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Burning Modes and Oxidation Rates of Soot: Relevance to Diesel Particulate Traps

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Outline

I. Current Oxidation Status

II. Alternative Burning Modes via HRTEM

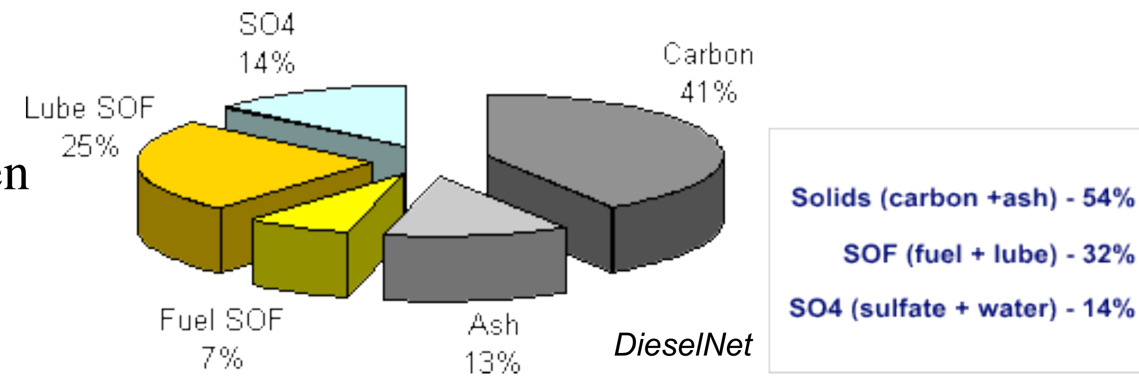
III. Nanostructure Quantification via Image Analyses

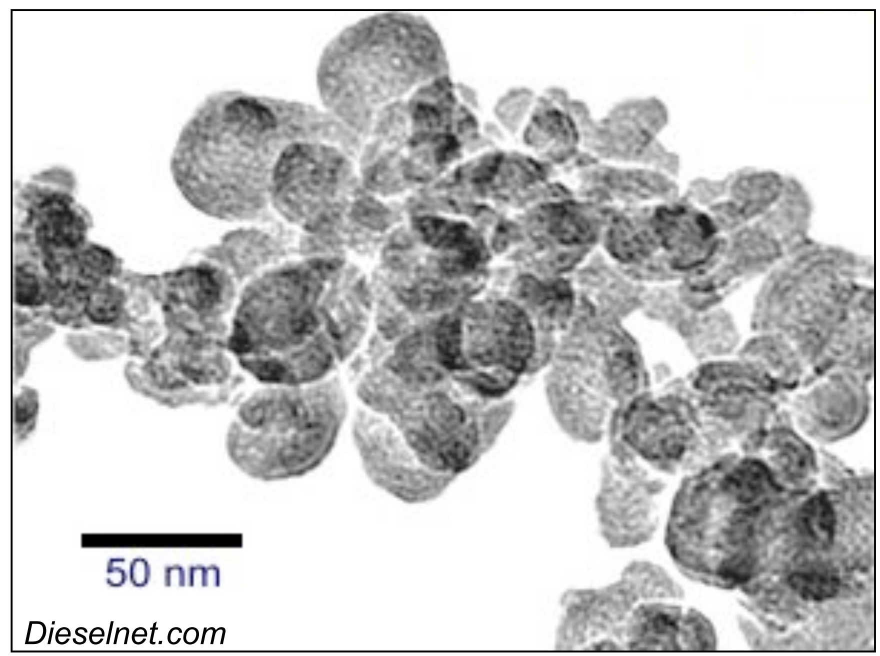
IV. Current Efforts

V. Conclusions

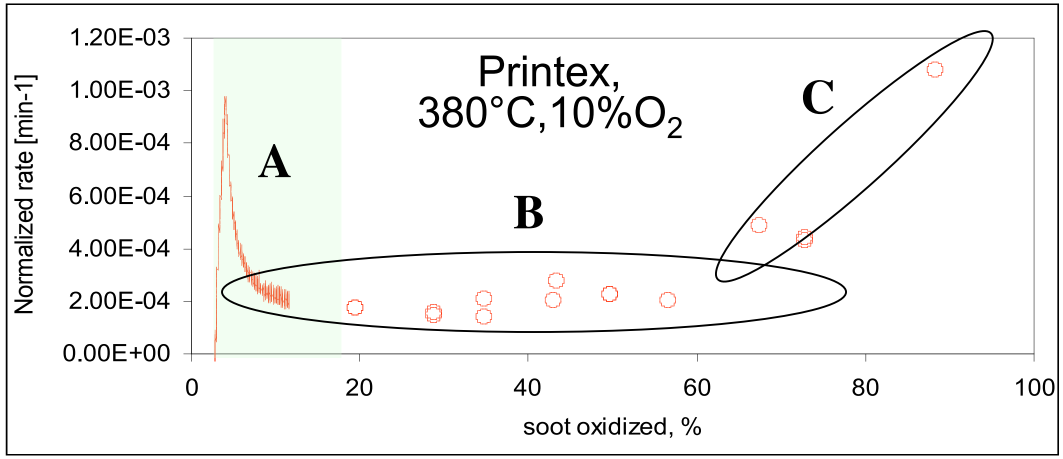
What is Diesel Particulate Matter ?

- Composition:
  - –"Dry carbon"
    - turbostratic graphite
    - initial evidence of fulleren structures in some cases
  - –Adsorbed HCs
  - –Inorganic materials
    - Lube oil ash, H_2SO_4, HNO_3, H_2O
- Nanostructure
  - \- Amorphous, fullerenic, graphitic
- Morphology:
  - –Primary particles: ~20-40 nm
  - –Agglomerates: 0.1-1 micron





Reactivity evolution over a life cycle of a soot particle

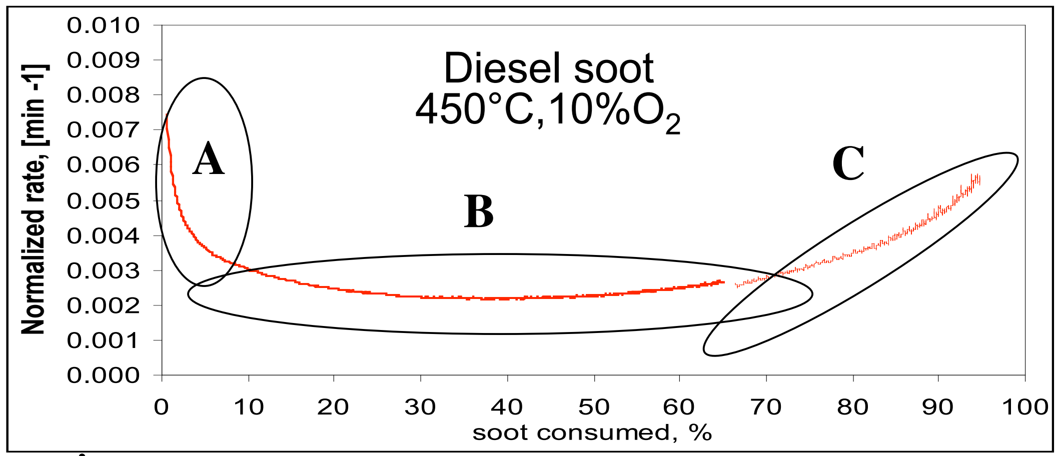


Printex

A: High reactivity due to ambient aging

B: Steady-state oxidation

C: Steep increase



Diesel Soot

A: High reactivity due to:

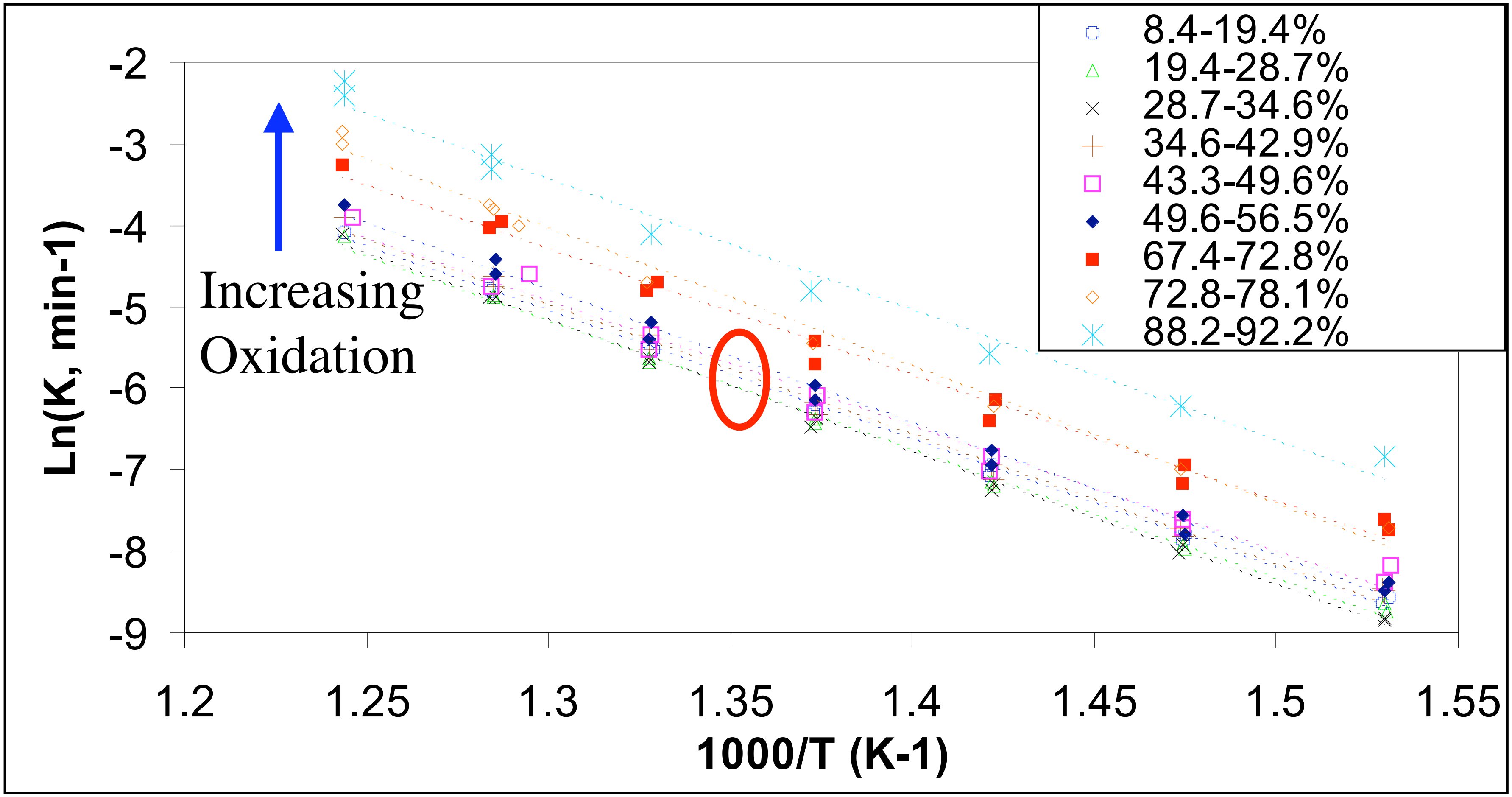
– Adsorbed HC; ambient aging

B: "Steady-state" oxidation

C: Increased reactivity at later stages of oxidation

$$r = \mathbf{A} \cdot exp(-\mathbf{E_a}/RT) \cdot [C]^{\mathbf{a}} \cdot [O_2]^{\mathbf{b}} \cdot [H_2O]^c$$

Progressive oxidation



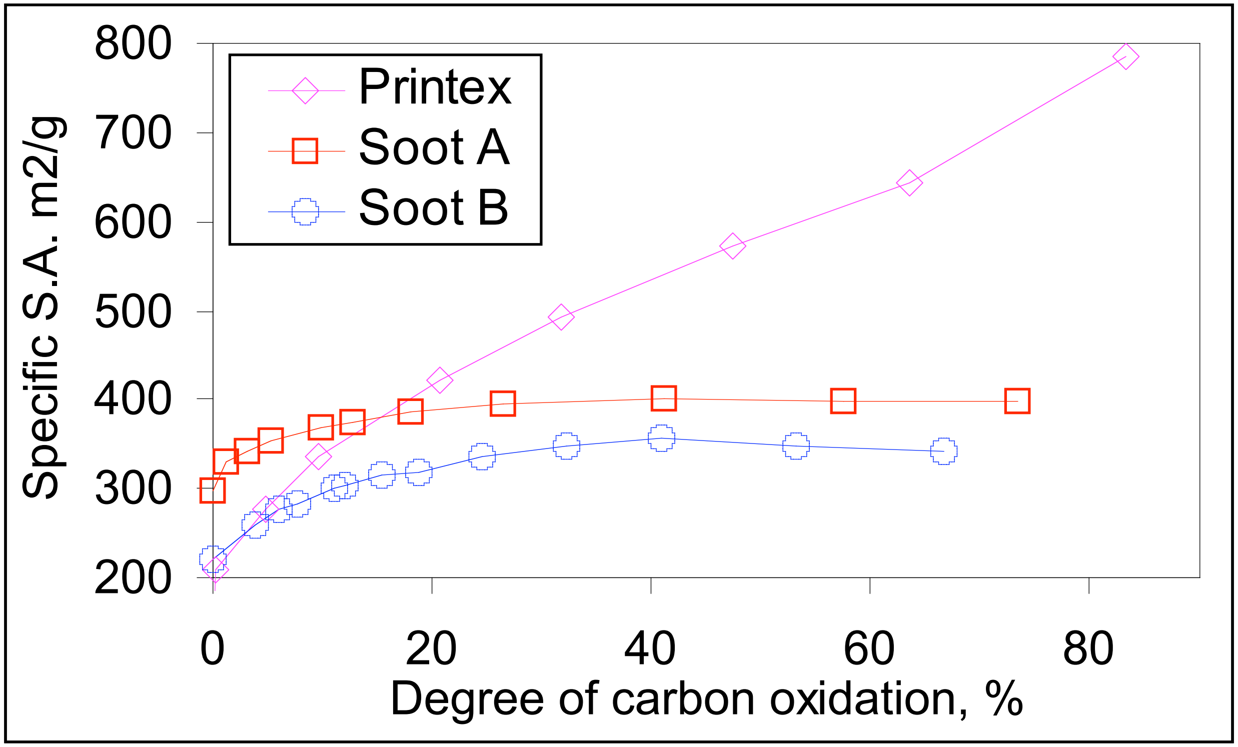
Reactivity is increasing with degree of oxidation:

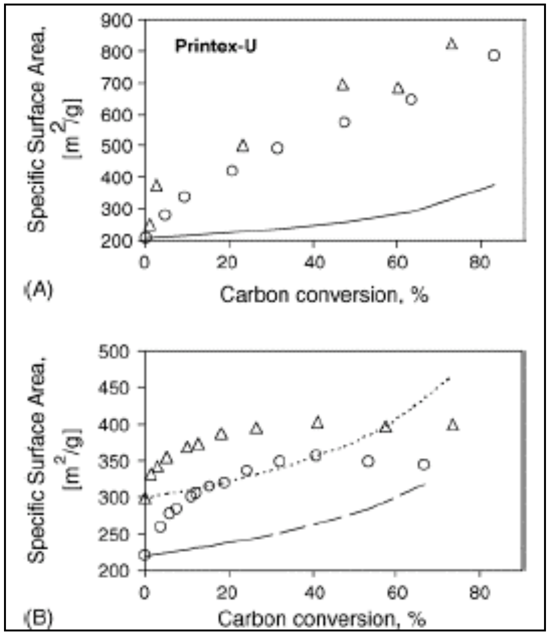
– No measurable changes of *Ea*, or *reaction order in* O_2

* Reaction *chemistry* appears to be independent of the degree of carbon oxidation.

* *Number (density)* of reactive sites (A) appears to be near constant!

Specific Surface Area*





A. Yezerets, et al. Applied catalysis B: 61 (2005), 134-143.

–BET surface area measured in-situ at different stages of oxidation

–samples pre-treated by thermal desorption

*** Development of the reactivity does not appear to correlate directly with the specific surface area**

*** Need a different parameter which would correlate with the number of active sites**

*Courtesy: Dr. Do Heui Kim, (PNNL)

Puzzles (thus far):

* Comparative changes in reactivity

* Comparative evolution of surface areas

Advantages of electron microscopy (HRTEM)

* Direct observation without property assumptions

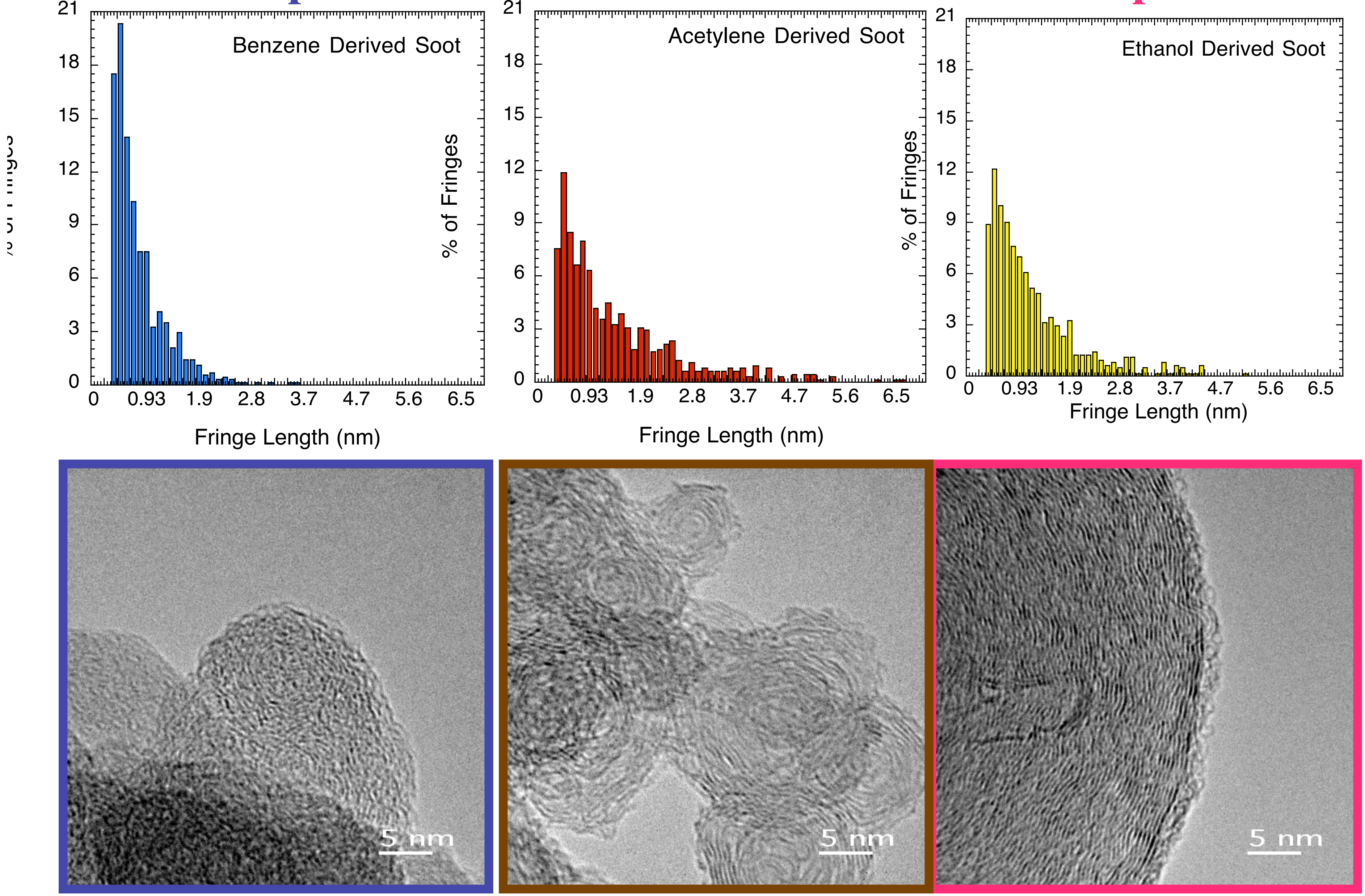
* Potential to reveal changes in nanostructure (during oxidation)

* Correlate oxidation characteristics (rate) with nanostructure

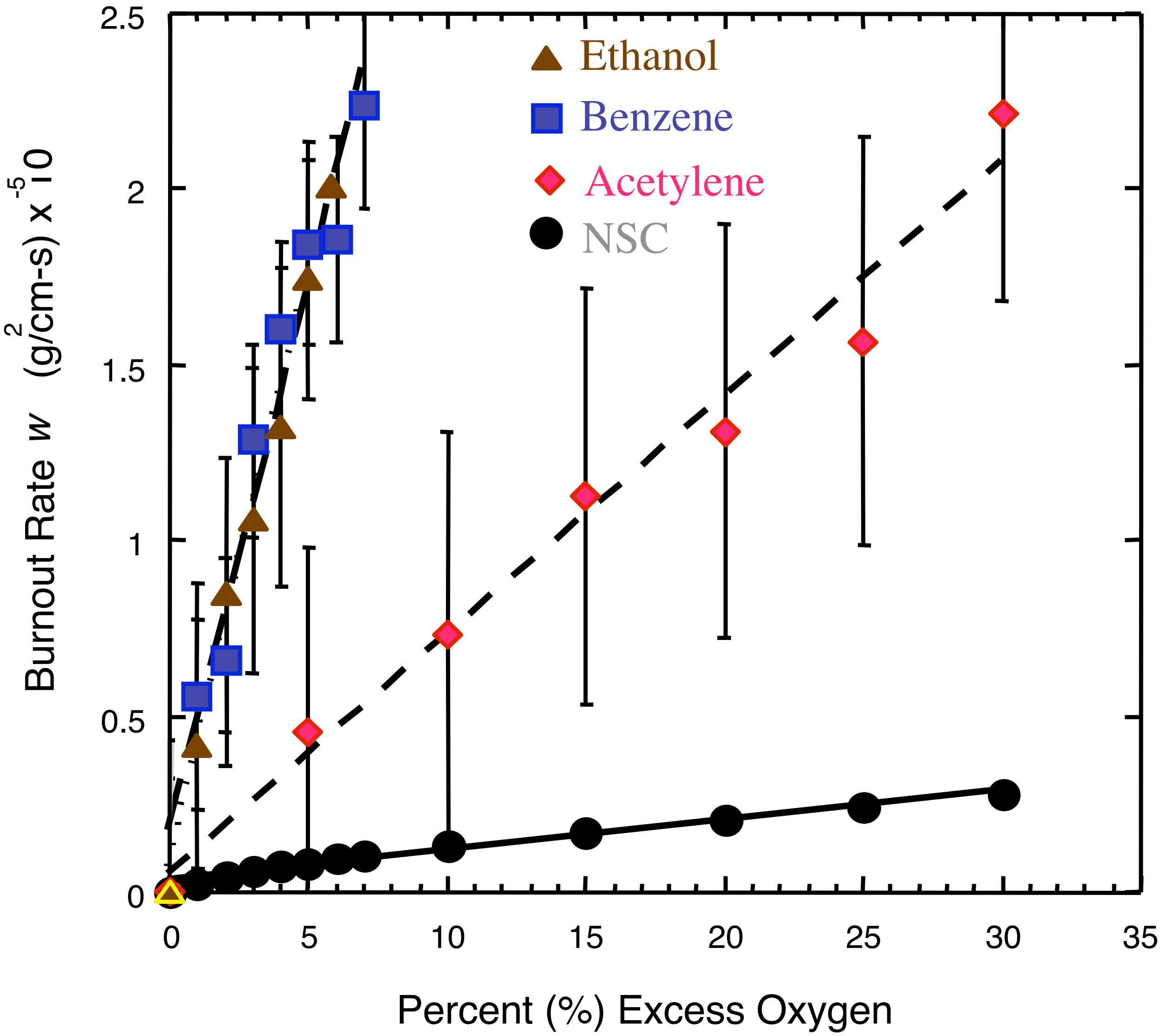
………*What changes in nanostructure?*

Nanostructure and Implications: Reactivity

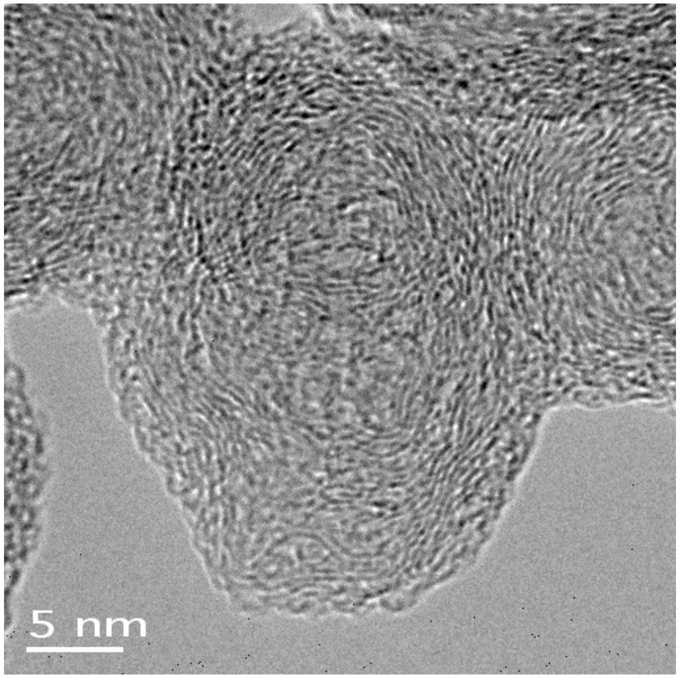
Amorphous | Fullerenic | Graphitic

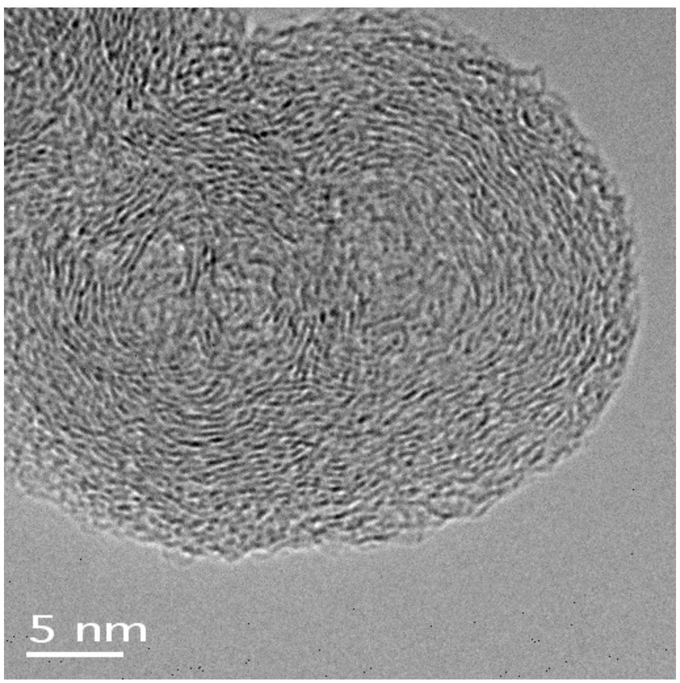


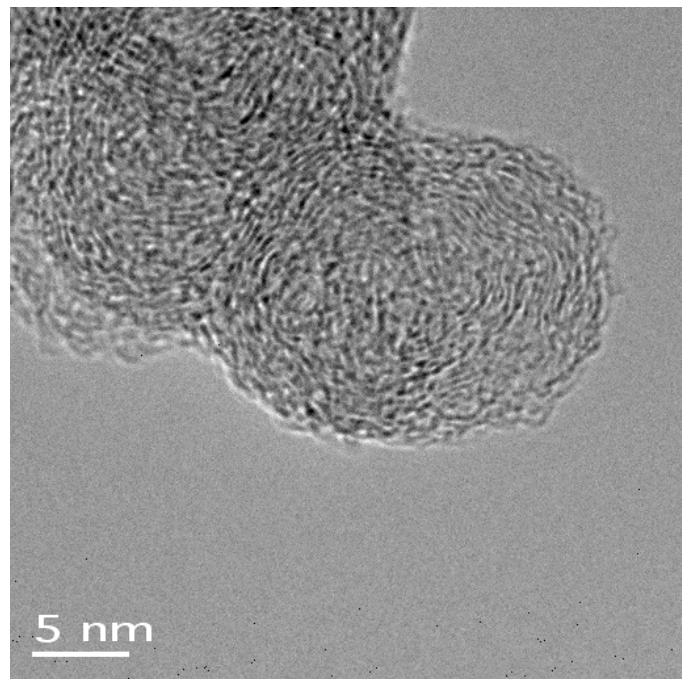
Soot Burnout Rates



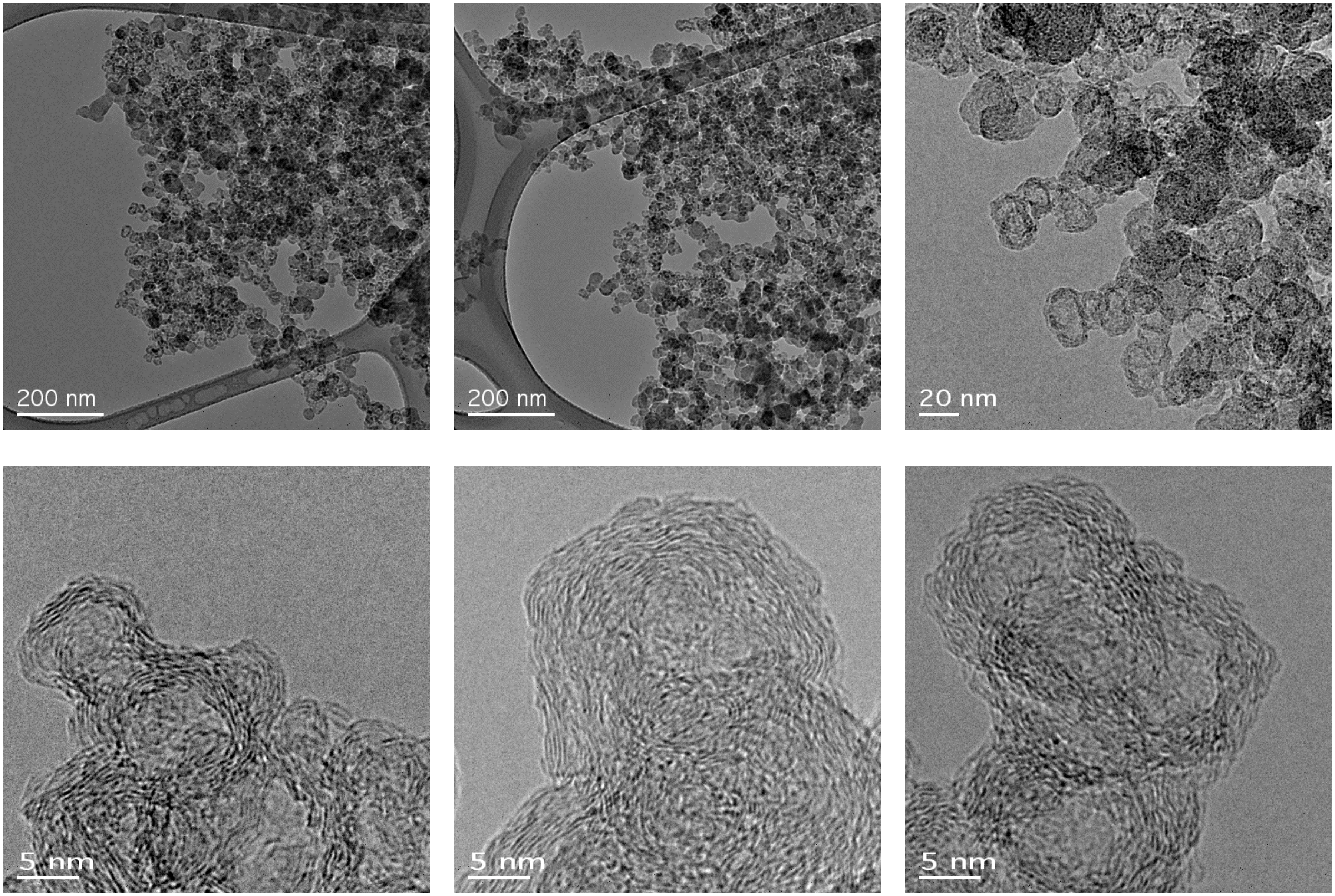
ENG-A - Original from Trap



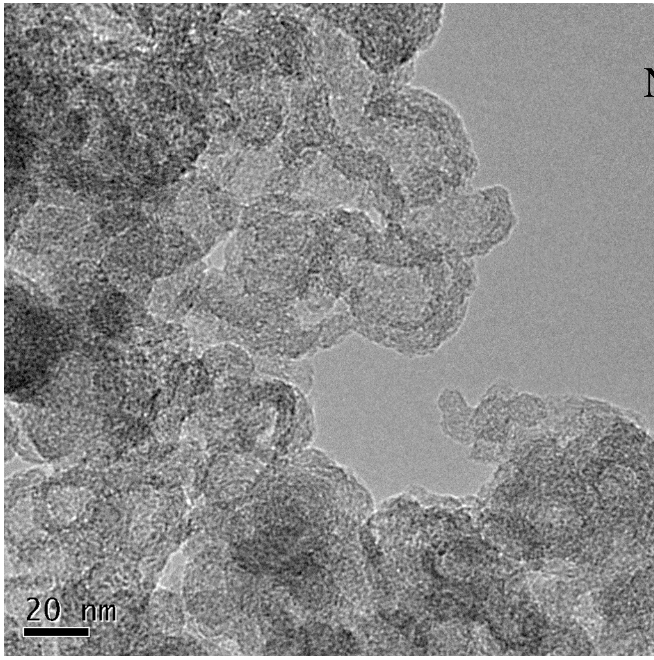




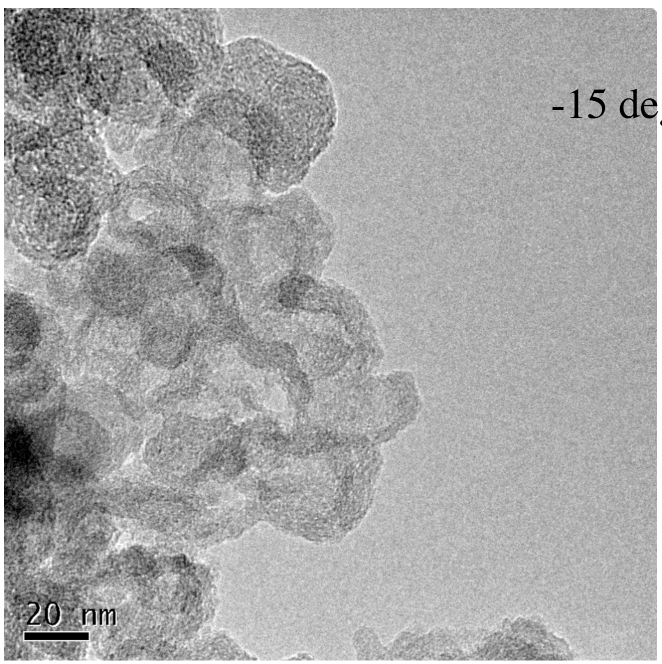
ENG-A - Post partial Oxidation (TGA, 50%)



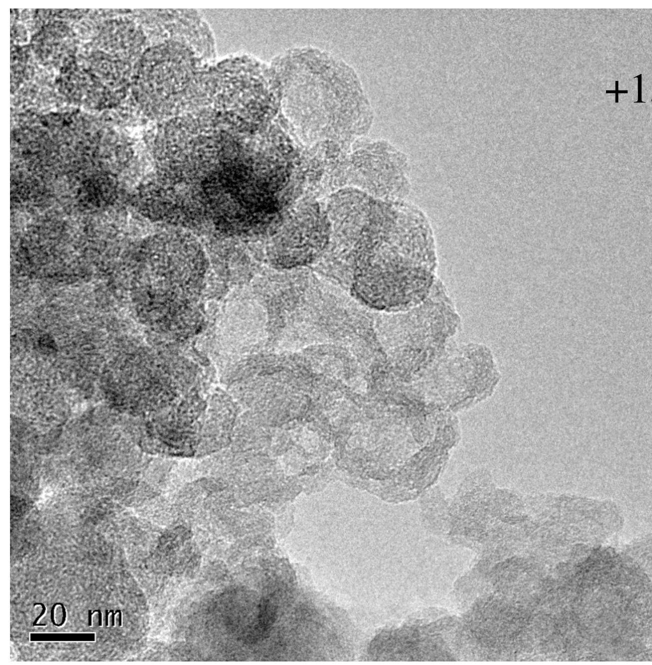
ENG-A 75%
Burnout
Hollow particles
viewed though
Successive tilts



No tilt

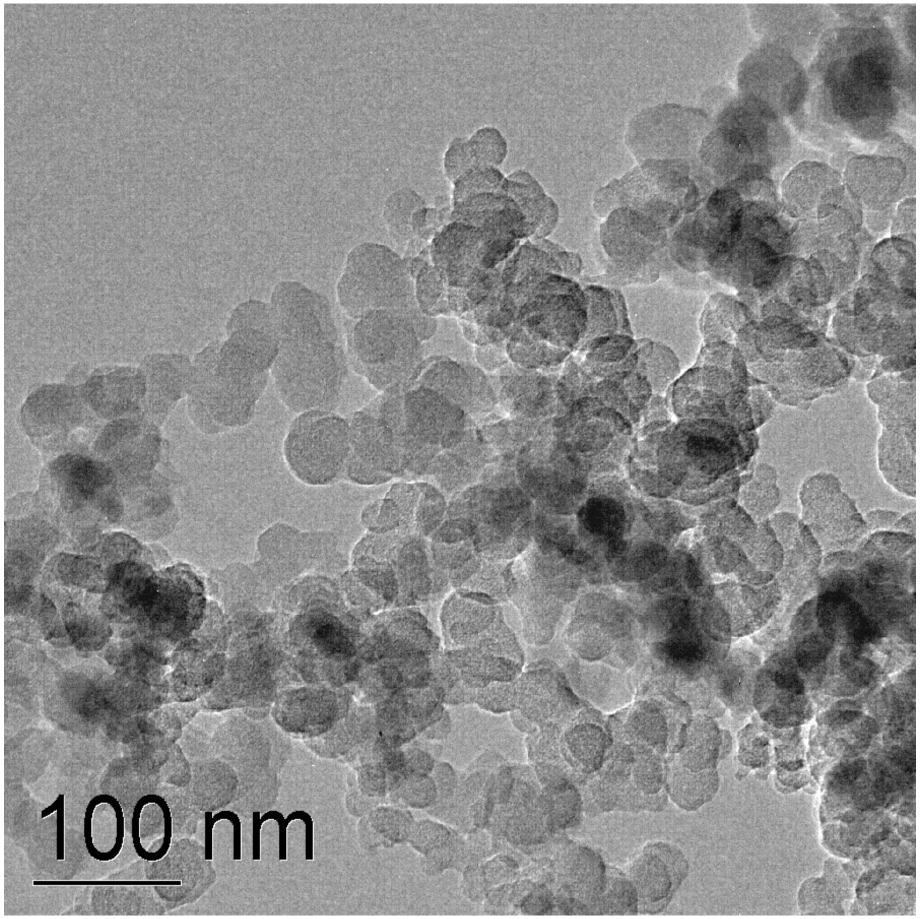


-15 degree tilt

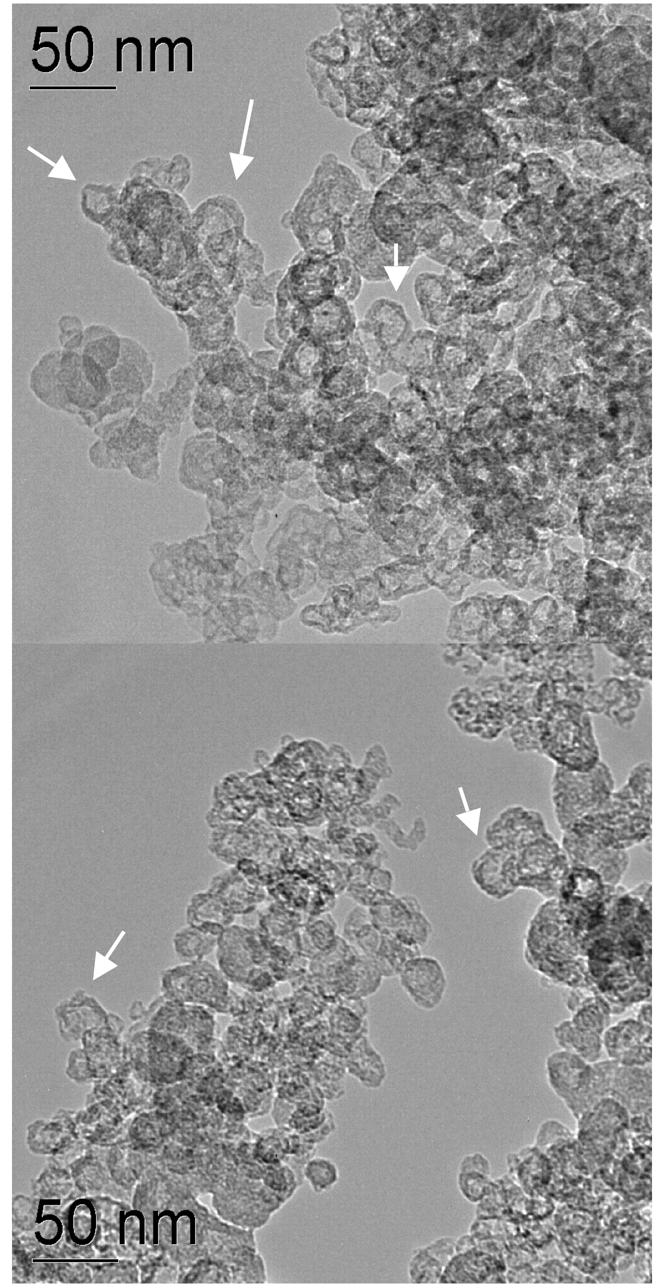


+15 degree tilt

Eng-A: Oxidized at 450 °C



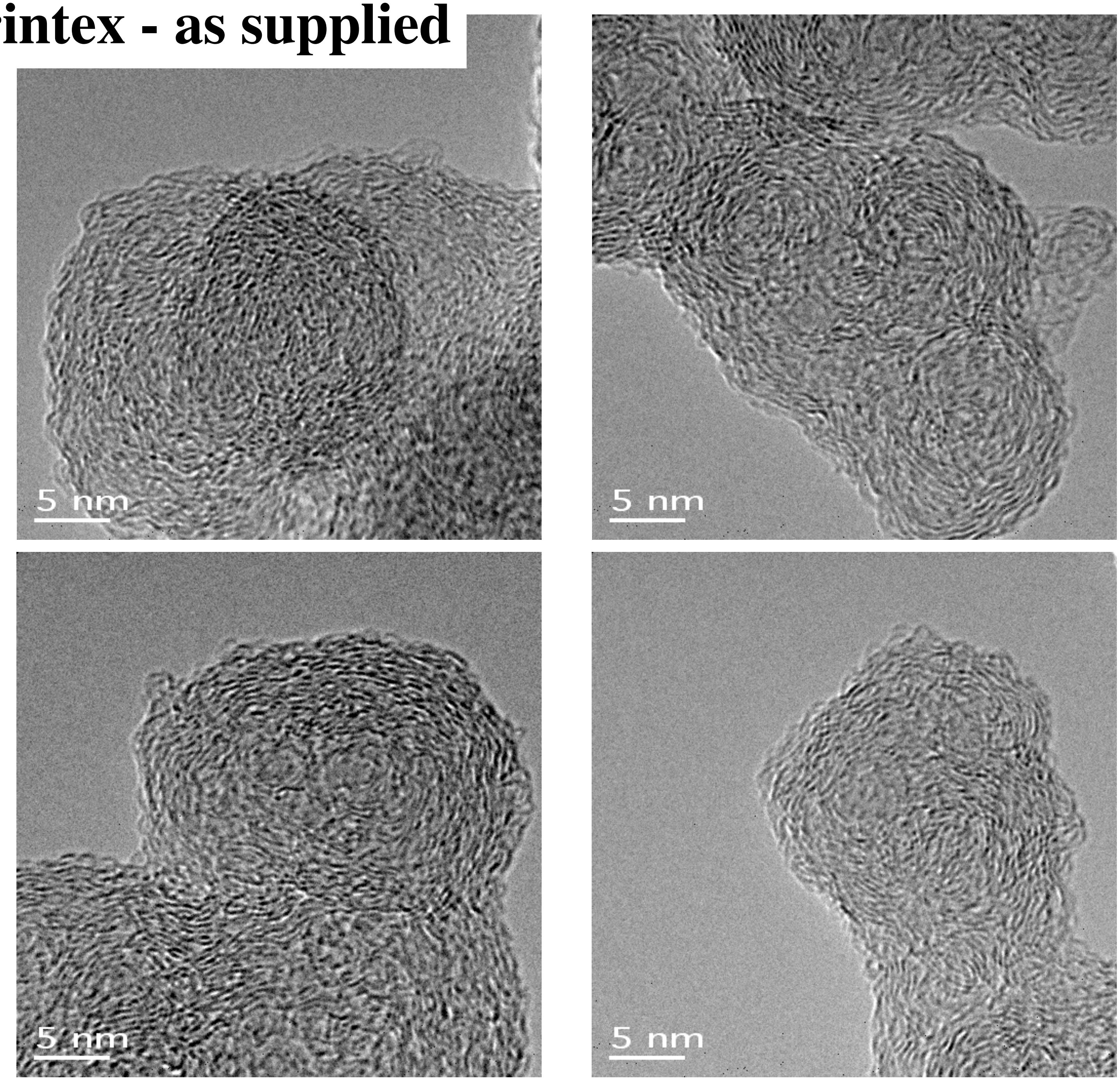
Eng-A: As-received
"Solid particles"



"Hollow particles"

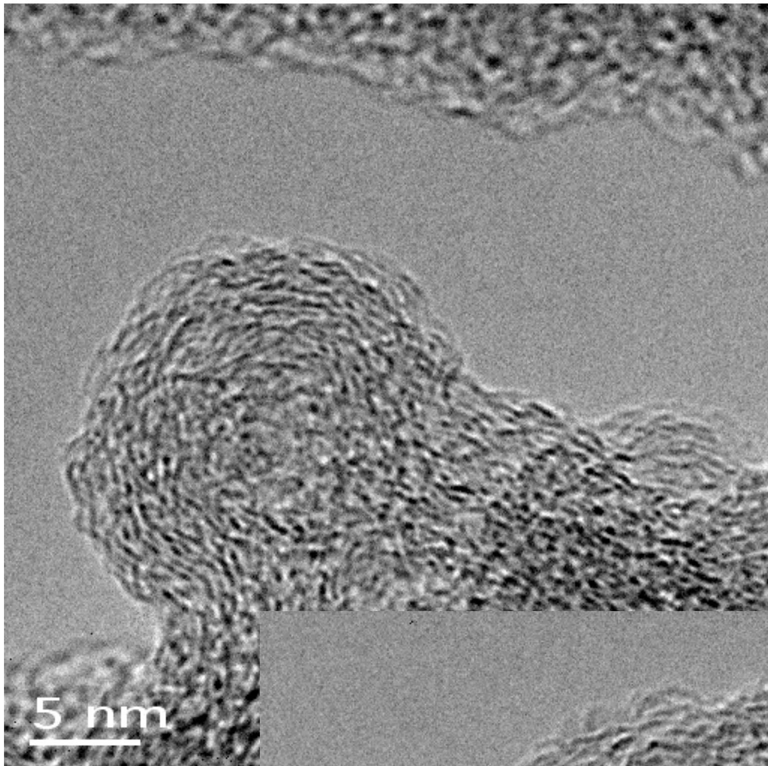
PNNL

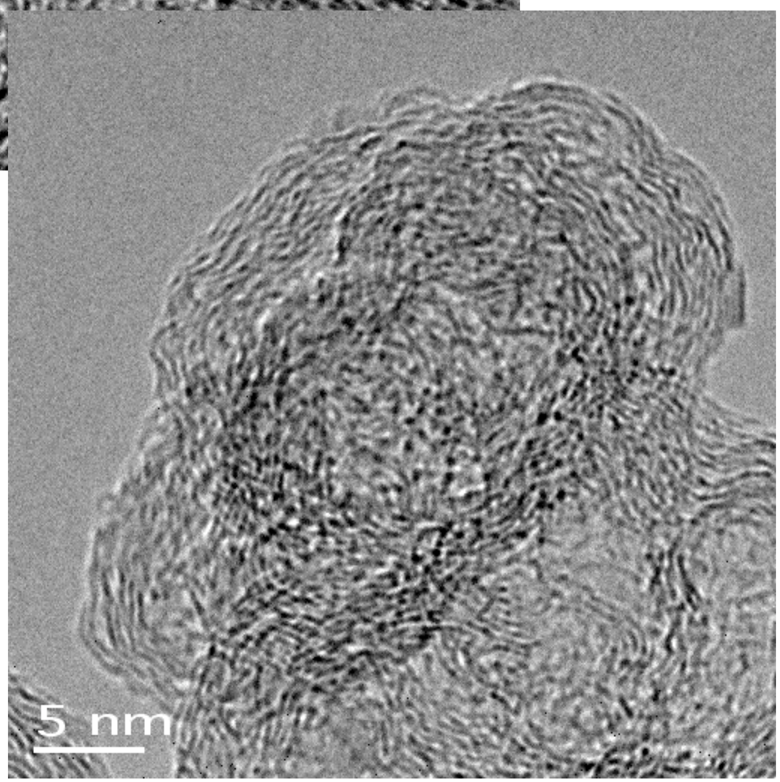
Printex - as supplied

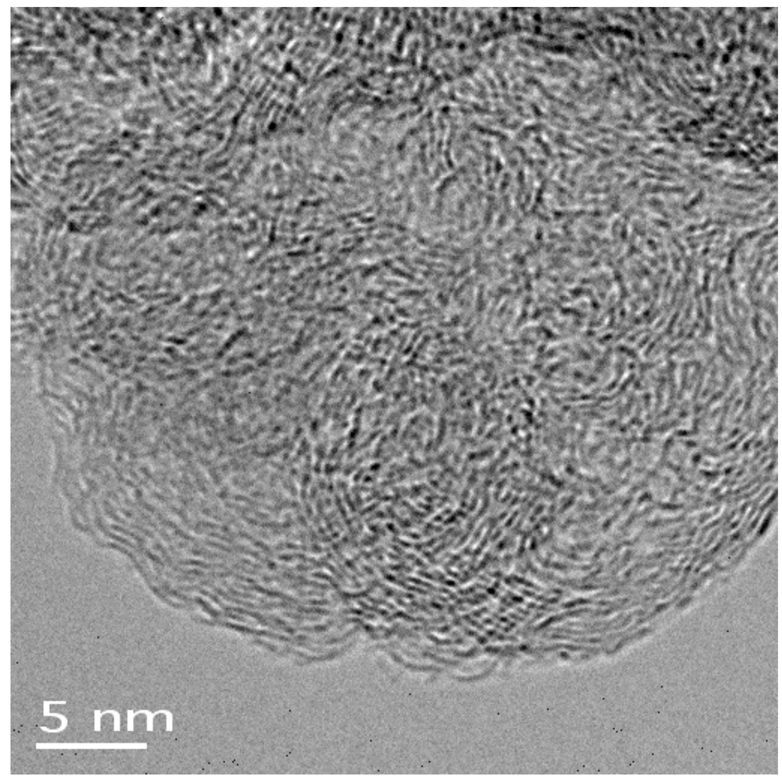


Printex - Post Partial Oxidation

50% Burnout, via TGA



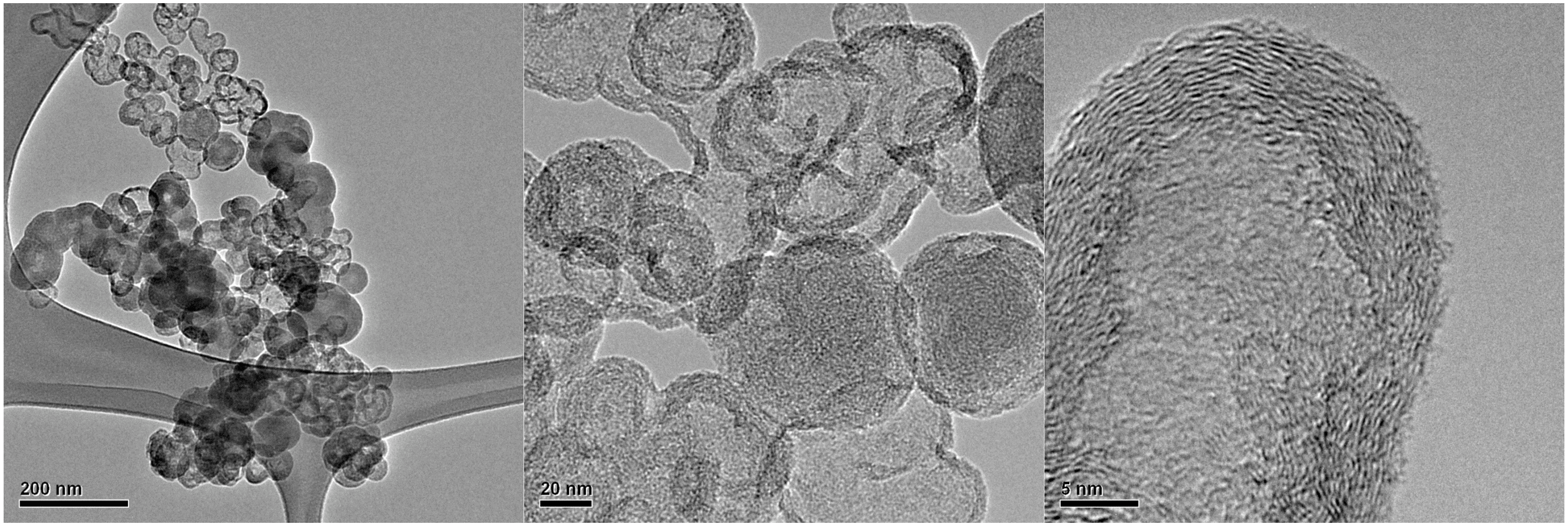




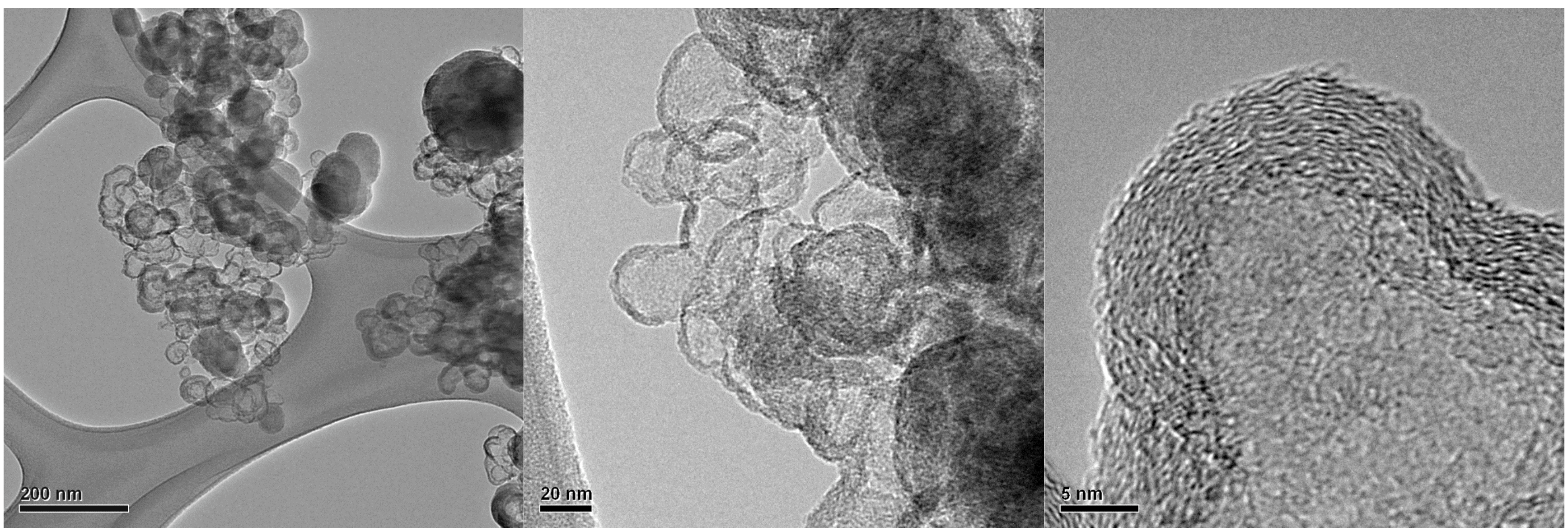
Summary of Results

Sample designation	**Ash contents, wt %**	**SOF contents, wt%**	**Observations**
ENG(A)	6.5 ± 0.5%	9 ± 1%	No shells/capsules
Printex-U™	<0.5%	4 ± 1%	No shells

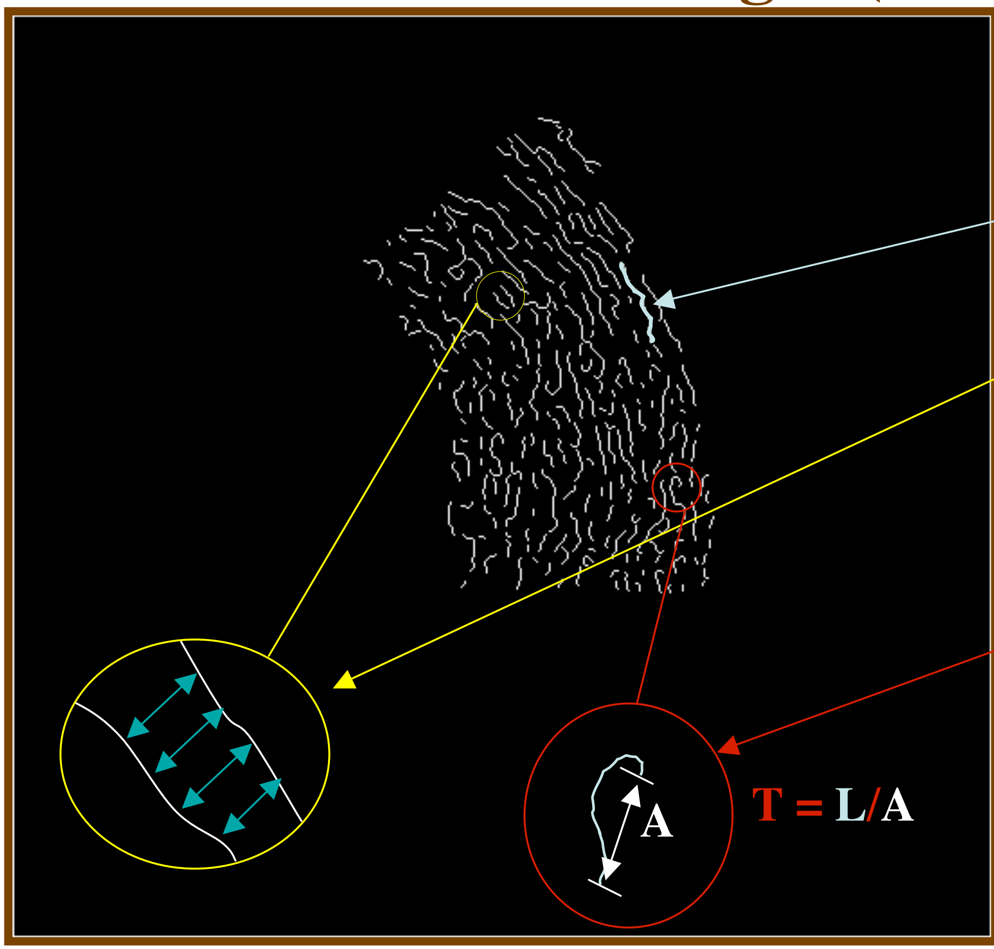
<u>Does Internal burning correlate with either ash or soluble organic fraction (SOF) content??</u>



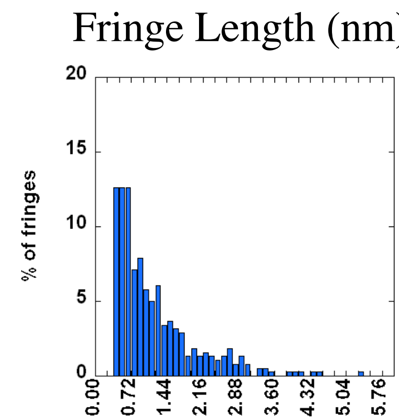
A Carbon Black

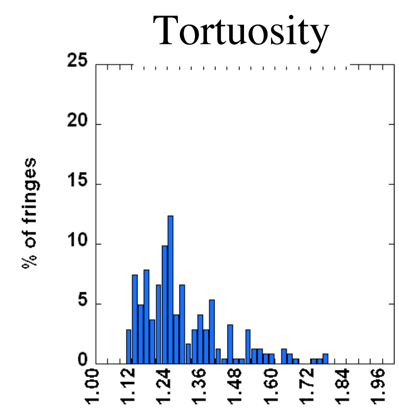


Statistical Properties Extracted From HRTEM Images (of soot nanostructure)



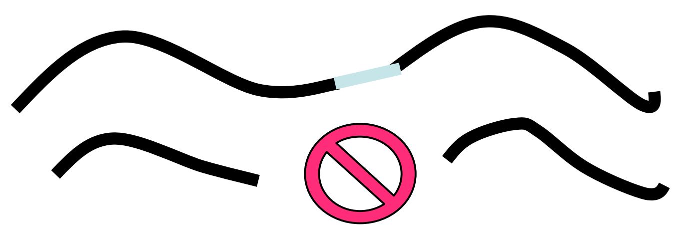
- Position
- **<u>Length</u>**
- Fringe Separation
- Orientation
- **<u>Tortuosity</u>**
- Fringe Density





*** Other inputs**

- **–Maximum join distance**
- **–Minimum fringe length**



Interpretation(s)

A. Densification - a pseudonym for graphitization

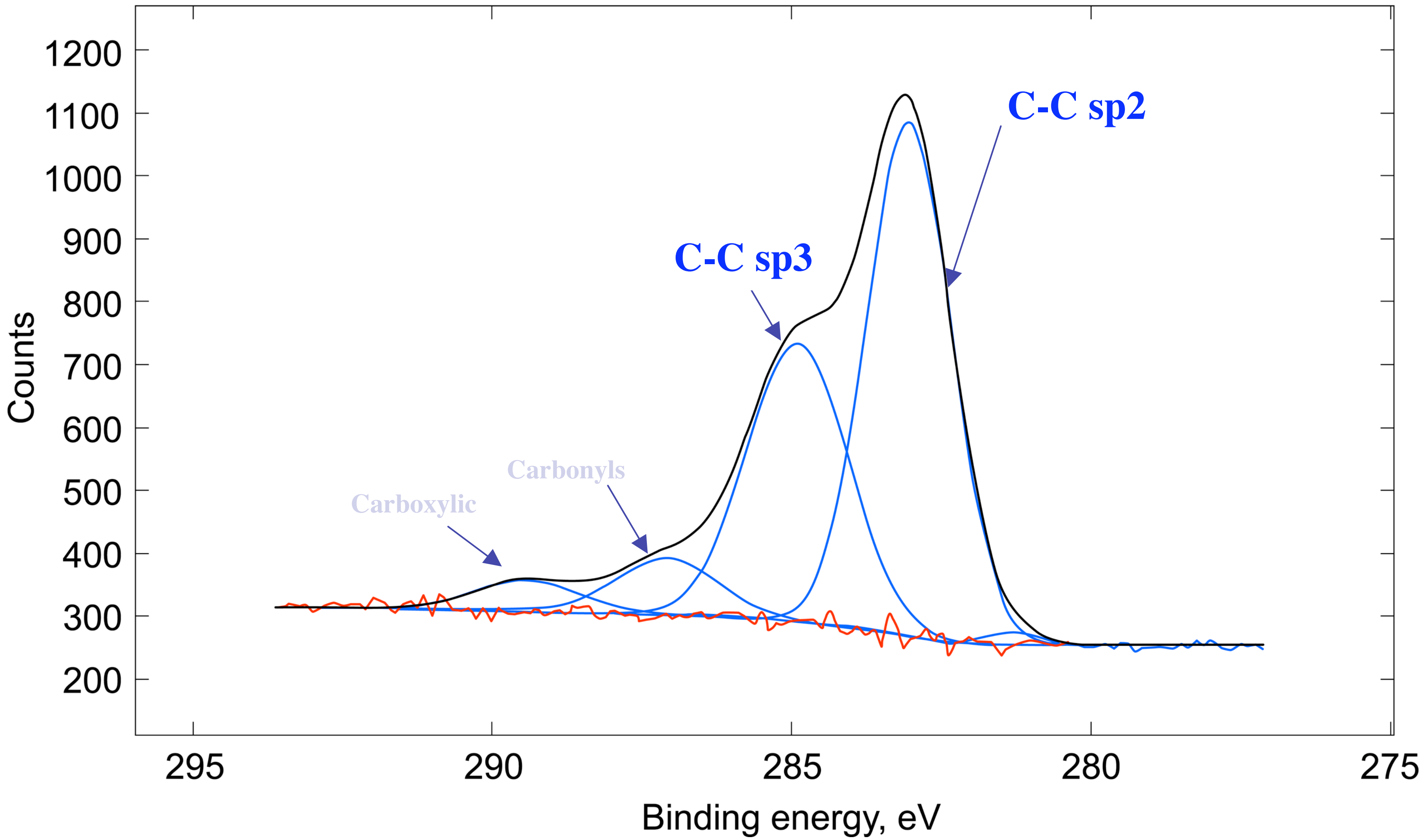
1. Thermally induced densification
Creation of radicals by **thermal** evolution of volatiles or loss of H-atoms permits lamella growth

2. Oxidation
Creation of radical sites by **oxidative** removal of amorphous carbon or loss of H-atoms

B. Internal Burning - disordered carbon and/or trapped volatiles preferentially burnout

Trap conditions could promote both densification and/or volatile evolution.

XPS-Characterization of Carbon Nanostructure



Conclusions

* Burning mode dependent upon nanostructure and oxidation conditions
  (ash and SOF are not unique predictors)
* Diesel soot and Printex U exhibit nearly identical activation energies and burning rates and even similar active site numbers ***BUT*** vastly different ***surface area*** evolution!
  * Measures other than surface area are needed for modeling *burning mode and rate*.

(A key feature will link the distribution of active sites to the nanostructure)

* Convolved with initial nanostructure are the change(s) enabled by oxidation.

Implications:

* Latter stage burnout will strongly depend upon burnout mode
* Soot burning mode(s) could affect regeneration efficiency and models.
* DPF regeneration costs fuel and each cycle limits lifetime.

Costs money!