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Diesel Soot in the Electron Microscope

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Diesel engine soot, a fraction of particulate matter (PM), stems from the exhaust of diesel engines. As it can penetrate deep into the lungs of people exposed to this pollutant it causes severe health risks. Therefore, over the last decade, worldwide legislation has tightened emission limits of the engines. Whereas the current Euro III engine [1] may emit 100mg PM per kWh the Euro IV engine in 2005 is allowed only one fifth of the previous amount. But these are still macroscopic requirements. For an understanding of the soot production or better for it's reduction by chemical means the morphology and the microstructure of the particles must be studied. This is where the electron microscope comes in.

We start as reference with the soot we all hate bellowing black from a diesel exhaust, referred to as Black Smoke soot. In figure 1 we see relatively large primary particles whose size varies between 25 and 50 nm, exhibiting a typical core shell structure

In order to demonstrate the progress we show in fig.2 soot particles from the improved Euro IV engine. Here, primary particles, varying in size from 2 to 20 nm, agglomerate to irregular shapes without defined profiles; particles with multiple nuclei arise from strongly bent ribbons. Large nuclei allow for continuously bent structure units and even for flat sections of neighbouring structures. In short, the agglomerates gain stability by graphene-type dispersive interaction between the bent strands of the ribbons. The inset shows that the primary particles exhibit multiple-shell structures like fullerenes. The same fullerenic morphology occurs in soot produced in the laminar flame of a benzene/oxygen/argon - mixture.

The measures to improve the performance of commercial vehicles were successful in reducing the total mass emitted particles per kilowatt-hour.
But at the same time the measures produce very fine, mainly fullerene like soot and this changed the chemical reactivity: the old paradigm in electron microscopy- structure and function.

The fullerene-like soot may be the result of the optimised mixing behaviour of air and diesel fuel (air/fuel >1.3) in the combustion chamber. The optimised combustion process in Euro IV as compared to preceding diesel engines prevents the formation of precursor molecules necessary for the growth of conventional spherical soot particles. Our investigations reveal that through the measures taken to decrease soot emission, the new, low-emission Euro IV diesel engine tested in the present work produces carbon particulate consisting of fullerenic primary particles. The optimised combustion conditions prevent the formation of larger, more stable spherical soot particles. The size of the new soot particulate is smaller, and the size-distribution narrower than that of soot produced in the Black Smoke. The Euro IV engine soot exhibits a highly defective microstructure and is much more easily oxidised, making its elimination through engine-internal oxidation possible [2,3].

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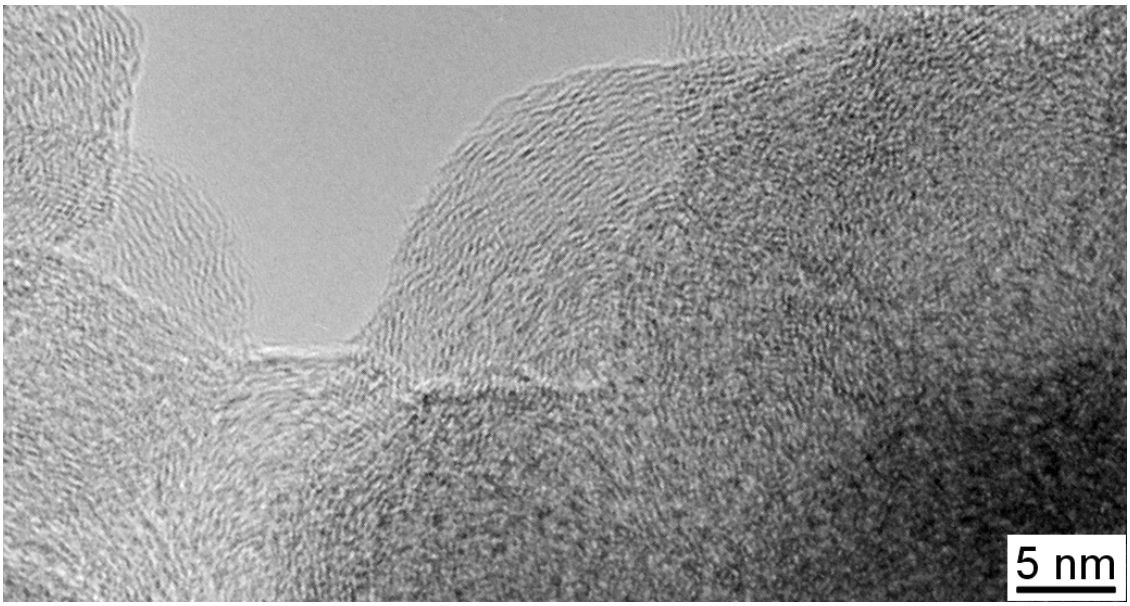

Figure 1: Black Smoke soot.

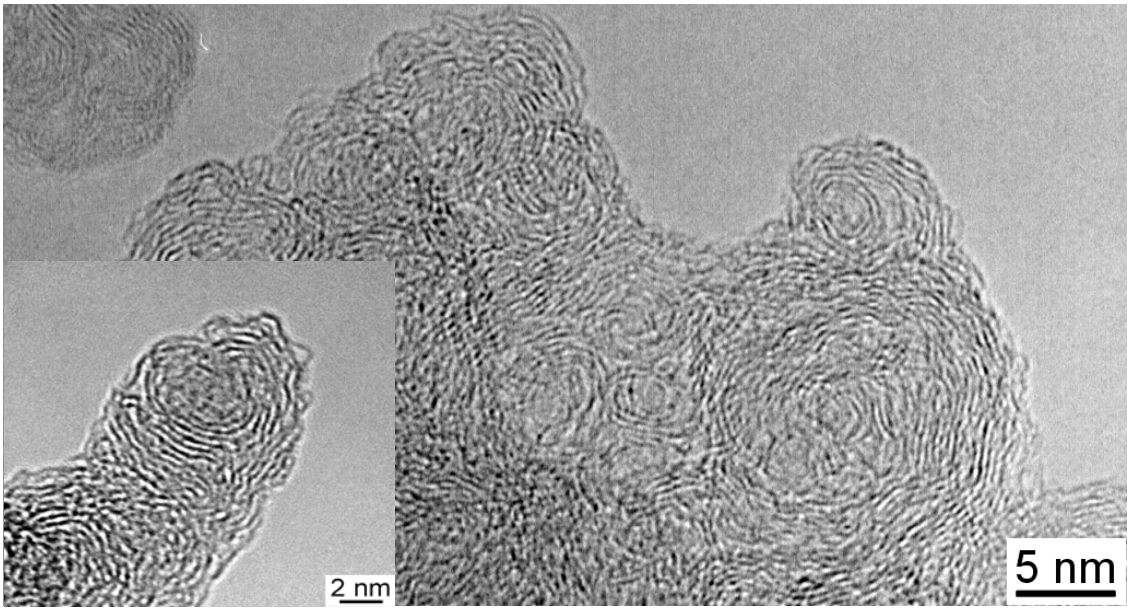

Figure. 2: Fullerene-like soot of Euro IV diesel engine.

Reference:

[1] http://www.dieselnet.com/standards
[2] D.S. Su, J.-O Müller, R. Jentoft, D. Rothe, E. Jacob, R. Schlögl, *Topics in Catalysis,* 30 (2004) 241
[3] D.S. Su, R.E. Jentoft, J.-O. Müller, C. Simpson, K. Müllen, A. Messerer, R. Nießner, R. Schlögl, *Catalysis Today*, 90 No. 1-2 (2004) 127
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