Structure - Reactivity Investigations on Diesel Engine Soot

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The investigation of bulk and surface properties of soot and carbon black is important in order to understand their overall behaviour towards oxidation. The fundamental processes of soot oxidation have to be investigated to design continuously regenerating particulate traps of Diesel engines. Studies have already been conducted, most of them on soot and carbon black oxidation did not attempt a detailed investigation of the microstructure or general morphology. Many studies have ignored the fact that several structural types of carbon have been used as model substances in oxidation, reactivity or atmospheric studies including flame soot, carbon black, and amorphous carbon, reflecting the common opinion (or assumption) that the structure of soot particles differs little even if they stem from various sources or are prepared under different synthesis conditions.

We present the application of high-resolution transmission electron microscopy to study the microstructure of Diesel engine soot, spark discharge soot, black smoke soot and carbon black samples. The heavy duty Diesel engine soot nanoparticles that are generated in a low-emission Diesel engine indicate a change in the formation mechanism of the soot. The soot nanoparticles are defective, functionalized and highly reactive. Soot particles from Diesel engines emitting black smoke present in contrast to the low emitting Diesel engine, the typical and well known core-shell morphology. Measurements conducted with electron energy loss spectrometry indicate a high graphitisation in the case of the black smoke soot as well as in the case of the carbon black and a lower graphitisation in the case of the low emission Diesel soot and spark discharge soot.

To further correlate the structure with the reactivity towards oxygen, functional groups and nanostructure of the carbon samples were investigated with thermogravimetry, diffuse reflectance infrared fourier transform spectroscopy and X-ray photoelectron spectroscopy. When comparing soot from a heavy duty Diesel engine, soot from a Diesel engine in black smoking conditions, spark discharge soot, and the furnace carbon black it is found, that the amount of defects plays, as well as the functionalization, an important role in the onset of combustion in the TG/TPO experiments. Clear differences in reactivity towards oxidation are observed. The combustion starts at 150 °C for the spark discharge soot, for the low emission Diesel engine soot at 380 °C, for the black smoke soot at 500 °C, for the carbon black at 550 °C. The burnout temperature, where the oxidation is completed is for the spark discharge soot at 620 °C, for the low emission Diesel engine at 590 °C, for the black smoke soot and the industrial carbon black at 690 °C. Apparently, the defective carbons oxidise faster than well graphitised soot samples. This can be correlated with the microstructure, as already described, and the functionalization of the soot materials. The XPS measurements reveal a high functionalization with oxygen and hydrogen in the case of the spark discharge soot and the low emission Diesel engine soot, in contrast to the black smoke soot and the carbon black.

The fact that soot from modern low emission Diesel engines is more easily oxidised, might give new impulses for exhaust treatment technologies. One has also to be aware that model soot substances have to be carefully chosen and investigated for any future development. These findings may have consequences for health risk assessment and for future exhaust treatment systems.

The internal reduction of soot particle emission may not be automatically beneficial for environmental protection and for reducing the epidemiological effect on human health. The advancement of technology in engine management carries new risks, as the soot becomes biologically accessible with a large amount of functional groups on defective sites of the rough soot particle surface.

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In this presentation ...

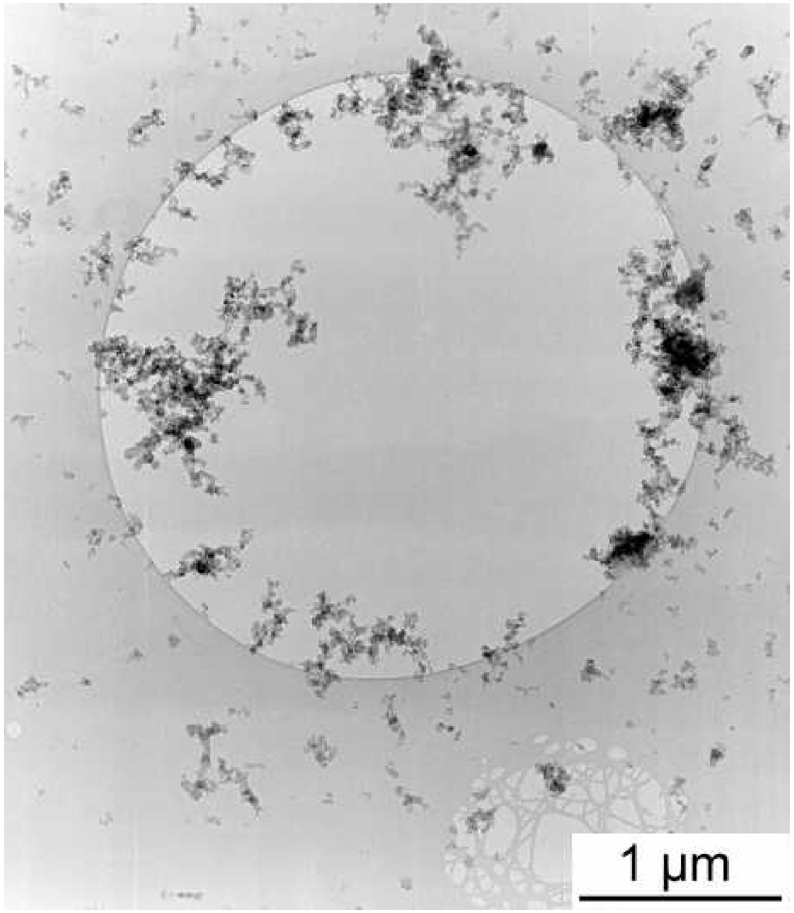
- Investigatons

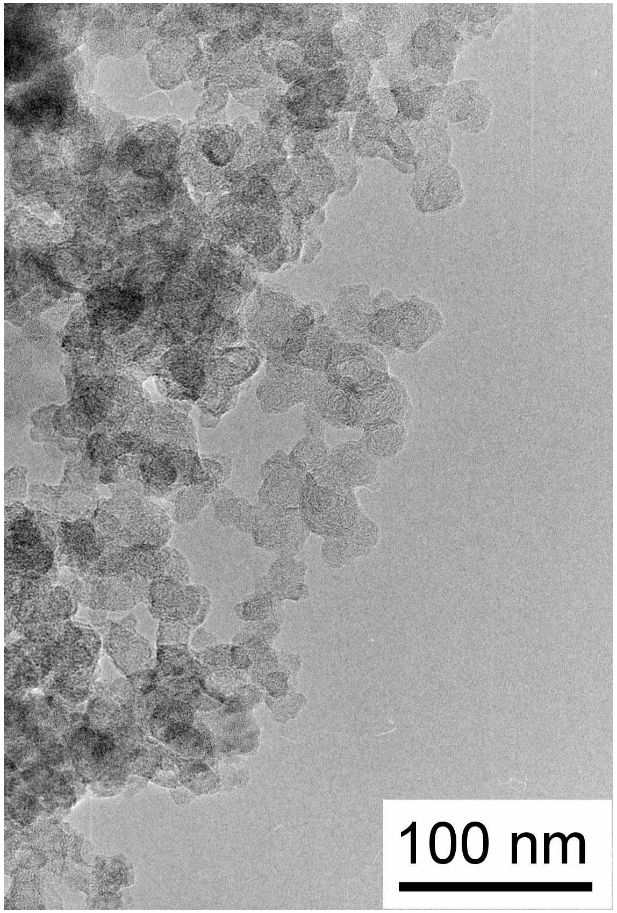
- Soot
- Carbon Black

- Morphology TEM / HRTEM
- Functional Groups XPS
- Reactivity TG / TPO

- Summary

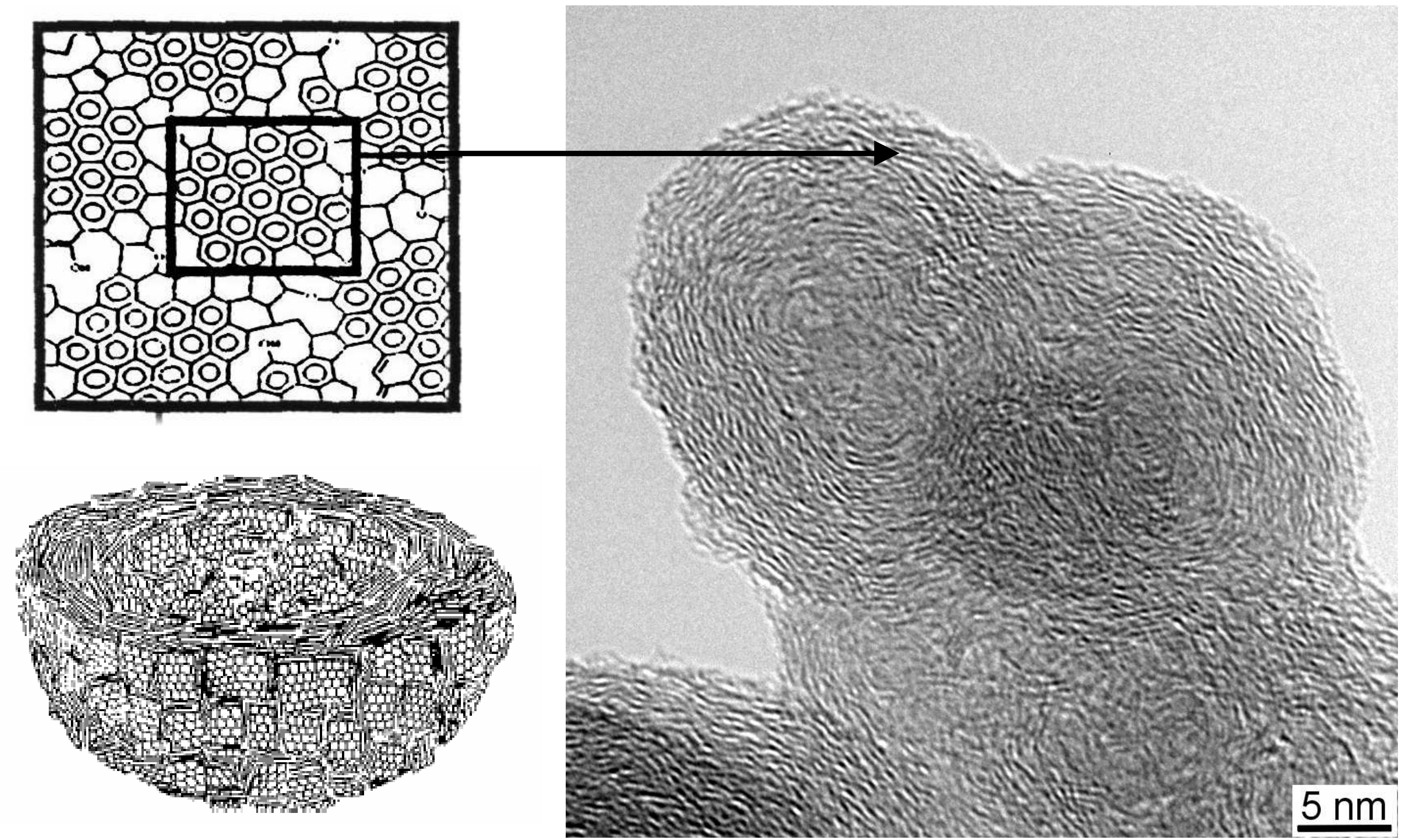
Diesel Engine Soot



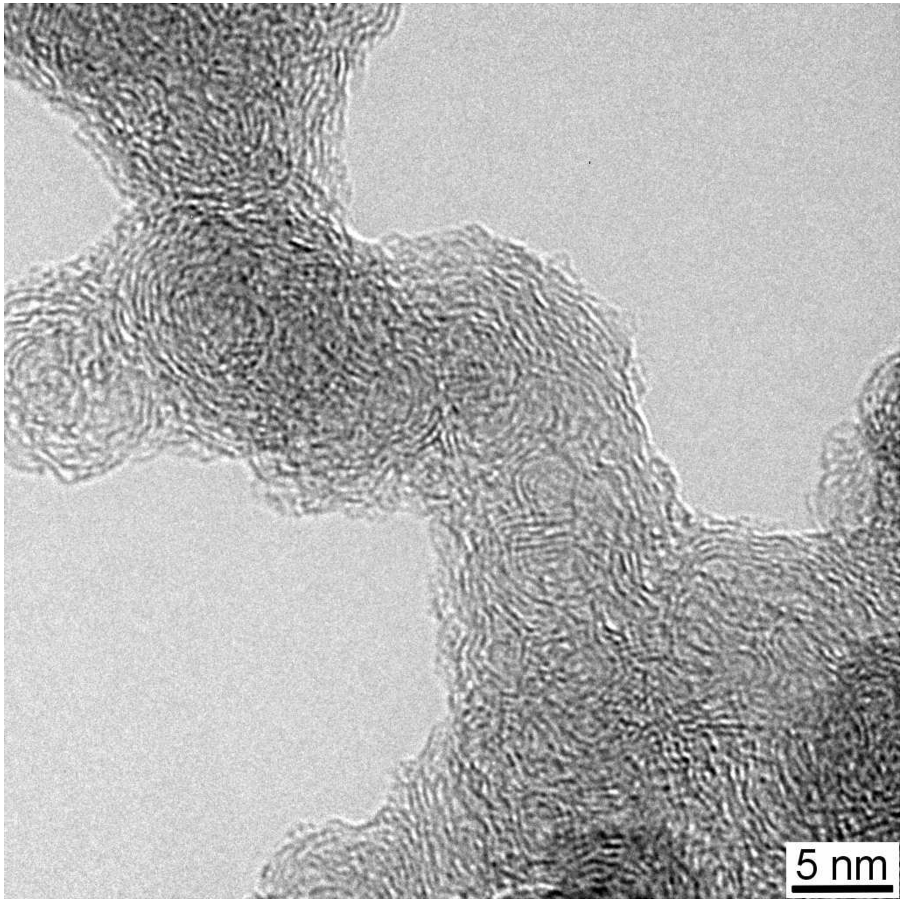


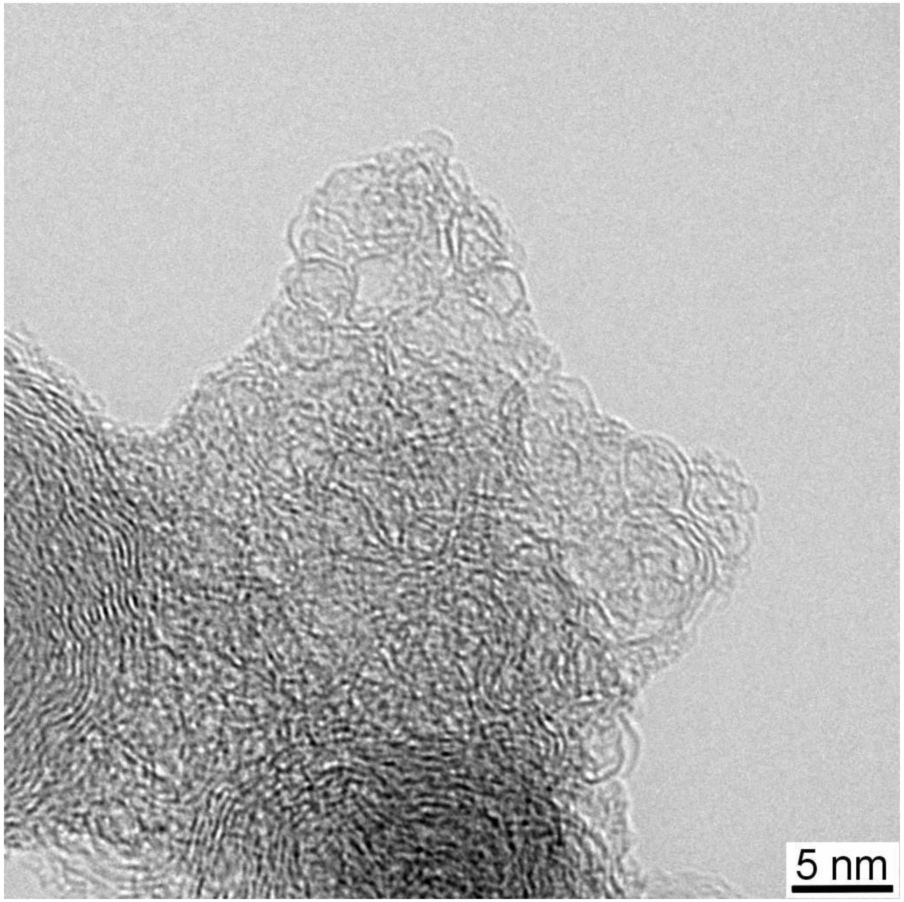
Soot directly collected from the exhaust stream of the diesel engine.

Soot: General Microstructure



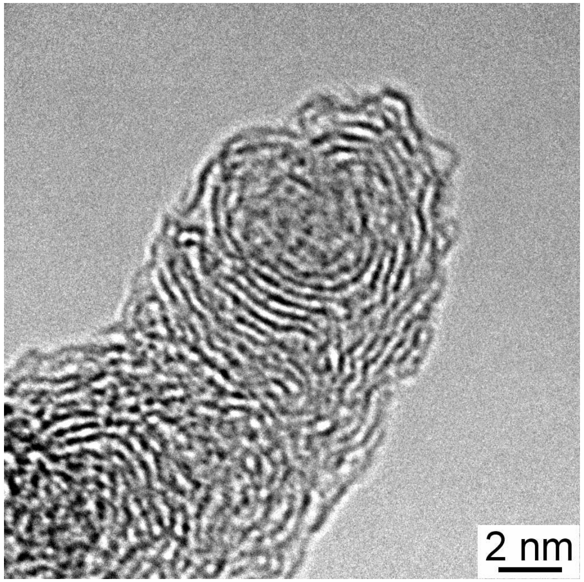
Euro IV Heavy Duty Diesel Engine Soot

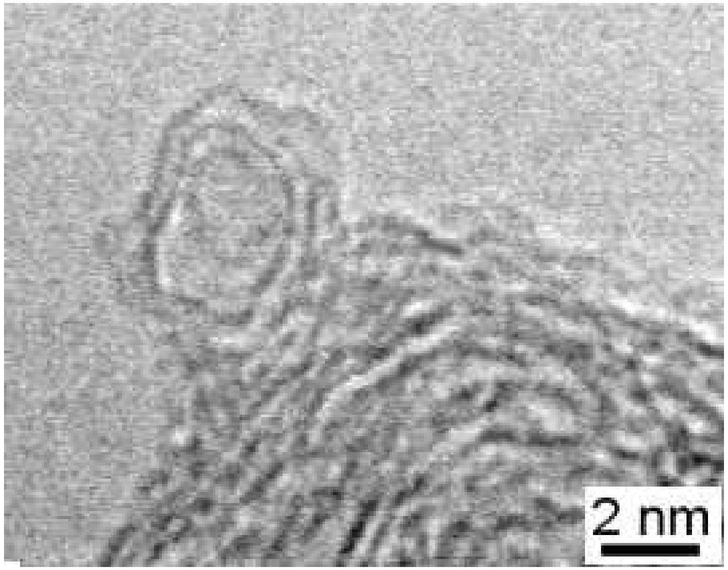


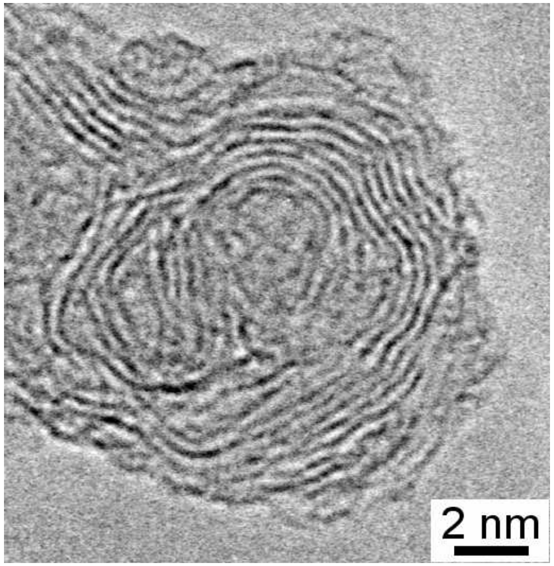


Soot from heavy duty diesel engine set to fulfil Euro IV conditions

Fullerenoid Soot



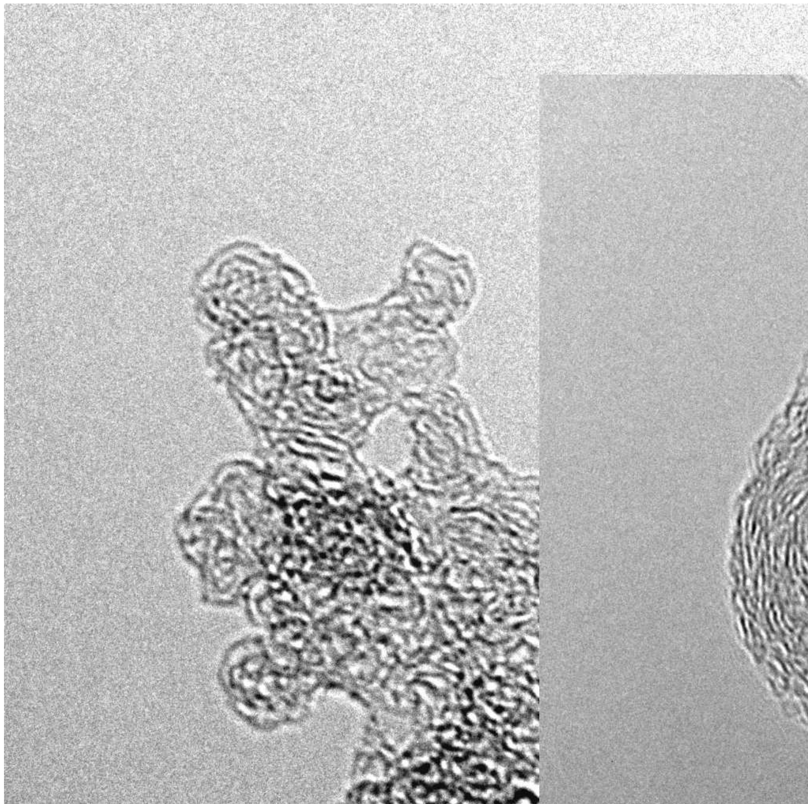




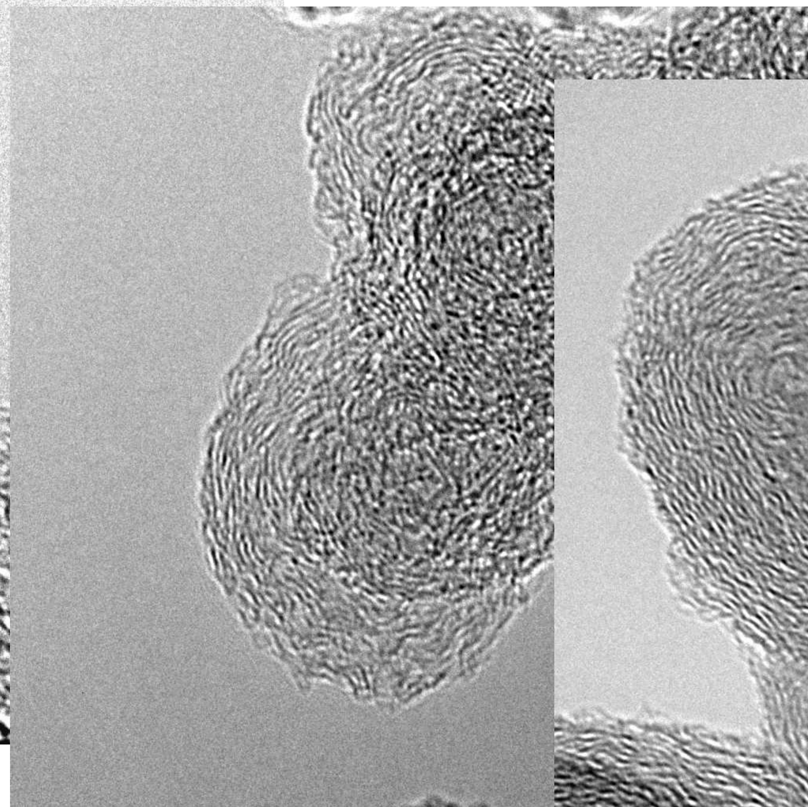
Primary particles with very strong bent graphene layers. The particles are bound to large agglomerates by sharing graphitic layers.

The fullerenoid structures are found on the surface of primary particles

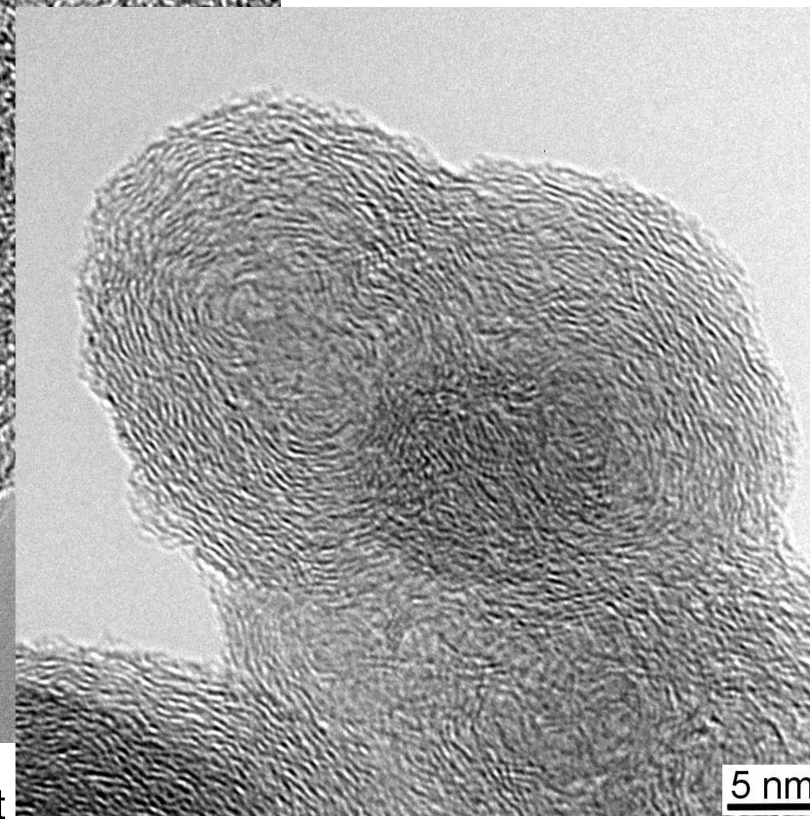
Carbonaceous Materials



GfG Soot



Furnace Soot



Black Smoke

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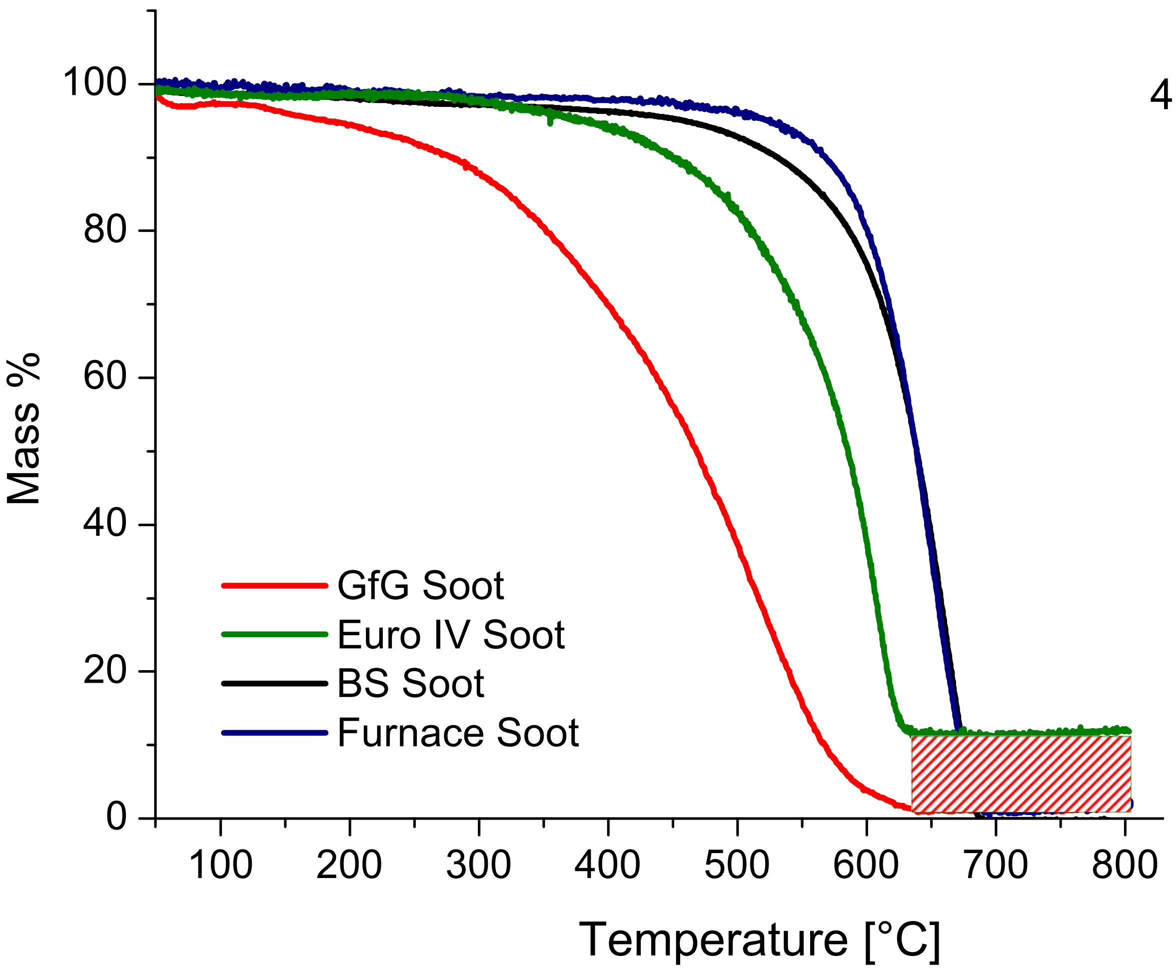
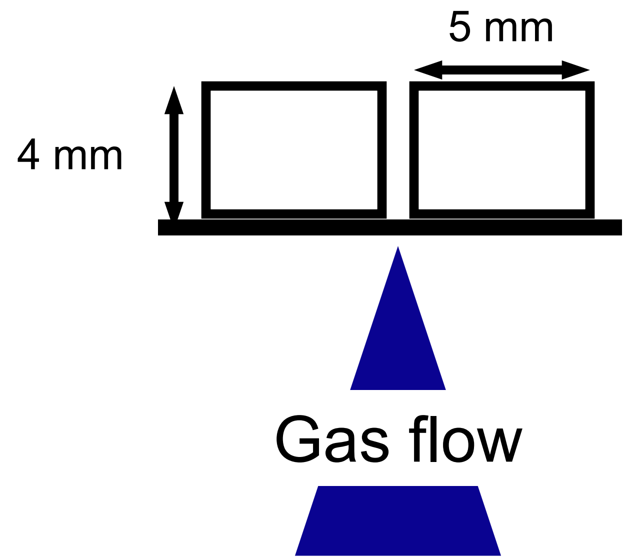
TG / TPO



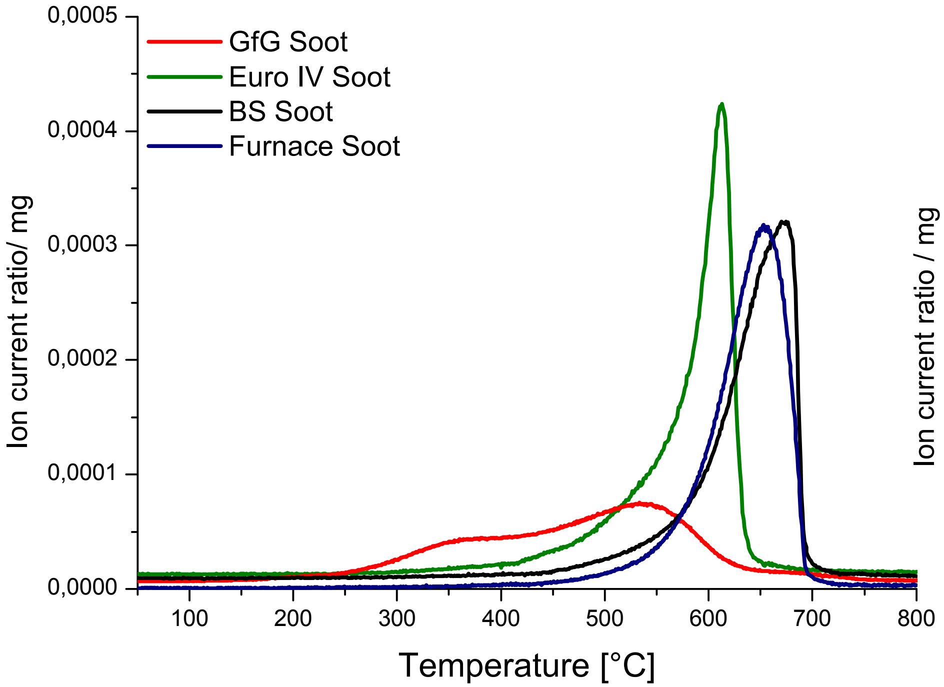


TG-DTA/DSC setup:

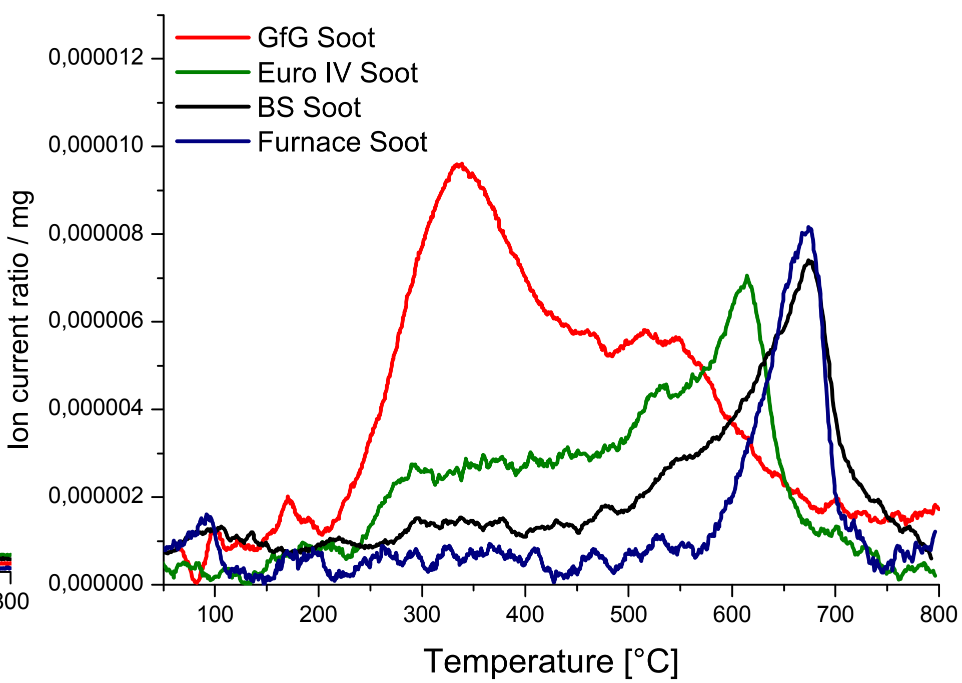
- Al_2O_3 crucibles
- 5% O_2 in N_2
- 100 ml/min / 1bar
- Sample load: 1-2 mg

TG / TPO

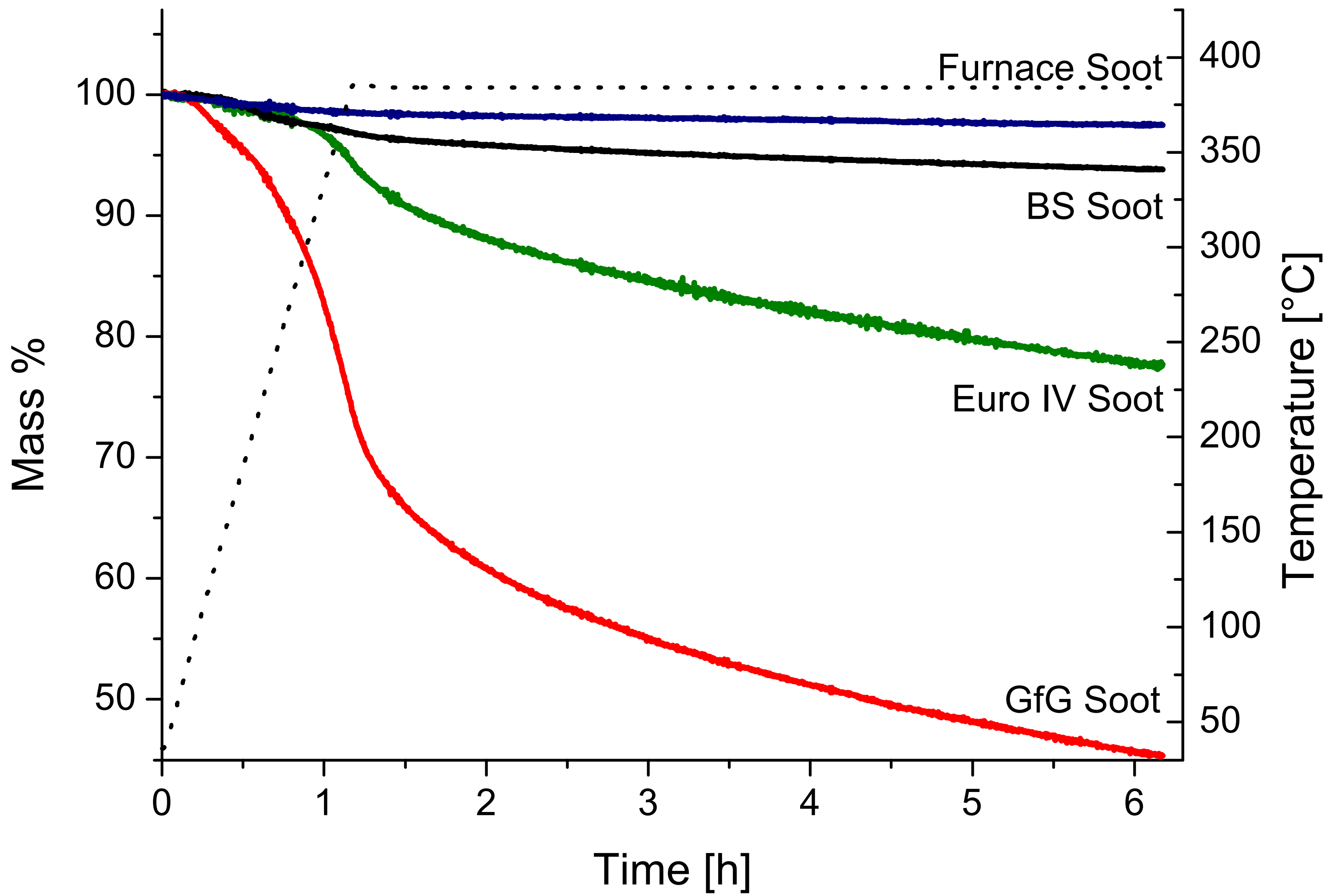
CO_2 m/e = 44



H_2O m/e = 18



TG: Isothermal Experiments



Summary

- TEM and HRTEM reveals differences in soot morphology
- Soot formation in the diesel engine. Soot microstructure (and reactivity) dependent on formation
- Microstructure induced functionalization (XPS)
- Microstructure induced reactivity (TG / TPO)
- Reactivity of soot reflects dimensions of graphene segments and degree of curvature. Larger graphenes possess relatively fewer edge site carbon atoms relative to those within basal plane positions. Superimposed on this is a distribution of curvature.

Acknowledgements

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