

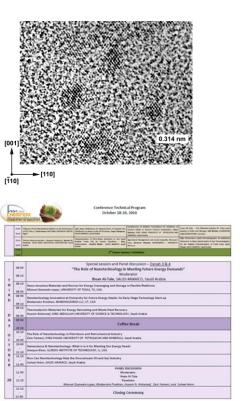


Innovative Technologies for Tomorrow's Energy Demand

8th International Conference & Exhibition on Chemistry in Industry Bahrain, Oct. 2010

The Role of Nanotechnology in the Petroleum and Petrochemicals Industries

[The Role of Nanotechnology in Meeting Future Energy Demands]





Zain Hassan Yamani CENT Director KFUPM-Dhahran-KSA

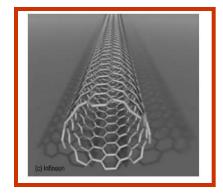


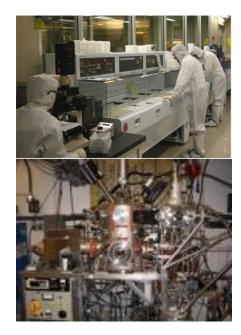






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- 6. Conclusions

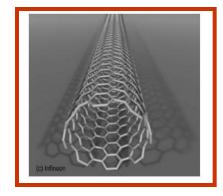


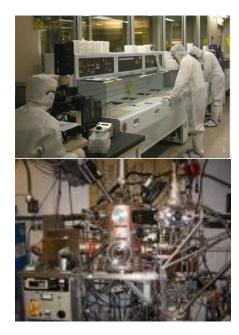






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Erosion and Corrosion Nanocoatings for Oil & Gas Industry, David Reisner, INFRAMAT, USA

Fabrication of In2O3 Nanostructures And Their Hydrogen Gas Sensing Properties, Ahsanulhaq Qureshi, KING FAHAD UNIVERSITY OF PETROLEUM AND MINERALS, Saudi Arabia

> **Carbon Nanotubes and Manganese Dioxide as A Fixed Bed Composite For Lead** (II) Removal From Water, Tawfik Awadh, KING FAHAD UNIVERSITY OF PETROLEUM AND MINERALS, Saudi Arabia

> > Synthesis of Mesoporous Chromium Silicates Molecular Sieves in Strong Acidic Media by Assembly of Preformed CrS1 Precursors with Triblock Copolymer, L. Chérif, Algeria

The effect of nanostructuring and composition modification on the oxidation behavior of stainless steel coatings, A. Al-Mathami, SAUDI ARAMCO, Saudi Arabia

Influence of ZnO Nanoparticle Addition on the Performance of PVC Films, I. Elashmawia, NATIONAL RESEARCH CENTRE, Egypt

From yesterday's two sessions on nanotechnology.. it looks like we know it all 😊

Polymer Nanocomposites – Research Advances, Bander Al-Farhood, SAUDI BASIC INDUSTRIES CORPORATION, Saudi Arabia

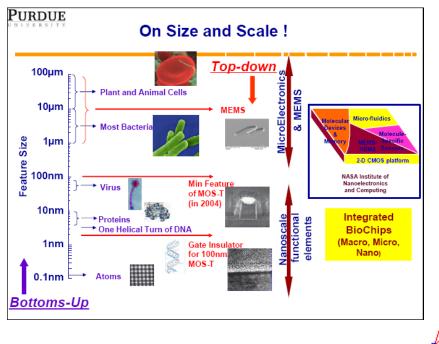




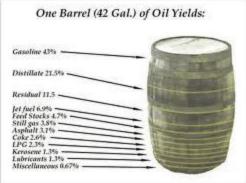
What does "Nano" have to do with huge (large-scale) industries?

Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.

http://www.nano.gov/html/facts/whatIsNano.html





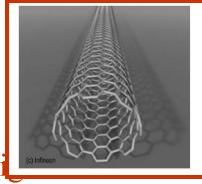








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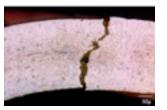






Petroleum and Petrochemicals Industries [the big picture]



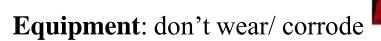


Feedstock:

- Find it
- Improve it



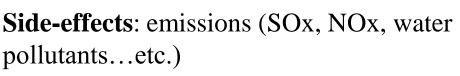
- Selectivity
- Yield



Product quality: purity, strength, specs ...



Safety: corrosive materials, inflammable materials, poisonous gases.



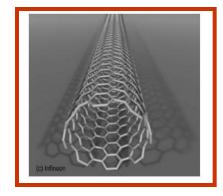


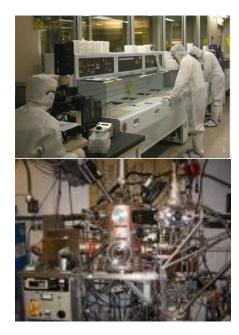






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How is nanotechnology 'special'?

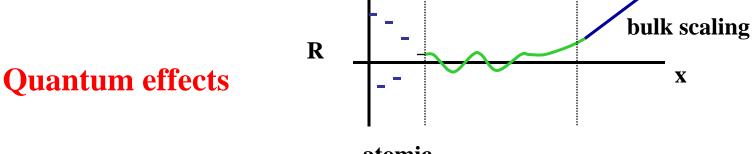
Optical qualities





Bulk Gold = Yellow



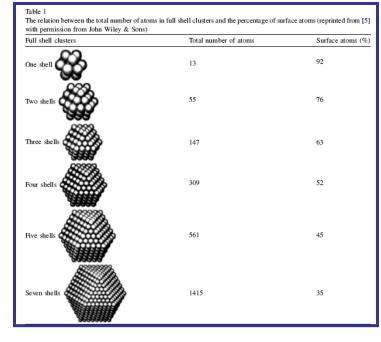


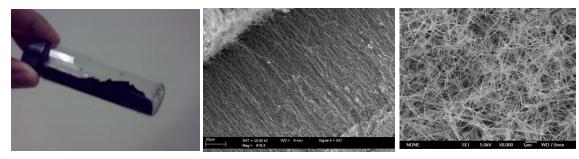
atomic





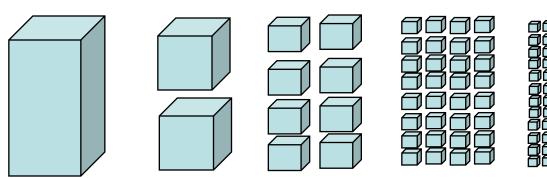
How is nanotechnology 'special'?





Extremely important for catalysis, sensors, purification and the like.

Specific surface



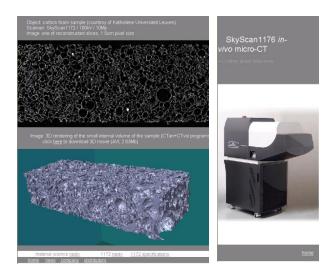




How is nanotechnology 'special'?

Nanomaterials are really.. really "tiny"..

Video



We can 'see' through sandstone and carbonate plugs!!

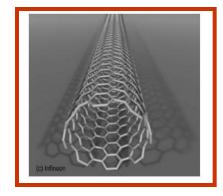


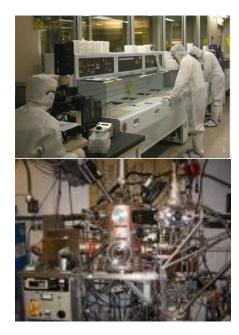
The whole micrograph is only 1/5 of a hair-width!!





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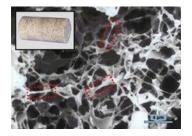
Prelude

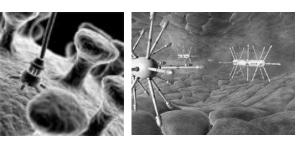
Nanotechnology cartoons I 'had' problems with: Robots in blood arteries

Then, S. Aramco (2008) shocked me! Robots 7000 ft below ground in complete darkness, wandering 'inside' rocks





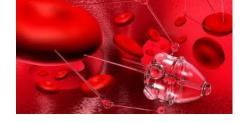




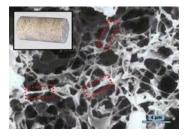


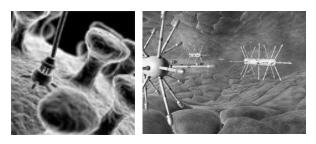
DHAHRAN, November 19, 2008 -- The EXPEC Advanced Research Center (EXPEC ARC) won the prestigious New Horizons Idea Award at the 2008 World Oil Awards. The award was granted for the research and innovation of Resbots (reservoir robots).

Resbots are nanorobots, less than 1/100th the size of the human hair, that can move through the reservoir. They will be deployed as a microscopic army with injected water into the reservoir. During their journey, they will analyze reservoir pressure, temperature and fluid type, and store that information in onboard memory. They will then be picked up from the produced crude at the producing wells to download that information and tell us everything about the reservoir they have encountered during their journey, thus effectively mapping the reservoir.

















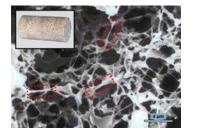


2 years later: Novel Hybrid Reservoir Nano-Agents for Enhanced Oil Recovery

Proposal submitted by Z. Yamani et. al. for S. Aramco EXPEC ARC funding!!







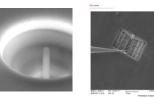
Goal: smart tracing, sensing, and sniffing devices for on-line implementation in oil fields

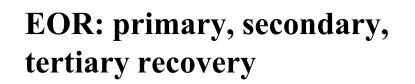












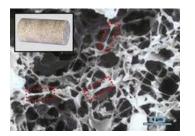
Improve on current single well chemical tracers (SWCT)

Measure residual oil saturation

Map the oil reservoir









There are a LOT of difficulties and uncertainties; yet, **IF** this technology improves EOR by even a single percent, that is a LOT of **Oil**!!





Challenging problem:

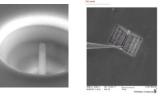
- "right" size,
- dispersibility,
- functionalization,
- harsh environment,
- choice of markers/ sensitive detection (chemical, optical, electrical, magnetic)









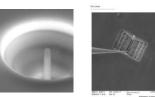








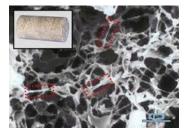






Bring resbot to life?? (active vs. passive)

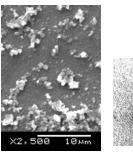


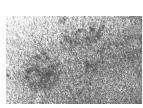


Propulsion; Navigation; Communication; Ammunition;

(for now!!)

The resbots are not 'really' robots.. but rather (just) 'agents'









NT in Petroleum-PTT challenges

Corrosion: inhibitors, coatings..

Proppants

Artificial lifting (break emulsion, remove nasty gases)

Water shut-off

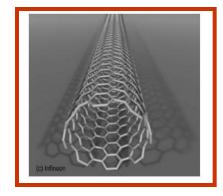
Visco-elastic surfactants

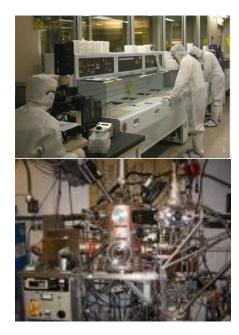
MRF: Magnetic rheological fluids





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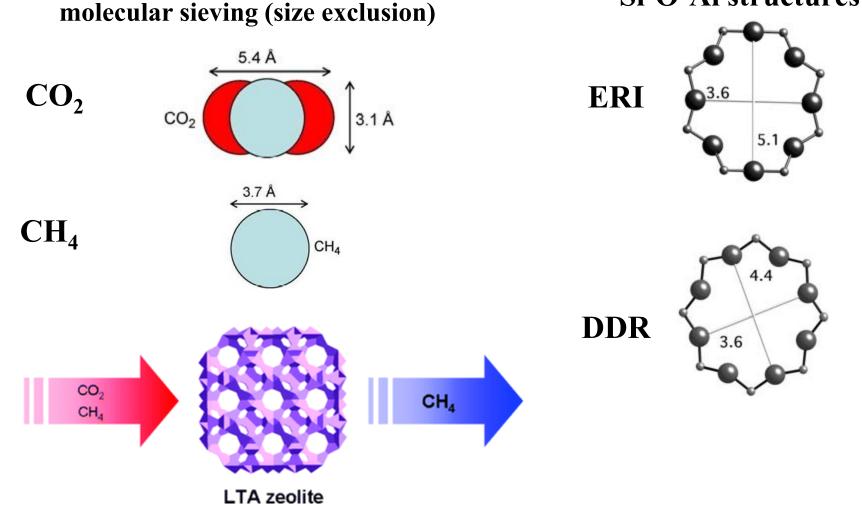






NT in Petroleum-clean gas

Crystalline aluminosilicates Si-O-Al structures



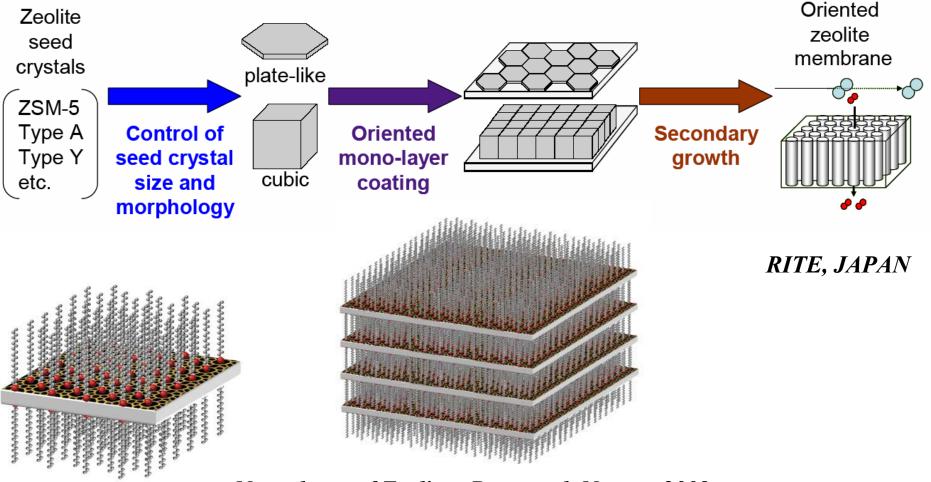
Krishna, van Baten, J. Membrane Sci. 2010, Palomino, et al Langmuir 2010





NT in Petroleum-clean gas

Hierarchical Nano-manufacturing



Nanosheets of Zeolites, Ryoo et al, Nature, 2009.



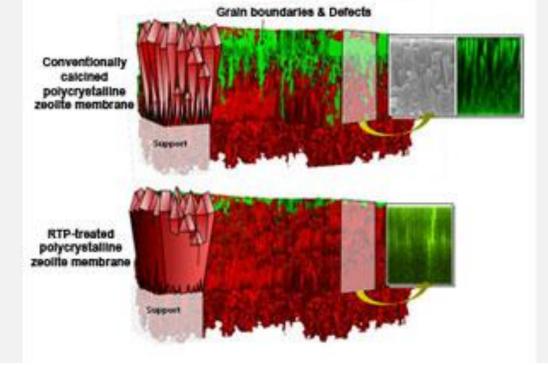


NT in Petroleum-clean gas

Challenges (1) Defects

Cracks and grain boundaries

1. Rapid Thermal Treatment



Tsapatsis group, Science, 2009

2. CVD to fill intercrystallines with amorphous silica (Nakao lab, Univ Tokyo)

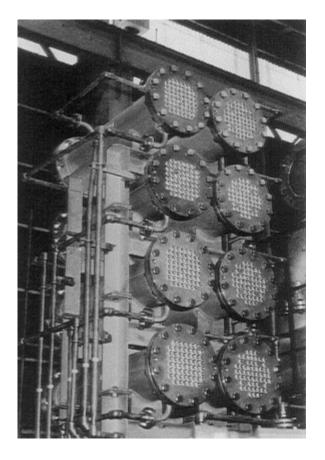




Challenges (2) Scale up

- NaA zeolite crystals had been synthesized hydrothermally.
- On the surface of a porous tubular support (12 mm OD, 80 cm L and 1 µm average pore size).
- The plant is equipped with 16 modules, each of which consists of 125 pieces of NaA zeolite membrane tubes.

Mitsui, Japan (2001)

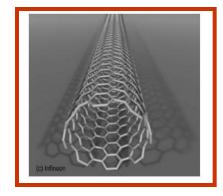


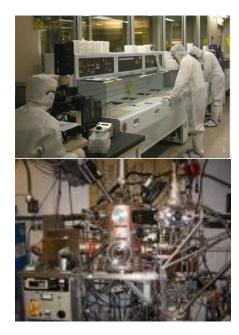






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NT in Petroleum- catalytically selective products and clean environment

Hasn't catalysis 'always' been nano? Or is it just a fad and a fancy name

Rational design.. zeolites.. an (nano) art.. not just science..

BASF.. in 1940s'.. try out 2500 of catalysts to specifically address one reaction. [trial and error].

Now, we study what are the active sites.. and *design* the materials such as to provide that specific activity.

The effect of "nano"-particle.. gold is noble, but nano-gold is not \leftarrow it is active!! Fischer Tropsch [gas to liquid]..controlling the size of the particle enhanced the activity.

2-D and 1-D materials do exist.





NT in Petroleum

catalysis by rational and computational design

Density-functional theory (DFT)

Electron density is a very convenient variable

- Physically observable
- Has intuitive interpretation
- Depends only on three spatial coordinates

DFT Simulations:

• Energetics and stability of catalytic surfaces

- Particle nucleation, agglomeration, and sintering
- Surface reconstruction
- Surface alloys vs. bulk alloys
- Surface segregation
- Gas-solid interactions
 - Adsorption strength
 - Reaction kinetics
 - Molecular transport
 - Mechanistic aspects

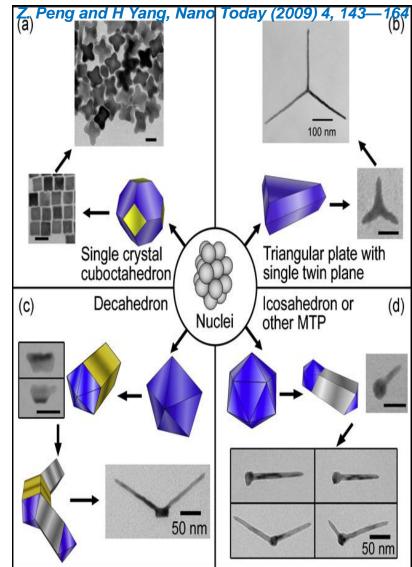
Computational approach for predicting properties and function of nano-engineered catalytic surfaces



NT in Petroleum- catalytically selective products and clean environment

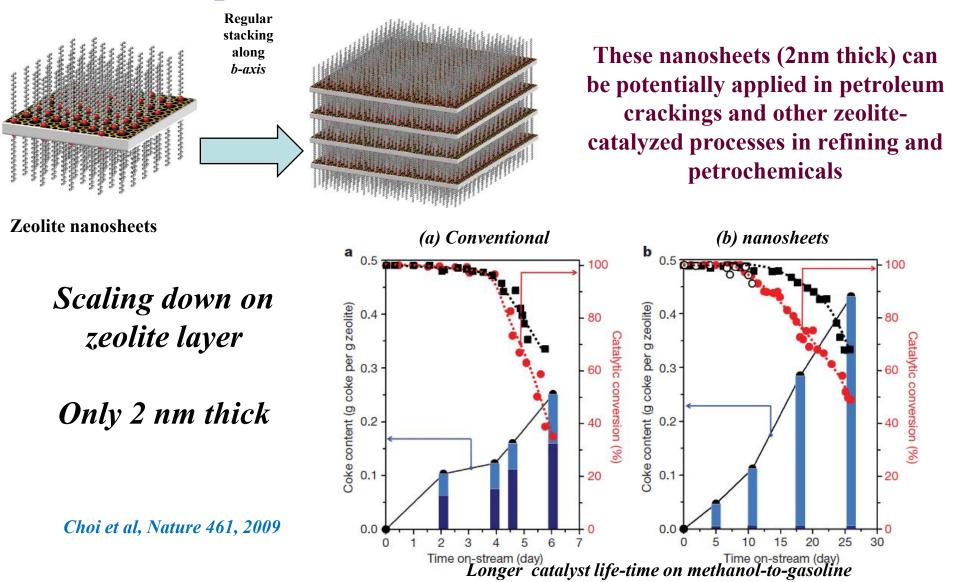
Nanostructure materials catalysts have attracted great attention due to:

- Enhanced catalytic activity and durability in catalytic processes, such as HDS of fuels, hydrogen generation, fuels to chemicals conversion,.. etc.
- Better control of their chemical and physical properties, such as surface functionalities, pore size, surface area, etc.
- Variety of methods to engineer the materials , namely solvo/hydro thermal, mircowave, temperature programmed reaction, atomic layer deposition, ion beam deposition, etc.
- Possibility of being prepared and used with and without support





NT in Petroleum- catalytically selective products and clean environment





JSM-6701F



NT in Petroleum- catalytically selective products and clean environment

ppm cm ⁻² hr ⁻¹	120	Branched Paraffin Olefin	а
	100	Other alkanes Methane	
	80	- Mediane	
	60		
	40	-	6
	20	-	9
	0	NT/Pt-460 NT/Pt-600	NT/Cu-600
	200		
г. ц	200 150	- CO H ₂	b
			b
ppm cm ⁻¹ hr ⁻¹	150		ь

Nitrogen doped TiO2 nanotube array films with Pt (NT/Pt) and Cu (NT/Pt) cocatalyst annealed at 460 and 600°C under sunlight illumination (a) hydrocarbon generation and (b) CO and H₂ generation rates Nano lett. 9 2009 731

SEI

CH4, H2,O2 CO-CATALYST

Depiction of cocatalyst loaded flow-through nanotube array membrane for high rate photocatalytic conversion of CO2 and water vapor into hydrocarbon fuels

Nanostructured materials for CO₂ storage electrochemical conversion of CO₂

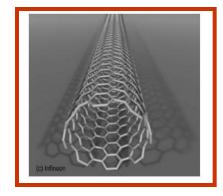
5.0KV

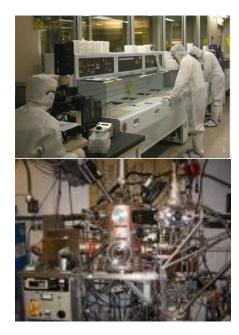
X20.000





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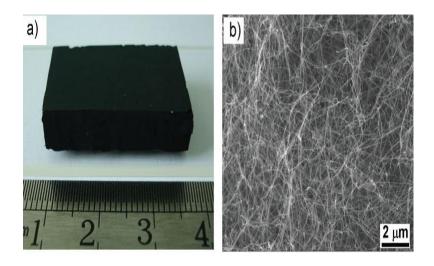






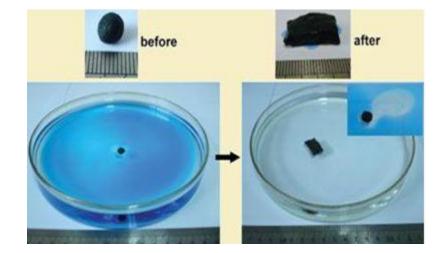
NT in Petroleum- clean environment

Nanotechnology For Clean Air and Water



CNTs can absorb up to 180 times of its weight for wide range of oils and solvents in water *X. Gui et al., Adv. Materials, Adv. Mater. 2010, 22, 617–621*

Nanotechnology can improve the quality of our live



Nano metal oxide as air purification catalyst







NT in Petroleum-tough materials

Advanced Ceramics & Their Applications

- *Structural:* Wear parts, bioceramics, cutting tools, engine components, armour.
- *Electrical:* Capacitors, insulators, integrated circuit packages, piezoelectrics, magnets and superconductors
- *Coatings:* Engine components, cutting tools, pipes, rotors, propellers, turbine blades and industrial wear parts
- Chemical and environmental: Filters, membranes, catalysts, and catalyst support

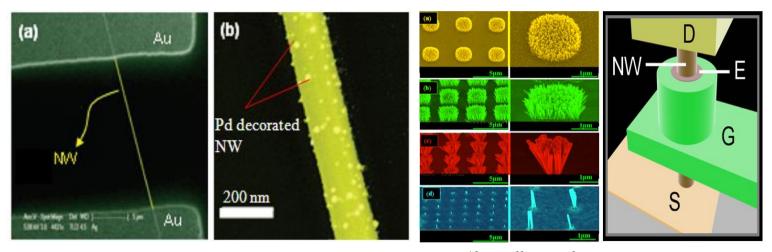






NT in Petroleum- 3S detection of H_2 , H_2S , NO_x ,...

Future Sensors



Miniaturization scaling down..

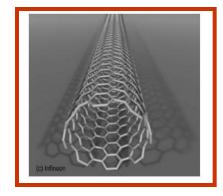
Ahsanulhaq et al Nanotechnology 18 2007 485307 Vertical Single Nanowire device

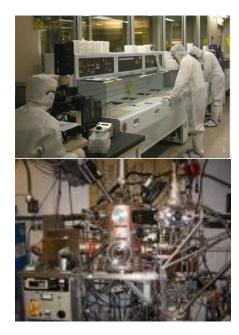
Sub 100 nm Patterning





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NT in Petrochemicals Industry

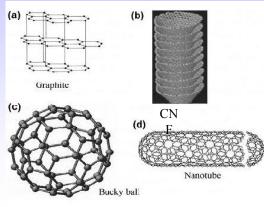
Nanomaterials for the Petrochemicals Industry



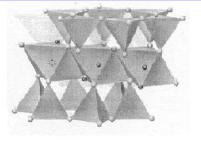




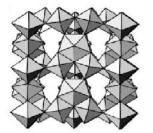
Nanomaterials Carbon, Inorganic and Hybrid



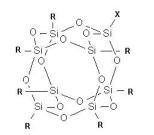
Carbon nanomaterials



Nanoclay/ layered silicate www.nanocor.com



Zirconium Tungstate



POSS Nanoparticle, Hybrid

- > Nanosize materials have different properties than microsize materials.
- > Very high surface to volume ratio.
- > High strength to weight ratio.
- > Exceptional mechanical, thermal, and electrical properties.





Polymer Nanocomposites

Polymer nanocomposite is defined as combination of polymer matrix and a material which has at least one dimension in nanometer scale.

Looking for a jump in qualities at low levels of incorporation (less than 1%).

- Improved Mechanical Properties
- Improved Barrier Properties
- Flame Retardant Properties
- Improved Electrical and Thermal Conductivities
- Lower Thermal Expansion
- Low Specific Gravity Compared to Traditional Composites

Degree of property enhancement is a function of particle dispersion and Matrix-Particle interaction.





Polypropylene- Layered Silicate (Clay) Nanocomposite

Mechanical Properties of Injection Molded HPP Nanocomposites

Process	PP Type	Addition Level (%)	Tensile Mod. (Mpa)	Flexural Mod (Mpa)	HDT (C)
Injection	Homopolymer	-	1412	1148	87
Molding	(Low melt flow)	6%	2804 (+98%)	2043 (+78%)	116 (+33%)
Injection	Homopolymer	-	1327	1196	86
Molding	(medium melt flow)	6%	2180 (+64%)	1777 (+49%)	109 (+26%)

Barrier Properties of Polyolefin Nanocomposite Films

Film Process	РР Туре	Addition Level (%)	OTR (cc-mil/m² day)	CO2 (cc-mil/m ² day)	H2O (g-mil/m² day)
Cast	Random	-	3.35 E+03	1.38 E+04	0.22
	Copolymer	6%	2.54 E+03 (+24%)	0.72 E+03 (+47%)	0.19 (+14%)
Cast	TPE	-	1.82 E+03		
		6%	1.27 E+03 (+30%)		

Substantial improvement

in the Mechanical and in

the Barrier properties of

nanocomposites of

injection- molded and

extruded polypropylene

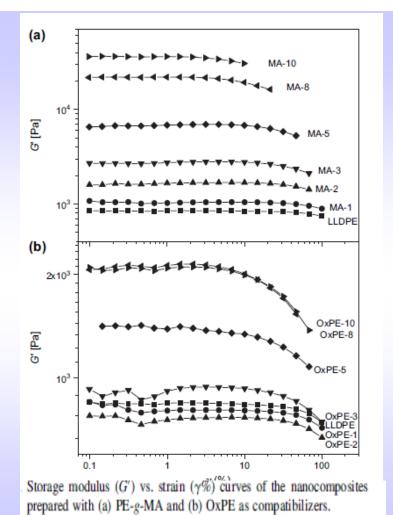
at small (6 %) nanofiller

fraction





Functionalized Polyethylene/ Clay Nanocomposites



Properties of Extruded Nanocomposites of Maleated Polyethylene , and of slightly Oxidized Polyethylene containing Exfoliated Layered Silicate

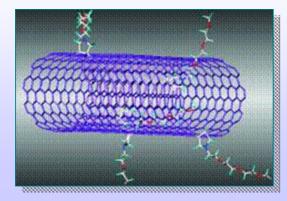
Greater than an order of magnitude improvement in modulus for both modified polyethylenes



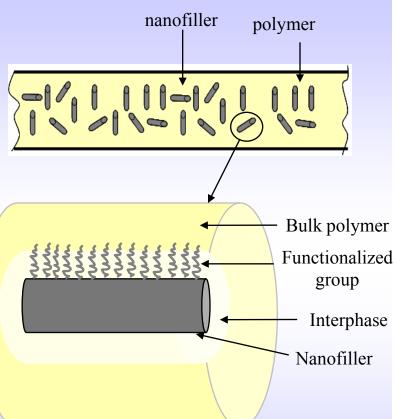


In Search of a Quantum Leap in performance improvement at less than 1% nanoparticle

- Proper functionalization of nanomaterials is critical for increased matrix compatibility and optimum dispersion
- Performance of a nanocomposite is based on three characteristic.
 - > Properties of polymer and nanofiller.
 - Interfacial interaction between the nanofiller and the polymer matrix.
 - > Orientation of the nanofillers.



Functionalized Carbon nanotube







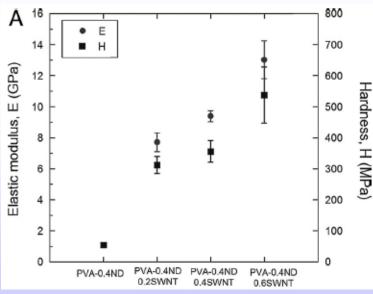
Mechanical Properties of Polyvinyl Alcohol (PVA)-Nanocarbon Composites

Extraordinary synergistic effect on the mechanical properties of polymers resulting from incorporating binary combinations of nanocarbons

 Nanotubes and nanodiamond
 Nanotubes and graphene

At 1 % or less of Nano Carbon Mixture

Material	Hardness (MPa)	Modulus (GPa)
PVA	38	0.66
PVA – 0.2 ND	43.7	0.87
PVA – 0.6 SWNT	290	7.8
PVA – 0.4 SWNT + 0.2 ND	367	9.30
PVA – 0.4 ND + 0.6 SWNT	550	13



ND = Nanodiamond

(CNR. Rao, Proceedings of the National Academy of Sciences, PANS, 106, 32,13187, 2009)

Elastic Modulus (E) and Hardness (H) for PVA Composites with Binary Nanoparticles



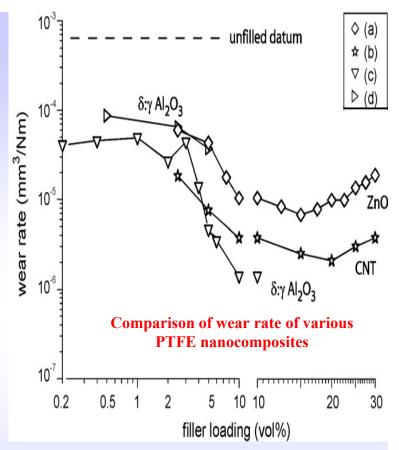


Wear Rate Reduction in Polymers by the Incorporation of Nanomaterials

Fluoropolymers (TEFLON)

Characteristics

- Low Friction
- High Temperature
- Chemically Inert
- Hydrophobic
- High Wear Rate
 - Lower wear rate by incorporation of filler particles - at the expense of other properties
 - **Nanofillers** more effective at small percentages can have high number density and surface area



It takes 10% of unfunctionalized nanoparticle to lower the wear by 2 orders of magnitude

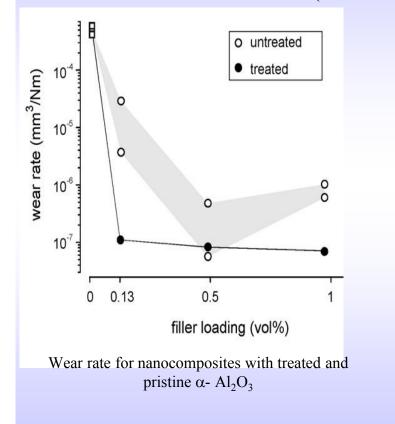


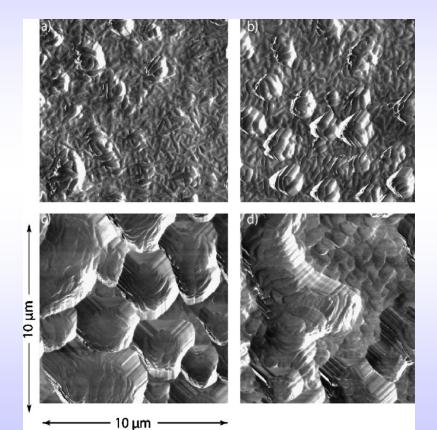


Teflon Nanocomposites (PTFE) with Functionalized Nanoparticles

> Alpha Alumina (α -Al₂O₃) Surface functionalized with fluorinated Groups

Show an Unprecedented four order of magnitude drop in wear rate of PTFE at a 1% volume of α- Al₂O₃ (W.G. Sawyer, et. al., Wear, 267, 653, 2009)





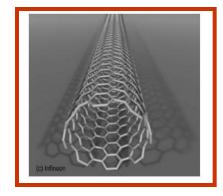
AFM of a) PTFE, b) 0.5 vol. % Δ : Γ Al₂O₃-PTFE, c) 0.5 vol. % 40nm treated α -phase Al₂O₃-PTFE, and d) 0.5 vol. % 40nm untreated α -phase Al₂O₃-PTFE.

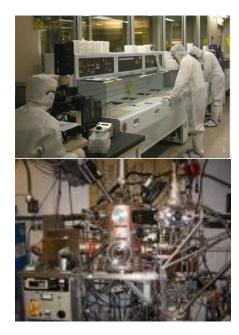




Outline

- 1. We need no introduction?!!
- 2. Petroleum and Petrochemicals Industries [the big picture]
- 3. How is nanotechnology (NT) 'special'?
- 4. NT in Petroleum and Petrochemicals
- 5. CENT as an example
- 6. Conclusions



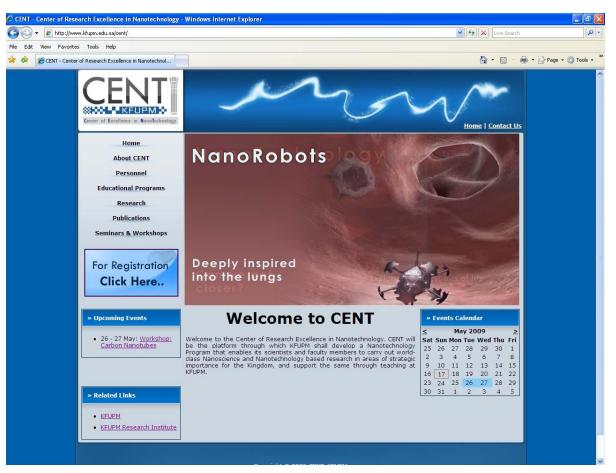






What is CENT?

Center of Excellence in NanoTechnology



www.kfupm.edu.sa/cent





CENT: Vision and Mission

Vision:

CENT shall be an internationally recognized leading research center that develops innovative research and cutting edge knowledge in the field of Nanoscience and Nanotechnology

Mission:

CENT will be the platform through which KFUPM shall develop a Nanotechnology Program that enables its scientists and faculty members to carry out world-class Nanoscience and Nanotechnology based research in areas of strategic importance for the Kingdom, and support the same through teaching at KFUPM.





CENT: Objectives

1. To build up a world class human resources research capacity including highly qualified scientists and staff and trained graduate students in the field of nanomaterials synthesis and their characterization & applications.

2. To develop a research infrastructure including state of the art facilities that enables the Center to achieve its goals.

3. To develop innovative nanotechnology-based solutions in strategic areas for the Kingdom related mainly to petroleum and petrochemicals industries.

4. To establish Industrial Partnerships with relevant companies and entrepreneurships as a step toward commercialization, in coordination with DTV.

5. To contribute to the development of teaching graduate programs and training students in the field of nanotechnology.

6. To promote public awareness regarding the benefits and the risks of nanotechnology.





CENT Areas of Focus

focusing on the petroleum and petrochemicals industries

- 1. Nano-engineered Catalytic Materials
- 2. Nano-structured Materials for Sensing Applications
- **3. CNT Applications**





Equipments



Focused Ion Beam Stations



Gas Chromatograph



Gas Chromatograph Mass Spectrometer



Tensile testing machine for metals and polymers



Ultra Performance LC



Advanced Optical Microscope



Autoclave





Spectrofluorometer with combined steady state and lifetime capabilities



Raman System



Furnace



Pulsed Laser Deposition System



Semiconductor device analyzer



Glove Box



Surface area analyzer



Tunable pulsed dye laser





Potentiostat/galvanostat



Contact Angle Measuring Device



Planetary Ball Mill Machine





Sputtering Device

Ultra Sonicator



Solar Simulator

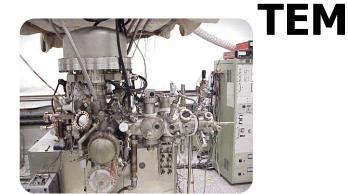


XPS XRD

monneter







http://www.veeco.com/promo/innova/

SEM

AFM/ STM



PVD/ CVD



Lasers





CENT Capabilities and Research Areas of Interest

Development of highly active and nanostructured catalysts for ultra-clean fuel. This includes the removal of sulfur and nitrogen containing compounds. In addition, removal of heavy metal complexes from natural gas is also under the scope of CENT research activities.

CENT team has the expertise to conduct research and development activities in the area of nano-composites, such as PP/CNT, PE/CNT, PTFE/CNT, etc., for many applications, including electronic packaging, coating, and electrochemical devices.

CENT team has also the expertise and "know how" to convert the oil residues into manageable and valuable products.

Develop sensors with quick responses and cost effective. With expertise of CENT team, it is possible to invent new nanostructured materials for sensing volatile organics and inorganics with ultra-low concentrations.

Research and development of catalyst based on core-shell and nanostruture materials for clean energy processes, such as photocatalysis, hydrogen generation, carbon carbon, and fuel cells.





CENT sponsored NSTIP Projects [May 2010]

Development of advanced and functional nano-structured mesoporous zeolites for hydrodesulphurization and other catalytic applications in petroleum and petrochemicals

Zeolite Nanosheets as a Materials Platform for Improved Refining Catalysts

Carbon Nanofibers Grown on 3-D Solid Structures for Applications in Energy-Related Catalysis

Development and characterization of high surface area metal carbides modified mesoporous carbons and ceramics for clean fuel and catalysis applications

Development of nano-structured metal phosphides for ultra-clean fuel and fuel cell applications

Development of Nitrogen-Modified CNTs as Pt-Free Catalysts for Fuel Cells

Electrochemical engineering of nano-structured materials for clean energy and energy conversion applications

Synthesis of Metal-Organic Framework Nanostructures for uptake of CO₂ and Hydrogen Storage

Design of Smart Fluids for Acid Delivery in Well Stimulation Treatment





CENT sponsored NSTIP Projects [May 2010]

Electrospinning of Semiconductor Metal-oxide and Polymer Nanofibres for Ultra-sensitive Amperometric Sensor

Synthesis of Mesoporous and Microporous Metal-oxides Nanostructured Materials for Hydrocarbons and NO_x Sensors

Comparative Study of Conversion of Carbon dioxide into high-value hydrocarbons using nano- structured materials by solar and laser irradiation

Development of highly efficient visible-light-driven nanostructured materials for photocatalytic applications

Photocatalytic Splitting of Water over mixed metal oxyhalides-based Catalyst using Laser Radiation

Activity of laser enhanced nano-structured oxides of tungsten, nickel, zinc, iron and titanium against Candida and Aspergillus

Lanthanide-doped oxide nanoparticles for Multi-modality Molecular Imaging Agents





Other Activities/Programs Maintained by CENT

Bi-weekly seminars

Developing CENT labs on campus

Publishing papers Patent Applications

Workshops under preparation

Visiting professors

Graduate Program

CENT Affiliates Meetings

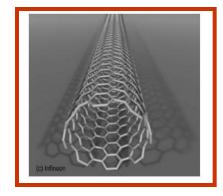
Collaborative Research

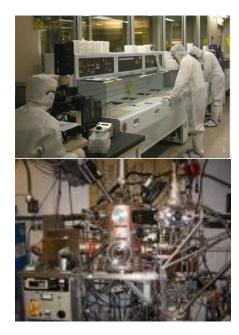




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Conclusions

- Nanotechnology is an interesting subject. 🙂
- Nanotechnology is not 'all' fake dreams!! 🙂 🙂
- There many challenges ahead of us.
- Nanotechnology has a LOT to do with the petroleum and petrochemicals industries
- CENT: nanotechnology platform at KFUPM-Dhahran-KSA.
- In coordination with other sisters centers and industries, we are developing human competency, building capacity, transferring experience, and advancing technology in the fields of:
 - 1.Catalysis,
 - 2.Gas sensing, and
 - 3.Environment [including photocatalysis and CNT work]





Acknowledgements:







The CENT research teams, both employees and affiliates









Thank you for your attention