Production of few-layer graphene by catalytic-CVD

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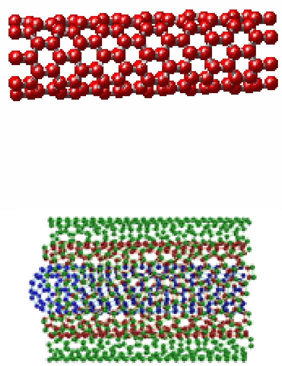
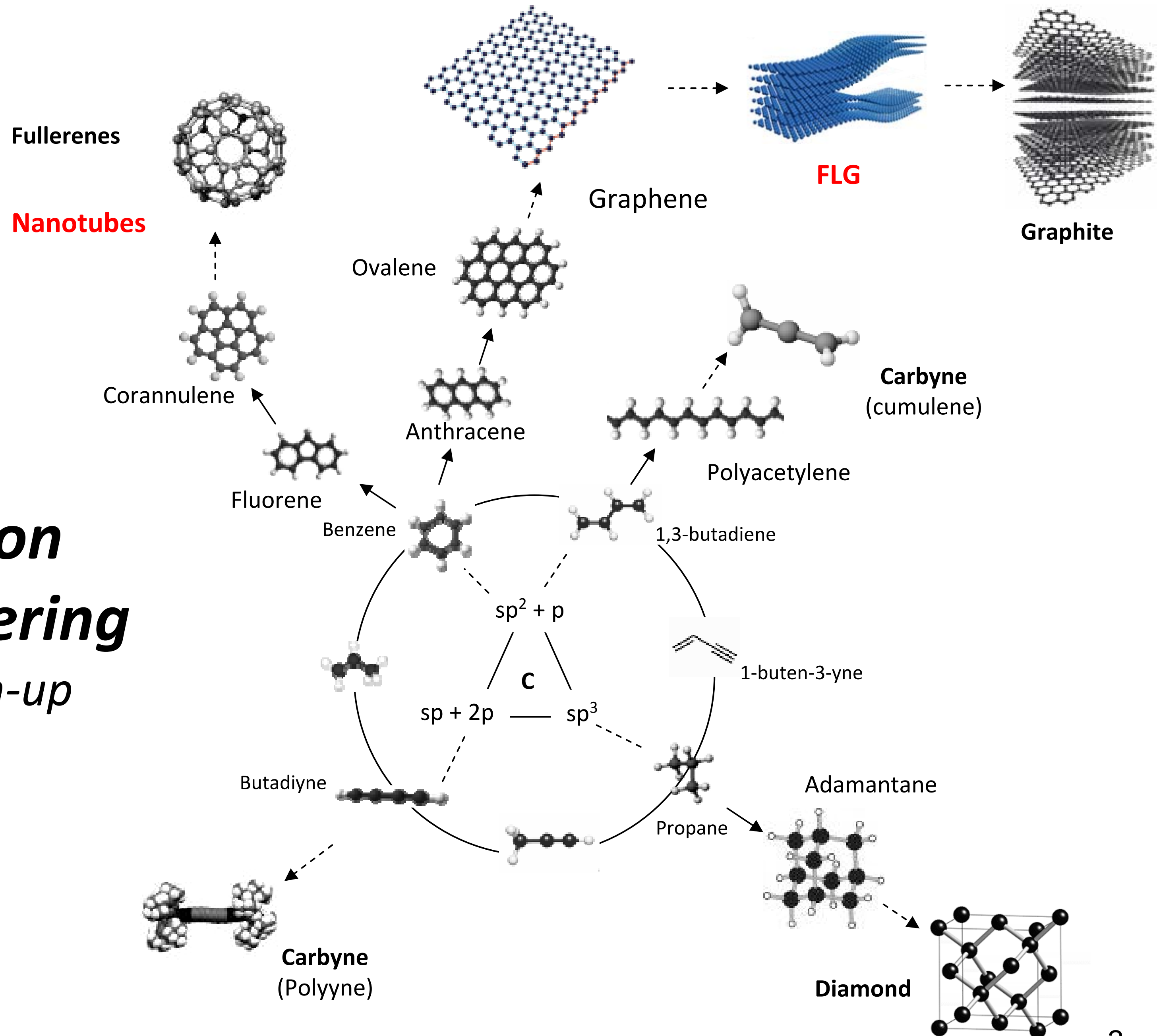
Atelier de prospective du GFP
Graphène et nanocomposites polymères
Paris, 16 avril 2013



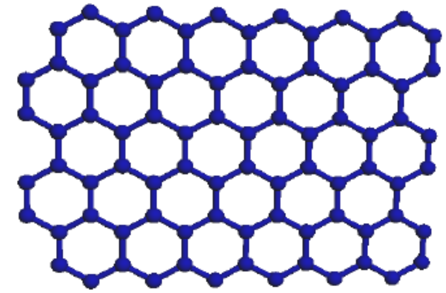
Carbon engineering

Bottom-up

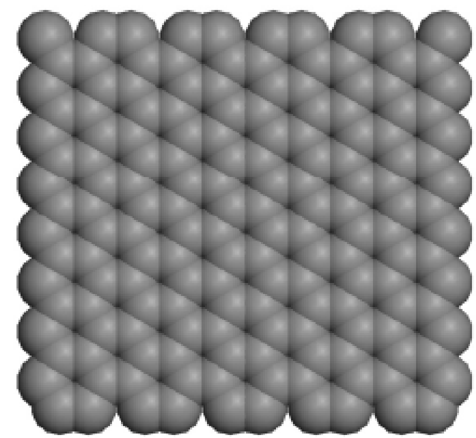


P. Serp, in Comp. Inorg. Chem. II **2013.**

Why graphene?



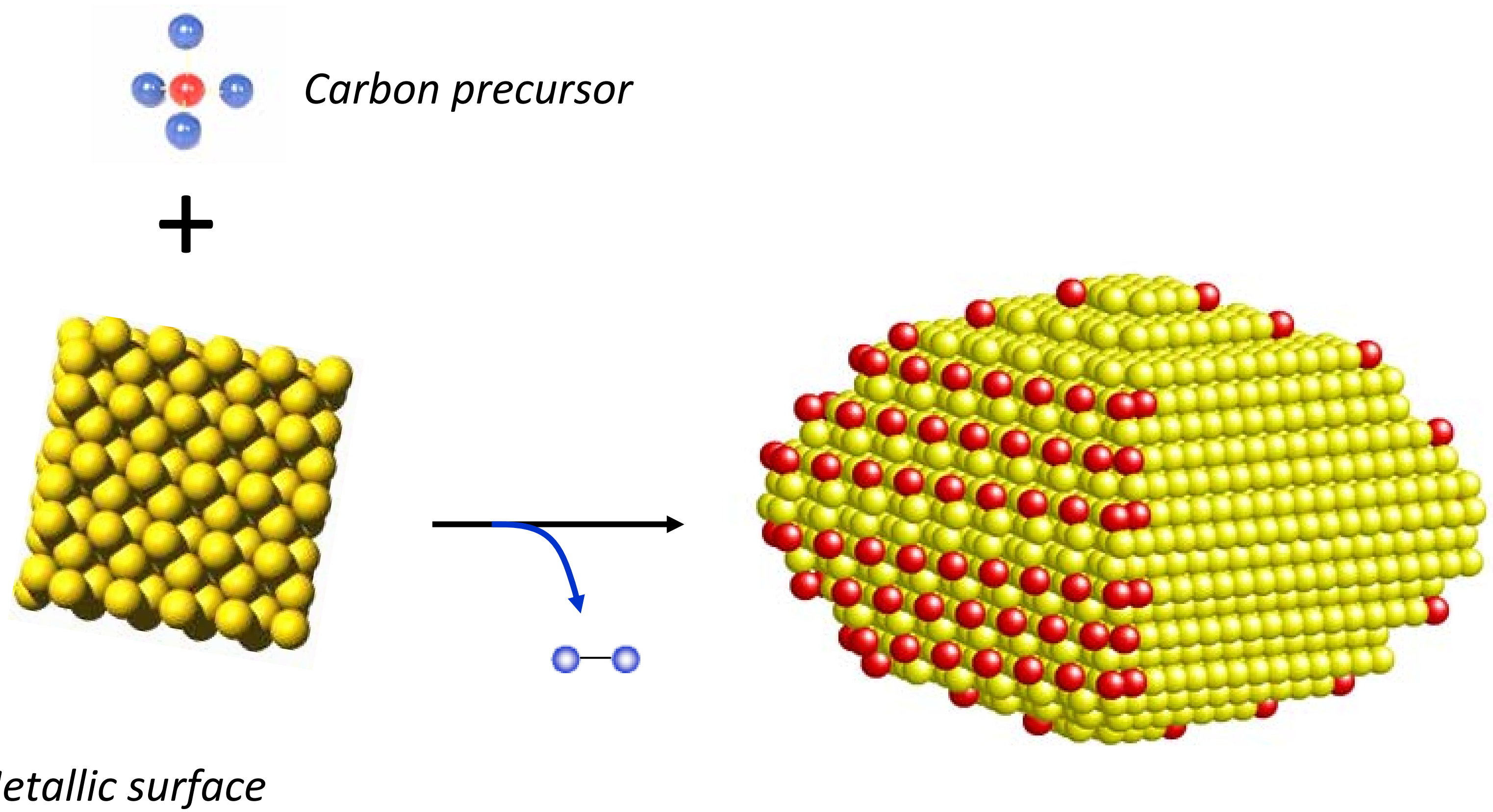
- ~ 1100 GPa modulus, fracture strength ~ 130 GPa
- Low density ~ 2 g/cm^3
- Thermal conductivity ~3000 W/m-K in plane - but highly anisotropic; ~ 2 W/m-K out of plane
- Electrical conductivity: ballistic electron transfer; high mobility
- High specific surface area (limit: 2630 m^2/g)
- Physical properties can be 'chemically tuned'
- Barrier material - impermeable if defect-free?
- High temperature 'base' (support) material (in reducing or neutral conditions)



Graphene is thus a material of great interest and also multilayer graphene and ultrathin graphite (such as <1 μm thick)

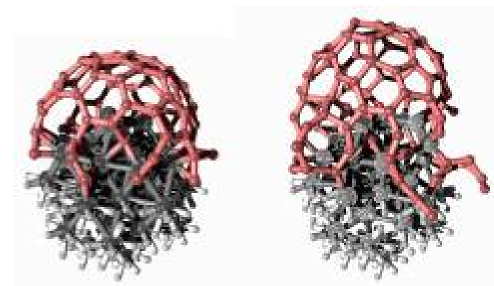
Catalysis for nanocarbons: a minimalist catalysis…

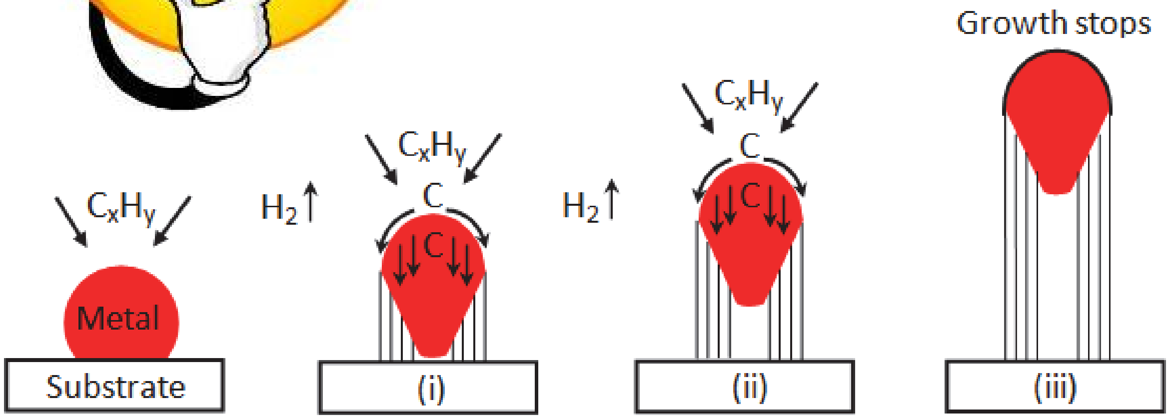
Rapidly a two-player game

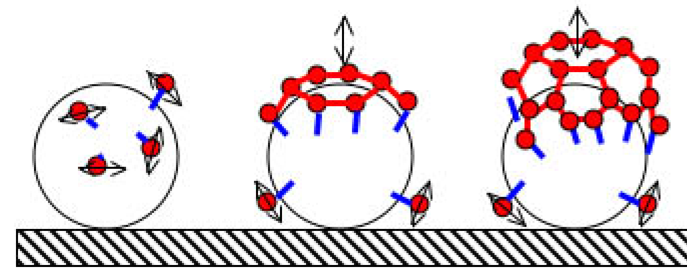


Carbon nanotubes (CNTs) growth mechanism

A catalytic process…
A template effect

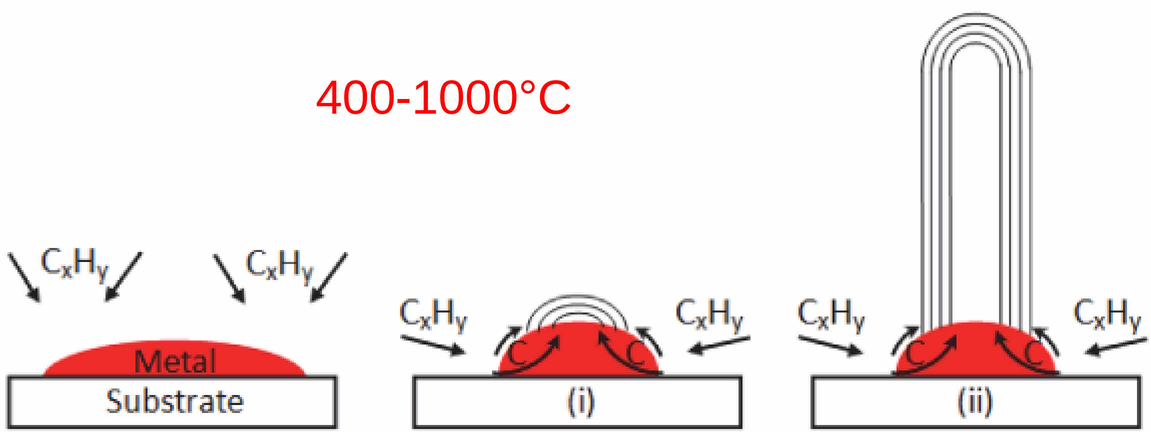






rds: often C diffusion

400-1000°C

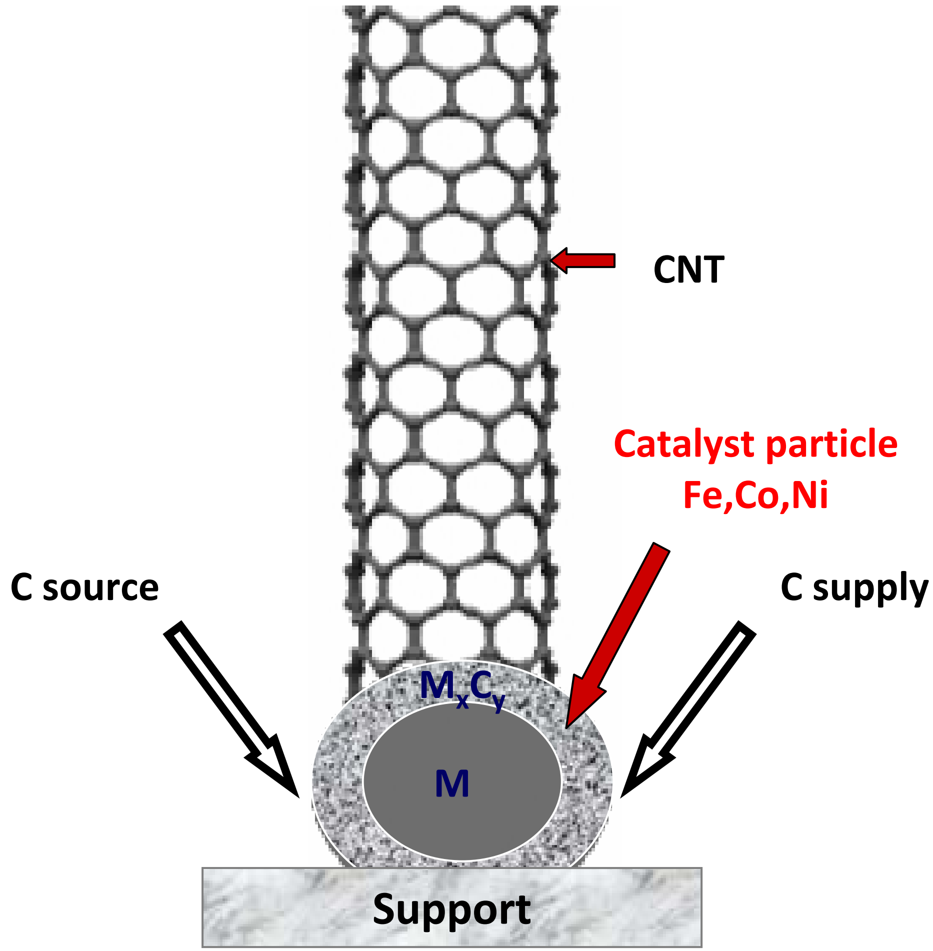


*RTK Baker, J. Catal. 26, **1972**, 51.*

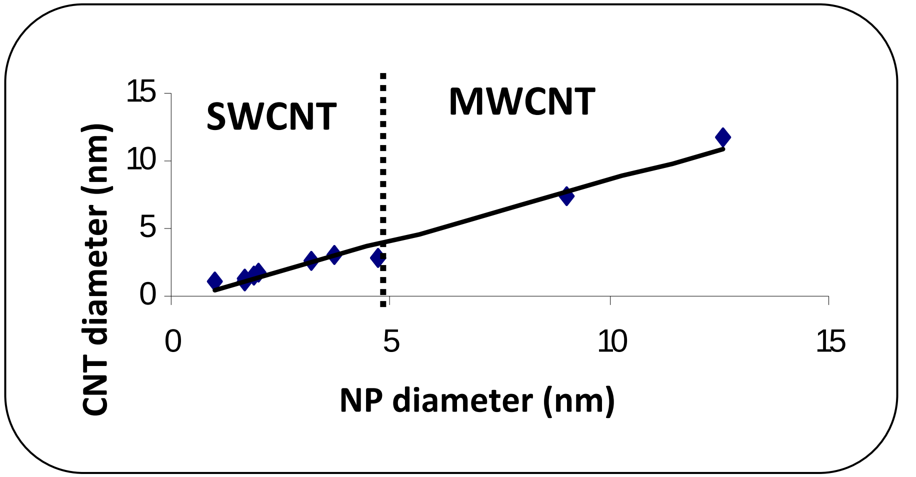
P. Serp « Carbon Materials for Catalysis, Wiley, 2009

Designing selective catalyst for CNT growth

A very peculiar reaction



T = 500 – 1000°C

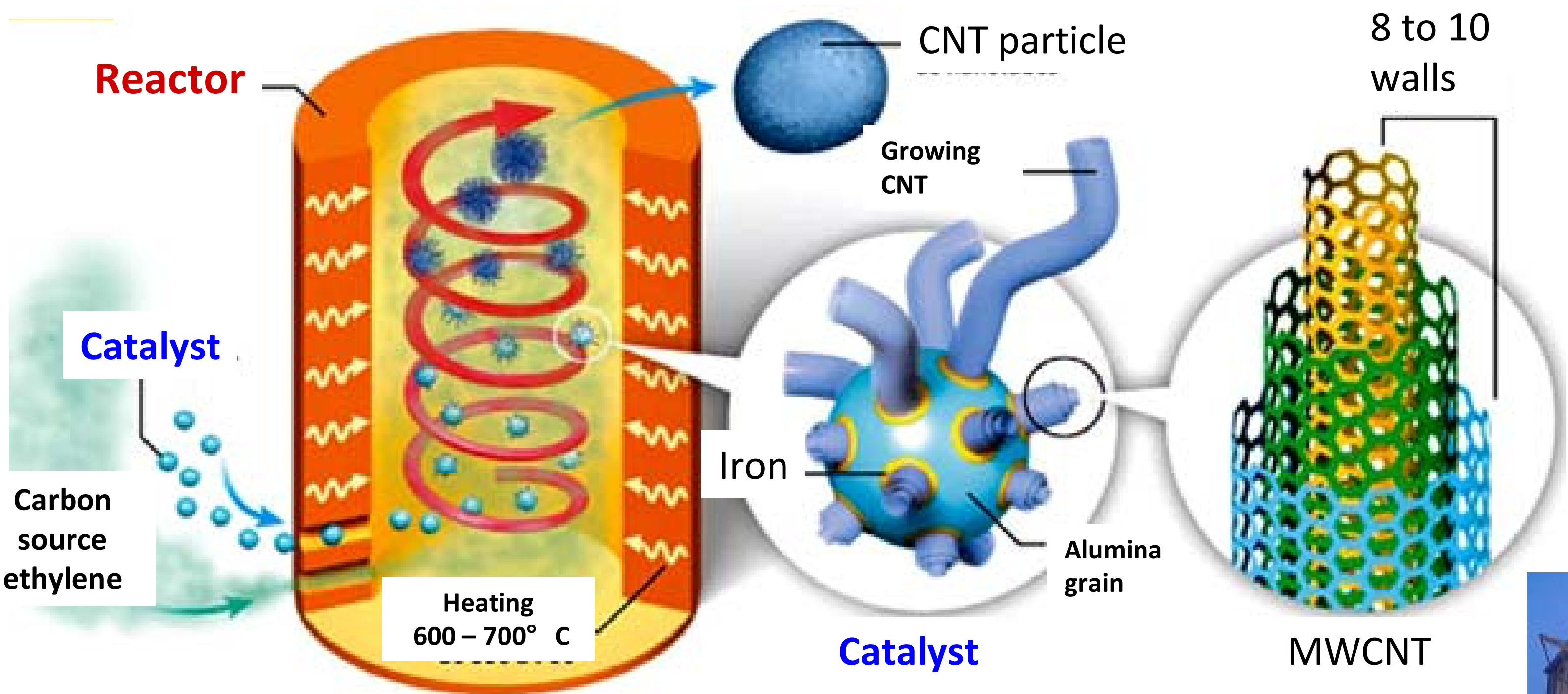


- Catalyst particle size
- Metal-Support Interaction
- Metastable carbides
- Carbon diffusion in the metal
- CVD operating conditions

*E. Lamouroux et al. Catal. Rev. – Sc. Eng. 49, **2007**, 341.*

CNT synthesis – a bottom-up approach

Fe/Al_2O_3 catalyst / Ethylene / Fluidized Bed Reactor

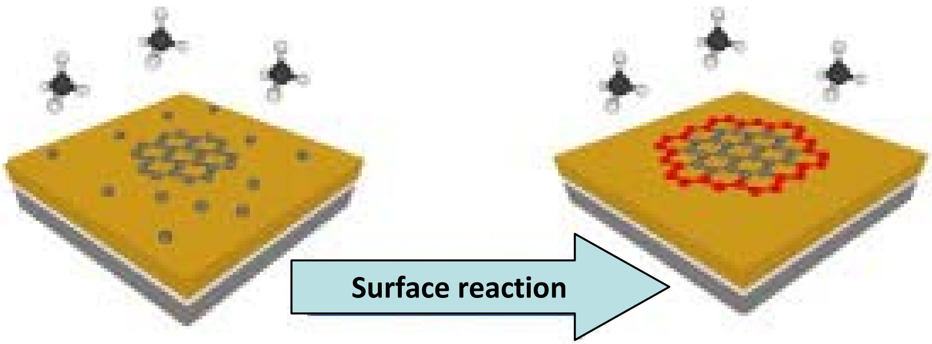


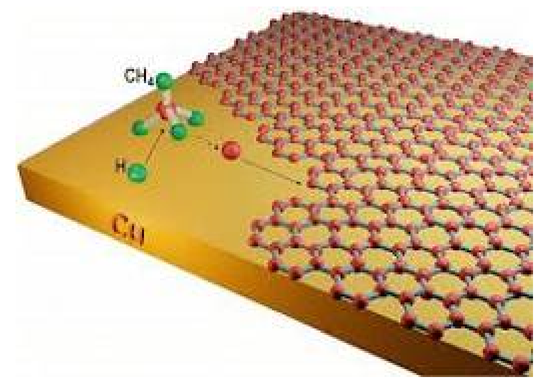
ARKEMA

P. Serp, et al. ***2001****, WO03/002456A2*
D. Venegoni et al. Carbon, 40, ***2002****, 1799.*

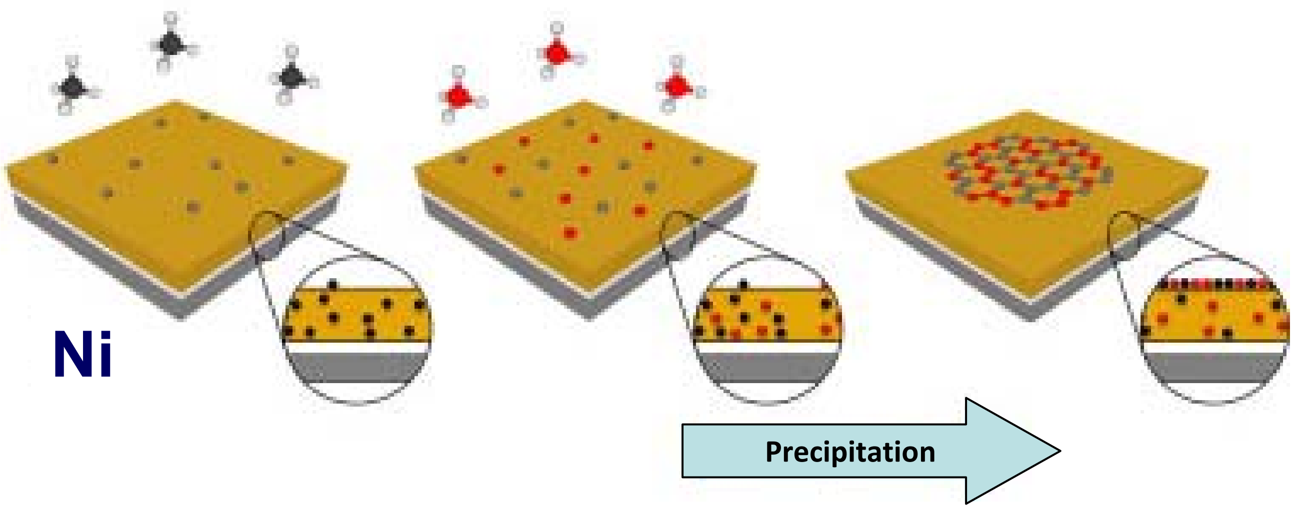
Graphene growth by CVD – planar catalytic substrates

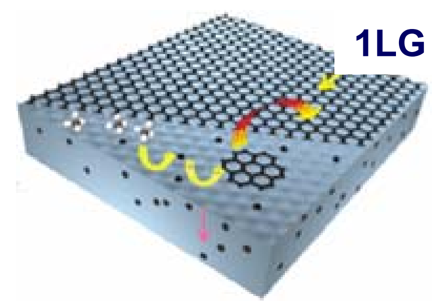
Cu





Ni



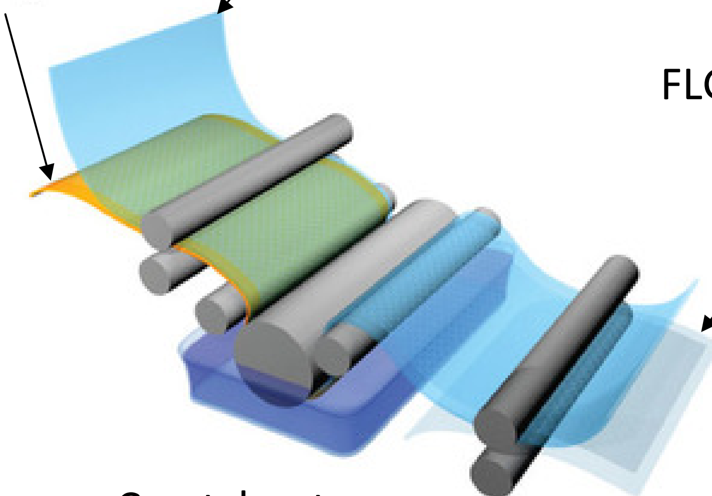


*Y. Zhang et al. Nano Research 5, **2012**, 402.*

Flexible, conductive, translucent surfaces capable of absorbing light

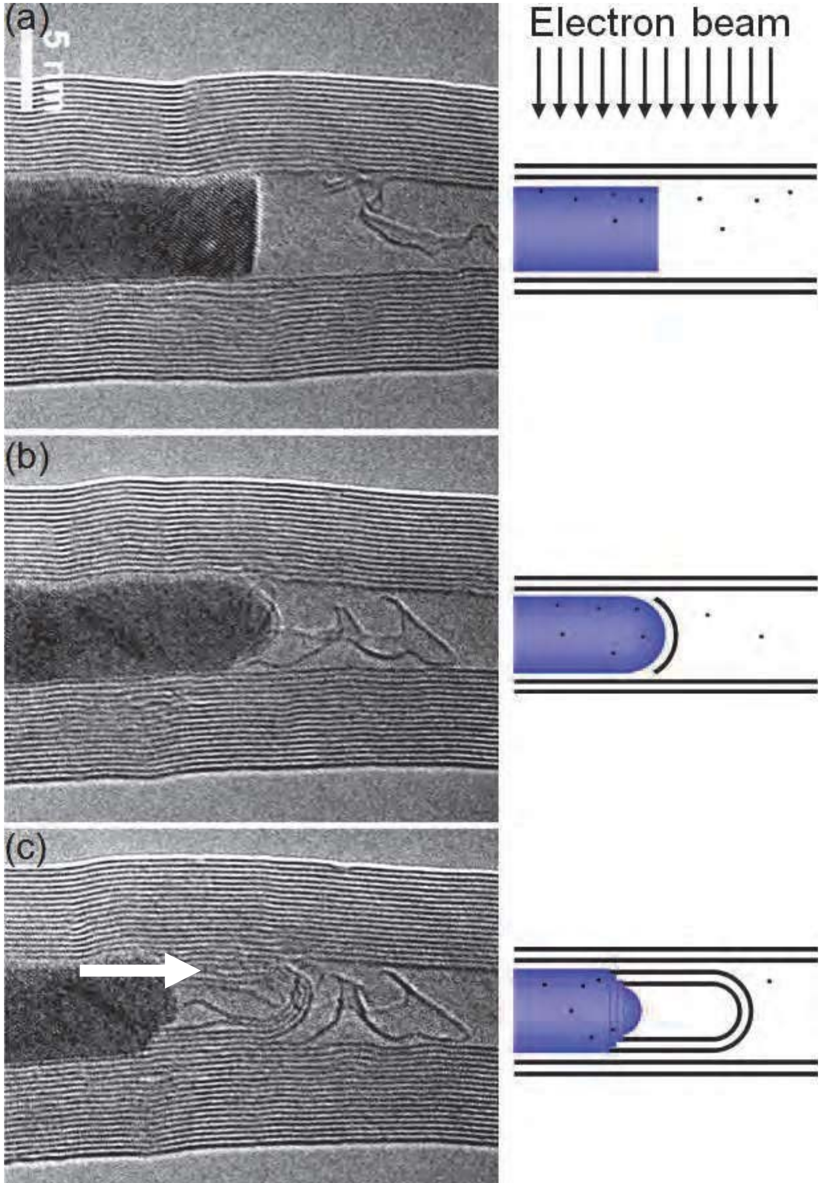
Large area graphene

*P. Yong et al. Nature Nanotech. 5, **2010**, 559.*



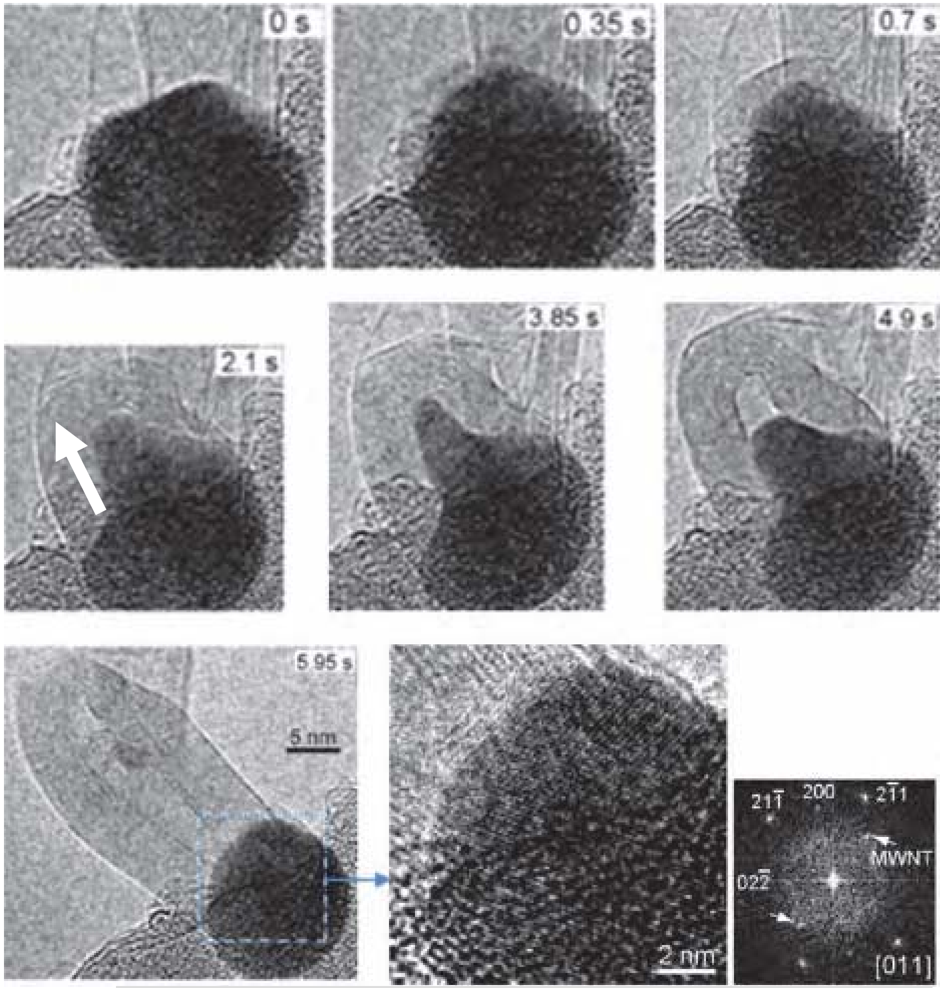
Graphene/FLG powders – which catalytic substrates?

The mechanical, thermal, electrical and structural properties of graphene make it possible to obtain ***composites*** with potential applications in many fields because of their improved properties.



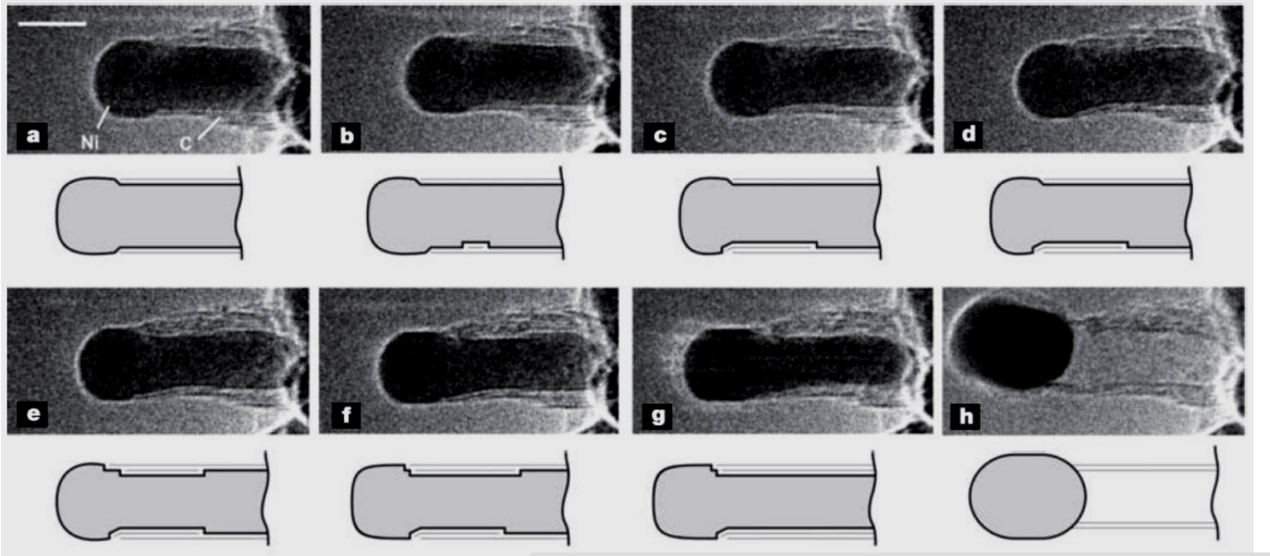
M. Kumar et al. J. Nanosci. Nanotech, 10, **2010**, 3739

Iron catalyst at 600°C - acetylene

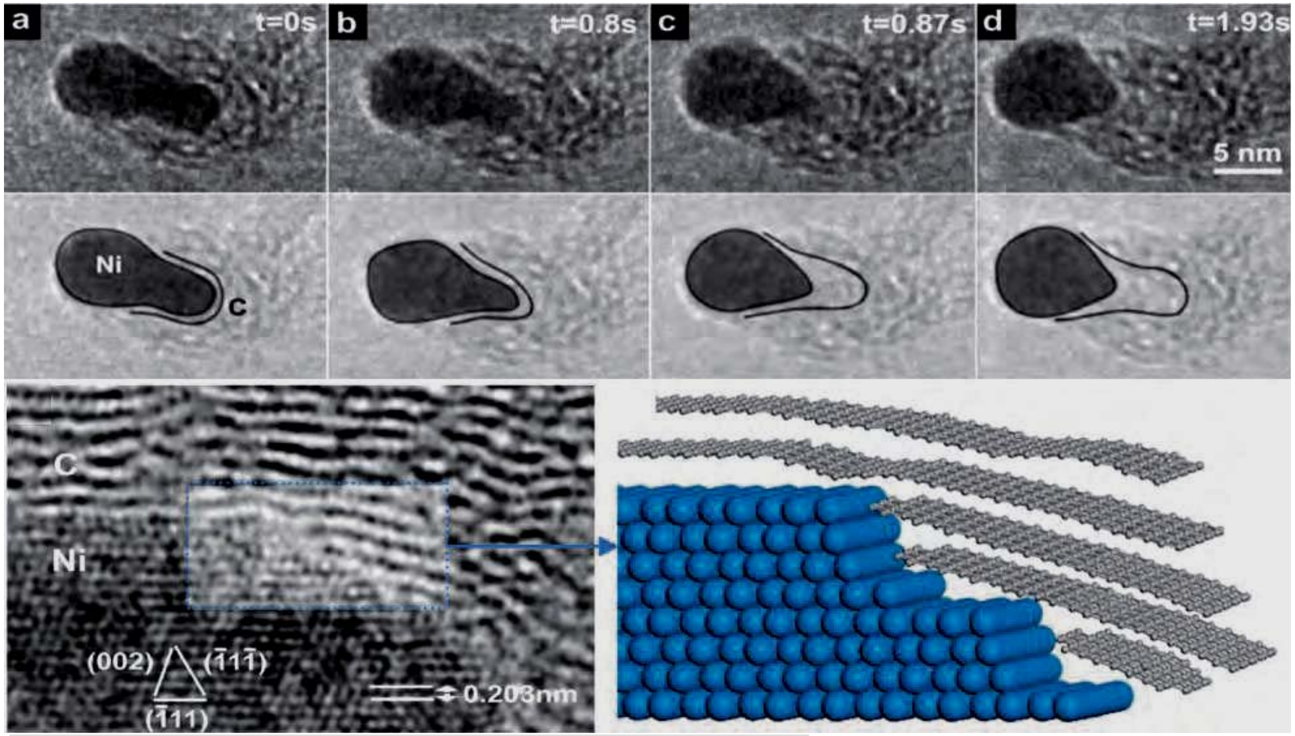


Yoshida et al. *Nano Lett.* 8, **2008**, 2082-2086.

Elongation/contraction process

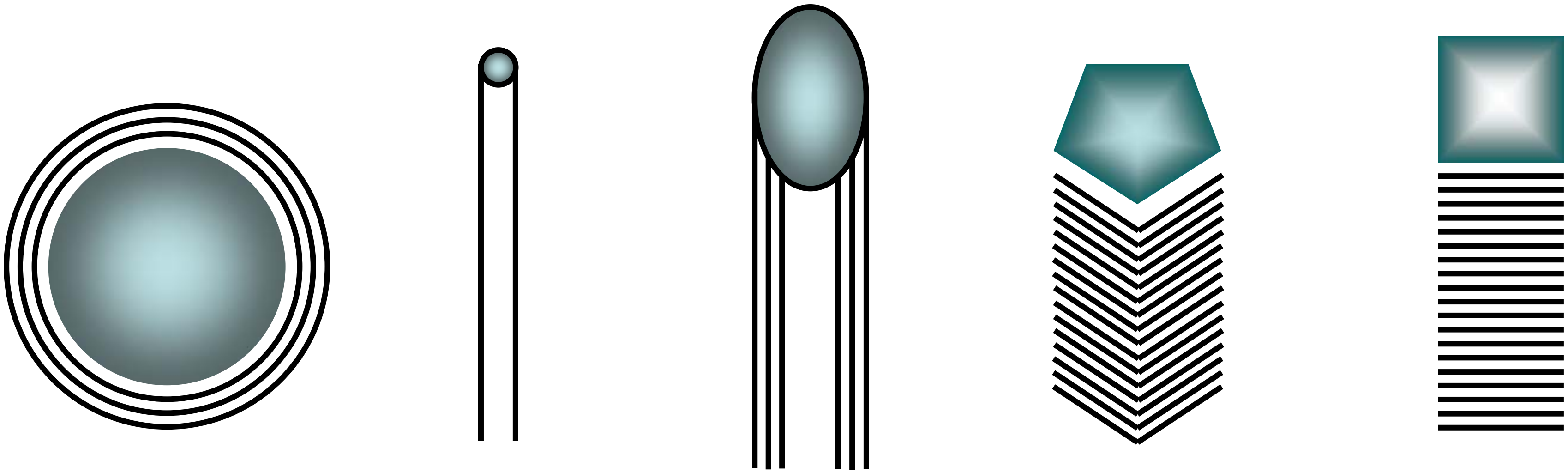


*Helveg et al. Nature 427, **2004**, 426-429.*



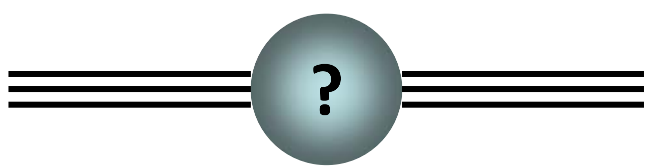
*Hofmann et al. Nano Lett. 7, **2007**, 602-608.*

How to control carbon diffusion/precipitation?



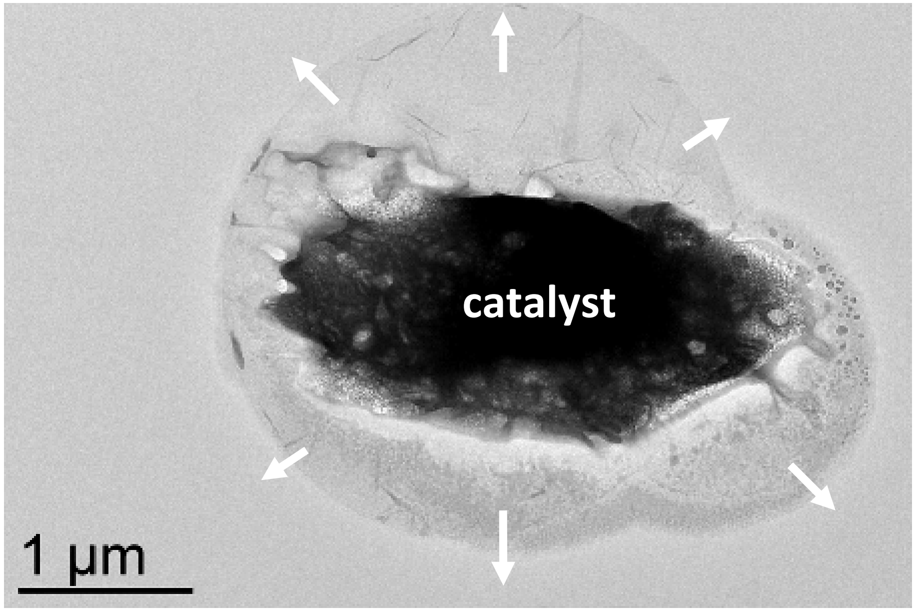
C onion | SWCNT | MWCNT | CNF *Herring bone* | CNF *Platelet*

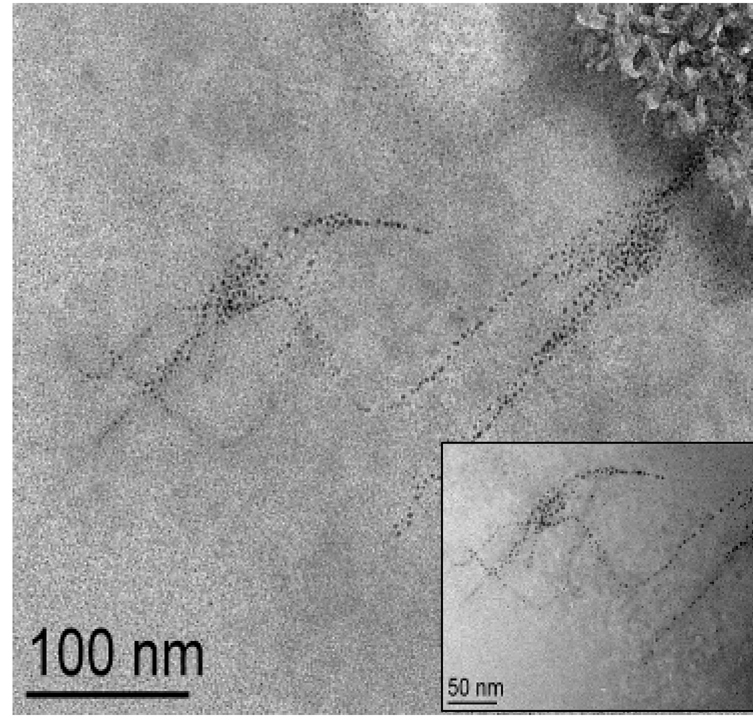
FLG

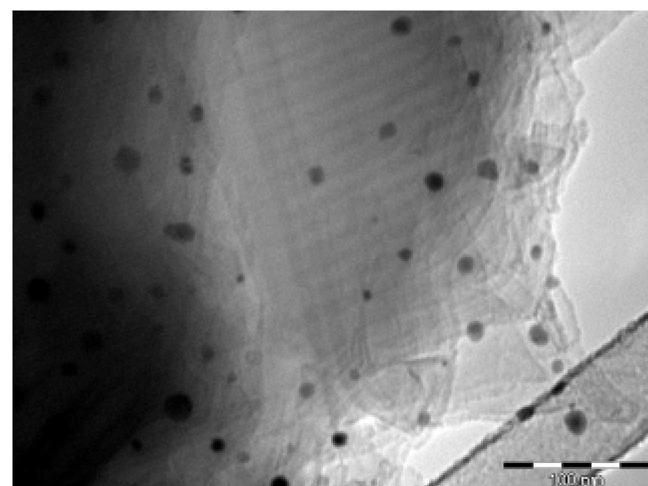


Cπ-Cπ *vs* M-Cπ interaction
C-support interaction
Anisotropy (composition)

Catalytic synthesis of few layer graphene (FLG)







R. Bacsa, P. Serp, FR 11.03952 (2011)

CVD synthesis process for graphene

Carbon in gas phase (C_2H_4 or other hydrocarbons) —— **600-1000°C** (Horizontal/fluidized bed) ——→ **Solid carbon (few layer graphene)**

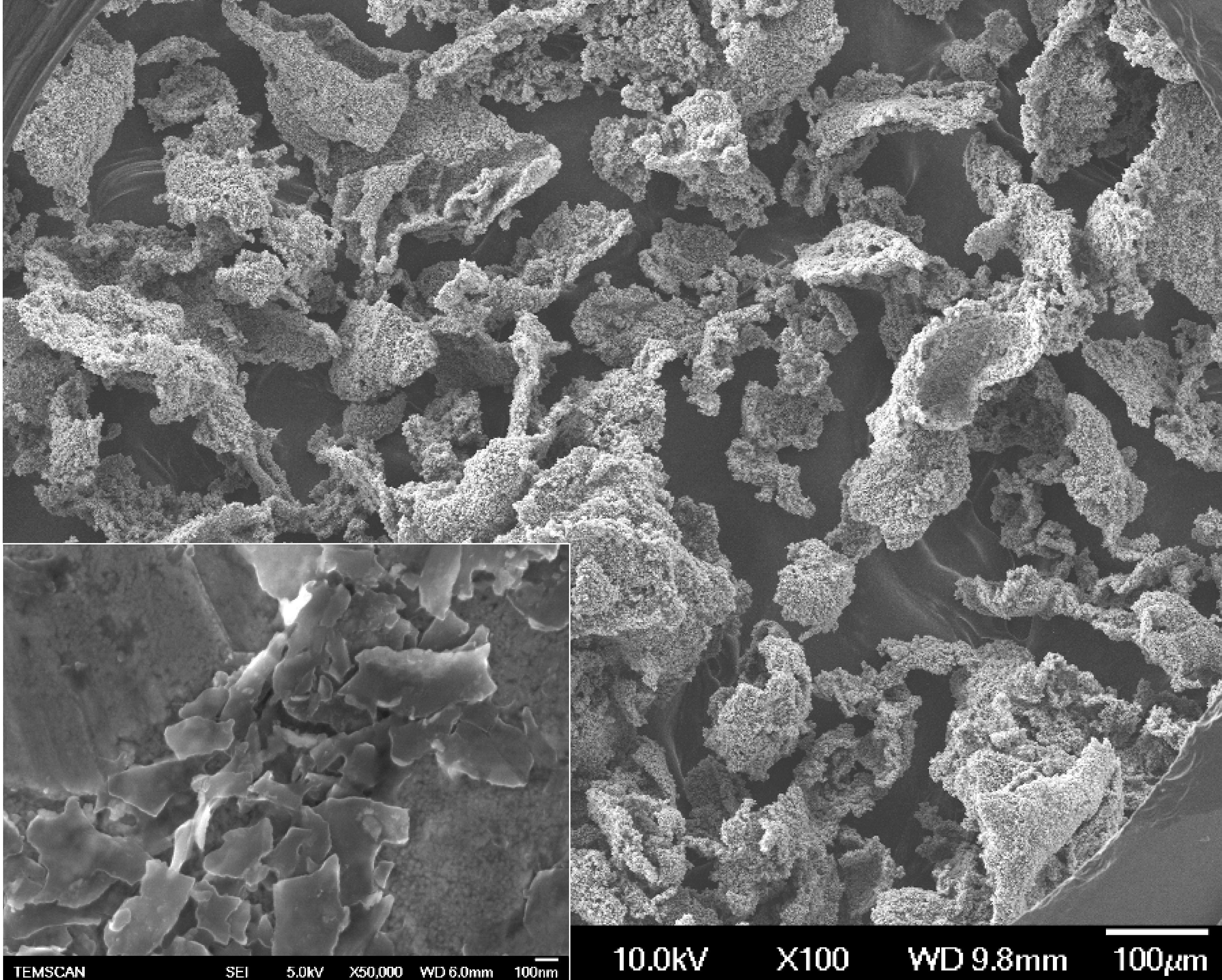
Catalyst = Mixed oxides containing Co, Fe, Ni, Cu

Nanometric oxide powder → (Ar/H_2) → Anneal → (C_2H_4, 650°C) → Composite containing graphene → (Acid treatment) → **FLG**

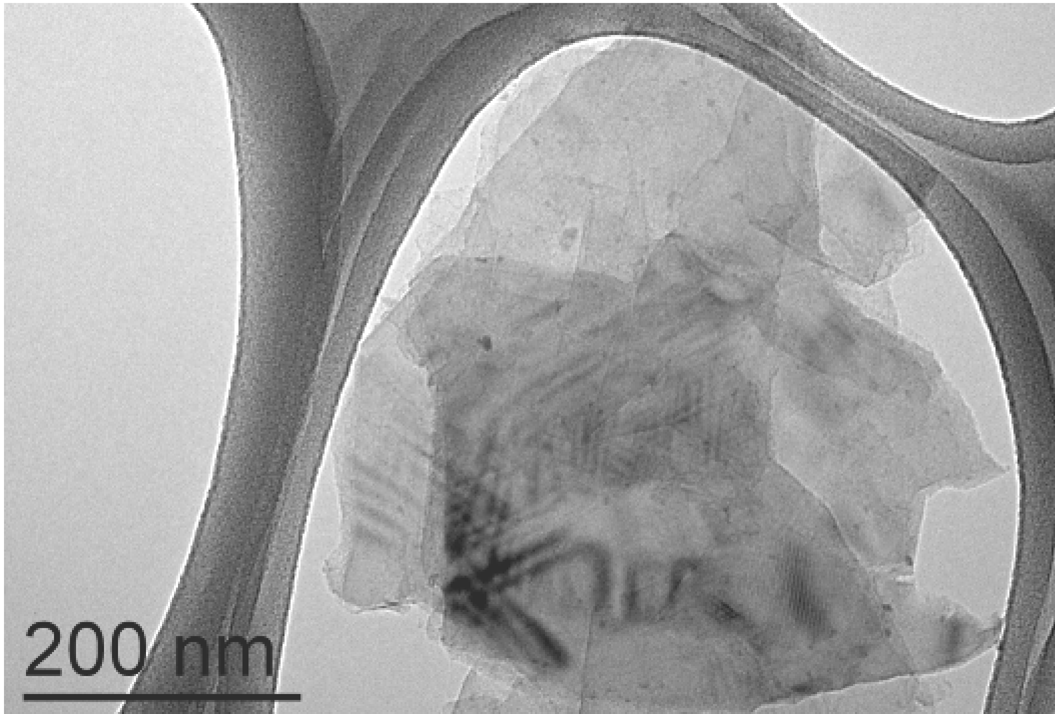
- **Low temperatures of production**
- **Selective production of CNT, FLG and CNT-FLG hybrids**
- **Lower cost of production**
- **In situ doping, domain size and thickness control**

R. Bacsa, P. Serp, FR 11.03952 (2011).
J. Beausoleil, R. Bacsa, B. Caussat, P. Serp, FR 11.62270 (2011).

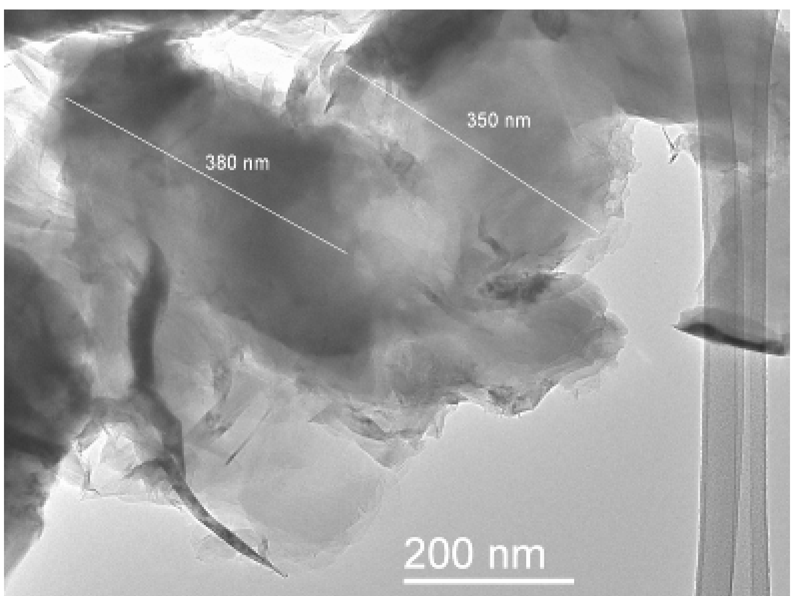
CVD reactor

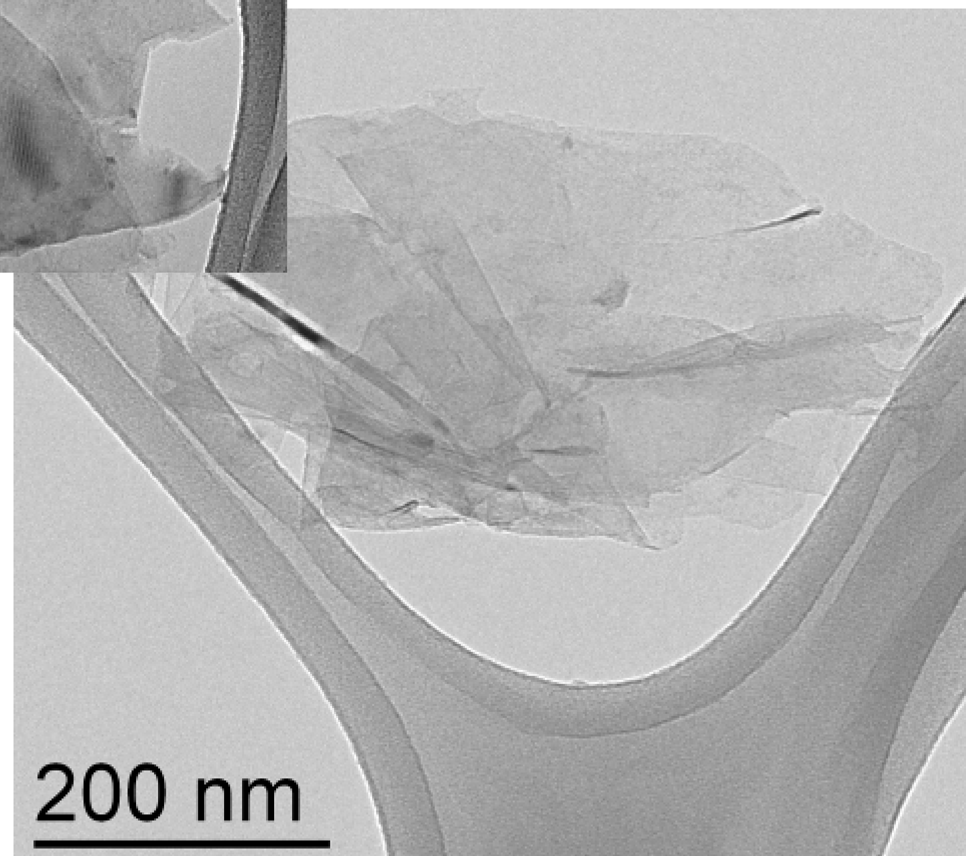


TEMSCAN SEI 5.0kV X50,000 WD 6.0mm 100nm
10.0kV X100 WD 9.8mm 100μm

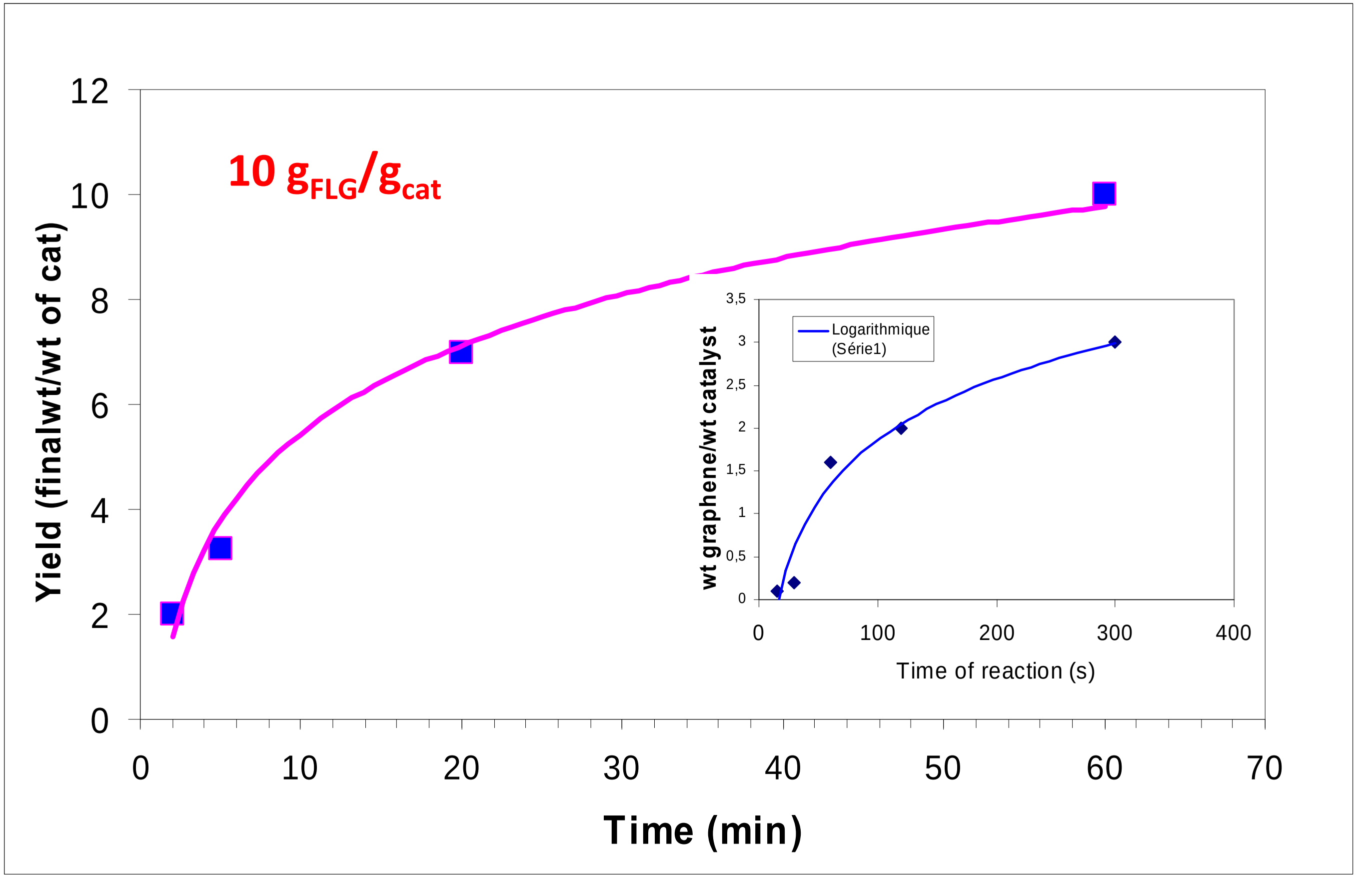


Catalyst:
M/M’ ratio
Particle size



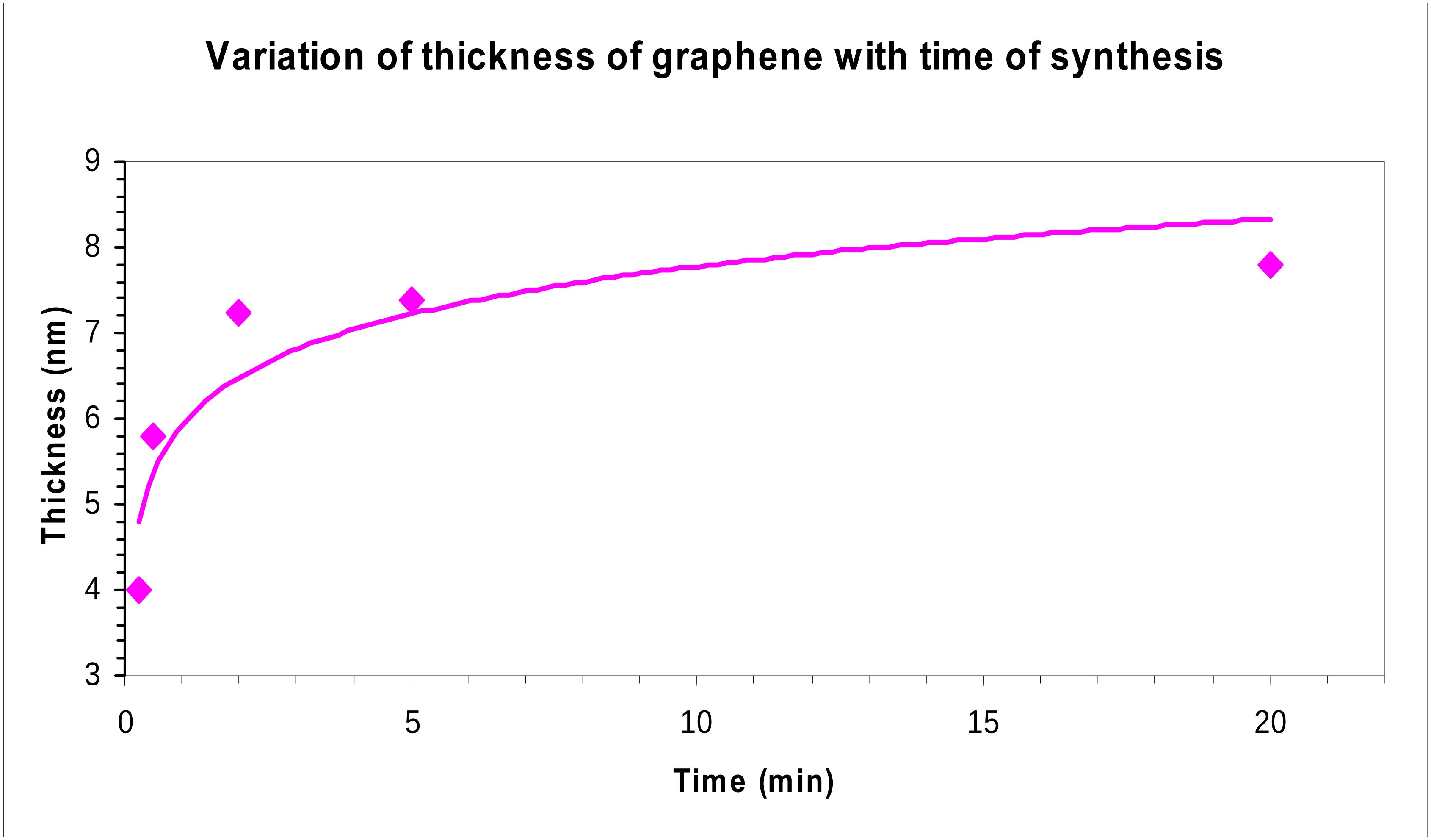


Reaction yield

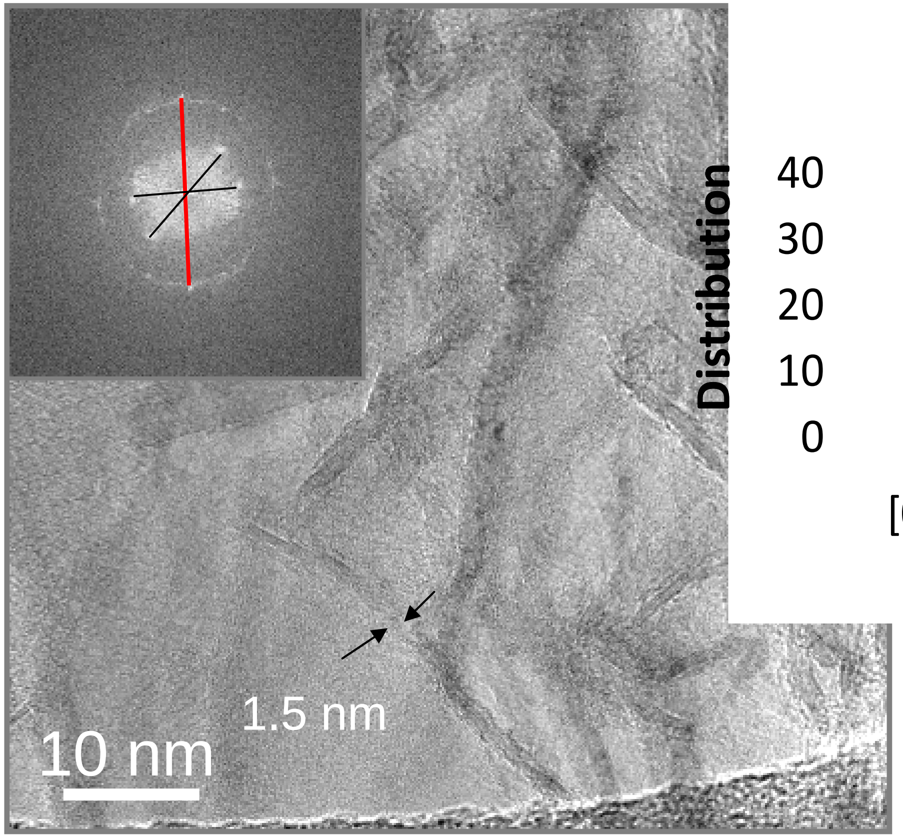


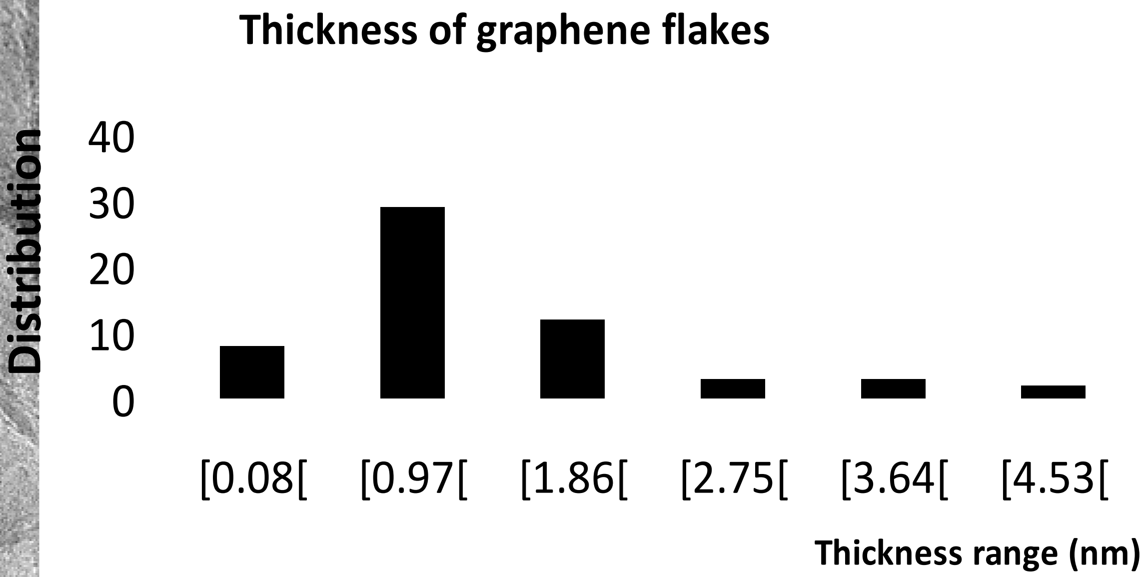
$$X = \frac{\text{Wt. of catalyst} + \text{carbon after reaction}}{(\text{Wt of catalyst})}$$

Thickness variation



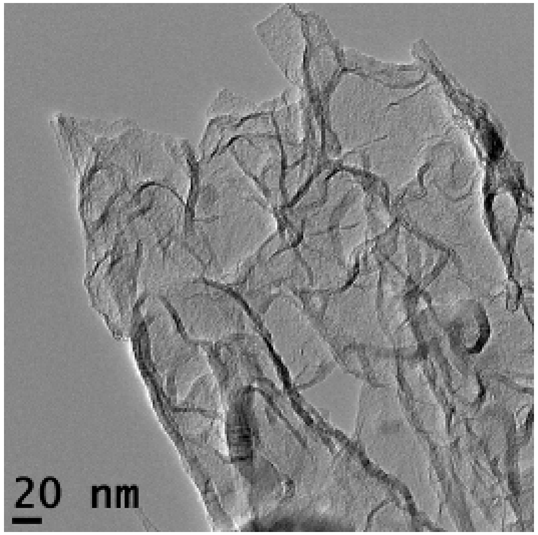
Thickness distribution for purified FLG





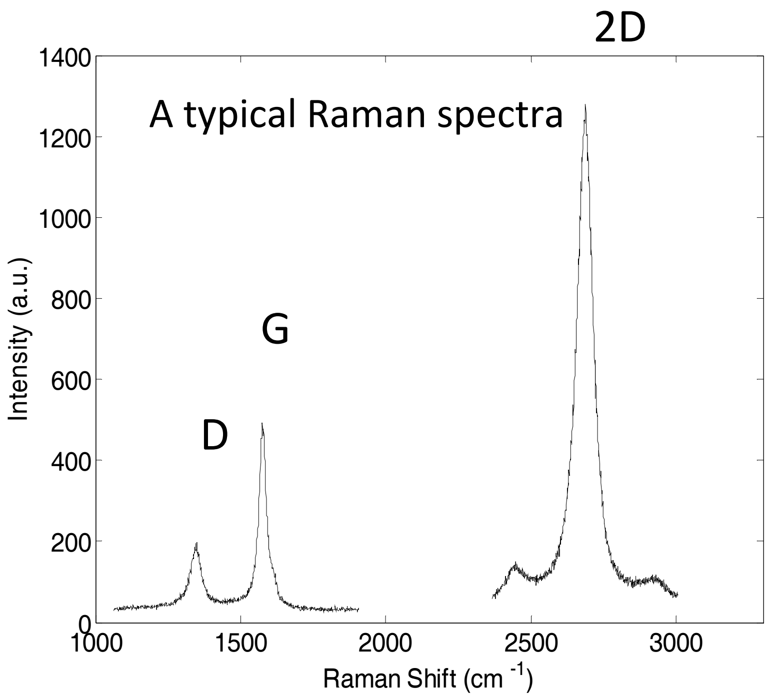
d_{002} = 0.34 nm

d_{100} = 0.21 nm



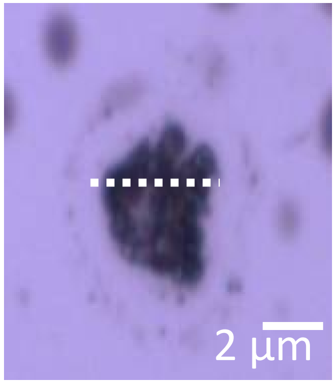
Petal like flakes of thickness ranging from 1-5 graphene layers

Raman mapping of purified FLG

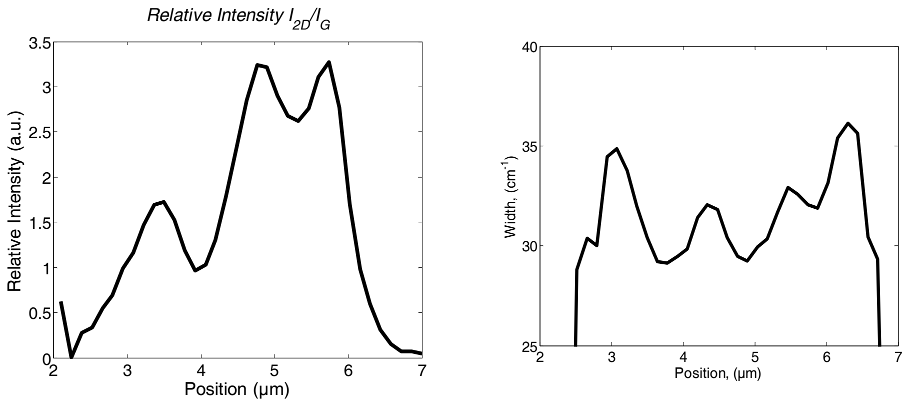


Spectrometer Xplora (Horiba Inc.), 532 nm

Optical microscope image of the FLG agglomerate



Raman spectra were taken along the white line: 50 points, step 0.14 μm



2D band is 2-3 times more intense than G band: typical for graphene

Profile of the relative intensity I_{2D}/I_G *and the width of the 2D band*

D.R. Lenski et al. J. Appl. Phys. 110, 013720 (2011)

Purified FLG properties

Oxygen content

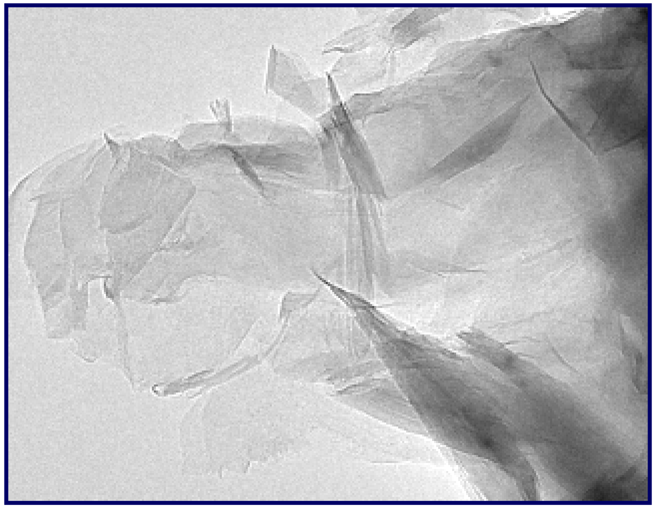
< 1% XPS

Chemical Purity

98.5%

Production

10g/h



Thickness

1-8 nm average (3-20 layers)

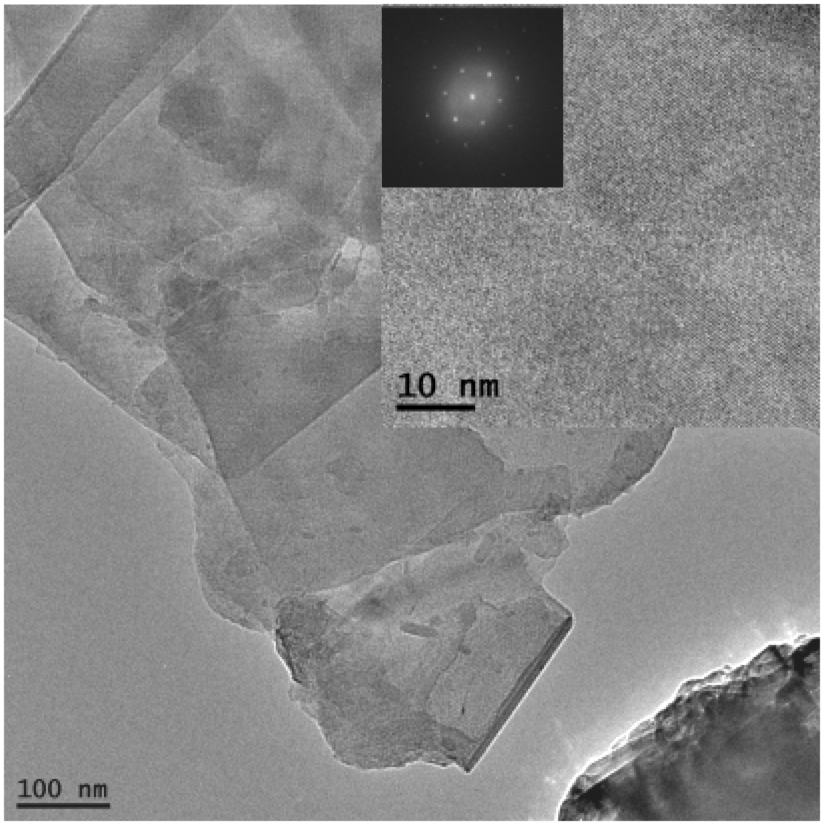
Domain size

0.2 – 0.4 μm

High crystallinity

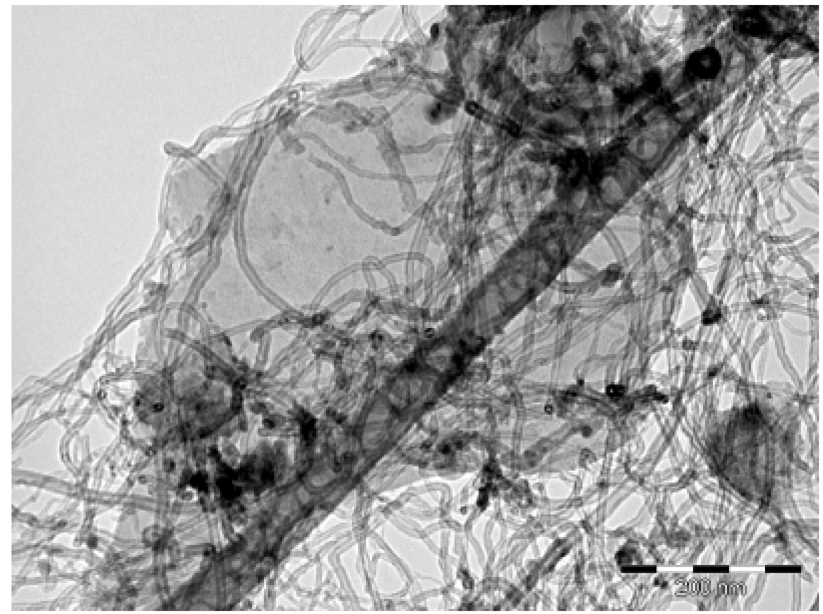
Raman 2D/G ≥ 1

Catalytic synthesis of FLG and FLG@CNT composite powders



Few layers graphene

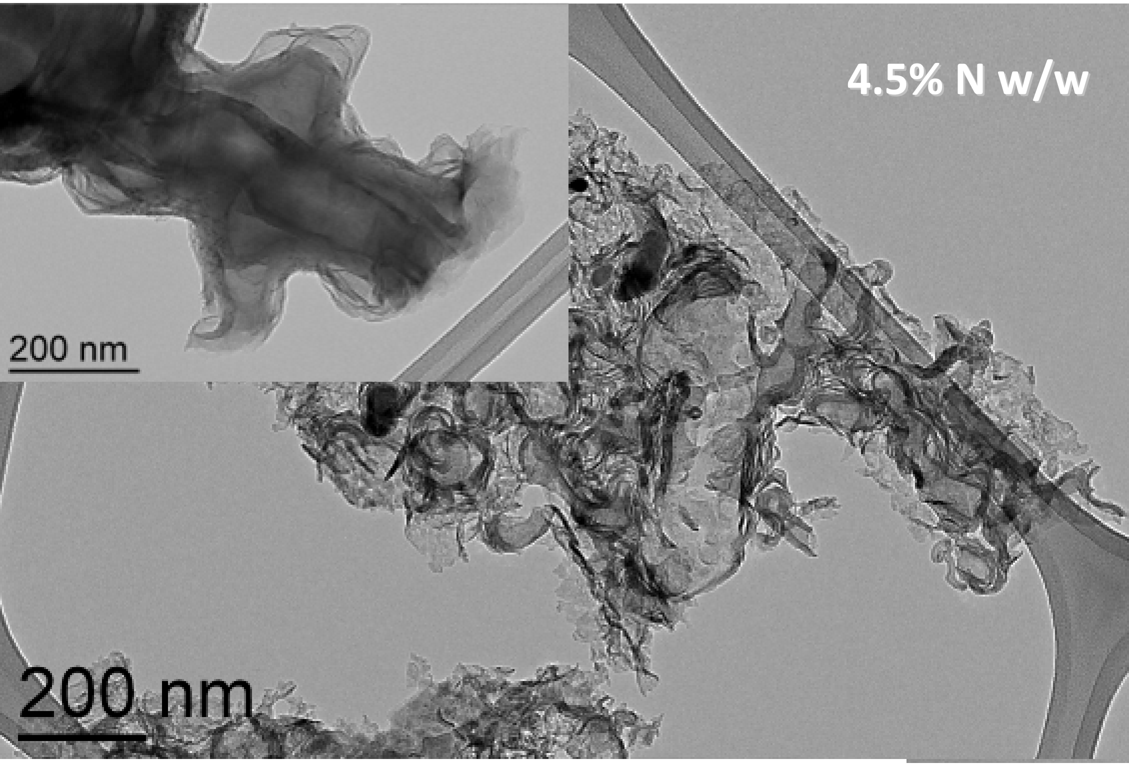
Productivity : 10g/h

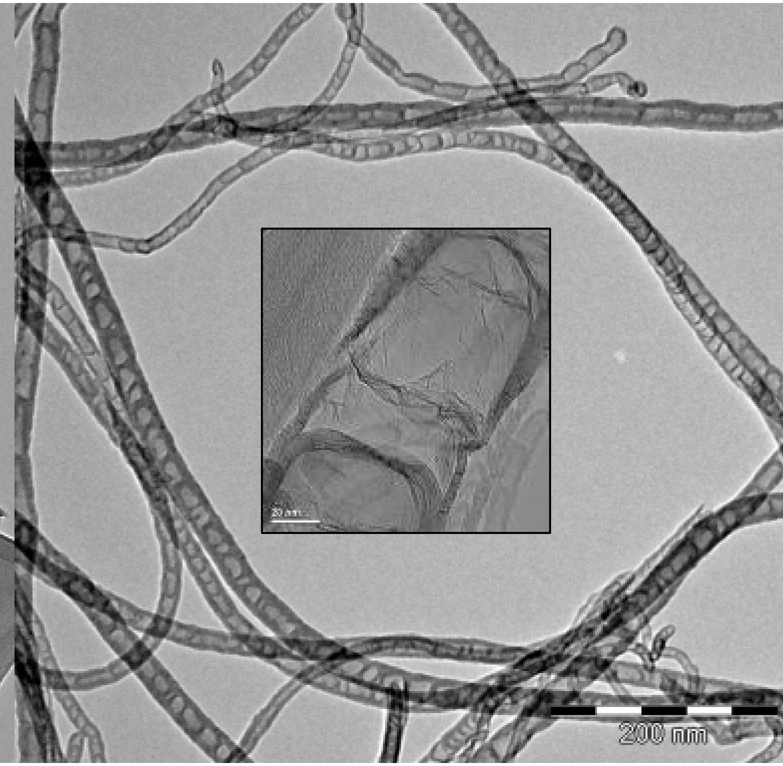


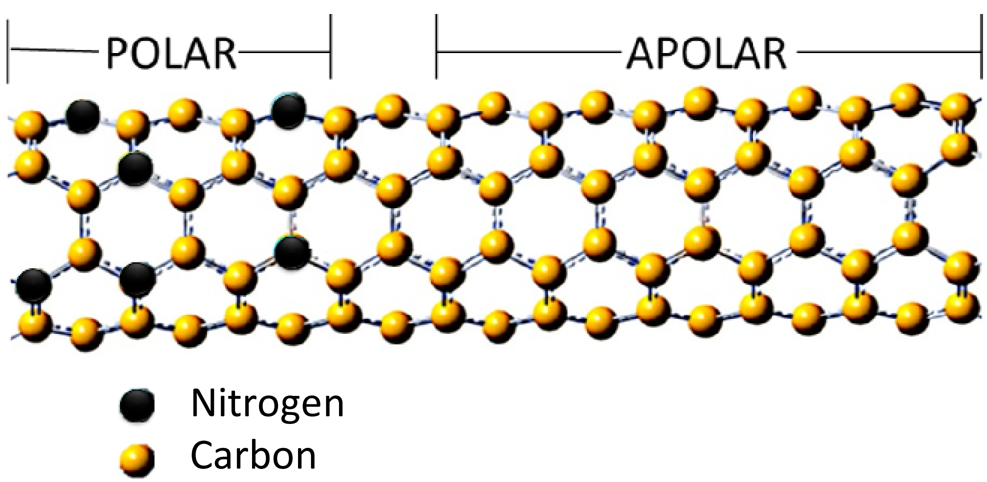
Composite powder CNT/graphene

Productivity : 30g/h

Catalytic synthesis of N-doped FLG and CNT

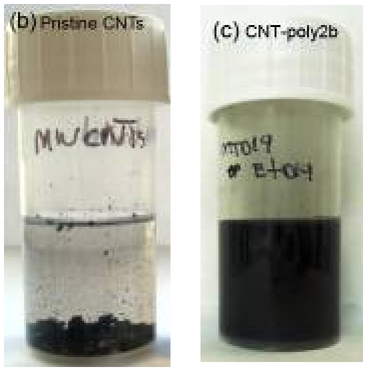






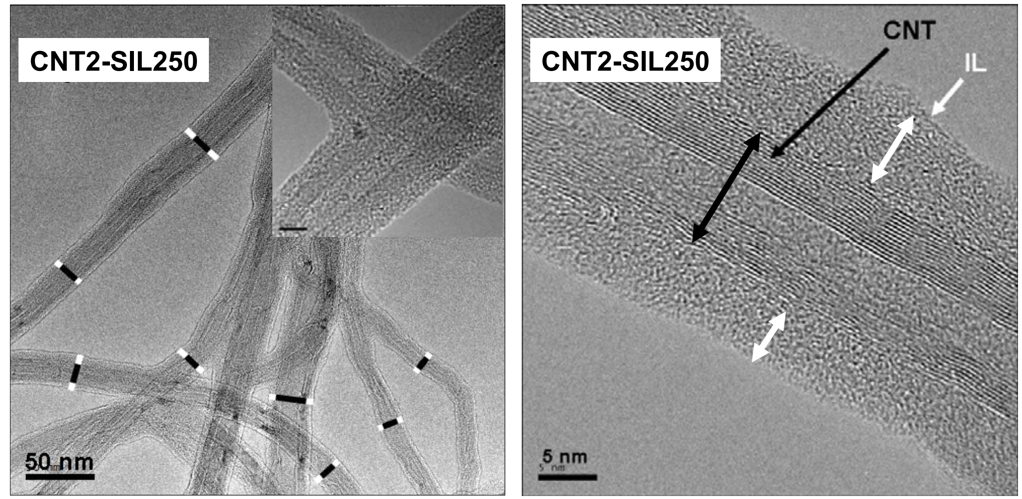
FLG dispersion???

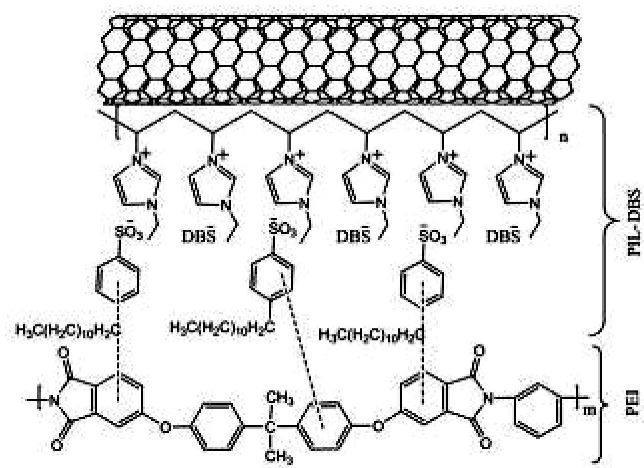
CNT/graphene & Ionic Liquids



dispersion

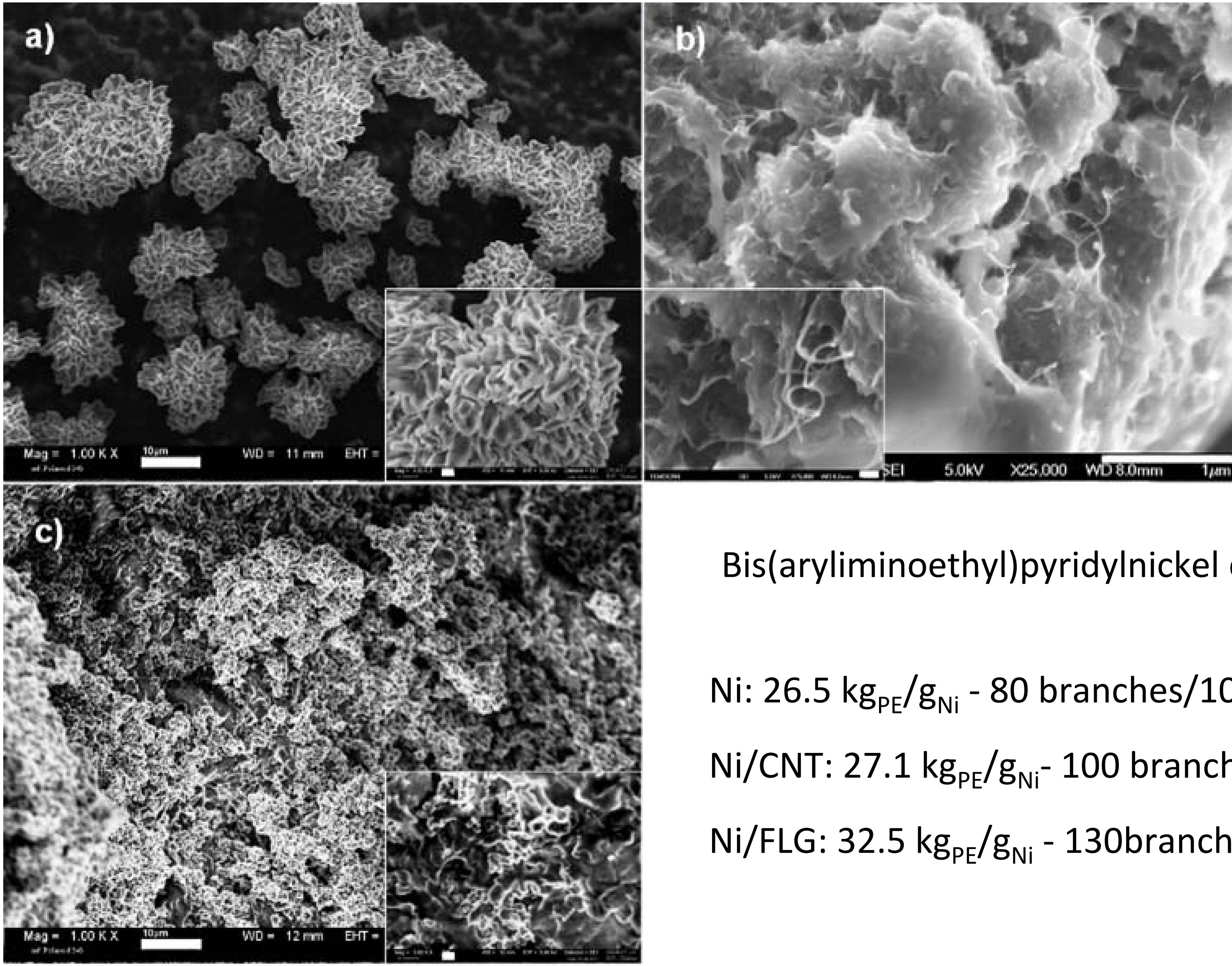
hydrogels
organogels





*M. Tunckol, et al. Carbon, 50, **2012**, 4303.*
*M. Tunckol, et al. Carbon, 57, **2013**, 209.*

Dispersion of CNT and FLG in PE waxes



Bis(aryliminoethyl)pyridylnickel chlorides

Ni: 26.5 kg_{PE}/g_{Ni} - 80 branches/1000C

Ni/CNT: 27.1 kg_{PE}/g_{Ni}- 100 branches/1000C

Ni/FLG: 32.5 kg_{PE}/g_{Ni} - 130branches/1000C

Acknowledgements

LCC

R. Bacsa
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W. Bacsa

Raman

le LABORATOIRE DE GÉNIE CHIMIQUE UMR 5503 TOULOUSE

B. Caussat

SEVENTH FRAMEWORK PROGRAMME

ARKEMA

CNT-FLG composites