Plasma Sources for Nanomaterials and Nanodevices

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Self-Organization Subpanel, August 12, 2015

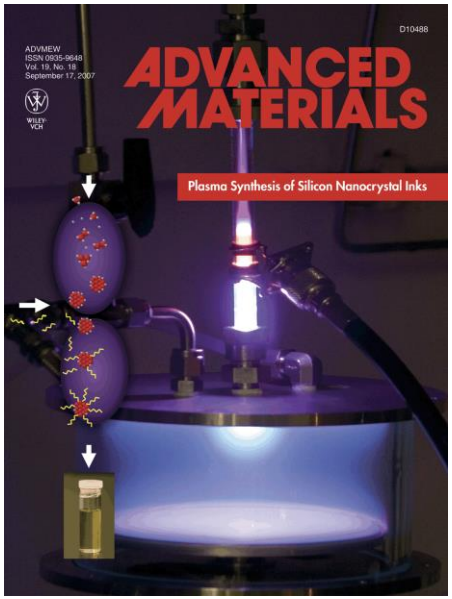
Outline

- **Plasma-driven nucleation of nanoparticles (Sankaran).**
- **Plasma-nanoparticle interactions (Sankaran).**
- **Plasma-based nanosynthesis methods (Raitses).**
- **Self-organization in nanosynthesis plasmas (Raitses).**
- **What are frontiers?**

Role of the plasma in nanomaterial synthesis.

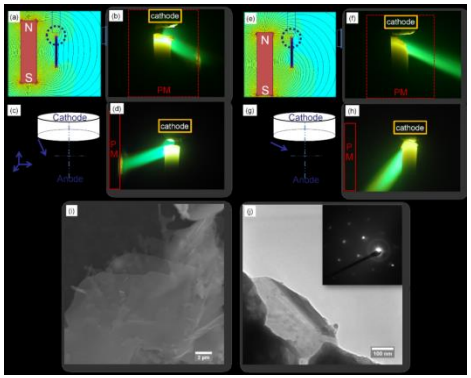
Recent Advances in Plasma Synthesis of Nanomaterials

- **High-purity, high-temperature materials, non-equilibrium chemistry**



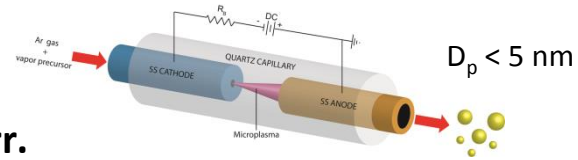
Low pressure plasma synthesis of silicon nanoparticles.

Mangolini and Kortshagen, Advanced Materials, 2007



Magnetically controlled arc synthesis of graphene at 500 Torr.

Keidar's group, Nanoscale, 2010



D_p < 5 nm

1 atm, room T

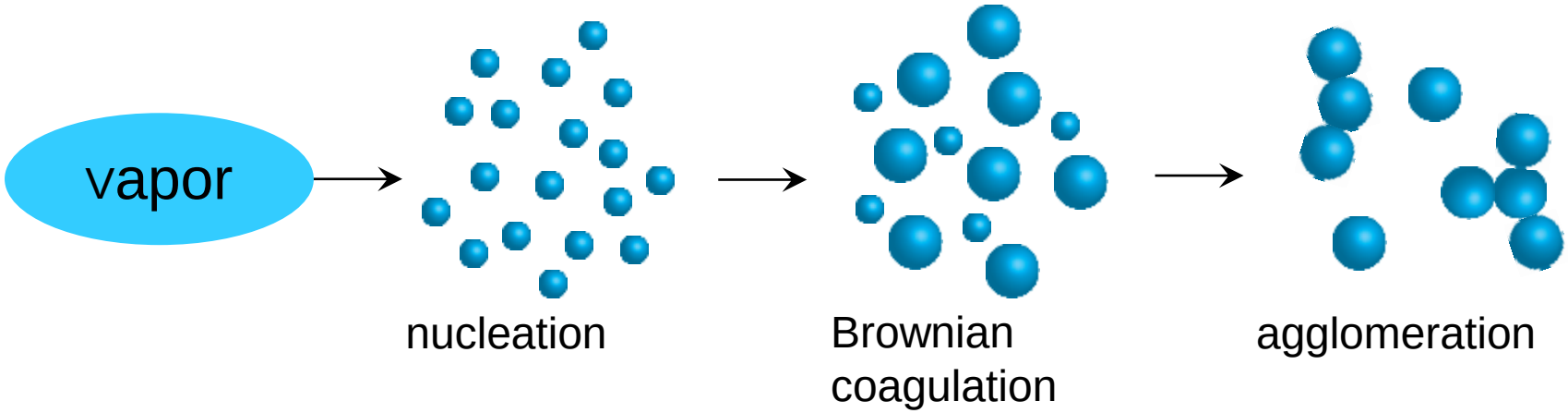
Microplasma synthesis of nanodiamonds at 1 atm. pressure

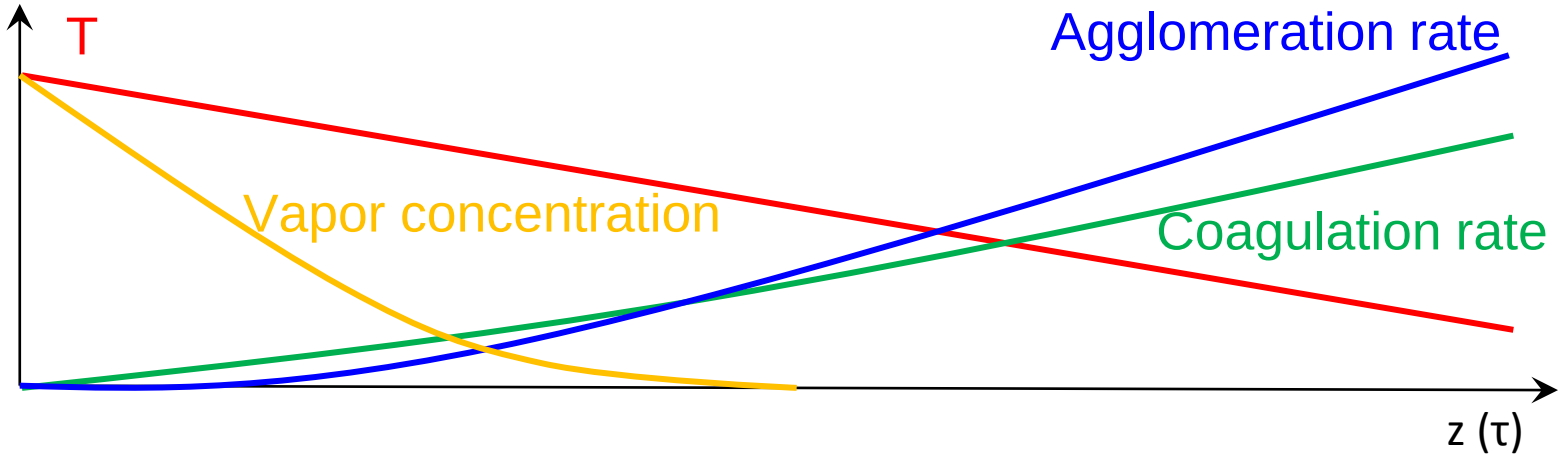
Sankaran's group, Nature Comm. 2013

Plasma-Based Nanomaterial Synthesis – Status Quo

- **Low-pressure methods use non-equilibrium plasma (T_e ~1-10 eV, $T_{i,a}$ < 0.1 eV) to support non-thermal synthesis processes:**
    - **Plasma kinetics and gas-phase chemistry are important, but not well understood, which explains the absence of validated predictive modeling capabilities.**
- **Atmospheric pressure methods use higher-density, non-thermal and thermal plasmas to achieve higher synthesis yield at lower cost as compared to low-pressure plasma methods.**
    - **Role of the plasma in nucleation and growth of nanoparticles *is not* the focus of experimental and theoretical research, and not understood so far.**
    - **Absence of reliable quantitative data on plasma and nanoparticles in synthesis region.**
    - **A critical issue – poor control of synthesis and selectivity.**

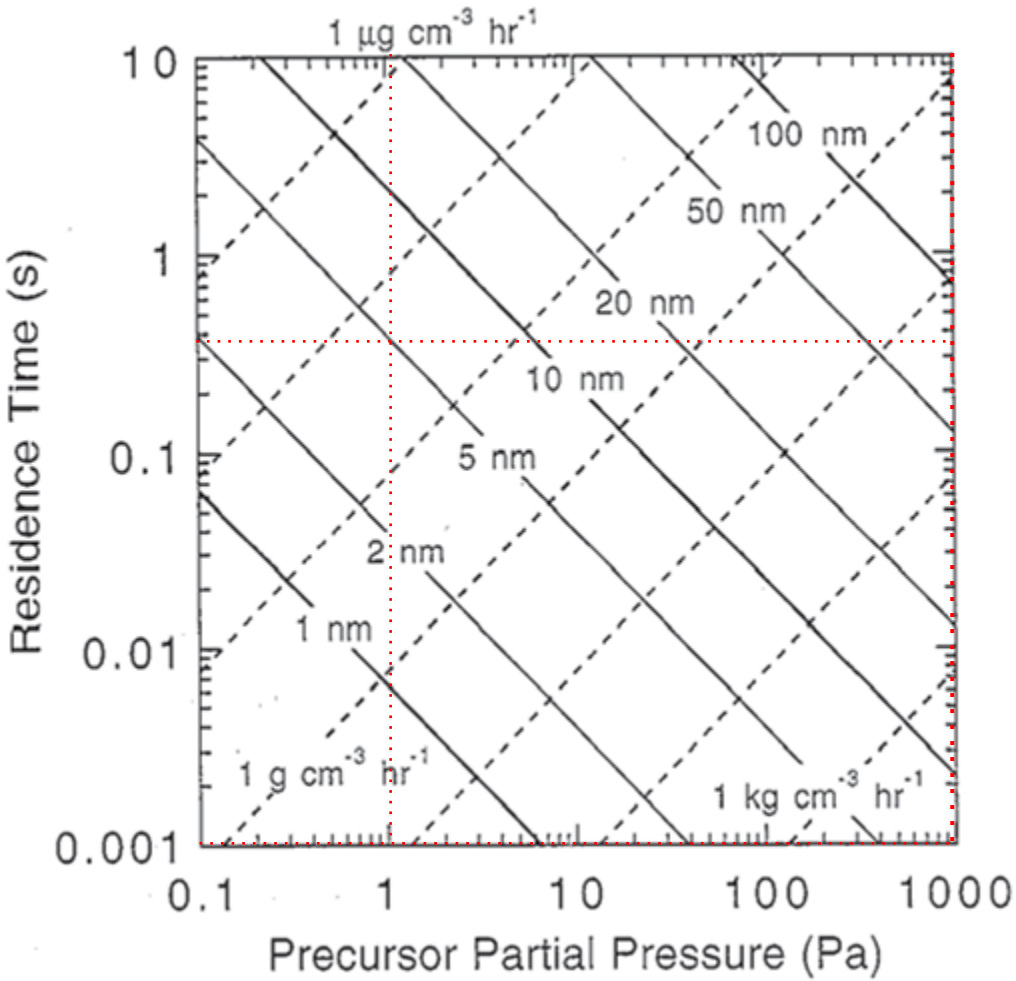
Homogeneous Nucleation of Nanoparticles





Importance of Residence Time and Precursor Concentration

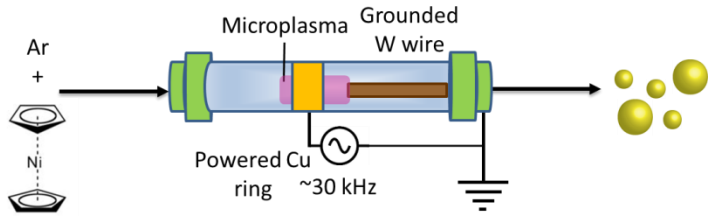
Isopleths of NP growth by coagulation

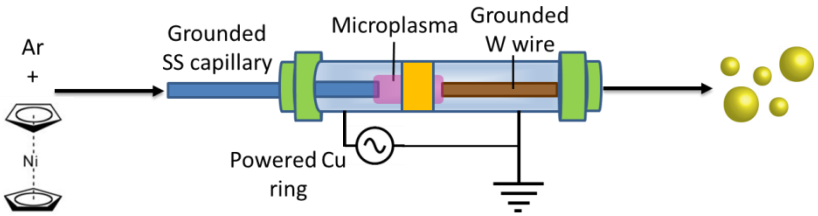


- 1% at 1 Torr is ~1 Pa
- Residence time to produce 5 nm particles must be <~0.5 s
- 1% at atmospheric pressure is ~1000 Pa, residence time must be <1 ms!
- Assumes the same reactor volume and 100% efficiency at all conditions

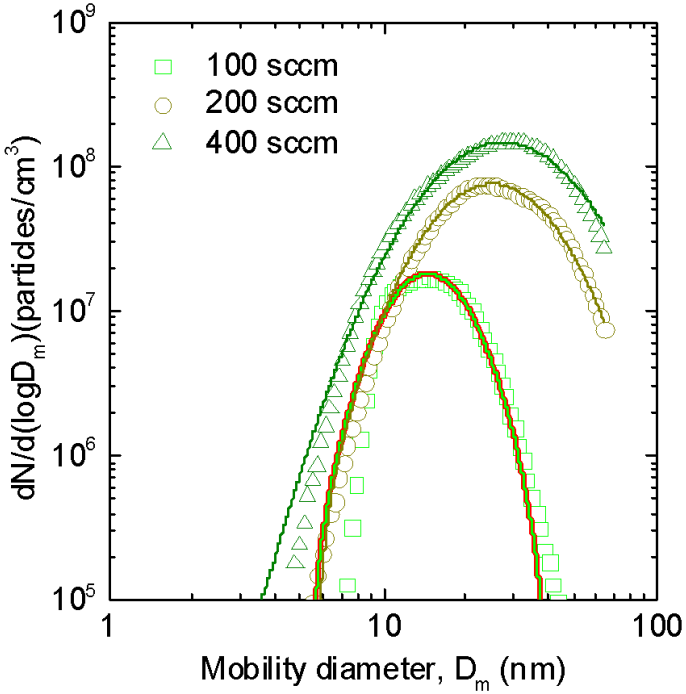
Flagan *et al.*, *Mat. Sci. Eng. A* **204**, 113 (1995).

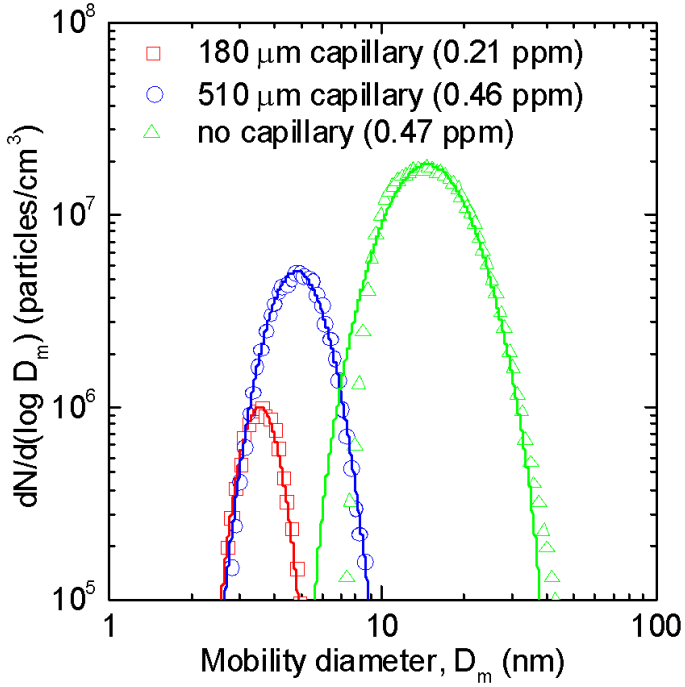
Example of Result from Laboratory





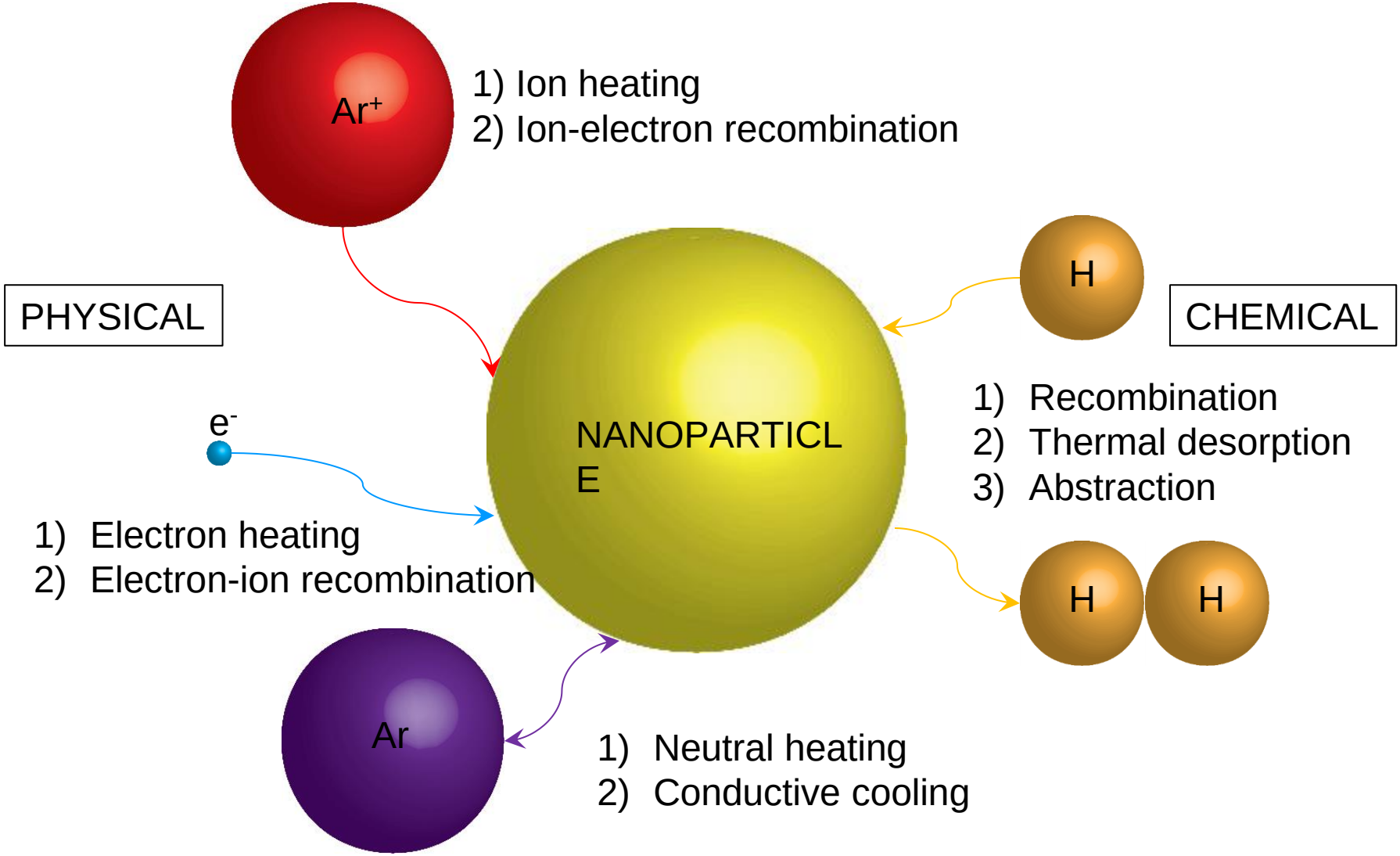
Downstream measurements with aerosol instrument:





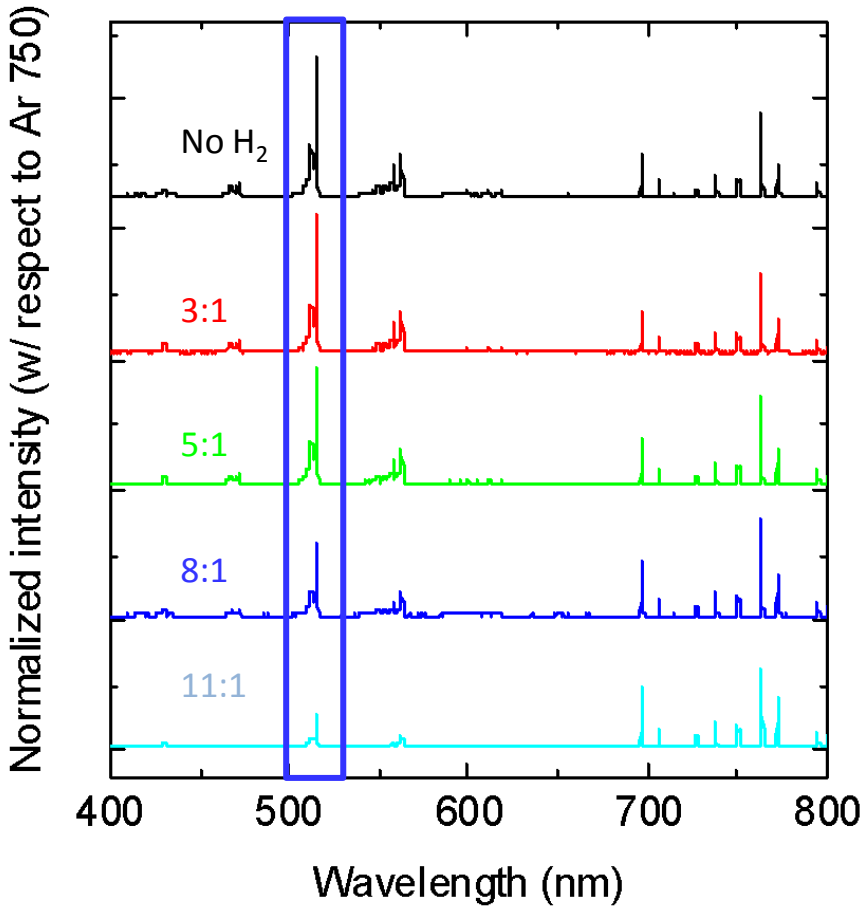
Flow rate alone doesn't control particle nucleation/growth. There are coupled effects involving plasma properties.

Plasma-Nanoparticle Interactions: Heating and Reactivity

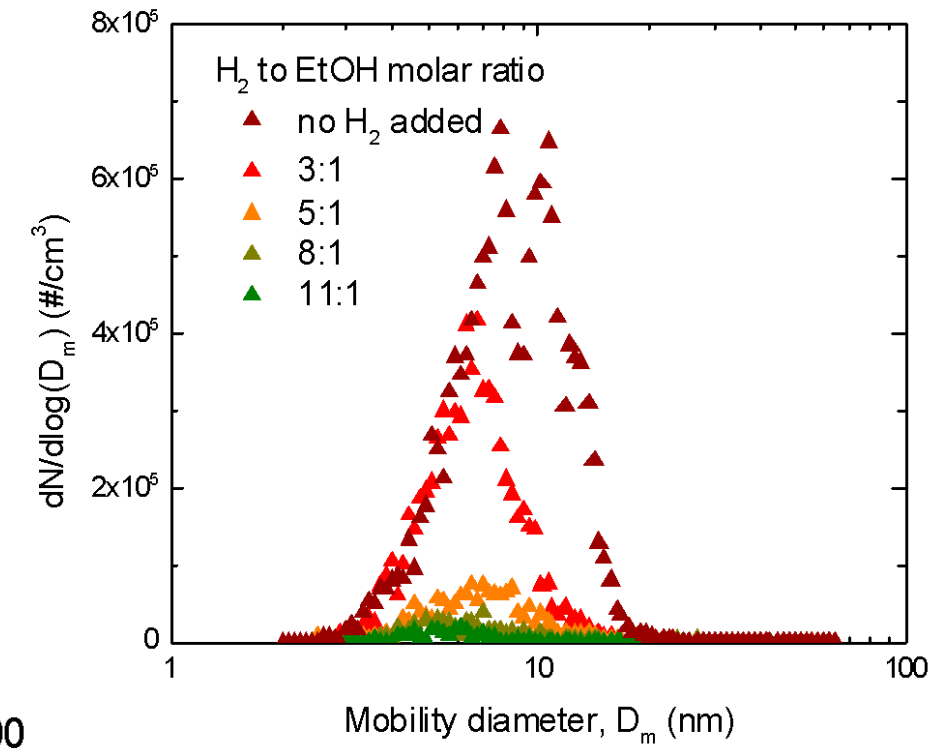


Example of Result from Laboratory

OES



Aerosol measurements



Carbon particle formation is suppressed by H_2 gas (atomic hydrogen).

Atmospheric Pressure Plasmas for Nanosynthesis – Highly Complex Plasmas

- **Partially ionized (N_i~ 10^{12} -10^{15} cm^{-3}), highly collisional plasma.**

  Collisions with neutral atoms are dominant.

- **Highly stratified plasmas with large density and temperature gradients, combining regions with nearly equilibrium and non-equilibrium plasmas, T_e ~ 1eV, T_i ~ 0.5 eV, T_a ~ 0.01-0.5 eV.**

- **Flowing plasma, with free or forced convection.**

- **Charged nanoparticles, 10^7 -10^{11} cm^{-3} , nucleate and growth from atomic clusters to 100's nm nanostructures.**

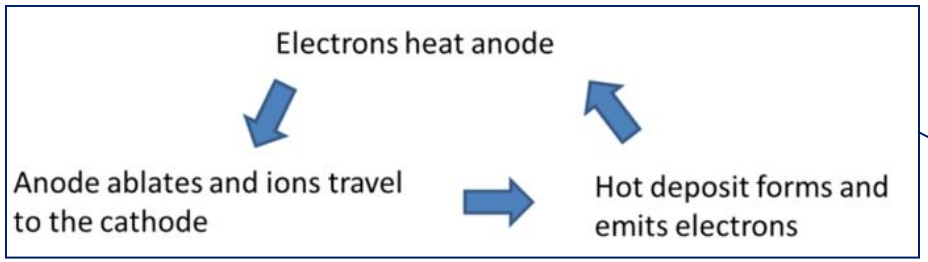
  Charging is weaker than in low pressure plasmas - smaller T_e and thermionic electron emission.

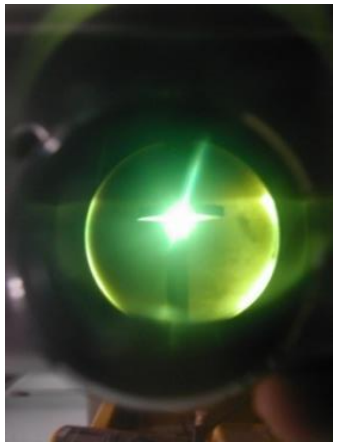
- **A strong coupling between plasma and materials processes:**

  Plasma affects the whole chain of nanosynthesis processes and resulting nanoparticles, while nanoparticles affect the plasma: Plasma losses and cooling (including radiation), energy distribution etc.

Self-Organization of Plasma and Nanosynthesis Processes in Atmospheric Pressure Carbon Arc Discharge

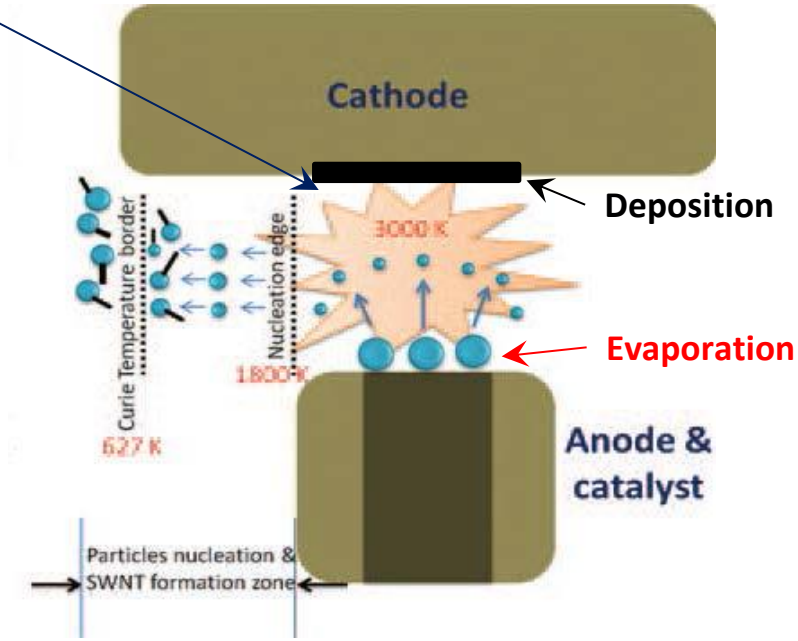
- Evaporation of graphite anode provides a supply of carbon atoms and catalyst atoms, which are ionized in the arc plasma.
- Plasma and evaporation/deposition processes are self-organized to sustain the arc discharge:





Arc core:

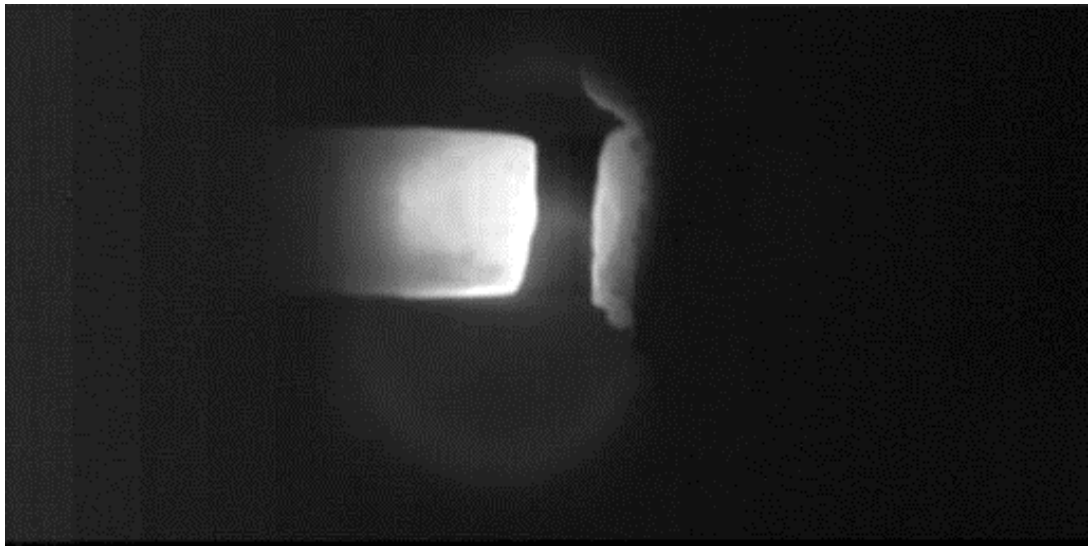
$N_e \sim 10^{15}$ cm^{-3}
$T_e \sim 1$ eV,
$T_i \sim 0.5$ eV
$T_a \sim 0.1$-0.3 eV



- <u>Hypothesis # 1:</u> Nucleation and growth of nanotubes occur in a colder non-equilibrium plasma region outside the hot core of the arc.
- <u>Hypothesis # 2:</u> Plasma density and residence time of nano particles determines the size of the synthesized nanotubes.

Convection and electrode processes affect energy balance and residence time!

Discharge Instabilities May Affect Self-Organization



Imaging of DC carbon arc discharge at 500 torr He 20 V and 70 A

- Characteristic frequency ~ 20-50 Hz.
- Mechanism – not well understood, but could be convective or near-electrodes?
- CNT synthesis time ~ 20-30 msec.
- Arc oscillations can be responsible for poor selectivity of arc nanosynthesis.

Frontiers Plasma Science Challenges

- **Collisional plasma with nanoparticles is hard to diagnose:**
  - **Probes are invasive, contaminated with nanoparticles, no solid probe theory for measurements in highly collisional atmospheric pressure plasmas.**
  - **OES and laser diagnostics are obscured by nanoparticles, laser can be invasive due to effect on nanoparticles (sublimation, charging, disintegration).**
  - **Standard laser scattering methods will produce a combined signal, which includes contributions of Thomson scattering on free electrons and Rayleigh scattering on neutral components.**
- **Development of advanced experimental methods and theory of laser-based diagnostics of such complex plasmas is required.**
- **Modeling needs to be multi-component, multi-scale, multi-phase, possibly MHD, to capture all physics of nanosynthesis plasma.**

What Are Frontiers of Plasma Science?

<u>The main frontier</u>: ***Role of the plasma and plasma characteristics in nanomaterial synthesis.***

<u>Plasma science questions:</u>

1. **What are the plasma characteristics where nucleation and growth of nanoparticles occur? What are the physical mechanisms, governing these plasma characteristics?**
2. **How plasma and materials processes are self-organized? How plasma processes (e.g. convection, instabilities) can affect and control selectivity?**
3. **What are the effects of mutual interactions of nanoparticles with plasma (charging, radiation emission and absorption, heating) on nucleation and growth of nanoparticles and their transport in plasma (agglomeration, disintegration, separation etc.)?**
4. **Can the presence of plasma cause reduced synthesis temperature compared to chemical methods- low temperature synthesis?**
5. **What are suitable diagnostic tools for measurements in plasmas with nanoparticles?**
6. **What plasma simulation methods can predict plasma characteristics with nanoparticles?**