Nanofabricação

14 a 18 de juho de 2008

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- *Prof. Dr. José Gomes Filho / gomes@cbpf.br*

Nanofabricação

Aula 1 – Prof. Gomes

14 jul 2008

"allons enfants de la patrie..."

- Apresentação da Disciplina
- Objetivo
- Metodologia
  - aulas teóricas
  - "hands off“
  - enfoque prático

- Bibliografia:
  - Livros acessíveis na Biblioteca/CBPF,
  - Papers vários
  - Sites "confiáveis" (Univ’s, Lab’s e C.Pesq’s)

- Vários Tópicos em Inglês >> any problem?

Nanostructures and Nanotechnology

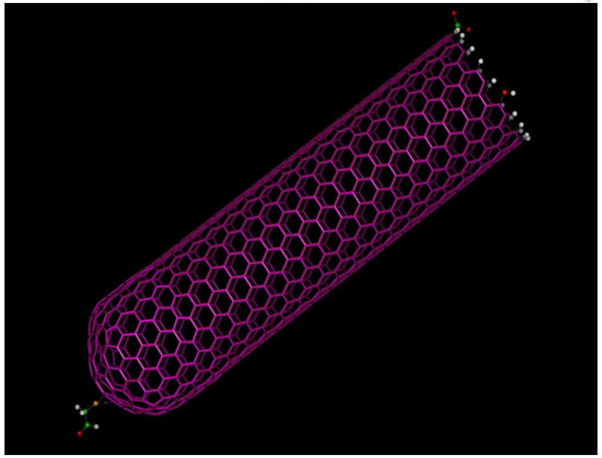
"There's plenty of room at the bottom!"

Richard Phillips FEYNMAN, 1959

- Materials behave differently when structured at the nm scale than they do in bulk.
- Technologies now exist that allow engineering of materials on the nanometer scale.
- Nanostructured materials are useful now, and will be phenomenally more so in the near future.
- Fundamental overlap between physics, chemistry, biology.
- Current situation may be similar to that of electronics in ~ 1955.

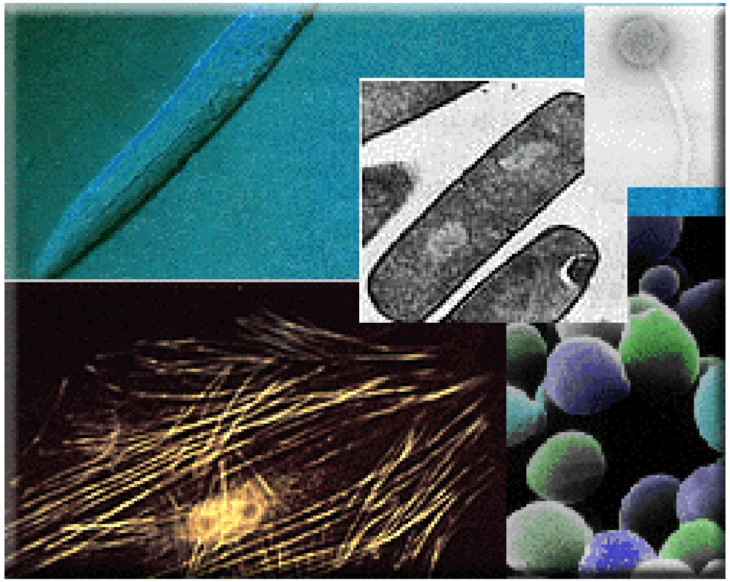
Nanostructure: a piece of material with at least one dimension less than 100 nm in extent.

What is Nanotechnology?



• Nanotechnology is the study, design, creation, synthesis, manipulation, control and application of functional materials, devices, and systems through control of matter and energy at the nanometer scale (1–100 nanometers, one nanometer being equal to 1 × 10–9 of a meter).

• Exploitation of novel phenomena, including the properties of matter, energy, and information at the molecular, atomic, and sub atomic levels.



• Creating and using structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.

Nanotechnology

– ***novel phenomena, properties and functions at nanoscale,***
which are nonscalable outside of the nm domain

– ***the ability to measure / control / manipulate matter at the nanoscale***
in order to change those properties and functions

– ***integration along length scales, and fields of application***

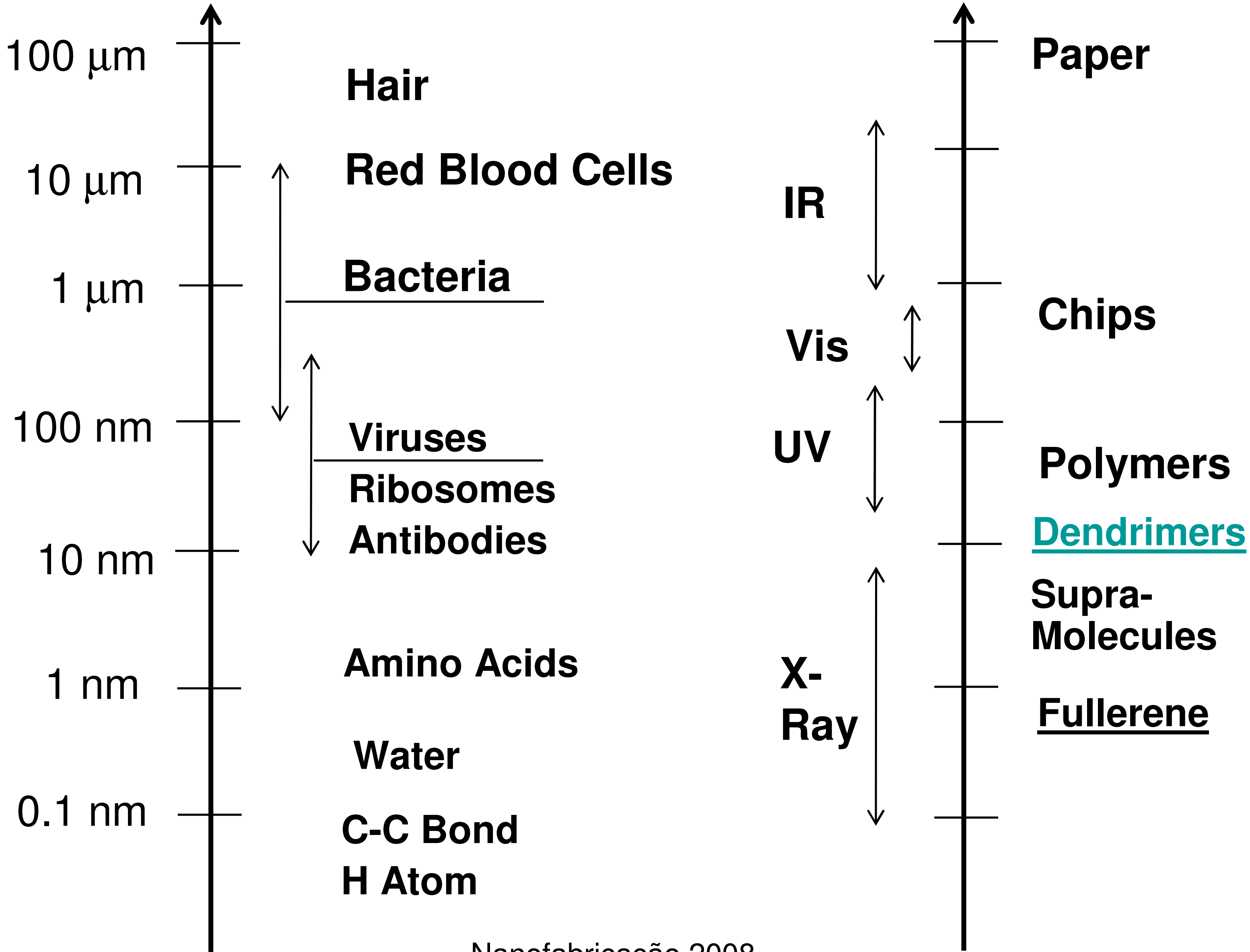
Orders of Scale

- Giga – billion, 10 e9
- Mega – million, 10 e6
- Kilo – thousand, 10 e3
- Milli – 10 e^{-3}
- Micro – referring to small, also 10 e^{-6}
- Nano – 10 e^{-9}
- Pico – 10 e^{-12}
- Femto – 10 e^{-15}

OBS:

- *"Macro" – referring to big or visible*
- *"Meso" – intermediate level(between micro-mili)*

Length Scale from 0.1 nm to 100 micron



Nanoscale Dimensions

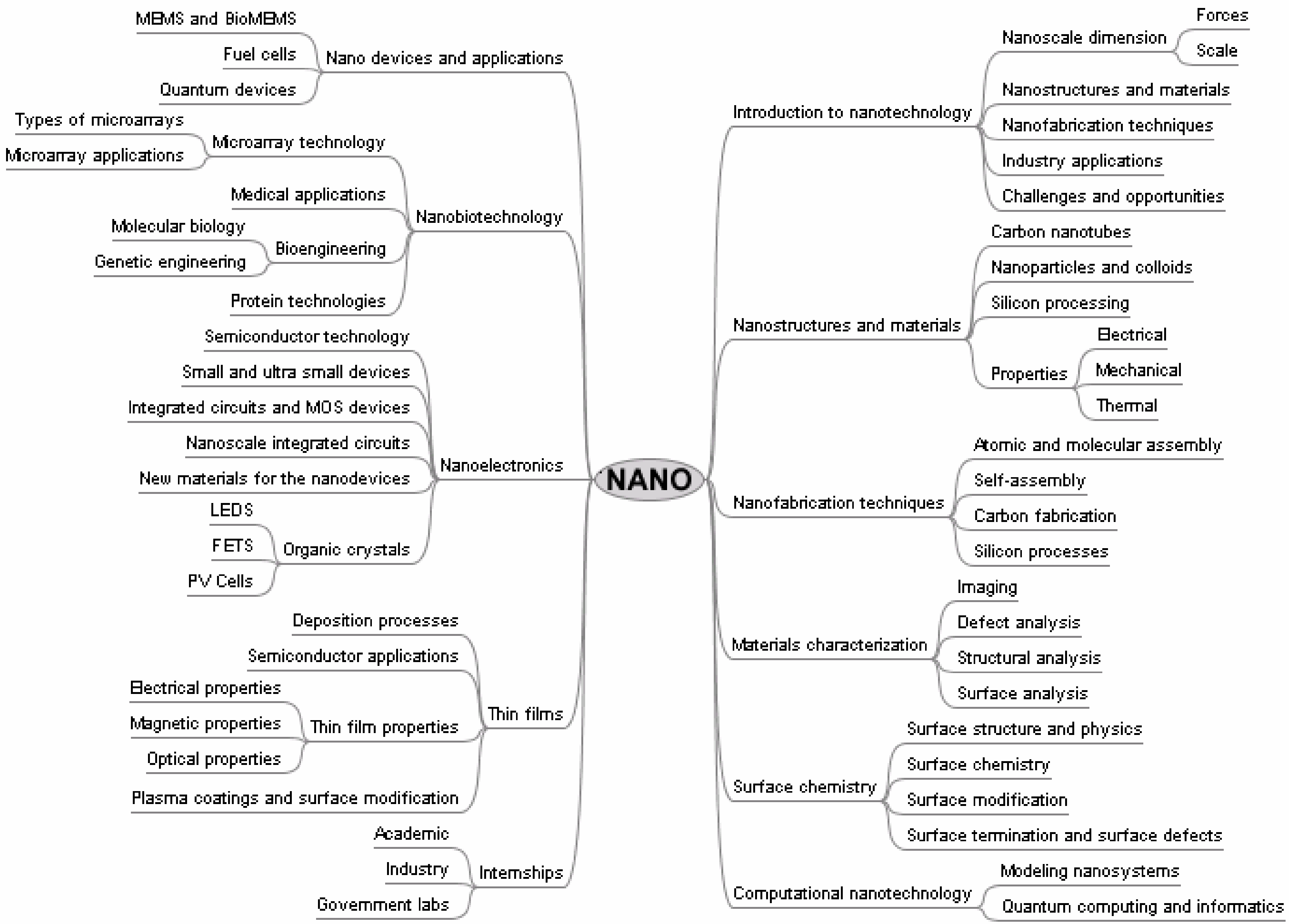
- Matter
- Energy
- Information
- Forces
- Quantum states
- Time

Nanotechnology touches the 'inner universe'

- ***Quantum scale*** dimension
  - Small ***things***
  - Short ***times***
  - Small ***numbers***
  - Low ***probabilities***
- Things happen ***differently at nanoscale***

A pesquisa e o desenvolvimento em dimensões abaixo de 1 μm, até se aproximar das escalas moleculares e atômicas (nm e Å), levaram ao surgimento de novos campos de estudo denominados Nanociências, Nanotecnologia e Nanoengenharia, em analogia às áreas primitivas associadas.

Estes campos encontram-se em plena emergência e visam o conhecimento e o domínio dos fenômenos característicos, o desenvolvimento de técnicas de fabricação de estruturas nessas escalas (nanofabricação) e o projeto de novos materiais com novas propriedades (materiais nanoestruturados).


NANO
Nano devices and applications
MEMS and BioMEMS
Fuel cells
Quantum devices
Nanobiotechnology
Microarray technology
Types of microarrays
Microarray applications
Medical applications
Bioengineering
Molecular biology
Genetic engineering
Protein technologies
Nanoelectronics
Semiconductor technology
Small and ultra small devices
Integrated circuits and MOS devices
Nanoscale integrated circuits
New materials for the nanodevices
Organic crystals
LEDS
FETS
PV Cells
Thin films
Deposition processes
Semiconductor applications
Thin film properties
Electrical properties
Magnetic properties
Optical properties
Plasma coatings and surface modification
Internships
Academic
Industry
Government labs
Introduction to nanotechnology
Nanoscale dimension
Forces
Scale
Nanostructures and materials
Nanofabrication techniques
Industry applications
Challenges and opportunities
Nanostructures and materials
Carbon nanotubes
Nanoparticles and colloids
Silicon processing
Properties
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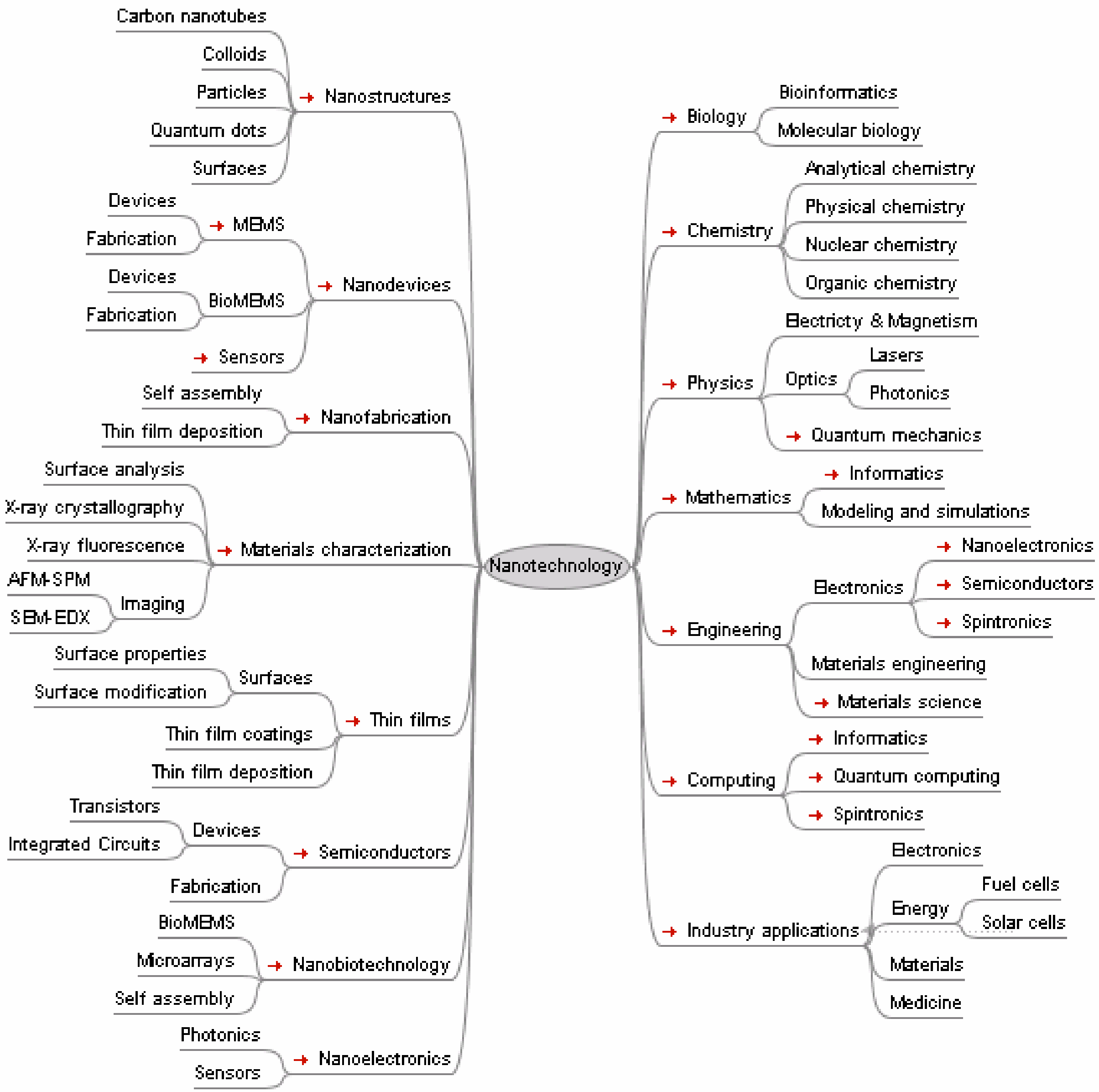
Nanofabrication techniques
Atomic and molecular assembly
Self-assembly
Carbon fabrication
Silicon processes
Materials characterization
Imaging
Defect analysis
Structural analysis
Surface analysis
Surface chemistry
Surface structure and physics
Surface chemistry
Surface modification
Surface termination and surface defects
Computational nanotechnology
Modeling nanosystems
Quantum computing and informatics


Nanotechnology
Nanostructures
Carbon nanotubes
Colloids
Particles
Quantum dots
Surfaces
Nanodevices
MEMS
Devices
Fabrication
BioMEMS
Devices
Fabrication
Sensors
Nanofabrication
Self assembly
Thin film deposition
Materials characterization
Surface analysis
X-ray crystallography
X-ray fluorescence
Imaging
AFM-SPM
SEM-EDX
Thin films
Surfaces
Surface properties
Surface modification
Thin film coatings
Thin film deposition
Semiconductors
Devices
Transistors
Integrated Circuits
Fabrication
Nanobiotechnology
BioMEMS
Microarrays
Self assembly
Nanoelectronics
Photonics
Sensors
Biology
Bioinformatics
Molecular biology
Chemistry
Analytical chemistry
Physical chemistry
Nuclear chemistry
Organic chemistry
Physics
Electricty & Magnetism
Optics
Lasers
Photonics
Quantum mechanics
Mathematics
Informatics
Modeling and simulations
Engineering
Electronics
Nanoelectronics
Semiconductors
Spintronics
Materials engineering
Materials science
Computing
Informatics
Quantum computing
Spintronics
Industry applications
Electronics
Energy
Fuel cells
Solar cells
Materials
Medicine

Revolução para a humanidade, devido à possibilidade de organização sistemática e manipulação da matéria em escala nanométrica e mesmo atômica.

Em muitos casos os dispositivos, estruturas e sistemas são bem maiores, porém suas propriedades e as técnicas utilizadas para fabricá-los envolvem conceitos e métodos baseados na escala nanométrica.

O próprio embasamento teórico para explicar certos fenômenos pode requerer readequações quando se trata de escalas “nano”.

Muitos materiais quando sofrem redução abaixo de aproximadamente 100 nm em uma ou mais de suas dimensões, começam a exibir características diferentes por vezes explicadas pela mec.quântica.

Certos materiais chegam p.ex. a se tornarem mais ou menos condutores de corrente elétrica, ou de calor, possuírem propriedades mecânicas diferentes (dureza, módulo de elasticidade) ou até mesmo passarem a ser ferromagnéticos, enquanto normalmente não o seriam

A engenharia de materiais através das técnicas de nanotecnologia adequadas e do conhecimento correspondente advindo da pesquisa em nanociência, possibilita projetar sua estrutura próximo à escala atômica, influenciando diretamente, p.ex., o comportamento dos elétrons no interior da matéria, os quais, por possuirem um caráter também ondulatório, se mostram sensíveis à geometria nanoscópica do meio.

Desta forma se torna possível alterar as propriedades fundamentais de um material, sem alterar sua composição química.

Os componentes em nanoescala possuem alta razão área-volume, fazendo deles ideais para uso em materiais compostos, sistemas reagentes, transporte intracorpóreo de medicamentos e armazenamento de energia. O tamanho finito das entidades materiais comparados com a escala molecular, determina um aumento da importância relativa da tensão superficial e dos efeitos eletromagnéticos locais, tornando os materiais nanoestruturados mais duros e menos quebradiços.

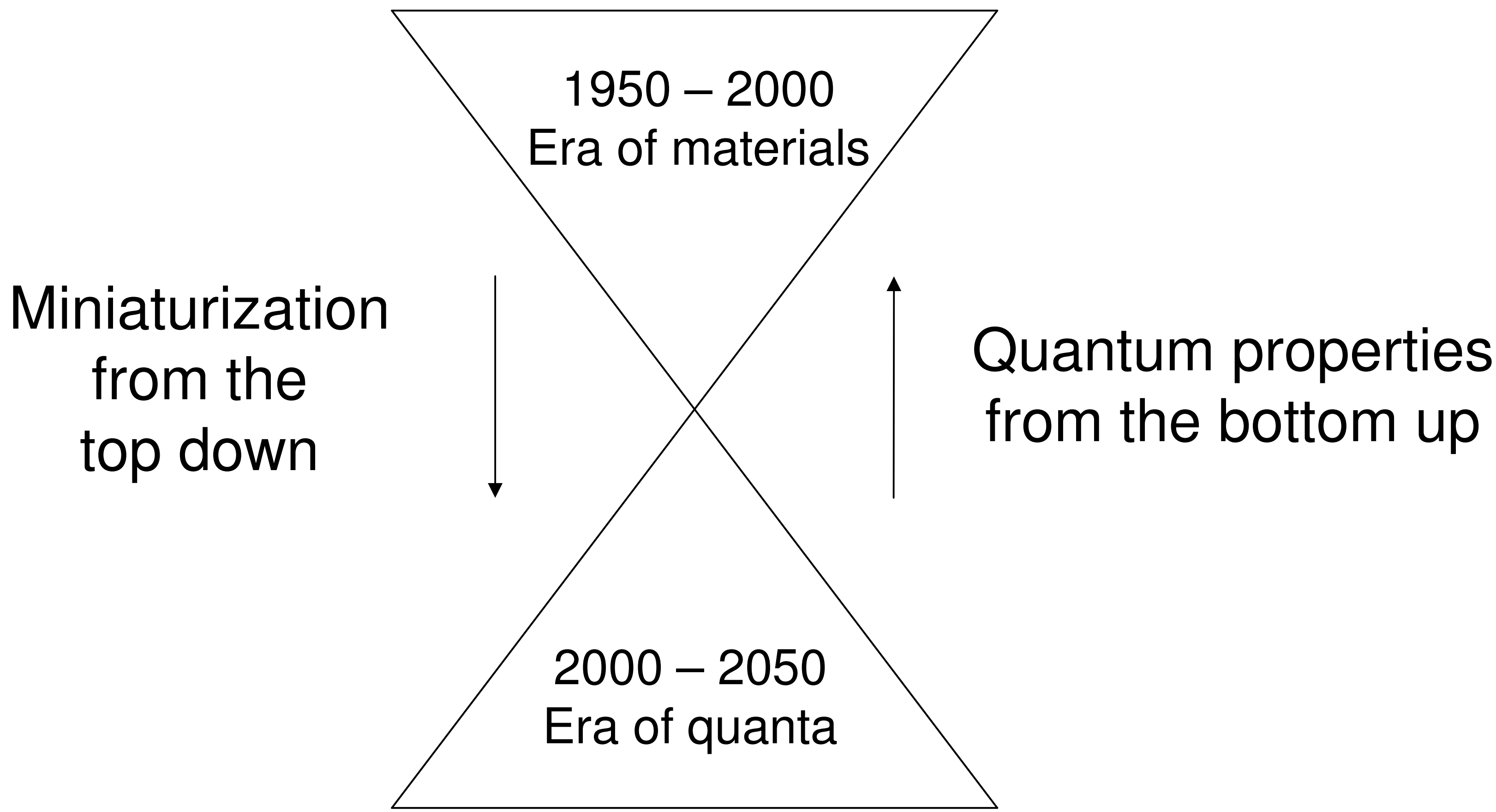
As escalas de comprimento de onda de interação de vários fenômenos ondulatórios se tornam comparáveis ao tamanho da entidade material, tornando os materiais adequados para várias aplicações, como p.ex. as optoeletrônicas e nanomagnéticas.

A nanoestruturação de superfícies visando criar sítios com propriedades magnéticas específicas, seja localmente ou se estendendo a escalas mais amplas, como centímetros ou milímetros >> objetiva desde a fabricação de mídias de gravação magnéticas com cada vez maior densidade de informação (bits/cm2) e melhor qualidade de resposta (tempo, estabilidade, nível de ruído etc.) >> até a fabricação de sensores baseados em efeitos magnéticos peculiares como os magnetoópticos e os vários tipos de magneto-resistência e magnetoimpedância // desenvolvimento da spintrônica

exemplos de fenômenos e aplicações tecnológicas em nanoescala :

- **magneto-resistência gigante em materiais nanocristalinos;**
- **nanocamadas com barreiras seletivas ópticas;**
- **nanocamadas de revestimentos duros e extra-duros;**
- **dispersões de nanopartículas com propriedades optoeletrônicas;**
- **detectores químicos e biológicos nanoscópicos;**
- **sistemas ultraminiaturizados de transporte intracorporal de medicamentos;**
- **nova geração de laseres;**
- **catalisadores nanoestruturados;**
- **sistemas em chip único com cada vez maior nível de integração;**
- **produtos baseados em nanotubos de carbono;**
- **materiais reforçados por nanopartículas;**
- **novos isolamentos térmicos;**
- **sistemas de nanoinjeção de tintas;**
- **novos filmes finos e ultrafinos para armazenamento de informações magnéticas, ópticas, piezoelétricas etc.;**
- **dispositivos moleculares;**
- **ferramentas nanoestruturadas de alta dureza.**
- **etc.**

Nanoscale Paradigm



Concept by Hilary Lackritz

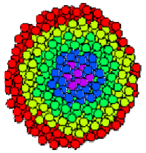
How Nanotech Impacts Properties of Materials

Nanotechnology enables discrete control of desired materials properties:

- **Mechanical**
  - Dictated by particle size (Griffith criteria), morphology and strength of interfaces (chemistry and roughness)
- **Thermal**
  - Emissivity influenced by particle size and enhanced surface area/roughness
  - Thermal conductivity controlled by particle size (phonon coupling and quantum effects) and nano-scale voids
- **Electrical**
  - Nano structure and defects influence conductivity and bandgap energy (conductivity, current density, thermoelectric effects)
  - High aspect ratios enhance field emission and percolation threshold
- **Optical**
  - Transparency and color dominated by size effects
  - Photonic bandcap controlled by size ($\lambda/10$) and nanostructure

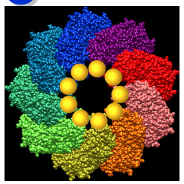
Industrial Prototyping and Nanotechnology Commercialization

FOUR GENERATIONS



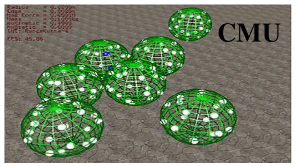
1st: Passive nanostructures (1st generation products)
Example: coatings, nanoparticles, nanostructured metals, polymers, ceramics

~ 2000



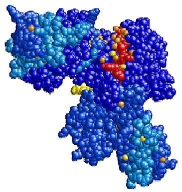
2nd: Active nanostructures
Example: 3D transistors, amplifiers, targeted drugs, actuators, adaptive structures

~ 2005



3rd: Systems of nanosystems
Example: guided assembling; 3D networking and new hierarchical architectures, robotics, evolutionary

~ 2010



4th: Molecular nanosystems
Example: molecular devices 'by design', atomic design, emerging functions

~ 2015-2020

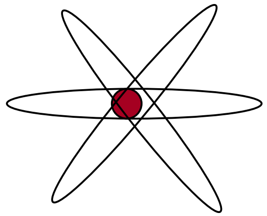
New R&D Challenges

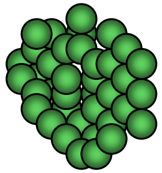
AIChE Journal, 2004, Vol. 50 (5), M. Roco

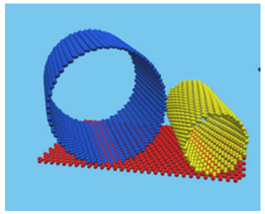
Atomic Properties

Bulk Properties

Discrete States







Coninuum of states (bands)

Elastic moduli etc...

Example: a copper atom has no Young's modulus or conductivity, but a 1g chuck of copper does. What about a 1000 atom cluster of copper?

Hypothesis:

- Electronic
- Mechanical
- Frictional
- Optical
- Magnetic

Properties depend on

- Size of object
- Specific Geometry of object
- Specific environment of object

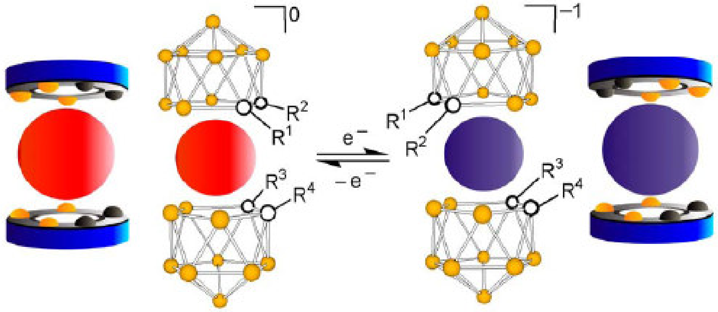
MEMS e NEMS (micro/nanoelectromechanical systems).
sistemas eletromecânicos micro e nanométricos de importância p.ex. na indústria aeroespacial >> a miniaturização de tais componentes possibilitará p.ex. diminuição dos custos de lançamento (peso total das espaçonaves e satélites espaciais). Ex: efeitos magnéticos em dimensões reduzidas >> micro/nanomotores, micro/nanoengrenagens de baixo atrito, micro/nanossensores, dispositivos de guiamento inercial, de visão adaptativa, de ressonância nanomecânica e outros micro/nanoinstrumentos. Baixa massa, baixo consumo de potência (são controlados por baixíssimos níveis de tensão-corrente), associados a novas capacidades e propriedades características das dimensões ultra-reduzidas >> particularmente os dispositivos atuados eletromagneticamente têm se mostrado os mais estáveis mecanicamente.

Nano & Chemistry

- Precision ***placement*** (yes)
- Molecule by ***molecule*** (maybe)
- Working with moles (a lot)
- ***Surface*** chemistry (always)
- ***Particles*** and colloids (if small enough)
- Chemists ***guide*** atoms and molecules to particular ***places*** (with help from ***nature***)

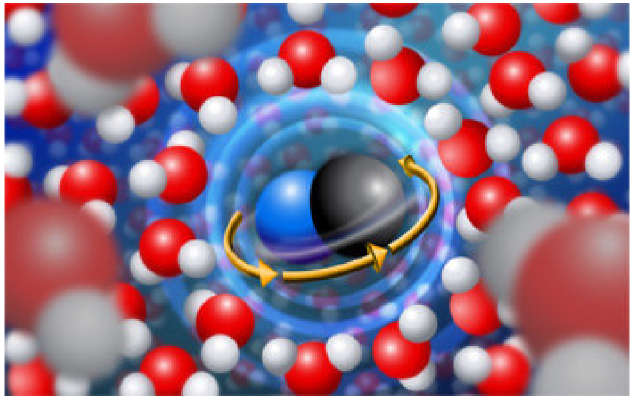
Nano & Chemistry

Making Things



- Organic and Macromolecular Chemistry (OMC)
  - Organic Dynamics
  - Organic Synthesis

- Inorganic, Bioinorganic, & Organometallic Chemistry (IBO)



Measuring and Modeling

- Analytical & Surface Chemistry (ASC)

- Physical Chemistry (PC)
  - Theoretical & Computational Chemistry
  - Experimental Physical Chemistry

NANOELECTROMAGNETISM

NANOSTRUCTURES:

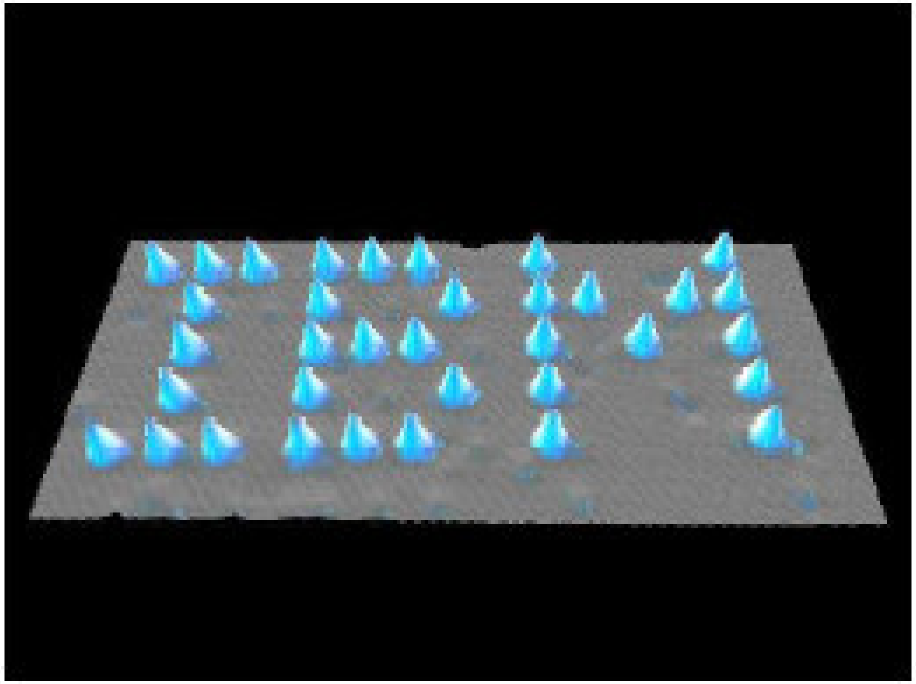
Quantum wires and quantum dots, fullerenes, nanotubes, sculptured thin films, atomic clusters, nanocrystallites, *etc.*

- **Spatial inhomogeneity**
- **Quantization of the charge carrier motion**

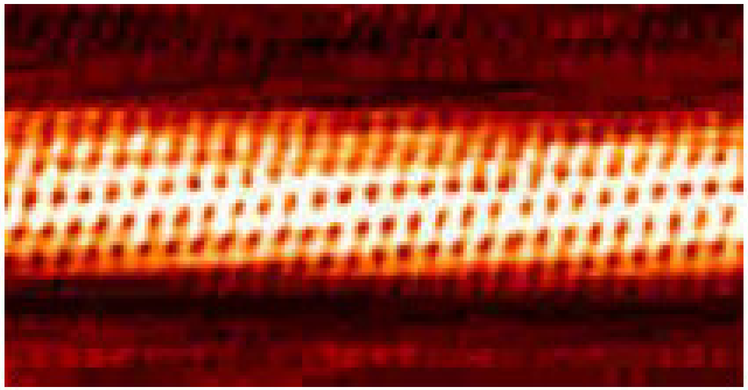
complex geometry
complex electronics

Tools: scanning tunneling microscopy

- STM (1986) allows imaging of surface topography of conductors with atomic resolution.
- Surface manipulation also possible.
- May also be used as atomic-resolution probe of local electronic states.



Images from Eigler at IBM.

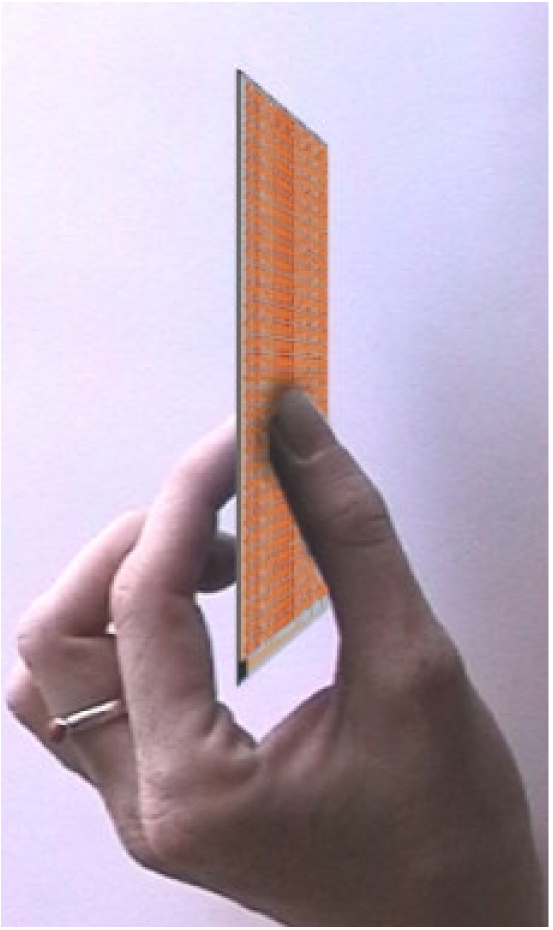


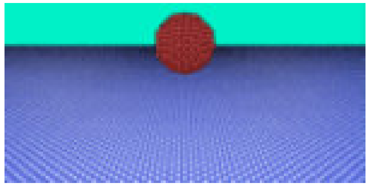
Images from Cees Dekker.

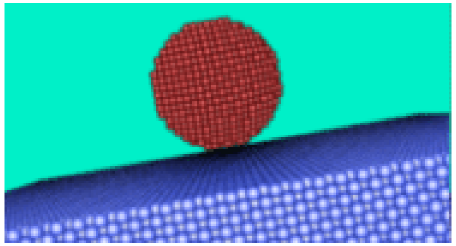
Thin Film Deposition

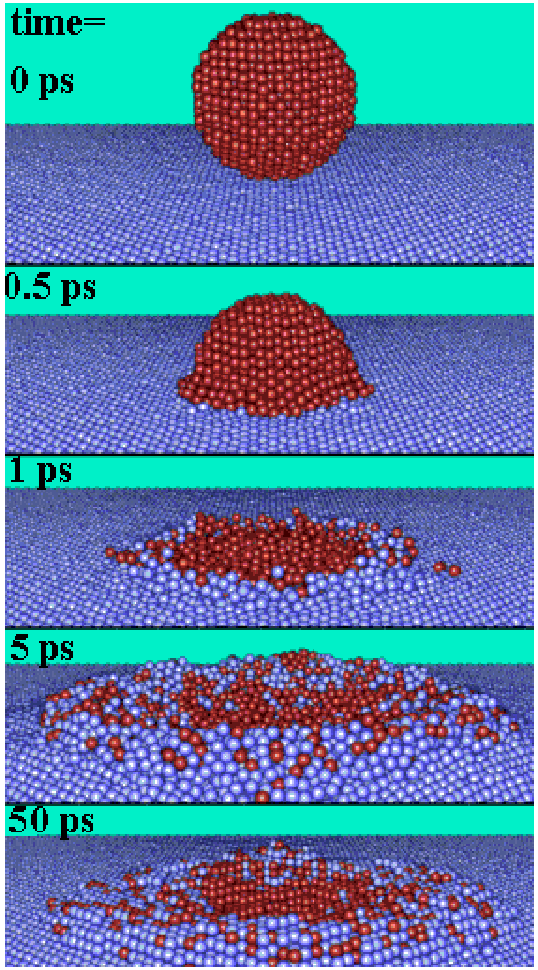
- Layer by layer ***deposition***
  - Most thin film layers are 10 to 1000A thick
  - Deposition can occur one monolayer at a time
- Atom by atom ***nucleation***
  - Clusters of atoms influence each other
  - Ordering process can occur very quickly
- Tailored ***properties*** based on ***process***
  - Optical, electrical, and magnetic
  - Interfacial chemistry can be critical

Thin Film Deposition









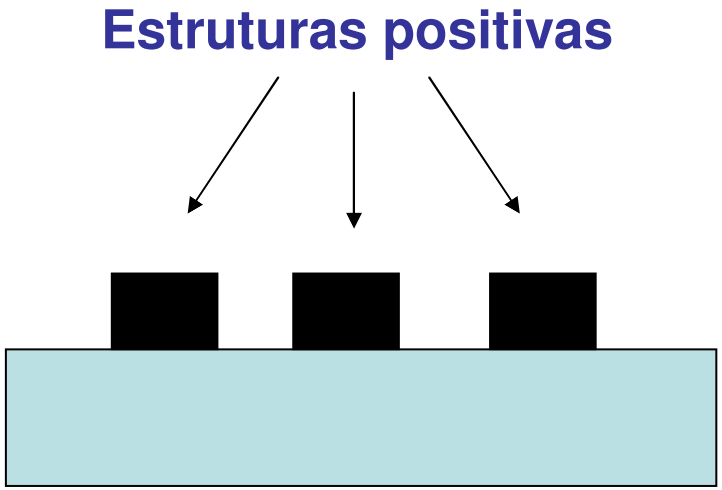
http://www.fmf.uni-freiburg.de/projekte/pg_cluster/projekt_cluster/eci/eci_sim_e.html

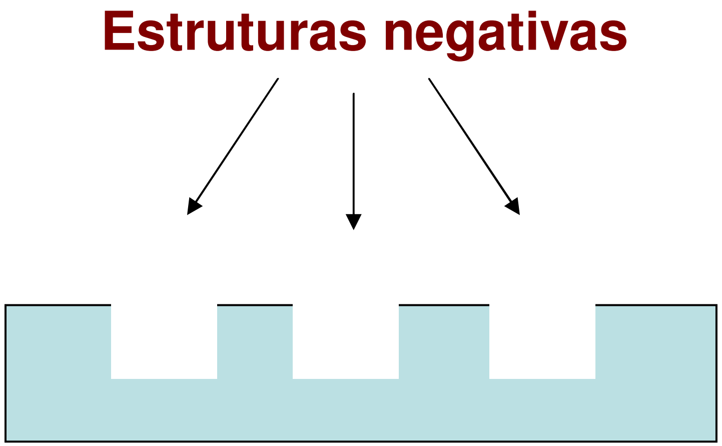
NANOESTRUTURAS INDIVIDUAIS

As estruturas individuais podem ser formadas por uma ou mais camadas de materiais cujas propriedades (p.ex.magnéticas) variam de camada a camada de acordo com o comportamento desejado . Tais materiais podem ainda ser condutores, semicondutores ou isolantes, p.ex., quando se deseja explorar efeitos como o tunelamento.

Sua fabricação sobre a superfície suporte, ou substrato, pode ser executada de modo denominado "positivo", seja isoladamente ou em arranjos (arrays), como pontos (dots) de diferentes formatos (retangulares, circulares, triangulares, elipsoidais etc), diferentes organizações espaciais e razões de aspecto, ou fitas "planas" (stripes, belts), fios, anéis (rings), zigue-zagues etc. Todos estes elementos também podem ser fabricados em sua versão negativa (antidots, antistripes etc), sendo os mesmos erodidos p.ex. por meio de plasmas ou quimicamente corroídos em um filme (ou conjunto de multicamadas) matriz, geralmente através de uma máscara devidamente pré-estruturada.

SIMPLIFICADAMENTE



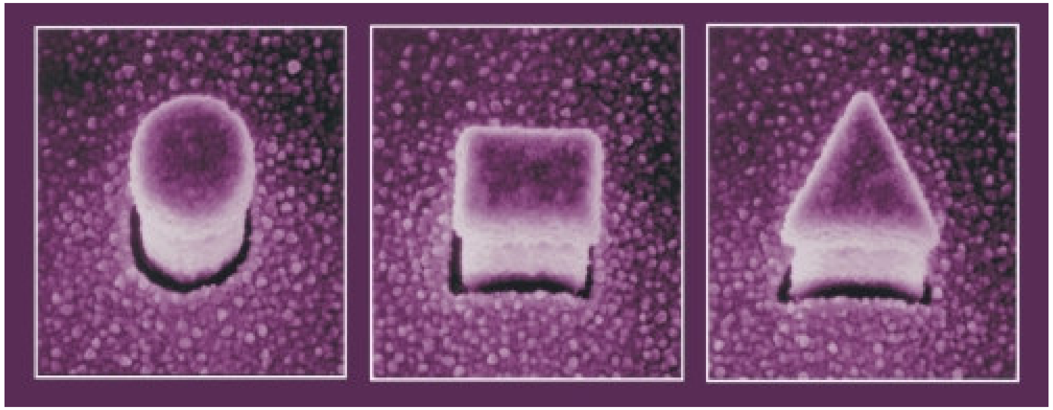


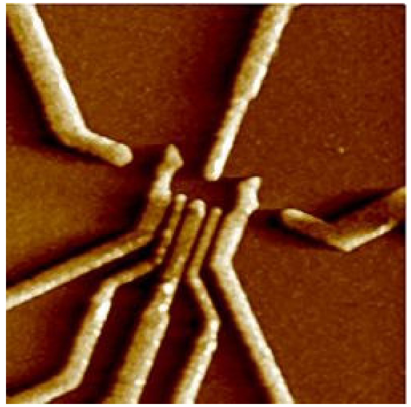
Sejam as estruturas positivas ou negativas, elas se utilizam, em alguma etapa de sua fabricação, de um processo de deposição adequado, que pode ser evaporação, sputtering, MBE (molecular beam epitaxy), CVD (chemical vapor deposition) , PECVD (Plasma-enhanced chemical vapor deposition), PLD's (pulsed laser deposition) e outros, em particular, da deposição eletroquímica (eletrodeposição), que, quando adequável, possui grandes vantagens de custo-benefício.

Quantum Dots

- Quantum ***confinement***
  - *Energy and information* ***states***
- Small atomic assemblies
- Ex: Used in solar collection devices
  - With very high quantum efficiencies
- Applications in memory storage
- Applications in ***quantum computing***

Quantum Dots





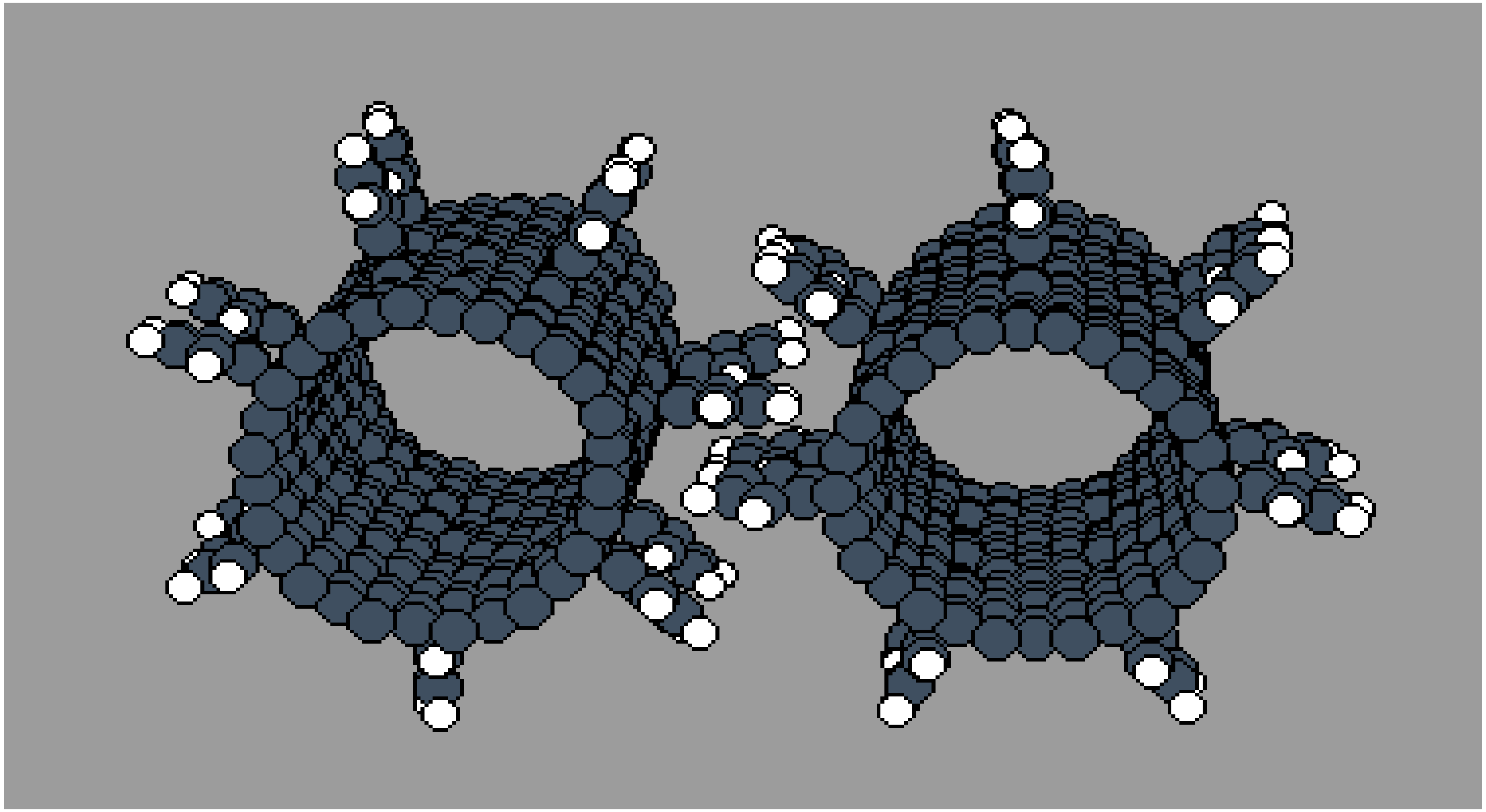
Quantum dots are small devices that contain a tiny droplet of free electrons. They are fabricated in semiconductor materials and have typical dimensions between nanometers to a few microns. The size and shape of these structures and therefore the number of electrons they contain, can be precisely controlled; a quantum dot can have anything from a single electron to a collection of several thousands. The physics of quantum dots shows many parallels with the behavior of naturally occurring quantum systems in atomic and nuclear physics. As in an atom, the energy levels in a quantum dot become quantized due to the confinement of electrons. Unlike atoms however, quantum dots can be easily connected to electrodes and are therefore excellent tools to study atomic-like properties. There is a wealth of interesting phenomena that have been measured in quantum dot structures over the past decade.

http://qt.tn.tudelft.nl/research/qdots/

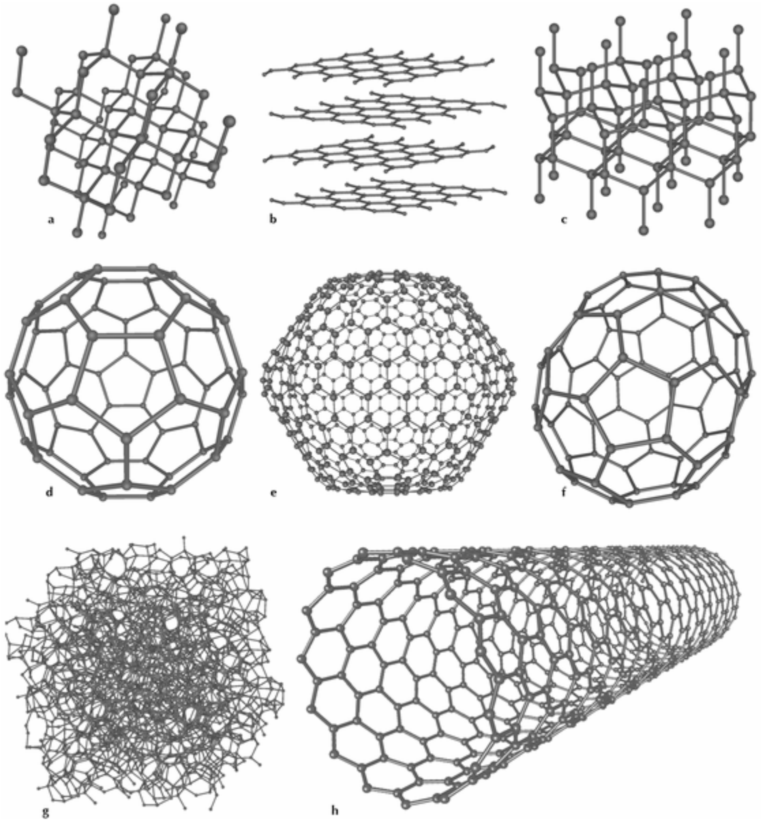
Carbon Nanotubes

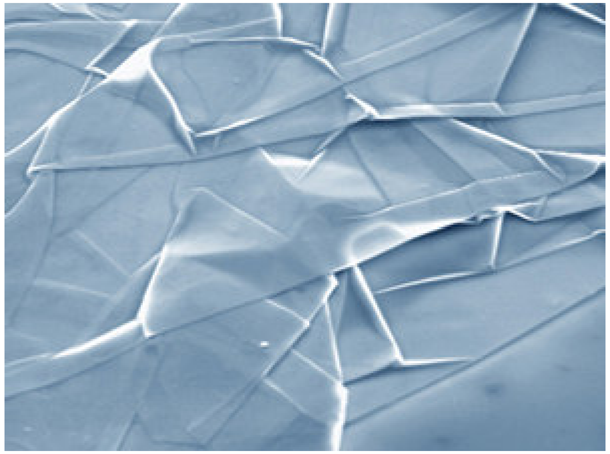
- Like graphite but all coiled up
- Typically 10 Angstroms in diameter
- Two key parameters ***control properties***
  – m/n ratio determines electrical conductivity
- SWNT and MWNT*
  – Transistors, heat sinks, hydrogen storage
- *Carbon fibers have come a long way!*

Carbon Nanotube Structures



Carbon Nanostructures

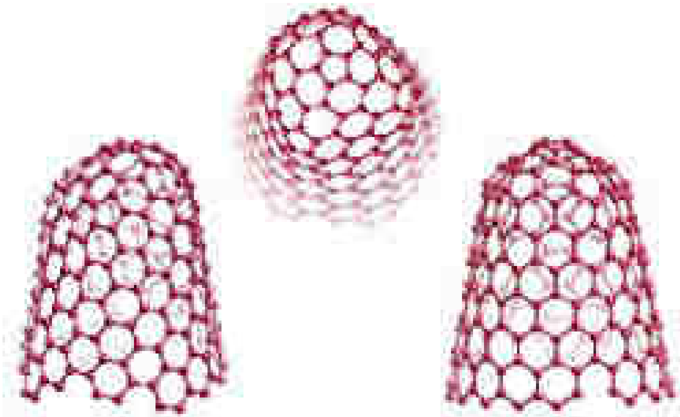


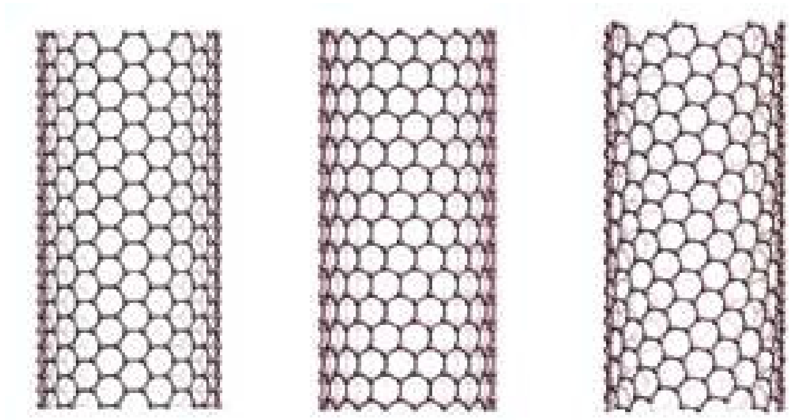


(*) **truly two-dimensional crystals**
http://www.grapheneindustries.com/?Wha
t+is+graphene%3F

- Graphite and diamond are the most widely known types of carbon structures
- However, carbon forms other interesting types of “NANO-structures”
    - These include: fullerenes, nanotubes, graphene*, nanocones

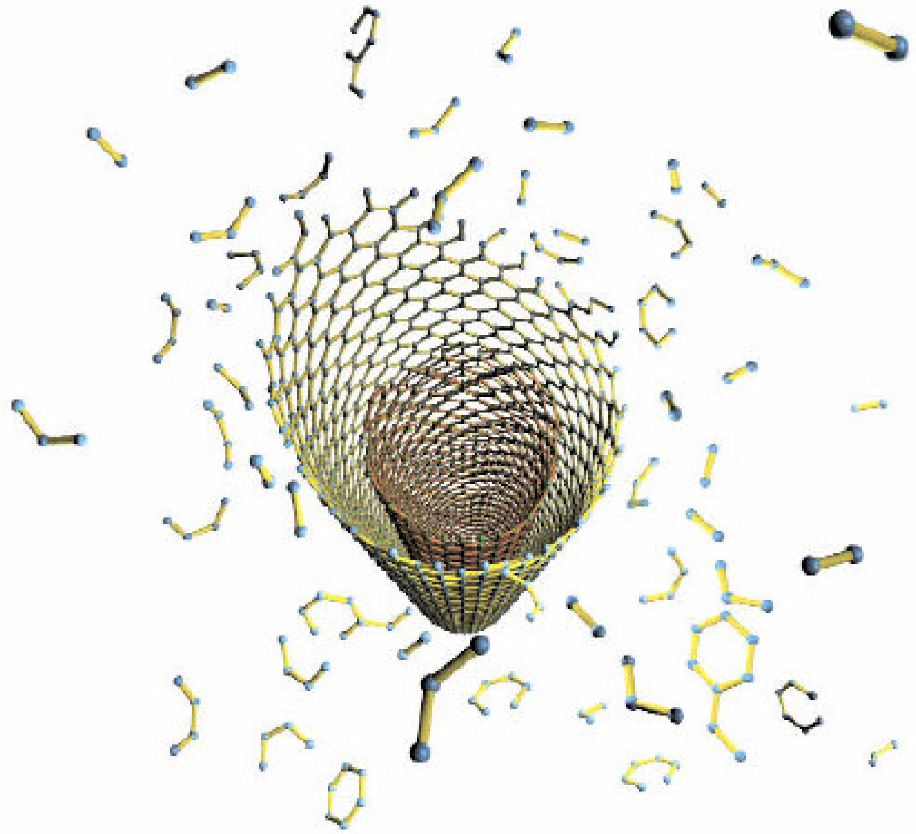
Nanotubes / Nanohorns





The electrical properties of nanotubes / nanohorns can change, depending on their molecular structure. The "armchair" type has the characteristics of a metal; the "zigzag" type has properties that change depending on the tube diameter—a third have the characteristics of a metal and the rest those of a semiconductor; the "spiral" type has the characteristics of a semiconductor.

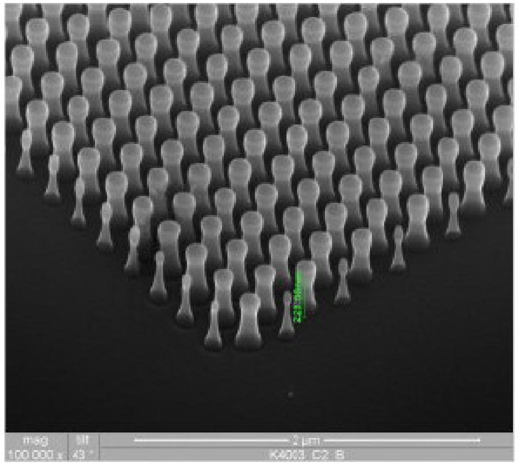
Self Assembled Nanostructures?

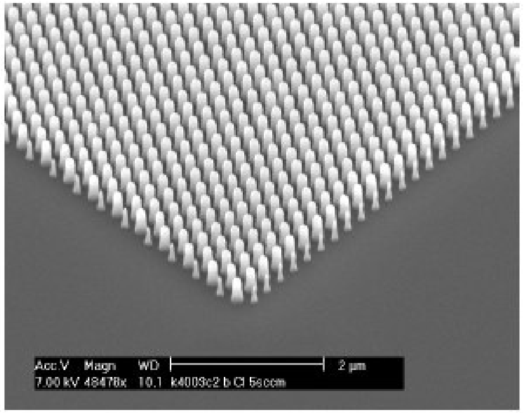


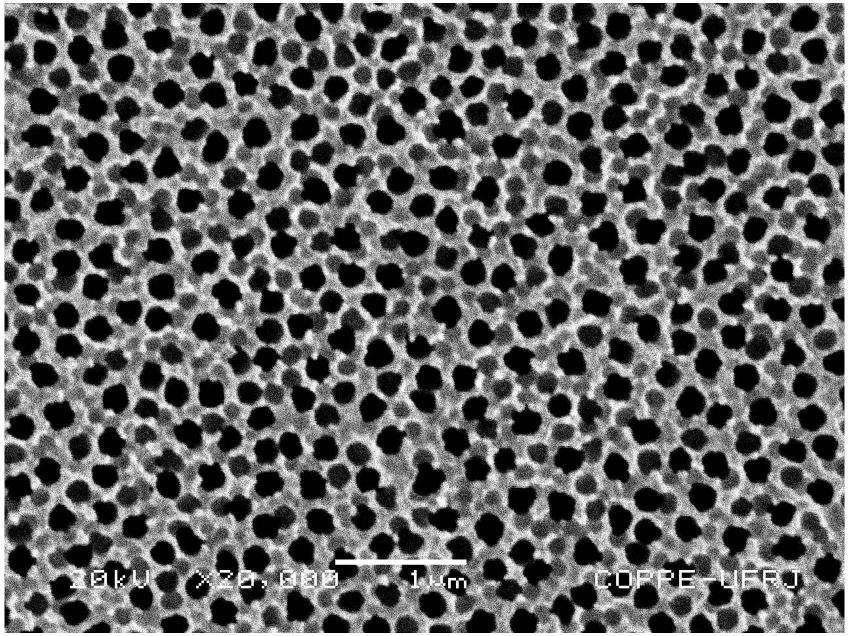
ARRANJOS ("ARRAYS")

I
- **Periódicos**
- **Ordenados**
- **Anisotrópicos**

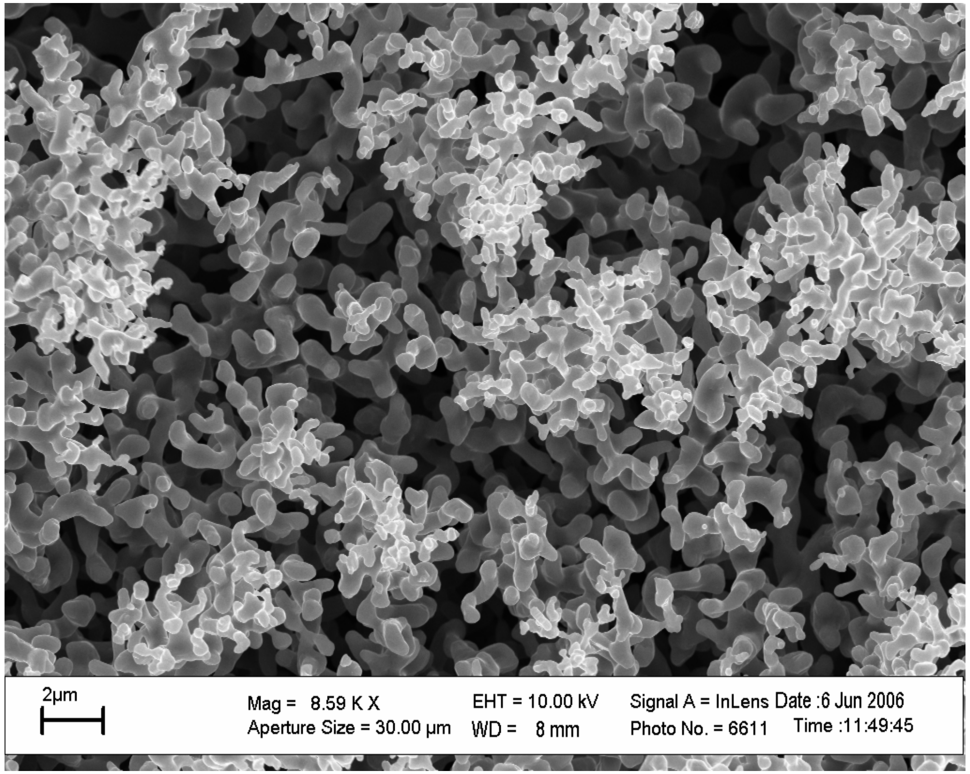
II
- **Aperiódicos**
- **Desordenados**
- **Isotrópicos**



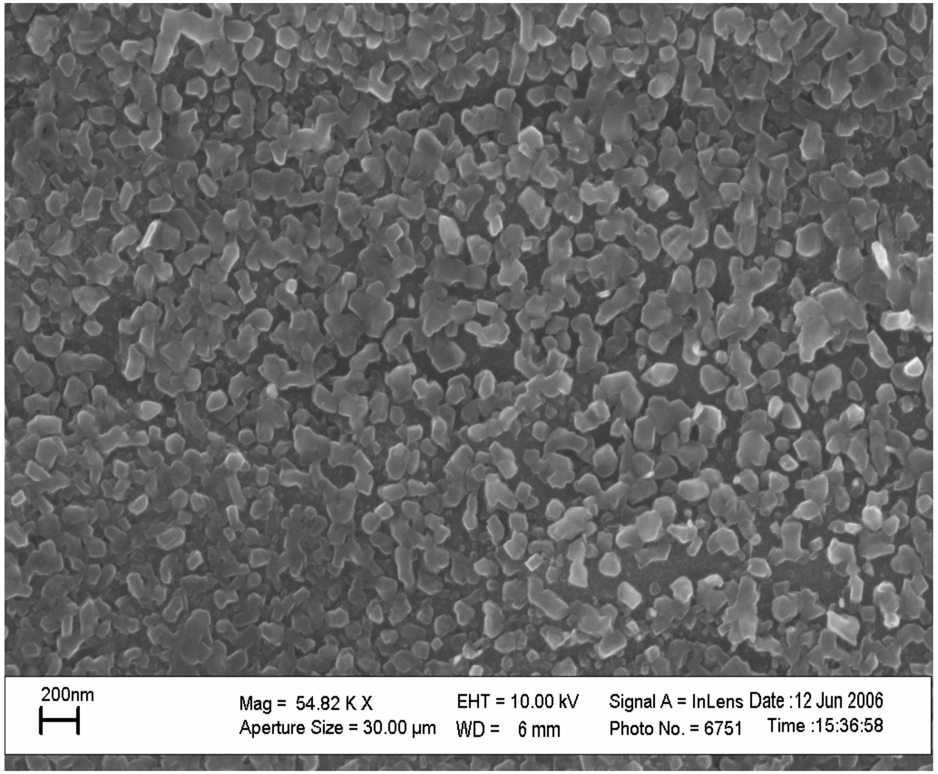




SEM Images Titanium Oxide (TiO2) Nanoparticles

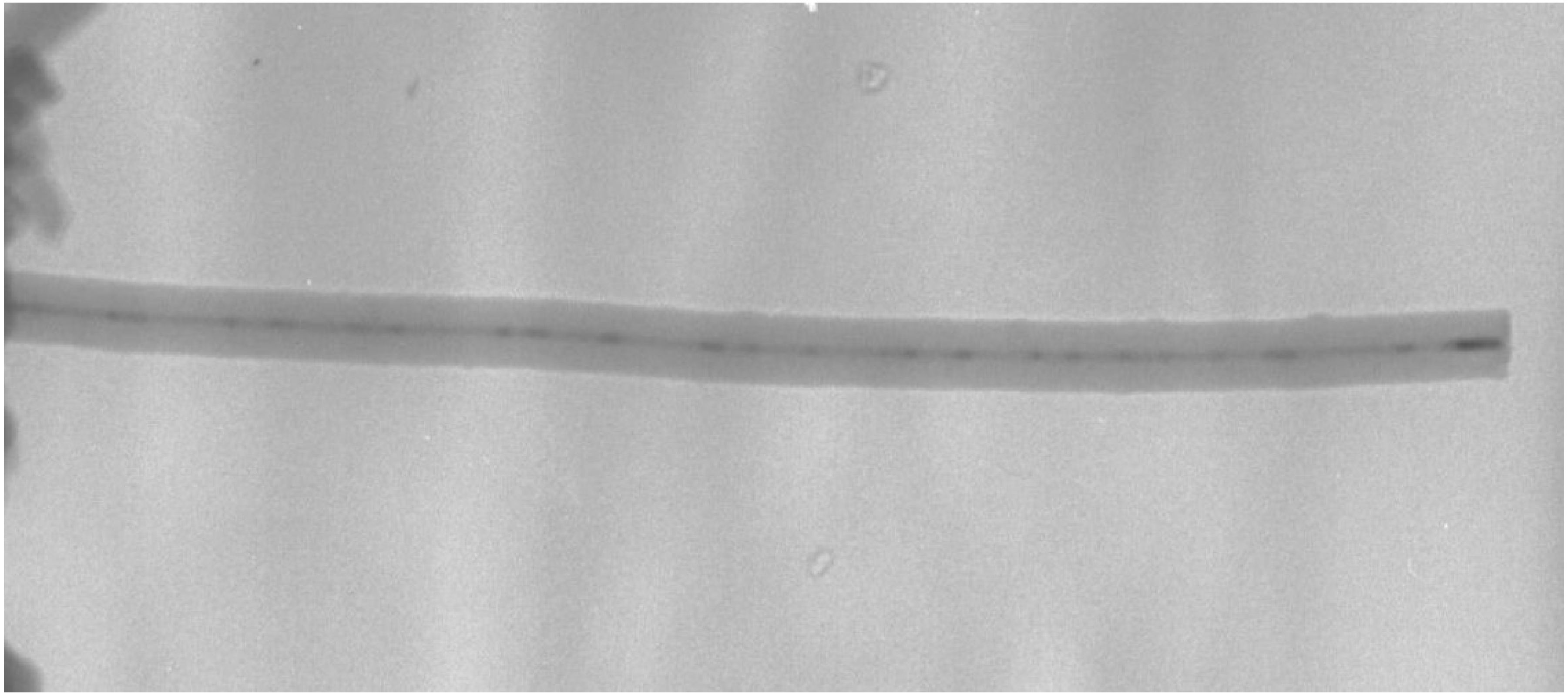


Attempt # 3



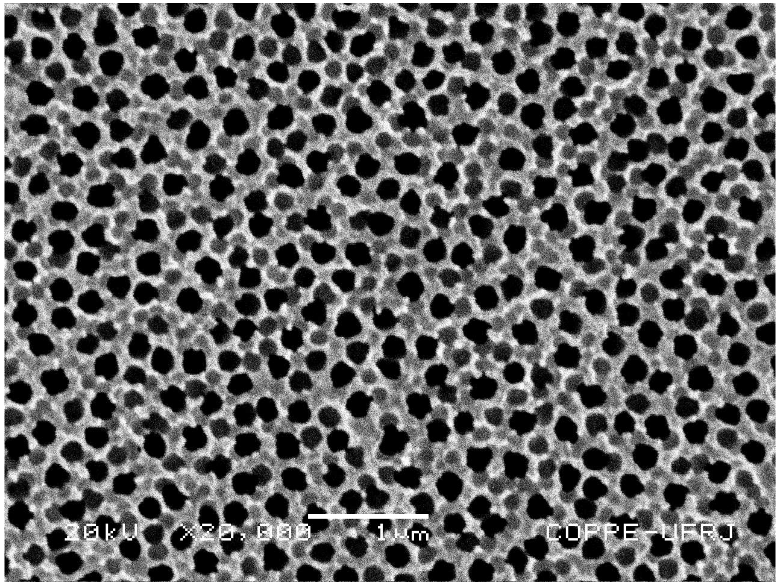
Attempt # 4

TEM Image Tin Oxide (SnO_2) Nanowires

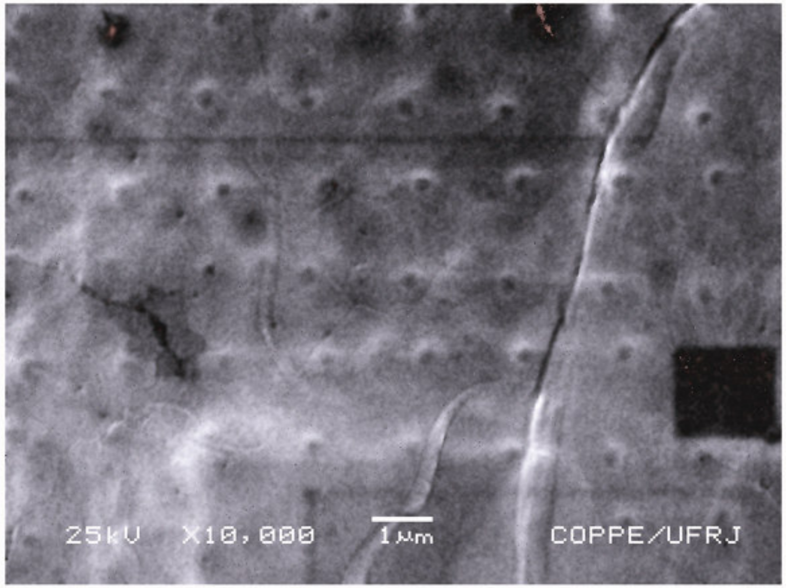


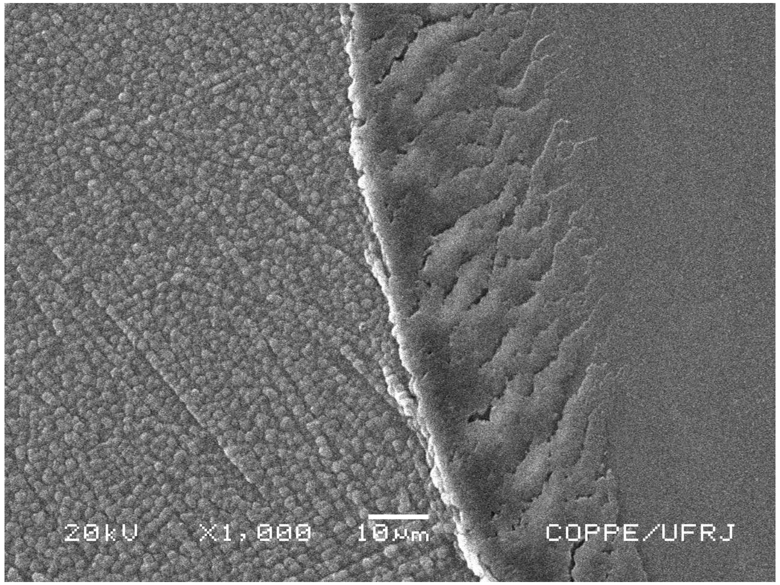
Attempt #2 - Silicon

PAM COMERCIAL

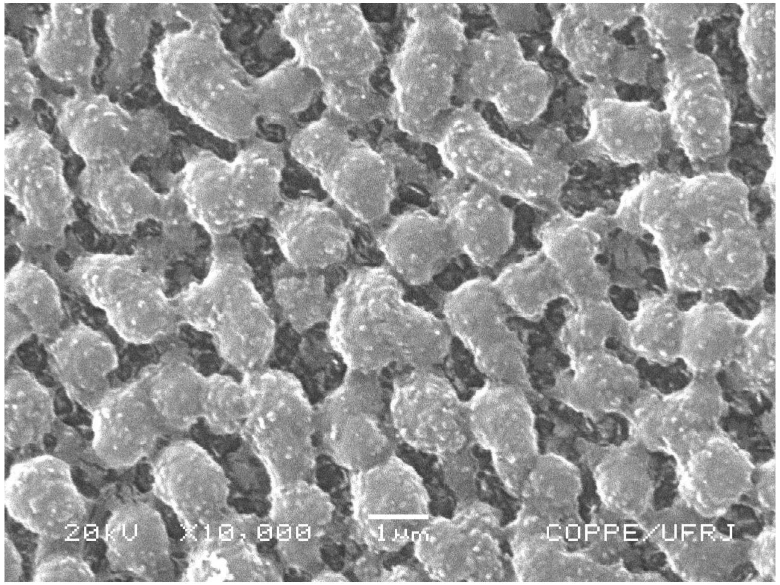


PARAFINA



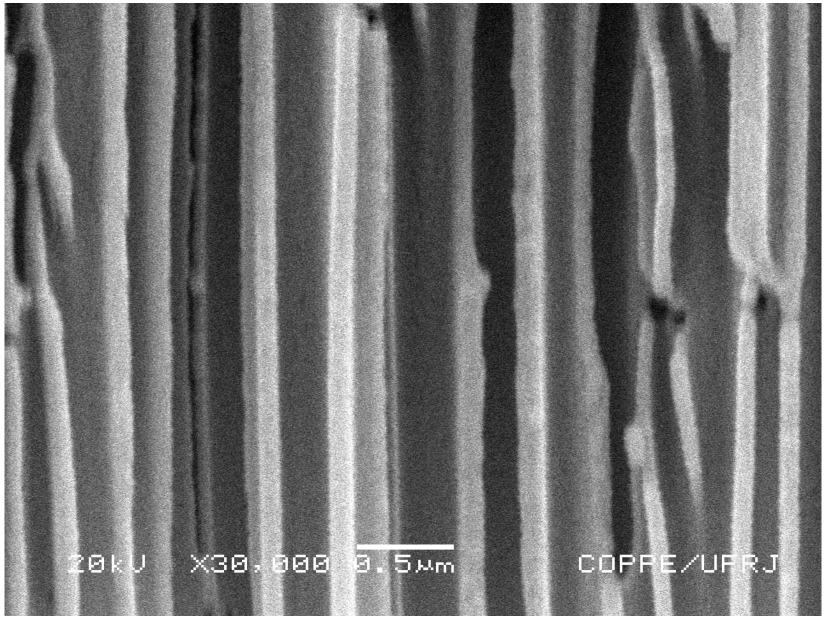


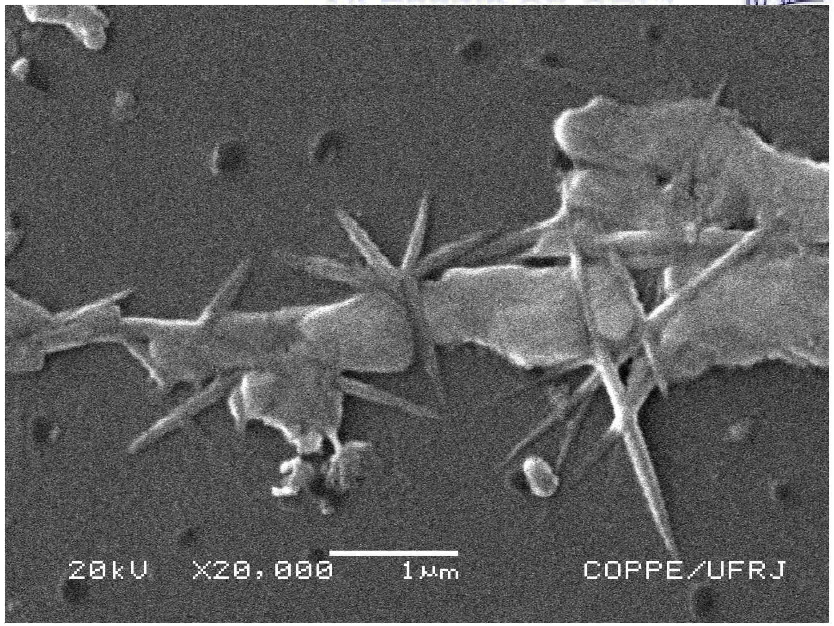
SUPERBONDER

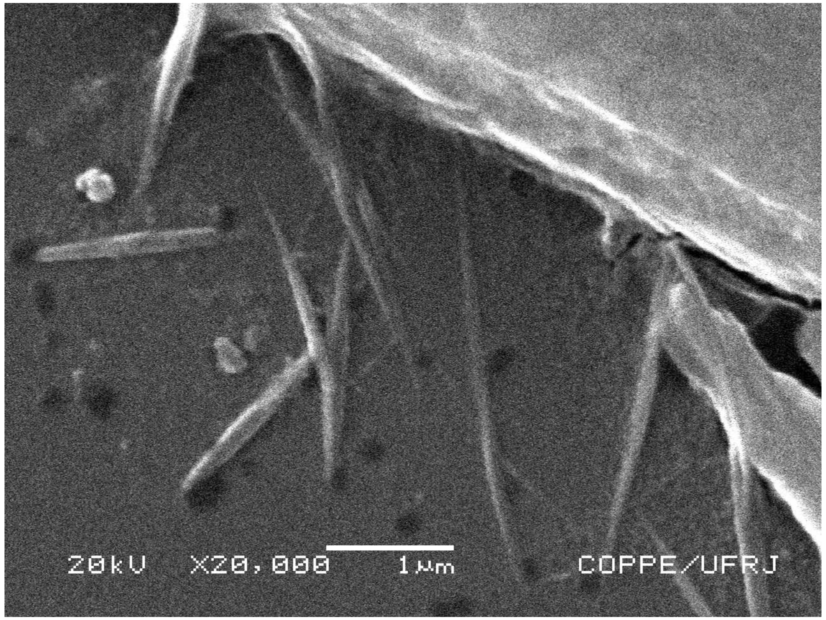


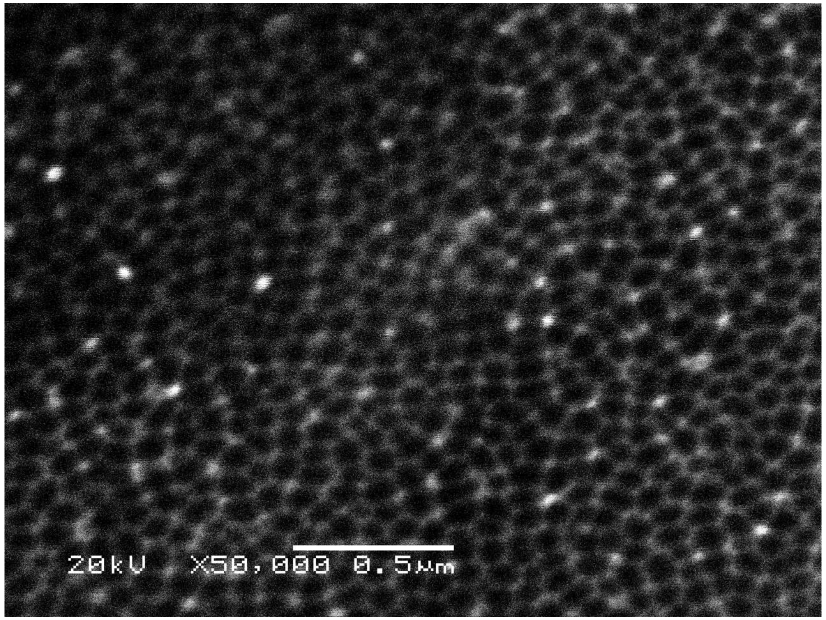
SUPERBONDER

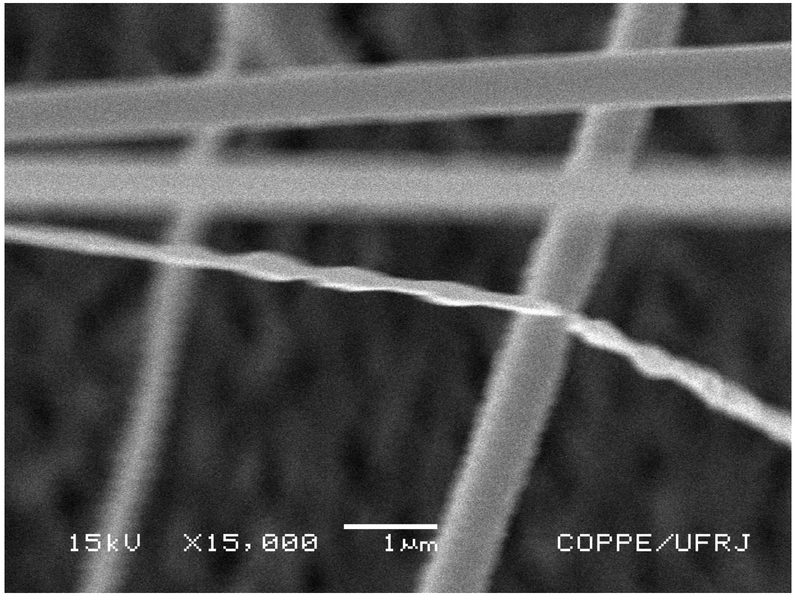
Imagens: Prof. Gomes - MEV da COPPE/UFRJ

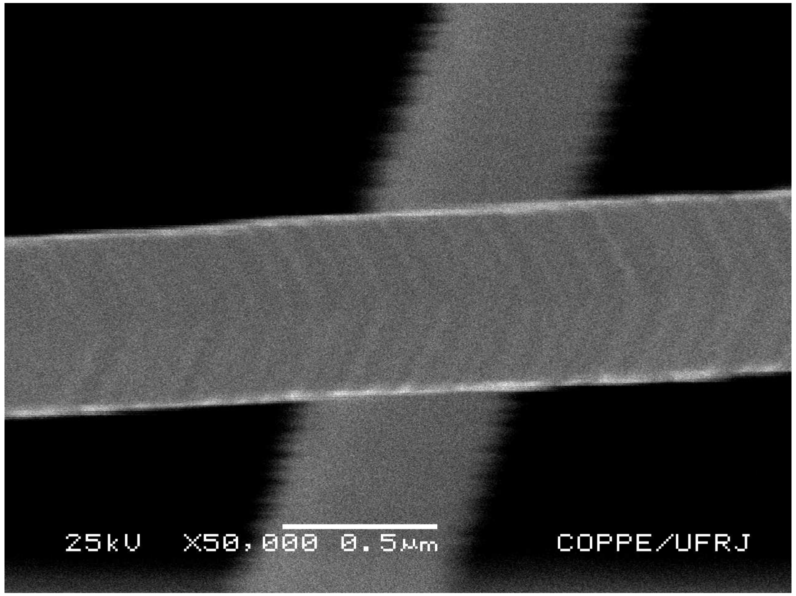

20kV X30,000 0.5µm COPPE/UFRJ

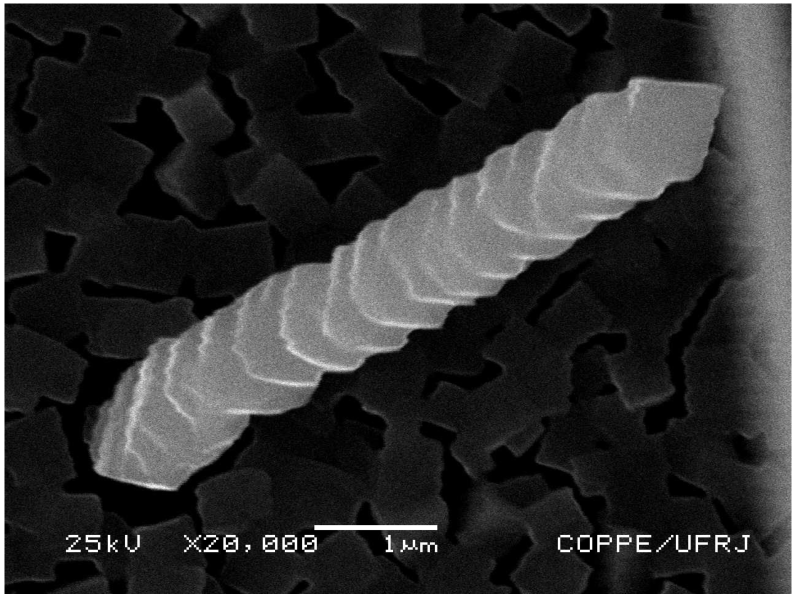

20kV X20,000 1µm COPPE/UFRJ

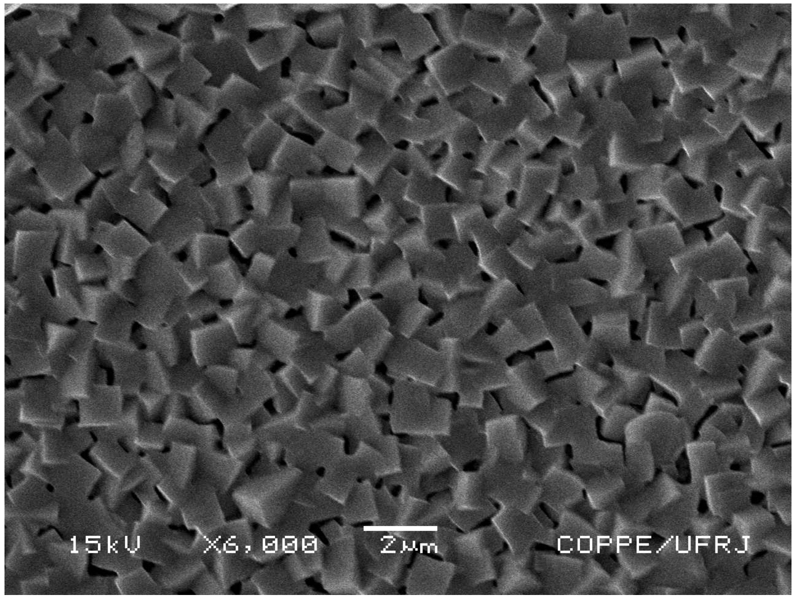

20kV X20,000 1µm COPPE/UFRJ


20kV X50,000 0.5µm


15kV X15,000 1μm COPPE/UFRJ

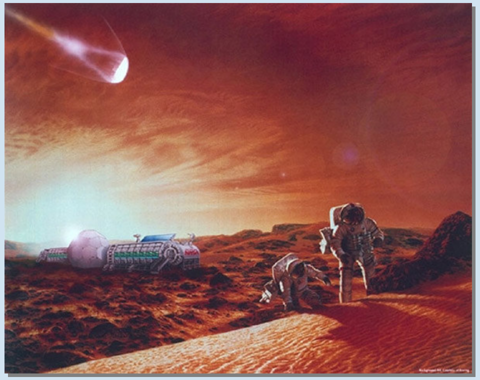

25kV X50,000 0.5μm COPPE/UFRJ


25kV X20,000 1μm COPPE/UFRJ


15kV X6,000 2μm COPPE/UFRJ

Estudo de Caso: Nanotecnologia Espacial (fonte: NASA)

Impact of Nanotechnology on Spatial Tech



- New and Powerful computing technologies
  - Onboard computing systems for future autonomous intelligent vehicles; powerful, compact, low power consumption, radiation hard
  - High performance computing (Tera- and Peta-flops)
    - processing satellite data
    - integrated space vehicle design tools
    - climate modeling

- Smart, compact devices and sensors
  - Ultimate sensitivity to analytes
  - Discrimination against varying and unknown backgrounds
  - Ultrasmall probes for harsh environments
  - Advanced miniaturization of all systems

- Microspacecraft/Micro-Nanorovers
  - "Thinking" Spacecraft with nanoelectronics/nanosensors
  - Size reduction through multifunctional, smart nanomaterials

Ten Most Significant Benefits

- Reduce vehicle structural weight by a factor of 3
- Application Tailored Multi-functional Materials
- Thermal Protection and Management
- Reliable Reconfigurable Radiation/Fault Tolerant Nano-electronics
- On-board Life Support Systems
- On-Board Human Health Management
- 30% lighter EVA Suit
- Micro-craft (< 1 kg) with functionality of current 100 kg spacecraft for science and inspection
- Ultra-Sensitive and Selective Sensing
- Modeling Fabrication Processes for Nano-to-Micro Interfaces

Nano-sensors and Instrumentation

Goals

Enable missions with nano-sensors:

- Remote sensing
  - Viewing there
- Vehicle health and performance
  - Getting there
- Geochemical and astrobiological research
  - Being there
- Manned space flight
  - Living there

Hard Problems

- Band-gap engineered materials
- Control Atomic layers of substrates
- Template pattern controls
- Dark current reductions
- Readout electronics
- Assembly of large arrays
- Modeling, simulation and testing
- Upward integration into macro-systems

Value to Space Systems

- 10X to 100X smaller, lower power & cost
- Tailorable for very high quantum efficiency
- Tailorable for space durability in harsh environments
- Improved capabilities at comparable or reduced cost
- Mission enabling technology

State of the Art (all ground based)

- Designer bio/chemical sensors
  - Characteristic Properties of Molecules
  - Functionalized structures (CNTs, etc.)
- Assembly of nano-structures
  - Template development
  - Electro-static control
  - Nano-fluidics/separation tools

NASA

Nanomaterials

Goals

Reliable, consistent, on-demand production of durable nanomaterials to support Space Missions:

- Control of morphology and structure over all length scales (nm to m's)
- Scalability to practical quantities
- Ability to produce materials with resources on other planets
- Long-term (years) durability in severe environments

Hard Problems

- Ability to reliably and consistently control functional material synthesis and assembly from nano to macro scales
- Understand and counteract effects of long term exposure in complex/extreme environments on materials durability and properties
- Understand/model/predict nanoscale phenomena

Value to Aeronautic and Space Systems

- 5-fold increase in specific strength and stiffness over conventional composites
- Integral power generation, storage and self-actuation with a total aerial weight of $0.8Kg/m^2$ & 1.0 kw/kg power generation
- Material with near zero H2 permeability
- Electrode materials for reversible fuel cells
- Life Support: catalysts /absorptive materials for efficient, low volume environmental revitalization
- 50% lighter TPS and radiation shielding
- 10X higher thermal conductors (EVA suits, habitats, etc)

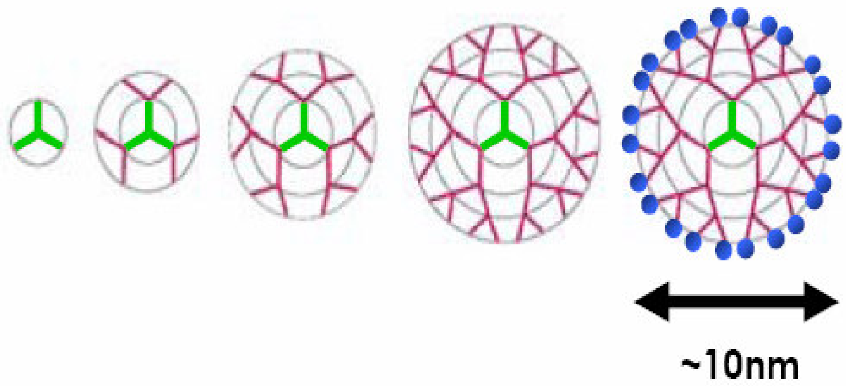
State of the Art

- Self assembly & biomimetic processes enable micron scale structure control – need control over 100's of meters
- Single wall carbon nanotubes (CNTs) production at 100 gram/day – need precise control of length and chirality
- CNT doped polymers and fibers have been produced with high strength and electrical conductivity – need to scale to >100m
- Polymer cross-linked aerogels produced with 300X the strength of conventional aerogels – need to scale to $>10m^2$

FIM DA 1a AULA

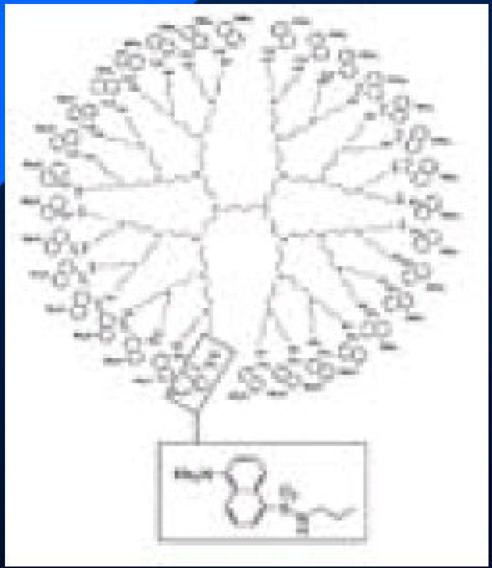
Dendrimers: Macromolecules with controlled, complex surfaces

Dendrimers are well-defined, highly-branched synthetic macromolecules suitable for pharmaceutical applications. They are synthesised by surrounding a core molecule with layers of branching elements. The resulting dendrimer is either used in this "uncapped" state or its surface can be functionalised by conjugation of active groups.



WHAT WOULD A DENDRIMER LOOK LIKE?

Molecular structure of a dendrimer



3-D representation of a Dendrimer