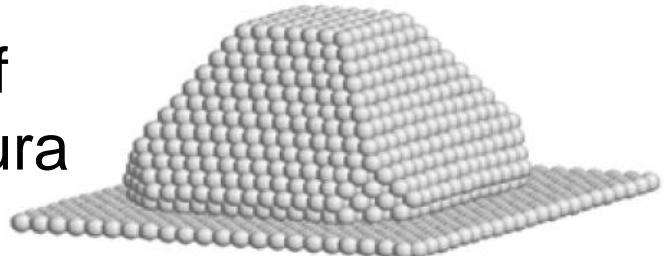




Norwegian University of  
Science and Technology

**TMT4320 Nanomaterials**  
**September 28<sup>th</sup>, 2016**

- TNN3 and NN-Synthesis routes-  
Chemical methods (sol-gel and  
precipitation) and consolidation of  
Nanopowders-Special guest: Laura  
Rioja-Monllor



# Last lecture

- Solid Oxide Fuel Cells
  - O<sub>2</sub>-SOFC
  - H<sup>+</sup>-SOFC
- Batteries
  - Li-ion batteries
  - Metal-air batteries

# Today lecture

- Synthesis of nanomaterials: chemical methods:
  - Sol-gel processing
  - Precipitation/co-precipitation
- Consolidation of nanopowders: sintering problem.

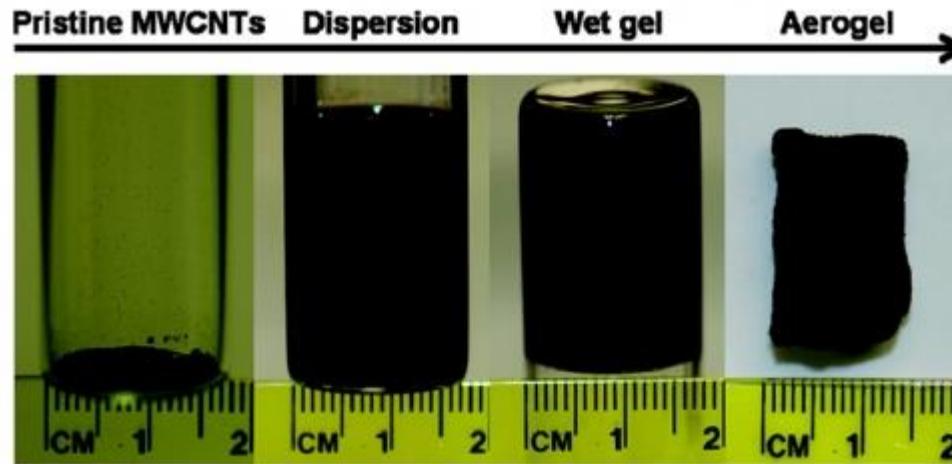
# Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles

Brian L. Cushing,\* Vladimir L. Kolesnichenko, and Charles J. O'Connor\*

*Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana 70148-2820*

- Introduction
  - Precipitation / coprecipitation
    - Nucleation and growth
    - Various synthesis methods for metals, oxides and chalcogenides
  - Sol-gel processing (today)
    - Fundamentals
    - Synthesis methods
    - Pechini method
  - Microemulsions
  - Hydrothermal/solvothermal processing
  - Templated synthesis (today)
  - Biomimetic synthesis
  - Surface-derivatized nanoparticles
- } Read on your own in Cushing and summary in additional notes.

# Aerogel technology



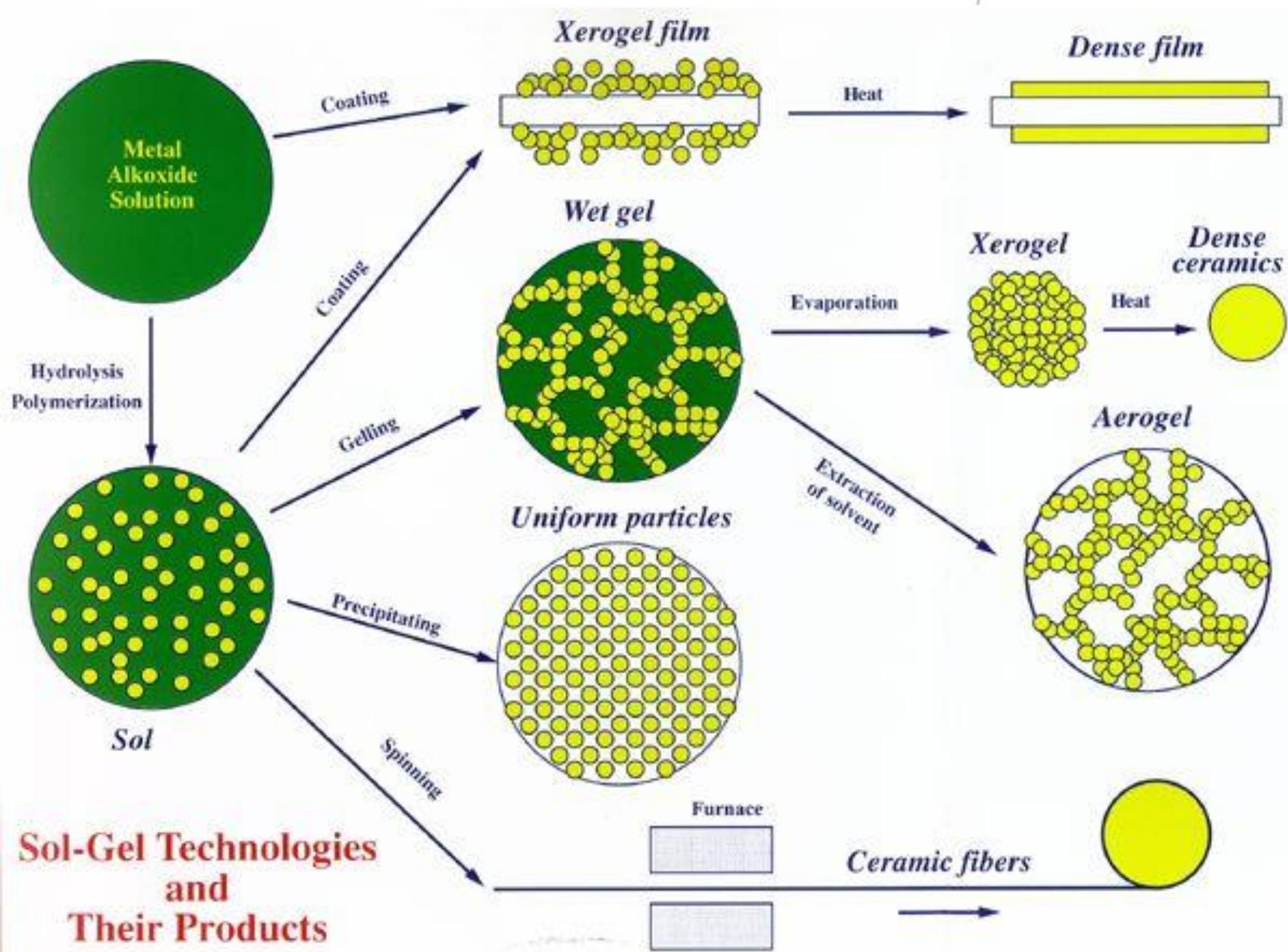
<http://www.aerogel.org/?p=1878>

<http://www.youtube.com/watch?v=kHnen2nSmDY>

Aspen Aerogels: <http://www.aerogel.com/>

# Sol-gel processing

- Hydrolysis and condensation of alkoxide-based precursors such as  $\text{Si(OEt)}_4$  (tetraethyl orthosilicate, or TEOS)
- An **alkoxide** is the conjugate base of an alcohol and therefore consists of an organic group bound to a negatively charged oxygen atom
  - Can be written as  $\text{RO}^-$ , where R is the organic substituent
- In general, “alkoxide” is also used to name compounds with alkoxide groups such as TEOS



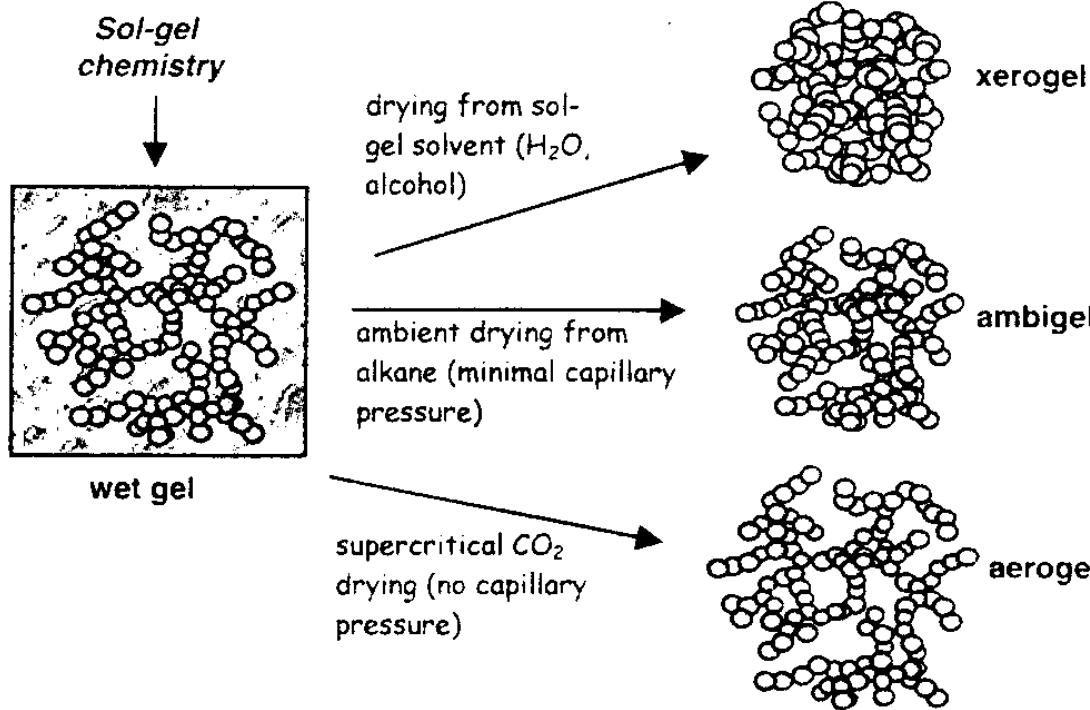
# Steps in sol-gel processing

1. Formation of stable solutions of the alkoxide or solvated metal precursor (the *sol*)
2. **Gelation** – formation of an oxide- or alcohol-bridged network (the *gel*) by a polycondensation or polyesterification reaction
3. **Ageing (syneresis)** – polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from the gel pores

# Steps in sol-gel processing

4. **Drying** – water and other volatile liquids are removed from the gel network
5. **Dehydration** – surface-bound M-OH groups are removed
  - Stabilizing the gel against rehydration
  - Usually calcination of the monolith at temperatures up to 800 °C
6. **Densification** and decomposition of the gels at high temperatures ( $T > 800$  °C)
  - The pores of the gel network are collapsed, and remaining organic species are volatilized
  - This step is normally reserved for the preparation of dense ceramics or glasses

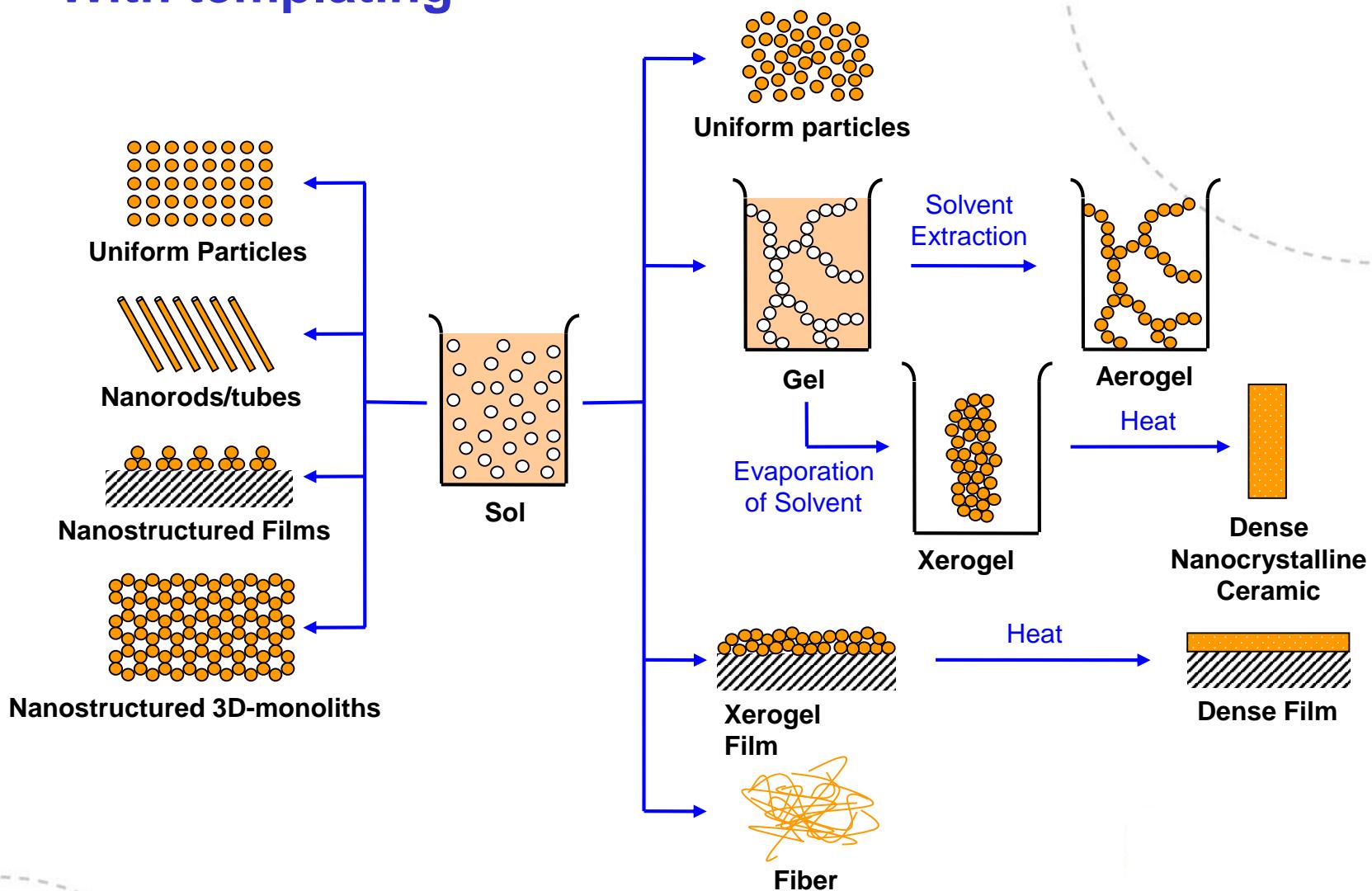
# Xerogel and aerogel formation



- **Xerogel**
  - Collapse of the gel structure
  - Capillary forces induce stresses on the gel
- **Ambigel**
  - Drying from alkane
- **Aerogel**
  - Maintains the gel structure
  - Supercritical solvent extraction

# Without templating

## With templating



# Sol-gel synthetic methods

- Oxides
- Other inorganics
- Nanocomposites

# Sol-gel synthesis of oxides

- Important to distinguish between:
  - Xerogel or aerogel being the end **product**
  - The xerogel or aerogel serves as a **precursor** that is subsequently calcined, sintered, and so forth.
- Most aerogel reactions yield amorphous nanoparticulate products. Need calcination to become crystalline.
- Calcination normally also leads to agglomeration.
- Example:  $\text{Fe}_3\text{O}_4$  nanoparticles (see additional notes for details)

# Sol-gel syntheses of other inorganics

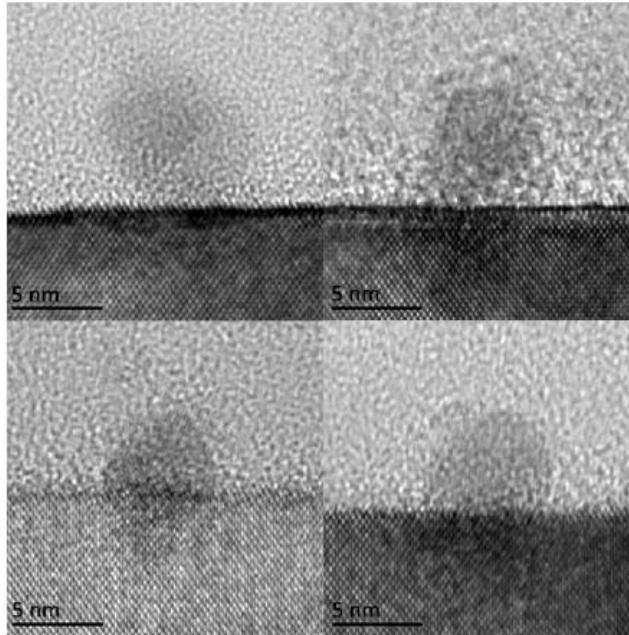
- Sol-gel methods are most commonly used to synthesize oxides, but syntheses of carbides, nitrides, and sulfides are also known.
- Major difference between sol-gel synthesis of oxides and other inorganics:
  - Hydrolysis reactions which always produce hydroxides and oxides must be avoided.
  - Perform the reactions in **aprotic solvents** under **inert atmospheres**.

# Sol-gel processing of nanocomposites

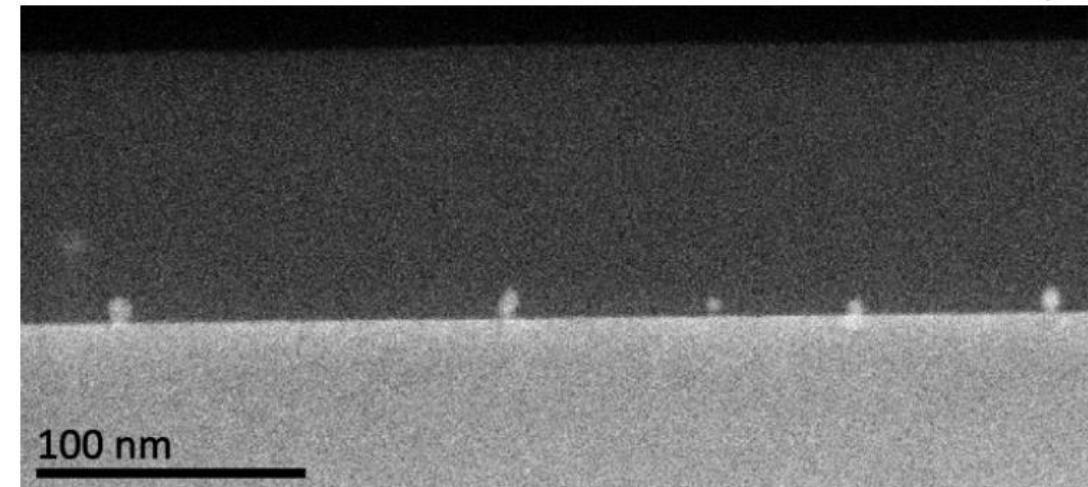
- Allow metal oxides or metal chalcogenides to hydrolyze and condense simultaneously with silicon alkoxides
  - The metal-containing nanoparticles become dispersed in an amorphous silica matrix
- Three major syntheses routes for production of sol-gel-based nanocomposites
  1. Mix a preformed colloidal metal (or oxide) with a sol containing the matrix-forming species followed by gelation,
  2. Direct precipitation of metal, metal oxide, and so forth nanoparticles within a pre-hydrolyzed silica sol.
  3. Complex the metal to a functionalized silane and reduce the metal prior to hydrolysis/condensation

# NTNU research

- CdSe/ZnS core/shell quantum dots dispersed in a silica ( $\text{SiO}_2$ ) thin film



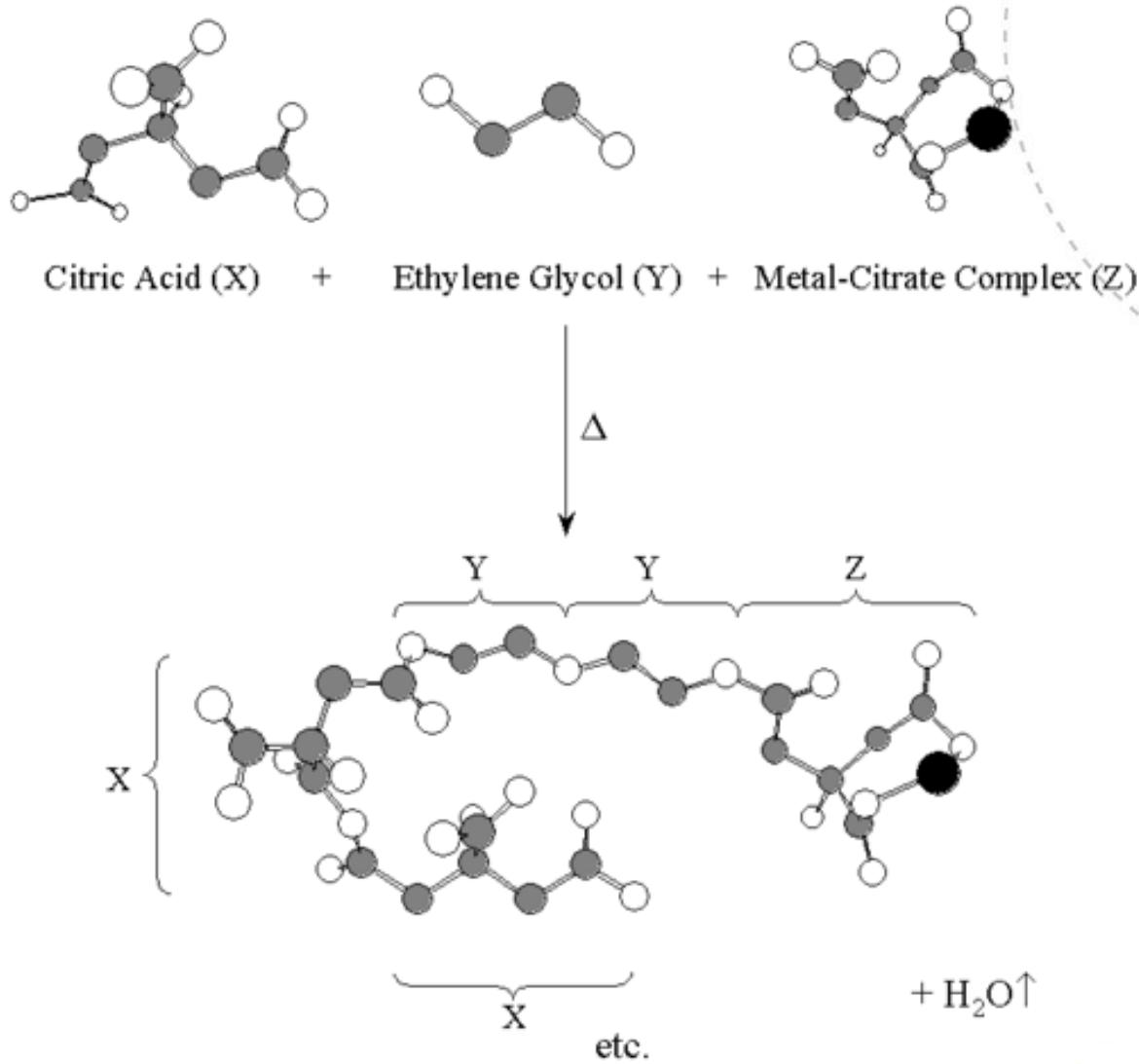
Four different CdSe/ZnS quantum dots in a silica matrix at high magnification.



TEM dark field image of CdSe/ZnS quantum dots in a silica film.

# Pechini method

- A modified sol-gel process used for metals with unfavorable hydrolysis equilibria.
- Main characteristics of the Pechini method are:
  - Bi- and tridentate organic chelating agents (i.e. citric acid) are used to form **complexes** of alkali metals, alkaline earths, transition metals, or even nonmetals
  - Gelation is obtained by adding a **polyalcohol** (i.e. ethylene glycol) to establish linkages between the chelates by a polyesterification reaction
  - After drying, the gel is heated to initiate **pyrolysis** of the organic species, resulting in agglomerated submicron oxide particles



Conceptual representation of the condensation between a metal cation, citric acid, and a polyol: the early stages of the Pechini method.

- **Advantage**
  - Elimination of the requirement that the metals involved form suitable hydroxo complexes
- **Limitations**
  - Lack of control over particle size, shape, and morphology
  - Mainly spherical particles are produced
- Most frequently used to prepare fine particles which are compacted and sintered into dense ceramic pellets

# Example: BaTiO<sub>3</sub>

- Precursors
  - BaCO<sub>3</sub>
  - Ti(O*i*Pr)<sub>4</sub>
- Citric acid as chelating agent
- Ethylene glycol as polymerization agent
- Calcination temperature 700-1000 °C
- Product size 50-340 nm
- See Table 5 in Cushing for other examples

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- Biomimetic synthesis
- Surface-derivatized nanoparticles

Today

# Precipitation and coprecipitation

- Precipitation – formation of a solid (a precipitate) in a solution during a chemical reaction
- Coprecipitation – simultaneous precipitation of multiple species in more complex systems (ex. binary, ternary and quarternary metal oxides)

# A few definitions

- **Solution**: a homogeneous mixture composed of two or more substances
- **Dispersion**: a system in which one compound exist in dispersed state in a phase with another chemical composition or another state of matter
  - **Suspension**: a dispersion of non-colloidal solid particles in a liquid
  - **Sol**: a dispersion of colloidal solid particles in a liquid
  - **Emulsion**: a dispersion of liquid in liquid
- **Colloidal size**: at least one dimension within 1-1000 nm
- **Colloid**: a particle (solid, liquid or gas) or a large molecule of colloidal size

# Precipitation - Introduction

- Precipitation reactions tend to exhibit the following characteristics:
  1. Products are sparingly soluble species formed under conditions of **high supersaturation**.
  2. **Nucleation** is the key step of the precipitation process → large number of small particles are formed.
  3. **Ostwald ripening** and **aggregation** can dramatically affect the size, morphology, and properties of the products.
  4. **Reaction conditions** influencing the mixing process (rate of reactant addition and stirring rate) are relevant to product size, morphology, and particle size distribution.

- Precipitation usually induced by chemical reactions
  - Chemical reactions should result in products with low solubilities
- Methods for inducing precipitation
  - Addition/exchange reactions
  - Chemical reduction
  - Photoreduction
  - Oxidation
  - Hydrolysis
  - Temperature changes
  - Concentration changes

# Reduction of metals in aqueous solutions

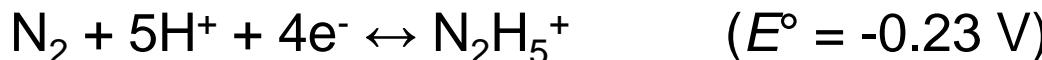
- Chemical reduction of metal cation:



- Corresponding oxidation process:



- Two common reducing agents:



**Table 1. Representative Sampling of Nanoparticulate Metals Precipitated from Aqueous Solutions**

metal	starting material	reducing agent	stabilizer <sup>a</sup>	notes	avg diam (nm)	ref
Co	Co(OAc) <sub>2</sub>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	none		~20	44
Ni	NiCl <sub>2</sub>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O + NaOH	CTAB	reaction performed at 60 °C	10–36	45
Ni	Ni(OAc) <sub>2</sub>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O + NaOH	none		(10–20) × (200–300) rods	44
Cu	CuSO <sub>4</sub>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	SDS		~35	44
Ag	AgNO <sub>3</sub>	ascorbic acid	Daxad 19		15–26	46
Ag	AgNO <sub>3</sub>	NaBH <sub>4</sub>	TADDD		3–5	47
Pt	H <sub>2</sub> PtCl <sub>6</sub>	potassium bitartrate	TDPC	60 °C	<1.5	48
Au	HAuCl <sub>4</sub>	trisodium citrate	S3MP	simultaneous addition of reductant and stabilizer	not stated	49

<sup>a</sup> CTAB = cetyltrimethylammonium bromide (see section 4); SDS = sodium dodecyl sulfate; Daxad 19 = sodium salt of high-molecular-weight naphthalene sulfonate formaldehyde condensate; TADDD = bis(11-trimethylammoniumdecanoylethoxyethyl)-disulfide dibromide; TDPC = 3,3'-thiodipropionic acid; S3MP = sodium 3-mercaptopropionate

- The sizes are in general larger than those for metals reduced in microemulsions (reverse micelles)

# Precipitation of metals by reduction from non-aqueous solutions

- If  $E^\circ$  for the reduction reaction  $M^{n+} + ne^- \rightleftharpoons M^0$  is highly negative, an aqueous solvent cannot be used because the reducing agents capable of supplying electrons to the metal will reduce water



- Must use more stable solvents
- Example: Au nanoparticles in nonpolar solvents (see additional notes for details).

Table 2 in Cushing et al. lists other relevant examples

# Precipitation of metals by decomposition of metalorganic precursors

- The thermolysis of organometallic precursors in the presence of a polymer
- Typically, a metal complex such as  $\text{Co}_2(\text{CO})_8$  is decomposed at 130-170 °C under inert atmosphere in ethylene glycol solvent:

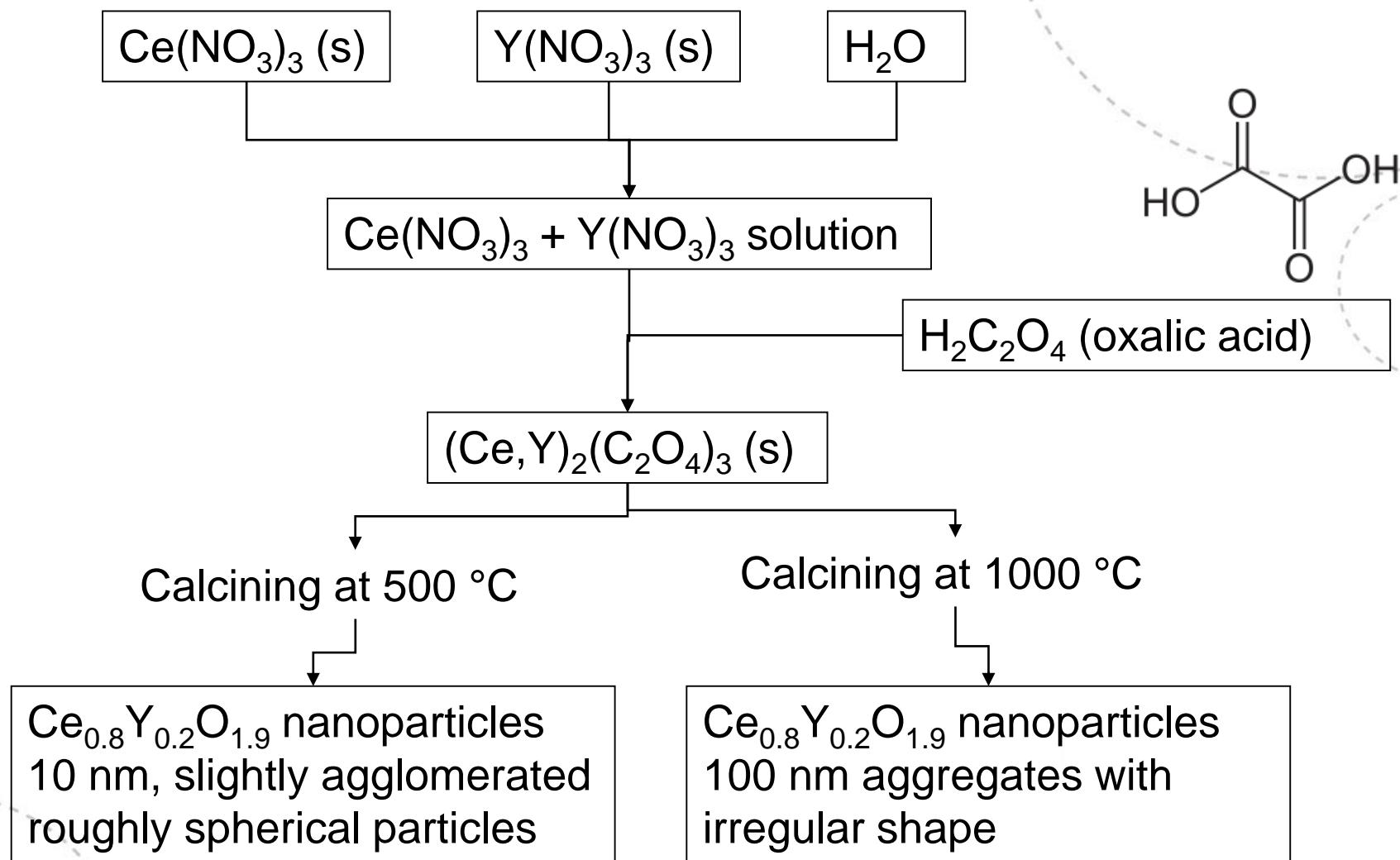


- 45 nm Co particles capped with PVP have been prepared by this approach

# Precipitation of oxides from solutions

- Less straightforward than the precipitation of metals
  - Aqueous or non-aqueous
- Reactions can be broken into two categories:
  - those that produce an oxide directly
  - those that produce what is best termed a precursor that must be subjected to further processing (drying, calcination, etc.)
- Production of monodispersed nanoparticles often require a capping ligand or other surface-bound stabilizer to prevent agglomeration of the particles

# Precipitation of $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$ from aqueous solution



**Table 3. Summary of Reactions for the Precipitation of Oxides from Aqueous Solutions**

compd	starting material	ppt agent	stabilizer	conditions	product size (nm)
VO <sub>2</sub> (B)	NH <sub>4</sub> VO <sub>3</sub>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	none	calcined 300 °C	35
Cr <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	none	calcined 500 °C	30
$\gamma$ -Mn <sub>2</sub> O <sub>3</sub>	KMnO <sub>4</sub>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	none		8
MnFe <sub>2</sub> O <sub>4</sub>	MnCl <sub>2</sub>	NaOH	none	100 °C	5–25
	FeCl <sub>3</sub>				
Fe <sub>3</sub> O <sub>4</sub>	FeCl <sub>2</sub>	NH <sub>4</sub> OH	H <sup>+</sup>	N <sub>2</sub> atm	8–50
	FeCl <sub>3</sub>				
NiO	NiCl <sub>2</sub>	NH <sub>4</sub> OH	CTAB	annealed 500 °C	22–28
ZnO	ZnCl <sub>2</sub>	NH <sub>4</sub> OH	CTAB	annealed 500 °C	40–60
SnO <sub>2</sub>	SnCl <sub>4</sub>	NH <sub>4</sub> OH	CTAB	annealed 500 °C	11–18
Sb <sub>2</sub> O <sub>3</sub>	SbCl <sub>3</sub>	NaOH	PVA	annealed 350 °C	10–80

# NTNU research - Spray pyrolysis

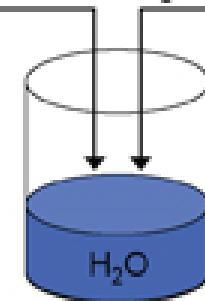
- Precipitation of oxides because of water evaporation
  - Reduced solubility
  - Supersaturation
- Rapid cooling
  - Reduces the growth

1

**Solution**

Selected nitrates

Complexing agents



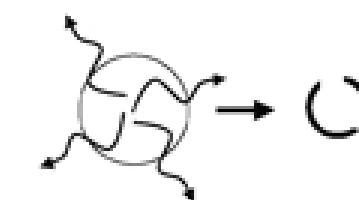
2

**Atomization**

Two phase nozzle

**Evaporation / Drying**

Droplets dried to hollow fragmentet spheres.



3

4

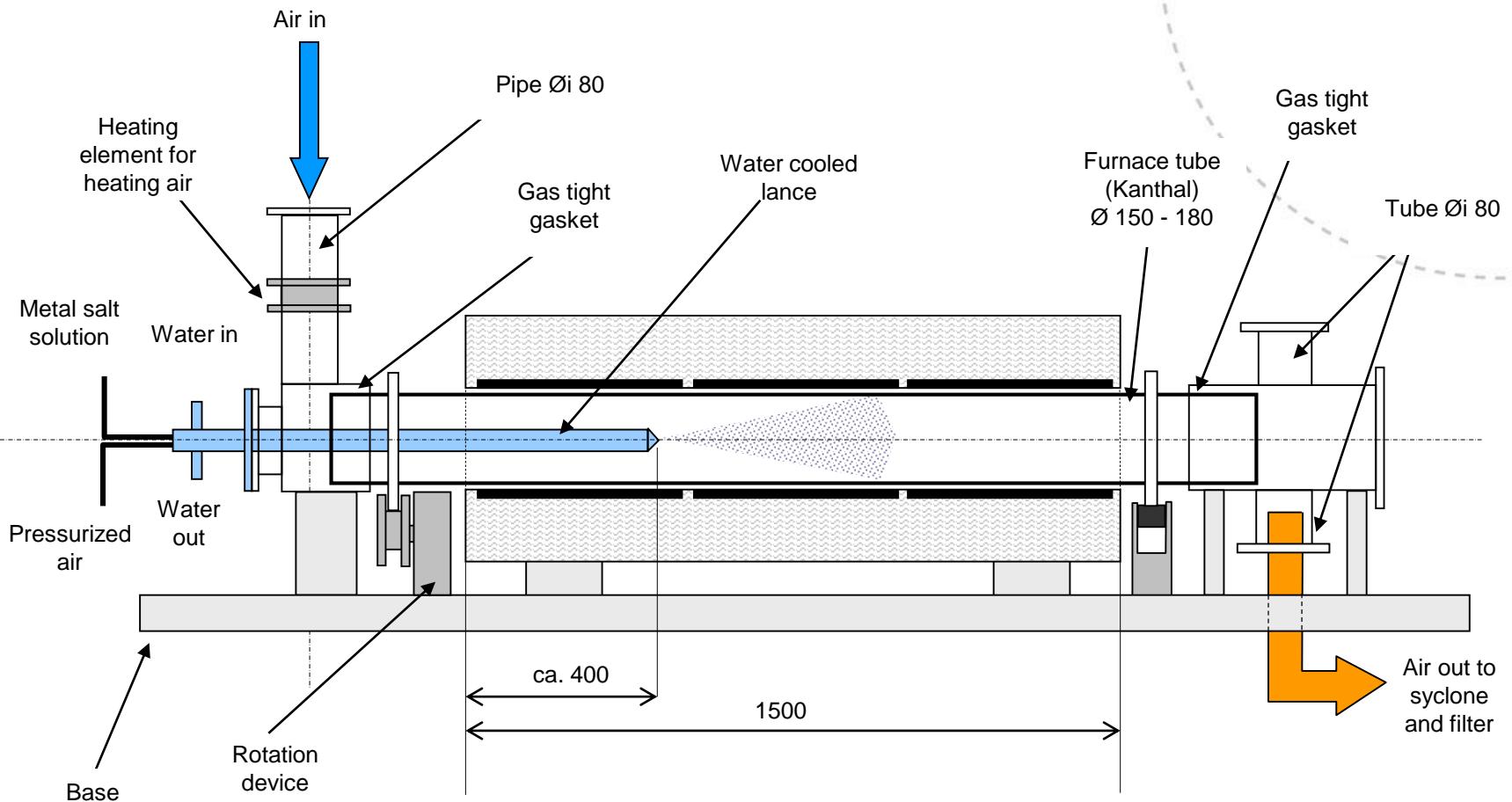


# Spray pyrolysis equipment at NTNU



- Pilot scale equipment
- Solution pumped through a nozzle (1.0 mm) with a pumping rate of < 8 dm<sup>3</sup>/h
- Temperatures at nozzle: 850°C and at outlet: 450-550°C
- Powder collected with a cyclone

# Spray pyrolysis unit



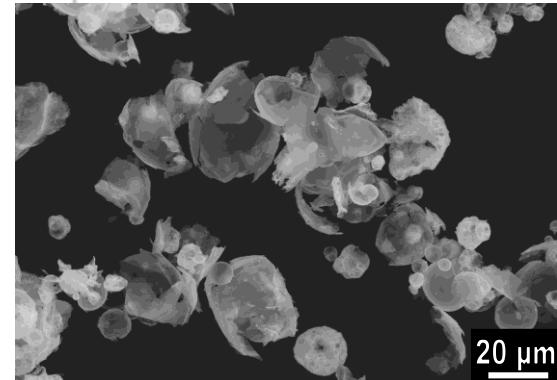
Spray pyrolysis furnace - NTNU

Ove Paulsen -  
SINTEF Materialteknologi

# Powder characteristics

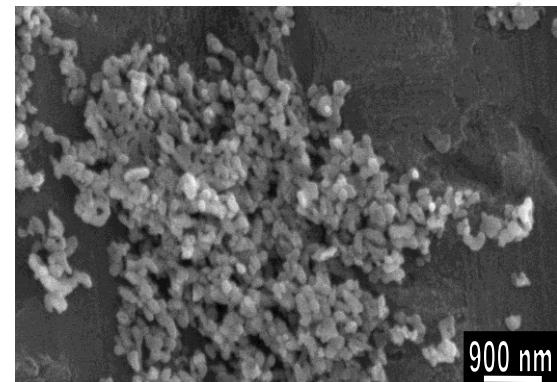
- As-synthesized powder from spray pyrolysis:

- Large, soft, spherical agglomerates
  - Nearly phase pure  $\text{LaNbO}_4$



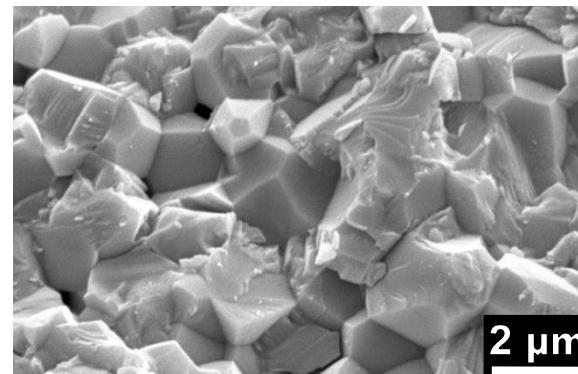
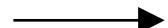
- Calcined 800 °C for 10 h and milled

- Small particles ( $\sim 100 \text{ nm}$ )
  - Phase pure  $\text{LaNbO}_4$
  - Excellent sintering properties



- Sintering at 1200 °C for 6 h

- 99% density
  - Fracture surface: grain size 1-4  $\mu\text{m}$



# Precipitation of oxides from nonaqueous solutions

- Good for precipitating dissimilar metals that cannot be simultaneously precipitated from aqueous solution.
- $\text{LiCoO}_2$ 
  - Cathode in Li-ion batteries
  - $\text{LiOH}$  is a common precursor
    - Cannot be precipitated from aqueous solution
    - Low solubility in alcohols
  - How do we solve this problem
    - Coprecipitation of  $(\text{LiOH} + \text{Co(OH})_2$ )
  - Calcination of hydroxide mixture is necessary ( $400\text{-}700\text{ }^\circ\text{C}$  in air to yield 12-41 nm  $\text{LiCoO}_2$ )
- See additional notes for example on  $\text{BaTiO}_3$ .

# Coprecipitation of metal chalcogenides by reactions of molecular precursors

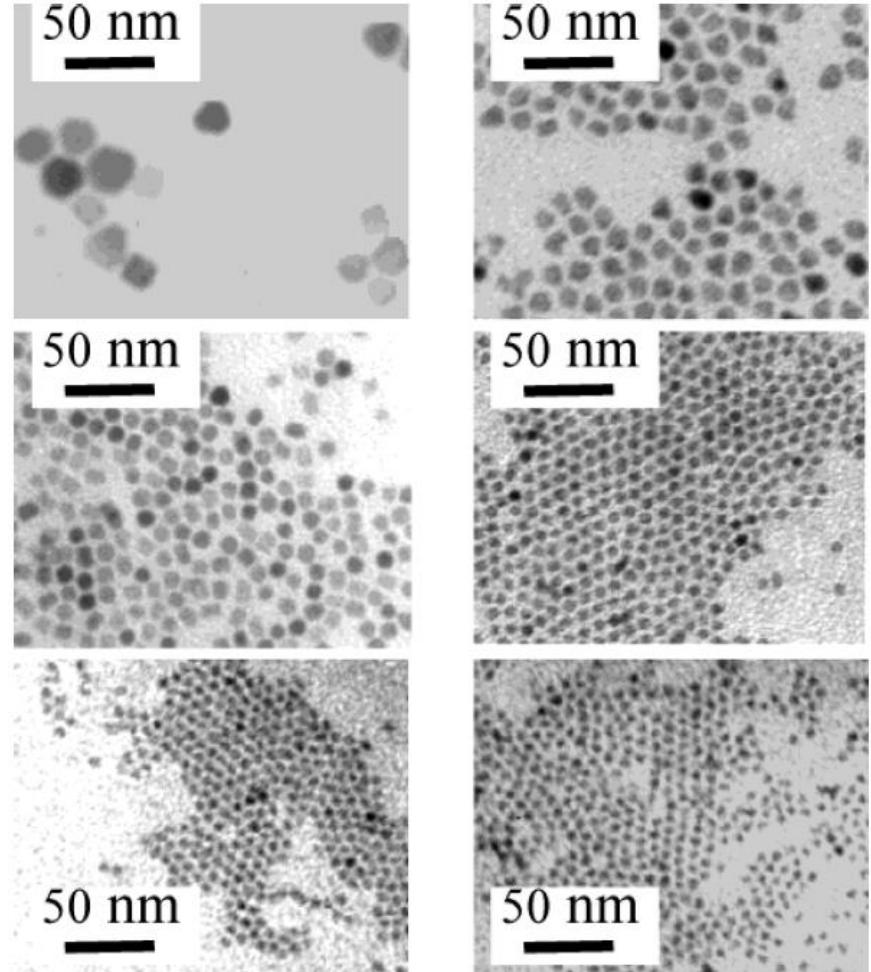
- II-VI and III-V semiconductors
- Thermolysis
- Separation of the nucleation step and the crystal growth step has resulted in processable, highly crystalline nanoparticles with extremely narrow size distributions
  - Nucleation step at higher temperature
  - Growth at lower temperature



# Cadmium chalcogenides

- Cd-precursor: Cd(CH<sub>3</sub>)<sub>2</sub>
- Chalcogen source molecules:
  - [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>S
  - [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>Se
  - R<sub>3</sub>PSe (R = C<sub>4</sub>-C<sub>8</sub> *n*-alkyl)
  - R<sub>3</sub>PTe
- Rapid injection of a room-temperature solution containing both precursors into preheated (340-360 °C) solvents
  - Rapid nucleation
- Lowering the temperature to 280-300 °C hinders further nucleation and the relatively slow nanocrystal growth takes place until the reactants are consumed

- Cadmium carboxylates can be used as cadmium precursors
- Can control size and shape by tuning concentrations of the reagents and reaction temperature
- Elimination of toxic dimethylcadmium



TEM micrographs of different sized wurtzite CdSe nanocrystals (as-prepared) synthesized in stearic acid related solvents.

# Learning objectives Cushing review

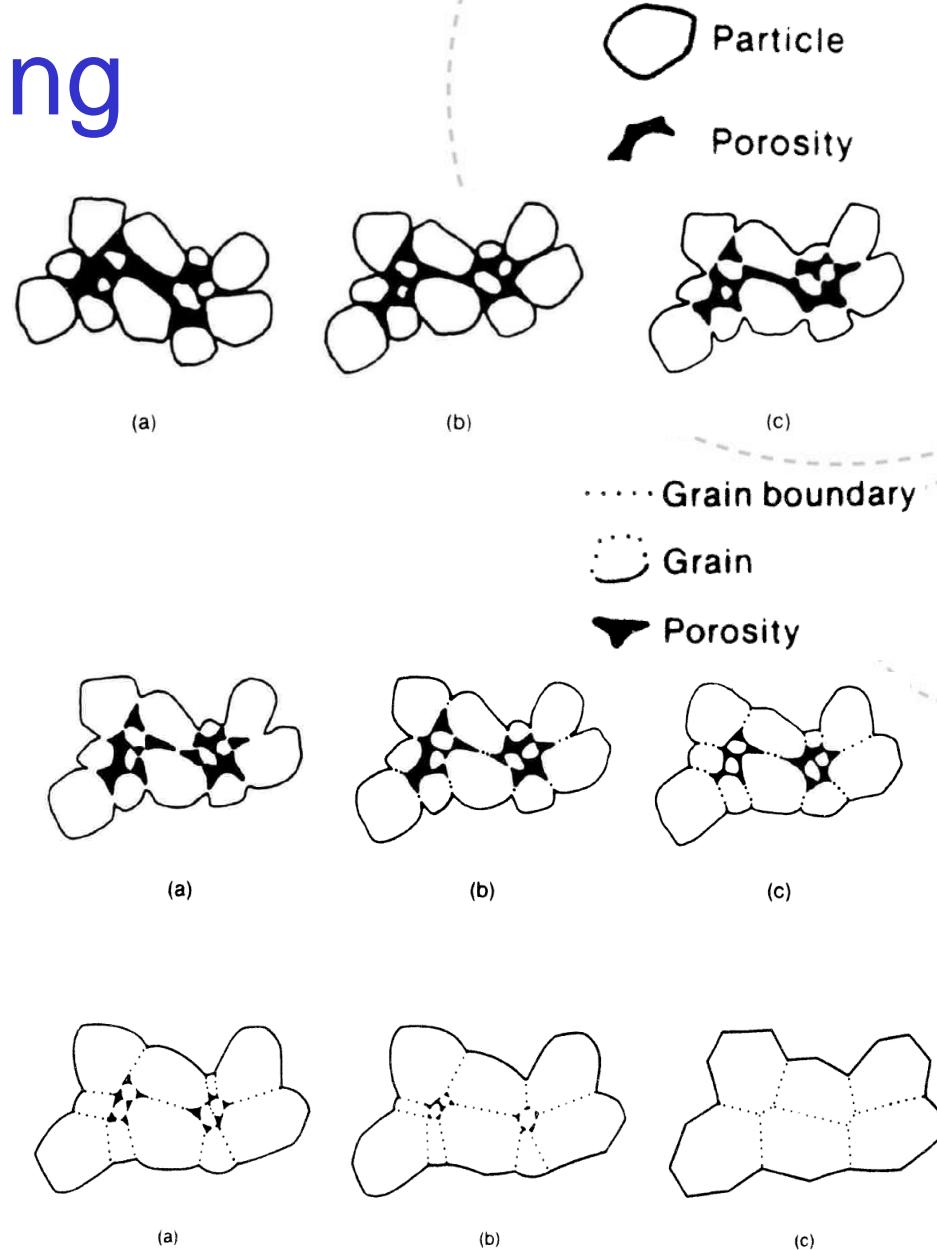
- Have an overview over various methods to produce nanoparticles by wet-chemical (liquid) methods
- Principles of synthesis methods, not details
  - Metal synthesis by reduction
  - Precipitation of oxides
  - Two-step synthesis of metal chalcogenides (nucleation, then growth)
- Sol-gel: hydrolysis and condensation reactions
- Synthesis of Au and BaTiO<sub>3</sub> by various methods
- Advantages and limitations of various methods
- Important: Read additional notes posted on it's learning!!!

# 21 - Bulk nanostructured materials obtained by powder sintering

- Sintering → consolidation of a dispersed material under the action of heat, without total melting of the material
- Two competing phenomena during sintering:
  - **Densification**, which should generally be favored, and
  - **Grain growth**, which should generally be opposed or at least controlled
- There are 3 stages of sintering

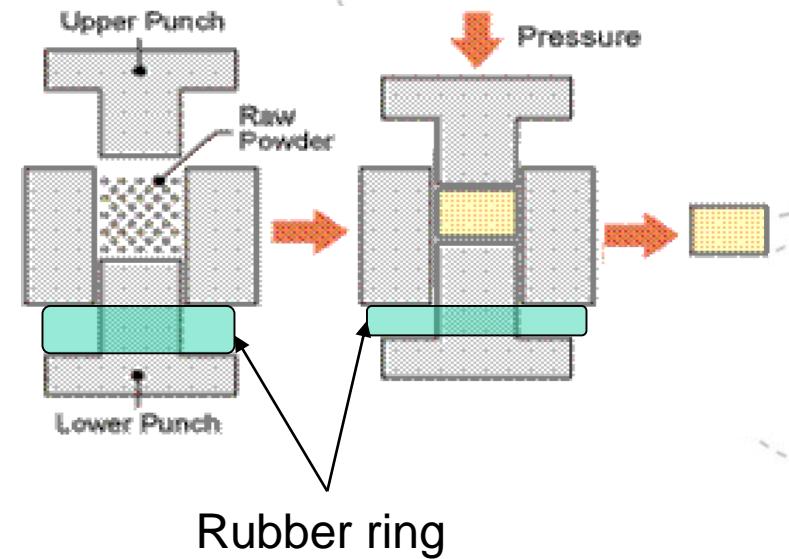
# 3 stages of sintering

- **Initial stage:** rearrangement, and neck formation
- **Intermediate stage:** neck growth, grain growth, high shrinkage, and continuous pore phase
- **Final stage:** Much grain growth, discontinuous pore phase, elimination of grain boundaries



# Different sintering conditions

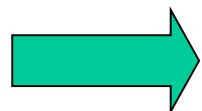
- Natural sintering
  - The material to be sintered is simply heated in a furnace
- Sintering under pressure
  - Hot pressing
  - Hot isostatic pressing
- Sintering in microwaves
  - Rapid and uniform heating of powder
- Sintering under electric discharge
  - Spark plasma sintering (SPS)



# Preserving nanostructure during sintering

- When sintering nanostructured powders (individual nanograins or nanostructured micrometric agglomerates) it is crucial to **restrict grain growth**, while **promoting the densification process**
- To preserve or limit loss of nanostructure:
  - Shortened sintering times
  - Keep temperatures as low as possible

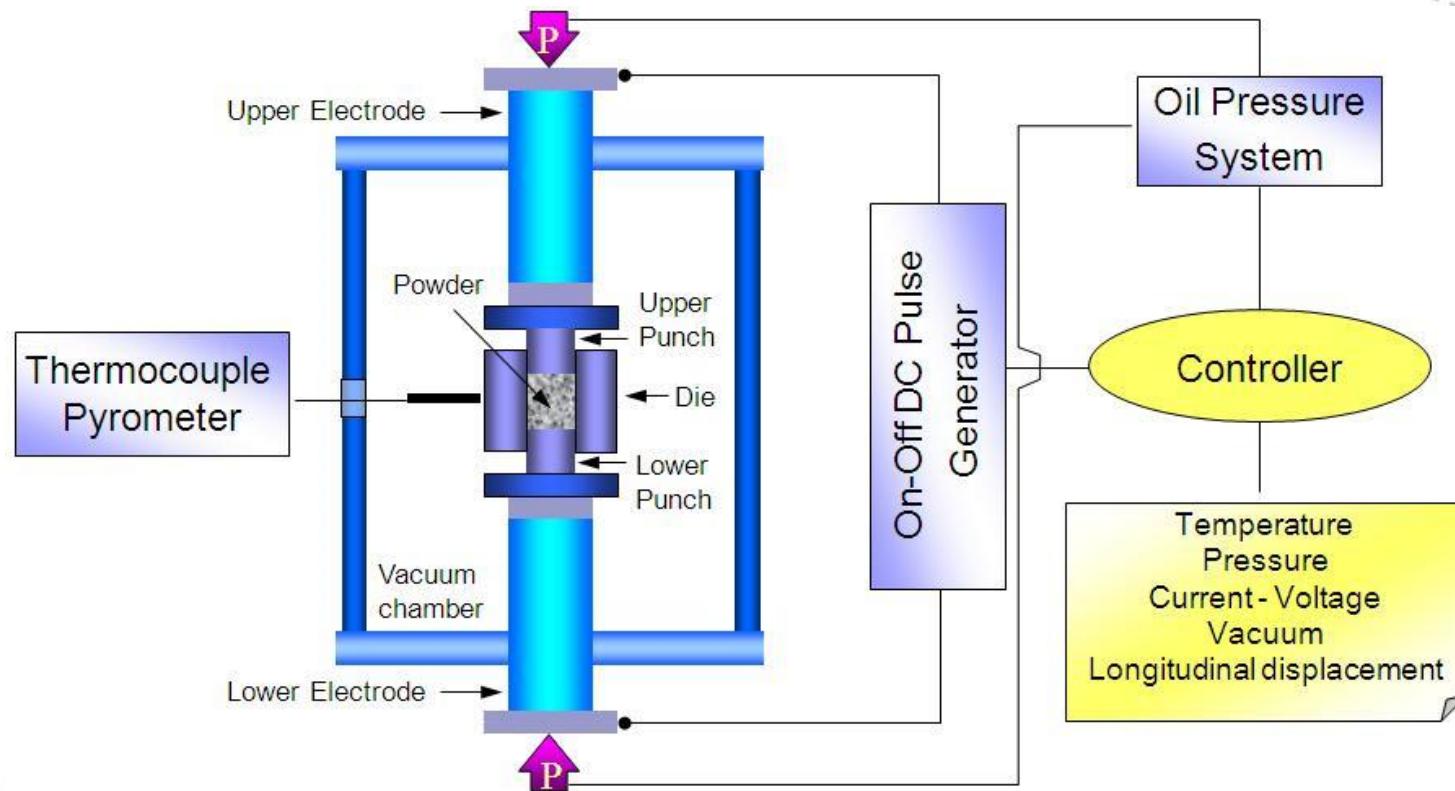
How do we achieve this?



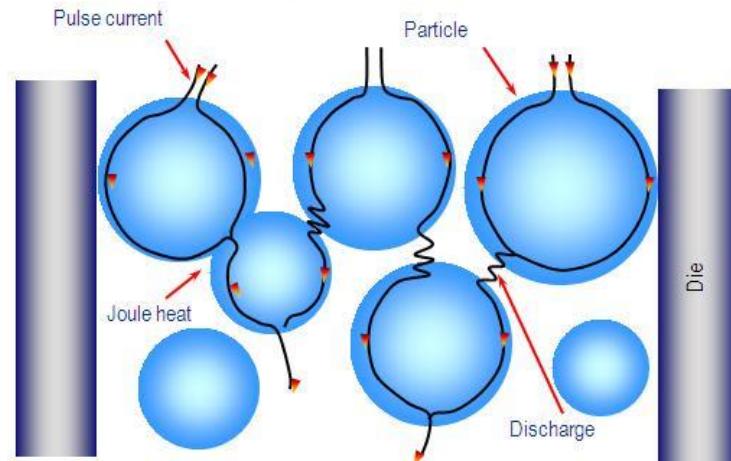
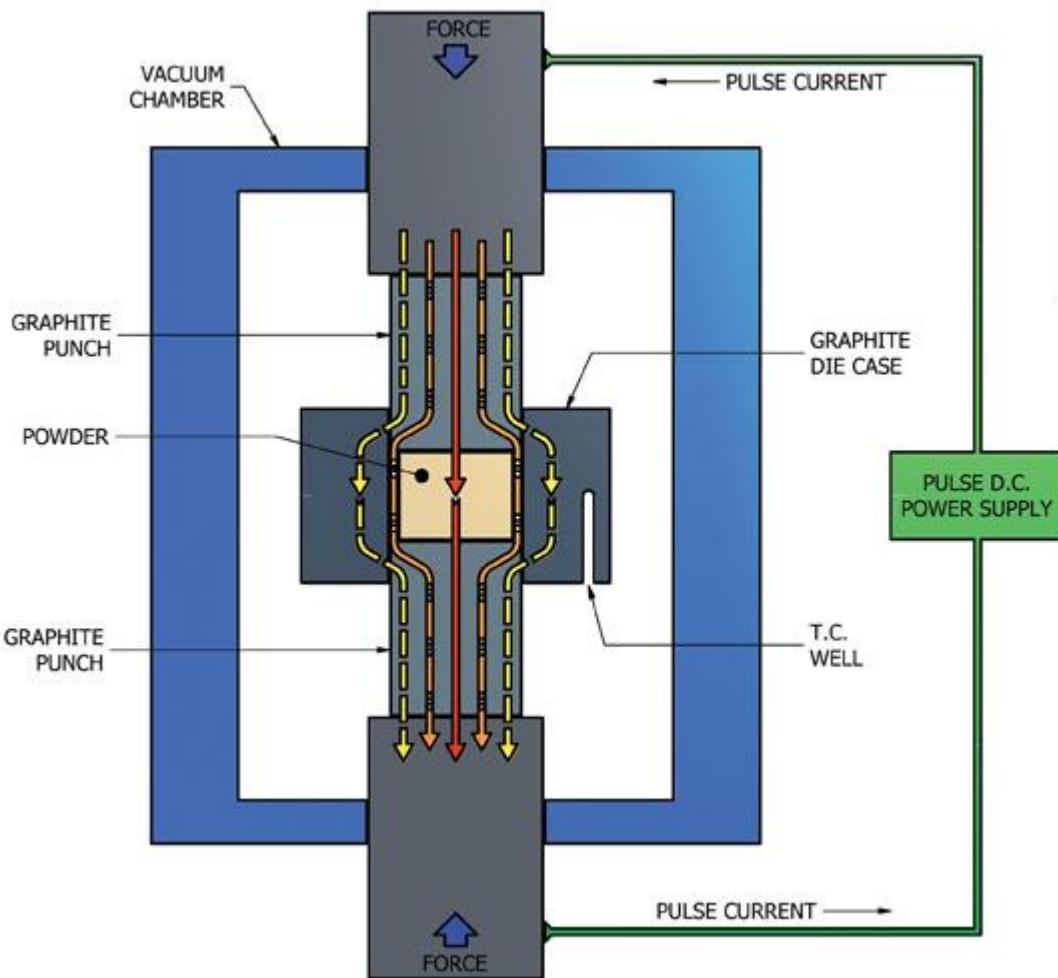
Spark plasma sintering!

# Spark plasma sintering

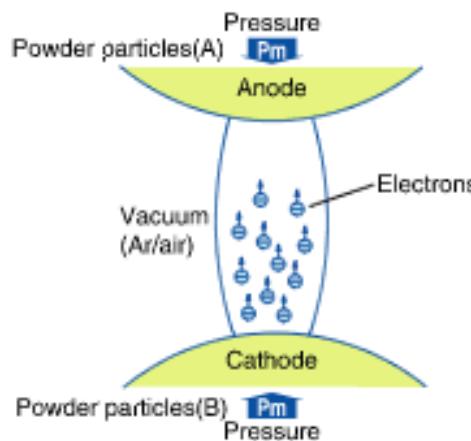
- The densification process combines uniaxial compaction with an intense electric discharge (between 2 000 and 20 000 A) in a few ms.



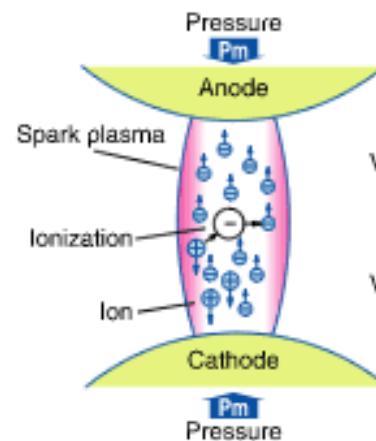
Basic configuration of an SPS machine.



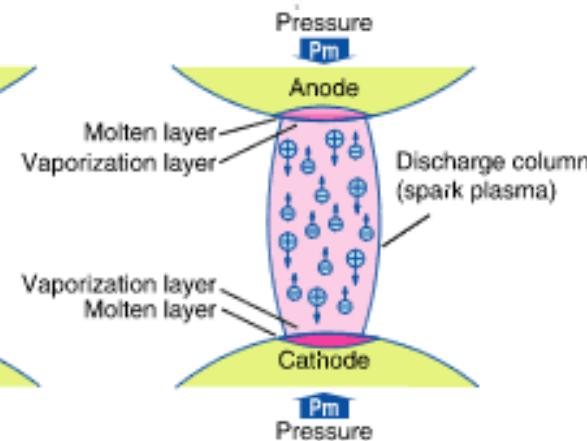
ON-OFF pulsed current path through the machine.



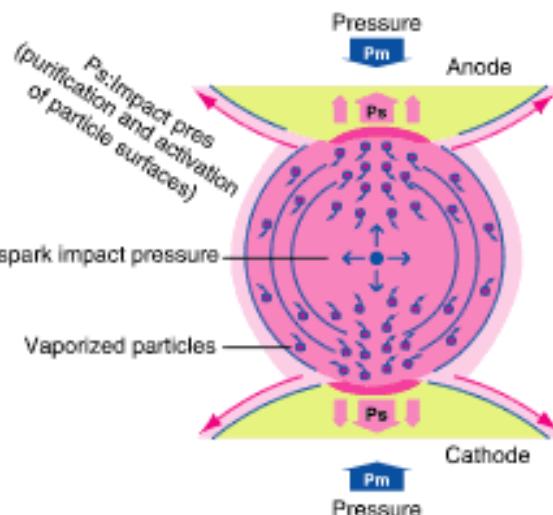
(I) Initial stage of spark discharging by ON-OFF pulse energization



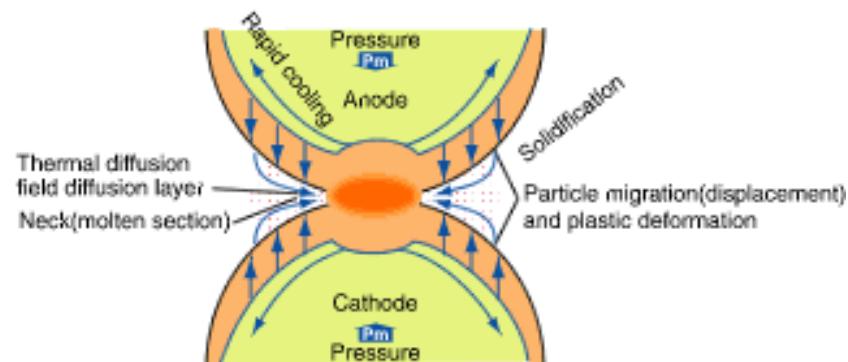
(II) Generation of spark plasma



(III) Vaporization and melting actions on the particles surfaces



(IV) Generation of spark impact pressure, sputtering of vaporized/molten particles



(V) Neck formation by spark plasma

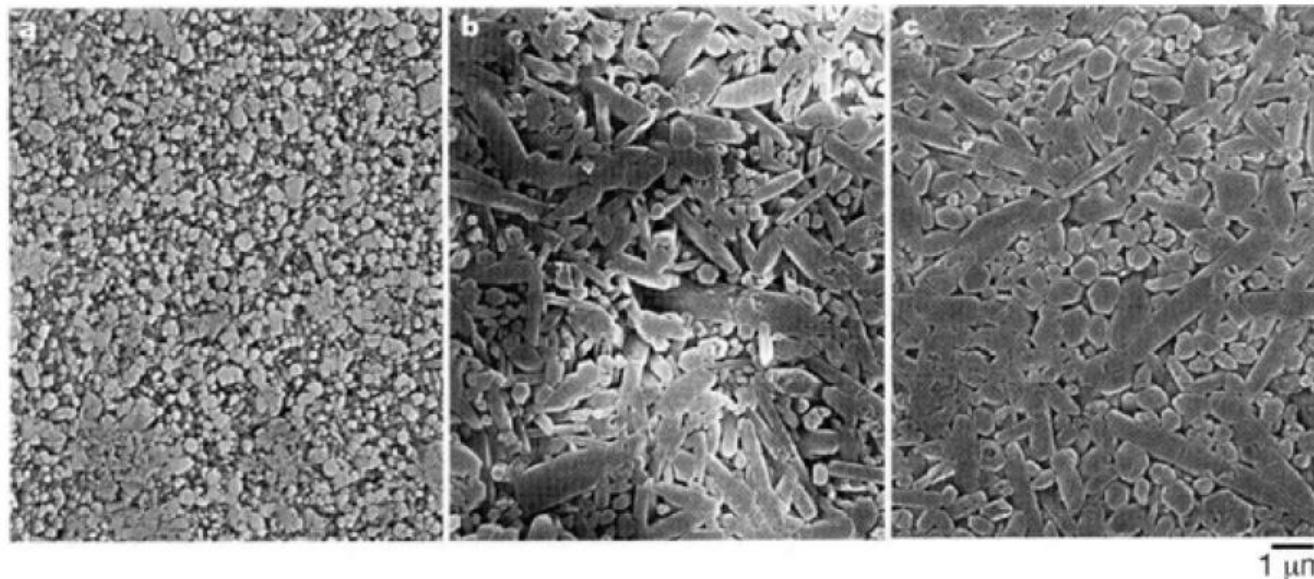
# Main advantages of SPS

- Low operating cost
- Shorter sintering times
- Lower temperatures than traditional high-pressure sintering processes
- Also possible to consolidate and assemble different types of materials such as nanomaterials, composites, and functionally graded materials



# Example: $\beta$ -sialon

- Ceramic alloy based on the elements silicon (Si), aluminium (Al), oxygen (O) and nitrogen (N)

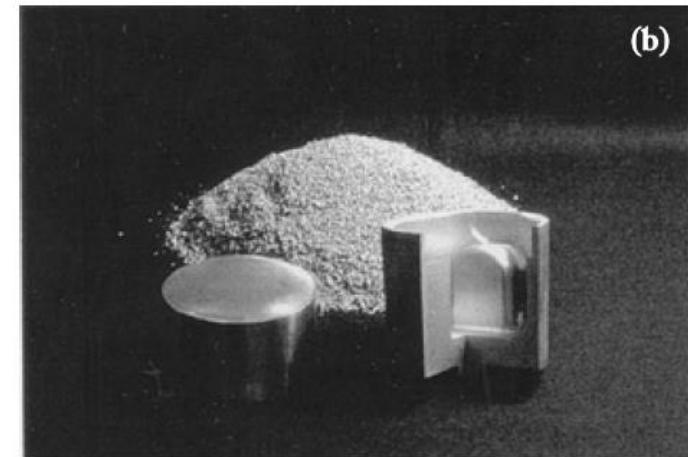
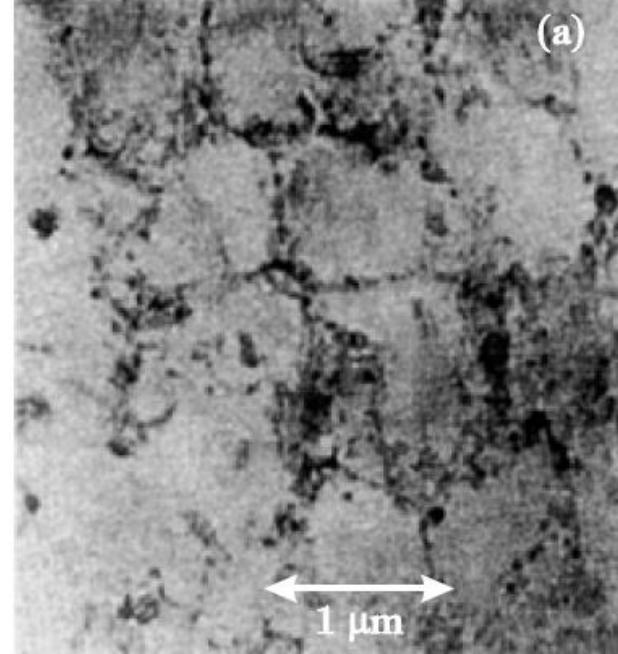


$\beta$ -sialon produced by SPS. (a) Without holding the temperature at 1600 °C. (b) Holding the temperature at 1600 °C for 1 min. (c) Holding the temperature at 1600 °C for 10 min.

# Example: Al-Si alloys

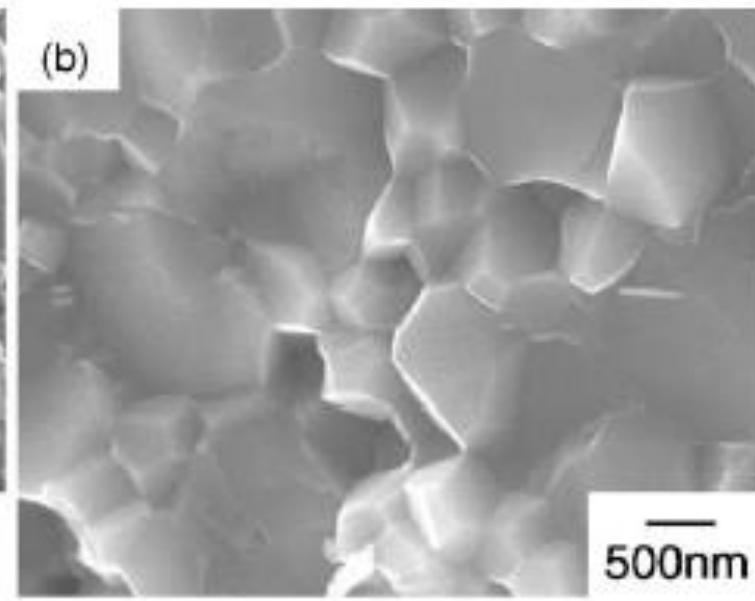
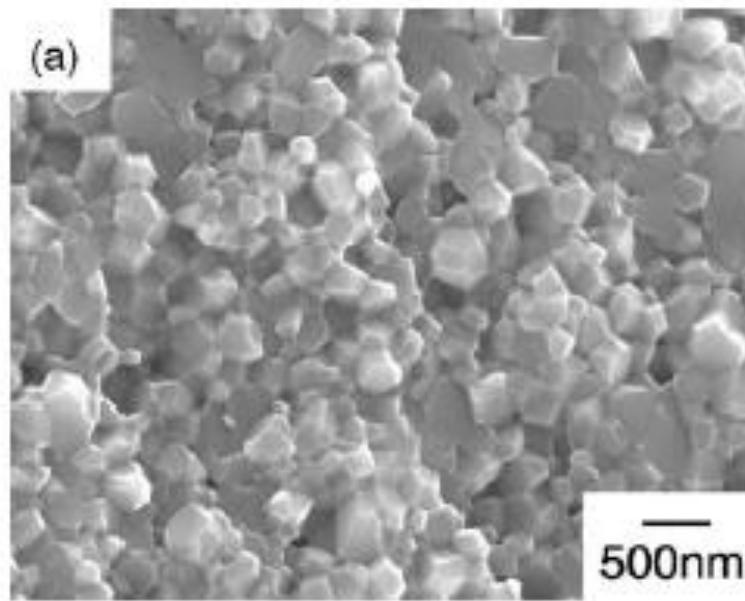
- Nanometric powders of aluminum–silicon alloys (> 12% at. Si) prepared by atomization
  - Sintering conditions:
    - 450–500 °C
    - 100–110 MPa
    - Sintering time was less than 20 min (including ramping and hold time)
- ➔ “Extremely fine” microstructure (< 1  $\mu\text{m}$ )
- ➔ Plastically deformed to produce the required 3D object

TEM image of an Al–17Si alloy synthesised by SPS.



# Sintered $\text{TiO}_2$

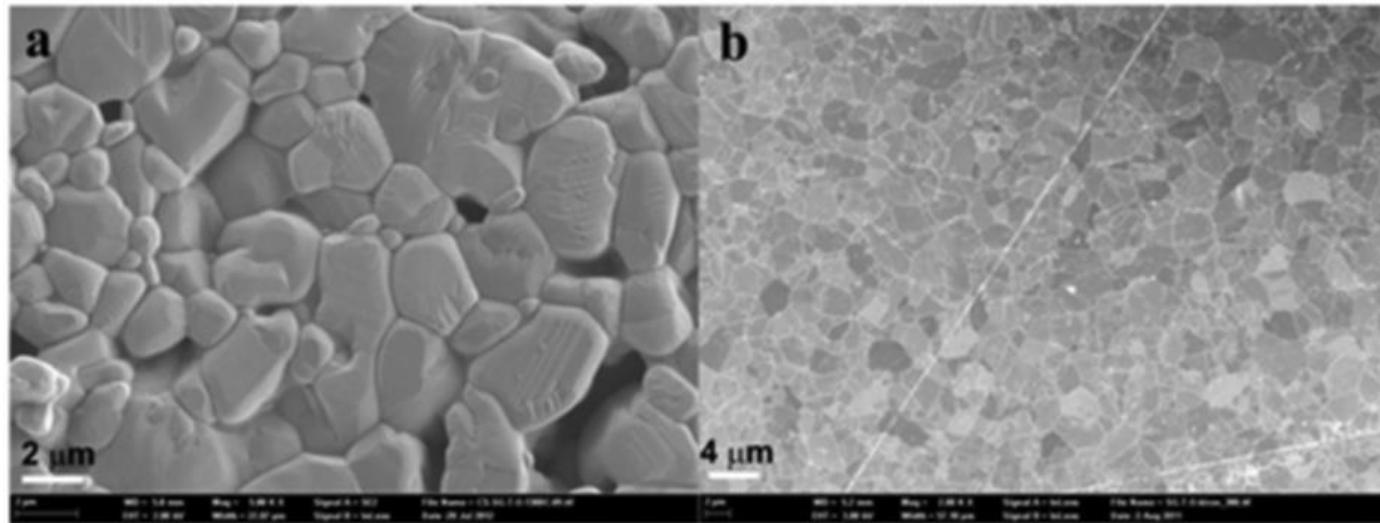
Fractured surfaces of sintered  $\text{TiO}_2$  specimens:



**Spark plasma sintering**  
at 700 °C for 1 h

**Conventional sintering at**  
900 °C for 1 h

# TiO<sub>2</sub> by SPS



Conventional sintering  
at 1300 °C for 5 h

Spark plasma sintered  
and annealed at 1000 °C  
for 1 h

# Learning objectives chapter 21

- Sintering
  - Definition
  - Mechanism
  - Densification versus grain growth
- Spark plasma sintering
  - Basic principles
  - Advantages