Doping and growth of carbon nano-structures -a next generation material

By
Malay Jana

Under the supervision of
Prof. Subrata Ray & Prof. Anjan Sil

Department of Metallurgical & Materials Engineering
Indian Institute of Technology Roorkee

Outline

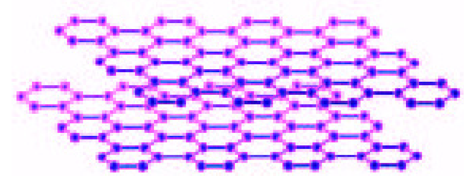
- History
- Some motivating properties
- Applications
- Some results with discussion
- Conclusions

History of carbon nano-structures

- In **1970s, Morinobu Endo** prepared the first carbon filament of nanometer dimensions
- **Richard E. Smalley** (**Nobel Prize winning in 1996**) discovered the **buckyball (C60)** and other **fullerenes (1985)**
- In **1991, Sumio Iijima** had been using TEM to analyze new type of finite carbon structure, that is composed of **needle-like tubes**

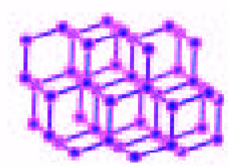
Why do Carbon Nanotubes form?

Carbon → Graphite (Ambient conditions)
sp^2 hybridization: planar



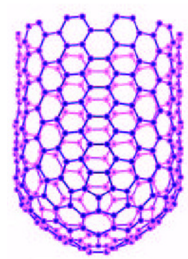
graphite

Carbon → Diamond (High temperature and pressure)
sp^3 hybridization: cubic

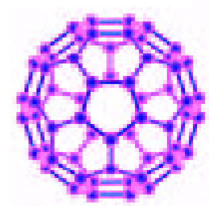


diamond

Carbon → **Nanotube/Fullerene (certain growth conditions)**
sp^2 + sp^3 character: cylindrical

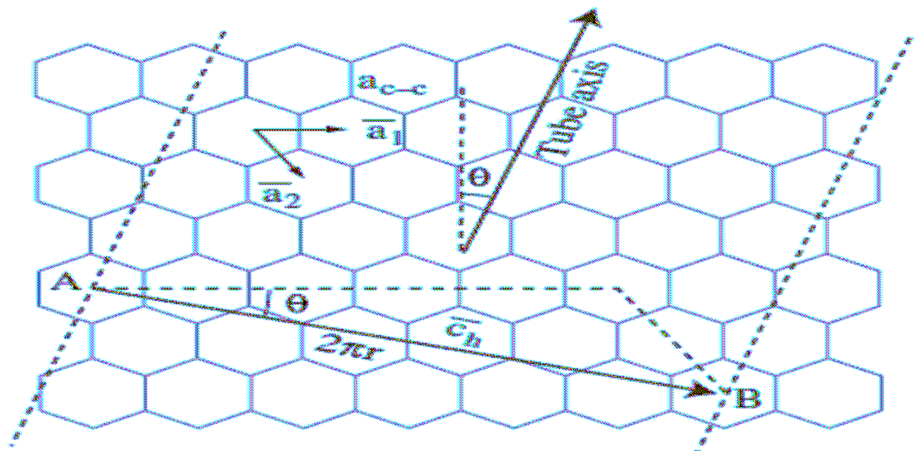


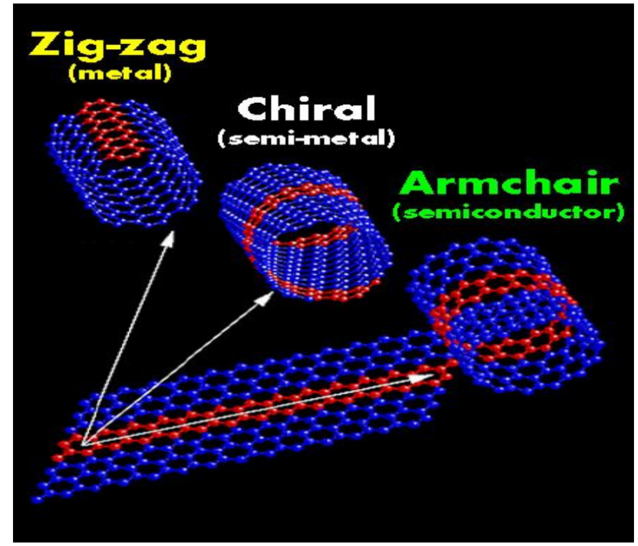
(10, 10) nanotube



C_{60} fullerene

Iijima S., *Nature* 354, 56 (1991); Smalley R. E. et al., *Science* 273, 483 (1996)



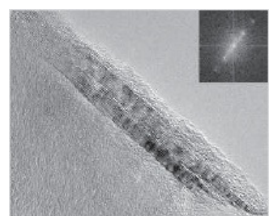


The chirality, or "twist" of the nanotube

The electronic properties of nanotubes are directly dependent on the chiral vector

Damascas blades famous for their remarkable strength and sharpness

CNTs inside damascas blade ➡



Nature, 2006

Young's modulus	SWCNT	1054 GPa
	MWCNT	1200 GPa
Tensile strength	SWCNT	~60 GPa
	MWCNT	~150 GPa
Current density	10^9 A/cm^2	
Electric conductivity	1.5 kW-cm	
Thermal conductivity	2000 W/m.K	

Popov Valentin N., *Mater Sc and Engg. R.* 43, 61 (2004)

Common applications

Suggesting a new generation **high strength & light weight material** for **current & future green technologies**

- Structural composites (Boeing 787, steel, buildings,etc)
- Energy storage
- Molecular (Nano) electronics & devices
- Conductive plastics
- Conductive adhesives & Connectors
- Thermal materials (conduct or insulate)
- Catalytic & biomedical supports
- Others

Development of nano porous anodic aluminium oxide (PAAO) substrate:

Degreasing of Al strips

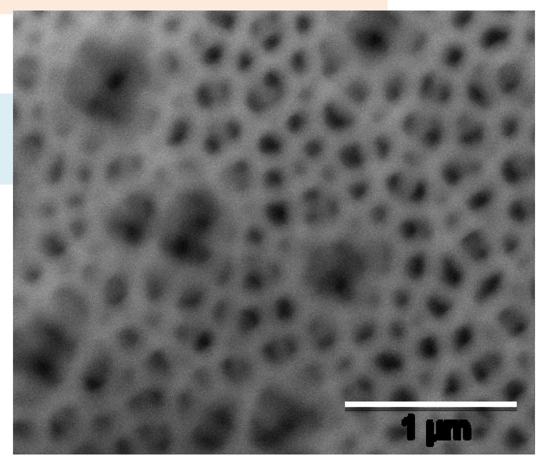
Electropolished using solution of Ethyl alcohol (99.9%) and Perchloric acid (70 %) in 5:1 ratio

1st step nodized at a constant voltage of 80 V for 30 min in 5 wt % Phosphoric acid electrolyte

Removal of porous alumina film by chemical etching using Phosphoric (6 wt %) and Chromic acid (1.8 wt %) at 80 □C

2nd step anodization under identical conditions

A regular array of pore



Preparation of nano-sized metal oxide catalyst particles:

Aqueous saturated solution of mixtures of each of the metal salts with varied Cu % (0.5-20)

\+

Chelating agent of Citric acid monohydrate

↓

Slow stirring & heating simultaneously at 65 -84 □C to form a gel to get desired average particle size

↓

Drying at 120 □C for 12 hrs

↓

Calcination in air (5 hrs, 800 □C)

↓

Ground to powders

Details of doping and size distribution of oxide catalyst particles:

Sample Designation	Doping level of Cu (wt %)	Size distribution (nm)	Mean Size (nm)	
			Zetasizer	Image-J
Co	0	167-691	583.4	581
CoCu1	1	88-424	327.3	350
CoCu10	10	71-391	251.0	225
CoCu20	20	137-663	531.9	500
NiCu10	10	39-84	71.51	60
NiCu15	15	45-165	91.28	97
NiCu20	20	70-173	141.8	130
FeCu0.5	0.5	233-444	339.7	329
FeCu1	1	296-516	387.7	362

Flow chart for carbon nano-structure (CNS) production:

Dispersion of catalyst particles using in iso-propanol onto the substrate

↓

Catalyst particles supported substrates placed in a furnace at 600 □C

↓

Ammonia gas was introduced at atmospheric pressure

↓

Temperature raised to 640 □C

↓

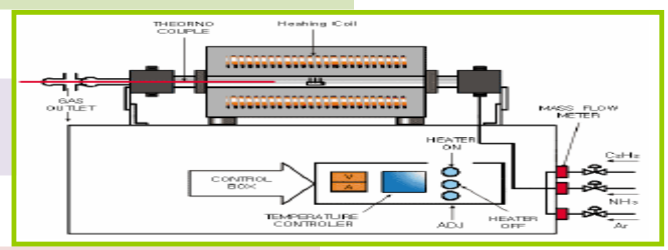
Acetylene gas introduced along with flowing ammonia gas for ~15 min

↓

CNS with other forms of carbonaceous materials

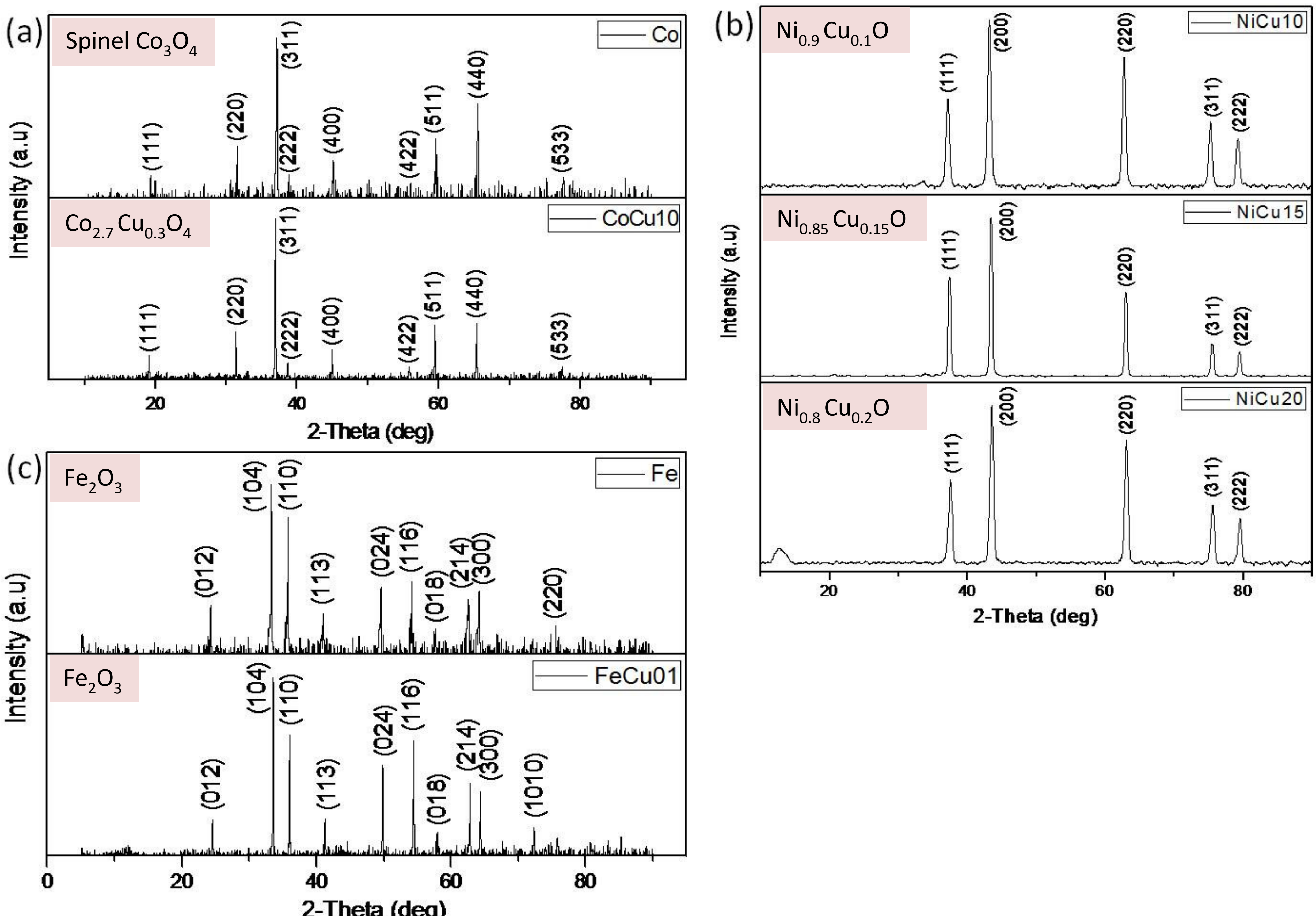
↓

Cleaning and washing



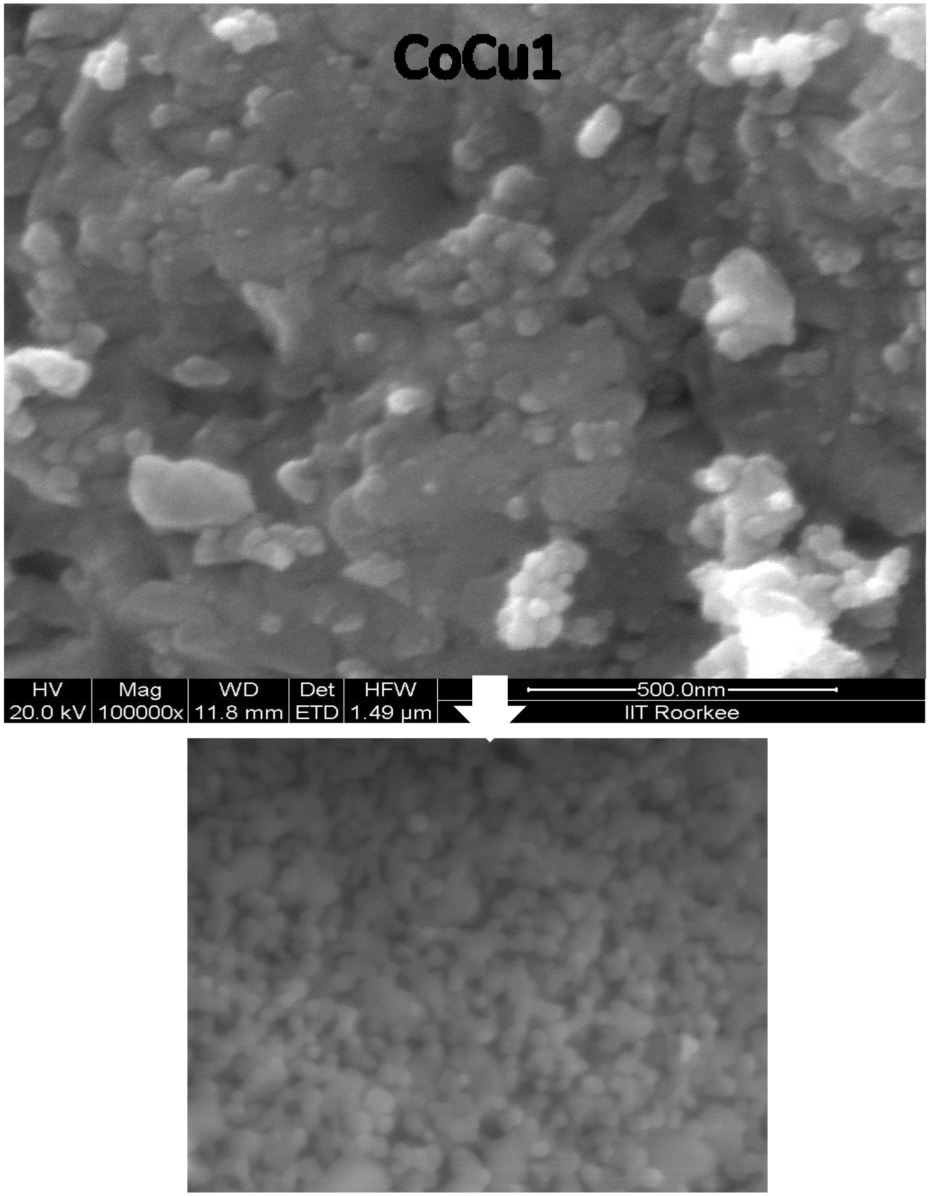
↓

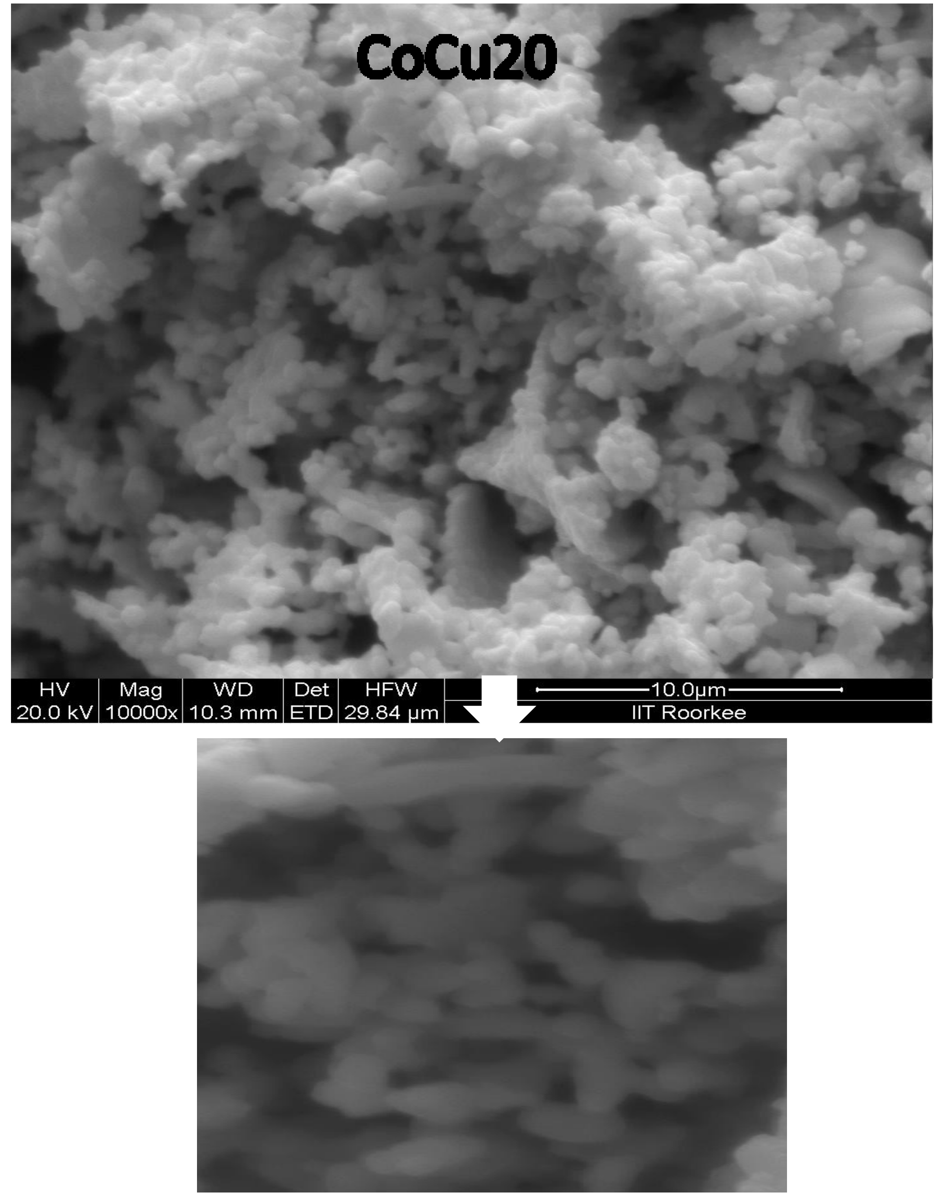
Dried in an oven at 120 □C to get final product

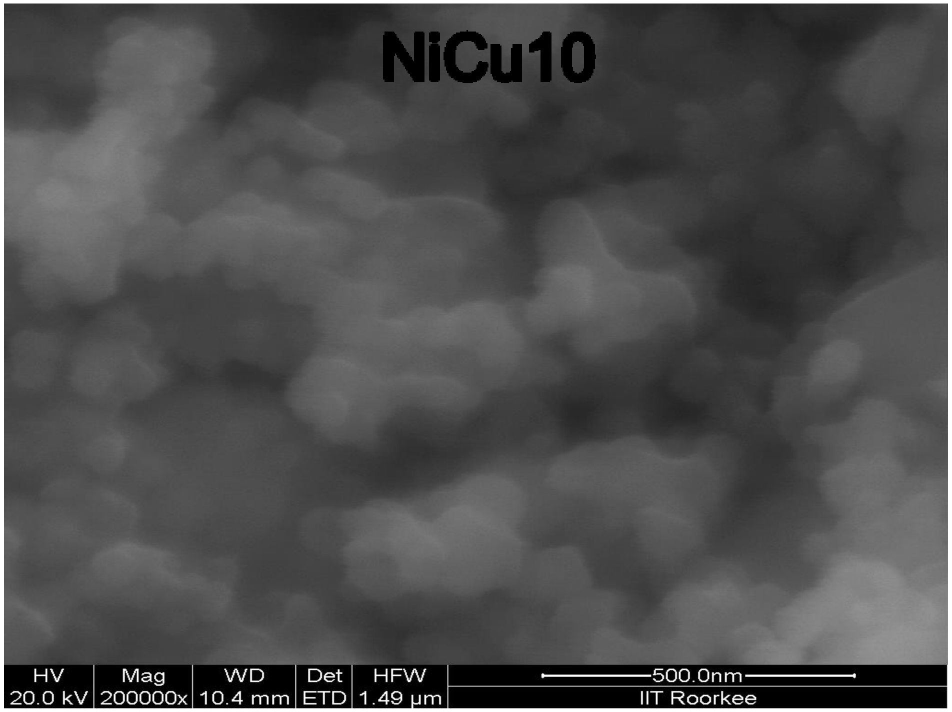


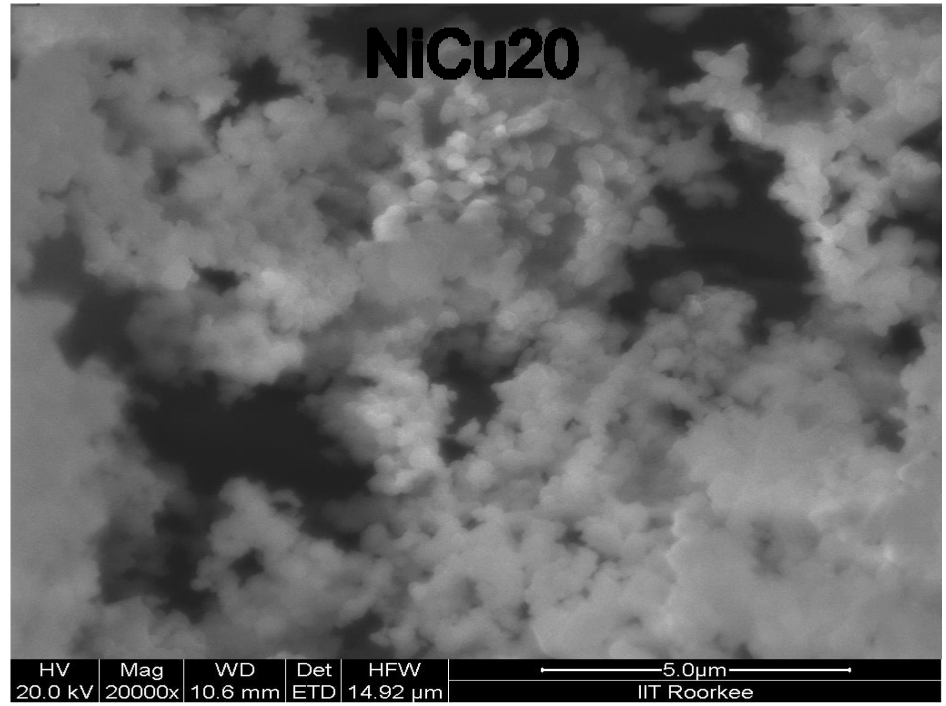
XRD pattern of (a) $Co_{3-x}Cu_xO_4$; (b) $Ni_{1-x}Cu_xO$ and (c) $Fe_{2-x}Cu_xO_3$ catalyst

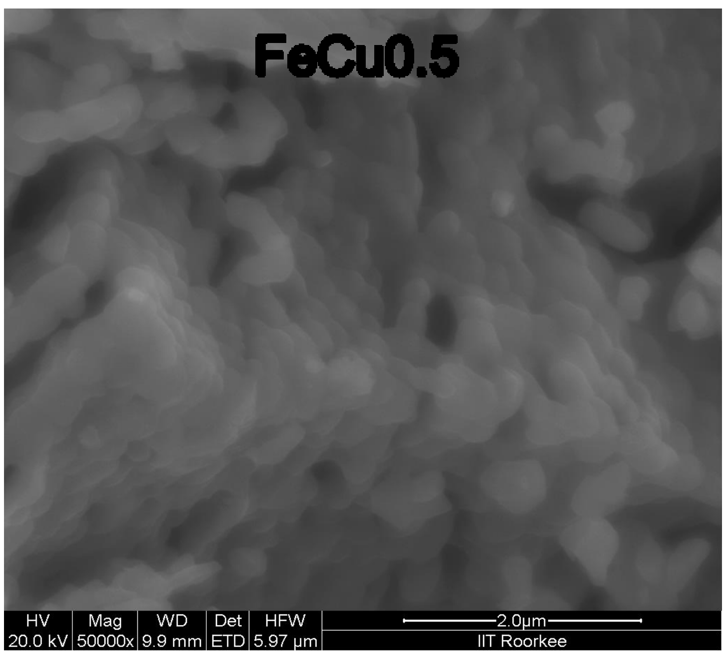
Typical FESEM micrographs of some of calcined oxide catalysts

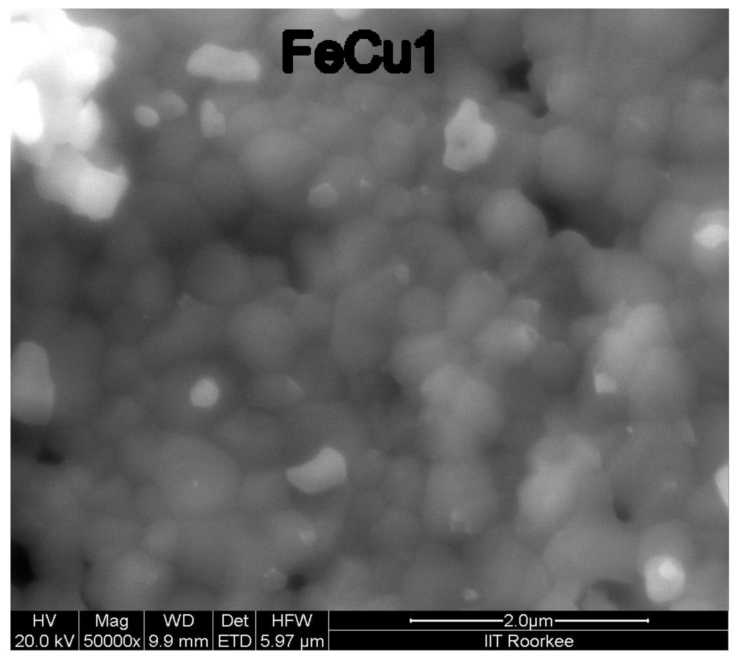





NiCu10
HV 20.0 kV
Mag 200000x
WD 10.4 mm
Det ETD
HFW 1.49 µm
500.0nm
IIT Roorkee

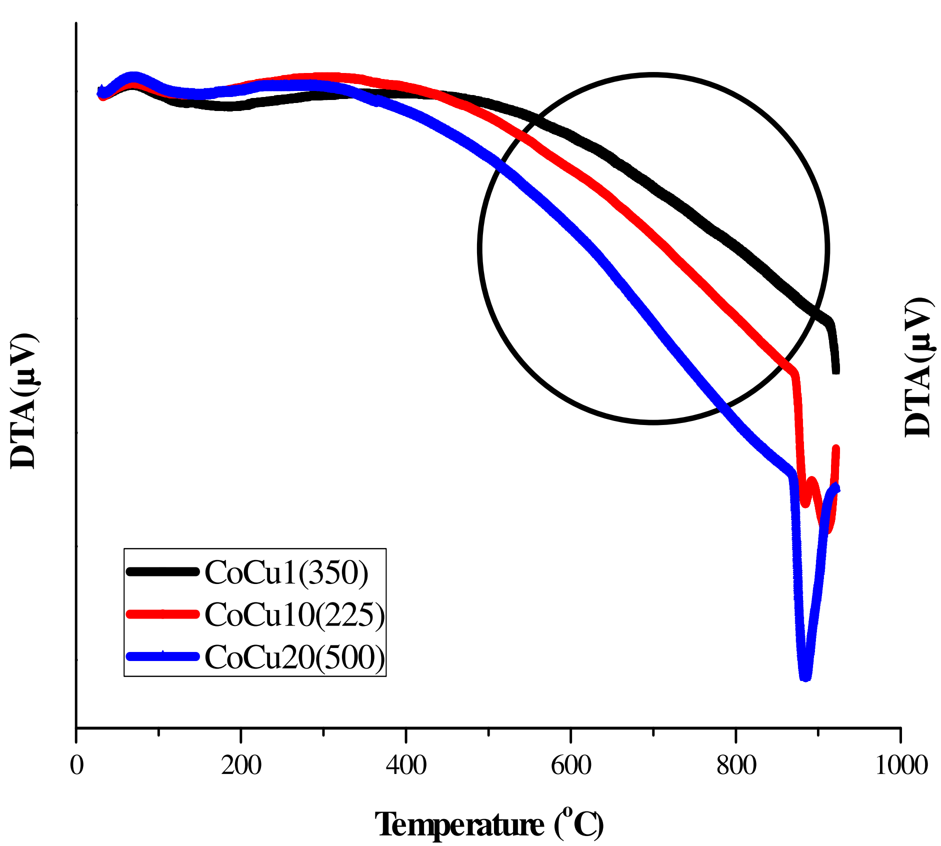

NiCu20
HV 20.0 kV
Mag 20000x
WD 10.6 mm
Det ETD
HFW 14.92 µm
5.0µm
IIT Roorkee

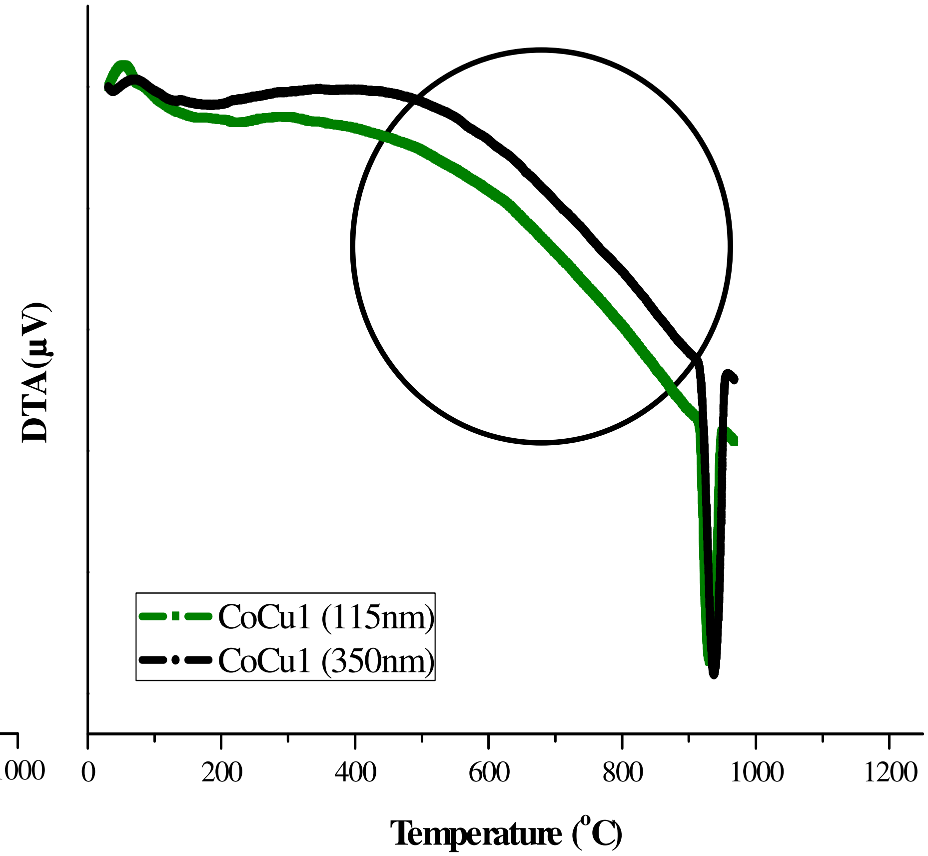

FeCu0.5
HV 20.0 kV
Mag 50000x
WD 9.9 mm
Det ETD
HFW 5.97 µm
2.0µm
IIT Roorkee


FeCu1
HV 20.0 kV
Mag 50000x
WD 9.9 mm
Det ETD
HFW 5.97 µm
2.0µm
IIT Roorkee

DTA curves for different composition and different particle size of some doped Co oxide catalyst

Beginning of a broad endothermic peak, within a sharp endothermic peak is embedded

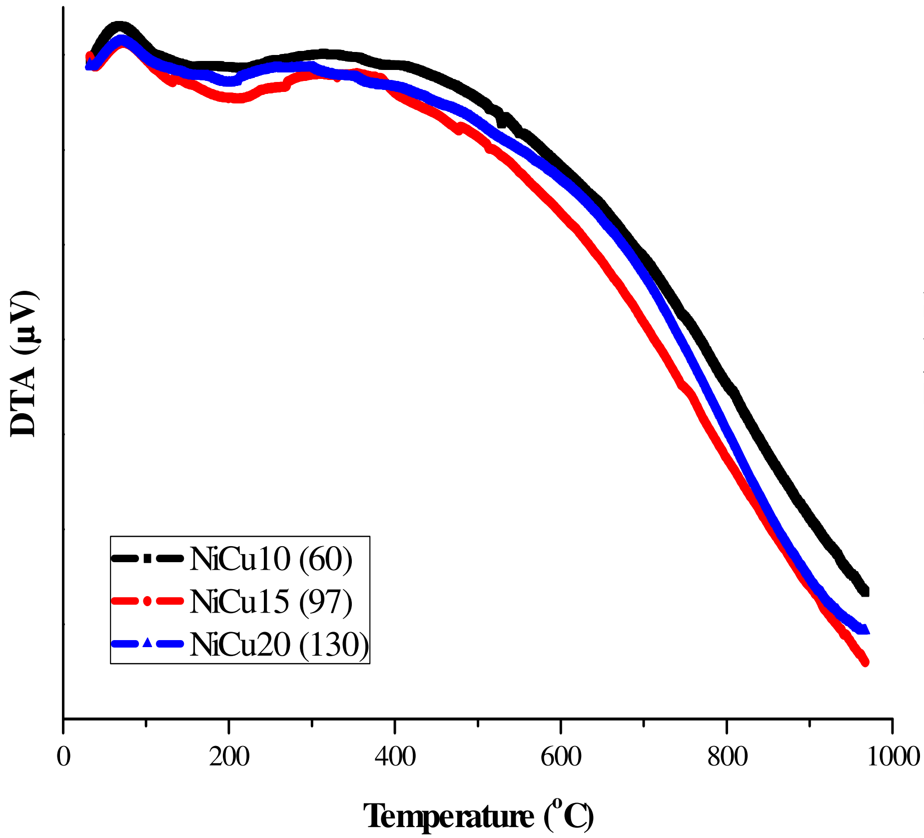


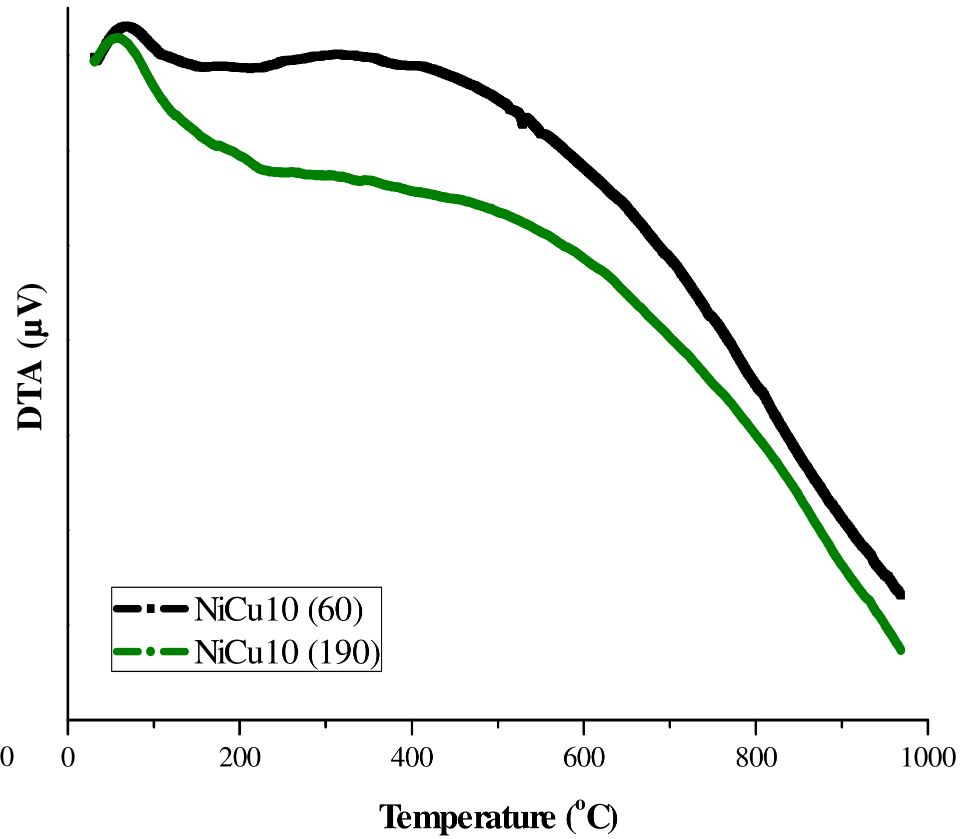


- Different slope
- Different starting melting point

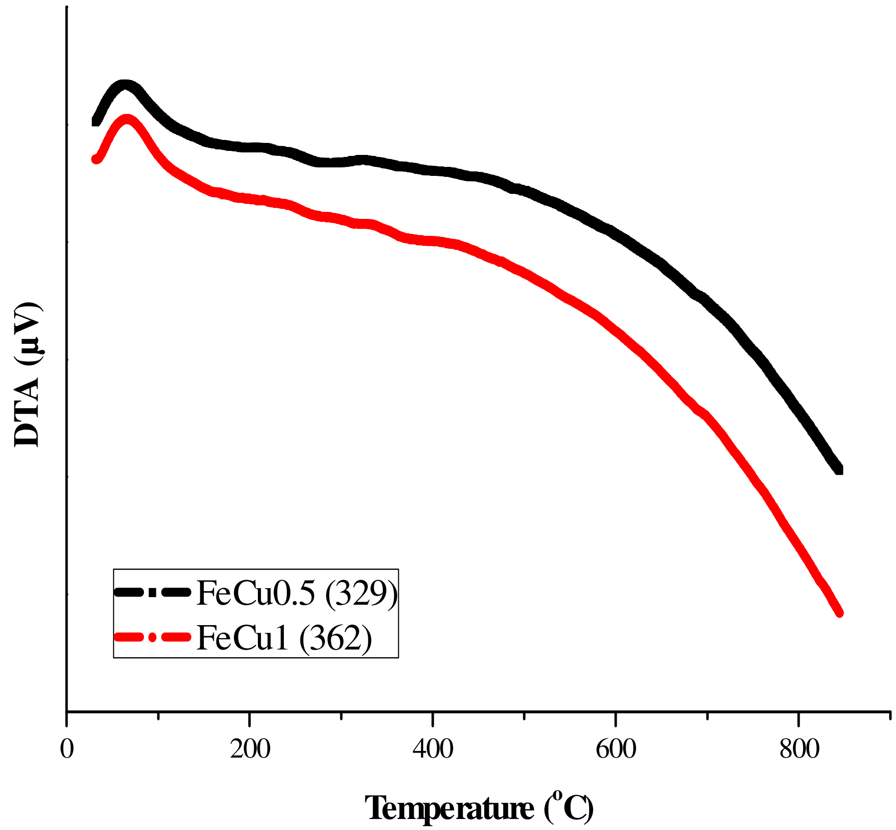
- Similar slope
- Different starting melting point

DTA curves for different composition and different particle size of some doped Ni oxide catalyst





DTA curves for different composition of some doped Fe based oxide catalyst



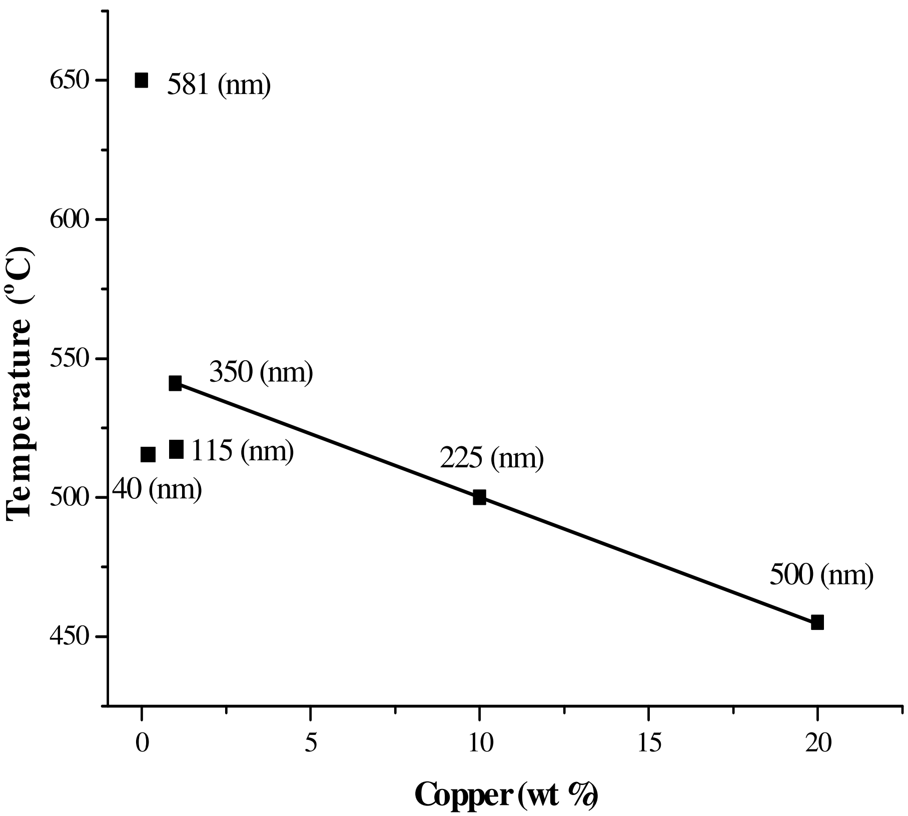
- Shows a broad endothermic peak with a bigger size of particles - slope change is narrow compared to others

The effect of doping and size of the catalyst on the start of melting as indicated by DTA result:

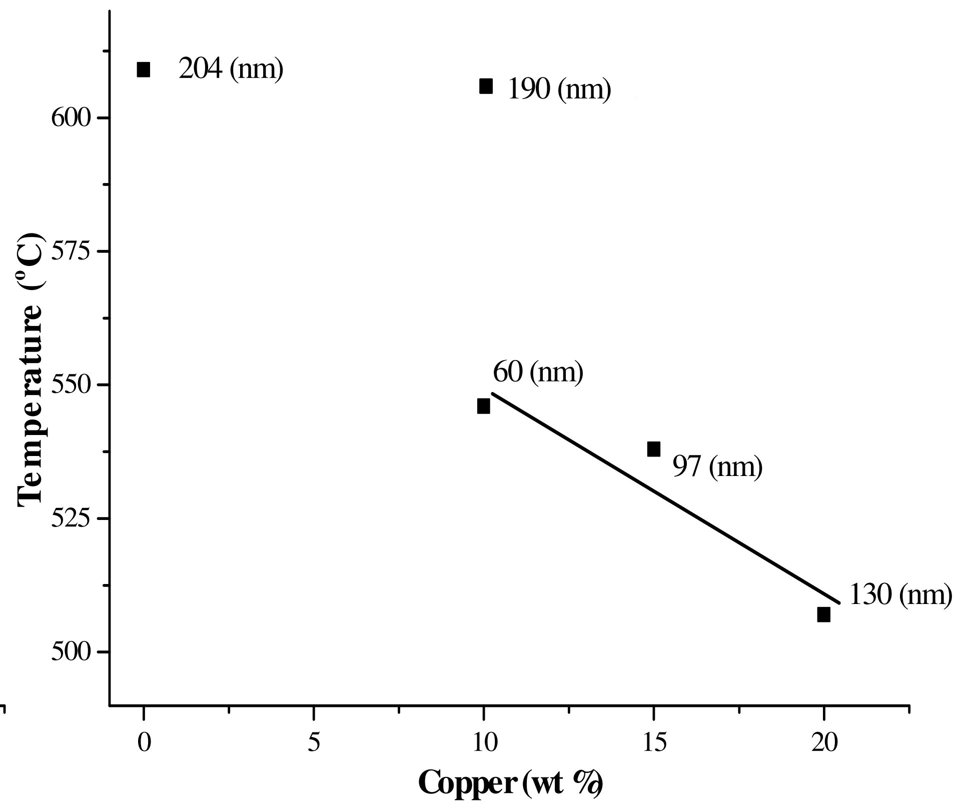
Sample designation	Mean Size (nm)	Smallest Size (nm)	Start of melting phenomena (°C) from DTA
Co	40	19	516
CoCu1	350	88	541
CoCu10	225	71	500
CoCu20	500	137	455
NiCu10	60	39	546
NiCu15	97	45	538
NiCu20	130	70	507
FeCu0.5	329	233	>640
FeCu1	362	296	>640

Variation of start of melting with increase level of doping for Co and Ni based oxide catalysts

Co based catalyst

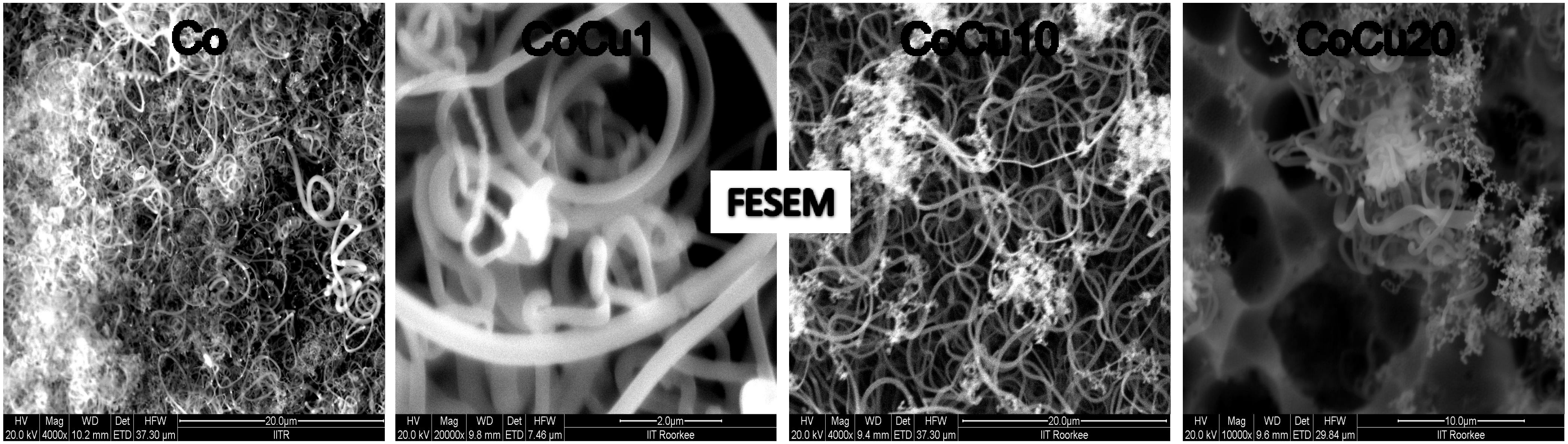


Ni based catalyst

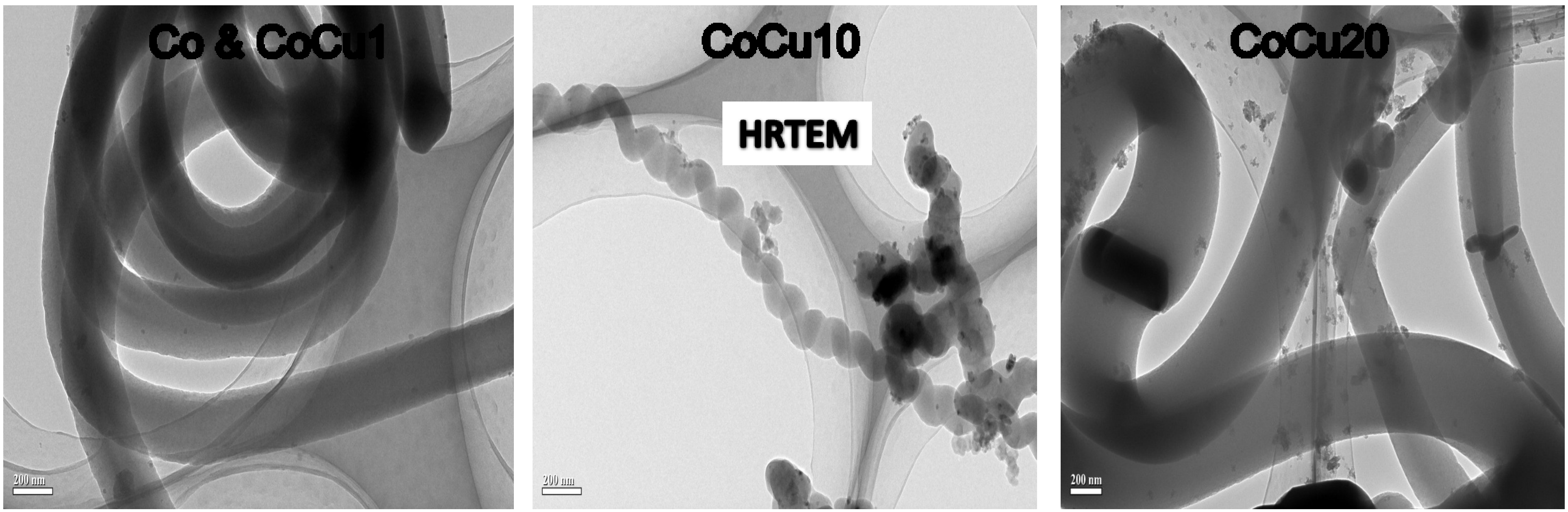


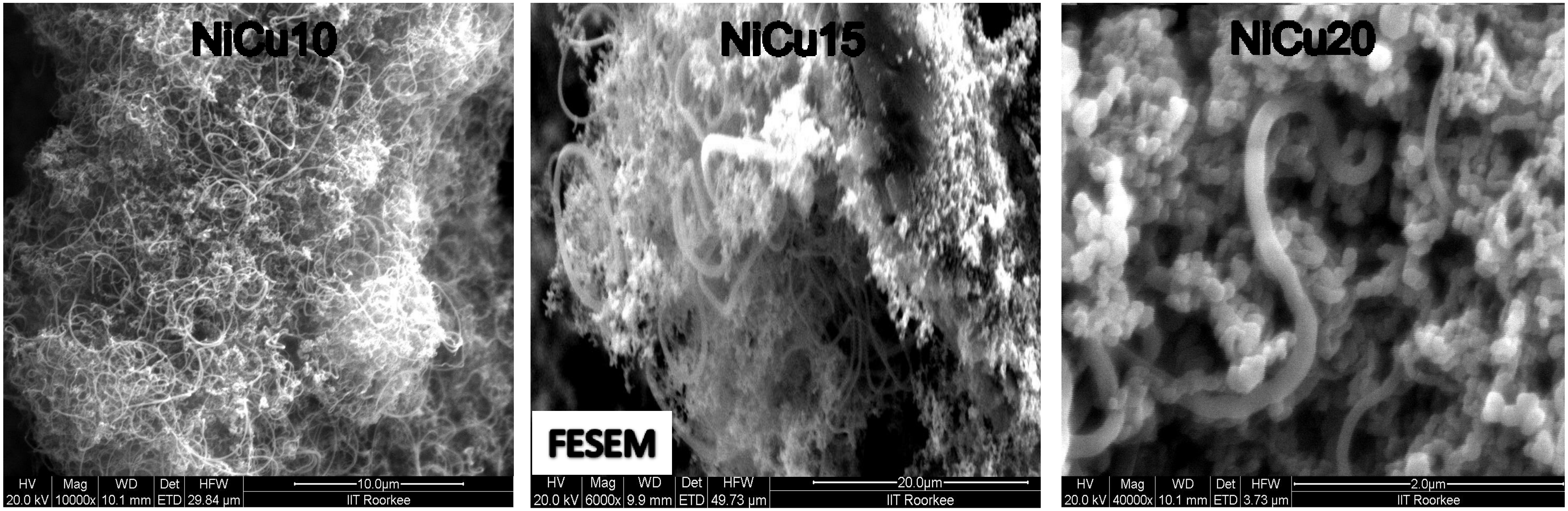
Observed nanostructures with different size and doping level of catalysts:

Catalyst	Particle size range (nm)	Observed nano-structures	Diameter distribution of the CNS (nm)
Co	19-59	Tube & nano-spheres	55-339
CoCu1	88-424	Tube & nano-spheres	134-256
CoCu10	71-391	Fiber –straight/helical & nano-spheres	131-147
CoCu20	137-663	Tape, Fiber & nano-spheres	210-590
NiCu10	39-84	Tube, Fiber-straight/helical & nano-spheres	8-248
NiCu15	45-165	Tube, Fiber & nano-spheres	49-211
NiCu20	70-173	Fiber & nano-spheres	54-165
FeCu0.5	233-444	Chains of nano-spheres	141-200
FeCu1	296-516	Chains of nano-spheres	74-131

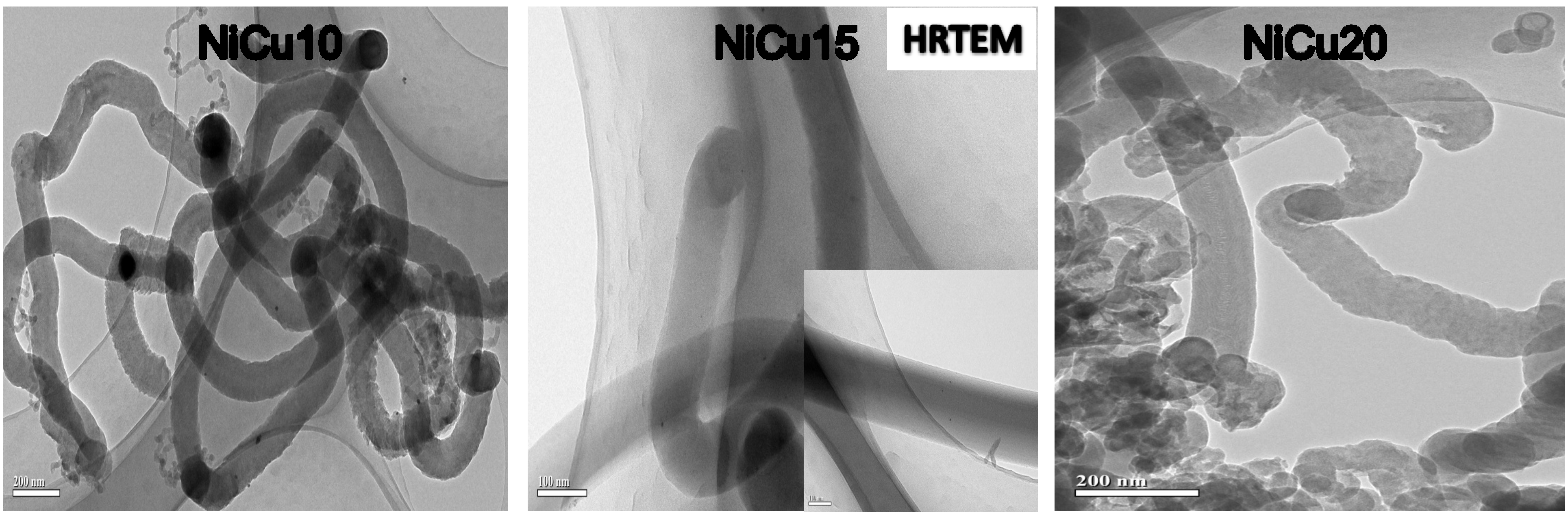


Observed carbon nanostructures grown over Co oxide based catalyst

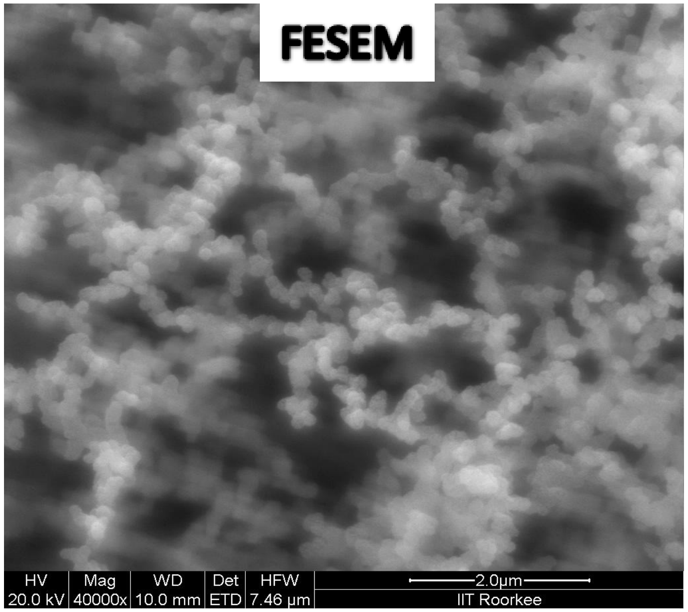


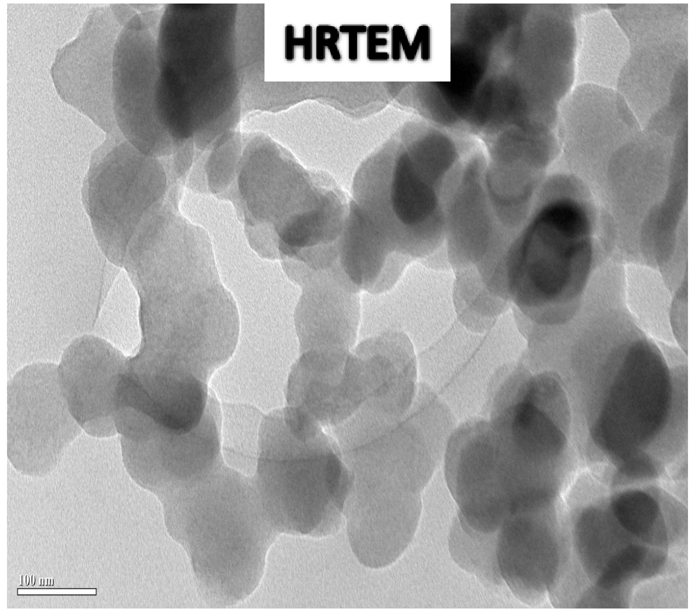


Observed carbon nanostructures grown over Ni oxide based catalyst

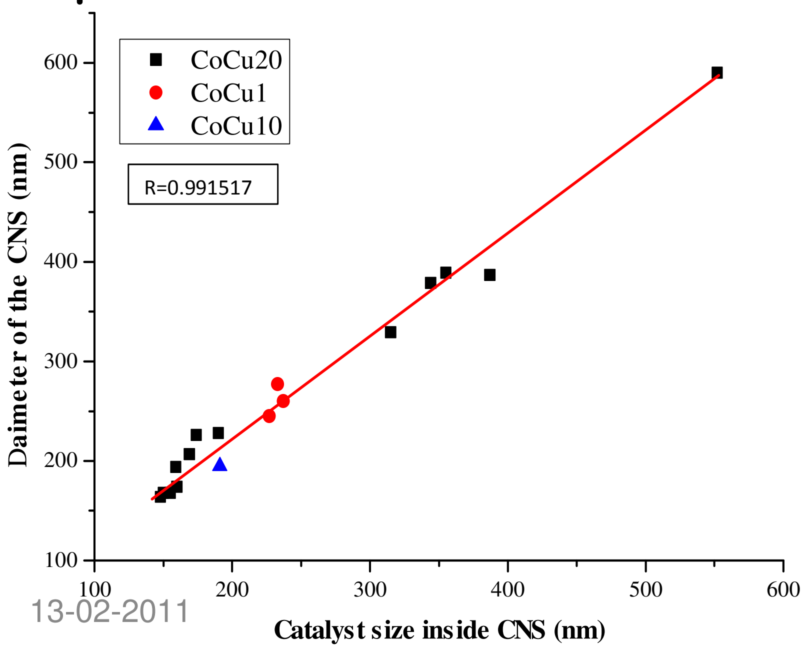


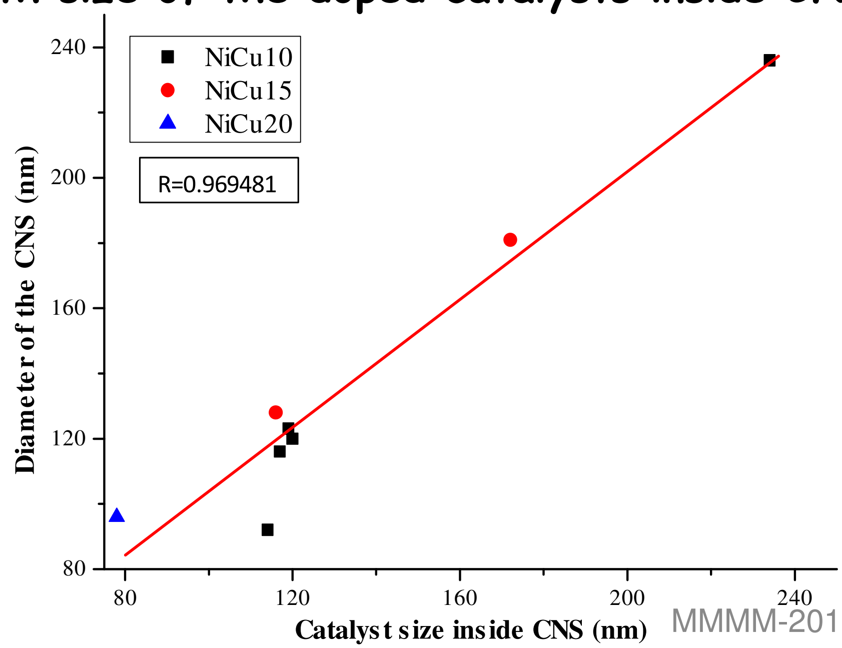
Observed nanostructures (Nano-spheres) grown over Fe oxide based catalyst





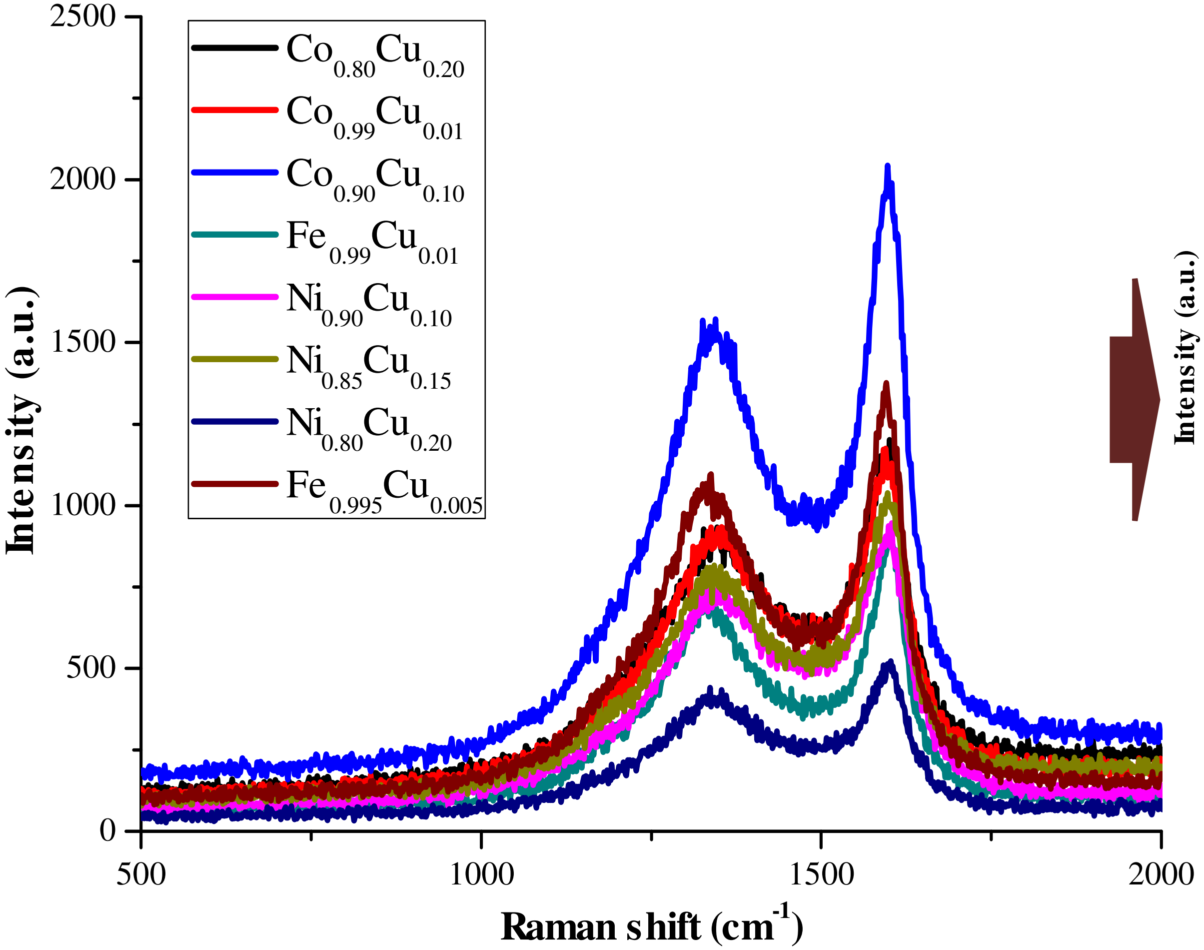
Dependence of diameter of the CNS with size of the doped catalysts inside CNS

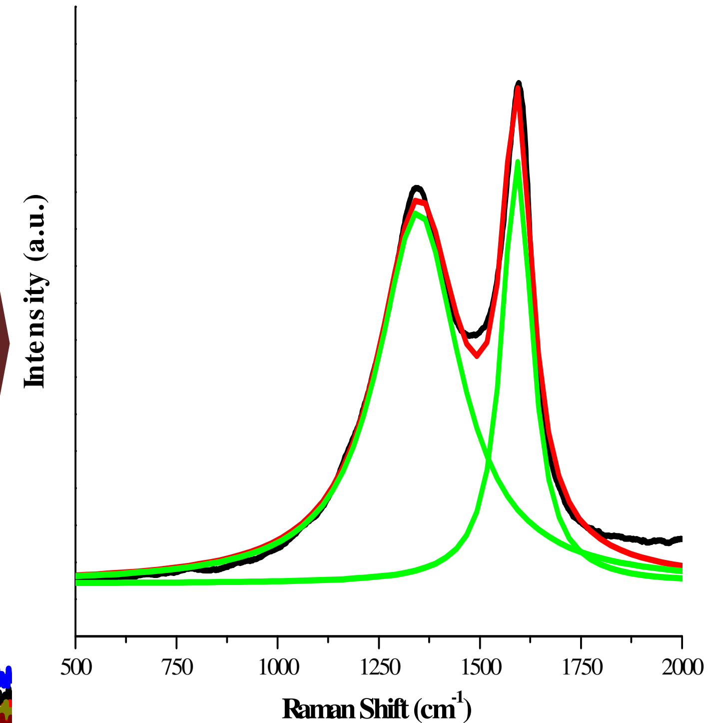




Raman spectrum of the CNS formed by different copper doped catalysts

Degree of graphitization depends on **FWHM** and $\mathbf{I_d/I_g}$





Black:	Original
Red:	After Smoothing
Green:	After Lorentzian fit

The peaks appearing at ~1590 and ~1345 cm^{-1} are attributed to G and D-bands respectively.

Conclusions:

- Formation of different type of carbon nano-structures (multi-walled) through a distinctly different mechanism involving surface melting of the catalyst.

- Doping provide an important tool for getting the desired type of CNS by
    - Surface melting and the thickness of the molten layer &
    - Changes in the shape & size of the catalyst.

So for commercialization it needs industry to come for bulk production- Which in turns is very much in need for use in any structural applications.

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Thank You!!