Approaches to Measurement of Airborne Engineered Nano-Objects

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CDC
CENTERS FOR DISEASE CONTROL AND PREVENTION

National Institute for Occupational Safety and Health
NIOSH

What is “nano”? - ISO 27687:2008

- Nanoscale
  - ~ 1 nm to 100 nm
- Nano-object
  - 1 to 3 external dimensions in nanoscale
- Major categories of nano-objects
  - Nanoparticle: 3 external dimensions
  - Nanofiber: 2 external dimensions
  - Nanoplate: 1 external dimension

Why Care about Nano-Objects?

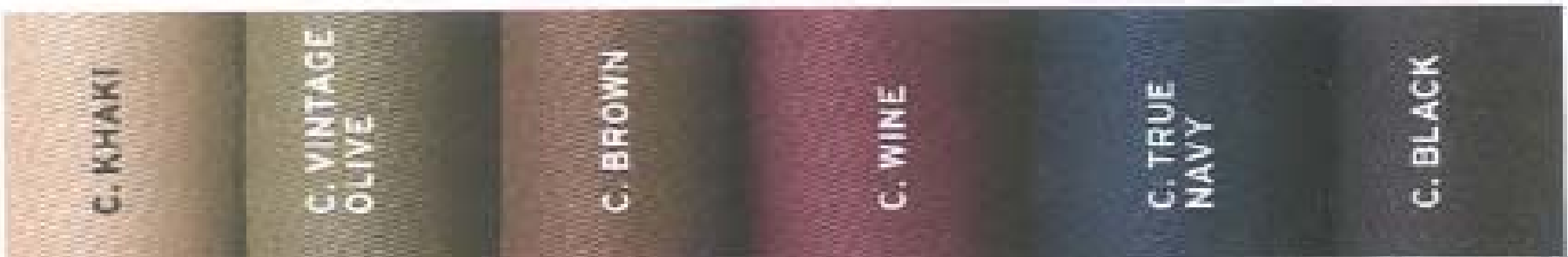
C. Performance Dress Twills with NANO-TEX. Our Nano-Tex® finish makes spills bead up – but all you'll feel is soft 100% cotton fabric. We include an alterable waistband with Ban-Rol®, French fly, lined crotch. Button-through back pockets. Hemming is free. Machine wash. Imported. Colors, below.

Pleated Front

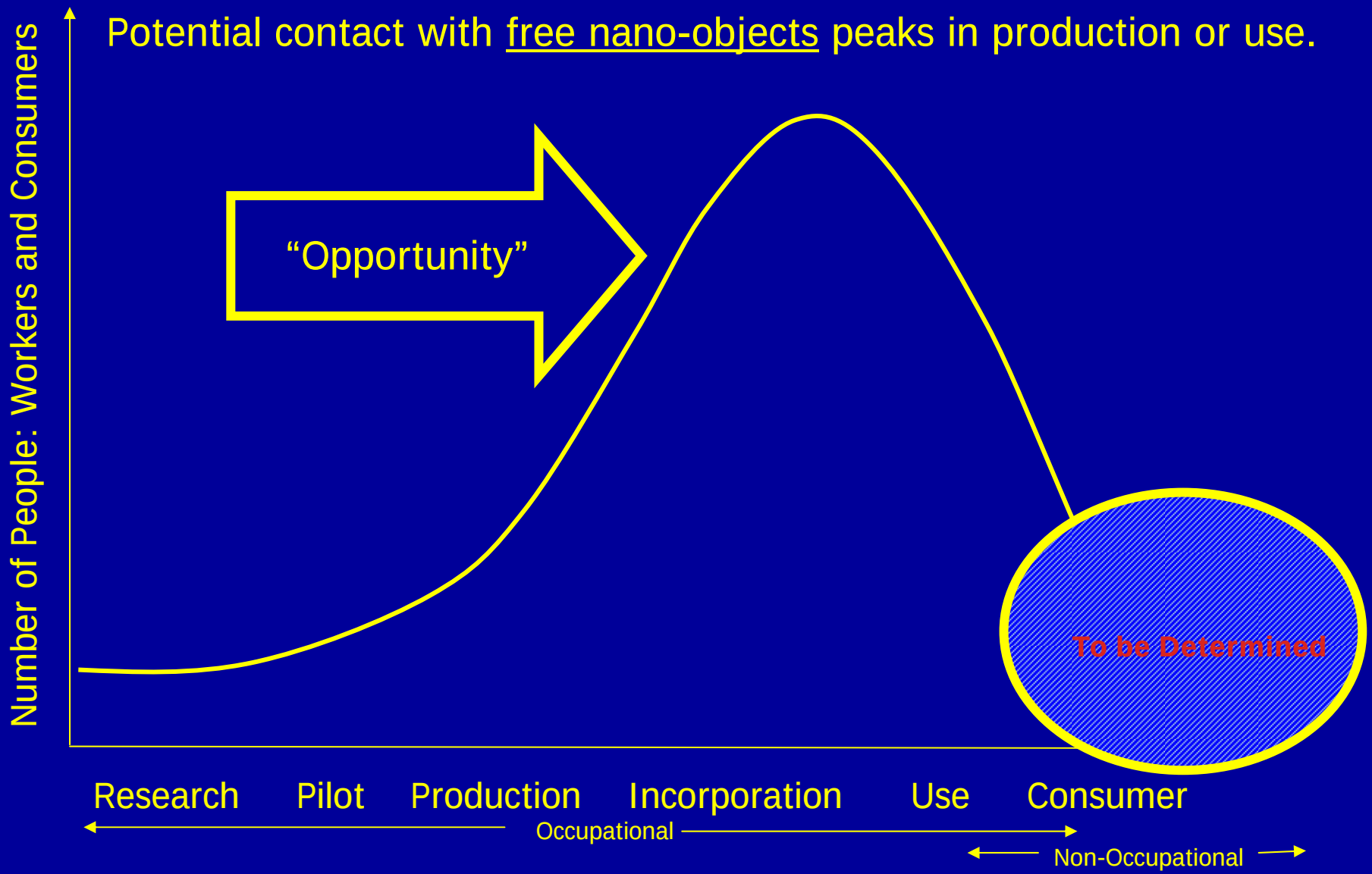
R Regular even 30-46, odd 31-37.	04483-82K8	$49.50
L Long even 34-46.	04483-92K2	$55.00
S Short even 30-36.	00902-42KX	$49.50
B Big even 48-52.	16602-62K8	$59.50
BT Big/Tall even 48-52.	16602-72K2	$59.50

Plain Front (not shown)

R Regular even 30-46, odd 31-37.	04483-62K9	$49.50
L Long even 34-44.	04483-72K3	$55.00



Where is the Exposure?



Current Concerns for Nano-Objects

- Oxidative stress
- Pulmonary inflammation
- Early interstitial lung fibrosis and granulomas
- Asbestos-like pathogenicity
- Translocation from respiratory tract
  - Oxidative damage in human blood serum
  - Inflammatory and pro-clotting effects in blood

Parameters That Could Affect Nano-object Toxicity

- Size
- Shape
- Composition
- Solubility
- Crystalline structure
- Charge
- Surface characteristic
- Attached functional groups
- Agglomeration
- Impurities

NIOSH Nanotoxicology Summary

- Nano-objects under investigation
  - SWCNT, MWCNT, TiO_2, CB, metal oxides, nanowires, and nanospheres
- Target organs
  - Lung, skin, brain, cardiovascular system
- End points
  - Inflammation, oxidant stress, fibrosis, translocation

Risk Assessment: Ultrafine TiO_2

NIOSH draft recommended exposure limits (RELs):

- 1.5 mg/m^3 fine TiO_2
- 0.1 mg/m^3 ultrafine TiO_2
- Reflects greater inflammation & tumor risk of ultrafine on mass basis
- www.cdc.gov/niosh/review/peer/tio2/

Same message: The OEL for a material in its 'large' form may not be appropriate for the nano form

Hazard and Risk Picture - CNTs

Aspiration of SWCNT resulted in:

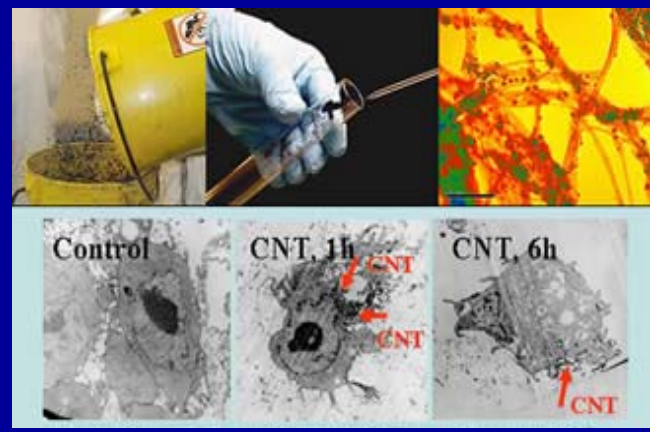
- Rapid but transient inflammation and damage
- Granulomas and fibrosis at deposition sites of large agglomerates of SWCNT
- Rapid and progressive interstitial fibrosis at deposition sites of dispersed SWCNT
- Results were verified with inhalation study

Message:

- SWCNTs more fibrogenic than an equal mass of ultrafine carbon black or fine quartz

- Doses approximated exposure at the PEL for graphite (5 mg/m^3) for 20 days

Message: The PEL for the 'large' form of a material may not be a good guide for the nano form.



Graphics courtesy of Andrew Maynard and Anna Shvedova

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Existing Measurement Tools

- Condensation particle counter
- Optical particle counter
- Diffusion charger
- Aerosol photometer
- Electrostatic lo… …sure impa…
- Scanning… …ity particle…
- Wi… …ge particle… …ometer
- … …way depos… …rticle surface area analyzer
- NanoM…
- Pla… …assette (25- or 37-mm)
- Electrostatic precipitator

Lack specificity for engineered nano-objects

Lack of validation for these tools

NIOSH Nano-Object Exposure Assessment: A Progression

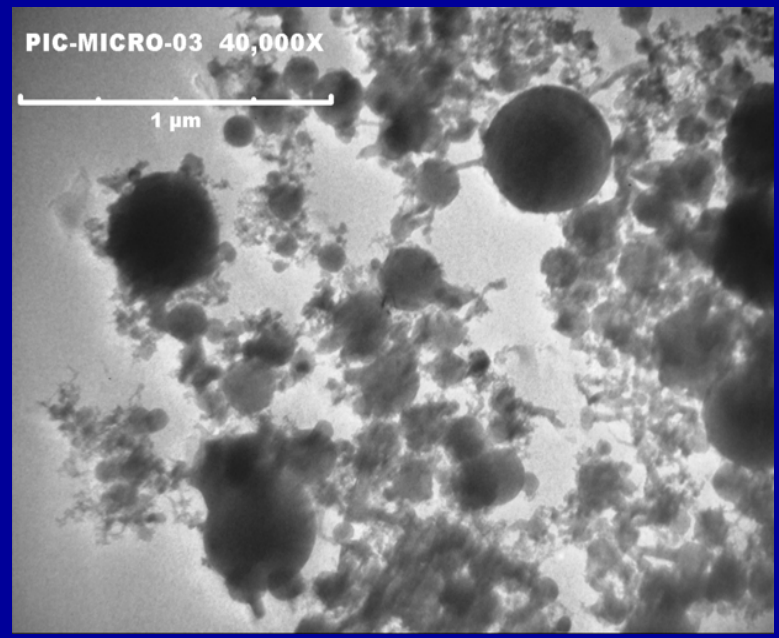
- Initial screening: Baseline assessment
- Detailed investigation: Baseline as a guide to more detailed investigation
- Long-term personal exposure surveillance

Baseline Assessment

- What has been used?
  - Particle count in conjunction with broad size information
  - Aerosol sampling
  - Elemental mass: Metals, carbon
- Has it been successful?
  - Instruments and a ‘trained eye’
  - Good for a ‘yes/no’ approach on emissions and controls
- Limitations
  - Instrument overload
  - Area versus personal monitoring

Correlate Simple and Complex Measurements

Starting Point



TEM analysis of aerosol

Mass, size distribution,
surface area, etc.

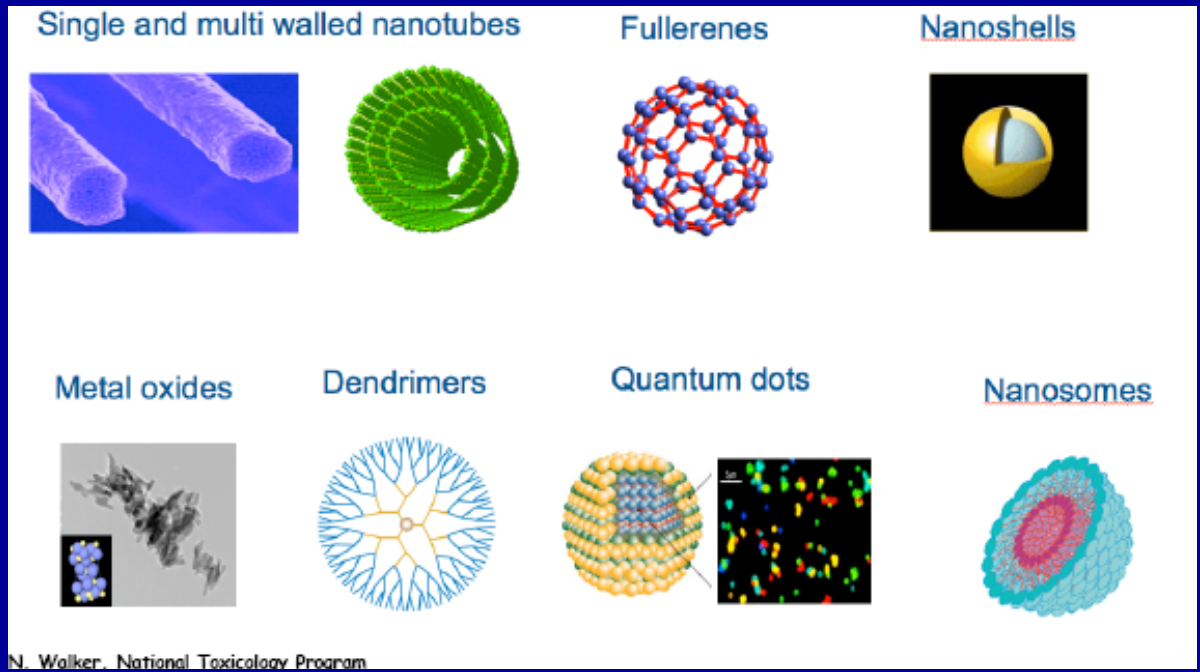
Detailed Investigations

- An additional level of complexity
- Particle size distribution: by size and number
  - SMPS and ELPI
- Mass (element) by size
  - MOUDI and personal impactors

Additional metrics = less portable

What are our Critical Needs?

- Standard protocols
  - Exposure measurement
  - Sample analysis



Standards for Measurement

- Biologically relevant metrics
  - Mass, number, surface area, etc.
- Suitable reference materials
- Validated exposure assessment tools
  - Measurements linked to biological mechanism
- Validated protocols
  - Demonstrated accuracy and precision

Standards for Analysis

- Analysis of airborne nano-objects
  - Preserve object in native state
  - Measure linked to tox mechanism of interest
  - Validated

- Measurement can not alter parameter being measured
  - Example 1: nano-object size
  - Example 2: nano-object surface area

Example 1: Particle Size

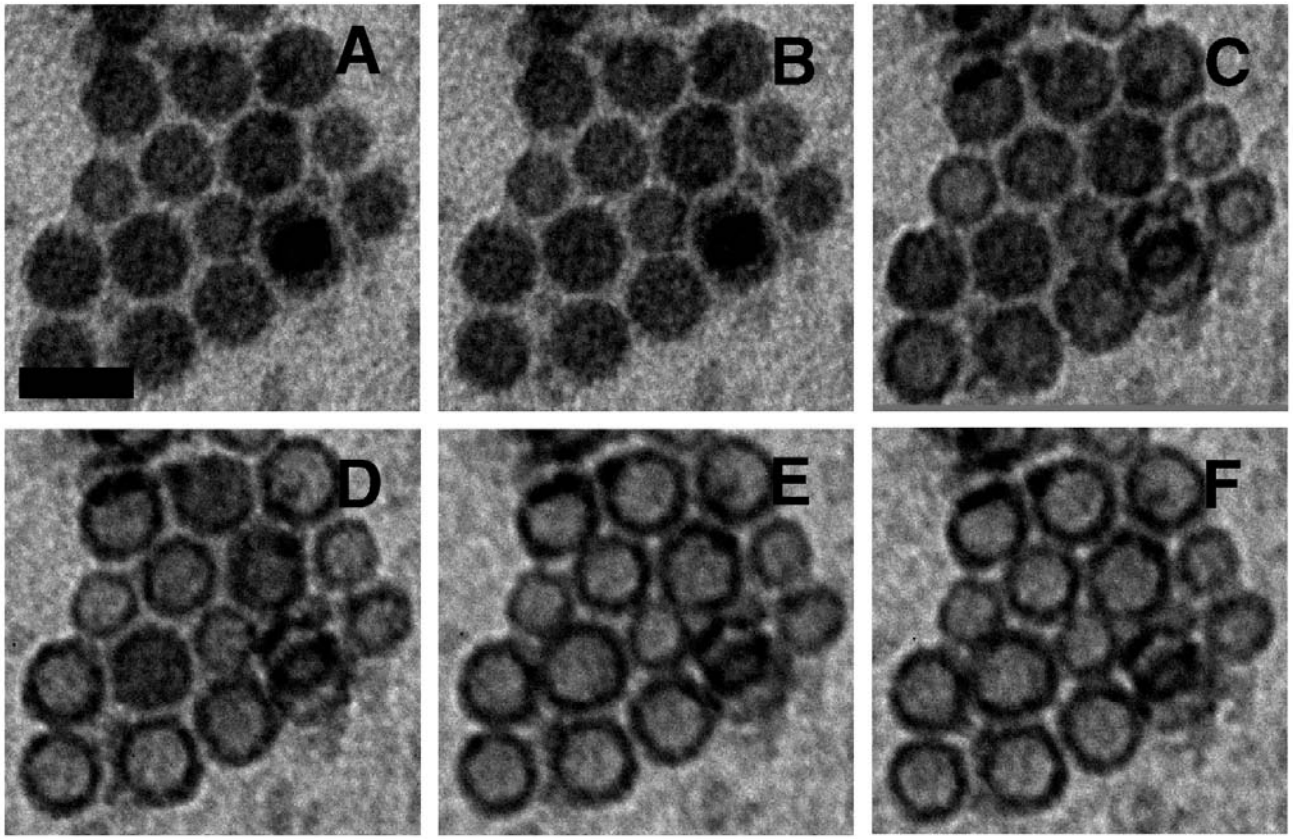
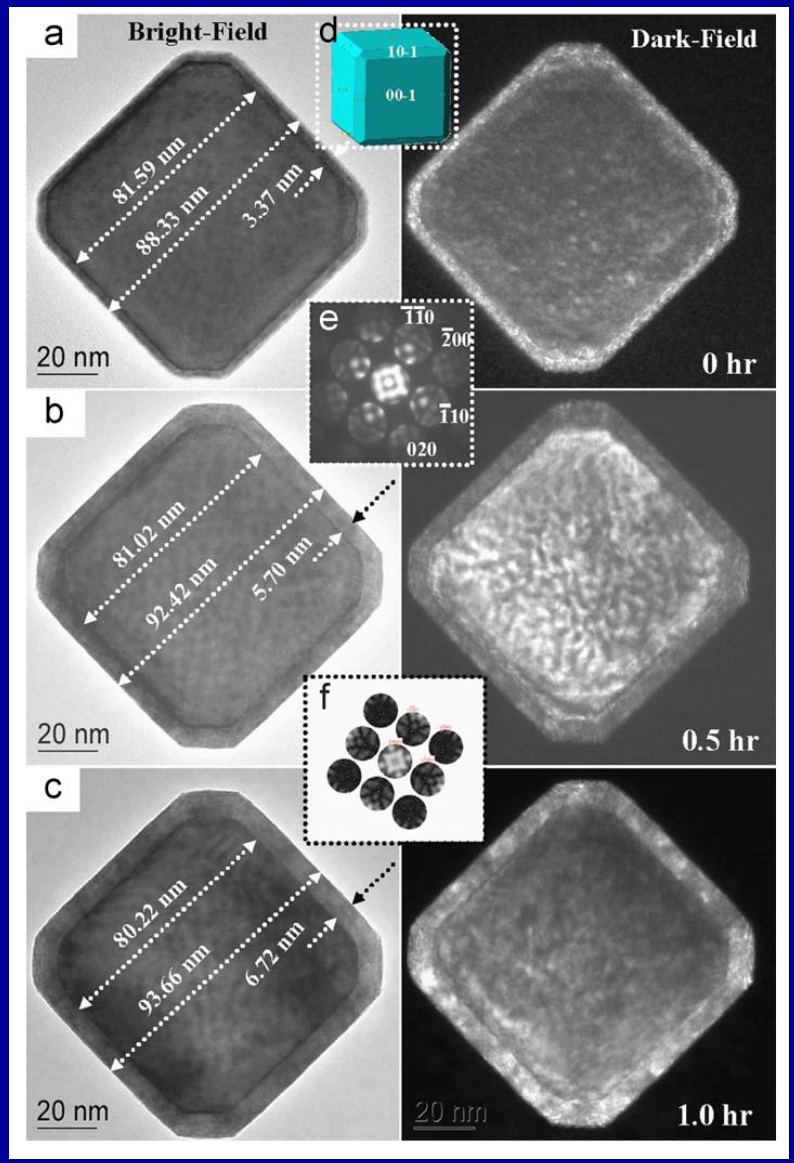


Figure 3. Low resolution TEM images of amorphous Fe oxide particles acquired at approximately (A) 0; (B) 20; (C) 40; (D) 50; (E) 60; and (F) 120 s exposure in the 80 keV beam. Scale bar is 15.

Latham et al. JACS. 128:12632-12633 (2006)

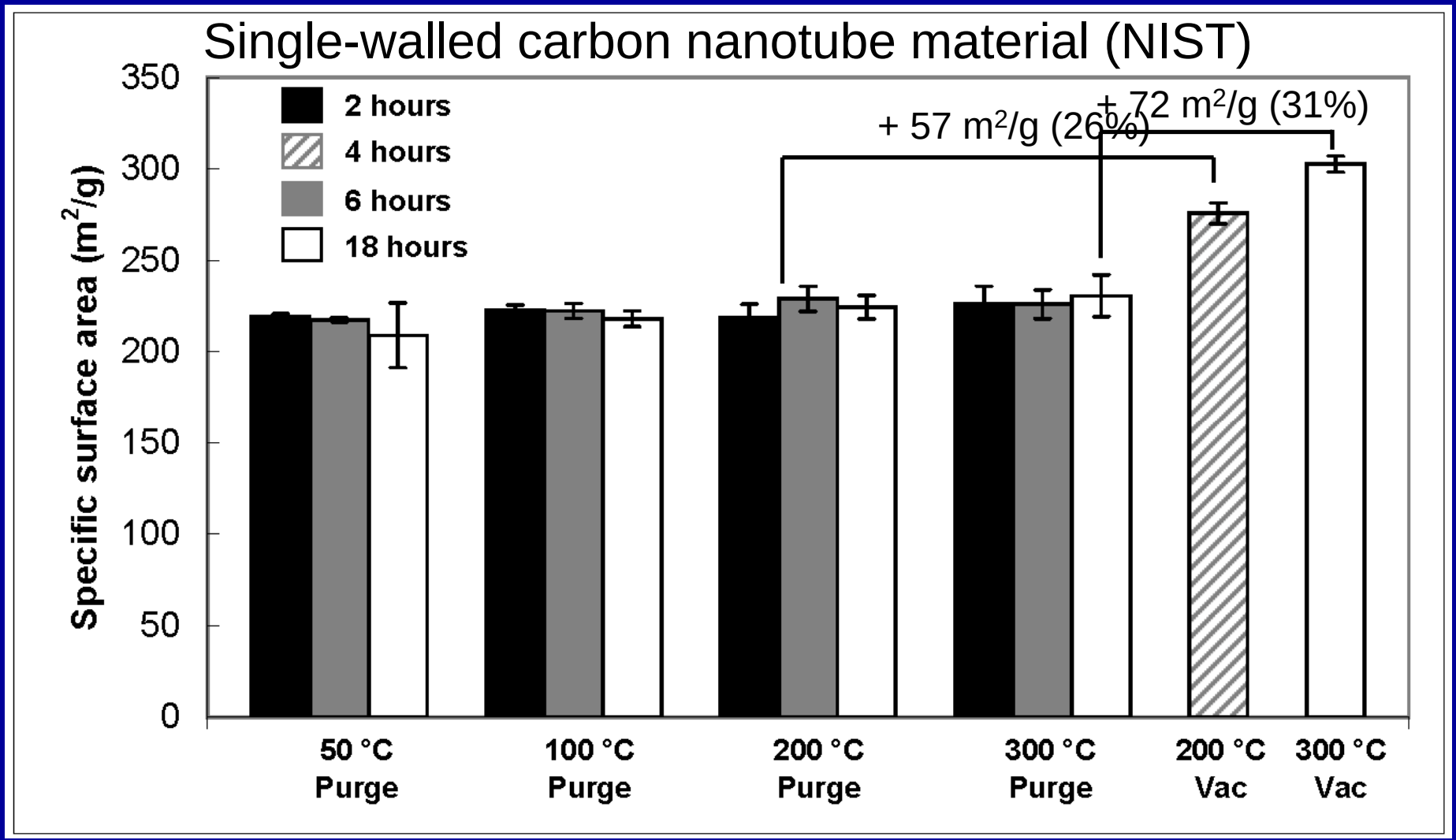
Example 1: Particle Size



Thickening of oxide layer results in change in particle size by ~ 6nm

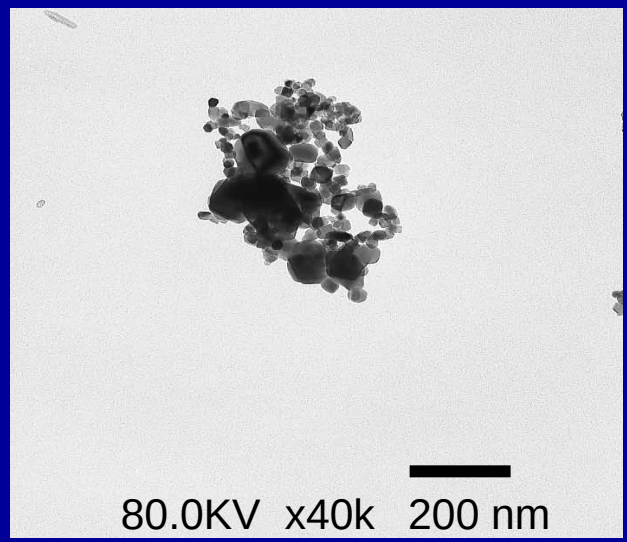
Wang et al. Ultramicroscopy. 108:43–51 (2007)

Example 2: Particle Surface Area



Summary of Needs

- Reference materials
- Tools to measure airborne nano-objects
  - Specificity: nanoscale vs nano-object
  - Biologically relevant metric
  - Personal samplers
- Standard protocols
  - Sample collection
  - Sample analysis



Titanium dioxide

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