Extended summary

Nanoparticle characteristics of exhaust and soot-in-oil from a light duty diesel engine

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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 migrates to the boundary layer, and then into the oil film, early in the expansion stroke. Consequently, the morphology, agglomeration and other characteristics of soot-in-oil are quite different to exhaust soot. The form taken by this soot-in-oil is of interest because of the potential influence on oil properties, for example, and for insights to the history of particle formation and growth.
The exhaust soot and soot-in-oil samples used in the study were from a high pressure common rail (HPCR) direct injection four-cylinder diesel engine meeting Euro 4 emissions requirements. High Resolution Transmission Electron Microscopy (HRTEM) is commonly used to investigate the characteristics of exhaust agglomerates, to understand the structure and distribution of the carbon sheets in the primary particles and the nanostructure morphology. Primary particles from used oil samples have the advantage to show structure as it was at the time of adsorption into the engine oil, which prevented further oxidation. 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. Solvent extraction technique was found to minimise the stress on soot agglomerates and gave sufficient separation of oil and soot to allow conventional TEM results to be obtained; but this is not sufficiently oil-free for high resolution analysis of primary particles. Five stages of centrifugation of soot-in-oil agglomerates suspended in heptane followed by solvent replacement with cyclohexane, produced samples with minimal remnant oil and hydrocarbon contamination, suitable for high resolution TEM analysis; centrifugation is found to produce a differing particle size distribution to samples produced using the solvent extraction process [1].
Solvent extraction, diluting the oil in heptane, followed by dispersion onto the grid and a 30 second O2/Ar plasma clean is suitable for limited TEM imaging, as shown in Fig 1 and Fig 2, but not for high resolution analysis due to carbon contamination. The centrifugation process has been used for HRTEM; it modifies the distribution of size and shape of agglomerates, as reported in Fig 3, but not primary particles.

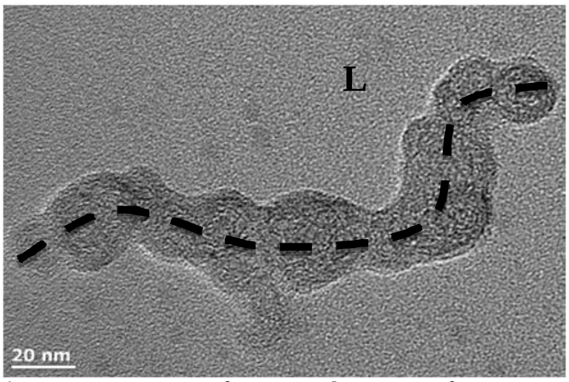

Fig.1 TEM picture of soot agglomerates from engine oil. Sample prepared using solvent extraction L=200nm

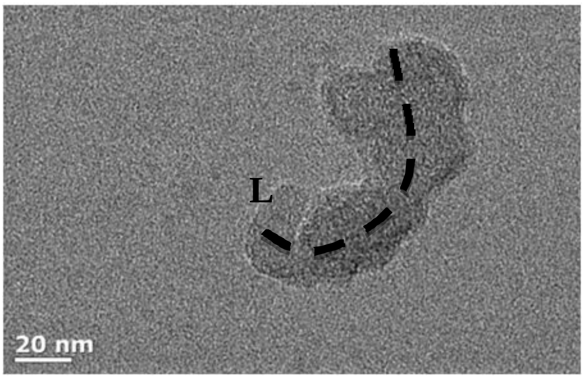

Fig.2 TEM picture of soot agglomerates from engine oil. Solvent extraction followed by diethyl ether bath. L=105nm

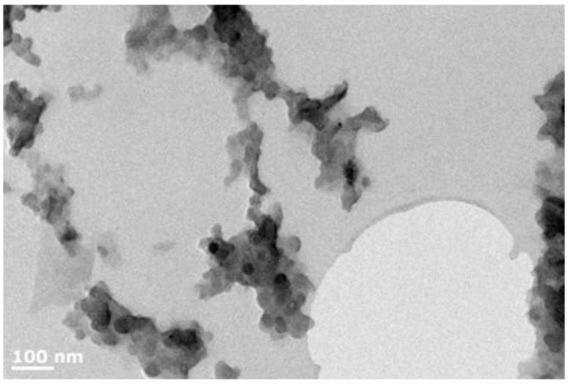

Fig.3 TEM picture of soot agglomerates from engine oil. Sample prepared using centrifugation

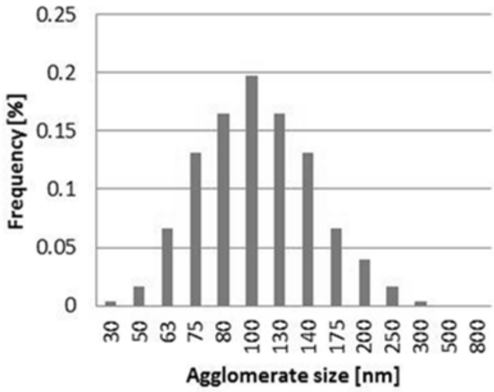

Fig.4 Length of agglomerates from engine oil. Sample prepared using solvent extraction without centrifugation.

Frequency distributions of soot-in-oil agglomerate length are given in Fig 4. These dimensions are the maximum values of length (L) of projected two-dimensional images of agglomerates. The lengths were measured using an open architecture image processing program, ImageJ. Agglomerates not subjected to centrifugation have a modest branched morphology and average size of 100nm. A full exhaust soot agglomerate characterisation was not performed; the exhaust soot particles analysed in this work showed a majority of clusters of agglomerates with few chainlike particles as reported in Fig 5 and Fig 6.

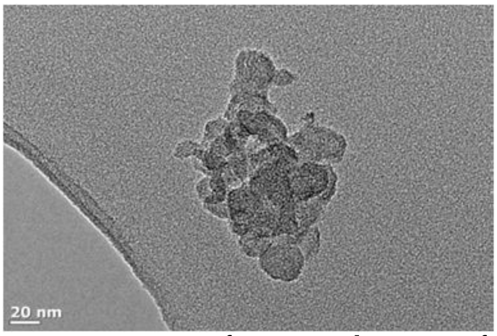

Fig.5 TEM picture of soot agglomerates from exhaust

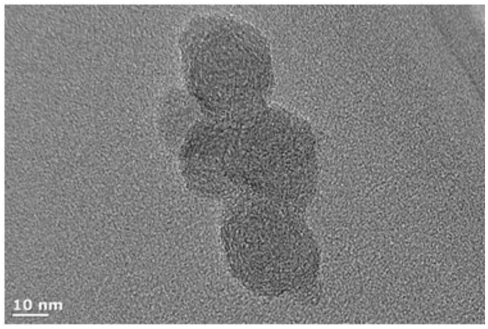

Fig.6 TEM picture of soot agglomerates from exhaust

Soot-in-oil agglomerates were found to be composed of primary spherical particles of 12-40nm. Core-shell structure is clearly visible in Fig 5 and Fig. 6. Soot adsorption into the engine oil prevented oxidation of the primary particles. The classic core shell structure is present in all particles from soot in oil samples, with an outer shell of 6-12nm thick.

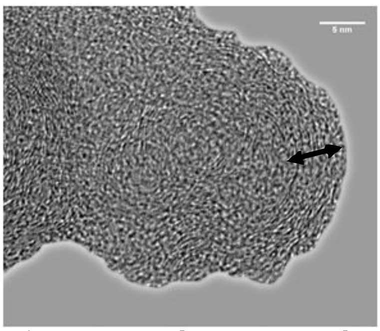

Fig.5 Soot-in-oil primary particle. Diameter 25nm. Outer shell 6.5nm (support-film removed manually)

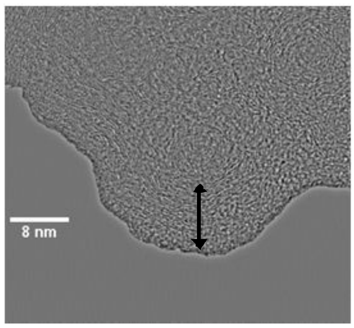

Fig.6 Soot-in-oil primary particle. Diameter 31nm. Outer shell 11nm (support-film removed manually)

In literature, primary particles from Euro IV diesel exhaust soot are reported having a bucky-onions structure and size ranging from 3 to 15nm with averaged size of 13nm; the majority of particles do not exhibit a core-shell structure [2]. The exhaust soot primary particles analysed in this work exhibit a primary particle size of 5-28nm with an outer shell of 0-4nm, HTEM images of exhaust primary particles are given in Fig.7 and Fig.8. The support-film, originally part of the image, has been removed manually to enhance primary particle visualisation. Soot-in-oil differs from exhaust soot in that it has not been subject to oxidation processes to the same extent and hence the outer shell structure is more likely to remain intact. Soot surface nanostructure is of interest because of the potential influence on its reactivity and oxidation rates.

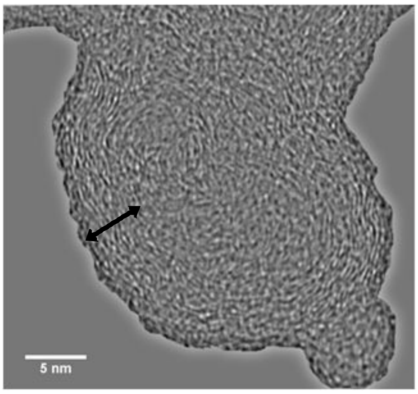

Fig.7 Exhaust primary particle.
Diameter D=22nm. Outer shell 3.8nm
(support-film removed manually)

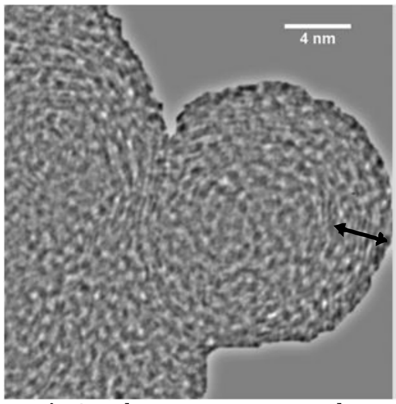

Fig.8 Exhaust primary particle.
Diameter 16nm. Outer shell 3nm
(support-film removed manually)

The length and orientation of the graphene layer determines the soot graphitisation, and consequently its reactivity. The nanostructure of the primary particles does not differ significantly between both soot samples; tortuous graphene segments constitute the outer shell, if not completely oxidised, and look comparable to naked eye. Defects and incomplete layers are present. Although the graphitic structure indicates a rigid structure, the defects make the outer shell prone to oxidation. It is then possible that the shell is almost completely oxidised during the expansion and exhaust stoke; exhaust particles will then be smaller and will not show the core-shell structure as reported by Su et al. [2].

References

[1] La Rocca, A., Di Liberto, G., Shayler, P.J., Fay, M.W. The nanostructure of soot-in-oil particles and agglomerates from an automotive diesel engine. Tribology International, 2013:61: 80-87.
[2] Su DS, Jentoft DE, Muller JO, Jacob E, Simpson CD, Tomovic Z, Mullen K, Messerer A, Poschl U, Niessner R, Schlogl R. Microstructure and oxidation behaviour of Euro IV diesel engine soot: a comparative study with synthetic model soot substances. Catalysis today, 2004;90:127-132

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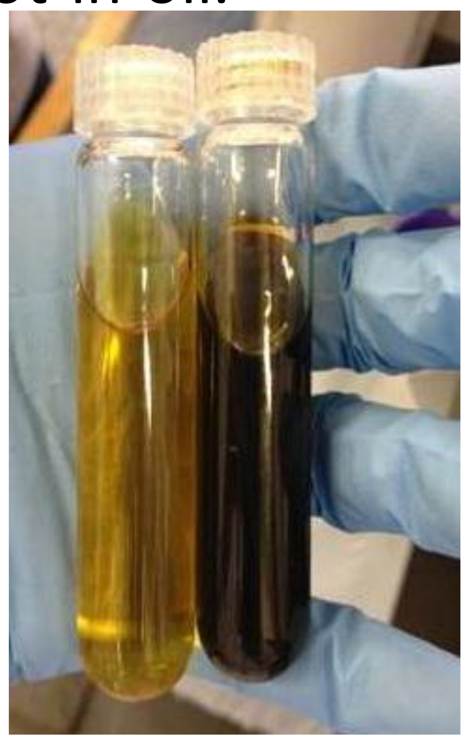
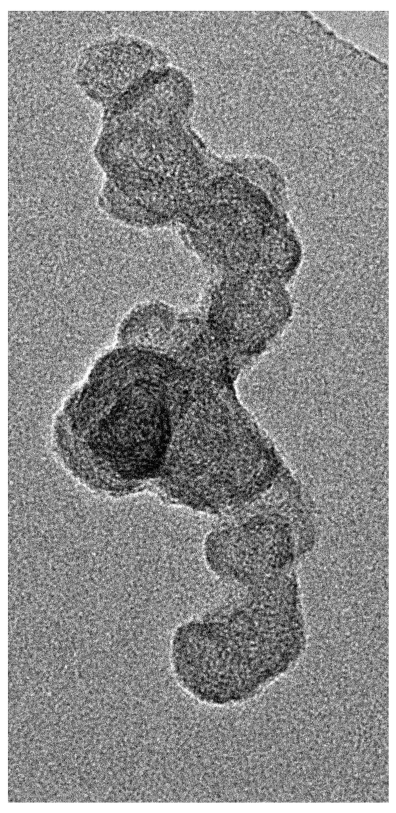
1. Objectives: To analyse characteristics of soot-in-oil from modern light duty automotive engines, examine the effect of sample preparation on the size of soot particle agglomerates and compare characteristics of exhaust soot and soot-in-oil.



2. Introduction: Most of the particulate matter produced by the combustion process in a diesel engine is expelled with the exhaust gases into the exhaust. A small proportion is transferred from the cylinder to the lubricating oil. The form taken by the soot-in-oil is of interest because of the influence on oil properties, engine performance and wear and for insights to the history of particle formation and growth.

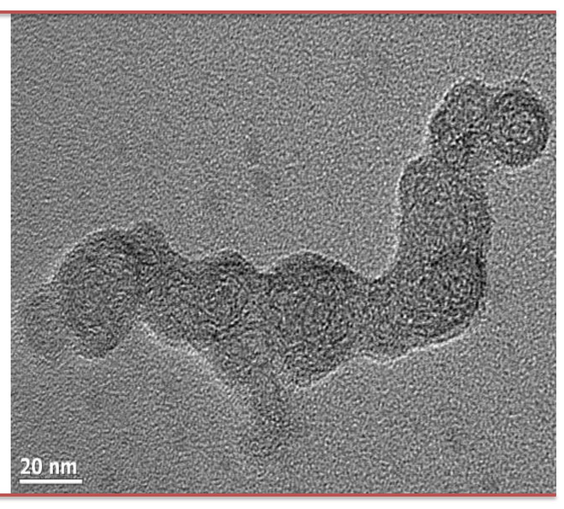
Soot migrates into the oil film early in the expansion stroke; consequently, the morphology, agglomeration and other characteristics of soot-in-oil are quite different to exhaust soot. Soot-in-oil has not been subject to oxidation processes to the same extent and hence the outer shell structure is more likely to remain intact.



3. Soot diagnostics: Transmission Electron Microscopy (TEM), is commonly used to characterise exhaust soot nanoparticles. Oil environment make the soot-in-oil investigation highly challenging as oil acts as contaminant for TEM. Solvent dilution and centrifugation are commonly used to prepare specimen for HRTEM.

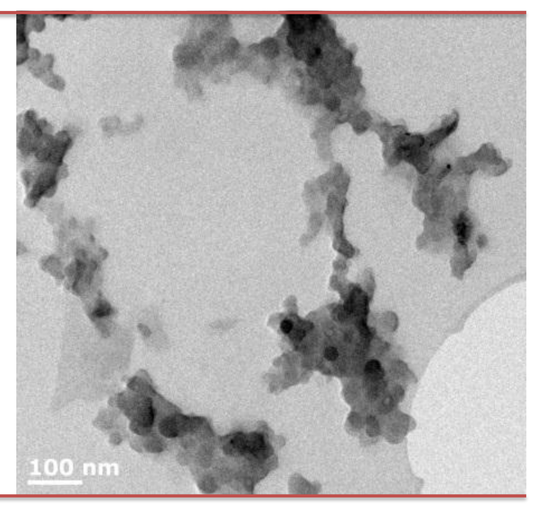
(I) Sample dilution

Does not alter agglomerate size
Gives sufficient separation of oil
Allows conventional TEM analysis



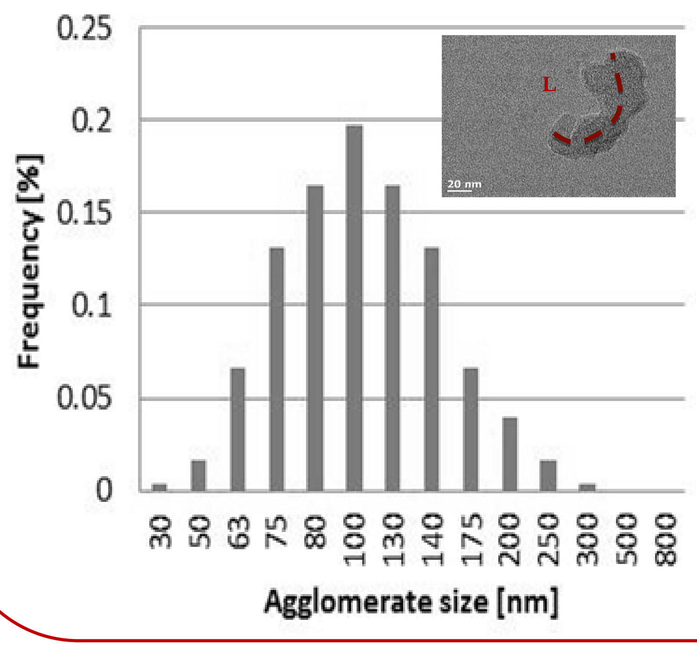
(II) Centrifugation

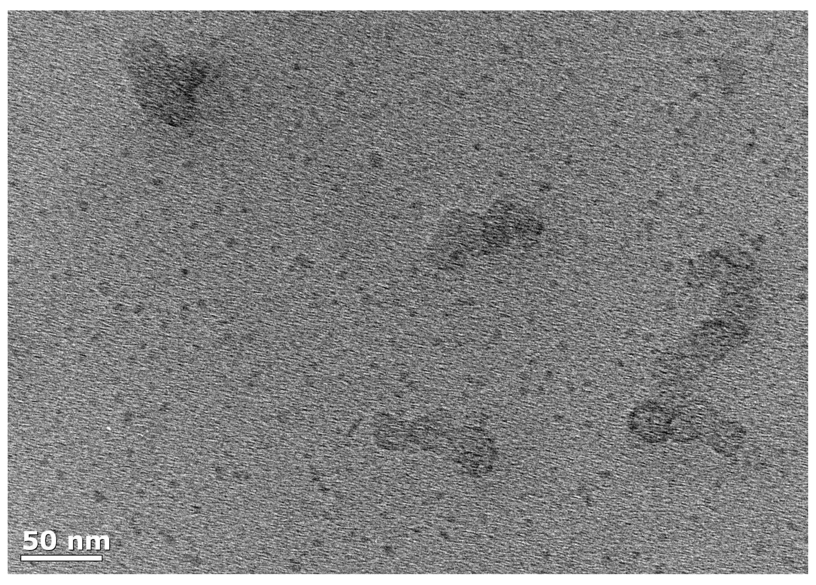
Causes particle agglomeration
Reduces oil contamination
Allows high resolution TEM



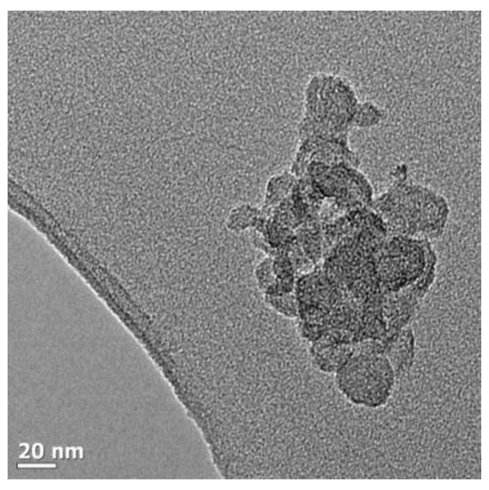
4. Results: Soot agglomerates have a modest branched morphology, and exist in clusters and chainlike structures. Soot-in-oil agglomerates not subjected to centrifugation, have a modest branched morphology with average length of 100nm and are composed of spherical primary particles of 12-40nm. Exhaust soot shows smaller primary particles with outer shell almost completely oxidised.

Soot-in-oil agglomerates - (I)

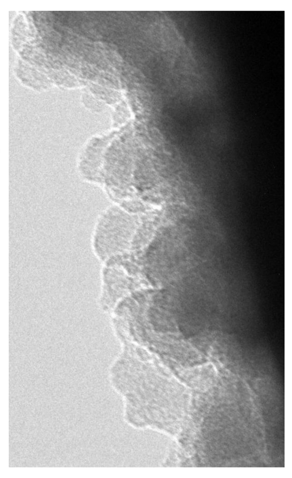




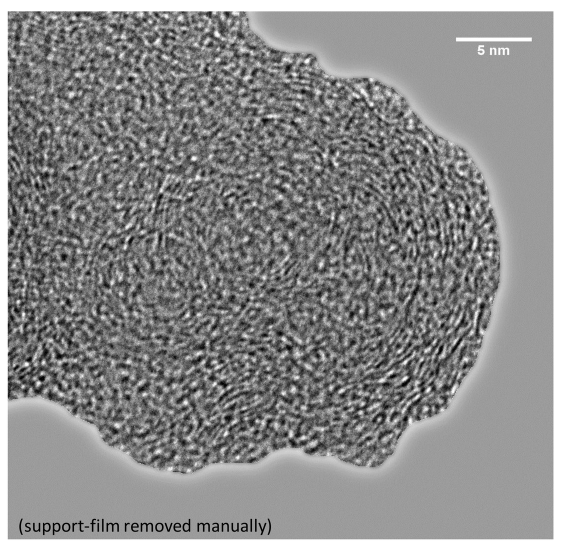
Exhaust soot agglomerates - (I)



The irregular shapes of the agglomerates are typical of exhaust soot shapes where branched morphology is predominant



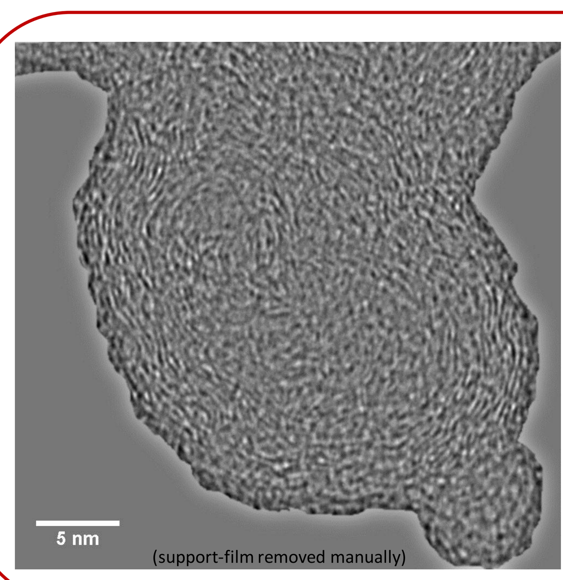
Full exhaust soot agglomerate characterisation to be completed



Soot-in-oil primary particle - (II)

Diameter 25nm. Outer shell 6.5nm

The classic core shell structure is clearly visible in all particles from soot in oil samples



Exhaust primary particle - (II)

Diameter D=22nm. Outer shell 3.8nm

The exhaust soot primary particles exhibit a primary particle size of 5-28nm with an outer shell of 0-4nm.

If present, primary particles' nanostructure of outer shell from both soot samples is not significantly different; tortuous graphene segments constitute the outer shell and look comparable to naked eye.

5. Conclusions

Centrifugation is not necessary for TEM studies of agglomerate characteristics, but essential in the preparation of samples for HRTEM. It modifies the distribution of size and shape of soot agglomerates but not the primary particles. Soot-in-oil agglomerates shows modest branching and largest size smaller than the 300nm with spherical primary particles of 12-40nm. Exhaust primary particles are generally smaller (<30nm), with outer shell partially or completely oxidised (0-4nm) .

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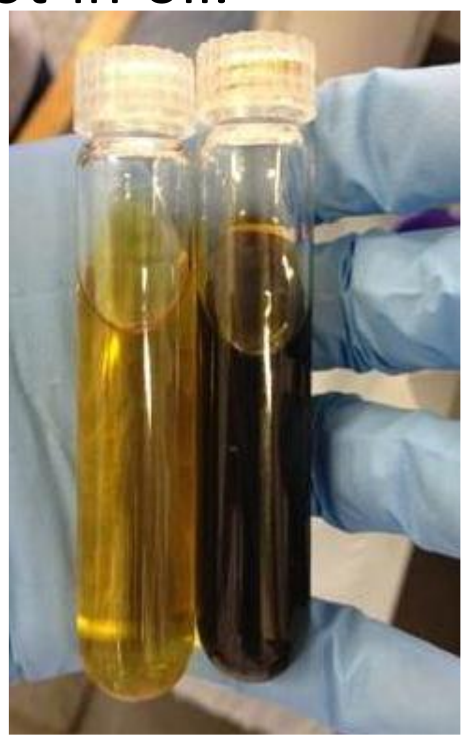

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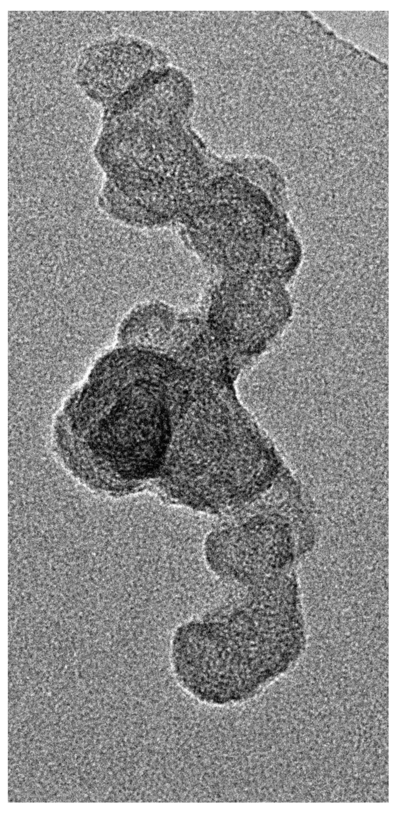

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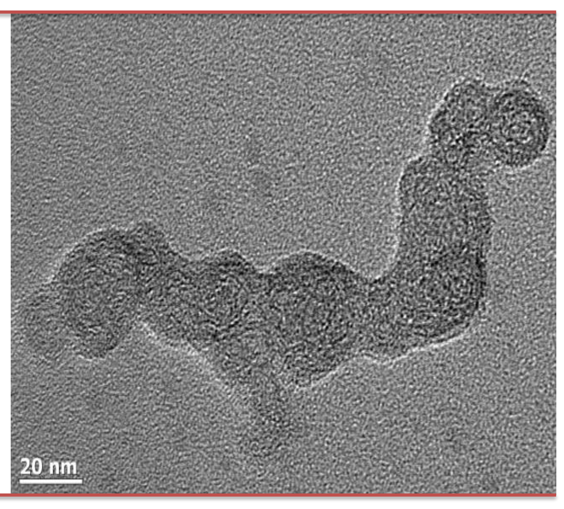

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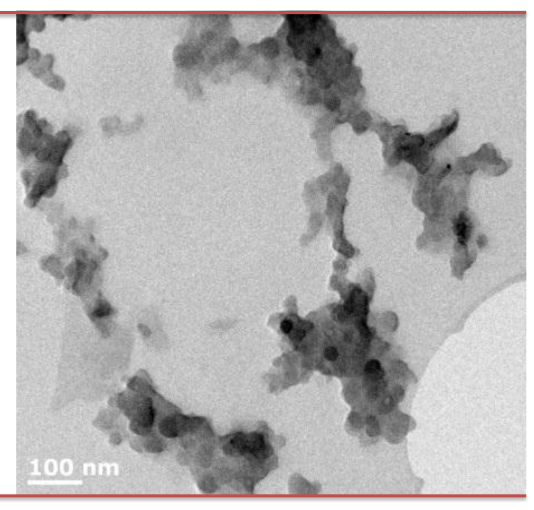

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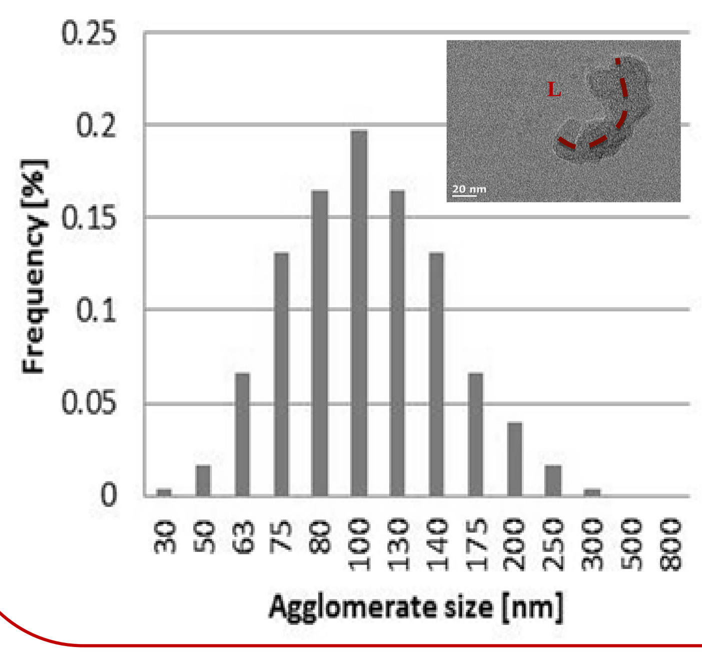

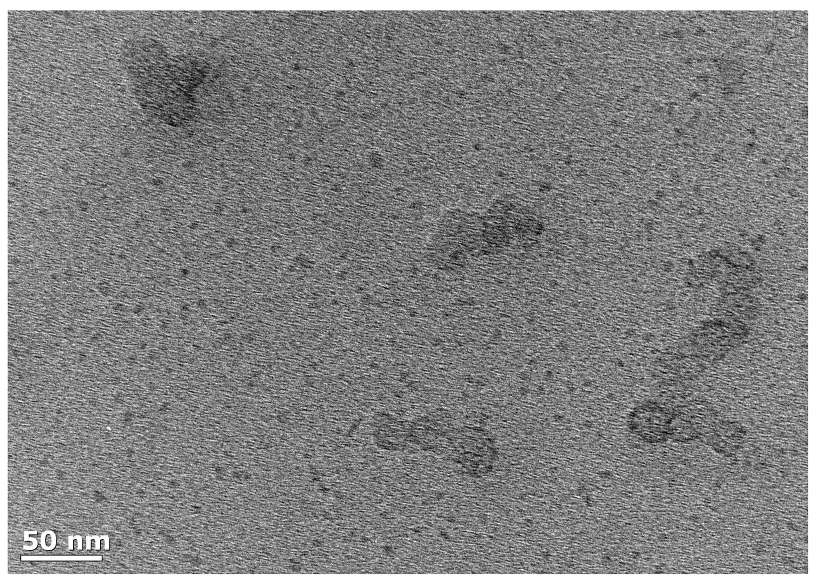

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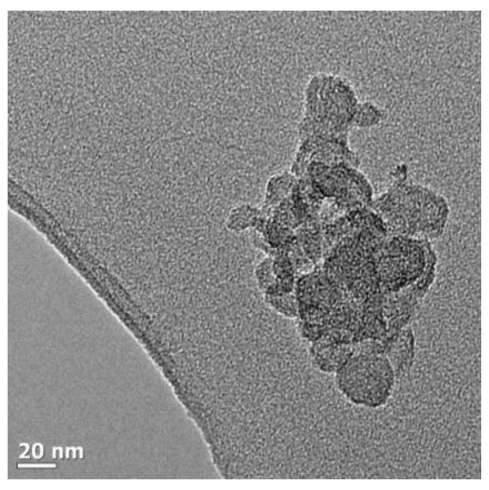

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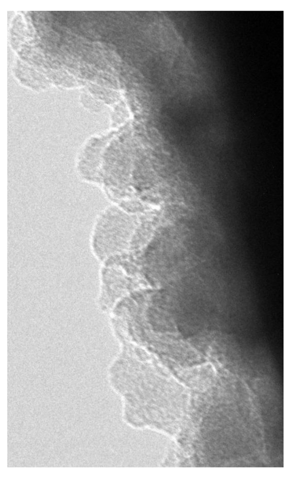

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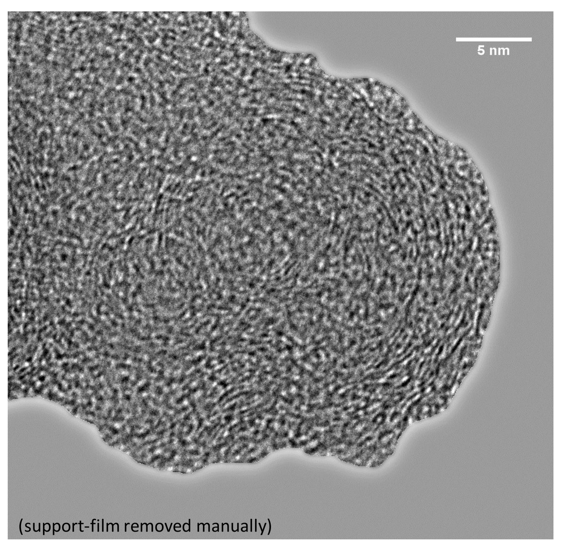

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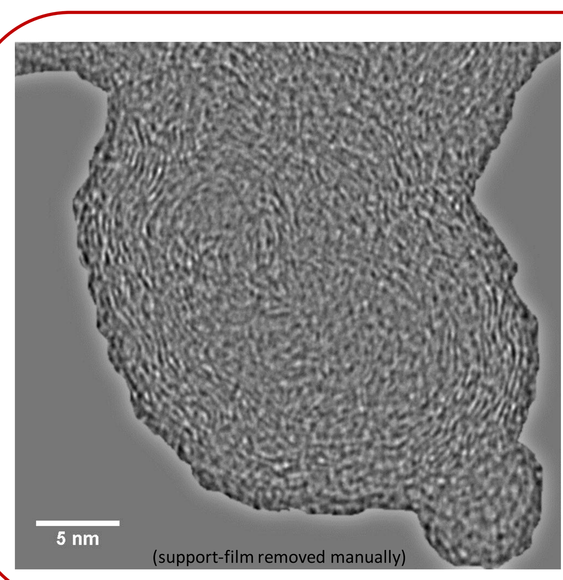

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