Nanomaterial Synthesis

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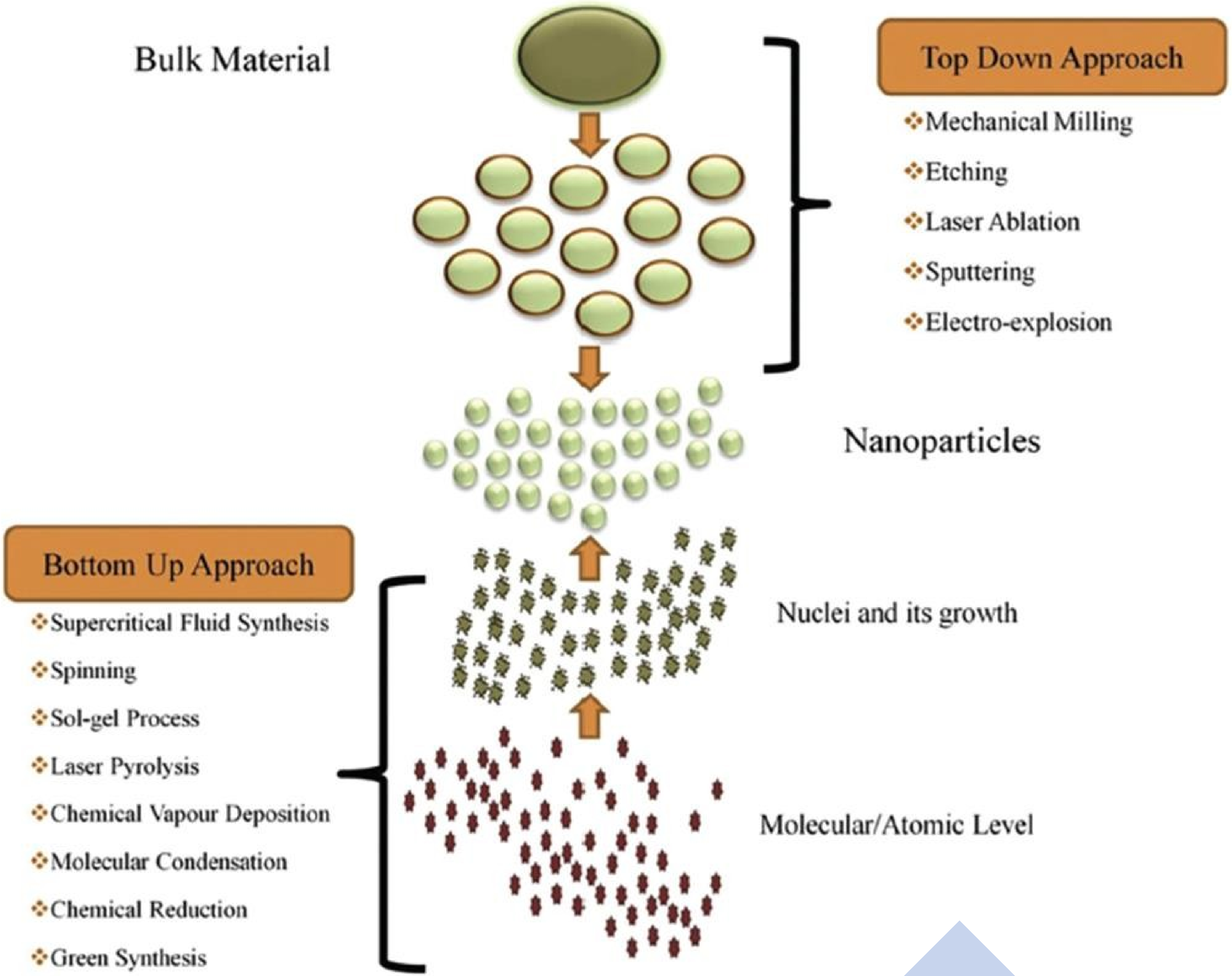
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Colloidal Methods

- **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 **-150 nm** and are controlled by the initial concentrations of the reactants and the action of the stabilizing reagent.

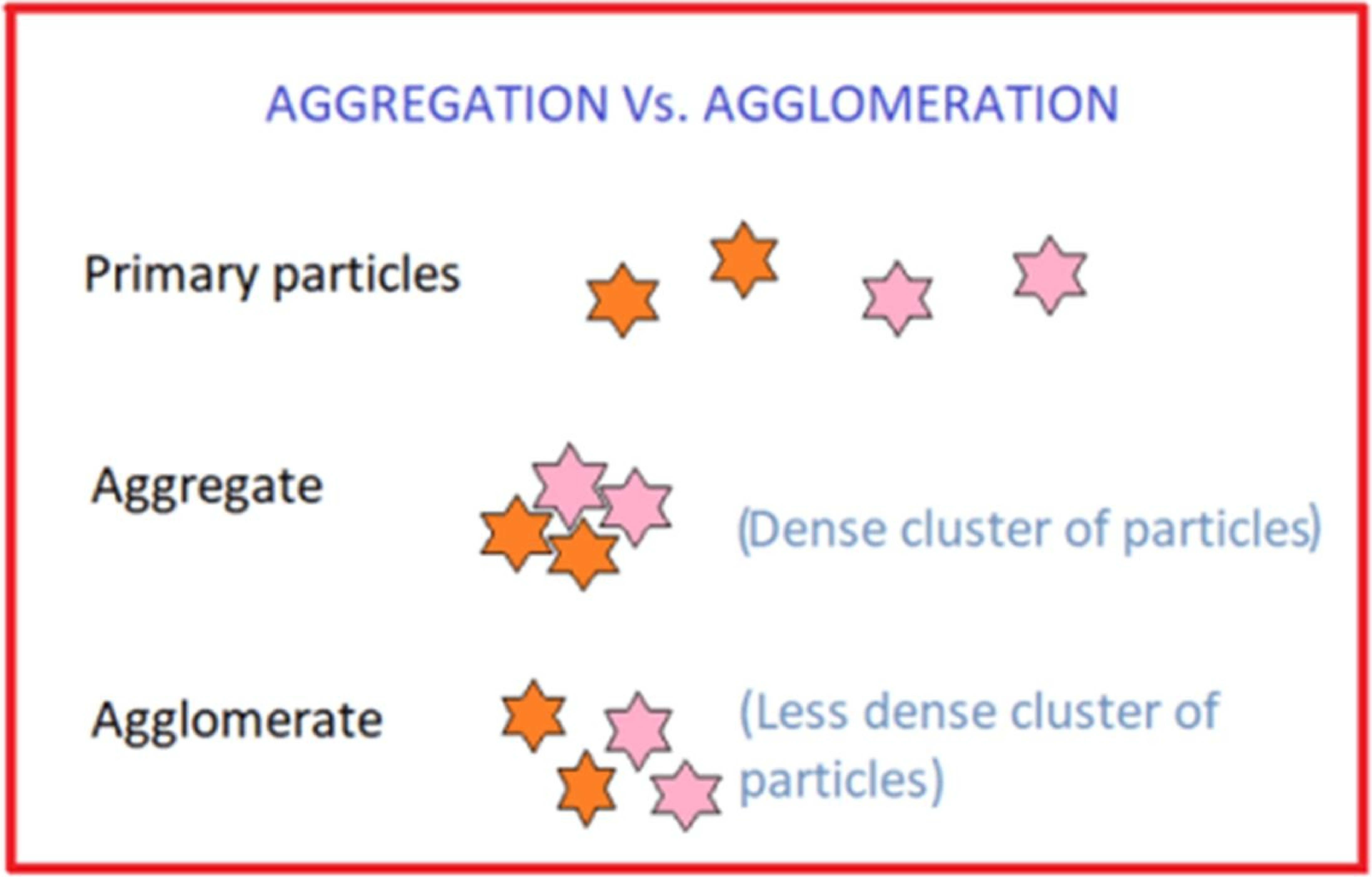
What is Aggregation?

Aggregation is the process of formation of clusters of particles via gathering small particles by forming **strong chemical bonds between the particles**. The final product of this process is an “aggregate”. Usually, the aggregates are very dense clusters of particles since there are strong bonds between the particles. Therefore, these clusters of particles are small comparatively.

What is Agglomeration?

Agglomeration is the process of formation of clusters of particles via gathering small particles by forming **weak physical interactions with each other**. The end product of this process is an “agglomerate”.

https://www.differencebetween.com/difference-between-aggregation-and-agglomeration/


AGGREGATION Vs. AGGLOMERATION
Primary particles
Aggregate
(Dense cluster of particles)
Agglomerate
(Less dense cluster of particles)

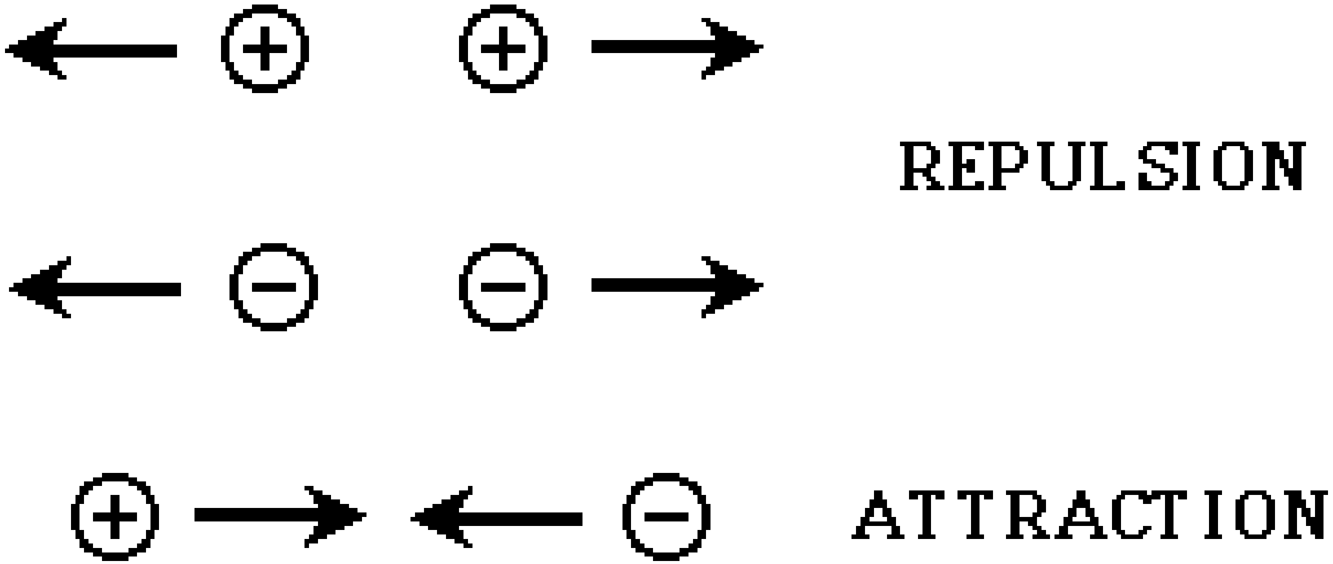
Aggregation vs Agglomeration

More Information Online WWW.DIFFERENCEBETWEEN.COM

	Aggregation	Agglomeration
DEFINITION	The process of forming clusters of particles by gathering small particles via forming strong chemical bonds between the particles.	The process of forming clusters of particles by gathering small particles via forming weak physical interactions with each other.
CHEMICAL BONDING	Aggregation forms strong chemical bonds between particles.	Agglomeration forms weak physical interactions between particles.
END PRODUCT	Aggregation forms an "aggregate" as the end product.	Agglomeration forms an "agglomerate" as the end product.
DENSITY	Usually aggregates formed from aggregation are dense.	The agglomerates formed via agglomeration are less dense.
SIZE	Aggregates are relatively small because the particles are very close to each other due to strong bonding between them.	Agglomerates are relatively large because the particles are not that much close to each other due to weak bonding between them.

Electrostatic repulsion: is the result of interaction between the electrical double layers surrounding particles or droplet.

When two positively or two negatively charged particles come closer to each other they repel from each other.



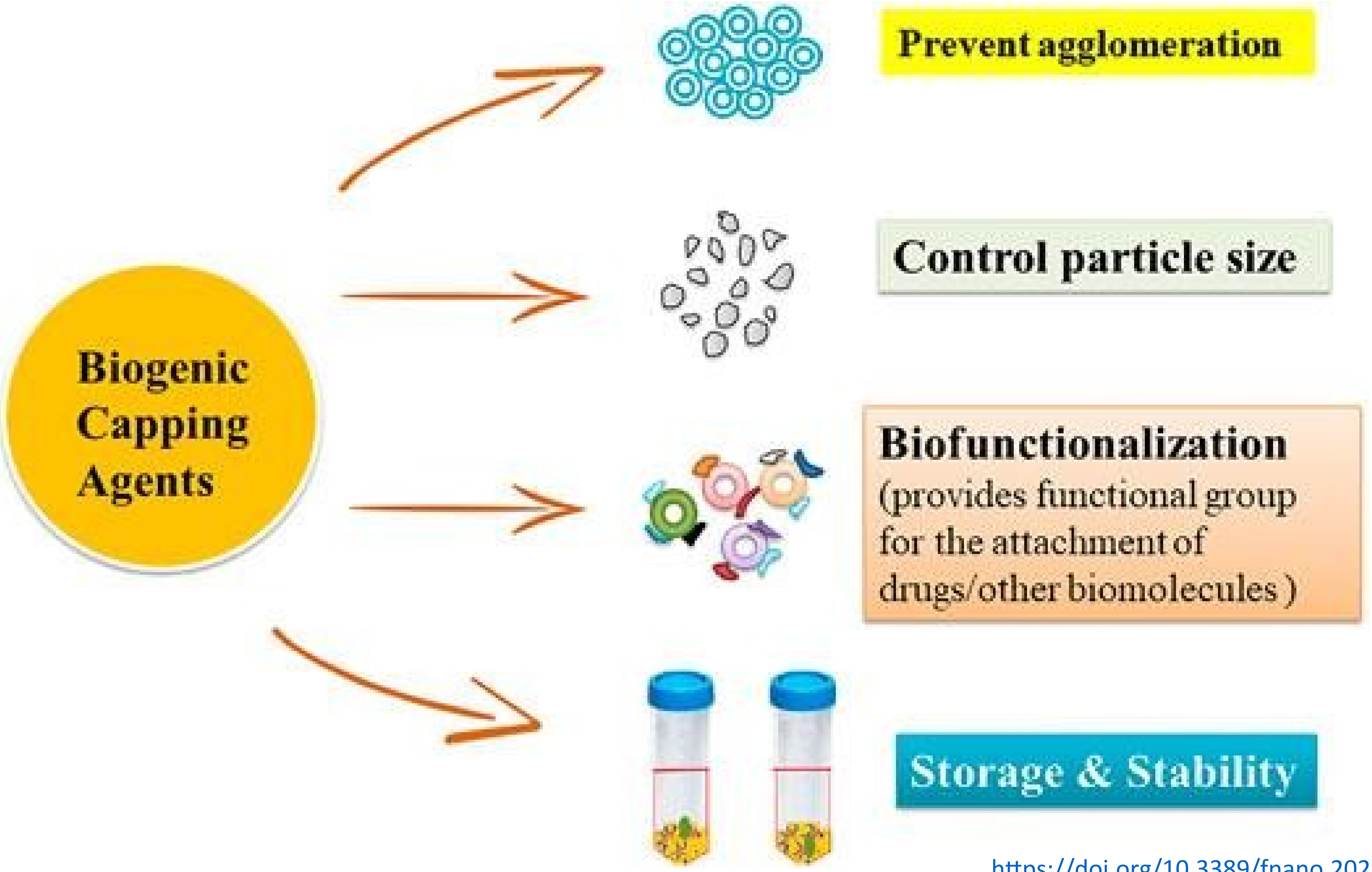
Capping/stabilizing agents: ligands, surfactants, polymers, dendrimers, biomolecules

- The use of coating nanoparticle with surfactant or polymer is to prevent aggregation of the particles due to nanoparticles high surface energy.
- It also controls the size of the particles during synthesis process.
- Capping of nanoparticles can be checked using TEM (Transmission Electron Microscope)

Capping agents

- Capping agent would help preventing the nanoparticles from growth. Final product could be either a solid or liquid.
- Stabilizing agent could be used to prevent agglomeration of the nanoparticles. Here too, the final product could be either a solid or liquid.
- Dispersing agent also helps in preventing agglomeration, but the final product must be a liquid.
- There may be just one material, for example the PEG, which could serve all the three roles mentioned above. That is the reason why all these terms are being used by the researchers in common.

PEG: Poly Ethylene Glycol



https://doi.org/10.3389/fnano.2021.801620

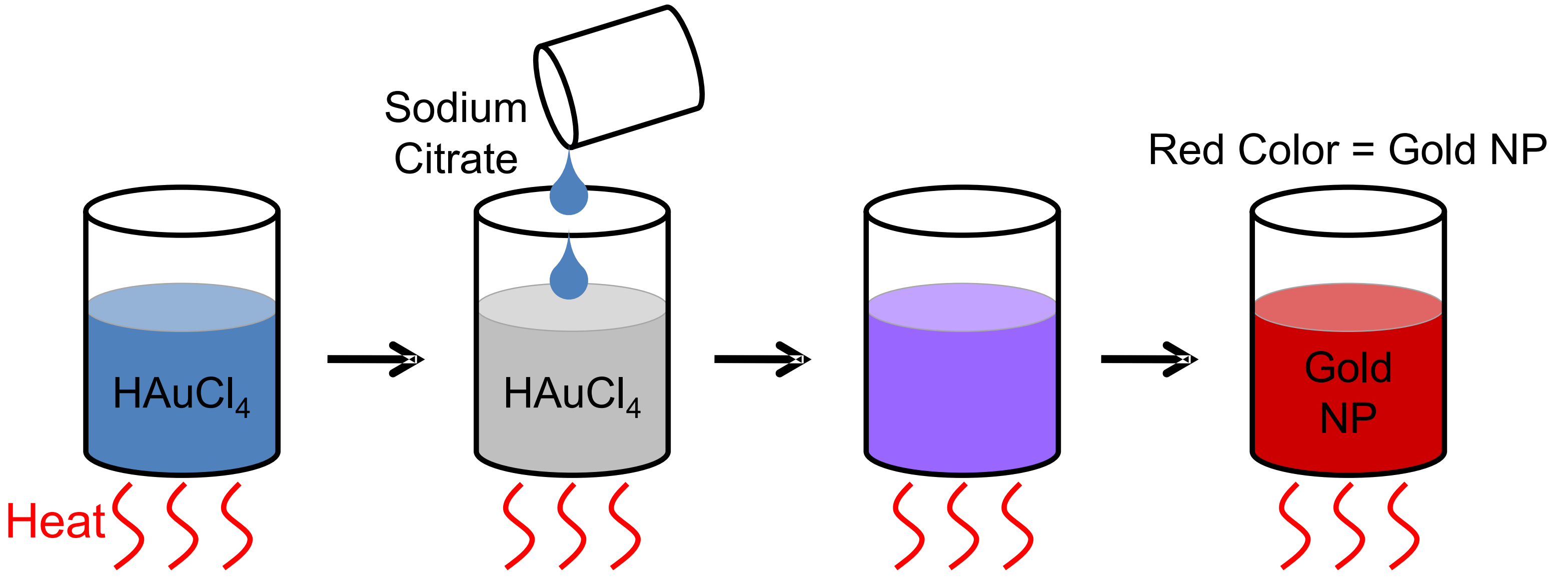
Colloidal Chemical Methods

- The synthesis of: **Gold particles**
  - 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:

- $Au^{3+}(aq) + 3e^- \rightarrow Au(s)$
- $C_6H_5O_7^{3-}(aq) + H_2O(l) \rightarrow C_5H_4O_4^{2-}(aq) + CO_2(g) + H_3O(aq) + 2e^-$

Gold Nanoparticles Formation

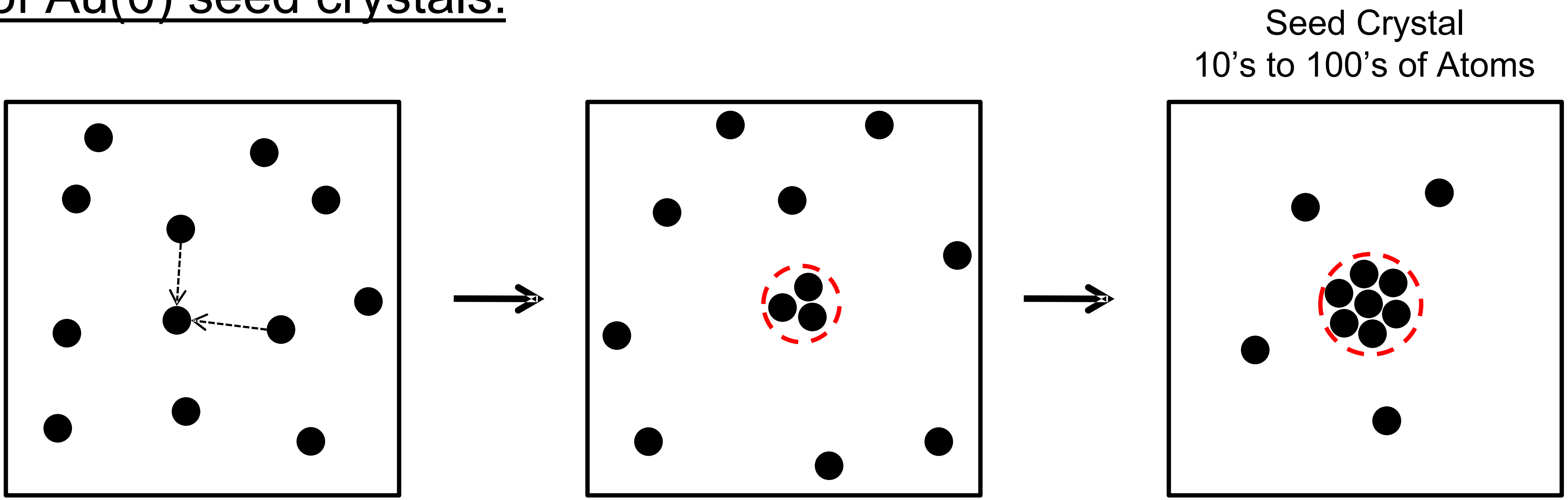


1. Heat a solution of chloroauric acid ($HAuCl_4$) up to reflux (boiling). $HAuCl_4$ is a water soluble gold salt.
2. Add trisodium citrate, which is a reducing agent.
3. Continue stirring and heating for about 10 minutes.
   - During this time, the sodium citrate reduces the gold salt **(Au^{3+})**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

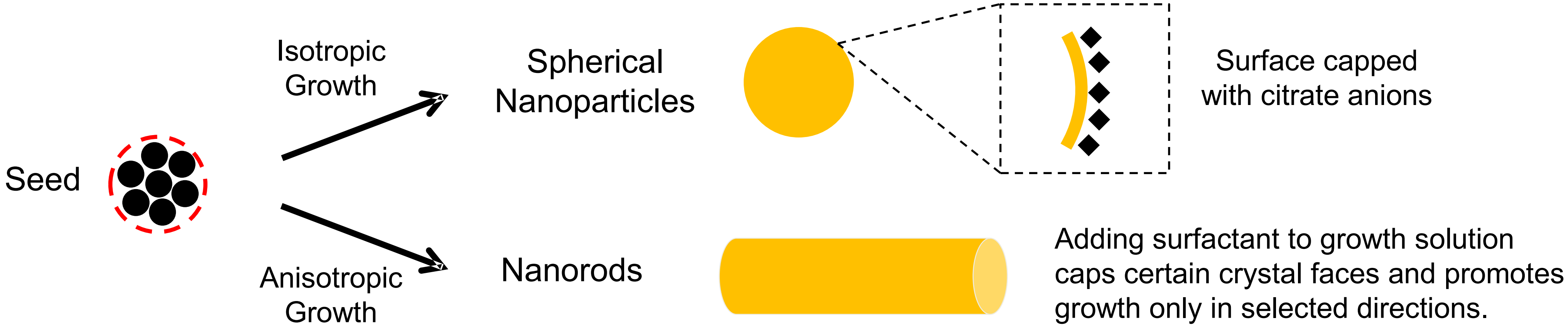
http://mrsec.wisc.edu/Edetc/nanolab/gold/index.html
J. Chem. Ed. 2004, 81, 544A.

Reduction of gold ions: Au(III) + $3e^- \rightarrow$ Au(0)

Nucleation of Au(0) seed crystals:



Growth of nanoparticles:



- Examples: **Molybdenum**

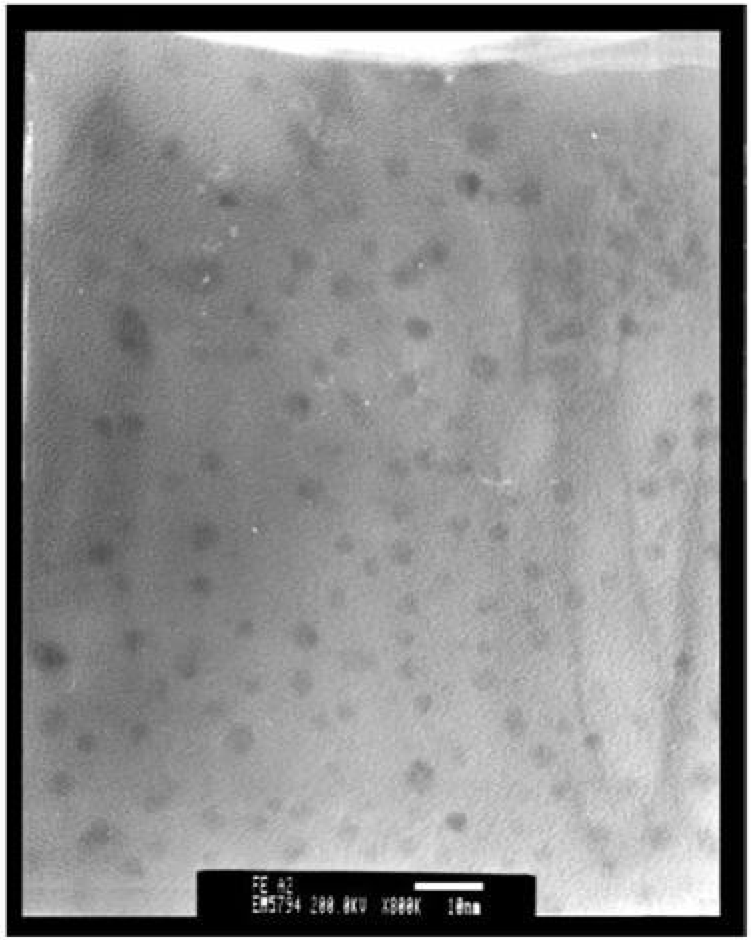
  - 1-5 nm molybdenum nanoparticles can be created at room temperature by reducing $MoCl_3$ in a toluene solution in the presence of sodium triethylborohydride ($NaBEt_3H$).

  - Reaction equation:

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

- Examples: **Iron**

  - The TEM image to the right shows 3 nm Fe nanoparticles produced by reducing $FeCl_2$ with sodium borohydride (NaBH4) in xylene.
  - Trioctylphosphine oxide (TOPO) was introduced as a capping agent to prevent oxidation and aggregation

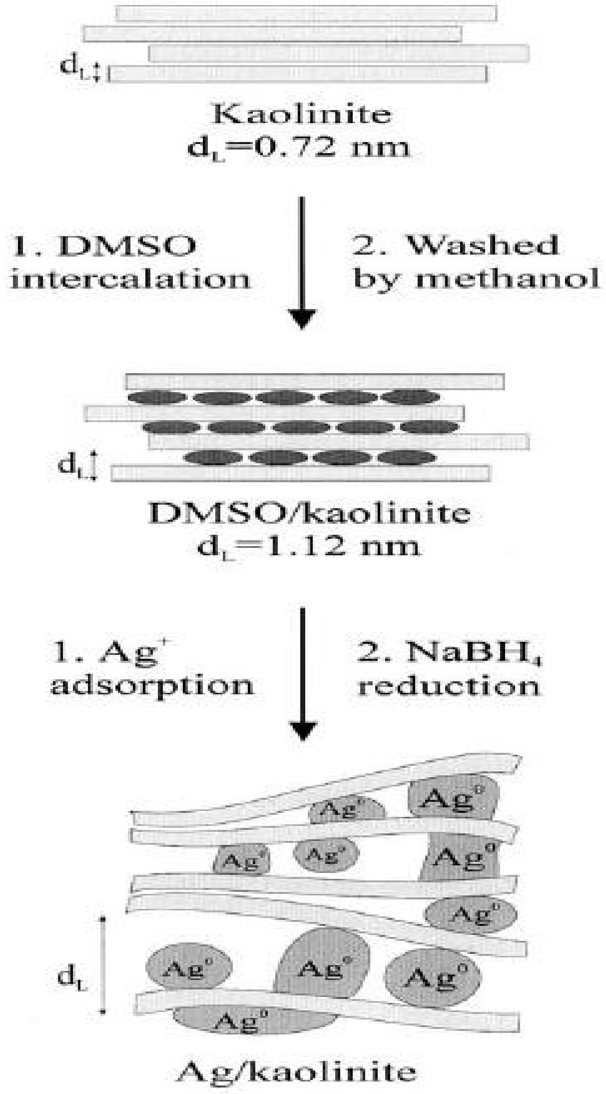


TEM image of Fe nanoparticles

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

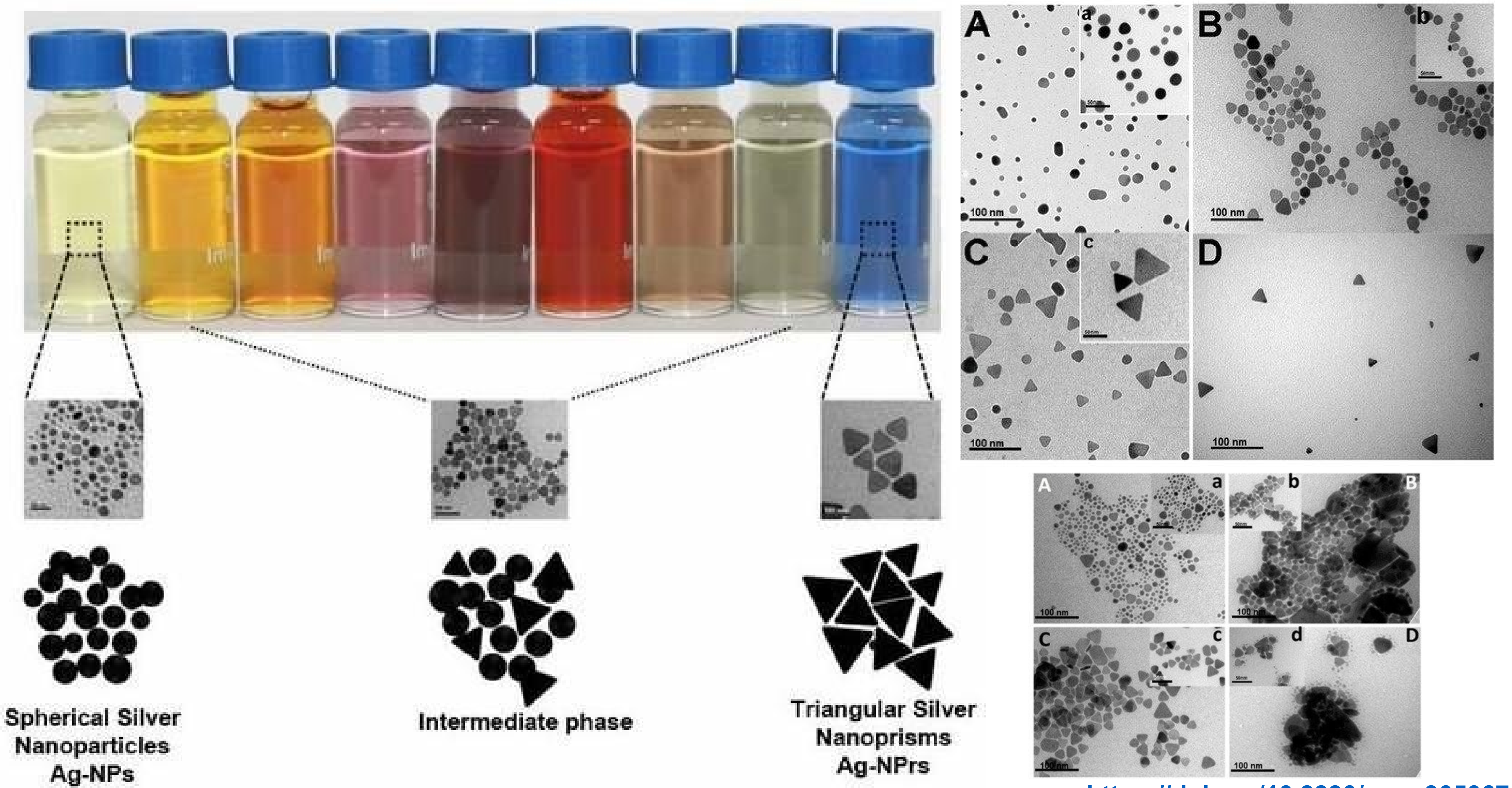
Examples: Silver

- The reduction of AgNO3 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 nano-particles on kaolinite.

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



https://doi.org/10.3390/nano9050674

Thermal Decomposition

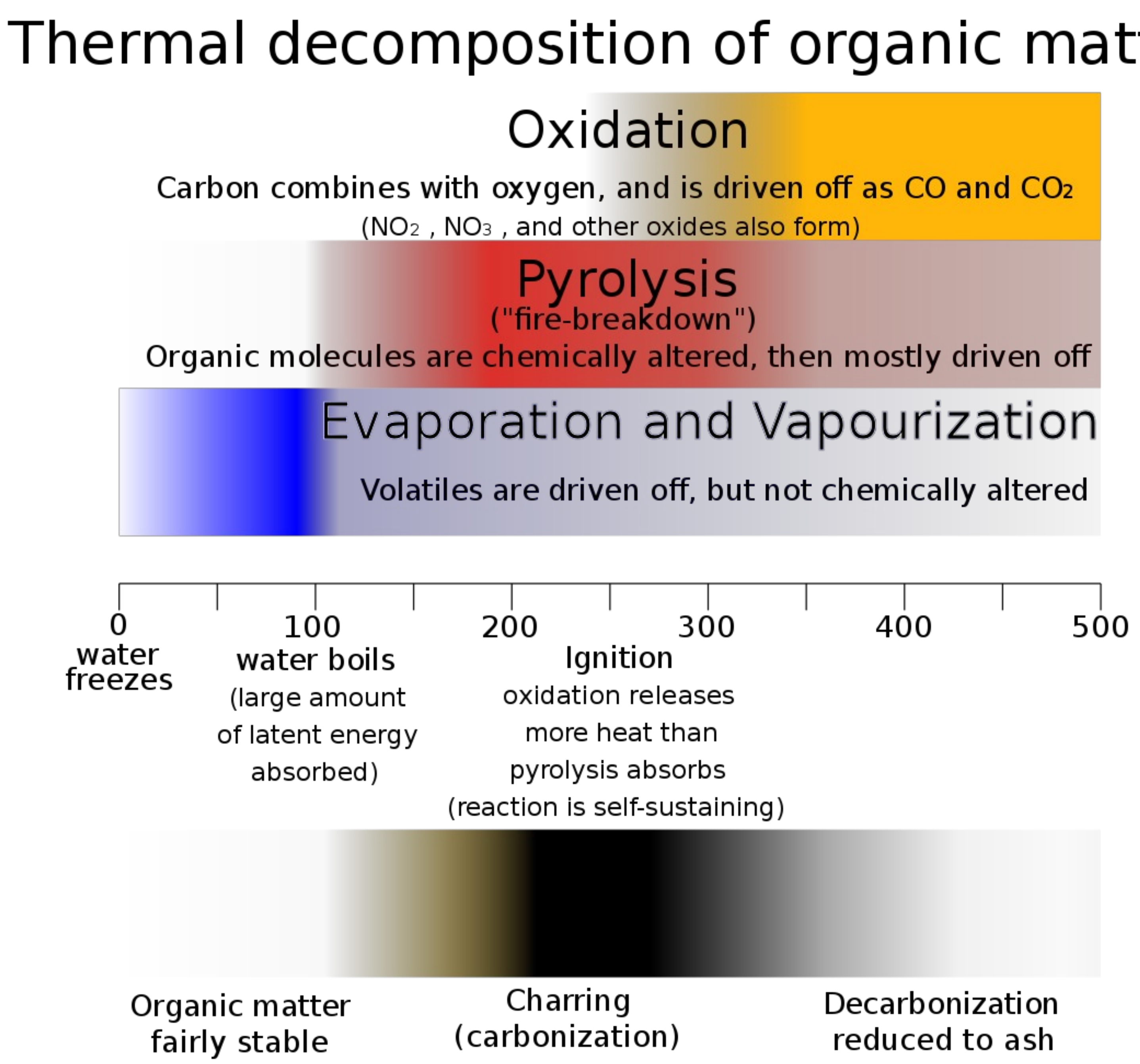
- **Thermal decomposition i**s the chemical decomposition of a substance into its constituents by heating.
- A s**olid bulk material i**s heated beyond its decomposition temperature in an evacuated furnace tube.
- The precursor material may contain metal cations and molecular anions, or metal organic solids.

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

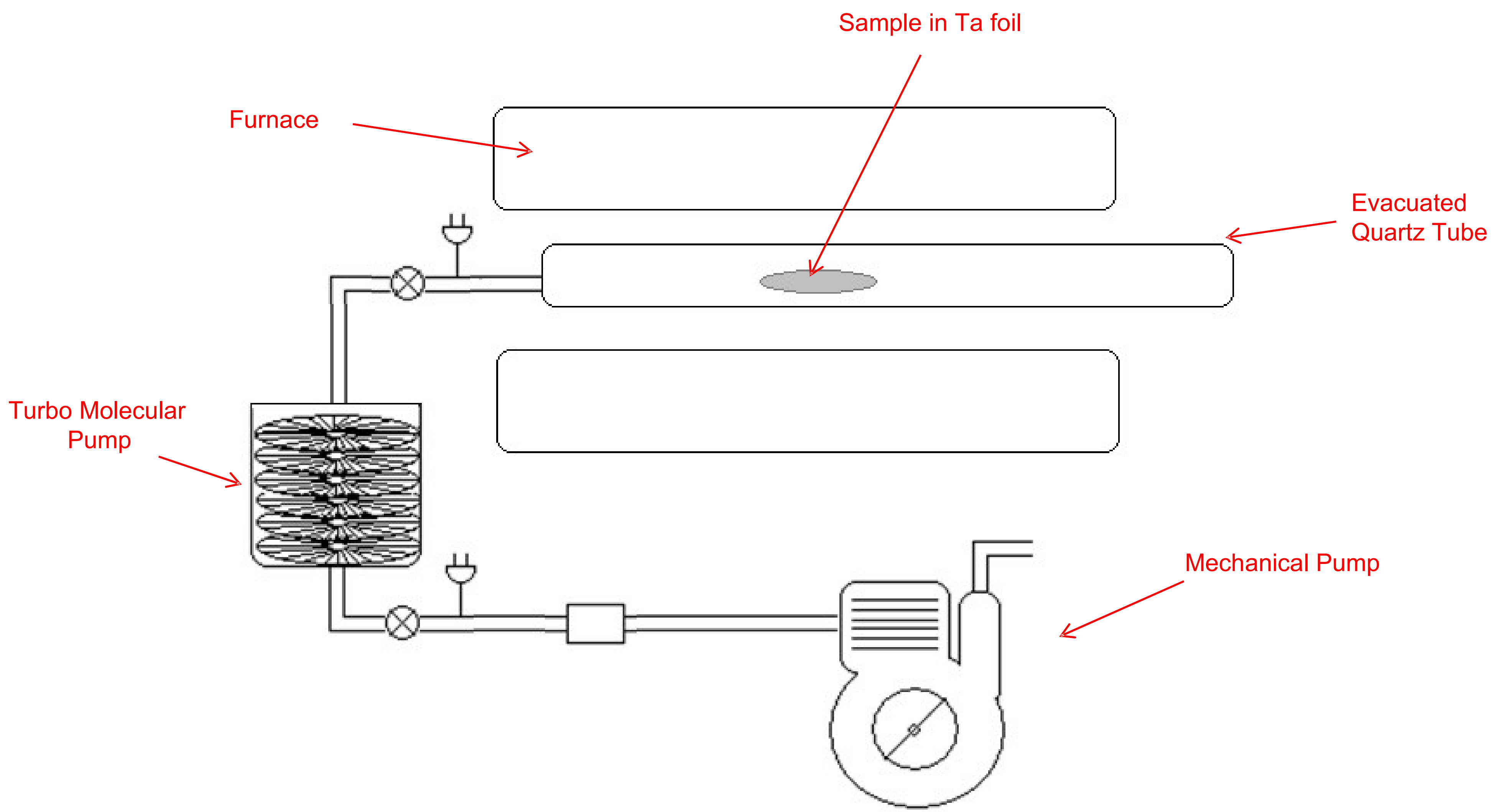
- **Example**: $2LiN_3(s) \rightarrow 2Li(s) + 3N_2(g)$

Lithium particles can be synthesized by heating LiN_3 in a quartz tube under vacuum.

When heated to **375ºC** the nitrogen outgases from the bulk material and the Li atoms coalesce to form metal nanoparticles.


Thermal decomposition of organic matter
Oxidation
Carbon combines with oxygen, and is driven off as CO and CO2
(NO2 , NO3 , and other oxides also form)
Pyrolysis
("fire-breakdown")
Organic molecules are chemically altered, then mostly driven off
Evaporation and Vapourization
Volatiles are driven off, but not chemically altered
0
100
200
300
400
500
water freezes
water boils
(large amount of latent energy absorbed)
Ignition
oxidation releases more heat than pyrolysis absorbs
(reaction is self-sustaining)
Organic matter fairly stable
Charring (carbonization)
Decarbonization reduced to ash

Thermal Decomposition Apparatus

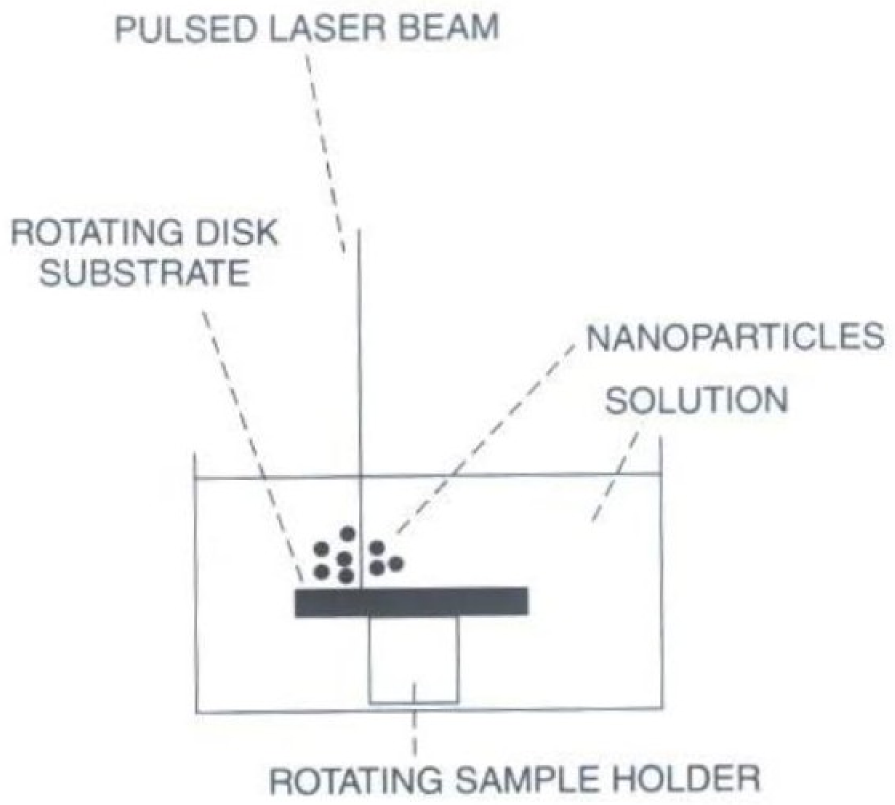


Pulsed Laser Methods

- 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.

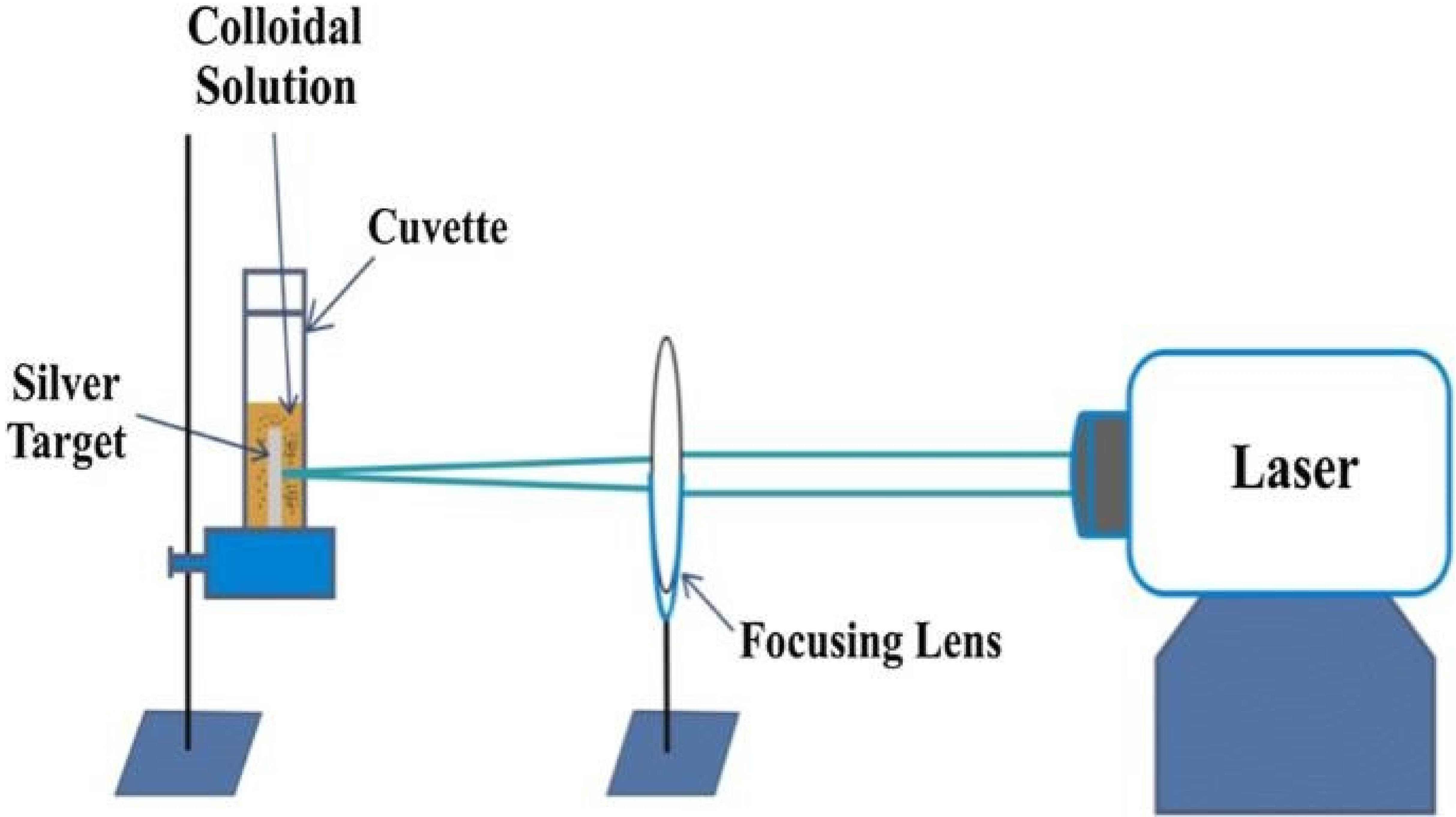
Poole, C., Owens, F. *Introduction to Nanotechnology*. Wiley, New Jersey. 2003

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



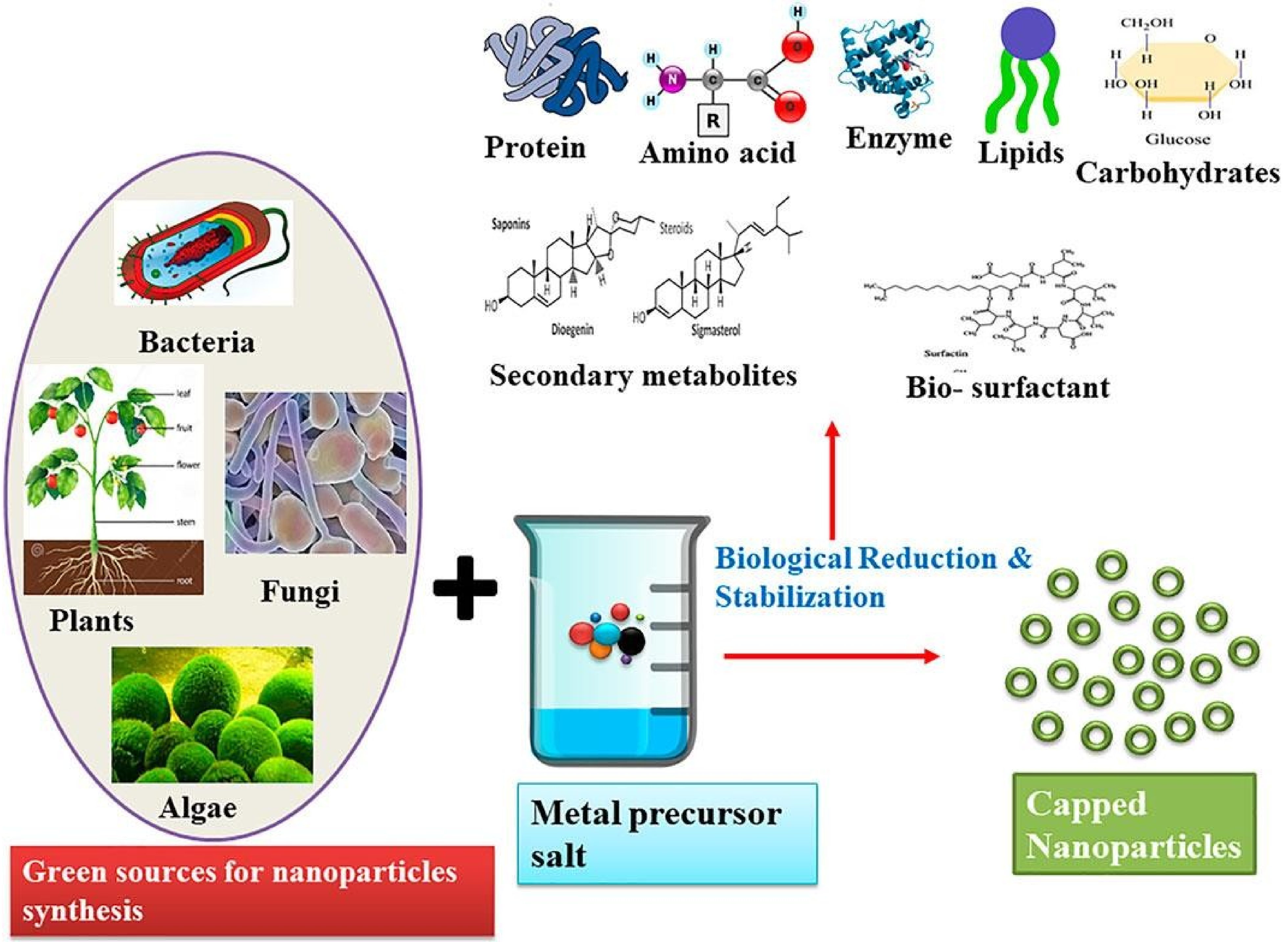
https://doi.org/10.1007/s11082-019-1902-0

Green Chemistry Route

Green Chemistry or Biological method involves using an environment-friendly green chemistry-based approach that employs unicellular and multicellular biological entities such as actinomycetes, fungus, bacteria, viruses, yeast, and plants

Noble metallic NPs like as **gold**, **silver,** and **platinum** are widely recognized for their importance in organic chemistry, bioelectronics, and medicines.

These noble metals are widely synthesized by wet chemical method using the reducing agents such as **sodium borohydride**, **potassium bitartrate**, **methoxypolyethylene glycol**, or **hydrazine** and the stabilizing agent such as **sodium dodecyl benzyl sulfate** or **polyvinyl pyrrolidone (PVP)**.



Protein
Amino acid
Enzyme
Lipids
Glucose
Carbohydrates
Saponins
Steroids
Dioegenin
Sigmasterol
Secondary metabolites
Surfactin
Bio- surfactant
Bacteria
Plants
Fungi
Algae
Biological Reduction & Stabilization
Metal precursor salt
Capped Nanoparticles
Green sources for nanoparticles synthesis

Biological method offers a clean, nontoxic, and environment-friendly method of synthesizing the NPs with a wide range of sizes, shapes, and compositions.

Compared to biological methods which use bacteria and fungi, the plant-based biosynthesis methods have several advantages such as:

(i) avoid the use of specific, well-conditioned culture preparation and expensive isolation techniques,

(ii) safe,

(iii) relatively short production times,

(iv) a lower cultivation cost, and

(v) a relatively simple process that can be easily scaled up for large-scale production of NPs.

Plant extracts act both as reducing agents and stabilizing agents during the synthesis of NPs.

The green chemistry approach, on the other hand, consists mostly of **three steps:**

1. the solvent medium,
2. an ecologically benign reducing agent (e.g., sugar or -d-glucose), and
3. the nontoxic substance for NP stabilization.

Furthermore, reducing agents are nontoxic, gentle, renewable, and affordable.

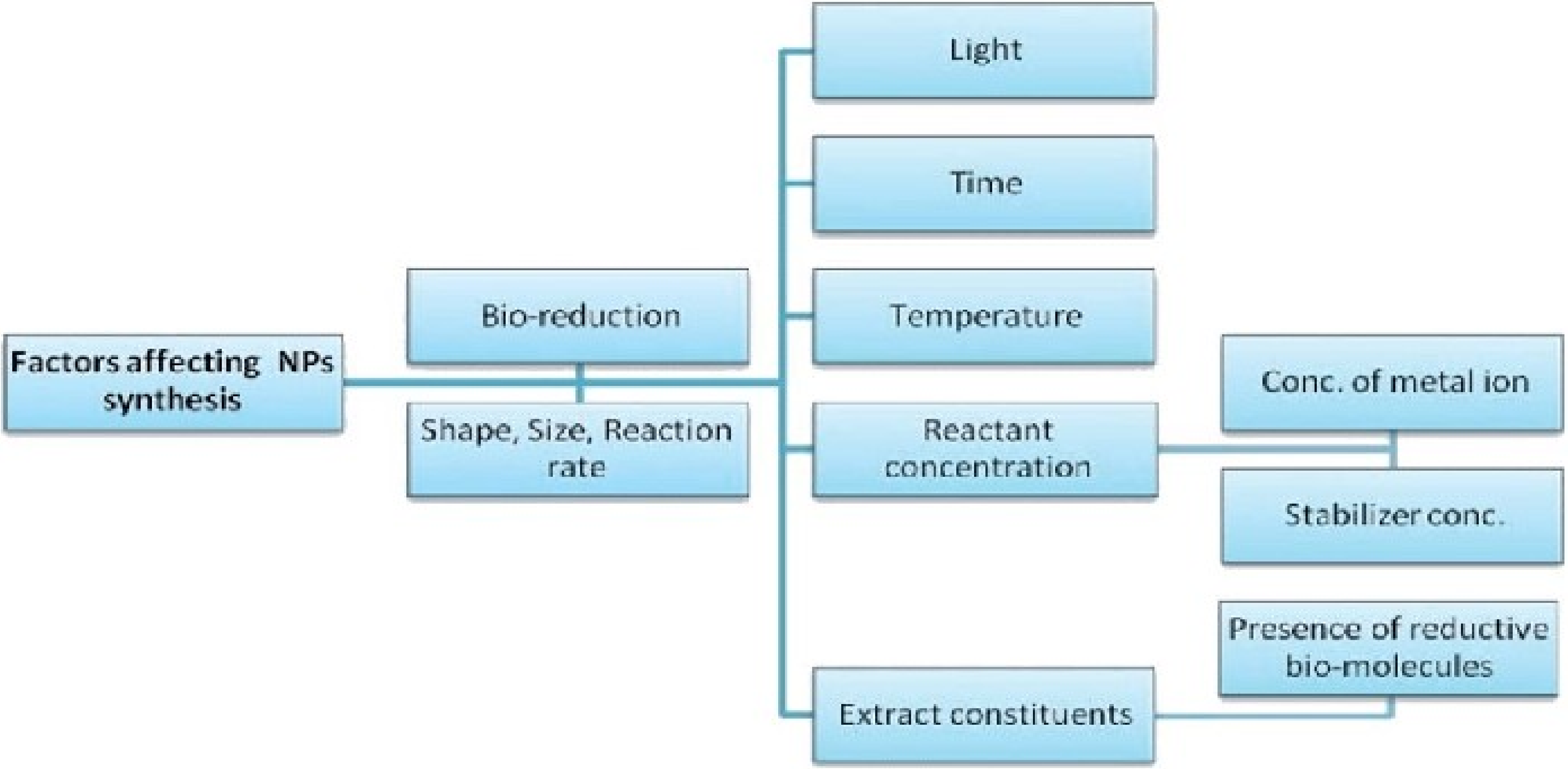
To protect or passivate the NPs surface, the green chemistry approach employs **starch** as a protective agent.

Furthermore, **caffeine/polyphenols** operate as a reducing and capping agent for Ag and Pd NPs, making them environmentally friendly multifunctional materials. Caffeine, the most commonly utilised medication, is highly water soluble, has minimal toxicity, and is biodegradable.

A Summary of Extracts of Plants, Metal Salts, Synthesized Nanoparticle, and Their Sizes

Sr. No.	Plants/Extract of Plants	Name of Metal Salt	Type of Nanoparticles Synthesized	Particle Size (nm)	Ref.
1	*Rosa rugosa*	Silver nitrate, auric acid	Ag, Au	11–12	[48]
2	*Chenopodium album* leaf	Silver nitrate, auric acid	Ag, Au	10–30	[44]
3	Apiin	Silver nitrate, chloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$)	Ag, Au	7.5–23	[39]
4	*Hibiscus rosasinensis*	$AgNO_3$, $HAuCl_4 \cdot 3H_2O$	Ag, Au	14	[43]
5	*Euphorbia Jatropha* latex	Zinc nitrate	ZnO	50	[52]
6	*Punica granatum* peels	Copper acetate monohydrate $[Cu(CH_3COO)_2 \cdot H_2O]$	CuO	40	[49]
7	*Eucalyptus globulus*	Iron nitrate 9-hydrate	Fe_2O_3		[51]
8	Coffee, tea	Silver nitrate, $PdCl_2$	Ag, Pd	20–60	[46]
9	*Azadirachta indica*	$H_2PtCl_6 \cdot 6H_2O$ (aqueous)	Pt	5–50	[45]
10	*Aspalathus linearis*	$SnCl_4 \cdot 5H_2O$	SnO_2	2.1–19.3	[40]

Factors Affecting Size and Morphology of NPs



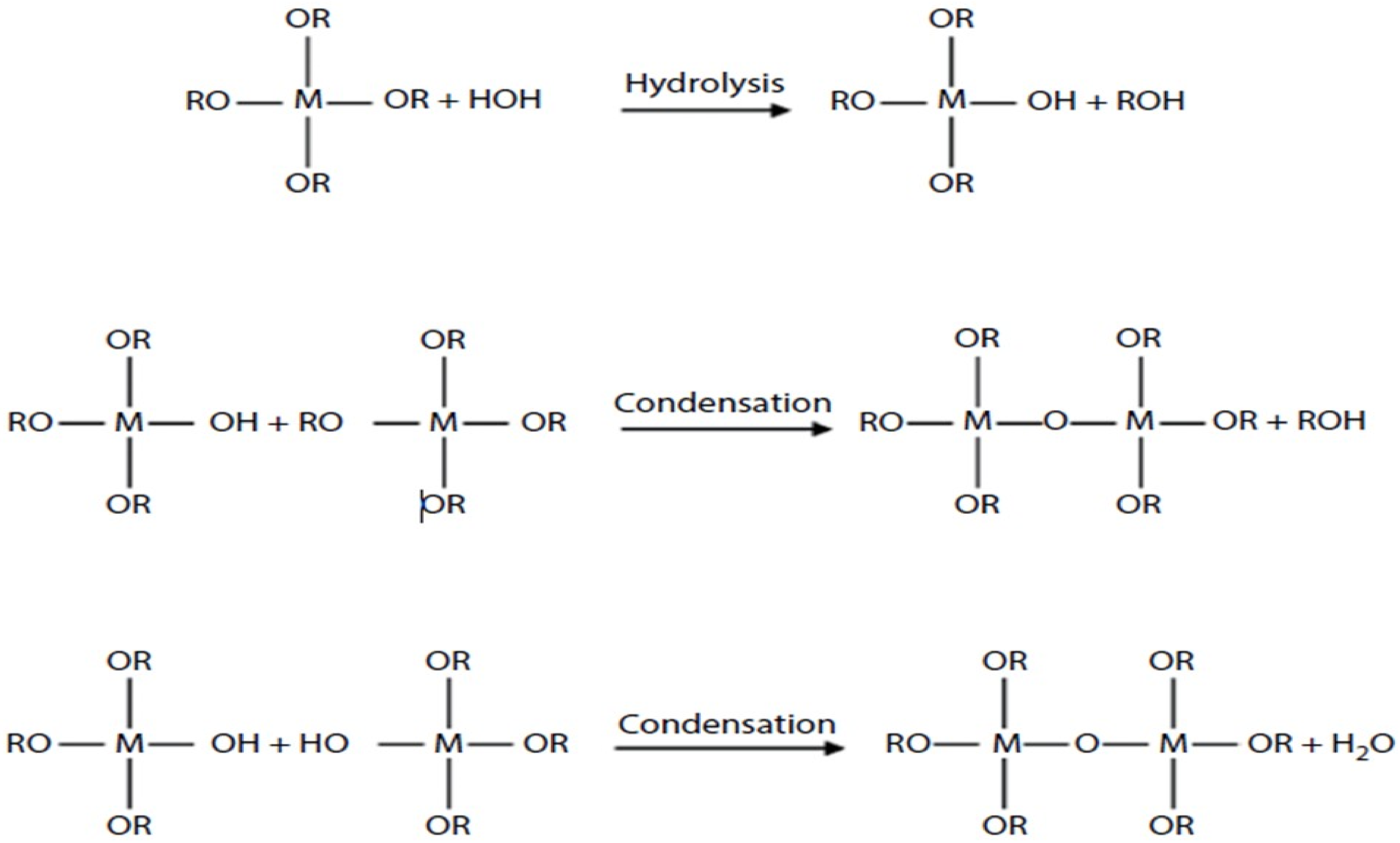
https://doi.org/10.1039/C9RA02225B

Sol-gel Method

The **sol-gel technique** is one of the most interesting and adaptable approaches for producing nanomaterials at low temperatures and cheap cost.

A **"Sol"** is defined as a stable dispersion of colloidal particles or polymers in a solvent, whereas colloid is defined as suspension of dispersed solid particles (1–1000 nm). The gel consists of a **3D** continuous network, which encloses liquid phase.

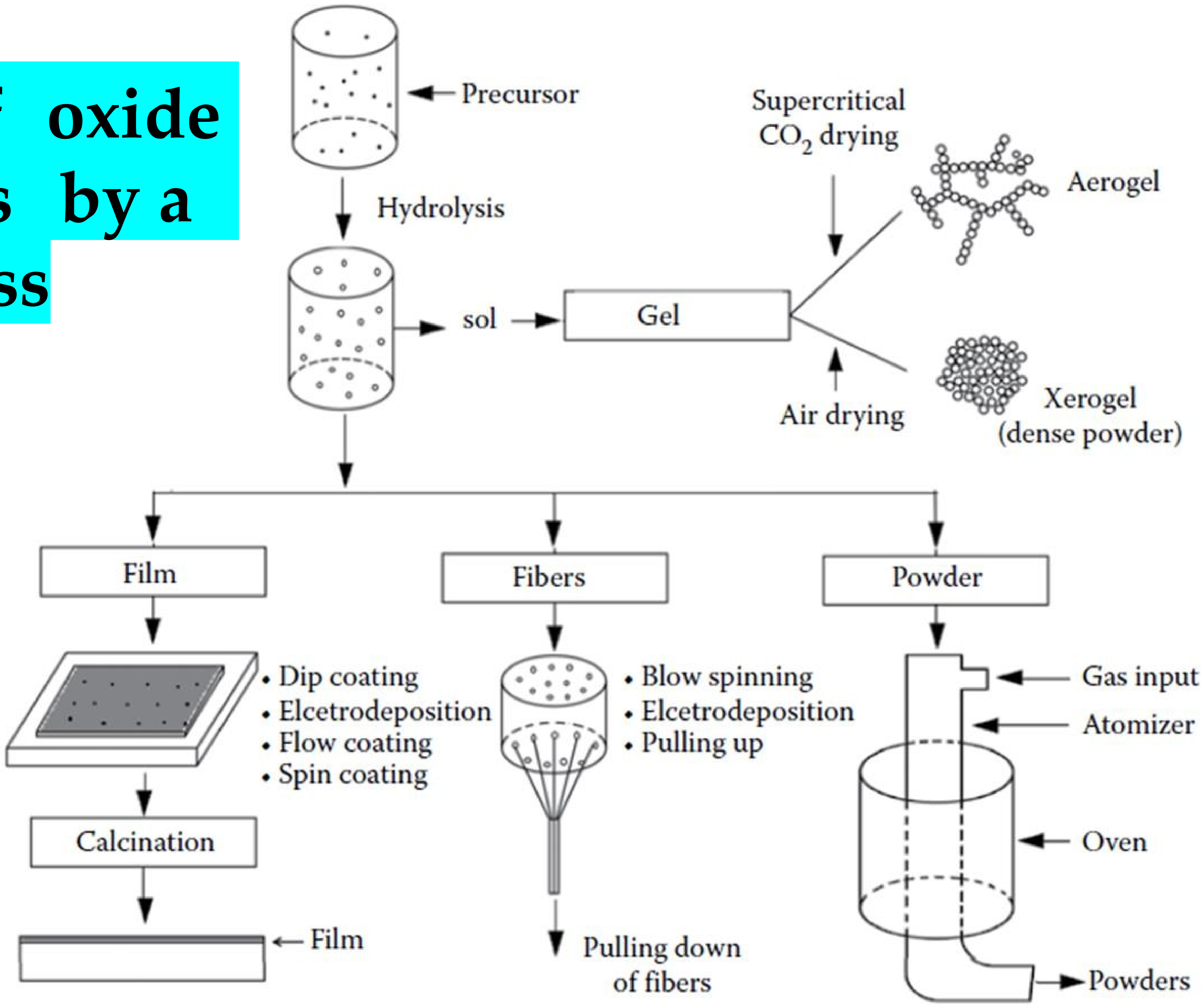
Sol-gel processes are categorized into aqueous based that involved **water** during reaction and **alcohol** based that excludes water. Sol-gel process involves **hydrolysis** and **polycondensation** reactions using water as a medium.



where R = $-CH_3$, $-C_2H_5$, $-C_3H_7$, etc.

M = Metal cation (e.g., Ti^{4+}, Si^{4+})

Synthesis of oxide nanoparticles by a sol-gel process




250
200
150
100

Thank you