RJ LeeGroup, Inc.

Analysis. Consulting. Development.

April 23, 2009

Nanoparticle Characterization using Advanced SEM/STEM Instrumentation

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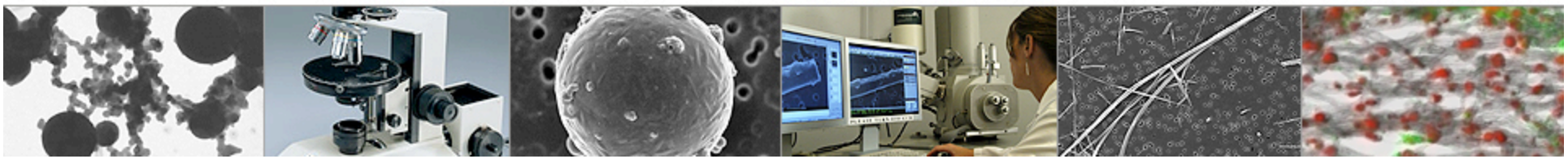

Outline

- What are nanoparticles?
- Historical uses of nanoparticles
- Complementary TEM and FESEM analyses
- Advanced SEM/STEM technology
- Examples
- Application: Industrial Hygiene
- Case Study
- Summary

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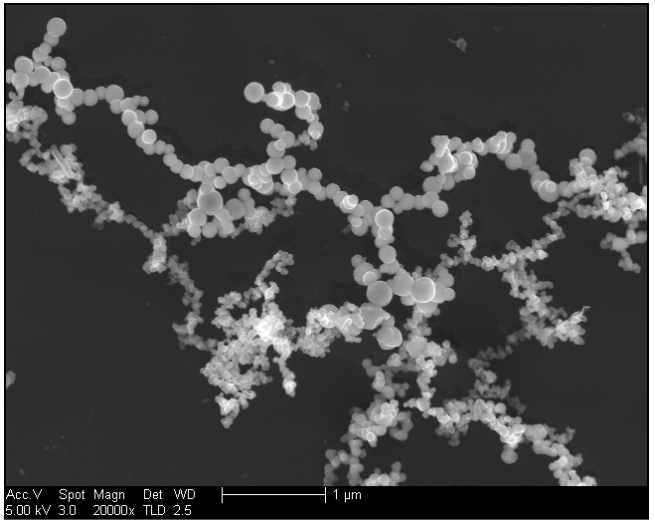
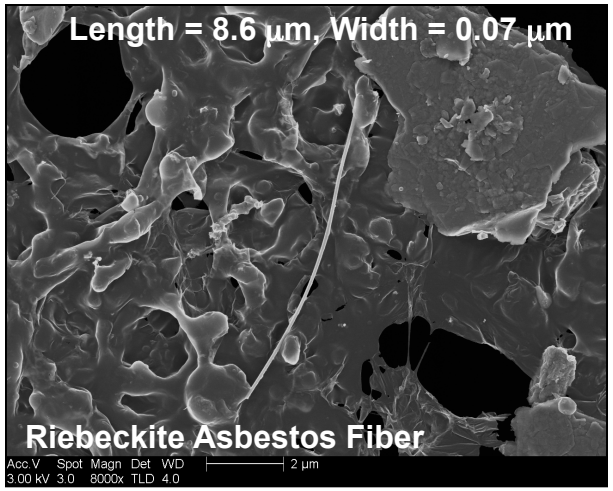
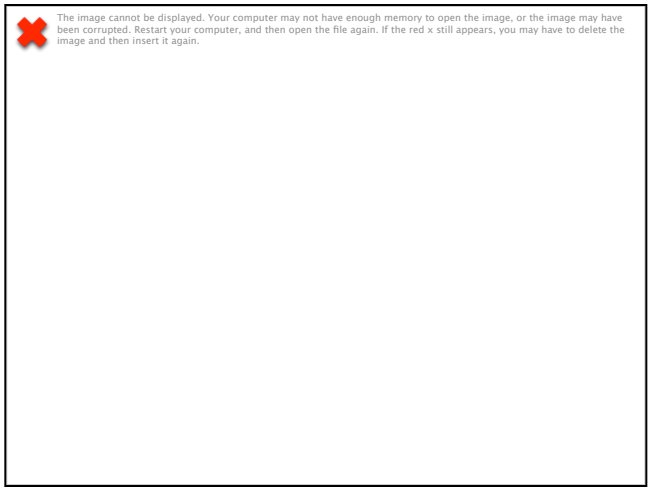


ASTM Definition of Nanoparticle

- **nanoparticle,** n—in *nanotechnology*, a sub-classification of ultrafine particle with lengths in two or three dimensions greater than 0.001 micrometer (1 nanometer) and smaller than about 0.1 micrometer (100 nanometers)…..

- **ultrafine particle**, n—a particle smaller than about 0.1 micrometer (100 nanometers) in diameter.

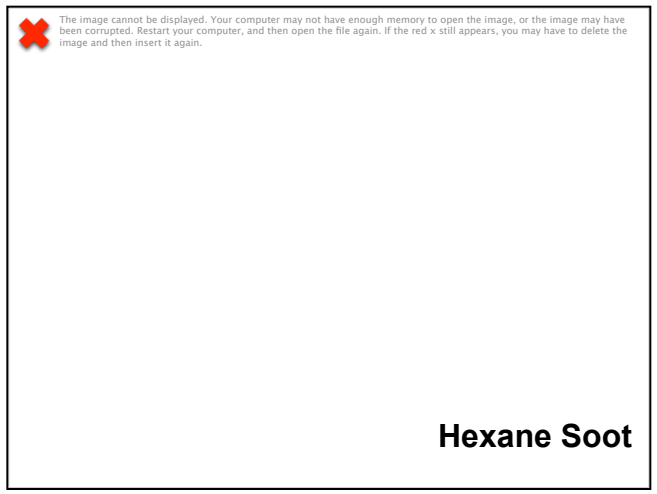




ASTM E 2456-06, Terminology for Nanotechnology, American Society for Testing and Materials, West Conshohocken, PA 19428-2959, 2006.

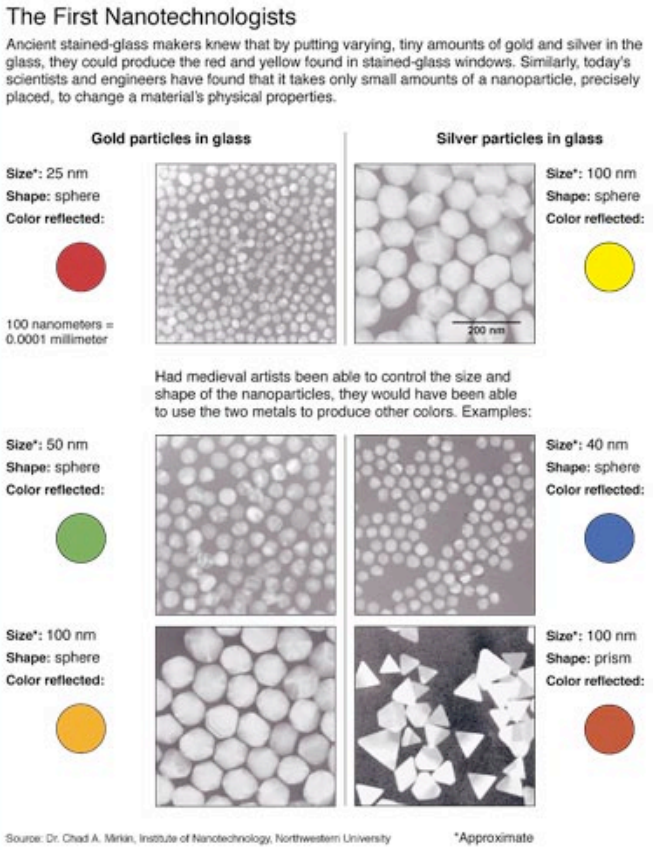
Where are nanoparticles?

- Natural and anthropogenic origins
  - Naturally occurring
    - Asbestos, volcanic ash, forest fire smoke, biological structures (brochosomes)
  - Combustion particles
    - Soot, metal oxides, welding fumes
  - Engineered nanoparticles
    - Carbon nanotubes, carbon and metal nanoparticles, pigments, carbon black



Early Uses of Nanoparticles

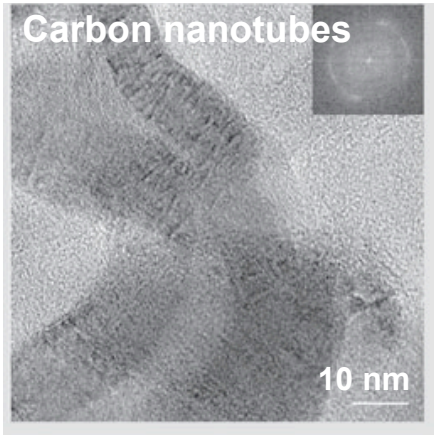
- Stained windows from the16th and 17th centuries:
  - Added gold chloride to molten glass resulting in a red tint
  - Added silver nitrate to molten glass resulted in a yellow tint
- Analysis of glass from this era revealed gold and silver nanoparticles; reflected red and yellow light, respectively

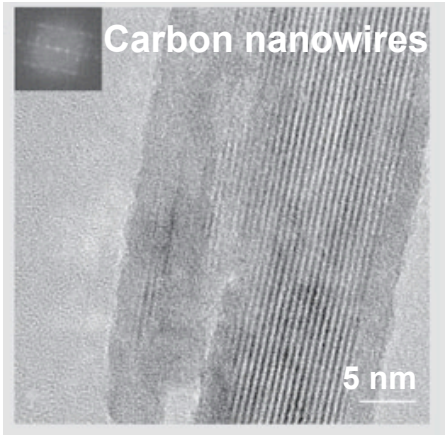


Chang, Kenneth, "Tiny Is Beautiful: Translating 'Nano' into Practical," New York Times, 22 February 2005, Science Desk Section.

Early use of Nanostructures

- 12th-18th century Middle Eastern Damascus blades had features not found in European steals
  - Superior mechanical properties (strong/flexible)
  - Extremely sharp
  - Wavy banding pattern
- In 2006, dissolved portion in hydrocholoric acid and analyzed by HRTEM – composite material
  - Carbon nanotubes
  - Nanotubes we protecting nanowires of iron carbide
- "Wootz" ore from India
  - Small traces of metals including vanadium, chromium, manganese, cobalt and nickel
- Combination of forging process and impurities
  - At high temperatures the impurities in the Indian ores could have catalyzed the growth of nanotubes from carbon





Reibold, M., A.A. Levin, W. Kochmann, N. Patzke, D.C. Meyer, "Materials: Carbon Nanotubes in an Ancient Damascus Saber," Nature, 444 (2006), 286.

Complementary TEM and FESEM Techniques for the Characterization of Nanoparticles

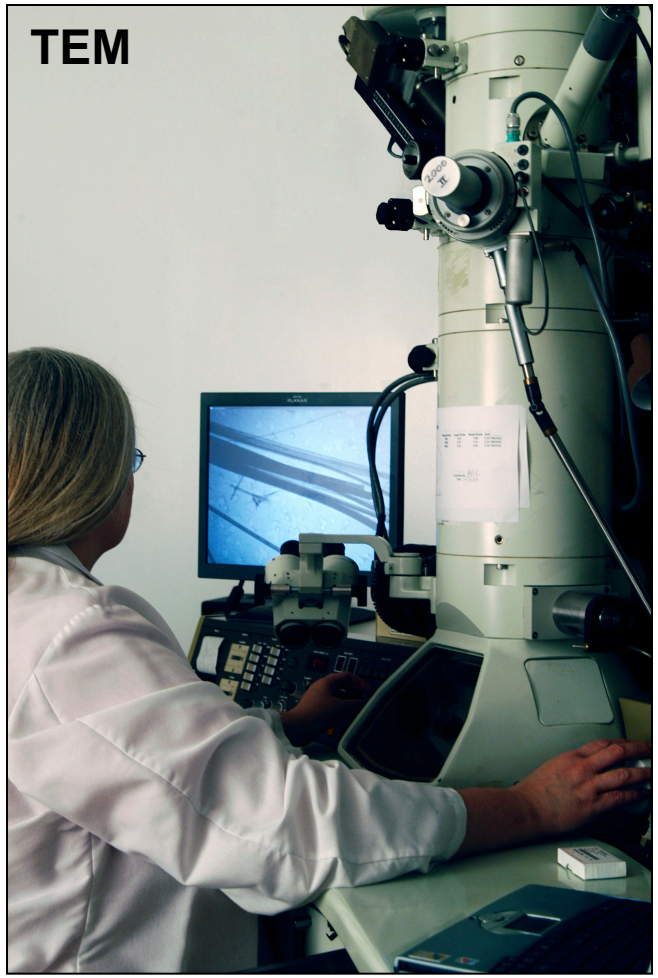
TEM

- High Resolution/High Magnification Images
- Provides chemistry (EDS)
- Provides crystallography (SAED)
- Provides projection image (no surface details and limited morphology)
- Limited Sample Size

FESEM

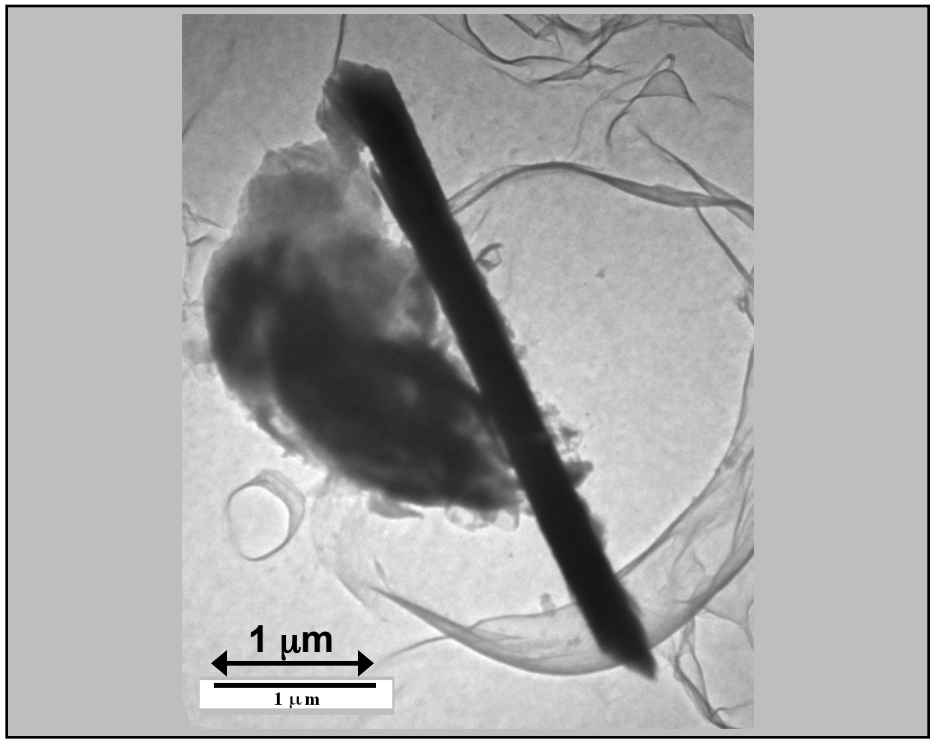
- FESEM provides comparable magnifications to TEM
- Detailed Surface Characteristics and Three-Dimensional Appearance
- Depth of Field
- Provides chemistry (EDS), but no crystallographic information
- Large Sample Capacity

What if we combine TEM and FESEM?

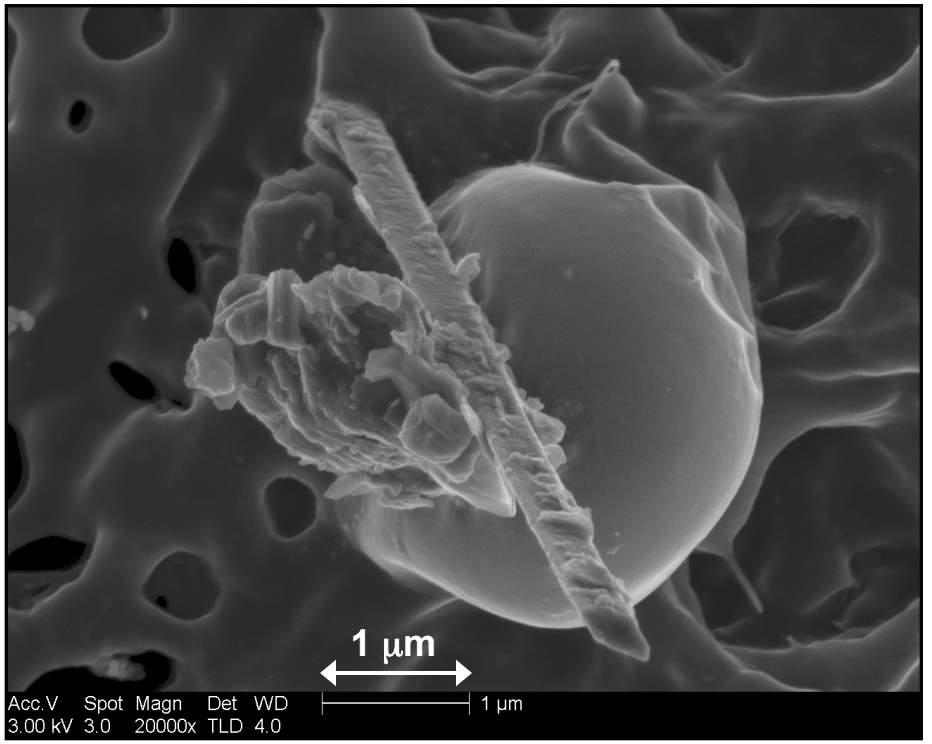


Complementary TEM and FESEM Characterization

TEM Image

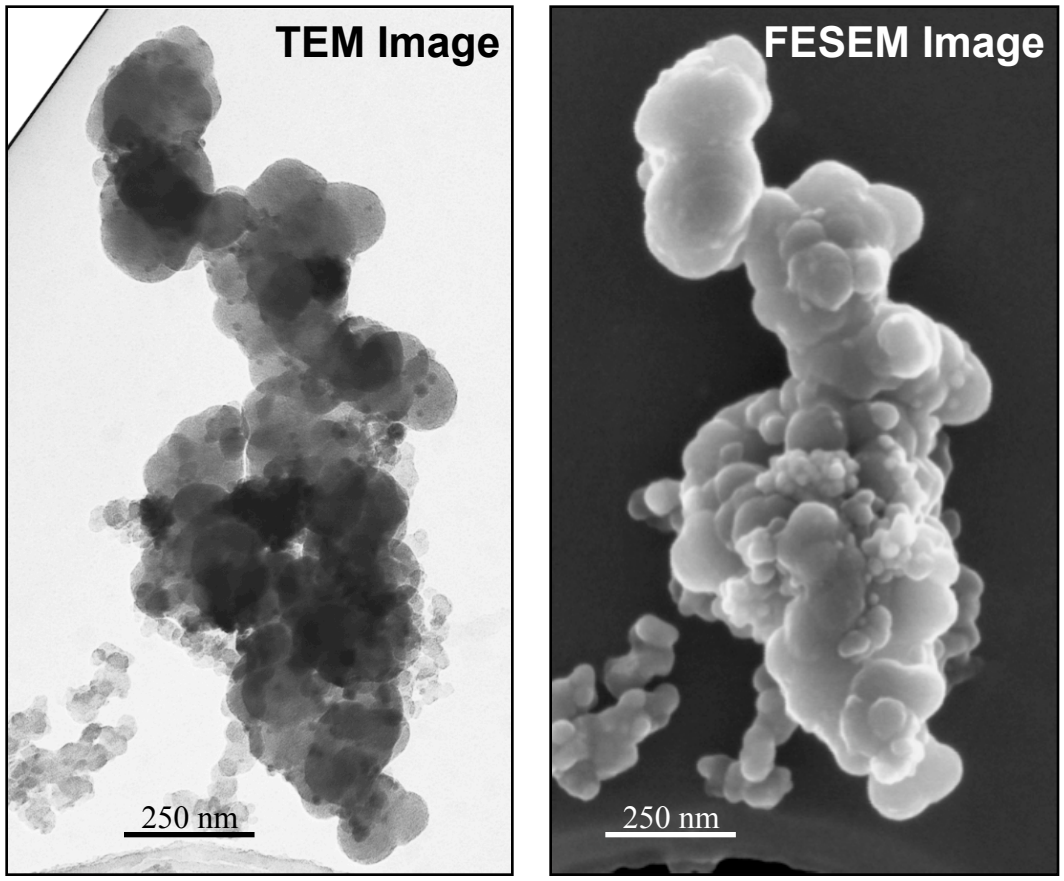


FESEM Image



What appears to be a long, thin fiber in the TEM image is revealed in the FESEM image to be a prismatic particle coming out of the plane of the projection screen. The particle was identified (EDS/SAED) as a richterite particle.

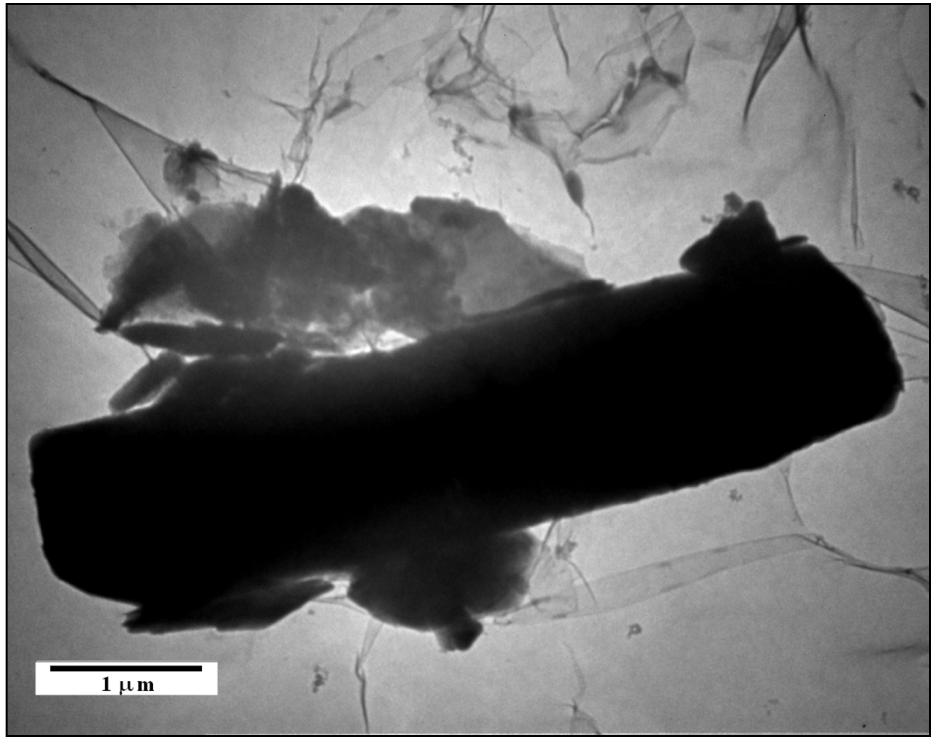
Complementary TEM and FESEM Characterization



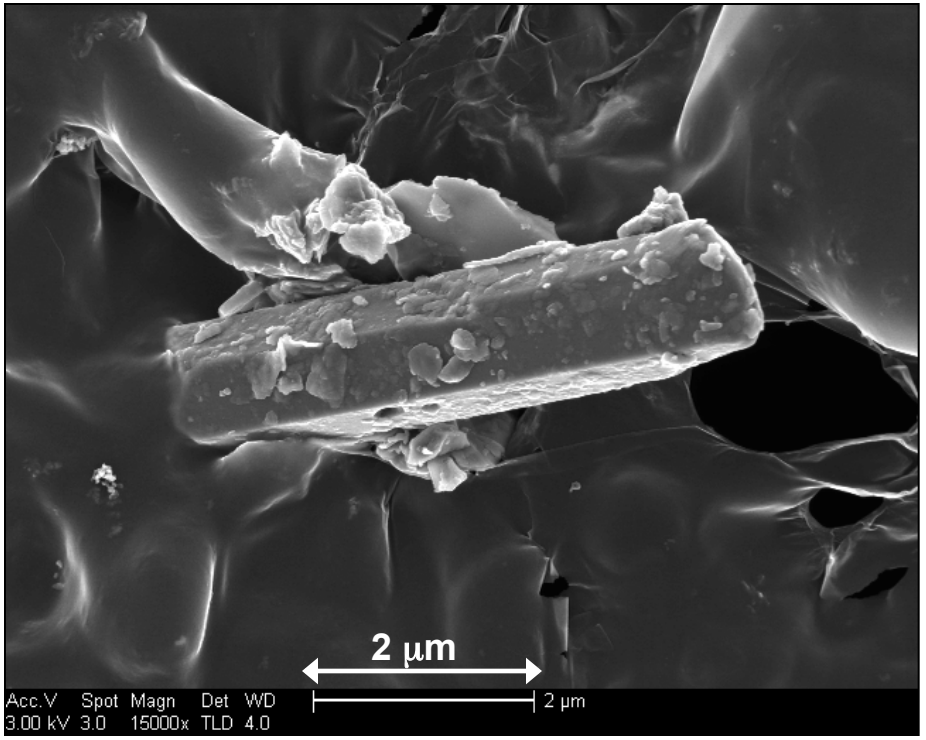
An aggregate of soot particles.

Complementary TEM and FESEM Characterization

TEM Image

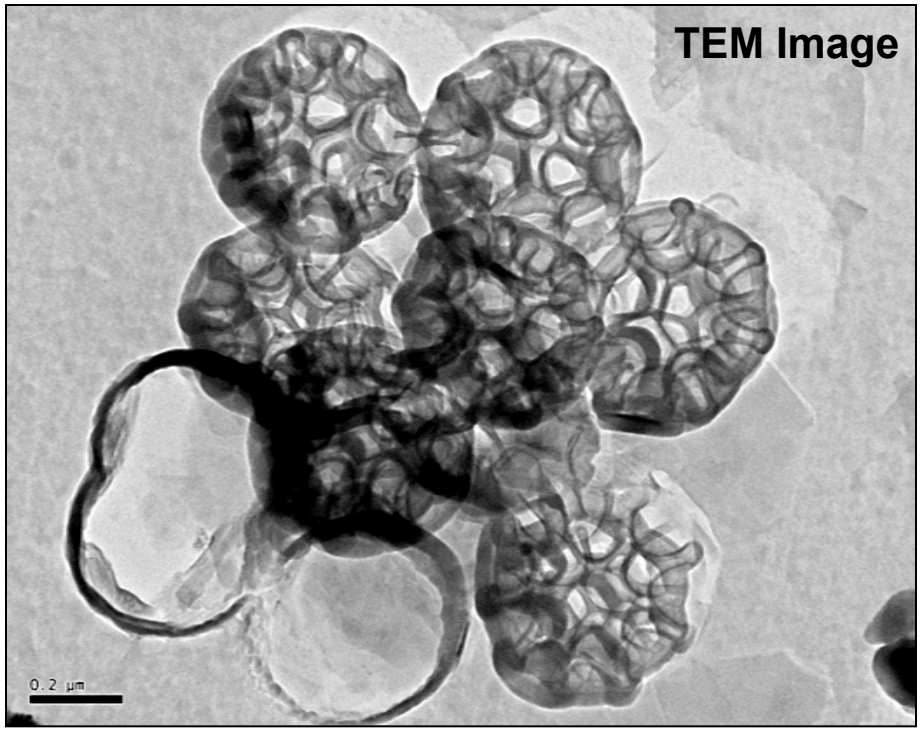


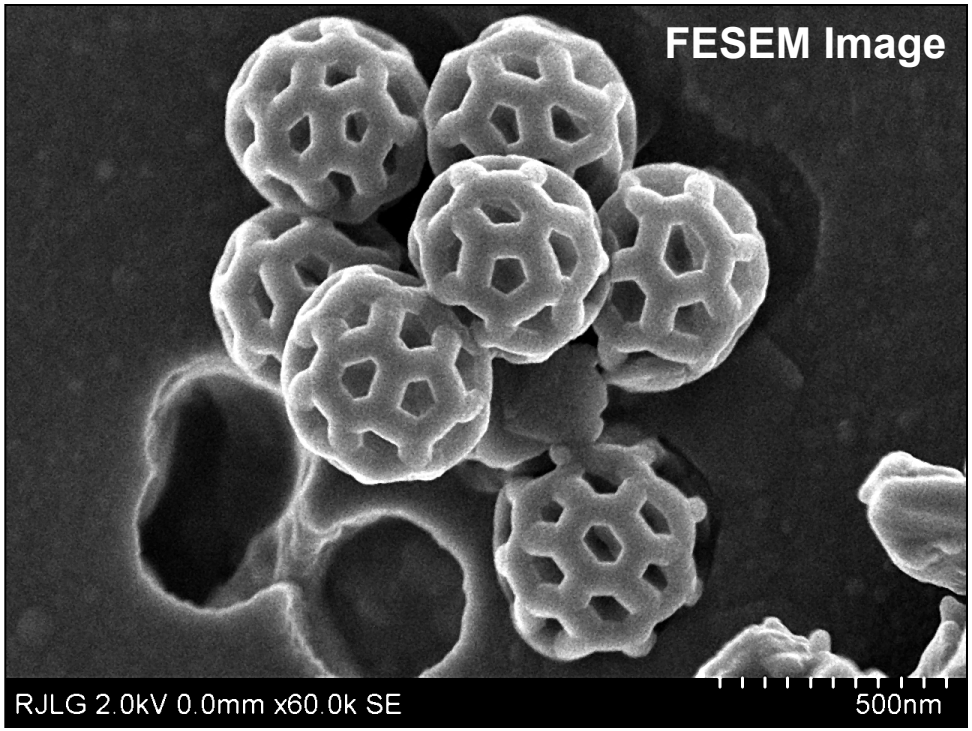
FESEM Image



What appears to be a long, thin particle in the TEM image is revealed in the FESEM image to be a prismatic particle. The particle was identified as an aluminum silicate mineral fragment.

Complementary TEM and FESEM Characterization



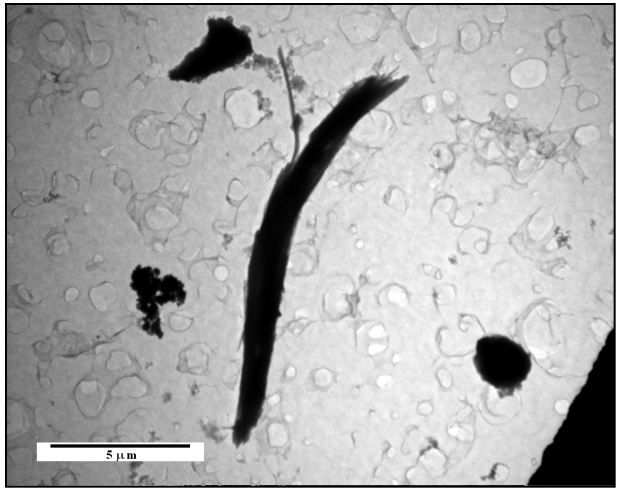


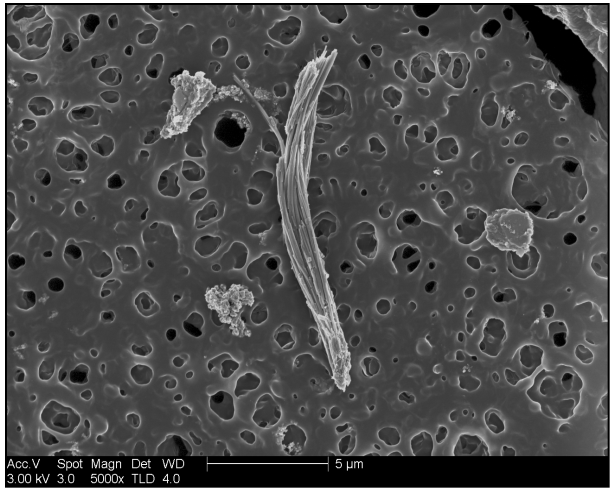
An aggregate of brochosomes.

Challenges of Complementary TEM and FESEM Analyses

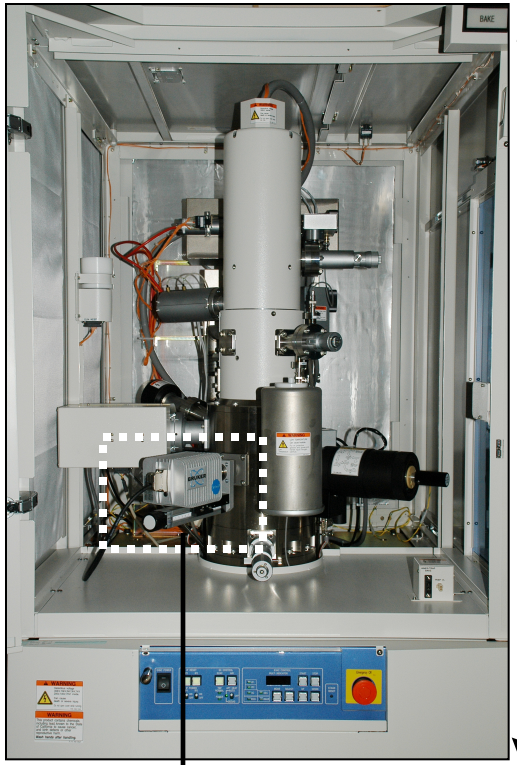
- Transferring samples between microscopes
  - Relocation
  - Orientation
  - Appropriate side of the grid (TEM to SEM)

- SEM working distance for EDS vs. high-resolution images





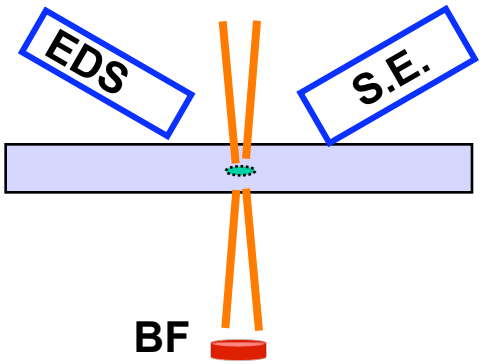
Advances in Electron Microscopy High-Resolution FESEM/STEM

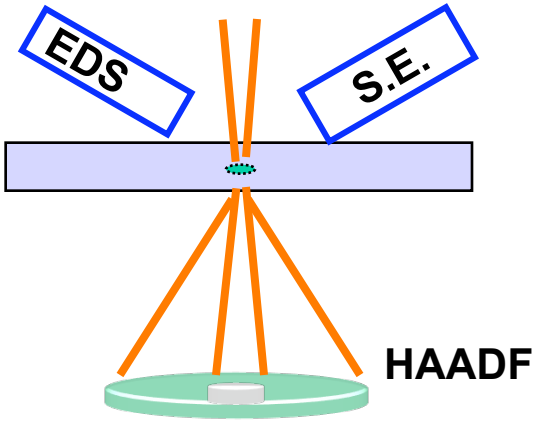


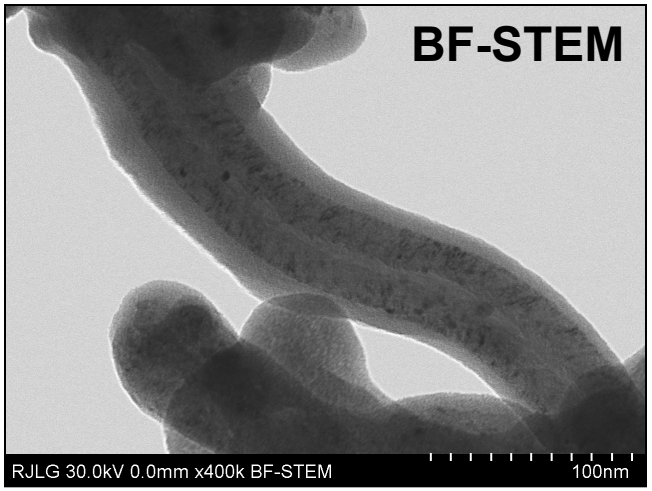
Bruker 30 mm^2 SDD

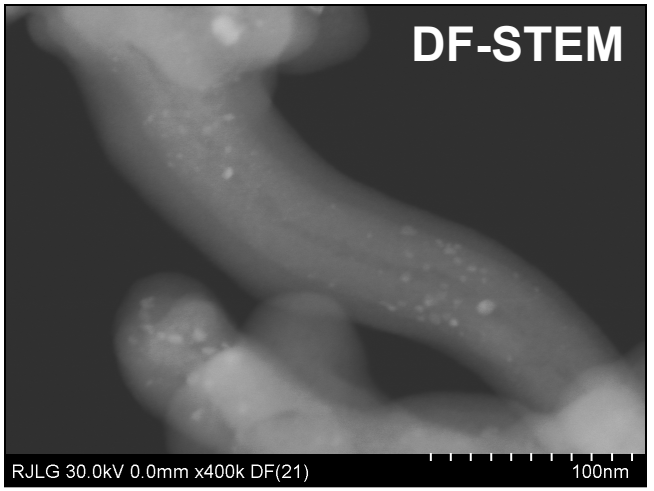
- 30 kV cold field emission
- Magnifications up to 2,000,000X
- Secondary electron imaging
- Bright field-STEM and Dark field-STEM imaging
- Energy dispersive X-ray spectroscopy (EDS)
- Switch between all operation modes without changing the specimen position (including EDS)
- Change accelerating voltages easily

BF-STEM and DF-STEM imaging

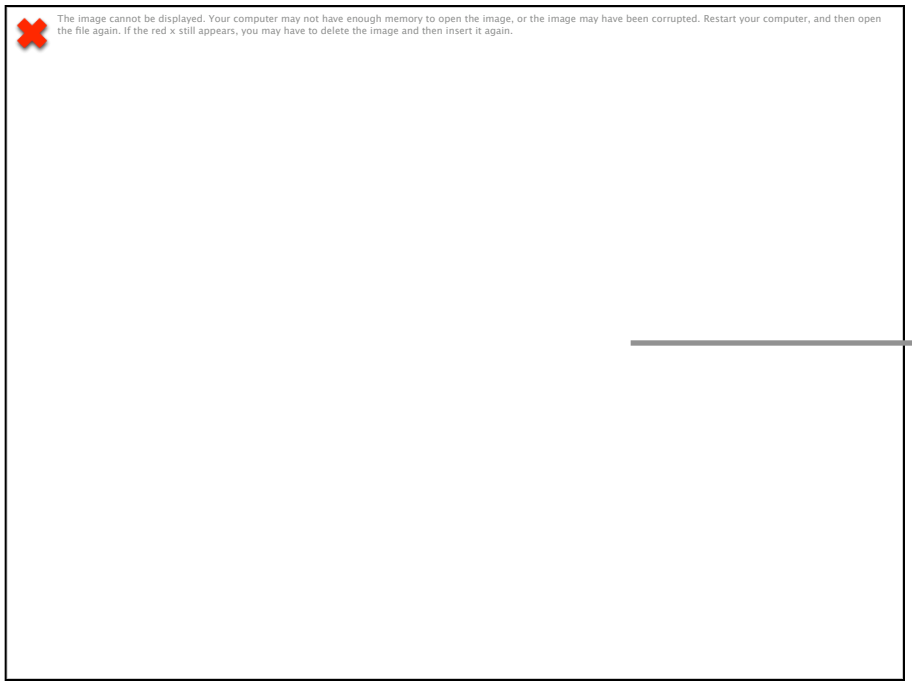




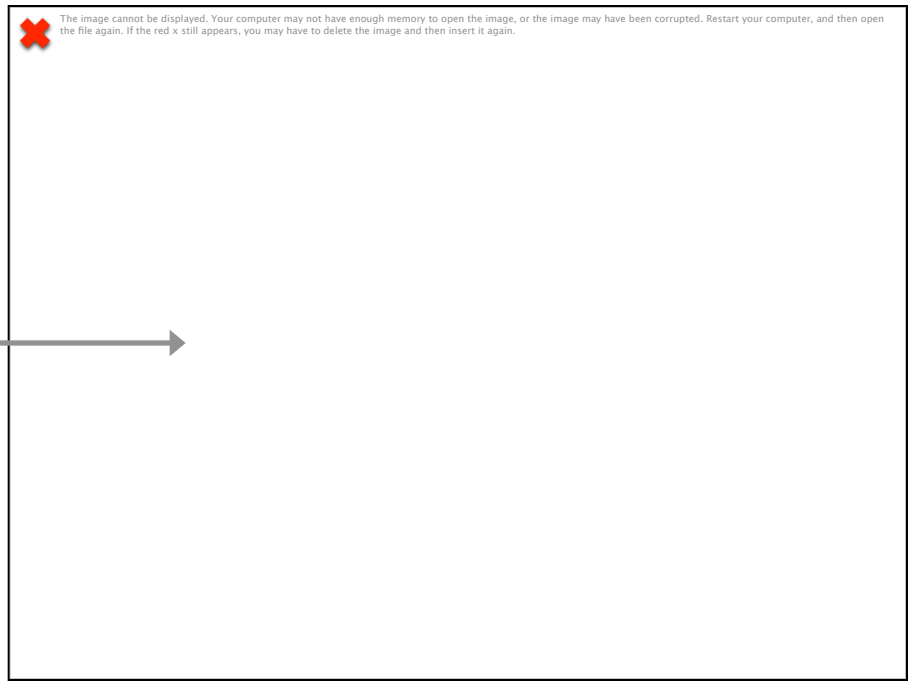




Gold Nanoparticles

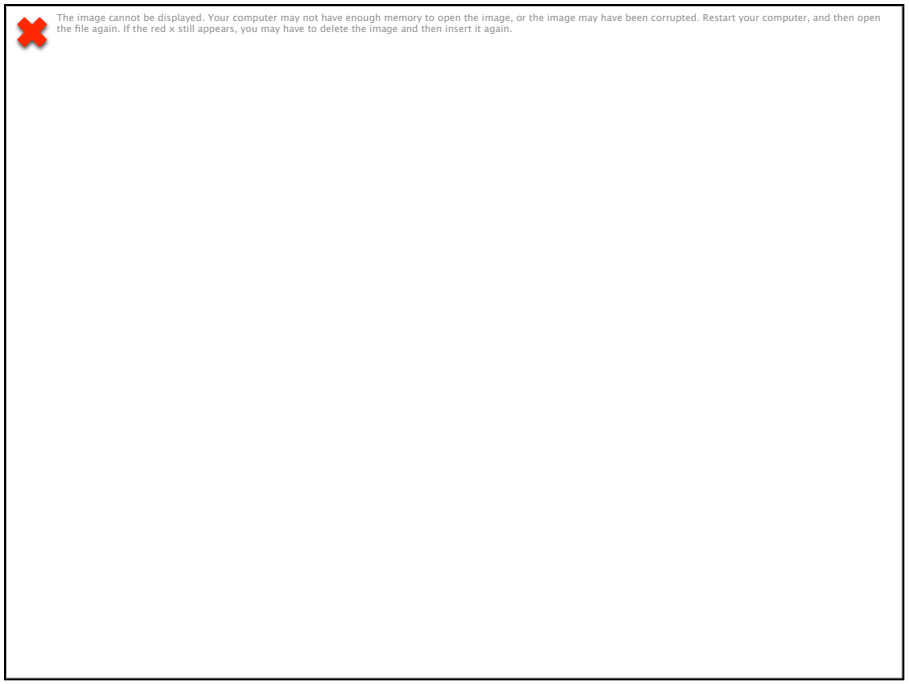


Secondary Electron Image

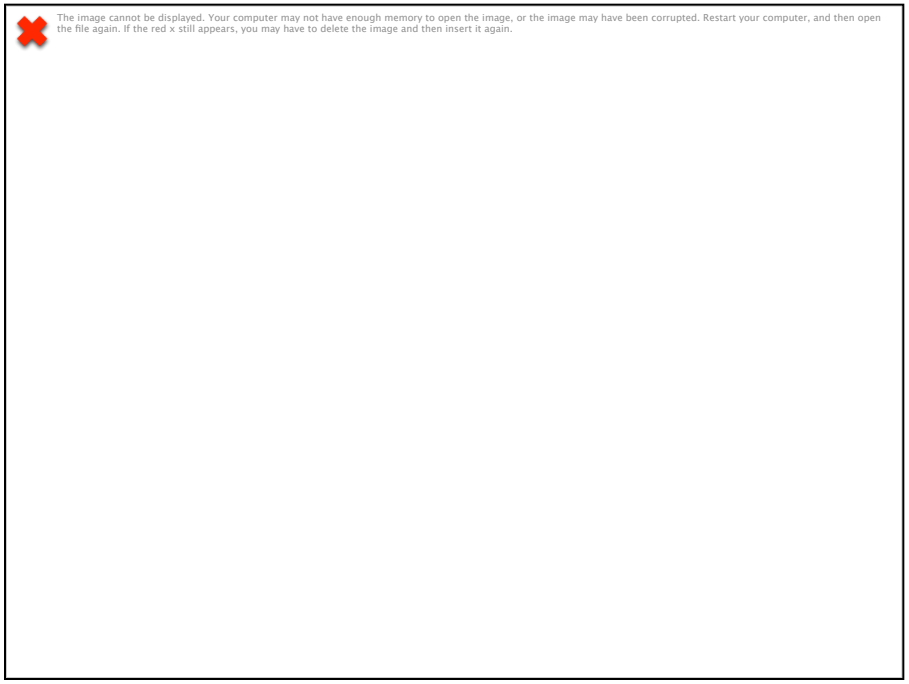


Secondary Electron Image

5 nm TiO_2 particles

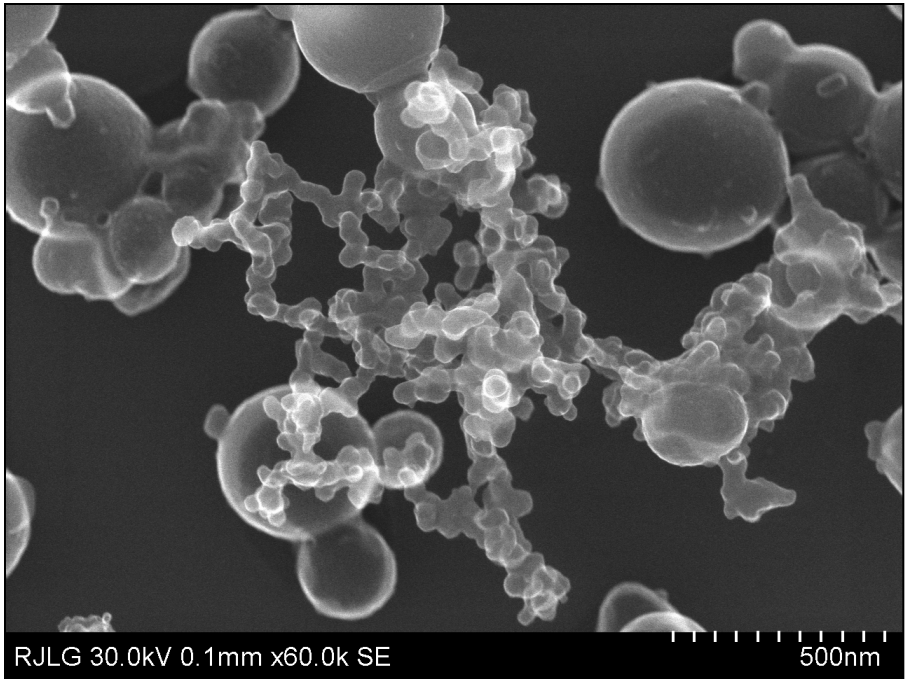


Secondary Electron Image



Secondary Electron Image

Wood Smoke – CA Fires



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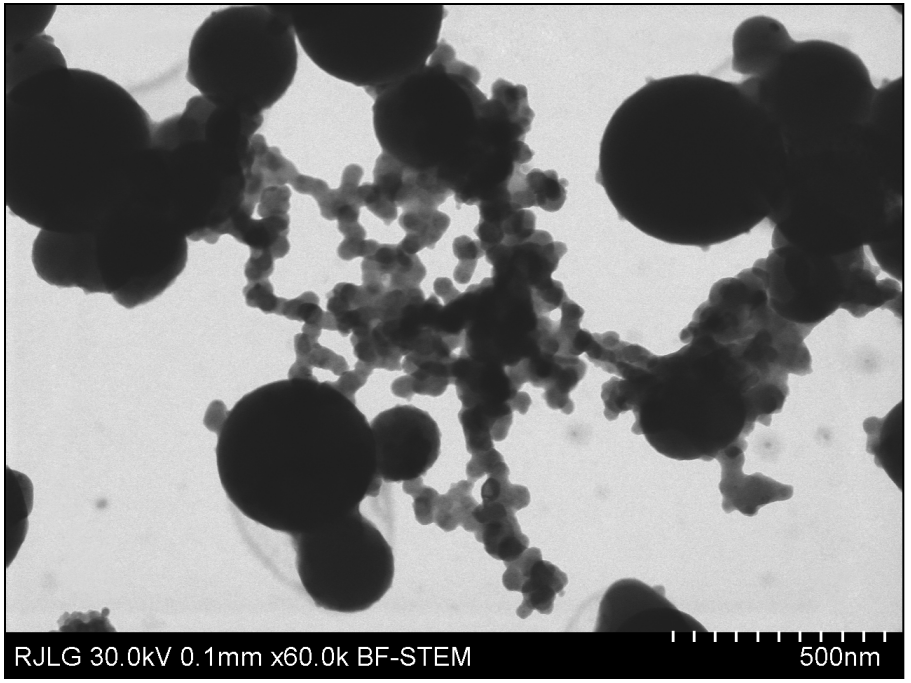
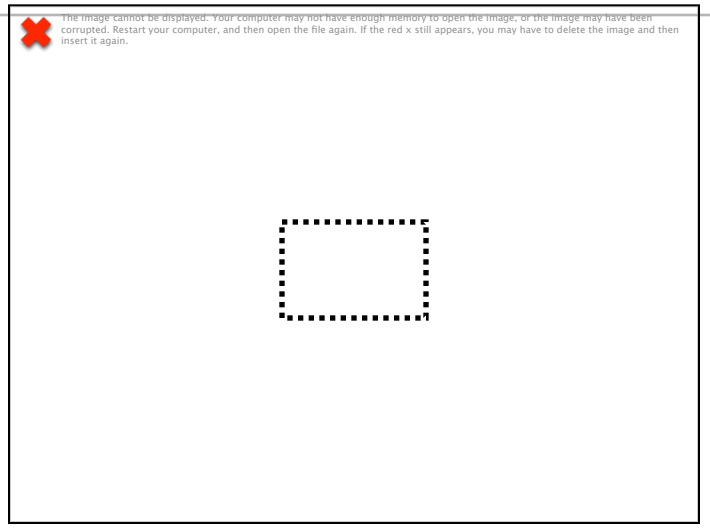


BF-STEM Image

April 23, 2009

Carbon Black



Secondary Electron Image

BF-STEM Image

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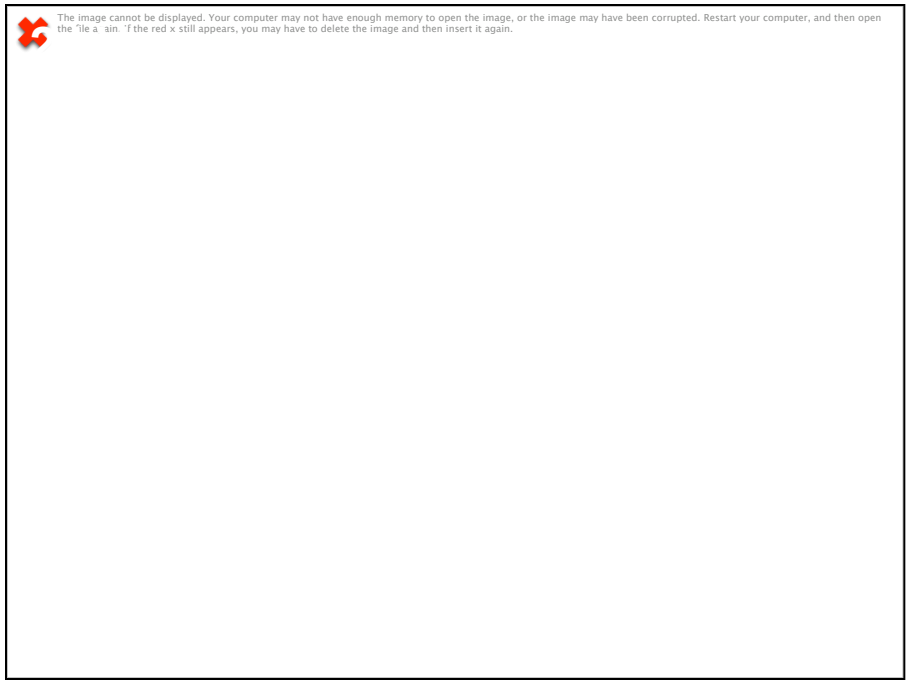
Welding Fumes – 2 kV and 30 kV Comparison



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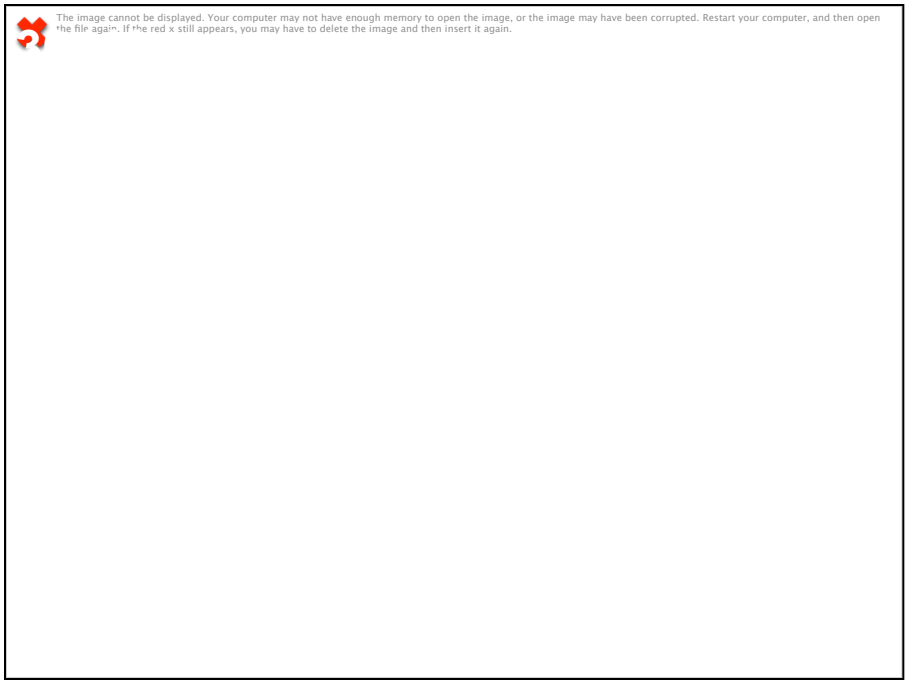

Secondary Electron Image

Welding Fumes

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BF-STEM Image

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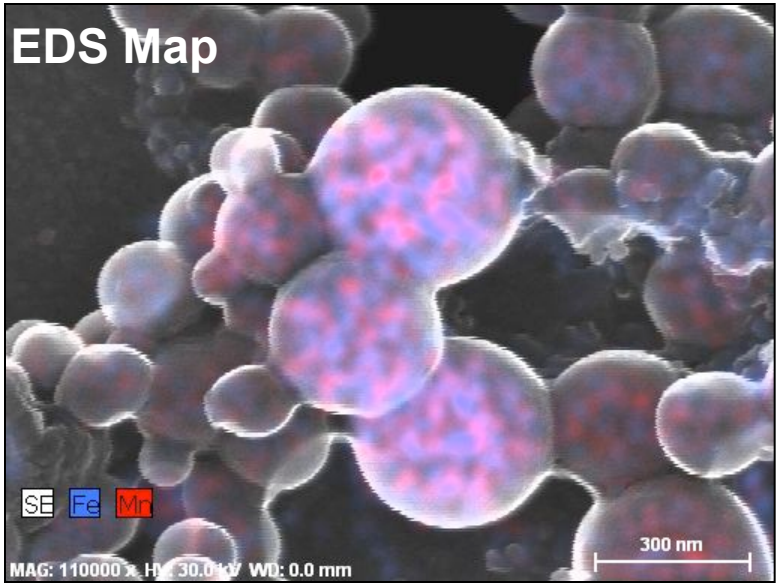

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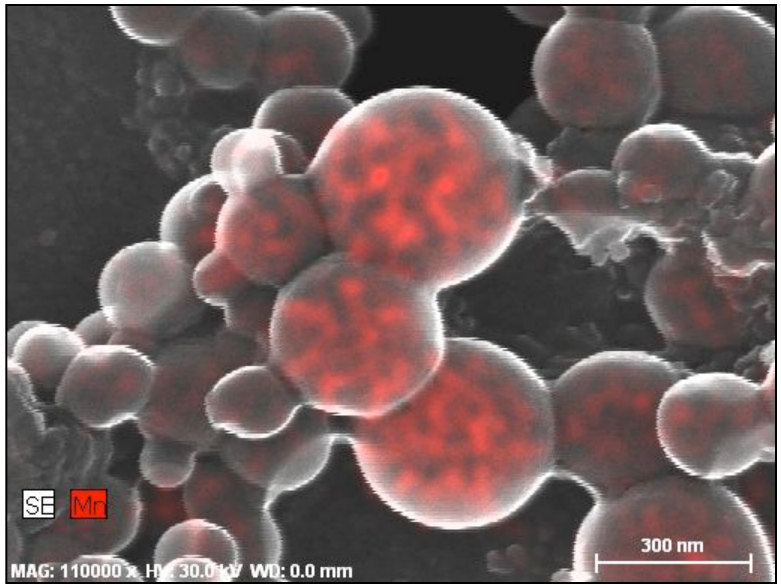
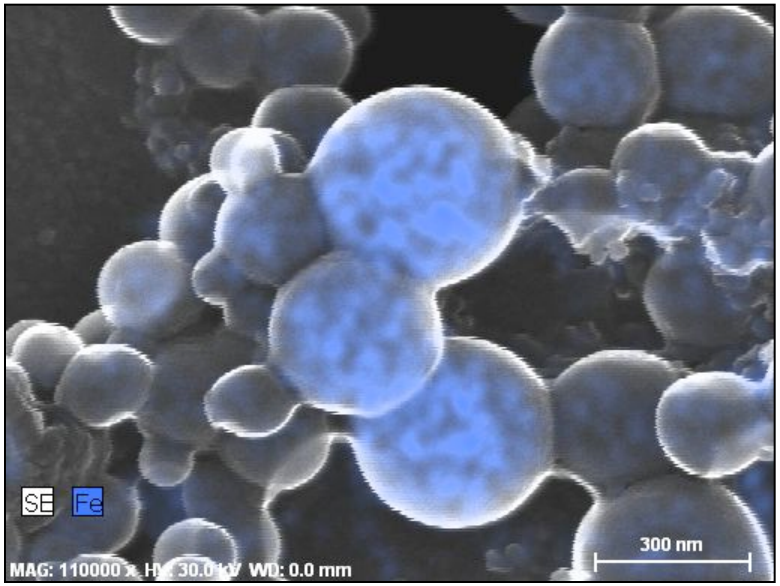
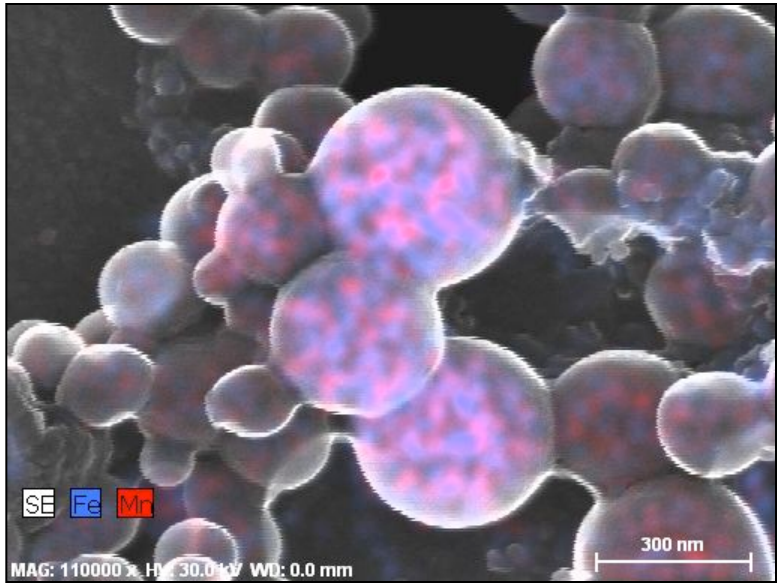
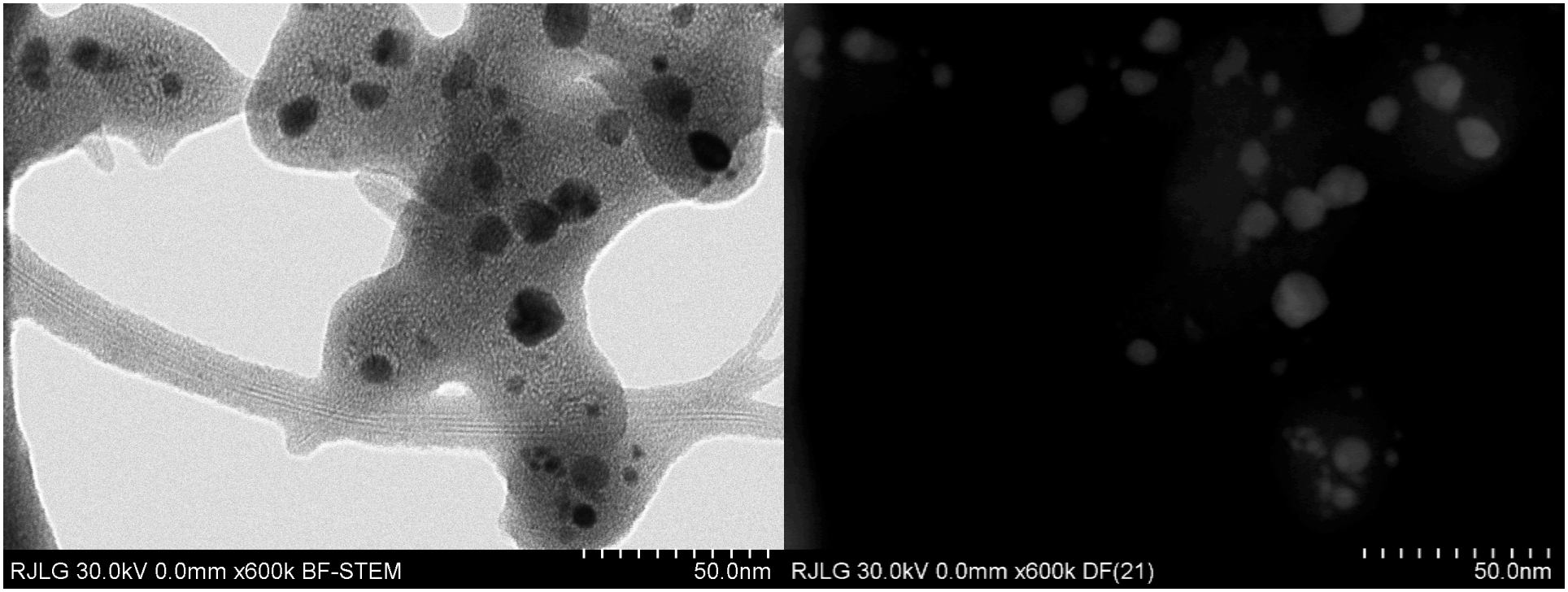






NIST Candidate Reference Material



M. Pacurari, et al. 'Raw Single-Wall Carbon Nanotubes Induce Oxidative Stress and Activate MAPKs, AP-1, NF-κB, and Akt in Normal and Malignant Human Mesothelial Cells', Environmental Health Perspectives, Vol. 116, No. 9, Sept. 2008.

Acknowledgement: Mark Hoover, NIOSH and Mike Postek, NIST

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Analysis. Consulting. Development.

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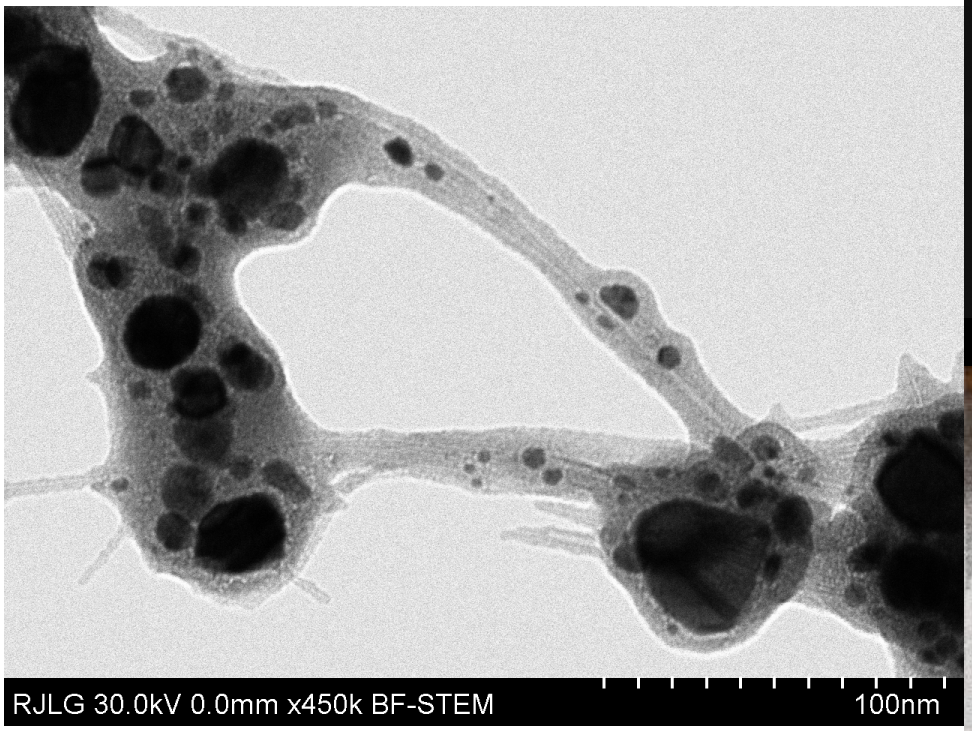
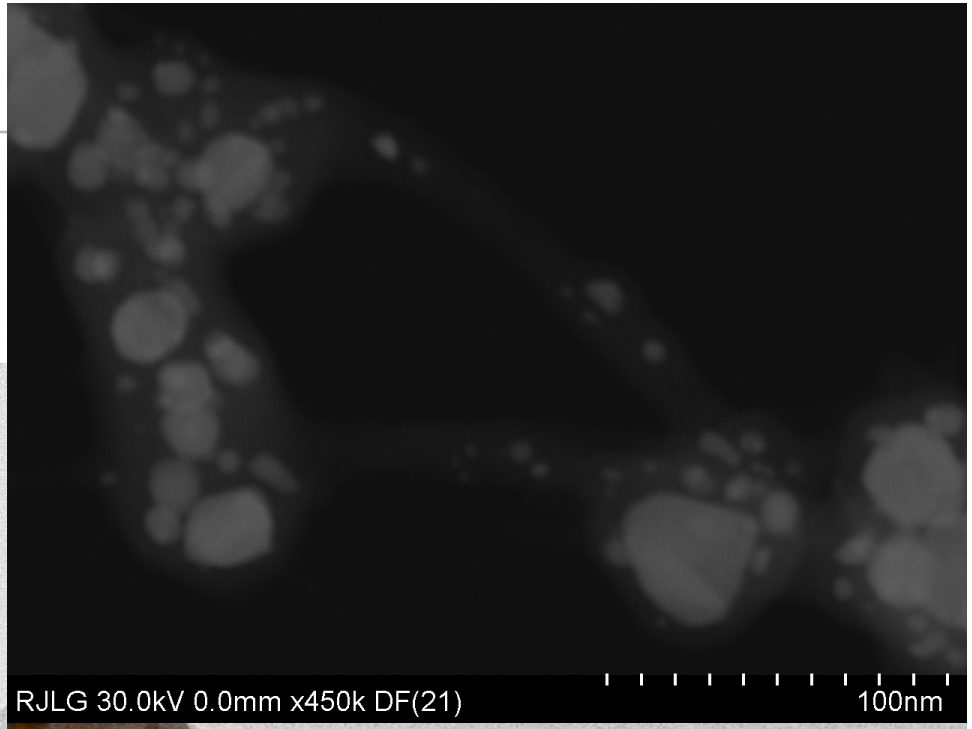
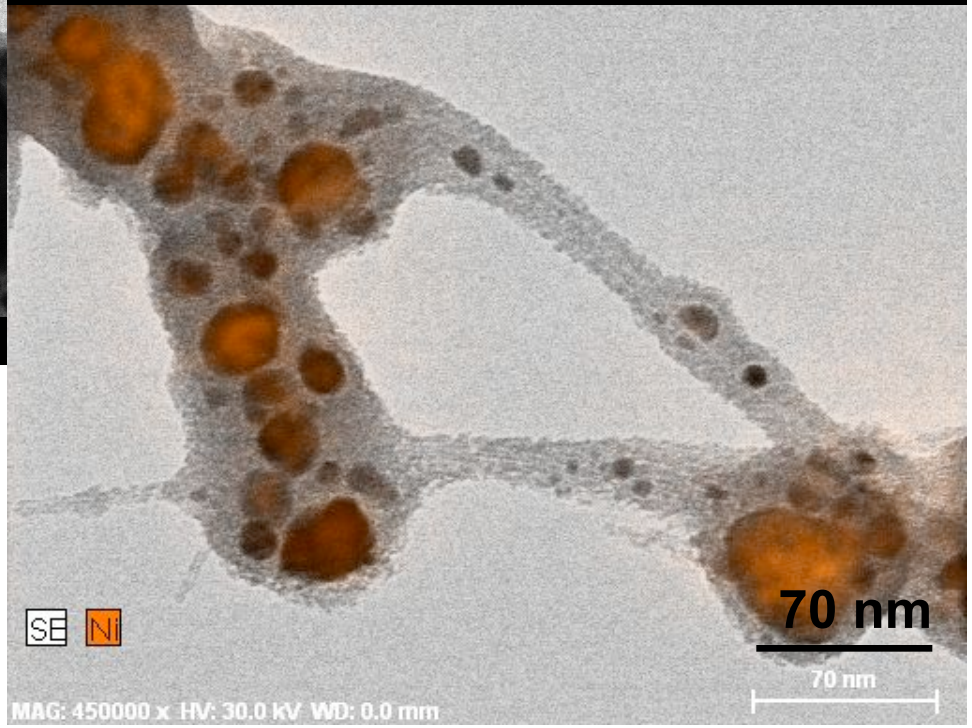
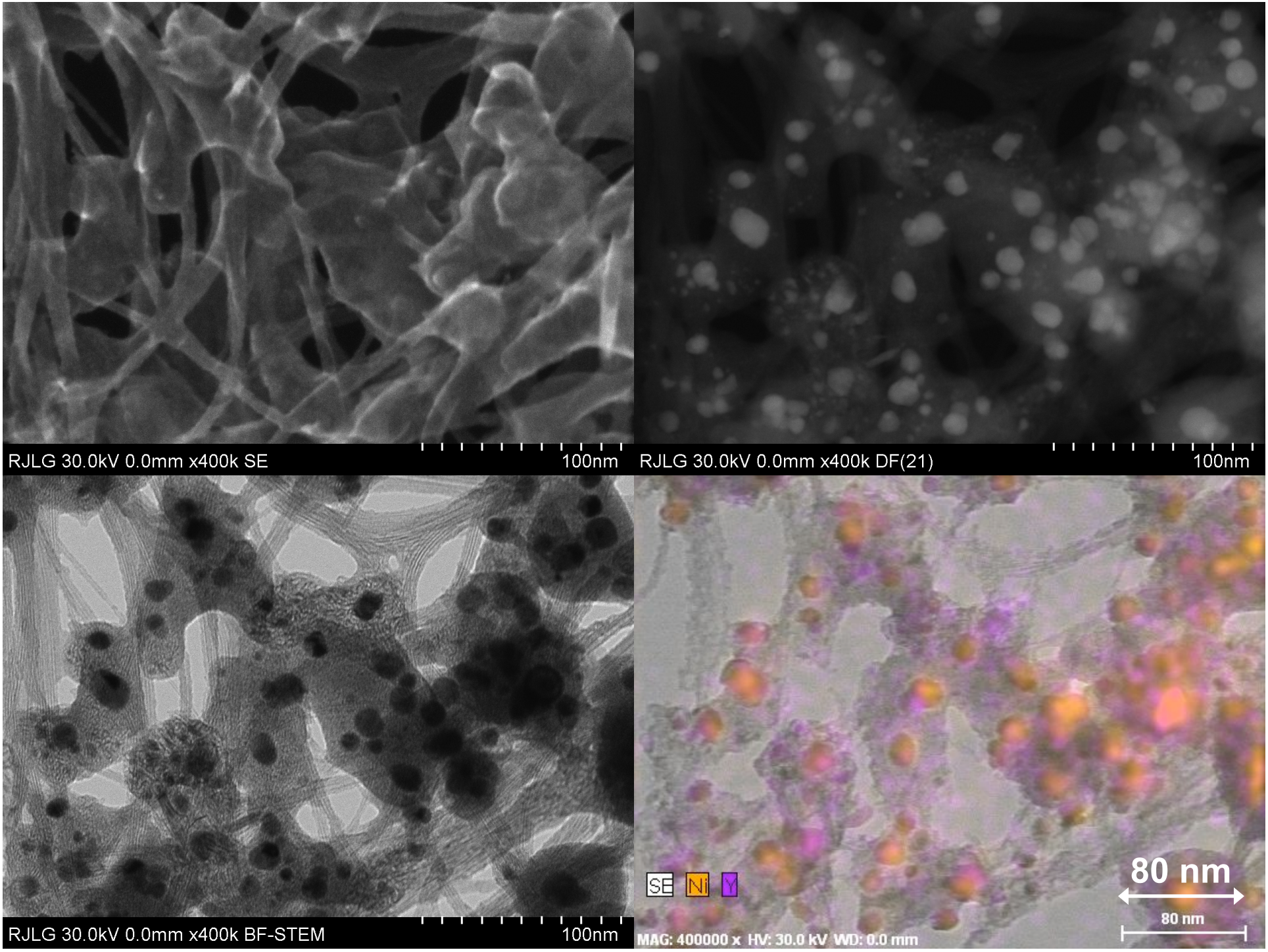






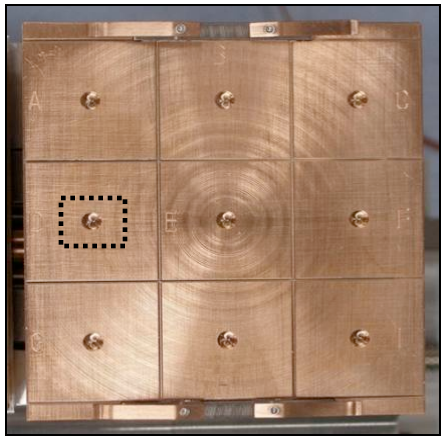

RJLG 30.0kV 0.0mm x400k SE
100nm
RJLG 30.0kV 0.0mm x400k DF(21)
100nm
RJLG 30.0kV 0.0mm x400k BF-STEM
100nm
SE
Ni
Y
80 nm
80 nm
MAG: 400000 x HV: 30.0 kV WD: 0.0 mm

X-ray Photoelectron Spectroscopy (XPS) for Surface Characterization

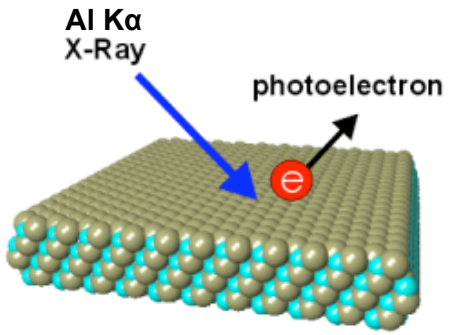
Thermo Scientific K-Alpha XPS

XPS Capabilities

- Conductive or insulating samples
- Qualitative and quantitative elemental surface analysis
- Chemical state information
- Sampling depth: ≤ 10 nm
- Analytical spot size: 30-400 µm

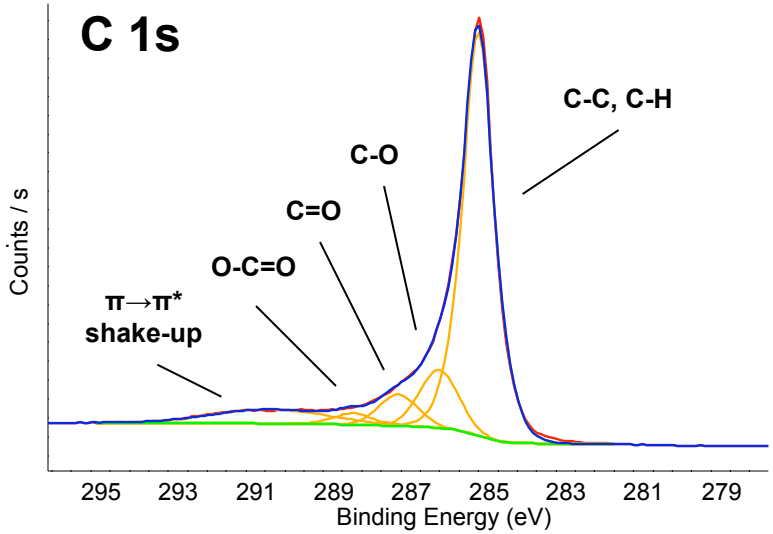


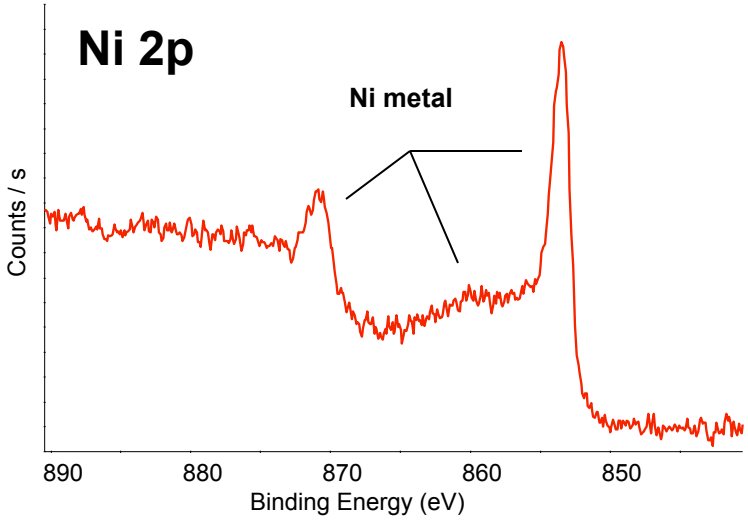
Powder Holder (60 mm x 60 mm)

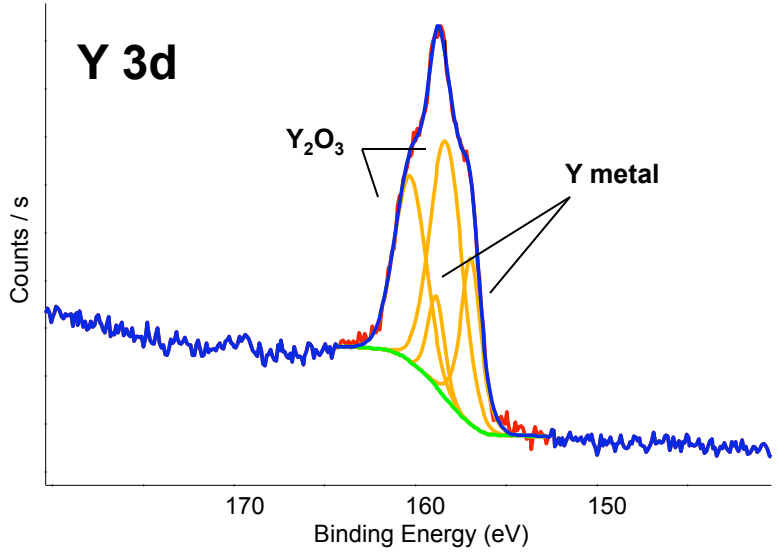


XPS Characterization of Proposed NIST SWCNT Standard

- Surface composition (atomic %): C – 94.1; O - 4.8; Ni - 0.4; Y - 0.7
- Carbon chemical structure was primarily graphitic plus some oxygenated functional groups
- Nickel was primarily metallic
- Yttrium was a mixture of metal and oxide (Y_2O_3)

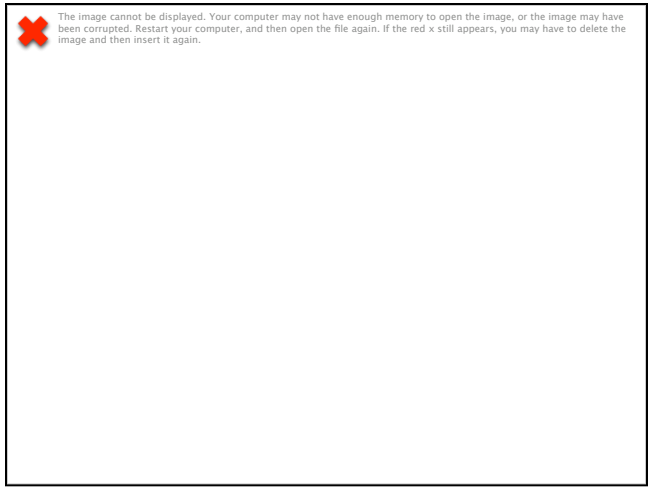




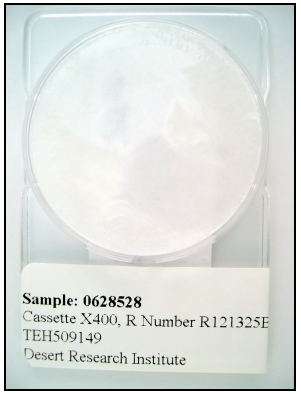


Application: Industrial Hygiene

- Question: What is on the worker exposure filter (particle shape, morphology, chemistry)?
- Question: Does the material on the worker exposure match a source material?
- Question: What is approximate concentration (similar to asbestos)?
- Efficiency = Time/Cost
- RJLG exploring the use of S-5500 as primary tool for application
  - No diffraction
  - No high-resolution TEM images

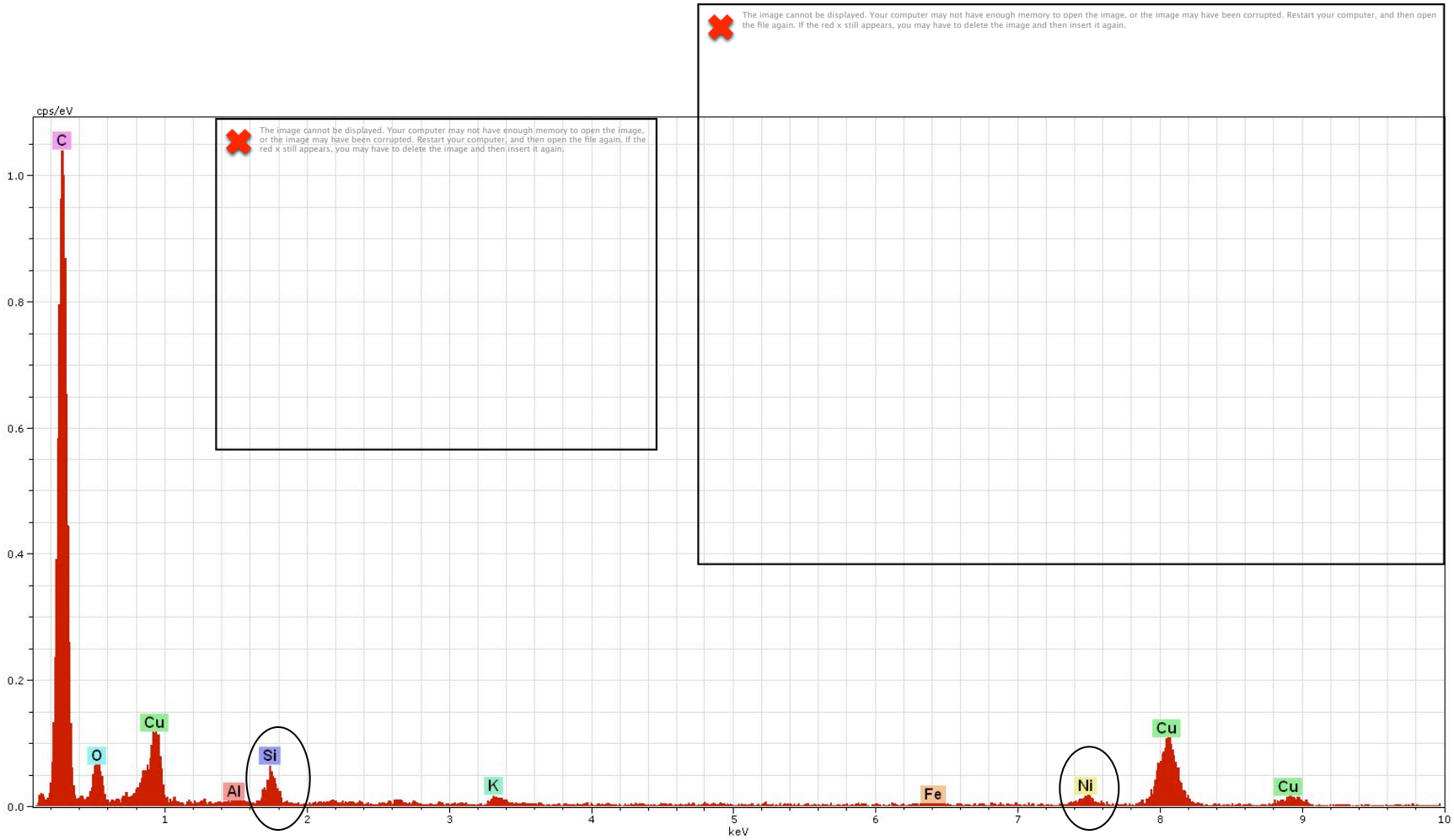


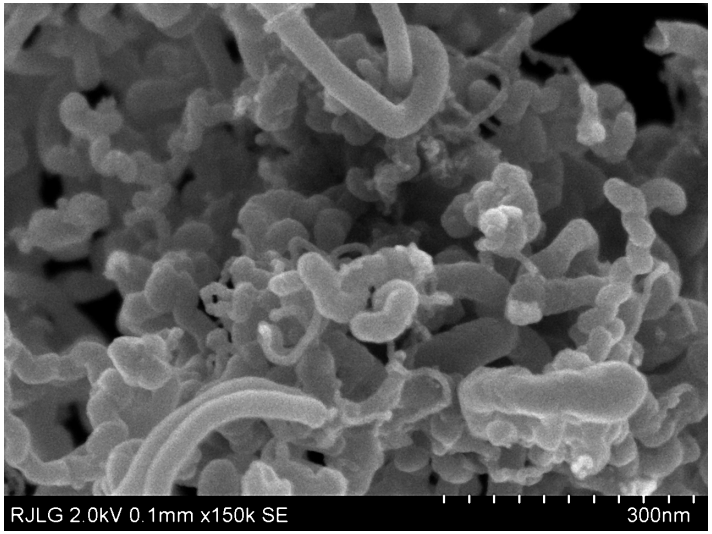
Case Study

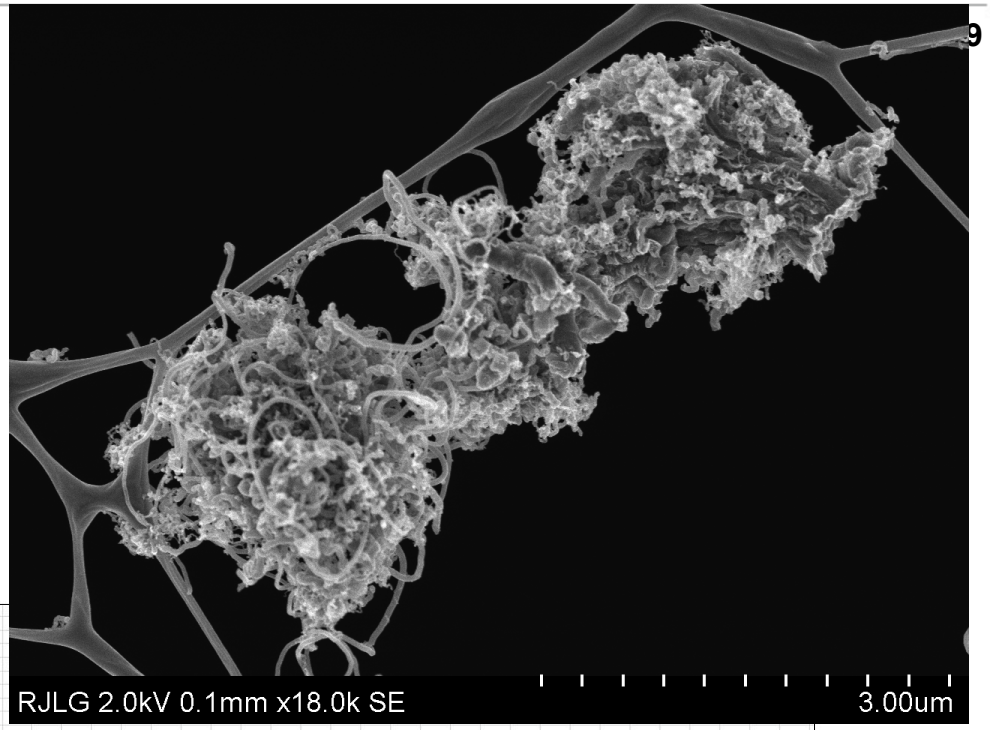


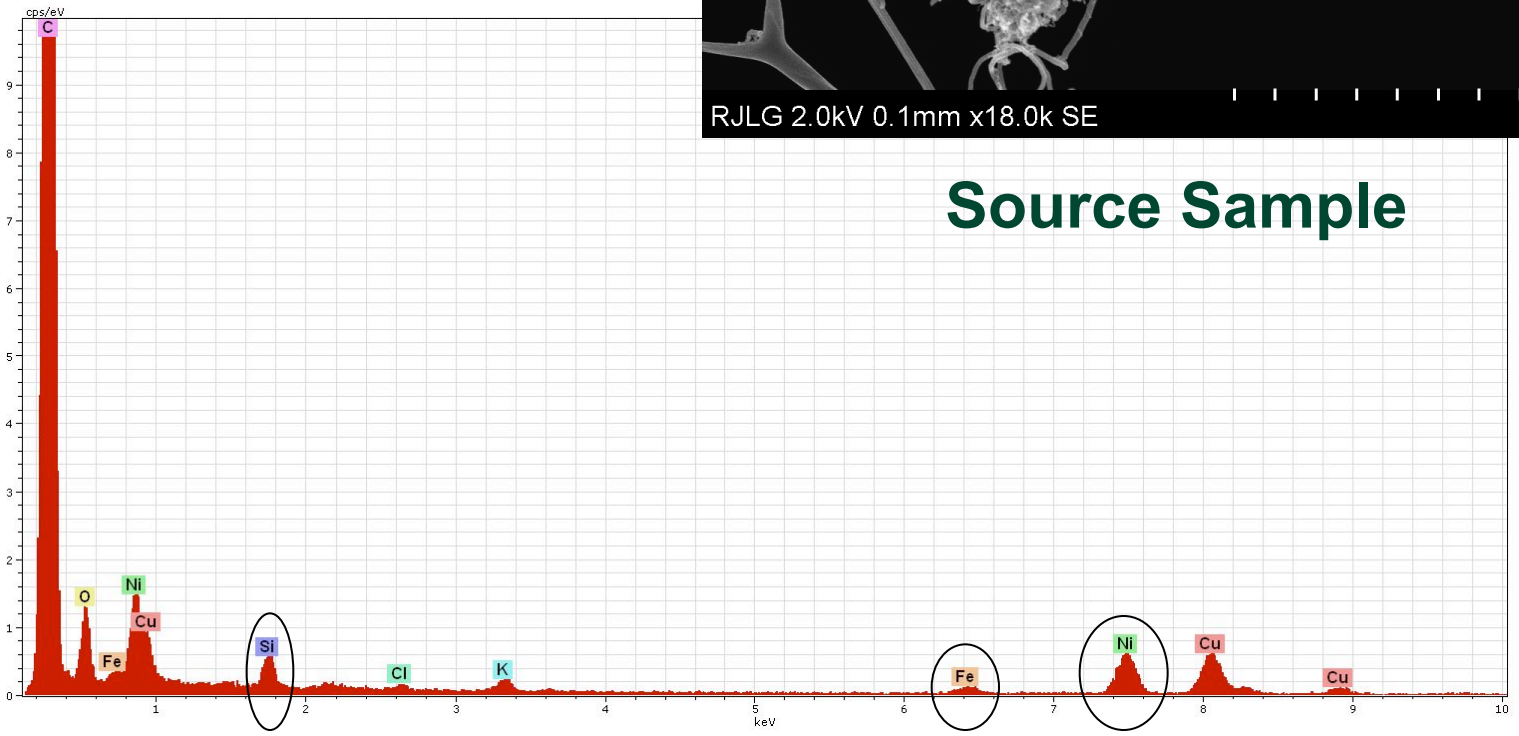
- Source: CVD used in the growth of diamond
- Samples Collected:
  - Bulk/Source sample: Suspended in isoproponol and deposited on a filter
  - 2 worker exposure samples: Standard direct TEM preparation method
  - 1 field blank sample: Standard direct TEM preparation method
- Utilize a phased approach to microscopy analysis:
  - Level I: Screening analysis provides basic information on sample characteristics
  - Level II: Provides more detailed analysis on size, morphology and chemical characteristics
  - Level III: In-depth research analysis
  - Conforms with NIOSH graded approach (M. Hoover)

Source Material



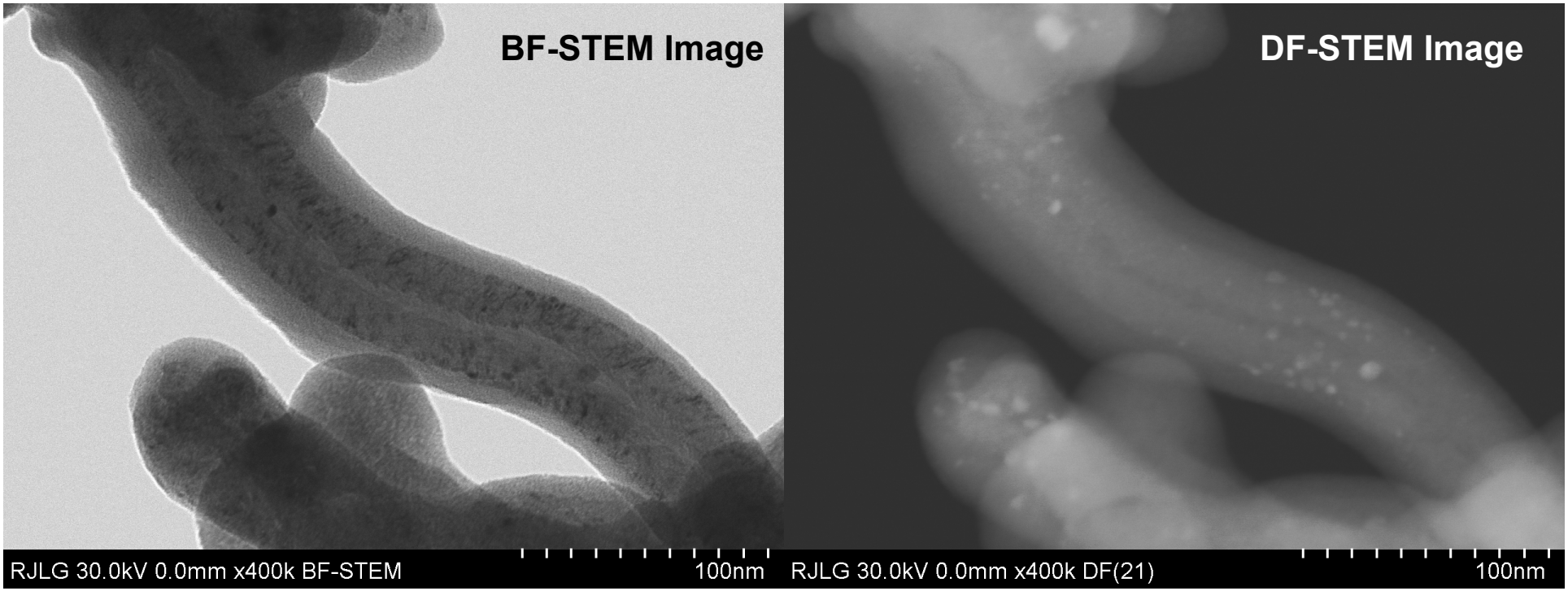




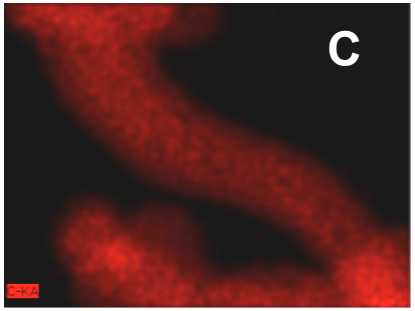


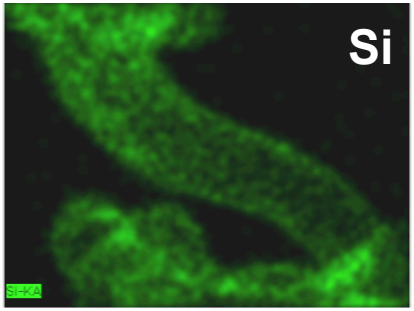
Source Sample

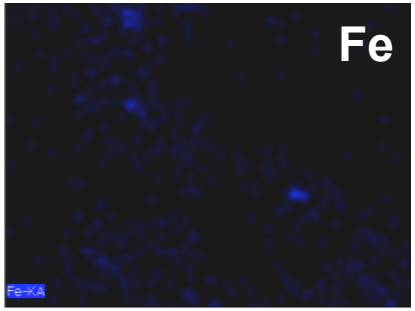
Source Material

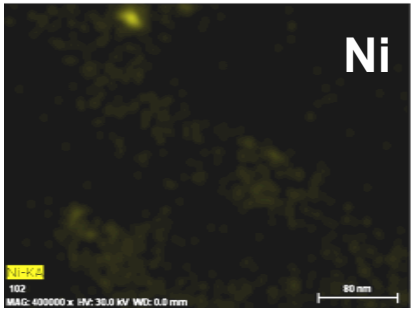


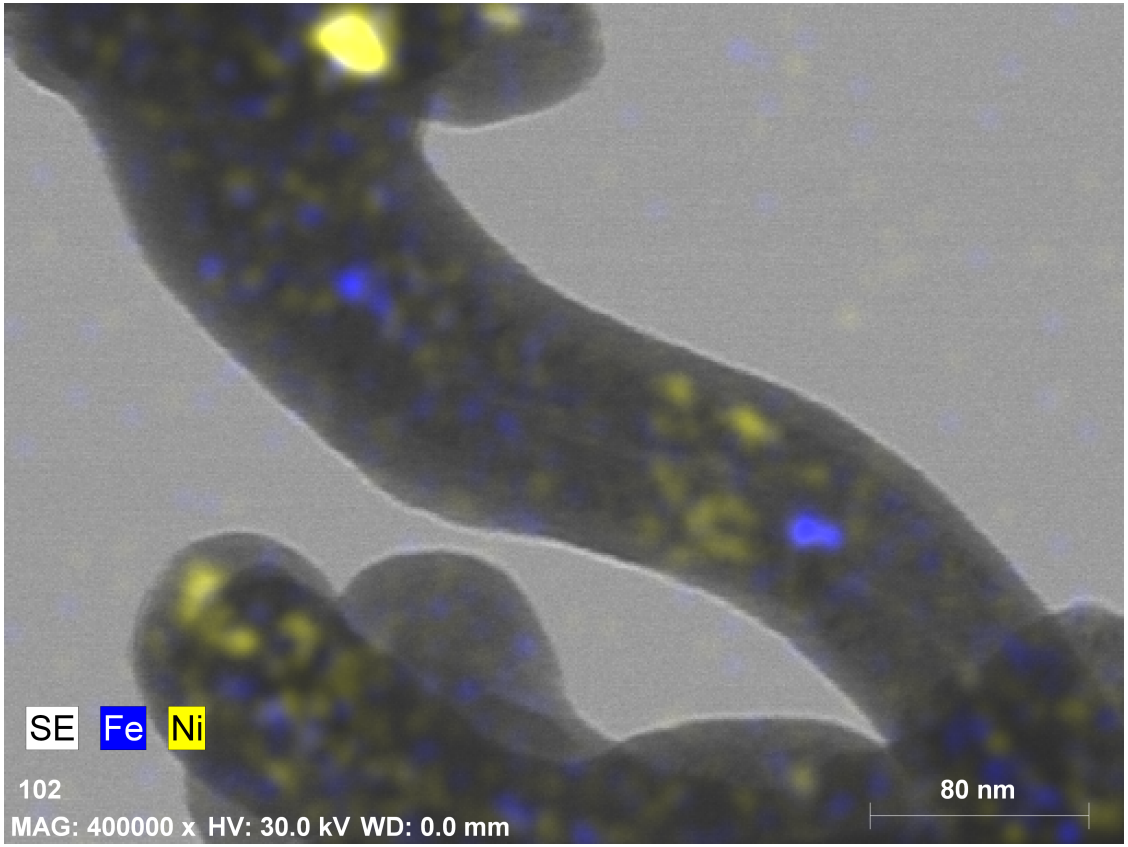
Example of Carbon Nanotubes with ultra-fine nickel and iron particles from the carbon particulate source material


C

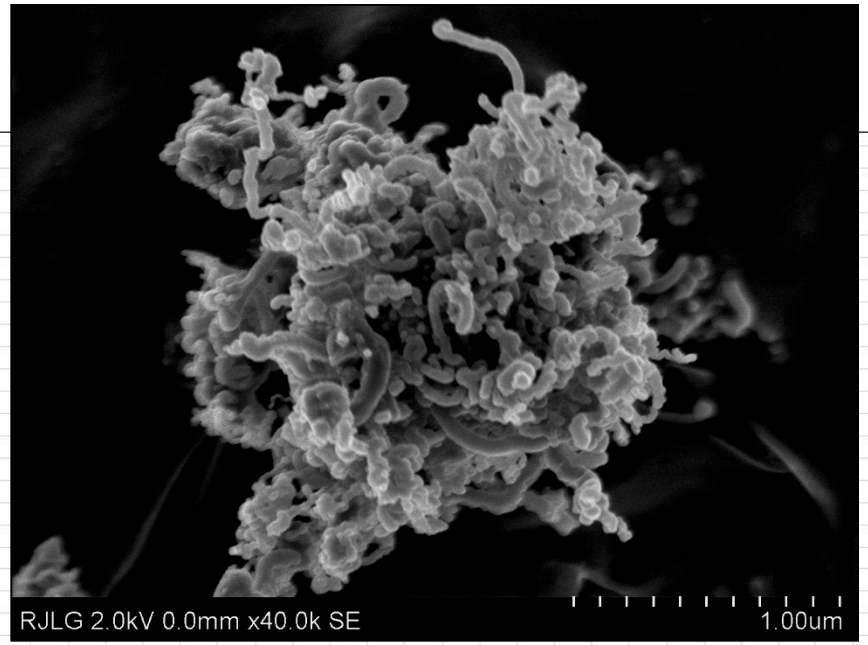

Si


Fe


Ni
102
80 nm


SE
Fe
Ni
102
80 nm
MAG: 400000 x HV: 30.0 kV WD: 0.0 mm

Worker Exposure Sample – Initial Analysis



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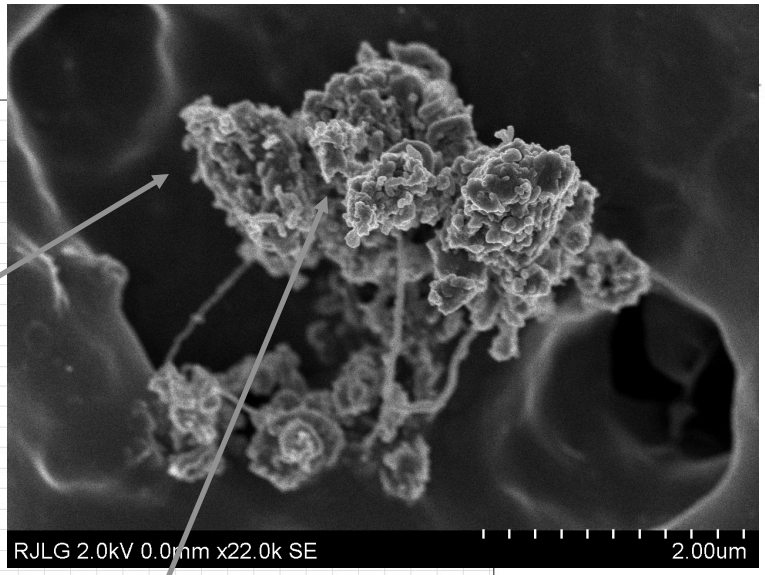
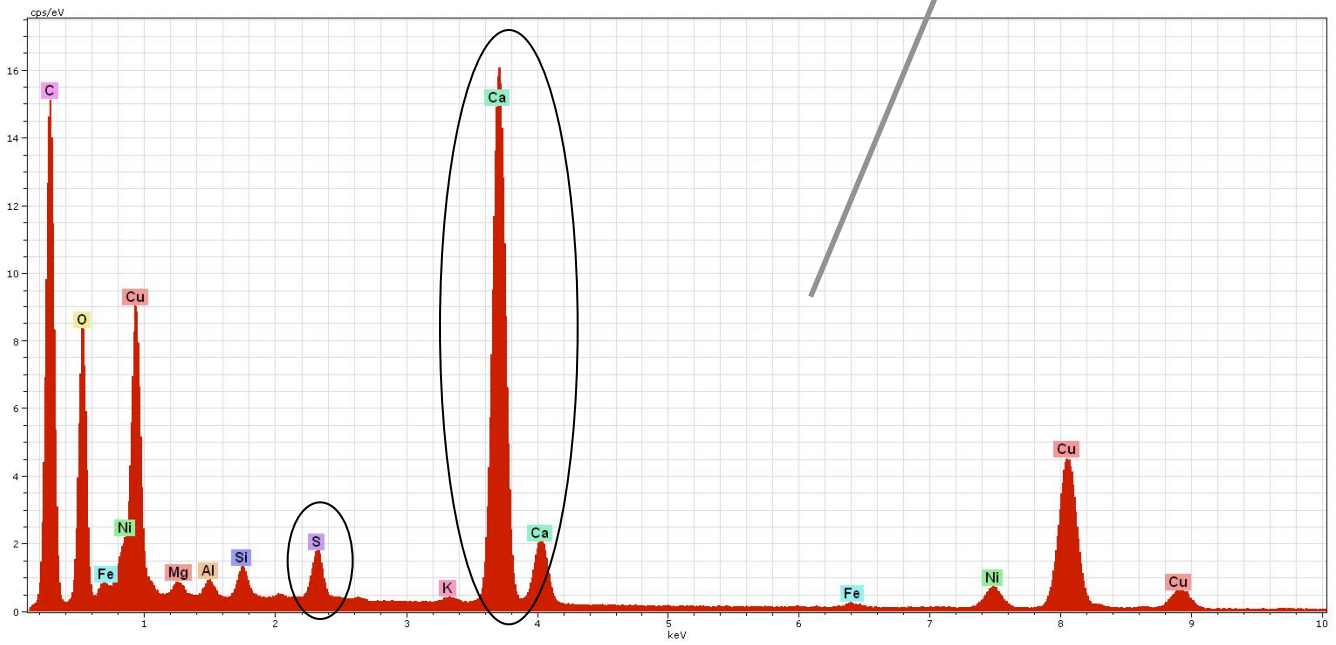
Cr not detected on bulk source sample

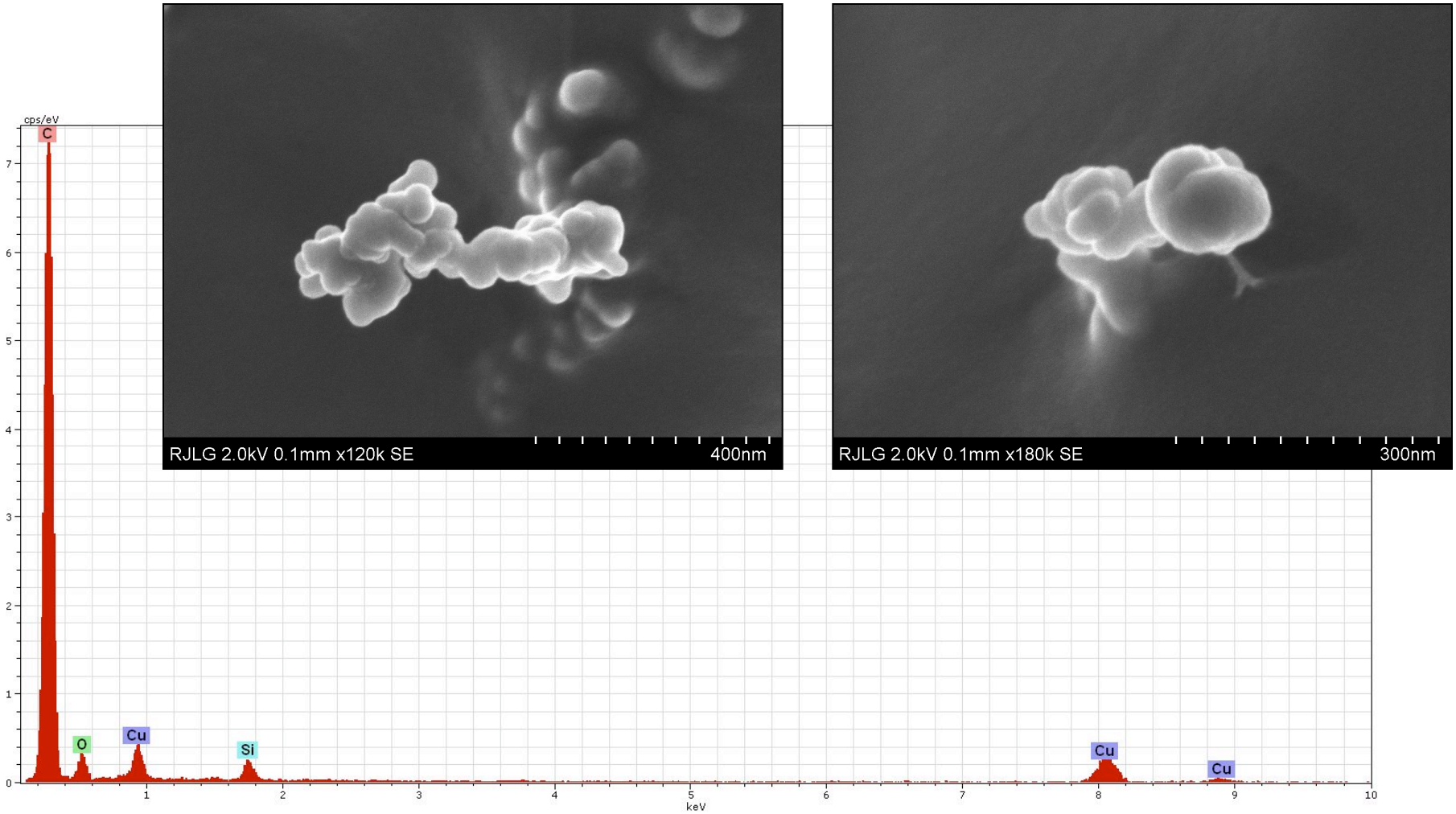
RJ LeeGroup, Inc.

Ca and S not detected on bulk source sample





Worker Exposure – Detailed Analysis



Case Study: Challenges

- Develop sampling technology capable of collecting nanoparticle samples directly on suitable substrate
  - TEM grids
  - Polycarbonate filters/MCE filters
- Source and worker exposure sample collection times (suitable loading)
- Time/Cost Effective Microscopy Analysis
- Perform simultaneous sampling using real time and filter based methods

Summary

- Advanced analytical tools are available for the characterization of nanoparticles
  - Simultaneous SE, BF-STEM, DF-STEM, EDS
  - No Diffraction, no high-resolution TEM images
- Variety of Materials: Pharmaceuticals, welding fumes, carbon black, carbon nanotubes
- Industrial Hygiene Applications
  - Sample in a smart manner
  - Analyze samples in a smart manner
  - Sampling and analysis protocols are evolving and will continue to evolve as more information becomes available