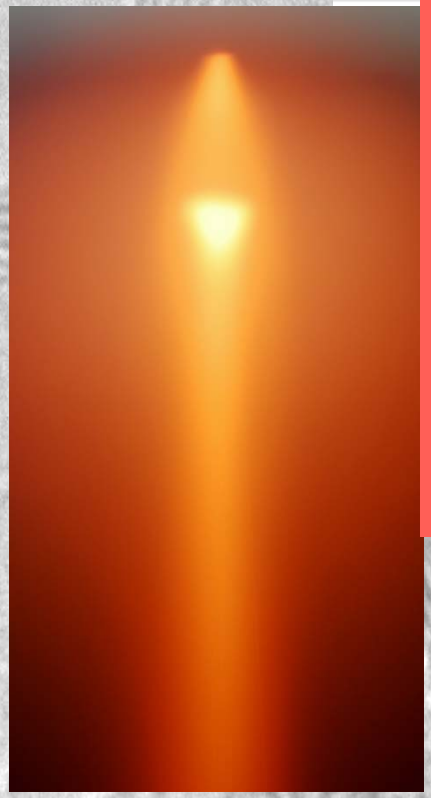
Synthesis of stacked graphene sheets by a supersonic thermal plasma expansion technique and the effect of sample collection chamber pressure



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We are primarily plasma people.....

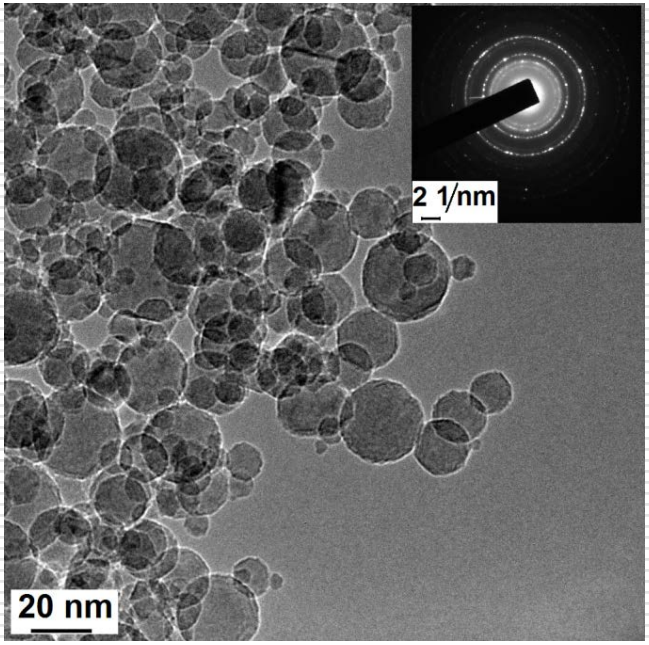
- So here we will mostly concentrate on those aspects of plasma systems which may contribute positively in enhancing material properties, in this case of graphene here.

- Undoubtedly, the bulk production rate is the biggest advantage of thermal plasma assisted materials synthesis techniques.

Picture below shows an intense thermal plasma beam Issuing from a plasma torch at Atmospheric pressure

Some other major advantages include….

- ✓ Induces good crystallinity because of the very high processing temperature.
- ✓ Most often a single step, rapid and continuous process.
- ✓ Clean process, with less hazardous effluent.
- ✓ Less impurity.
- ✓ A wide variety of reactants possible.

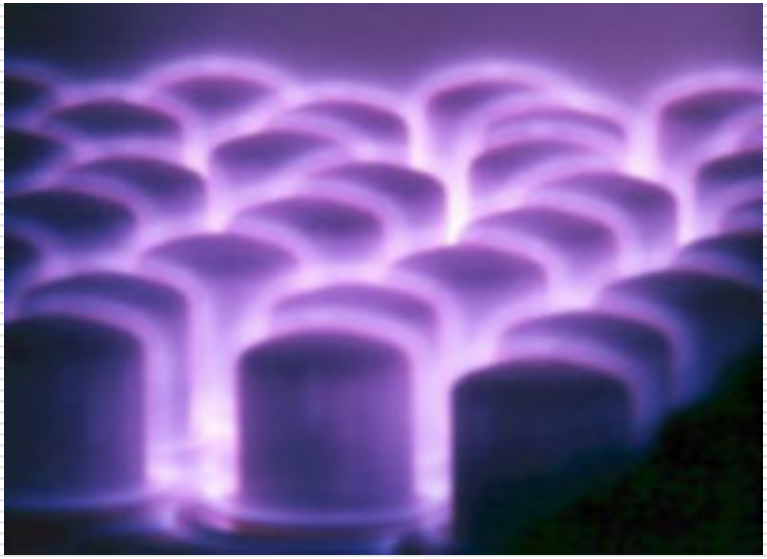


TEM photograph of highly crystalline, well dispersed alumina nanoparticles synthesized by plasma technique

So, what is Plasma ?

Plasma is an ionized gas consisting of atoms, electrons, ions, molecules, molecular fragments, and electronically excited species (*informal definition*)

The difference between thermal and non-thermal plasma

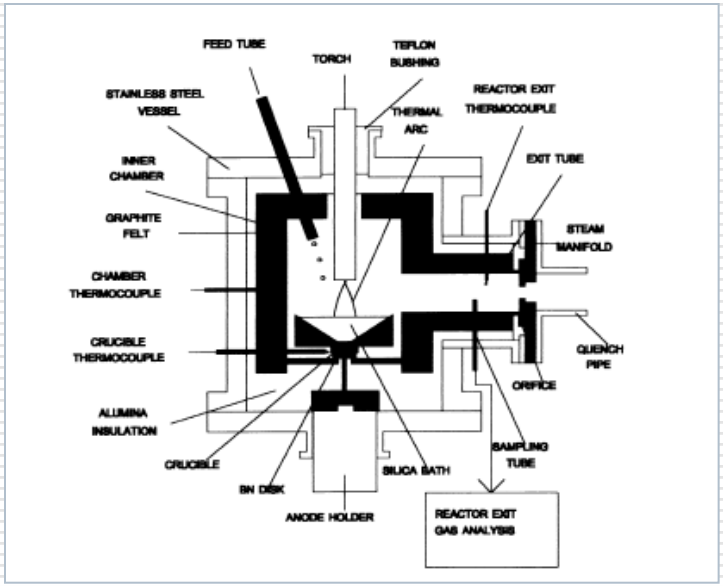


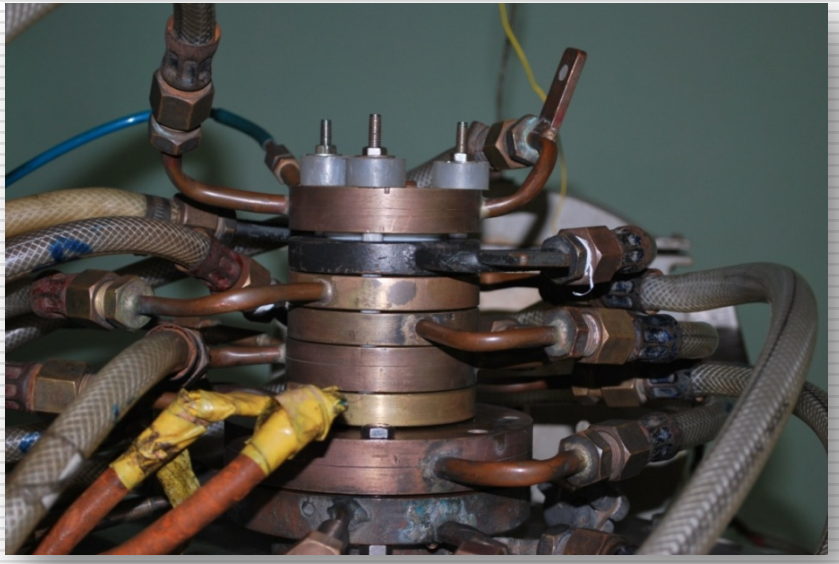
Non-thermal glow discharge Plasma being used for surface engineering

- If $T_e \approx T_i$ then we have a thermal plasma; Plasmas produced at atmospheric pressure are mostly this type.

- If $T_e \gg T_i$ then plasma is non-thermal or non-equilibrium or cold plasma; Plasmas produced under vacuum are mostly non-thermal plasma.

Two types of thermal plasma torches used for materials processing……





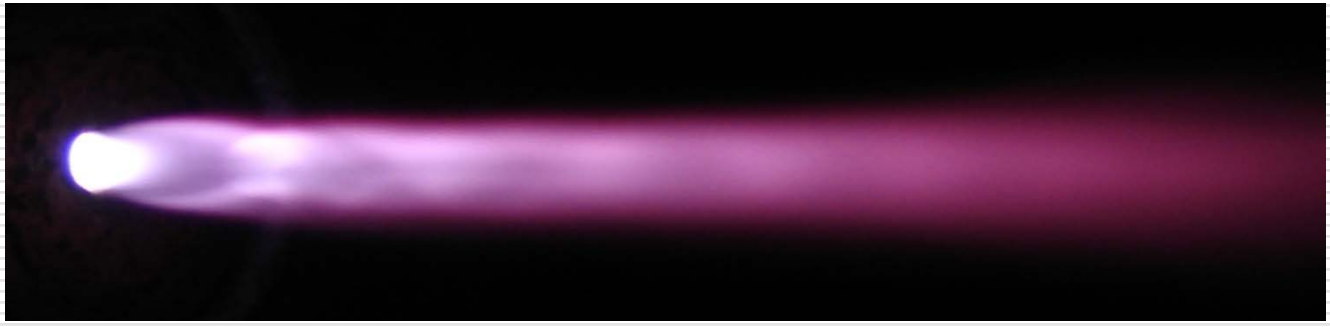
Transferred arc plasma torch used by Munz for synthesis of alumina nanoparticles

The non-transferred segmented torch we used for producing a supersonic plasma beam

Our Experimental System

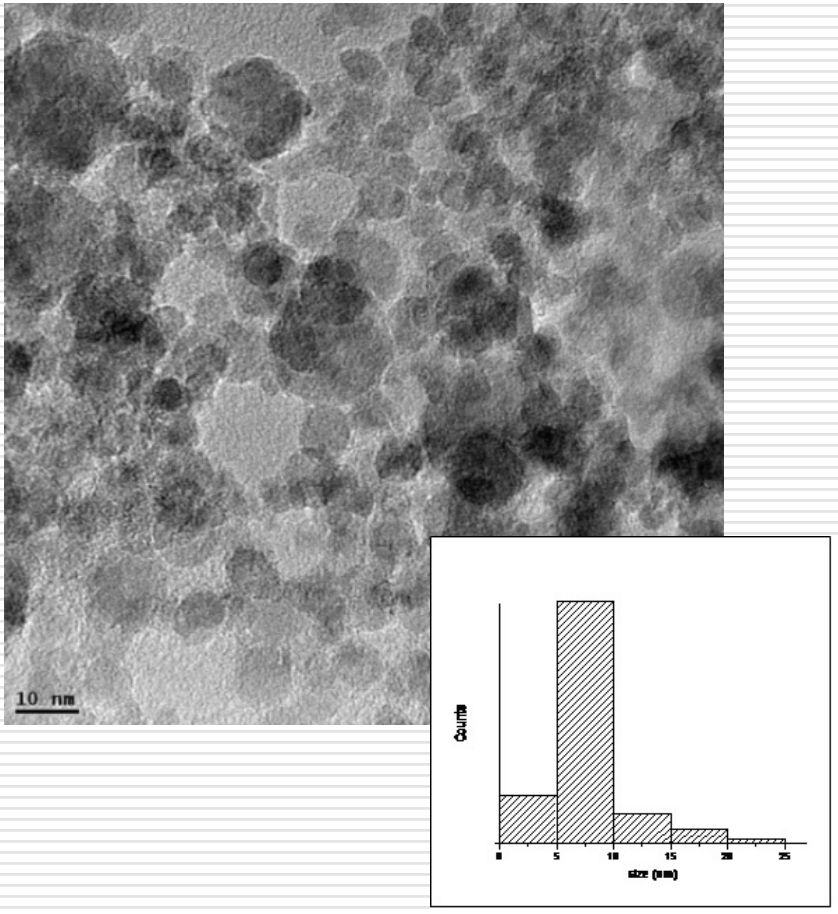
The Plasma Expansion Method

- The plasma beam is accelerated in to supersonic velocity as it is expanded into a low pressure sample collection chamber while moving through a converging nozzle.
- The nozzle expansion can convert the pressure and thermal energy into the kinetic energy of the plasma beam. This results in a very high rate and also uniform cooling.
- As opposed to gas mixing cooling, during expansion the plasma is also accelerated in the forward direction, which reduces agglomeration.



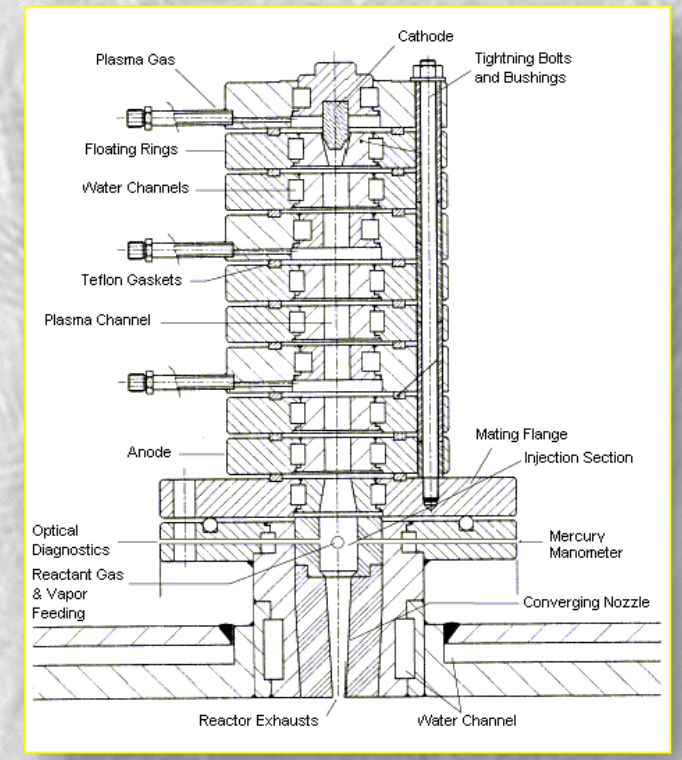
Advantages of the plasma expansion technique

- An intense (10^6-10^7 K/s) and also uniform cooling results in to smaller particles with a narrow size distribution.
- Less particle agglomeration
- Several control knobs like plasma power, reactant concentration, reactant feed location and sample collection chamber pressure.
- Physical separation of plasma production with particle growth zone.
- Long supersonic beam offers extended residence time at higher temperature which enhances crystallinity.



Our experiments on synthesis of nanosized stacked graphene sheets

- There is active search for graphitized nanostructured carbon with typically higher electrical conductivity combined with large specific surface area, to be used as a catalyst in Fuel Cell applications.
- We were using the same nanoparticle reactor for synthesis of these nano carbons, taking advantage of the extended residence time in the supersonic plasma beam, which is likely to enhance crystallinity of the material.
- Pressure in the sample collection chamber was used as one of the most important control parameter.



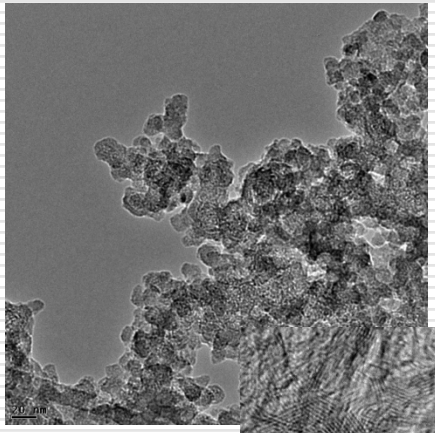
The Experiments

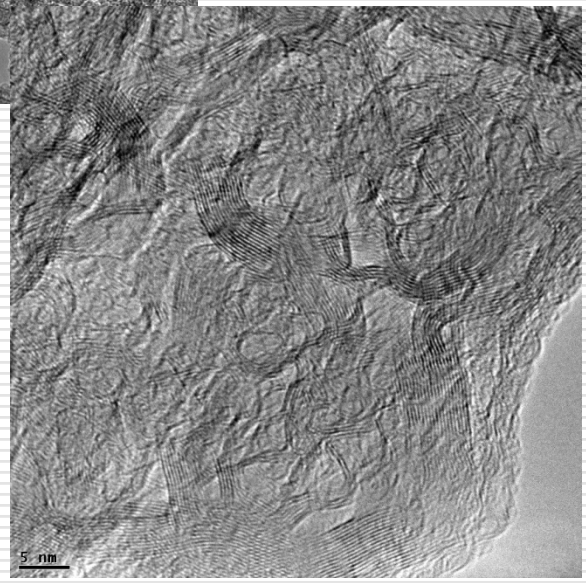
Control knobs in the system

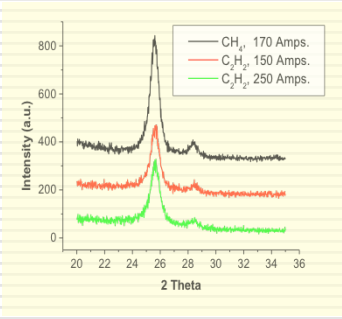
- Plasma Current (150-250 Amperes).
- Sample Collection Chamber Pressure (10, 300 and 600 mbar).
- Location of Reactant Injection (hot zone and Colder Tail Plasma).
- Catalyst for Better Crystallization (Ferrocene and Cobaltocene).
- Carbon Precursors (Acetylene, Methane and Graphite).
- Sample collection substrate temperature.
- Plasma Gas Flow Rate (10-20 lpm).
- Number of Floating Rings in the Torch (3-5) Sample Collection Point (120 and 220 mm).

TEM and XRD characterization of the product

- TEM Shows primary particles of less than about 20 nm, fused together forming branched aggregates.
- Higher magnification reveals crumpled nano-sheets of carbon inside these structures.
- XRD measures the interlayer distances (d_{002}) of the synthesized carbon to be in the range of 3.42 to 3.47 A^0 (Graphite is 3.36 A^0).







BET specific surface area characterization of the product

- BET gives specific surface area of the product (acetylene, 150 ampere plasma current, 10 mbar sample collection chamber pressure) in the range of 340-360 m^2/g.
- The same sample had a graphitization of 3.47 A^0.
- To our knowledge this is the best combination of both graphitization (3.47 A^0) and large surface area (340-360 m^2/g), by a plasma assisted method, most suitable for the intended applications

We can compare our values (surface area and graphitization combination) with some other recent results…

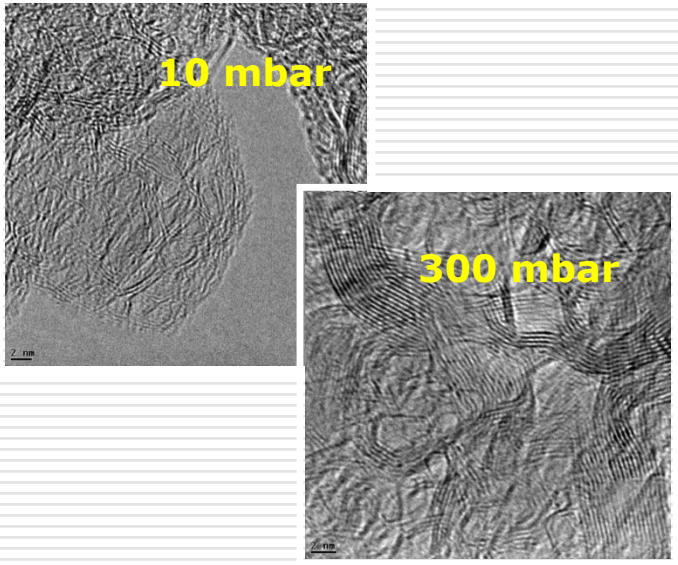
i. 3.46 A^0/53 m^2/g and 3.52 A^0/385 m^2/g, Kim *et al.* 2005 IEEE transaction on plasma science 33(2): 813-823

ii. 4.03 A^0/30 m^2/g and 3.55 A^0/119-345 m^2/g, Pristavita *et al.* 2010 Plasma Chemistry Plasma Processes 30: 267–279

iii. 3.55 A^0/112-156 m^2/g, Xiao-Feng *et al.* 2010 Plasma Chemistry Plasma Processes 30: 75-90

Effect of sample collection chamber pressure

- Stacking of individual Graphene sheets in a single layer increase with increasing pressure.
- This may explain the higher specific surface area (340-360 m^2/g) of our very low pressure synthesized carbon nanomaterials.
- Crystallization of the material improves drastically with pressure.
- Crystallization also improves substantially as the feed material is injected at a point with higher temperature. Injecting at the tail had resulted a graphitization of 3.83 $A^{0.}$

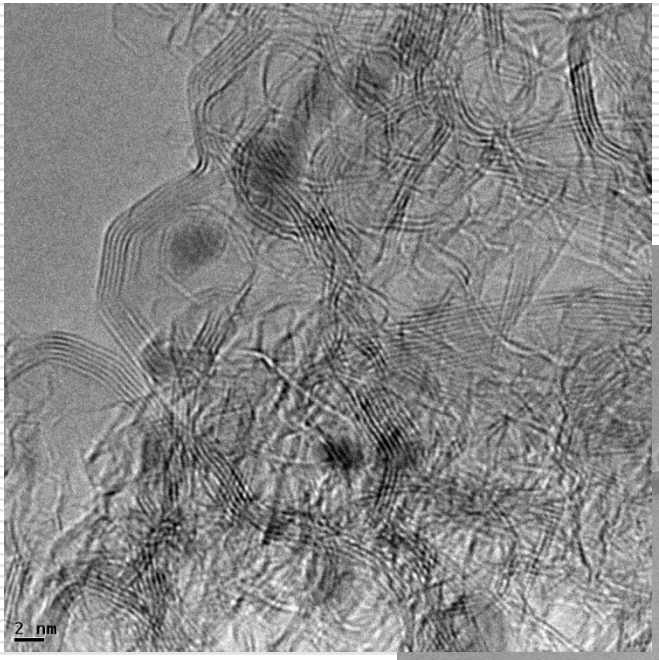


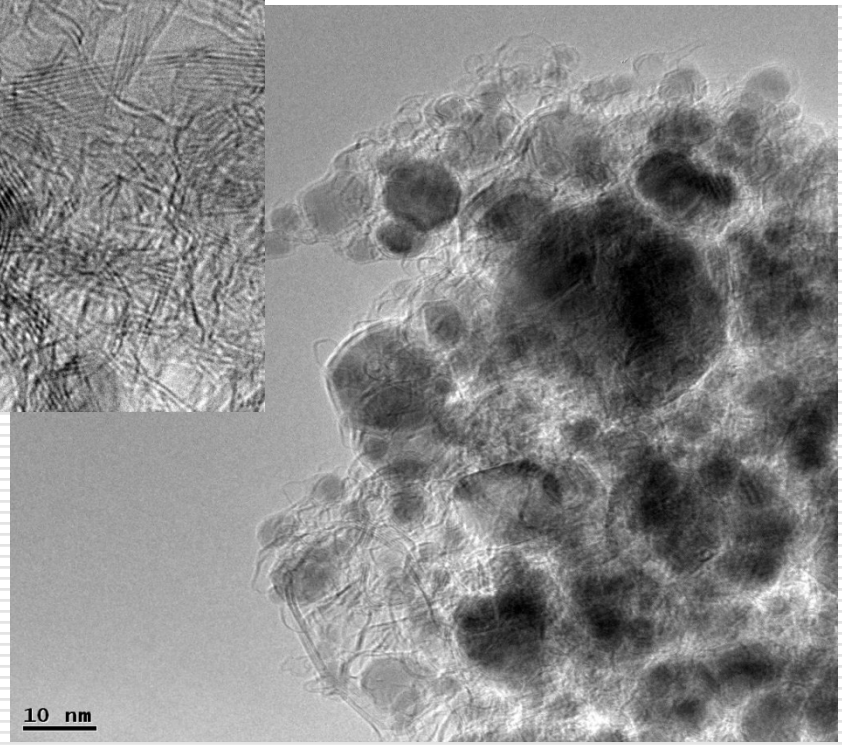
XRD measured d_{002} distances	
Pressure in mbar	Distance in A°
10	3.47
300	3.42
600	3.41

Effect of co-injected metal particles and heated up particle collecting substrate

• Co-injecting Ferrocene ($Fe(C_5H_5)_2$) and depositing on a heated substrate (350 C) had improved crystallinity substantially even at 10-20 mbar pressure in the sample collection chamber.

• Some TEM photographs shows what is considered to be a single graphene sheet.

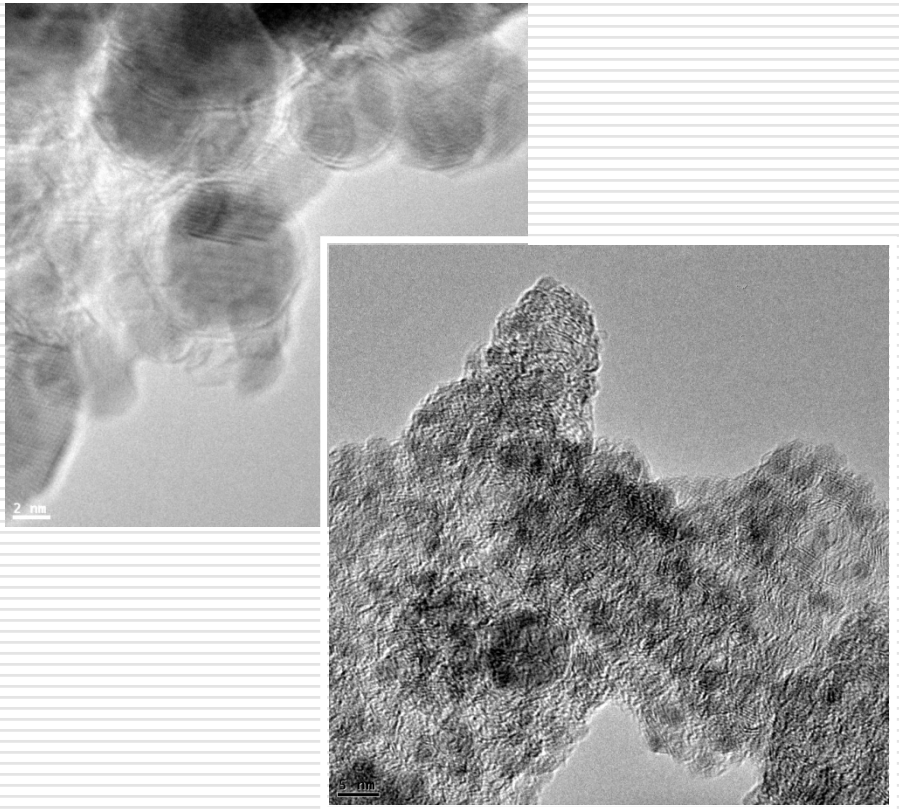




Graphene sheet encapsulated iron nanoparticles

• Another important observation was formation of iron nanoparticles encapsulated in few graphene layers, which have many different application potential including in Cancer treatment.

• TEM shows uniform, carbon capped iron nanoparticles of 2-3 nanometers sizes, which is much smaller compared to any other thermal plasma assisted method and only comparable to laser assisted techniques.




Thank You!