Combining HRTEM, EELS and RAMAN for determining structure and reactivity of Soot

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Keywords: Soot, EELS, graphitization, reactivity

Soot generated in the combustion process of Diesel engines is potentially harmful for the human body due to the risk of penetration into the lungs [1, 2]. Recent results [3] have shown that the harmfulness of soot is directly related with its nanostructure (defective sites, curvature and amount of oxygen). One way to face this problem is to address special posttreatment with the goal to trap or burning off the particulate before emitted to air. The aim of the work is to gain more insight in the reactivity of soot and establish a structure-reactivity correlation. In order to reach this goal it has been studied here how the nanostructure and electronic structure of the soot particle surface are modified by conditions present in the exhaust system (oxidation treatment with 5% oxygen in inert gas up to 500°C).

The nanostructure of Euro IV, Euro VI (generated under European Standard Emission Conditions) and GfG (spark discharge generator) soot have been investigated by means of EELS, HRTEM, electron diffraction and compared with other nanostructured carbon materials used as model system: HOPG as reference for 100 % sp^2 hybridized carbon and Furnace Black as reference for fullerene like structures.

The morphological analysis by TEM shows that in contrast to graphite samples, soot samples are characterized by a complex heterogeneous structure which includes graphitic and non-polar molecular carbon. HRTEM reveals that the samples contains beside of graphene BSUs that are build up by twisted ribbons with molecular units sitting on them (Figure 1).

Changes in the curvature due to the oxidation process are summarized in the table reported in Figure 2 for GfG, Euro IV and Euro VI. The GfG sample shows the highest bending from all investigated samples. Due to the heat and oxidation treatment the curvature is flattening allowing to conclude about a better ordering and reduced reactivity. Euro IV and VI show higher values for the curvature, indicating weaker bending. The slightly higher bending for untreated and oxidized Euro VI compared to Euro IV suggest a higher defect density and higher functionalization in the Euro VI sample. The curvature of grapheme ribbons is an important indicator for its defect content as deviations from planarity are linked with vacancies that affect the reactivity. This was already theoretically [4] calculated and experimentally observed [5]

Information about the atomic structure of the samples are obtained by EELS measurements of the C K edge. Those measurements are performed using magic angle conditions to by-pass the dependence of the spectrum resonance (π^* and σ^*) on the relative orientation of incident electron beam/sample which occurs due to the anisotropy character of graphite and graphite-like materials. Figure 3a shows the changes in the sp^2/sp^3 ratio of the investigated samples during the oxidation treatment. For GfG a significant increase in sp^2 bonded carbon is observed due to oxidation while the same treatment leads to a less pronounced increase in the ratio of sp^2/sp^3 bonded carbon for both Euro IV and VI. These results correlate with Raman data (Figure 3b) and also with curvature measurement. Raman data in Figure 3b show a sharpening of the D and G band due to the oxidation for GfG which

W. Grogger, F. Hofer, P. Pölt (Eds.): MC2009, Vol. 3: Materials Science,
DOI: 10.3217/978-3-85125-062-6-570 , © Verlag der TU Graz 2009

is correlated with increase of structural order. For Euro IV and VI there is no significant change in the shape of D and G band visible indicating no or minor modifications in the structural order.

The results shown here lead to the conclusion that oxidation of soot occurs with a preferential oxidation of highly disordered carbons on the surface (molecular carbon). This results to an apparent increase in the overall structural order visualized by the increase of the sp^2/sp^3 ratio. This is also reflected in the changes of the curvature.

Combining this results with XPS/NEXAFS data of the oxygen functional groups present on the soot samples allows to determine the reactivity of those soot samples, as the functional groups present on the surface are linked with the curvature induced defective sites.

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The support for this work by DFG grant is kindly acknowledged.
MAN is kindly acknowledged for providing the Euro4/6 samples

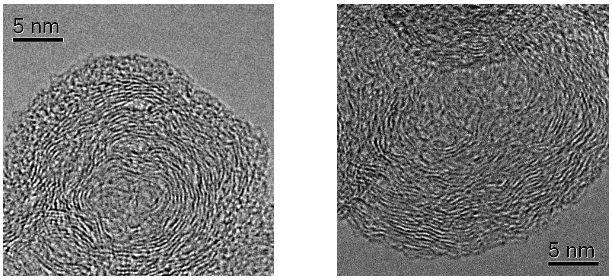

Figure 1. Left side: TEM micrographs of Euro IV showing a complex heterogeneous structure which includes graphitic and non-polar molecular parts (BSU); right side: molecular parts are removed after oxidation treatment

curvature [nm]	MV	STDEV
GfG RT	0.61	0.12
GfG 500℃	0.63	0.12
Euro IV RT	0.67	0.08
Euro IV 500℃	0.71	0.08
Euro VI RT	0.65	0.11
Euro VI 500℃	0.67	0.11

Figure 2. Statistical measurements of the curvature analysis for GfG, Euro IV and Euro VI before (RT) and after oxidation treatment (500°C)

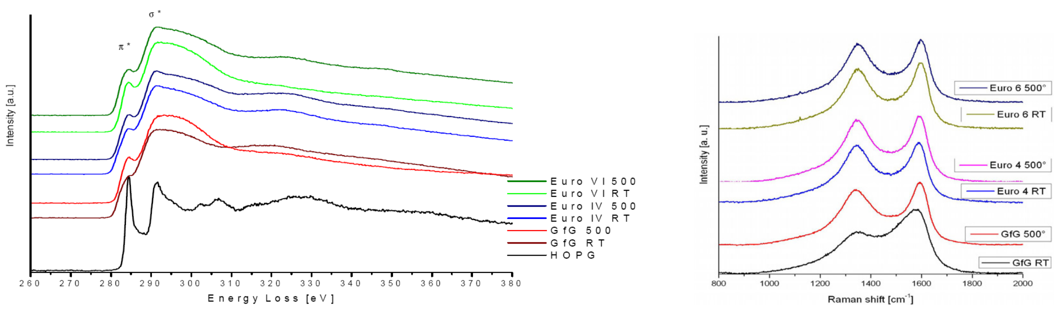

Figure 3. a) EELS C K-edge measurements under magic angle conditions reveal changes in sp^2/sp^3 hybridization due to oxidation and heat treatment; b) Raman spectroscopy data show also increase in the structural order

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