Building College-University Partnerships for Nanotechnology Workforce Development

Nanoparticle Synthesis and Applications

Outline

- Nanoparticle Synthesis
  - Colloidal Chemical Methods
  - Attrition
  - Pyrolysis
  - RF Plasma
  - Thermal decomposition
  - Pulsed Laser Method
- Some Nanoparticle Applications

Colloidal Methods

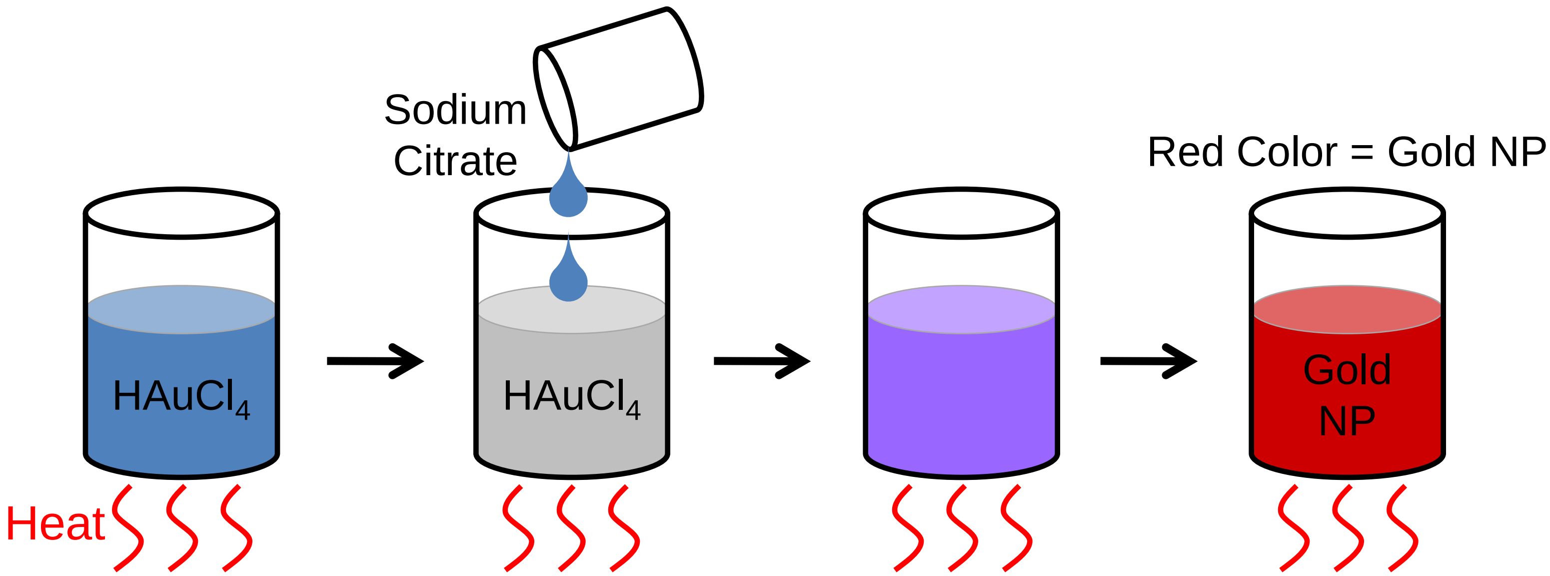
- Colloidal chemical methods are some of the most useful, easiest, and cheapest ways to create nanoparticles.
- Colloidal methods may utilize both organic and inorganic reactants.
- Typically, a metal salt is reduced leaving nanoparticles evenly dispersed in a liquid.
- Aggregation is prevented by electrostatic repulsion or the introduction of a stabilizing reagent that coats the particle surfaces.
- Particle sizes range from 1-200nm and are controlled by the initial concentrations of the reactants and the action of the stabilizing reagent.

Colloidal Methods

- Examples: Gold
  - A common method for preparing colloidal gold nanoparticles involves combining hydrogen tetrachloroaurate ($HAuCl_4$) and sodium citrate ($Na_3C_6H_5O_7$) in a dilute solution.
  - Upon dissociation, the citrate ions ($C_6H_5O_7^{3-}$) reduce Au^{3+} to yield 30-40 nm gold particles.

  Half reaction equations:
    - Au^{3+}(aq) + $3e^-$ → Au(s)
    - $C_6H_5O_7^{3-}$(aq) +H_2O(l) → $C_5H_4O_4^{2-}$(aq) + CO_2(g) + H_3O(aq) + $2e^-$

Example: Formation of Gold Nanoparticles



1. Heat a solution of chloroauric acid ($HAuCl_4$) up to reflux (boiling). $HAuCl_4$ is a water soluble gold salt.
2. Add trisodium citrate, which is a reducing agent.
3. Continue stirring and heating for about 10 minutes.
   - During this time, the sodium citrate reduces the gold salt (Au^{3+}) to metallic gold (Au^0).
   - The neutral gold atoms aggregate into seed crystals.
   - The seed crystals continue to grow and eventually form gold nanoparticles.

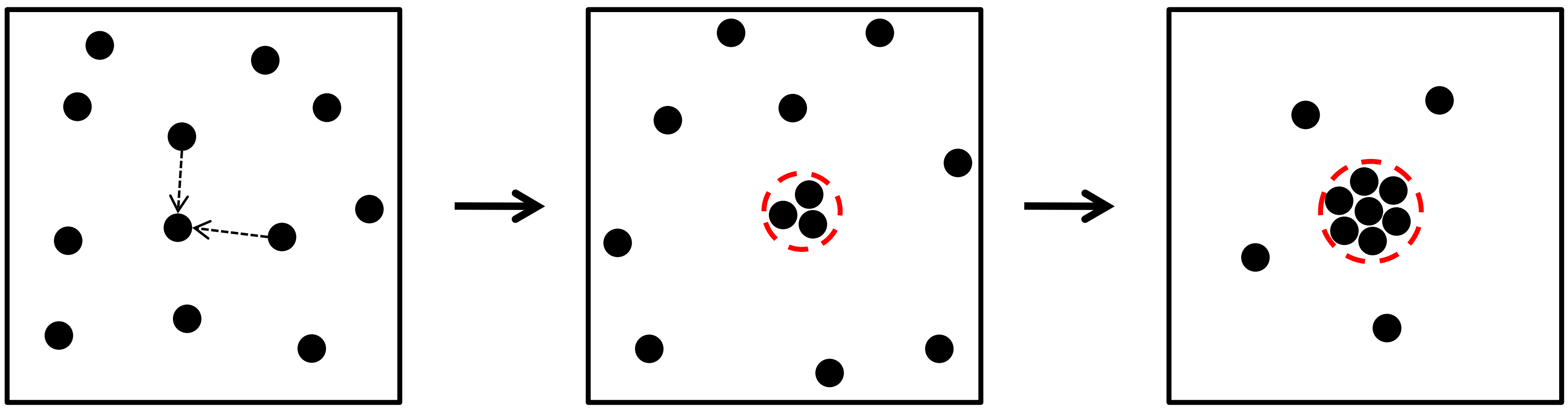
http://mrsec.wisc.edu/Edetc/nanolab/gold/index.html
J. Chem. Ed. 2004, 81, 544A.

Example: Formation of Gold Nanoparticles

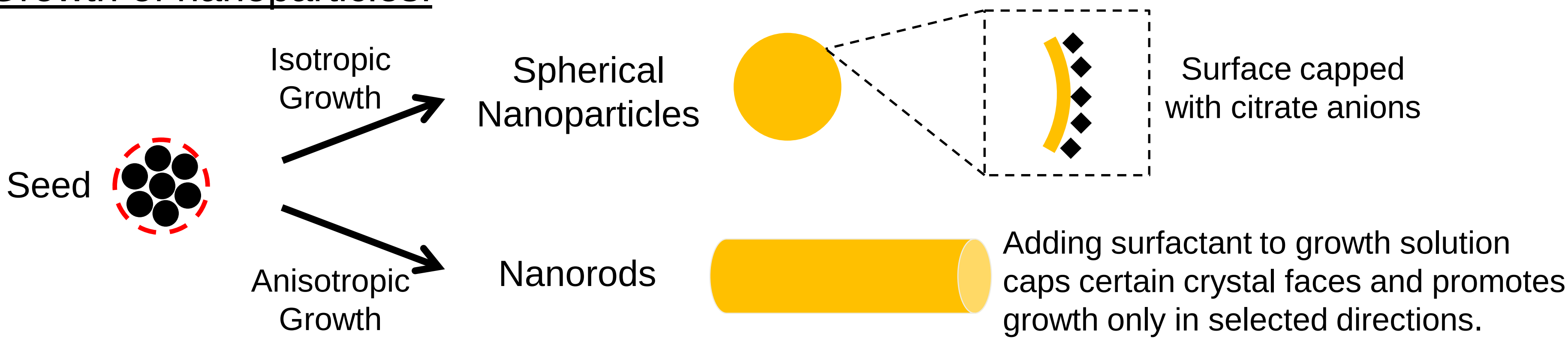
<u>Reduction of gold ions:</u> $Au(III) + 3e^{-} \rightarrow Au(0)$

<u>Nucleation of Au(0) seed crystals:</u>

Seed Crystal
10's to 100's of Atoms



<u>Growth of nanoparticles:</u>



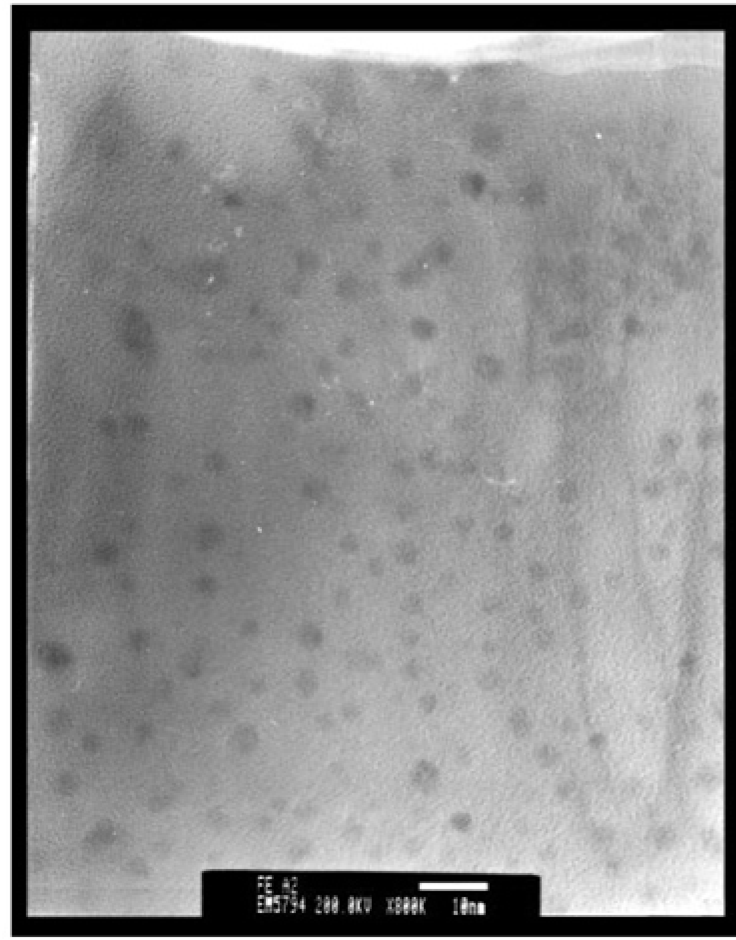
Colloidial Methods

- Examples: Molybdenum
  - 1-5 nm molybdenum nanoparticles can be created at room temperature by reducing $MoCl_3$ in a toluene solution in the presence of sodium triethylborohydride ($NaBEt_3H$).
  - Reaction equation:

    $MoCl_3 + 3NaBEt_3H \rightarrow Mo + 3NaCl + 3BEt_3 + (3/2)H_2$

Colloidal Methods

- Examples: Iron
  - The TEM image to the right shows 3nm Fe nanoparticles produced by reducing $FeCl_2$ with sodium borohydride ($NaBH_4$) in xylene.
  - Trioctylphosphine oxide (TOPO) was introduced as a capping agent to prevent oxidation and aggregation

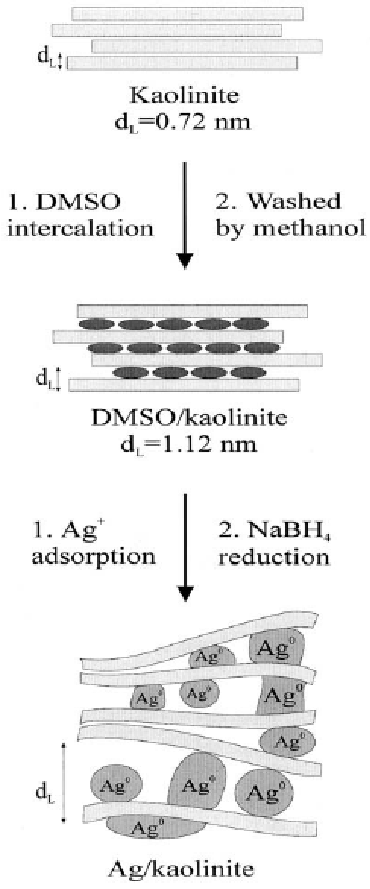


TEM image of Fe nanoparticles

Phys. Chem. Chem. Phys., 2001, 3, 1661È1665

Colloidal Methods

- Examples: Silver
  - The reduction of $AgNO_3$ by $NaBH_4$ in aqueous solution can produce small diameter (<5nm) silver nanoparticles
  - In one reported method, the reduction takes place between layers of kaolinite, a layered silicate clay material that functions to limit particle growth.
  - Dimethyl sulfoxide (DMSO) is used as a capping agent to prevent corrosion and aggregation of the Ag particles.



Schematic illustration of the preparation of Ag nanoparticles on kaolinite.

R. Patakfalvi et al. / Colloids and Surfaces A: Physicochem. Eng. Aspects 220 (2003) 45/54

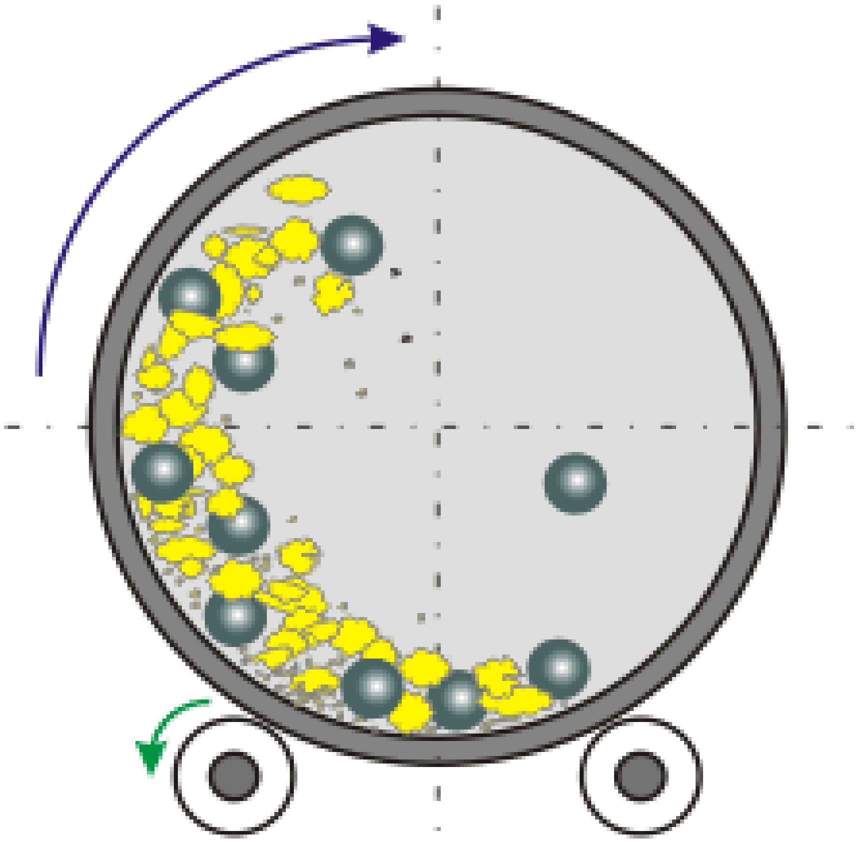
Attrition

- Attrition is a mechanical method for creating certain types of nanoparticles.
- Macro or micro scale particles are ground in a ball mill, a planetary ball mill, or other size reducing mechanism.
- The resulting particles are separated by filters and recovered.
- Particle sizes range from tens to hundreds of nm.
- Broad size distribution and varied particle geometry.
- May contain defects and impurities from the milling process.
- Generally considered to be very energy intensive.

Cao, Guozhong. *Nanostructures and Nanomaterials: Synthesis, Properties & Applications.* Imperial College Press. 2004

Attrition: Rotary Ball Mill

- A hollow steel cylinder containing tungsten balls and a solid precursor rotates about its central axis.
- Particle size is reduced by brittle fracturing resulting from ball-ball and ball-wall collisions.
- Milling takes place in an inert gas atmosphere to reduce contamination.



http://www.ktf-split.hr/glossary/image/ball_mill.gif

Attrition

- Attrition Examples

Composition	Attrition technique	Grain size (nm)	Attrition time (h)
Fe-Co powders	Rotary ball mill	10–15	30
Fe	Vibratory mill	20	4
NiAl	Vibratory mill	12	100
Ni silicides	Vibratory mill	10–17	30
Fe-C	Horizontal ball mill	4.7	500
Fe_3Al	Vibratory mill	12.6	100

Claudio L. De Castro, Brian S. Mitchell. Nanoparticles from Mechanical Attrition.

Department of Chemical Engineering, Tulane University, New Orleans, Louisiana, USA

Outline

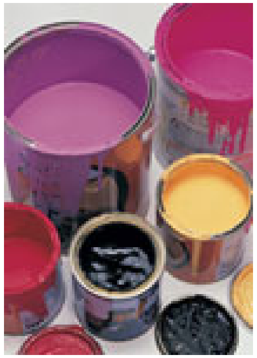
- Nanoparticle Synthesis
  - Colloidal Chemical Methods
  - Attrition
  - Pyrolysis
  - RF Plasma
  - Thermal Decomposition
  - Pulsed Laser Method
- Nanoparticle Applications

Pyrolysis

- History
- System Overview
- Aggregation and agglomeration
- Impact of oxygen flow
- Jet design
- Flame quenching
    - Nozzle quenching
    - Electrostatic Charging

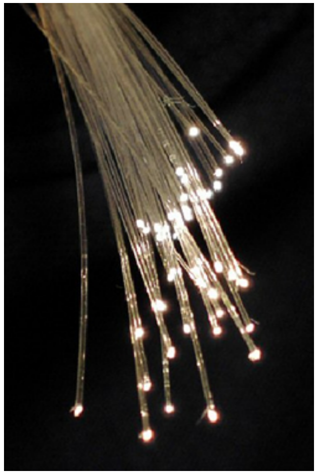
Pyrolysis: Material Applications

Tires



Paints

TiO_2



Optical fibers

Carbon Black

Inks

Makeup

SiO_2

Flowing aid

Images clockwise from top left:
1. Tire <www.Safercar.gov>
2. Paint cans <http://www.ndhealth.gov/wm/PollutionPreventionAndRecyclingProgram/MercuryContainingDevicesProducts.htm>
3. Optical Fibers <https://lasers.llnl.gov/publications/photons_fusion/2009/january_february.php>
4. Vitamans <www.fda.gov/AboutFDA/WhatWeDo/History/ThisWeek/ucm117726.htm>
5. Makeup <https://pa-online.pa.gov.sg/NASApp/sdsol/sdsol/common/Bring_Out_Best_In_You.htm>
6. Ink Quil < http://www.orovalleyaz.gov/Town_Government/Town_Clerk/notary_services.htm>

Annual Production of Flame made materials

- Carbon black – 8 million tons $8 billion
- TiO_2 - 2.5 million tons, $5 billion
- SiO_2 2.0 million tons, $2 billion

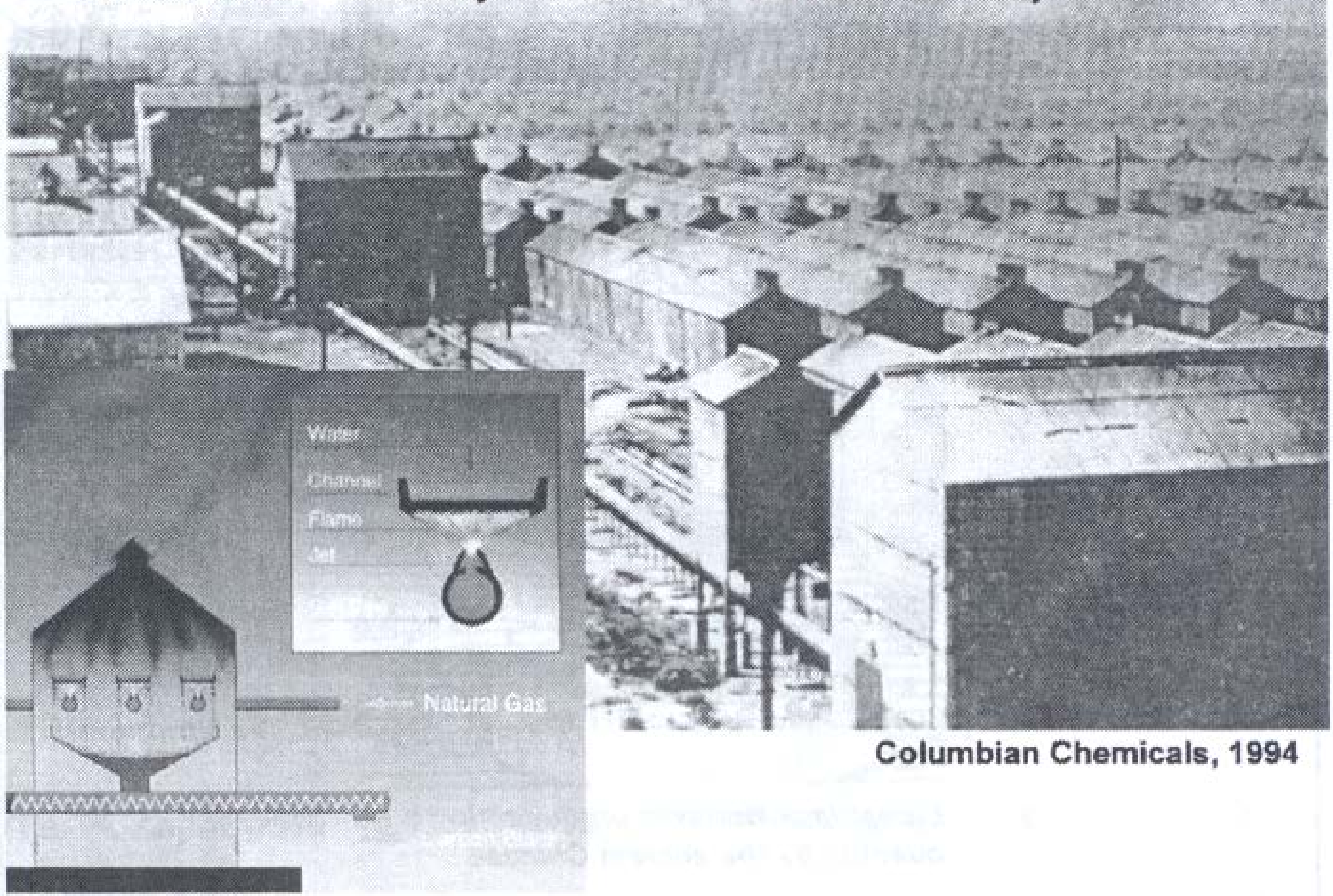
History: Advertisement in Farbe & Lacke (1949) of SiO_2 nanoparticles

Between 4 to 20 millimicron is the particle size of ***aerosil****, the new additive for the lacquer industry.*

Please ask for the new brochure at Degussa, Carbon Black Dept., Frankfurt

Pratsinis, Sotiris E., Functional Nanoparticles and Films Made in the Gas-phase. Nano Science and Technology Institute, Cambridge. 2008

Channel Plant, Texas Panhandle, 1940's



Columbian Chemicals, 1994

Degussa, 1996

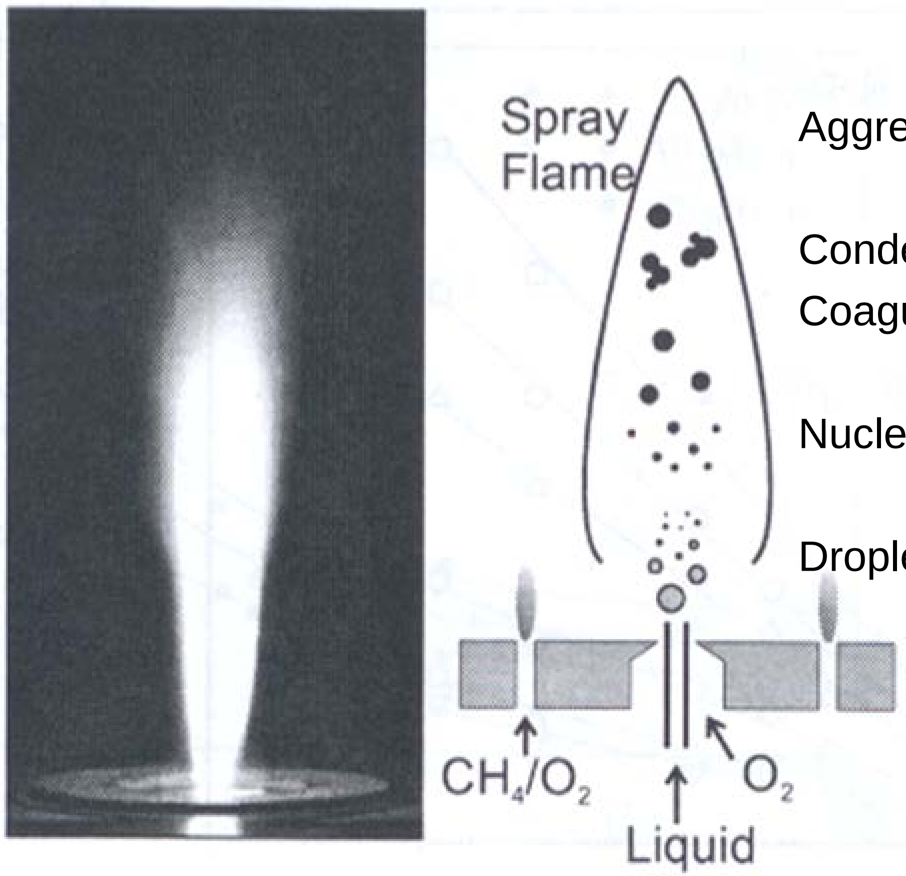
Pratsinis, Sotiris E., Functional Nanoparticles and Films Made in the Gas-phase. Nano Science and Technology Institute, Cambridge. 2008

Pyrolysis

- **Pyrolysis** is a popular method for creating nanoparticles, especially oxides. A precursor (liquid or gas) is forced through an orifice at high pressure and burned.
- The resulting ash is collected to recover the nanoparticles.
- Large volume of gas leads to high rate of material synthesis

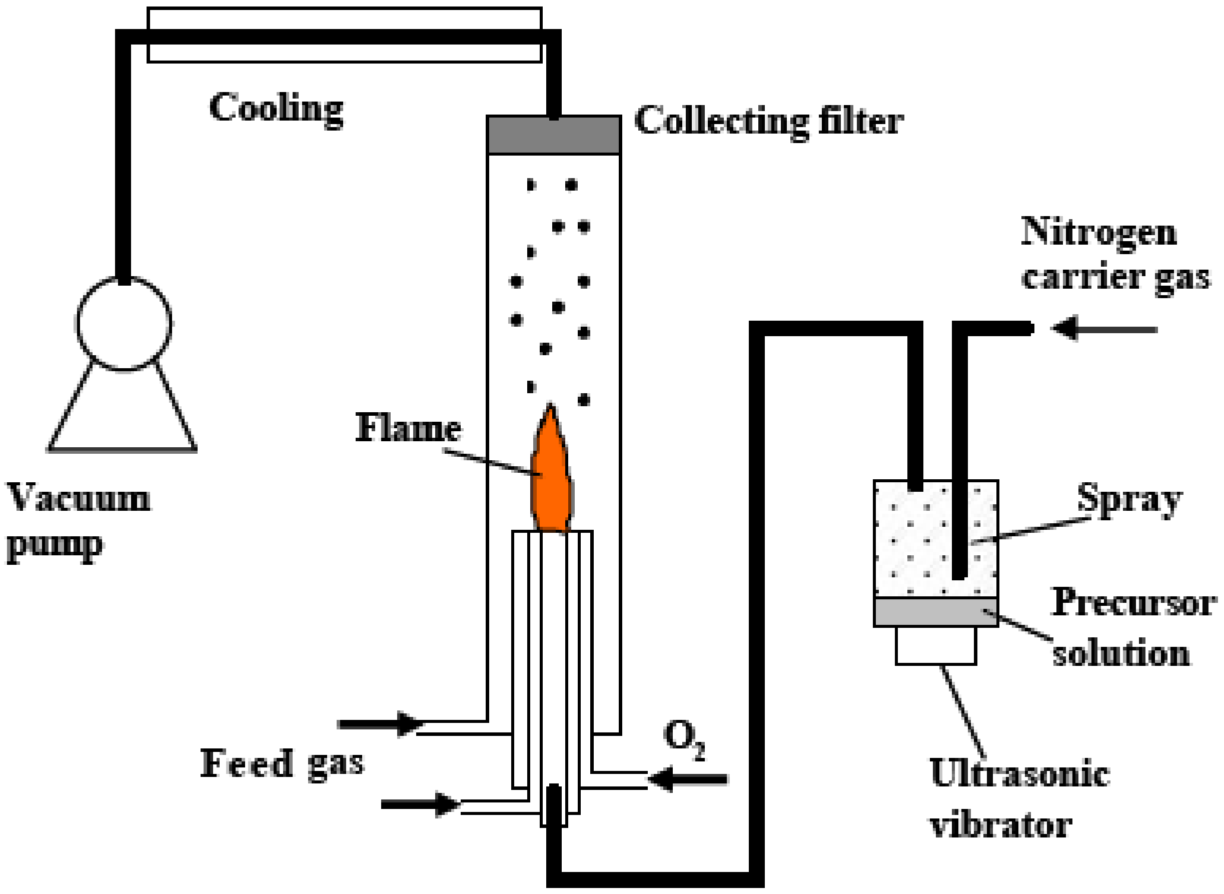
Flame Spray Pyrolysis (FSP)

- Versatile
- Large Variety of precursors
- Controllable
- Scalable



Mädler et al., *J. Aerosol Soc.* **33**, 369-389 (2002)

Pyrolysis: System Overview



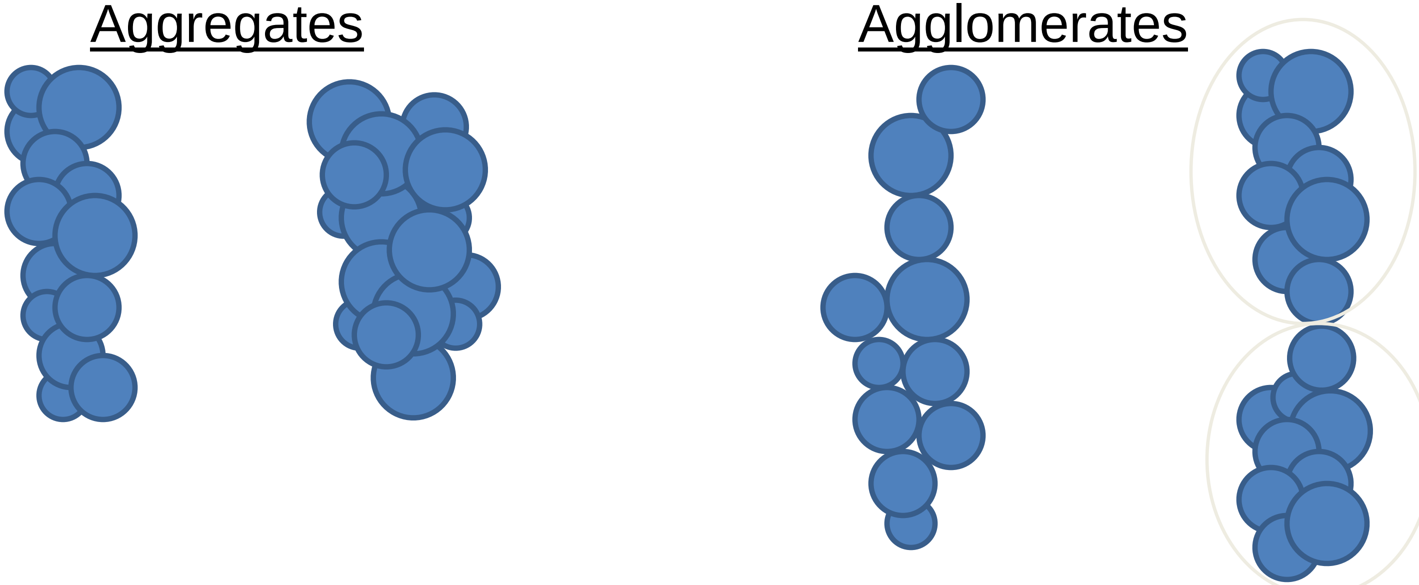
Xiao Q., Yiguang J., Stefan B. and Nan Y. *Synthesis of Y2O3:Eu Phosphor Nanoparticles by Flame Spray Pyrolysis*. Princeton University, Princeton, NJ

Pyrolysis

Aggregates and Agglomerates:

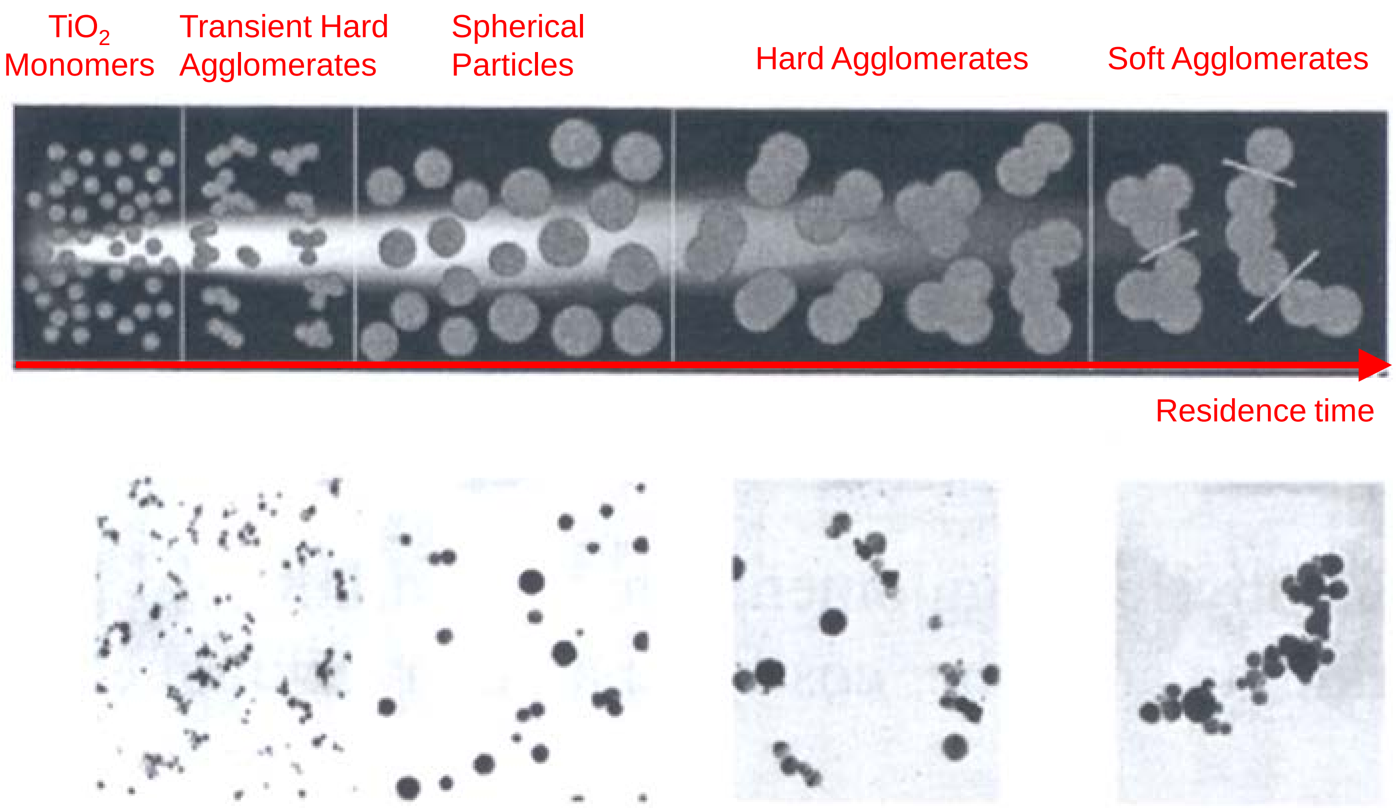
- Aggregate – An assemblage of particles rigidly joined together by chemical or sinter-forces.
- Agglomerate – A loosely coherent assembly of particles and/or aggregates held together by weak interactions
- Current aerosol instruments cannot distinguish between them.

Aggregates Agglomerates



Pyrolysis

Agglomerate Formation Sequence



Images: O. Arabi-Katbi, SEP, P.W.Morrison, C.M. Megaridis (2001), *Combust. Flame* **124**: 560.

Pyrolysis

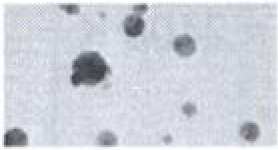
Degree of agglomeration matters:

- Agglomerated
  - Fillers
  - Catalysts
  - Lightguide preforms
  - Particles for CMP
- Non-agglomerated
  - Pigments
  - Composites
  - Electronics
- Distinction between hard and soft agglomerates is largely empirical.
- Controlled agglomeration can minimize post-grinding and other costly separation techniques.

Pratsinis, Sotiris E., Functional Nanoparticles and Films Made in the Gas-phase. Nano Science and Technology Institute, Cambridge. 2008

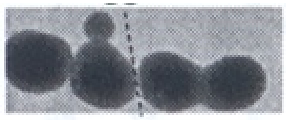
Pyrolysis

Non-Agglomerates

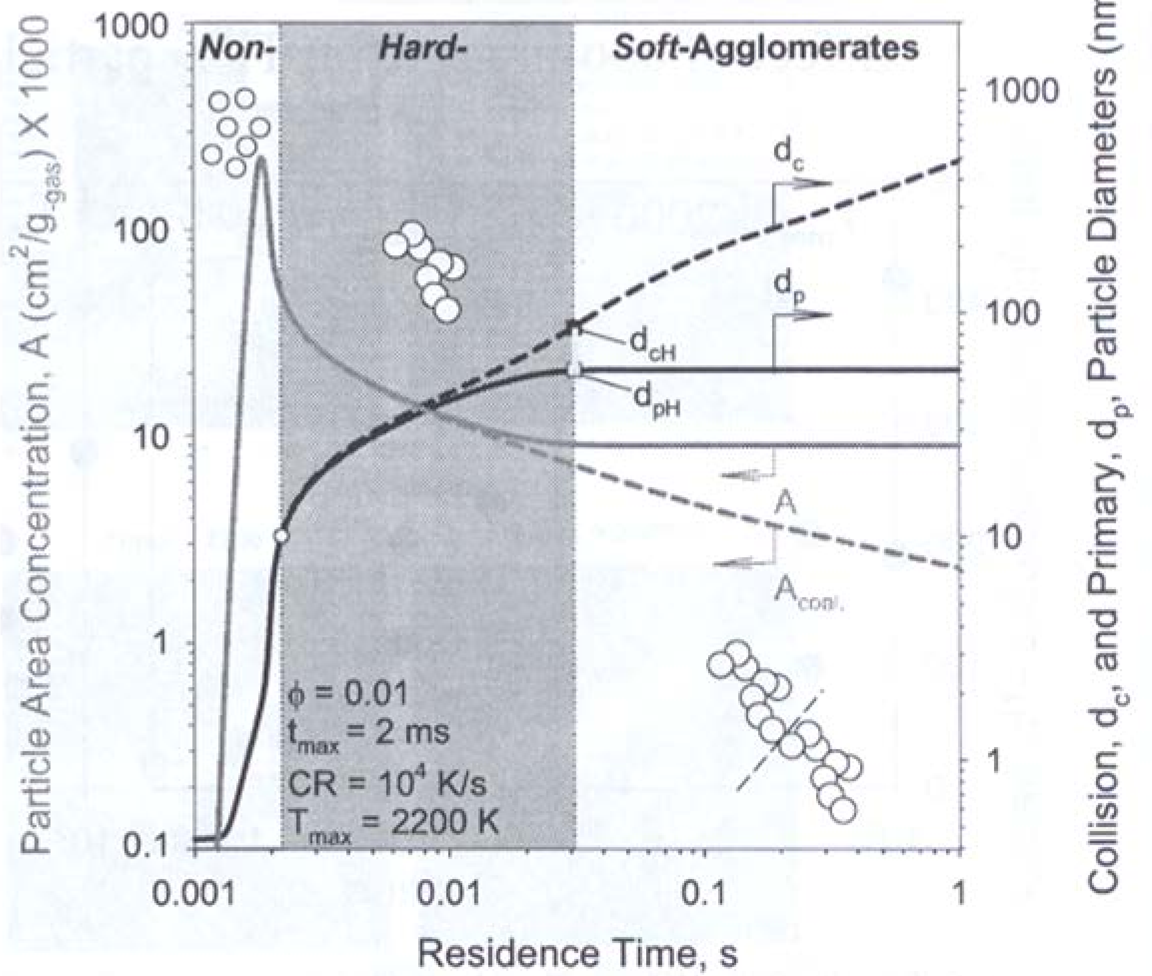


Hard Agglomerates

Soft Agglomerates

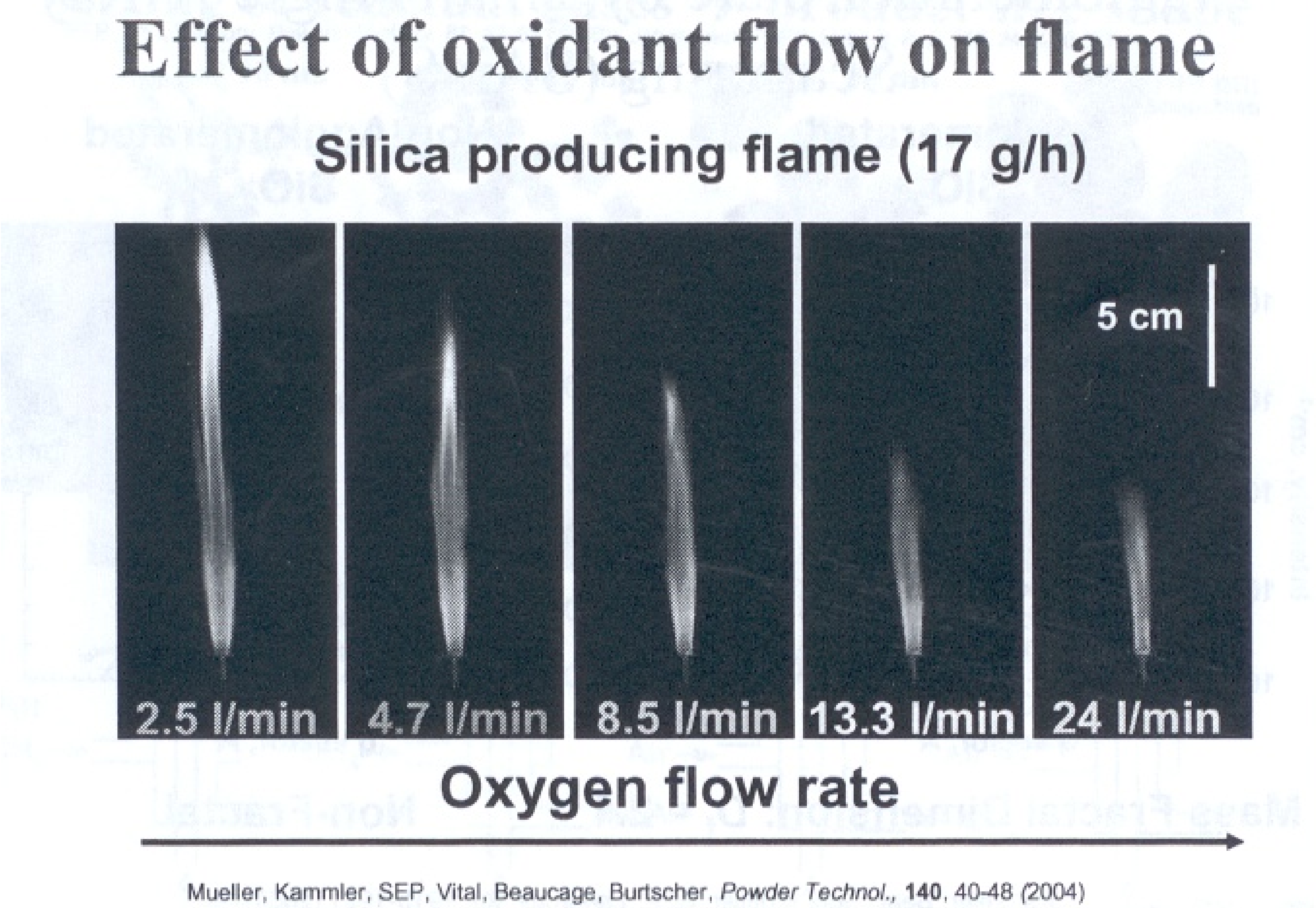


Regions of Agglomeration



Pratsinis, Sotiris E., Functional Nanoparticles and Films Made in the Gas-phase. Nano Science and Technology Institute, Cambridge. 2008

Pyrolysis


Effect of oxidant flow on flame
Silica producing flame (17 g/h)
5 cm
2.5 l/min
4.7 l/min
8.5 l/min
13.3 l/min
24 l/min
Oxygen flow rate
Mueller, Kammler, SEP, Vital, Beaucage, Burtscher, Powder Technol., 140, 40-48 (2004)

Pyrolysis

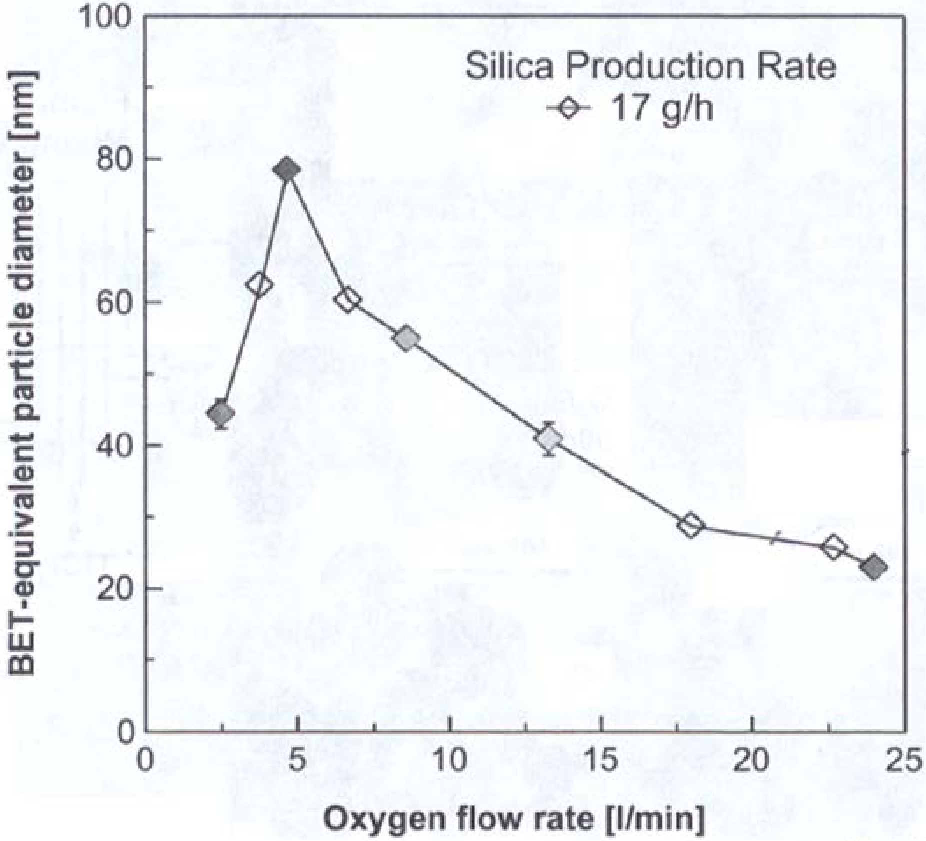
Impact of oxygen

- Aids in combustion
- Provides chemistry in the reaction
- Acts as a dilutent, cools the flame, prevents agglomeration
- All of these variables can be decoupled by burner design. Which is cheaper than increasing oxygen flow.

Pyrolysis

Particle Size Controlled by O_2 Flow

- Excess oxygen makes the flame burn cooler resulting in smaller diameter particles



T_{HMDSO}: 5°C

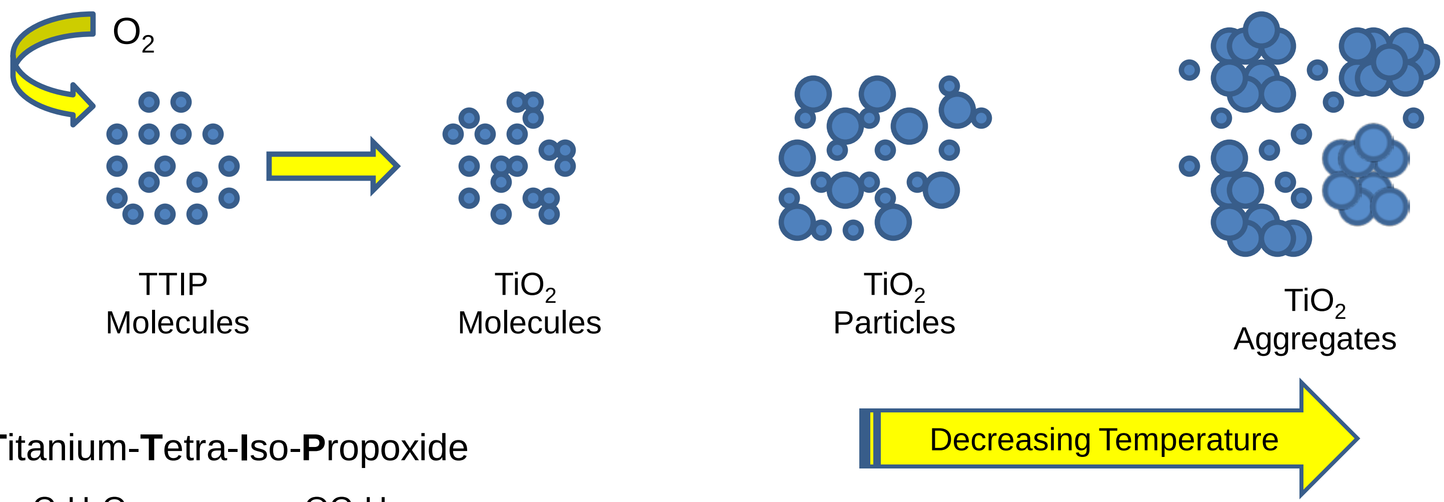
N_2 = 2.9 l/min

CH_4 = 1.4 l/min

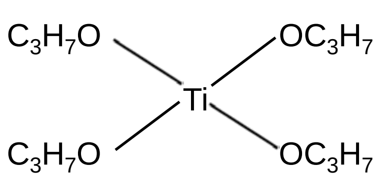
Mueller, Kammler, SEP, Vital, Beaucage, Burtscher, *Powder Technol.*, **140**, 40-48 (2004)

Pyrolysis

Particle Formation and Growth by Gas Phase Chemical Reaction, Coagulation, Sintering and Surface Growth:

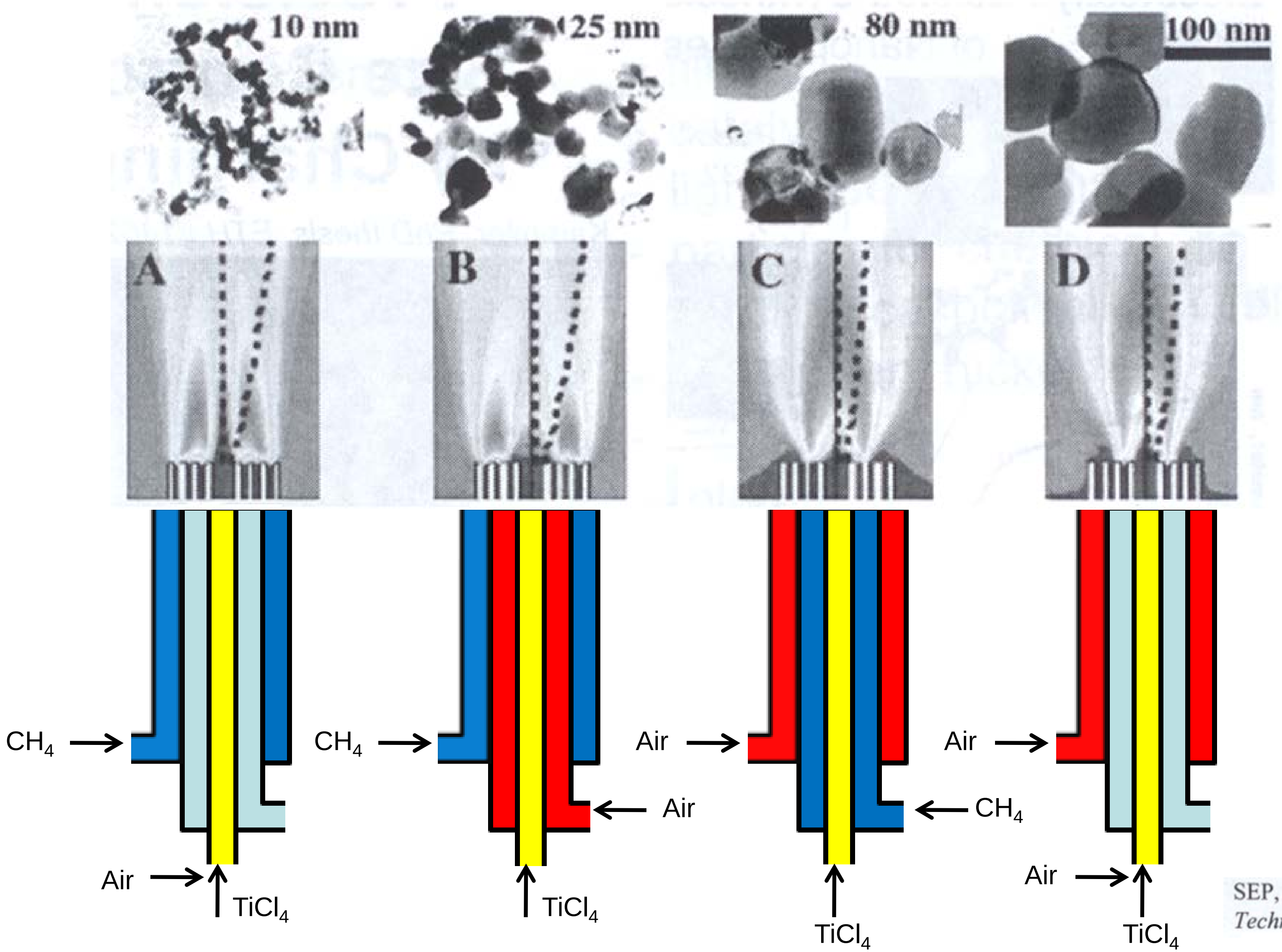


Titanium-**T**etra-**I**so-**P**ropoxide



Pratsinis, Sotiris E., Functional Nanoparticles and Films Made in the Gas-phase. Nano Science and Technology Institute, Cambridge. 2008

Pyrolysis: Jet Design

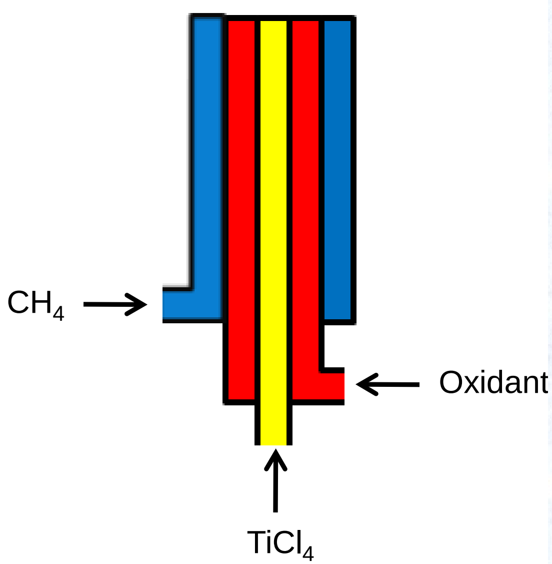


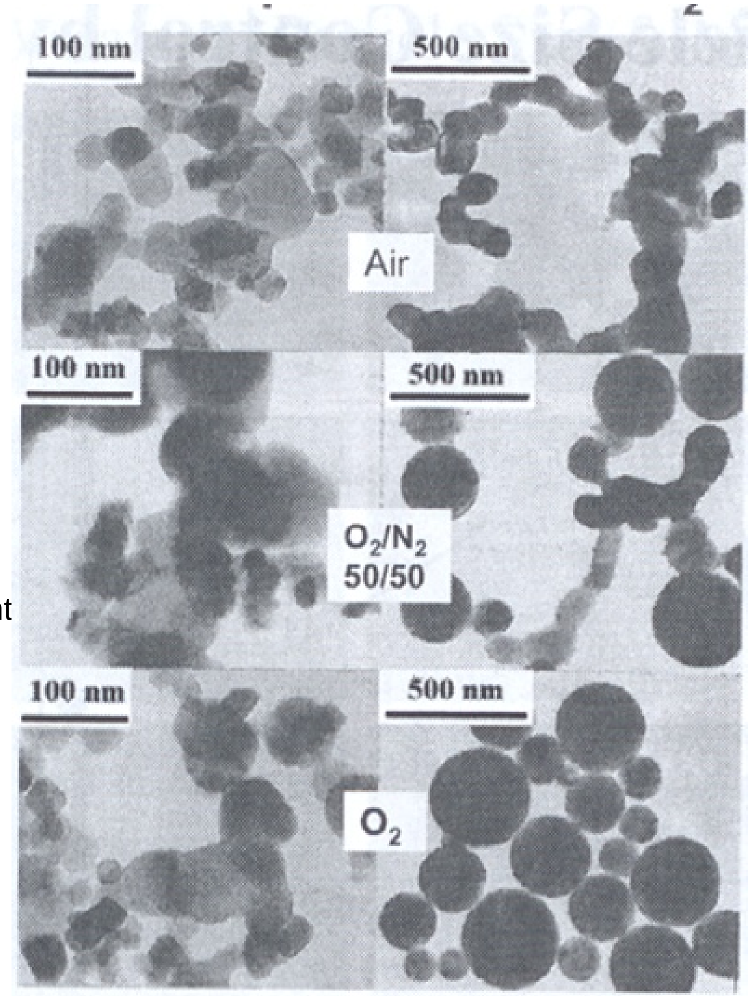
SEP, Zhu, Vemury, *Powder Technol.* **86**, 87-93 (1996)

Pyrolysis: Jet Design

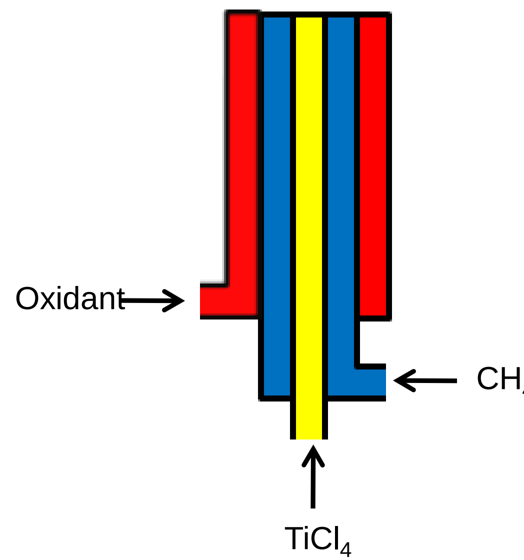
Effect of Oxidant Composition on TiO_2 Morphology:

Flame mixing B





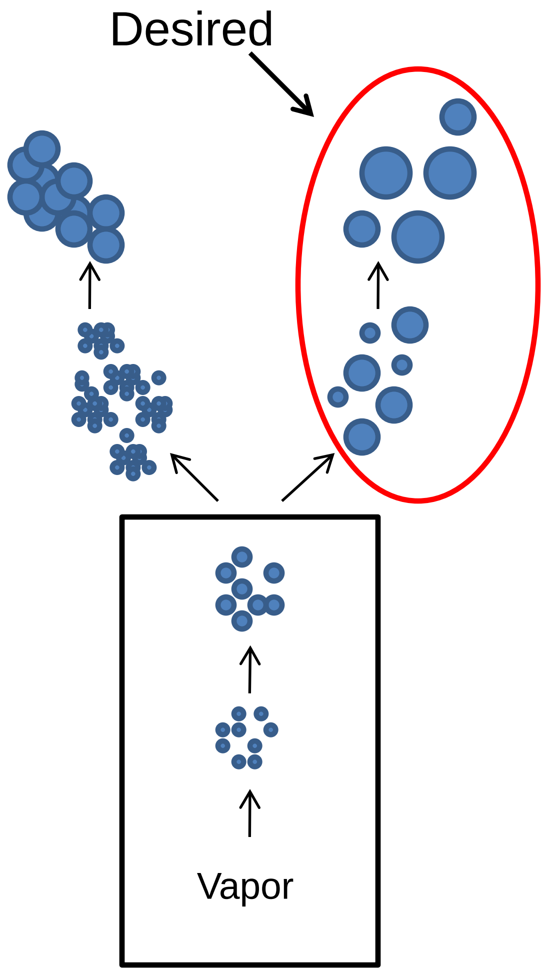
Flame mixing C



W. Zhu, SEP, ACS Symp. Ser. **622**, 64-78 (1996).

Pyrolysis: Nozzle Quenching

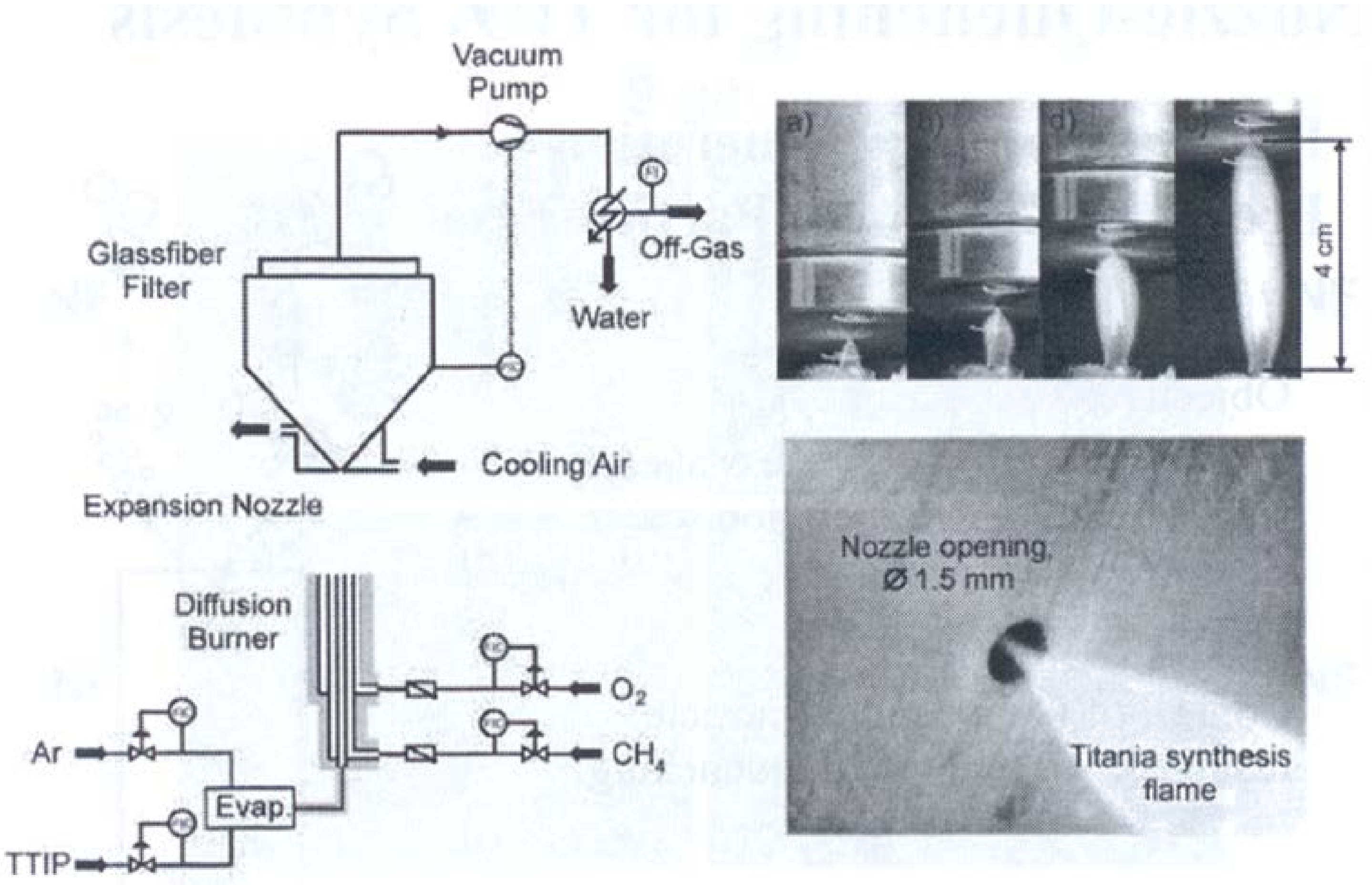
- Flame length is controlled by rapid quenching
- Prevents agglomeration by inhibiting growth processes in the early stages of growth.
- Provides precise control of particle size



Pratsinis, Sotiris E., Functional Nanoparticles and Films Made in the Gas-phase. Nano Science and Technology Institute, Cambridge. 2008

Pyrolysis: Nozzle Quenching

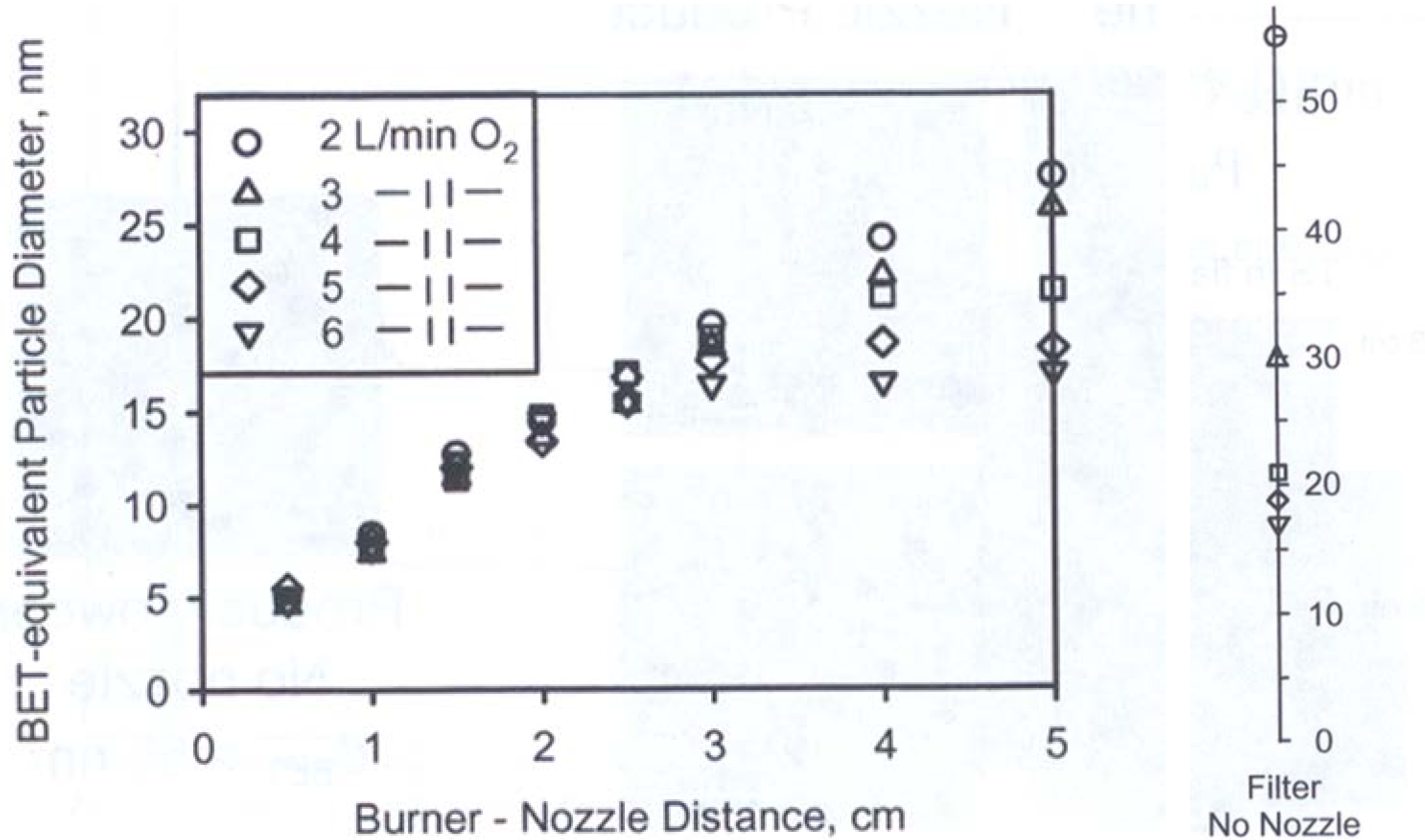
Nozzle Quenching controls flame length and particle size.



Wegner, Stark, SEP, *Mater. Lett.* **55**, 318 (2002)

Pyrolysis: Nozzle Quenching

TiO_2 Particle Size Control by Nozzle Quenching



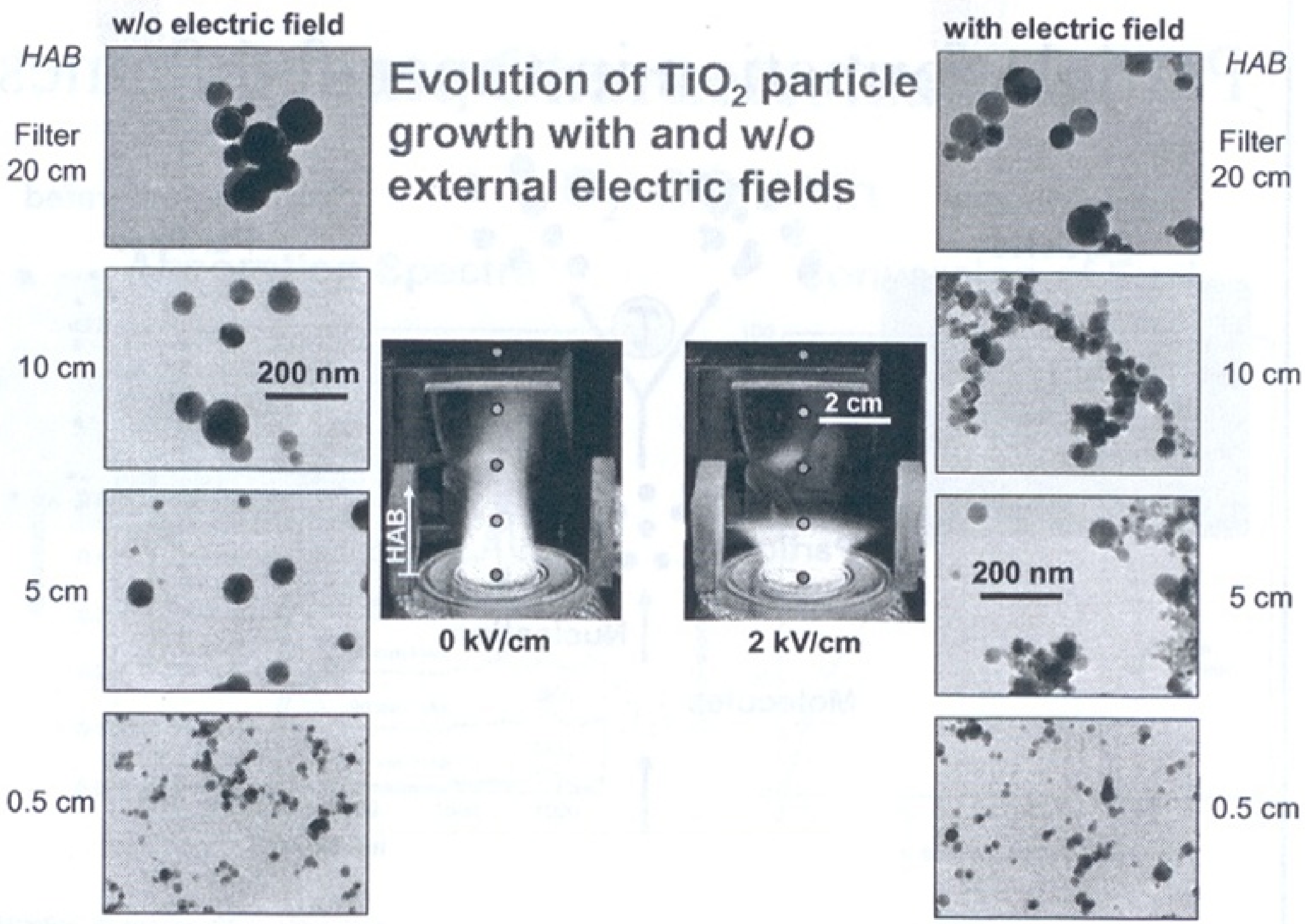
Pratsinis, Sotiris E., Functional Nanoparticles and Films Made in the Gas-phase. Nano Science and Technology Institute, Cambridge. 2008

Pyrolysis: Electrostatic Charging

- Particle size can also be controlled by generating an electric field across the flame.
- A large electric field (hundreds of kV/m) is generated between two plate electrodes situated on opposite sides of the flame.
- Similar to nozzle quenching, the electric field limits particle growth by reducing the residence time in the high temperature region of the flame.
- In addition, the electric field charges the particles. This results in electrostatic repulsion between newly formed particles, preventing coagulation.

S. Vemury, S.E. Pratsinis, L. Kibbey, Electrically-controlled flame synthesis of nanophase TiO_2, SiO_2, and SnO_2 powders. JMR, Vol. 12, 1031-1042. 1997.

Pyrolysis: Electrostatic Charging



Kammler, Jossen, Morrison, SEP, Beaucage, *Powder Technol.* **135**, 310 (2003)

Pyrolysis: Advantages & Disadvantages

- Pyrolysis is a high yield method that can fulfill the strong demand for nanoparticles.
- Can be customized to produce unique nanoparticles.
- Broad distribution of particle sizes and morphology.

Outline

- Nanoparticle Synthesis
  - Colloidal Chemical Methods
  - Attrition
  - Pyrolysis
  - RF Plasma
  - Thermal Decomposition
  - Pulsed Laser Method
- Nanoparticle Applications

RF Plasma Synthesis

- The starting material is placed in a pestle and heated under vacuum by RF heating coils.
- A high temperature plasma is created by flowing a gas, such as He, through the system in the vicinity of the coils.
- When the material is heated beyond its evaporation point, the vapor nucleates on the gas atoms which diffuse up to a cooler collector rod and form nanoparticles.
- The particles can be passivated by introducing another gas such as O_2.
- In the case of Al nanoparticles the O_2 forms a thin layer of AlO_3 around the outside of the particle inhibiting aggregation and agglomeration.
- RF plasma synthesis is very popular method for creating ceramic nanoparticles and powders
- Low mass yield.

Poole, C., Owens, F. *Introduction to Nanotechnology*. Wiley, New Jersey. 2003

RF Plasma Apparatus

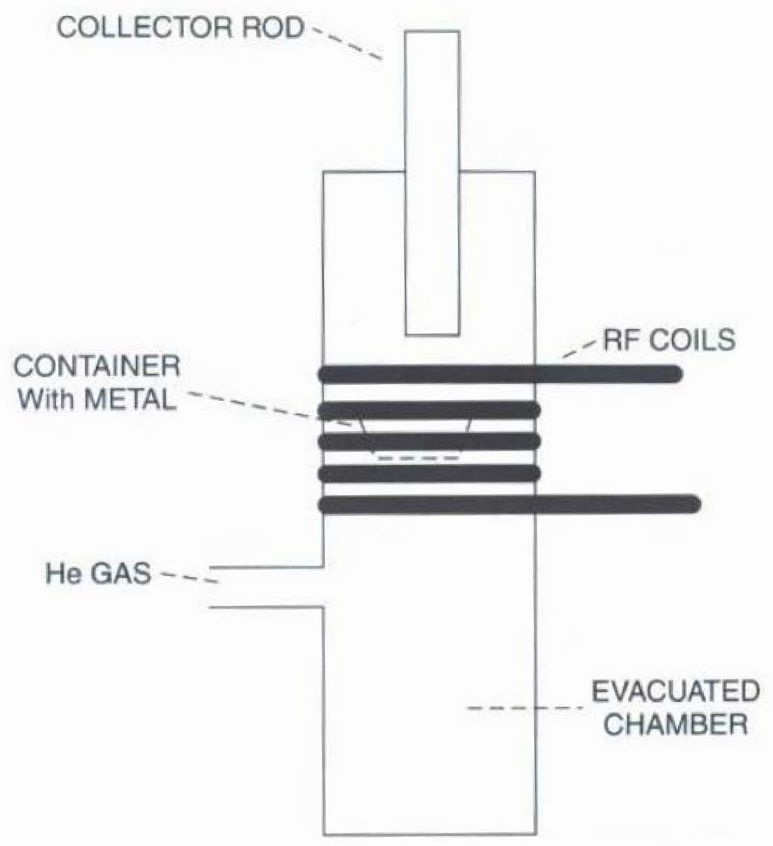


Illustration of apparatus for the synthesis of nanoparticles using an RF-produced plasma.

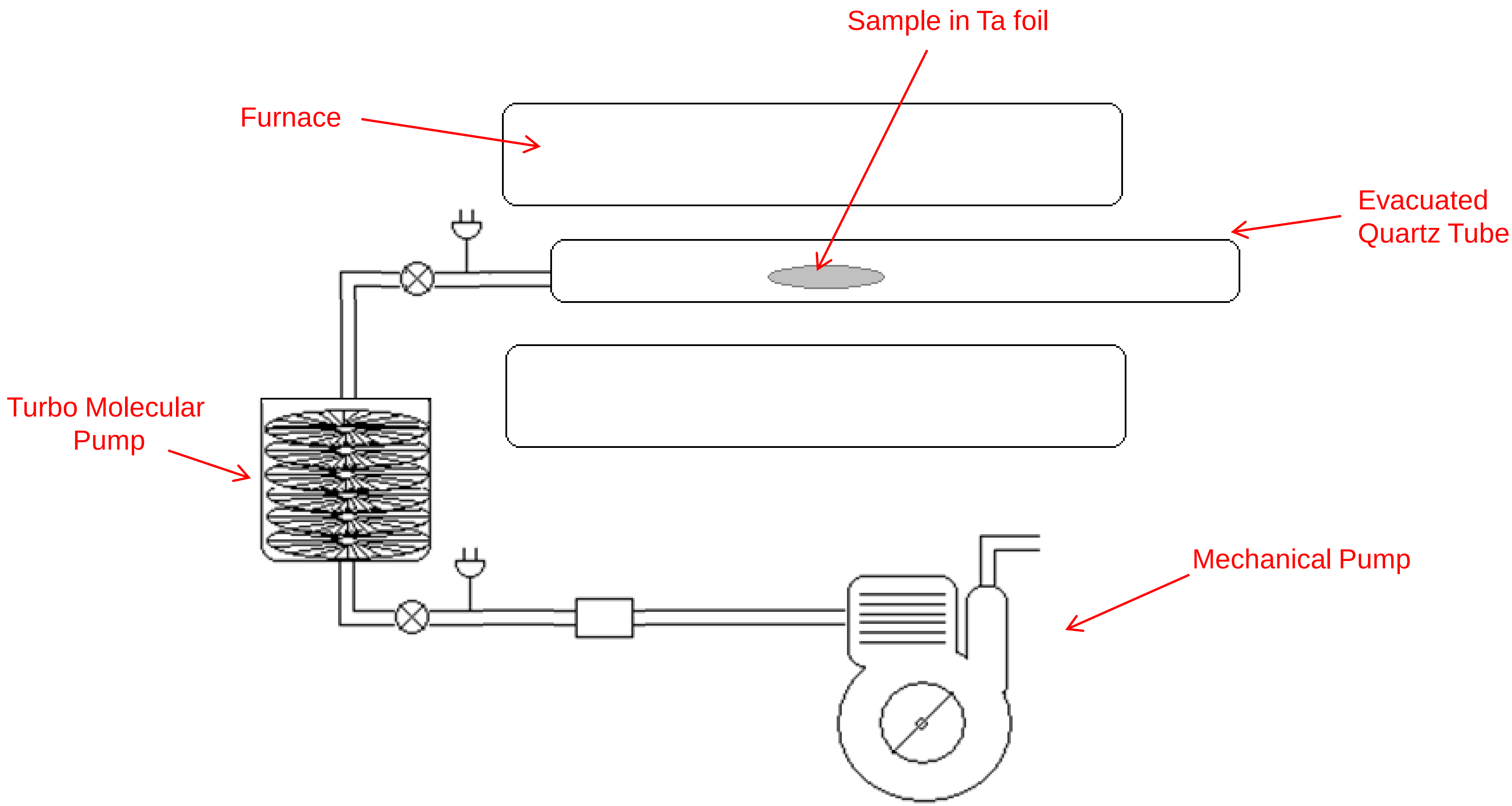
Poole, C., Owens, F. *Introduction to Nanotechnology*. Wiley, New Jersey. 2003

Thermal Decomposition

- Thermal decomposition is the chemical decomposition of a substance into ins constituents by heating.
- A solid bulk material is heated beyond its decomposition temperature in an evacuated furnace tube.
- The precursor material may contain metal cations and molecular anions, or metal organic solids.
- Example: $2LiN_3(s) \rightarrow 2Li(s) + 3N_2(g)$
  – Lithium particles can be synthesized by heating LiN_3 in a quartz tube under vacuum.
  – When heated to 375^{o}C the nitrogen outgases from the bulk material and the Li atoms coalesce to form metal nanoparticles.

Poole, C., Owens, F. *Introduction to Nanotechnology*. Wiley, New Jersey. 2003

Thermal Decomposition Apparatus



Outline

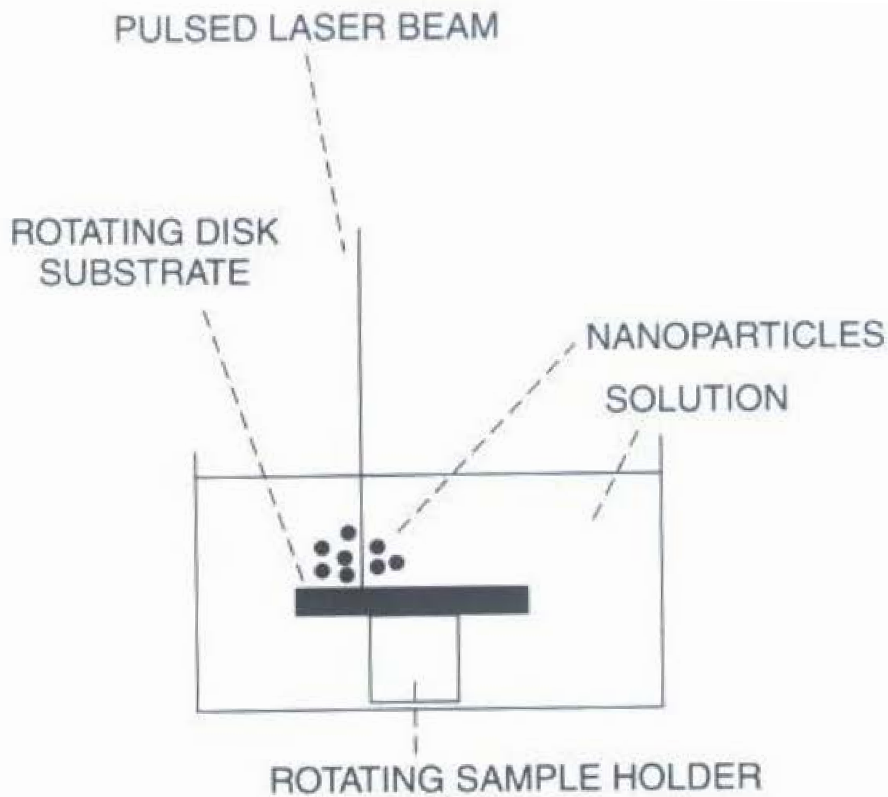
- Nanoparticle Synthesis
  - Colloidal Chemical Methods
  - Attrition
  - Pyrolysis
  - RF Plasma
  - Thermal Decomposition
  - Pulsed Laser Methods
- Nanoparticle Applications

Pulsed Laser Methods

- Pulsed Lasers have been employed in the synthesis silver nanoparticles from silver nitrate solutions.
- A disc rotates in this solution while a laser beam is pulsed onto the disc creating hot spots.
- Silver nitrate is reduced, forming silver nanoparticles.
- The size of the particle is controlled by the energy in the laser and the speed of the rotating disc.

Poole, C., Owens, F. *Introduction to Nanotechnology*. Wiley, New Jersey. 2003

Pulsed Laser Apparatus for Ag Nanoparticles



Apparatus to make silver nanoparticles using a pulsed laser beam that creates hot spots on the surface of a rotating disk. [Adapted from J. Singh, *Mater. Today* **2**, 10 (2001).]

Poole, C., Owens, F. *Introduction to Nanotechnology*. Wiley, New Jersey. 2003

Nanoparticle Applications: ZnO

- Zinc Oxide has opaque and antifungal properties.
- Used as UV blocking pigments in sunscreens, cosmetics, varnishes, and fabrics
- Incorporated in foot powders and garden supplies as an antifungal.
- ZnO nanowires can improve the elastic toughness of bulk materials

Nanoparticle Applications: TiO_2

- Titanium Dioxide is used as an inorganic white pigment for paper, paints, plastics, and whitening agents.
- TiO_2 nanoparticles are used as UV blocking pigments in sunscreens, cosmetics, varnishes, and fabrics.
- TiO_2 has unique photocatalytic properties that make it suitable for a number of advanced applications:
  – Self-cleaning glass and antifogging coatings
  – Photoelectrochemical cells (PECs)
  – Detoxification of waste water
  – Hydrolysis

Nanoparticle Applications: Fe

- 50-100nm Iron nanoparticles are used in magnetic recording devices for both digital and analog data.
- Decreasing the diameter to 30-40nm increases the magnetic recording capacity by 5-10 times per unit.

Nanoparticle Applications: Iron Oxide

- Iron Oxide nanoparticles have unique magnetic and optical properties.
- Iron oxide nanoparticles can be translucent to visible light while being opaque to UV light.
- Applications include UV protective coatings, various electromagnetic uses, electro-optic uses, and data storage.

Nanoparticle Applications: Iron Alloys

- Iron-platinum nanoparticles have increased magnetism and it is predicted that 3nm particle can increase the data storage capacity by 10 times per unit area.
- Iron-palladium nanoparticles 100-200nm in diameter have been shown to reduce toxic chlorinated hydrocarbons to nontoxic hydrocarbon and chloride compounds.

SCIENCE VOL 287 17 MARCH 2000

Nanoparticle Applications: Alumina

- Alumina (Aluminum Oxide) is used in Chemical Mechanical Polishing (CMP) slurries, as well as ceramic filters.
- Nano-alumina is used in light bulb and fluorescent tube coatings because it emits light more uniformly and allows for better flow of fluorescent materials.

Nanoparticle Applications: Ag

- Silver has excellent conductivity and has been used as an antimicrobial material for thousands of years.
- Silver's anti-microbial potential increase with increased surface area.
- Applications include biocides, transparent conductive inks, and antimicrobial plastics, and bandages.

Nanoparticle Applications: Gold

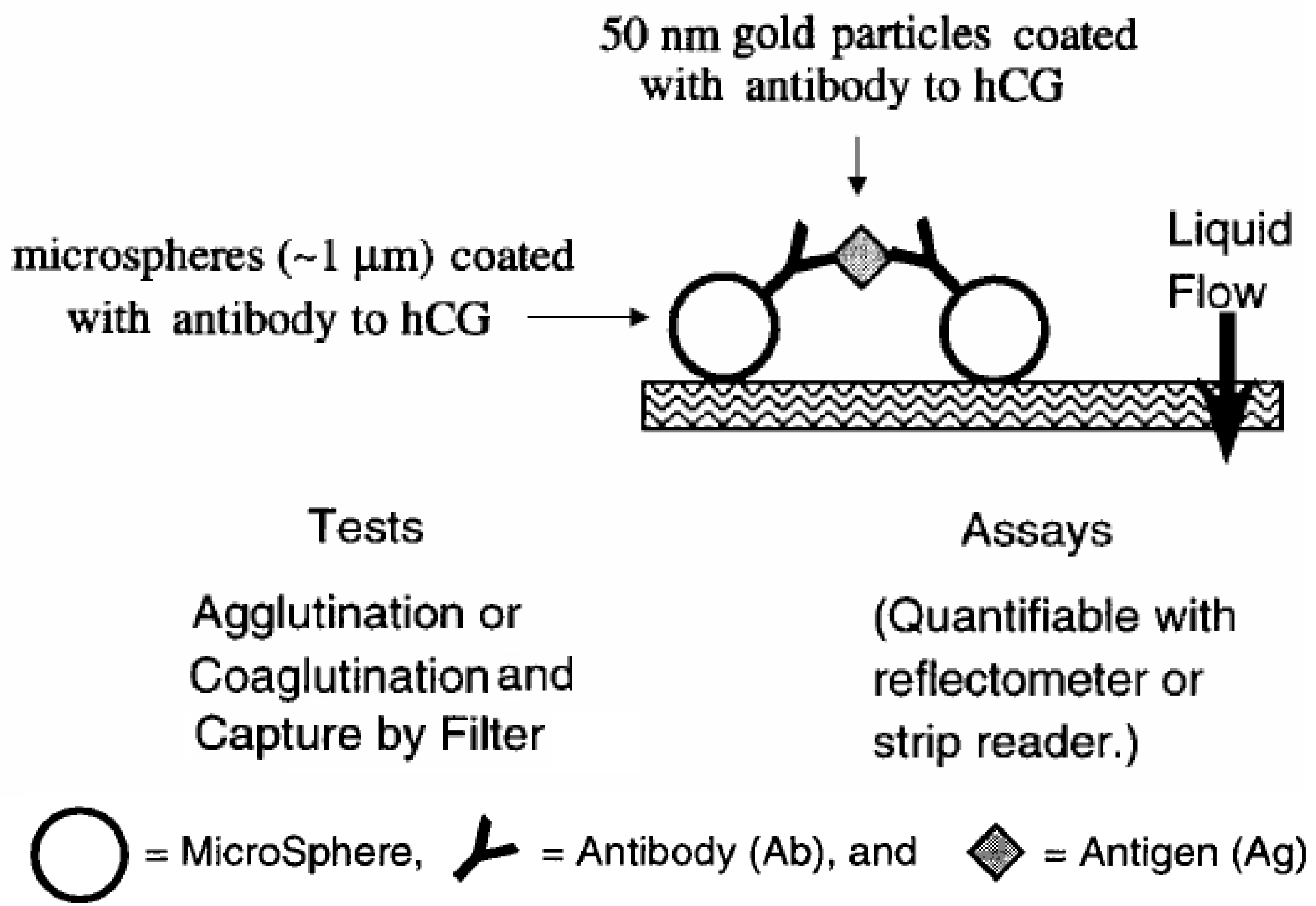
- Gold nanoparticles are relatively easy to produce compared to other types of nanoparticles due to its high chemical stability.
- Uses for gold nanoparticles are typically catalytic and include DNA detection and the oxidation of carbon monoxide.
- Gold has superior conductivity allowing gold nanoparticles to be used in various probes, sensors, and optical applications.

Nanoparticle Applications: Gold

- The First Response® home pregnancy test uses 1μm polystyrene sphere and 50nm gold particles coated with an antibody to human chorionic gonadotropin (hCG), a hormone produced during pregnancy.
- When urine containing hCG comes in contact with the polystyrene-gold-antibody complex, the nanoparticles coagulate into red clumps. Fluids pass through a filter where the clumps are caught yielding a pink filter.
- Suspended (un-coagulated) nanoparticles pass through the filter and no color change occurs.

Bangs, L. B. *New Developments in Particle-based Immunoassays*. Pure & Appl. Chem. Vol. 68, No 10 p 1873-1879. 1996

Nanoparticle Applications: Gold



Bangs, L. B. *New Developments in Particle-based Immunoassays*. Pure & Appl. Chem. Vol. 68, No 10 p 1873-1879. 1996

Nanoparticle Applications: ZrO

- Zirconium Dioxide nanoparticles can increase the tensile strength of materials when applied as a coating.
- This has many possible applications in wear coatings, ceramics, dies, cutting edges, as well as piezoelectric components, and dielectrics.