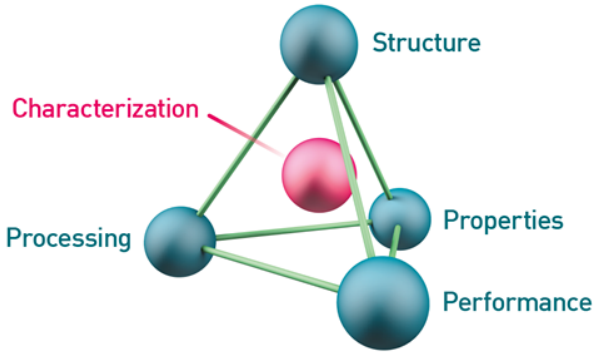
M5052
CHARACTERIZATION OF MATERIALS AND NANOMATERIALS

Graduate Program in Nanotechnology



Tecnológico de Monterrey

PROF. YADIRA I. VEGA CANTÚ

COURSE OBJECTIVES

- Present the principles and applications of some of the basic techniques for characterization of materials and nanomaterials
- Present the principles and applications of some techniques needed specifically for nanomaterials characterization

- Learning Objectives: At the end the student should be able to select a characterization technique for a material or nanostructure based on the type of material and properties to measure

- Final Project Objective: Linking the class topics to the current research projects of the students

SYLLABUS

1. Introduction to Instrumental Analysis and Interactions of Light and Matter
2. Vibrational Spectroscopy: Infrared Spectroscopy, Raman Spectroscopy, SERS
3. Molecular Spectroscopy:
    - 3.1 UV-vis
    - 3.2 Fluorescence
4. X-Ray Methods:
    - 4.1 Diffraction XRD
    - 4.2 XRF, EDS, XPS
5. Introduction to Optical Microscopy and Nanoscopy
6. Electron Microscopy
    - 6.1 SEM
    - 6.2 TEM
    - 6.3 Other EM (etc.)
7. Scanning Probe Microscopies
    - 7.1 STM
    - 7.2 AFM
    - 7.3 other SPM
8. Thermal Analysis: TGA, DTA, DSC, TMA, DMA

BACKGROUND KNOWLEDGE REQUIRED OF ENROLLED STUDENTS

- **Bonding in solids**
    - Ionic
    - Covalent
    - Metallic
- **Structure of crystalline solids**
    - Crystalline structures, amorphous
- **General properties of materials**
    - Metals
    - Ceramics
    - Polymers
- **Basic concepts in nanomaterials**
    - Nanoparticles
        - Metallic, oxides
    - Quantum dots
    - Carbon nanomaterials
        - Carbon nanotubes, graphene, fullerenes

RECOMMENDED TEXTBOOKS

- J.P. Sibilia [Ed.] "A Guide to Materials Characterization and Chemical Analysis" 2nd. ed., Wiley-VCH (1996)
  - *Contains basic descriptions and examples of applications to materials for a large variety of chemical and materials characterization techniques*
- Encyclopedias of Science or of Chemical Technology
  - *These usually have entries or chapters explaining different analytical techniques*
- Douglas A. Skoog, F. James Holler, Stanley R. Crouch "Principles of Instrumental Analysis" 7th. ed. Cengage Learning, 2017
  - *A classic textbook of instrumental analysis*
  - *Mexican edition in Spanish may be cheaper: D.A. Skoog, F.J. Holler, S.R. Crouch "Principios de Análisis Instrumental", 7a ed., México : Cengage Learning, 2018*

SUPPLEMENTARY TEXTBOOKS

- **W. D. Callister and D. G. Rethwisch**
  - Fundamentals of Materials Science: An Integrated Approach
- W. Smith, J. Hashemi, "Foundations of Materials Science and Engineering," McGraw-Hill
- J. Shackelford, "Introduction to Materials Science for Engineers", Pearson, Prentice Hall.
- G. Hornyak, et al. "Introduction to Nanoscience and Nanotechnology", CRC Press.
- Additional/Supplementary reference books:
  - Materials Science
  - Chemistry of Materials
  - Solid State Chemistry

DR. YADIRA I. VEGA

- Tecnológico de Monterrey
  - School of Engineering and Sciences (IEC)
  - Advanced Manufacturing Focus Group
  - Department of Sciences, area Chemistry and Nanotechnology
  - Innovation Center in Design and Technology

- Office: A1-404-C
- Office hours (unofficial): Monday 14:30 - 17:00, Wednesday 11:30 - 13:00 h
- **Please notify in advance**

Contact:
yadira.vega@itesm.mx

Yadira Vega-Cantu @yivega Yadira Vega-Cantu

- **Preferably, contact me during office hours (8:00 - 18:00)**

DR. VEGA'S ACADEMIC BACKGROUND

TECNOLÓGICO DE MONTERREY®
- B.S. in **Chemistry**
- M.S. in **Chemistry**

RICE
- Ph.D. in **Chemistry**
- Post-doctoral training in **Chemistry**

Instituto Potosino de Investigación Científica y Tecnológica, A.C. IPICYT
- 2005 - 2012 Research Professor
- **Advanced Materials** Division

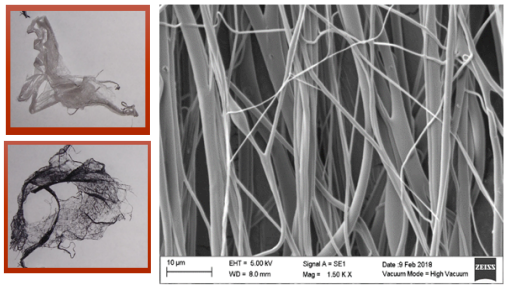
Universidade Federal de Pernambuco
- 2012 - 2015 Visiting Professor
- Graduate Program in **Materials Science**

TECNOLÓGICO DE MONTERREY®
- 2016 - Currently Research Professor
- School of Engineering and Sciences
- Innovation Center in Design and Technology
- **Advanced Manufacturing** Focus Group
- Department of **Chemistry and Nanotechnology**

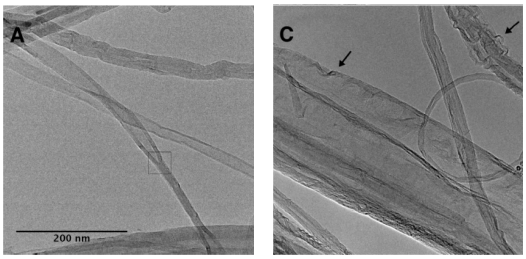
DR. YADIRA I. VEGA: RESEARCH

Nanomaterials
Carbon Nanostructures: Production, Functionalization, Characterization, Properties & Applications

Nanocarbon Hybrid Systems



Nanoribbons



Composite Materials

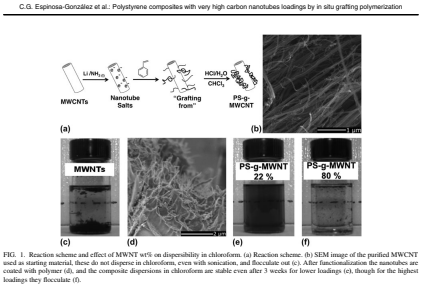
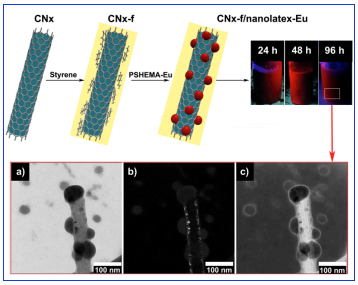


FIG. 1. Reaction scheme and effect of MWNT wt% on dispersibility in chloroform. (a) Reaction scheme. (b) SEM image of the purified MWCNT used as starting material, these do not disperse in chloroform, even with sonication, and flocculate out (c). After functionalization the nanotubes are coated with polymer (d), and the composite dispersions in chloroform are stable even after 3 weeks for lower loadings (e), though for the highest loadings they flocculate (f).

Photoluminescent Nanomaterials

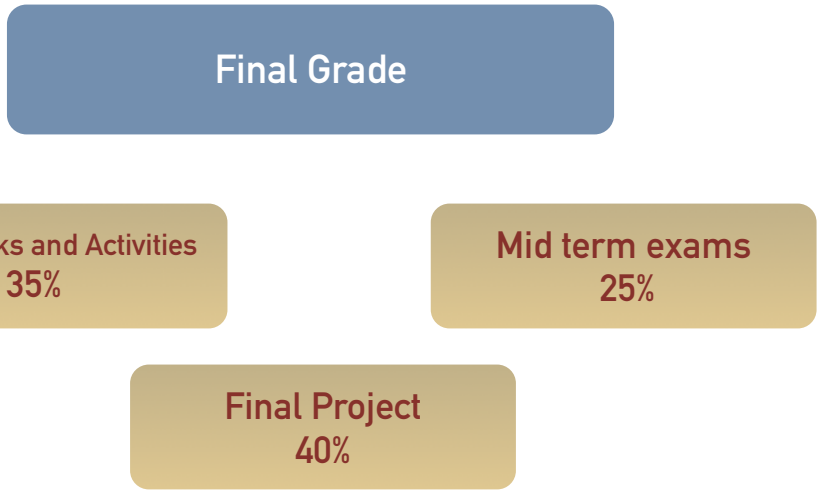


COURSE ASSESSMENT: DISCUSSION OF EXAMPLES

- *After each topic each student should look for one scientific paper showing an example of application of the analysis technique for materials or nanomaterials*
  - *Journal should be indexed in Journal Citations Reports or Scopus, preferably with a Q1 or Q2 ranking*
    - *Articles from predatory journals are not acceptable*
  - *All papers should be uploaded to a shared folder*
  - *Each student should prepare one slide of their own article and upload it to the shared folder*
    - *Both Files should follow the format Name-Surname-Paper-Name*
      - *Also upload supporting information if necessary*
- *Uploaded examples will be discussed in class*
  - *All the students should read at least all the slides of their peers for in-class discussion*

COURSE ASSESSMENT

- *Final grade will have a numeric value of 1 - 100*
- *Exams and activities will be graded with a numeric value of 0 - 100*



Midterm grades reported will be an average of the grades of homework and activities and the exams from that period

PARTICIPATION

- We will have an active discussion during class, therefore, student participation is extremely important.
- Students have to participate in all designated activities on and off class.
- Other ways to participate: pay attention to lectures, participate on course's discussion boards.

FINAL PROJECT

- Proposal of Characterization of **materials or nanomaterials related to your research project**.
- Individual
- Must be **novel and original**
- Due on the last day of class
  - Points will be deducted for projects delivered after the due date
- Oral presentation at the end of the semester

- **One progress draft** will be due after the mid term period:
  - Around March 8th 2019

CLASS ATTENDANCE

- Tec official attendance rules will be observed:
  - **This year, the figure of "EF" (exceso de faltas) disappears; which means there is not an absence limit in order to be granted a final grade. HOWEVER:**
  - Attendance *still* will be registered at the beginning of the class session. If a student arrives after roll-call is her or his obligation to inform the instructor at the end of the session, and to make sure the absence is removed.
  - Tardiness will be counted in 15 minutes sets. If a student is late more than one hour, a complete absence will be registered.
  - Absences and tardiness will be counted starting today
  - **If you are late to any exam or activity, no extra time will be given**.
  - **If you do not show up in a day where a quiz or other graded activity was done, those will not be replaced and a grade of "0.00" will be granted.**
  - If you fall asleep, are talking to others, not paying attention, then instructors could consider to register an absence.

→ ***Class attendance will be registered even without conducting a roll call***

- Students with more than 9 h of absence will have a grade of "0.0" in participation

COURSE GUIDELINES AND POLICIES

- All exams and activities are individual:
  - Copying or transcribing in an exam will invalidate the answer or even the complete exam without opportunity for a second-chance exam.
  - Nullified exams will be graded with a "DA"
  - Any kind of academic dishonesty will not be tolerated: to offer or to recibe aid, plagiarism, cheating, etc.
- Students should not chat during lectures and presentations.
- It's very important to participate in and out of lectures.
- At the end of the semester, there are will be no extra activities of make up projects, nor second-chance exams.

USE OF CELL PHONES, TABLETS, LAPTOPS, ETC.

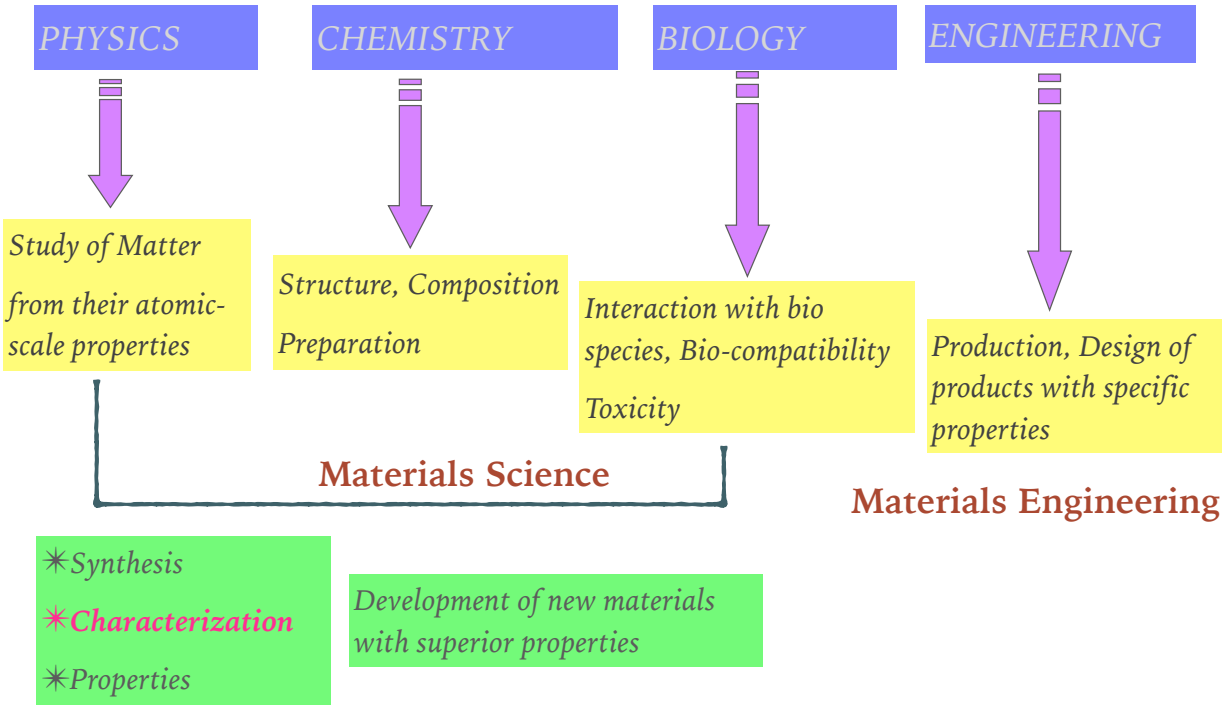
- Comprehension and discussion during lectures is very important, so the students should avoid any distractions.
- Mobile devices will be used to look for information during lectures and activities.
- Devices should stay in "mute" or "do not disturb" mode during lectures.
- Phone calls should be taken only in case of emergency, please leve the classroom to do so. Preferably let the professor know in advance.
- **Recording (filming) lectures or people can be done only upon previous authorization.**

Recommendations for success…

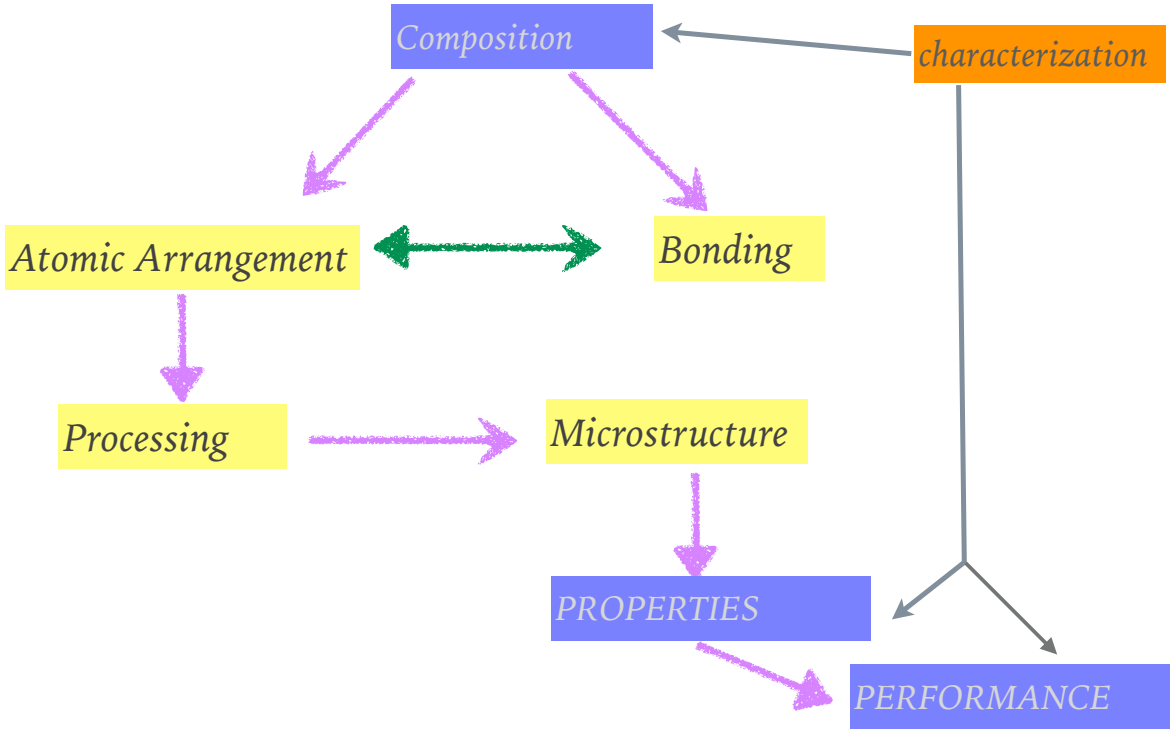
- ***Self-study is critical***
- *Find a study buddy, or even better, a study group*
- *Do not skip class*
- *Do not wait until you fail an exam to seriously start studying or to ask for help*
- *When doing homework, make sure you understand thoroughly every exercise. Do not just "deliver homework"*
- ***Do not hesitate to ask ANY question***
- *Be well prepared for the exams*
- ***Be responsible** for your own situation, actions and your own success*

INTRODUCTION: STUDY OF MATERIALS

STUDY OF MATERIALS

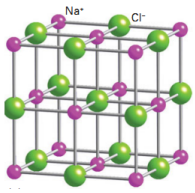


PROPERTIES OF MATERIALS



CLASSIFICATION BY ATOMIC ORGANIZATION

Crystalline solids



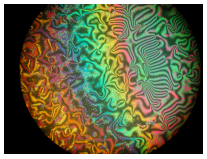
rock salt crystals

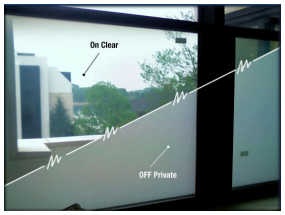
Semi crystalline / amorphous solids

Polymers

glass

Liquid crystals



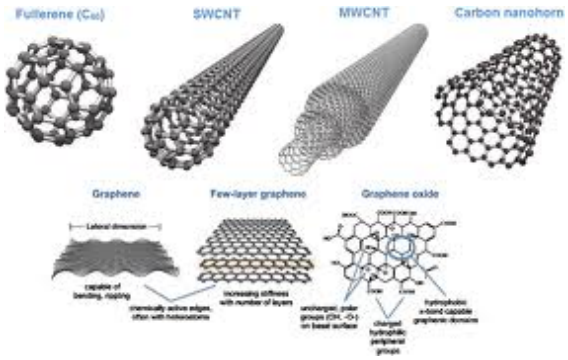


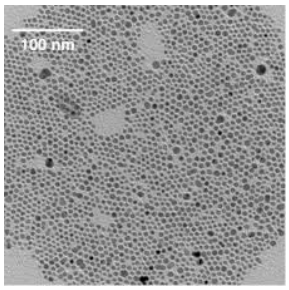
liquid crystals on windows

EXAMPLE: ADVANCED MATERIALS

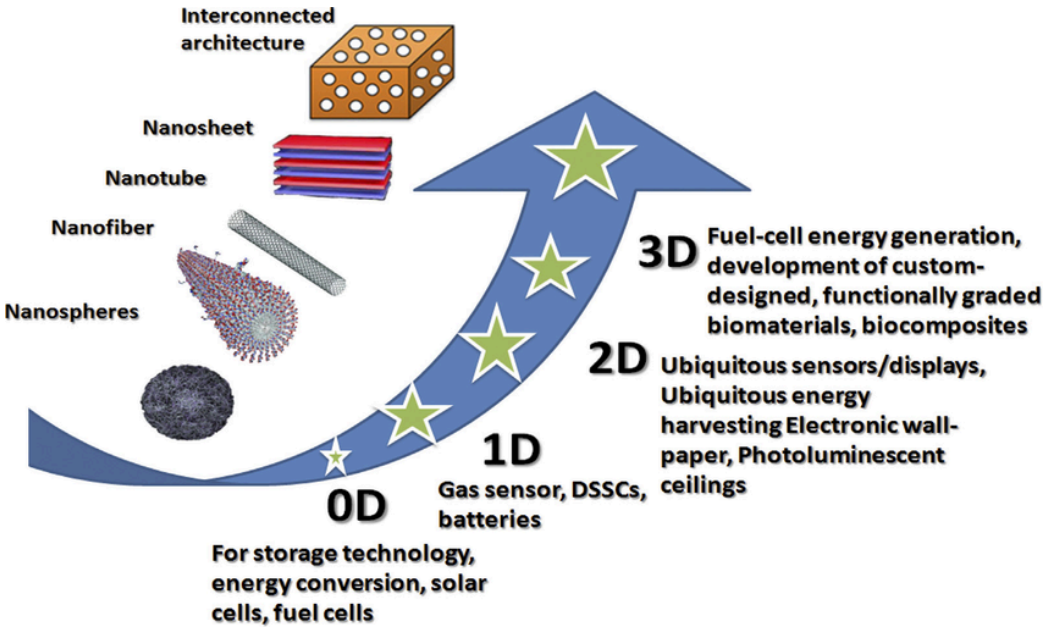
Nanomaterials

- Materials produced by simple materials at the atomic level
- Produced by nanotechnology: Ability to arrange atoms in different ways (bottom up)
- Dimensions in the order of nanometers (10^{-9}), less than 100 nm



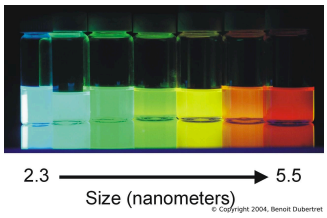


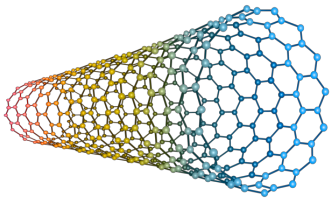
CLASSIFICATION BY DIMENSIONALITY

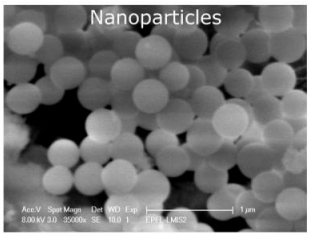


https://www.researchgate.net/publication/303423807_Nitrogen-doped_Titanium_Dioxide_an_overview_of_material_design_and_dimensionality_effect_over_modern_applications/figures?lo=1

NANOMATERIALS & NANOTECHNOLOGY NEED UNDERSTANDING OF MATER FROM THE ATOMIC AND MOLECULAR POINT OF VIEW







STUDYING OF MATERIALS AND NANOMATERIALS

NANOTECHNOLOGY

WHAT IS NANO?

"Nano" derived from the Greek

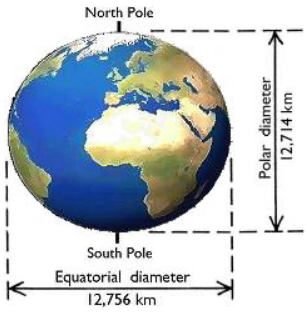
"Nannos" → very short man

NANO... IT'S A MATTER OF SCALE

Nano = 10^{-9}

1 nanometer = 0.000 000 001

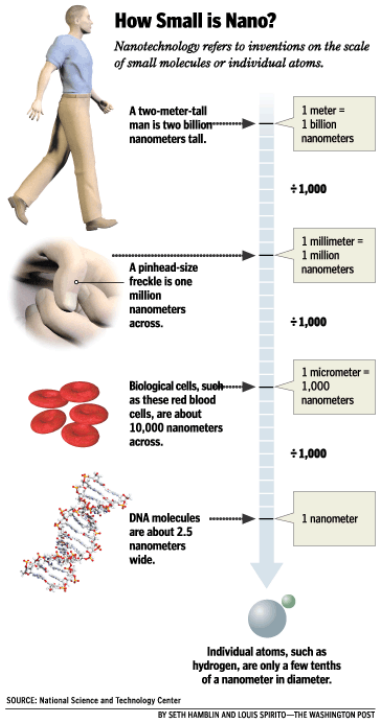
10^{-9} m

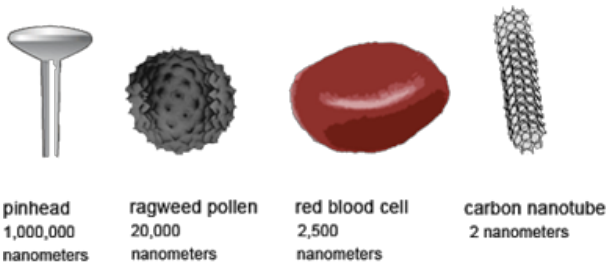


22 cm

0.7 nm

HOW SMALL IS NANO?



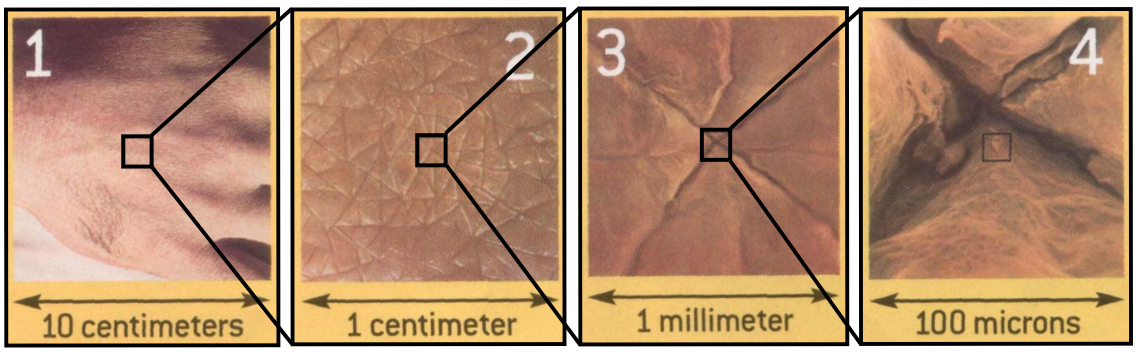


http://www.next.cc/journey/tools/nano-technology

http://www.washingtonpost.com/wp-srv/nation/daily/graphics/nanasize_020204.html

HOW SMALL IS NANO?

Consider a human hand:

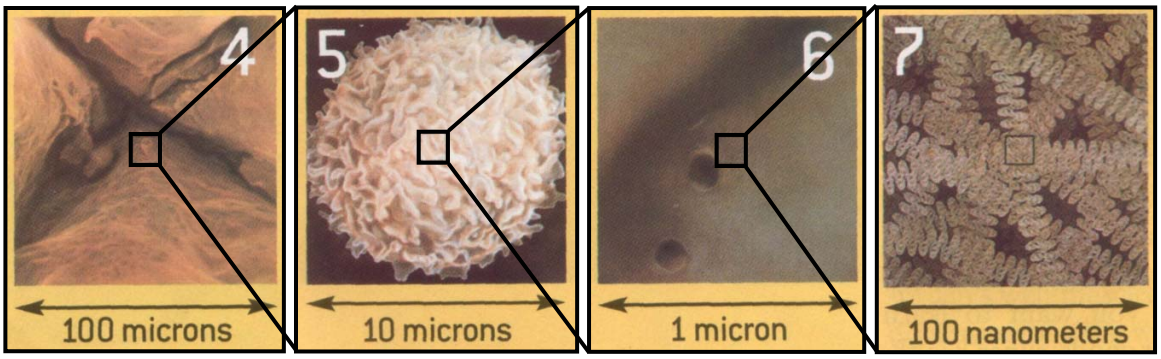


Skin

M. Hersam, *Introduction to Nanometer Scale, Science and Technology,* hersam-group.northwestern.edu/

HOW SMALL IS NANO?

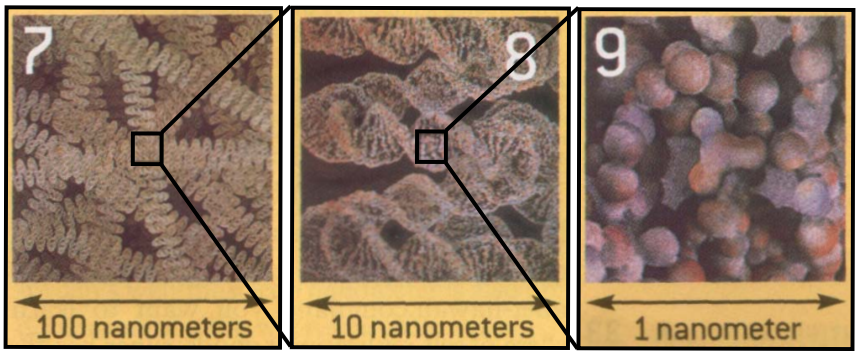
Consider a human hand:

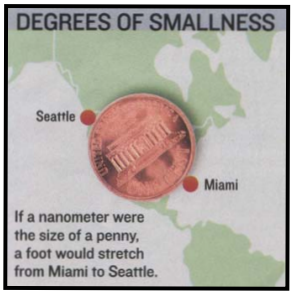


M. Hersam, *Introduction to Nanometer Scale, Science and Technology,* hersam-group.northwestern.edu/

HOW SMALL IS NANO?

Consider a human hand:





M. Hersam, *Introduction to Nanometer Scale, Science and Technology,* hersam-group.northwestern.edu/

NANOSCIENCE & NANOTECHNOLOGY

THE SCIENCE AND TECHNOLOGY OF THE SMALL OF THE VERY VERY VERY

"Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nm, where unique phenomena enable novel applications"

"Nanoscience is the study of materials that exhibit remarkable properties, functionality and phenomena due to the influence of small dimensions"

"Nanotechnologies are characterization, production application of structures and systems by controlling shape and size at nanometre scale "

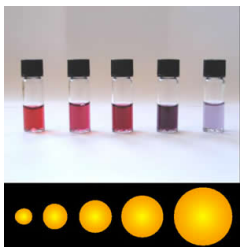
"Nanoscience is the study and of very small things and across all other the other science fields, such as chemistry, biology, physics, materials science, and engineering"

NANOTECHNOLOGY

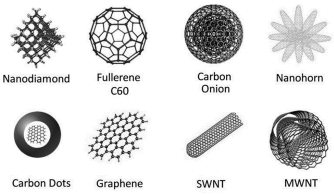
Materials Properties change at the nanoscale

bulk *nano* *Ancient nanotechnology*

gold



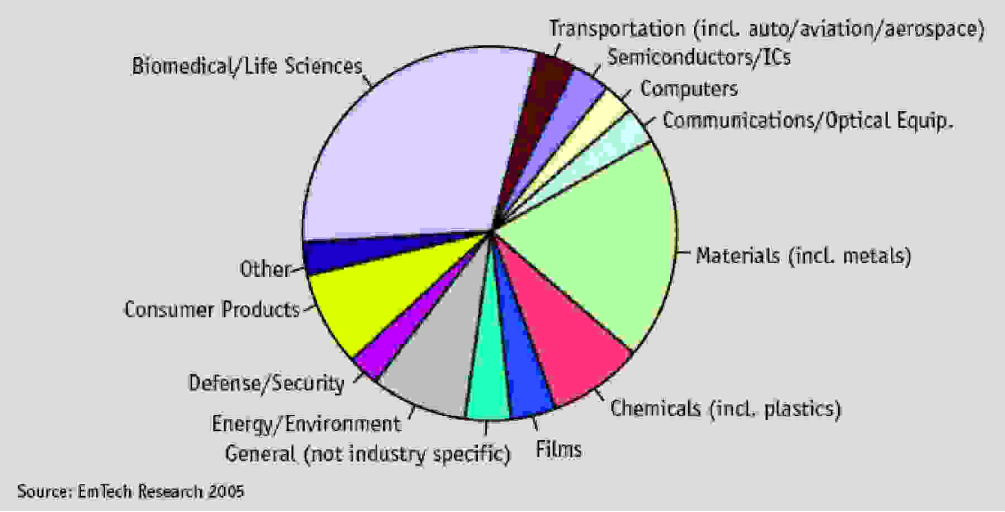
carbon



THE SCIENCE OF ATOM-SIZE OBJECTS WILL RESHAPE THE ECONOMY

http://library.cqpress.com/cqresearcher/document.php?id=cqresrre2016061000

APPLICATIONS OF NANOTECHNOLOGY BY INDUSTRY



A FEW BASIC DEFINITIONS

Nanoscale: in the order of 1 - 100 nm

Nanostructure structure of size between molecular and microscopic scales

Nanomaterial: material having at least one dimension at the nanoscale

Nanoscience: study of phenomena and processes at the nanoscale

Nanotechnology: the use of nanoscience for practical applications

NANOSCIENCE AND NANOTECHNOLOGY

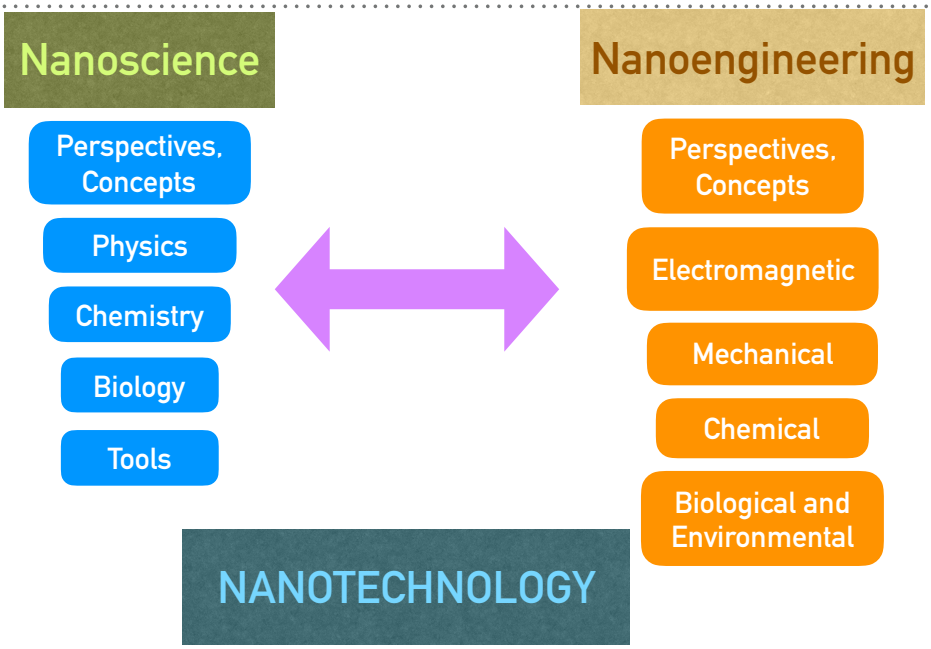
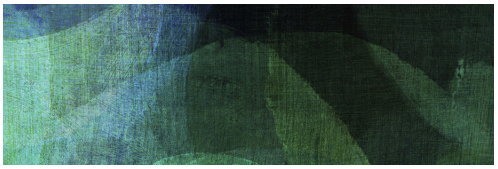
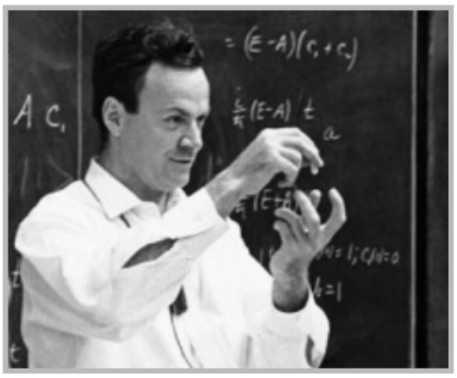


Figure modified from: G. L. Hornyak, H. F. Tibbals, J. Dutta, J. J. Moore; "Introduction to Nanoscience & Nanotechnology" . CRC Press. 2009

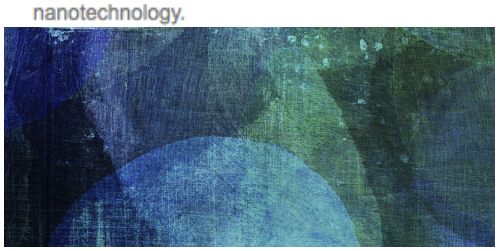
"THERE'S PLENTY OF ROOM AT THE BOTTOM"

Cal Tech 1959

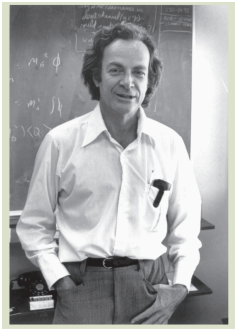




Physicist Richard Feynman, the father of nanotechnology.



> *I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle. This field is not quite the same as the others in that it will not tell us much of fundamental physics (in the sense of, 'What are the strange particles?') but it is more like solid-state physics in the sense that it might tell us much of great interest about the strange phenomena that occur in complex situations. Furthermore, a point that is most important is that it would have an enormous number of technical applications. What I want to talk about is the problem of manipulating and controlling things on a small scale.*
>
> RICHARD FEYNMAN, CALTECH, 1959 [FIG. 1.0],
> *"There's Plenty of Room at the Bottom"*



Nobel Prize laureate Richard Feynman at the blackboard.

G. L. Hornyak, H. F. Tibbals, J. Dutta, J. J. Moore; "Introduction to Nanoscience & Nanotechnology" . CRC Press. 2009

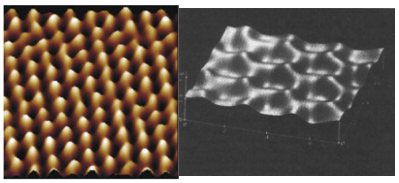
BRIEF HISTORY OF NANOSCIENCE AND NANOTECHNOLOGY

1959 Richard Feynman "There's Plenty of Room at the Bottom"

1979 Norio Taniguchi uses the term "Nano-Technology" to describe materials manipulation in the nanoscale (in the context of miniaturization of microprocessors)

1960 - 1980 Mesoscopic systems: Materials between the micro and nanoscale

1981 Development of the Scanning Tunneling Microscope (STM)
Individual atoms could be seen
First tool capable of manipulation at the atomic scale
Modern nanotechnology began



BRIEF HISTORY OF NANOSCIENCE AND NANOTECHNOLOGY (2)

1983 -1985 Discovery of Semiconducting Quantum Dots
Coloidal CdS particles semiconductors

1985 Discovery of Fullerenes

H. Kroto, R. Curl, R. Smalley (Rice University)
Carbon nanotechnology began

1986 Development of the Atomic Force Microscope (AFM)

1986

K. Erick Drexler publishes "Engines of Creation: The Coming Era of Nanotechnology"

Proposes "molecular nanotechnology"
Concept of "molecular assembler"
This idea is considered to be not feasible by nano science researchers

BRIEF HISTORY OF NANOSCIENCE AND NANOTECHNOLOGY (3)

1991 Discovery of Multiwalled Carbon Nanotubes by Iijima

1993 Discovery of Single-Walled Carbon Nanotubes

By Iijima and by Bethune et al.

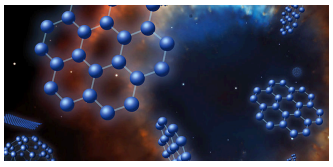
1999

USA launches the National Nanotechnology Initiative

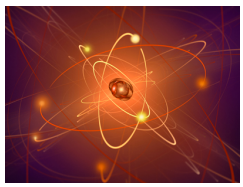
The recognition of Nanotechnology as a distinct field of study launches several research projects and initiatives around the world.

Nanoscience and Nanotechnology are now recognized as interdisciplinary fields of study which allow applications not formerly possible and enable new business opportunities

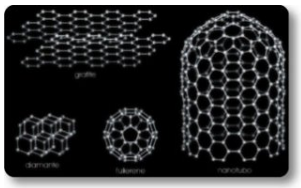
PRODUCING NANOSTRUCTURES: BOTTOM-UP



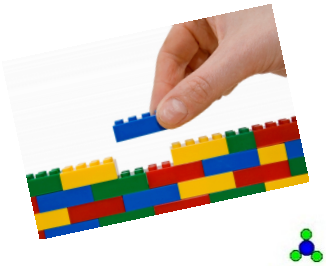
molecules

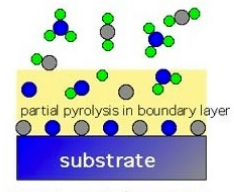


atoms



nanostructure

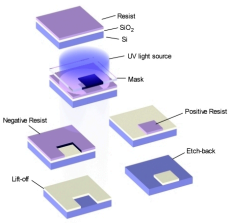




- Nanostructures from molecules and atoms
- CVD
- Wet chemistry
- Self-assembly

PRODUCING NANOSTRUCTURES: TOP DOWN

"Every block of stone has a statue inside it and it is the task of the sculptor to discover it." - Michelangelo



photolithography

La fille du Marin by Philippe Faraut

Graphene by the Scotch tape method

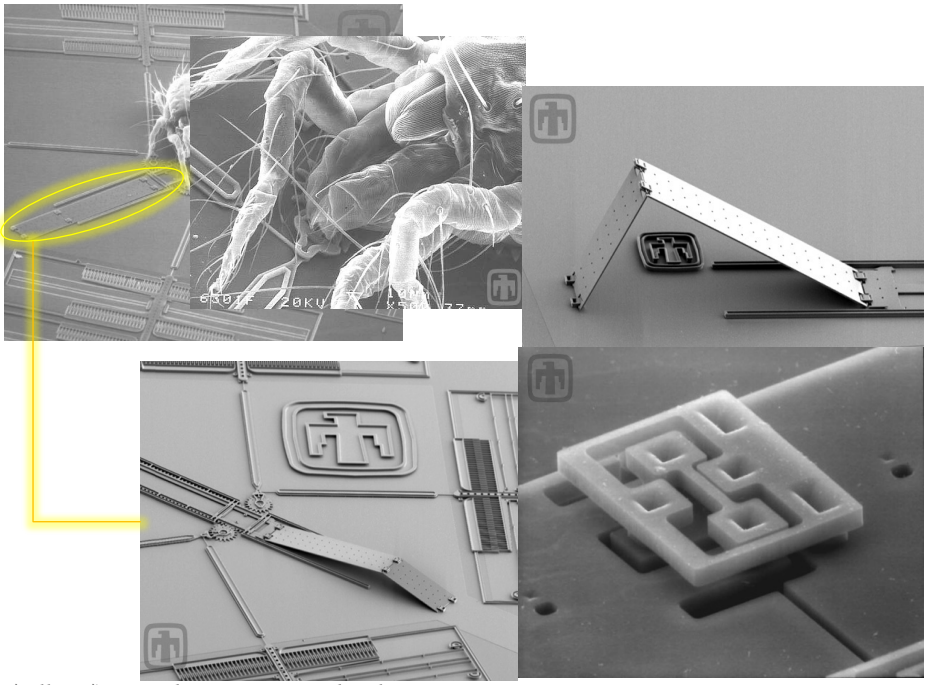
- Nanostructures from removing the excess material. From bulk or microscale to nano.

TOP DOWN: MEMS/NEMS

http://www.memx.com/

- Micro - & Nano-Electro-Mechanical Systems
- Produced with technology developed for semicondutor microcircuits and computer chips
  - Litography masks, physical and chemical etching, etc.

MEMS & NEMS



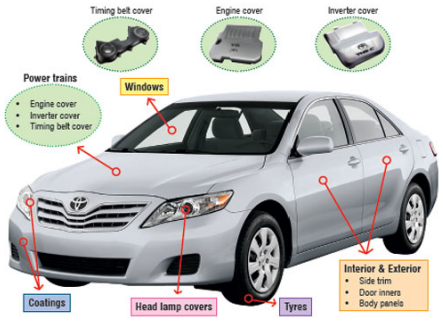
mems.sandia.gov/gallery/images_bugs_on_mems.html
mems.sandia.gov/gallery/images_mirrors.html

NANOTECHNOLOGY-BASED FORMULATIONS

- Incorporation of nanostructured materials
  - Most produced by bottom-up methods

Important Aspects

- Uniform **dispersion** & **distribution** in a medium is very important
- Many are used as **intermediate goods**, instead of final consumer products



http://www.nanowerk.com/spotlight/spotid=23934.php

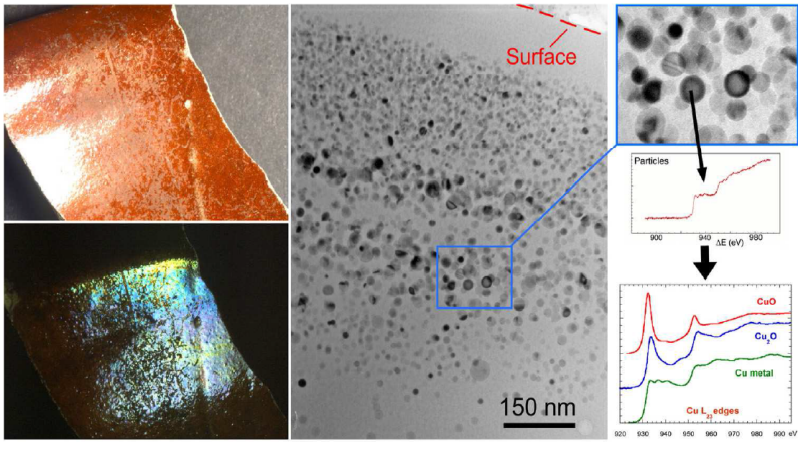
HOW OLD ARE THE OLDEST KNOW APPLICATIONS OF NANOTECHNOLOGY?

NANOMATERIALS BEFORE THE NANOTECHNOLOGY ERA

NANOPARTICLES ON ANCIENT TIMES

- Bronze age: (1200 -1100 B.C.) glasses found in Italy contain copper nanoparticles that give them a red color

- Celtic red enamels (400–100 B.C.) contain Cu (and cuprous oxide) nanoparticles



Philippe Sciau (2012). "Nanoparticles in Ancient Materials: The Metallic Lustre Decorations of Medieval Ceramics", in *The Delivery of Nanoparticles*, Dr. Abbass A. Hashim (Ed.), ISBN: 978-953-51-0615-9, InTech, http://www.intechopen.com/books/the-delivery-of-nanoparticles/nanoparticles-in-ancient- materials-the-metallic-lustre-decorations-of-medieval-ceramics

NANOPARTICLES ON ANCIENT TIMES

- Damascus Steel (Middle age) in 2006 carbon nanotubes were discovered in a blade

http://www.nature.com/news/2006/061113/full/news061113-11.html

- Ancient Chinese and Japanese ceramics: contained Cu oxides nanoparticles

Metal_nanoparticles_in_contemporary_potters_master_pieces_Lustre_and_red_pigeon_blood_potteries_as_models_to_understand_the_ancient_pottery ancient-pottery.pdf

NANOPARTICLES ON ANCIENT TIMES

- Lycurgus Cup, Rome, 4th century: **Au** and **Ag nanoparticles**
  - "The most spectacular glass of the period, fittingly decorated, which we know to have existed"

The Romans may have first come across the colorful potential of nanoparticles by accident, but they seem to have perfected it. (The Trustees of the British Museum / Art Resource, NY)

- Dichroic glass
- Transmission Electron Microscopy analysis in 1980 showed the presence of nanoparticles (50-100 nm) of a Au & Ag (30:70) alloy

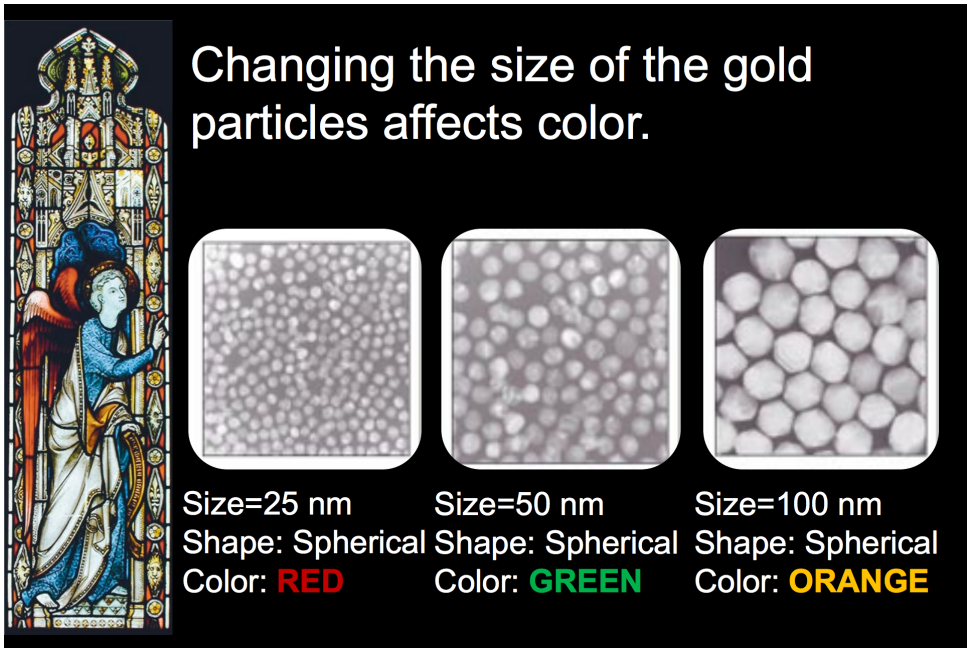
https://en.wikipedia.org/wiki/Lycurgus_Cup

www.britishmuseum.orgresearchcollection_onlinecollection_object_details.aspxobjectId=61219&partId=1&searchText=lycurgus+cup&page=1

NANOPARTICLES ON ANCIENT TIMES

➤ Stained Glass: metallic nanoparticles

79
Au
Gold
196.967

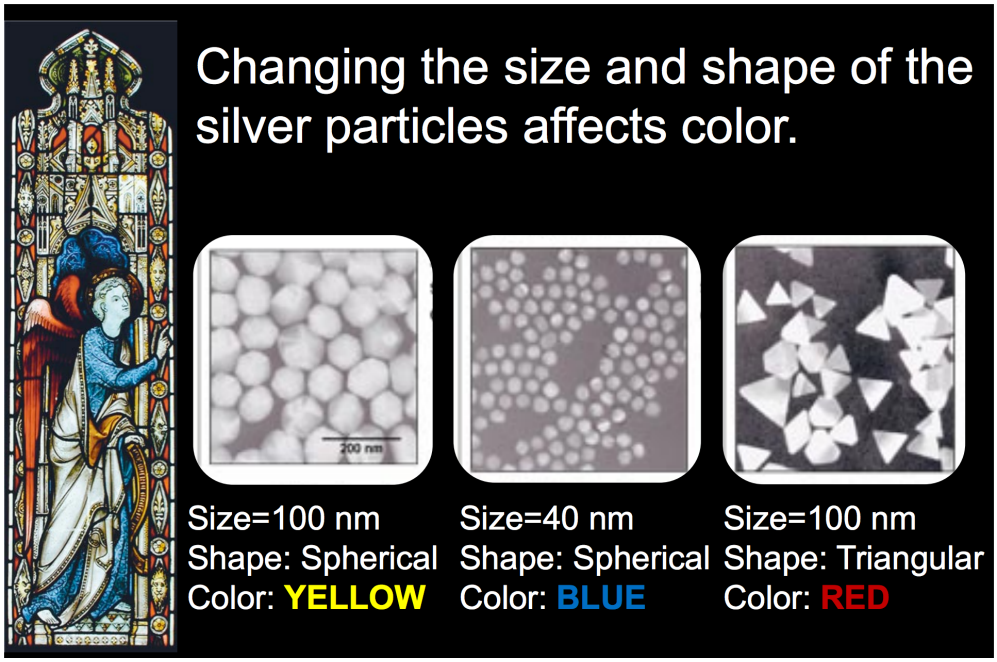


http://www.nisenet.org/sites/default/files/catalog/uploads/2474/stainedglasscart_classpresentation_jan10.ppt.pdf

NANOPARTICLES ON ANCIENT TIMES

➤ Stained Glass: metallic nanoparticles

47
Ag
Silver
107.868



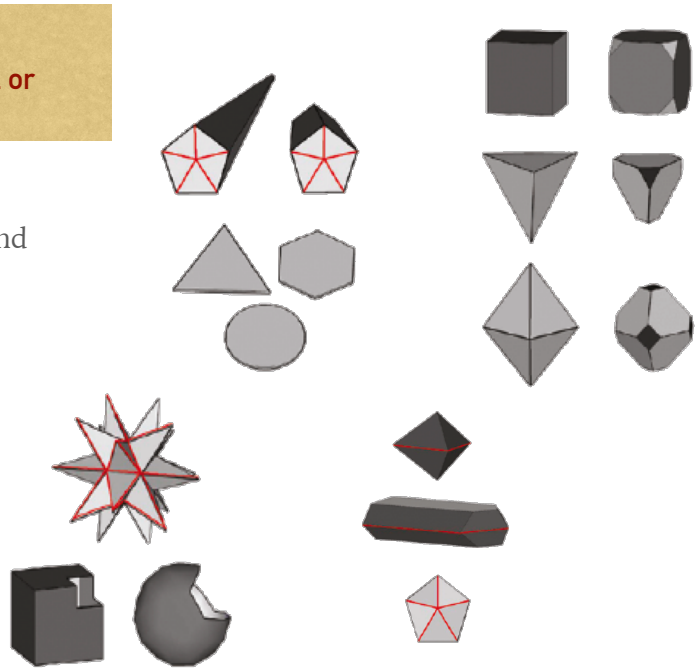
http://www.nisenet.org/sites/default/files/catalog/uploads/2474/stainedglasscart_classpresentation_jan10.ppt.pdf

NANOPARTICLES TODAY

Structures of any material about 100 nm or less

Composition:
metallic, ceramic, polymeric, biological or hybrid

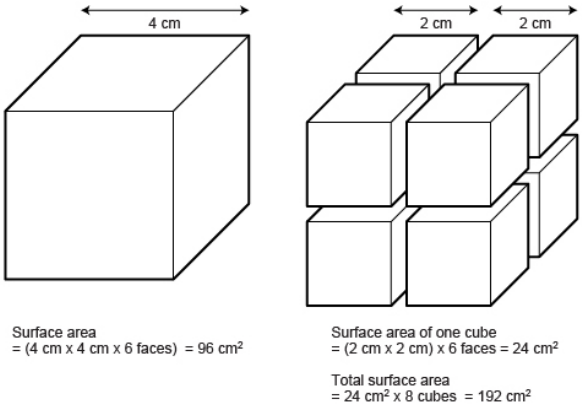
- Many morphologies are possible
- Named according to **composition** and **geometry**:
  - E.g.: Titanium nanorods, gold nanoclusters, zinc oxide nano whiskers, carbon nanotubes, etc.



NANOPARTICLES TODAY

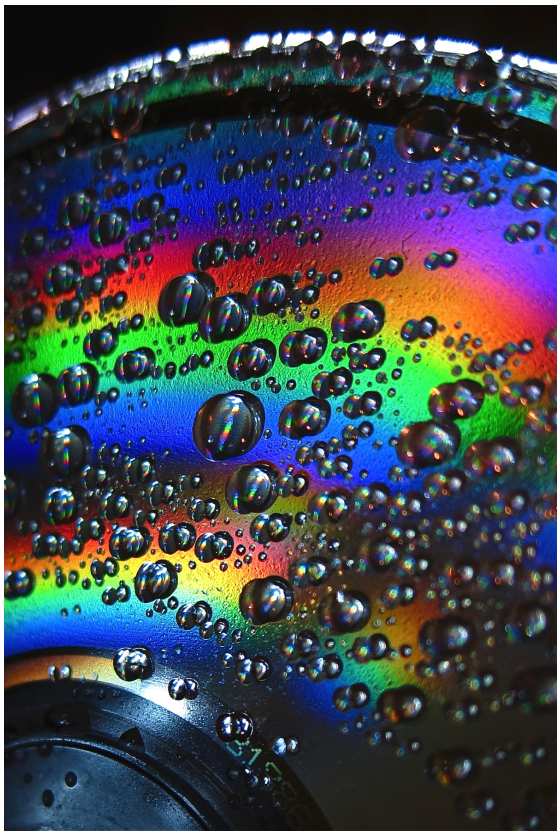
- Intentional and controlled synthesis is what defines these particles as products from nanoscience and nanotechnology

High surface to volume ratio



- In 2 g of Al nanoparticles of 100 nm diameter there are enough particles to give 300,000 to every human being on Earth

http://www.bbc.co.uk/schools/gcsebitesize/science/21c/materials_choices/nanotechnologyrev1.shtml



THE ELECTROMAGNETIC SPECTRUM