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TEM and HRTEM of Soot-in-oil particles and agglomerates from internal combustion engines

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Abstract. Over time, the performance of lubricating oil in a diesel engine is affected by the build-up of carbon soot produced by the combustion process. TEM and HRTEM are commonly used to investigate the characteristics of individual and agglomerated particles from diesel exhaust, to understand the structure and distribution of the carbon sheets in the primary particles and the nanostructure morphology. However, high resolution imaging of soot-in-oil is more challenging, as mineral oil is a contaminant for the electron microscope and leads to instability under the electron beam. In this work we compare solvent extraction and centrifugation techniques for removing the mineral oil contaminant, and the effect on particle size distribution.

1. Introduction

Most of the particulate matter produced by the combustion process in a diesel engine is expelled with the exhaust gases into the exhaust system, but a small proportion is transferred to the lubricating oil. Soot-in-oil differs from exhaust soot in that it has not been subject to oxidation processes to the same extent. Hence, the outer shell structure is more likely to remain intact. The nanostructure of the soot surface is of interest because of the potential influence on its reactivity and oxidation rates. The length and orientation of the graphene layers on the soot surface determine soot graphitisation and consequently the reactivity of the soot particles. Shorter layers will result in more edge sites, and therefore more reactivity. Soot in oil does not agglomerate as much as exhaust soot.

High resolution TEM is commonly used to examine exhaust soot [1, 2], but the presence of mineral oil in soot-in-oil samples complicates TEM analysis. Cryogenic vitrification and imaging have been used to analyse soot-in-oil in the past, but issues related to viscosity of the typical used engine oil lead to localised thick layers [3,4].

Solvent extraction has been used to prepare suitable samples for TEM, although significant engine oil remains that is an issue due to contamination in the TEM. Subsequent centrifugation has been reported to produce samples suitable for HRTEM; however there are indications in the literature that the increased stresses involved in this process have modified the characteristics of the soot agglomerates.

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2. Experimental

Samples of soot extracted from engine oil were prepared using a solvent extraction process, diluting the oil at a dilution ratio of 1:60 in heptane. This produces a heptane solution containing a much lower oil content, and also at a suitable low viscosity to allow deposition onto a carbon coated TEM grid. Following deposition, the solvent evaporates rapidly to leave soot particles of varying sizes and aggregations. This process puts little strain on the soot aggregates, so is expected to reveal a structure typical of the soot as it was in the engine oil. The centrifugation process is performed on the diluted oil/heptane solution by five stages at 14,000 rpm for 90 minutes at 25°C, following the work of Clague et al [5].

For TEM analysis, after preparation, 3 microlitres of the soot suspension in heptane were dispersed onto amorphous carbon or graphene oxide TEM support films obtained commercially from Agar Scientific. Graphene oxide films, which have only recently become commercially available, are particularly advantageous for work of this nature, as the reduced contribution to the image from the supporting film makes identification of the structures in the smaller soot primary particles more straightforward. The solvent extraction samples were given a 30 second O₂/Ar plasma clean in a Fischione Model 1020 Plasma Cleaner prior to imaging in the TEM.

Imaging of solvent extraction samples was performed at liquid nitrogen temperatures using a Gatan 914 Cryo-tomography holder. Imaging of centrifugation samples was performed using a standard JEOL single tilt holder. TEM analysis was performed in a JEOL 2100F TEM equipped with a Gatan Orius CCD camera.

3. Results and Discussion

Samples of soot in oil after solvent extraction only were found to be suitable for conventional TEM (Figure 1), showing the overall structure of the soot particles and the level of agglomeration. The soot agglomerates were found to be comprised of 12-40nm sized primary particles. These formed a mixture of chain-like structures and clusters of spherules. The presence of 2nm particles was also observed; these are also found in samples of the clean oil (not shown), and are ascribed to be an oil additive. However, high resolution TEM of samples prepared by solvent extraction was not practical due to the rapid build-up of carbon contamination in most areas of the TEM grid investigated, rapidly obscuring the structure of interest, even at liquid nitrogen temperatures.

In comparison, the five-step centrifugation process was found to produce samples suitable for HRTEM analysis, at room temperature, without the need for a plasma cleaning stage subsequent to dispersal onto the TEM grid (Figure 2). The nanostructure of the primary particles from soot samples shows tortuous graphitic segments constituting the outer shell, with defects and incomplete layers present, indicating that these particles will be reactive. However, the centrifugation process was found to have altered the structure of soot aggregates, although it does not appear to have altered that of the primary particles [6].

Dispersion of centrifuged samples onto graphene oxide grids was found to give superior imaging of the soot structures in comparison to dispersion onto conventional amorphous carbon film grid. The reduced contrast from the support film is particularly beneficial when observing small, light element structures such as the soot primary particles in this study.

Soot-in-oil agglomerates were found to be composed of primary spherical particles of 12-40nm. The core-shell structure is clearly visible. Primary particles from used oil samples show the structure as it was at the time of adsorption into the engine oil, which prevents further oxidation. The classic core shell structure is present in all particles from soot in oil samples, with an outer shell of 6-12nm thick.

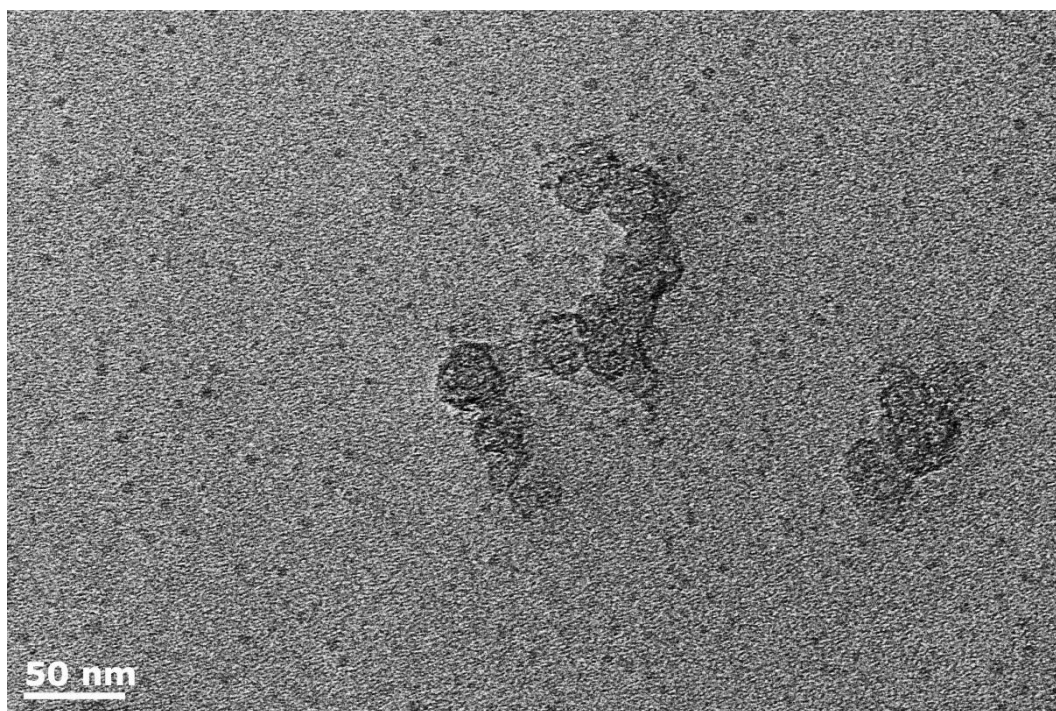


Figure 1 –TEM image of soot extracted from engine oil following solvent extraction, deposited on a conventional amorphous carbon film.

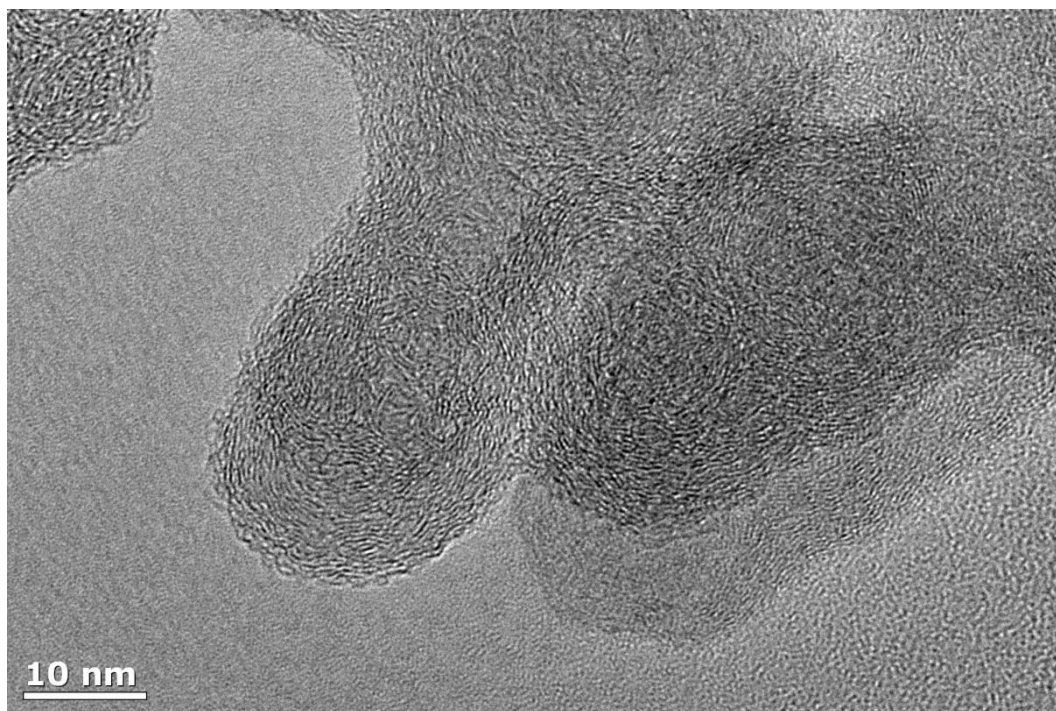


Figure 2 – HRTEM image of soot particles extracted from engine oil following solvent extraction and ultra-centrifugation. This sample was dispersed onto a graphene oxide support grid to give a reduced contrast from the supporting film.

4. Conclusion

Samples produced by solvent extraction were found to be sufficiently clean of mineral oil to analyse the aggregate structure of soot-in-oil. A centrifugation process subsequent to solvent extraction was found to produce samples with minimal remnant oil and hydrocarbon contamination, suitable for high resolution TEM analysis, but is found to produce a differing particle size distribution to samples produced using the solvent extraction process. Analysis of samples using both methods can be combined to obtain a full understanding of the soot-in-oil structure. Graphene Oxide support grids are beneficial for HRTEM analysis of such nanoscale, light element structures.

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