Nanotube growth mechanisms and chirality control from modeling and experiments

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Many ways to obtain Carbon Nanotubes ...

Do nothing and let Mother Nature do it for you ...
Many ways to obtain Carbon Nanotubes ...

Do nothing and let Mother Nature do it for you

Carbon Nanotubes found in ancient Damascus sabre ~ 400 years old

Many ways to obtain Carbon Nanotubes ...

Search the bibliography ...
Many ways to obtain Carbon Nanotubes ...

Search the Bibliography ...

Even focusing on CNT synthesis, impossible to summarize in one hour

My apologies to those I discarded / forgot / misunderstood

More to read in:
High temperature Nanotube synthesis

Arc discharge or laser ablation:
- produce fullerenes,
- multiwall Nanotubes
- Nanohorns ...
- With catalyst (e.g. Ni): Single Wall NTs

High quality tubes
Not up-scalable for controlled mass production

WITH catalyst:
Single-Wall CNTs (bundled)

WITHOUT catalyst:
Multi-Wall CNTs + fullerenes, etc ...

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Catalytic Chemical Vapor Deposition (CCVD)

Supported (surface bound) catalyst

Catalytic dissociation of gaseous carbon-bearing molecules (CH₄, C₂H₆, C₂H₄, C₂H₂, CO, etc ...)

Catalyst acts as a template:  \textit{nano}particles \Rightarrow \textit{nano}tubes

\textit{thick and flat catalyst layer} \Rightarrow \textit{graphene}

Features:

- Scalable, lower temperature, more controlled conditions
- Long synthesis times (minutes / hours)
- Used to grow Nanotube carpets, enables control of tube density on a surface
Super Growth Pilot Plant

From 2012, 70 companies shipped, 2015 Commercial Plant Planned
(courtesy K. Hata)

Christophe Bichara
Catalytic Chemical Vapor Deposition (CCVD)

Main features:
- Catalyst Nanoparticles are formed in situ (from e.g. ferrocene)
- Short synthesis times (seconds / minutes)
- No substrate / catalyst interaction, but other specific issues

Floating catalyst / aerosol CVD

Cambridge Continuous CVD process for making CNT fibre

Fibre winding rate: 5 - 100 (m/min)

Floating catalyst CVD pilot for nanotube fibers

Koziol, Windle - Cambridge

- Injection system
- Reactor
- Fibre collection
General ideas

Confining carbon atoms or reactive species is required, but not sufficient. It may lead to:
- Fullerenes
- Amorphous carbon
- Nanotubes, nanohorns etc ...

Second aspect is to optimize nanotube production:
- Nucleation (number of active NPs)
- Growth (efficiency / rate ...)
- Prevent growth termination

A chemical engineering problem?

Certainly yes, ...

... but detailed mechanisms are still not understood
Outline

Part 1 - Basics:
  o Nucleation / growth / termination
  o Energetics / Thermodynamics (feedstock, catalyst, carbon)
  o Process conditions

Part 2 - What is more or less under control:
  o Multiwall growth
  o Vertically aligned NT carpets / forests
  o Tube / NP diameter

Part 3 - More controversial:
  o Growth model
  o Computer simulation
  o Chiral selectivity

Personal conclusion
Surface bound CCVD: root growth

**Nanotube growth stages**

- **Particle formation**
- **Incubation**
- **Nucleation**
- **Growth**
- **Defect formation and healing**
- **Deactivation**

**Open questions**

- Control NP size distribution?
- Super-saturation?
- Control cap structure?
- Growth mechanisms?
- When/how is tube structure defined?
- How to avoid?
- Incubation
- Nucleation
- Growth
- Defect formation and healing
- Deactivation

**Tip growth**: switch tubes and NP
**Floating catalyst**: remove substrate

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Stability of carbon precursor versus graphite?

Standard free energy of formation $\Delta G^0_r$ versus Temperature

$\text{CH}_4 \Leftrightarrow T > 700 \text{ C}$
$\text{CO} \Leftrightarrow T < 700 \text{ C}$

Valid for general trends, actual experimental situation might be slightly different!
Empirical criteria for «efficient» catalysis of MWNT:

- sufficient carbon solubility (1-5 at %) in metal catalyst at growth $T^\circ$
- After saturation, C precipitation starts without carbide phase formation
- If carbides form, C diffusion in metal and carbide should be fast enough ...

Fe, Ni and Co are efficient catalysts for NT growth sometimes associated with Mo, Ru, W ...

Transition metal catalysts (3)

Carbon interaction with metal catalyst surface from DFT calculations:
Various metals (Ni, Co, Fe, noble metals ...)

Order of magnitudes
- Cohesive energy carbon (diamond, graphite) \( \approx -7.5\) eV/atom
- Transition metals: Ni \( \approx -4\) eV/atom;

Difficult because very different bonding situations:
- Atomic carbon interacts strongly with metal
- Graphene has almost zero interaction with metal
- Limitations in DFT for weak bonds (van der Waals ...)

Octahedral interstitial
Subsurface interstitial
In all DFT calculations C in graphene is the most stable

- Ni, Pd, Pt : subsurface atomic C most stable
- Cu, Ag, Au : C₂ dimers on surface most stable

C at Ni (211) step edge more stable than subsurface

Abild-Pedersen et al. PRB 73, 115419 (2006)

Yazyev et al. PRL 100, 156102 (2008)
Adhesion energy of tubes with ≠ (n,m) on pure metals calculated by DFT

- Stronger for Ni, Co, Fe than Au, Cu
- Depends on tube chirality:
  - 0.8 - 1.8 eV / C for armchairs
  - 1.6 - 2.8 eV / C for zig-zag

- Relevance of these calculations?
  - ... relaxations, reconstructions, C dissolution, ...
Typical process conditions

Catalyst preparation
- Deposition: evaporation, sputtering, spin-coating...
- Drying /calcination
- Temperature annealing: oxidation, reduction

Nanotube growth
- Temperature range: 500-1000°C
- Vector gas: Ar, He, \((N_2)\)
- Carbon precursor pressure: from several bars (e.g. CO) to a few Pa (e.g. C\(_2\)H\(_2\))
- Additional ambient: H\(_2\)O, H\(_2\), O\(_2\) in the 1-500 ppm range
Fundamentals are known, but nanosize and time scales are challenging

Requires: physics and chemistry investigation techniques (TEM, XPS, Raman, XRD ...) chemical engineering approach to deal with complex system

Difficult to compare different experimental results, with sometimes contradictory claims
Part 1 - Basics:
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Part 3 - More controversial:
  - Growth model
  - Computer simulation
  - Chiral selectivity

Personal conclusions
Nucleation and growth of multiwall tubes

Thanks to large size and slow growth, \textit{in situ} TEM is possible


Catalyst NP’s are large > 6 nm \textit{crystalline} though highly \textit{deformable}

reshaping of NP during growth

Bulk carbon diffusion is likely
Nucleation and growth of multiwall tubes

1) Metal NP is soft and sticks to the carbon wall
2) Quick detachment and retraction of NP
3) Step edges are clearly visible

Yoshida et al., Nano Letters 2008

Catalyst structure and chemistry may change during growth (Fe $\rightarrow$ Fe$_3$C)

Sharma et al. Nano Letters, 9, 2, 689–94, 2009
Vertically aligned Nanotubes carpets / forests

Idea is to grow **dense** forest of nanotubes for electric or heat conduction

Process:

1. Deposit metal Film
   - Catalyst film deposition
   - e.g. Fe layer on Al$_2$O$_3$

2. Reduce metal in Hydrogen
   - Nanoparticle formation by dewetting

3. Forest growth by CVD
State of the art of nanotubes carpets / forests

Quality of tubes: Single, double ... walls + carpet thickness.
   Tube diameter: 1.5-3.0 nm
   Mass density 0.003-0.1 g/cm³ - Surface density $10^{13}$ tube / cm²
   Length: up to ~ cm

Catalyst NP’s density:
   Surface energies set limits on NP diameters.
   How to go beyond? See Robertson’s group: APL 95, 17, 173115 (2009) and ...

Catalyst efficiency
   Only a small fraction of NPs are catalytically active

Recipes available at
   http://www.nanocarbon.jp/index_e.shtml

Christophe Bichara
Many materials (with oxygen) as growth enhancers

Advanced Material, 21, 1 (2009)
Control of tube diameter via process parameters

Optimal parameter domain for small-diameter SWNTs

\( \text{Temperature (°C)} \)

\( \text{Ethanol partial pressure (Pa)} \)

- No growth
- Small
- Medium
- Large

- Feedstock: ethanol
- Catalyst: Ni/SiO\(_2\)

\( \text{In situ} \) Raman supports size-dependent processes of activation/deactivation

More details: V. Jourdain, talk C9, Tuesday, 10.30 am

Picher et al., ACS Nano 5, 2118 (2011)
First step towards full control of SWNT structure is control of diameter

Post growth TEM measurements of SWNT and NP diameters $\phi$ generally yield:

$$\frac{\phi_{SWNT}}{\phi_{NP}} \approx \text{in (0.5 - 1) range}$$

TEM measurement on samples at different growth times shows that $\frac{\phi_{SWNT}}{\phi_{NP}}$ can evolve during synthesis

Tangential mode favored by slow growth conditions

<table>
<thead>
<tr>
<th>Synthesis time</th>
<th>Nuclei</th>
<th>Nanotube</th>
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<tbody>
<tr>
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<td>perp.</td>
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<tr>
<td>40 s</td>
<td>65</td>
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<tr>
<td>2 min</td>
<td>70</td>
<td>30</td>
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<tr>
<td>10 min</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td>30 min</td>
<td>45</td>
<td>55</td>
</tr>
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</table>

Nasibulin et al. Carbon 2005
Hiraoka et al. Carbon 2006

Fiawoo et al. PRL 195503 (2012)

M.F. Fiawoo

Christophe Bichara
SWNT and Nanoparticle diameter correlation

Raman + AFM on well separated ultralong tubes on a surface show that changing temperature can reversibly change tube diameter

Authors suggest change of carbon solubility and interfacial properties as a possible cause

Thanks to difficult and time consuming systematic analysis of 
substrate / catalyst / reactants / process conditions 
(interdependent parameters)

Substantial progress made on understanding / controlling growth of
- Multiwall nanotubes
- Nanotube carpets / forests
- SWNT diameter
- Preparation, state and quality of substrate (porosity ...)
- How to limit particle coarsening (MCM’s, surf. segreg. of Co from solid sol$	ext{on}$)
- Substrate and catalyst formation and pre-treatments (oxidation/reduction)
- Catalyst deactivation (encapsulation by C, coarsening of NPs ...)
- ...

Also very important
Outline

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Personal conclusions

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Simple model for SWNT growth - Yakobson + coworkers

Growth of nanotube similar to spiral growth of crystal

Feng Ding et al. PNAS 2009

Simple calculations show that growth rate is proportional to chiral angle

- Near armchair tubes grow faster
- Experimental support from in situ growth in Field emission microscope at LPMCN (Lyon), showing rotation of of FEM pattern

Controversial:

- Role of catalyst particle?
- Implies C₂ dimers attachment at kinks?

- Tomanek:
  http://www.rsc.org/chemistryworld/News/2009/February/10020901.asp

M. Marchand et al, NanoLetters 9, 8, 2961 (2009)
Measurement of individual tube growth rate

One **single** tube grown per plot... growth rate measured *in situ* by Raman

Higher chiral angles tend to grow faster ...

Computer simulation of SWNT Growth

Interatomic interaction model
- Metal + carbon
- Quantum Chemistry, DFT-based, Tight binding, empirical

Computer simulation techniques
- Energy relaxations (→ relative stabilities of simple structures) *ab initio OK*
- Molecular Dynamics.
  - TB or empirical

- Monte Carlo methods:
  - TB or empirical
  - grand canonical for open systems
  - force-biased for efficiency

Gavillet *et al.* PRL 2001

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Interatomic interaction model

- Metal + carbon
- Quantum Chemistry, DFT-based, Tight binding, empirical
- Accuracy / transferability

Computer simulation techniques

- Energy relaxations (→ relative stabilities of simple structures) \textit{ab initio OK}

- Molecular Dynamics.\footnote{Time scale < nanoseconds in MD > seconds in experiments}
  TB or empirical

- Monte Carlo methods :\footnote{structural quality, defects ?}
  TB or empirical

C atoms on flat Co surface diffuse to attach to tube cap

Gavillet et al. PRL 2001
Computer simulation: state of catalyst?

State of catalyst

○ During growth: small NP’s ($\phi \leq 2$ nm) are not crystalline because C incorporation larger ones: crystalline core (molten outer layer?)

○ Crystalline facets: unlikely for small NPs, in presence of C may exist for larger ones

○ Once formed, tube is stiff, metal NP is soft epitaxy of ideal structures on pure metal at 0 K is not relevant!

Ni-C tight binding model
Los et al. PRB 81, 064112 (2010)

Fe-C empirical model
Feng Ding et al. JVST A22, 1471 (2004)
Computer simulation: carbon solubility in Nanoparticle?

In situ XPS shows presence of carbon near surface (Fe-C bonds, also for Ni-C)

Hofmann et al., Nano letters 7, 602–8 (2007)

C solubility larger for smaller nanoparticles

C solubility smaller for smaller nanoparticles
Computer simulation: Nucleation?

Nucleation

- Takes place when NP is (sub-surface) saturated

  See also
  H. Amara et al. PRL 100, 056105 (2008)

- Chirality may change during nucleation / early growth

  E. C. Neyts et al. JACS 133, 43, 17225–31 (2011)
Computer simulation: growth?

Growth

- **Carbon insertion**
  - polyyn chains (TB models ...)
  - Carbon atoms of dimers \( \text{C}/\text{C}_2 \)
  - Models don’t include etchants and hydrogen...

- **Does not require steps**
- **Dewetting is driving force**
- **Interfacial properties are**
- **control by C solubility**

See poster # 244 and CCTN13


<table>
<thead>
<tr>
<th>Name</th>
<th>Journal/Citation</th>
<th>Reaction/Conditions</th>
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<td>CO / CoMo / silica</td>
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<td>CH4 / FeRu / silica / 850 C</td>
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<td>CO, MetOH, EtOH, C$_2$H$_2$ / CoMo</td>
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<td>C$_2$H$_2$ / Ni$<em>x$Fe$</em>{(1-x)}$ plasma synthesis</td>
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<td>Harutyunyan</td>
<td><em>Science</em> 326, 5949, 116-20 (2009)</td>
<td>CH4 + ambient / Fe / silica</td>
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<tr>
<td>Ghorannevis</td>
<td><em>JACS</em> 132, 28, 9570-2 (2010)</td>
<td>CH4 + H2 / Au / PECVD</td>
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<td>This conference</td>
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</table>

_Different ways of assigning chirality (Raman, Photoluminescence, electron diff., ...) may play a role_
Chiral selectivity?

Bachilo  *JACS* 125, 37, 11186-7 (2003)
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Zhu  *JACS* 133, 1224–1227 (2011)
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Yan Li  This conference

CO / CoMo / silica
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*C2H2 / NixFe(1-x) plasma synthesis*
*CH4 + ambiant* / Fe / silica
*CH4 + H2* / Au / PECVD
CO / FeCu / MgO
*CH4 / Ferrocene + S / Float. Cat.*
*CO + NH3/ Ferrocene/ Float.Cat.*
CO / FeCu / MgO

Some groups emphasize the role of **ambient or process** (PECVD)

Christophe Bichara
Chiral selectivity: role of precursor, ambient ...

Similar growth conditions:
• Fe nanoparticles on Si₃N₄ grid
• 800°C
... but changing precursor

TEM analysis
Electron diffraction to assign (n, m)

Chiral selectivity: role of precursor, ambient ...

Modifying the ambient \((H_2O+He)\) vs \((H_2O+Ar)\) leads to substantial modifications of NP shape (surface energies).

In situ TEM @500C

H\(_2\)O+He
Facetted NP

H\(_2\)O+Ar
Rounded shape NP

Fine tuning the experimental conditions, leads to a maximal selectivity of 96% metallic SWNT’s!


(9, 9) \(\phi\) NP < 2 nm
Chiral selectivity?

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CO / FeCu / MgO  
CH4 / Ferrocene + S / Float. Cat.  
CO + NH3/ Ferrocene/ Float.Cat.  
CO / FeCu / MgO

Many groups report use of **bimetallic** catalysts
Some are **phase separated**: 

**CuFe**: Fe NPs on Cu layer; **CoMo**: Co NPs on Mo oxide/carbide 

emphasis on process conditions

Chiral selectivity: state and role of bimetallic catalyst

Some are **Nanoalloys**:

- \(\text{Ni}_x\text{Fe}_{(1-x)}\) large solubility range, similar size and surface energies
- \(\text{FeRu}\) probably too, according to bulk phase diagram

**FeRu**

A way to control carbon solubility?

**Best selectivity for \(\text{Ni}_{27}\text{Fe}_{73}\)**

Chiang and Sankaran, *Nat. Mat.* (2009)

![FactSage diagram](image-url)

![Temperature vs Fe concentration](image-url)
Nanotube growth stages:

- Particle formation
- Incubation
- Nucleation
- Growth

Some answers ...
... personal conclusions

Summarizing ...
Catalyst Nanoparticle is one of the keys

Because of « high » temperature, issues with

- Chemical interactions
  - with substrate: oxidation, ...
  - feedstock + ambient: (surface-) carbides, facetting (?)
  - « Growth enhancers » to keep active NPs

- Size distribution and stability during synthesis
  - Ostwald ripening / Nanoparticle coarsening can be limited by:
    - use of templates (MCM’s, ...)
    - Different ways of « anchoring » the NPs

Keeping stable and active NPs is a necessary condition for controlled growth
Nucleation is a stochastic event, difficult to control

- **Use of oxygen-containing « growth enhancer » helps keeping NPs active**
  - Removing amorphous carbon coating
  - Maximizes the number of active NP’s

- **Very small energy differences between caps with different chiralities**
  - ... makes *me* doubt that it can be a key to chiral selectivity

- ???
Growth

Better control is gained with slow growth conditions

Multiwall nanotubes
  - large, crystalline though highly deformable NPs,
  - metal or metal carbide NPs are efficient
  - bulk carbon diffusion, step edges ...

Single wall nanotubes
  - much smaller NP’s
    - liquid or amorphous, possibly with crystalline core
  - carbon incorporation mechanisms are still largely unknown
  - wetting properties of NP/carbon wall interface are essential

Competing growth kinetics
  - carbon wall growth (chirality + catalyst dependent)
  - dewetting of nanoparticle (carbon solubility dependent, controlled via chemistry)
    ... might be critical for structural control
Thank you for your attention!

And thanks to

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François Ducastelle Chatillon France
Kim Bolton Univ. Gothenburgh
Anders Börjesson + Borås Sweden
Alexandre Zappelli CINaM - CNRS and AMU
Jan H. Los
Mamadou Diarra
Postdoc positions available

Experimental: Transmission Electron Microscopy
Annick Loiseau – LEM (CNRS and ONERA) – Paris

Theory and computer simulation:
Christophe Bichara – CINaM (CNRS) Marseille
Hakim Amara – LEM (CNRS and ONERA) – Paris
Any questions?