

Inorganic Materials Chemistry

C7780

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- **Lectures: PowerPoint presentations with recorded talk uploaded in the IS MU**

Course grading:

- 3 graded **homeworks** during semester
- Short **presentations** on a selected topic concerning materials chemistry
- Written final **exam** (100 pts, minimum 50 pts to pass)

Grading weights: final test 75%, homeworks 15%, presentation 10%.

Recommended Literature

**SCHUBERT, U., HÜSING, N., Synthesis of Inorganic Materials.
Weinheim: Wiley-VCH**

**CALLISTER, W.D.J., Materials Science and Engineering, An
Introduction. John Wiley and Sons**

**SMART, L., MOORE, E., Solid state chemistry : an introduction.
2nd ed. London: Chapman & Hall**

**INNOCENZI, Plinio, The Sol to Gel Transition, Springer
International Publishing**

**WHITE, Mary Anne, Physical Properties of Materials, 2nd
Edition, CRC Press**

**MUELLER, Ulrich, Inorganic Structural Chemistry, 2nd Edition,
Wiley**

Recommended Literature

**OZIN, G.A., ARSENAULT, A.C., CADEMARTIRI, L.,
Nanochemistry : a chemical approach to nanomaterials. 2nd ed.
Cambridge: RSC Publishing, 2009.**

**CADEMARTIRI, L., OZIN, G.A., Concepts of nanochemistry.
Edited by Jean-Marie Lehn. Weinheim: Wiley-VCH, 2009.**

FAHLMAN, B. D. Materials Chemistry. Springer 2018.

**LOWELL, S., SHIELDS J. E., Martin A. THOMAS, M. A.,
THOMMES, M. Characterization of Porous Solids and Powders:
Surface Area, Pore Size and Density. Springer 2004.**

**MITTEMEIJER, E. J. Fundamentals of Materials Science.
Springer 2011.**

Materials in Human History

Historical perspective:

New materials bring advancement to societies

- Stone age
- Bronze age
- Iron age
- Silicon age



Crescent Axes. The top Syrian, the bottom Egyptian.
about 1900 BC

Materials in Human History

50 000 B.C. Iron oxide pigments Lascaux, Altamira

24 000 B.C. Ceramics – fat, bone ash, clay

3 500 B.C. Cu metallurgy

Glass, Egypt and Mesopotamia

3 200 B.C. Bronze

1 600 B.C. Iron metallurgy, Hittites

1 300 B.C. Steel

1 000 B.C. Glass production, Greece, Syria

105 B.C. Paper, China

590 A.D. Gun powder, China

700 A.D. Porcelain, China



Materials in Human History - Metals

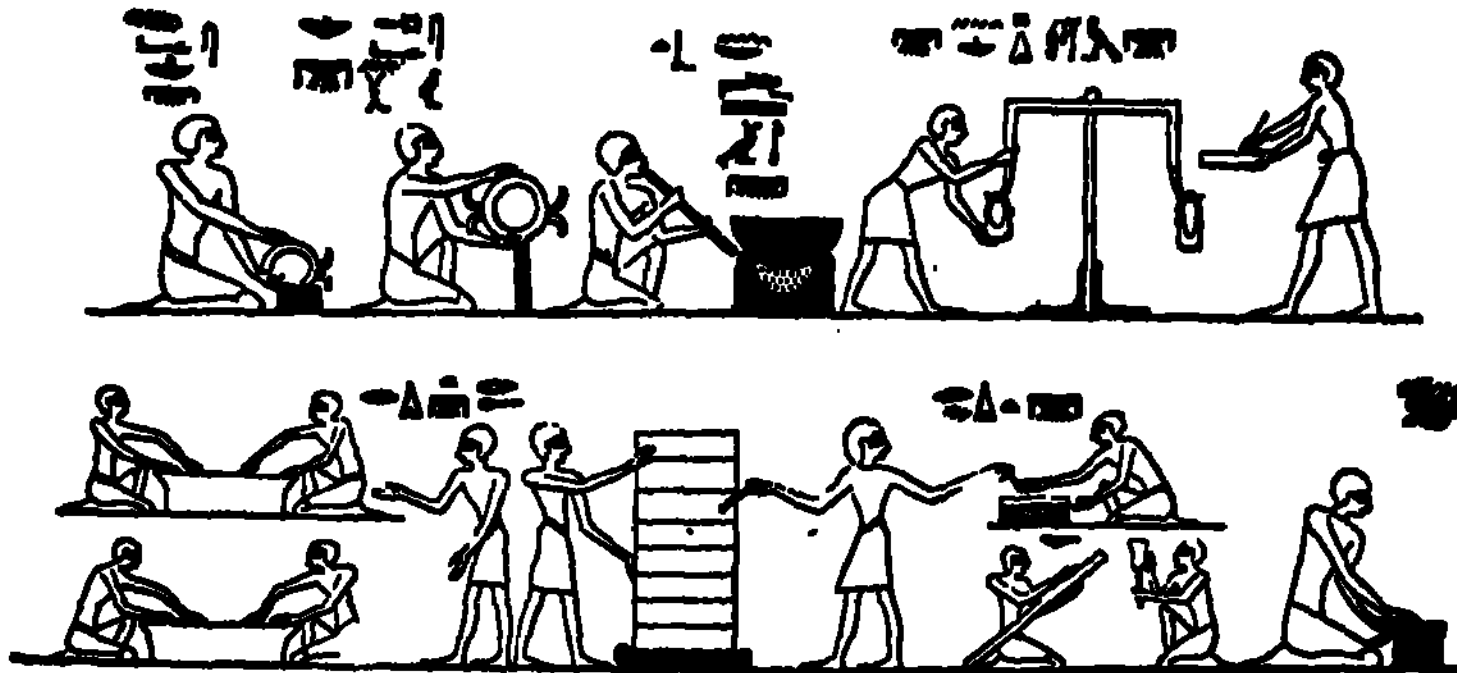


FIG. II.—EGYPTIAN GOLDSMITHS WASHING, MELTING AND WEIGHING GOLD.
BENI HASAN, 1900 B.C.

Materials in Human History - Ceramics

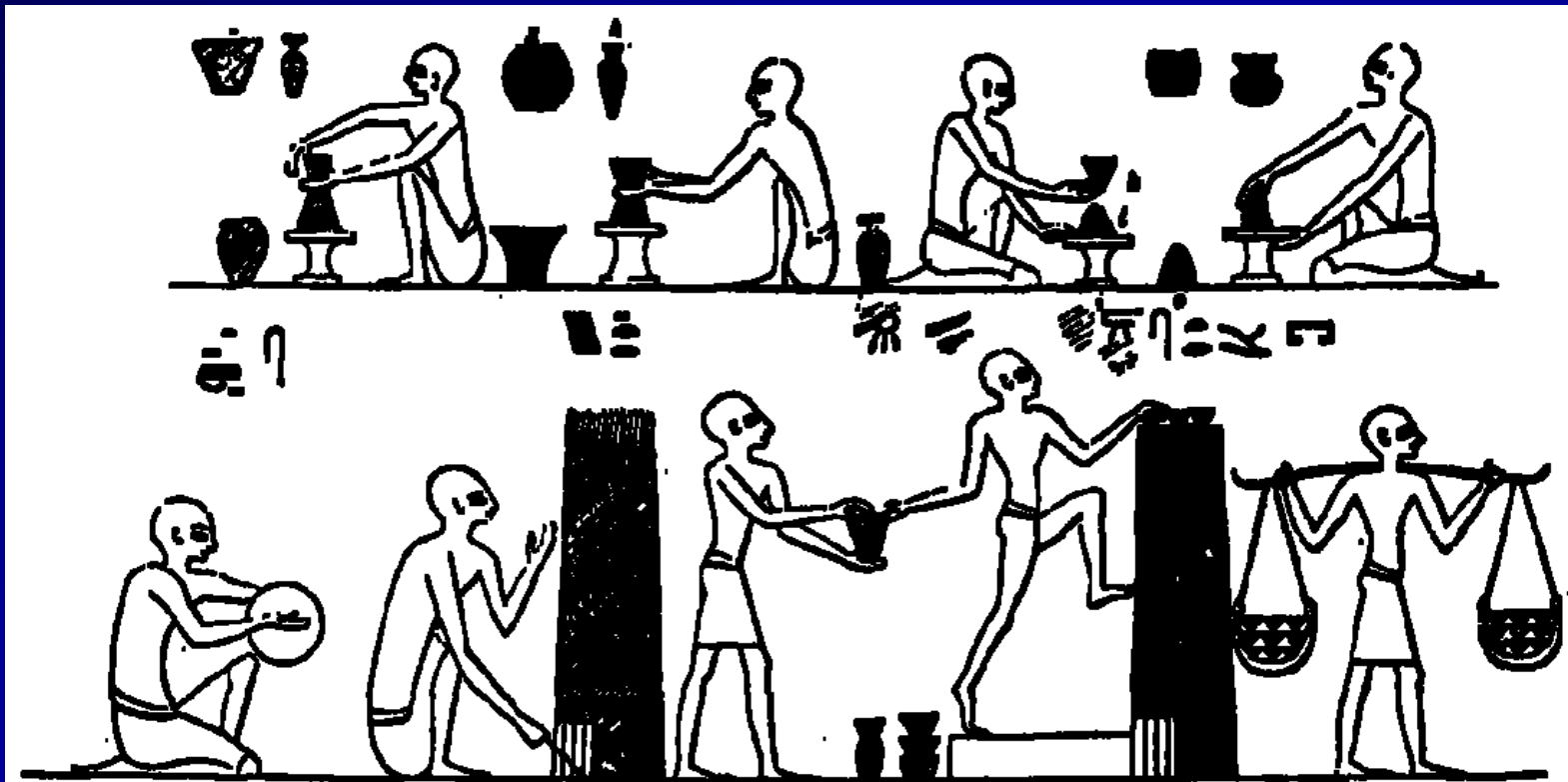
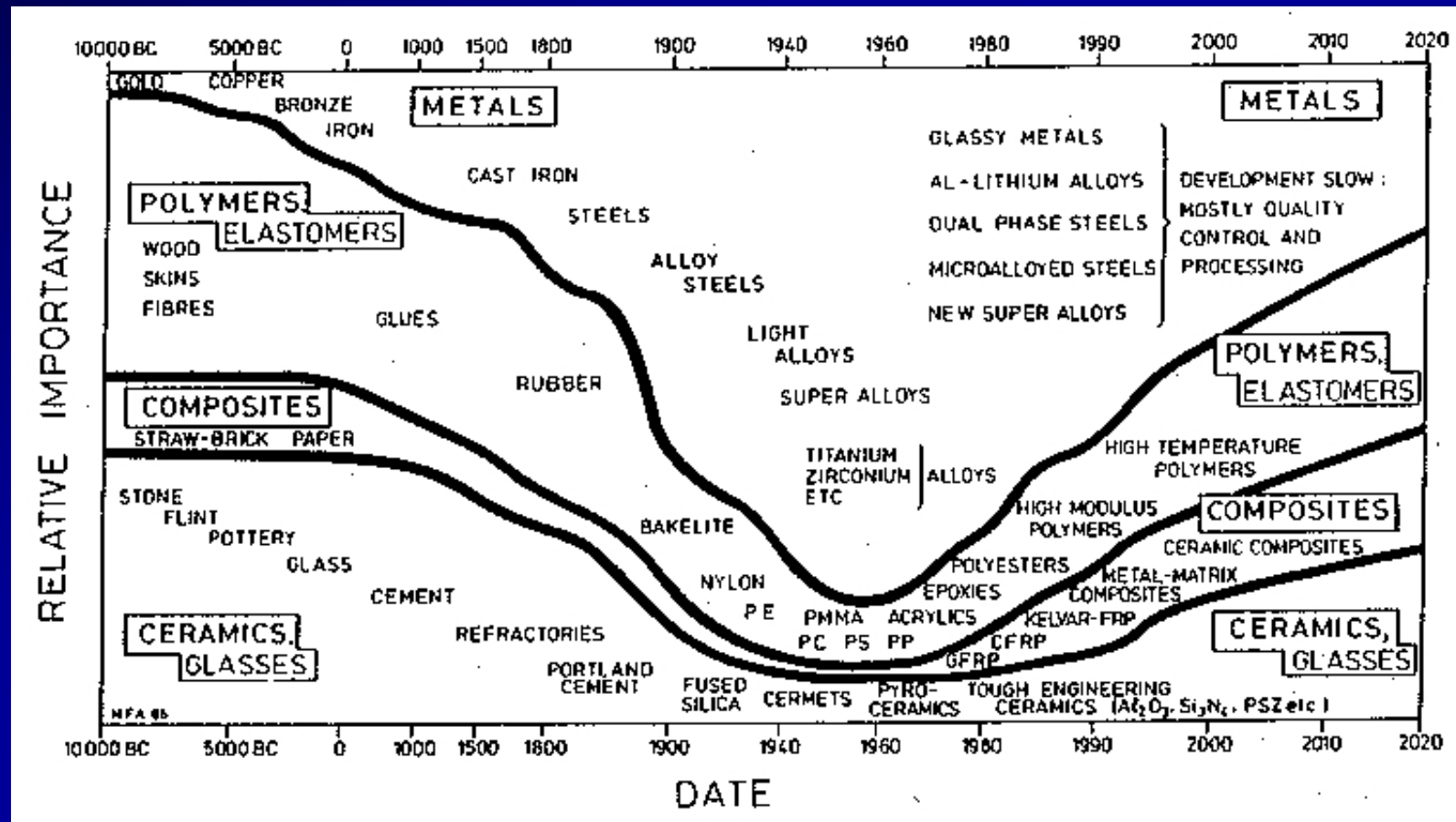


FIG. 12.—EGYPTIANS MAKING POTTERY, WITH FURNACE.
BENI HASAN, 1900 B.C.

Development of Materials in Human History



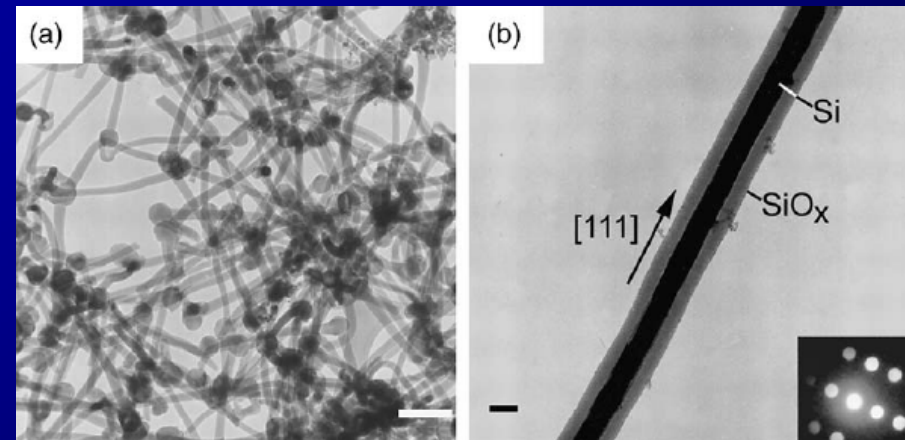
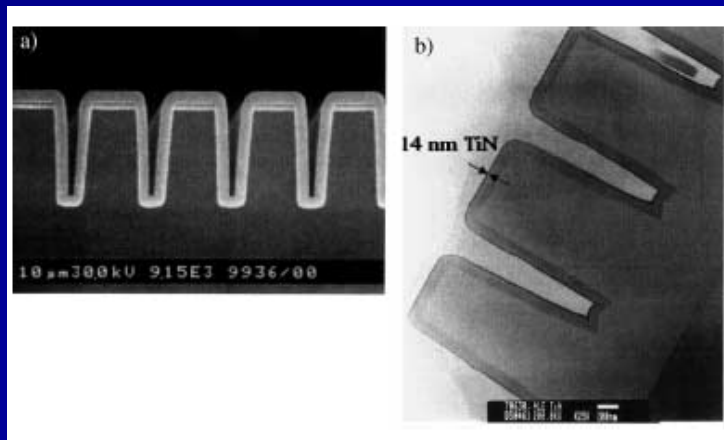
Compounds vs. Materials

- * **Chemical compounds**

 - single use** (pharmaceuticals, fertilizers, fuels)

- * **Materials**

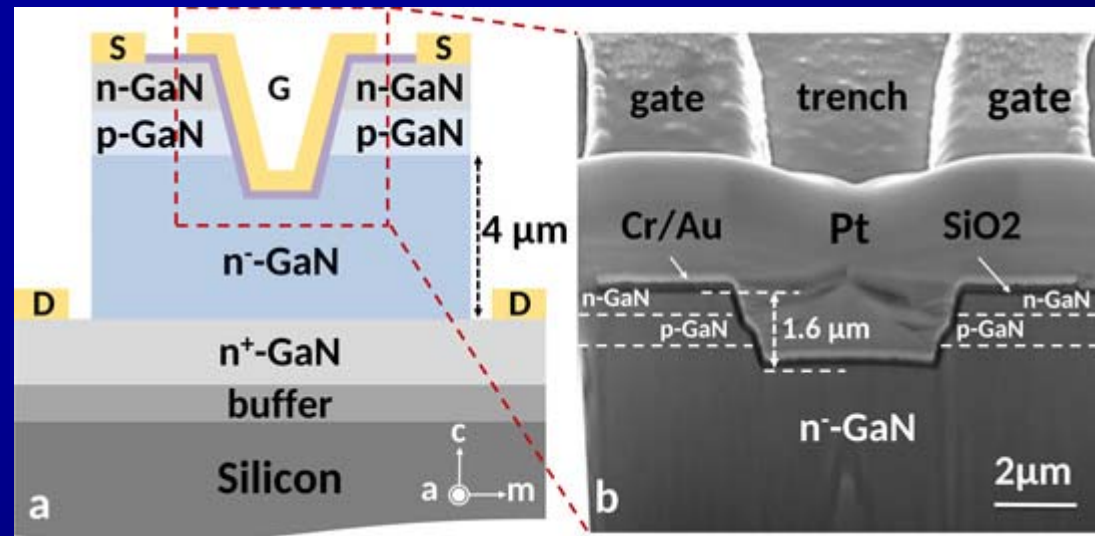
 - repeated or continual use
 - shaping



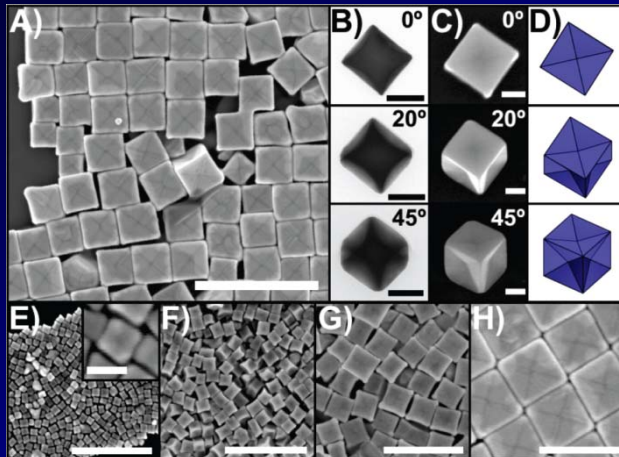
Shaping of Macro and Micro Materials



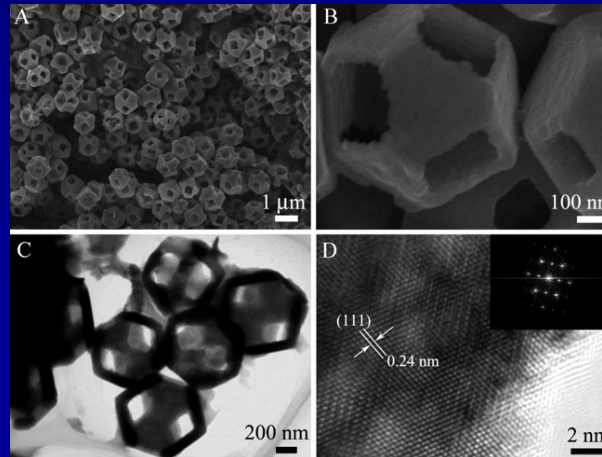
Ceramics
Glasses
Metals, Alloys
Polymers
Composites
Semiconductors



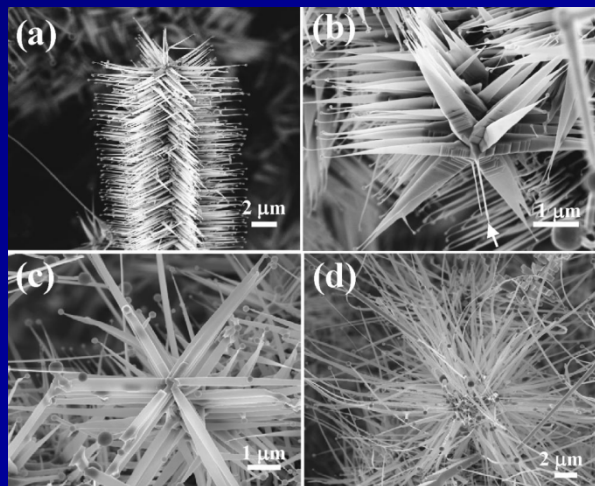
Shaping of Nanomaterials



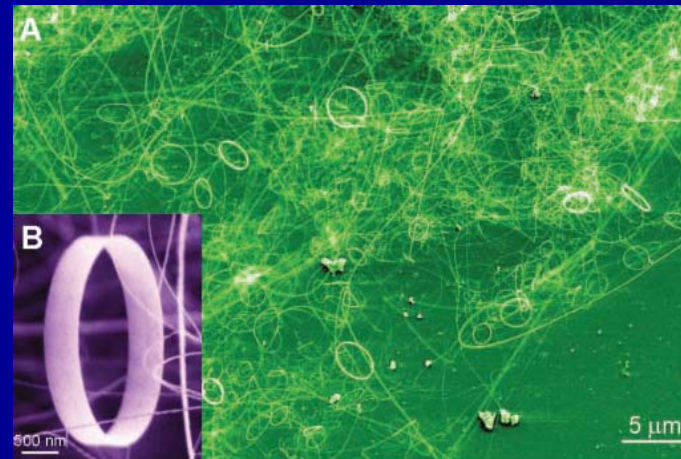
Au concave cubes



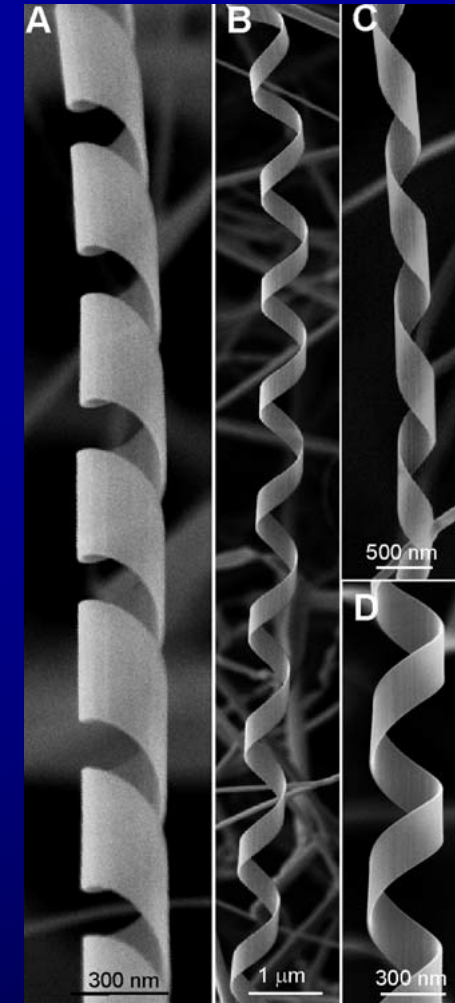
Cu₂O nanoframes



ZnO nanopropellers



ZnO nanorings



ZnO nanobelts

Classes of Materials

Ceramics (oxides, carbides, nitrides, borides)

Glasses (oxides, fluorides, chalcogenides, metallic)

Metals, Alloys, Intermetallics

Polymers - inorganic, organic, hybrid

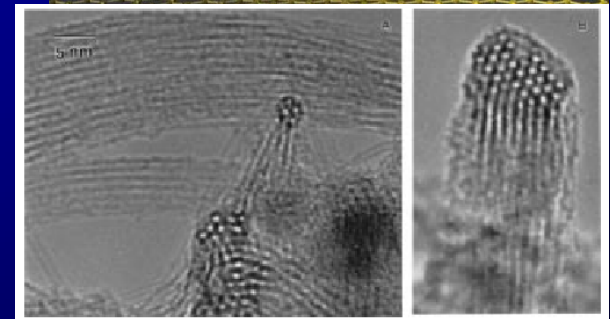
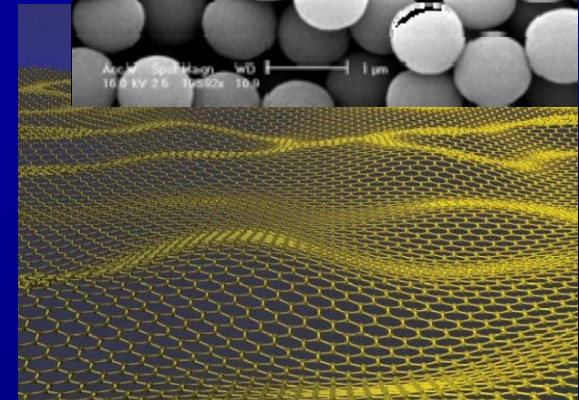
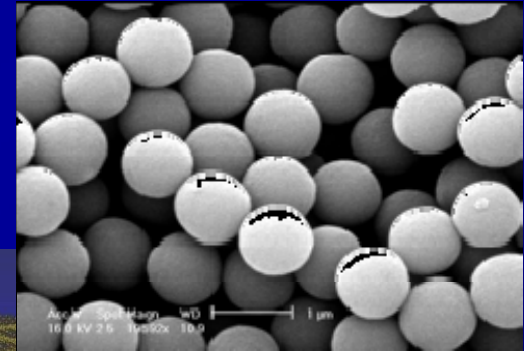
Semiconductors (Si, Ge, 13/15, 12/16 compounds)

Composites, Inorganic-Organic Hybrid Materials

Zeolites, Layer and Inclusion Materials

Biomimetic Materials, hydroxyapatite

Carbon-based Materials: Fullerenes, Fullerene Tubes, Graphene



Three Classical Classes of Materials

Metals	Ceramics	Polymers
Strong	Strong	Usually not strong
Ductile	Brittle	Very ductile
Electrical Conductor	Electrical Insulator	Electrical Insulator
Heat Conductor	Thermal Insulator	Thermal Insulator
Not transparent	May be transparent	Not transparent
Shiny	Heat Resistant	Low Densities

Properties of Materials

A property = a material trait, the kind and magnitude of response to a specific stimulus

Properties

Mechanical

Electrical

Thermal

Magnetic

Optical

Deteriorative (corrosion)

Catalytic

Biocompatibility

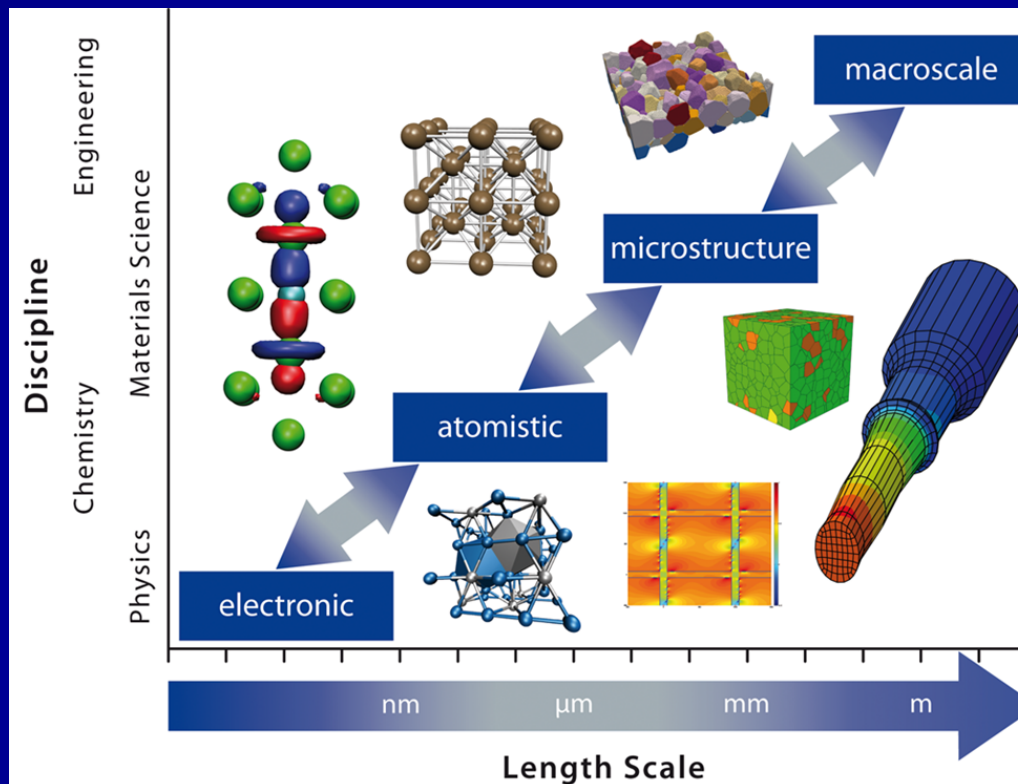
Materials Science:

Studies relationships between the structure and properties of materials

Materials Engineering:

Designing and engineering the structure of a material to produce a predetermined set of properties

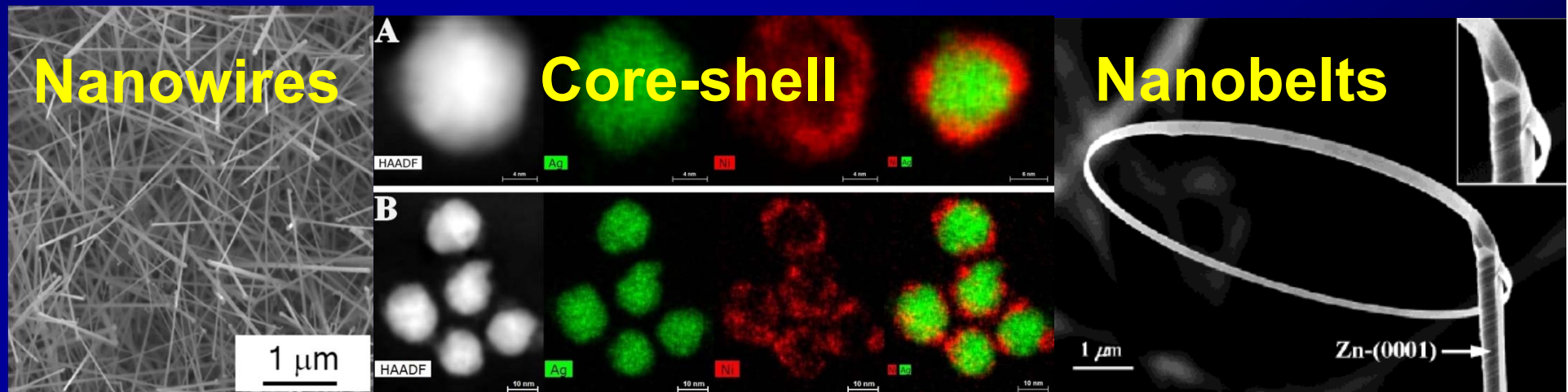
Processing Structure Properties Function



Materials Chemistry

Role of Materials Chemistry

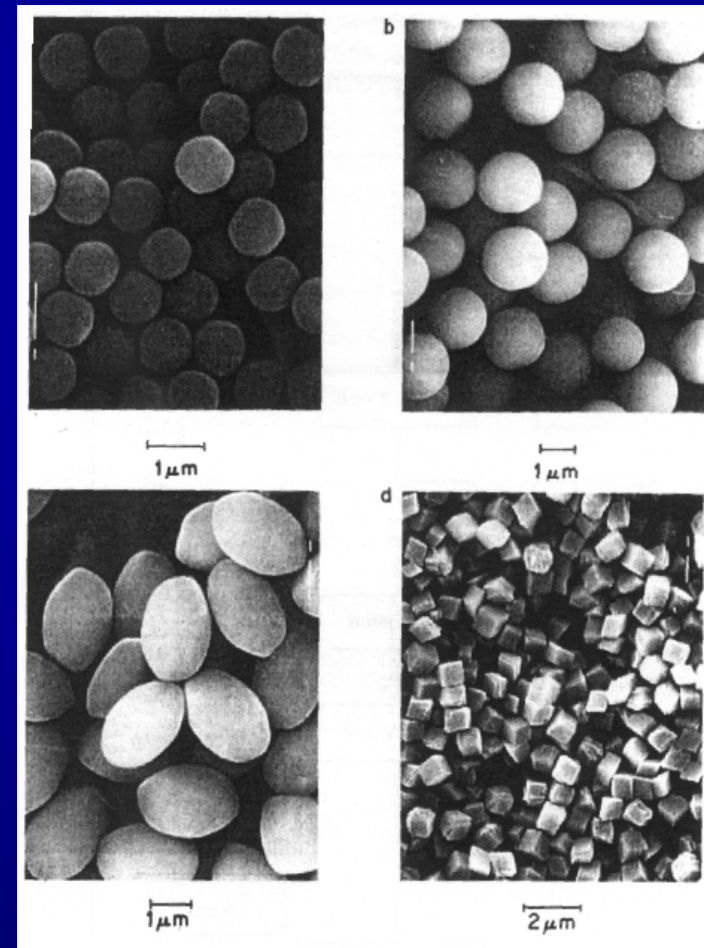
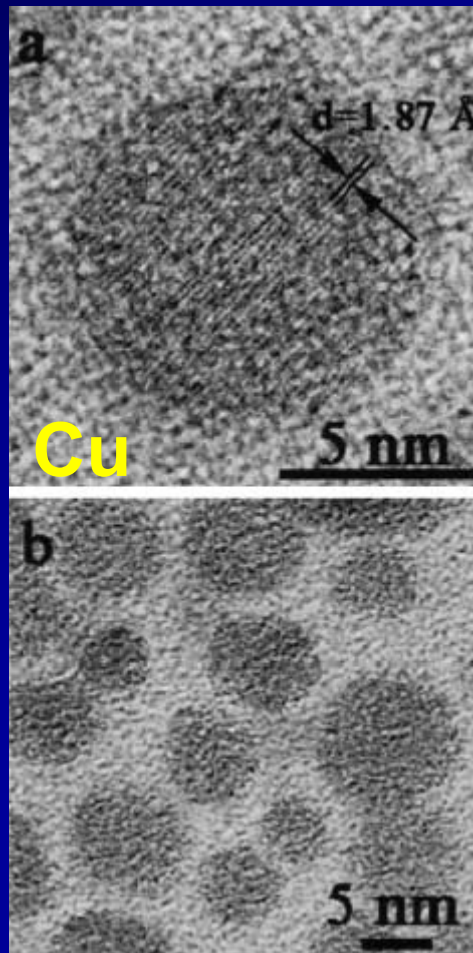
- Synthesis of new materials – new atom architecture
- Preparation of high purity materials
- Fabrication techniques for tailored morphologies (shapes and sizes)
- Fabrication of functional materials



Size of Particles

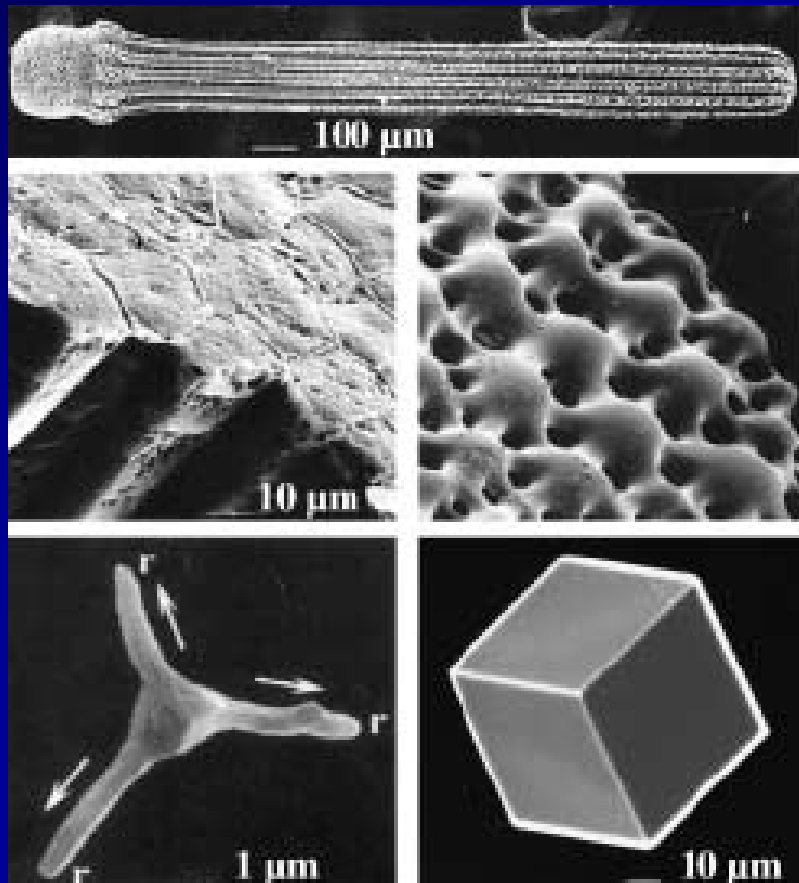
Nanoparticles 1 – 100 nm

Traditional materials > 1 mm

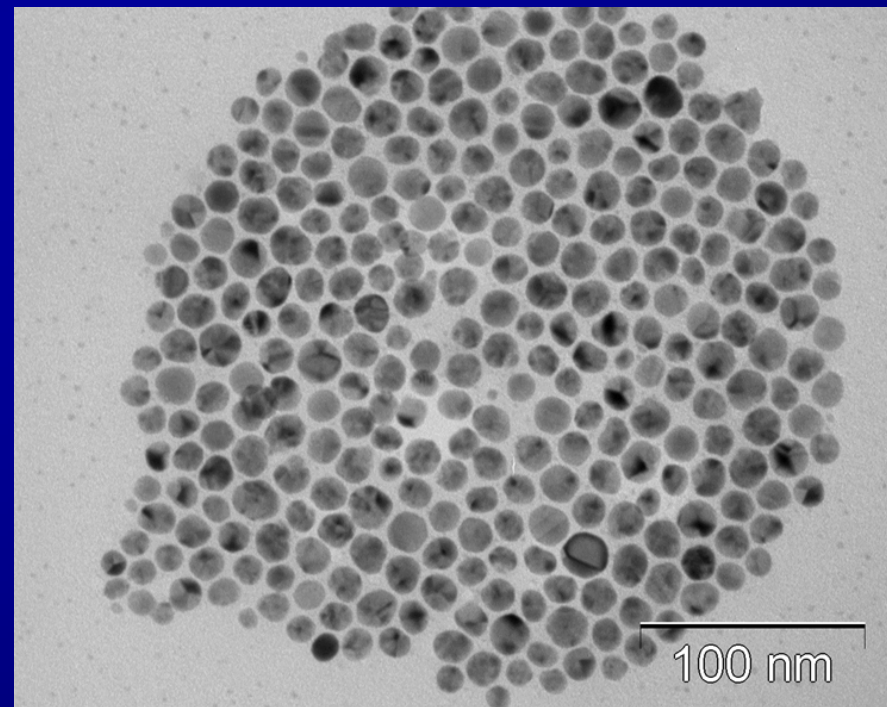


Shapes of Natural and Synthetic Single Crystals

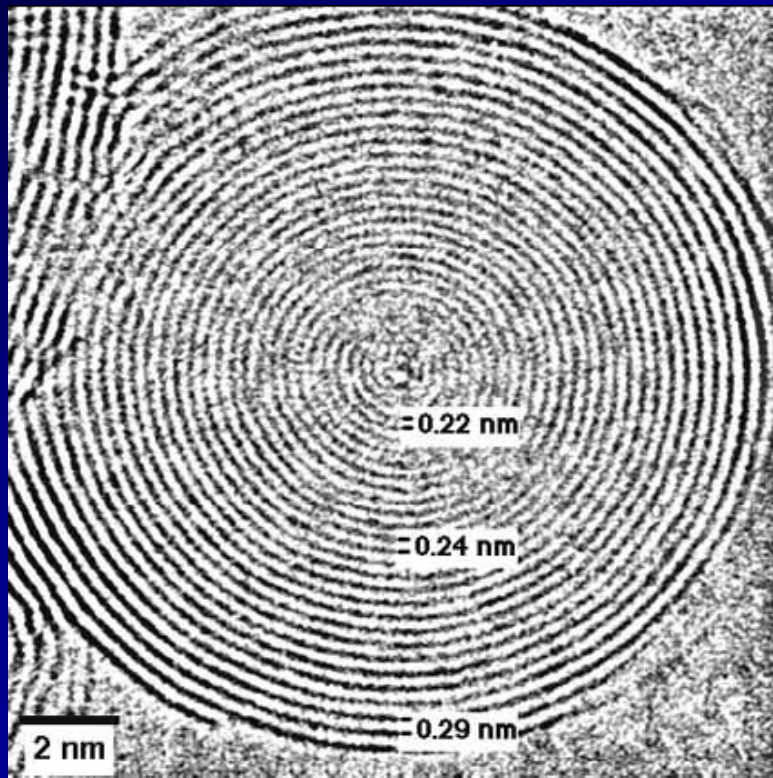
Calcite CaCO_3



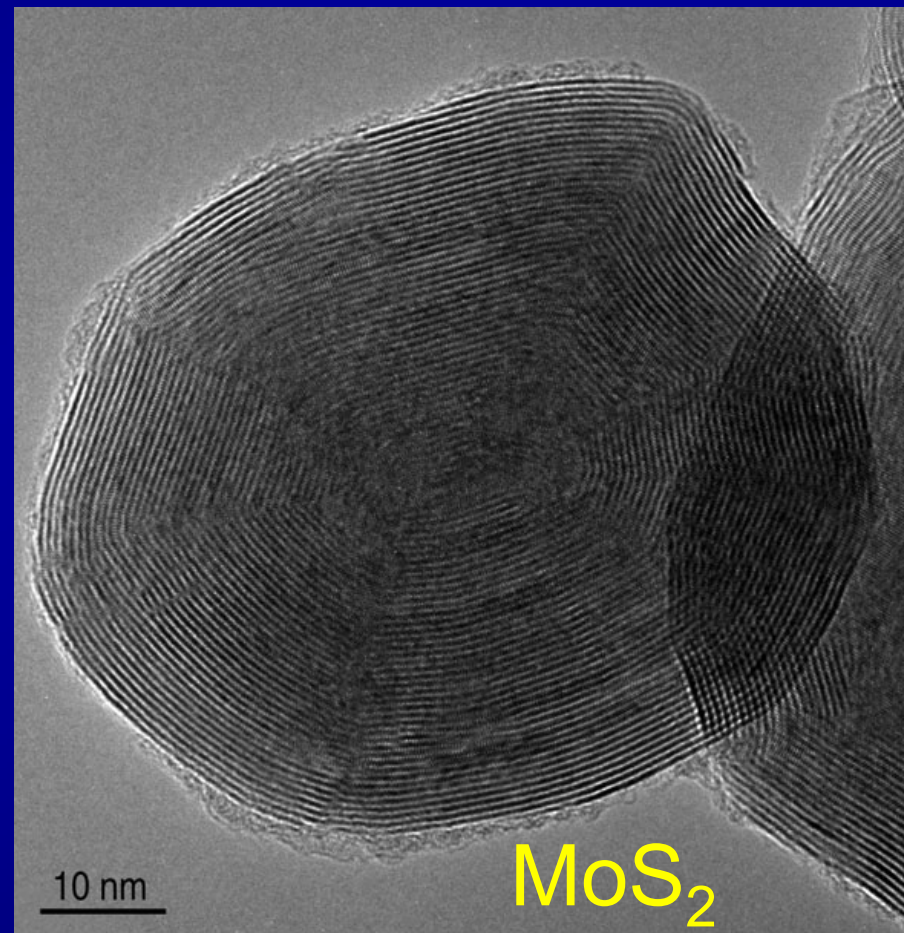
Cu-Ag nanoalloy



Onion-Like Particles

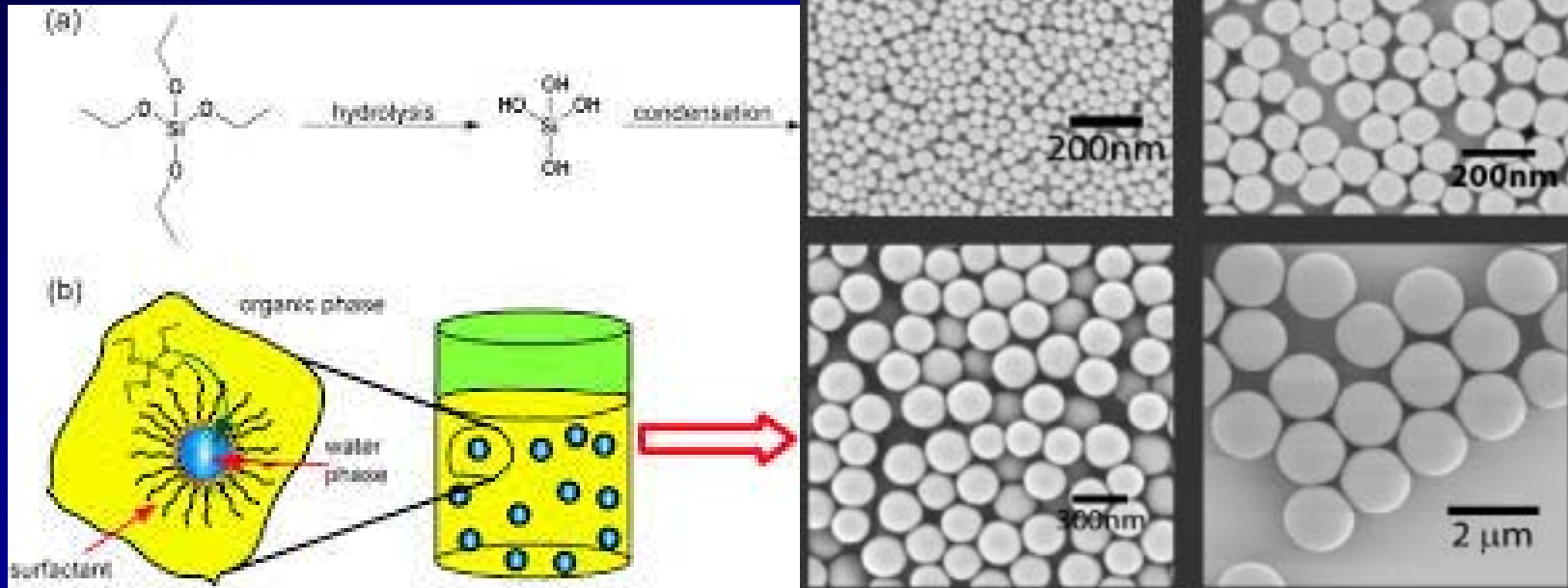


Graphitic

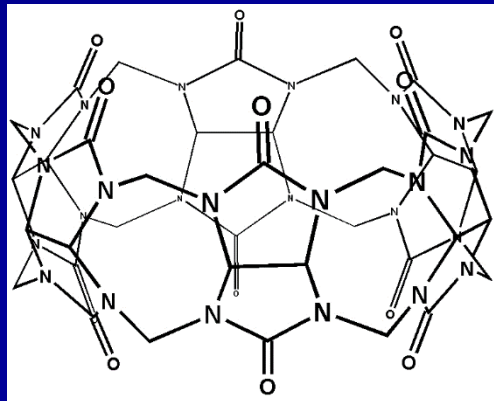


Functional Materials

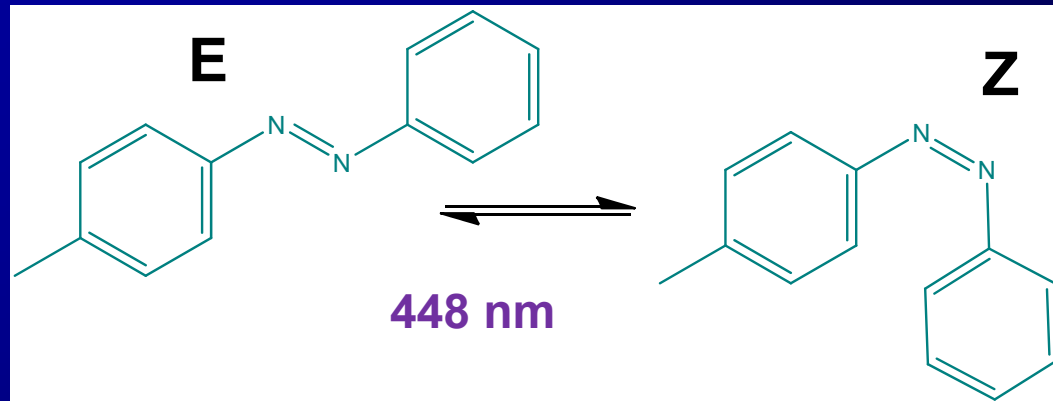
Synthesis of porous SiO₂ nanospheres



CB[6] = cucurbit[6]uril



Dynamic wagging motion by Z-E interconversion



Functional Materials

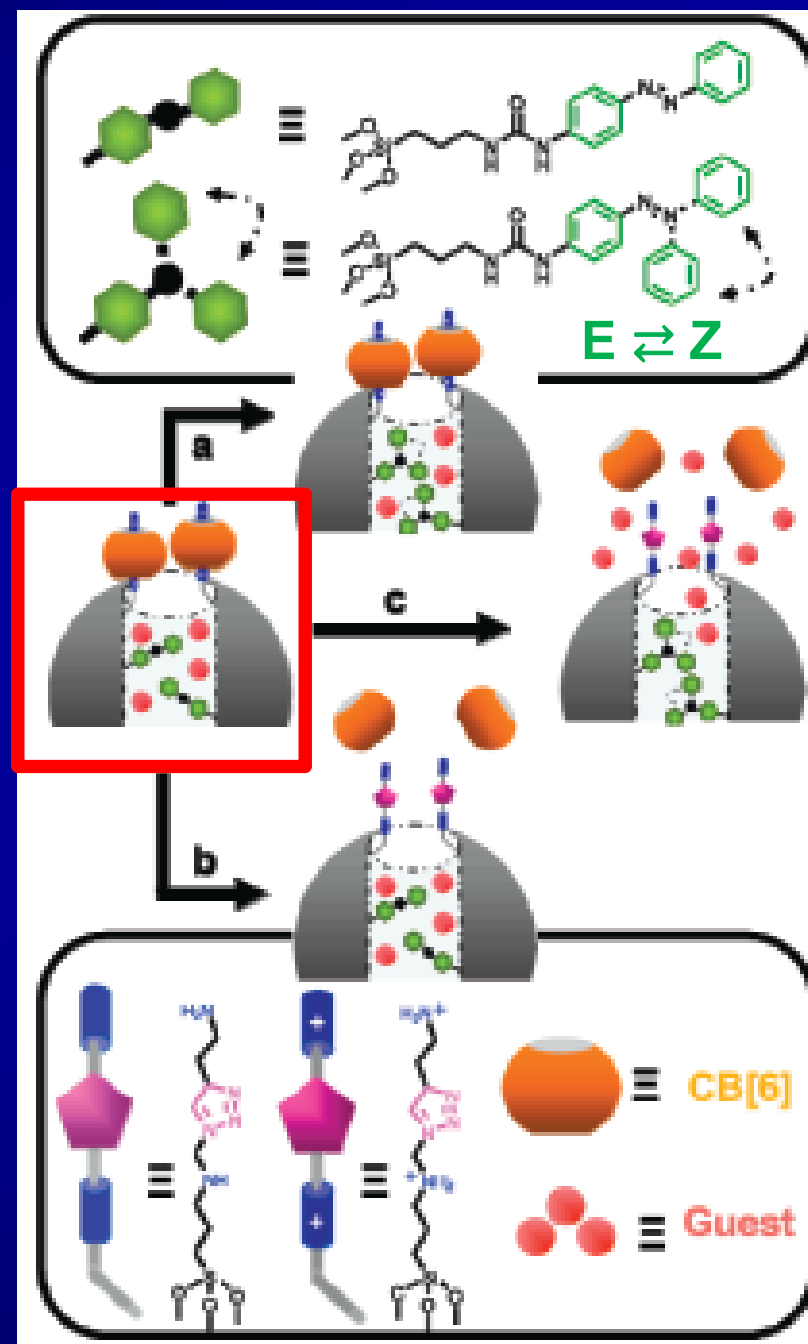
Dual-controlled nanoparticles exhibiting AND logic function

(a) Excitation with 448 nm light induces the dynamic wagging motion of the nanoimpellers, but the nanovalves remain shut and the contents are contained

(b) Addition of NaOH opens the nanovalves, but the static nanoimpellers are able to keep the contents contained

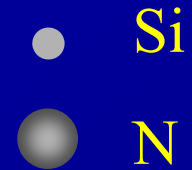
(c = a + b) Simultaneous excitation with 448 nm light AND addition of NaOH causes the contents to be released

CB[6] = cucurbit[6]uril

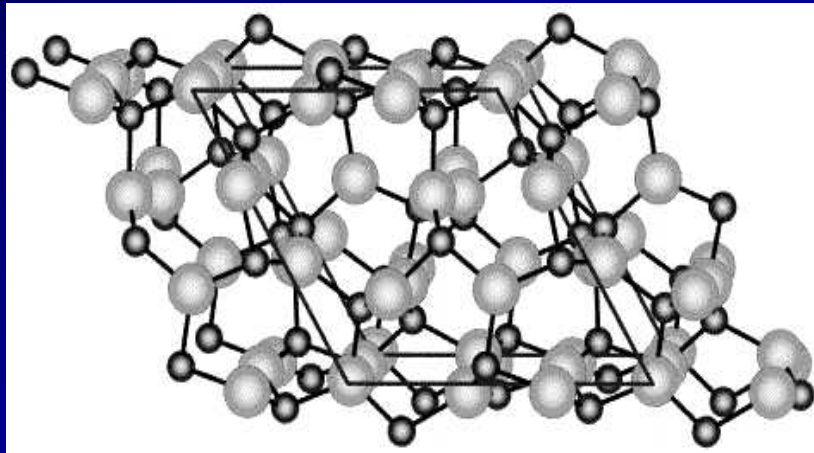


Functional Materials - Si_3N_4

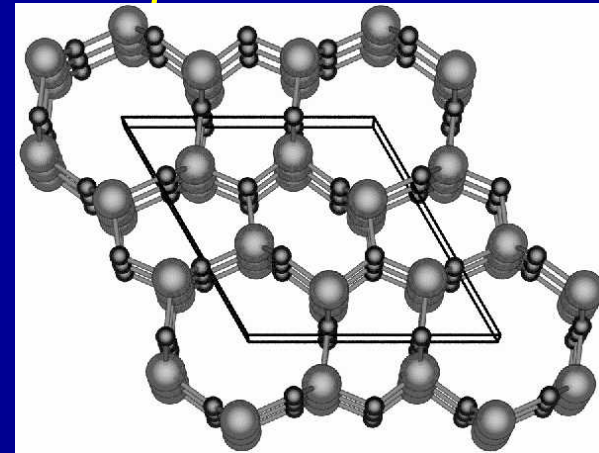
Hexagonal



α modification

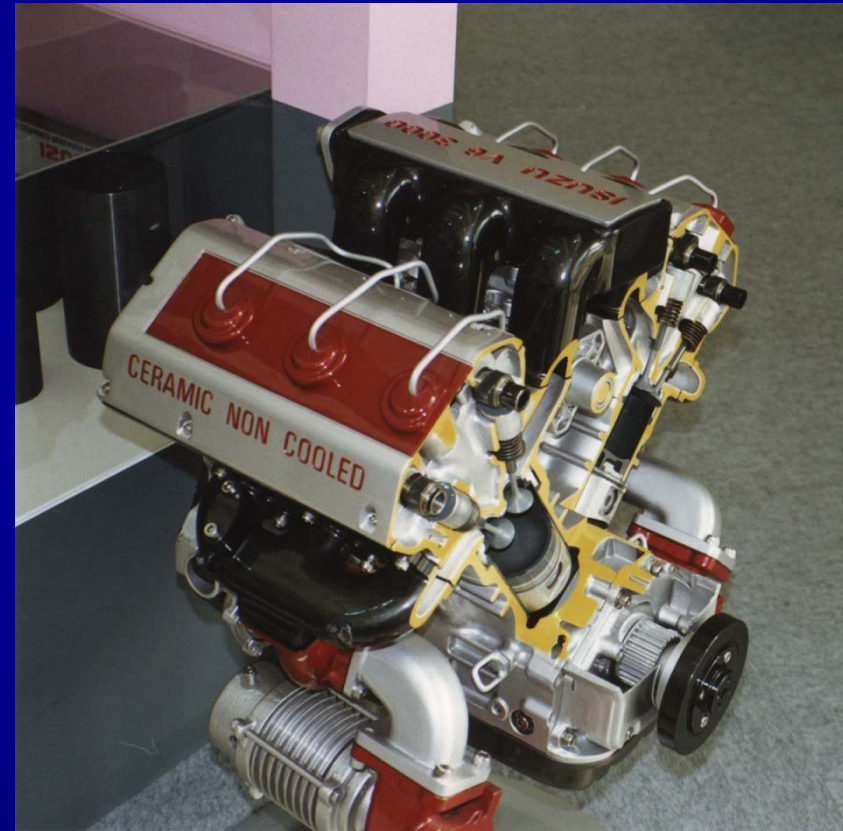
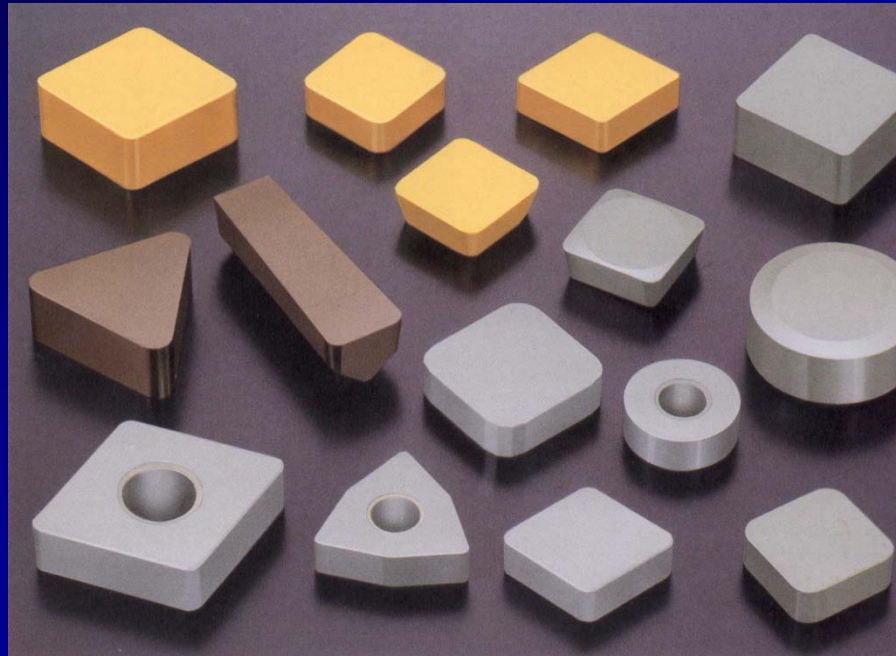


β modification



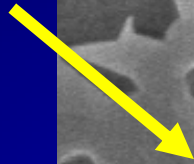
- Strong covalent bond (4.9 eV)
- Hardness (α -monocrystal, Vickers 21 GPa)
- Tensile Strength 1.5 GPa (β -whisker)
- Young modulus 350 GPa
- Decomposition temp. 1840 °C/1 atm N_2
- Density 3.2 g cm^{-3}

Si_3N_4 Ceramics

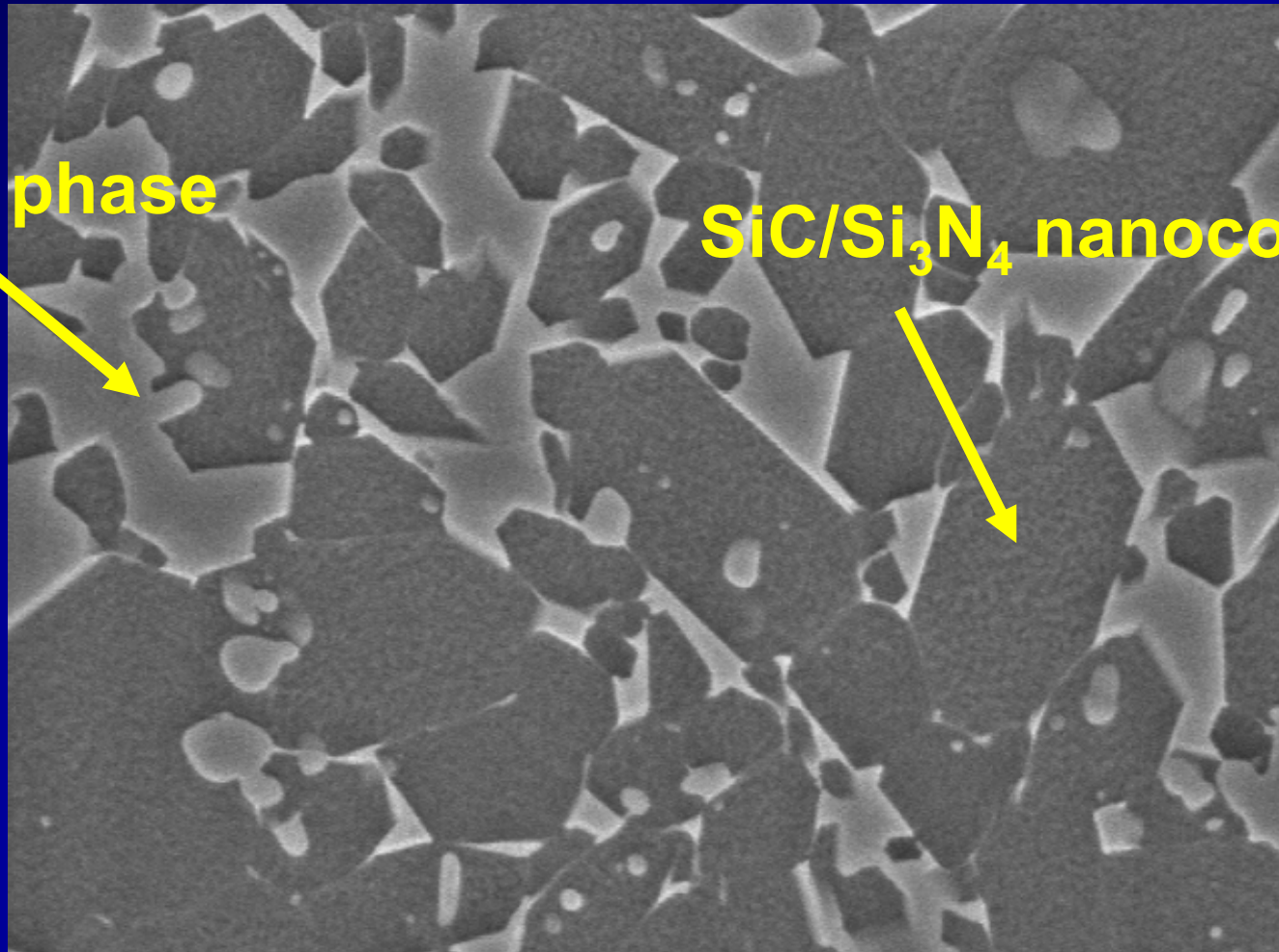
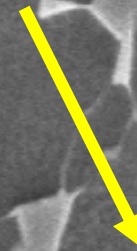


Microstructure of Materials

Glass phase



SiC/Si₃N₄ nanocomposite



x50000
#682011

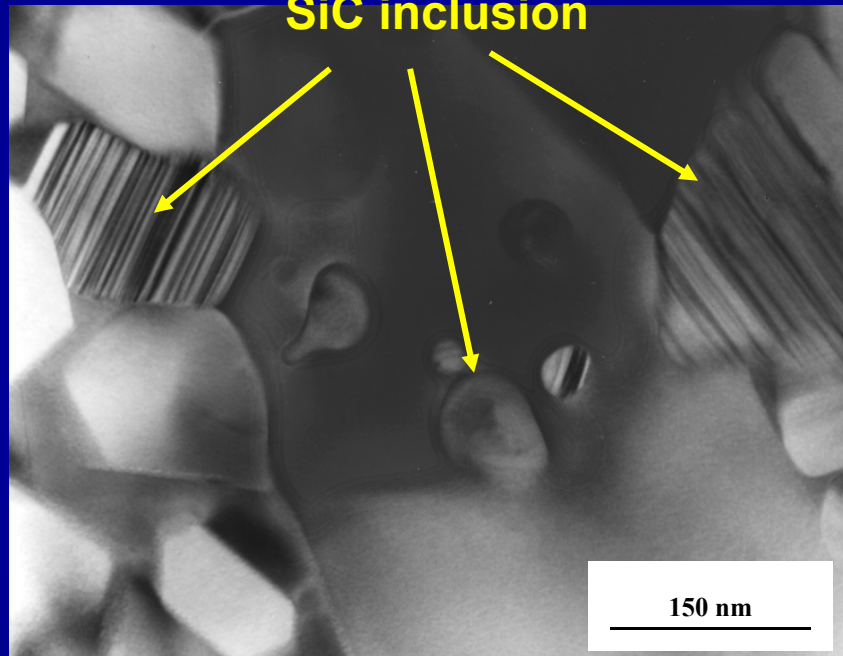
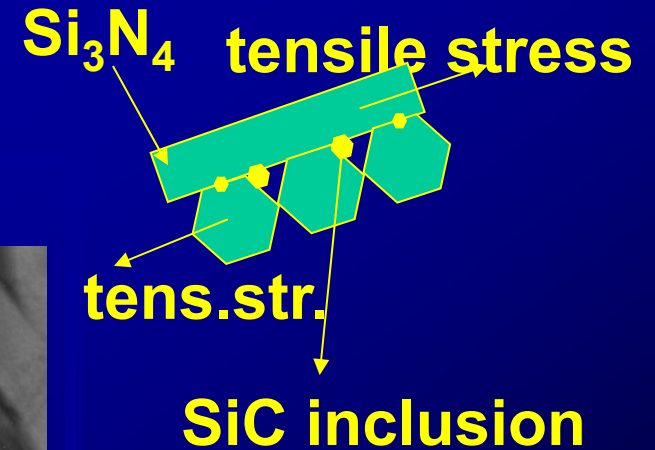
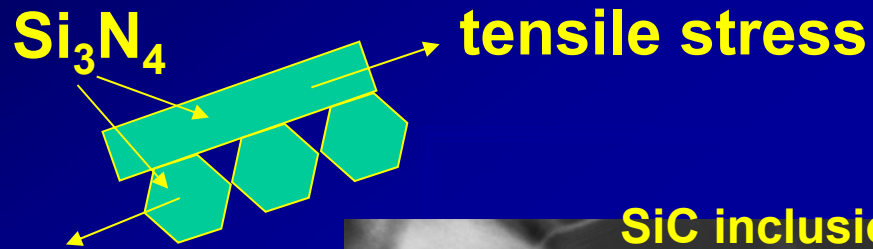
500nm
MPI/ALD/REM LA

3.00kV 2mm
DSM 982 GEMINI

Microstructure vs. Properties

Sliding of grains

Sliding of grains slowed down
improved mechanical properties



Materials Chemistry

Single crystals, defects, dopants, non-stoichiometry

Monoliths

Coatings

Thin or thick films - singlecrystalline, polycrystalline, amorphous, epitaxial

Fibers, Wires, Tubes

Powders – primary particles, aggregates, agglomerates
polycrystalline, amorphous, nanocrystalline (1-100 nm)

Porous materials

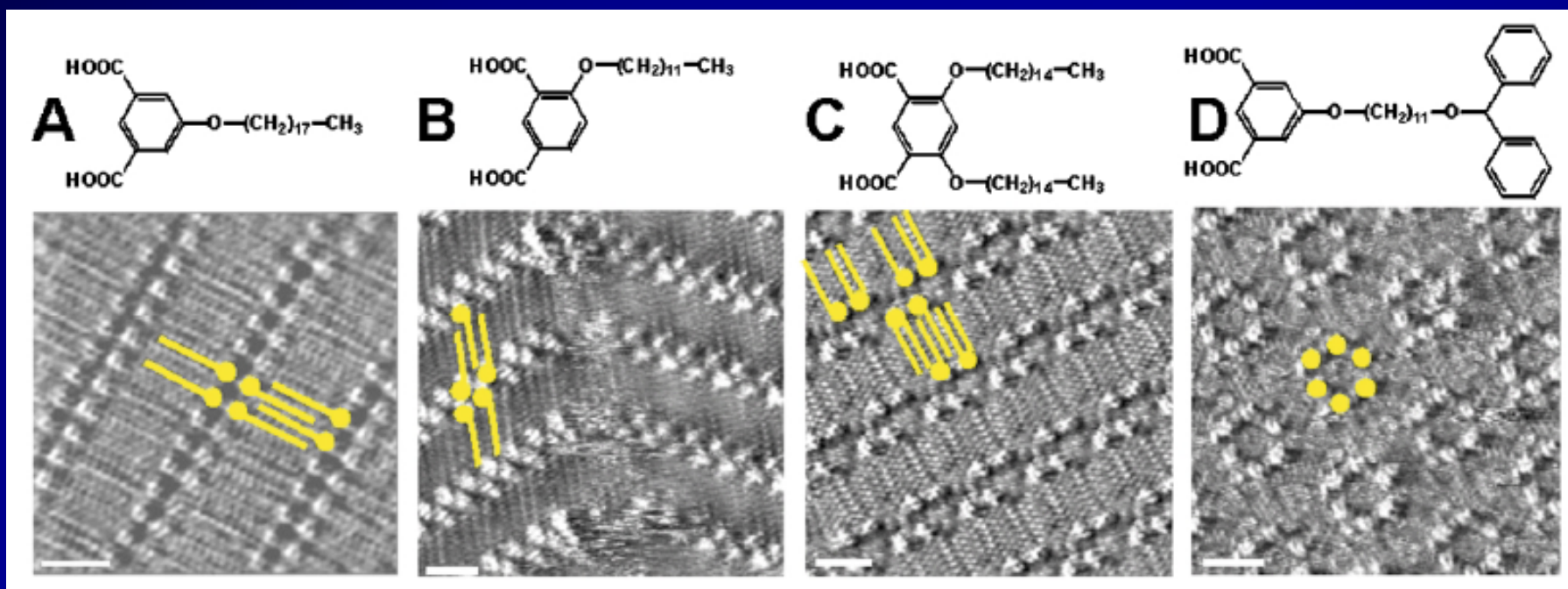
micropores ($< 20 \text{ \AA}$), mesopores (20-500 \AA), macropores ($> 500 \text{ \AA}$)

Micropatterns

Nanostructures – spheres, hollow spheres, rods, wires, tubes, photonic crystals

Self-assembly – supramolecular chemistry: rotaxenes, catenanes, cavitands, carcerands

Self-Assembling Monolayers



STM on HOPG

Materials Chemistry Tool Box

Direct reactions of solids – „heat-and-beat“

Precursor methods

Chimie douce, soft-chemistry methods, synthesis of novel metastable materials, such as open framework phases

Ion-exchange methods, solution, melt

Intercalation: chemical, electrochemical, pressure, exfoliation-reassembly

Crystallization techniques, solutions, melts, glasses, gels, hydrothermal, molten salt, high P/T

Vapor phase transport, synthesis, purification, crystal growth, doping

Materials Chemistry Tool Box

Electrochemical synthesis, redox preparations, anodic oxidation, oxidative polymerization

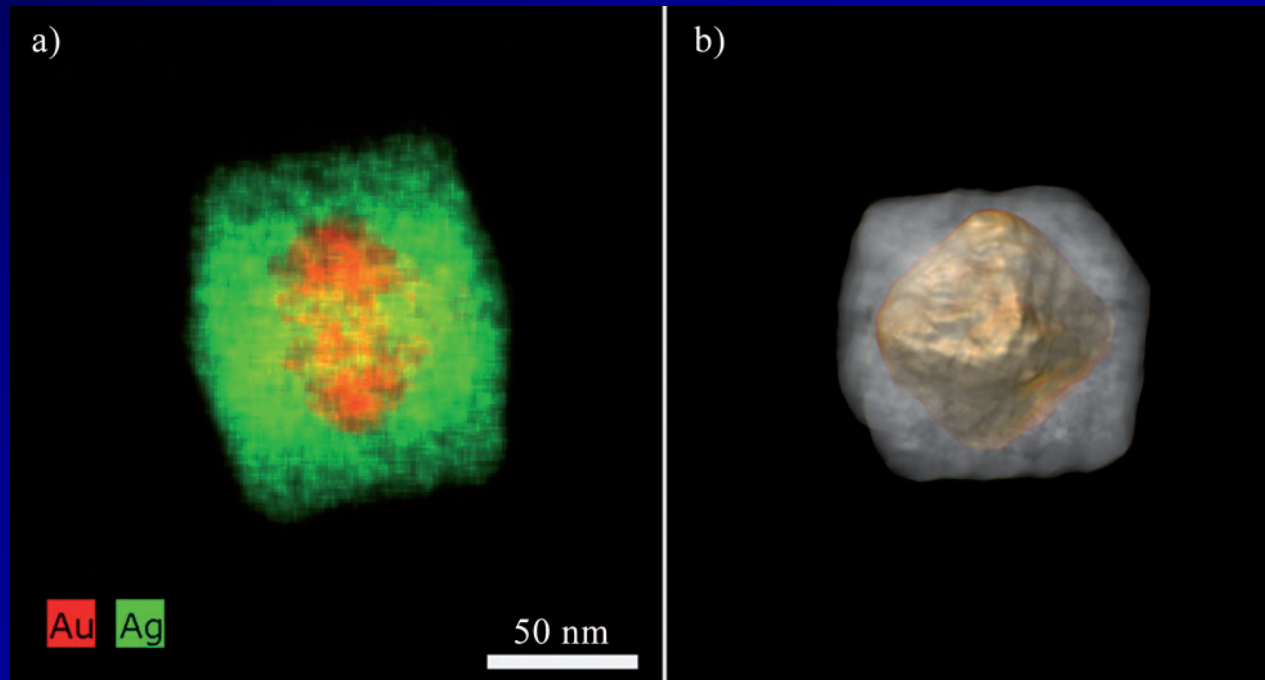
Preparation of thin films and superlattices, chemical, electrochemical, physical, self-assembling mono- and multilayers

Growth of single crystals, vapor, liquid, solid phase chemical, electrochemical

High pressure methods, hydrothermal, diamond anvils

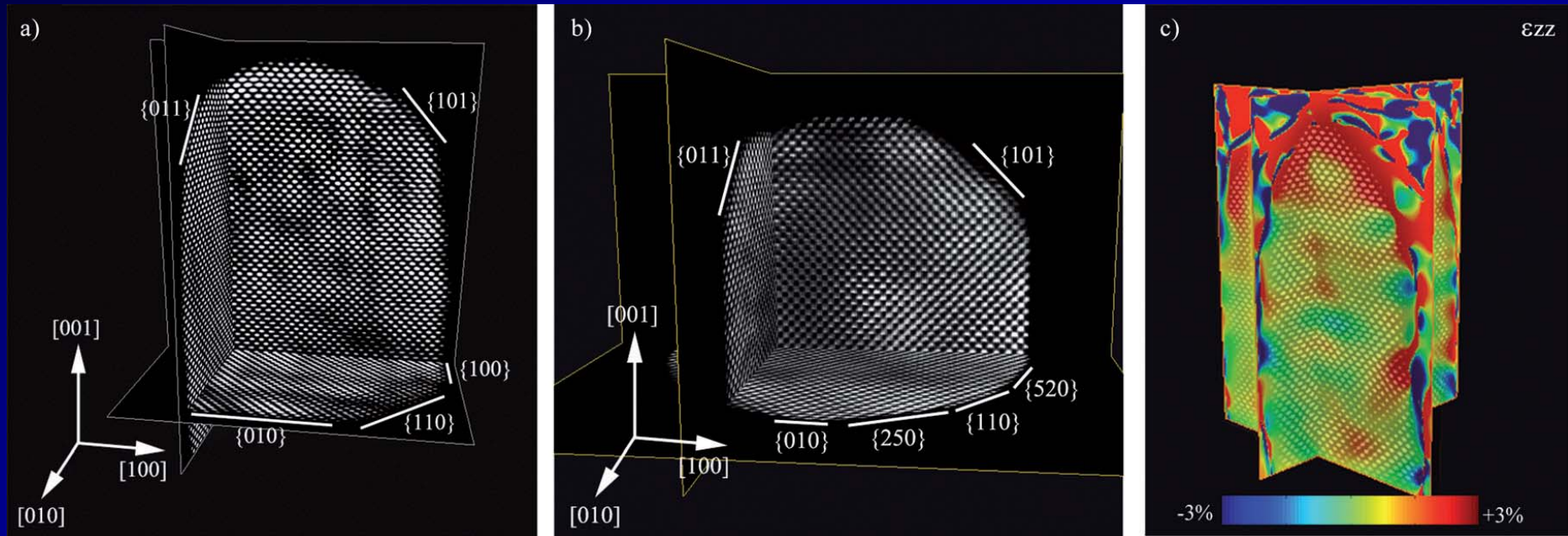
Combinatorial materials chemistry, creation and rapid evaluation of gigantic libraries of related materials

STEM - Imaging at Nanoscale



a) 2D EDX map of a Au@Ag nanocube. Based on a tilt series of 2D EDX maps the 3D reconstruction presented in (b) was obtained. The contrast in the 3D reconstruction is based on differences in chemical composition and it is clear that the core of the particle has an octahedral form.

TEM - Atomic Scale Imaging



Atomic scale reconstruction of Au nanorods. a,b) Orthogonal slices through the atomic scale reconstruction of Au nanorods prepared using different surfactants. The side facets of these rods can be clearly recognized. c) Strain measurement along the major axis of the nanorod.