



**UNIVERSITY OF ROME "LA SAPIENZA"**  
**NANOTECHNOLOGIES ENGINEERING**

# **NANOPARTICLES PRODUCTION FROM GAS PHASE**

## SYNTHESIS STRATEGIES

In gas phase, nanoparticles are produced by:

- evaporation of a target
- plasma formation of the target
- chemical reaction giving the target as a product

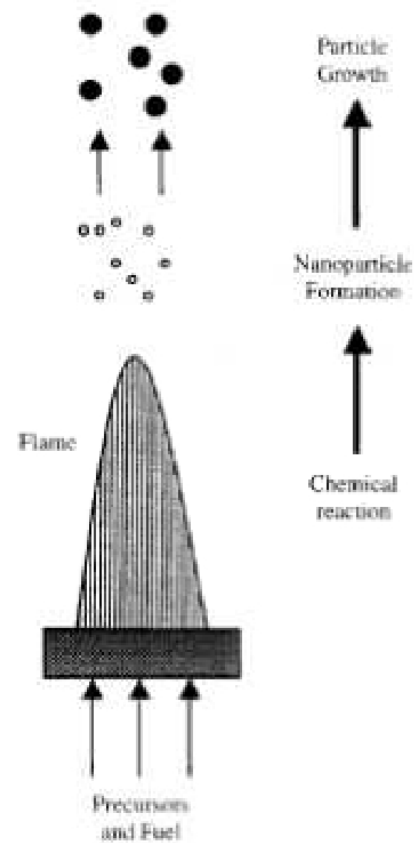
And recovered:

- by deposition of a solid from a condensing vapor stream
- by deposition of a product after chemical reaction in vapor phase.

The techniques require the vaporization of the material: not commonly used for ceramics, due to their low vapor pressure values.

# FLAME SYNTHESIS PROCESS

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## EXAMPLES FOR FLAME SYNTHESIS

Silica is produced starting from silica chloride and hydrogen. The produced silica is then separated by means of a cyclone, exhibiting a BET equal to 50-380 m<sup>2</sup>/g in nanosized aggregates.

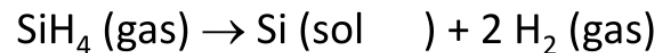
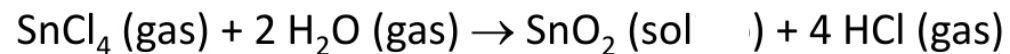
The produced quantity and quality depends on the mixing of the reactants, the flame temperature.

Advantages are: production of oxides at very small residence times, easy scale-up of the equipment and high purity;

Disadvantages are: tight agglomerates formation, heterogeneous residence times and temperature profiles in the reactor, not suitable for all targets.

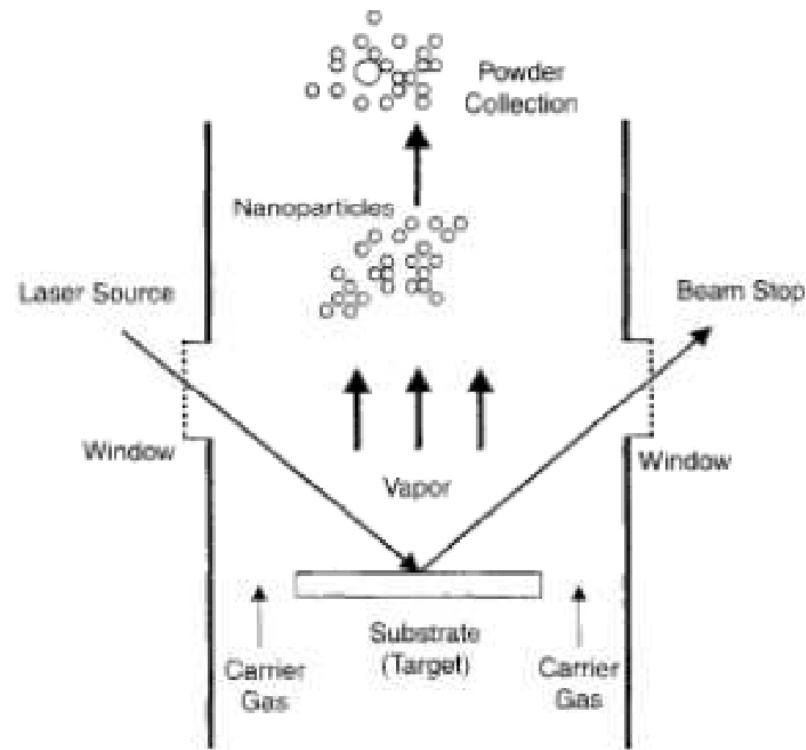
## CHEMICAL REACTION IN VAPOR PHASE

The reactions take place in a heated reactor by electrical resistances. Chlorides are used due to their low costs and low vaporization temperatures. Some reactions are:



The advantages are the same of the flame synthesis, but also the possibility to produce metals and semiconductors. Disadvantages are hard aggregates and huge aerosol formation.

# ASSISTED BY LASER (ABLATION)

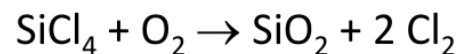


## **CVD (Chemical Vapor Deposition)**

The technique consists in the chemical reaction of two or more compounds in gas phase and the successive deposition of the produced solid material.

The technique results costly for those materials exhibiting low vapor pressure values (ceramics).

In the other cases, the technique offers all advantages working in gas phase; moreover, it is possible to address the composition of the product by controlling adequately the composition of the atmosphere, and can be used to produce a wide range of targets. In case using a furnace for the CVD technique, generally the raw material is a metal chloride. The reaction leads to the formation of the relevant oxide, such as:

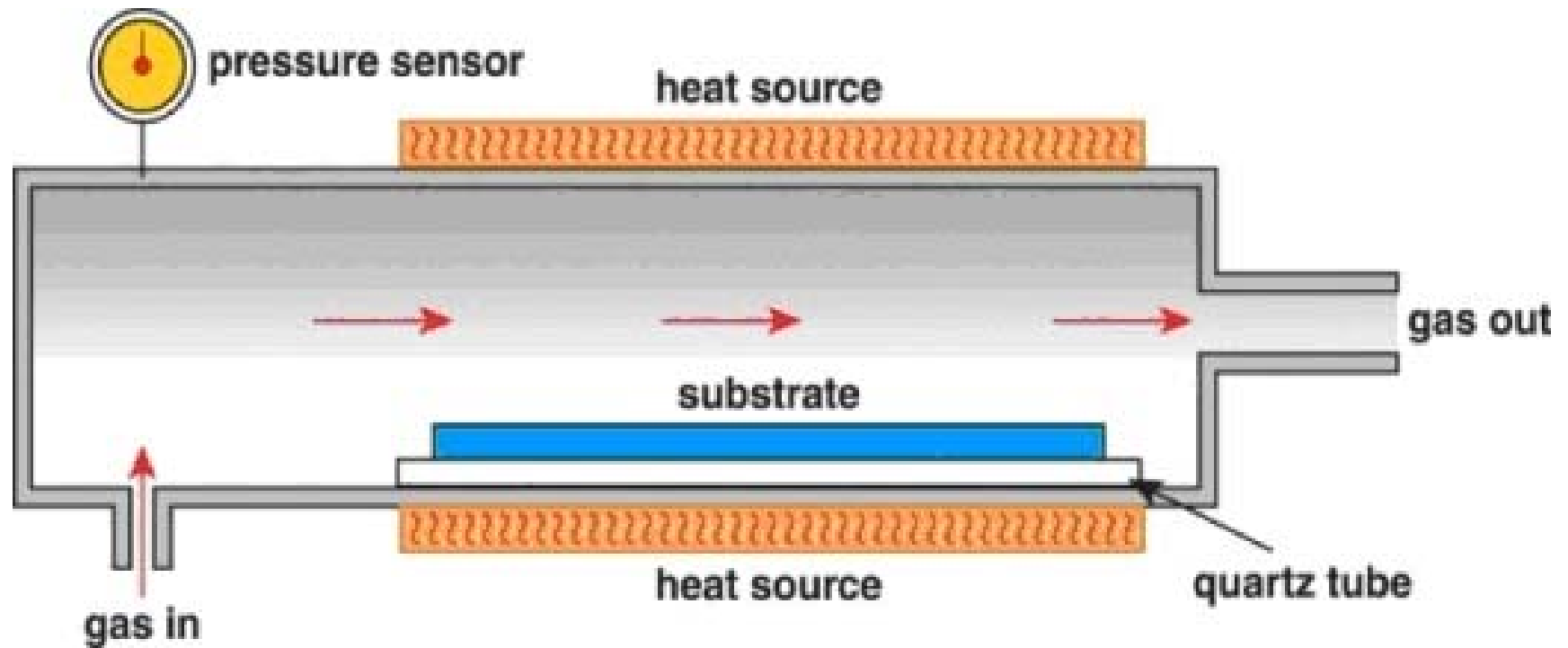


## **CVD (Chemical Vapor Deposition)**

- **APCVD: CVD atmospheric pressure;**
- **LPCV: CVD low pressure;**
- **MOCVD: CVD metallic–organic (gas with metal molecules bond to organic ones);**
- **OMCVD: CVD organic–metallic (gas with organic molecules bond to metallic ones);**
- **PECVD: CVD plasma enhanced;**
- **HDPCVD: CVD high density plasma enhanced;**
- **LACVD: CVD laser assisted.**

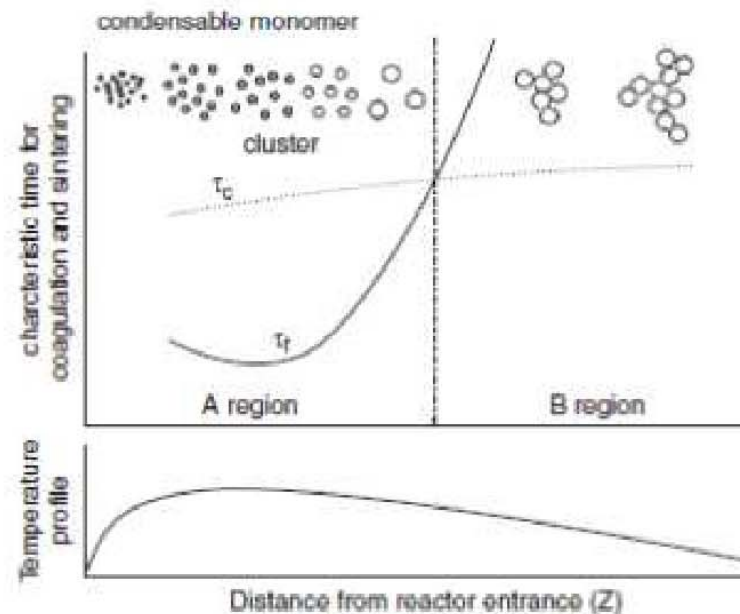


## CVD (Chemical Vapor Deposition)



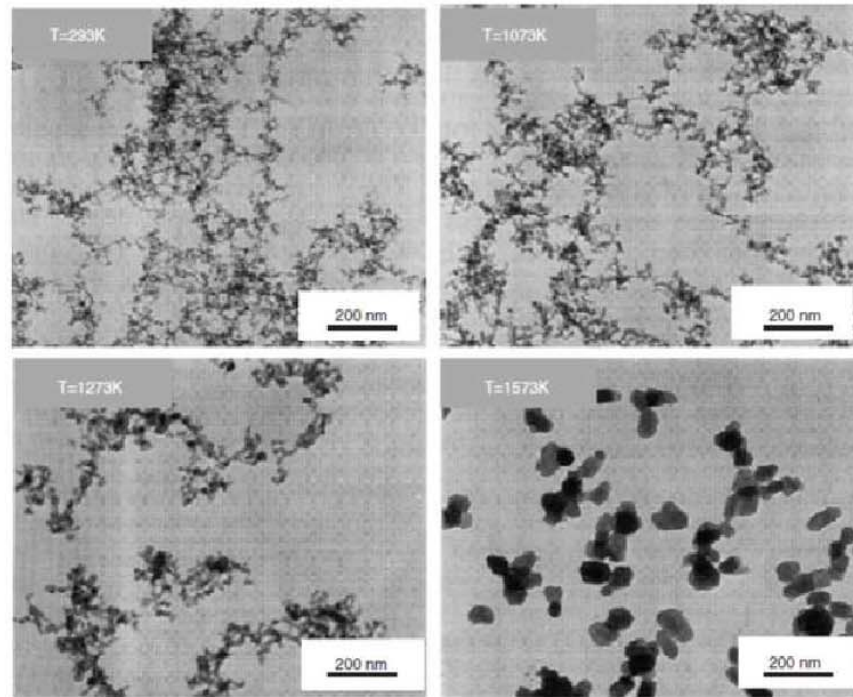
## OPERATING CONDITIONS

In particular, the temperature may have a great influence of the outcome of the process in terms of the morphology of the produced particles. In detail, coagulation and sintering phenomena concurs to the outcome: if the first is faster than the second one, the produced agglomerates are not spherical; in the opposite case, spherical particles are produced.



## EXAMPLE: TITANIA

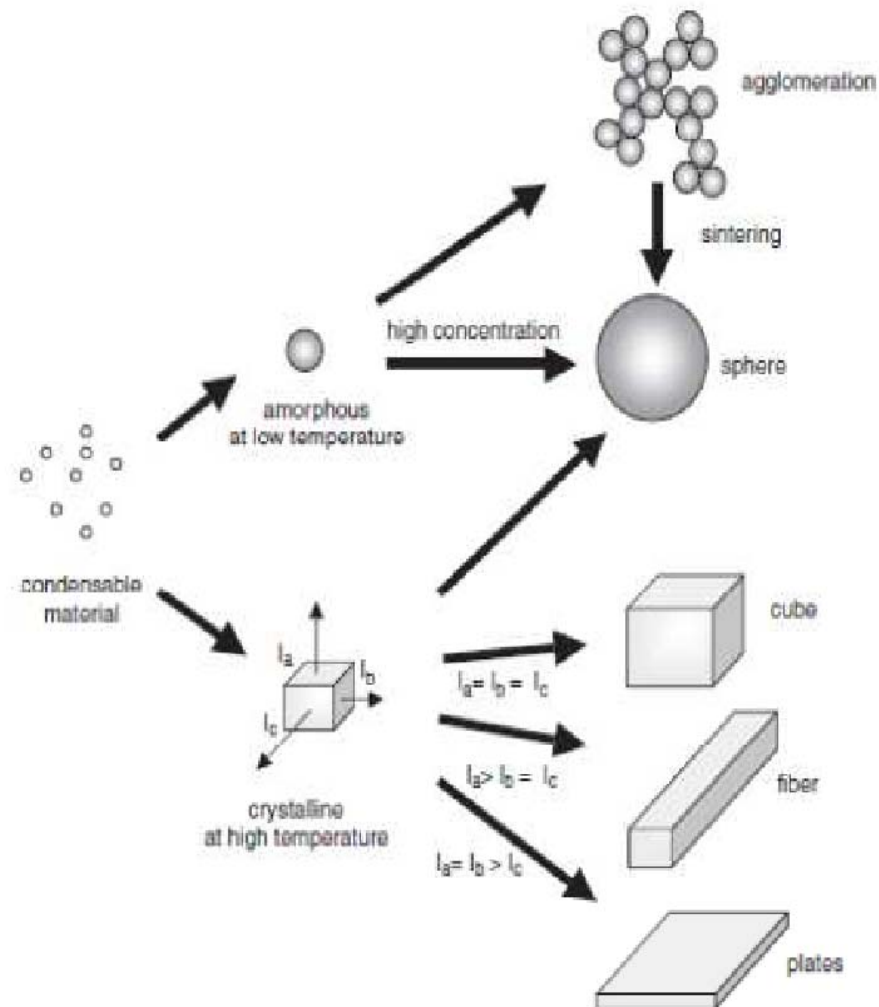
The production is performed by the thermal decomposition of titanium tetrahydroxide. Agglomerates are obtained except at 1300°C, where the production of spherical particles is given due to sintering.



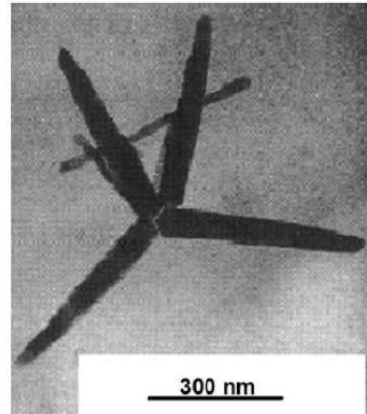
Morphology of the produced particles depends of the crystallinity of the target material.

Amorphous particles are produced at relative low temperatures and are generally of spheroidal shape, since growth rate is equal in all directions.

At higher temperatures, high crystallinity is achieved. Different growth rates in different directions will determine the habit (rods, cylinders, cubes). Only in case of equal growth rate in all directions, the habit may be spherical.



In case of zinc oxides, a star like shape is obtained, but only if the concentration of zinc is higher than a certain critical amount. At low concentration values of Zn, spherical zinc oxide particles are obtained.



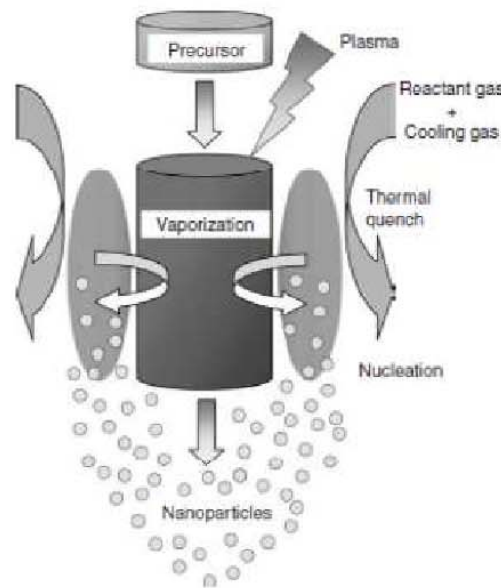
## PLASMA SYNTHESIS

Permits the production of large quantities of nanoparticles.

Permits to produce composite particles of different materials and different internal structures (not possible by other techniques such as CVD where the different vaporization temperatures of the materials will not allow the production of composites).

## METHOD

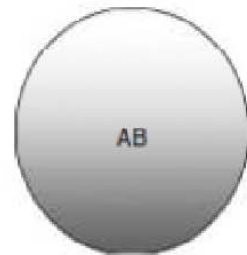
A high temperature plasma is irradiated on the material transported by a gas (air). The plasma will disassociate the material and allow the production of new chemical bonds (example: oxides) that will precipitate by cooling.



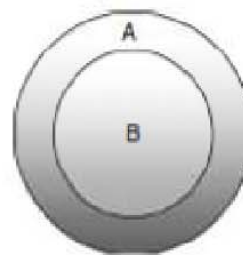


Products	Chemical formula (% means percent by mass)	Equivalent spherical diameter (nm)
Yttria stabilized zirconia	YSZ: $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$	30
Titanium silicon oxide	94% $TiO_2$ -6% $SiO_2$	60
	67% $TiO_2$ -33% $SiO_2$	70
	25% $TiO_2$ -75% $SiO_2$	100
	BTO: $BaTiO_3$	115
Samarium doped ceria – Nickel oxide	NiO-SDC: $x\%[(CeO_2)_x(Sm_2O_3)_{1-x}]-(100-x)\%NiO$	60
Lanthanum strontium manganese oxide	LSM: $(La_xSr_{1-x})MnO_3$	65
YSZ – Nickel oxide	$x\%YSZ-(100-x)\%NiO$	45
Ferrite	MO- $nFe_2O_3$	70
Cerium zirconium oxide	$(CeO_2)_x/(ZrO_2)_{1-x}$	15
Aluminum silicon oxide	$x\%Al_2O_3-(100-x)\%SiO_2$	110
Zirconium silicon oxide	50% $ZrO_2$ -50% $SiO_2$	25
Calcium silicon oxide	50% $CaO$ -50% $SiO_2$	93
Manganese doped zinc silicon oxide	$Zn_2SiO_4:Mn^{2+}$	50
Indium tin oxide	ITO: 95% $ln_2O_3$ /5% $SnO_2$	20

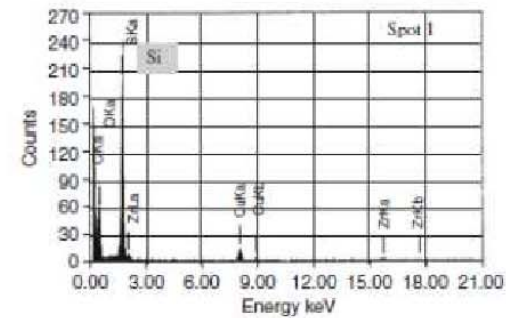
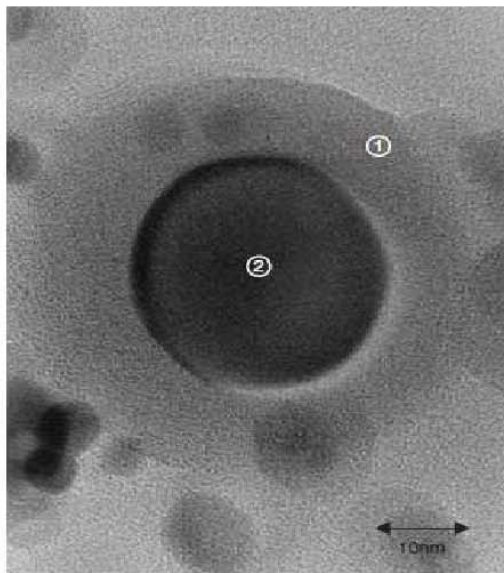
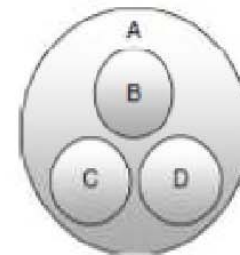
Compound, Solid solution particle



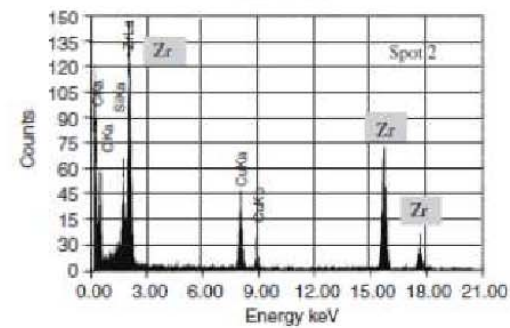
Coating particle



Dispersed multicomponent particle



1



2

## AEROSOL SYNTHESIS

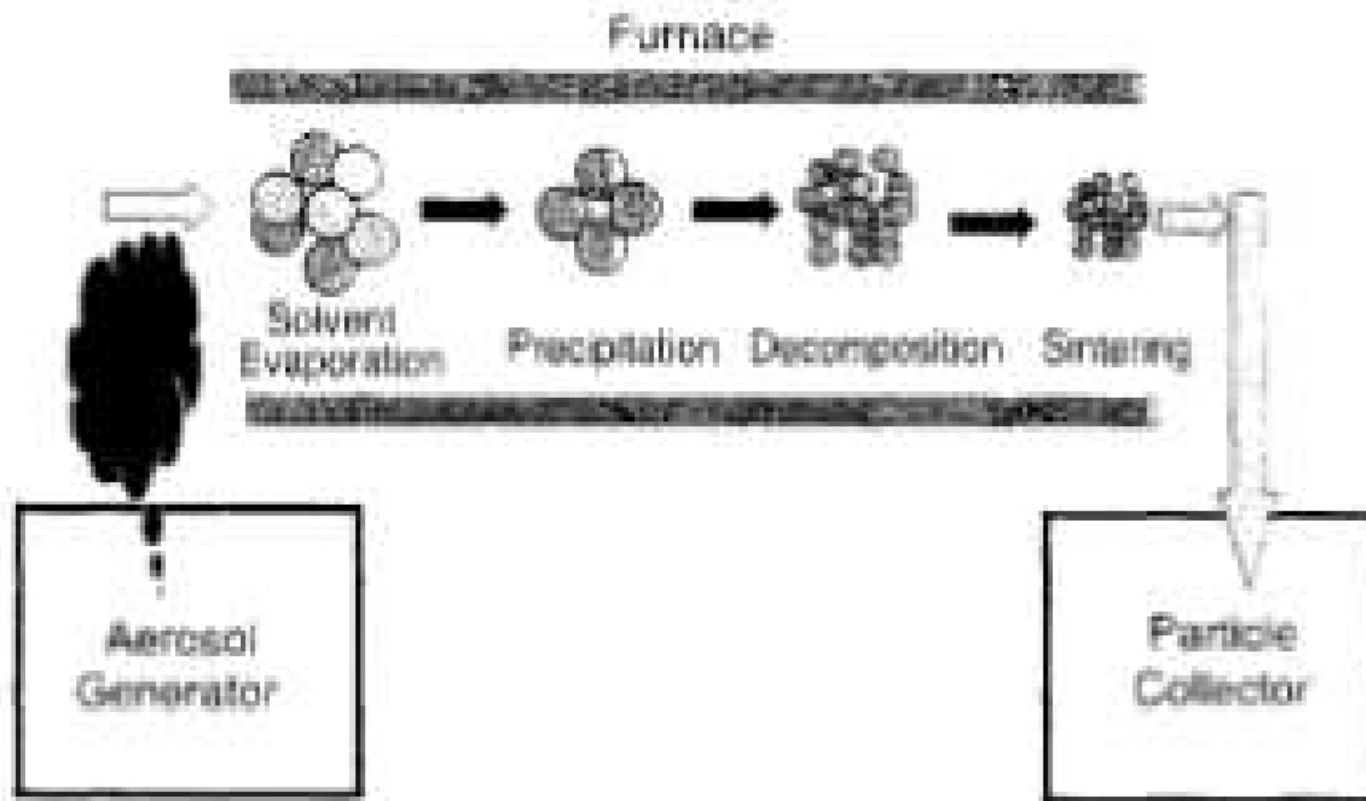
The starting material is a homogeneous liquid converted to aerosol. After this, the aerosol is converted to a gas suspension of solid nanoparticles.

The techniques are: aerosol pyrolysis and aerosol flame pyrolysis

The techniques are also called “spray pyrolysis” since the formation of the aerosol is given by a spray nozzle which generates very small liquid droplets suspended in a incoming gas phase.

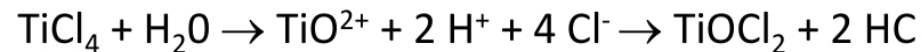
## METHOD – AEROSOL PYROLYSIS

Solvent evaporation → precipitation of the solid product (solute) → sintering

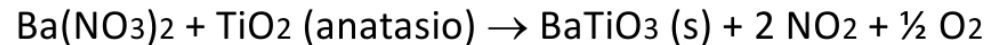


## EXAMPLE: Barium titante production

The first reaction is as follows:



At 380°C, the titania will shift to the anatase phase. In presence of barium nitrate, at 540-650°C, finally barium titanate is produced:



The advantages of this process are purity, spherical particles and no agglomeration; disadvantages are wide PSD, the necessity of high gas flow rates to avoid agglomeration, low productivities and difficulty in the scale-up.

## AEROSOL SYNTHESIS

The aerosol may be formed by a sprayer device. In this case, the starting liquid is formed by a metallic salt solution. The sprayer will eject the liquid in small droplets directly in a furnace, where:

1. The solvent will evaporate
2. The solute will diffuse
3. Drying
4. Precipitation
5. Reaction with the ambient gas of the precursor
6. Pyrolysis
7. Sintering

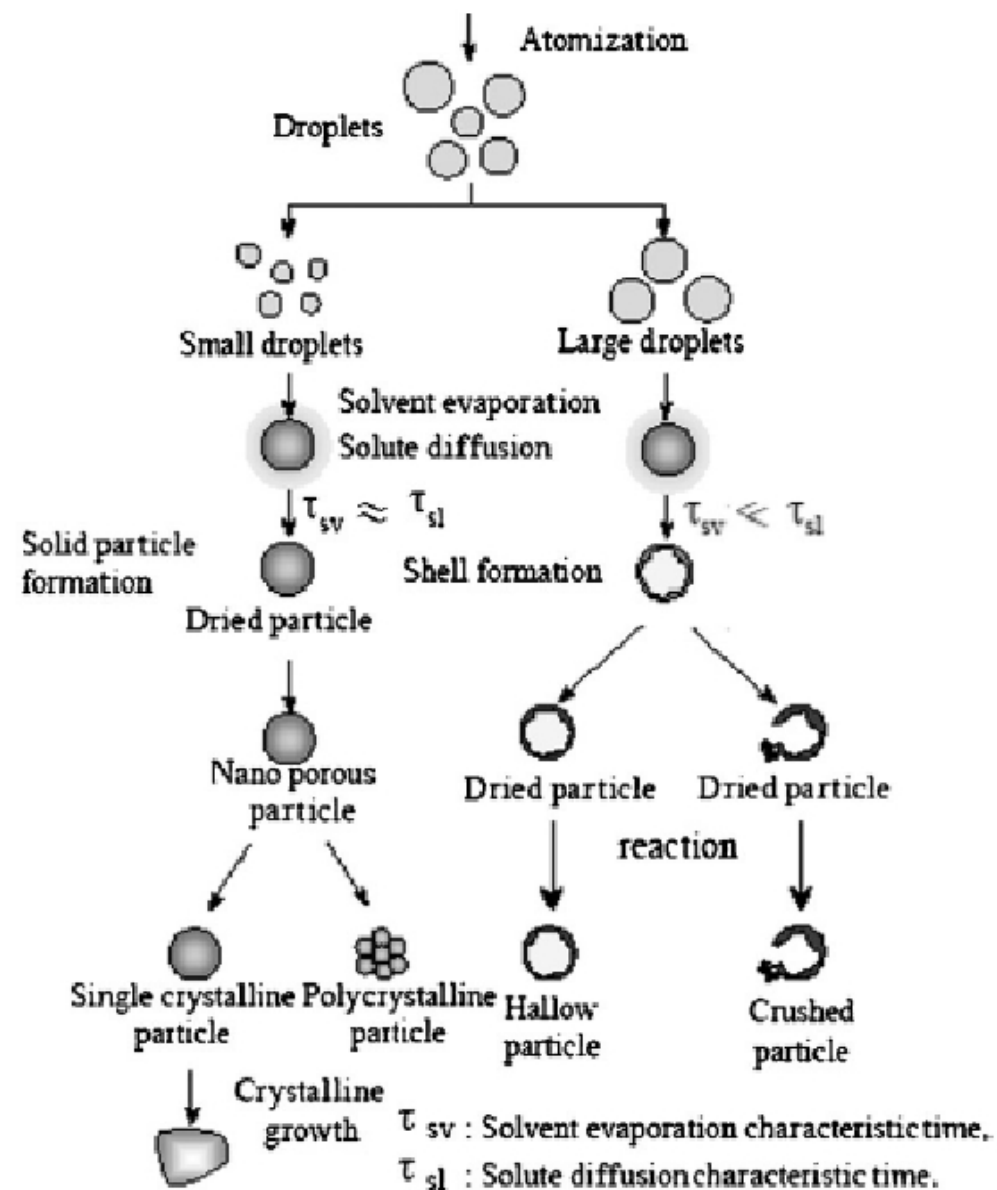
## MORPHOLOGY

The dimension and the morphology will depend on the concentration and velocity of the droplets: it is possible to obtain compact, porous or void particles.

The final morphology is a function of two characteristic times: solvent evaporation and solute diffusion.

In case of low heating rates and/or small droplets dimensions, coarse mono- or polycrystalline particles are obtained.

In case a near to the fusion temperature of the material is reached, spherical, dense and compact particles are obtained.

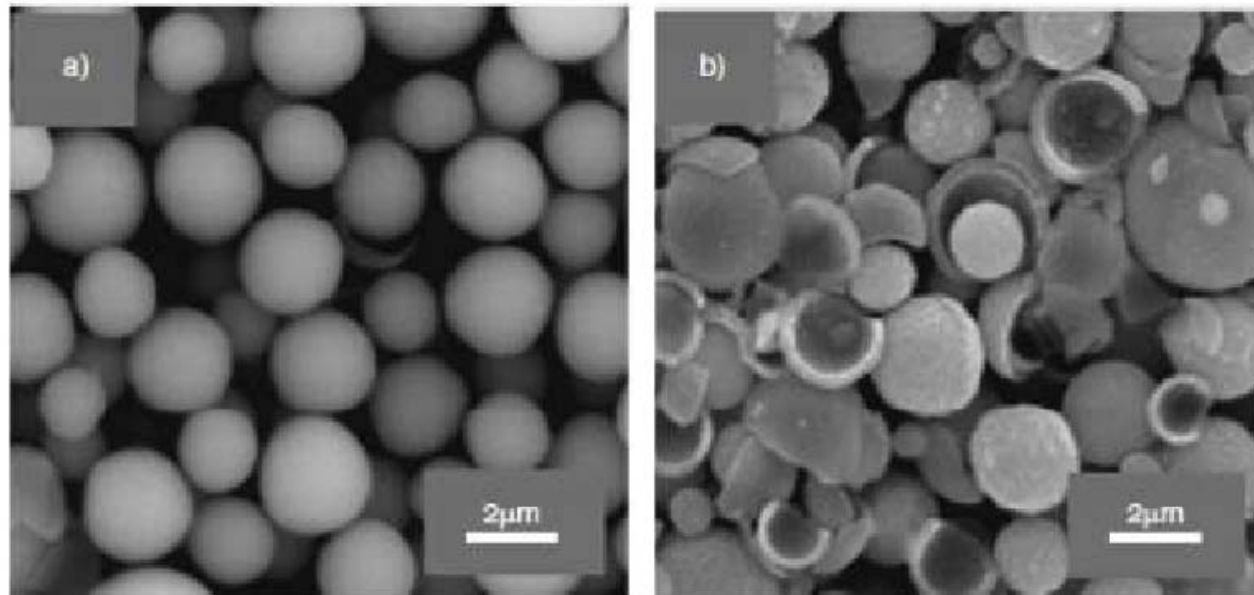




## EXAMPLE: ZIRCONIUM OXIDE

LEFT: low heating rate

RIGHT: high heating rate with void core particles and a porous shell  
(given by the evaporation of the solvent from the liquid core to the ambient)



# PVD

Physical Vapor Deposition is based on the condensation of a gas or a vapor up to solid particles.

Evaporation may be achieved by:

Direct evaporation, electron cannon, electric arc or laser

Advantages:

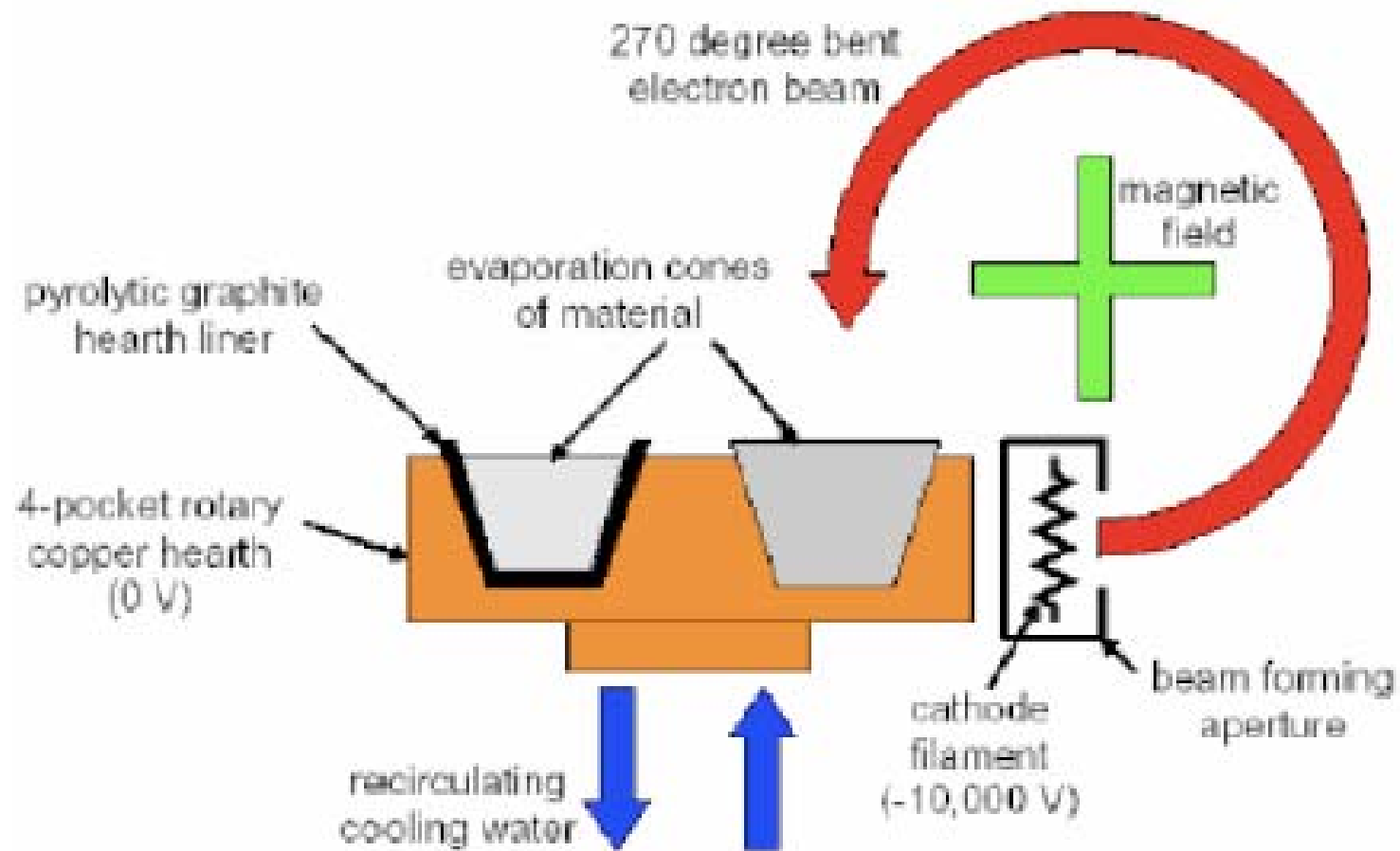
Production of ultrafine particles

Clear surfaces

Wide range of target materials

Flexibility in crystallinity control

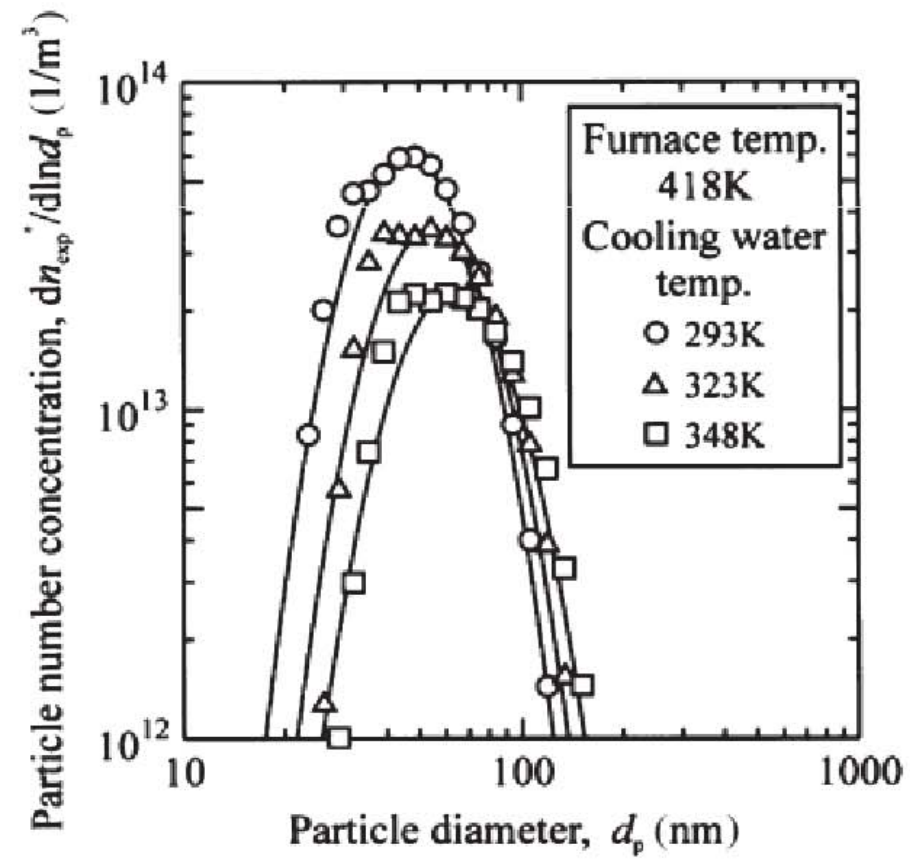
# Electron cannon

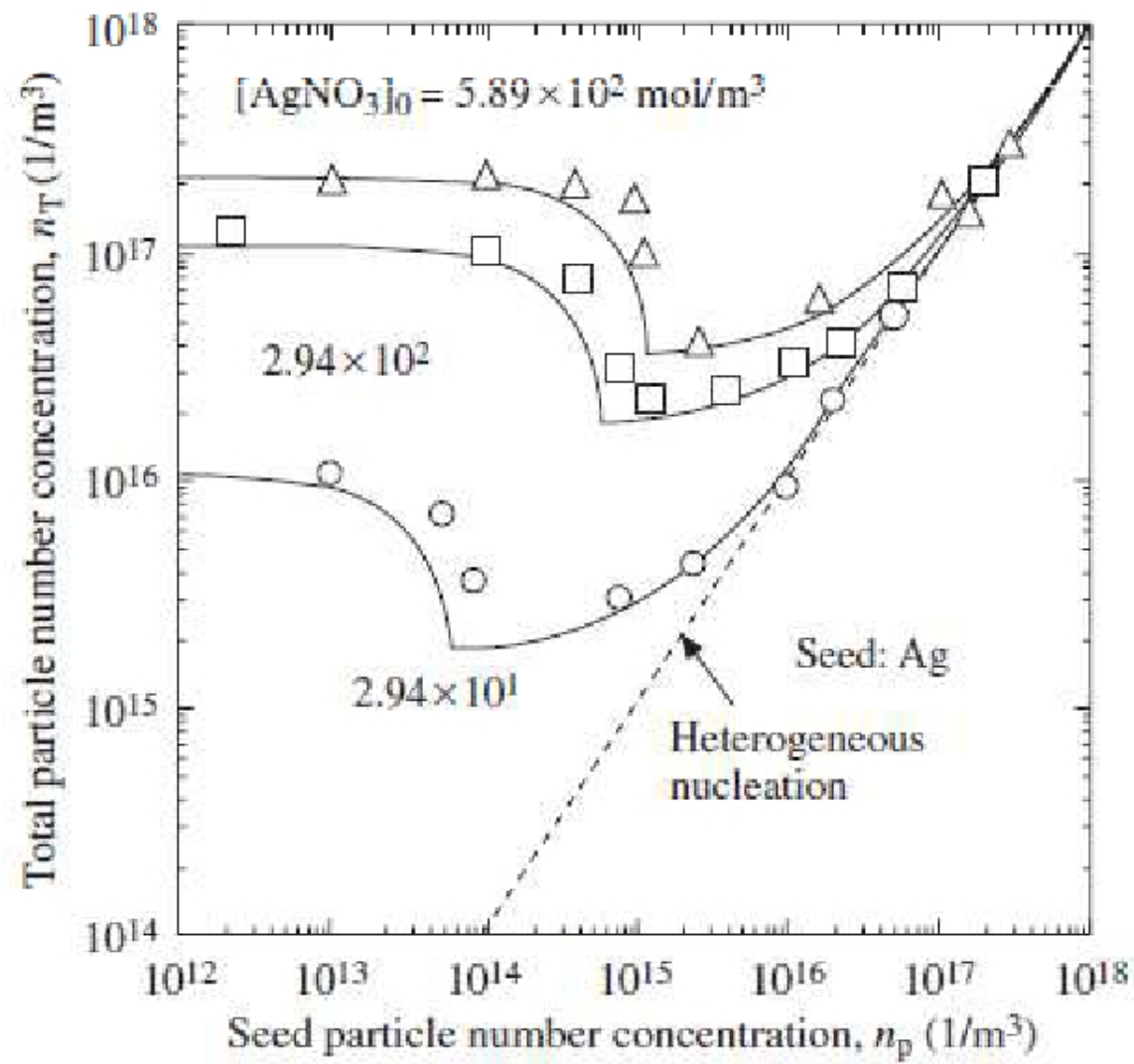


## METHODS

1. Evaporation of the material in void ambient or in presence of inert gas. Condensation is performed on cold surfaces.
2. The vaporized material is condensed on a cold material under void conditions.
3. A organic vapor is mixed to inert gas that transports the particles (seed) and send to a liquid nitrogen cooled reactor where heterogeneous nucleation occurs.
4. The gas transports some seeds in a cooled organic liquid trap, such as ethanol at low temperatures (-30°C up to -140°C)

## PARTICLE SIZE AS A FUNCTION OF THE COOLING TEMPERATURE





EFFECT OF SEEDING