Nanomaterials: Organic and Inorganic for Next Generation Diesel Technologies

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Introduction

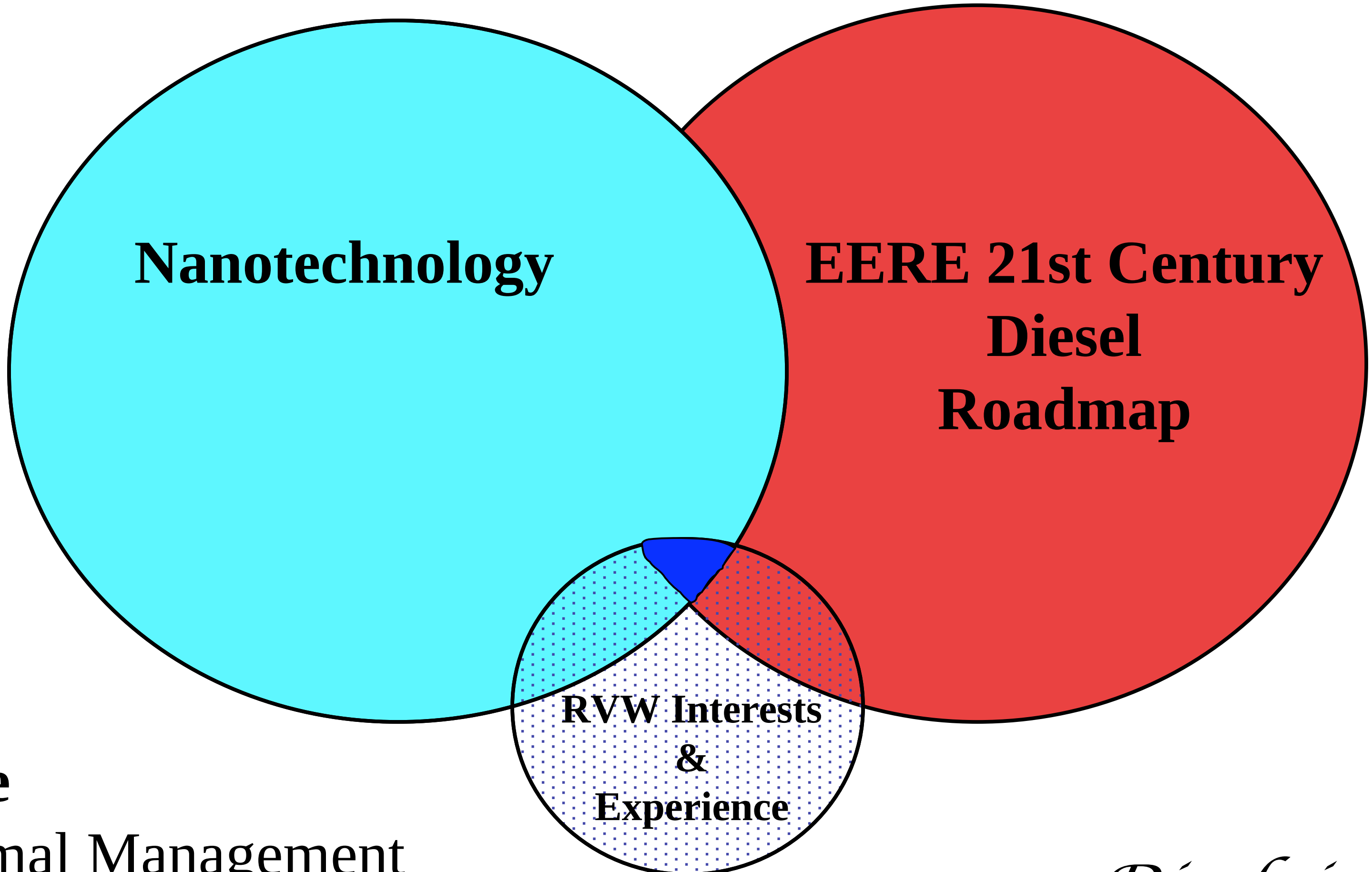
DOE's 21st Century Truck - Transportation

* Supports economic growt
* Is key to the country's energy security
* Enables an agile military

Examples of Nanotechnology Infusion

* BMW - Nano-oxide in clear coat laquer for paint protection
* GM – running boards for Safari and Astro vans from plastics reinforced with nanoclays.
* Hyperion - Electrostatic paint spraying using CNTs as additives
* Gold as catalyst, effectiveness, cost for oxidation of unburnt hydrocarbons and CO inside PEM fuel supplies & catalytic converters

Topic Selection Process



Outline

I. Thermal Management
II. Fuels and Lubricants
III. Energy Storag
IV. Materials Technologie
V. Combustion and Emission Control

Disclaimer

Fuel Cells
Thermoelectric Technology
Smart Materials
Catalysts

Thermal Management

Motivation

* EGR is the most popular near term solution for reducing NOX, but this could add 20-50% to coolant heat rejection systems.

* Conventional cooling-system components such as radiators, oil coolers, and air-conditioner condensers are already at or near practical maximum size.

* Reduce the size of present cooling system (heat exchanger, fluid reservoir and pump) to obtain a better aerodynamic profile and increase engine efficiency

* Coolants and lubricants are inherently poor heat transfer fluids

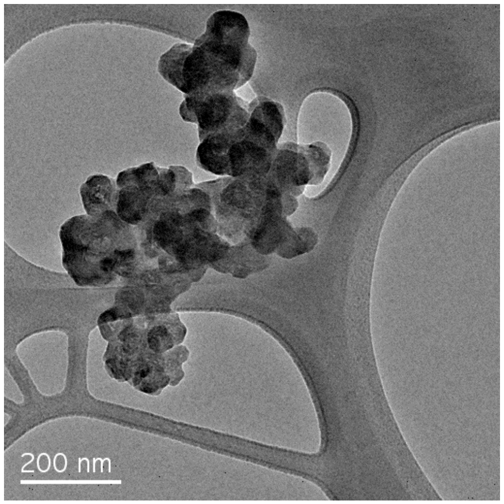
Advanced heat-transfer fluids: Nanofluid technologies

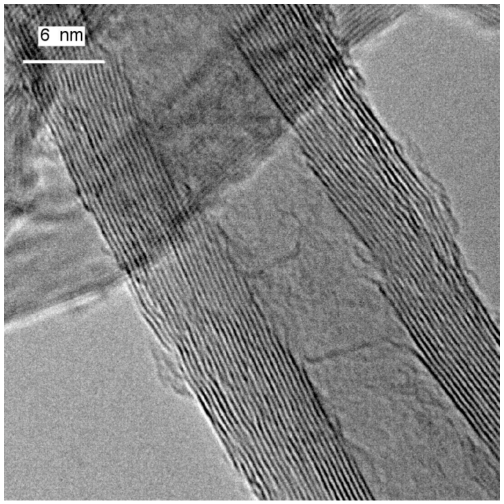
Thermal Management

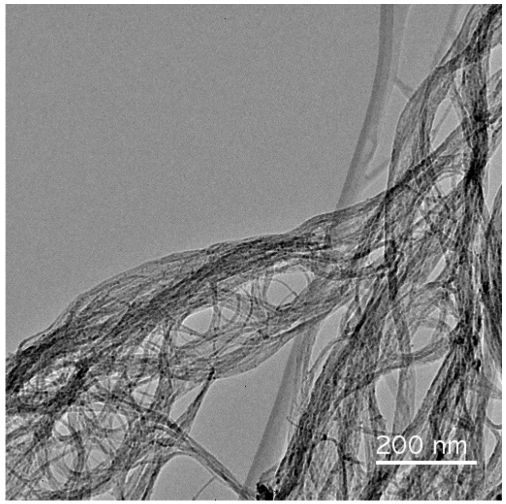
Limitations

* Measurement – Hot wire susceptible to convection, requires non-conducting solutions
* Materials – Nano-additives may cause abrasion and wear
* Particles – No images have been presented of individual nanoparticles. Instead aggregates and agglomerates
* Models- Several

Effective medium theory (EMT) models include the Maxwell-Garnett and Bruggeman, Hamilton-Crosser and Jeffrey and Davis models.







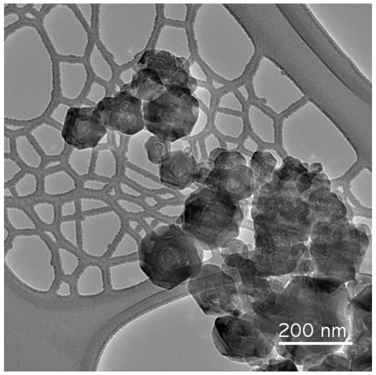
Thermal Management - Postulated Mechanisms

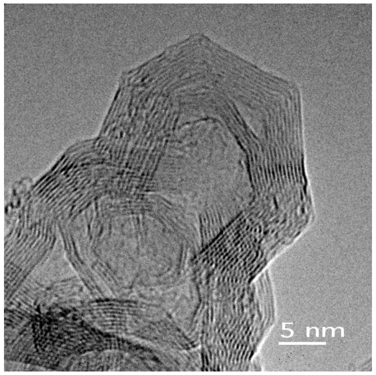
1. Brownian motion – Characteristic time to slow relative to fluid thermal diffusion
2. Interfacial ordering[1] – Liquid ordering at interface – small range
3. Ballistic transport[2] – Applicable for additives of extended length
4. Nanoparticle clustering – Network formation, i.e. Percolation

[1] Depends on thermal resistance at the interface (Kapitza conductance) Governed by phonon-phonon coupling.

[2] Depends upon additive thermal conductivity, defects, etc.

NanoMaterial	Thermal Cond.	% Increase H_2O
MWNT	0.58	4.6
MWNT-Funct.	0.65	16
R250-G	0.60	8.0
R250	0.61	5.6
R250-G-Funct.	0.66	19
R250-Funct.	0.65	17





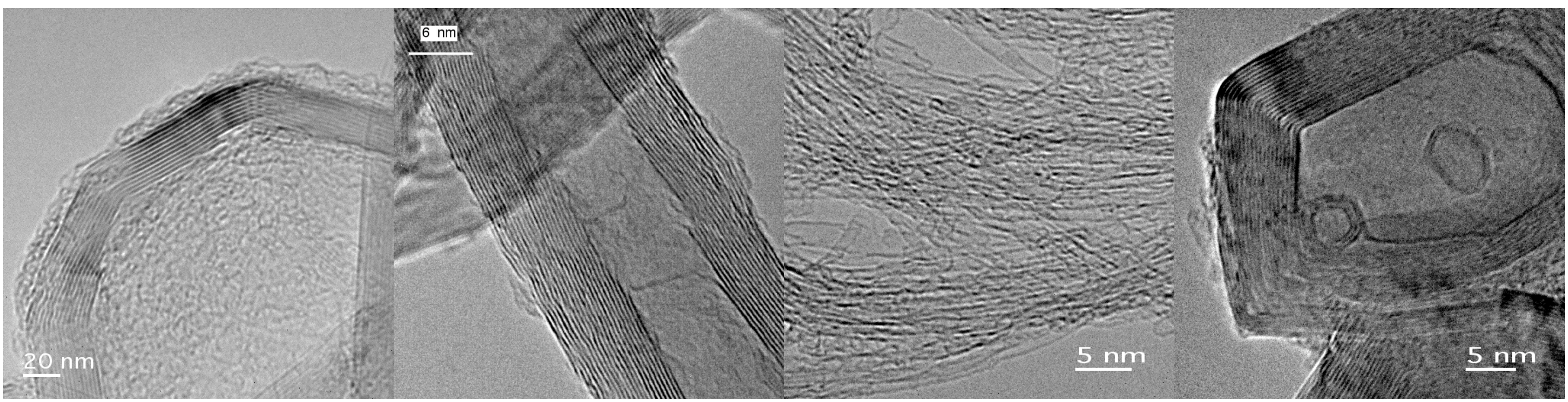
Friction and Wear

Needs

* Many critical components are lubricated by oil.
* Friction, wear and lubrication are important in virtually every approach for reducing energy consumption and wear.

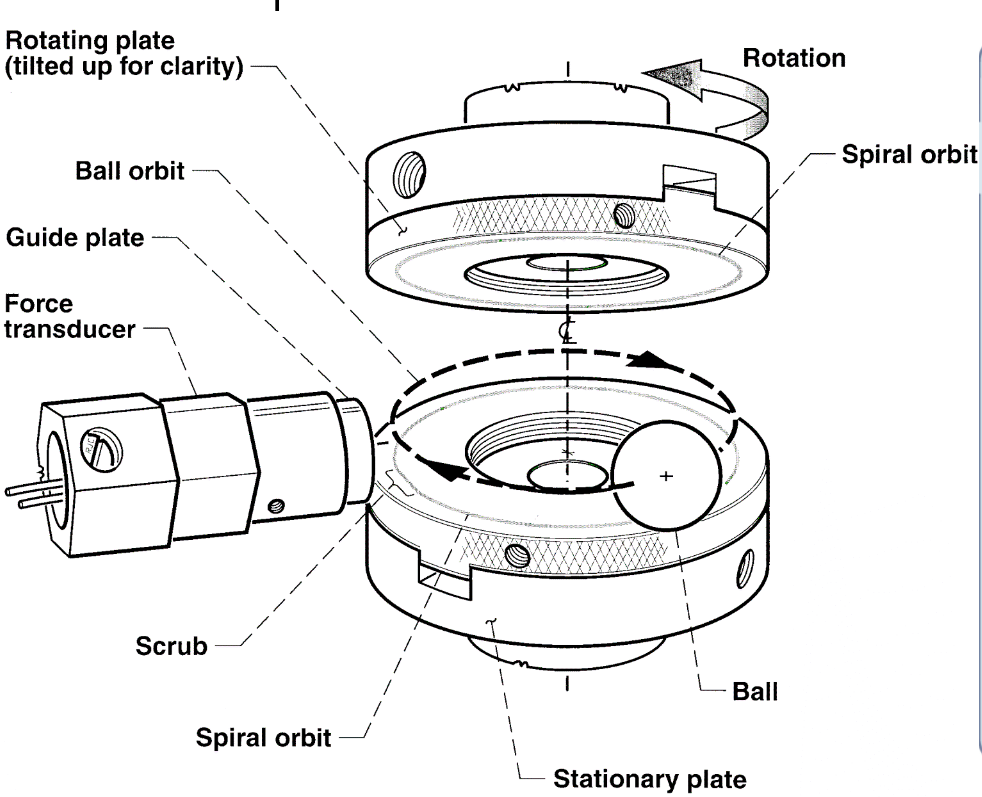
Improved lubricants, coatings and lubricant formulations will be important to addressing engine exhaust soot, sulfur and phosphorus and their impact on advanced aftertreatment technologies.

BN Shells MWNTs SWNTs Nano-Onions

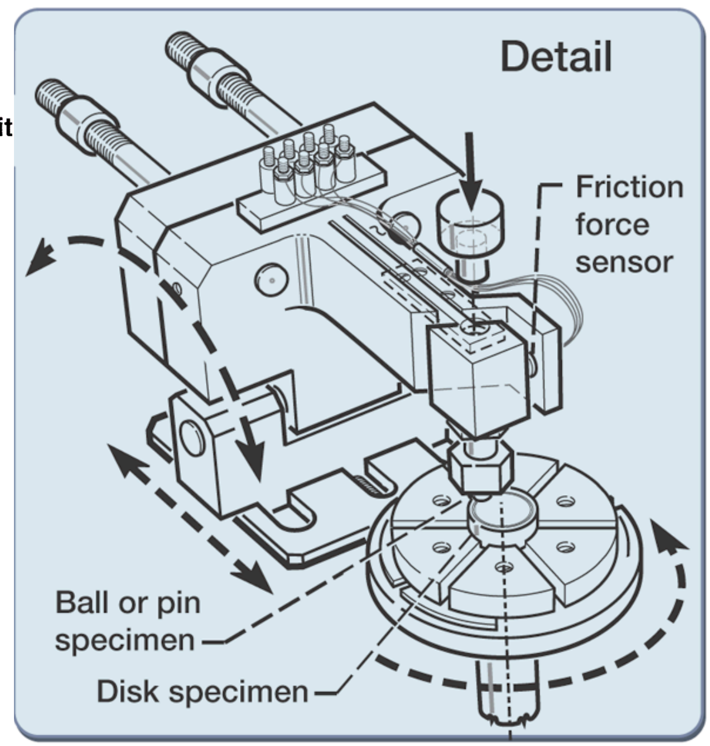


Tribometry Instrumentation

Spiral Orbit Tribometer (SOT)

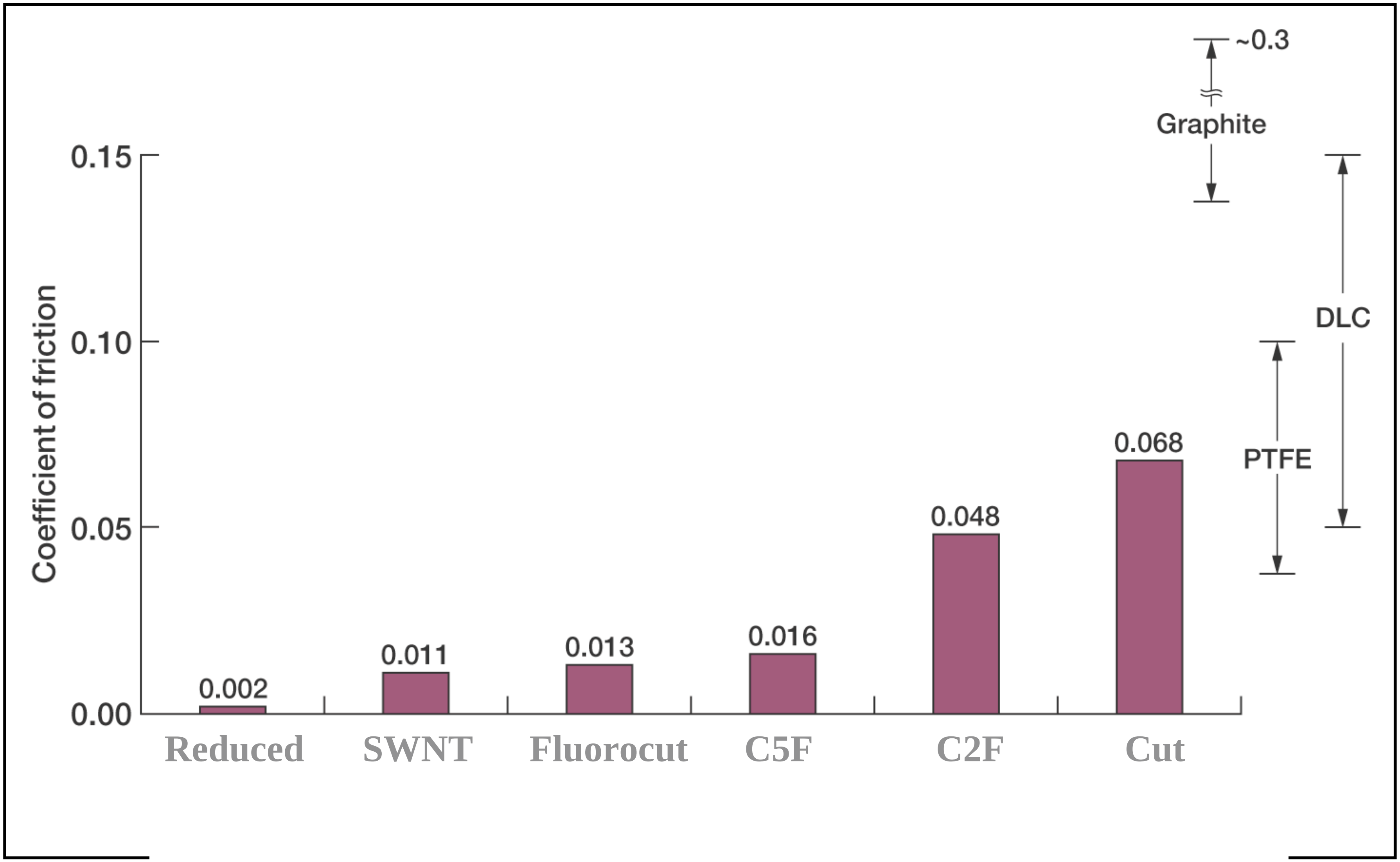


Pin on Disc Tribometer (POD)

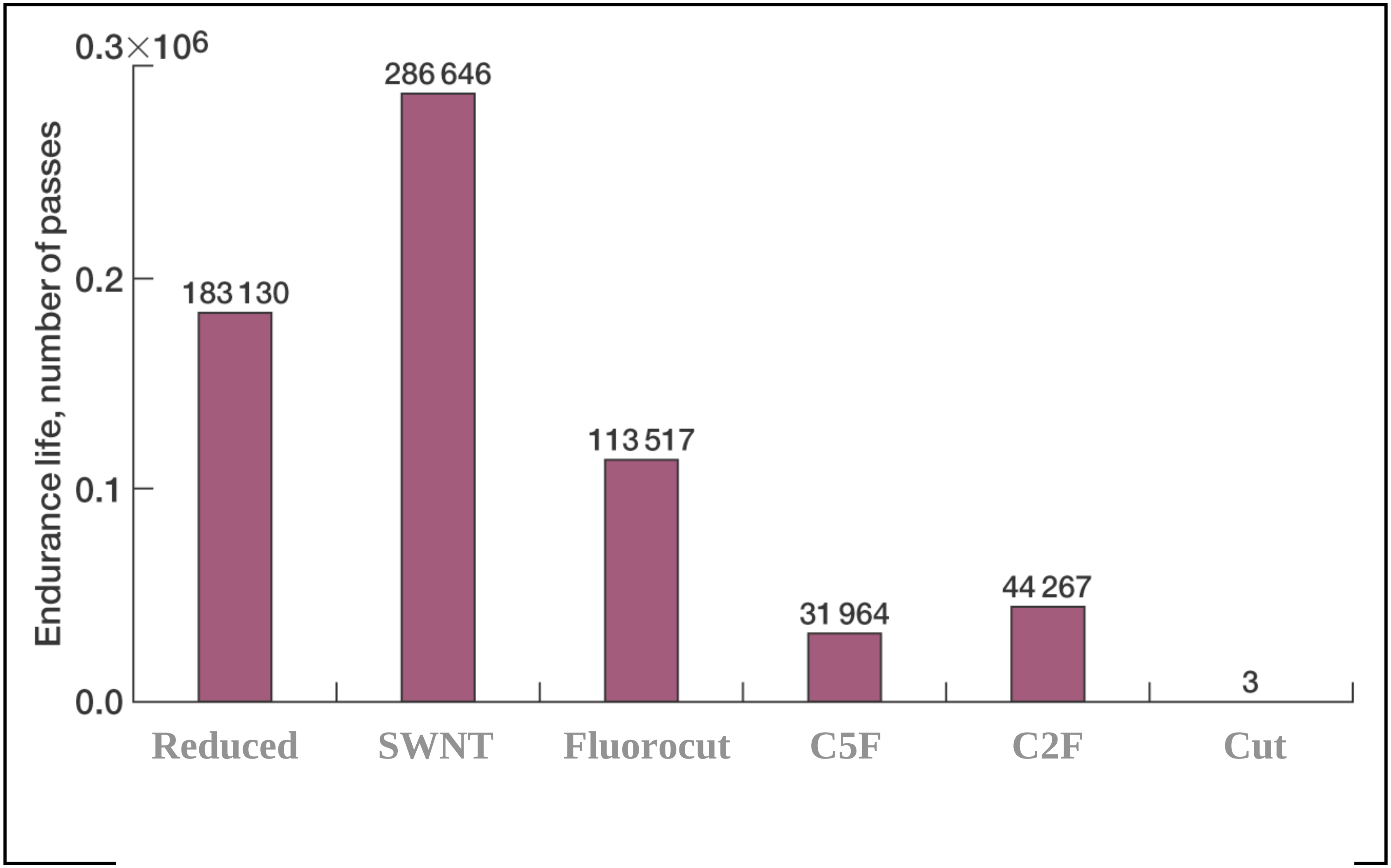


S.V. Pepper and E. Kingsbury, "Spiral Orbit Tribometry - Part 1: Description of the Tribometer©" Trib. Trans. 46 (2003) 57-64.

Coefficient of Friction for SWNTs in Contact With Sapphire in Air



Endurance Life for SWNTs in Contact With Sapphire in Air



Energy Storage

Motivation

Electrical storage systems are needed to capture energy from the generator, braking events (and other sources)
<u>and to return as needed.</u>

* Auxiliary power units such as fans, HVAC, etc.

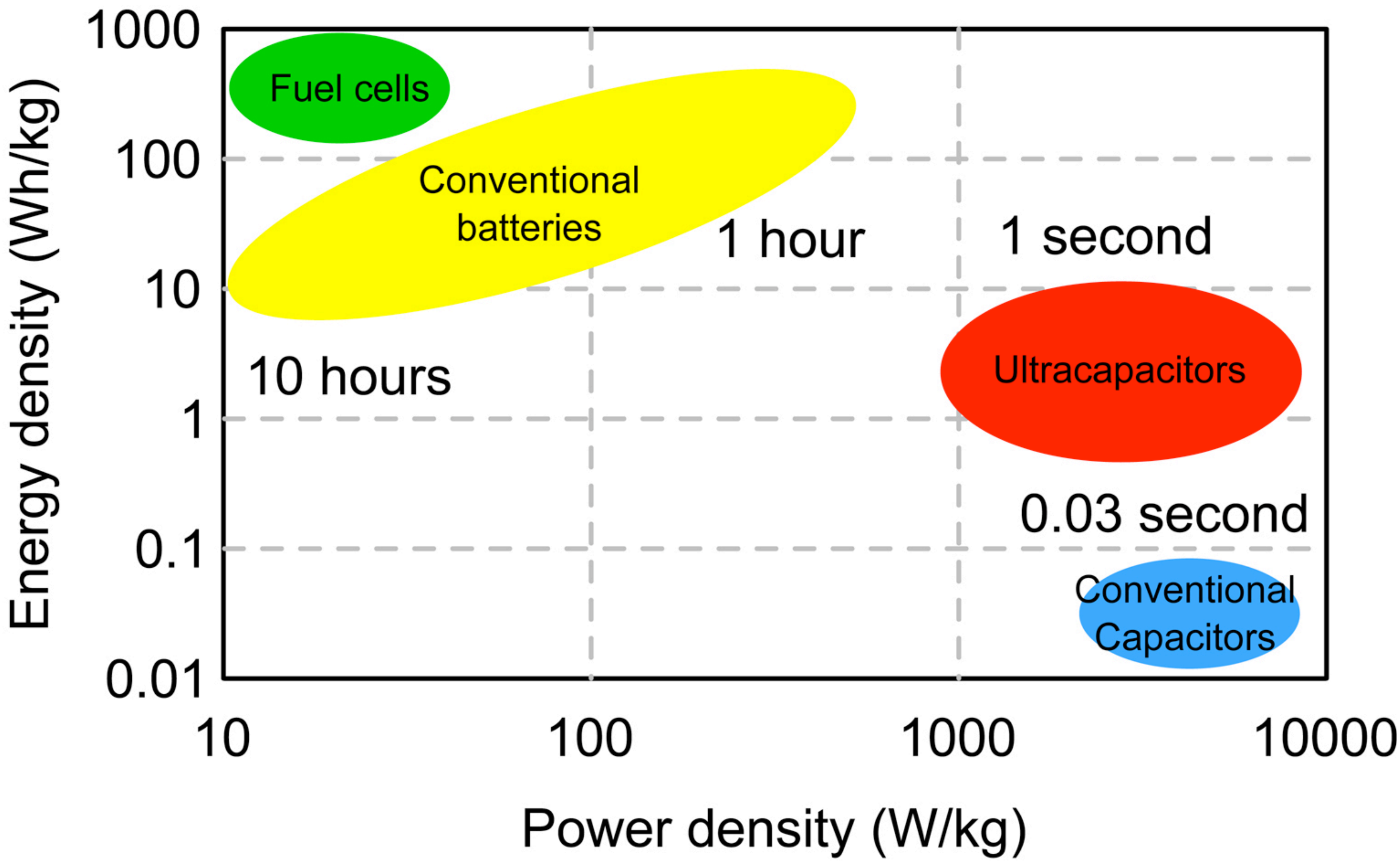
* To provide the “buffer” for low-speed torque in start-and-stop conditions.

* Hybrid Electric Propulsion Technologies

* <u>Approaches:</u>

Flywheels, batteries, ultracapacitors

Tradeoffs Between Batteries, Capacitors and Fuel Cells



Energy Storage - Projections

Batteries

Nanomaterials for higher intercalation/alloying capacity,
e.g. Anode materials including Sn, and Si.

Material	**Carbon**	**Tin**	**Silicon**
Li ion Capacity (mA-hr/g)	372 LiC6	790 Li2C	4200 Li4.4C

Ultracapacitors – Energy storage increased with surface area.

* High surface area of nanocarbons

* Combined Faradaic and pseudo-faradaic process <u>*Goal being 1kW/kg*</u>

Flywheels – Advanced carbon fiber composites

Power electronics necessary to operate the variable frequency input and output.

Future

Improvements in life cycle economics, power, storage capacity and energy efficiency are needed.

Materials

Motivation

* Reduction in weight can enables an increase in efficiency while reducing emissions

Objectives

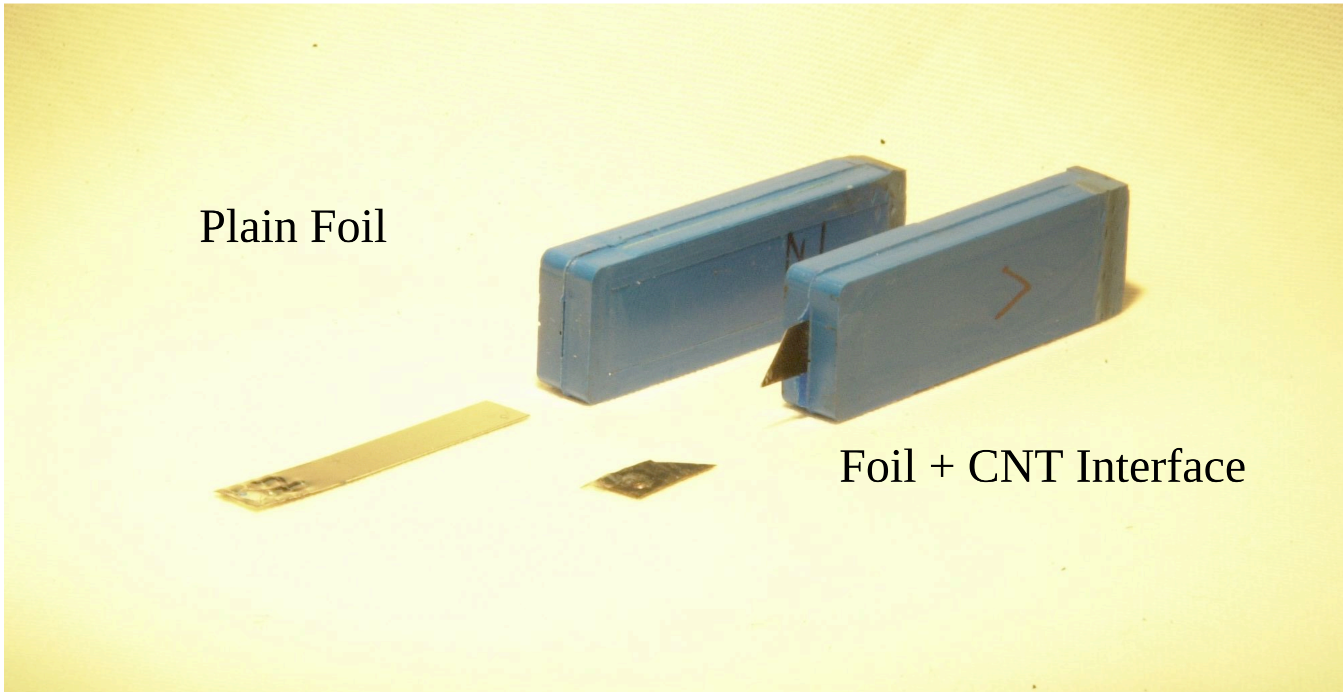
* Higher temperature, greater precision, and lighter weight

Property	CNT Additive %	Property Gain
Tensile Strength **Young's Modulus**	1-5% PMMA/PS	50% Gain 100% Gain
EM Shielding X-Band 1-10 GHz	~ 1% Polycarbonate, PS, PMMA	~ 20 dB
Electrical Conductivity S/m	0.1wt.% 1 wt. % 10 wt. %	0.1-1 1-10 10-100
Thermal Conductivity W/m-K	Epoxy 1%	100% (10s W/m-K feasible)

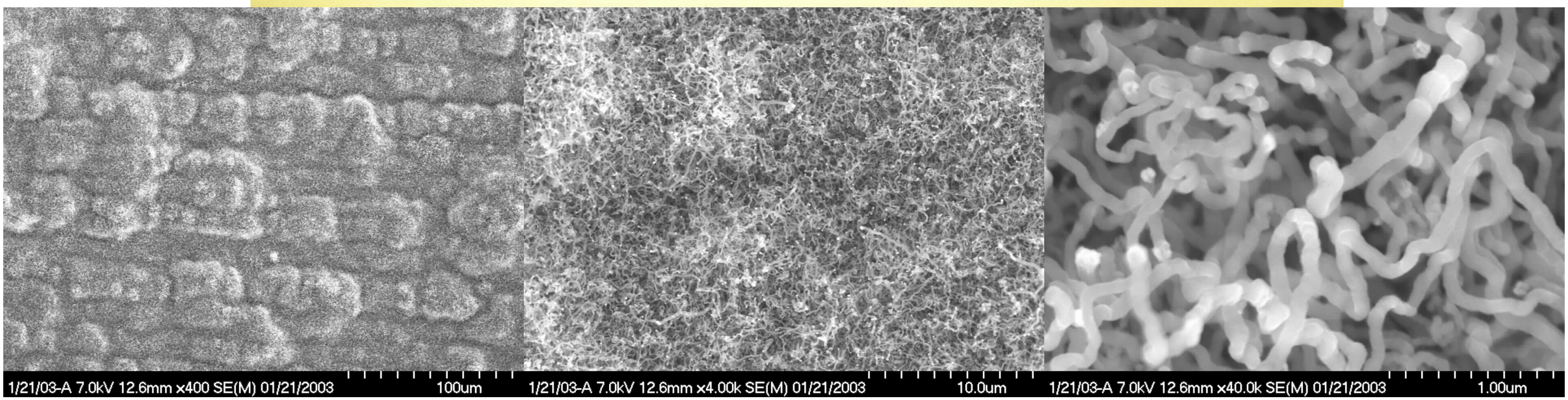
Issues: Costs, manufacturing and tooling (*integration*)

Polymeric Composites

Visual Results of Post Tensile Test Samples



SEM Images



Emissions Control Technologies

Sensors for

* Advanced Combustion Concepts (EGR, low-temperature, etc.)

* Exhaust Aftertreatment

2007-2010 EPA regulations

NOx @1.2 g/bhp-h

PM at 0.01 g/bhp-hr.

Time response critical

Presently no PM sensor and NOx inadequate

* Fuel Cells and Reformers

Sensors - Topics

1. Properties
2. Synthesis and characterization, SnO2, ZnO, In2O3 WO3 etc.
3. Integration
4. Performance

Carbon Monoxide	**1. Stored H2** **0.1 – 5 ppm** **Operational Temperature < 150 C** **Response Time 0.1 – 1 seconds** **Dry H2, 1 – 1700 atm.** **2. Reformate from stationary fuel processors** **100 – 1000 ppm** **Operational temperature 250 C** **Response time 0.1 – 1 seconds** **Gas environment, high-humidity reformer/partial oxidation gas** **H2O at 1-3 atm.**
H2 in fuel processor	**Measurement range: 25 – 100 %** **Operating temperature: 70 – 150 C** **Response time**
H2 in ambient air	**Measurement range: 0 – 2.5 %** **Temperature range: -30 C – 80 C** **Response time: < 1 second** **Gas environment: ambient air 10 – 98% humidity** **Lifetime: 10 years**
Sulfur compounds (H2S, SO2, organic sulfur	**Measurement range: 0.001 – 0.5 ppm** **Operating temperatures: - 40 C – 300 C** **Response time: < 1 min. at 0.05 ppm**
Fuel processor flow rate	**Measurement range: 30 – 7500 SLPM** **Temperature range: 0 – 100 C** **Gas environment: hihgh-humidity, reformer/partial oxidation gas (H2, CO2, N2, H2O)**
Ammonia	**Measurement range: 0 – 0.15 ppm** **Operating temperature: 70 – 150 C** **Selectivity: < 0.1 ppm from gas mixtures** **Lifetime: 10 years** **Response time: < 1 min. at 0.1 ppm** **Gas environment: high humidity reformer/partial oxidation gas, (H2, CO2, N2 and H2)**
Temperature	**Measurement range: -40 C – 150 C** **Response time: < 1 second** **Lifetime: 100 years** **Gas environment: high0himidity air or H2 at 1-3 atm.** **Insensitive to flow velocity**

Metal Oxide Semiconductor (MOS) Sensors

* Traditional MOS sensors use films or pellets of metal oxides.

  Problems include;

  - Little exposed surface area
  - Varying porosity
  - Sintering
  - Grain size

* Nanocrystalline Materials

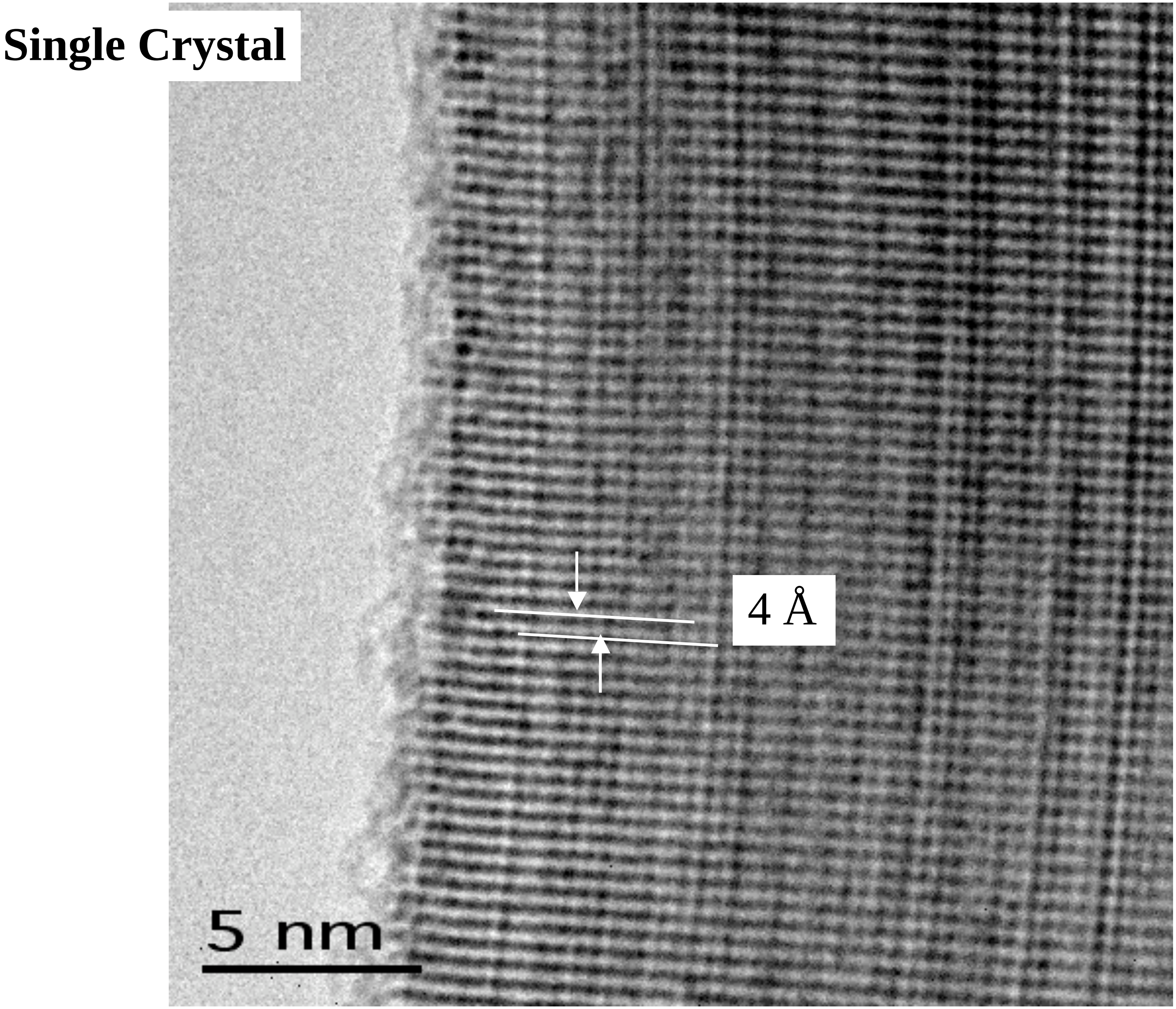
  + Tremendous increase in surface area (relative to bulk)
  + Potentially more reactive material
  + Controlled crystallinity

* Mechanism

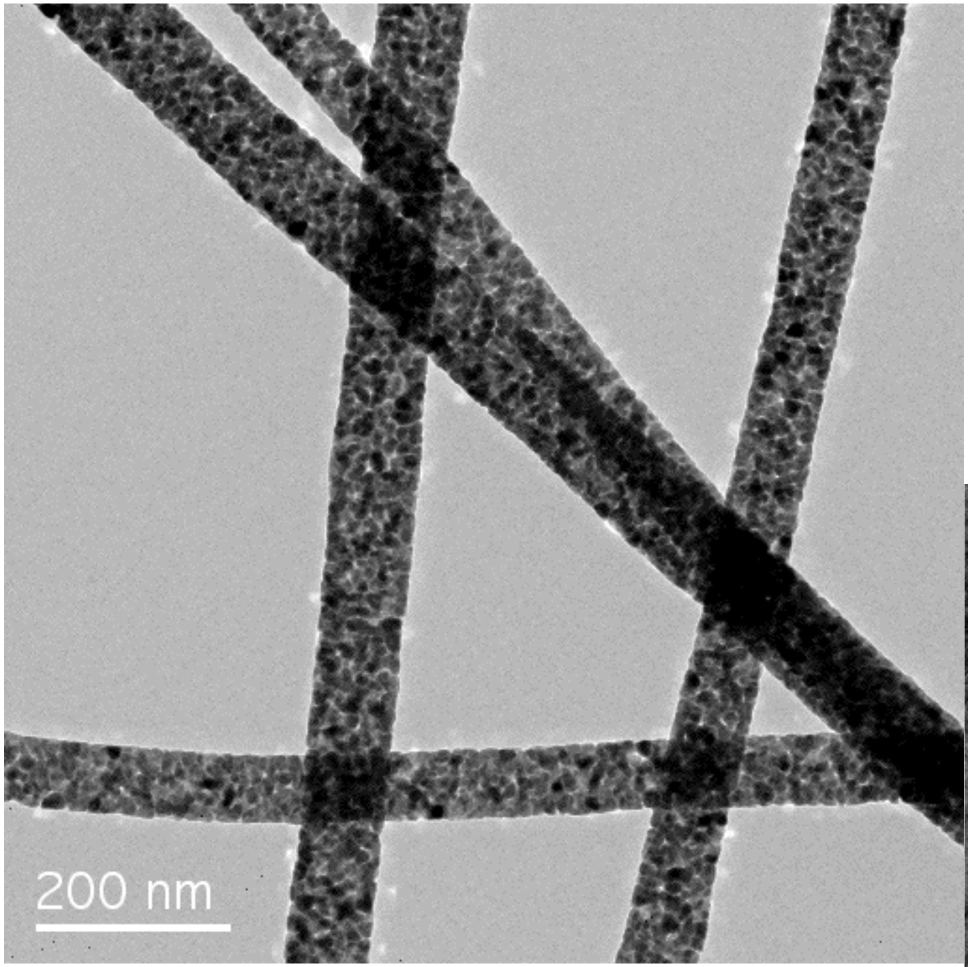
$$1/2O_{2(g)} + e^{-}_{cb} \Leftrightarrow O^{-}_{ad}$$

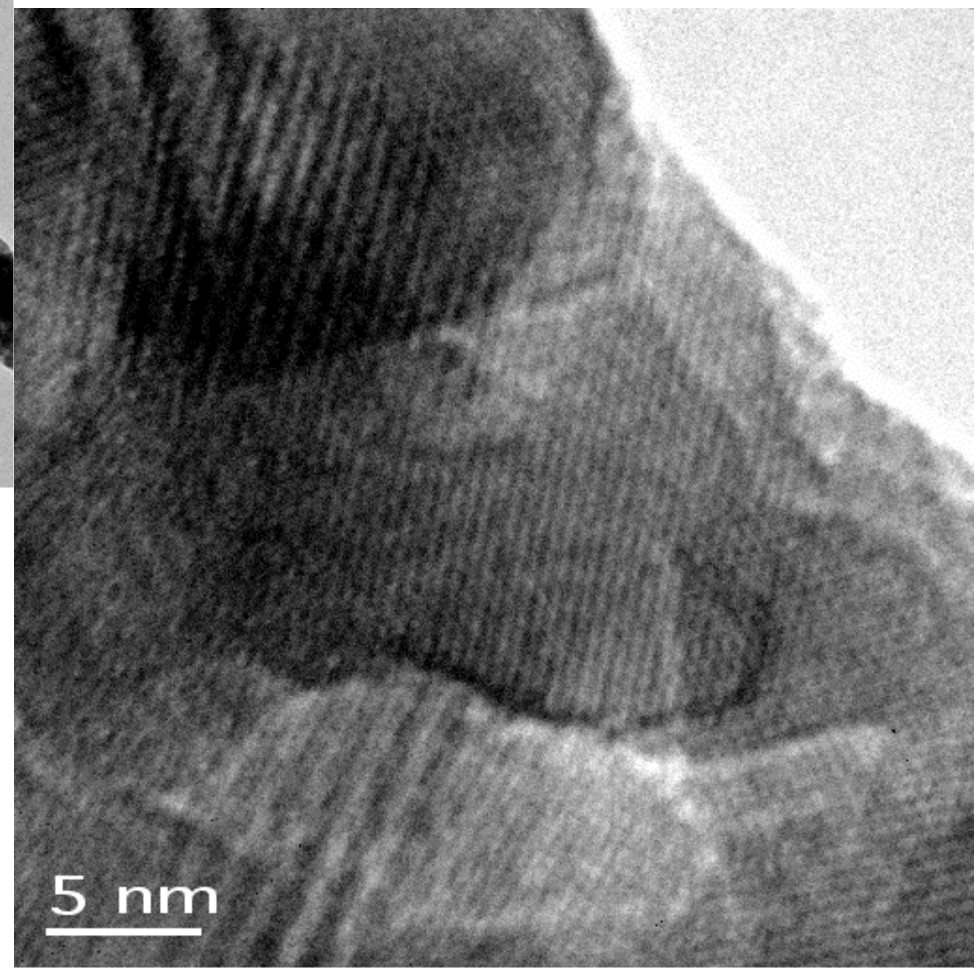
$$CO + O^{-}_{(ad)} \rightarrow CO_{2(g)} + e^{-}_{cb}$$

$$H_2, C_xH_y$$


Single Crystal
4 Å
5 nm

Electrospun Nanofibers - Transmission Electron Microscopy Images





Conclusions

* Nanotechnology is the **implementation** of nanomaterials

* Increased recognition of
interfacial processes and properties !

* **Surface area** matters!

* **Size** matters!

CNT Properties

Property	SWNTs	MWNTs	Comparison
Mechanical Tensile (GPa) Modulus (TPa)	100 ~ 1	63 ~ 1.2	1 (Steel) ~ 0.2
Thermal W/m-K	6000	2000	380 (Cu) 3200 (Diamond)
Electrical A/cm^2 Ohm-cm	$\sim 10^9$ $\sim 10^{-6}$	$\sim 10^9$ $\sim 10^{-6}$	10^6 (Cu) 4×10^{-6}
Cost	$500 / gram	$100/gram	$10/gram (Au)

* No synthesis process gives best of all three!
* Not all applications require these properties!