Plasma Synthesis of Nanomaterials: A joint challenge of plasma and materials sciences

Yevgeny Raitses

Princeton Plasma Physics Laboratory

Princeton University

yraitses@pppl.gov

SULI, PPPL

August 17, 2016

PPPL PRINCETON PLASMA PHYSICS LABORATORY

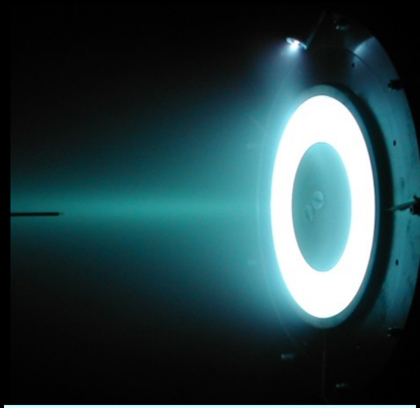
U.S. DEPARTMENT OF ENERGY | Office of Science

PRINCETON UNIVERSITY

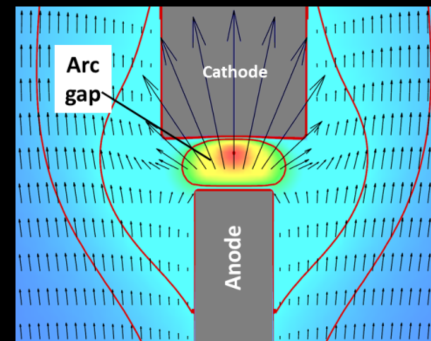
Low Temperature Plasma (LTP) Research at PPPL

Large thruster facility

Hall thrusters

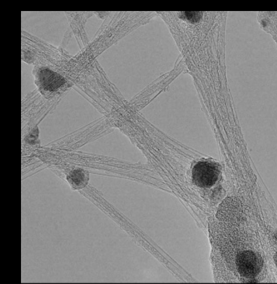


CFD simulations of atmospheric plasmas

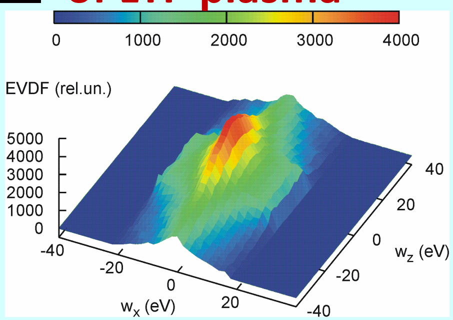


Plasma-based nanosynthesis

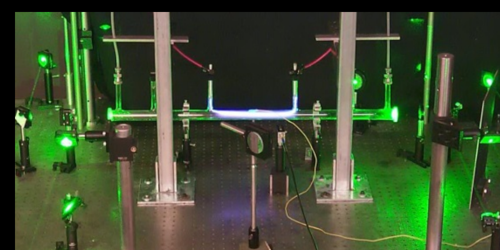
Plasma-produced nanomaterials



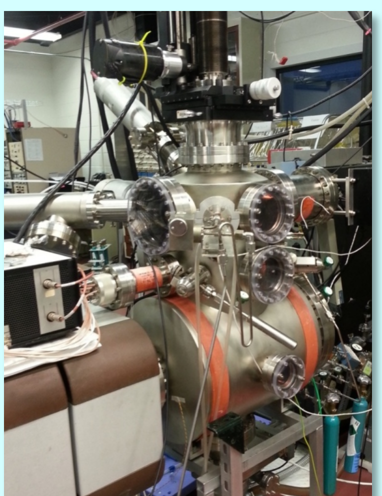
PIC simulations of LTP plasma



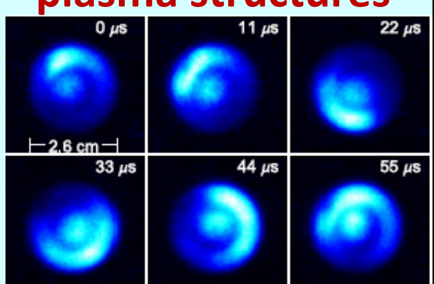
In-situ laser diagnostics of nanoparticles



Secondary electron emission from plasma-facing wall materials



Coherent ExB plasma structures

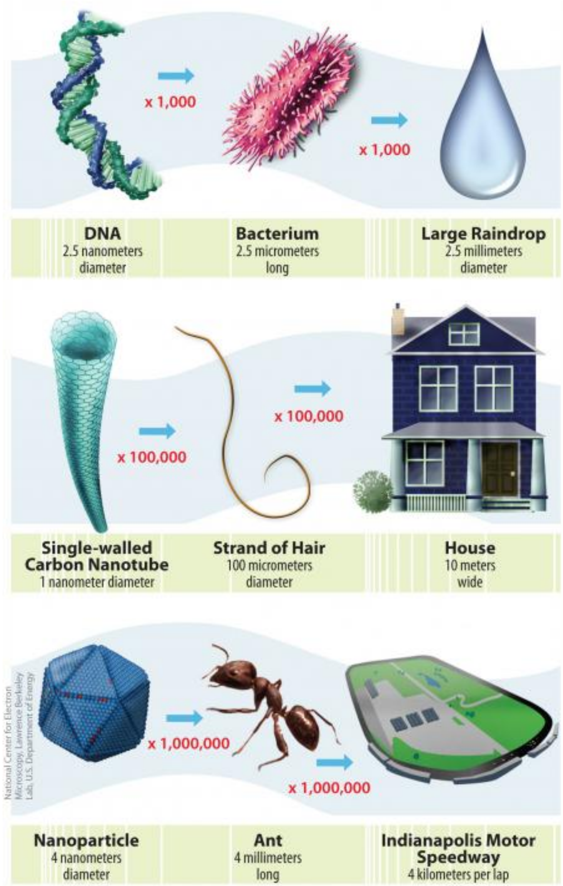


Reactive microplasmas for plasma catalysis

Plasma-based functionalization of nanomaterials

What’s nanotechnology?

- **Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications.**



- **Nanoparticles are effectively a bridge between bulk materials and atomic or molecular structures.**

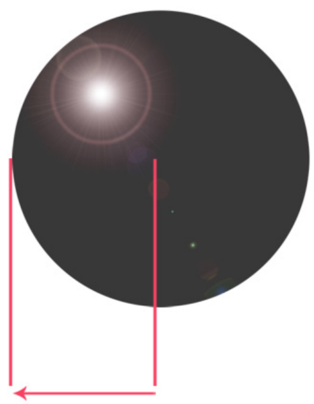
- **A bulk material should have constant physical properties regardless of its size.**

- **At nanoscale, properties such as melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity change as a function of the size of the particle.**

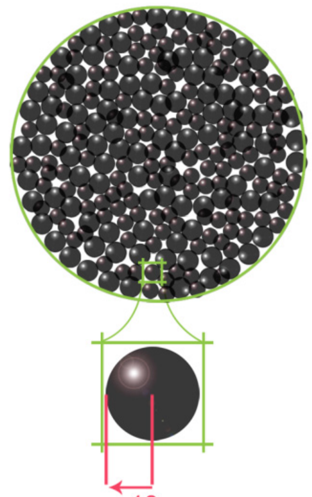
National Nanotechnology Initiative
www.nano.gov

Nanoscale dependent effects

Macro particle

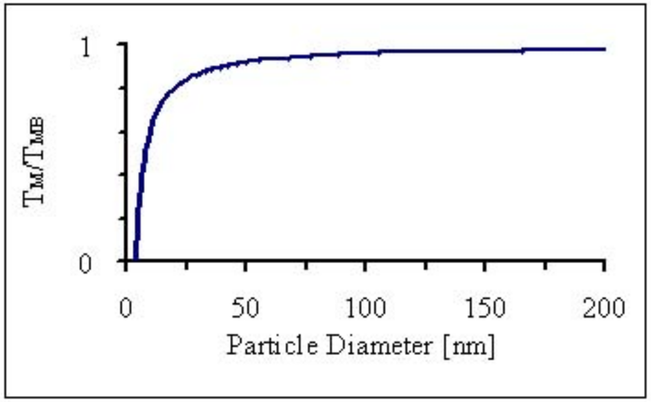


Macro sphere filled with nanoparticles



- **Increase of the surface-volume ratio, gives an increase in the total surface area.**
  - **Greater effects of surface atoms on phys. & chem. properties**

Example: Melting temperature depression for gold nanoparticles:



$$E = E_B\left(1 - \frac{d_{atom}}{D_{nano}}\right)$$

E_b is the bulk material cohesive energy

- **Increase of chemical and electrostatic potential gradients.**
- **Reduction of scattering events – inelastic mean free path is comparable with the size of the nanoparticle.**
- **Quantum effects - the energy bands are replaced by discreet energy states**

Current and potential applications of nanomaterials (not including bio-med)

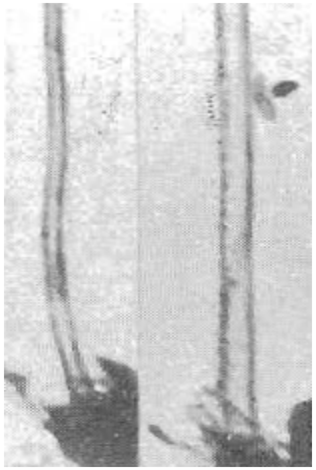
	Large-volume applications	Limited-volume applications	Key attributes
Present	Sporting goods such as golf shafts, tennis rackets, baseball bats etc., battery electrode additives, plastics additives and masterbatches, fuel line systems	Battery electrodes, boat hulls & decks, wind turbine blades, prepregs, scanning probe tips, sensors, catheters, membrane filters, flat panel displays, textiles, printing & packaging	Excellent mechanical and electrical conductivity properties, compatibility, high surface area (~1000 m^2/g), excellent chemical stability in acidic environments, distinguished optoelectronic properties, insensitivity to electromigration, excellent thermal conductivities and semiconducting properties
Near term (less than five years)	Supercapacitor electrodes, transparent conducting films, field emission displays, LCDs and OLED-based displays, fuel cell electrodes, inks for printing, adhesives	Electromechanical memory device, hydrogen-storage electrodes, biosensors, multitip array X-ray sources, probe array test systems, brush contacts, thermal-management systems	
Long term (beyond five years)	Power transmission cables, structural composites applications for aerospace and automobile, photovoltaic devices	Field-Effect Transistors (FET), interconnects, flexible electronics, drug-delivery systems	

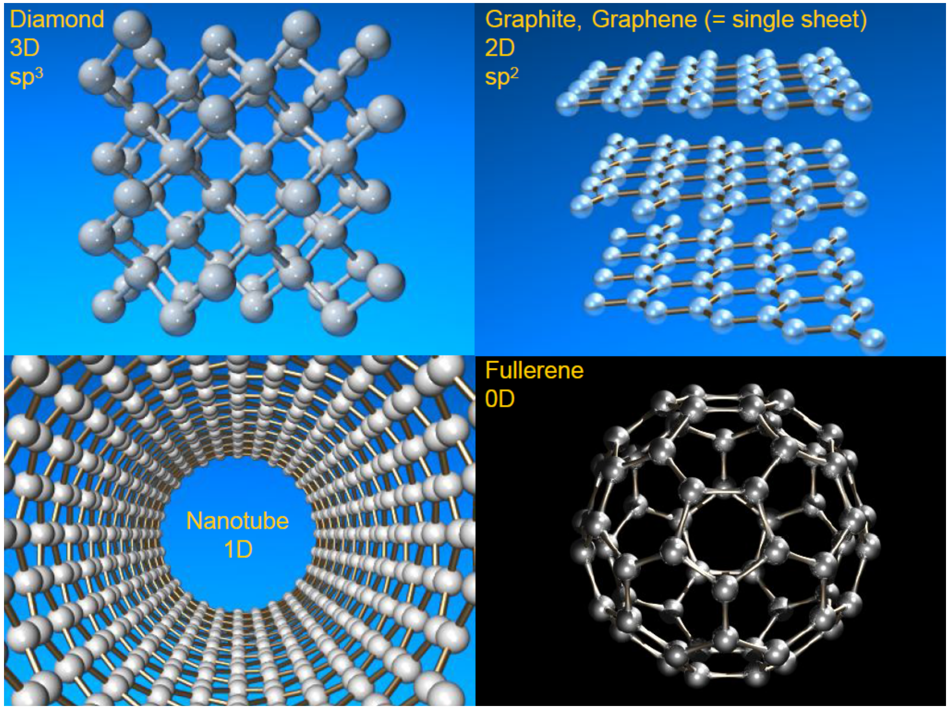
Nanowerk, August 2011

Examples of carbon nanostructures

- **Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).**
- **Conduction electrons free to move along the non-confined dimension/s.**

Single, double, multi-wall **nanotubes**
1-10 nm diam.



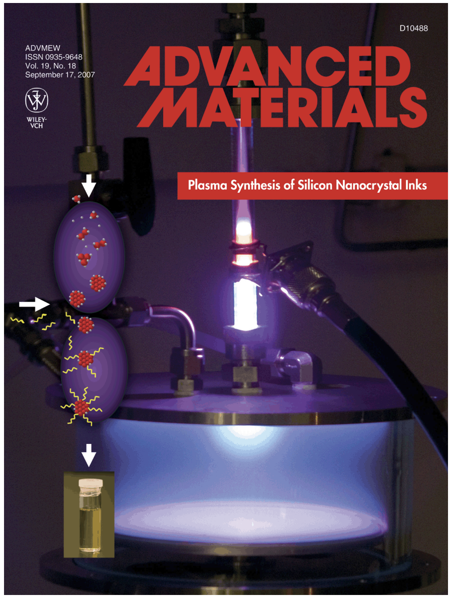


Buckyballs, C60, C70
~ 1 nm

- **Buckyballs – in 1985 by Kroto, Smalley, and Curl, Noble prize in 1996.**
- **Carbon nanotubes – in 1990 by S. Iijima.**
- **Discovered using carbon arc discharges.**

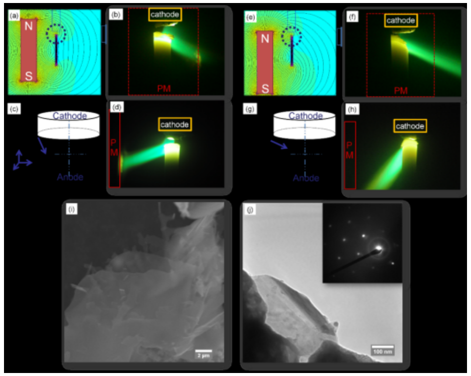
Plasma-based synthesis of nanomaterials

- **Many existing methods of nanosynthesis use low pressure (10^{-3}-10^{1} torr) and higher pressure (≤ 1 atm) plasmas to produce a broad range of nanomaterials with various nanostructures:**



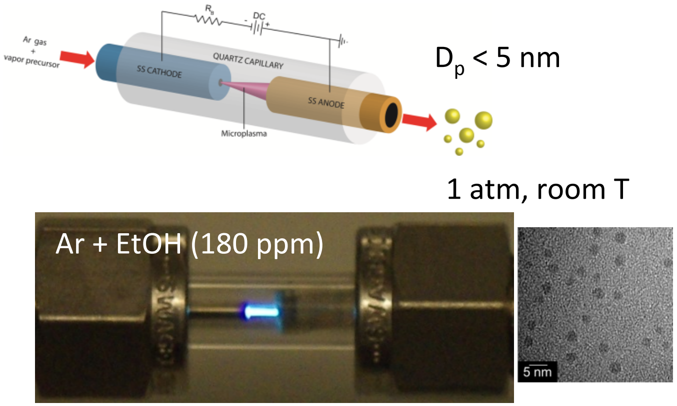
Low pressure plasma synthesis of silicon nanoparticles.

Mangolini and Kortshagen, Advanced Materials 2007, Univ. of Minnesota



Magnetic arc synthesis of graphene at 500 torr.

Volotskova et al, Nanoscale, 2010
GWU-PPPL-CSIRO



Microplasma synthesis of nano diamonds at 1 atm. pressure

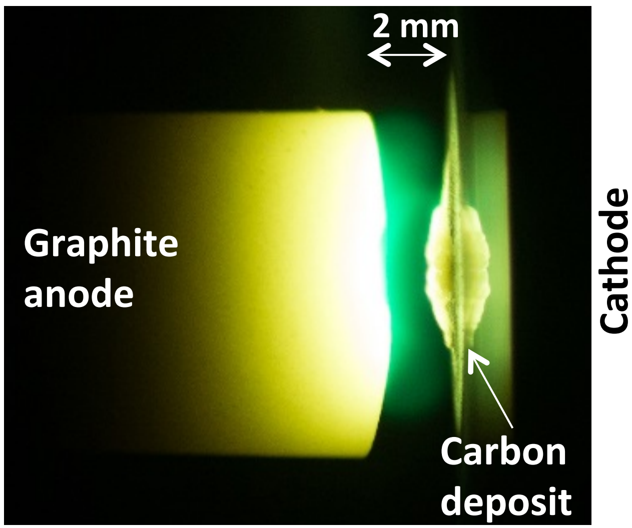
A. Kumar et al., Nature Comm. 2013
Case Western Reserve Univ.

Grand challenges of plasma-based nanosynthesis

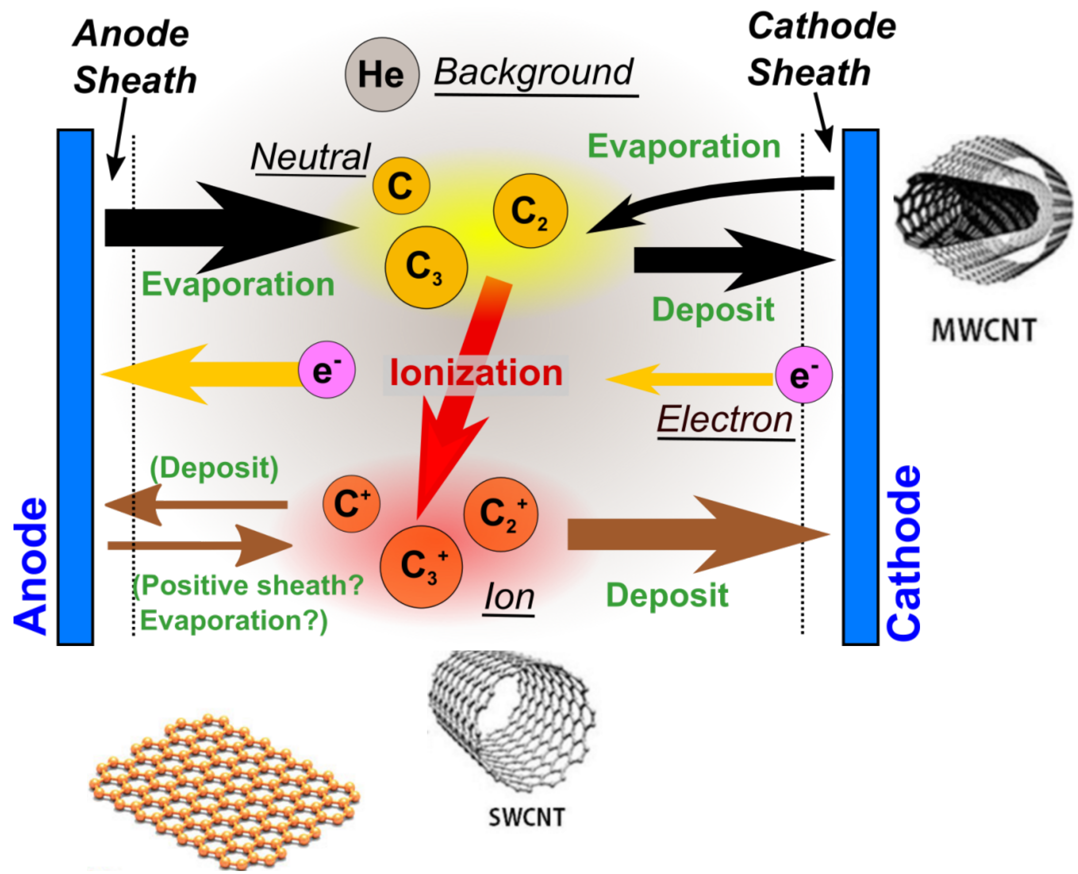
- **Low-pressure methods use non-equilibrium plasma (T_e ~1-10 eV, $T_{i,a}$ < 0.1 eV) to support non-thermal synthesis processes:**
  - **Plasma kinetics and gas-phase chemistry are important, but not well understood, which explains the absence of validated predictive modeling capabilities.**
- **Atmospheric 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 poorly characterized and not understood.**
  - **A critical issue – poor control of synthesis processes.**
- **Fundamental research of plasma synthesis is needed to address these challenges.**

Basic plasma and synthesis processes in the arc

- A versatile and extensively studied method of vaporization nanosynthesis
- Good for fundamental synthesis studies– different nanostructures synthesized at different arc conditions: C60, MWCNT, SWNT, graphene flakes, nanofibers
- Evaporation of the graphite electrode (usually anode) heated by the electric arc provides carbon feedstock to produce plasma and nanomaterials



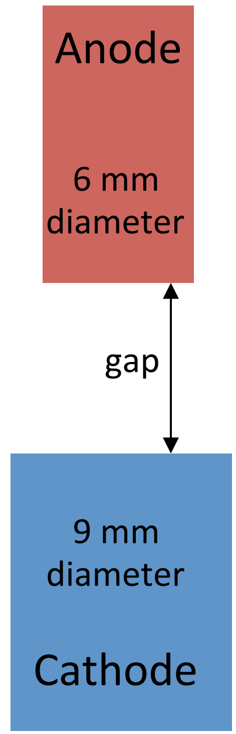
- 1-2 kW input power
- Helium buffer gas
- Atmospheric pressure
- 10 A/cm², 10's of Volts



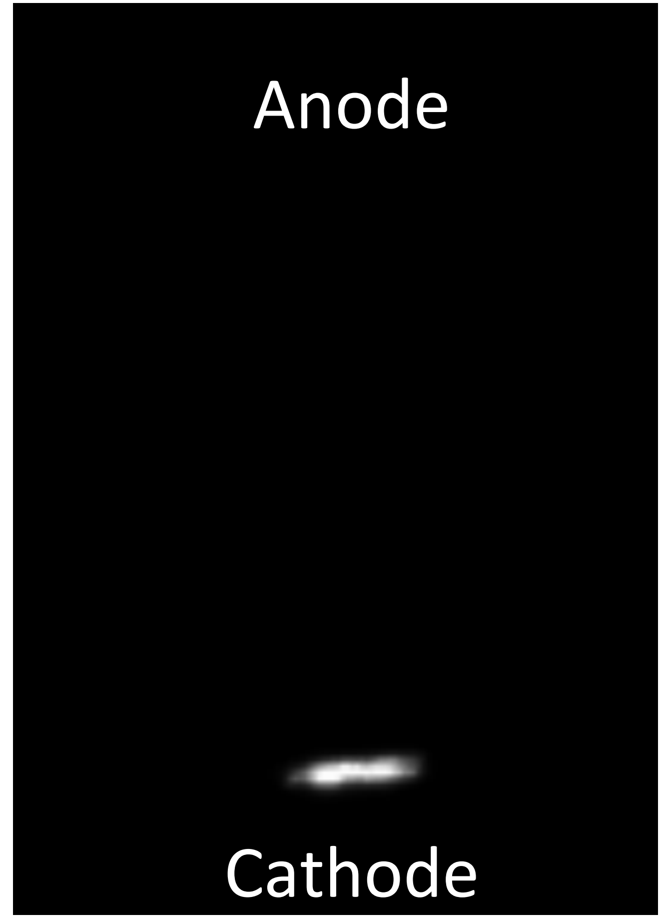
Ablation/deposition processes in the carbon arc

Run time: 1 min

low ablation mode, 23 V 45A



high ablation mode, 24 V 60 A

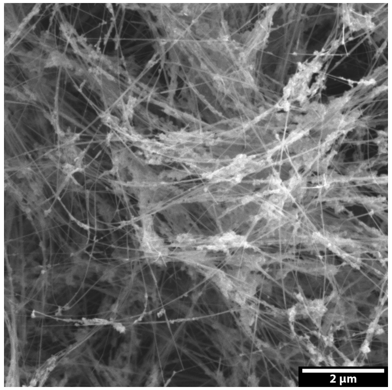


Recordings with filter at 656 nm, playing at 500 fps

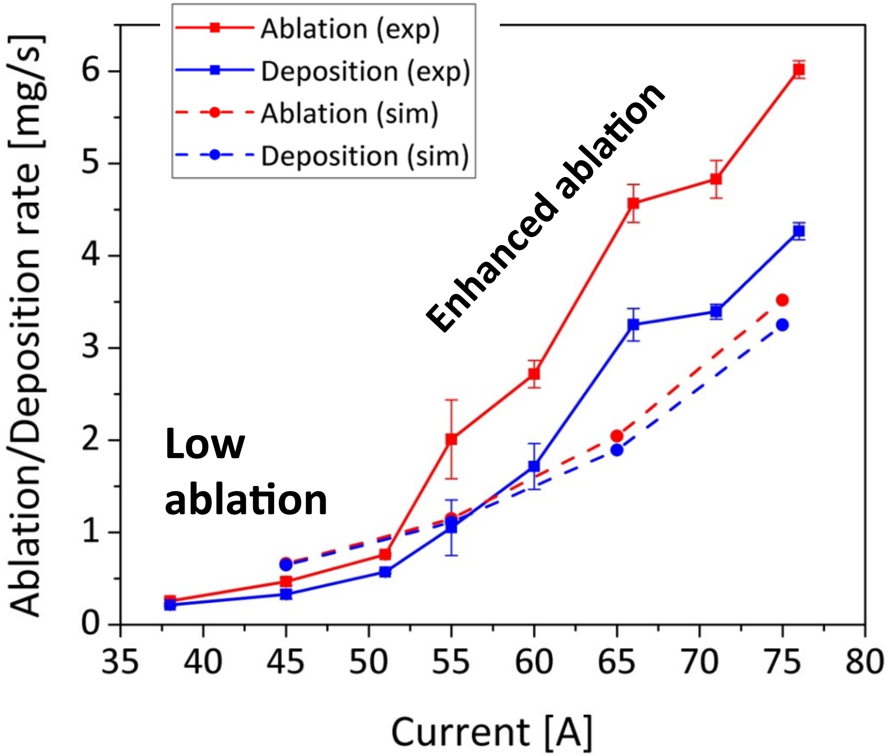
How arc generates carbon for synthesis

- Observed two ablation modes affecting the carbon feedstock for synthesis of nanotubes
- Modeling explains different ablation modes due to differences in the plasma-wall interaction at the anode

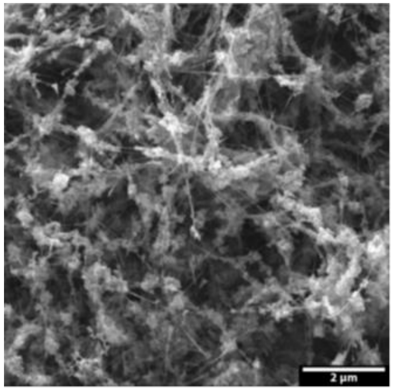
Low ablation



MWCNTs on the deposit



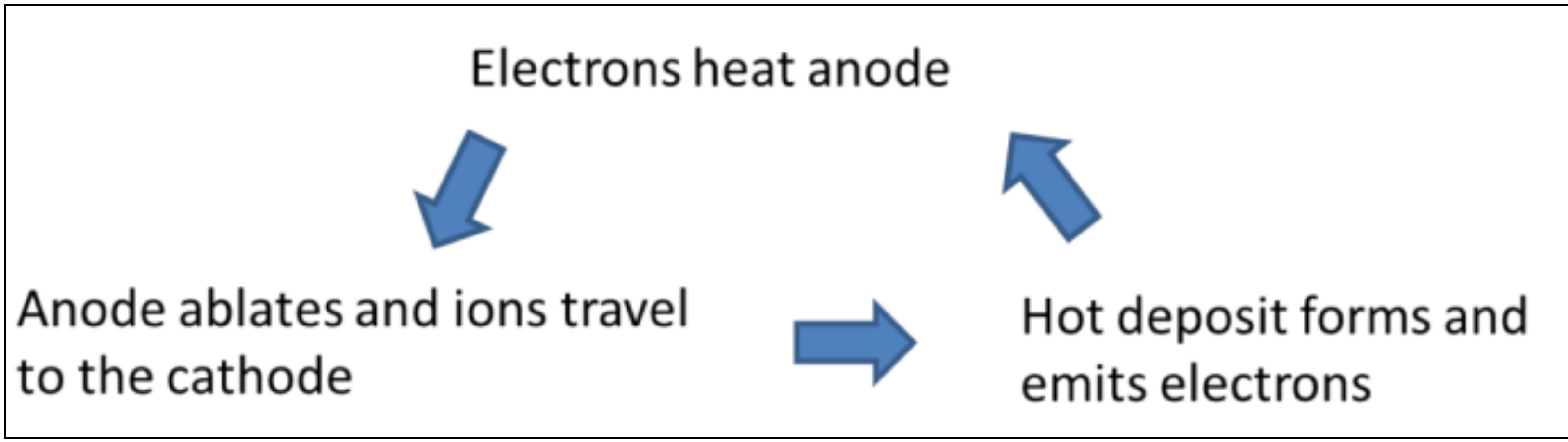
Enhanced ablation



MWCNTs on the deposit

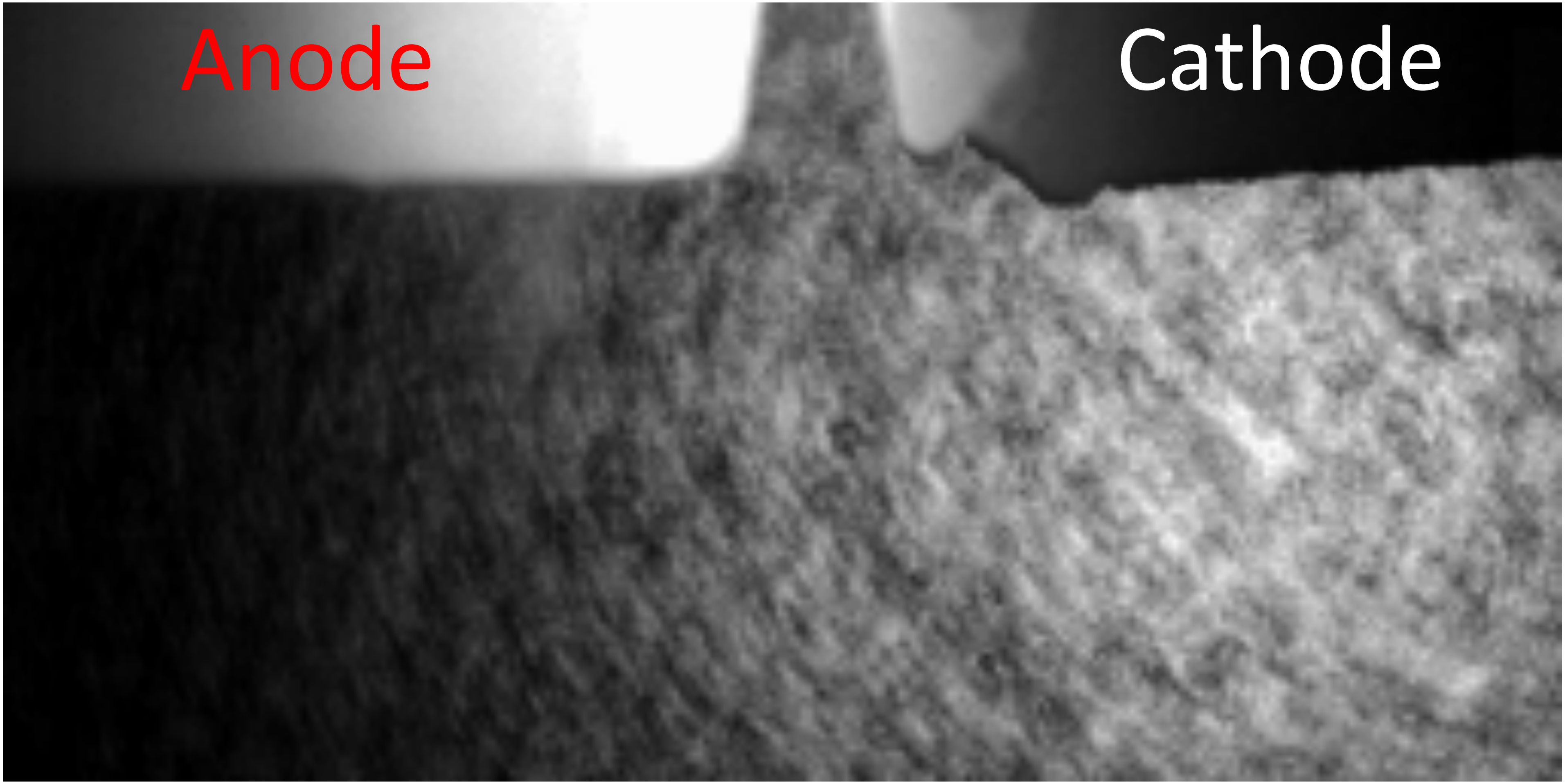
- Correlation between synthesis selectivity, yield, arc geometry and current:
  - Enhanced ablation → Higher C_2 density → Deposition with higher yield
  - Smaller ablation → Reduced carbon flux → Deposition with better selectivity

Self-organization of the carbon arc



Growth of carbon particles in the arc volume

Arc current 65 A, laser backlighting at 632nm, 60 kfps



Nucleation of single-walled carbon nanotubes (SWCNT)

Using *ab-initio* Car-Parrinello Molecular Dynamic simulations (10psec):

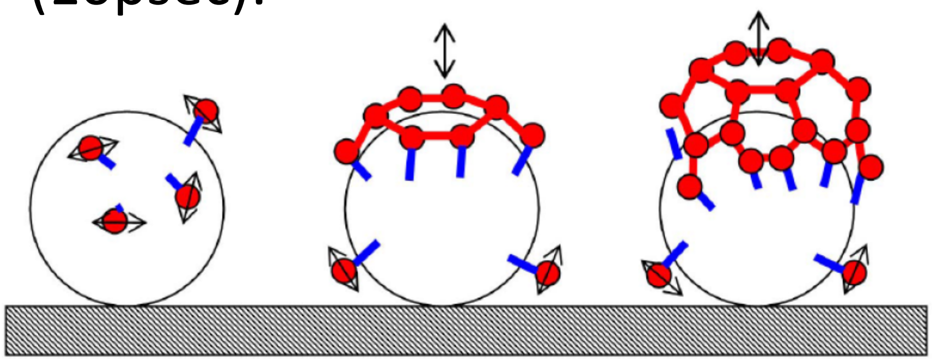


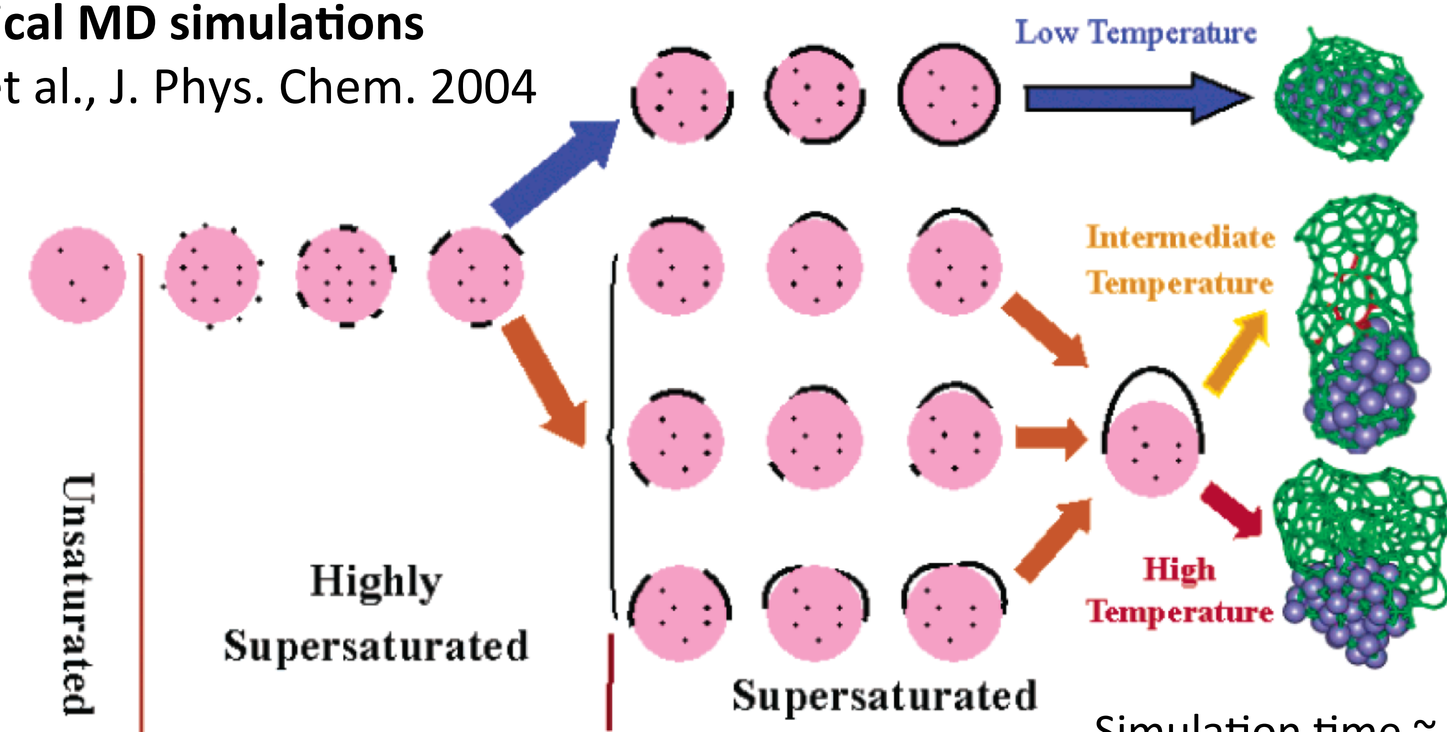
FIG. 3 (color online). Schematic representation of the basic steps of SWCNT growth on a Fe catalyst, as observed in *ab initio* simulations. (a) Diffusion of single C atoms (red spheres) on the surface of the catalyst. (b) Formation of an *sp*2 graphene sheet floating on the catalyst surface with edge atoms covalently bonded to the metal. (c) Root incorporation of diffusing single C atoms (or dimers).

J. –Y. Raty, Phys. Rev. Lett. ***95****, 096103 2005*

- **Carbon soluble transitional metal as catalyst.**
- **Carbon atoms (and dimers) get to into the catalyst nanoparticle.**
- **Once surface saturated with C, it starts to form as graphite sheet with fullerene cap.**
- **More C atoms can be inserted into Metal-C bond so the tube get growing longer.**
- **Role of the catalyst nanoparticle to keep one end of nanotube open to allow its growth and not closed with the cap as the top end of the nanotube.**

Growth of SWCNT

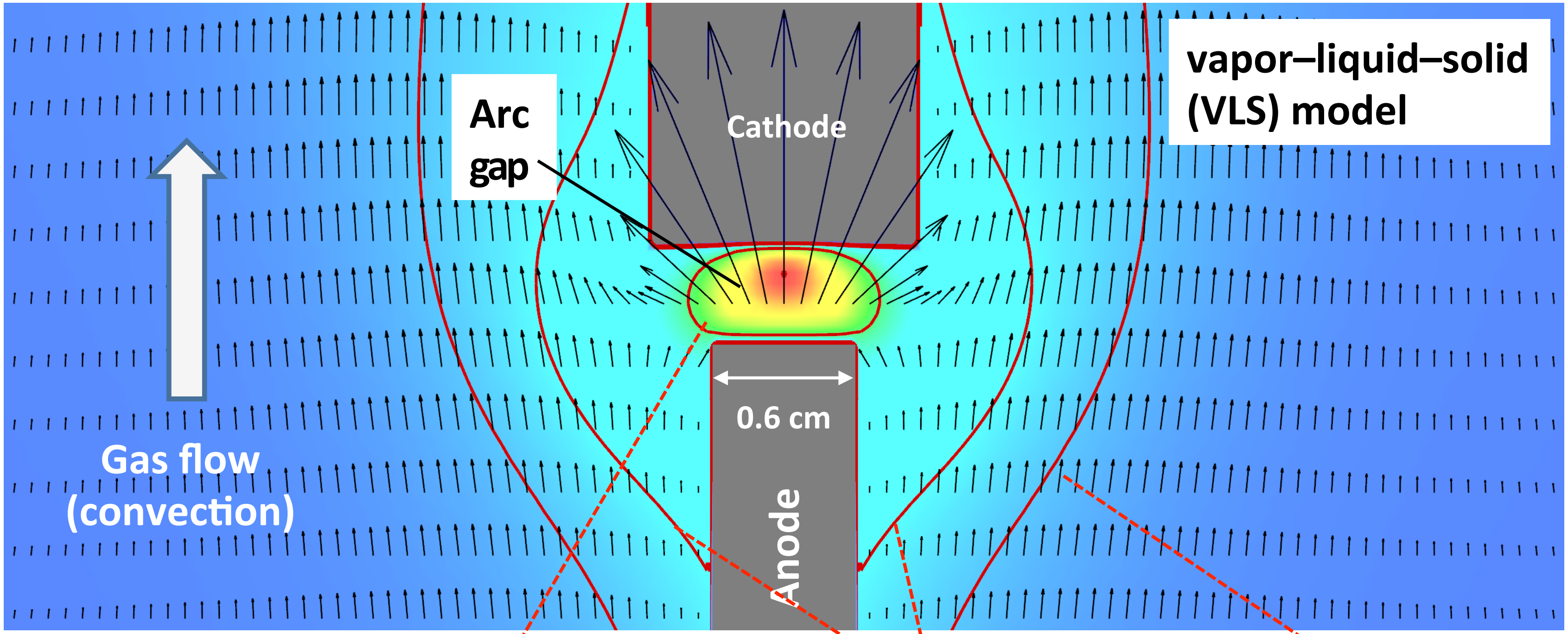
From Classical MD simulations
by F. Ding et al., J. Phys. Chem. 2004



Simulation time ~ 20 nsec

- **SWNT growth at temperatures between 800-1400 K.**
- **At lower temperatures the catalyst surface is encapsulated in a graphene sheet – no SWNT growth.**
- **High temperatures lead to an increased number of defects and a 3D soot-like structure is formed.**

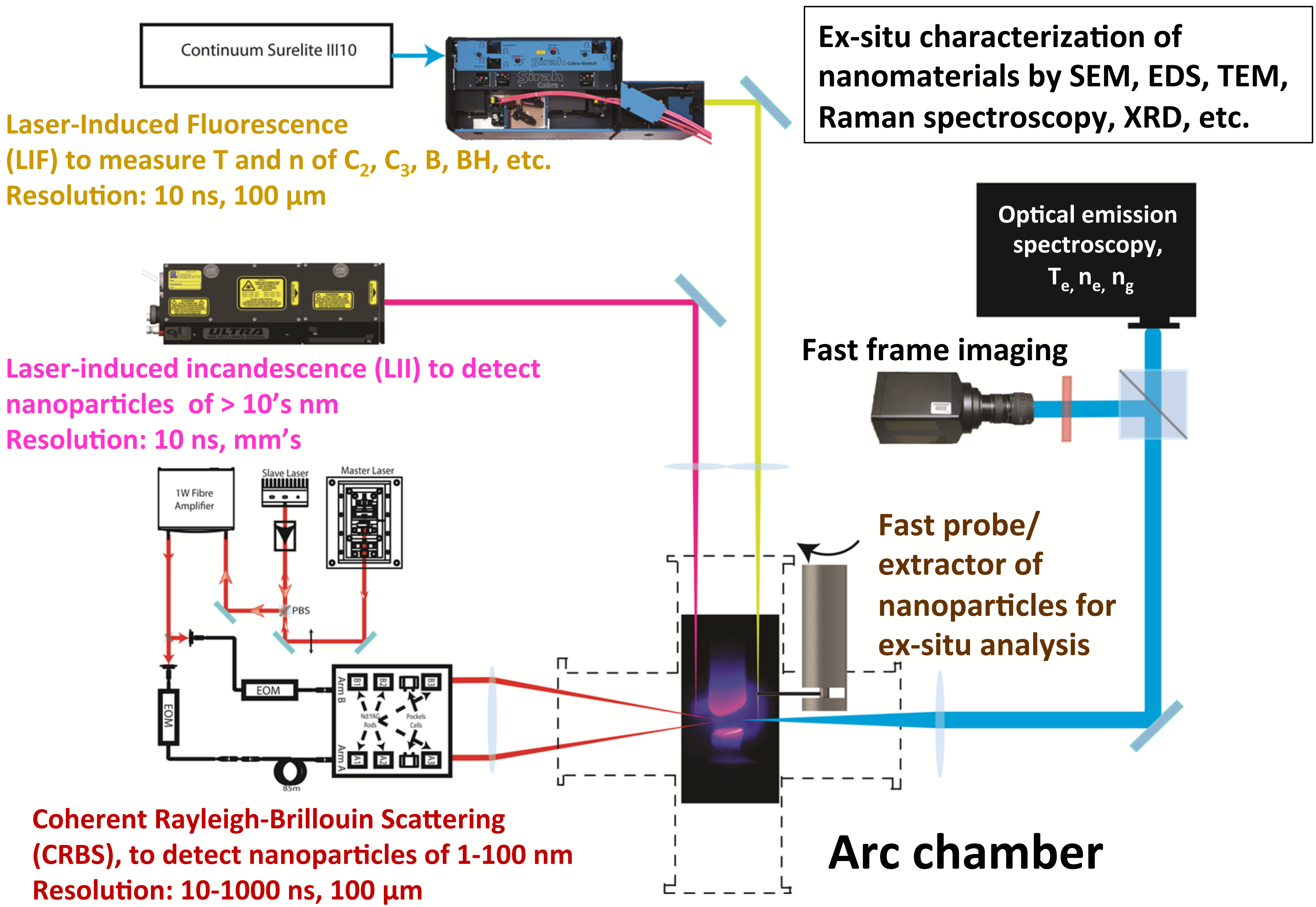
Proposed hypothesis of carbon arc nanosynthesis



Gas temperature, K

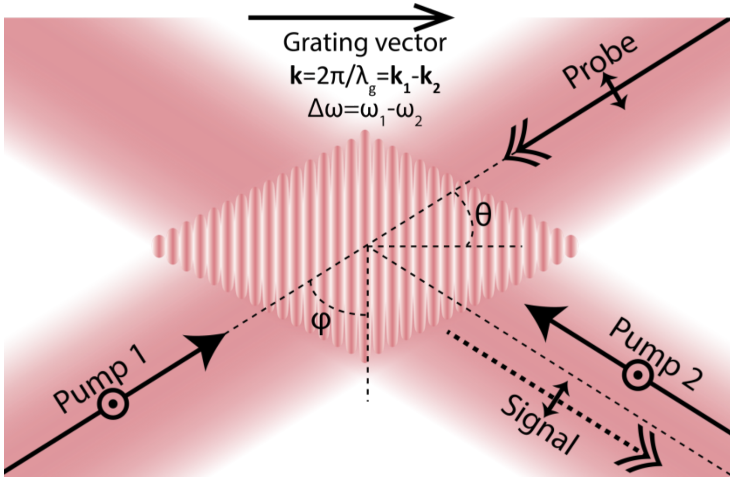
T = 4000 K	T = 1500 K	T = 1000 K
Evaporation, Dissociation	**Clusters, nucleation**	**Growth, bundling**
C ≈ $10^{17} – 10^{18}$ cm^{-3}	C ≈ $10^{15} – 10^{16}$ cm^{-3}	C ≈ $10^{14} – 10^{15}$ cm^{-3}
He ≈ $3 \cdot 10^{17}$ cm^{-3}	He ≈ $3 \cdot 10^{18}$ cm^{-3}	He > $3 \cdot 10^{18}$ cm^{-3}
C^+ ≈ $10^{14} – 3 \cdot 10^{16}$ cm^{-3}	C^+ ~ 10^{12} cm^{-3}	C^+ ≈ 10^{10} cm^{-3}

In-situ characterization of plasma and nanoparticles

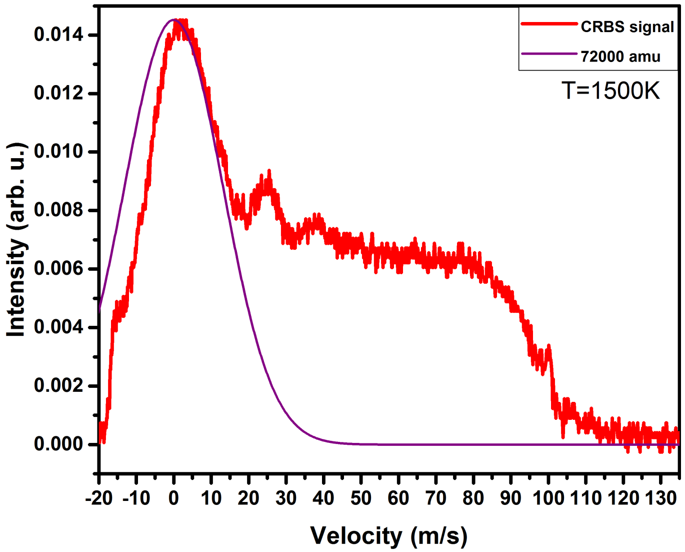


CRBS – unique in-situ diagnostic of nanoparticles in volume

- CRBS concept

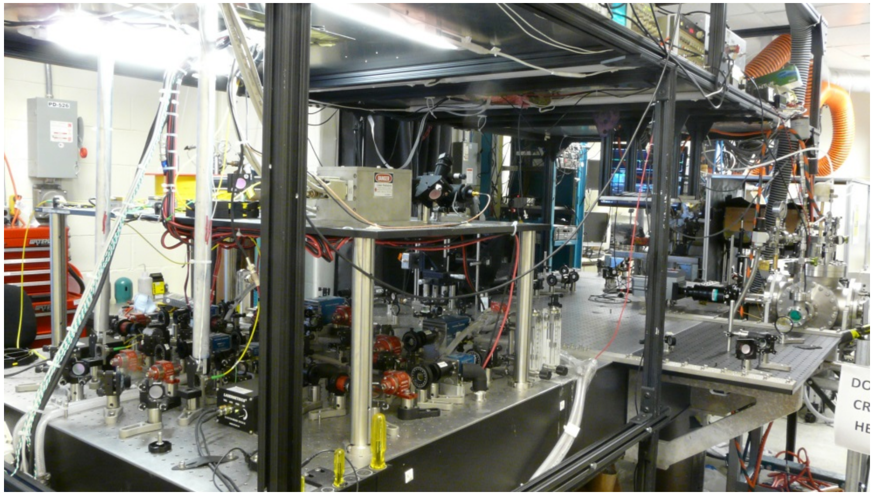


- Detected signal in carbon arc

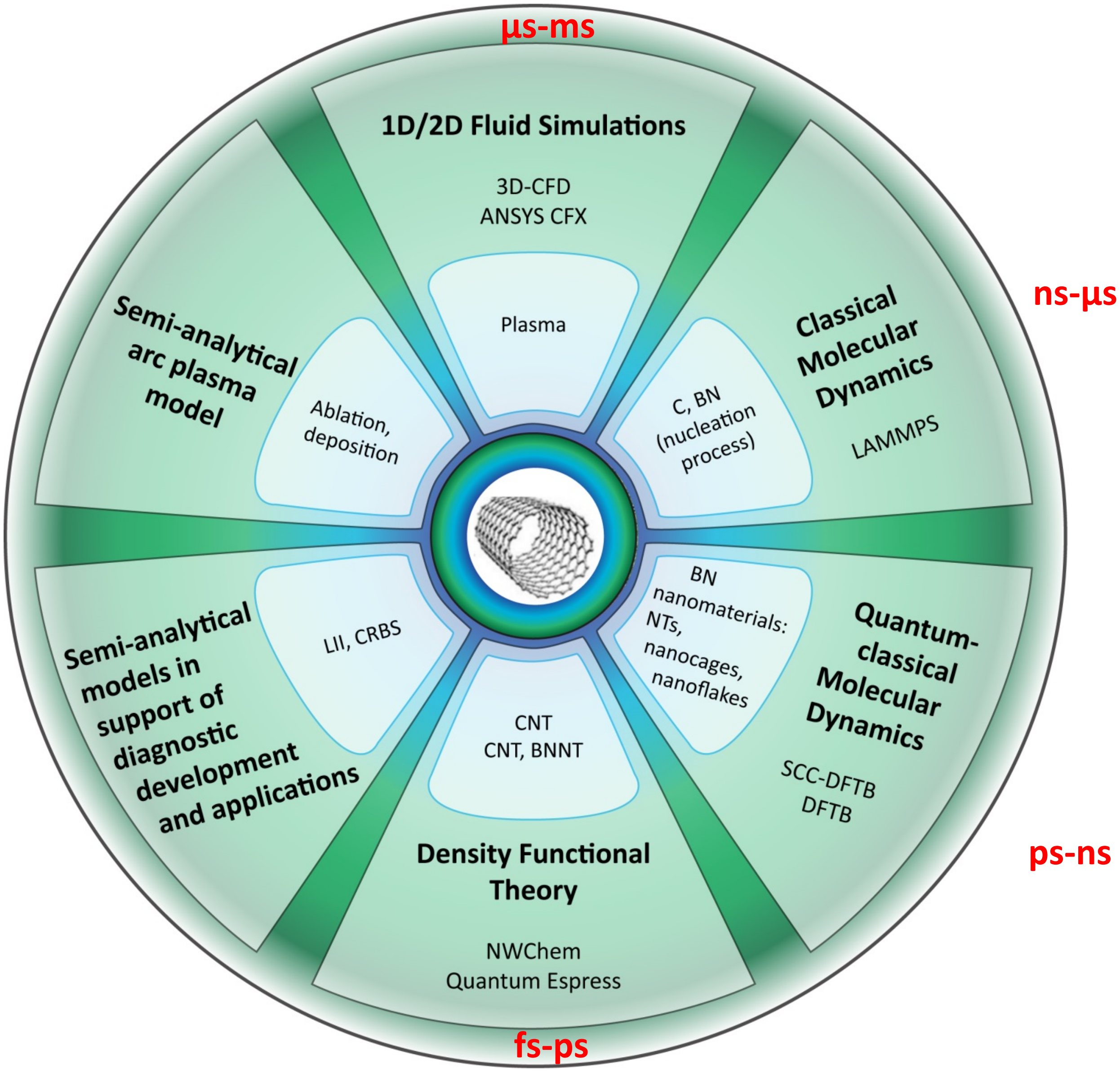


- Two beams form optical lattice by ponderomotive force to produce coherent scattered signal, *I↓signal* ∝(α[?]*N*)↑2
- Measures nanoparticle relative concentrations, Δ*N*, temperature or mass, and flow velocity
- Detection limits depend on densities and polarizabilities of gas and nanoparticles, α.
- Estimation for CNTs in arc: < 50 nm, ≥10^8 cm^{-3}

- CRBS setup



Computational tools used for simulations of arc plasma and nucleation and growth of nanostructures

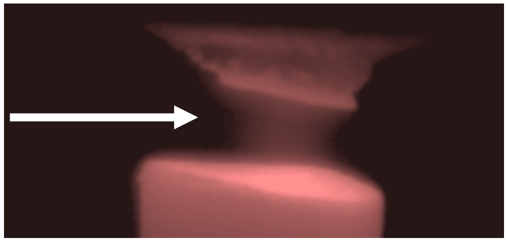


New results: complex structure of the carbon arc discharge for synthesis of carbon nanotubes

(a) Cathode

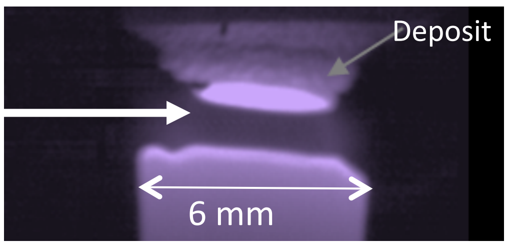
H_α (12 eV)

Anode



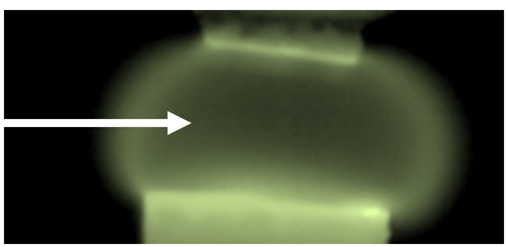
(b)

C I - emission (10.7 eV)



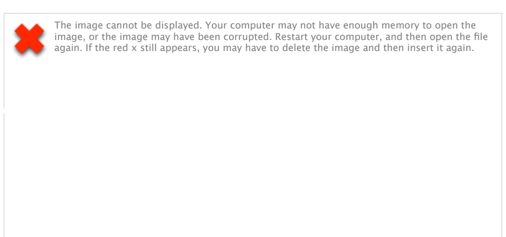
(c)

C_2 - emission (2.6 eV)



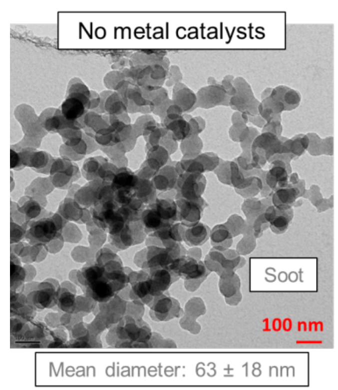
(d)

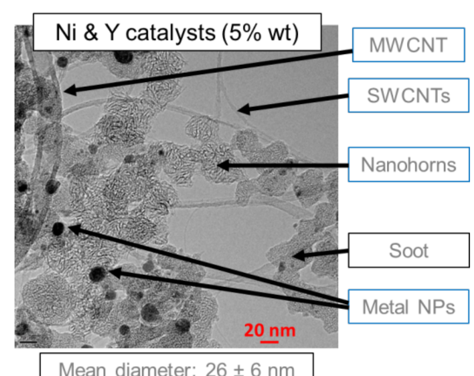
Carbon particles by pLII



- Measurements revealed arc regions with different gas/plasma phase properties & processes: evaporation (a,b), nucleation and growth of nanoparticles (c,d)
- Hot arc core is populated mainly with carbon atoms and ions (a) and colder arc periphery (c) populated mainly with C_2

Arc generated nanoparticles

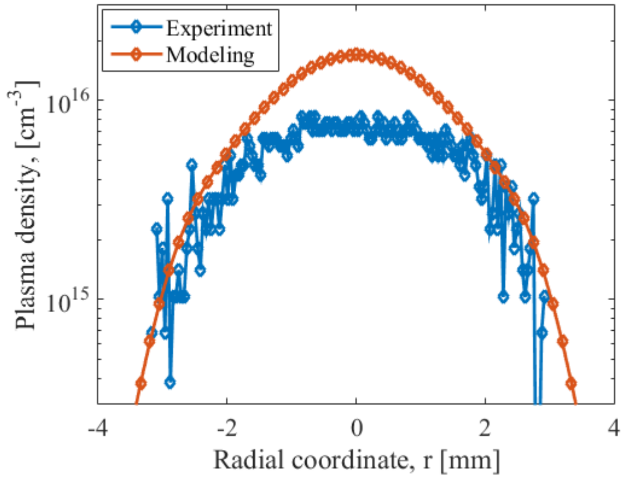




Towards predictive modeling of atmospheric plasma for synthesis of nanomaterials

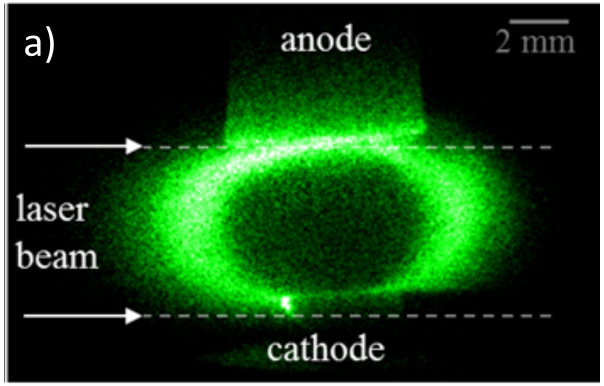
- **Plasma density obtained from H_α OES and 2-D CFD simulations**

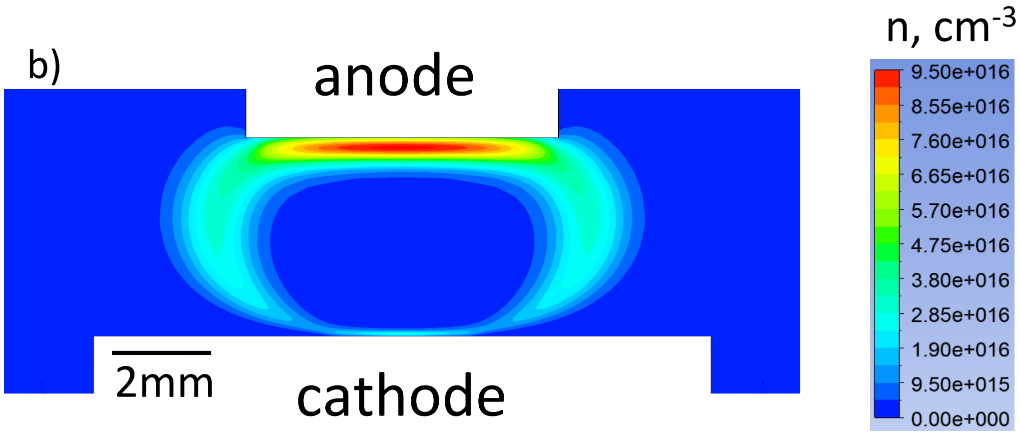
Arc operation: Current 55 A, He pressure 500 torr



- **Inhomogeneity of the arc plasma explained by the non-uniform distribution of the arc current and short collisional mean free paths**

- **C_2 density obtained from LIF (a) and 2-D CFD (b)**



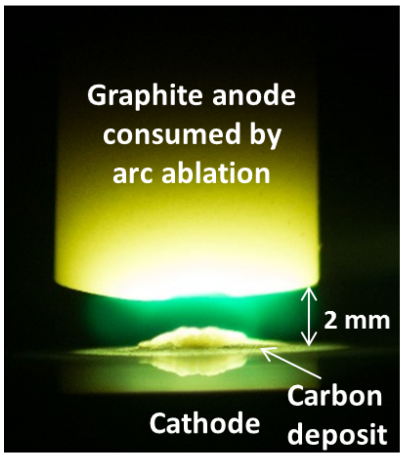


Formation of nanostructures in carbon arc:

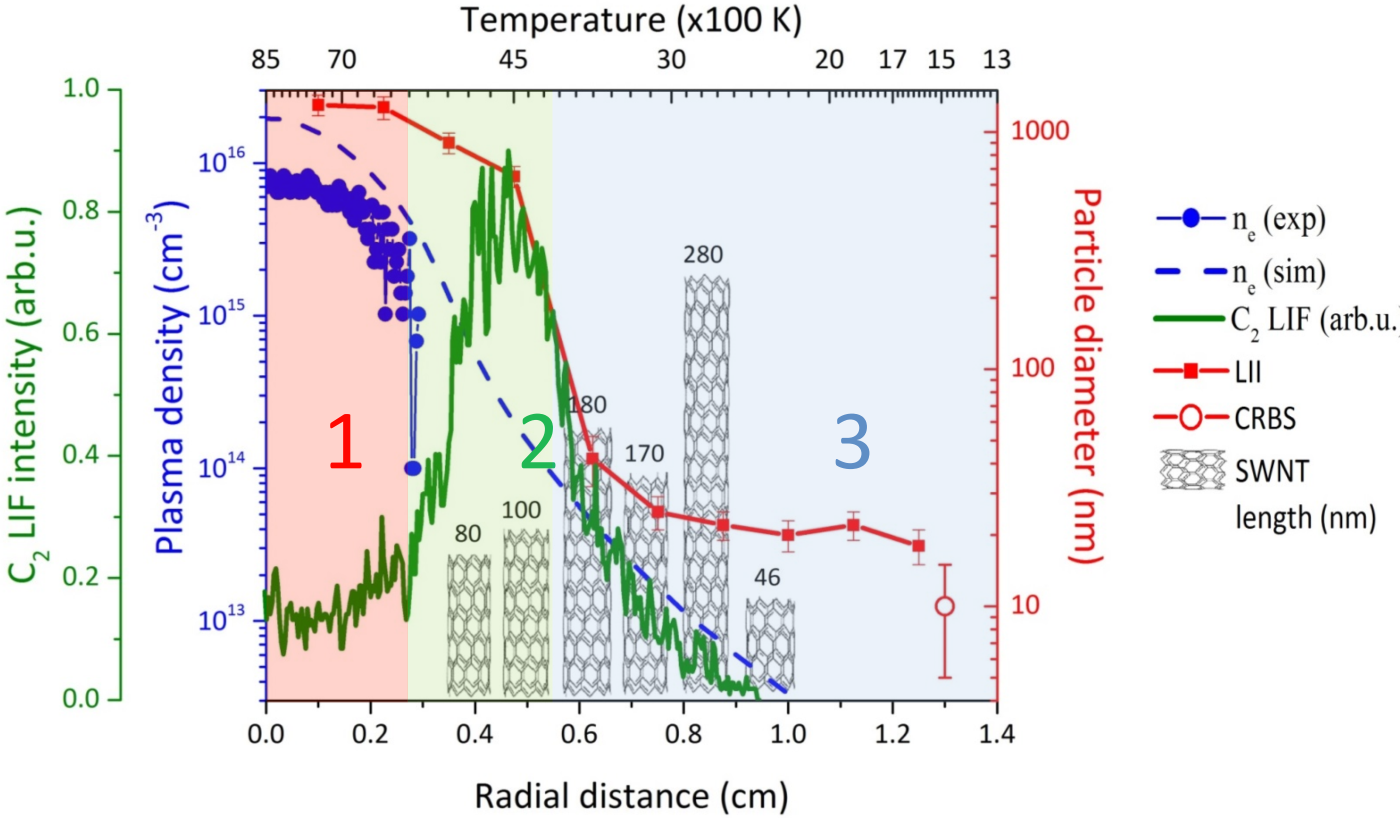
Summary of key results of in-situ and ex-situ measurements

1 – Evaporation   2 – Nucleation   3 – Growth

Atmospheric pressure carbon arc discharge



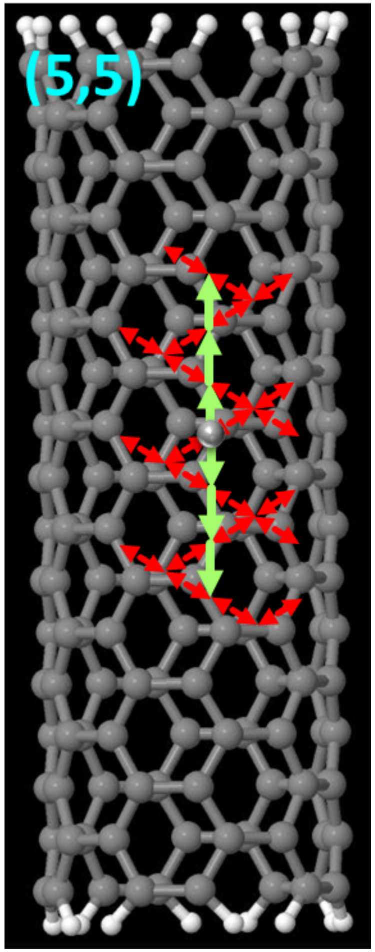
20V, 60A,
500 torr Helium



- **Arc current flows in the arc core (1). C_2 reaches maximum in region (2)**
- **CNTs are formed in non-equilibrium, colder plasma at the arc periphery (3)!**
- **Carbon particles observed: in the core (1) ~ 1 μm, at periphery ~20 nm**

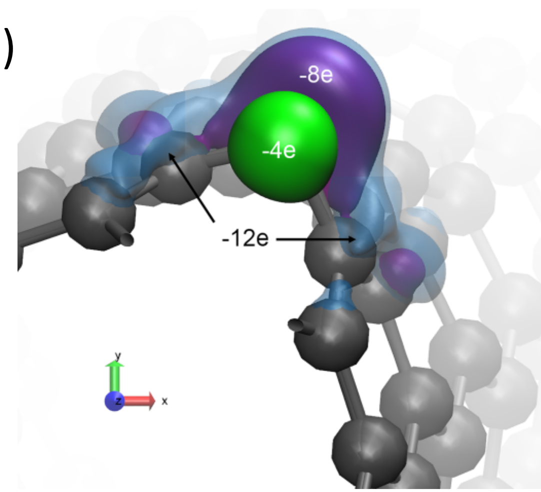
Charging of SWCNTs could help in their growth

a)

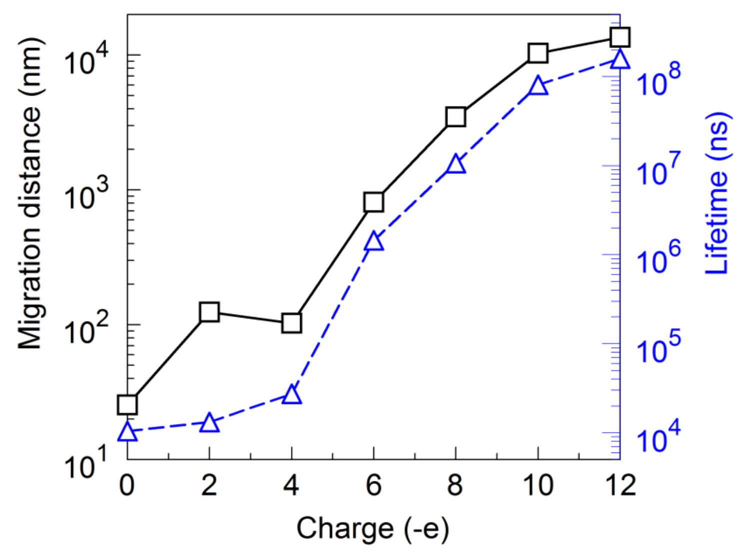


- Charging of nanoparticles and nanostructures is a plasma effect on nucleation and growth processes
- DFT and Kinetic Monte-Carlo simulations of charging effect
- Armchair (5,5) SWCNT (Fig. a)
- Charging of the CNT causes the higher adsorption energy E_a, increasing the migration distance, (Fig. c)

b)

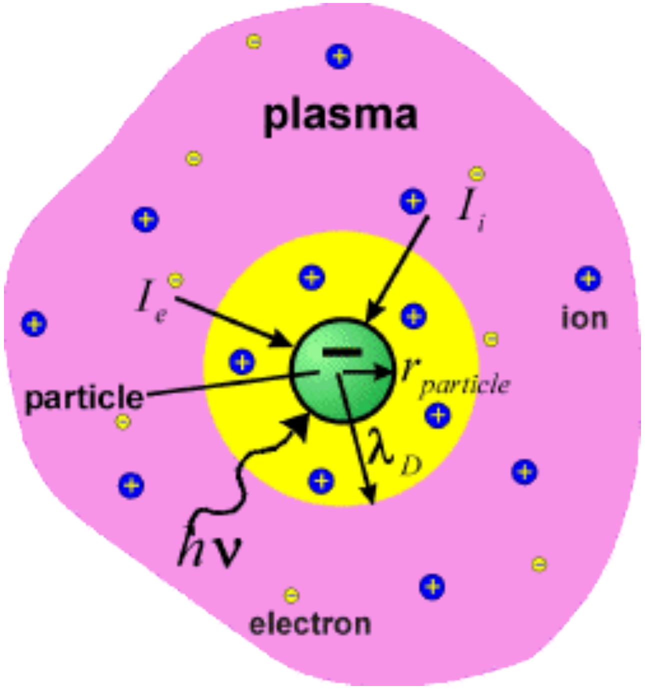


c)



DFT results (Fig. b)- additional charges distribute in the covalent bond space between adatom and CNT, increasing its covalent coupling

Charging of nanoparticles in arc plasma



http://www2011.mpe.mpg.de/theory/plasma-crystal/PKE/Hintergrund_e.html

Orbit motion limited approximation:

$$0 << \lambda_D << \lambda_{i,e}$$

λ_D ~ 0.2-1 µm

λ_i ~ 10 µm

Current balance, equilibrium particle temperature and floating potential

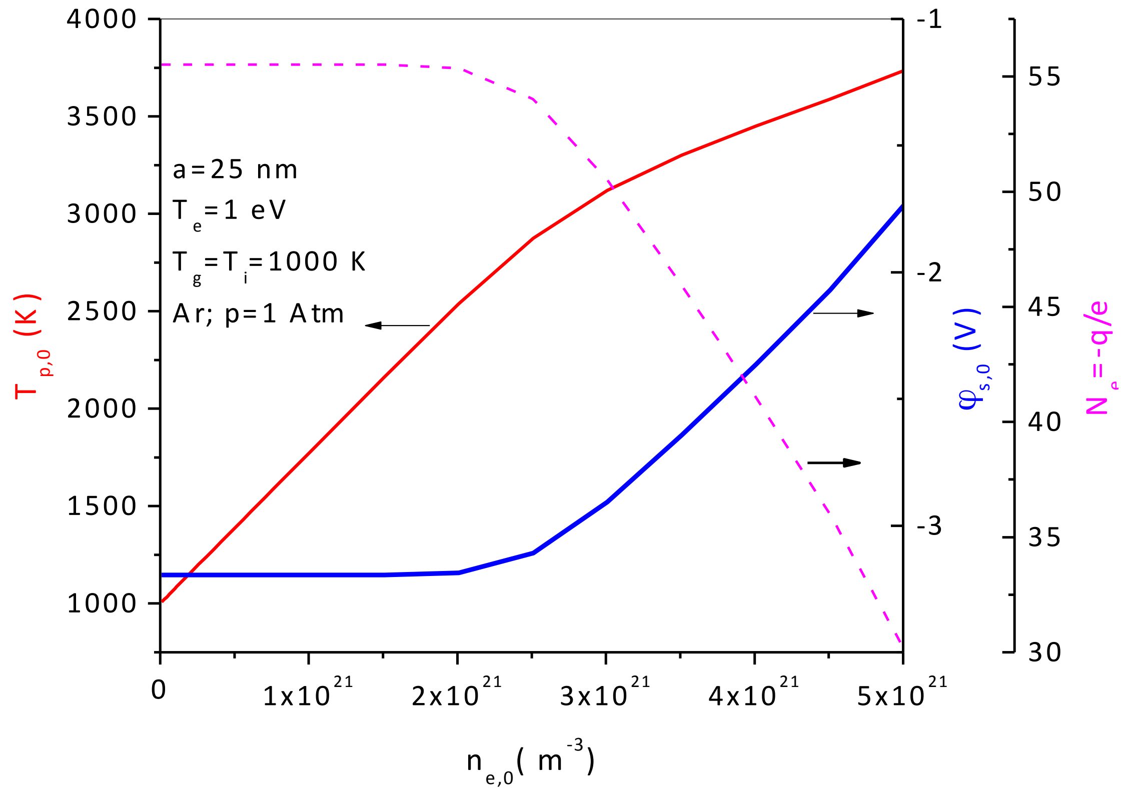
$$\frac{dq}{dt} = I_{e,tot} + I_i = I_e + I_{e,T} + I_i(1+\gamma) = 0$$

$$\varphi = q / C, \quad C = 4\pi\varepsilon_0 a$$

$$M_p c_p \frac{dT_p}{dt} = Q_e + Q_i - Q_{conv} - Q_{rad} = 0$$

Charging of nanoparticles in plasma, cont'd

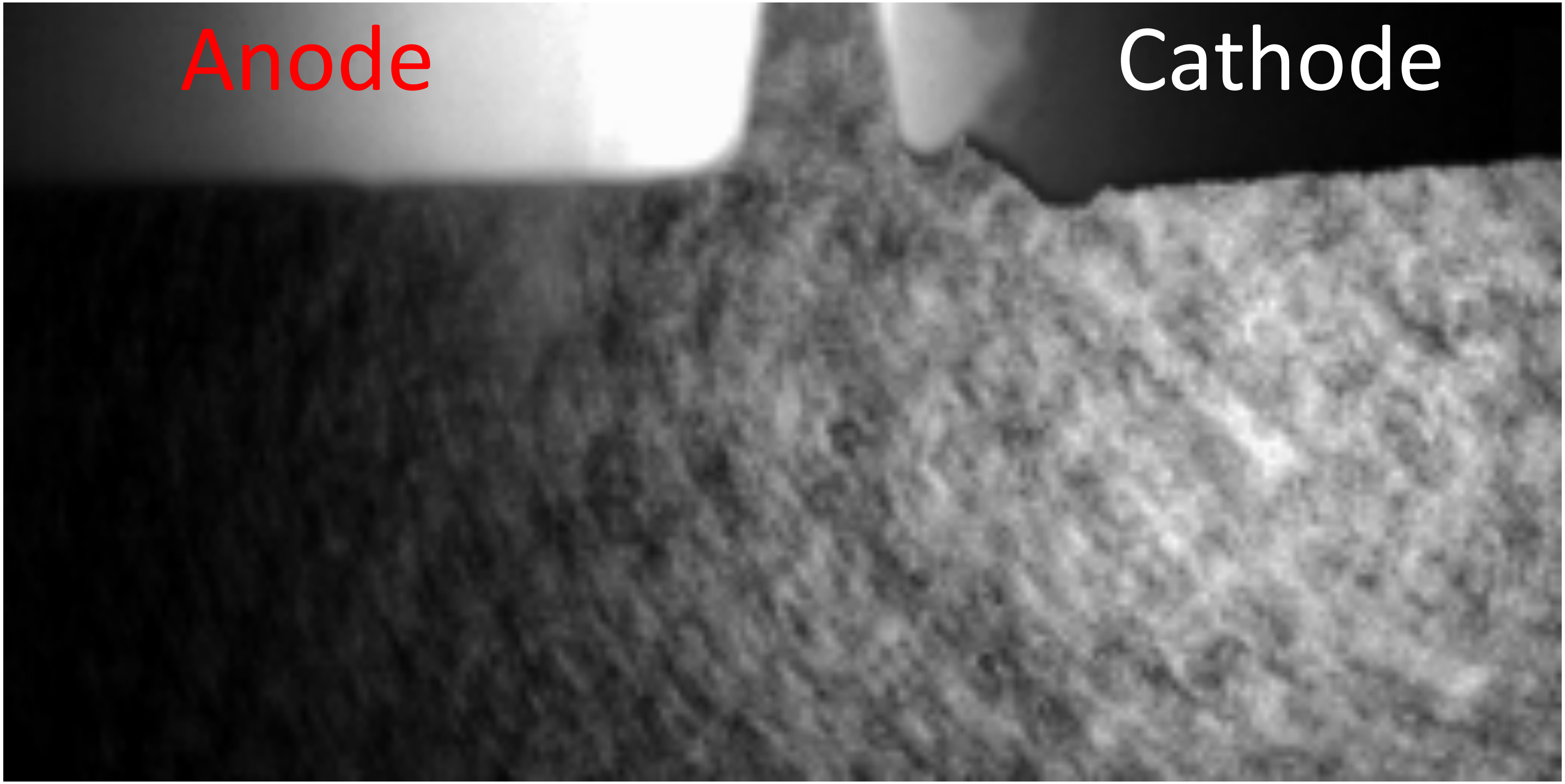
Nanoparticle temperature, potential and charge



- **For low pressure plasmas, charging of nanoparticles prevents their undesired agglomeration and bundling (for nanotubes).**
- **For atmospheric pressure plasma, charging of hot particles may not be as strong due to thermionic electron emission.**

Growth of carbon particles in the arc volume

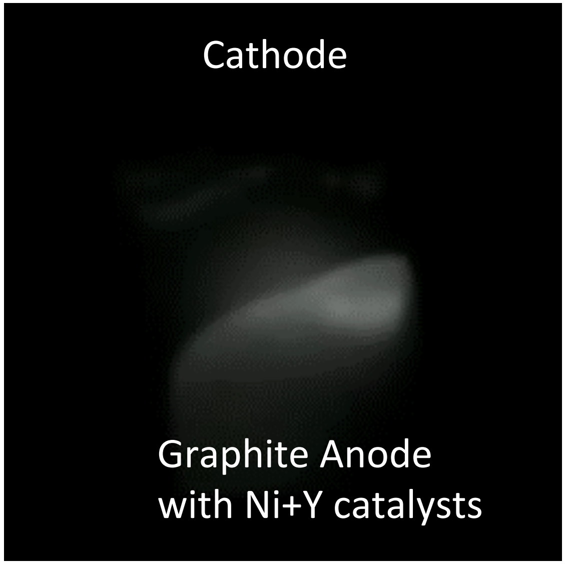
Arc current 65 A, laser backlighting at 632nm, 60606 fps

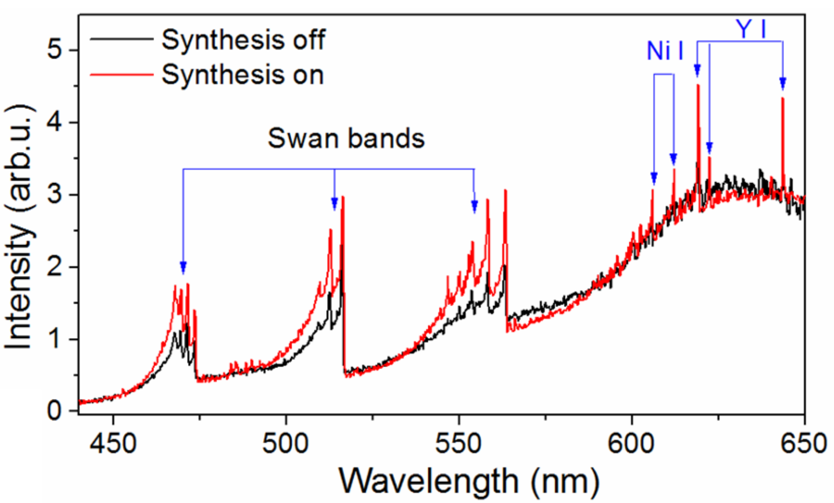


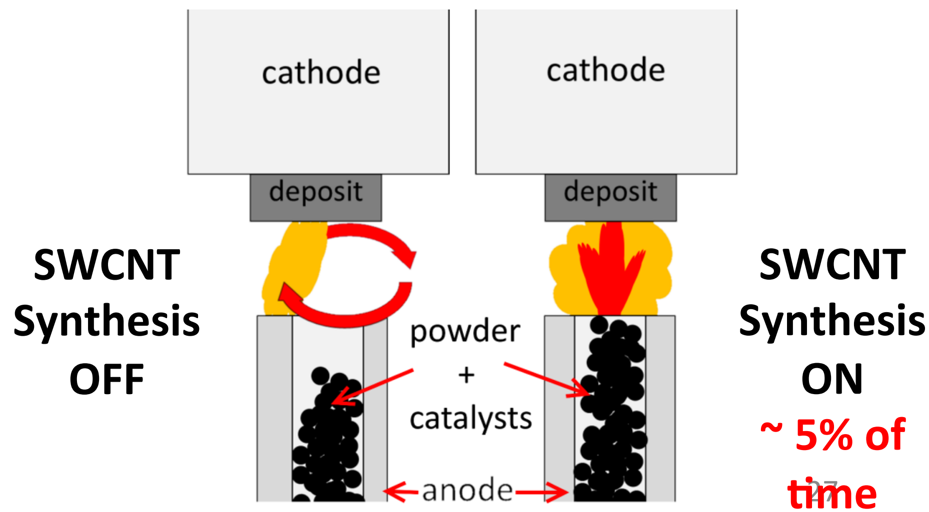
Arc oscillations cause unstable carbon feedstock

- **Synthesis of SWCNT by carbon arc with metal catalysts**
- **Metal – Carbon mixed powder filled in the hollow graphite anode rod**
- **Multi-mode oscillations: LF (10^2 Hz) and HF (10^3 Hz) modes, inside and outside the hollow anode**
- **Oscillations cause of low purity and poor selectivity of the arc synthesis**

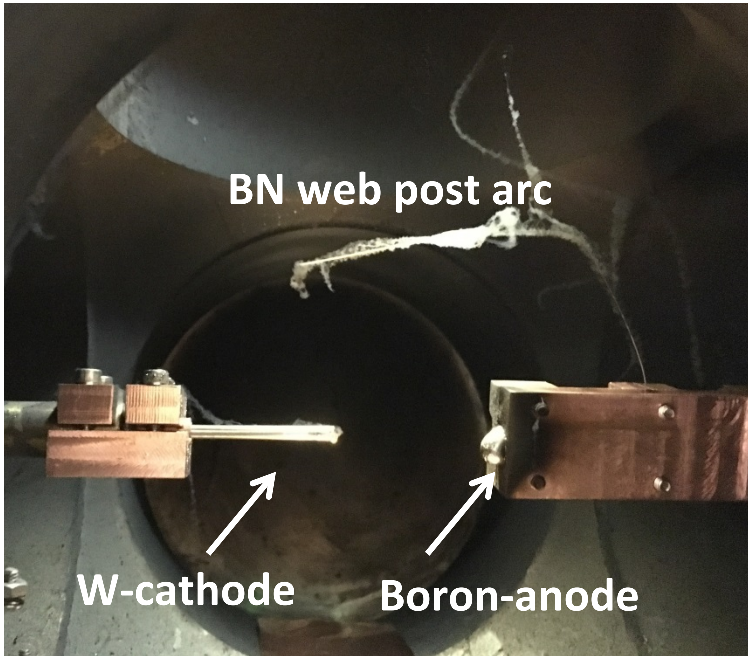
- **C_2 Filtered Fast Imaging, 10,000 fps**

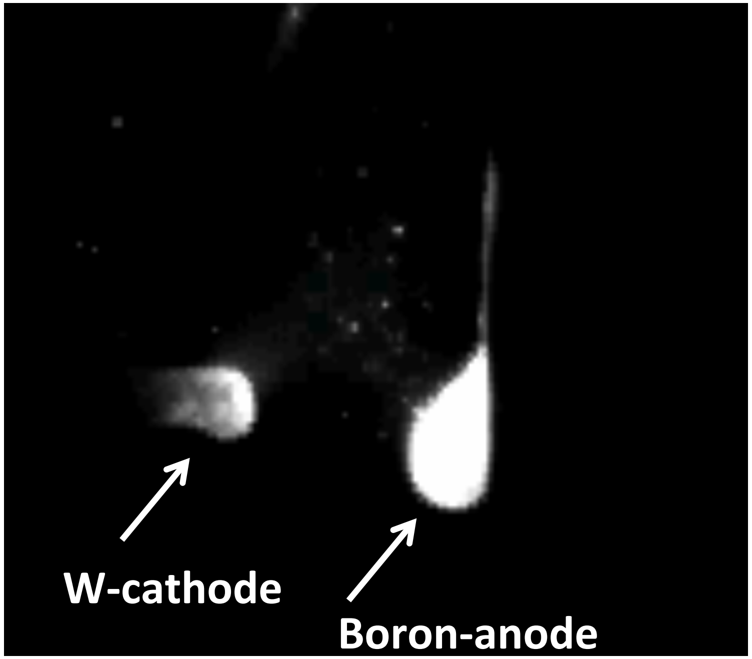






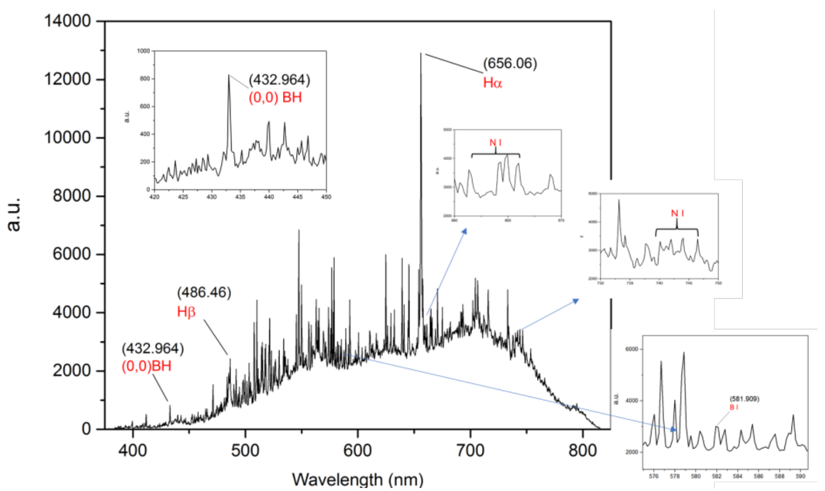
Synthesis of BNNT by arc discharge





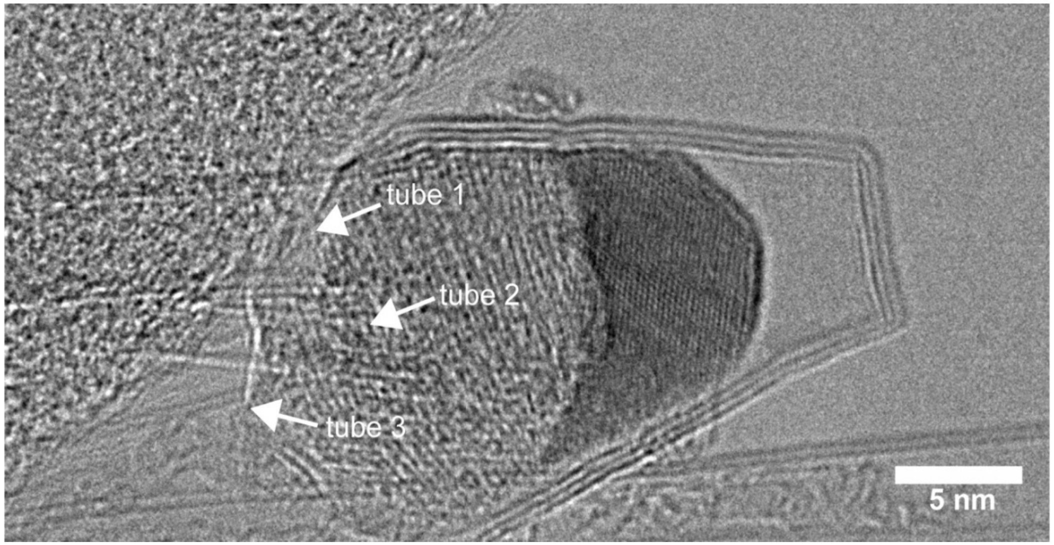
- **Boron-rich anode has 2% of Nickel and Cobalt to provide conductivity of the anode**
- **40V-40A arc at 400 torr of N_2 (Zettl's conditions, 2000)**
- **New regime: 40V-40 A arc at 400 torr, 75% N_2 – 25% H_2**

- **OES measurements for the N_2-H_2 regime**



BNNT – Root growth mechanism?

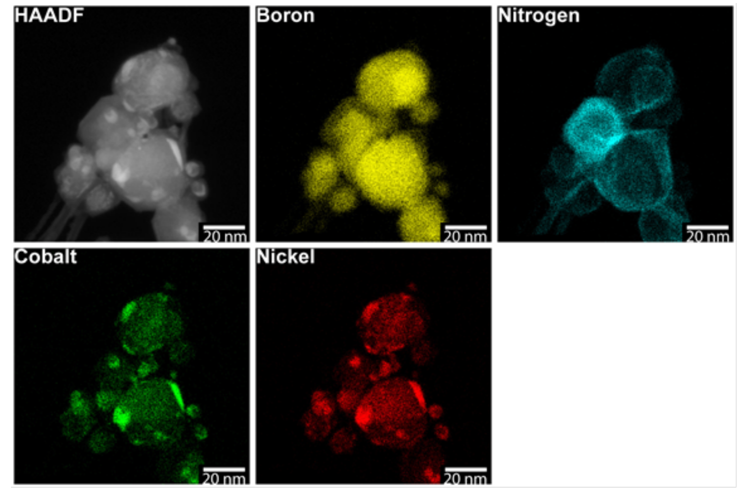
- **TEM image: Three BNNTs grown out of an unreacted boron nanoparticle wrapped by BN layers: Boron-rich (light) and Co/Ni-rich (dark)**

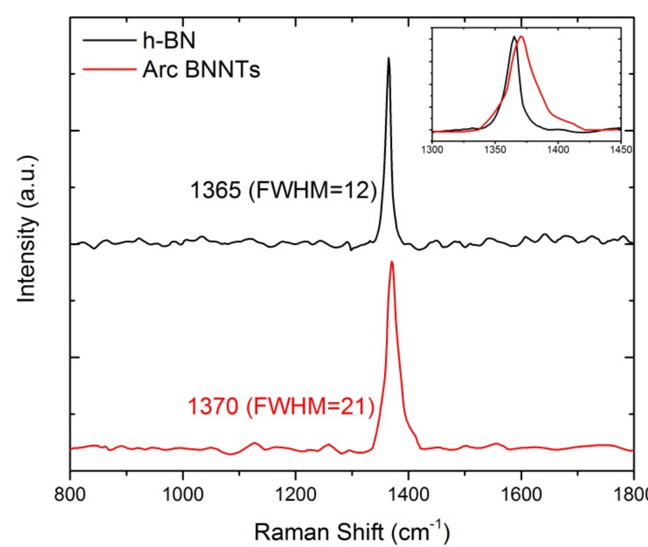


- **Raman spectra of bulk hexagonal boron nitride powder (black) and the arc synthesized BNNTs (red). Only the E_{2g} mode of hexagonal boron nitride was observed, and the blue shift observed in the synthesized BNNTs is characteristics of few-layer boron nitride**

- **EDS elemental mapping results**

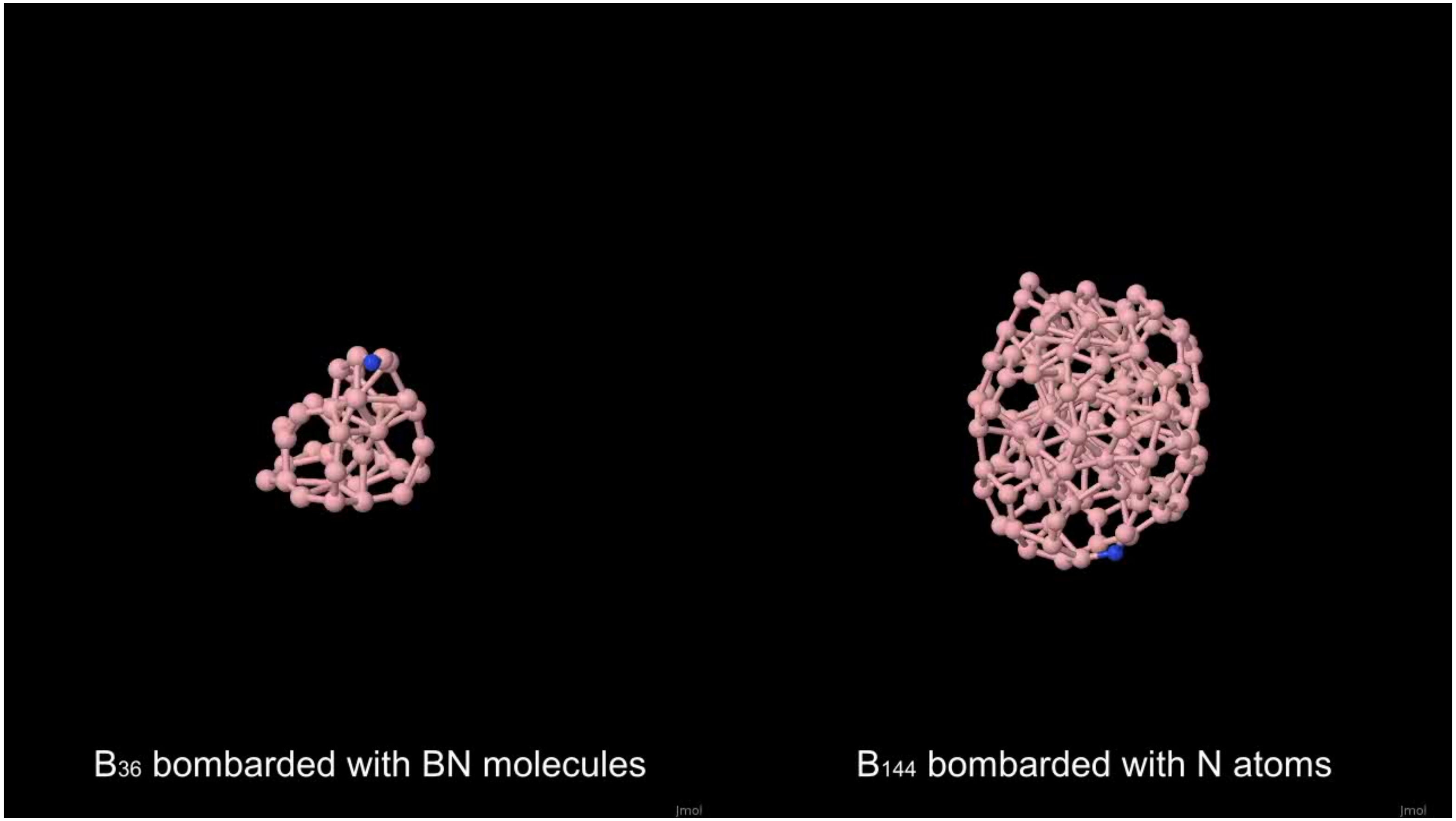
B and N show that the tube bundles on the lower left are boron nitride and the nanoparticles are wrapped by boron nitride





Encapsulation of boron particles

- Simulations by Quantum-Classical Molecular Dynamics with Density Functional Tight Binding Theory



B-pink
N-blue

- **Bombardment by BN (left) or N (right) of boron cluster shows encapsulation of boron clusters with BN layers; the effect is observed in experiments by our and other groups**

Summary

- Non-uniform arc current distribution determines spatial variation of the synthesis processes of CNTs.
  - In-situ characterization of plasma and nanoparticles, and arc modeling revealed that CNTs are formed in the plasma.
    - Predicted plasma effects: CNTs charging enhances growth of CNTs, impedes coagulation of soot particles and bundling of nanotubes, heating of nanoparticles above gas temperature.
  - Arc oscillations induced by ablation of the anode have adverse affect on synthesis selectivity and purity of synthesized products.
    - Solution - decouple processes for supply of carbon feedstock for synthesis and for sustaining the plasma.
- BNT arc synthesis:
  - Discovered a strong hydrogen effect on synthesis selectivity – the only method of exclusive synthesis of single-walled BNNT.
  - Predicted new mechanisms of growth of BN nanostructures (BNNT, nanoflakes, nanocages, etc.).

Laboratory for Plasma Nanosynthesis

Princeton Plasma Physics Laboratory

ABOUT | RESEARCH | **PEOPLE** | FACILITIES | PUBLICATIONS

LPN-PPPL Team

The LPN-PPPL collaborative team is assembled of high-level professional experts in the areas of theoretical and experimental plasma and materials sciences as well as advanced plasma and materials diagnostics.

PPPL PRINCETON PLASMA PHYSICS LABORATORY

PRINCETON UNIVERSITY

THE GEORGE WASHINGTON UNIVERSITY WASHINGTON DC

CASE WESTERN RESERVE UNIVERSITY EST. 1826 think beyond the possible

Stony Brook University

U.S. DEPARTMENT OF ENERGY | Office of Science

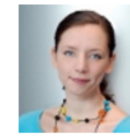

Yevgeny Raitses (PPPL)


Igor Kaganovich (PPPL)


Brentley Stratton (PPPL)


Roberto Car (Princeton Univ.)


Mikhail Shneider (Princeton Univ.)


Rachel Selinsky (PPPL)


lexandros Gerakis (PPPL)


Sophia Gershman (PPPL)


Kentaro Hara (PPPL)


Andrei Khodak (PPPL)


Michael Keidar (George Washington Univ.)


Alexnader Khrabry (PPPL)


Bruce Koel (Princeton Univ.)


Predrag Krstic (Stony Brook Univ.)


Longtao Han (Stony Brook Univ.)


James Mitrani (PPPL)


Valerian Nemchinsky (Keisa Univ.)


Angie Capece


Biswajit Santra (Princeton Univ.)


Mohan Sankaran (Case Western Reserve Univ.)


Vladislav Vekselman (PPPL)


Yao-Wen Yeh (PPPL)


Shurik Yatom (PPPL)

Acknowledgement

More information - http://nano.pppl.gov

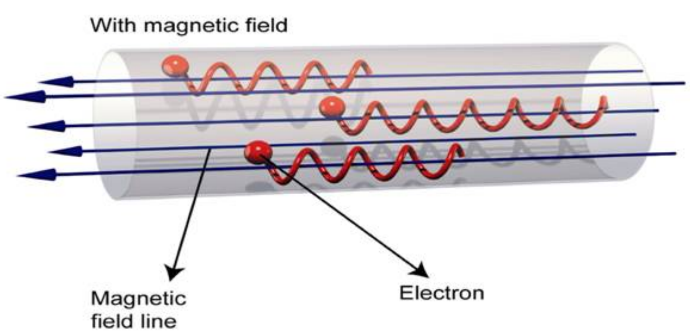
Arc movies courtesy of Tinyuan Huang, Vlad Vekselman, Sophia Gerhman, Shurik Yatom

U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division

Magnetized plasma to do materials science

- This LDRD research is on the use of the magnetic filter effect to produce a plasma with cold (< 1eV) electrons suitable for functionalization and atomic scale processing of complex 2-D nanostructures (nanofilms).
- Focus: hydrogenation of graphene, MoS_2, WS_2 etc.
- Deliverable: a new concept of the plasma-based functionalization
- Potential applications: hydrogen storage, new electronic and optical devices (because hydrogenation affect the bandgap of graphene) etc.

- Magnetic filter (MF) effect: stratified plasma with regions of different electron temperature

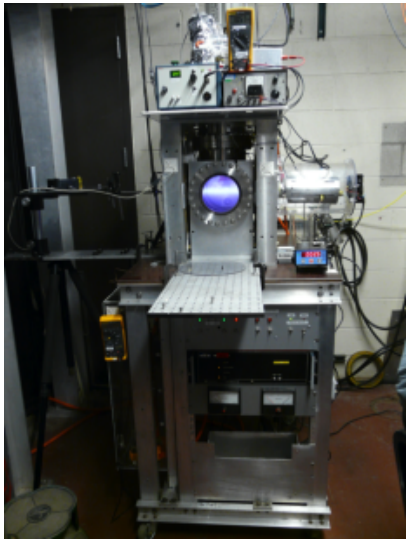


Electron cross-field displacement between collisions:

$$X \sim 2R_{Le} (\nu_{scat} / 2\nu_{loss})^{0.5}$$

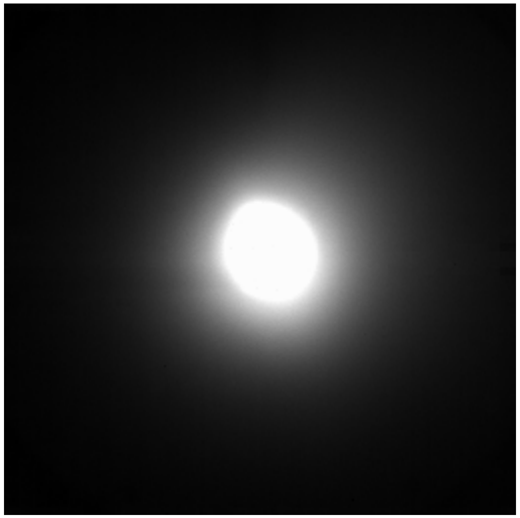
ν_{scat} electron-atom collisions, and Coulomb collisions $\propto 1/T_e^{3/2}$

- PPPL Filter Setup



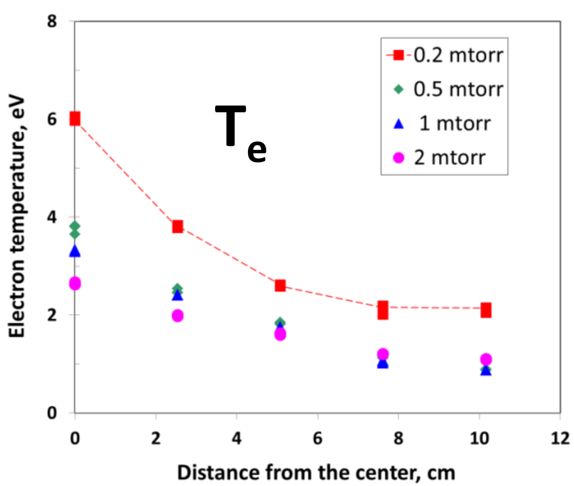
Characterization of magnetic filter

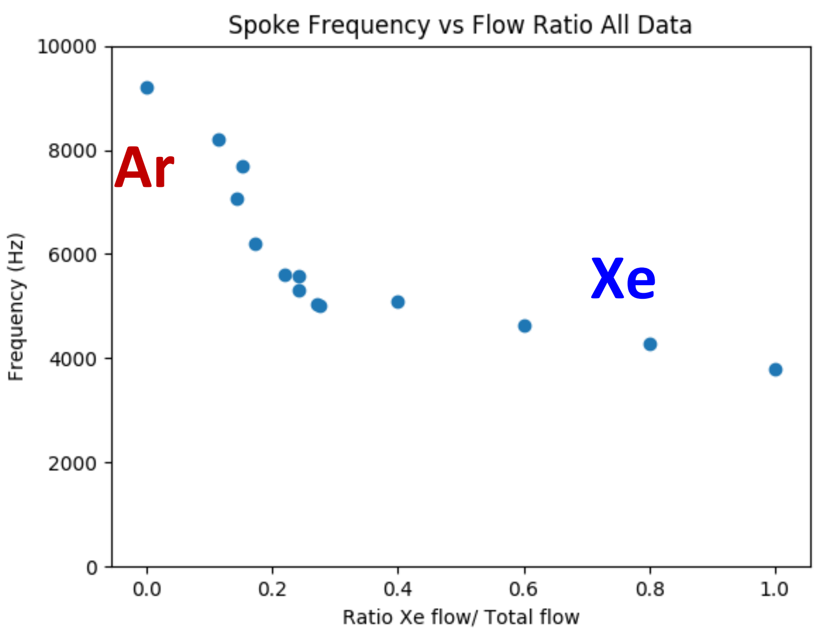
- **MF plasma unstable: spoke**



- **New results from probe, OES, fast imaging:**
  - **One spoke frequency for gas mixtures (e.g. Xe-Ar, Ar-H_2, Xe-H_2)**
  - **Spoke frequency follows the gas with highest ionization.**
  - **For hydrogenation – avoid the transitional region.**

- **Adverse effect of spoke on MF**

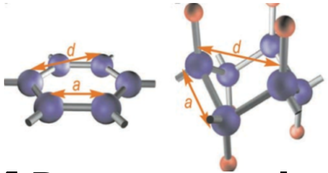




Parametric characterization of graphene hydrogenation in MF plasma

- **Experiments:**
  - **2D material samples (mono, bi, and tri layers graphene) loaded at different locations of the magnetic filter**
  - **Different MF parameters: magnetic field, pressure, power, etc.**
  - **Different treatment times**

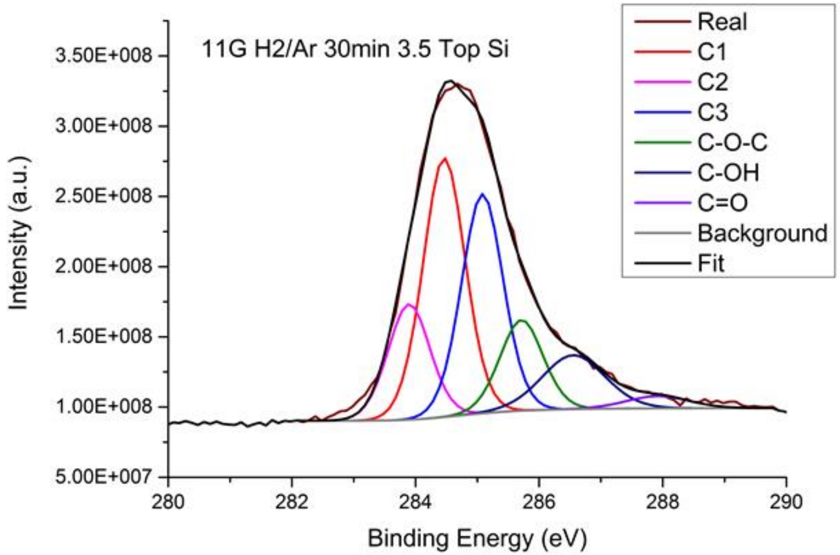
- **Characterization: Hydrogenation leads graphene sp^2 structure to transform to sp^3 structure.**

sp^2  sp^3

  - **Raman: The intensity ratio I_D/I_G of Raman peaks is to quantify the level of hydrogen.**
  - **XPS: H coverage=C3/(C1+C2+C3), C1 is C-C sp^2, C2 is neighbor of C-H. C3 is from sp^3. sp^3 could be from C-H and defect due to Ar bombardment.**
  - **TEM: to confirm the defect is from C-H not Ar bombardment**

Magnetic filter plasma allowed a record high hydrogen coverage

- **Results of X-ray photoelectron spectroscopy at PRISM**



38% H Coverage

H coverage=C3/(C1+C2+C3)

C1 is C-C sp^2,

C2 is neighbor of C-H,

C3 is from sp^3.

- **H coverage summary from the literature**

2009 Science	DC plasma. H coverage 10%
2009 ACS Nano	Capacitive coupled RF plasma. H coverage 17%
2010 APL	RF hydrogen plasma. H coverage 9%
2011, Carbon	Oxford Plasmalab 1000. H coverage less than 10%
2011 Advance Material.	STM hydrogen dose, Hydrogen coverage max 25.6%
2015, ACS nano	HPHT. H coverage 10%