Zero-Dimensional Nanostructures: Nanoparticles (1)

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Outline

- Introduction
- Ball Milling

- ***Nanoscience*** → the study of the phenomena at 1-100 nm
- ***Nanomaterials*** → *those which have structured components with at least one dimension less than 100 nm*

Zero-Dimensional Nanostructures → Nanoparticles

One-Dimensional Nanostructures → Nanowires and Nanorods

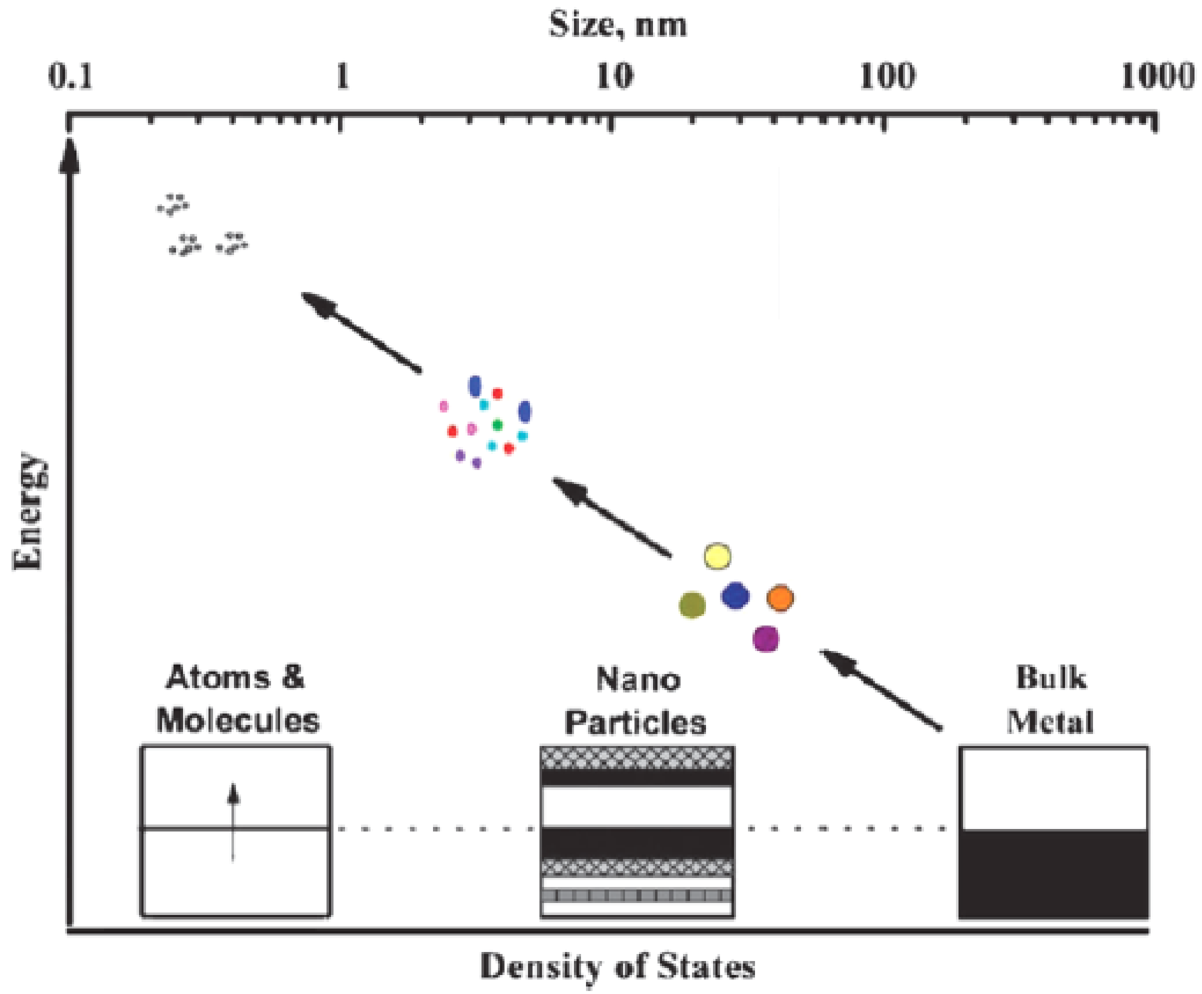
Two-Dimensional Nanostructures → Thin Films

- ***Nanoparticles*** are nanosized structures in which at least one of its phases has one or more dimensions (length, width or thickness) in the nanometer size range (1 to 100 nm) as depicted in figure 1.

The main characteristics of MNPs

- large surface-area-to-volume ratio as compared to the bulk equivalents;
- large surface energies
- the transition between molecular and metallic states providing specific electronic structure (local density of states LDOS);
- plasmon excitation;
- quantum confinement;
- short range ordering;
- increased number of kinks;
- a large number of low-coordination sites such as corners and edges, having a large number of ˝dangling bonds˝ and consequently specific and chemical properties and the ability to store excess electrons.

Figure 4. Relationship between nanoparticle size, energy and the principle of energy of states [Robin J. White-Chem. Soc. Rev, 2009, 38].



WHY "NANO"

Nanomaterials have superior properties than the bulk substances :

- Mechanical strength
- Thermal stability
- Catalytic activity
- Electrical conductivity
- Magnetic properties
- Optical properties
- ....

A wide range of applications:

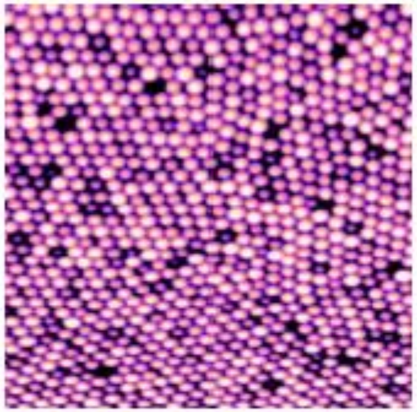
Quantum electronics, nonlinear optics, photonics, sensing, information storage and processing, adsorbents, catalysis, solar cells, superplastic ceramics…

New fields:

Nanofabrication, nanodevices, nanobiology, and nanocatalysis

Synthesis of Nanoparticles

- Mechanical
  - Ball milling
  - Attrition* milling
  - Mechanochemical processing
- Wet Chemistry
  - Sol Gel
  - Colloid chemistry
  - Impregnation
  - Super critical fluids



*Attrition: the act of rubbing together : friction; *also* : the act of wearing or grinding down by friction

- Gas Phase Synthesis
  - Plasma
  - Laser oblation
  - Chemical vapor synthesis
- Form in Situ
  - Lithography
  - Vacuum deposition
  - Spray Coating
- Thermal Routes
  - Aerosol reactor
  - Self propagating high temperature synthesis (SHS)
  - Exploding wire
- Others
  - Biomimetric
  - Microwave techniques
  - Ultrasound techniques

Ball Milling

(Mechanical alloying, Ball Milling)
Synthesis at room temperature, production of amorphous phase and intermetallic compounds, activation of sintering, obtaining nanoparticles and nanocomposites…

Main Processes

1a) Destruction of material, rupture of chemical bonds, formation of fresh surface

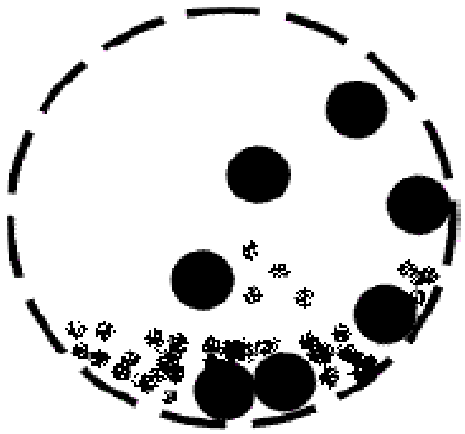
b) Aggregation, "Cold Welding"

2) Plastic deformation and deformation mixing

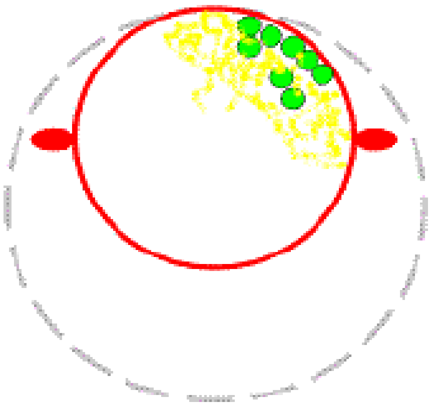
Zirconia (YSZ) grinding media is the most durable and efficient media for ball milling and attrition milling of ceramic materials.

Ball Milling

ball milling



High-energy ball milling



A ball mill, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. Ball mills rotate around a horizontal axis, partially filled with the material to be ground plus the grinding medium. Different materials are used as media, including ceramic balls, and stainless steel balls. An internal cascading effect reduces the material to a fine powder.

Ball Milling

1. Dry mechanical attrition of ceramic materials (purely elastic) to particles below ~ 1 μm is limited by the appearance of plastic deformation. This unusual phenomenon is probably caused by extremely high local temperatures developing in the grains. Wet grinding aided by chemical additives allows finer products, however, nanosized particles usually cannot be attained in ordinary mills. Therefore, the milling effectiveness of ceramics is greatly reduced as the top size decreases to the micrometric range.

2. Milling of metals may cause agglomeration into bigger particles, however, the size of the crystallites may decrease down to the nano range, and even further, leading to amorphous materials.

3.Chemical changes may take place during mechanical attrition, either by annealing the solid phases into new ones, or by introducing new substances from the environment.

4. Intensive mechanical attrition causes mill erosion, introducing impurities into the milled material.

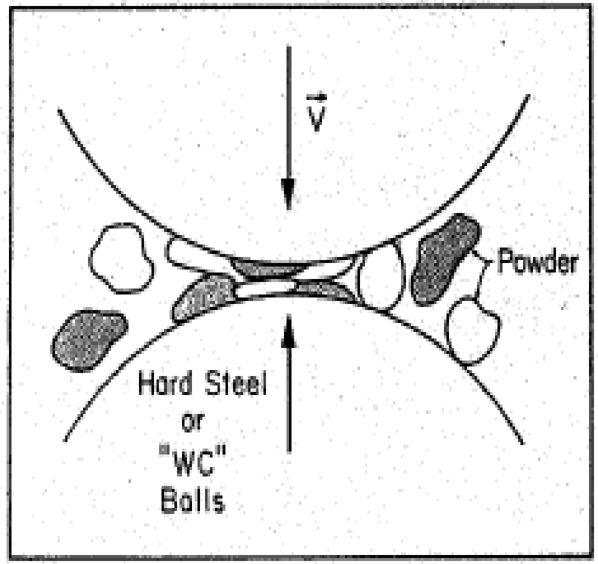


Figure 5.1. Schematic sketch of the process of mechanical attrition of metal powder.

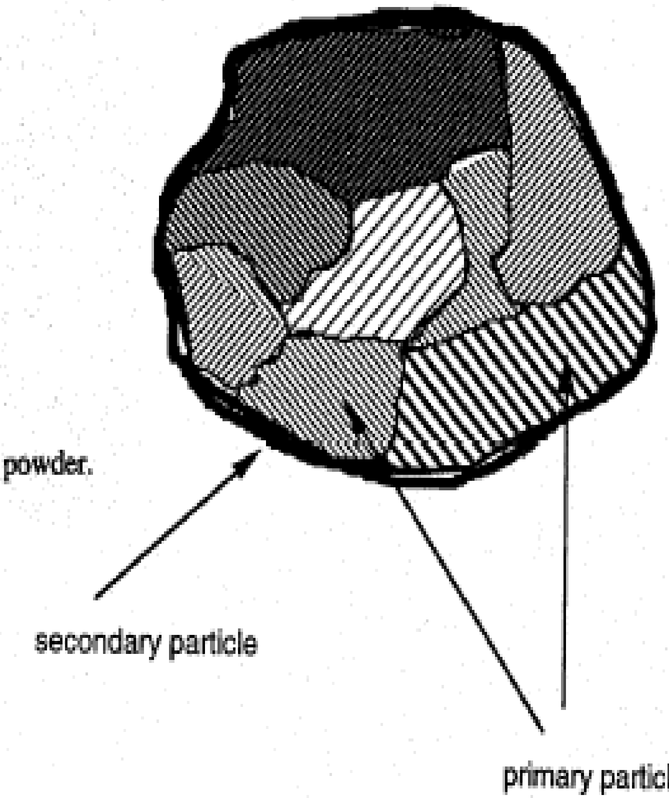


Figure 3.1. A schematic diagram showing the primary and secondary particles.

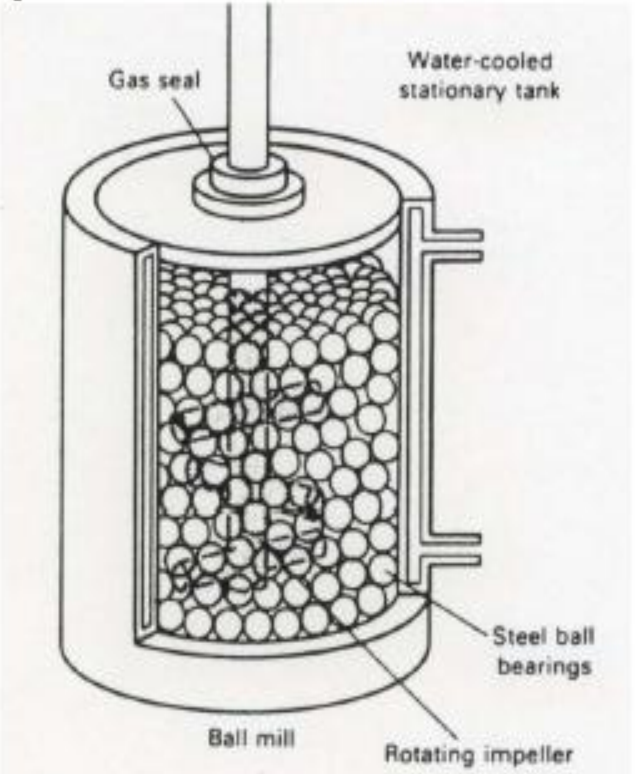
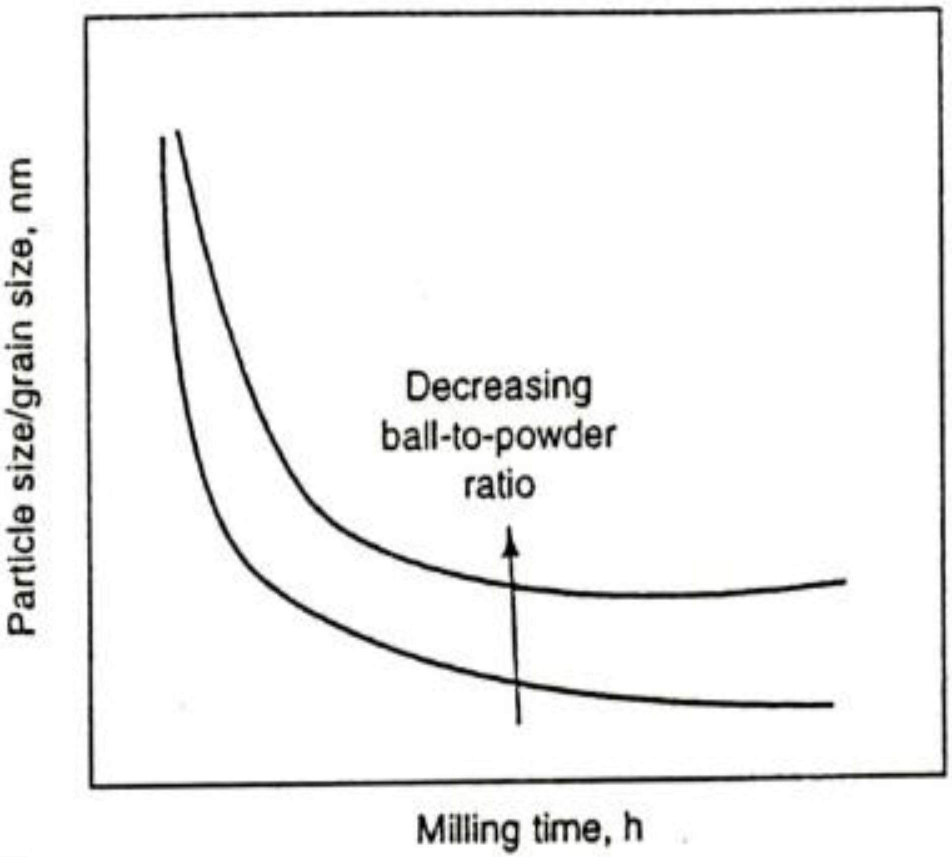
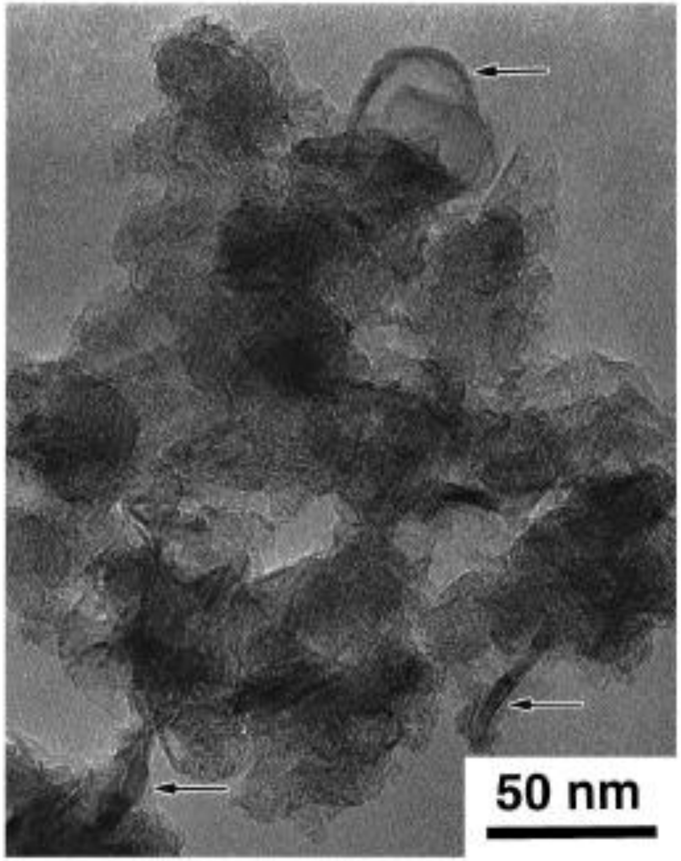


Figure 4.1. Arrangement of rotating arms on a shaft in the attrition ball-mill.



Lead antimony grinding media with aluminum powder

- To grind a sample in this device, you should already have reduced the particle size to less than 10 mm, using a mortar and pestle if necessary. Place your material in one of the bowls (shown in the lower right) and then add several balls (shown in a tray at the bottom). Samples can be run wet or dry. A cover is placed on the bowl and then the bowl is mounted in the machine. In the picture below, one bowl has been fastened down and the other has not yet been secured. Once the bowls are mounted and secured, the cover is lowered and the machine can be operated.
- Each bowl sits on an independent rotatable platform, and the entire assembly of four bowls is also rotated in a direction opposite to the direction of the bowl platform rotation. This action is a lot like the "teacup and saucer" rides commonly found in amusement parks. In planetary action, centrifugal forces alternately add and subtract. The grinding balls roll halfway around the bowls and then are thrown across the bowls, impacting on the opposite walls at high speed. Grinding is further intensified by interaction of the balls and sample. Planetary action gives up to 20 g acceleration and reduces the grinding time to about 2/3 of a simple centrifugal mill (one that simply spins around).



TEM micrograph taken from the graphite sample after milling for 15 h in a steel mill without ethanol, arrows showing the nanosized ribbons.

Ying Chen et al, APL, 74(19), 1999, 2782-2784

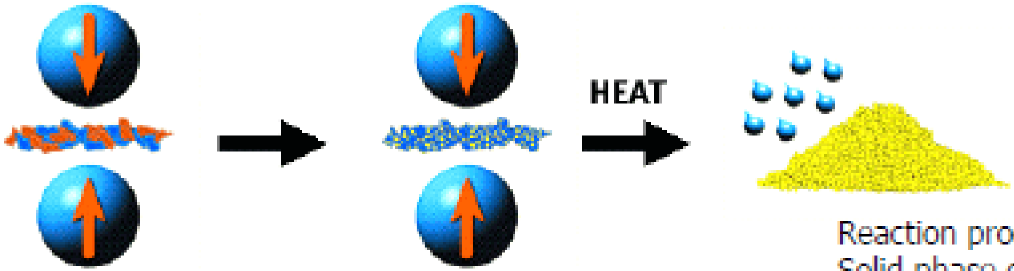
Advantages and disadvantages

- Broad size distribution
- Varied particle shape or geometry
- Significant amount of impurities from the milling medium
- Significant amount of defects resulting from milling
- Difficult to design and control so as to produce desired particle size and shape

- Commonly used in the nanocomposites and nanograined bulk materials

Mechanochemical Processing

- The Mechanochemical Processing (MCP) technology is a novel, patented solid-state process for the manufacture of a wide range of nanopowders. Dry milling is used to induce chemical reactions through ball-powder collisions that result in nanoparticles formed within a salt matrix. Particle size is defined by the chemistry of the reactant mix, milling and heat treatment conditions. Particle agglomeration is minimized by the salt matrix, which is then removed by a simple washing procedure.



Ball mill acts as a low temperature chemical reactor. Reaction process results from focal heat and pressure at contact surface.

Chemical reactions occur at nanoscale . Particles are kept apart by salt matrix. Low temperature enables controlled particle formation.

Reaction product is heat treated. Solid phase chemistry prevents particles from agglomeration. Salt removed through simple washing steps.

- The MCP process is distinguished from competing technologies by the solid-state nature of the process that enables the formation of equiaxed nanoparticles, with a narrow size distribution and low levels of agglomeration. A typical example is Advanced Nano's ~30 nm zinc oxide shown below.

Wet-Chemical Method

- Colloidal metallic nanoparticles (e.g., Au) are commonly made using this technique. As an example of a typical reaction:
  - Boil $HAuCl_4$ with vigorous stirring using magnetic stirring hot-plate.
  - Add Na3 citrate with stirring.
  - The yellow soln turns dark blue, then burgundy in mins.
  - Stir another 30 mins.

SOL-GEL PROCESSING

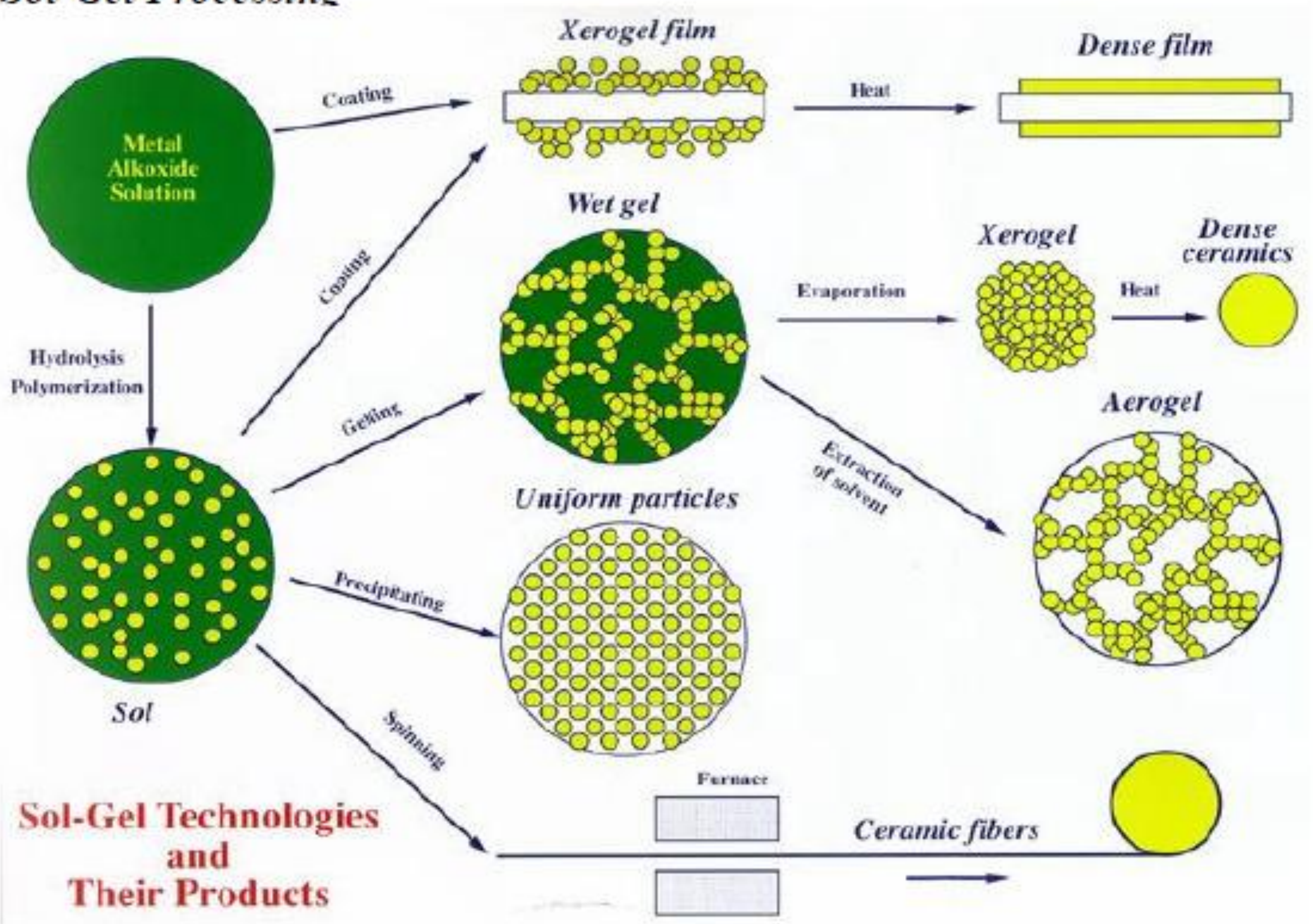
The sol-gel process is a wet-chemical technique that uses either a chemical solution (sol short for solution) or colloidal particles (sol for nanoscale particle) to produce an integrated network (gel).

Metal alkoxides and metal chlorides are typical precursors. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent. The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase (gel).

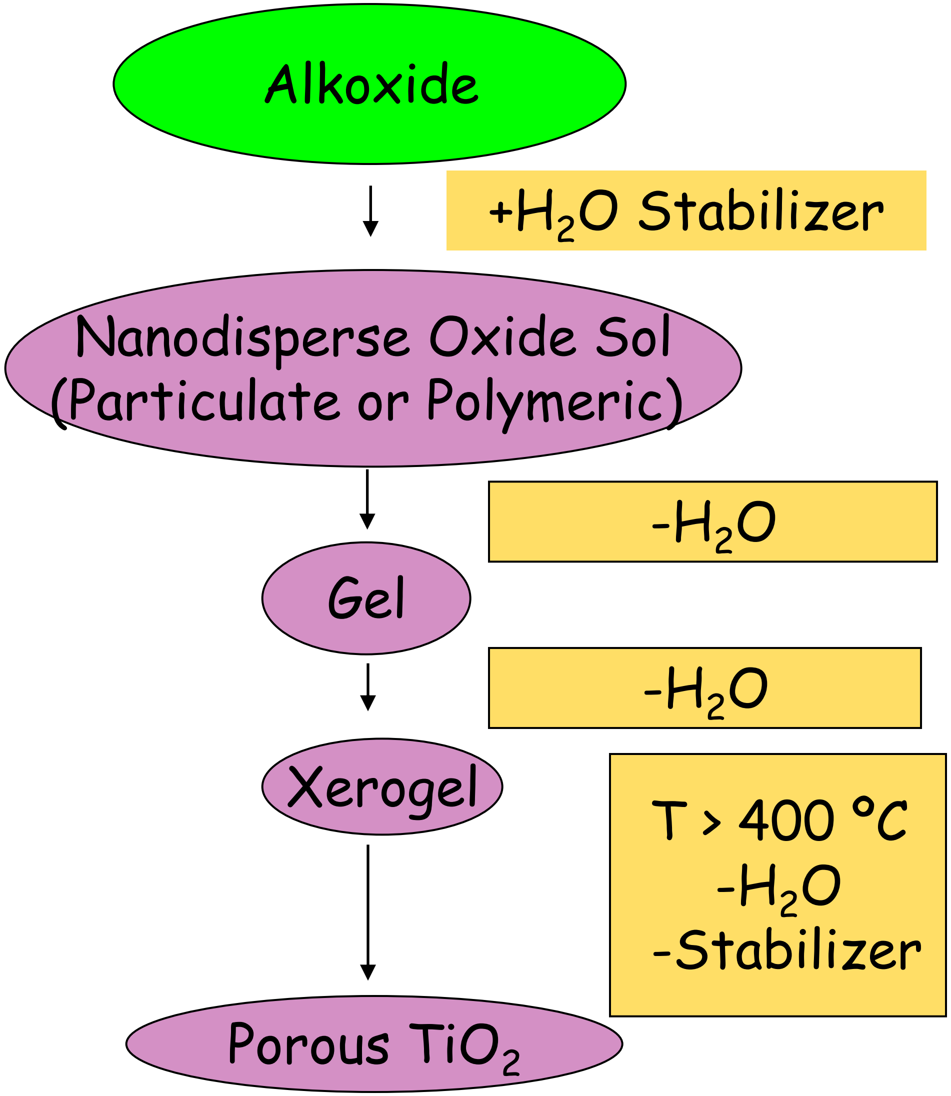
Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.

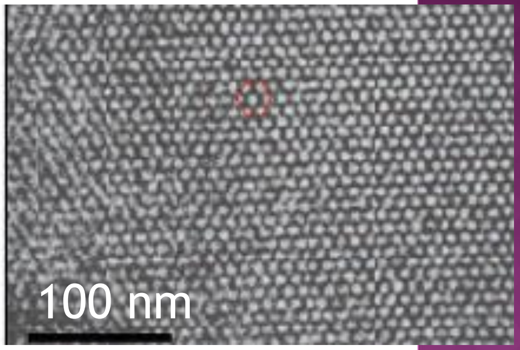
After a drying process, the liquid phase is removed from the gel. Then, a thermal treatment (calcination) may be performed in order to favor further polycondensation and enhance mechanical properties.

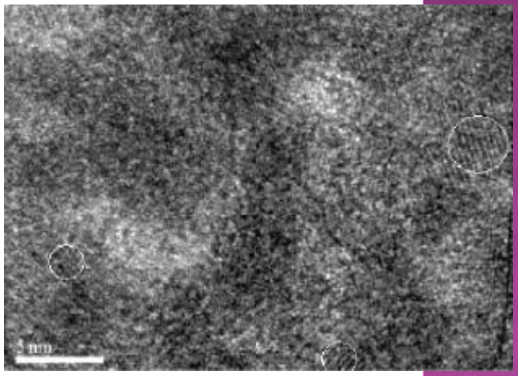
Sol-Gel Processing



EXAMPLE: TiO_2 NANOPARTICLE-MEDIATED MESOPOROUS FILM BY SOL-GEL PROCESSING



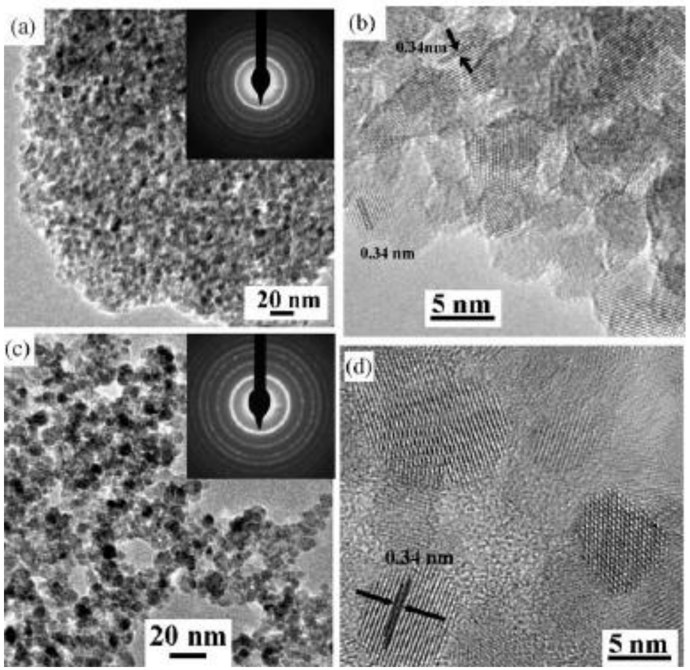




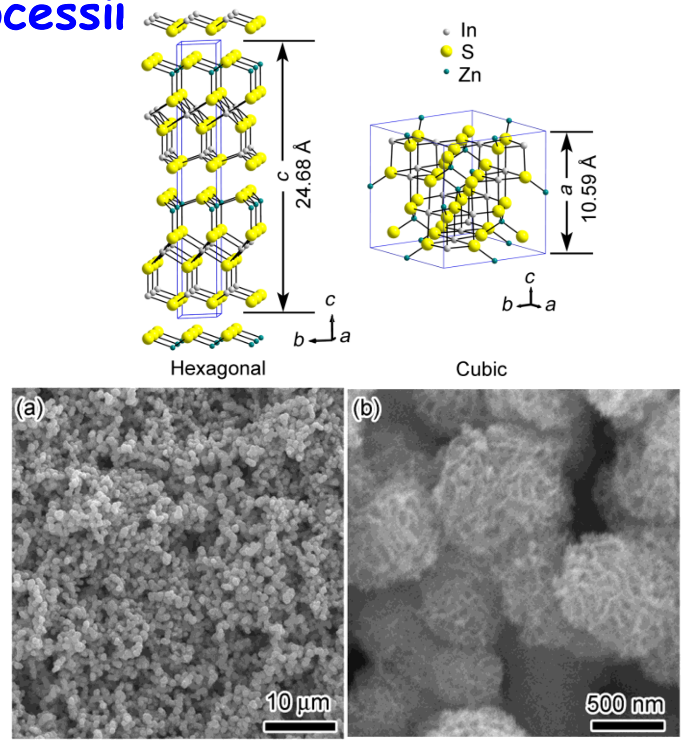
TiO_2 nanoparticle-mediated mesoporous film (Yu, J. C. et al. *Chem. Mater*. **2004**, 16, 1523.)

HYDROTHERMAL/SOLVOTHERMAL SYNTHESIS

In a sealed vessel (bomb, autoclave, etc.), solvents can be brought to temperatures well above their boiling points by the increase in autogenous pressures resulting from heating. Performing a chemical reaction under such conditions is referred to as solvothermal processing or, in the case of water as solvent, hydrothermal processi



TiO_2



$ZnIn_2S_4$

Yu, J. C. et al. *J. Solid State Chem.* 2005, *178*, 321; *Cryst. Growth Des.* 2007, *7*, 1444