Aerosol spray pyrolysis synthesis

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Outline

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3. **Methods of obtaining aerosol particles**
4. **Evolution of particle during pyrolysis**
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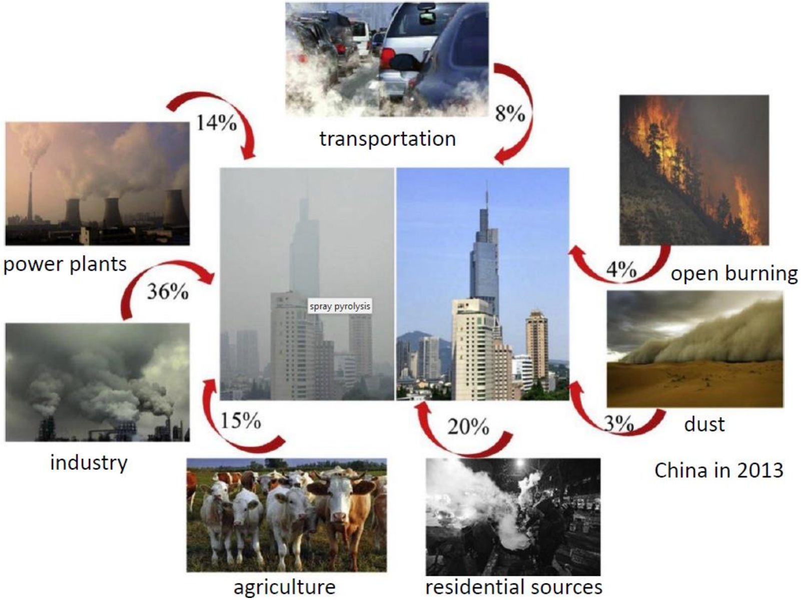
6. **Summary**



An aerosol is a dispersed system consisting of small solid or liquid particles suspended in a gaseous medium.

Particles can vary in size from nanometers to several micrometers
These particles can be of both natural and artificial origin. Aerosols are formed by mechanical grinding and atomization of solids or liquids: by crushing, milling, explosions, combustion, spraying with a nebulizer (e.g. pneumatic, ultrasonic, or electrostatic).

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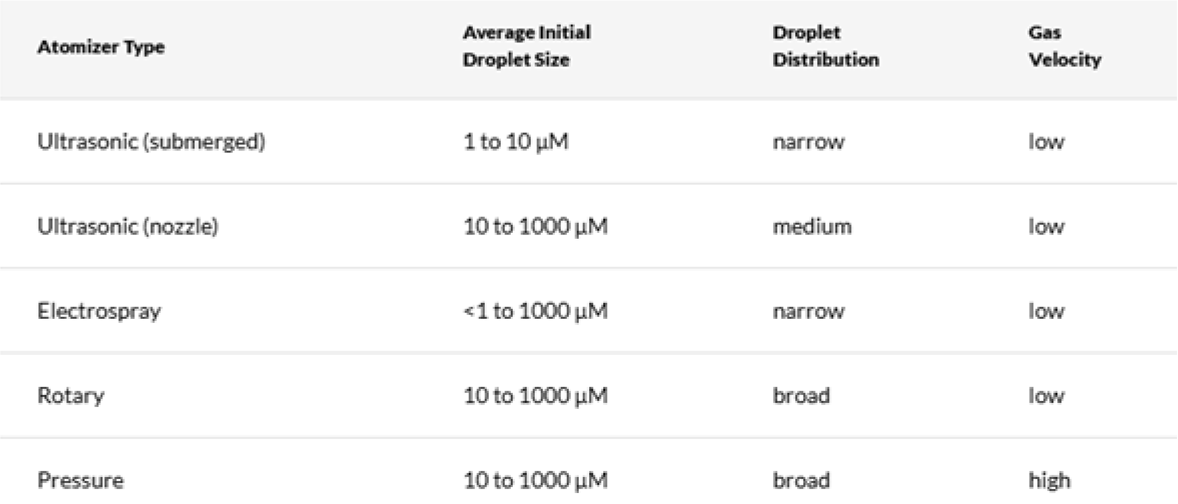
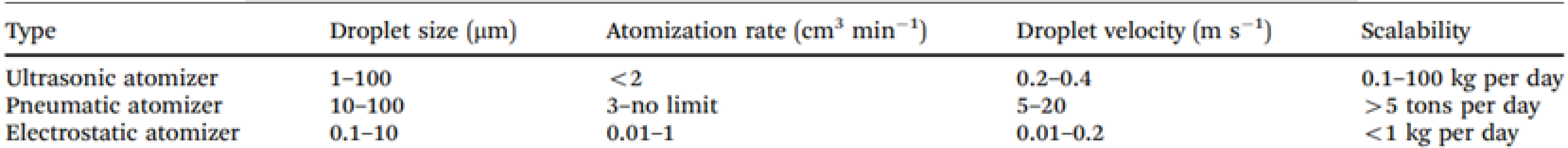
spray pyrolysis is

a method used to synthesize powders or thin films. The process involves two main steps: spraying (usually) a liquid precursor and pyrolysis, i.e. thermal decomposition at high temperatures, which results in the formation of a new phase.



Atomizer Type	**Average Initial Droplet Size**	**Droplet Distribution**	**Gas Velocity**
Ultrasonic (submerged)	1 to 10 µM	narrow	low
Ultrasonic (nozzle)	10 to 1000 µM	medium	low
Electrospray	<1 to 1000 µM	narrow	low
Rotary	10 to 1000 µM	broad	low
Pressure	10 to 1000 µM	broad	high



Type	Droplet size (µm)	Atomization rate ($cm^3\ min^{-1}$)	Droplet velocity ($m\ s^{-1}$)	Scalability
Ultrasonic atomizer	1–100	<2	0.2–0.4	0.1–100 kg per day
Pneumatic atomizer	10–100	3–no limit	5–20	>5 tons per day
Electrostatic atomizer	0.1–10	0.01–1	0.01–0.2	<1 kg per day

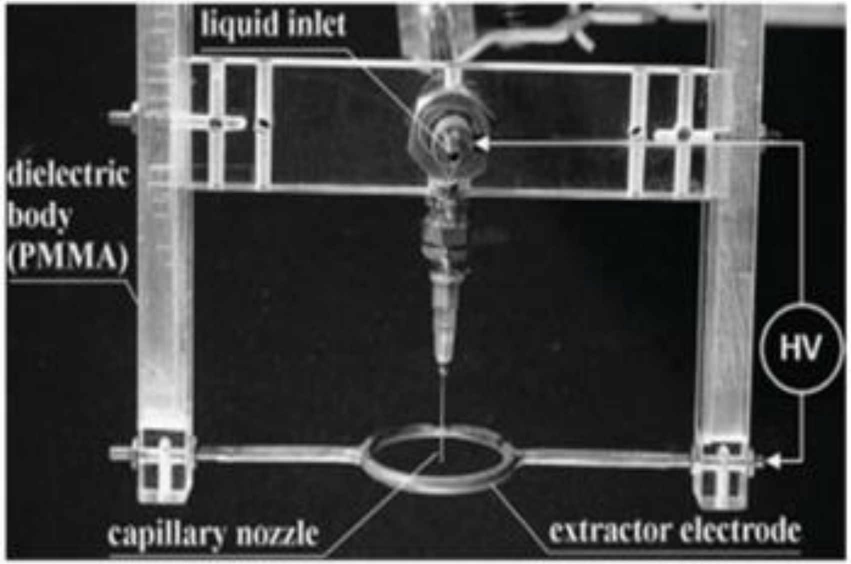
Electrostatic Spray

ESD set-up utilizes an electrostatic atomizer for the generation of an aerosol.

This spraying unit includes a high DC voltage power supply capable of providing voltages of up to 30 kV

a hollow metal needle with an inner diameter of 0.6 mm,

The liquid feeding unit consists of a syringe pump, a glas syringe, and a flexible tube



Ultrasonic Spray

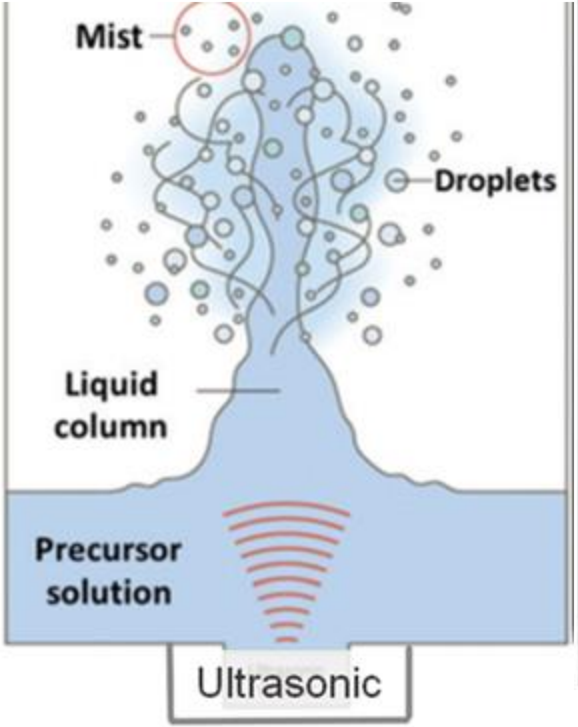
The mist maker is a widely commercial available type of nebulizer.

The nebulizer chip is a low-frequency 105 ± 5 kHz, low-power 2 W (left) frequency of the nebulizer is 1700 ± 50 kHz with a power of 30 W (right)

Processes during Ultrasonic atomization

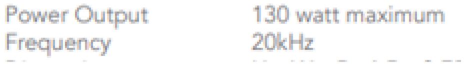
1) generation of capillary waves at the liquid-gas interface, which breaks at the crest of the wave at a certain amplitude (which is provided by the ultrasonic generator) and form liquid drops.

2) cavitation, i.e. the formation of bubbles in a liquid that can grow to tens of µm, and then implosively collapse. After the collapse (periodic hydraulic shocks) the stored energy is released in a very short time, which ruptures the liquid-gas interface and the liquid micron-sized droplets are formed on the surface of a liquid



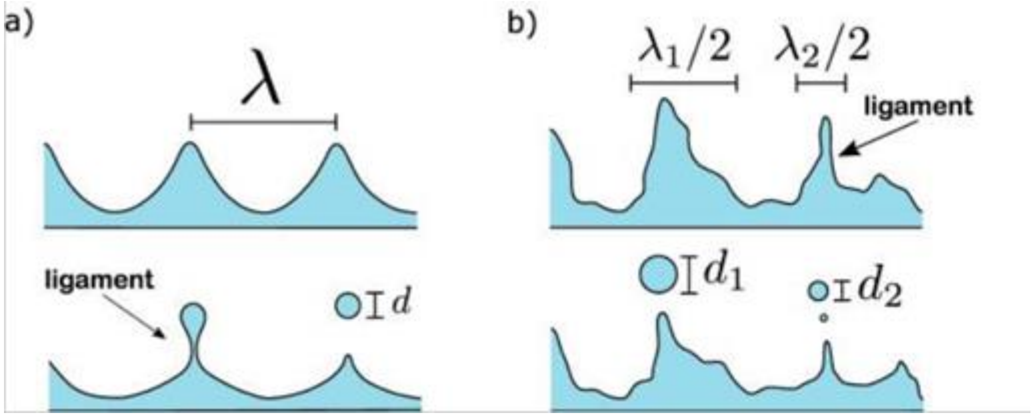
Ultrasonic probe and baths

Frequency 35 kHz



Power Output	130 watt maximum
Frequency	20kHz

Capillary wave mechanism



(a) Ideal case of standing capillary waves of wavelength *λ*. If the amplitude exceeds a certain value, equal sized ligaments are produced, leading to the break-off of monodisperse droplets of size *d* ~ *λ*. (b) Capillary waves in a system with maximum interference, leading to a distribution of wavelengths and amplitudes.

When the amplitude of the oscillations is large enough, droplets are detached.

$$D_{50} = \kappa\lambda = \kappa\left(\frac{8\pi\sigma}{\rho F^2}\right)^{1/3},$$

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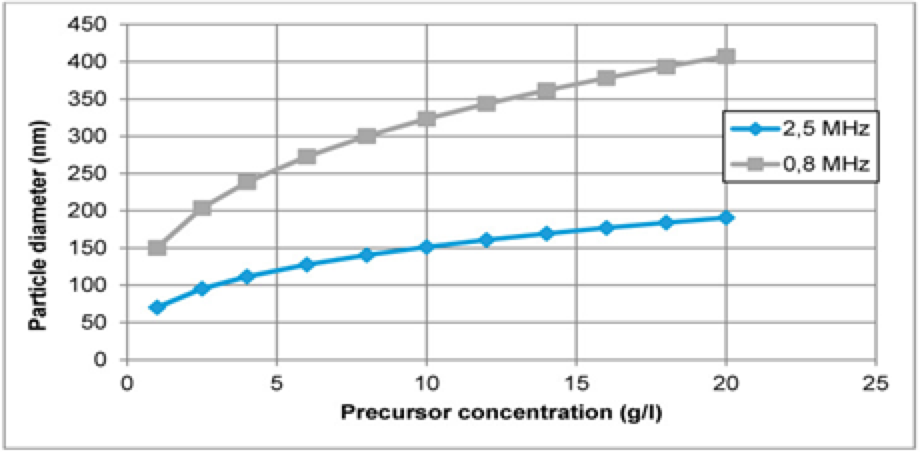
Lang equation, which establishes the relationship between the ultrasonic frequency and the diameter of droplets

$$D_{mat} = 0.34 \cdot \sqrt[3]{\left(\frac{8 \cdot \pi \cdot \gamma \cdot C_{sol} \cdot M_{mat}}{\rho_{sol} \cdot f^2 \cdot \rho_{mat} \cdot M_{sol}} \right)}$$

where D is the median droplet size or diameter (m), γ is the surface tension (N m^{-1}), ρ is the solution density (kg m^{-3}), f is the ultrasonic frequency (MHz) (C_{sol}, the solute concentration, ρ_{sol} density and M_{sol} molar mass; M_{mat} and ρ_{mat} are the molar mass and density of the desired material)



AuNPs with an ultrasound frequency of 0.8 and 2.5 MHz

The aerosol collisions not included into calculations

https://doi.org/10.1038/s41598-019-42599-8

https://pmc.ncbi.nlm.nih.gov/articles/PMC7476056/#B46-materials-13-03485

Aerosol spray pyrolysis synthesis schematic flow diagram

A) Ultrasonic aerosol fountain at 1.7 MHz. Schematic illustration of B) a typical laboratory scale USP apparatus.

1. droplet generation,

2. evaporation of solvents in the heated zone,

3. diffusion of reactants,

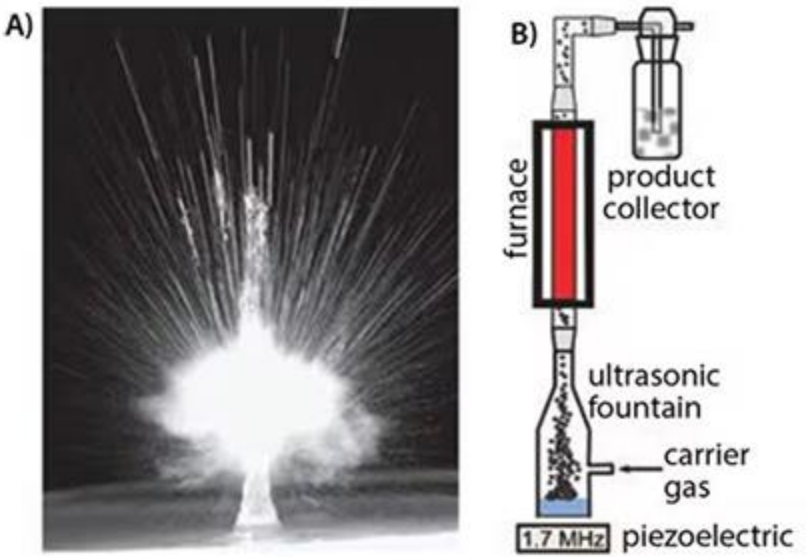
4. precipitation→ reaction,

5. escape of any product volatiles.

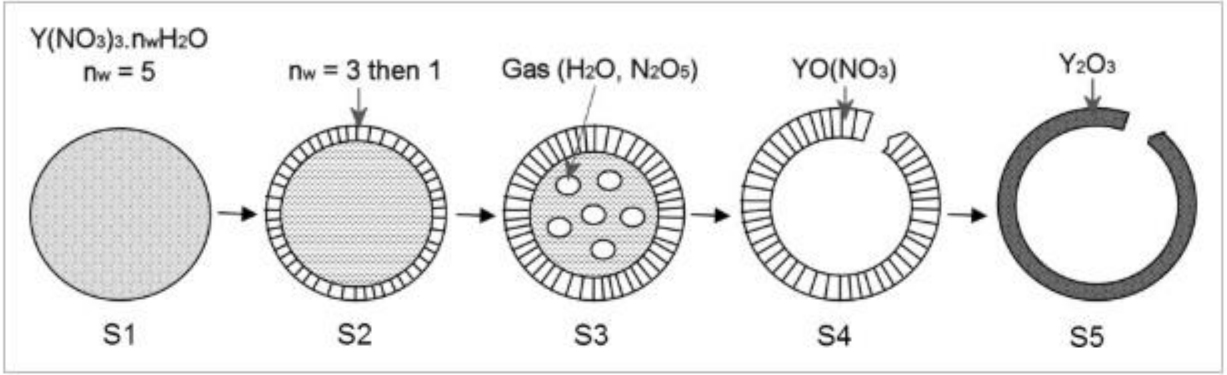
The nature of the final state is critically dependent on the phase of the material that remains after loss of the volatile solvent.

Spray drying - T lower than 300 C, where solvent evaporation and drying happens

Spray pyrolysis -above the decomposition temperature of the solute and chemical reaction occurs.



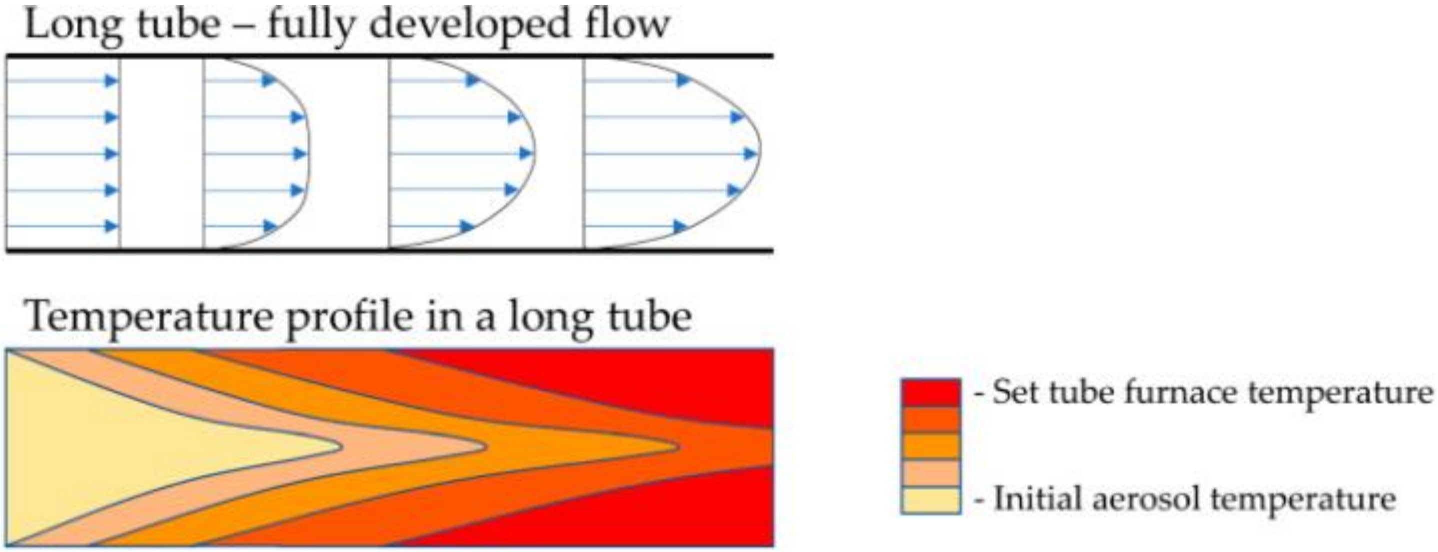
Example of droplet morphology evolution



- Hydrated yttrium nitrate looses progressively H_2O in the vapor state
- crust of low hydrated yttrium nitrate is formed (at 170°C)
- dehydration front moves progressively from the surface to the core
- if the permeability of the crust is too low and the gas pressure inside the particles too high lead to shell damage
- from about 450 to 1200°C, the oxide nitrate is progressively transformed into a pure oxide

doi/full/10.1002/aic.11375

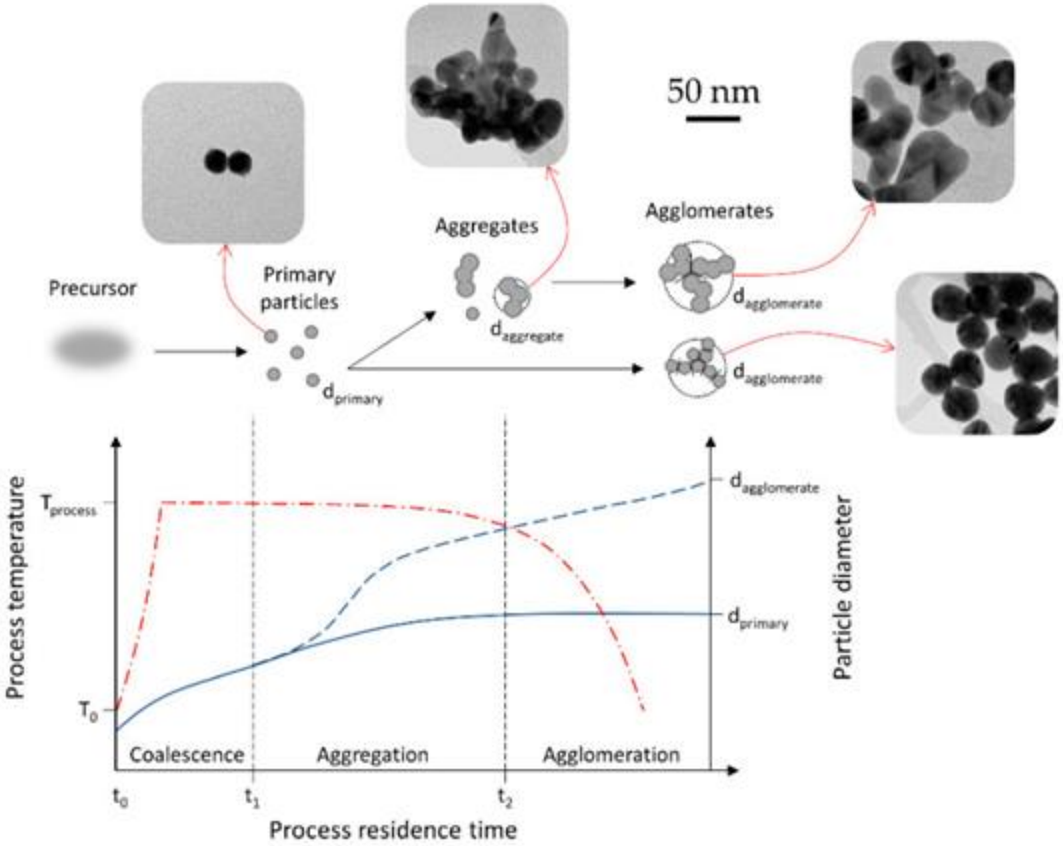
Temperature profile in reactor



The gas velocity profile in the reactor tube for a laminar flow and the temperature profile along the length of the tube

Residence time of the aerosol particles in the reaction furnace

- The red line represents the process temperature, while the blue line represents particle diameter.
- Decreasing the residence time led to more fine, spherical AuNPs.



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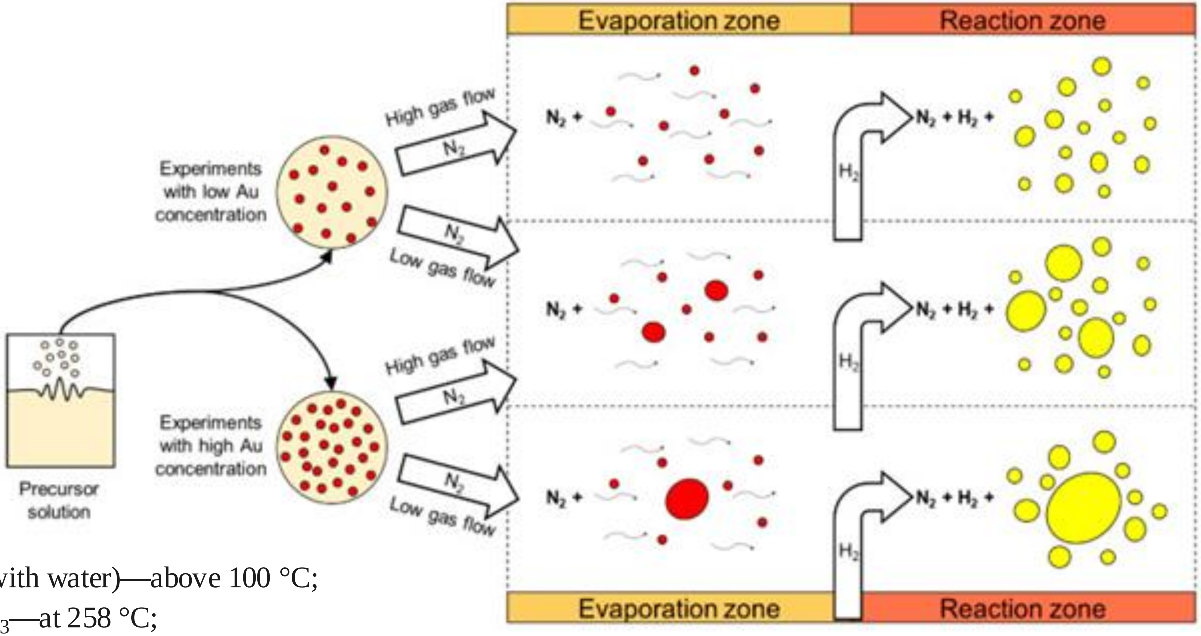
Concentration in the precursor solution and gas flow effect on size

The concentration of gold in the solution affects the solid-to-gas ratio in the process.

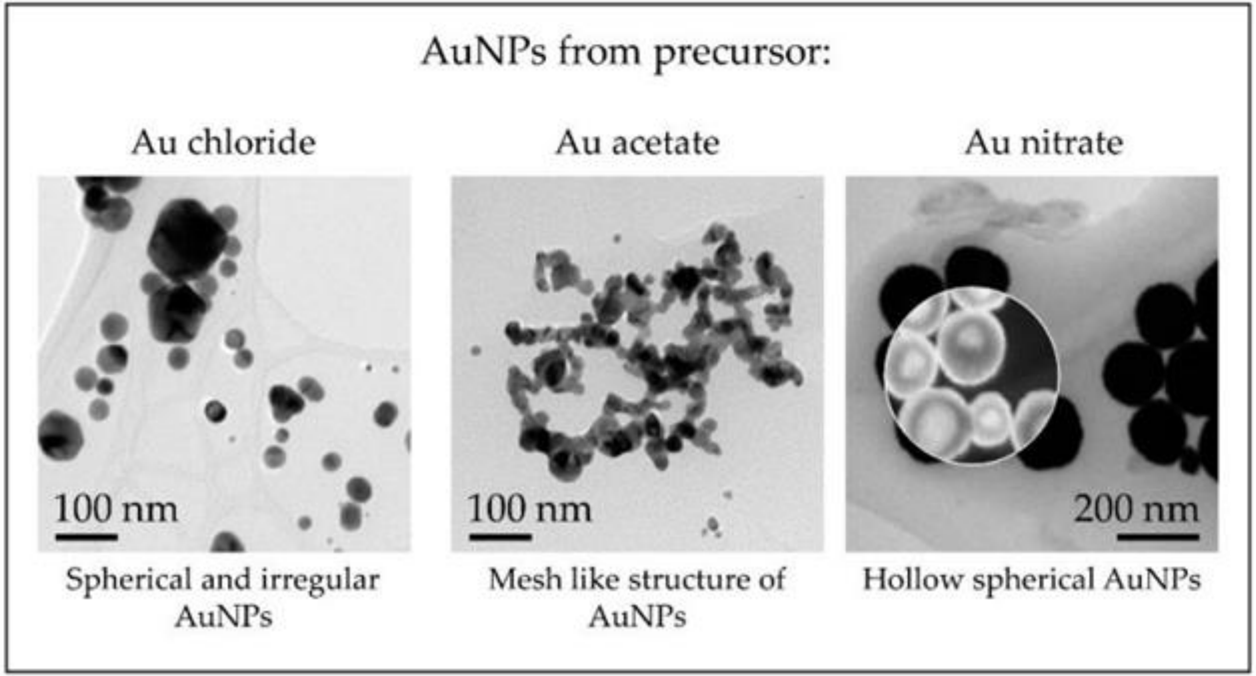
The gas flow determines the residence time, droplet evaporation, and particle reaction time.



1. Evaporation and droplet shrinkage ($HAuCl_4$ with water)—above 100 °C;
2. Thermal decomposition of $HAuCl_4$ into $AuCl_3$—at 258 °C;
3. Reduction of $AuCl_3$ with hydrogen gas and the formation of Au—above 300 °C;
4. Densification (sintering processes).

https://pmc.ncbi.nlm.nih.gov/articles/PMC7476056/#B59-materials-13-03485

Precursor effect

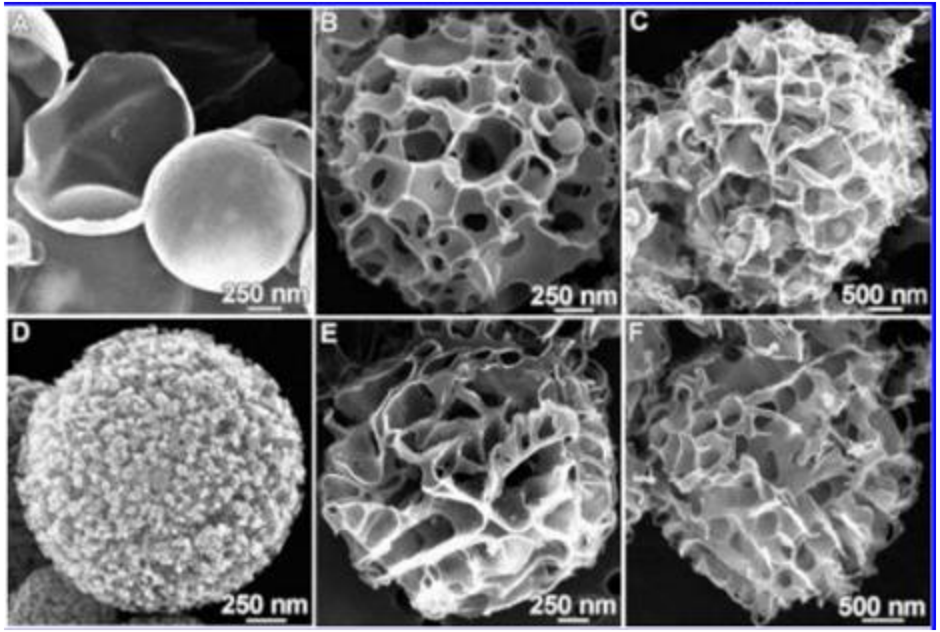


HAuCl4 $Au(O_2CCH_3)_3$ $HAu(NO_3)_4$

DOI:PMC7476056/#B37-materials-13-03485

https://sci-hub.ru/https://pubs.acs.org/doi/10.1021/ja064899h

Porous Carbon Powders Prepared by USP



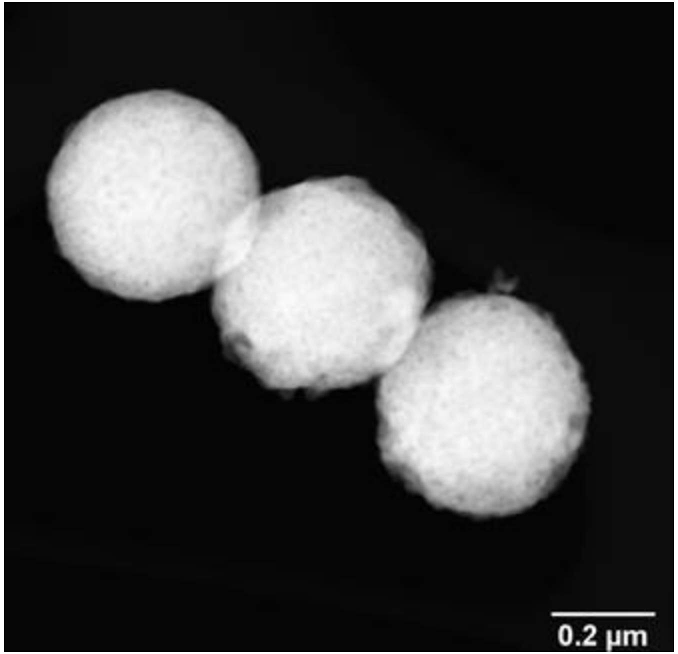
Melting points of the generated salts
LiCl 605 °C;
NaCl 801 °C;
KCl 770 °C.

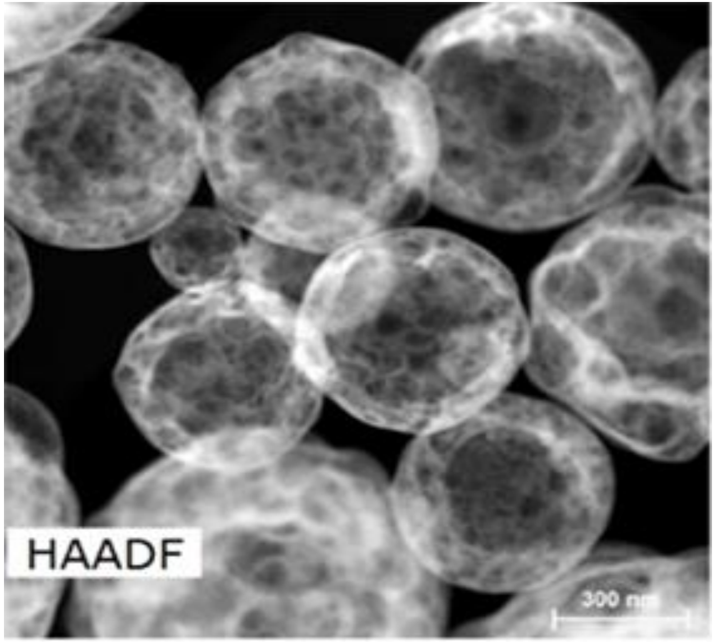
(Figure A) formation from heated aqueous droplets of LiCA: (1) water evaporates, leaving a droplet of solid LiCA; (2) **the LiCA then begins to melt;** (3) as the droplet temperature increases, the exterior LiCA decomposes, creating LiCl and carbon material; however, the interior, now molten, has yet to decompose; (4) the interior melt acts as a template and further source for the growing carbon shell.

In contrast, LiDCA (which forms mesoporous carbon 710 m2/g, Figure D) **melts long before decomposition**.

SEM images of USP porous carbons. Reaction conditions: 1.5 M solutions, **700 °C**, Ar at 1.0 slpm. Product from **(A) lithium chloroacetate**, LiCA, (B) sodium chloroacetate, NaCA, (C) potassium chloroacetate, KCA, (**D) lithium dichloroacetate**, LiDCA, (E) sodium dichloroacetate, NaDCA, and (F) potassium dichloroacetate, KDCA

$La_{1-x}Ca_xFe_{0.7}Ni_{0.3}O_{3-\delta}$ USP

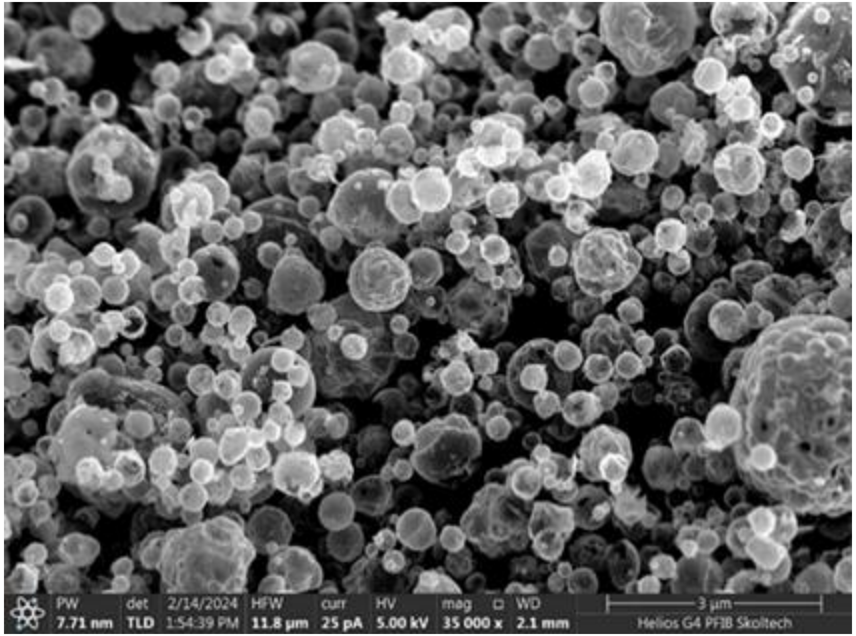




($V_{air\ flow}$ = 172 mL s^{-1}) tubular furnace pre-heated to 1100 °C. Powders were additionally annealed at 600 °C for 10 hours (left) and 850 °C and adding ozone O_3 to the air flow, additionally annealed at 600 °C for 5 hours (right)

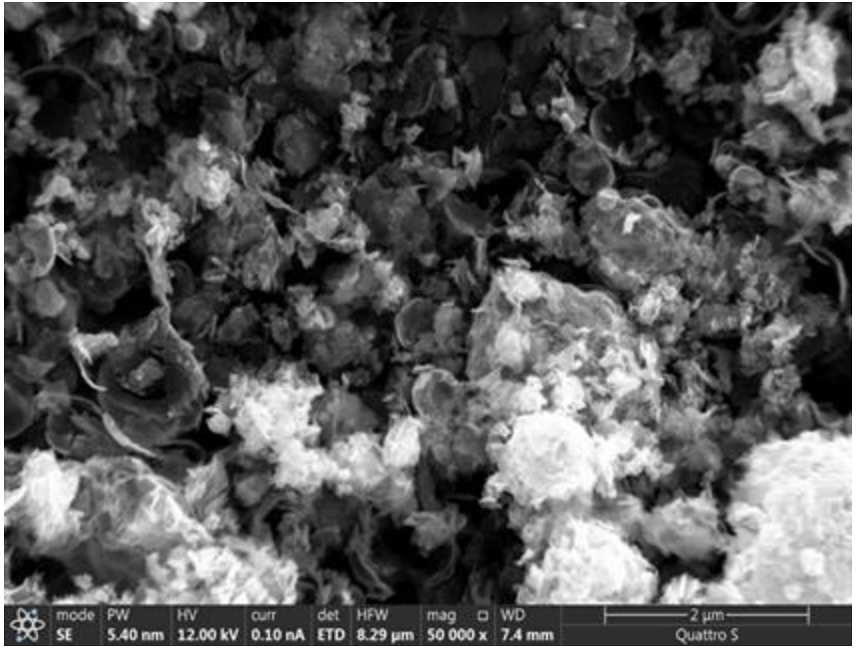
LCFN-RP, effect of concentrations

Nitrate concentration
5 [mg/mL]



45 m^2/g

20 [mg/mL]

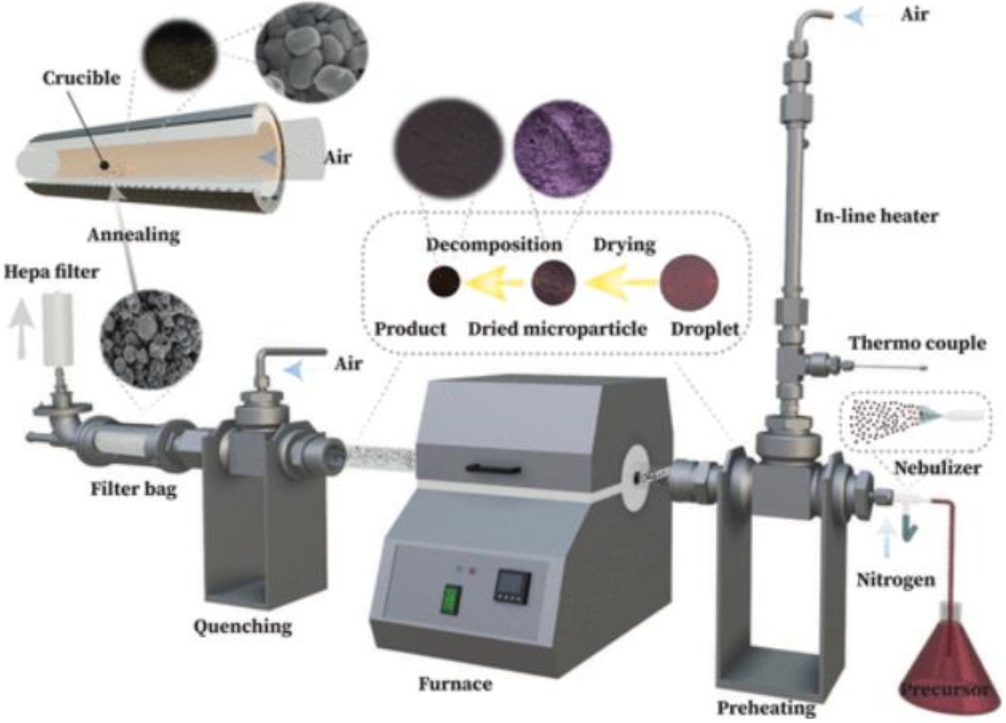


30 m^2/g

Layered-Oxide Cathode Materials

$Co(NO_3)_2 \cdot 6H_2O$ (T_{decomp} =300)
$Co(C_2H_3O_2)_2 \cdot 4H_2O$ (T_{decomp} = 360)
$LiNO_3$ (T_{decomp} = 700)
$LiC_2H_3O_2 \cdot 2H_2O$ (T_{decomp} = 460)

c = 1 mol/L
$T_{preheating}$ = 400 °C
$T_{achieved} \sim$ 230 °C
$T_{furnace}$ = 600–1000 ^{o}C
quenching section with air flow rate 30 L/min (reduced T)



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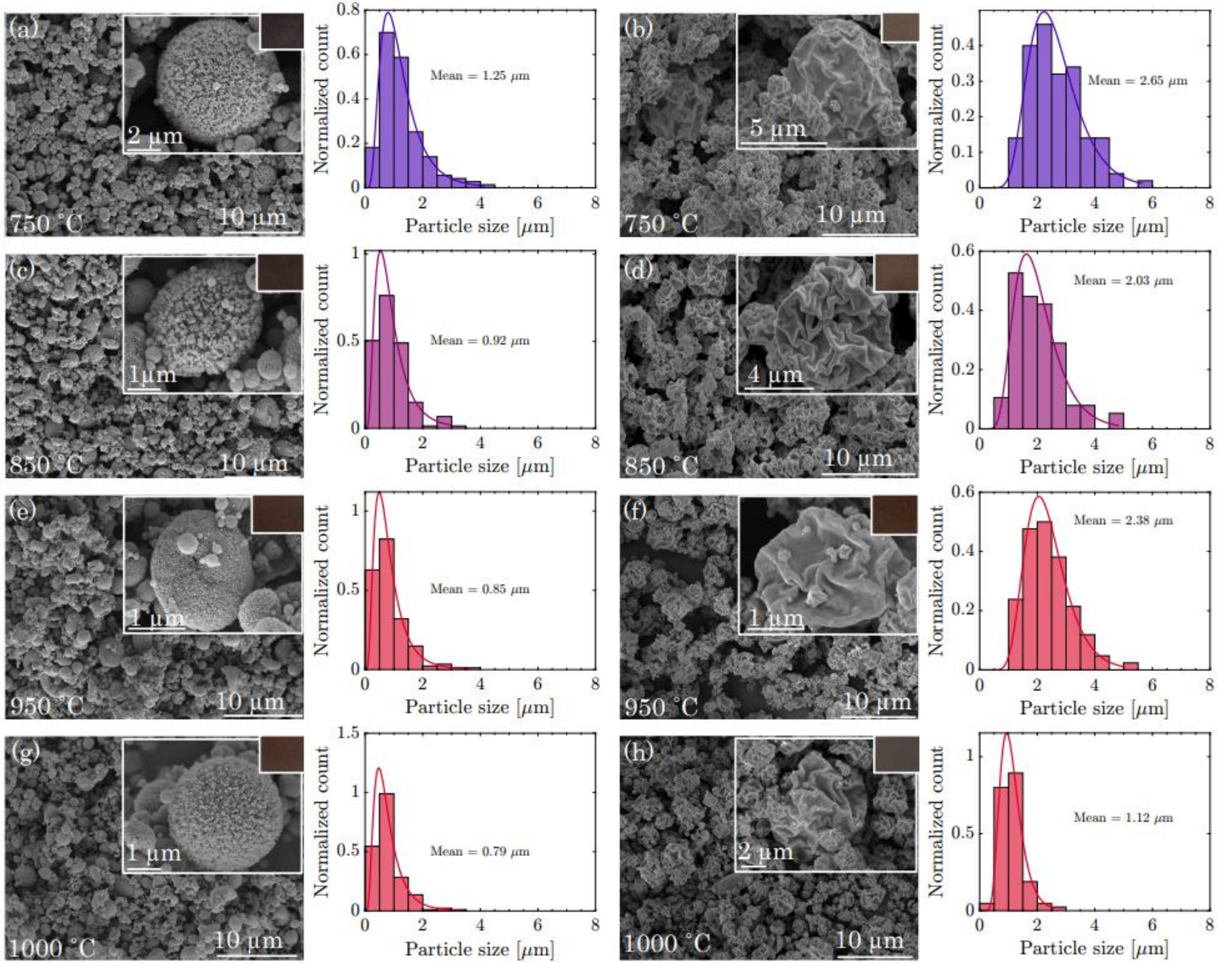
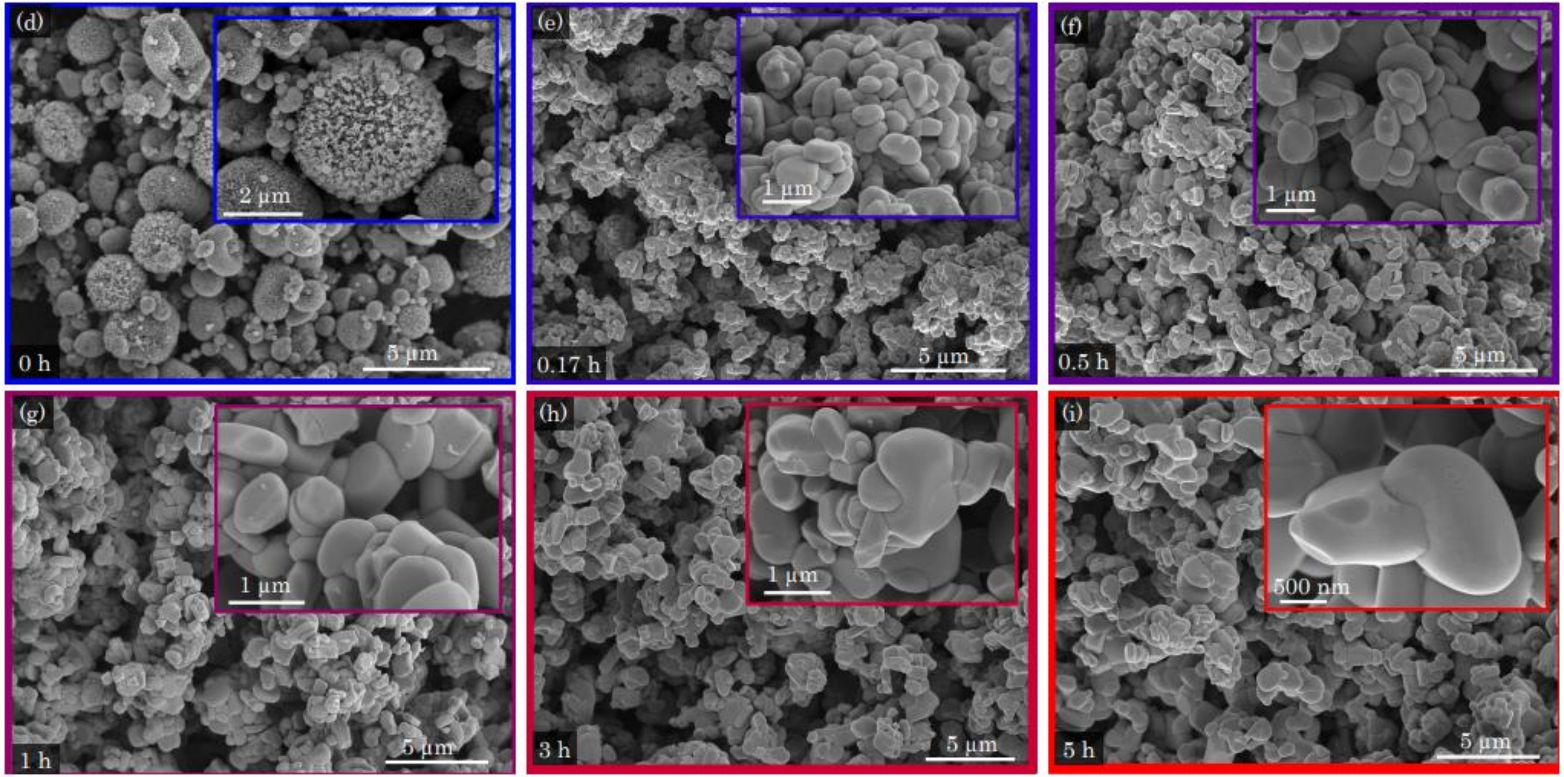


particles synthesized from nitrate precursors (a, c, e, g) and acetate precursors (b, d, f, h)



LCO particles synthesized from nitrate precursors at 900 ◦C, followed by annealing at 775 ◦C for various durations

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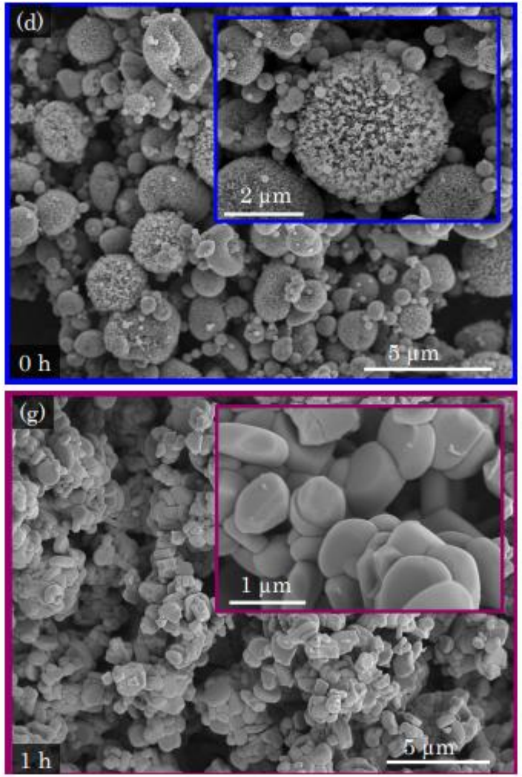
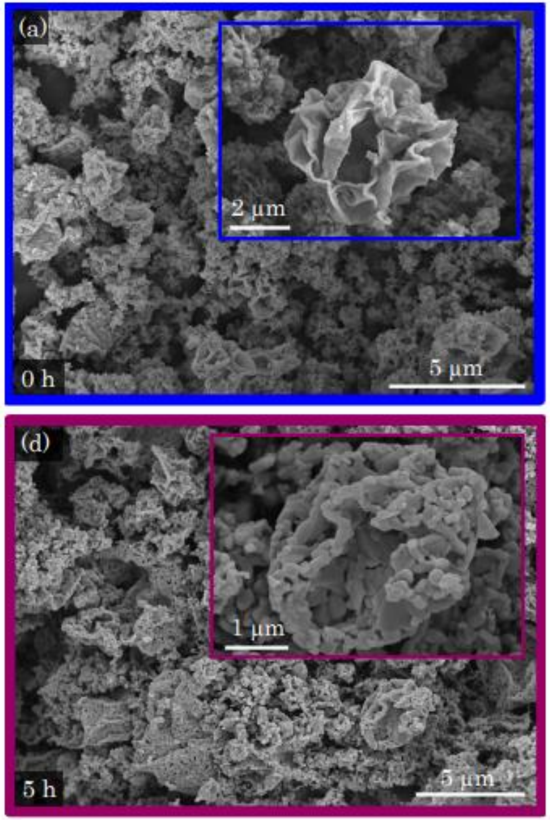


LCO particles synthesized from nitrate precursors at 900 ◦C, followed by annealing at 775 ◦C for various durations



synthesized from acetate precursors at 900 ◦C and annealed at 750 ◦C

Summary

1 The precursor must be dissolved in the liquid, but must not react with it. Water soluble metal salts (e.g. chloride, nitrate, acetate, hydroxides)

2 The product must not dissolve in the liquid, and must not react with the liquid

3 number of variables that can affect the final product:

1 concentration (solution, flow rate of aerosol),

2 atomization technique (droplet size)

3 temperature of furnace, temperature gradient

4 residence time in furnace (length of furnace, droplet velocity)

5 carrier gases and reaction gases (Ar, N2, He, O2, O3, air and e.c.t.)

Полые сферы с развитой поверхностью	Сплошные твердые сферы
Первоначально большой размер капли	Малый размер капли
Высокая температура печи. Быстрое испарение растворителя (grad)	Низкая температура печи и линейный профиль нагрева
Меньшая интенсивность подачи аэрозоля в реакционную зону	Большая интенсивность подачи аэрозоля в реакционную зону (увеличение паров растворителя)
Низкая концентрация растворенного вещества	Высокая концентрация растворенного вещества
Медленная диффузия растворенного вещества	Высокая скорость диффузии растворенного вещества

Thx

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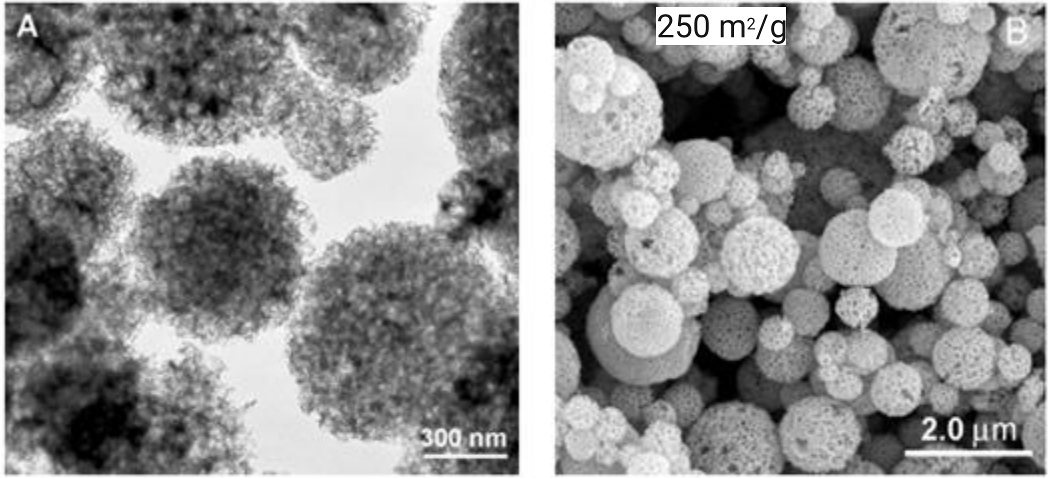
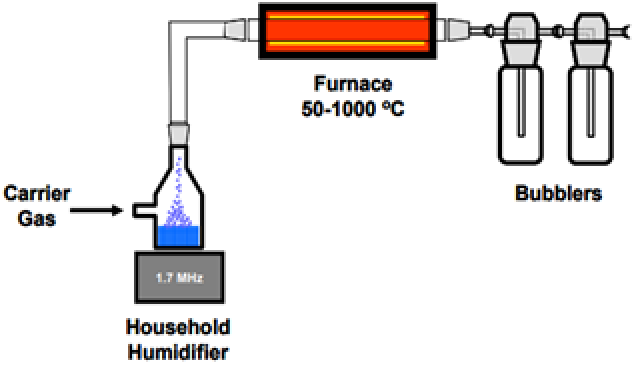
Sulfide synthesis



S.I. Figure 5: (A) TEM image of 20 nm silica templated USP MoS_2, after leaching of the colloidal silica. (B) SEM image of 80 nm silica templated USP MoS_2, after leaching of the colloidal silica.



https://pubs.acs.org/doi/10.1021/ja051654g