Structure and Cytotoxicity of Diesel Engine Soot Particulates

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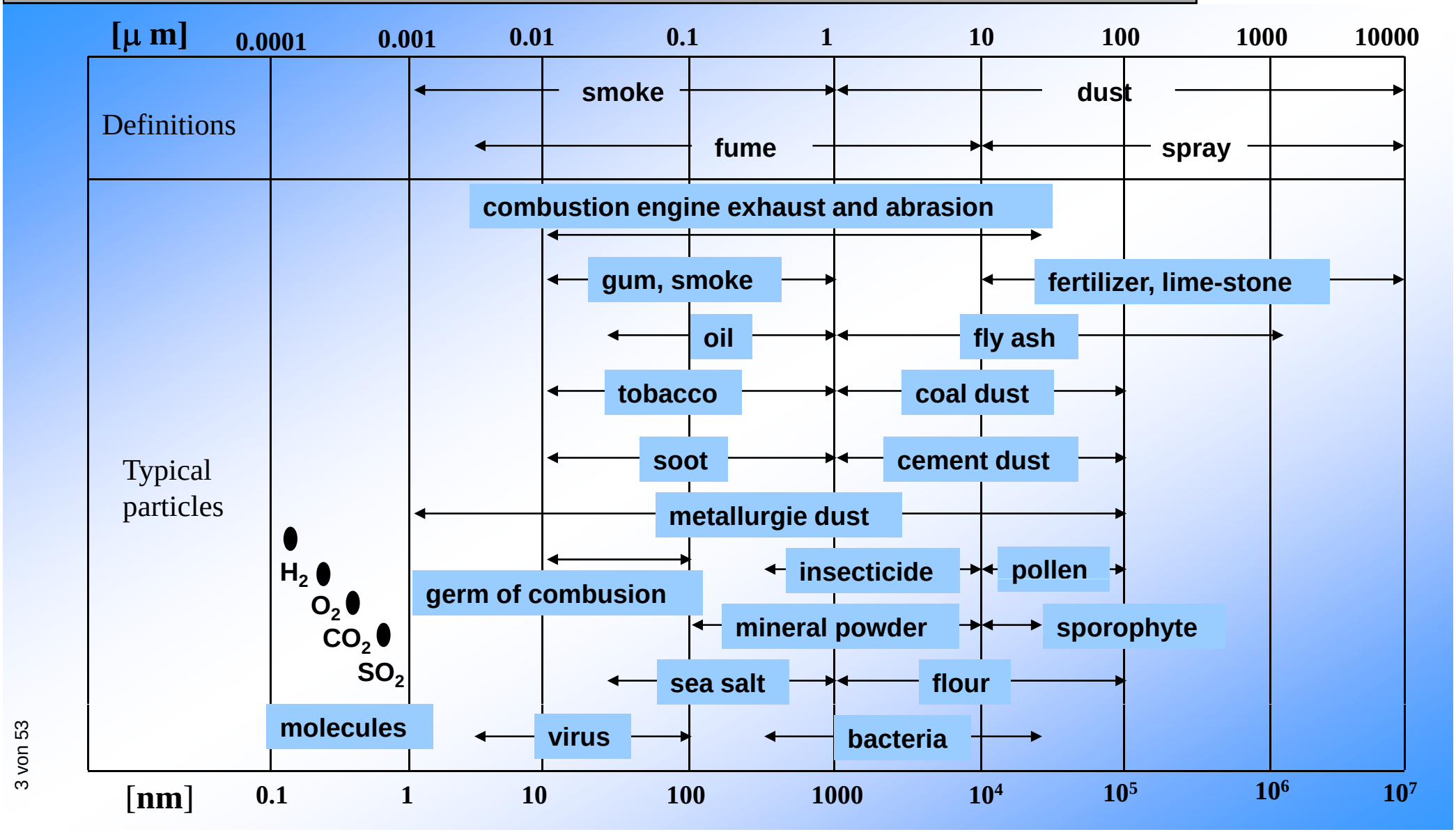
FHI der MPG

Outline

- Background
- Characteristic of Euro IV Diesel soot
- Reactivity of Euro IV Diesel soot
- Cytotoxic test
- Conclusion

Size of different particles



Defination

Soot (black carbon): **the mass of combusion-generated sp^2-bonded carbon.**

Organic carbon: **organic compounds or the carbon fraction of the aerosol that is not black.**

Diesel soot, a hot topic in envirenmental protection

MAX-PLANCK-GESELLSCHAFT

Greenpeace e.V. - 22745 Hamburg

Mit einfacher Technik gegen Dieselruß

Deutsche Autohersteller weigern sich,

Dieselautos von DaimlerChrysler, VW und anderen Autofirmen sind nicht mit Rußfiltern ausgerüstet, obwohl diese die Abgase zum Teil entgiften und die Men-

GEFAHRENQUELLE DIESEL

Rußpartikel lösen Mutationen aus

Forscher haben eine weitere Gefahr von Abgasen entdeckt: Mikro

tikel, die etwa von Dieselmotoren oder Stahlwerken in die Luft geb

Kampf gegen Diesel-Ruß:

Filter für alle Diesel-Fahrzeuge gefordert

Im Kampf gegen Gesundheitsschäden durch Diesel-Ruß hat ein breites Bündnis von Organisationen eine Filter-Pflicht für alle deutschen Diesel-Fahrzeuge gefordert.

Berlin (dpa) - Umweltverbände, Automobil- und Verkehrsclubs, Gesundheitsexperten und Kinderschutzorganisationen starteten am Montag in Berlin die Initiative «Kein Diesel ohne Filter». Ab Sommer 2003 dürften Diesel-Fahrzeuge grundsätzlich nur noch mit Rußfilter oder einer gleich wirksamen Technologie verkauft werden, verlangt die Allianz. Der Verband der Automobilindustrie (VDA) wies die Forderung zurück. Das Umweltministerium und die SPD-Fraktion begrüßten die Initiative.

Die Gruppen richteten schwere Vorwürfe gegen deutsche Automobilfirmen. Sie verweigerten anders als französische und italienische Autobauer die Einführung der Filter. Nach Schätzungen würden Rußfilter Diesel-Neuwagen um je 300 Euro ver-

Berliner Zeitung · Nummer 168 · Dienstag, 22. Juli 2003

Wissenschaft

Der Tod aus dem Auspuff

Kleinste Rußpartikel aus Dieselabgasen fordern jedes Jahr Tausende von Opfern

28.02.2003

Umwelt

Paris und Berlin ergreifen Initiative gegen Dieselruß

POTSDAM, 27. Februar (ap). Deutschland und Frankreich haben die EU-Kommission zur weiteren Verschärfung der ab 2005 geltenden Abgasverordnung aufgefordert. Die Luftverschmutzung durch Ruß und Stickstoff aus Dieselmotoren könne nach dem jetzigen Technikstand um 99

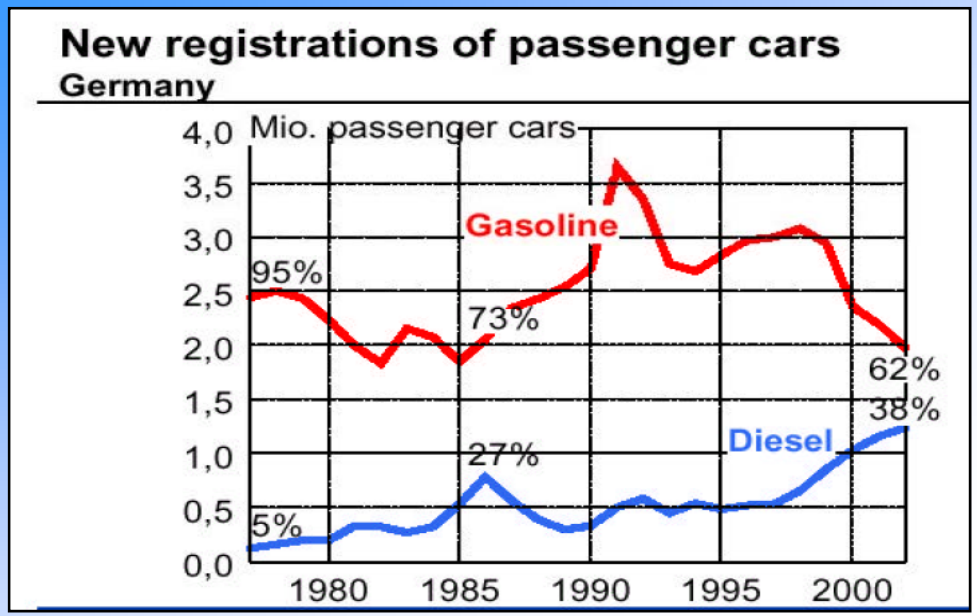
Die strenger
den technische
gelten. Sonst w
gesundheitsgef
derzeitigem W
res bis 2020 au
erklärte Trittin
für 2005 gepla
ro 4"-Norm im

EU verbietet Berliner Luft

Überhöhte Feinstaub-Konzentration in Souvenir-Dosen nachgewies
Umweltkommissar setzt Frist bis Jahresende

Berliner Luft in Dosen – ein beliebtes Reisemitbringsel für Touristen aus al
Doch nach dem Willen der EU wird es sie bald nicht mehr geben, sofern es d
nicht gelingt, die Luft in der Stadt generell von gefährlichen Feinstä
Dieselmotoren zu befreien. Dies geht aus einem Brief hervor,
Senatsumweltverwaltung jetzt aus dem Büro von EU-Umweltkommissar
Dimas erhalten hat. Es heißt darin, bei einer Stichprobe seien jetzt in mel
Prozent der überprüften Dosen diese Feinstäube in überhöhter Konz
festgestellt worden. Falls es der Verwaltung nicht gelingt, die Berliner Luft n
zu säubern, muss das Produkt bis zum Jahresende vom Markt genommen und unter
Aufsicht von Experten entsorgt werden.

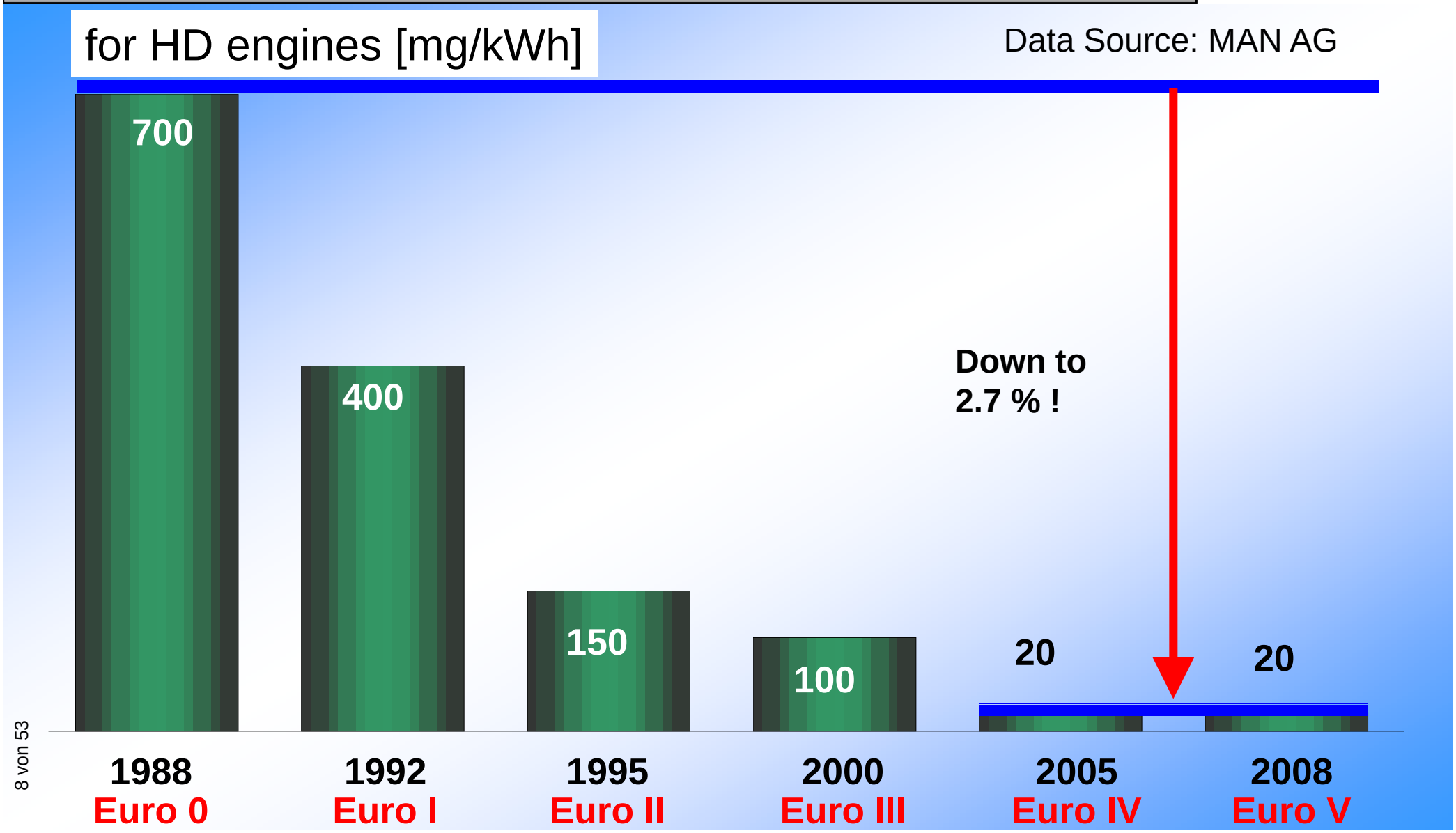
Automobile with Diesel engine



Diesel particulate standards of the European Union

Engine type	Light-duty diesel vehicle				Heavy-duty diesel vehicle	
Test cycle	ECE-15 + EUDC				ECE R-49 13 mode	
Unit of standard	g km^{-1}				g per kWh	
	Particulate standard		($HC + NO_x$) standard		Particulate standard	NO_x standard
	DI	IDI	DI	IDI		
1993(Euro-I)	0.19	0.14	1.36	0.97	0.36	9.0
1994(Euro-I)	0.14	0.14	0.97	0.97		
1996(Euro-II)	0.10	0.08	0.9	0.7	0.15	7.0
1999(Euro-III)	0.04	0.04	0.5	0.5	0.12	5.0
2004(Euro-IV)	0.025		0.025		0.02	3.5
2008(Euro-V)	0.025		0.025		0.02	2.0

Particle Emission of Commercial Vehicles: Delevepment of the standard 1988-2008



Reduction of emissions

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Changes in fuel: Alcohols;
Compressed natural gas
Vegetable oils (rapeseed, sunflower, soya bean)

Engine modification: Optimization of the combustion chamber geometry
Injection timing
High injection pressures
Turbocharging

After-treatment: Removal of NOx (selective catalytic reduction)
Removal of particulates
Paticulate traps (wall flow monolith)

Low Emission Diesel Engine

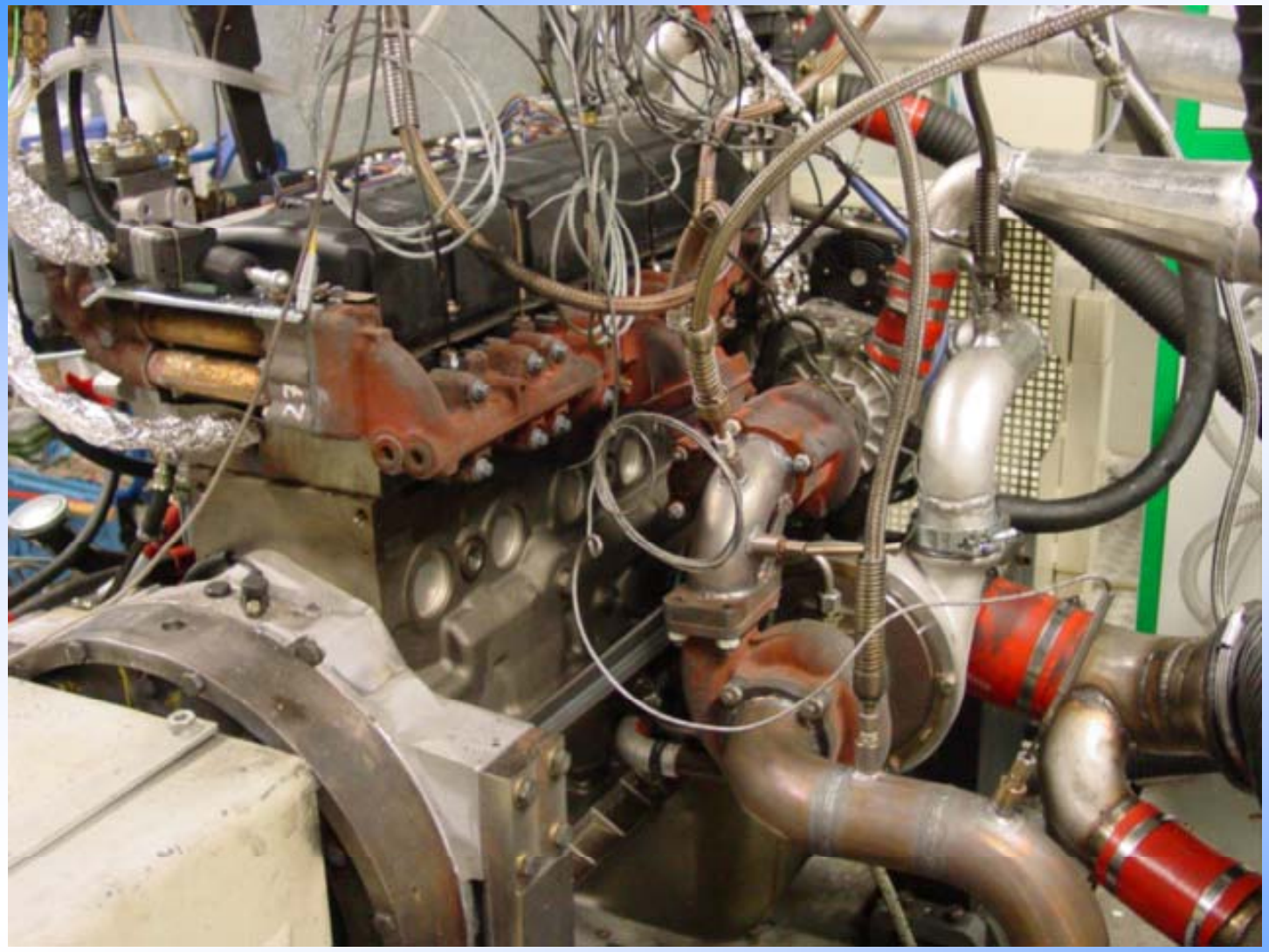
MAX-PLANCK-GESELLSCHAFT

1: Is the soot particulate produced under optimized fuel combustion conditions different from that produced in older engines ?

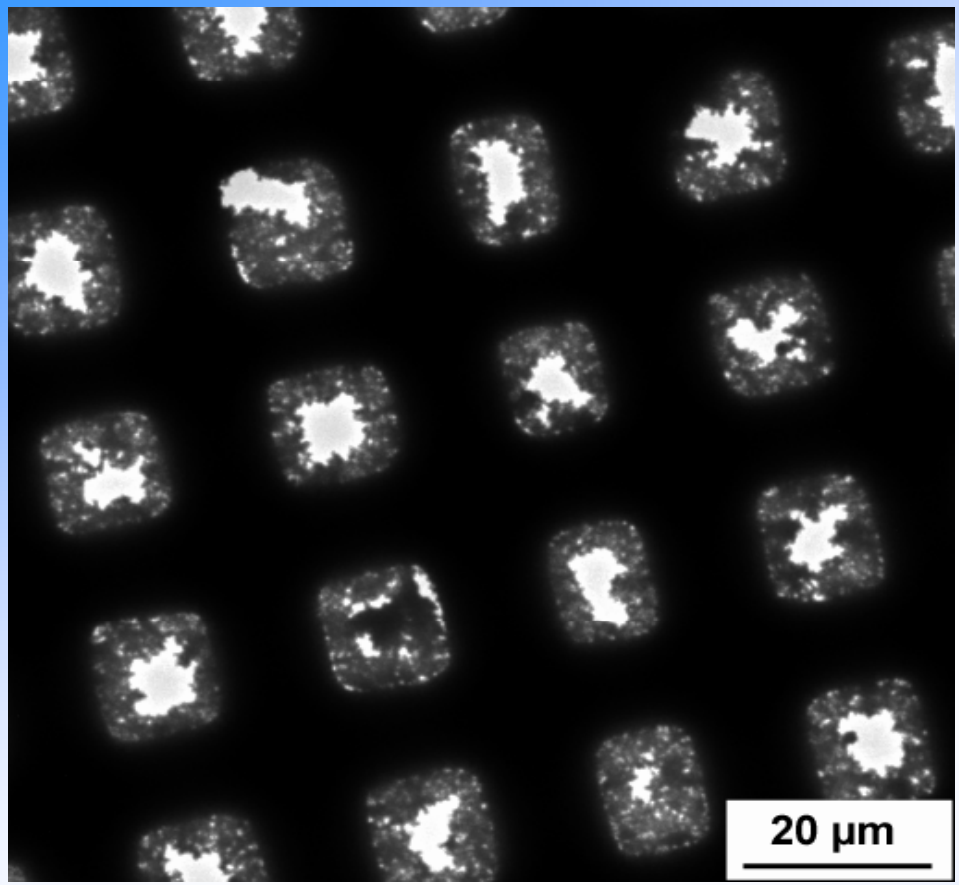
2: What is the chemical reactivity of Euro IV engine soot ?

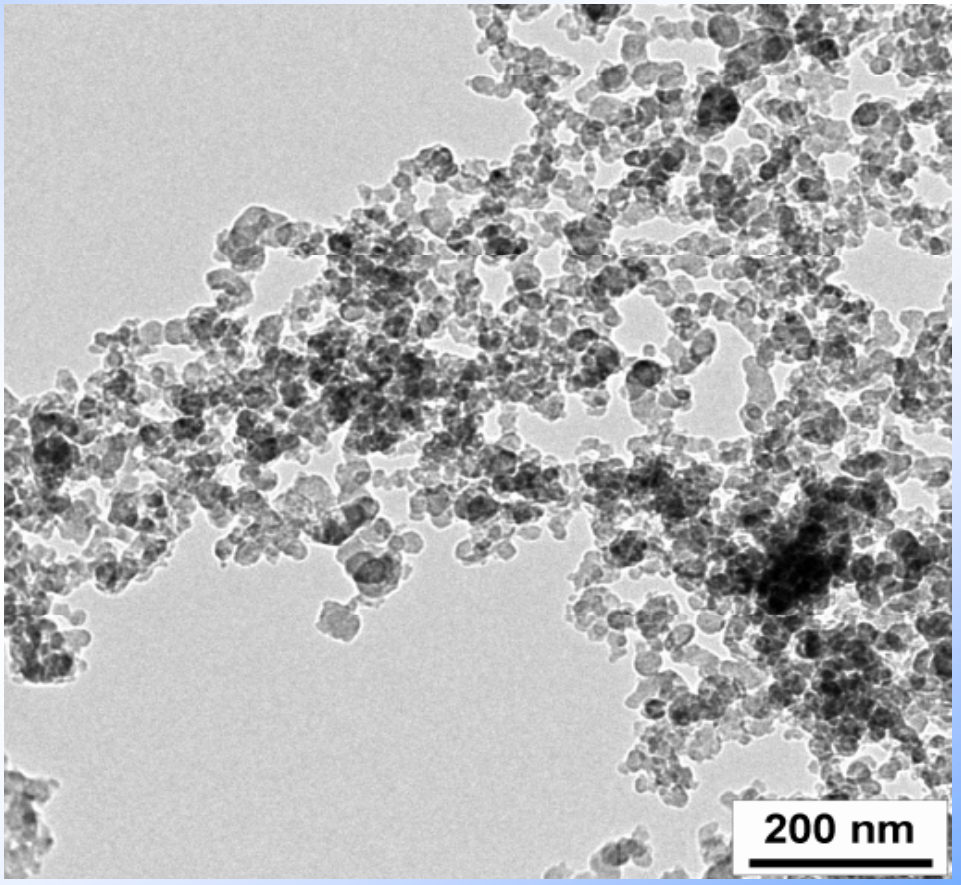
3: Does the Euro IV engine soot pose the same health risk as soot emitted from older diesel engines ?

EURO –IV Diesel Engine



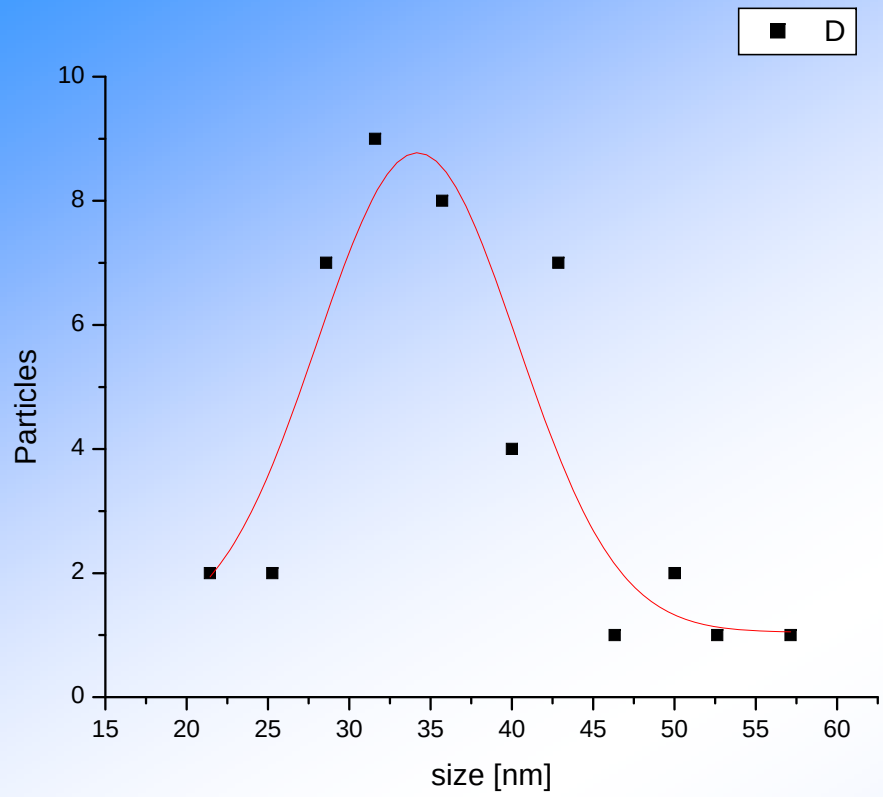
Euro IV Soot collected for TEM

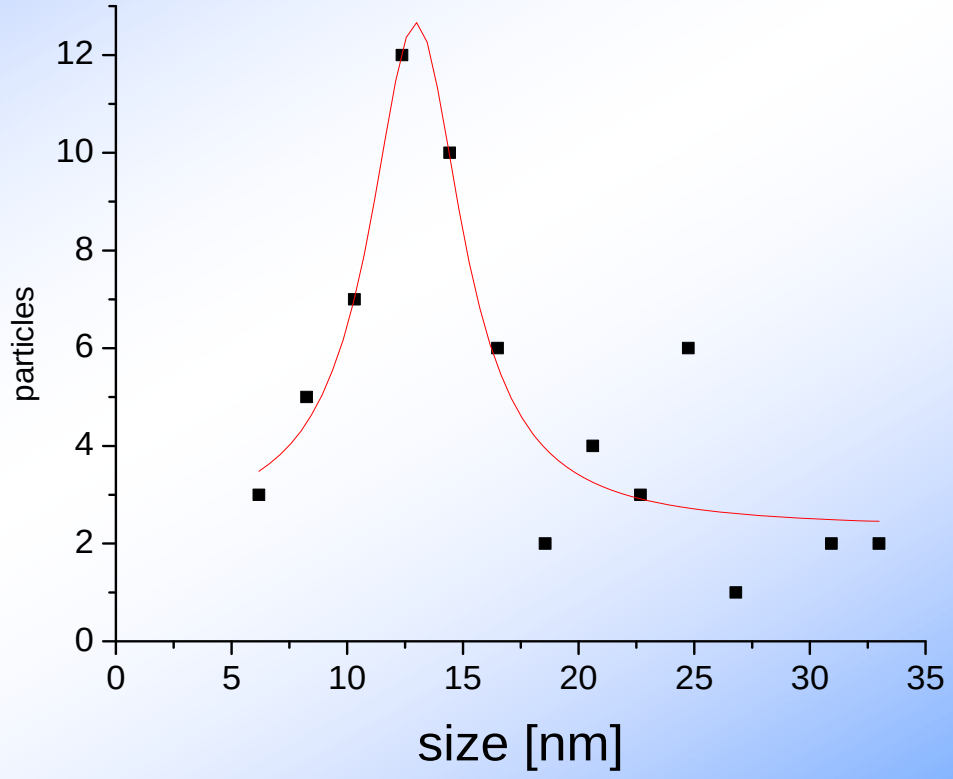




Soot collected on 1000 mesh Cu-Grid without any supporting carbon film.

Size-distribution of Soot Particles

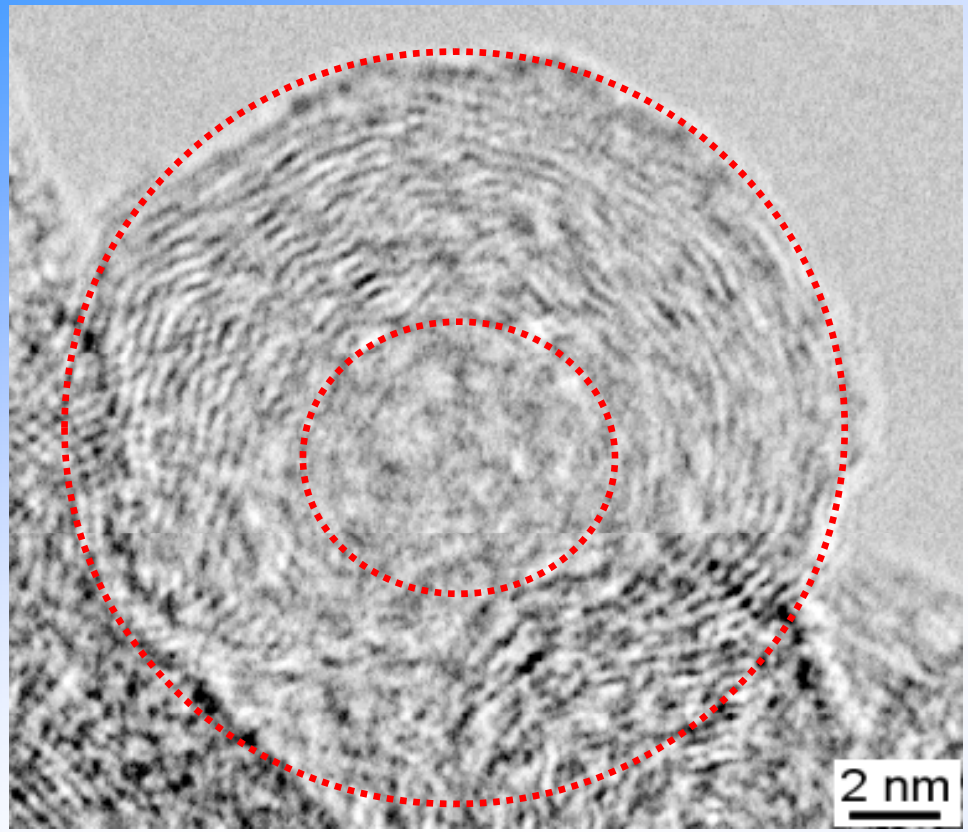




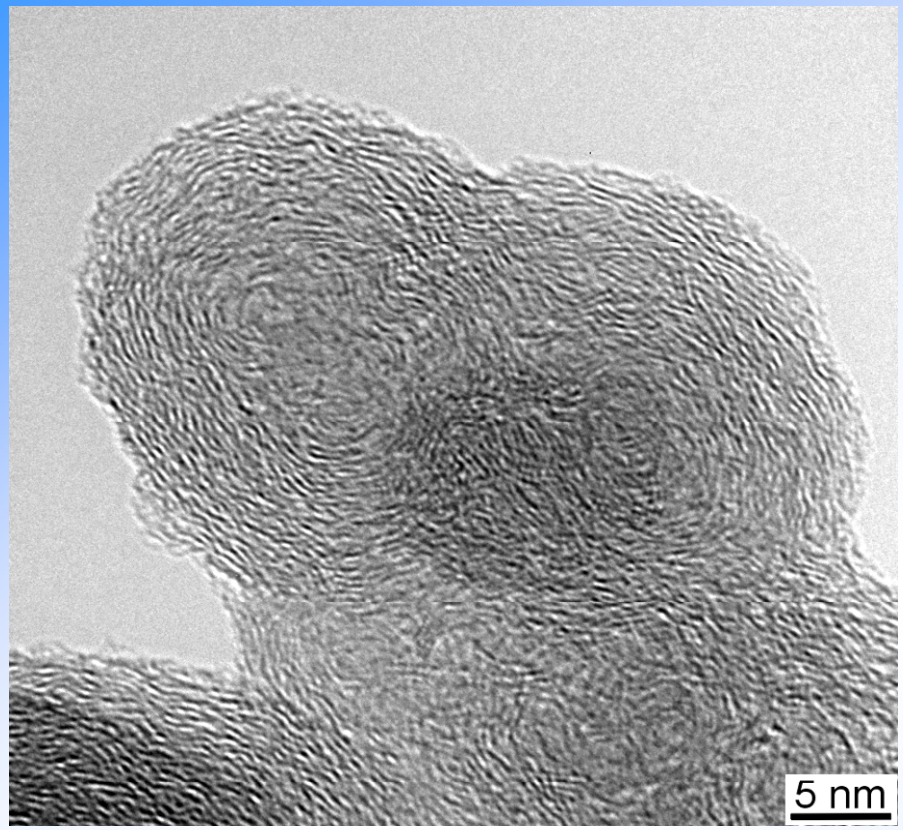
From a MAN Euro III engine run under black smoke condition

From a MAN Euro IV test engine

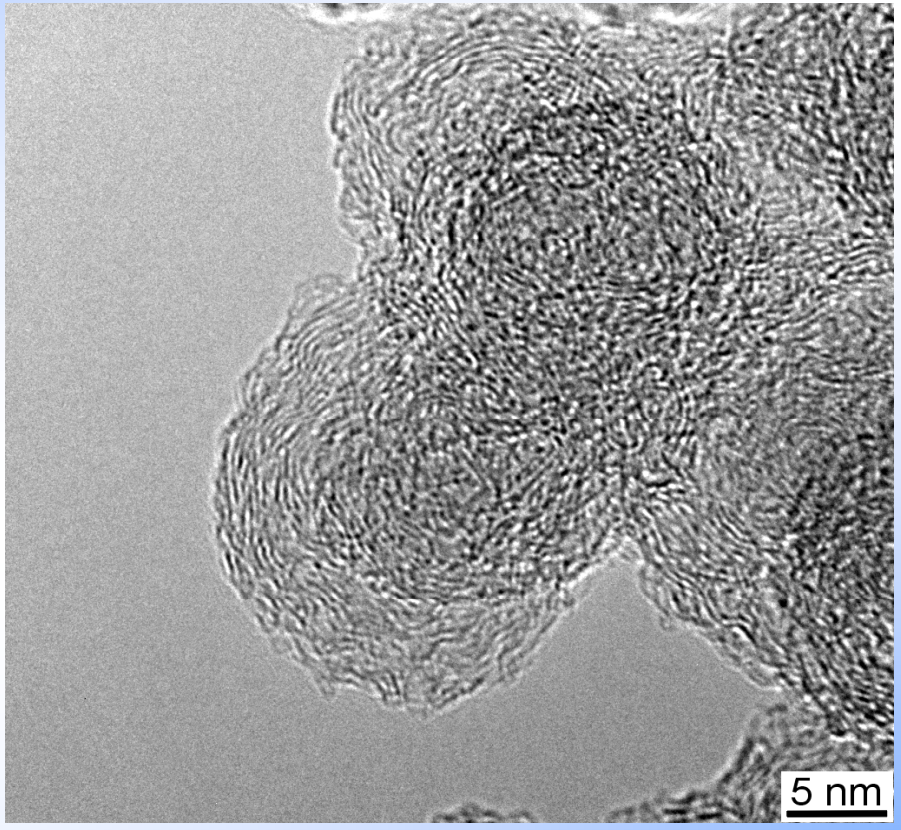
Polycyclic aromatic hydrocarbon (PAH) soot



Black Smoke and Furnace Soot

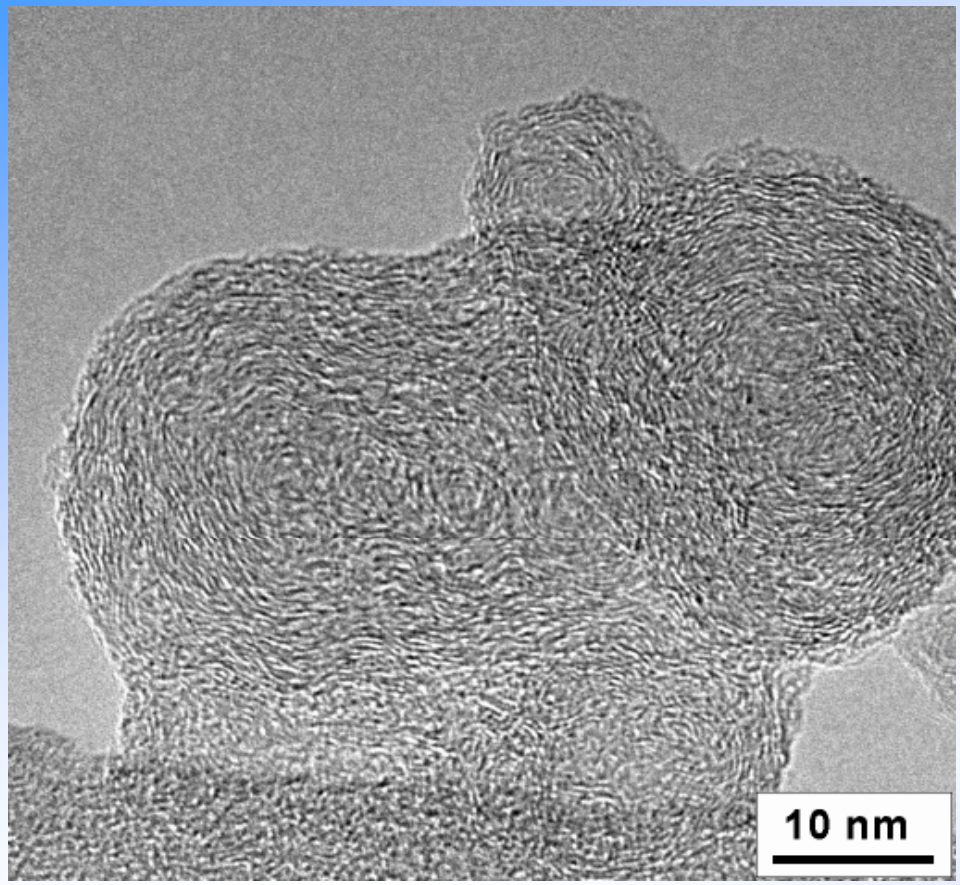


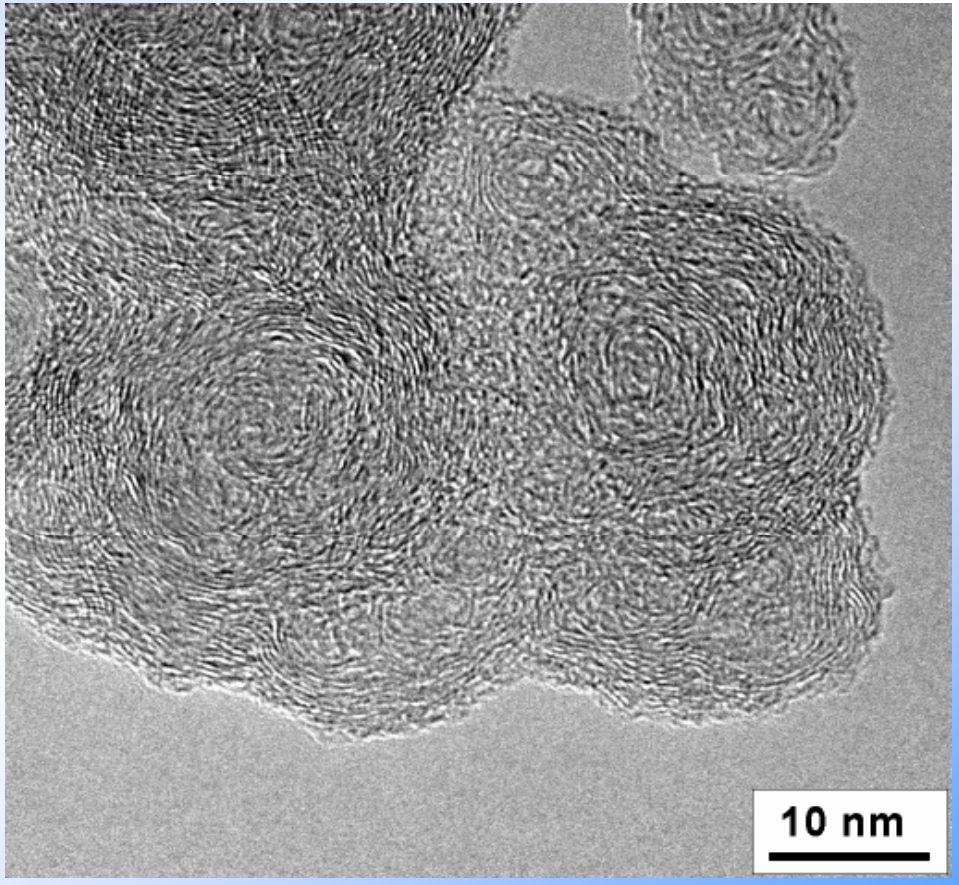
Soot from a black smoking diesel engine



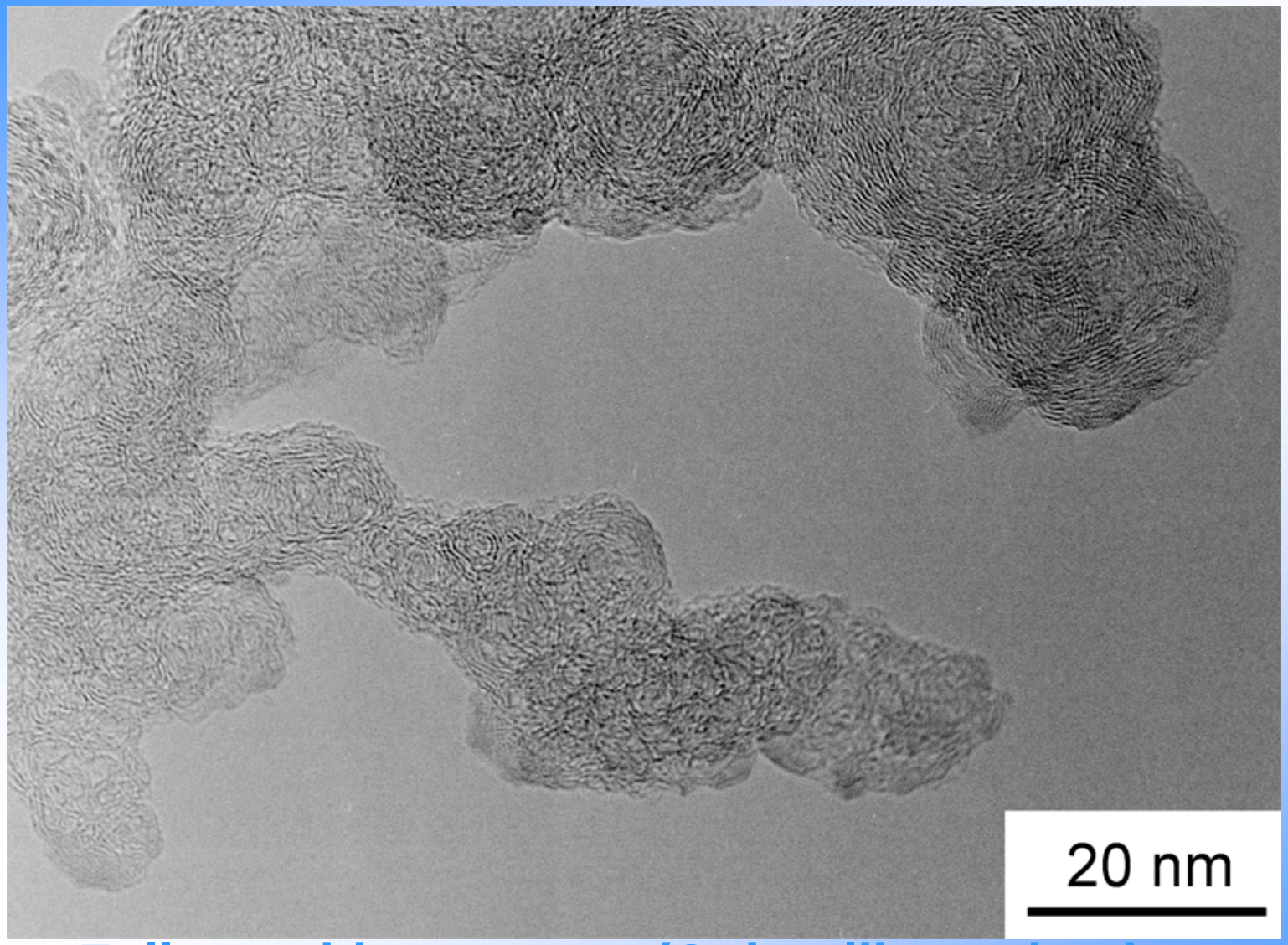
Furnace Soot FW1 from Degussa

Euro III Diesel Soot



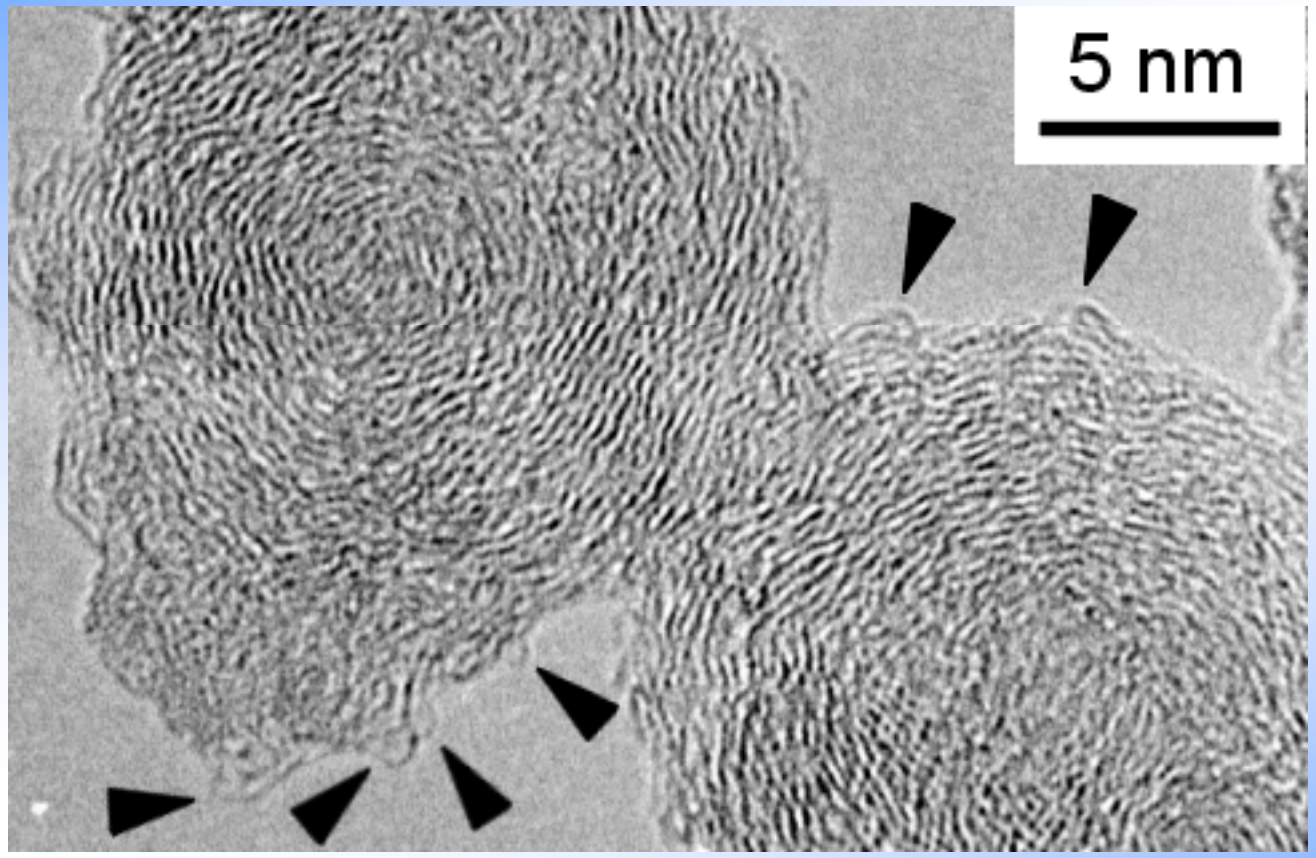


Euro IV Diesel Soot



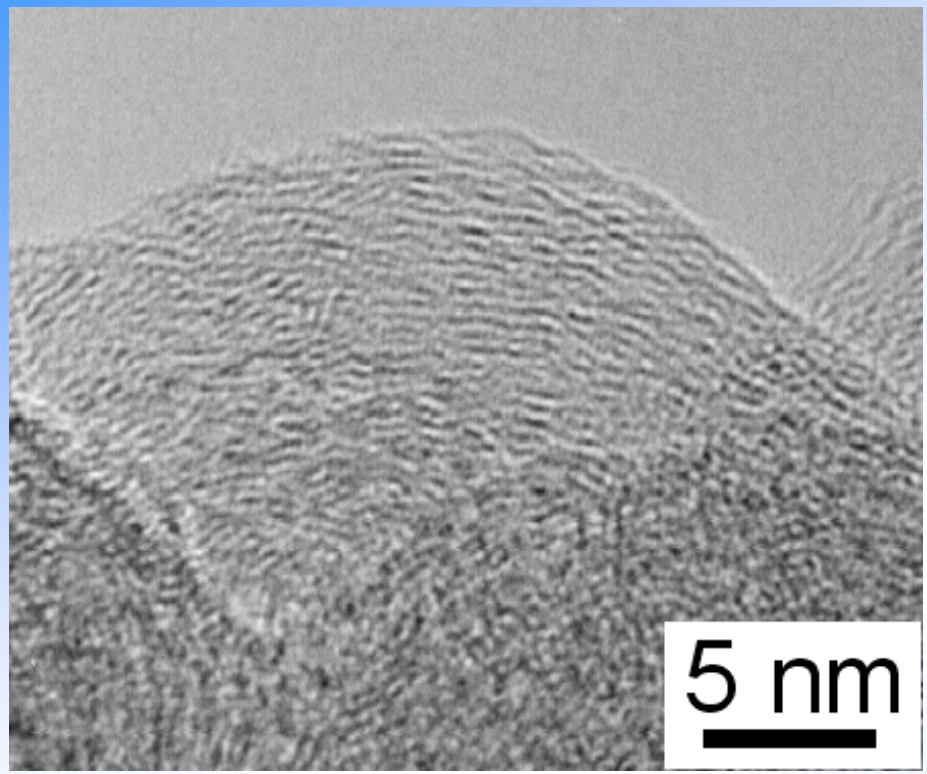
Fullerenoid aggregate (Onion-like carbon)

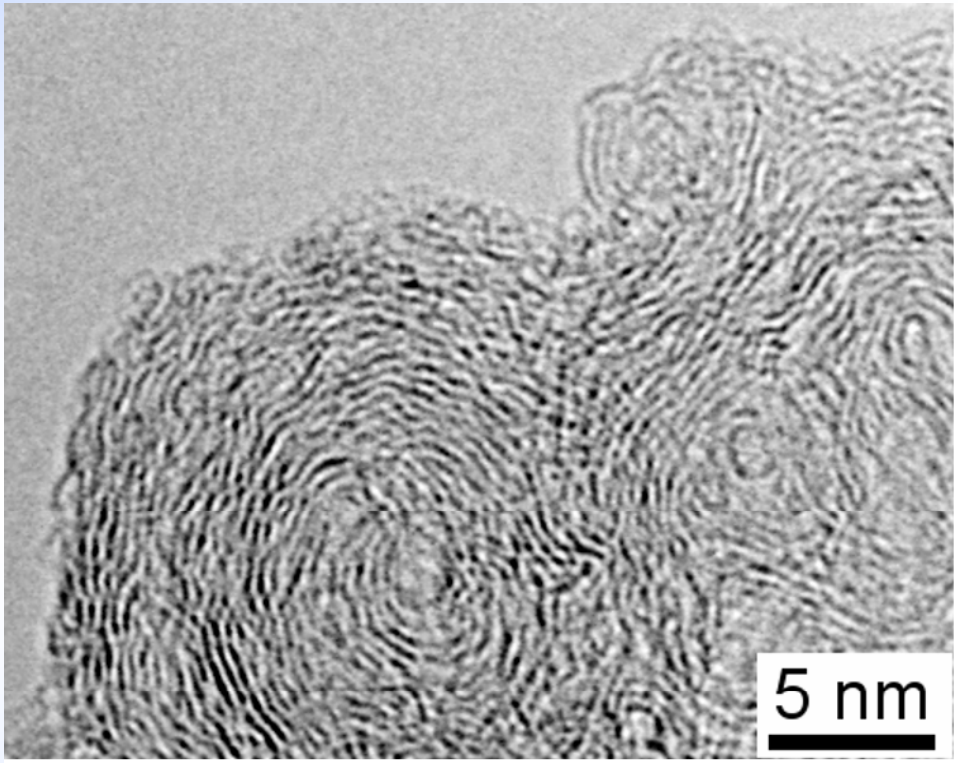
Euro IV Diesel Soot



Rough surface with fullerenes and fullerenoids

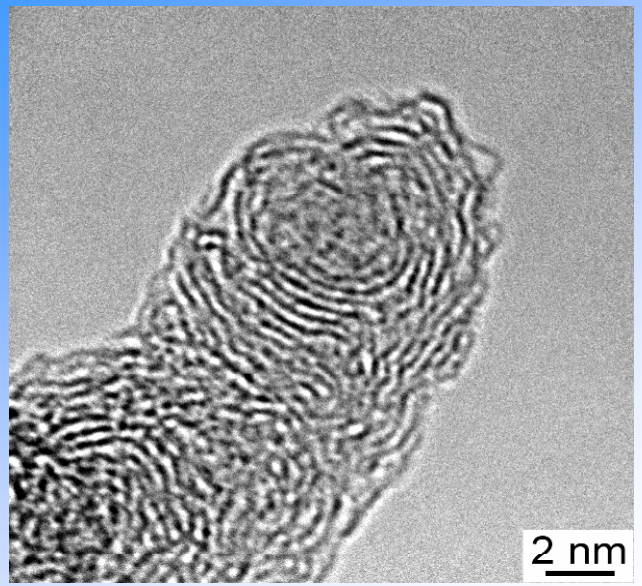
Euro III and IV Diesel Soot

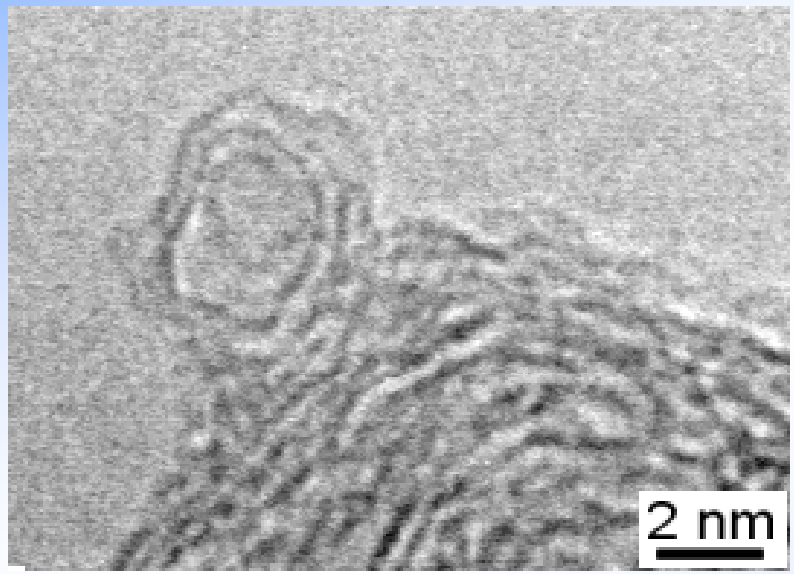


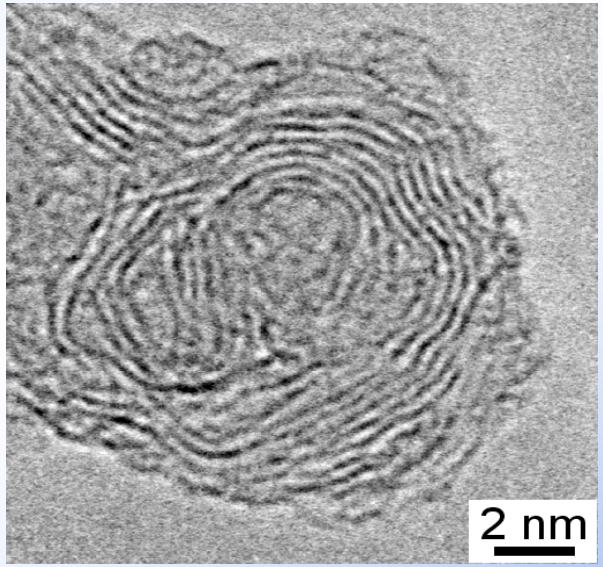


Heavy defective surface structure of Euro IV soot

Fullerenoid aggregate from an Euro IV engine

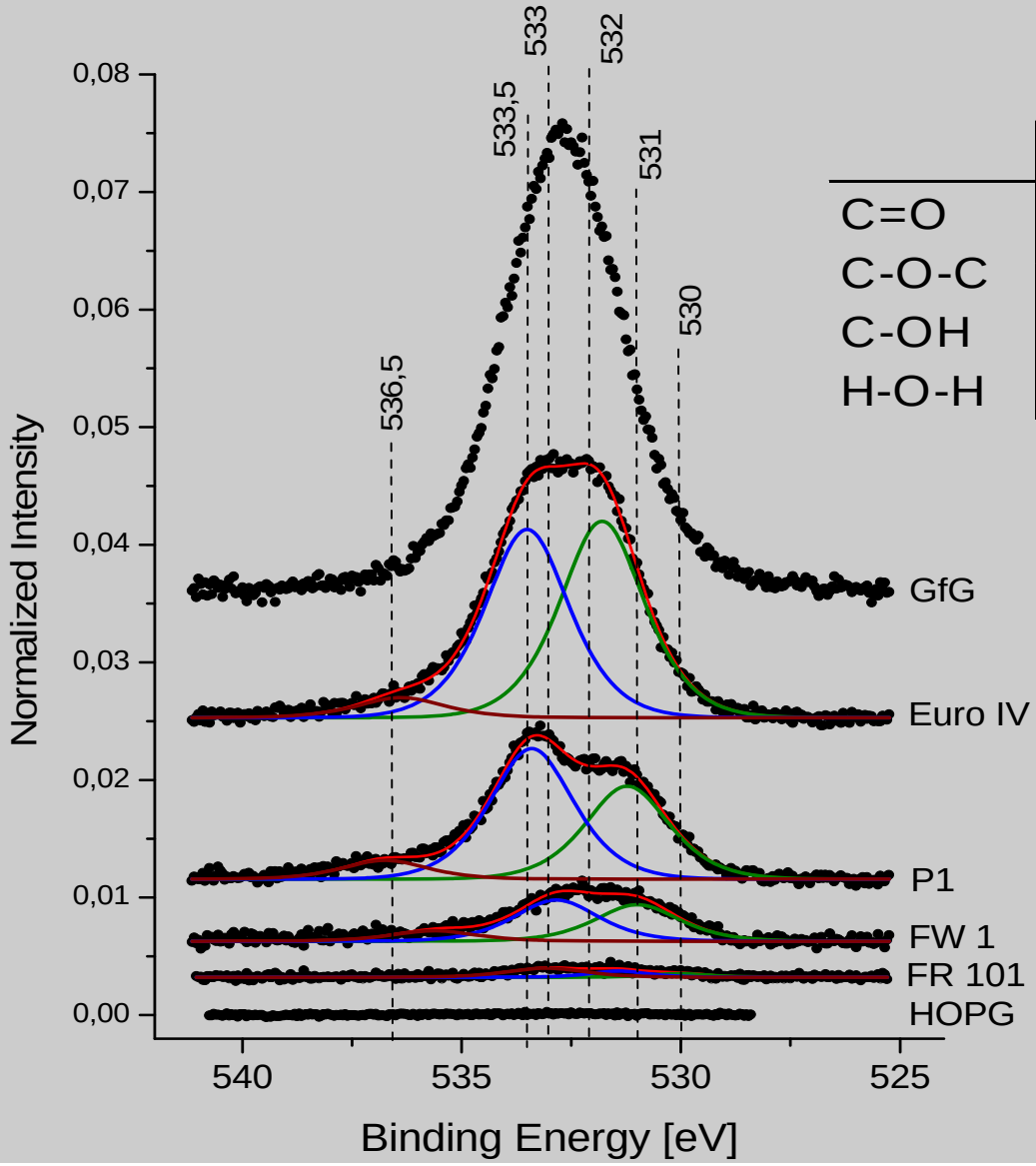




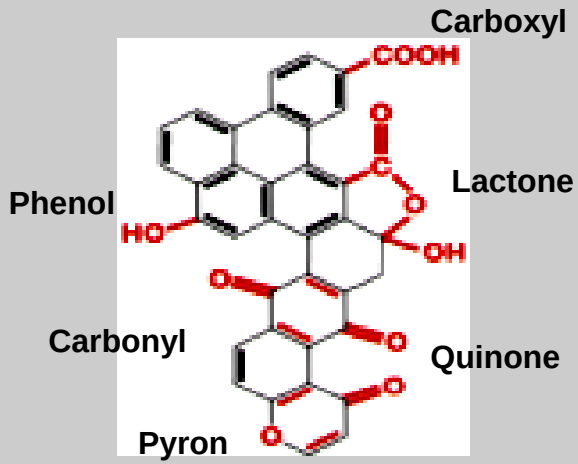


Primary particles with very strongly bent graphene layers. The particles are bounded on large agglomerate by sharing graphitic layers. The fullerenoid structures are found on the surface of primary particles

Surface Chemistry

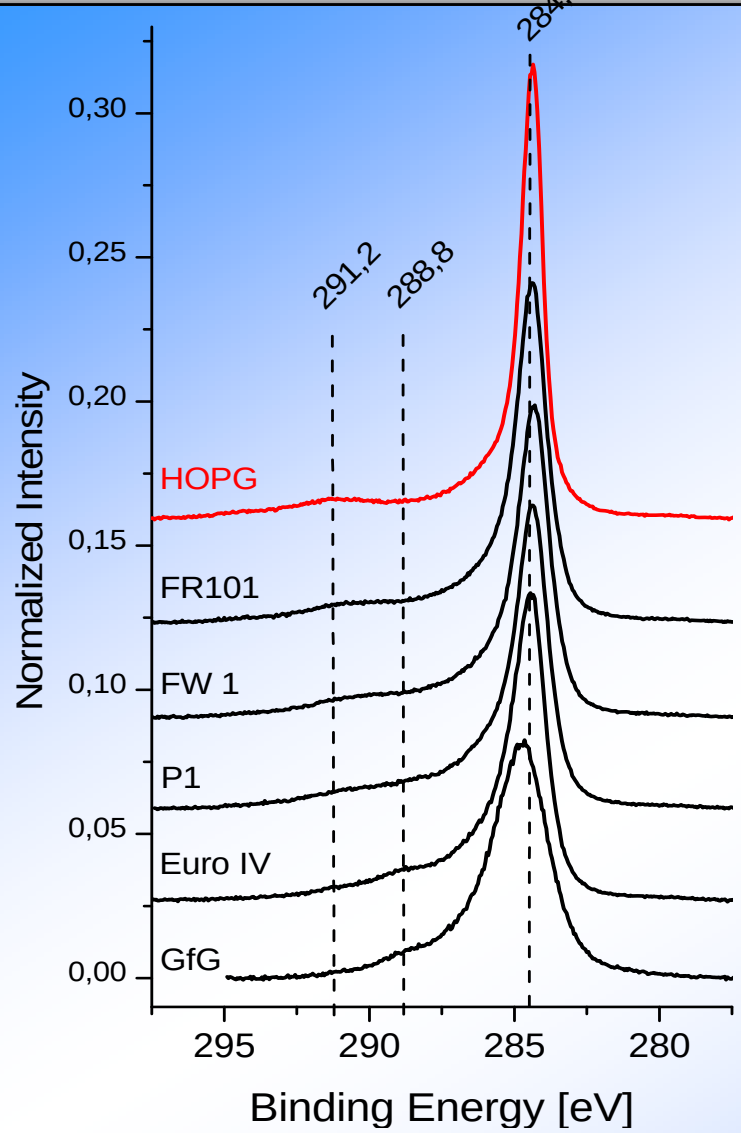


	B.E.
C=O	530,9
C-O-C	531,8
C-OH	533,5
H-O-H	536,4

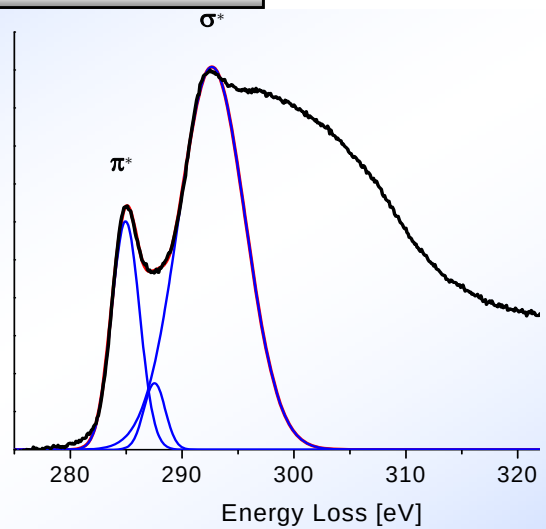


	C1s	O1s
GfG	83,14	16,86
Euro IV	87,98	12,02
P1	92,61	7,39
FW 1	97	3
FR 101	99,46	0,54
HOPG	99,8	0,2

Electronic structure



	FWHM
HOPG	0,91
Fr 101/33D	1,29
FW 1	1,37
Black Smoke P1	1,37
Euro IV - Soot	1,49
GfG-Soot	2,3



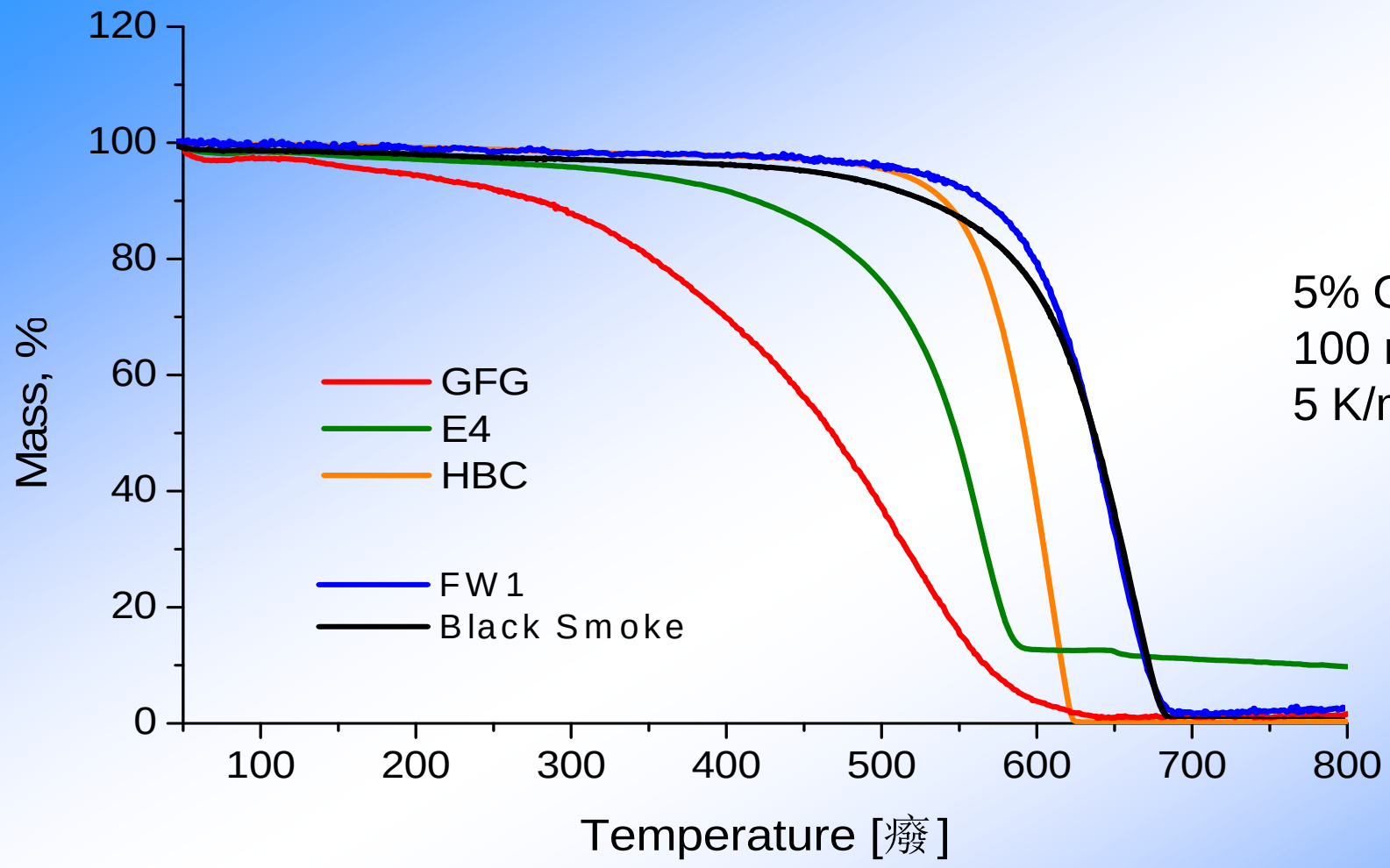
Degree of graphitisation correlates with the FWHM of the $C1_S$ intensity at 284,4 eV and also with the evolution of the shake up satellite (plasmon oszillations).

	Nsp^2 [%]	Nsp^3 [%]
Diamond (impure)	23	77
GfG-Soot	49	51
EuroIV-Soot	77	23
Black Smoke	90	10
Graphite	100	0

Summary I

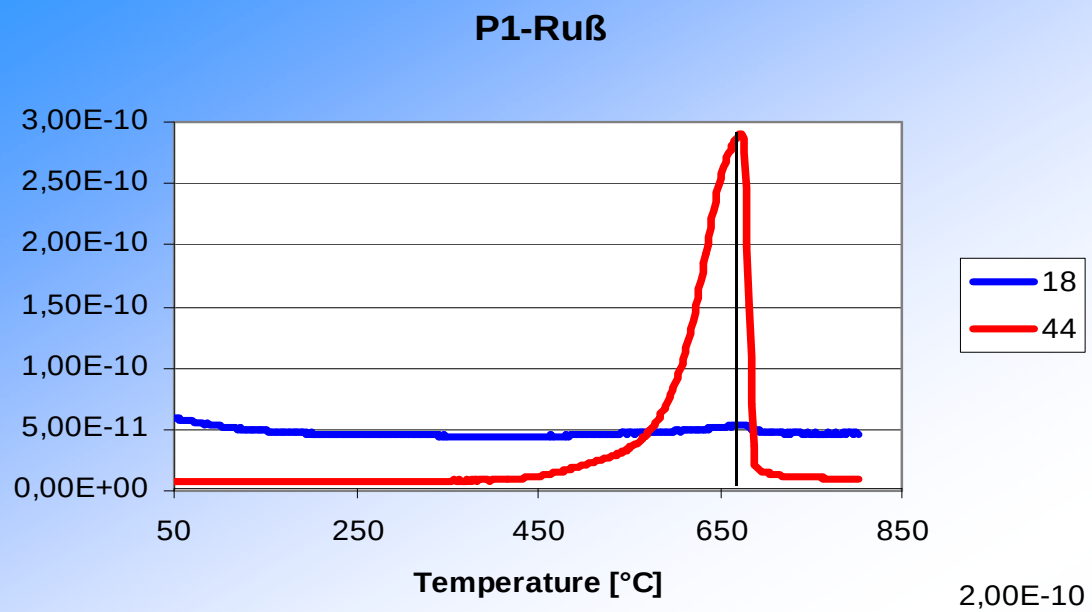
- **Emission rate and size distribution of soot**
  - ↑ **Lower emission (few soot mass)**
  - ↑ **Reducing of the particle-size distribution**
- **Microstructure (unexpected !)**
  - ↑ **Fullerene- and fullerenoid-like structure**
  - ↑ **Small graphene size and curvation**
  - ↑ **Aggregates and adsorption of fullerenes and fullerenoids on surface of large particles**
- **Electronic structure**
  - ↑ **Co-existence of 3- und 4-fold bond carbon**
  - ↑ **A certain amout of carbon in sp^3-hybridization**

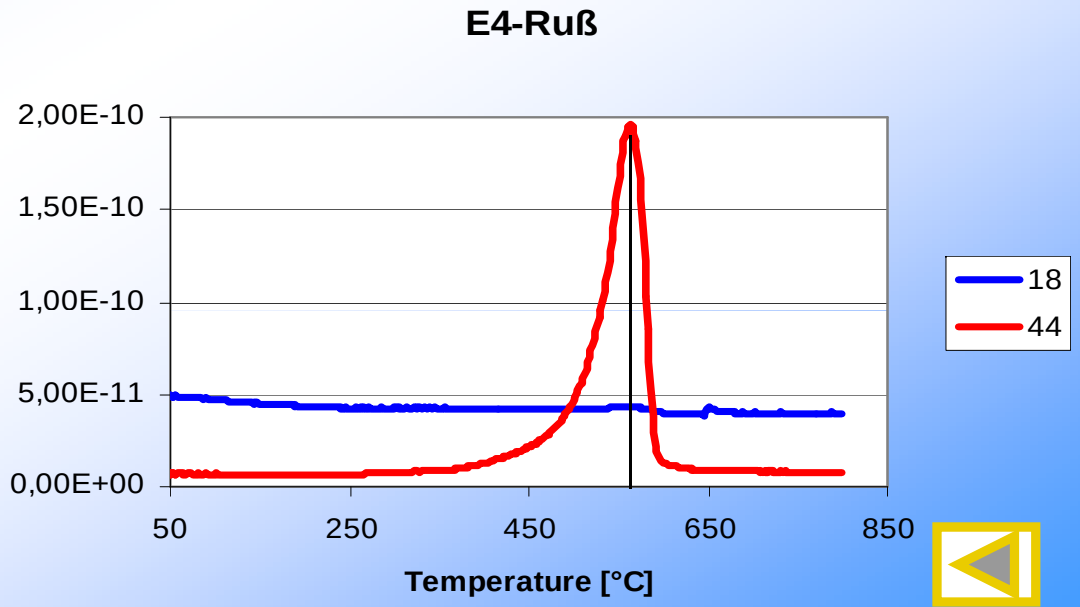
Oxidation: Thermogravimetry



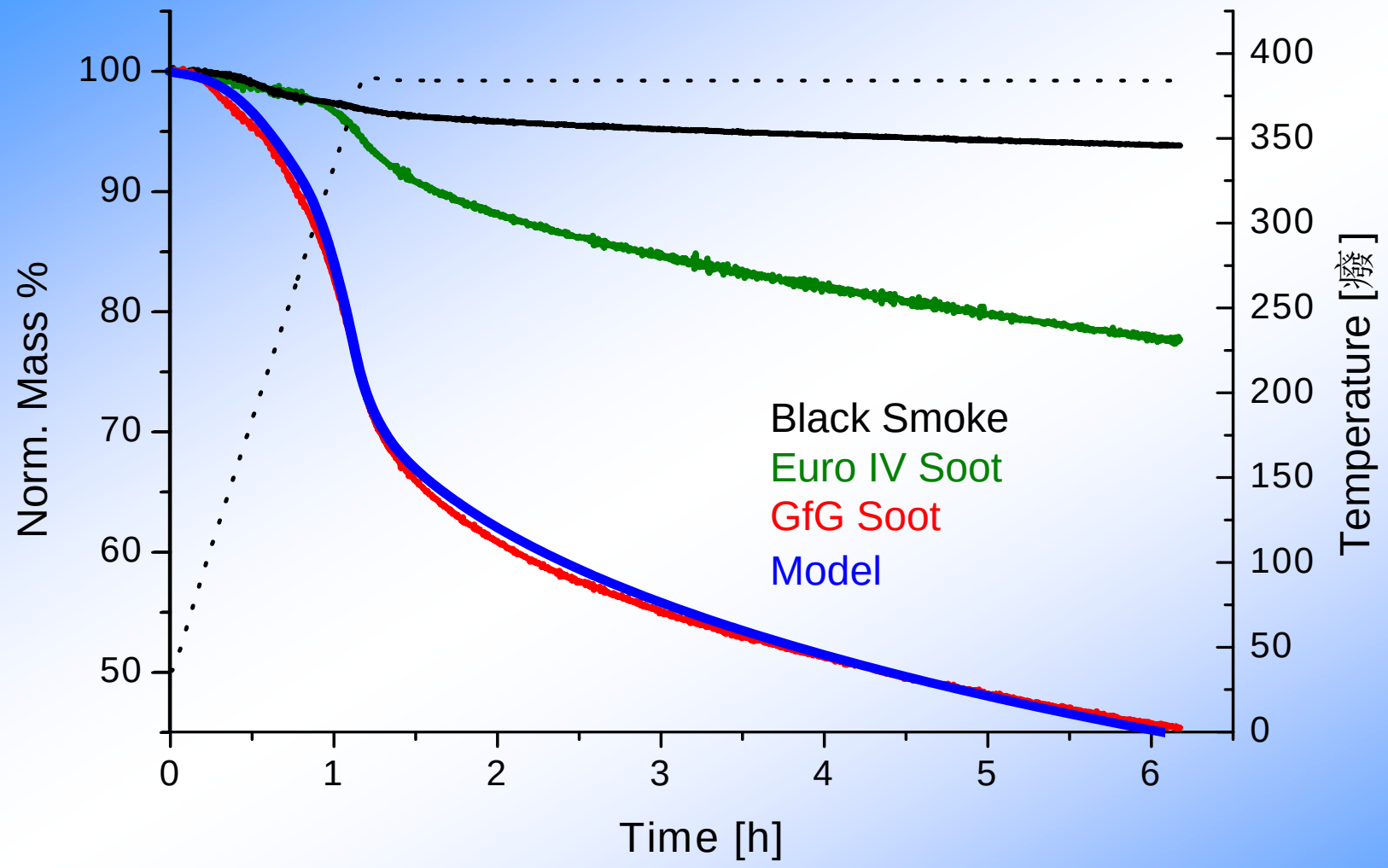
5% O_2 in N_2
100 ml/min / 1bar
5 K/min

Combustion of EURO III und IV Soot

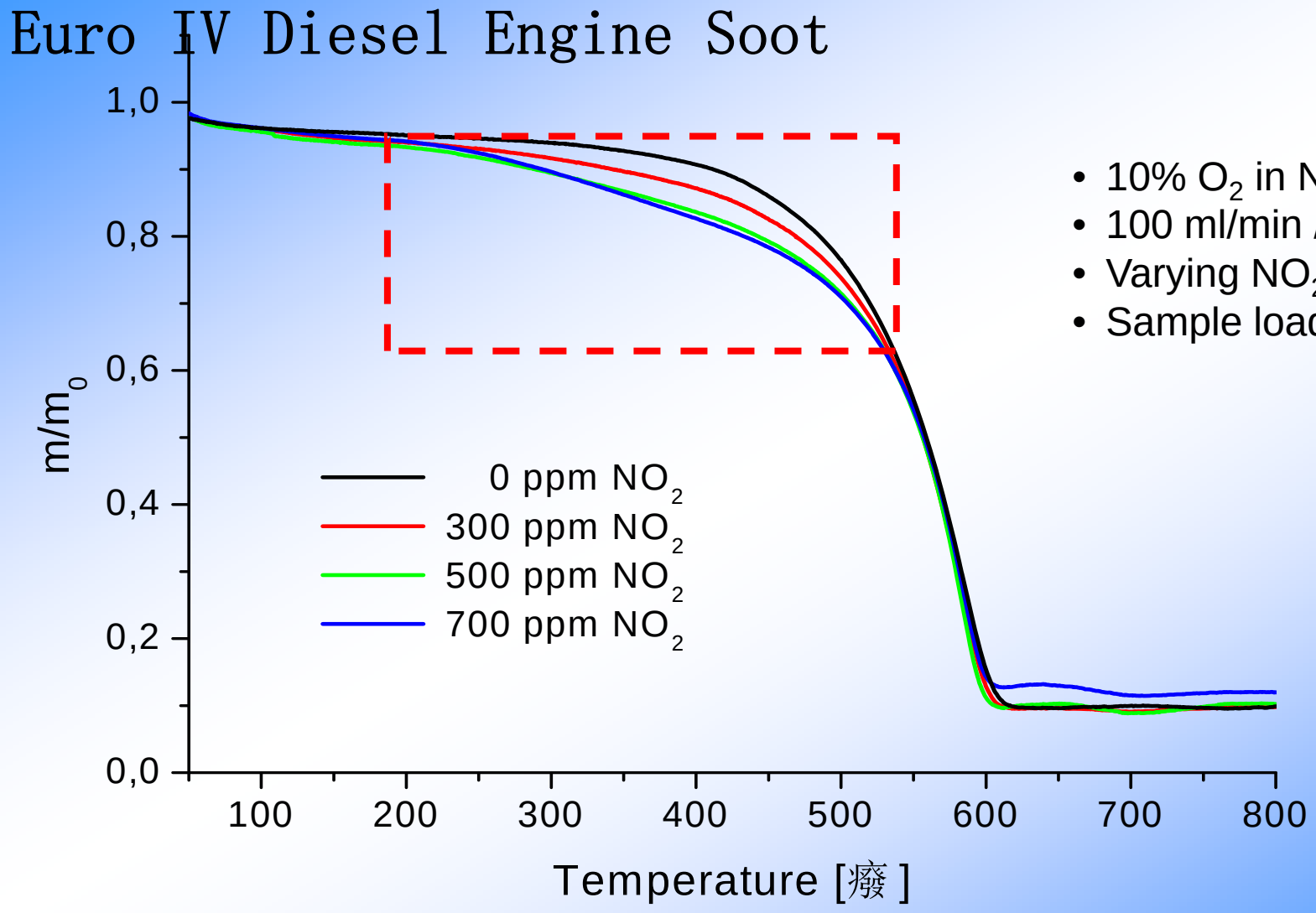




Isothermal Treatment



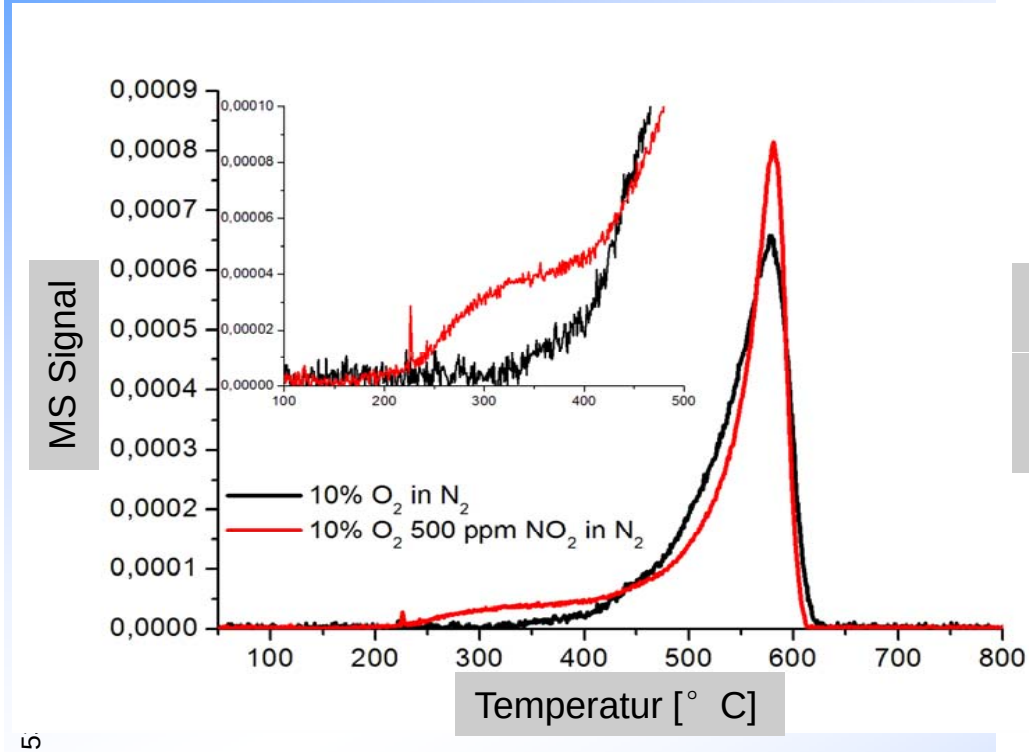
NO_2 Investigations



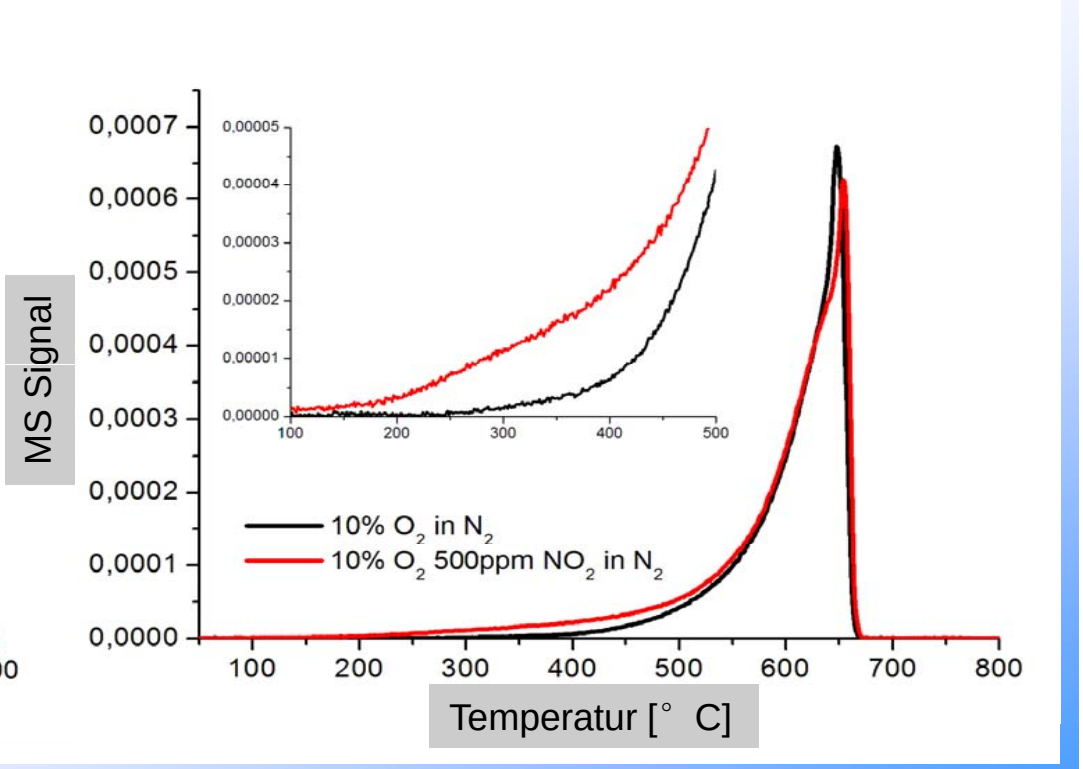
- 10% O_2 in N_2
- 100 ml/min / 1bar
- Varying NO_2 content
- Sample load: 1-2 mg

Oxidation with NO_2

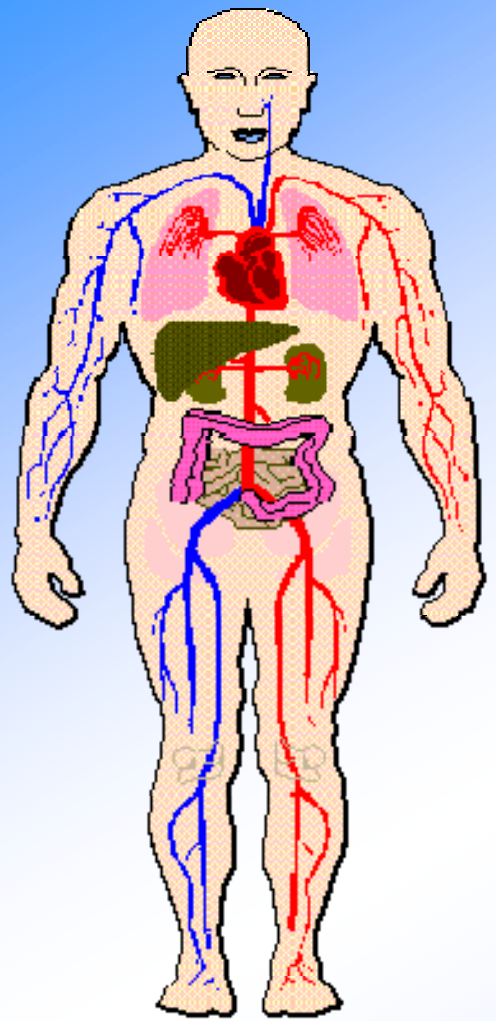
Euro IV Soot

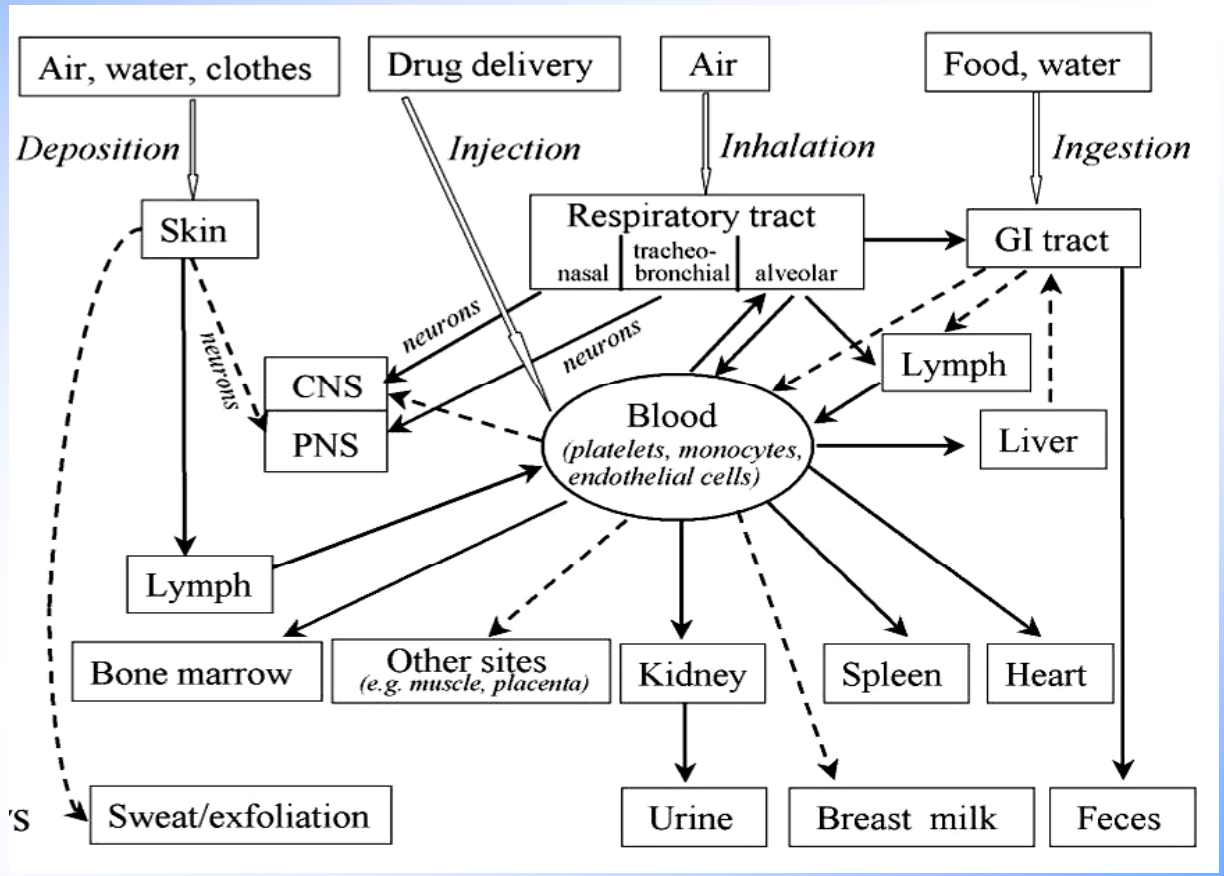


Black Smoke Soot



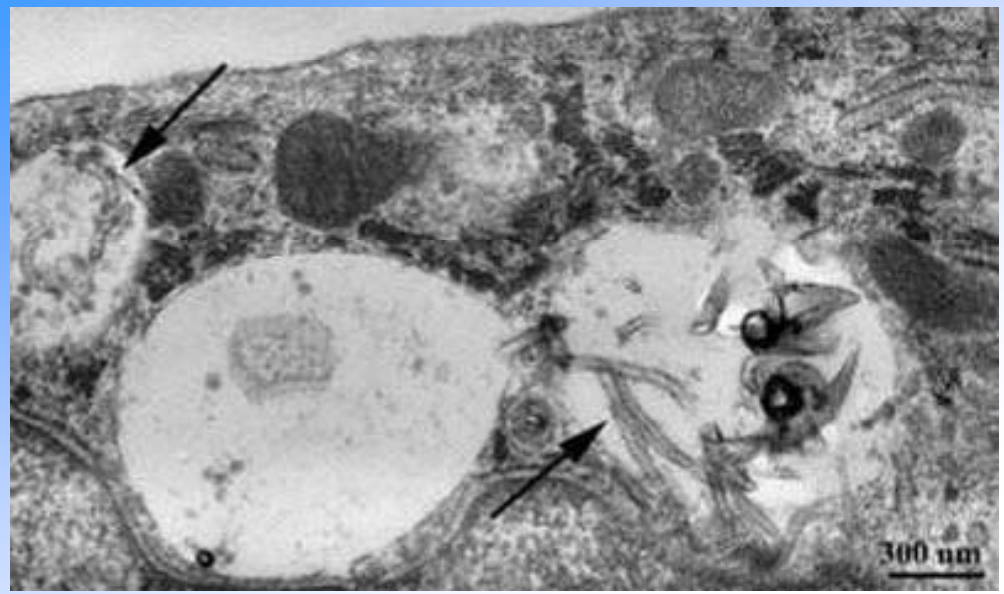
Possible uptake by skin, gastric tract and lung





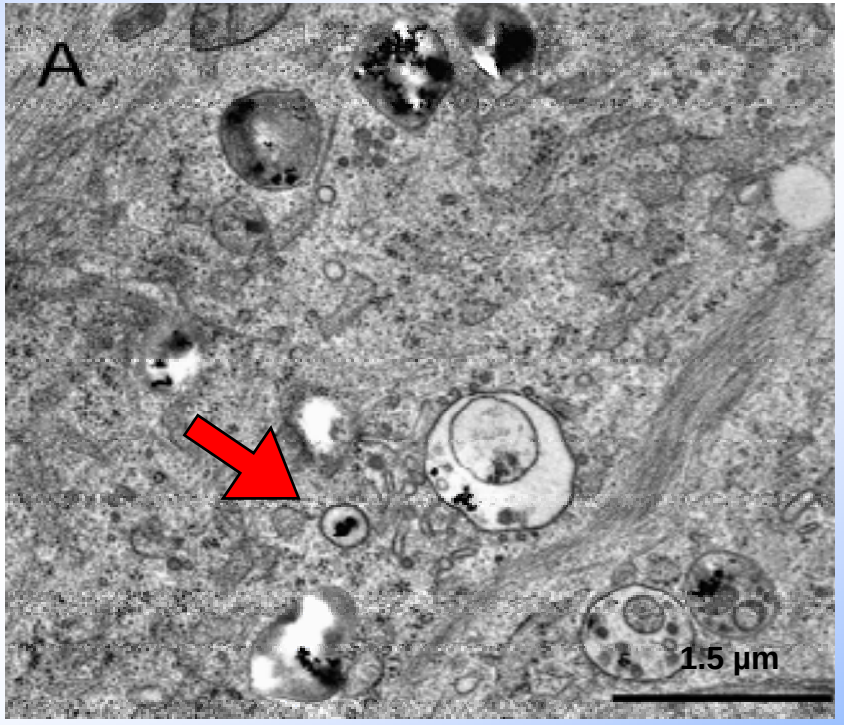
adapted from G. Oberdörster, 2005

Intracellular uptake of nano-sized material



Monteiro-Riviere et al. 2005

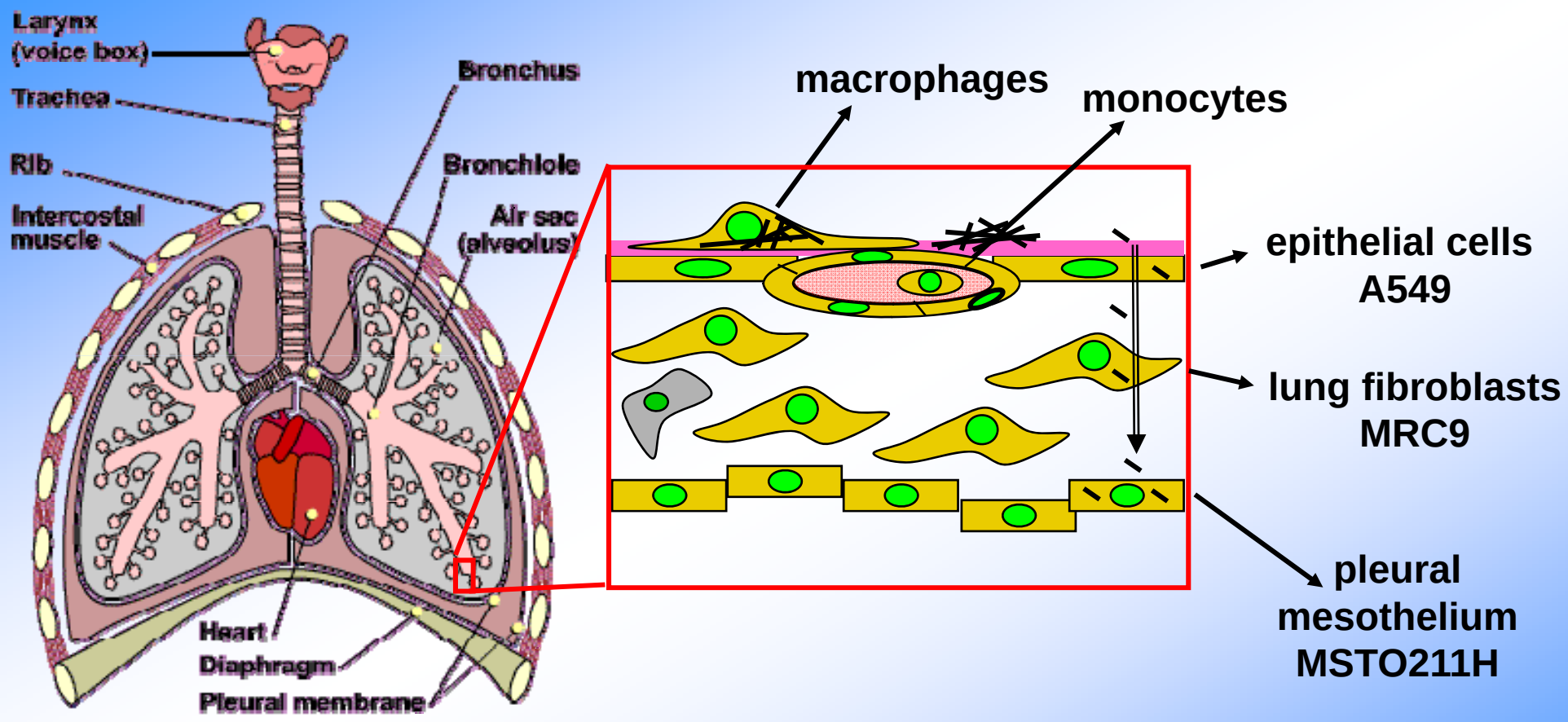
MWCNT in keratinocyte



Limbach et al. 2005

Ceria nanoparticles of 50 nm in lung fibroblast

Cell cultures: *in vitro* model



Cytotoxic test

MAX-PLANCK-GESELLSCHAFT

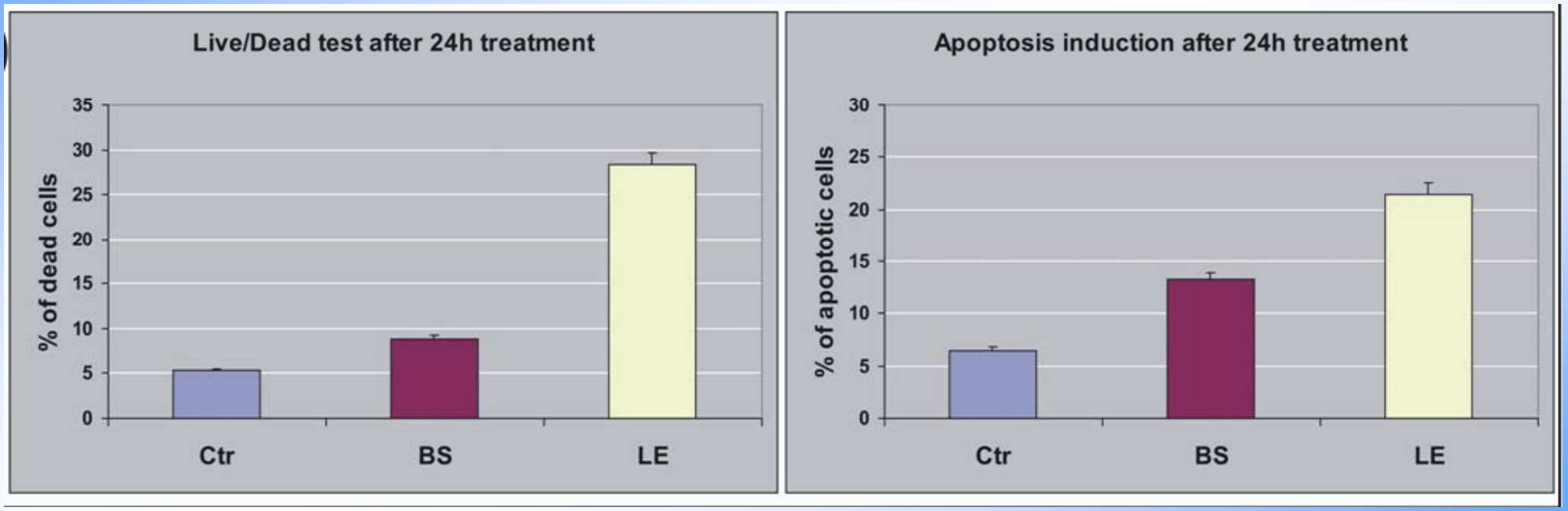
Assess the ability of soot to elicite an inflammatory response by human macrohpge cells *in vitro* and to be cytotoxic again these cells.

Macrophage, also know as antigen presenting immune system that react against all foreign body materials. When these cells get in contact with material particles or pathogen, they become activated and , after having phygocytosed particles, secrete a lot of chemical mediators of inflammation, very aggressive against either the host tissues and the foreign molecules or particles.

Evluation of dead cells by Live/Dead cell vitality array and of apoptotic cells.

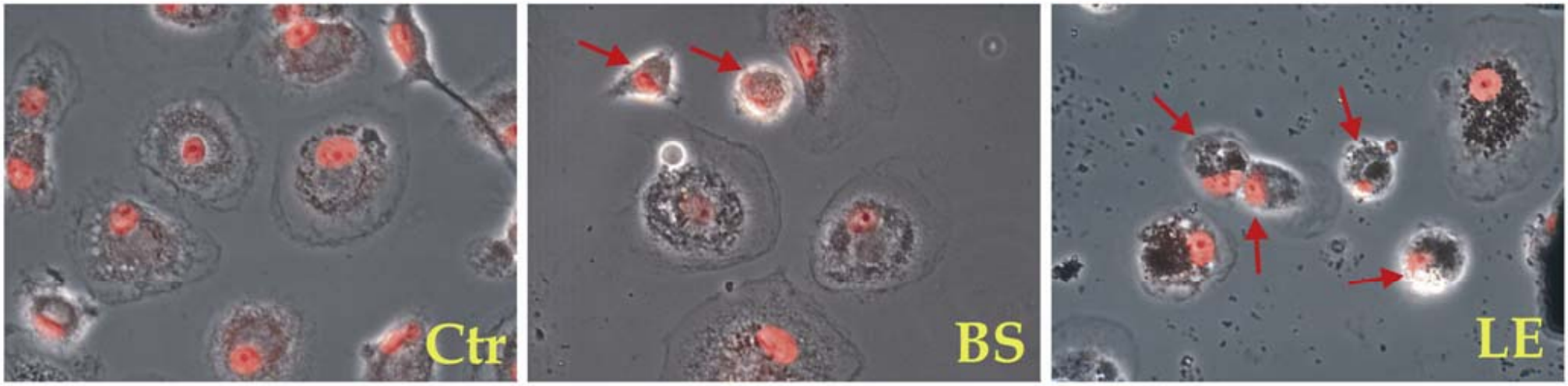
Cytotoxicity of BS and LE paticles on human MDMS

Evluation of dead cells by Live/Dead Cell Vitality Array (left panel) and of apoptotic cells (right panel)



MDMS: Monocyte-derived macrophage cell

Cytotoxicity of BS and LE paticles on human MDMS

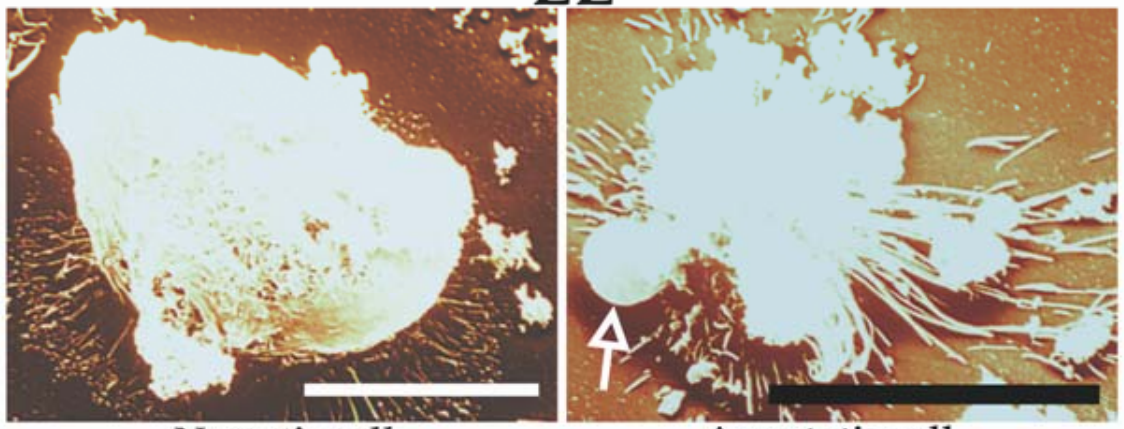


Apoptotic/necrotic cells (arrowed) in MDMS culture when treated with soot particles

Cytotoxicity of BS and LE paticles on human MDMS

Scanning elecgtron microscopy view of untreated (Ctr) and treated cells

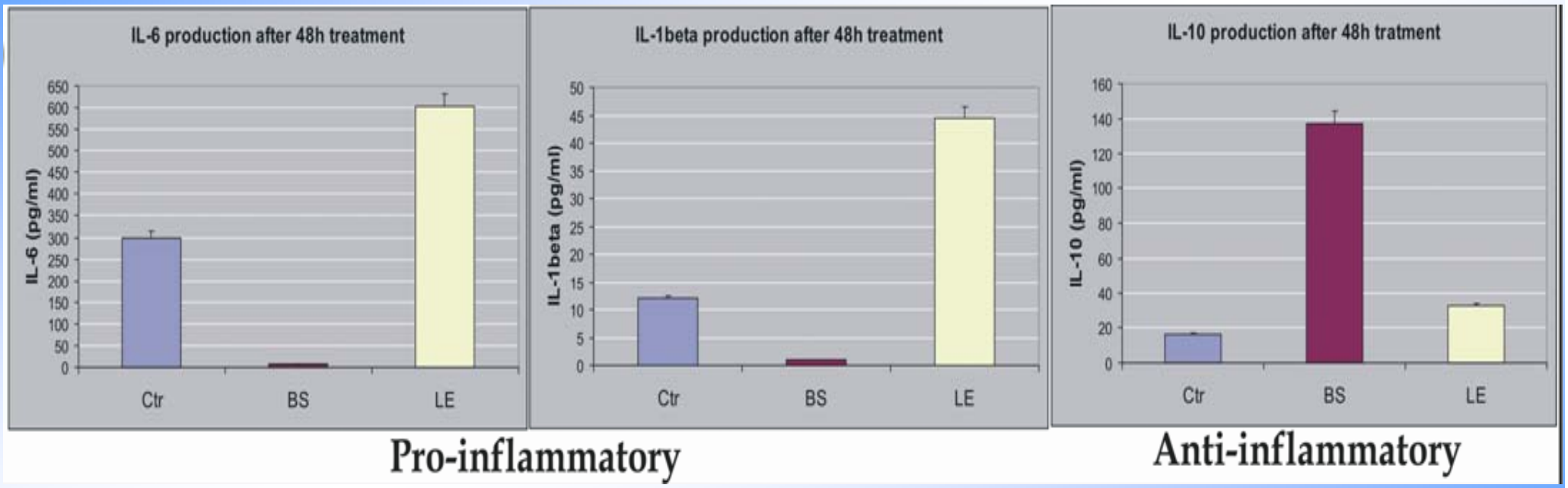
LE



Necrotic cell Apoptotic cell

Test of inflammatory potential

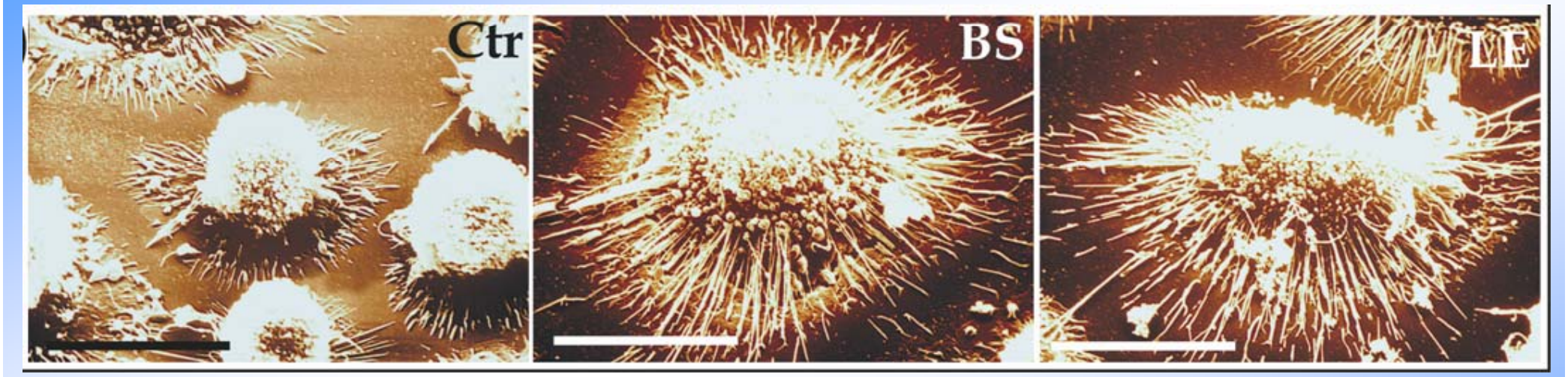
Effect of BS and LE soot particle treatment on pro- and anti-inflammatory cytokines production by MDMs



IL-1beta, IL-6: pro-inflammatory cytokines
IL-10: anti-inflammatory cytokines

Macrophage activation

Morphological changes of MDMs culture after soot particle treatment



20 µm

Summary II

- **Euro IV Diesel soot is chemical more reactive than conventional soot, low oxidation temperature**
- **Euro IV Diesel soot is more cytotoxic and have a high inflammaroty potential**

Conclusion

MAX-PLANCK-GESELLSCHAFT

Minimizing soot emissions

- is not automatically beneficial for human health
- makes soot particles more bio-available
- result in facile interfacing between the inorganic soot and the biosphere

The development of filtering technogloy must be directed to The removal of lultrasmall particles with pose a higher risk per gram to the biosphere than more conventional forms of large-particle soot

Surprising report in Bild

MAX-PLANCK-GESELLSCHAFT

NACHRICHTEN

VW erhöht die Schlagzahl

Neue Hoffnung für Tiguan-Kunden: VW reagiert auf die massive Kritik an den bis zu elf Monate langen Lieferzeiten für den neuen Kompakt-SUV (AUTO BILD 3/2008) und versetzt im Karosseriebau Roboter und Anlagenteile. Ziel der Umbauten: eine Steigerung der Kapazität von derzeit 440 auf 650 Autos täglich. Zudem verhandelt die Geschäftsführung mit dem Betriebsrat über weitere Sonderschichten im März und April. Bereits im Januar und Februar leisteten die Bandarbeiter zusätzliche Schichten.

Neue brisante Studie

Moderne Diesel gefährlich?

Kleinste Rußpartikel in Dieselabgasen können im menschlichen Körper Entzündungen auslösen und sogar wie Gift wirken. Zu diesem Ergebnis kommen die beiden Wissenschaftler Robert Schlögl und Dangsheng Su vom Berliner Fritz-Haber-Institut.

Trotz moderner Motoren und Filteranlagen werden noch immer Nano-Rußpartikel ausgestoßen, die mit einer Größe von zehn bis 15 Nanometer Durchmesser nicht halb so groß sind wie jene Rußteilchen, die ältere Dieselmotoren freisetzen. Wegen ihrer runden und leicht gebogenen Form könnten diese Teilchen für Umwelt und Gesundheit extrem gefährlich werden. Das ergaben Versuche mit Fresszellen des menschlichen Immunsystems. Weitere Experimente könnten den Verdacht bestätigen.

Zwei andere Eigenschaften machen Nano-Teilchen problematisch. „Keine Wand", so Su, „ist dicht genug, um die Partikel aufzuhalten." Das erschwere die Entwicklung neuer Filter. Zudem setzen sich große Rußteilchen nach Minuten am Boden ab. Nano-Partikel schweben aber tagelang durch die Luft.

Forschen im Nanobereich: Dangsheng Su versucht in Experimenten zu klären, wie gefährlich Nano-Partikel (unten) für den Menschen sind

Öko-An im Kom

Alternative sich durchset Prozent der de rer. Das ergab des AUTO BILD- Schon im Vorja zent große Cha Antriebe gese kenntnis der U 20 Prozent ach stärkt auf niec

Westeu leicht in

Der Pkw-Abs ist im Januar um über dem Vorj gen. Das hat da forschungsunte keting Systems Sieger war laut Mit einem Wach zent haben sich Westeuropa an vorbeigeschob

Kleiner scharf g

Acknowledgment

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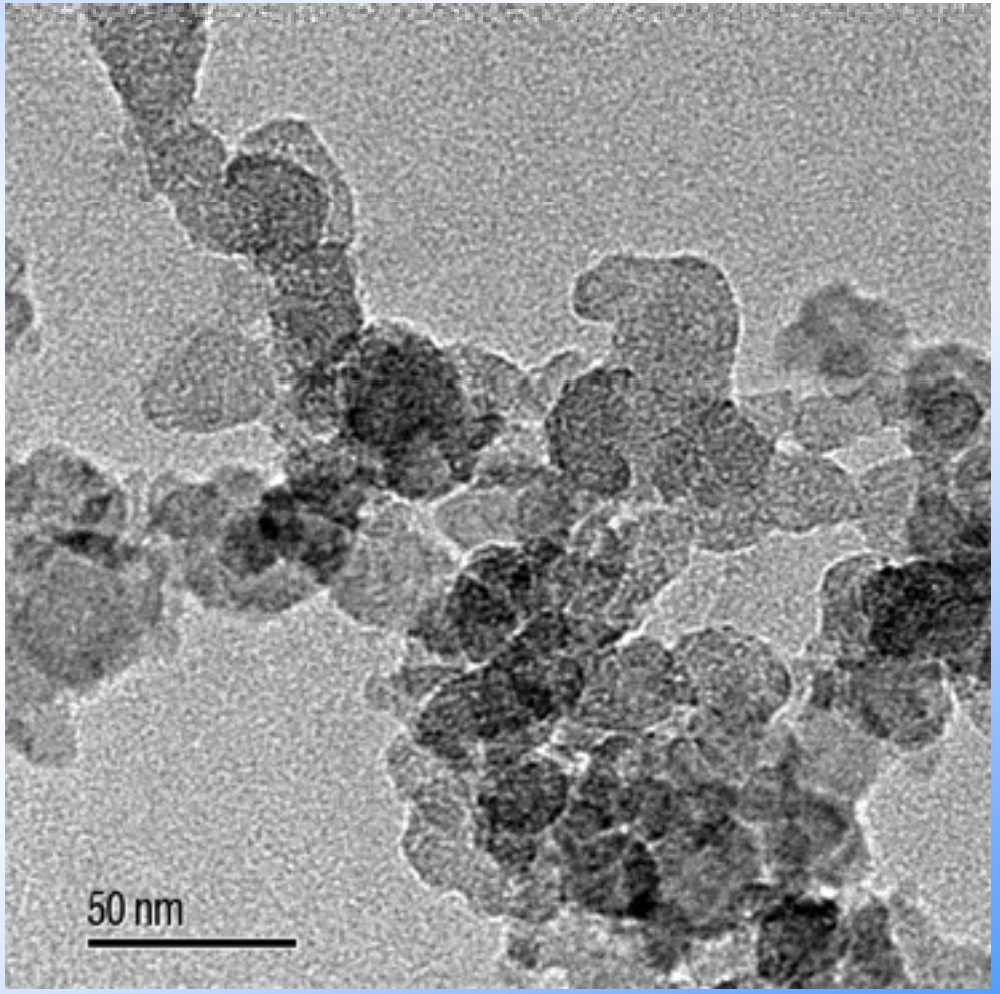
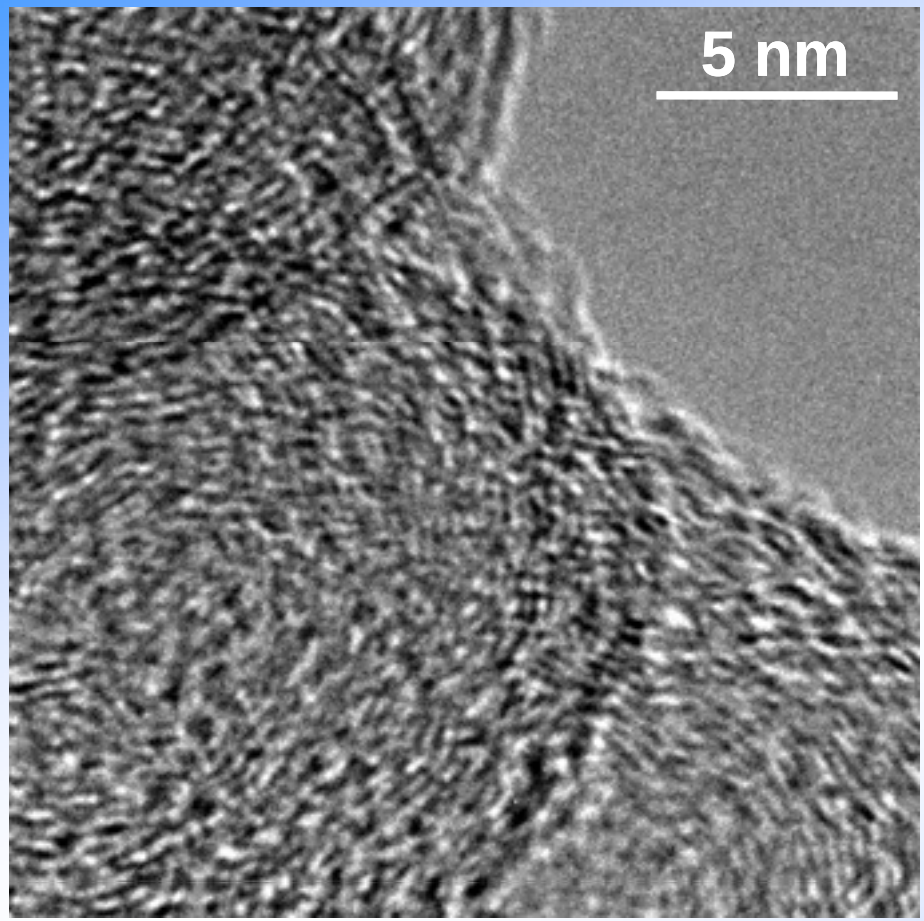
Jens-Oliver Müller, R. Jentoft, M. Swoboda, J. Kröhnert, R. Schlögl

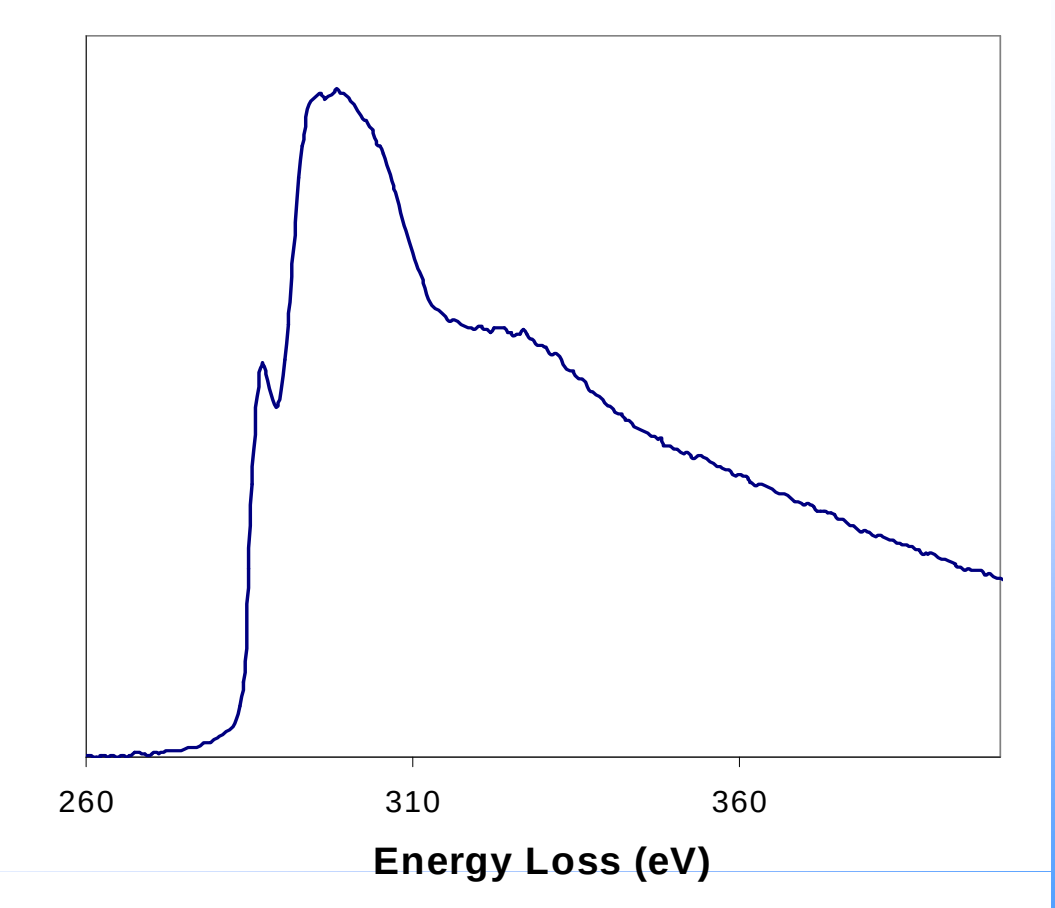
From birthday candle



HRTEM and EELS

Carbon K-ELNES





High-resolution imaging

Romantic candle light dinner...

Telegraph.co.uk

Romantic candles could cause cancer, say scientists

Candlelight may be key to creating the perfect atmosphere for a romantic dinner or a relaxing bath - but it could also be a dangerous one, claim American scientists.

By Richard Alleyne (http://www.telegraph.co.uk/journalists/richard-alleyne/) , Science Correspondent
Published: 7:00AM BST 20 Aug 2009

Researchers have found that the fumes from paraffin wax – the most common and cheapest form of candle wax – can be poisonous and even cause cancer.

They found that in unventilated spaces levels can build up and, over time, cause health problems such as allergies and asthma. In extreme cases they add to the risk of major disease, they said.

"An occasional paraffin candle and its emissions will not likely affect you," said Amid Hamidi, the co-author of the study at South Carolina State University.

"But lighting many paraffin candles every day for years or lighting them frequently in an unventilated bathroom around a tub, for example, may cause problems."

The study, published at American Chemical Society annual conference, involved burning the candles in a small chamber for around five hours and soaking up the chemicals released in charcoal Photo: GETTY

Besides the more serious risks, he also suggested that some people who believe they have an indoor allergy or respiratory irritation may in fact actually be reacting to air pollutants from burning candles.

Advice I: using LED candle for romantic dinner