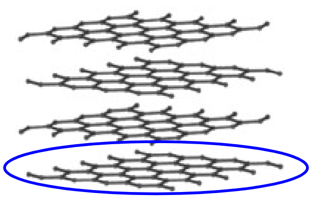
革新的マテリアルのプロセス基盤 カーボンナノチューブでの試行例

- 夢の材料をどう現実に？0→1→10→100→1000…
- マテリアル開発での0→1 vs プロセス開発での0→1
- コスト競争で勝てないから、我が国は品質で勝負…
  デバイス性能で勝てる根拠？
  プロセス性能で勝てない根拠？

Suguru NODA (野田 優)
Department of Applied Chemistry, Waseda University, Japan
noda@waseda.jp http://www.f.waseda.jp/noda/

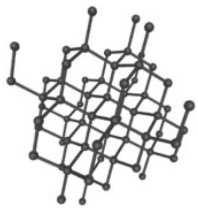
Carbon Nanomaterials

sp^2 → graphite

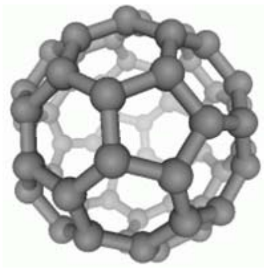


2D: graphene

sp^3 → diamond



0D: fullerene 1D: carbon nanotube (CNT)

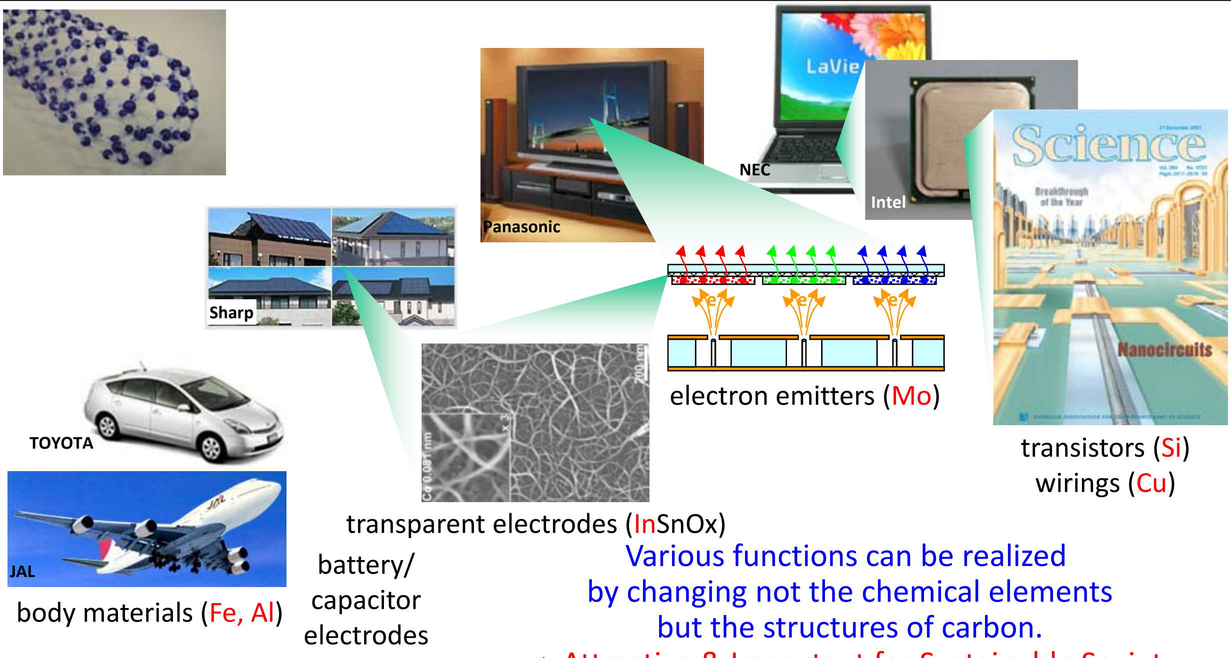


http://theor.jinr.ru/disorder/nano.html

SWCNTs: single-walled CNTs
FWCNTs: few-wall CNTs
MWCNTs: multi-wall CNTs

Dangling-bond less, 2D graphene sheet realizes stable 0~2D nanomaterials having both features of inorganic (strong, stable & conductive) & organic (soft & light) materials.

Rich Opportunities and Challenges with CNTs



Various functions can be realized
by changing not the chemical elements
but the structures of carbon.
→ Attractive & Important for Sustainable Society

Scientists/physicists showed their rich opportunities for innovative applications.
Challenges still remain in their practical production.
(high quality SWCNTs ~10^{4-6} USD/kg vs MWCNTs ~1×10^{2} USD/kg)

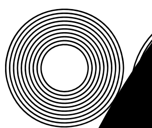
→ Mission for chemical engineers.

Various Carbon Nanotubes & Nanofibers

OCSiAl
TUBALL
http://ocsial.com/
single-wall
d = 1.5 nm
l > 5 µm
C > 85 wt%
CNT > 75 wt%
9 USD/g
(100 g)

MEIJO NanoCarbon
MEIJO eDIPS
http://meijo-nano.com/
single-wall
d = 1, 1.5, 2 nm
C > 50, 90, 99 wt%
1600–150 USD/g
(1 g)

CNano
FloTube 9000
http://www.marubeni-sys.com/cnt/cnano/
multi-wall (10–20)
d = 10–15 nm
l = 10 µm
C = 95–97.5 wt%
0.1 USD/g ?
(>kg)



Showa Denko
VGCF-H
http://www.sdk.co.jp/produc[redacted]
vapor grow[redacted]
d = 1[redacted]

A kind of "inorganic polymer made of only carbon"

Production Methods of CNTs

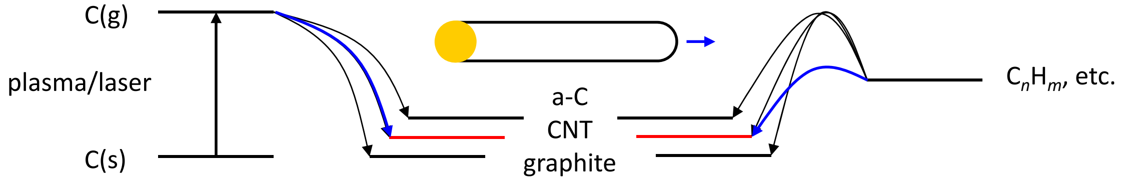
Physical Vapor Deposition

Carbon vapor is formed by heating solid carbon source by arc/laser.

Solid carbon including tubes is formed during cooling.

Chemical Vapor Deposition

Carbon-containing gas molecules are decomposed through chemical reactions, yielding solid carbon including tubes.



Metal nanoparticles as template & catalyst

High temperature (& solid C-source) ⇔ High crystallinity

Low temperature & gas C-source ⇔ Large production scale

> How to realize small catalyst particles (Fe, Co, Ni, etc.) at high reaction temperatures is an important key to establish production of thin CNTs.

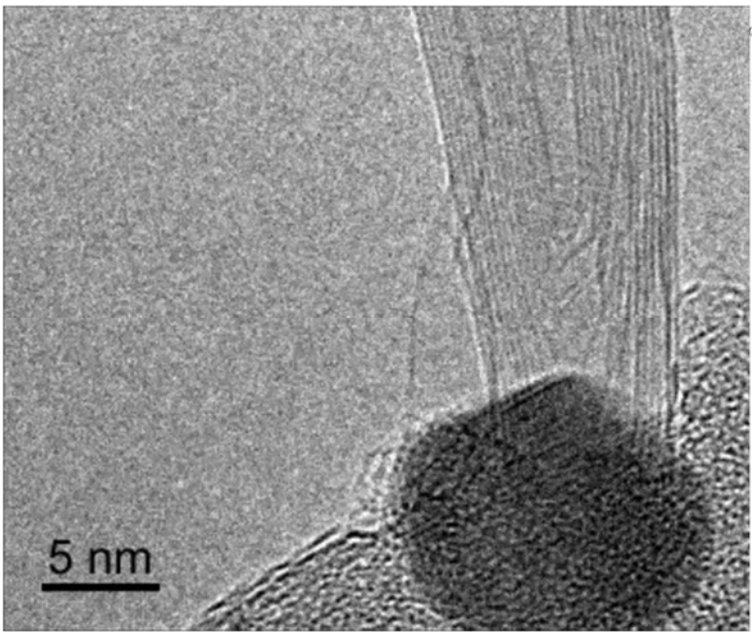
In Situ Observation of CNT Growth from a Catalyst

by environmental TEM, e-TEM

NANO LETTERS 2008 Vol. 8, No. 7 2082-2086

Atomic-Scale In-situ Observation of Carbon Nanotube Growth from Solid State Iron Carbide Nanoparticles

Hideto Yoshida,†,§ Seiji Takeda,*,†,§ Tetsuya Uchiyama,†,§ Hideo Kohno,†,§ and Yoshikazu Homma‡,§



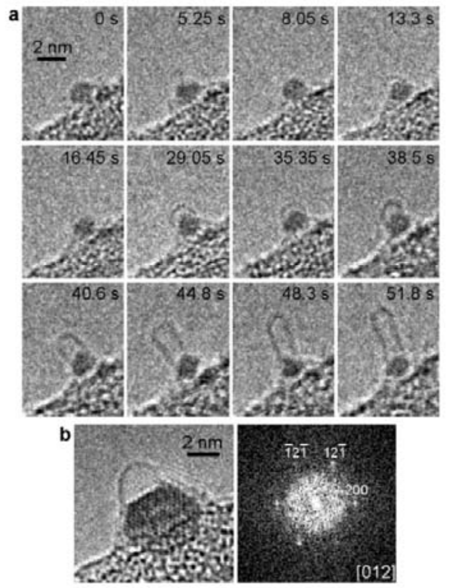
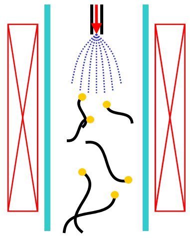


Figure 1. Nucleation and growth process of a SWNT from a NPC on a substrate. (a) Structural fluctuation of both carbon caps and a NPC is observed. The recording time is shown in images. (b) A snapshot of a NPC with a carbon dome. The NPC exhibits the lattice image and the corresponding extra diffraction in the Fourier transform. The NPC can be identified as Fe-carbide (cementite, Fe_3C) viewed along the [012] direction.

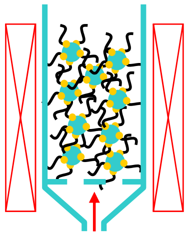
Various CVD Processes

(a) Floating Catalysts
SW: Rice (HiPco), Aalto, AIST (e-DIPS), etc.
MW: Showa-Denko (VGCF), Nikkiso (DIPS), etc.



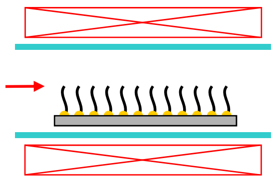
Catalysts floating in gas
○Continuous feeding, *in situ* formation
△Catalysts at low density
△Catalyst contamination
Reaction in 3D-space
→ Middle productivity
Products as aerosol
○Ready for dispersion

(b) Powder Catalysts
SW: Oklahoma (CoMoCAT), Tsinghua, etc.,
MW: NANOCYL, Bayer, Alchema, CNano



Catalysts on powders
・Continuous feeding possible, *ex situ* formation
○Catalysts at high density
△Catalyst contamination
Reaction in 3D-space
→ High productivity
Products as aggregates
・How to post-treat?

(c) Supported Catalysts
SW: UT (ACCVD), AIST (SuperGrowth), etc.
MW: Tsinghua (Super Aligned Tubes), etc.



Catalysts on substrates
・Continuous feeding possible, *ex situ/ in situ* formation
○Catalysts at high density
○Easy separation
Reaction in 2D-space
→ Small productivity
Products on substrates
○Direct implementation

多様なプロセス ⇔ 多様な構造 ⇔ 多様な用途
無数の組み合わせ、沢山の玉、それ以上に沢山の石

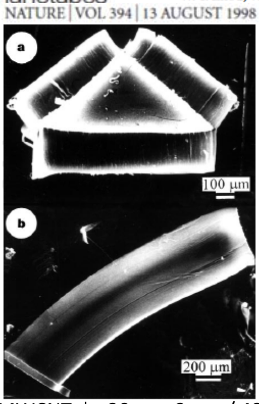
Vertically-Aligned Forests: MWCNTs → SWCNTs

Pioneering Work on MWCNTs

Large-Scale Synthesis of Aligned Carbon Nanotubes
W. Z. Li, S. S. Xie,* L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, G. Wang
SCIENCE • VOL. 274 • 6 DECEMBER 1996

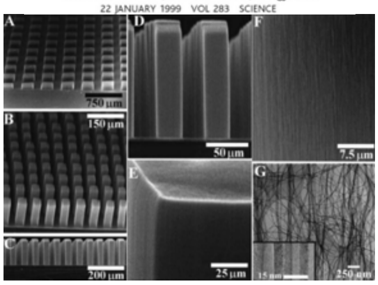
MWCNT, ϕ~ 30 nm, 50 µm/ 2 h (Fe/porous SiO_2, C_2H_2@700 °C)

Very long carbon nanotubes
Z. W. Pan, S. S. Xie*, B. H. Chang, C. Y. Wang, L. Lu, W. Liu, W. Y. Zhou, W. Z. Li
NATURE | VOL 394 | 13 AUGUST 1998



MWCNT, ϕ~ 30 nm, 2 mm/ 48 h (Fe/porous-SiO_2, C_2H_2@600 °C)

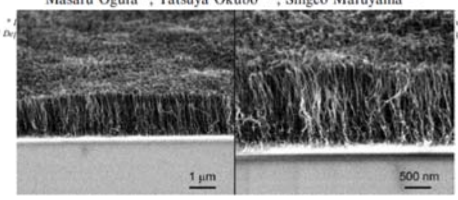
Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties
Shoushan Fan, Michael G. Chapline, Nathan R. Franklin, Thomas W. Tombler, Alan M. Cassell, Hongjie Dai*
22 JANUARY 1999 VOL 283 SCIENCE



MWCNT, ϕ~ 16 nm, 30–240 µm/ 5–60 min (Fe/porous-SiO_2, C_2H_4@700 °C)

Alcohol CVD of VA-SWCNTs

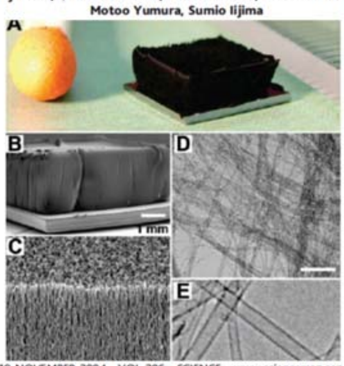
Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy
Chemical Physics Letters 385 (2004) 298–303
Yoichi Murakami, Shohei Chiashi, Yuhei Miyauchi, Minghui Hu, Masaru Ogura, Tatsuya Okubo, Shigeo Maruyama



Several years →

SuperGrowth of VA-SWCNTs

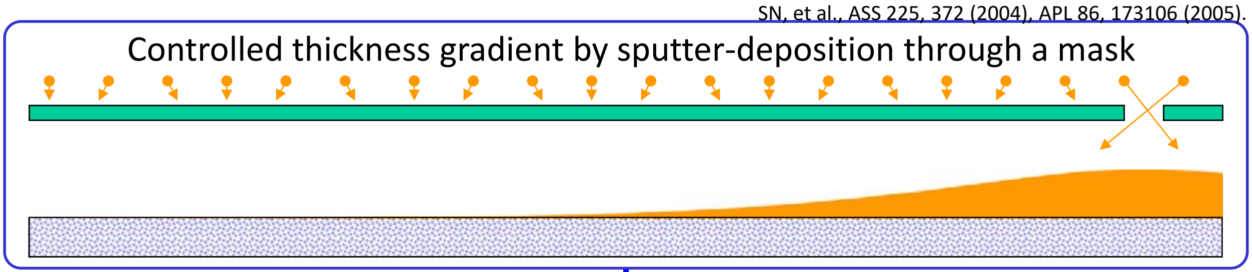
Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes
Kenji Hata,*† Don N. Futaba,* Kohei Mizuno, Tatsunori Namai, Motoo Yumura, Sumio Iijima

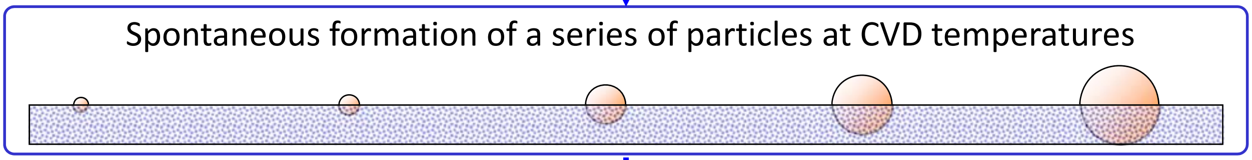


19 NOVEMBER 2004 VOL 306 SCIENCE www.sciencemag.org

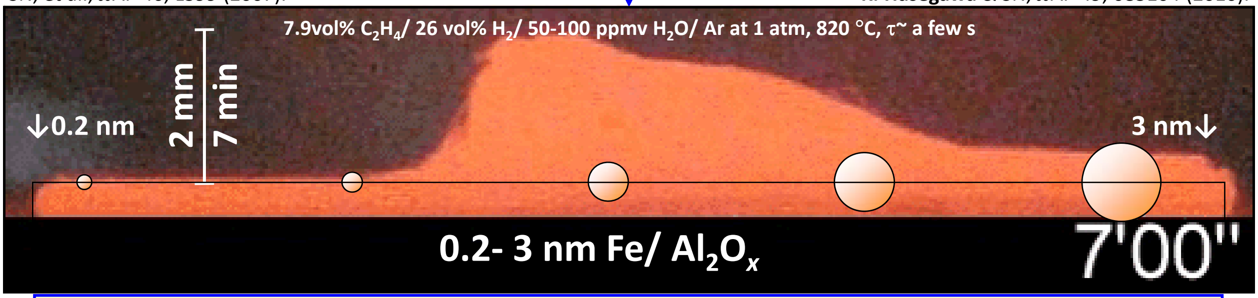
触媒の効果的な探索・最適化

SN, et al., ASS 225, 372 (2004), APL 86, 173106 (2005).



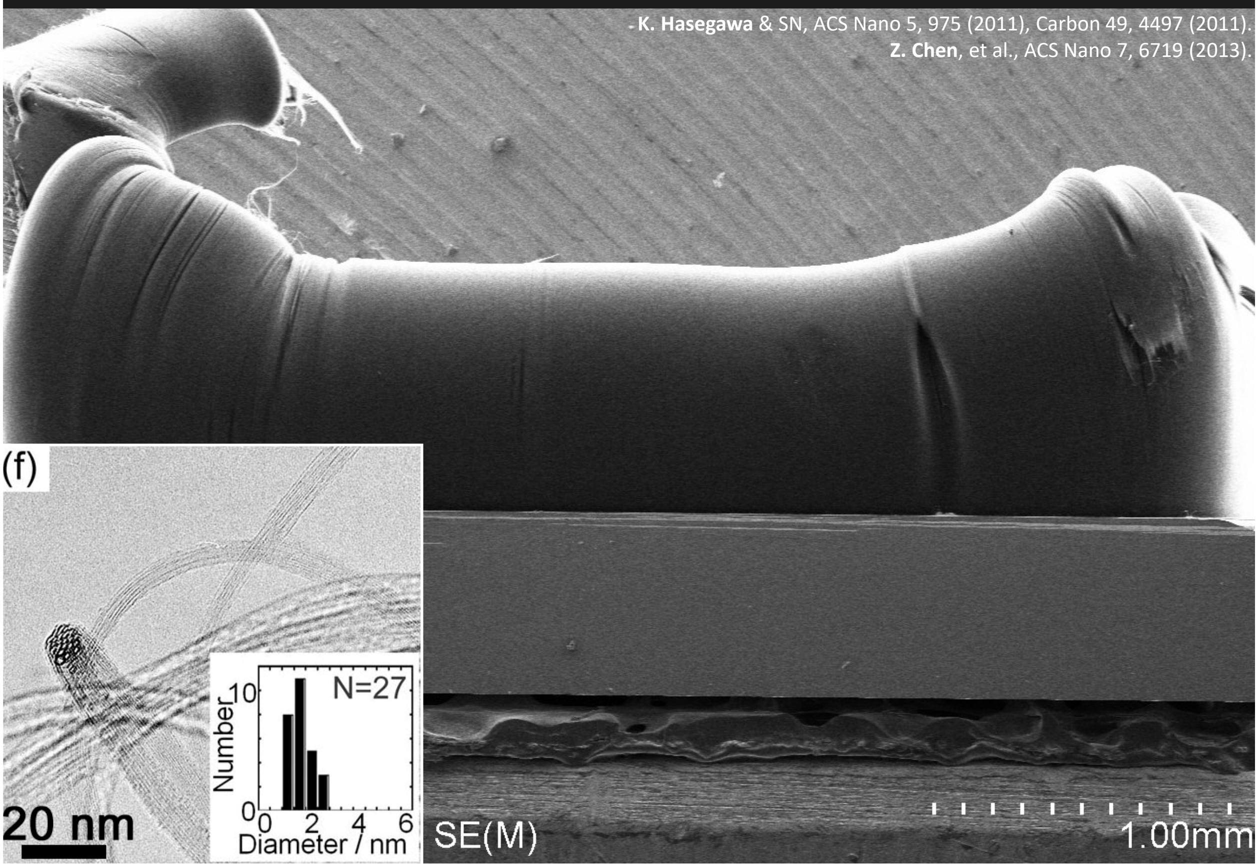


SN, et al., JJAP 46, L399 (2007). **K. Hasegawa** & SN, JJAP 49, 085104 (2010).



CNTs grow quickly. Extensive trial-error & activity/lifetime in one experiment.

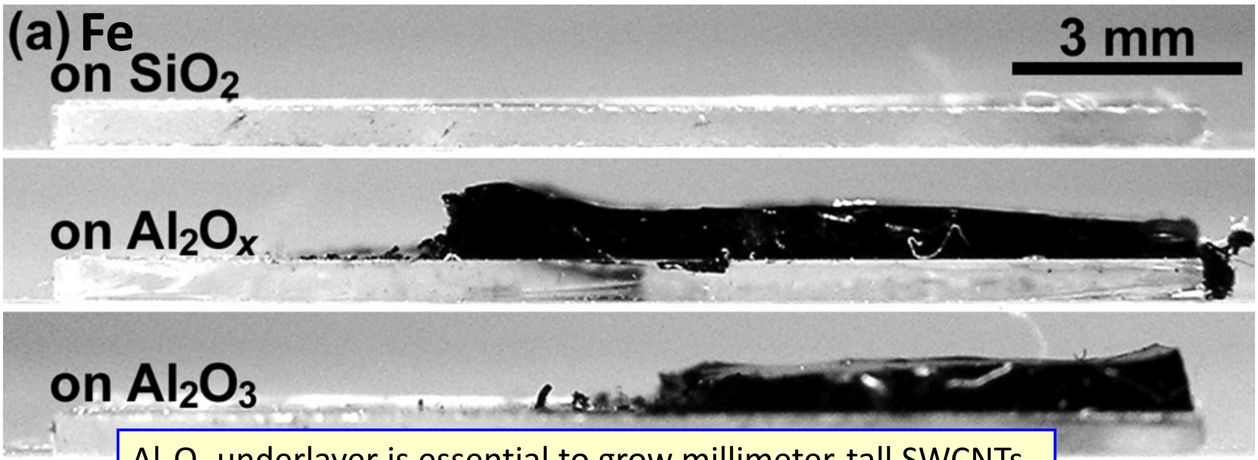
SWCNTs Grown on Flat Substrates



反応添加剤・触媒担体

SN, et al., JJAP 46, L399 (2007). **K. Hasegawa**, et al., JNN 8, 6123 (2008).

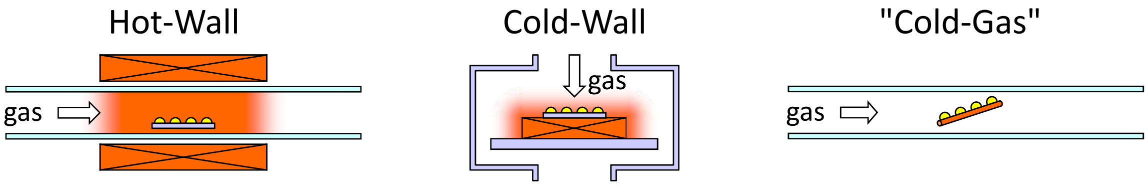
Even w/o H_2O addition, SWCNTs grow tall BUT under a limited window.
Water-assist is effective as reported by Hata, et al. in Science 306, 1362 (2004).



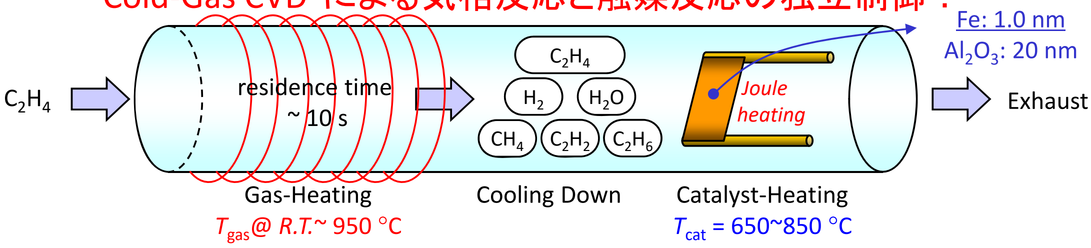
Al_2O_x underlayer is essential to grow millimeter-tall SWCNTs.

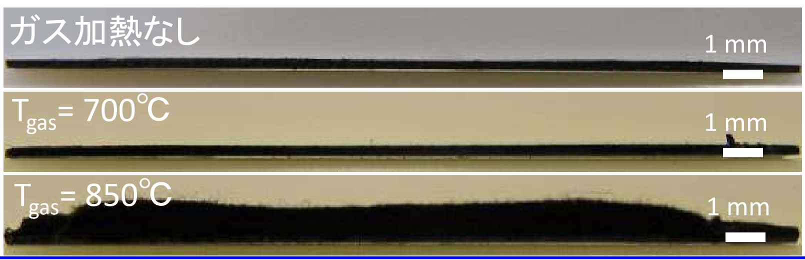
炭素原料 vs 反応前駆体

R. Ito, et al., MRS Spring Meeting (2008). **H. Sugime** & SN, Carbon 50, 2953 (2012).



"Cold-Gas CVD"による気相反応と触媒反応の独立制御！

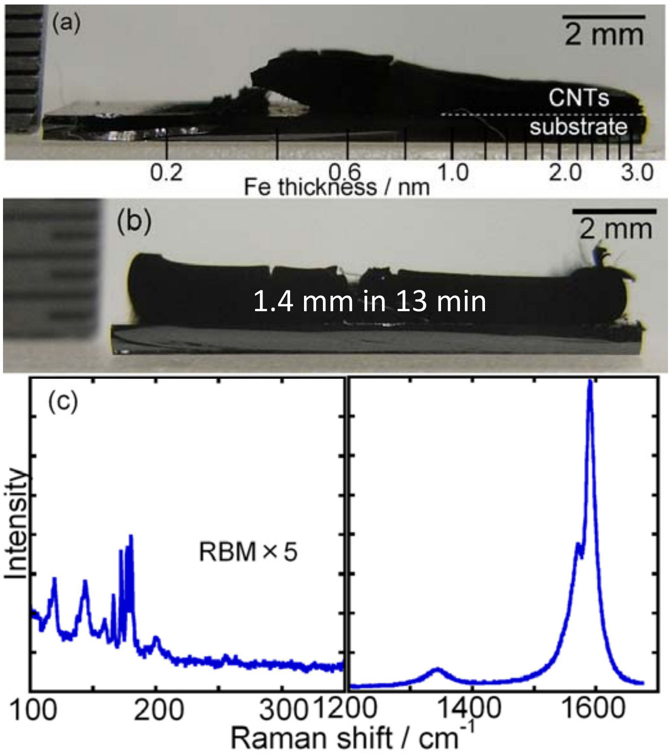




C_2H_4やC_2H_5OHから熱分解で生成するC_2H_2が前駆体!
C_2H_2を直接供給すると、ガスの加熱は不要

シンプル合成：C_2H_2/Ar

K. Hasegawa & SN,
ACS Nano 5, 975 (2011).

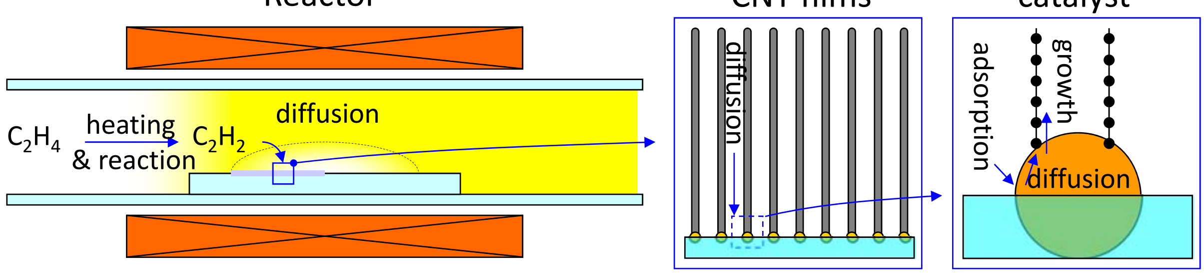


SWCNTs actually grow tall rapidly without additives.

What Is Occurring in the Reactor?

Series of Processes in Serial

C_2H_4 →(1) C_2H_2 (flow) →(2) C_2H_2 (film) →(3) C_2H_2 (cat) →(4) C (cat, in) →(5) C (cat, out) →(6) CNT



Rate Determining Steps

Serial: Slowest one governs the whole. Parallel: Fastest one governs the whole.

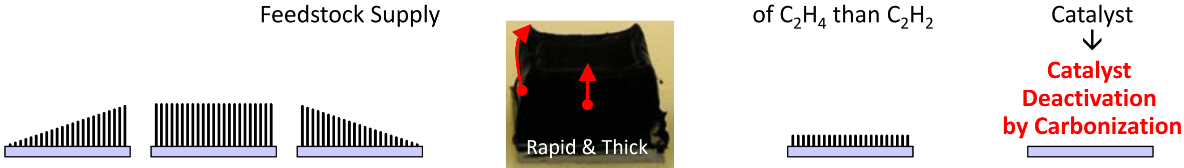
(1) Gas-Phase Reaction

(2) Gas-Phase Diffusion/ Feedstock Supply

(3) Diffusion in CNT Films

(4) Surface Reaction cf. Slower reaction of C_2H_4 than C_2H_2

(5) Diffusion in/ (6) Precipitation from Catalyst
↓
Catalyst Deactivation by Carbonization

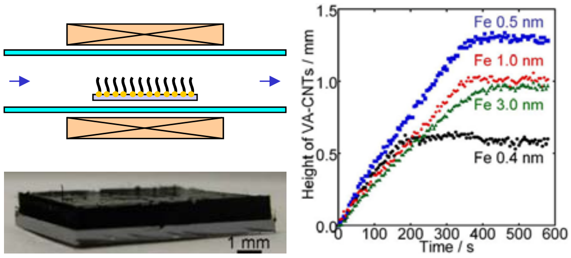


Identify the rate determining step → Efficiently control & newly design CVD

Why CNTs Grow? → How to Grow CNTs? (Previous)

Rapid Growth of VA-CNTs

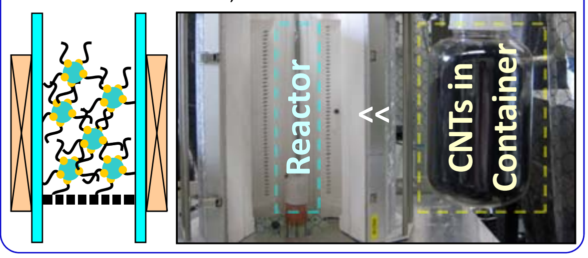
at a high cost (~ 800 ℃, 2D substrates)



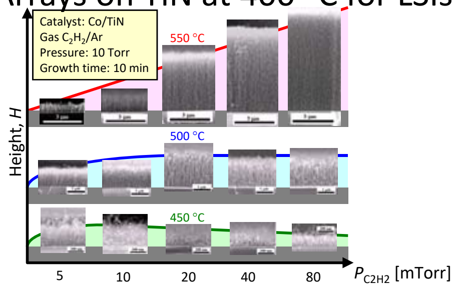
Continuous Production of Long CNTs

by Effectively Utilizing the Steady Growth Stage.

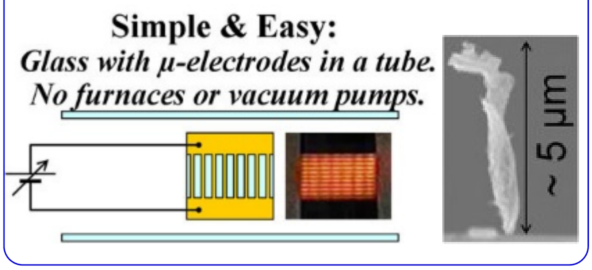
2D → 3D, Batch → Continuous



Low *T* Growth of 1 g/cm³ Dense CNT Arrays on TiN at 400 °C for LSIs



1 s-Growth of CNT Patterned Arrays on Glass for Flat-Panel Displays

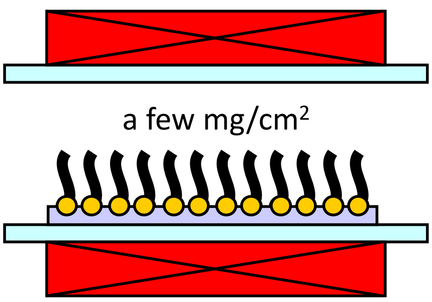


Customize CVD process to each application target.

Long CNTs from On-Substrate to Fluidized-Bed

from Semiconductor Process

VA-CNTs on 2D substrates

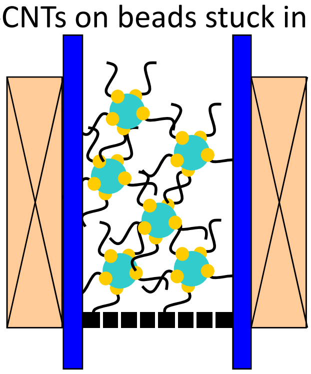


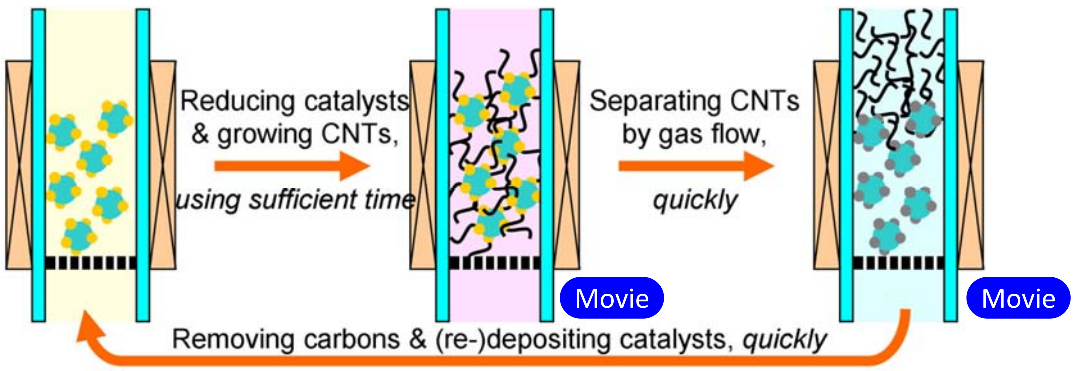
surface area ~ 1,000x

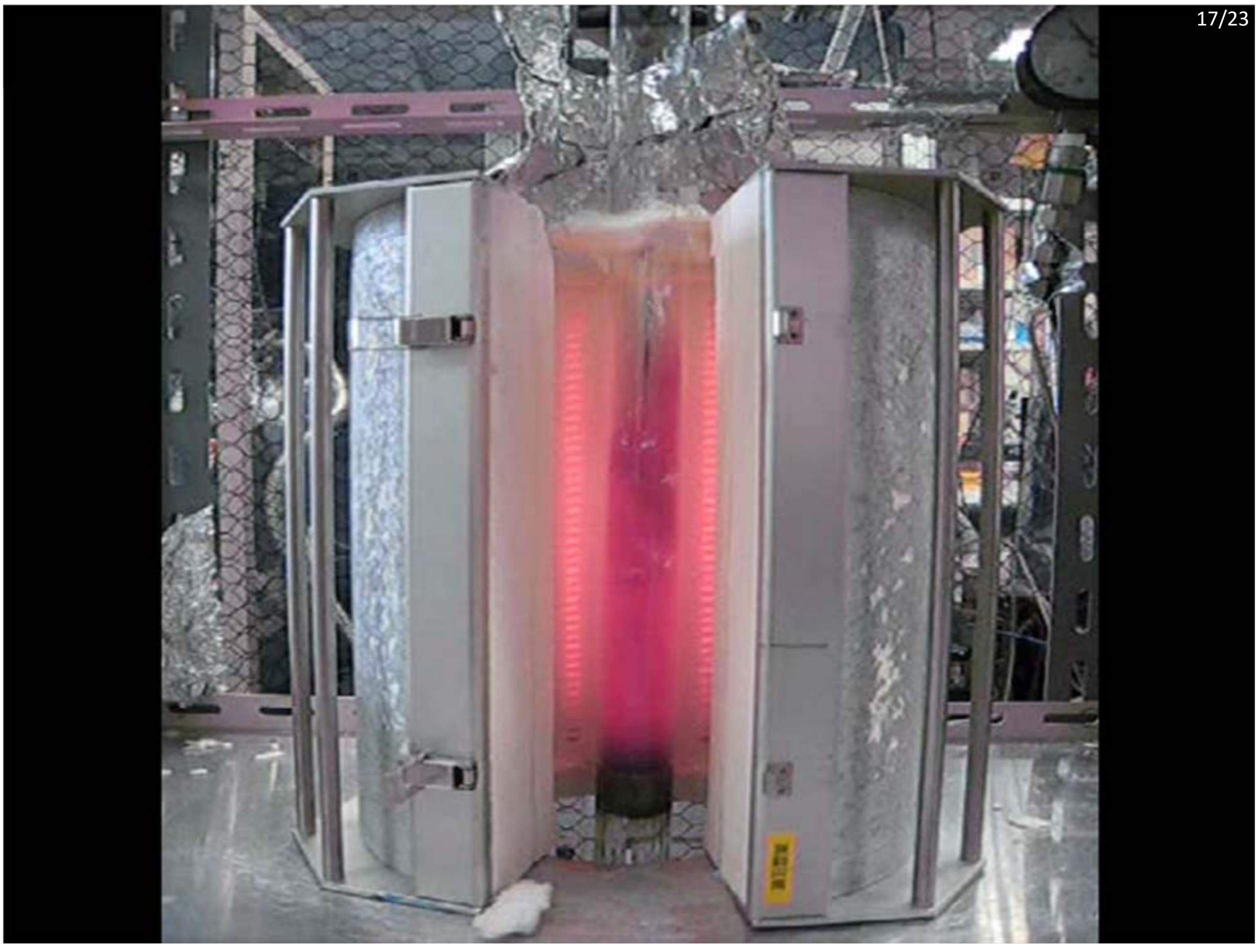
continuous process

to Chemical Process

VA-CNTs on beads stuck in 3D

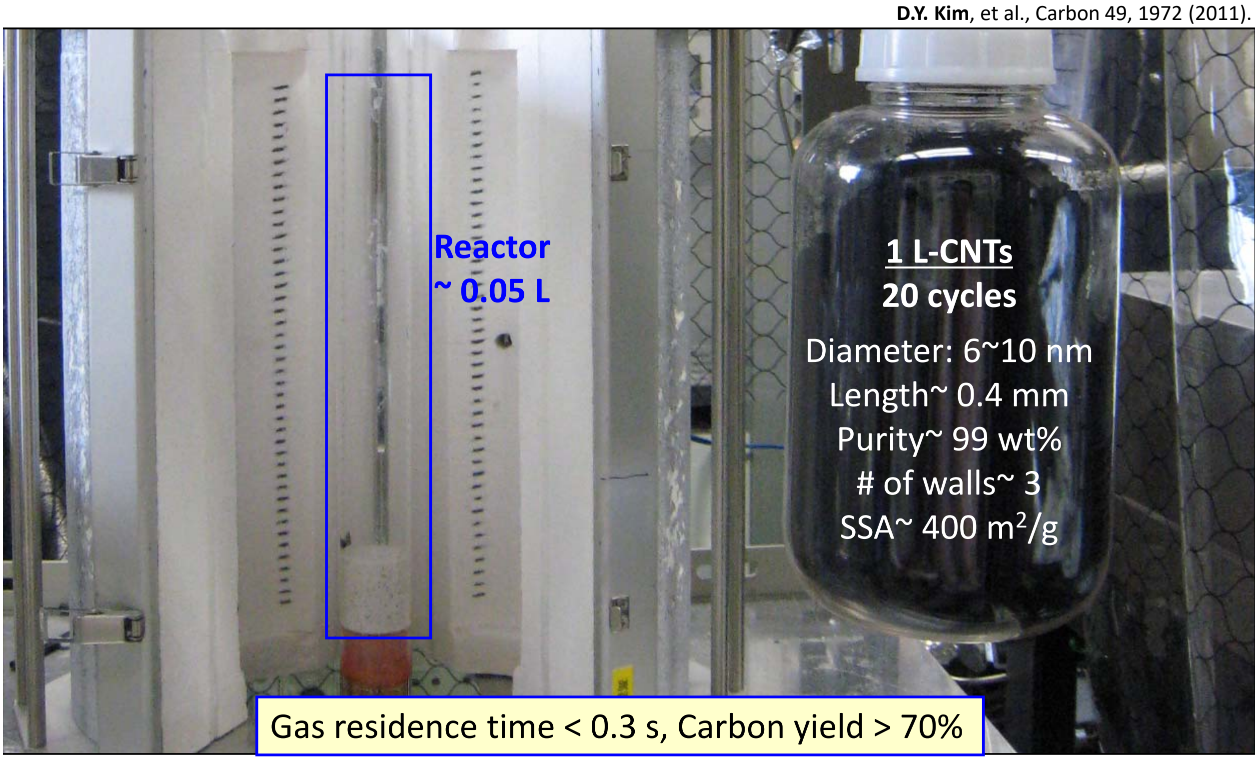






Small Reactor & Big Container

D.Y. Kim, et al., Carbon 49, 1972 (2011).



Reforming of C_2H_2 to CNTs + H_2!

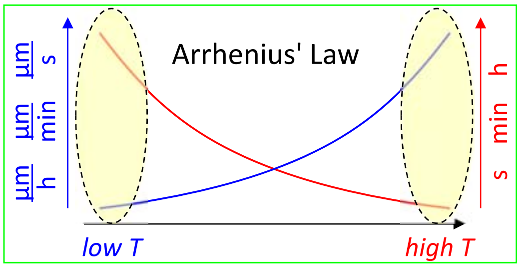
Si基板での実験と解析 → 速度情報 → プロセス設計（大学院の演習）→ ほぼ設計通りに

How to Grow CNTs on Display Glass?

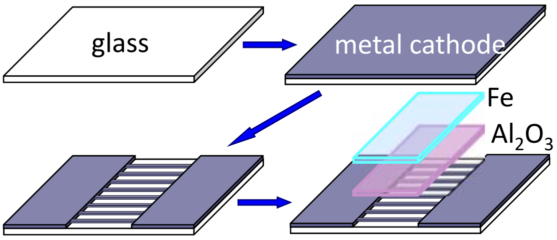
(a) Low temperature growth
- Glass-tolerable temperature
- Impractical process time

(b) High temperature growth
- Growth rate > µm/s
- Glass-tolerable process time

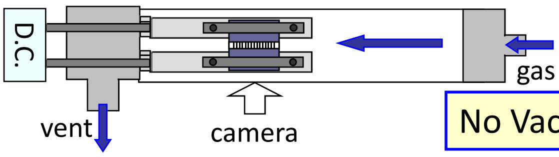
"Hot & instant" is another answer!

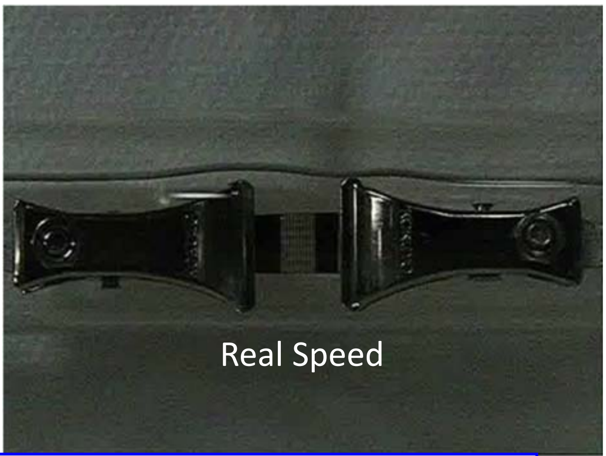


Sample preparation



CVD by pulse electrical heating



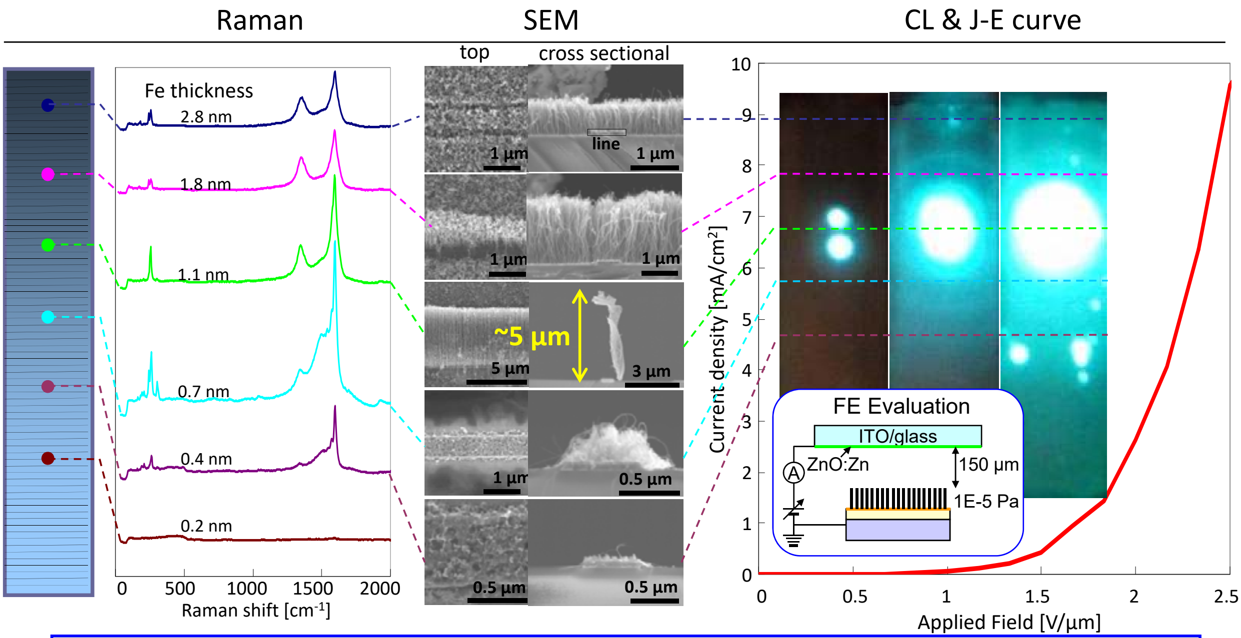


No Vacuum Pump, No Heater! Instant & Easy!

1-s-Fabrication of CNT Emitter Library

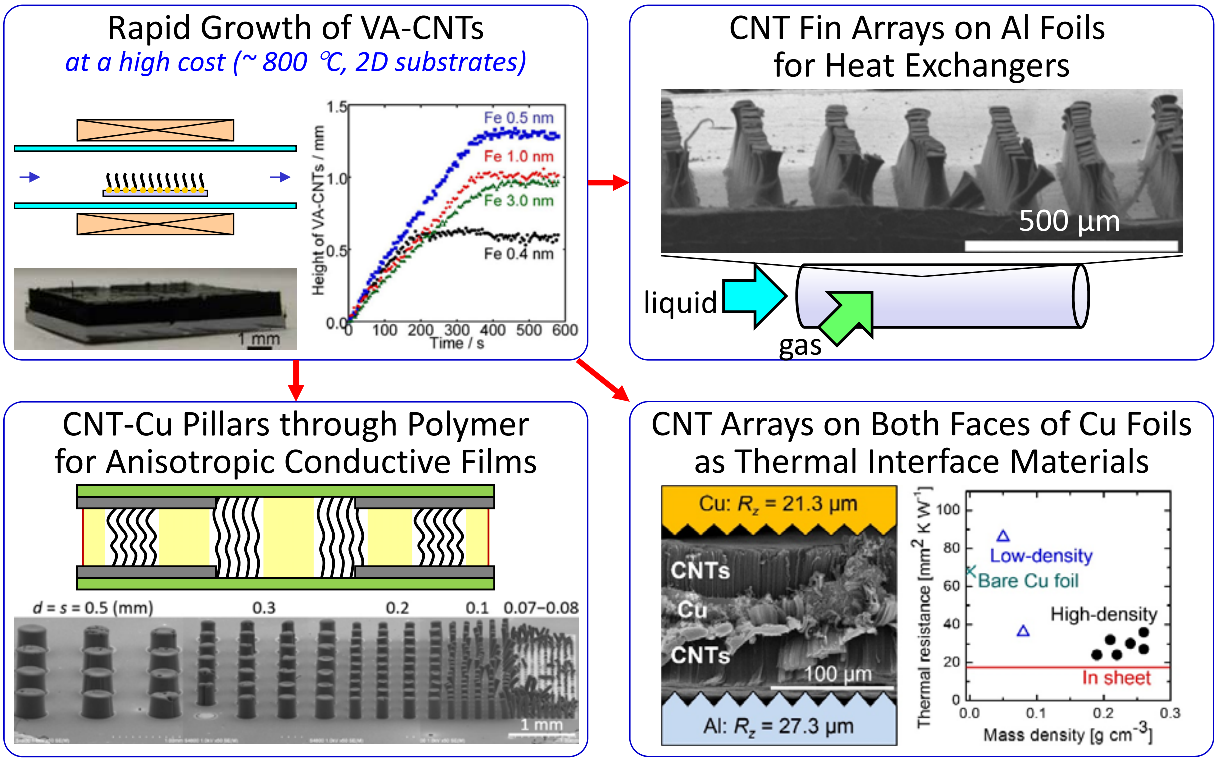
K. Sekiguchi, et al., Carbon 50, 2110 (2012).

Combinatorial Emitter Fabrication & Evaluation



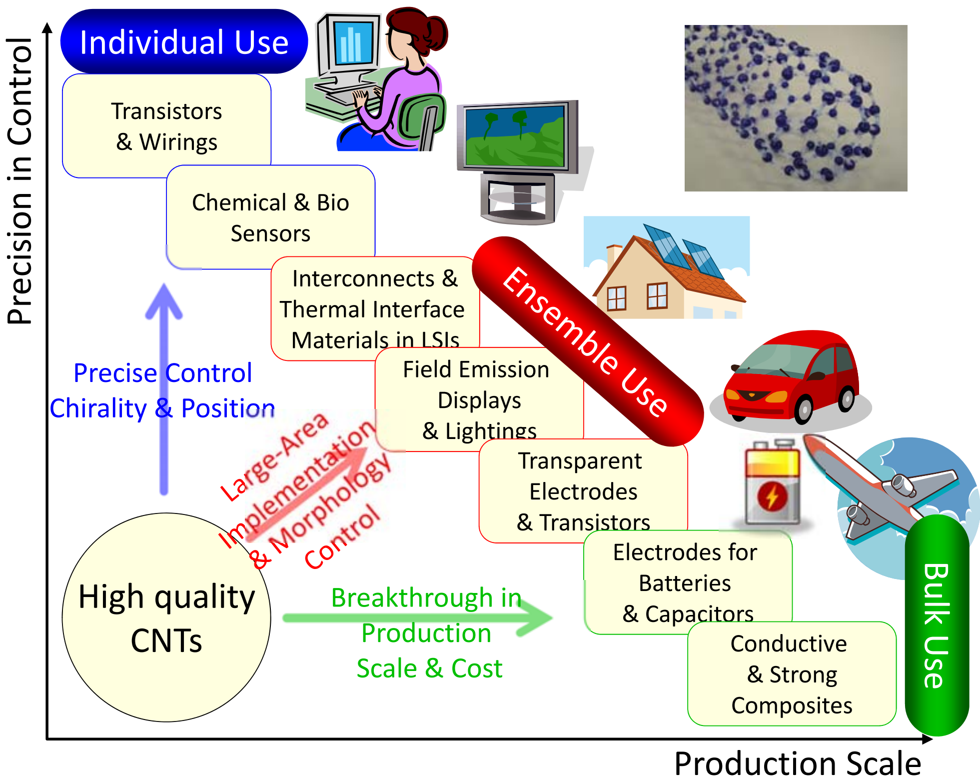
CNT growth is the easiest among various processes for emitter fabrication.
Easy implementation → Easy use for various purposes

Why CNTs Grow? → How to Grow CNTs?



Customize CVD process to each application target.

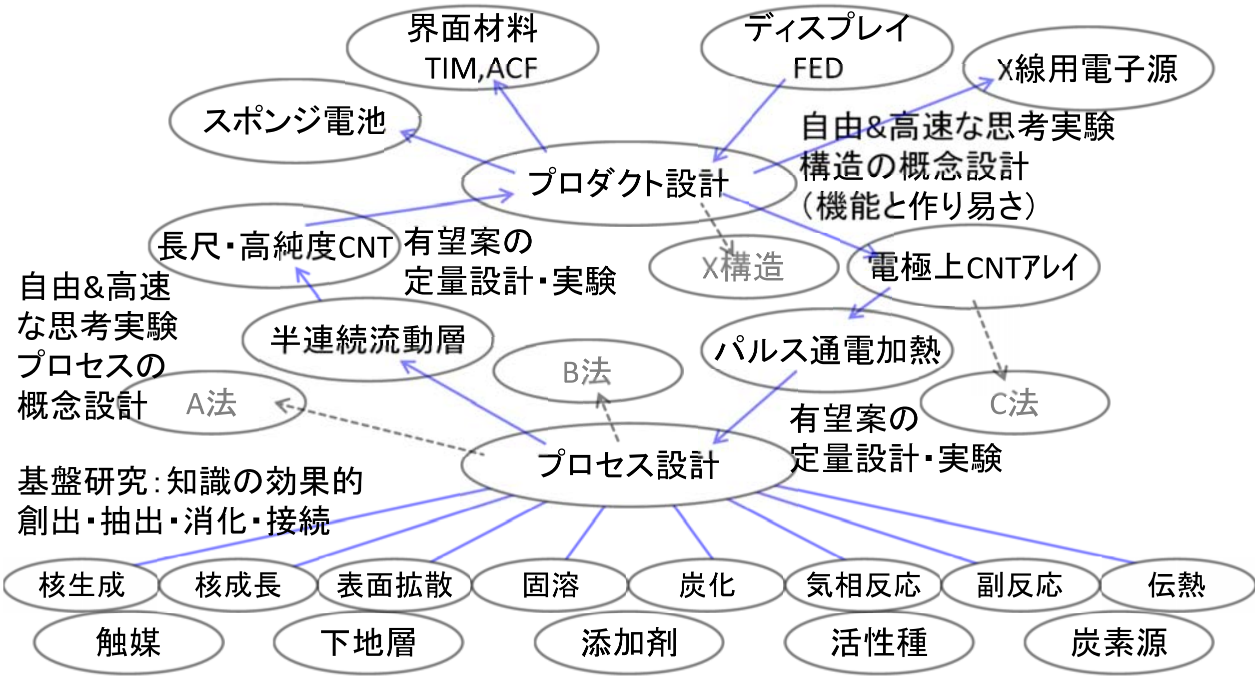
Opportunities & Production Challenges



Customizing CNT production processes to make dreams come true.

まとめ

先端材料の合成法は必ずしも合理的ではない。如何に合理的なプロセスを産み出す？



純粋研究と基盤研究、思考実験と定量設計、発想と類推、要素と組み合わせ
自由に積極的に繋げ、接続に無理がある箇所に未解明の科学、科学と工学の往来
思考実験を支援するプラットフォーム？（当面は）ヒト？