2}$. Note the formation of CaO polycrystals (and corresponding diffraction rings) in C.
Bottom row- BF-STEM images and FFTs (indicating the calcite $[4\bar{4}1]$ direction) at different accumulated fluences: D) $1.22x10^6e^-nm^{-2}$; E) $5.5x10^7e^-nm^{-2}$ and F) $1.87x10^8e^-nm^{-2}$.

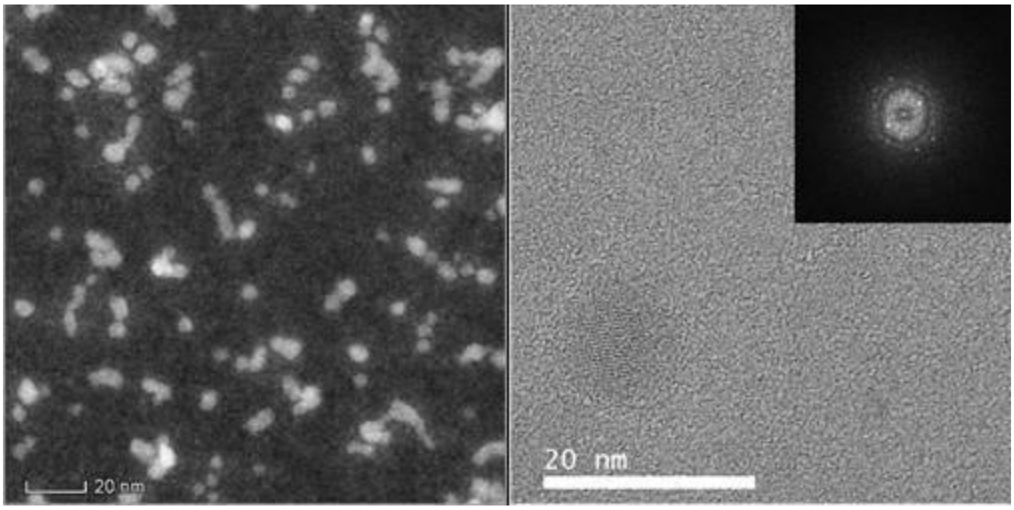

Figure 2 - Left) ADF-STEM of the commercial detergent particles. Labelled regions are suggestive of crystalline scattering. Right) Low-dose BF-TEM image of crystalline particle with FFT indicating the presence of crystallinity at 1.51, 1.88, 2.35, and 3.74Å d-spacings.