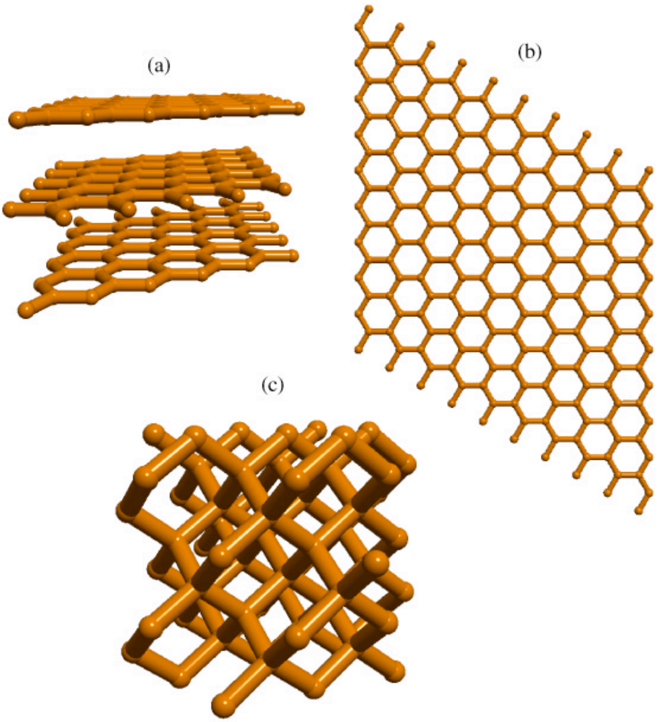
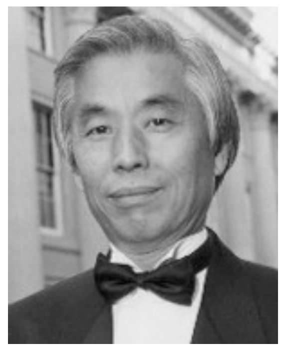
Film Thickness Dependence of the Fe Catalyst Size on Si_3N_4, Al_2O_3 and SiO_2 Substrates for the Synthesis of Vertically Aligned Carbon Nanotubes: A High-Throughput Approach

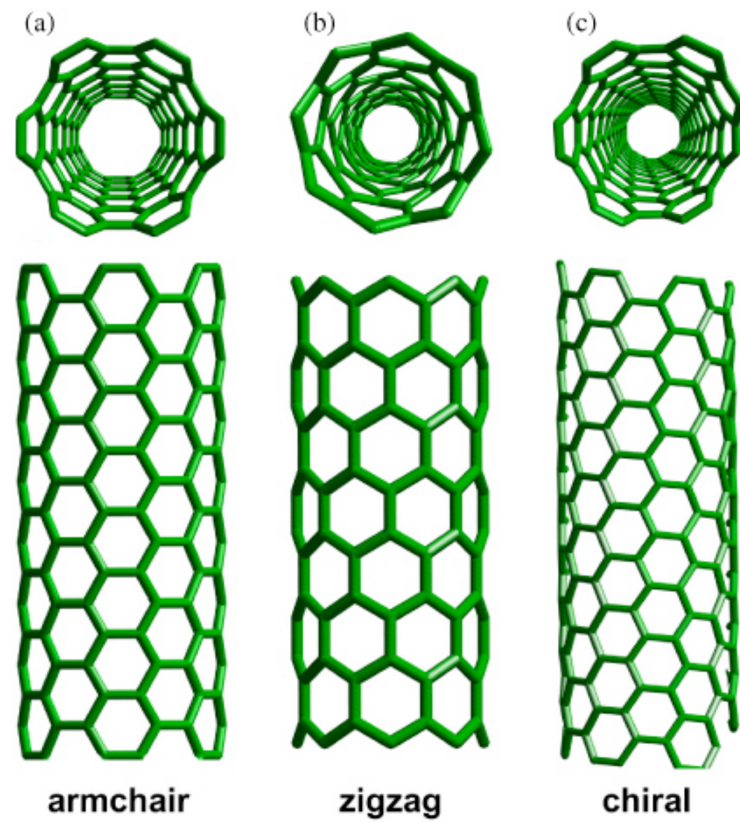
Pablo G. Caceres-Valencia
(*) The work was carried out by the author when he was on-leave from the University of Puerto Rico at Mayaguez, Puerto Rico PR 00681

Background



- Examples of the various structural forms of carbon
- a.） Three graphene sheets forming graphite；
- b.） Graphene；
- c.） Diamond



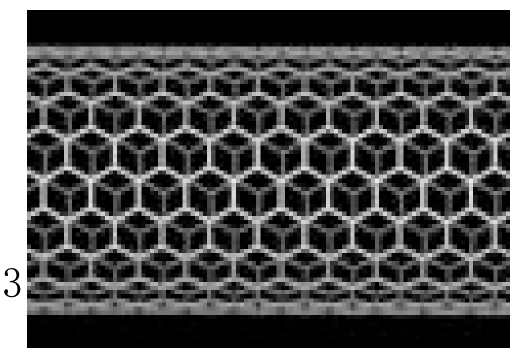


CNT's History

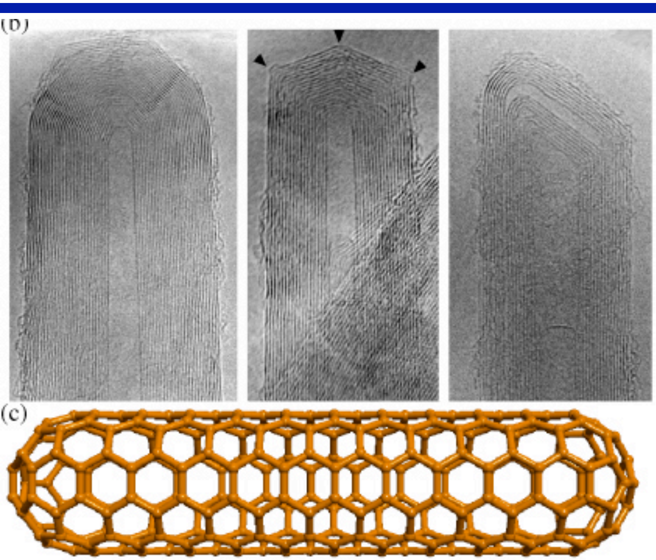
- Multi-walled Nanotubes 1991

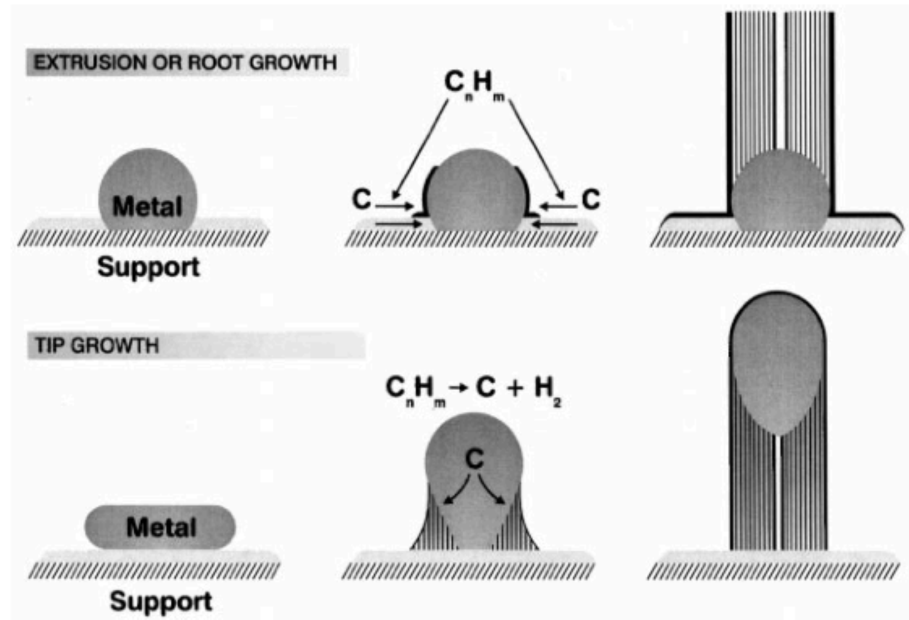
S. Iijima, Nature 354 (1991) 56

- Single-walled Nanotubes 1993



Background





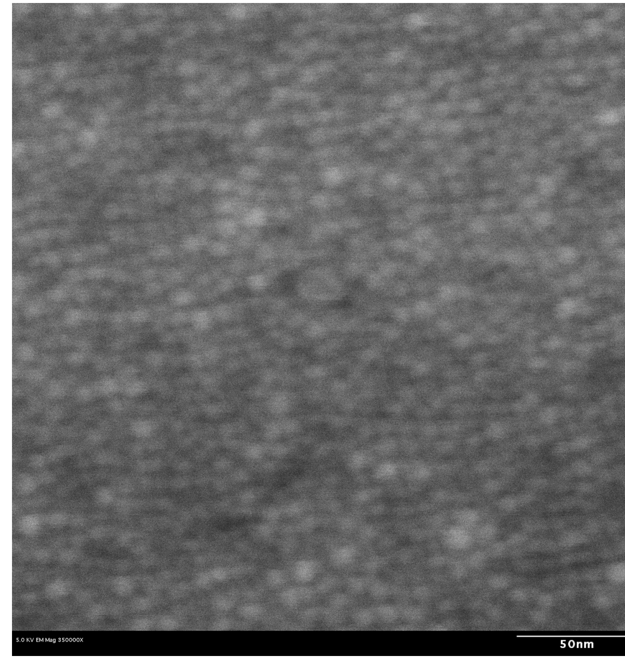
S.B. Sinnott et al., Chemical Physics Letters 315 (1999) 25–30

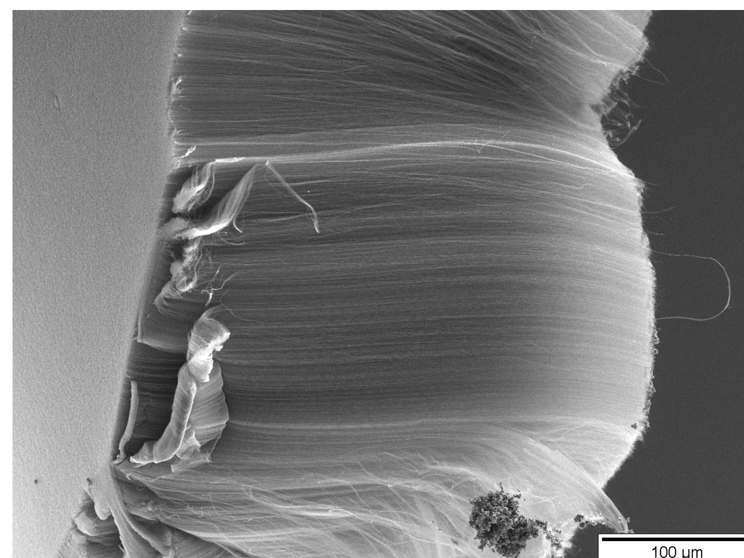
Background

Vertically aligned carbon nanotubes (VACNT's) of uniform diameter and length have the potential to be used as electro-chemical sensors[3, 4], electron field emitters[5-7], supercapacitors[8], via interconnects[9] and others.

The versatility of CNTs is based on the tuning of its properties to specific applications by controlling the diameter and chirality of the tubes. The former is directly related to the diameter of the catalyst particles[10-13].

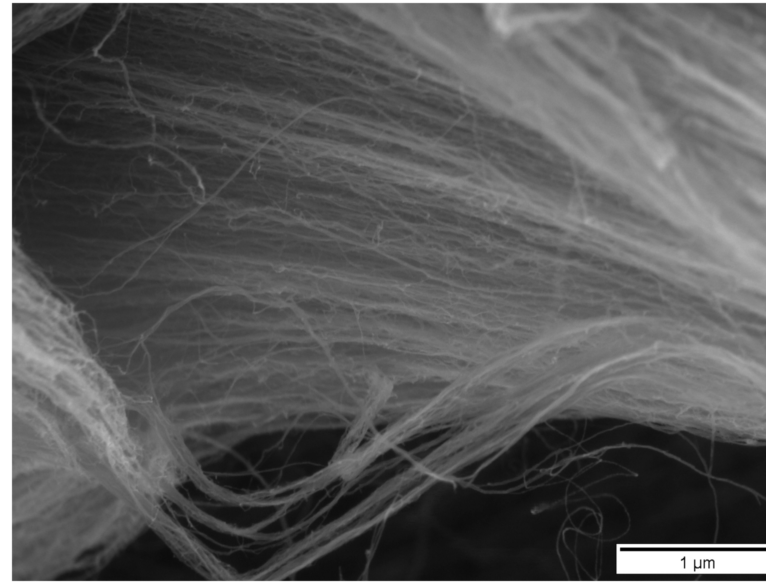
In thermal CVD, a transition metal catalyst such as Fe, Ni or Co is usually deposited onto a substrate as a uniform film using techniques such as sputtering or thermal evaporation. A subsequent annealing causes the catalyst film to fragment into nearly spherical particles with sizes that depends mainly on the initial thickness of the depositing layer, type of substrate and the annealing temperature.

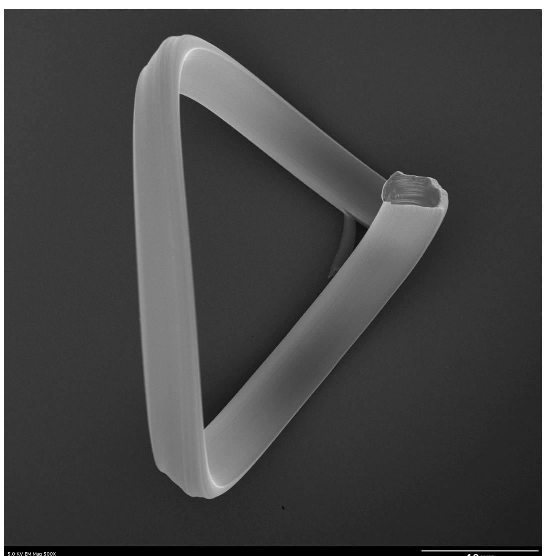


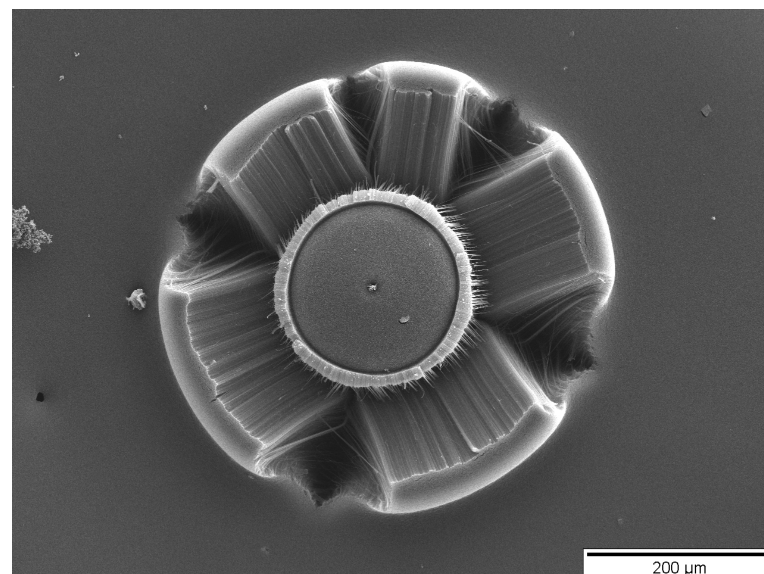


Background

The application of CNTs as interconnects requires the use of high CNT densities (10^{-2} to 10^{-1} particles/nm^2)[22, 30].
High CNT densities can only be achieved with high catalyst particle density by concomitantly increasing the catalyst area coverage and at the same time decreasing the particle size.
The highest achieved VACNT densities to date has been reported by Zhong et al[34] at $1/nm^2$ using controlled thin film thickness and a multilayer approach.

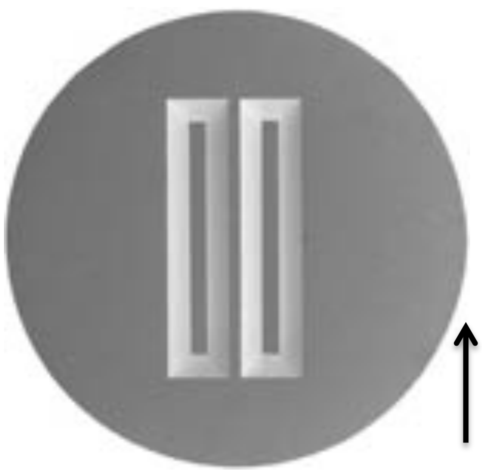


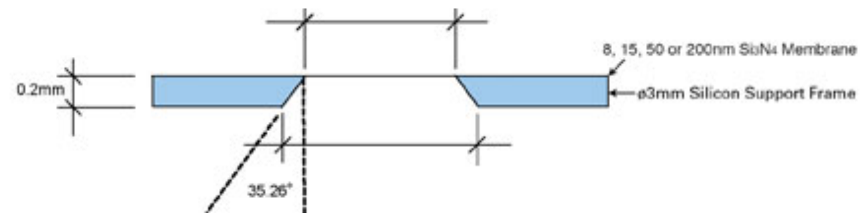




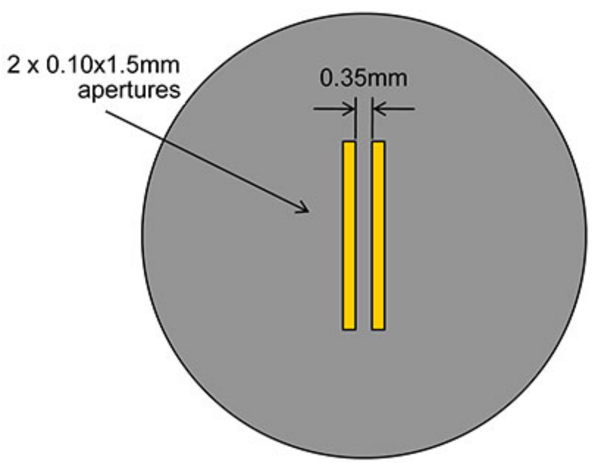
Experimental Techniques

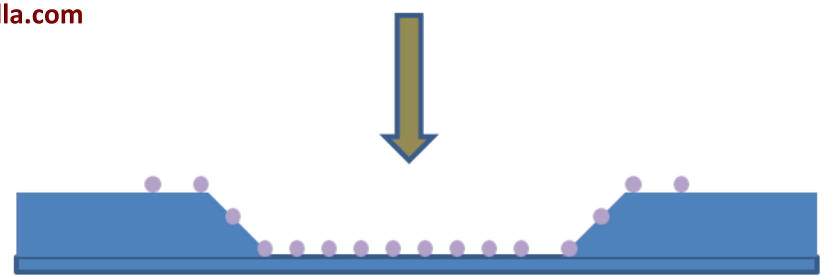
Electron transparent membranes of Si_3N_4 were acquired from Ted Pella for this investigation. All the membranes were sputtered with an iron film of gradient thickness. The maximum thickness at one end was 4.2nm.





Taken from www.tedpella.com





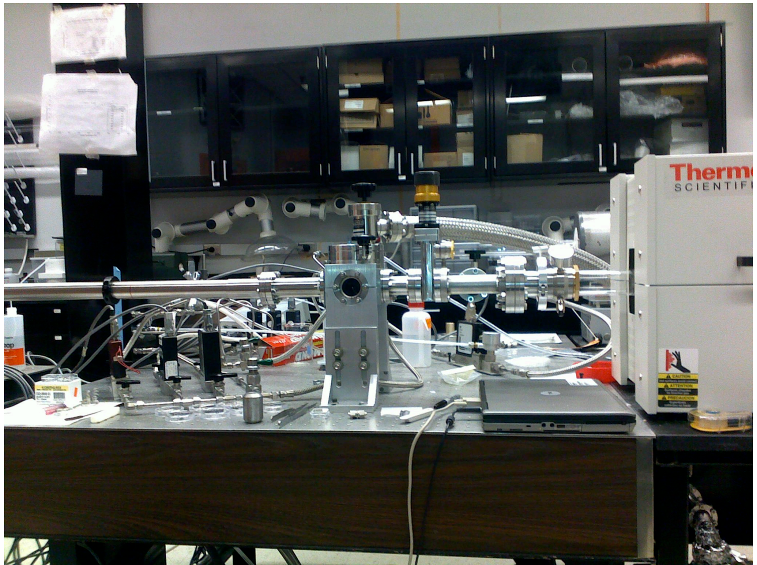
Experimental Techniques

a. For the studies on the SiO_2 and Al_2O_3 substrates, the Si_3N_4 membranes were sputtered with a 3nm uniform film of SiO_2 or Al_2O_3 prior to the Fe sputtering.

b. An ion-beam sputtering equipment and quartz and sapphire as target materials respectively were used for this purpose.

c. The membranes were subsequently annealed using a rapid insertion furnace kept at 675^{o}C under an atmosphere of flowing helium (200sccm) and hydrogen (250sccm). All samples were annealed for 16minutes.

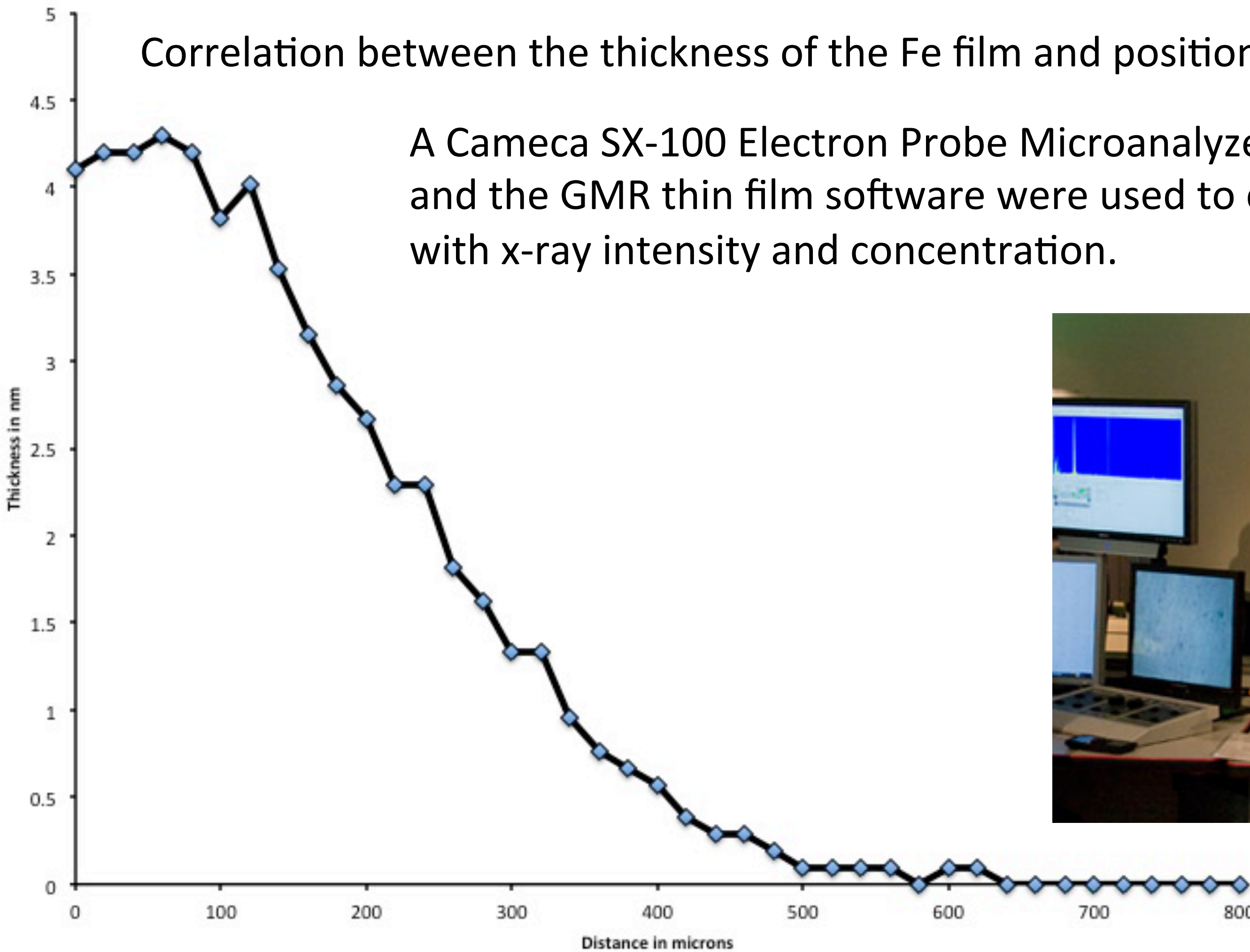
d. The annealed samples were observed under a Transmission Electron Microscope operating at 200kV.



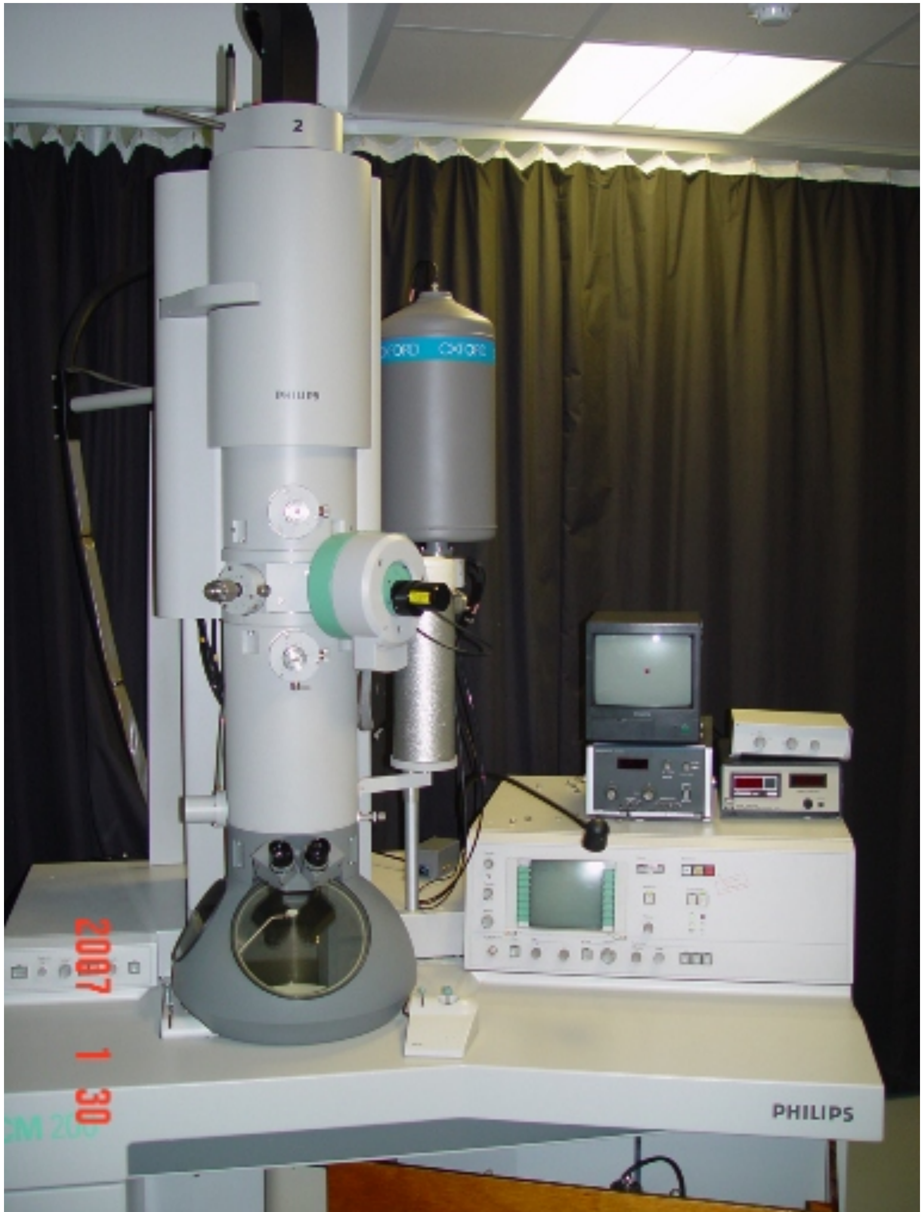
Catalyst thickness determined by position

Correlation between the thickness of the Fe film and position on the sample.

A Cameca SX-100 Electron Probe Microanalyzer operating at 15kV and the GMR thin film software were used to correlate position with x-ray intensity and concentration.



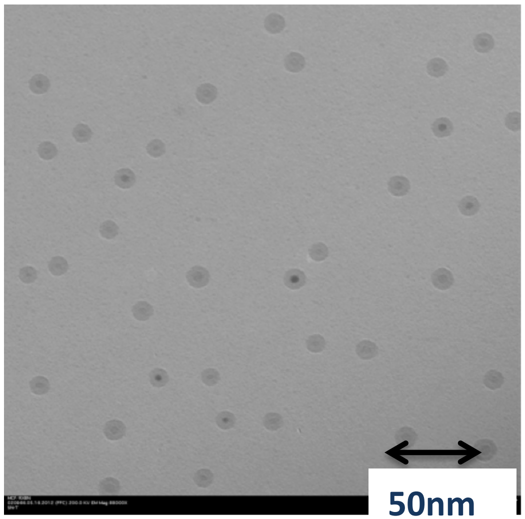
Transmission Electron Microscopy (TEM)



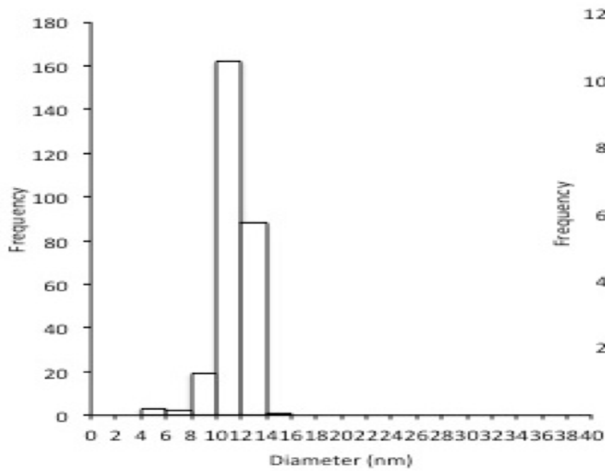
Acceleration voltage: Up to 200 kV
Point resolution: 0.19 nm
Line Resolution: 0.14nm
Side-entry computer controlled eucentric goniometer: ±EDX and 45º and ± 30º
EELS systems
Operation Modes: BF, DF, CBED, HRTEM, Microdiffraction, EDX and EELS

Post-heat treatment catalyst size vs. substrate 0.3 nm

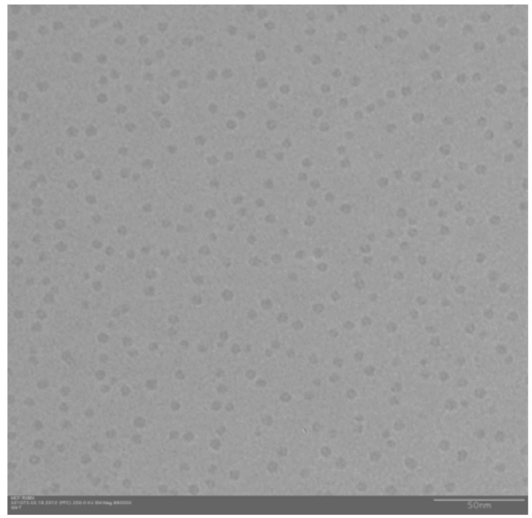
Si_3N_4



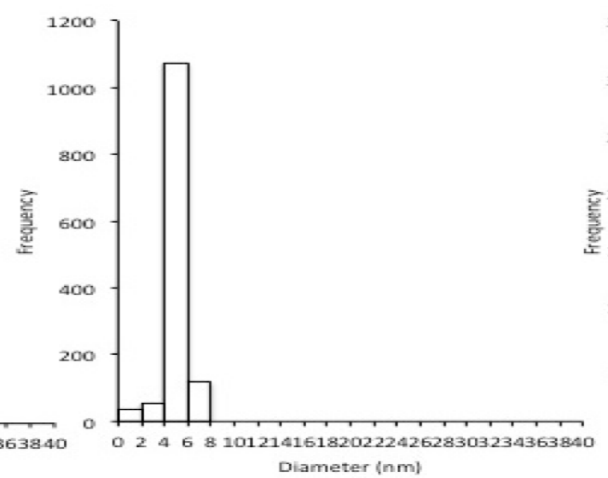
(a) 0.3nm



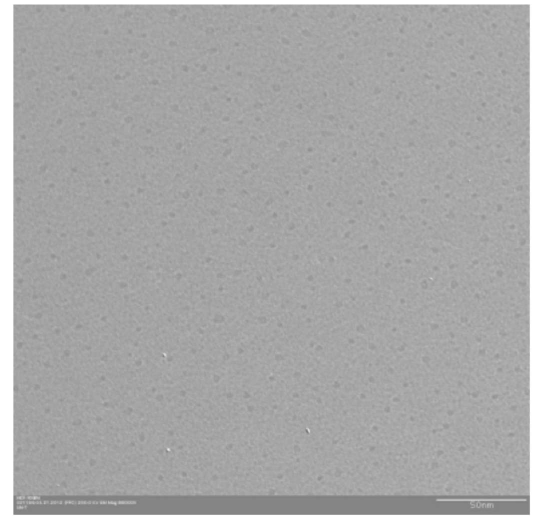
Al_2O_3



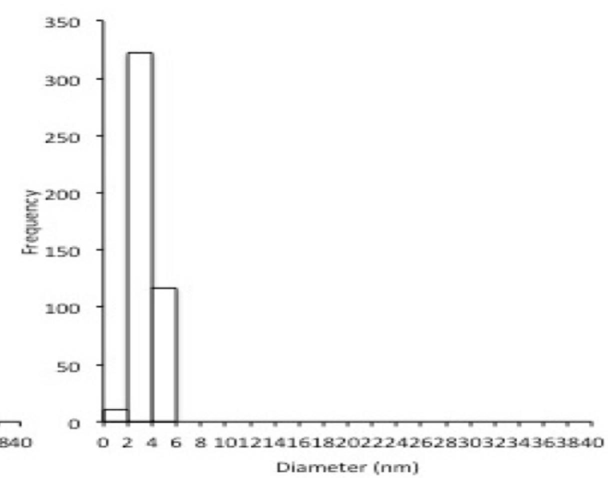
(b) 0.3nm



SiO_2-IBS

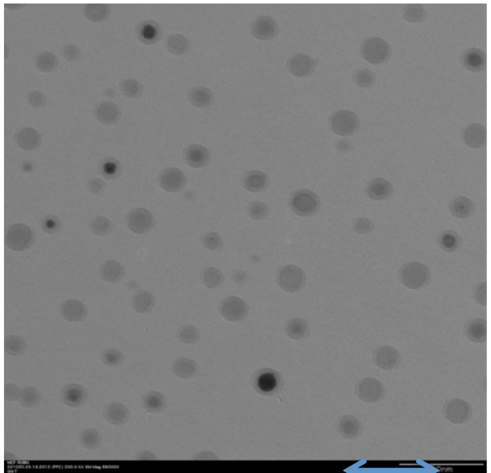


(c) 0.33nm

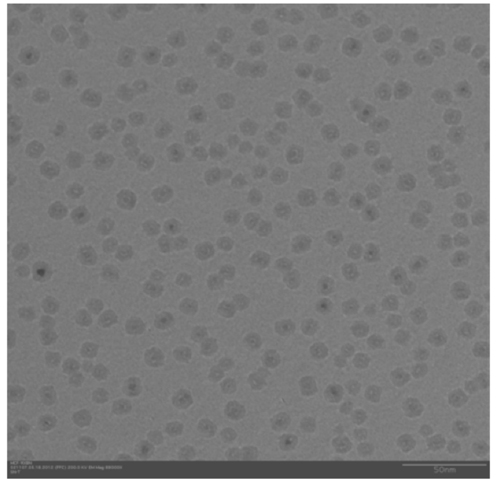


Post-heat treatment catalyst size vs. substrate 0.6 nm

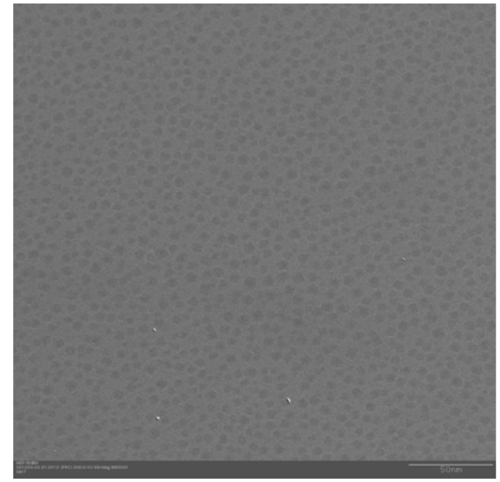
Si_3N_4 Al_2O_3 SiO_2-IBS



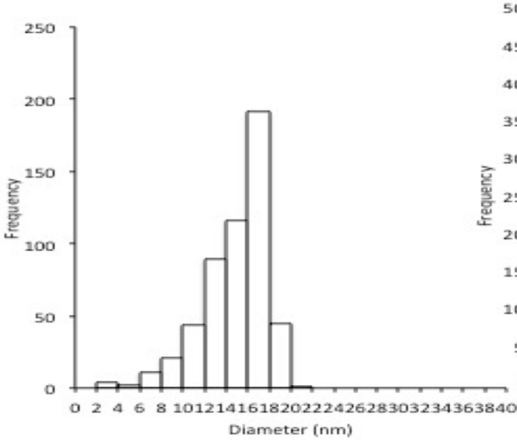
(d) 0.6nm 50nm

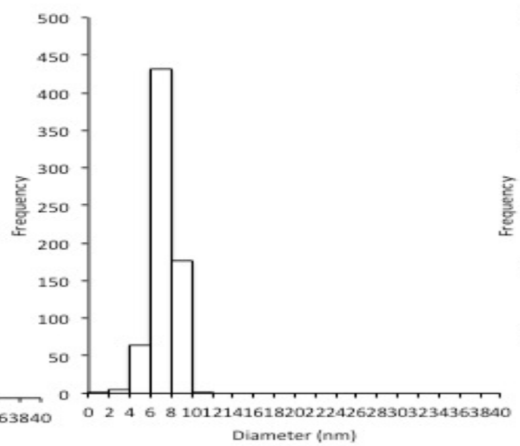


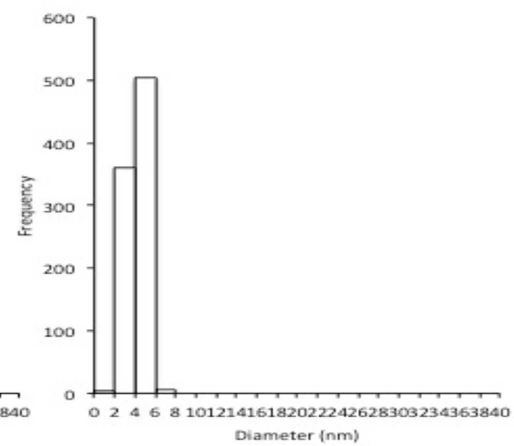
(e) 0.6nm



(f) 0.7nm

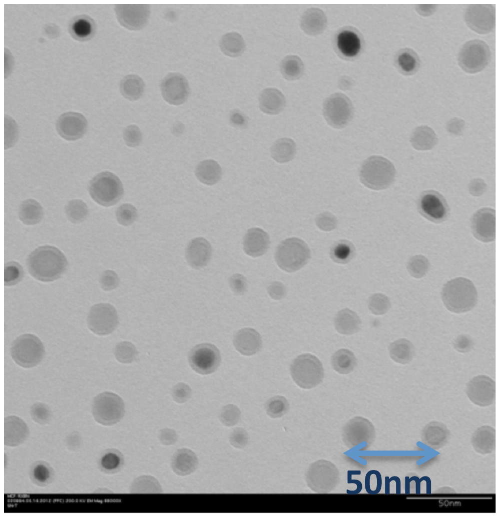






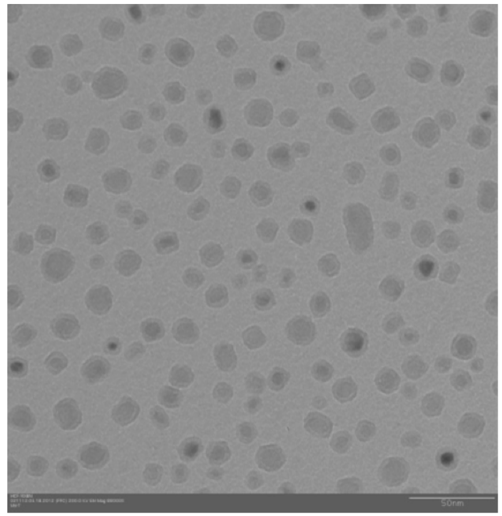
Post-heat treatment catalyst size vs. substrate 1.2 nm

Si_3N_4



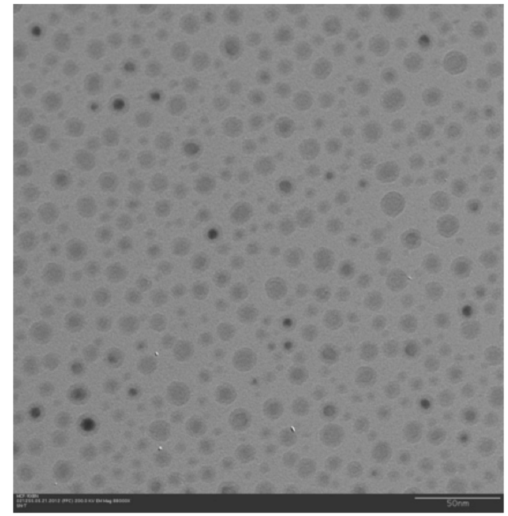
(g) 1.2nm

Al_2O_3

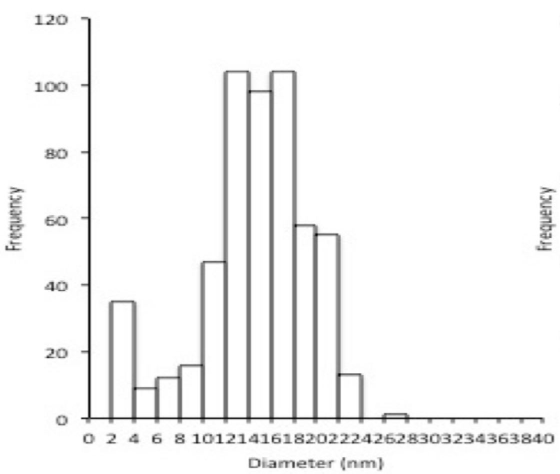


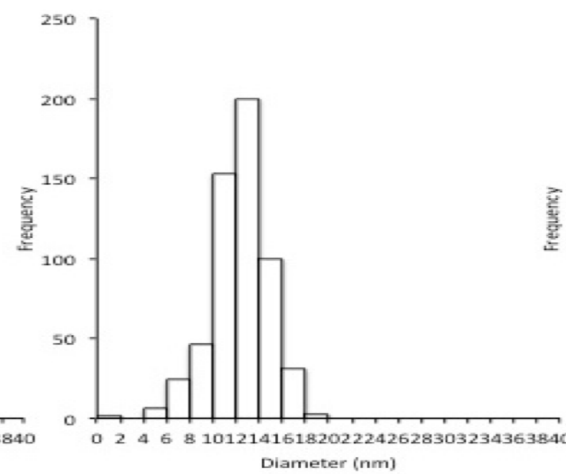
(h) 1.2nm

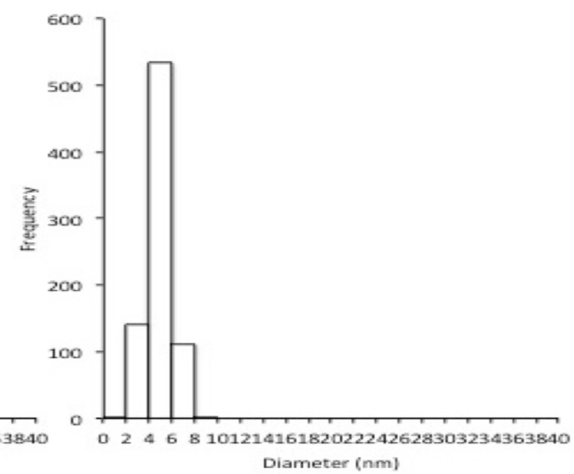
SiO_2-IBS



(i) 1.3nm

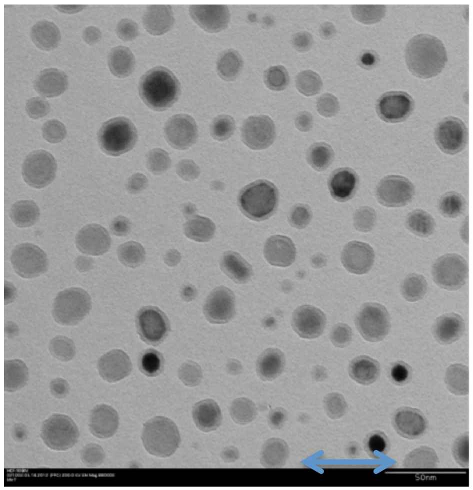






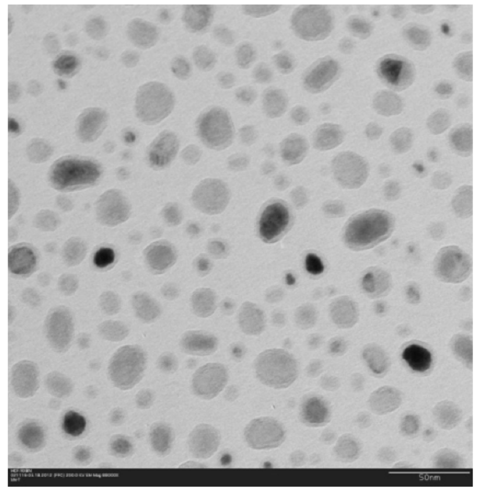
Post-heat treatment catalyst size vs. substrate 2.6 nm

Si_3N_4



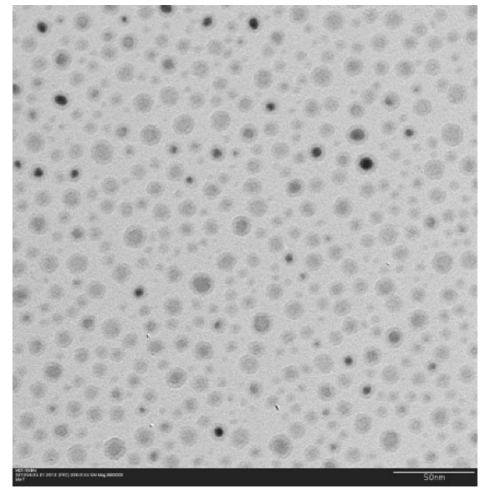
(j) 2.3nm 50nm

Al_2O_3

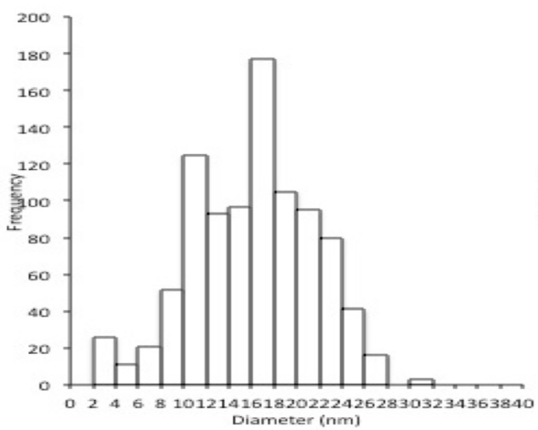


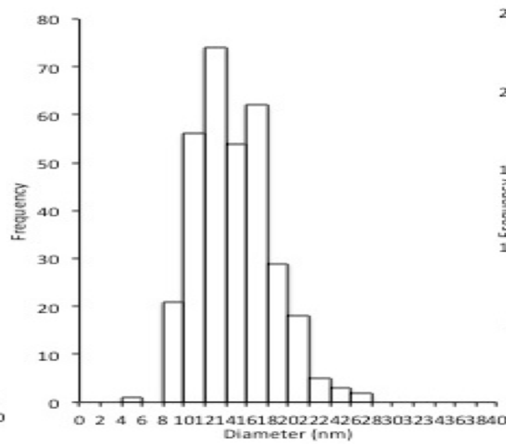
(k) 2.6nm

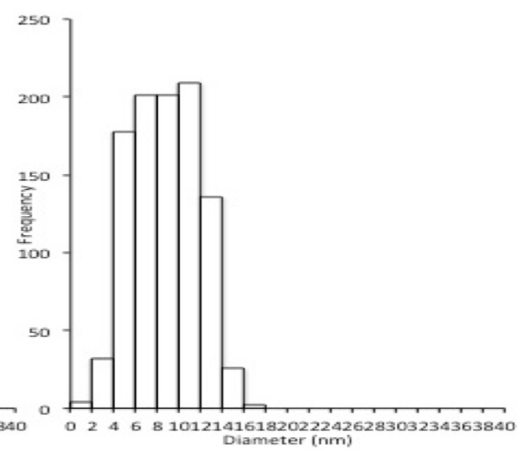
SiO_2-IBS



(l) 2.6nm

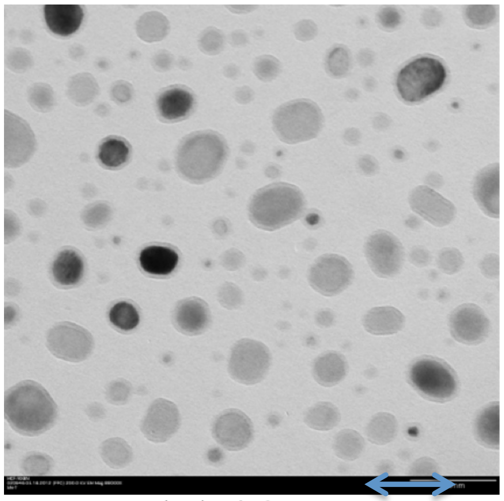






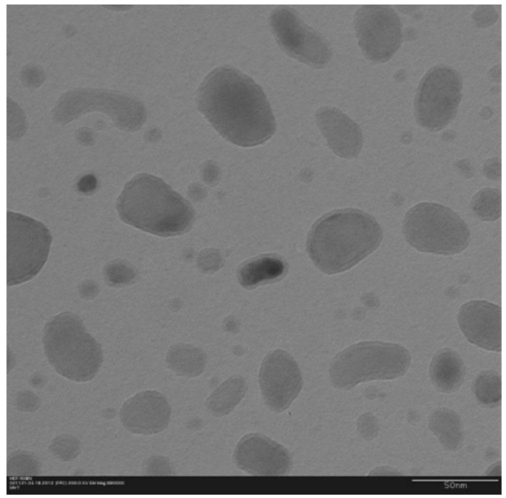
Post-heat treatment catalyst size vs. substrate 4.2 nm

Si_3N_4



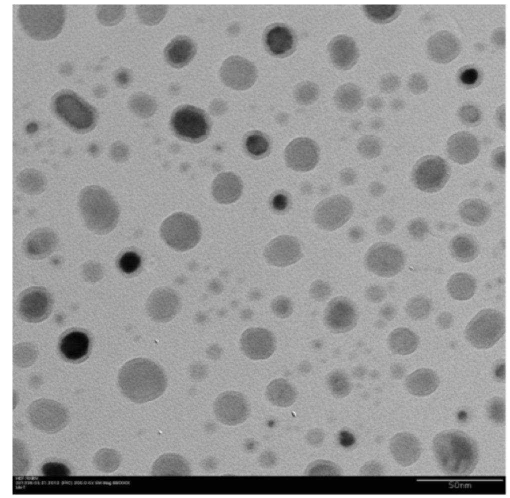
(m) 4.2nm

Al_2O_3

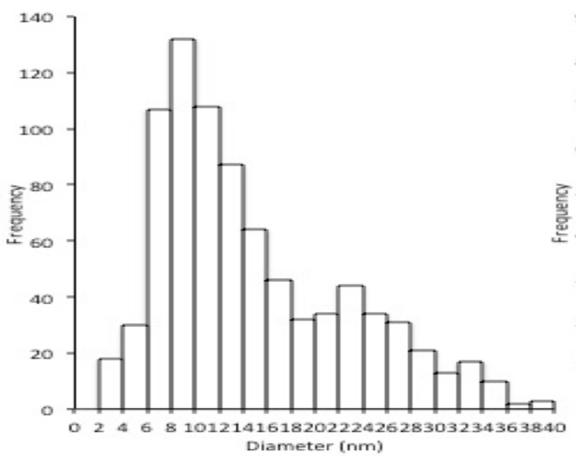


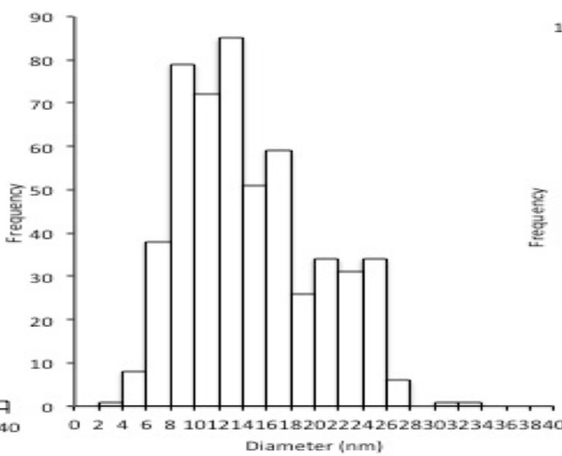
(n) 4.2nm

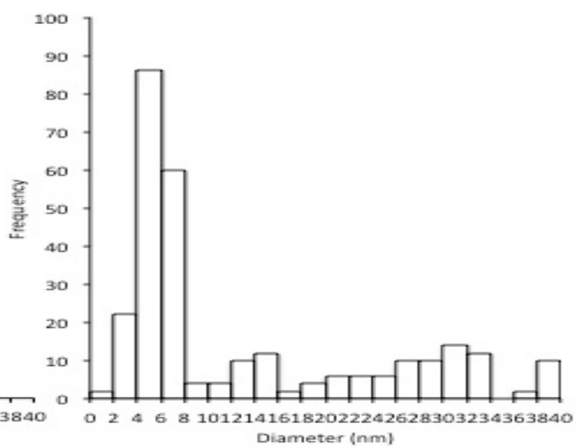
SiO_2-IBS



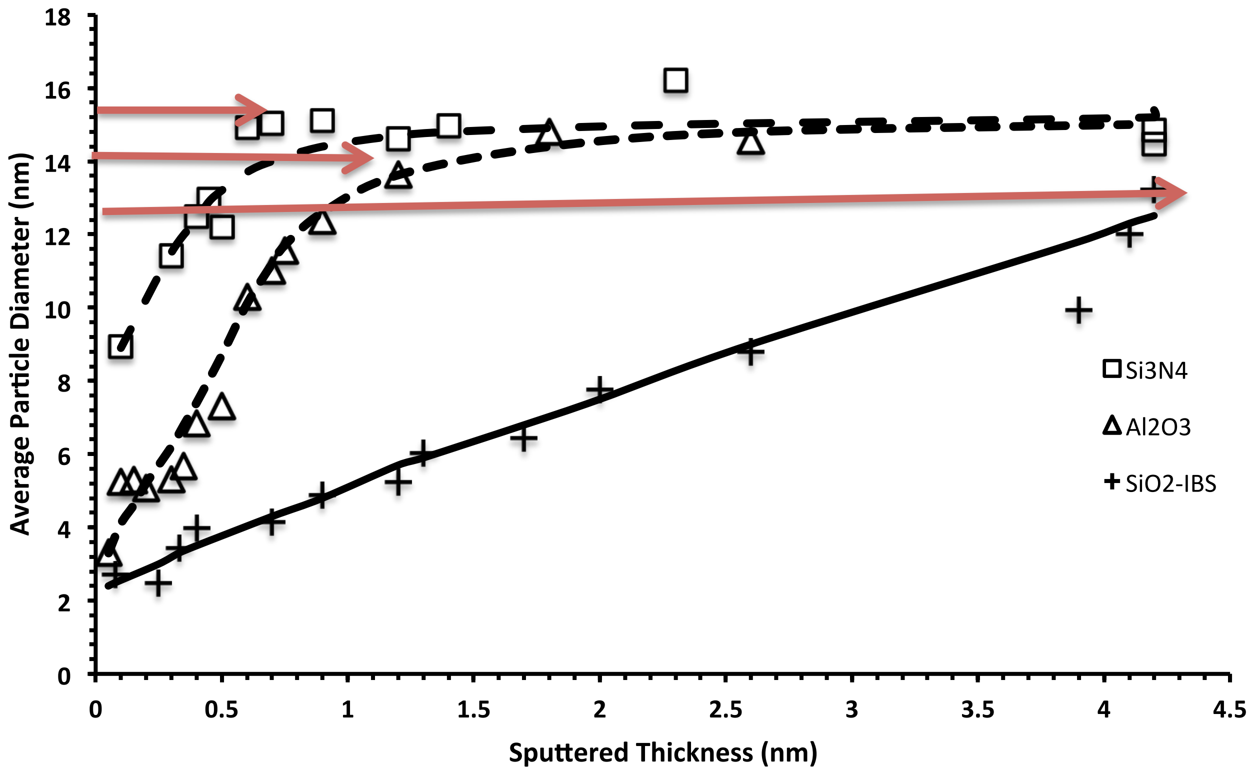
(o) 4.2nm







Post-heat treatment catalyst size vs. substrate

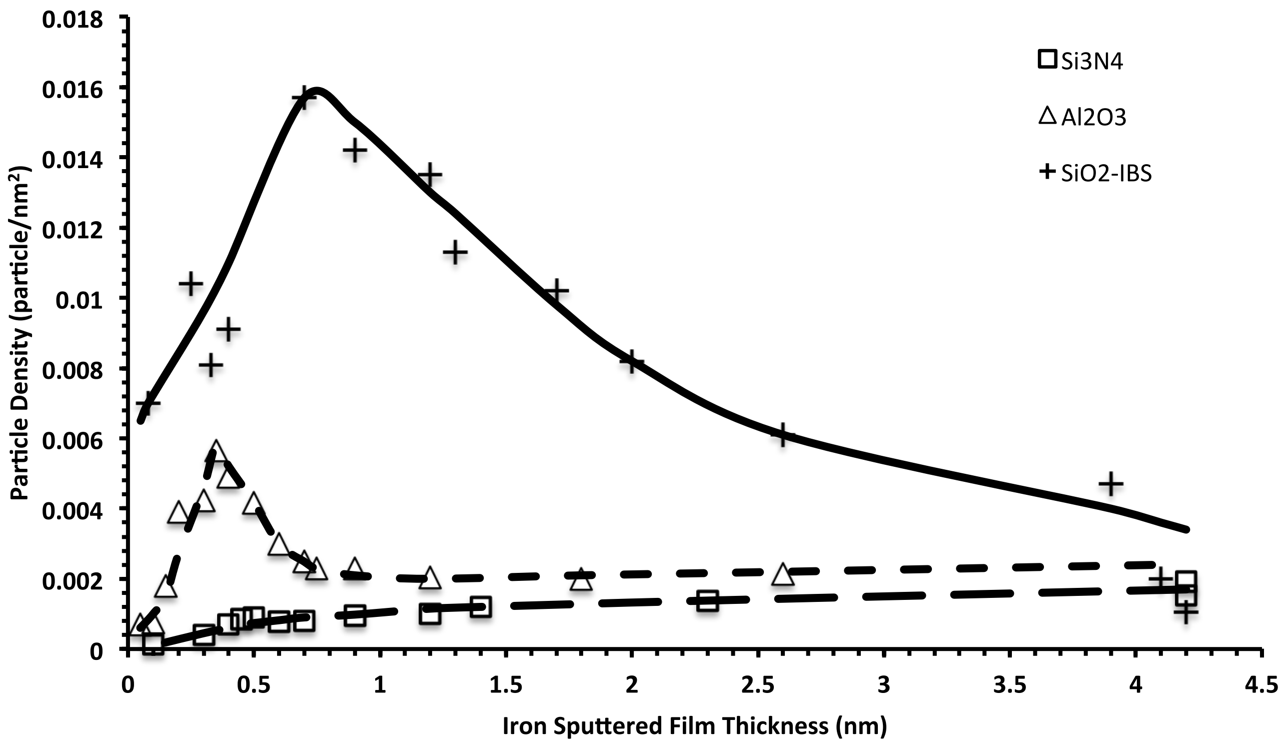


In Si_3N_4 substrate the average particle size of the catalyst is always large, even at very small sputtering film thickness (e.g. at 1.2nm of film thickness a 15nm particle develops).

In Al_2O_3 or SiO_2-IBS the average particle size obtained at very small thickness starts at 3.3 and 2.6nm respectively.

The rate of growth of the average diameter with film thickness for these substrates (as determined by the initial slope of the graphs) is faster in Si_3N_4 and Al_2O_3.

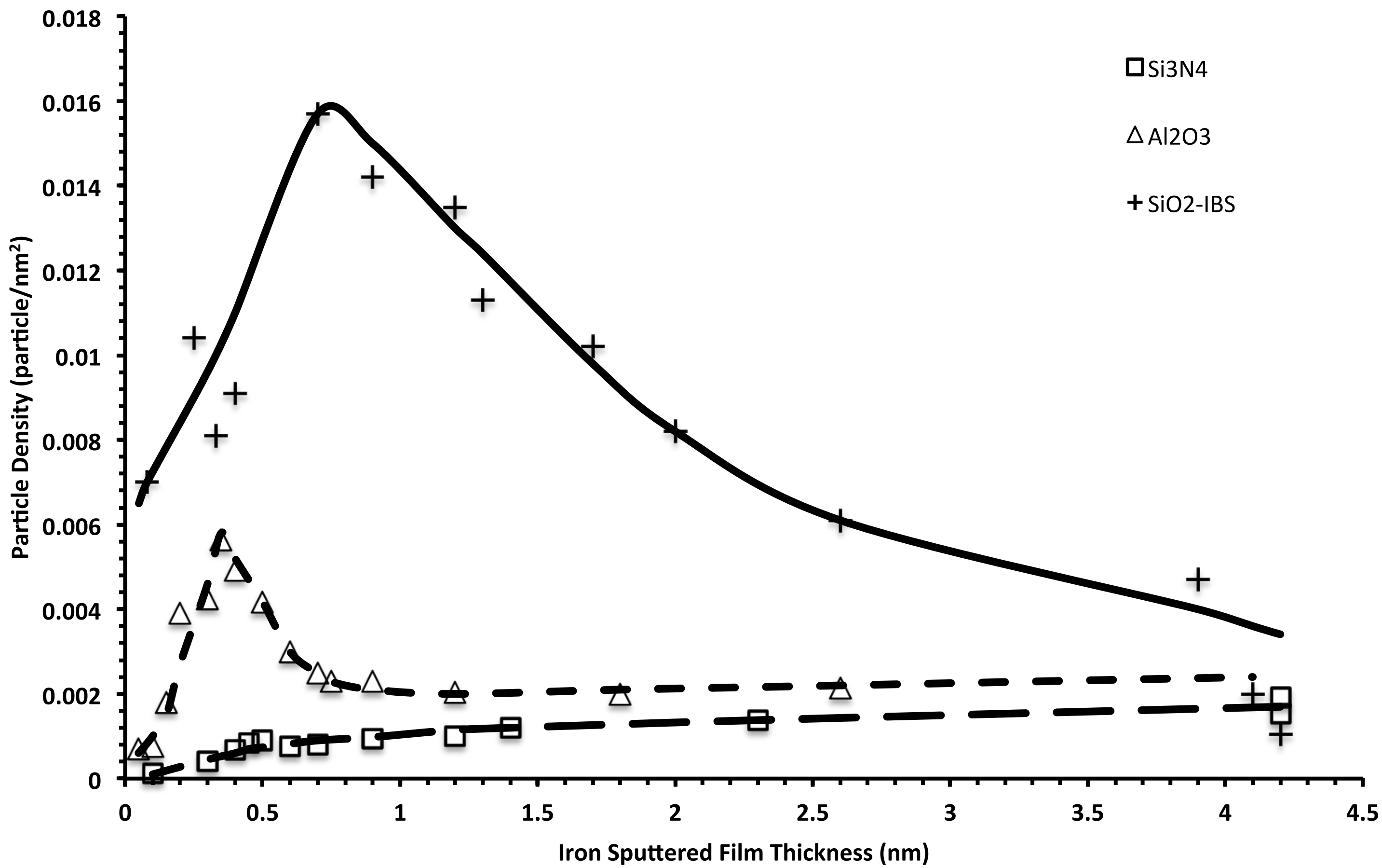
Particle Number Density vs. Catalyst Thickness



The Si_3N_4 has low particle densities for all the sputtered film thicknesses.
Particle densities of 10 (in 10^{-4} nm^{-2}) are reached at thickness of 0.5nm with an average particle diameter of 14nm and a wide PSD.
These particle density values are 10 times higher than the values obtained by Sigmore et al for ill formed carpets.

M.A. Signore, A. Rizzo, R. Rossi, E. Piscopiello, T. Di Luccio, L. Capodieci, T. Dikonimos, R. Giorgi; *Role of iron catalyst particles density in the growth of forest-like carbon nanotubes*; Diamond & Related Materials 17 (2008) 1936–1942

Particle Number Density vs. Catalyst Thickness

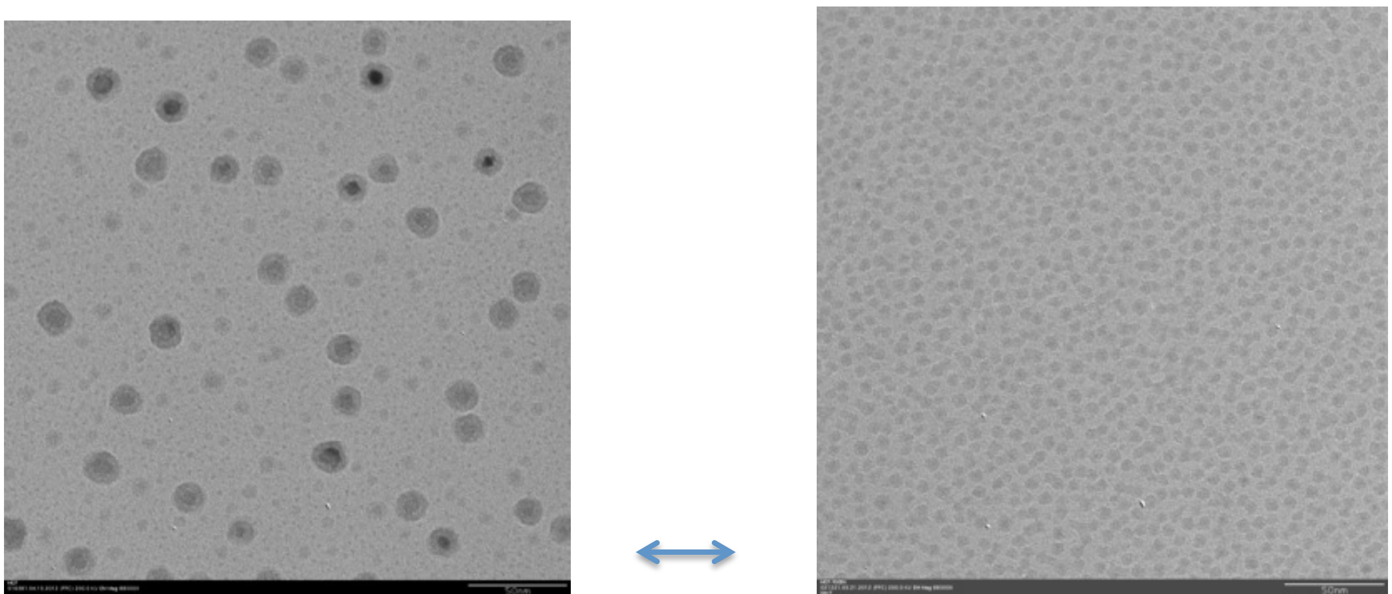


In Al_2O_3, ultra high density CNTs reaching $6x10^{-3}$ nm^{-2} can be formed with a 0.4nm thickness and an average diameter between 4-6nm.

Particle densities of $1.6x10^{-2}$ nm^{-2} are reached at thickness of 0.8nm with an average particle diameter of 3-4nm in the SiO_2-IBS substrate.

Catalyst Evolution on Thermal vs. IBS SiO_2

As the most widely used SiO_2 substrate is produced thermally, a SiO_2-thermal substrate was used to compare our TEM results. This comparison was also extended to a solid substrate (non-electron transparent) of Si/SiO_2 wafer.



50nm

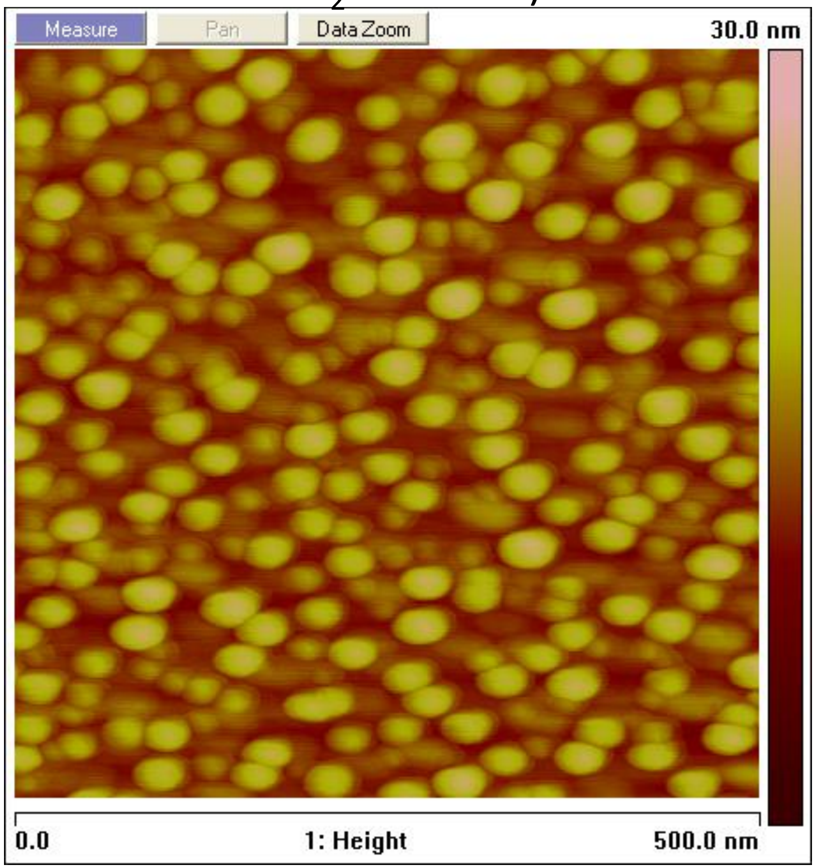
(a) 1.2nm SiO_2-Thermal (b) 1.2nm SiO_2-IBS

TEM images of catalyst on the SiO_2-thermal and SiO_2-IBS were compared for an initial Fe thickness of 1.2nm.
The SiO_2-thermal substrate behaves similarly to the Si_3N_4 substrate, that is, with a high initial catalyst particle size.

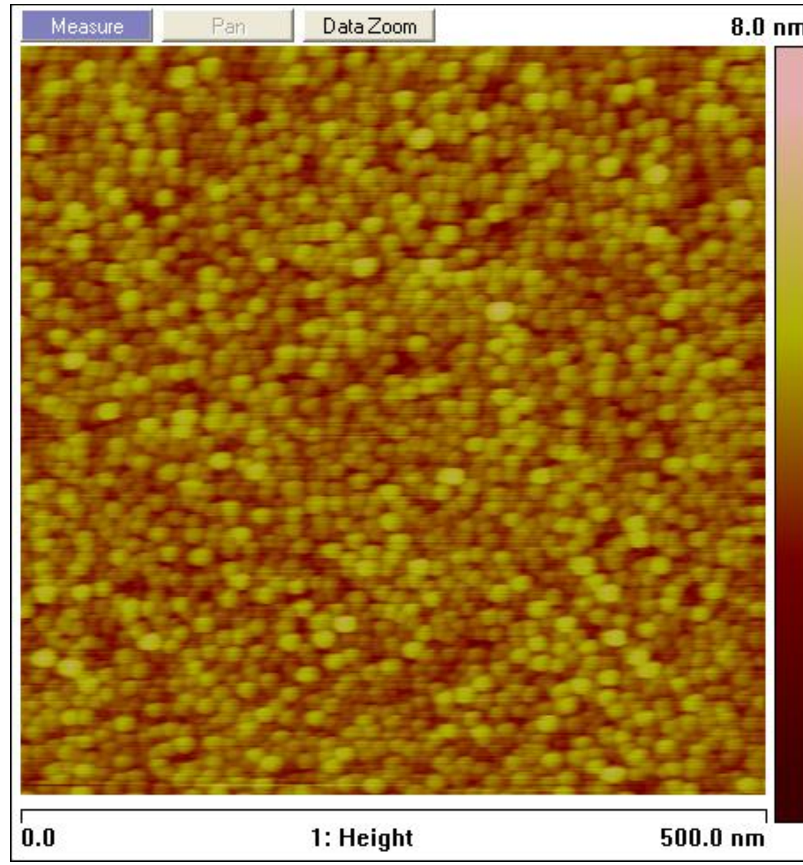
AFM Comparison Between Thermal SiO_2 and IBS- SiO_2 substrates

Fe-1.2nm + 675°C for 16m (He +H_2)

On Si wafer with a thermally oxidized film SiO_2 – 254nm)

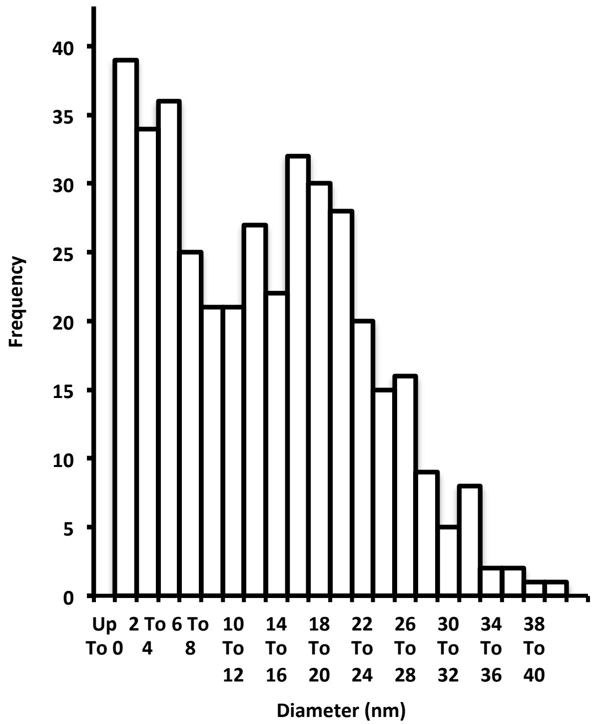


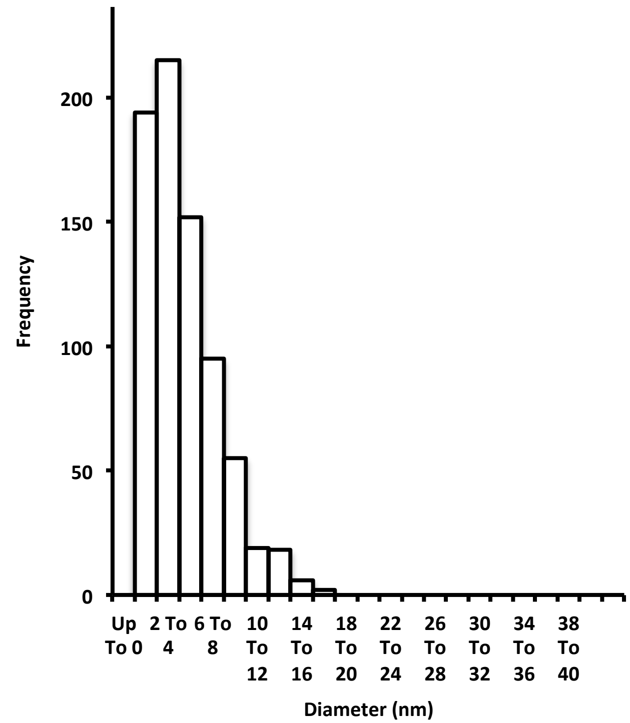
On Si + SiO_2 (254nm) + 3nm SiO_2 IBS



AFM Comparison Between Thermal SiO_2 and IBS- SiO_2 substrates

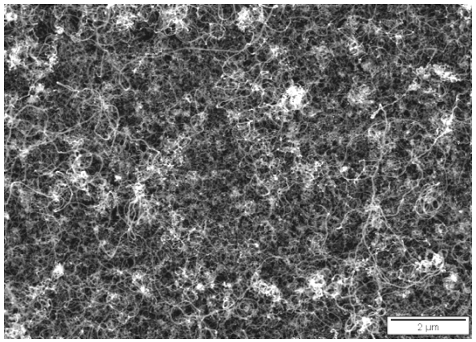
PSD from AFM micrographs of iron on SiO_2-thermal and SiO_2-IBS



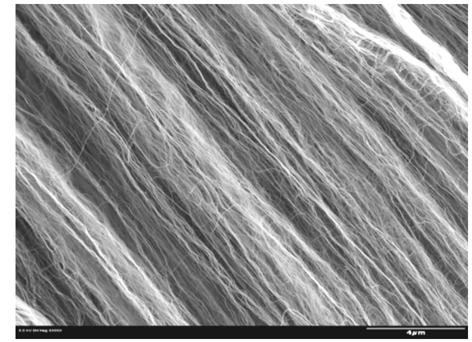


The PSDs obtained from the AFM images indicate that average catalyst particles are 14nm for SiO_2-thermal and 4nm for SiO_2-IBS that is, the Fe particles have grown 40 times more on the thermally oxidized substrate.
AFM results are similar to the TEM results.
The AFM results corroborate the suggestion that the Fe particle growth on SiO_2-thermal is similar to the Si_3N_4 substrate.

CNT Synthesis: Comparison between SiO_2-thermal and SiO_2-IBS – 0.6nm



After annealing at 675°C for 16m, synthesis was carried out at 775°C-16m

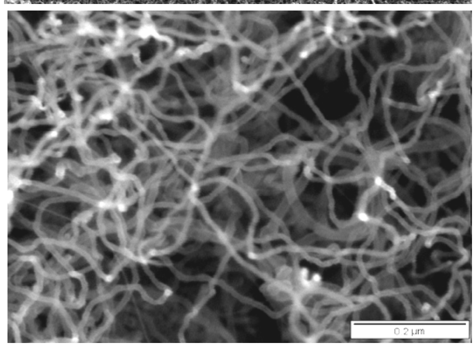


4mm

Non-aligned CNTs

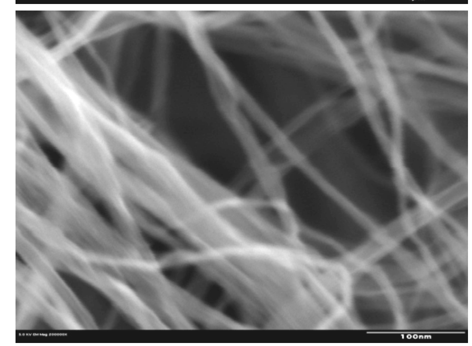
2mm

Aligned CNTs
Carpet height = 500microns

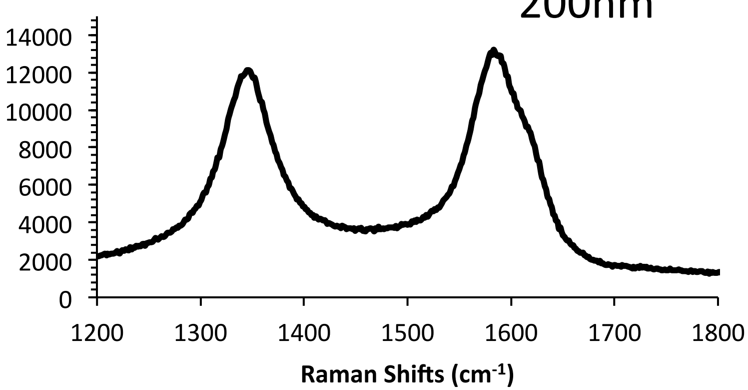


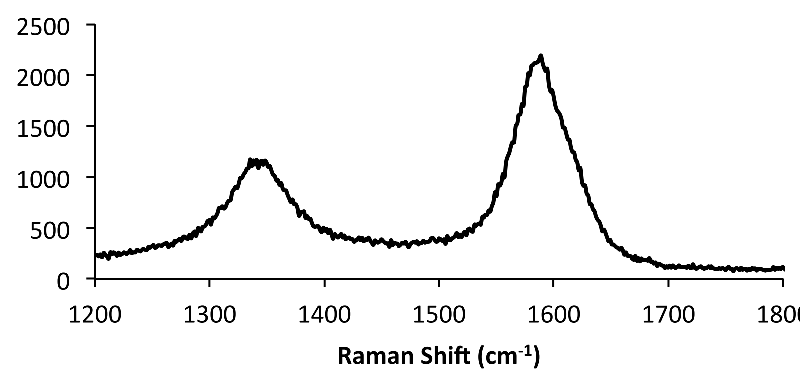
At this high synthesis temperature, OR takes place in SiO_2.

200nm

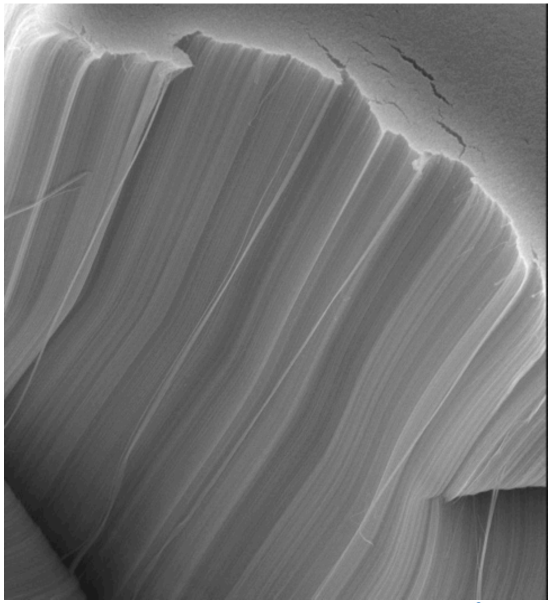


100nm



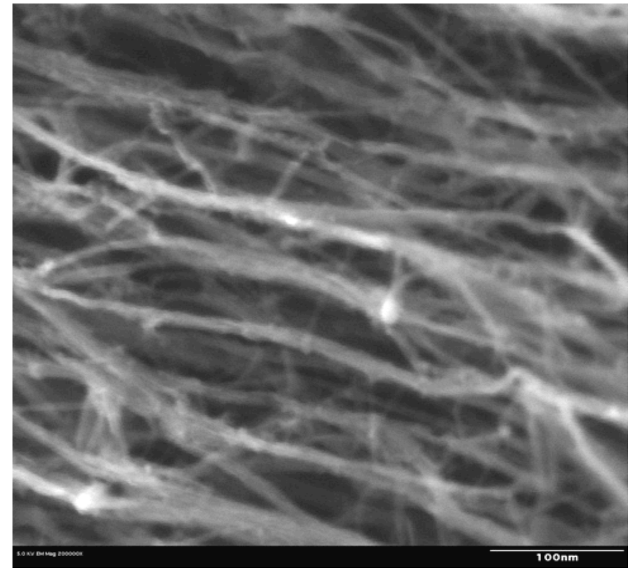


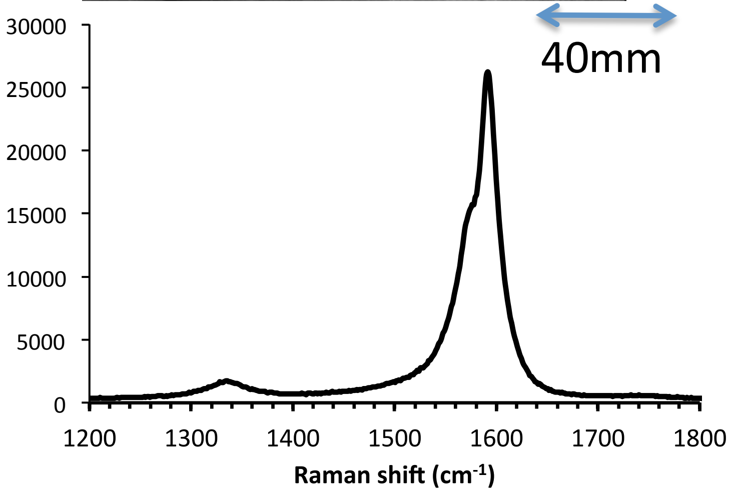
Synthesis of CNTs on Al_2O_3-IBS 0.6nm

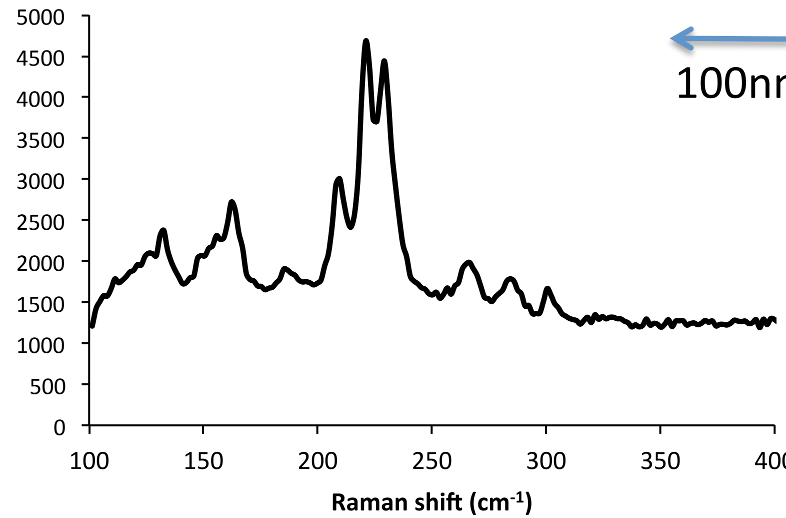


Aligned CNTs
Carpet height = 750microns

At this high synthesis temperature, OR is small in Al_2O_3.

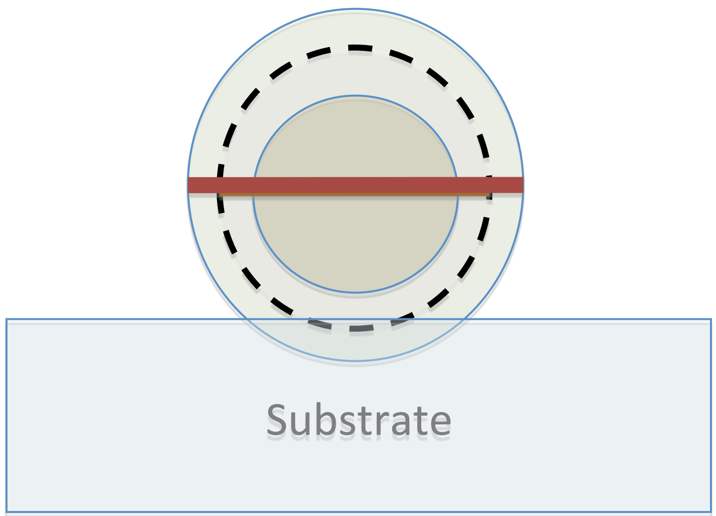




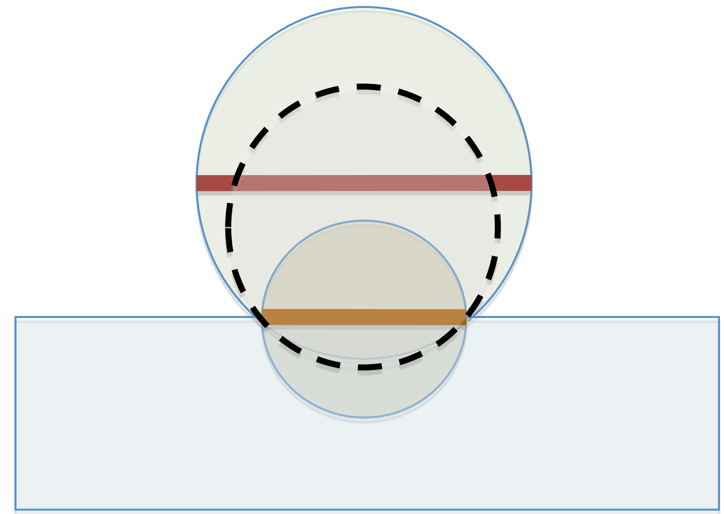


Contact Angle Measurements

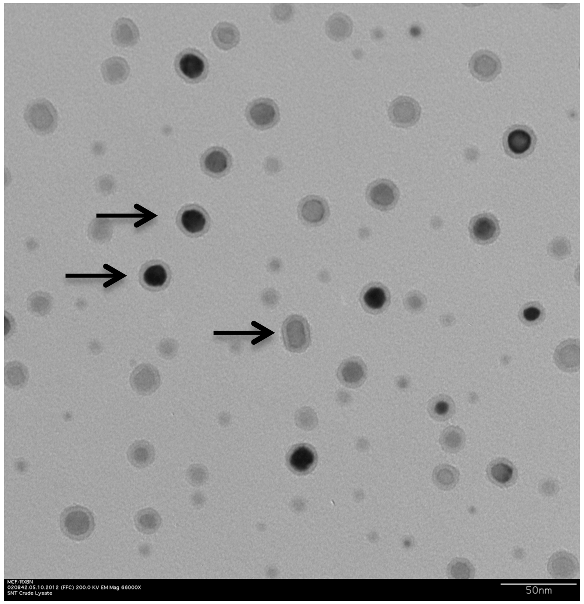
Core Shell:

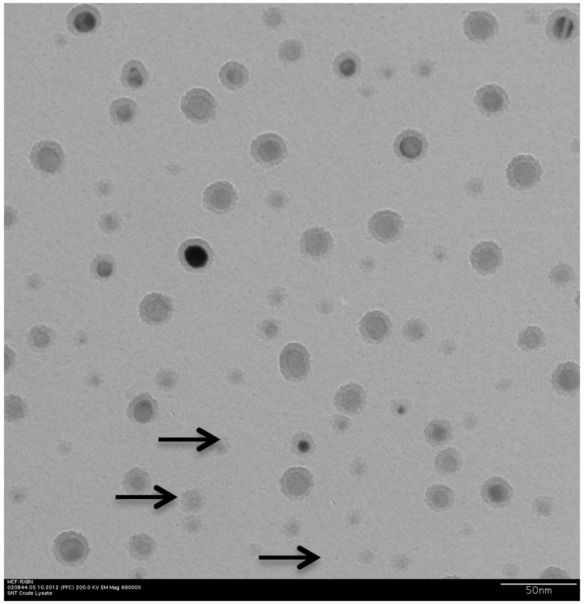


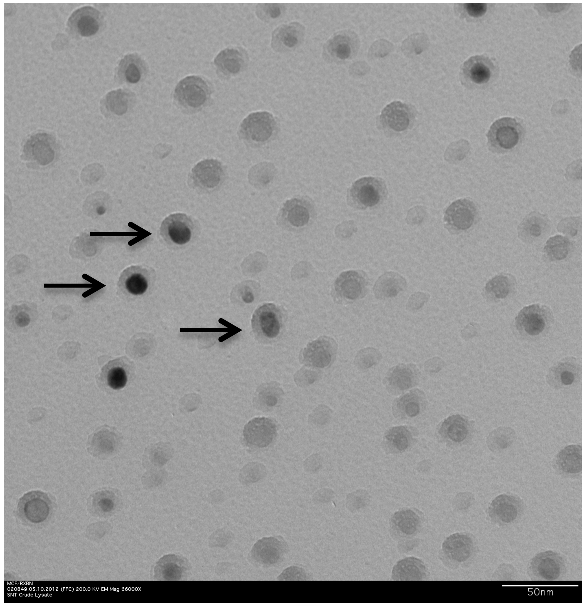
Attached to Substrate

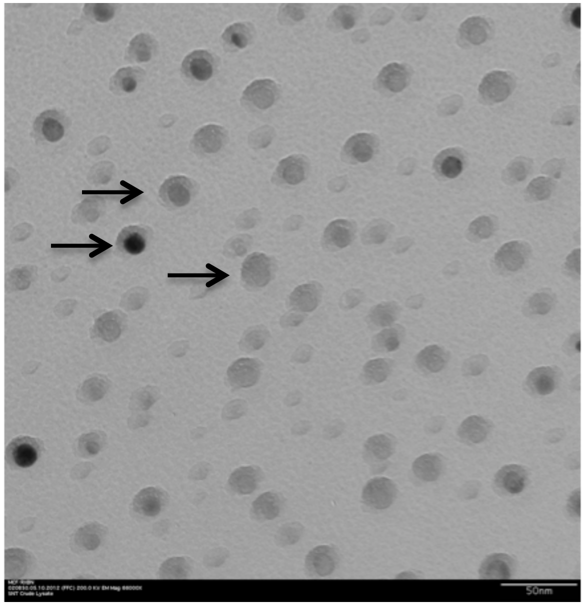


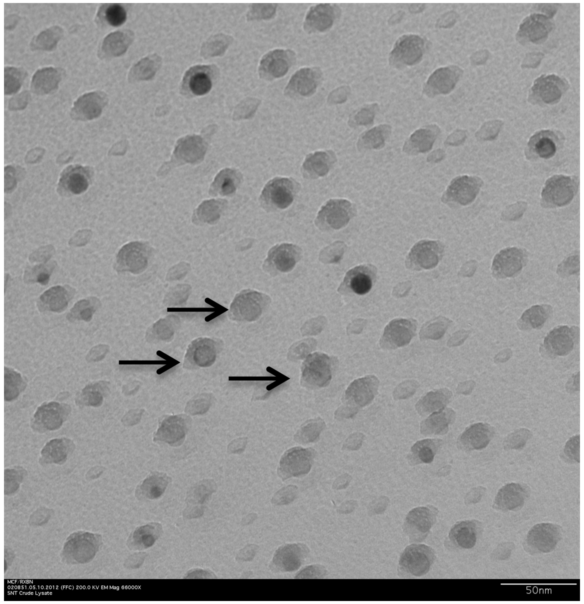
Tilting Experiments











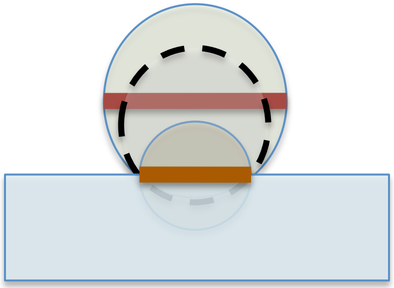


Figure. It shows the same area after different tilting angle. (a) 0 ; (b) 18 ; (c) 36 ; (d) 45 and (e) 54 degrees. A schematic of the position of the metallic core is given in (f).

Conclusions

a. The average particle size diameter measurements show two different linear behaviors. At small film thickness range the linear behavior is dominated by the catalyst-support interaction, while in the large film thickness range their behavior is independent of the type of substrate.
b. The growth of VACNTs is not solely controlled by a minimum areal particle density. The size of the particles and particularly a large spread of the PSD will induce uneven CNT growth and hence the formation of non-aligned CNT's.
c. The catalyst-substrate interaction is strongly influenced by the processing conditions of the substrate. When comparing thermal or IBS produced SiO_2 substrates, the latter showed to strongly enhance the nucleation of the Fe particles and reduce coalescence or the rate of the particle growth with increasing film thickness.
d. The optimum conditions for the growth of ultra-high density CNT can be obtained by controlling the catalyst-substrate interaction and by determining the effect of film thickness on the particle size and areal particle density,.
e. These parameters can also be tailored to produce ultra high density VACNTs with a large percentage of SWCNTs. For such, the effect of the synthesis temperature needs also to be tailored for each type of substrate.