FB100 Plasma Chemical Processes

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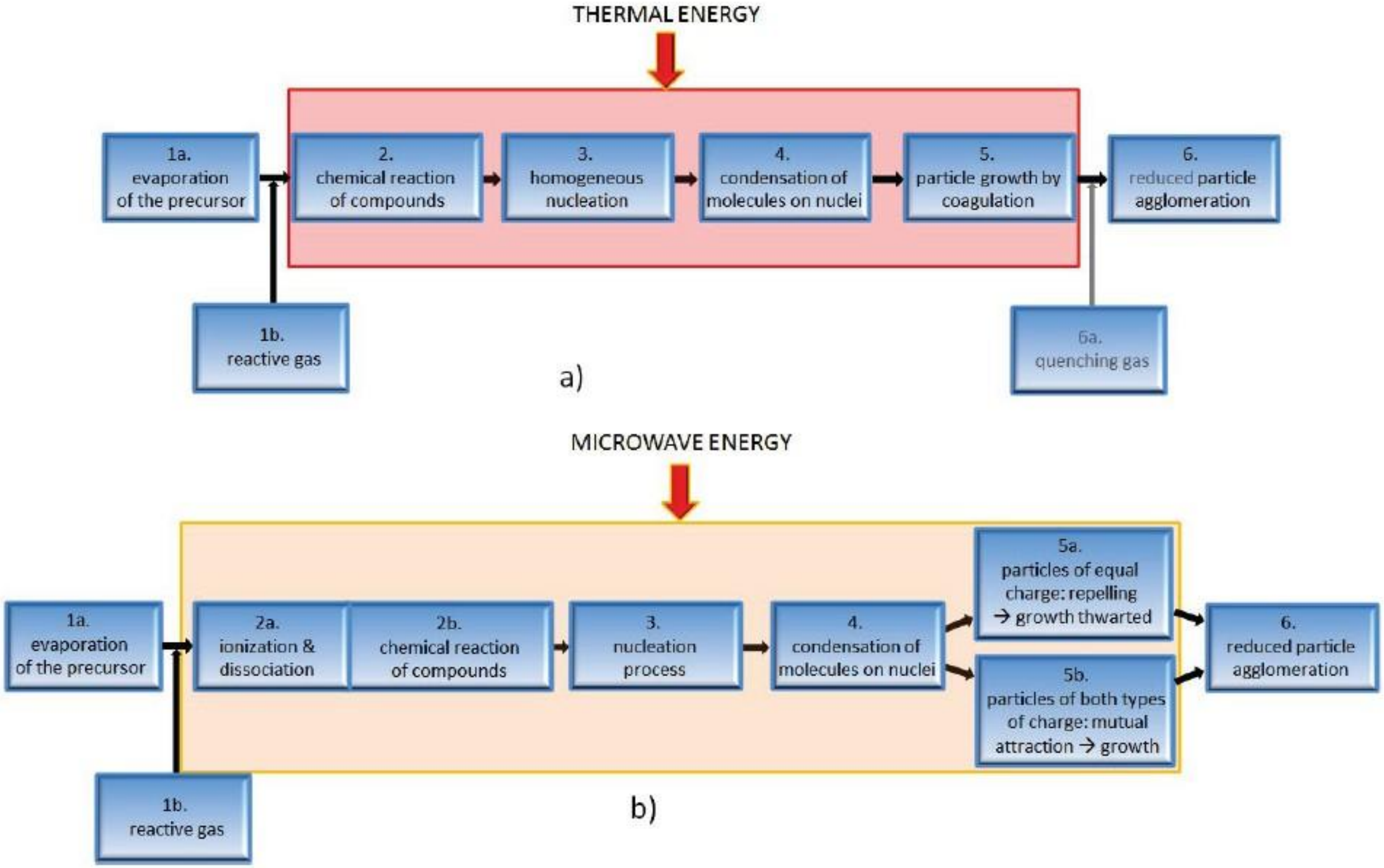
Outline

- Plasma synthesis of Nanoparticles
- Basics of Dusty Plasmas

Plasma synthesis of nanoparticles



Szabo D.V., Schlabach S., Inorganics, 2014, 2, 468-507.

Plasma synthesis of nanoparticles

- In plasma many input parameters such as pressure, flow rates, directly influence plasma parameters such as temperature and concentration of various species and can not be tuned independently
- Plasma synthesis of nanoparticles can be carried out in wide range of discharges driven from DC to RF (13.56 or 27.12 MHz) to MW (2.45 GHz) sources.
- Low pressure setups are limited from point of view of amount of precursor so especially rf or mw setups. Highest densities are achieved in laser plasmas. MW sources are industrially very easily scalable and there is a lot such power sources in the industry.

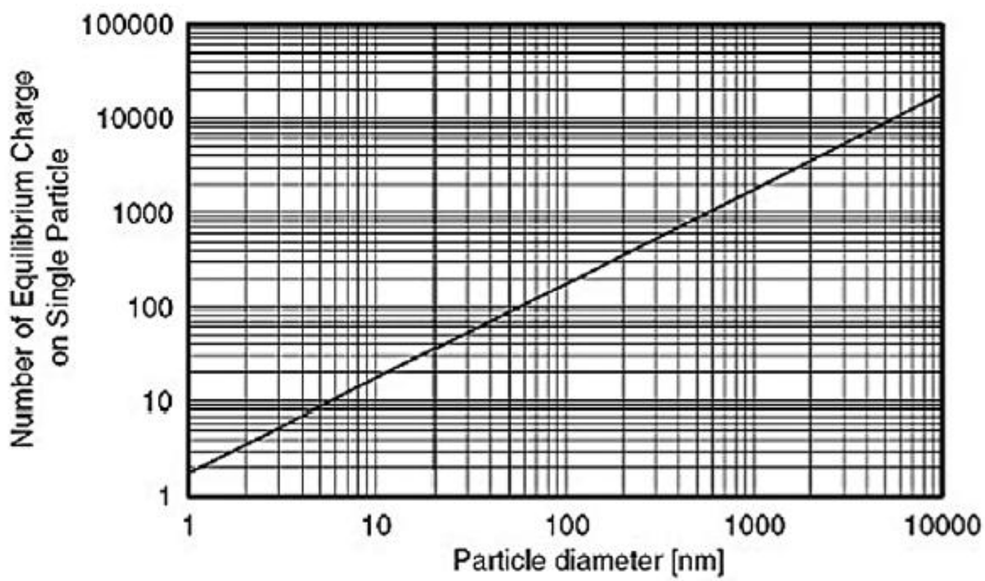
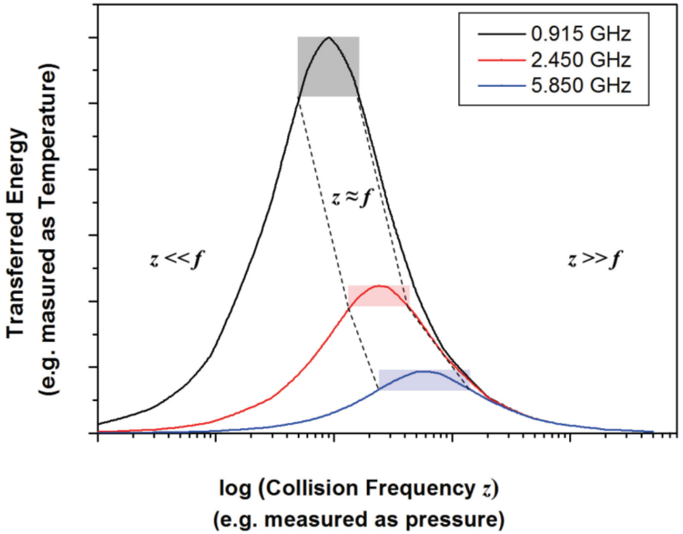


Fig. 9 Average number of electric charges carried by a single nanoparticle. The particle charge increases linearly with the diameter over many orders of magnitude.[21] Reproduced by permission of Springer.

Plasma synthesis of nanoparticles

- The plasma synthesis of nanoparticles differs from gas phase process due to the presence of charged species and charged nanoparticles during the synthesis
- Pressure, temperature and electric field frequency are important parameters influencing nucleation and growth of nanoparticles
- This is of course connected to thermal and non-thermal plasmas with their differences in electron and neutral/heavy species temperature. For different discharges, especially pressures, we will get different conditions for nanoparticle synthesis.
- Ability of nanoparticles to obtain charge and repel each other is connected with collision frequency and frequency of electric field of power source.
- There is direct relationship between frequency of source field f and collision frequency z

$E \sim (q/m)\,(z/(z^2+f^2))$
maximum is reached when z=f
for z << f electrons are ionizing the nanoparticles, nanoparticles have positive charge and are repeling each other (mw discharges).
for z ≈ f we have mix of positively and negatively charged nanoparticles which results in agglomeration.
for z >> f electrons are attached to nanoparticles surface, nanoparticles carry negative charge and repel each other (rf dicharges).
With increasing nanoparticle diameter increases the charge it carries



D. Vollath, Plasma synthesis of nanopowders, J Nanopart Res (2
Inorganics, 2014, 2, 468-507

Plasma synthesis of nanoparticles

- RF sources and configurations – capacitive and inductively coupled discharges with electrodes in or outside the reactor

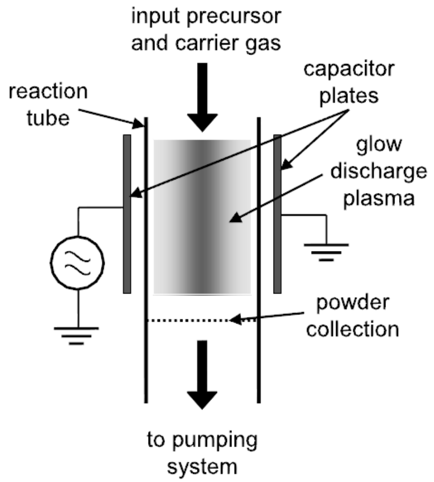
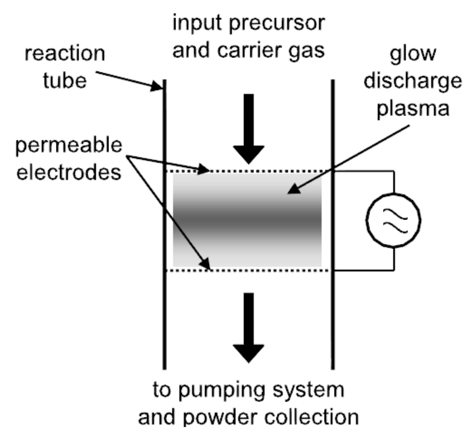
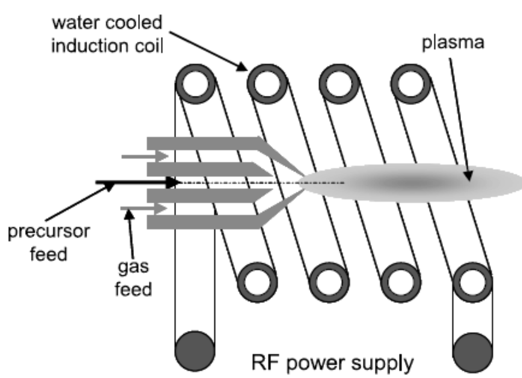


Fig. 10 General layout of a capacitive-coupled RF system for nanoparticle synthesis working at reduced pressure.





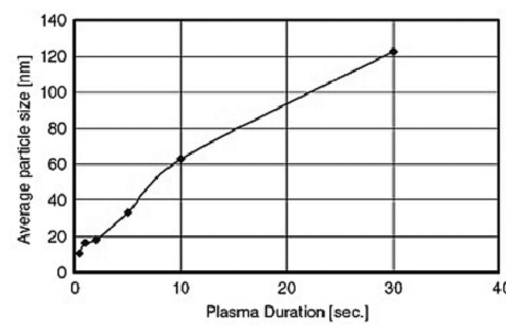
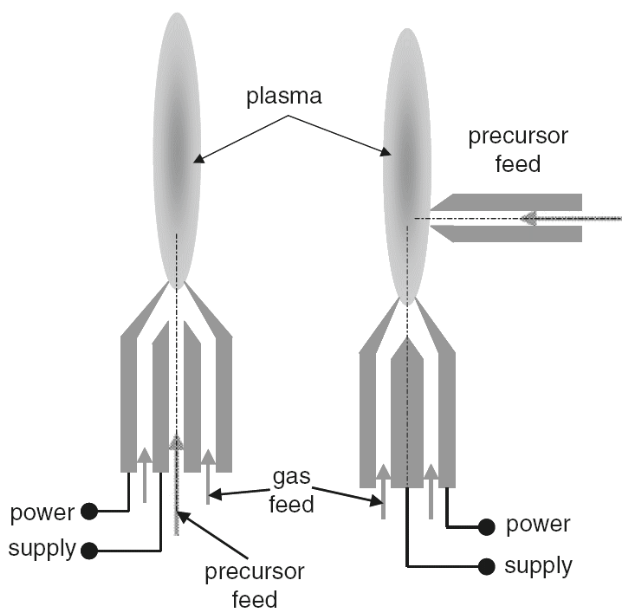
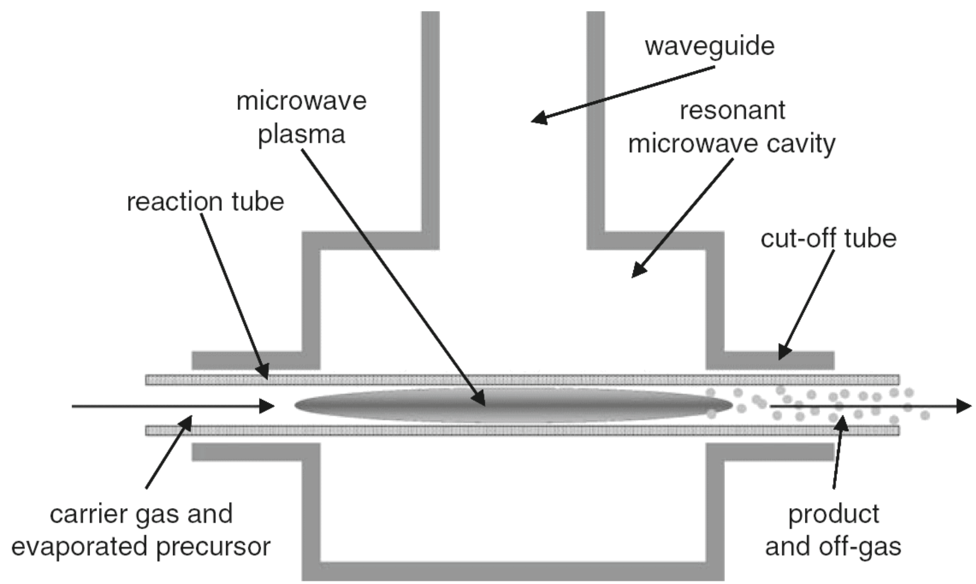


Fig. 12 Average particle size, obtained in a device according to Fig. 11, as a function of the plasma duration, which is the dwell time of the particles in the plasma.[24] Reproduced by permission of Springer.

Plasma synthesis of nanoparticles

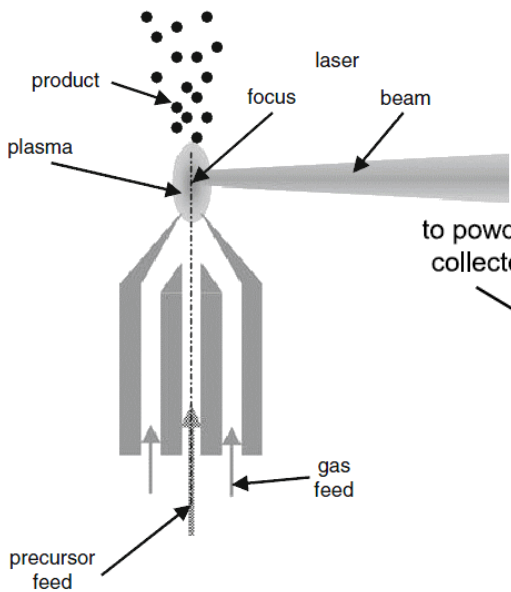
- Microwave plasma sources – thermal or close to thermal sources such as jets and torches and non-thermal sources such as low pressure resonance cavities or surface wave discharges (can be run also at atmospheric pressure)
- Central flow – coaxial or rotating gas feed of liquid or gas precursor, side feed mostly used for powder precursor, influence of nozzle design
- Quench gas rapid cooling of nano powder limits the aggregation of nanoparticles, one can also induce agglomeration by addition of neutralizing agent $H_2O > H^+ + OH^-$
- Influence temperature on crystallinity of nanoparticles

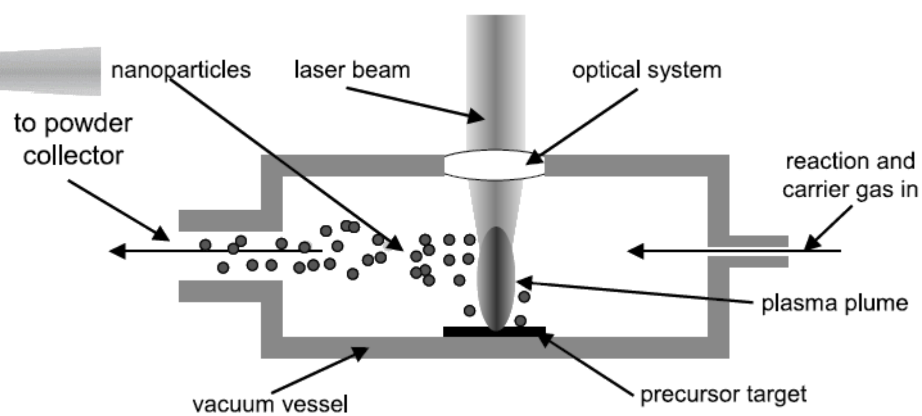


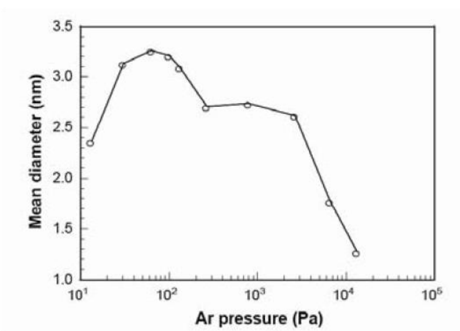


Plasma synthesis of nanoparticles

- Laser driven plasma have high density and high core temperature. The nanoparticle source can be in gas, liquid or solid form. Laser energy dissociates and ionizes precursors and created atoms and molecules form nucleation centers and grow into nanoparticles which eventually can agglomerate into bigger particles. During the plume expansion, the temperature decreases and, as the vapor gets supersaturated, particles are nucleated. Within the short time interval of supersaturation, the particles are formed. The lower the gas pressure in the system, the faster expands the plume; the shorter is the time for particle formation. This limits particle growth.
- However, with increasing supersaturation, the number of nuclei increases, a process that leads to small particles, too.
- In industry most often used lasers are CO_2 laser at 10,6 μm. To achieve efficient absorption in the gas medium SF_6 or C_2H_2 are added to gas mixture.

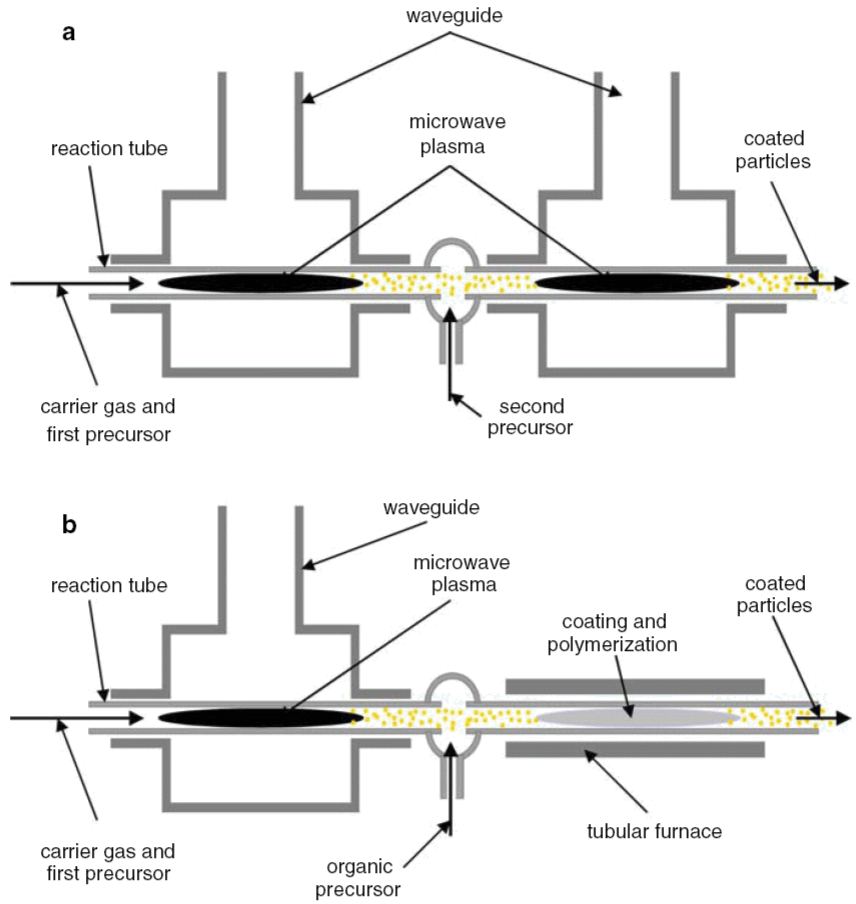


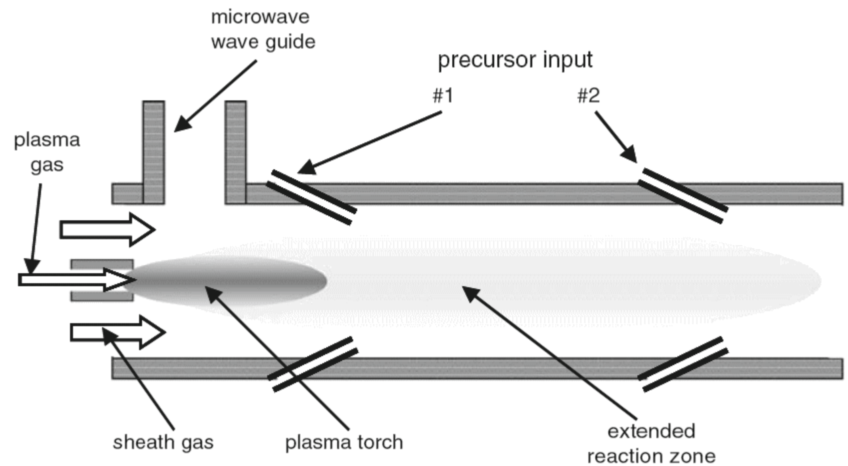




Plasma synthesis of nanoparticles

- Synthesized nanoparticles can be also functionalized. It would be of advantage to use the same plasma source for creating functional layer or coating. If its not possible two coupled setups are used.





Plasma synthesis of nanoparticles

- Influence of precursor densities/molecular weight on yield of nanoparticles for example for $SnCl_4$ and $Sn(C_4H_9)_4$. One also needs to take into account also by products of plasma reactions, if one can remove them by annealing or if they are incorporated into the nanostructures.
- Influence of microwave frequency is given by collision frequency relation, but because this frequency is almost always fixed in given device its not studied.
- Increased pressure leads to increase of particle diameter, one can also tube the repulsion process of nanoparticles as mentioned above.
- Higher microwave power usually leads to bigger amount of smaller particles which is probably related to increase of temperature and chemical reactivity which leads to higher number of nanoparticle nuclei. Higher reaction rates also lead to cleaner chemical composition and lower amount of un-reacted precursor.
- Residence time is plasma can influence properties of nanoparticles but it has to be investigated in detail and experiment setup must be adjusted to such fine tuning.

Plasma synthesis of nanoparticles

Table 1. Selection of different commercially available, solid, liquid, or gaseous, and volatile precursors typically used in microwave plasma nanoparticle synthesis.

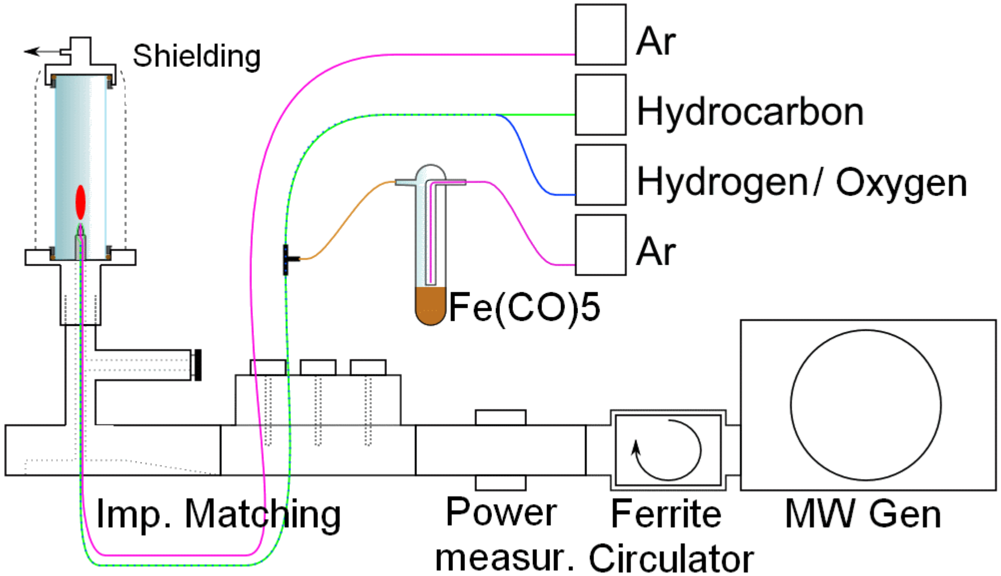
No.	Chemical formula [CAS-Number]	Name/synonym	Melting point/boiling point	Aggregate state	Remarks and hazards
1	$FeCl_3$ [7705-08-0]	Iron(III)chloride	304 °C/319 °C 120 °C sublimation	solid	Corrosive; hygroscopic; harmful; releases Cl
2	$SiCl_4$ [10026-04-7]	Silicon(IV)chloride Silicon-tetrachloride	−70 °C/57 °C	liquid	Moisture sensitive; corrosive to metals and tissues; irritant; releases Cl
3	$SnCl_4$ [7646-78-8]	Tin(IV)chloride Tin-tetrachloride	−33 °C/114 °C	liquid	Moisture and air sensitive; corrosive to metals and tissues; harmful; irritant; releases Cl
4	$TiCl_4$ [7550-45-0]	Titanium(IV) chloride Titanium-tetrachloride	−25 °C/136 °C	liquid	Moisture sensitive; corrosive to metals and tissues; irritant; releases Cl
5	$Fe(CO)_5$ [13463-40-6]	Ironpentacarbonyl	−20 °C/103 °C	liquid	Air sensitive; highly flammable; very toxic
6	SiH_4 [7803-62-5]	Mono-Silane Silicon-tetrahydride	−187 °C/−112 °C	gaseous	Extremely flammable; pyrophoric in air
7	$Sn(C_4H_9)_4$ [1461-25-2]	Tetra-n-butyltin	−97 °C/145 °C @ 10 mm Hg pressure	liquid	Harmful; toxic
8	$Ti(OC_4H_9)_4$ [5593-70-4]	Titanium(IV)-*n*-butoxide	−55 °C/206 °C @ 10 mm Hg pressure	liquid	Moisture sensitive; flammable; irritant
9	$Zr(OC_4H_9)_4$ [2081-12-1]	Zirconium(IV)-*t*-butoxide	3 °C/90 °C @ 5 mm Hg pressure	liquid	Moisture sensitive; irritant
10	$HC{\equiv}CH$ [74-86-2]	Acetylene	−82 °C (sublimation)	gaseous	Flammable; may cause fire flash
11	CH_4 [78-82-8]	Methane	−182 °C/−164 °C	gaseous	Flammable; explosive
12	$H_2C{=}CH_2$ [78-85-1]	Ethylene	−169 °C/−103 °C	gaseous	Highly flammable; may form explosive mixtures with air

Plasma synthesis of nanoparticles

Particle collection in plasma synthesis is carried out outside the reaction zone can main methods are mechanical filtering and cyclones. Very effective is also electrostatic deposition, possibly also done with addition of corona discharge. One can also use drift of particle in temperature gradient so call thermophoresis.

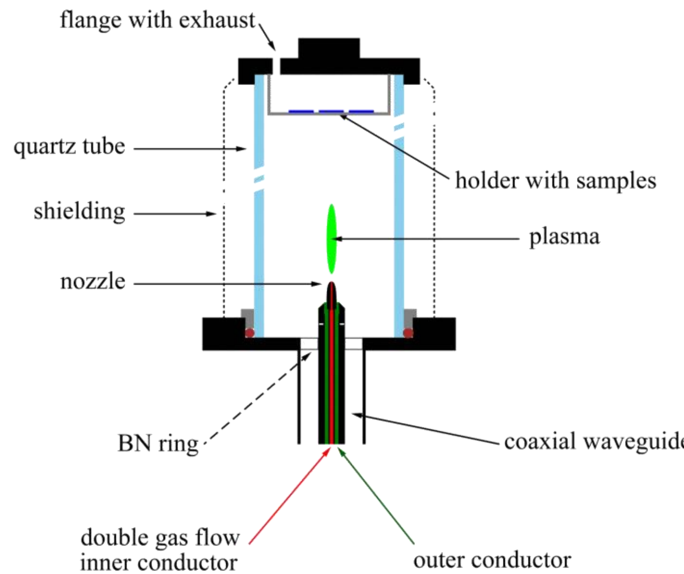
Nanoparticle size monitoring during the synthesis:
Laser-light-scattering methods - Thomson scattering, Photo-emission and photo-ionization methods, Modified Langmuir probe method etc. Y. Watanabe, Formation and behaviour of nano/micro-particles in low pressure plasmas J. Phys. D: Appl. Phys. 39 (2006) R329–R361.

Plasma synthesis of nanoparticles – iron oxides

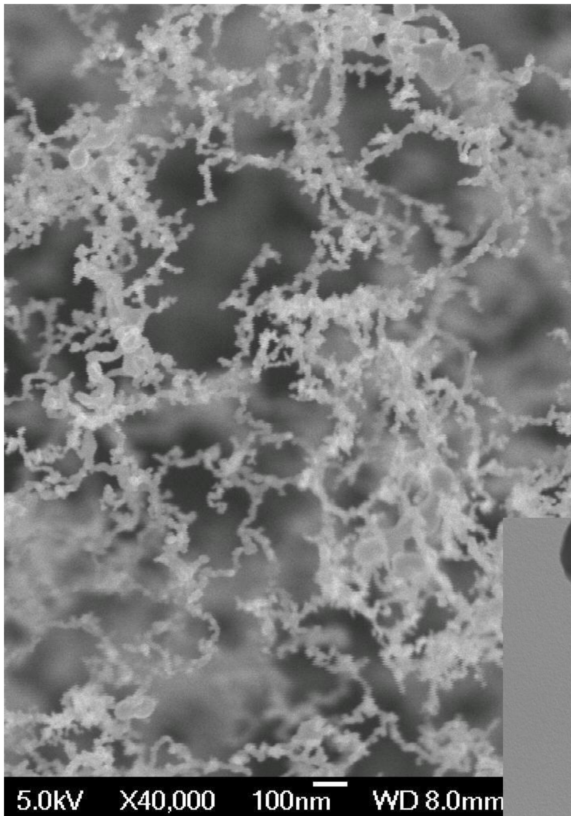


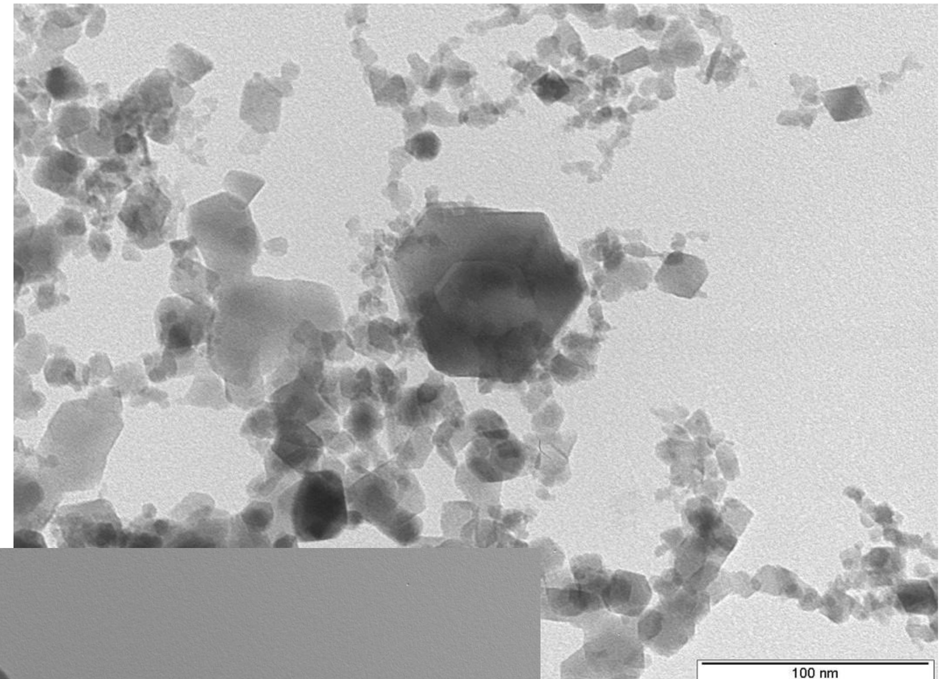
Microwave plasma torch operating at 2,45 GHz,
(100 – 300 W) max. 2 kW power, dual gas flow
Center - Ar(500-1500 sccm)/
Outer – O_2, H_2, hydrocarbons, (250-1000 sccm)
Deposition in volume or on substrates

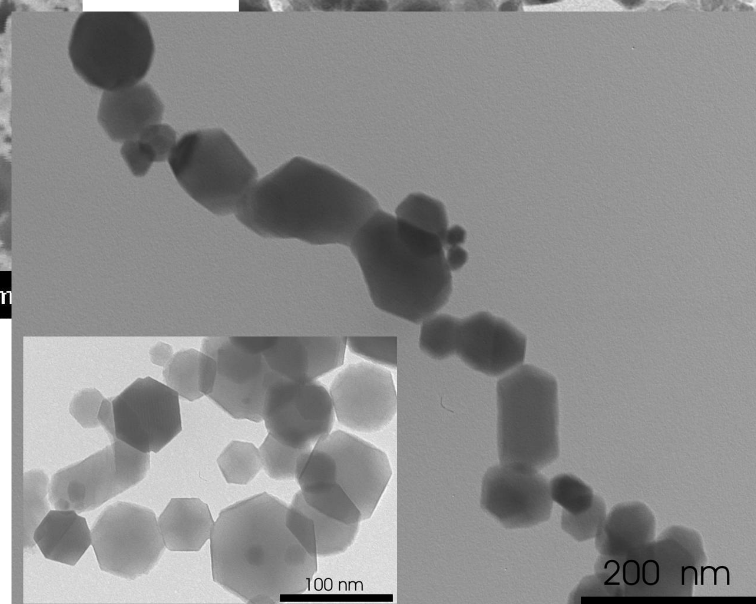
Plasma synthesis of nanoparticles – iron oxides



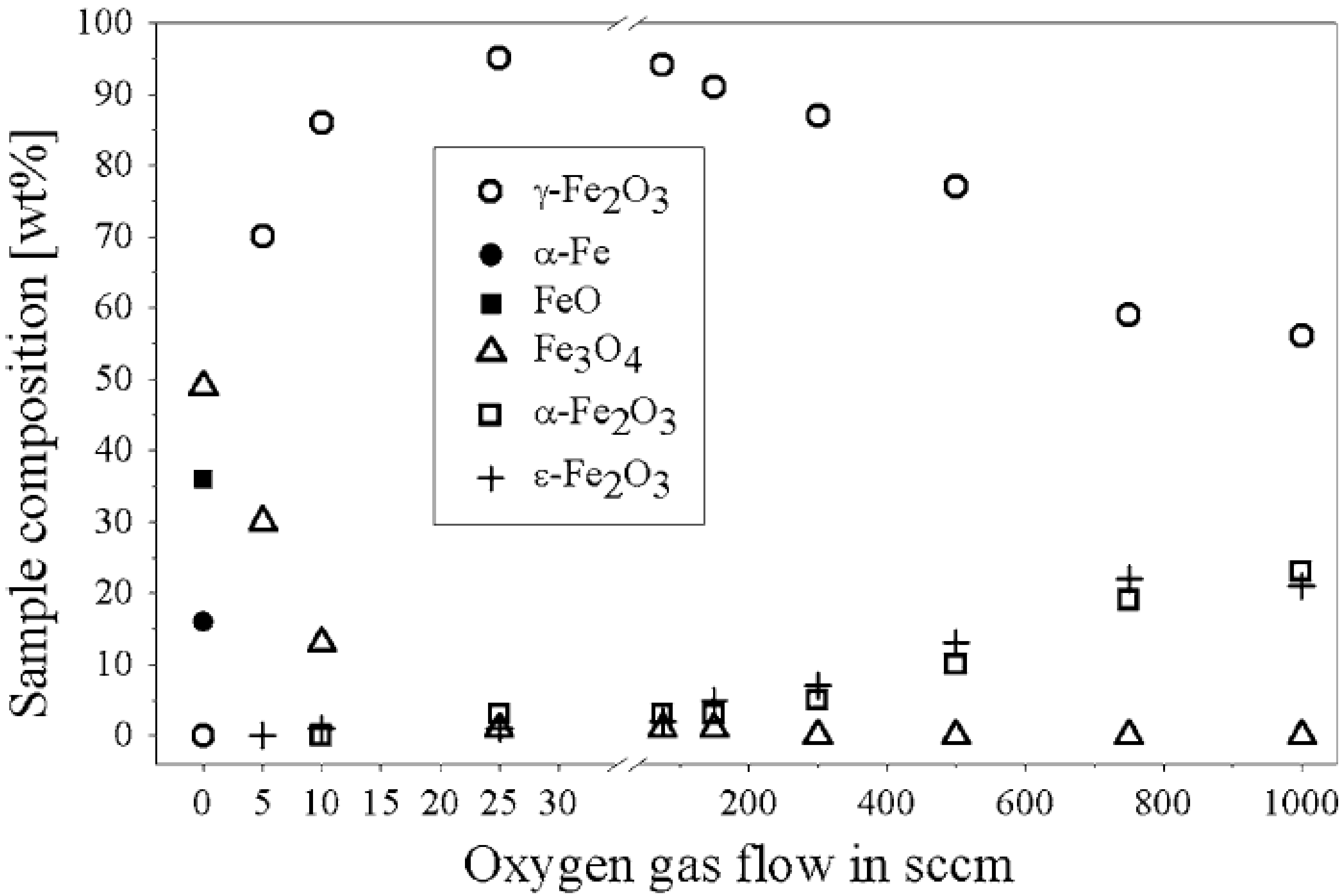
Plasma synthesis of nanoparticles – iron oxides

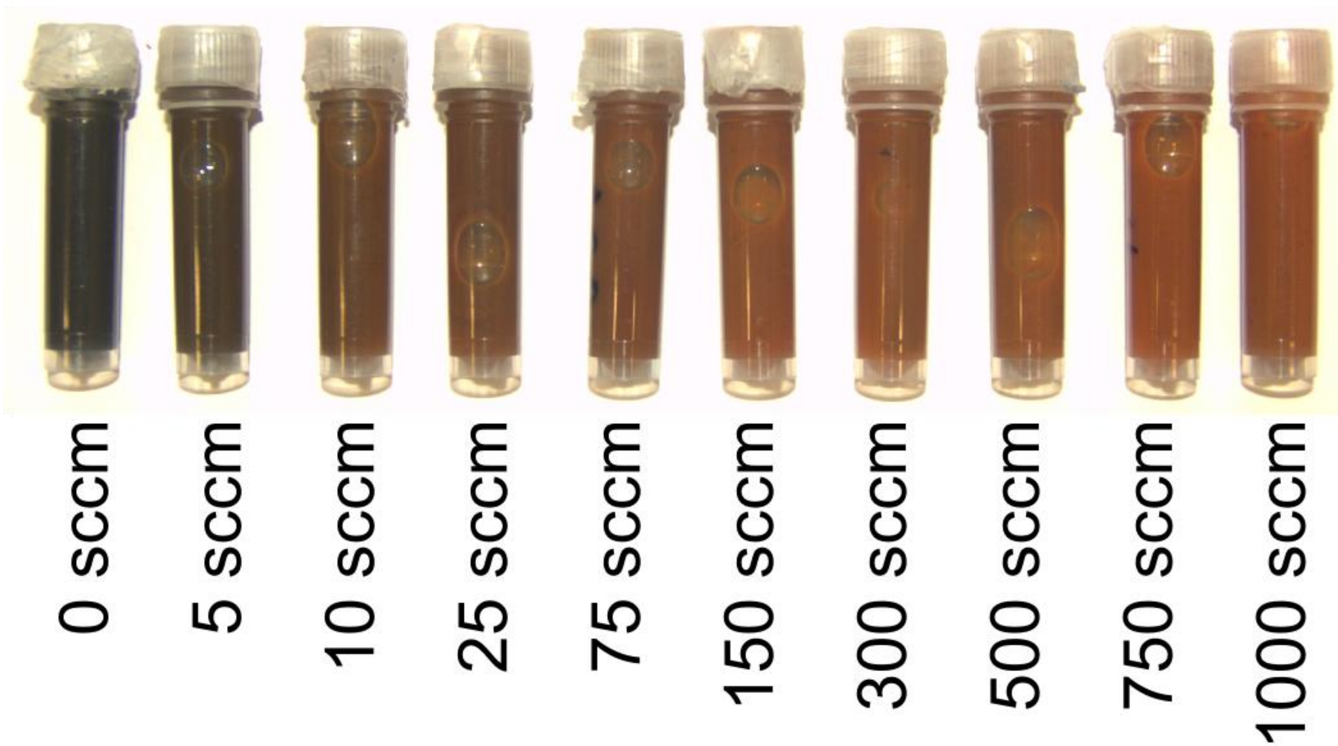






Plasma synthesis of nanoparticles – iron oxides




0 sccm
5 sccm
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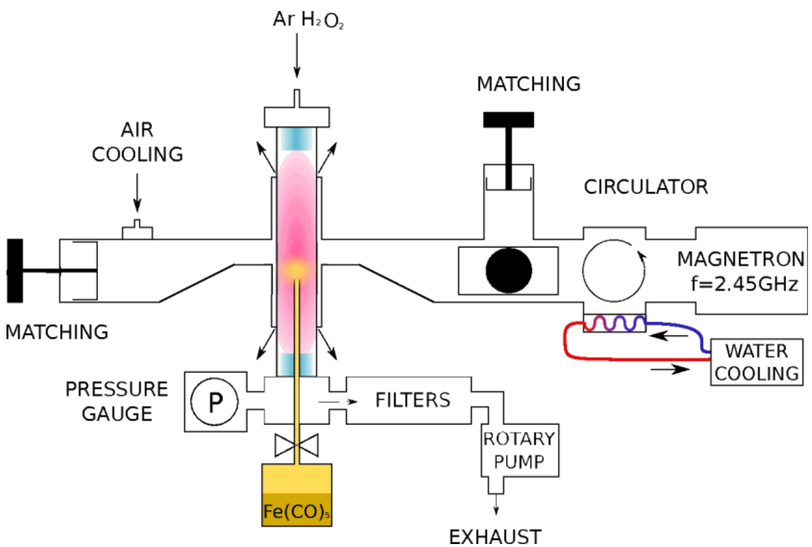
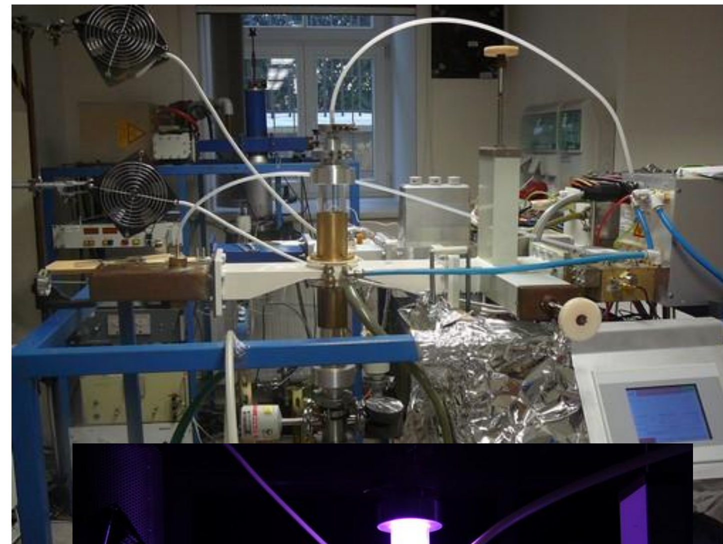
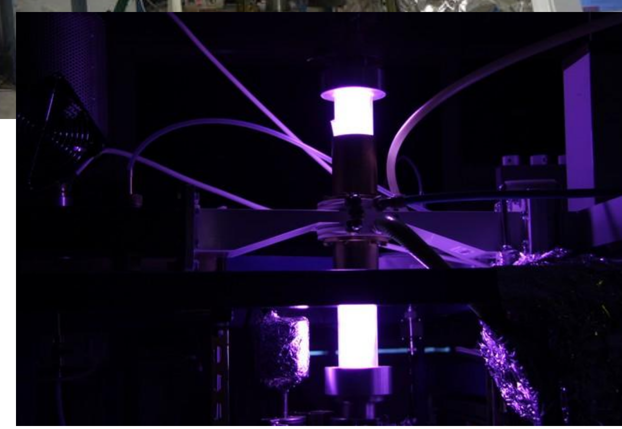
25 sccm
75 sccm
150 sccm
300 sccm
500 sccm
750 sccm
1000 sccm

Plasma synthesis of nanoparticles – iron oxides

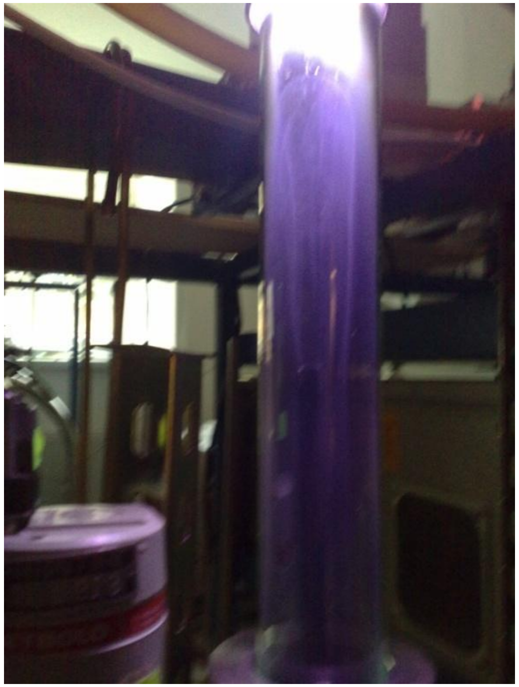






Low pressure surface-wave microwave discharge 2,45 GHz, (100 – 800 W) max. 2 kW power, operating pressure 500 – 10000 Pa,
Gas flows - Ar(500-1500 sccm),
O_2, H_2, hydrocarbons, (250-1000 sccm), iron pentacarbonyl

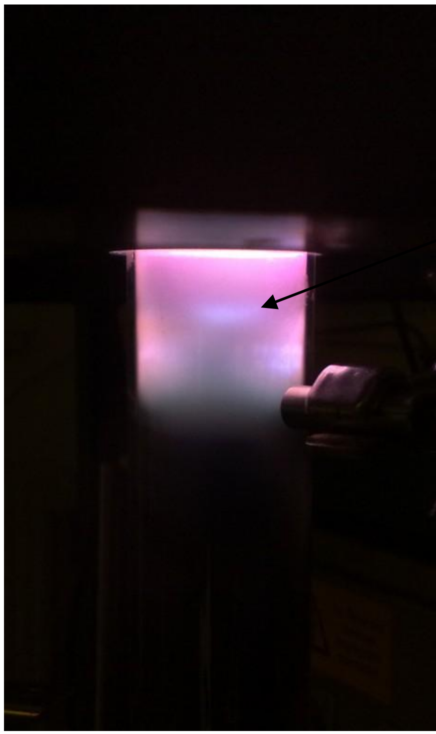
Plasma synthesis of nanoparticles – iron oxides



Ar discharge

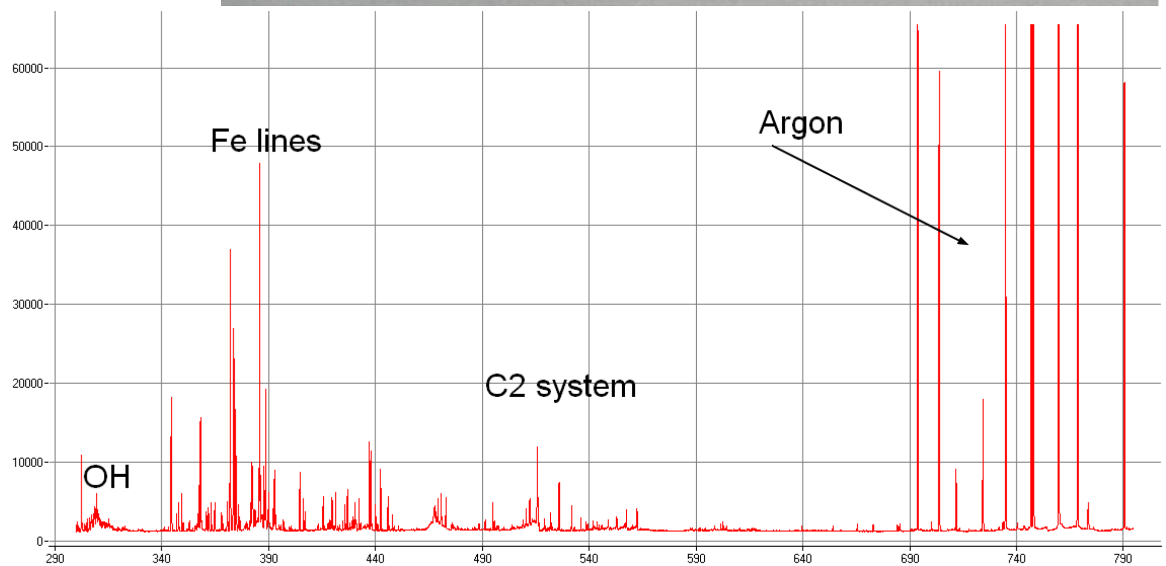
Ar + $Fe(CO)_5$ discharge

Plasma synthesis of nanoparticles – iron oxides

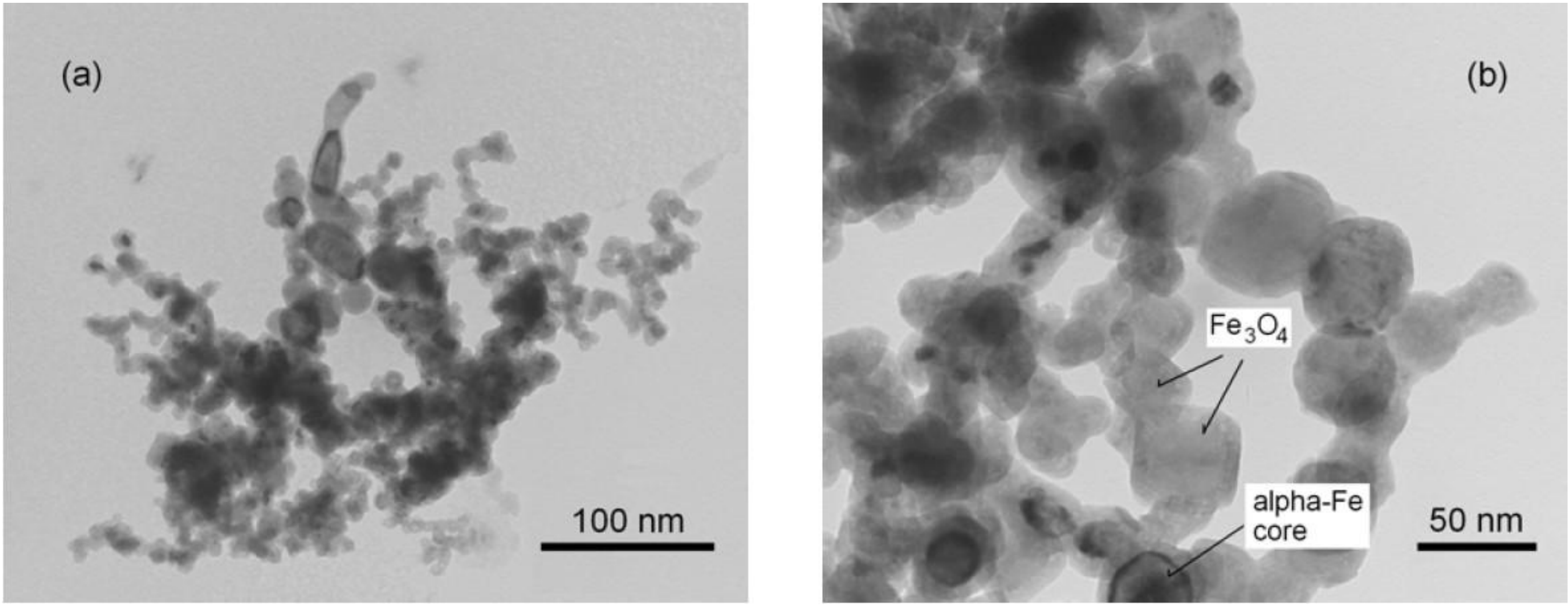


Iron cloud

$Fe(CO)_5$



Plasma synthesis of nanoparticles – iron oxides



Sample LP16 Ar 280 sccm, 500 W, Ar+$Fe(CO)_5$

Dusty plasmas

- Low-temperature plasmas containing charged nano or macroparticles.
- They are also called complex or colloidal plasmas. They exhibit collective behavior with strongly coupled particles.
- Dusty plasmas is that the particles can arrange in ordered crystal-like structures, so-called plasma crystals (1994).
- In the plasma, the particles acquire high negative charges of hundreds or thousands of elementary charges due to the inflow of electrons and ions. Then, the Coulomb interaction of neighboring particles by far exceeds their thermal energy: the system is strongly coupled. The spatial and time scales of the particle motion allow easy observation by video microscopy. Weak frictional damping ensures that the dynamics and kinetics of individual particles become observable. Thus, dusty plasmas enable the investigation of crystal structure, solid and liquid plasmas, phase transitions, waves and many more phenomena on the kinetic particle level.
- Dusty plasmas can be find in astrophysics, polymer plasma synthesis or semiconductor industry, where dust removal is essential for functionality of transistors or solar cells.

Dusty plasmas

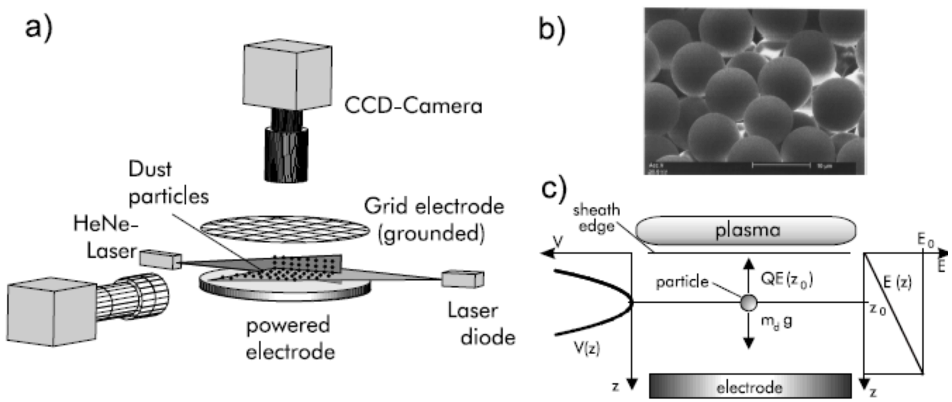
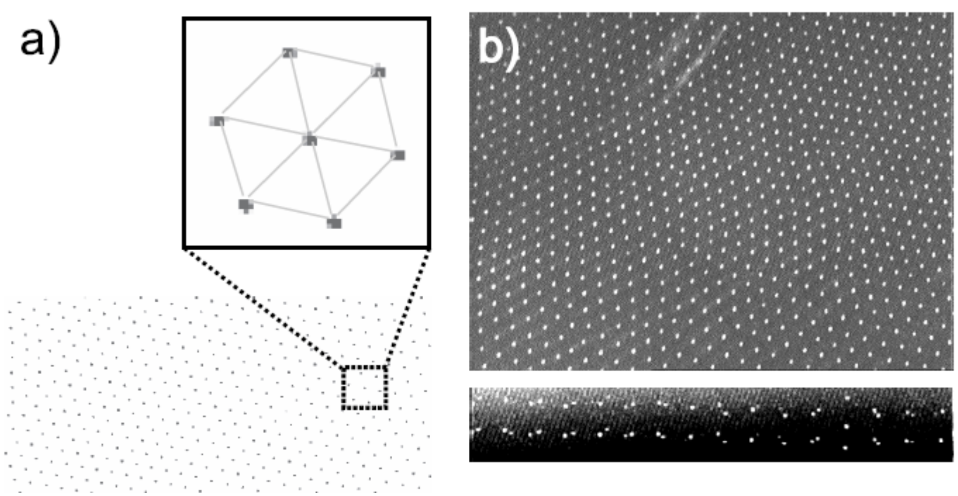
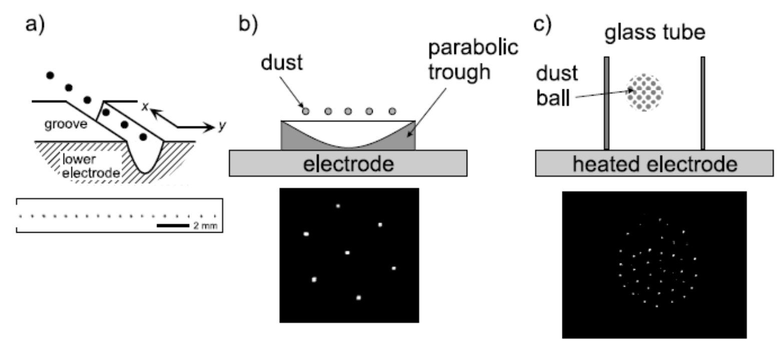


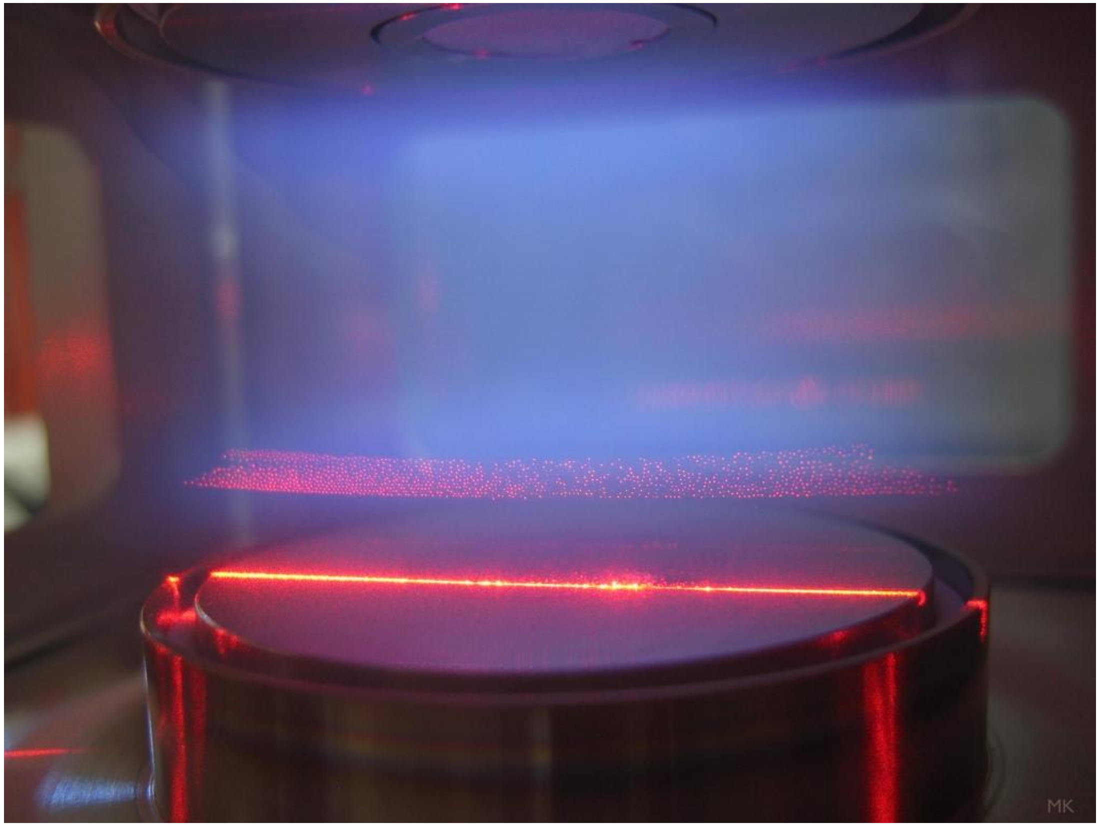
Figure 6.5: a) Scheme of the experimental setup in a typical experiment on complex plasmas. The particles are illuminated by vertical and horizontal laser sheets. The particle motion is recorded from top and from the side with video cameras. b) Electron micrograph of the melamine-formaldehyde (MF) particles typically used in the experiments. c) Trapping of the particles in the sheath of an rf discharge. See text for details.

Table 1. Forces acting on particle.

Force	Expression	Size dependence
Electrostatic force	$\boldsymbol{F}_q = Q\boldsymbol{E}$	d^1
Ion drag force	$\boldsymbol{F}_\mathrm{i} = n_\mathrm{i} m_\mathrm{i} \boldsymbol{u}_\mathrm{i} (u_\mathrm{i}^2 + v_{it}^2)^{1/2} \pi (b_\mathrm{c}^2 + 4 b_{90}^2 \Lambda)$	d^2
Gravity	$\boldsymbol{F}_\mathrm{g} = m_\mathrm{g} \boldsymbol{g}$	d^3
Gas viscous force	$\boldsymbol{F}_n = n_\mathrm{n} m_\mathrm{n} u_\mathrm{n}^2 (\boldsymbol{u}_\mathrm{n}/u_\mathrm{n})(\pi d^2/4)$	d^2
Thermophoretic force	$\boldsymbol{F}_T = -p\lambda d^2 (\nabla T_n / T_n)$	d^2
Diffusion force	$\boldsymbol{F}_\mathrm{d} = -\kappa T_\mathrm{p} \nabla n_\mathrm{p}$	—







http://www2011.mpe.mpg.de/pke/index_e.html

Dusty plasmas

- Dusty plasmas are at least three component plasmas (electrons, ions and dust). In this sense, dusty plasmas are comparable to negative ion plasmas.
- The typical charge on the charge carriers (dust) are of the order of 10 000 elementary charges which leads to strong coupling.
- The dust charge is variable and depends on the local plasma parameters. Thus, the charge becomes a dynamic variable.
- The dust mass is by orders of magnitudes larger than that of electrons and ions. Thus the dominant time scale is that of the dust plasma frequency ω_{pd} which is by orders of magnitude smaller than that of electrons and ions leading to convenient time scales for the observation of dynamic processes.
- The slow time scales allow that electrons and ions contribute to shielding which should results in different shielding scales.
- The dust size is not negligibly small leading to surface phenomena and forces which are unimportant in “usual” plasmas.
- Fundamentals of Dusty Plasmas Goree_LANL_PPSS07.pdf
- Dusty plasmas , V E Fortov, A G Khrapak, S A Khrapak, V I Molotkov, O F Petrov, Physics - Uspekhi 47 (5) 447 ± 492 (2004).