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Impact of Electron Beam Irradiation on Carbon Black Oxidation

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Background

The use of environmental transmission electron microscopy (ETEM) in oxidation studies of nanocarbons, such as carbon black (CB), has revealed new, and confirmed previously suggested, oxidation mechanisms [1]. However, connecting ETEM studies to technical processes (occurring at very different conditions) is not necessarily straightforward. Primarily, the influence of the electron beam can present a large issue that is not easily resolved. For nanocarbon oxidation, there is a clear increase in oxidation rate depending on the dose rate, however, there are few studies reporting any quantification of this effect [2].

To better understand the origin of the beam-enhanced oxidation rate, we note that CB reacts with oxygen gas only at active sites, imperfections in the graphitic shell. These active sites are inherent to CB but can also be generated through interactions with the electron beam through 3 distinct mechanisms. Firstly, ionized oxygen species can react directly with the graphitic shell of CB, these species can be produced through ionization interactions with either primary electrons (PE) or secondary electrons (SE). Additionally, active sites can be generated through atomic displacements in CB by PE. These three mechanisms; ionization of O2 by PE [3], ionization of O2 by SE [4], and atomic displacements by PE; have different underlying mechanisms and respond differently to variation of reaction and imaging conditions.

Methods

In our study, we have observed the oxidation of CB at varying electron dose rates and electron energies in two ETEM setups. Data were collected using electron energy loss (EEL) spectroscopy time-series for determination of an average oxidation rate over agglomerates, as calculated from the time-dependent decrease in the C-K signal. This data were complemented with data high-resolution time resolved image series to investigate the local effect on individual particles and to validate the EEL spectroscopy results.

Results

Our experiments show that in situ beam-enhanced CB oxidation is localized to the irradiated area, that the oxidation rate is not significantly affected by changes to the electron energy, and that the in situ beam enhancement is non-linear in nature. Additionally, the reaction only occurs in the presence of an oxidizing gas, i.e. not in inert gases like N2. These findings contradict that ionization by PE is the driving force behind the increase in oxidation rate in TEM, as the ionized species are expected to spread out over an area larger than the illuminated, and the rate at which ionized oxygen species is expected to approximately double as the electron energy is reduced from 300 keV to 100 keV. Similarly, oxygen ionization by SE, is also expected to increase when the electron energy is decreased, however, this mechanism may have a minor impact if the CB sample is located on a support, in which case an excess of SEs is generated. Rather, the results are consistent with atomic displacement as the main driving force; given that the electron energy required to knock an atom out of its lattice position is exceeded, the probability of displacement does not change to a large extent over the relevant electron energy scale. Additionally, atomic displacements can only occur where the electron beam has been located, and no damage is observed outside of the irradiated area.

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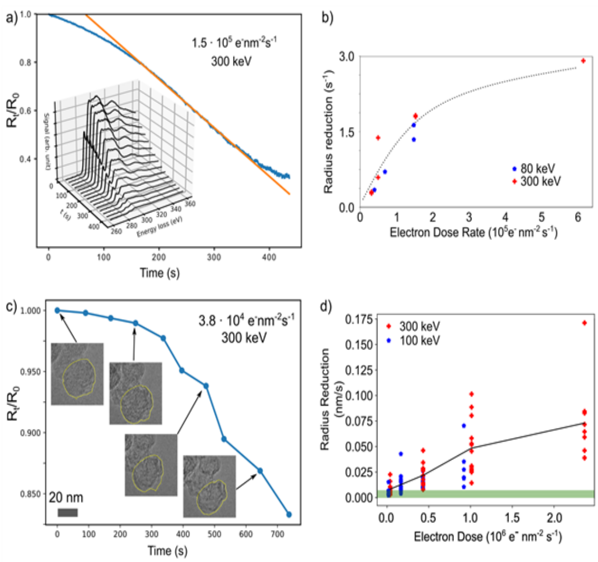
Conclusion

We have shown that CB oxidation is mainly affected by elastic high-energy electron-sample interactions, with a smaller contribution from inelastic electron-gas processes from secondary electrons emitted from the sample and sample support. While this process suggests that there are no safe conditions, the beam effect can be made vanishingly small compared to the intrinsic oxidation. We show how EELS can link processes seen at individual particles to whole agglomerates. This further illustrates the importance of comparing results obtained in the ETEM with results obtained via other methods such as TGA or its like.

Graphic

Figure: Summary of methods and primary results of study. a) EEL spectroscopy time-series (blue) of the C-K signal and linear fit (orange) to the linear region of the time-series. The inset illustrates selected average spectra from times s. b) The linear oxidation rate as calculated from the linear fit in time-series as in a) illustrating no significant difference between 80 keV and 300 keV. c) Results from an image time-series with insets showing a CB particle at various stages of oxidation. d) Aggregate results of image time-series, the green region represents an “inherent” oxidation rate with intermittent imaging.

Graphic:



Keywords:

Electron beam nanocarbon oxidation ETEM

Reference:

[1] H. Wiinikka et al. Carbon 2019, DOI: 10.1016/j.carbon.2019.01.007
[2] D. Wahlqvist et al. Carbon 2024, DOI: 10.1016/j.carbon.2023.118686
[3] A. L. Koh et al. Ultramicroscopy 2017, DOI: 10.1016/j.ultramic.2016.12.009
[4] H. Yoshida et al. Nanotechnology 2017, DOI: 10.1088/1361-6528/aa6a4c