# Ultra-long carbon nanotube forest via *in situ* supplements of iron and aluminum vapor sources

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## Ultra-long carbon nanotube forest via *in situ* supplements of iron and aluminum vapor sources

Check for updates

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Growth

WASEDA University

Mechanical & Electrical Characterization

国立大学法人 静岡大学 National University Corporation Shizuoka University

H. Sugime et al., *Carbon* **172**, 772-780 (2021).

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# Introduction

## Growth of carbon nanotube (CNT) forest

Several pioneering works of multi-wall (MW) CNT forests

WZ. Li et al., Science 274, 1701 (1996).
$Fe/SiO_2$
$C_2H_2$

ZW. Pan et al., Nature 394, 631 (1998).
$Fe/SiO_2$
$C_2H_2$

SS. Fan et al., Science 283, 512 (1999).
$Fe/SiO_2$
$C_2H_2$

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single-wall (SW) CNT forest

$H_2O$-assisted growth of 2 mm SWCNT forest

2 cm MWCNT forest

K. Hata et al., Science 306, 1362 (2004).
$Fe/Al_2O_3$
$C_2H_4$

importance of $Al_2O_3$ layer

Y. Murakami et al., Chem. Phys. Lett. 385, 298 (2004).
$Co\text{-}Mo/SiO_2$
$C_2H_5OH$

W. Cho et al., Carbon 72, 264 (2014).
$Fe/Gd/Al_2O_3$
$C_2H_4$

thin ←— Fe —→ thick
S. Noda et al., *Jpn. J. Appl. Phys.* 46, L399 (2007).

Spontaneous growth termination are key issues.

## Several phenomena during the growth

Change of $I_G/I_D$ in Raman spectra

Diameter increase of CNT

G. Eres et al., *J. Phys. Chem. B* 109, 16684 (2005).

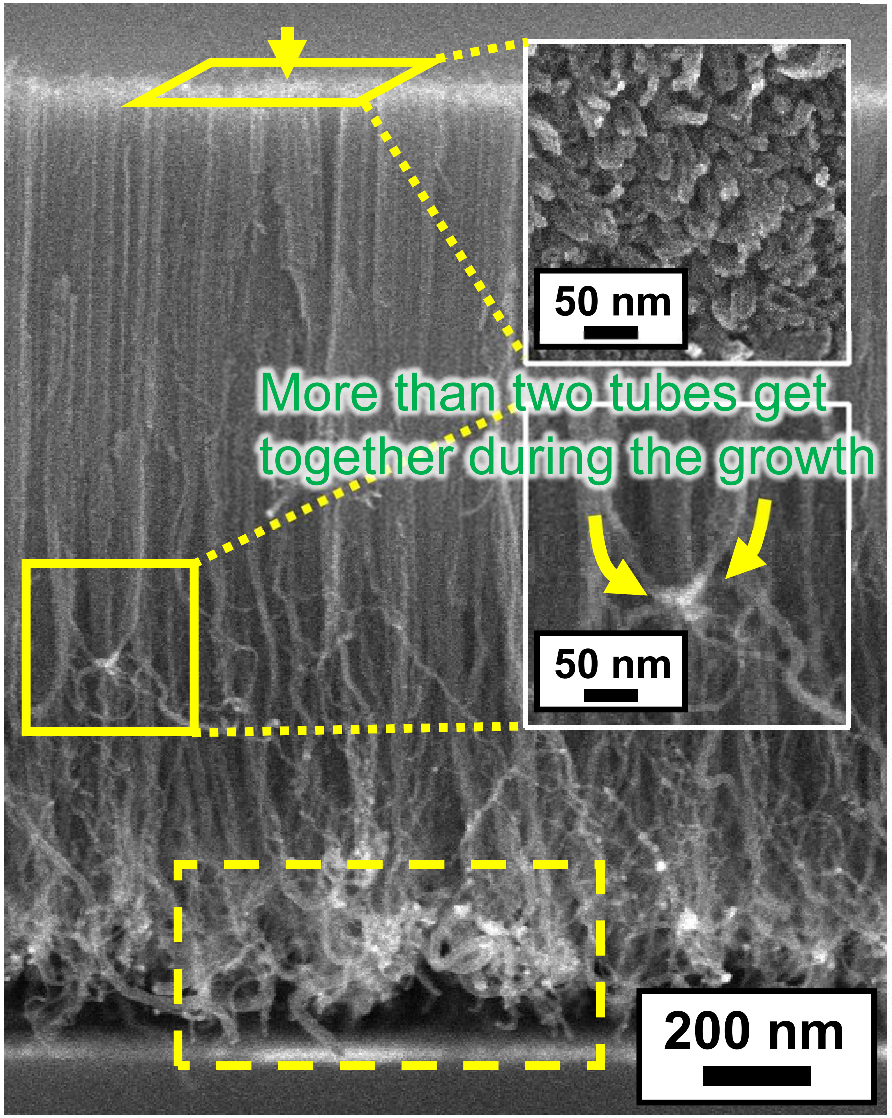
Alignment change

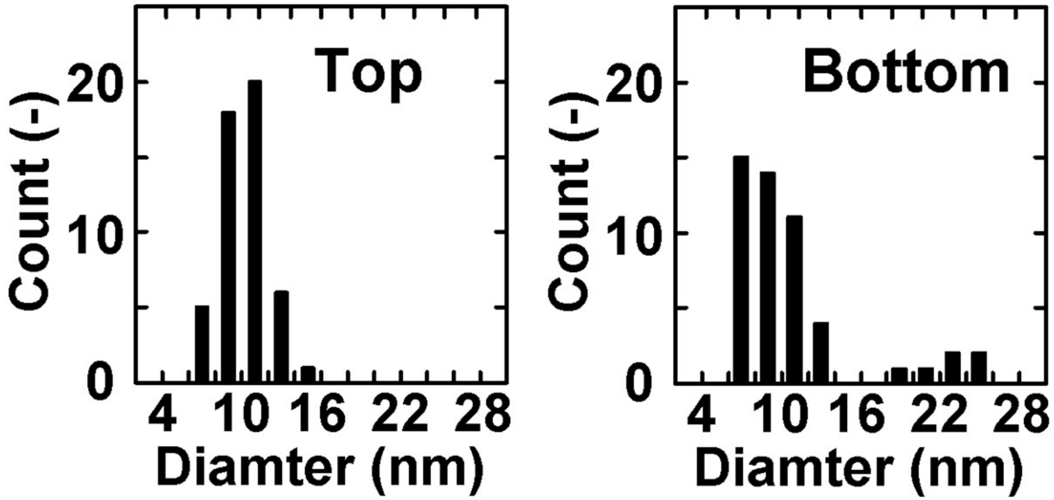
E.R. Meshot et al., *Appl. Phys. Lett.* 92, 113107 (2008).

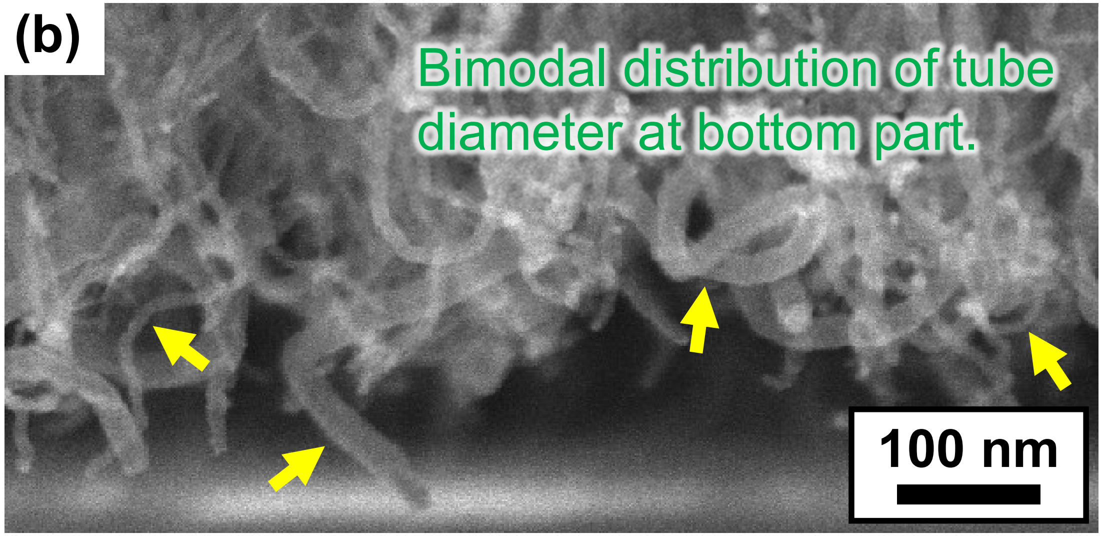
K. Hasegawa et al., *Appl. Phys. Express* 3, 045103 (2010).

# Morphology change & Growth termination

H. Sugime et al., *ACS Appl. Mater. Interfaces* **6**, 15440 (2014).

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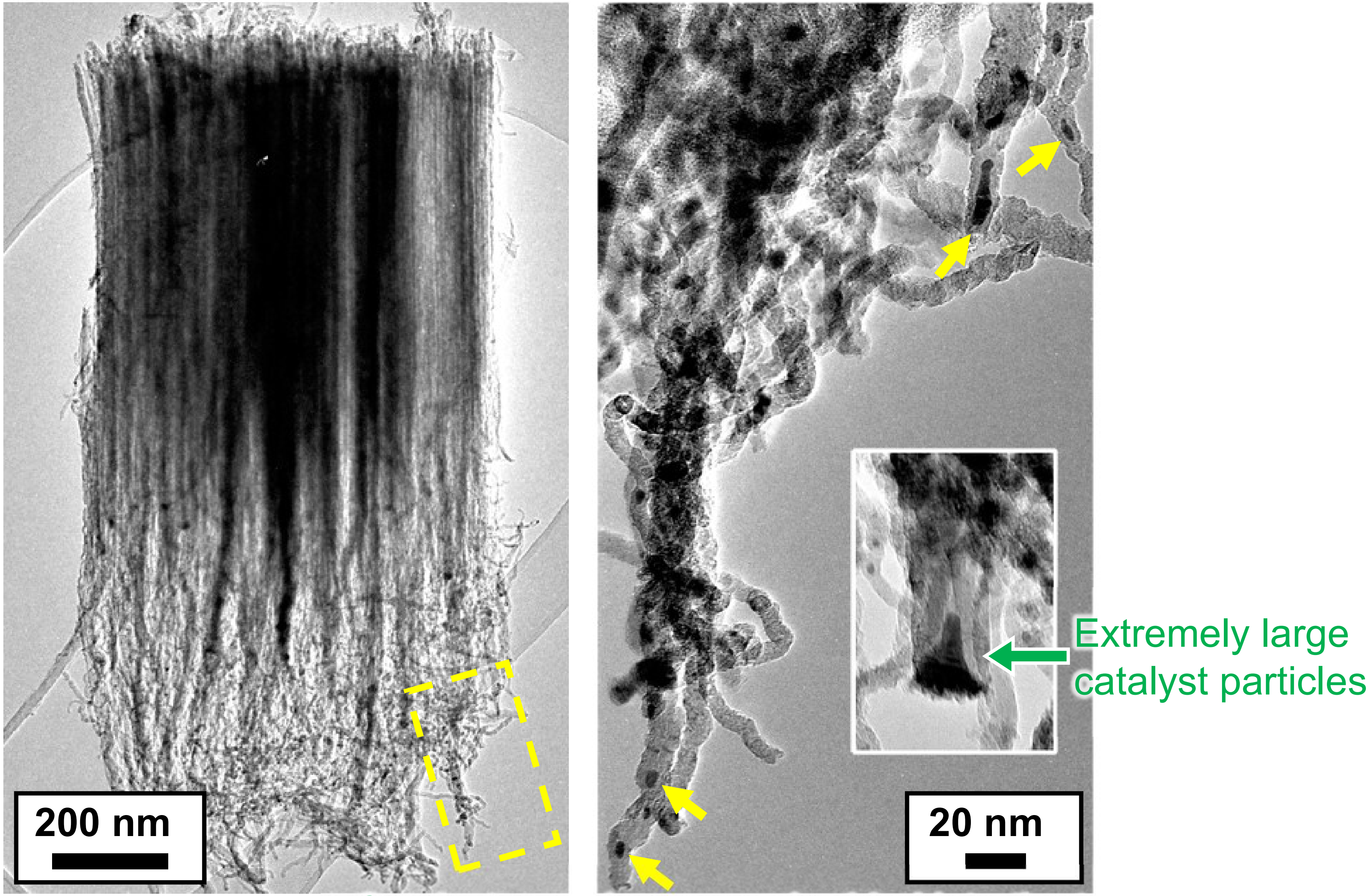
# Morphology change & Growth termination

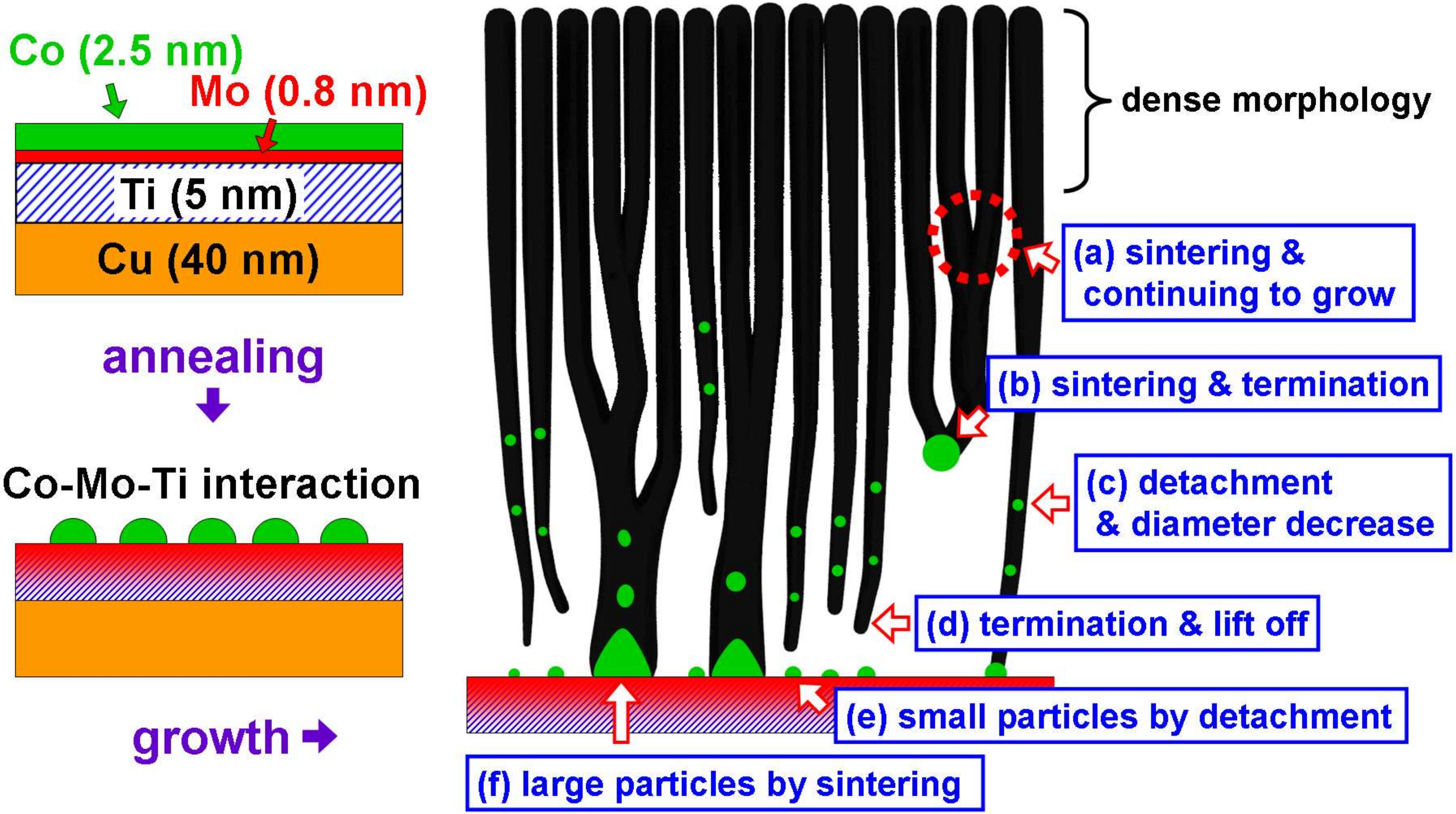
H. Sugime et al., *ACS Appl. Mater. Interfaces* **6**, 15440 (2014).




Catalyst particles are embedded into the tubes

# Morphology change & Growth termination

H. Sugime et al., *ACS Appl. Mater. Interfaces* **6**, 15440 (2014).




Several kinds of structural change of the catalyst nanoparticles occur simultaneously.

# Fe-Gadolinium (Gd) catalyst

Growth lifetime: ~13 h at 780 °C

W. Cho et al., *Carbon* 72, 264 (2014).

Fe/Gd/$Al_2O_3$

$C_2H_4$

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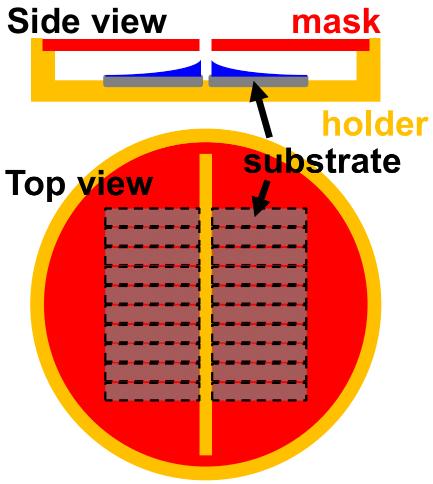
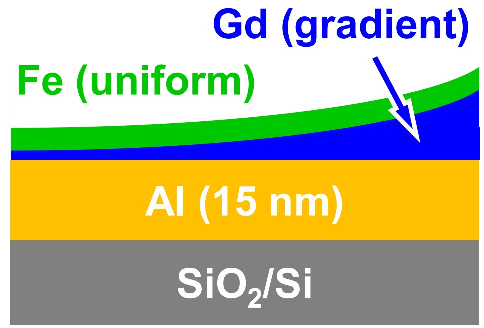
Too thick Gd inhibits the growth of CNT forests.

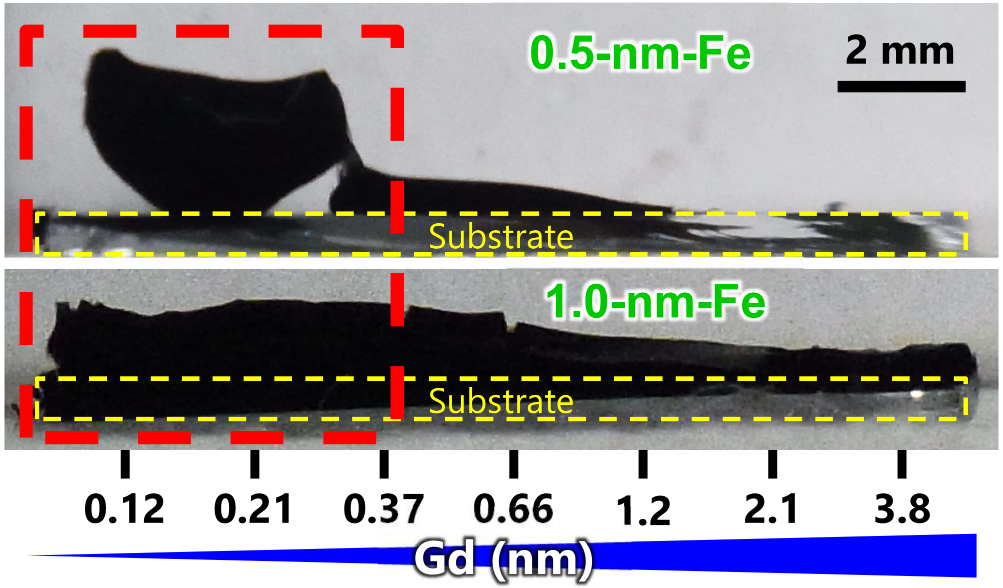
H. Sugime et al., *ACS Nano* **13**, 13208 (2019).

Application of Gd-added catalyst to the growth of single-wall CNT forest




combinatorial method
Sugime et al., *Carbon* **47**, 234 (2009).

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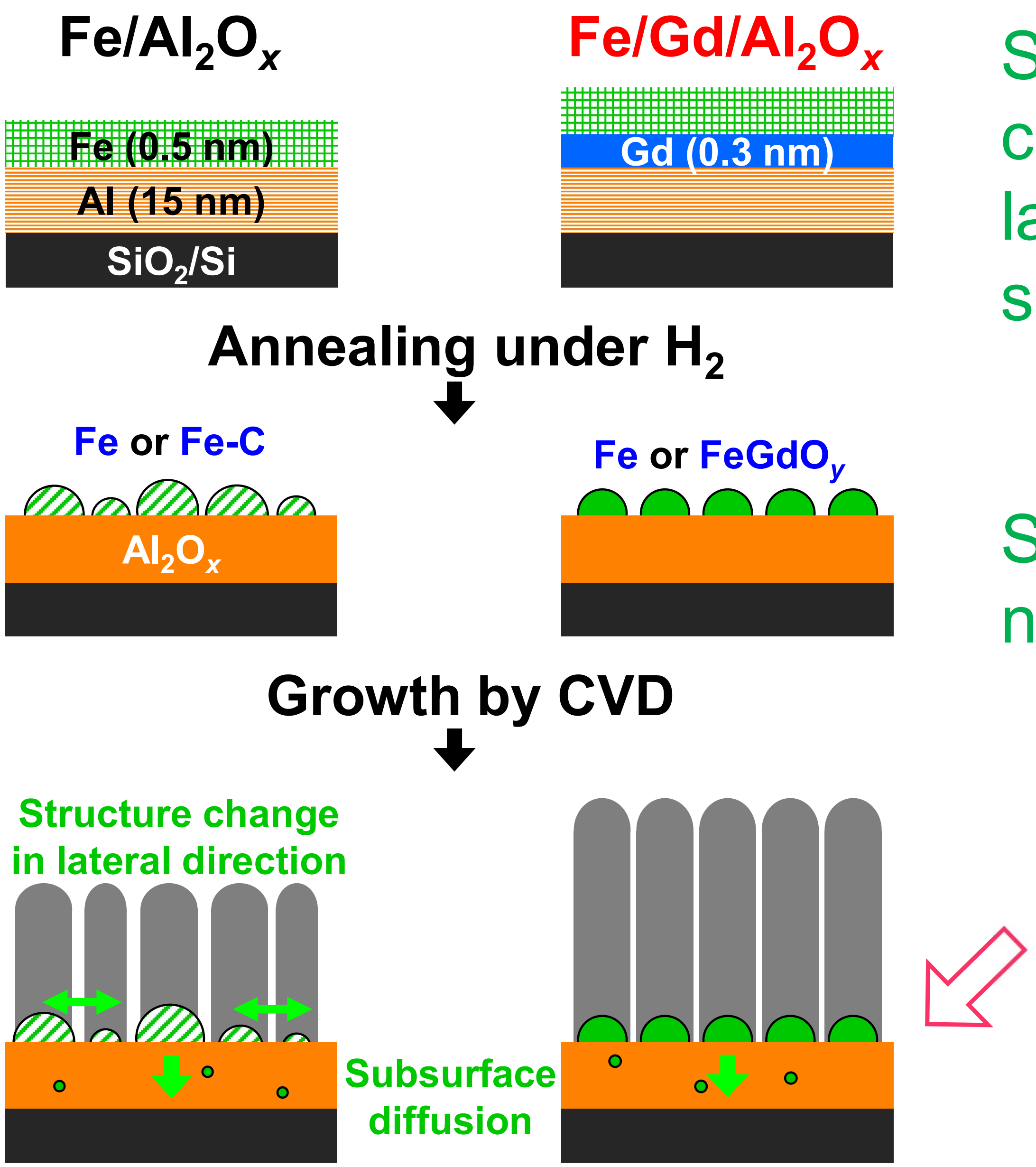
# Fe-Gadolinium (Gd) catalyst




Structural change of the catalyst nanoparticles in lateral direction was suppressed by adding Gd.

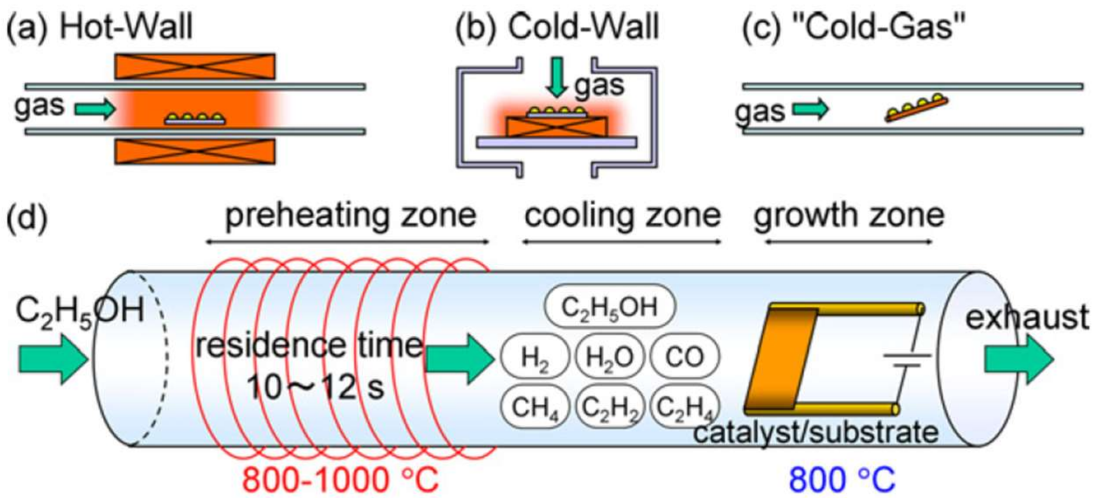
Subsurface diffusion was not suppressed.

How about supplying Fe from gas phase?

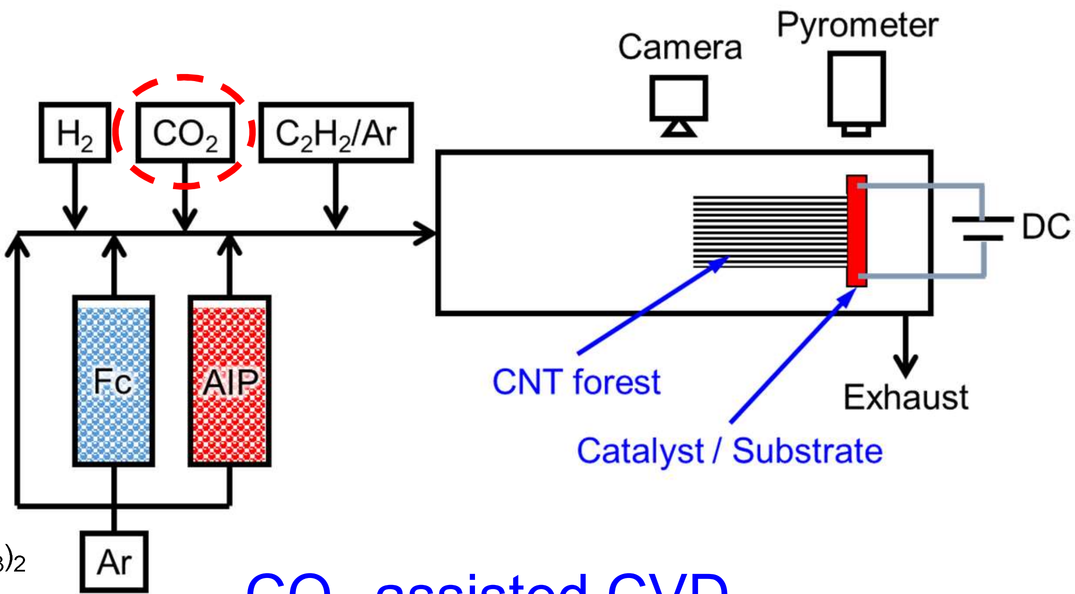
# Experimental

## Cold-gas CVD apparatus

H. Sugime et al., *Carbon* **50**, 2953 (2012).

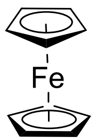




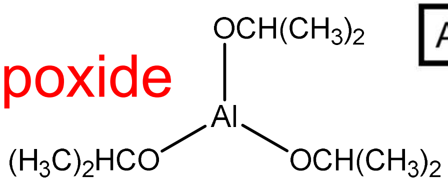



Gas-phase reaction & deposition on the reactor wall are suppressed.

Fc: Ferrocene




AIP: Aluminum isopropoxide




$CO_2$-assisted CVD

T. Sato et al., *Carbon* **136**, 143 (2018).

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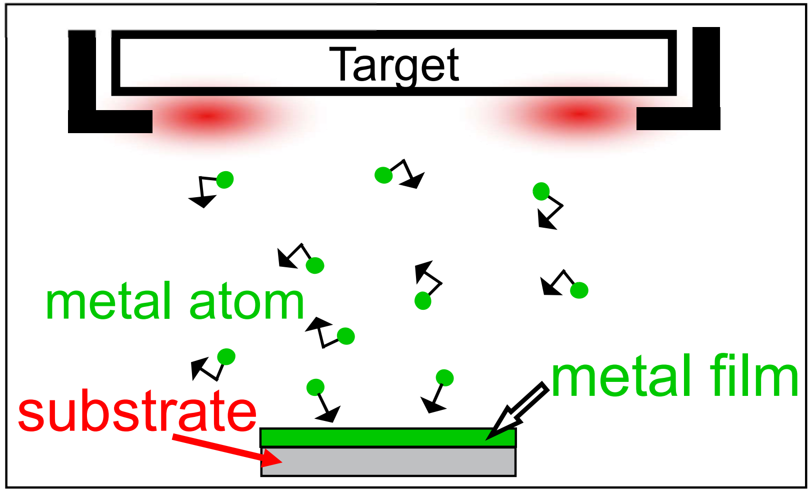
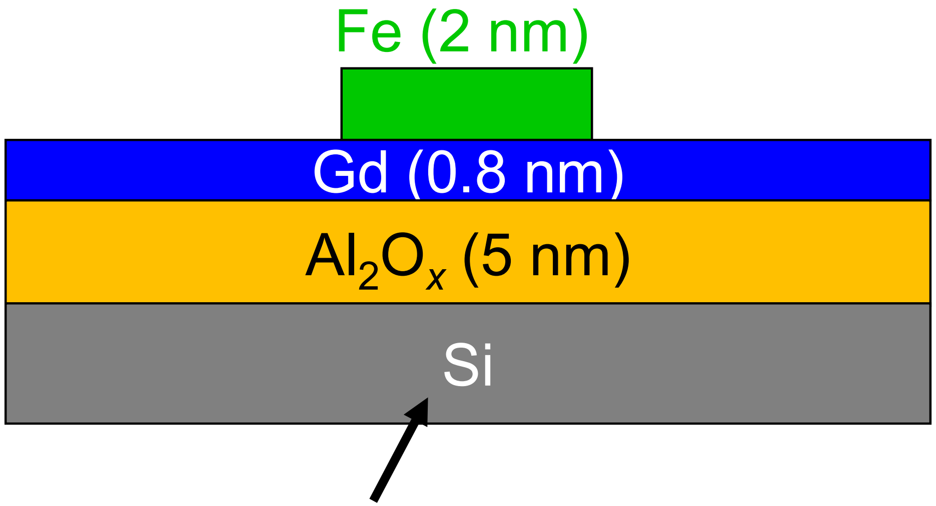
# Experimental

## Catalyst preparation

RF sputtering




Resistivity: 0.002 - 0.004 Ω cm


for good electrical contact

for higher growth rate

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# Results

no-growth-on-Gd/$Al_2O_x$-area


- Catalyst: Fe(2nm)/Gd(0.8nm)/Al(15nm)/Si sub
- $C_2H_2$(0.3%)/$H_2$(10%)/$CO_2$(0.5%)/Fc/AIP/Ar(carrier gas)
- $T_{sub}$: 750 °C, $P_{total}$: ambient pressure

Fc: Ferrocene, 0.6 ppmv

AIP: Aluminum isopropoxide, 0.03 ppmv

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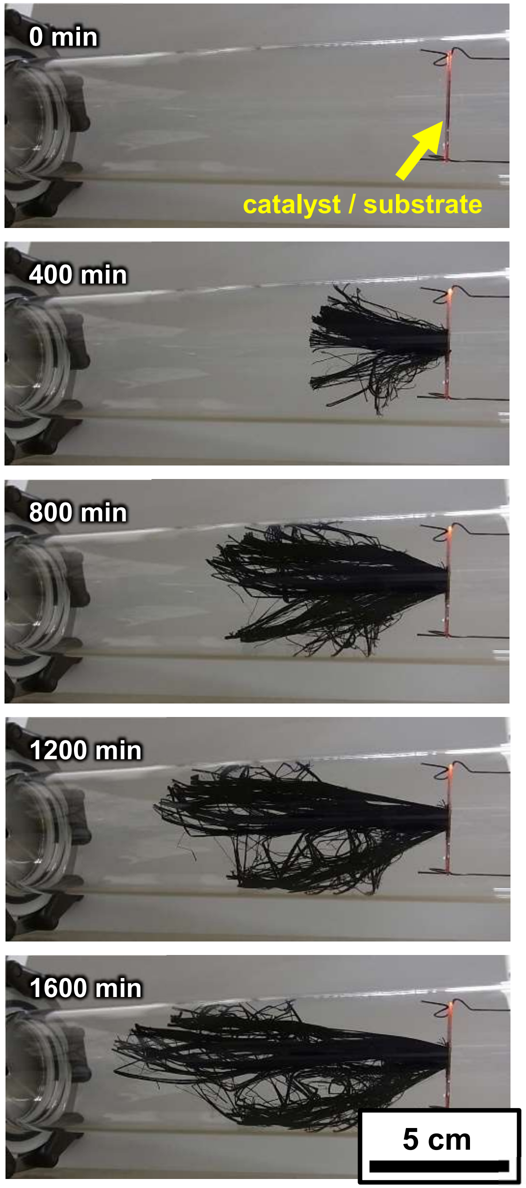
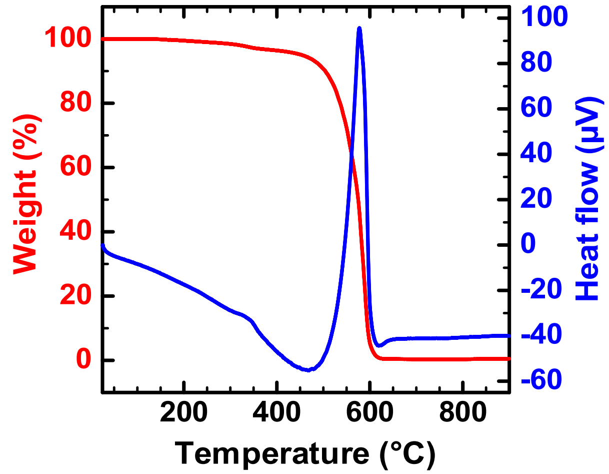
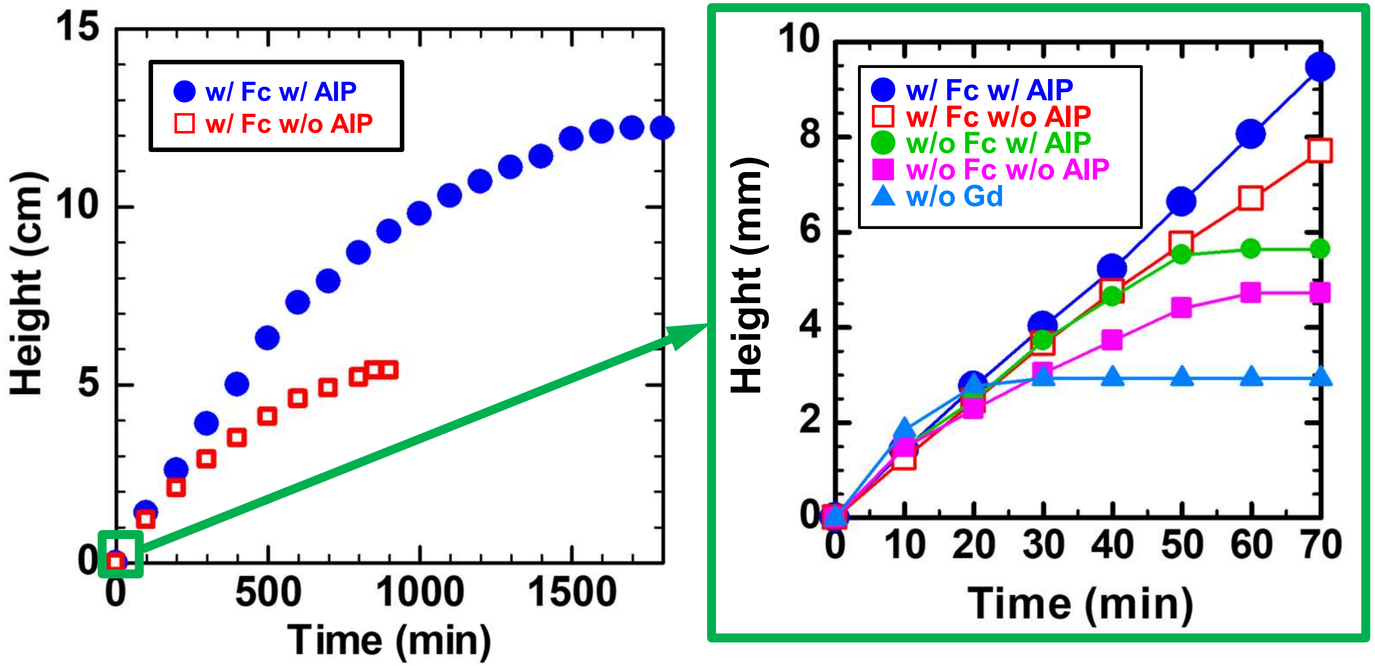
# Results





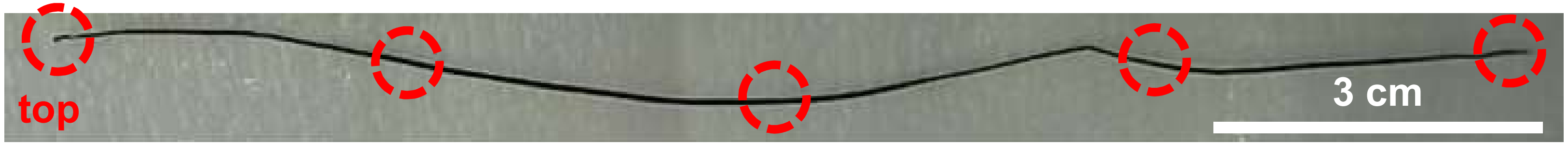


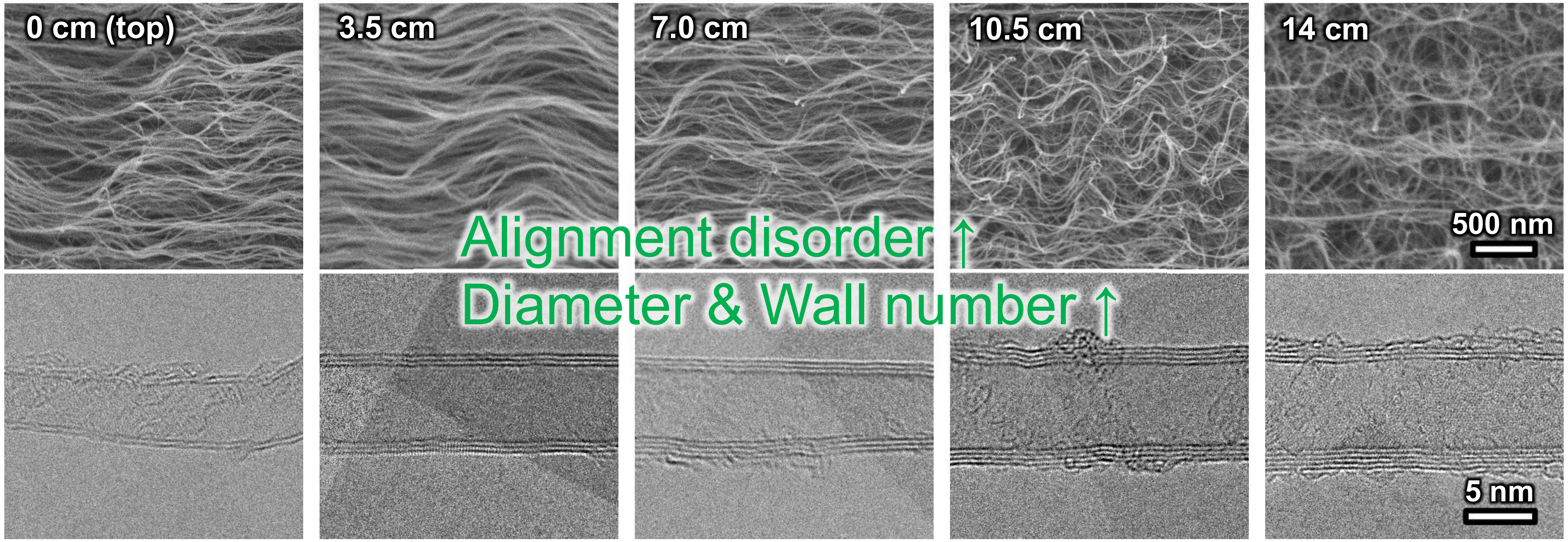



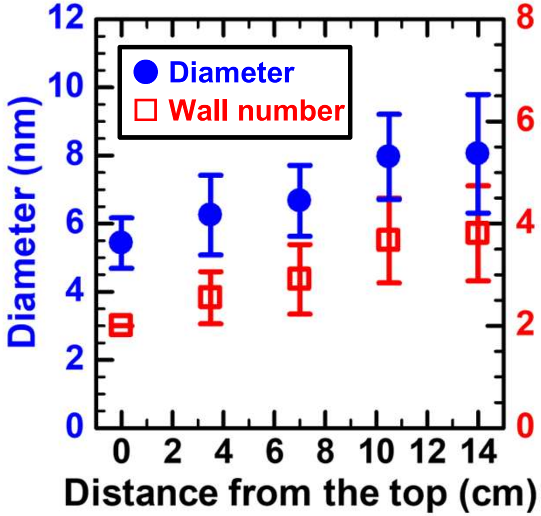

Average growth rate: 1.5 μm/s

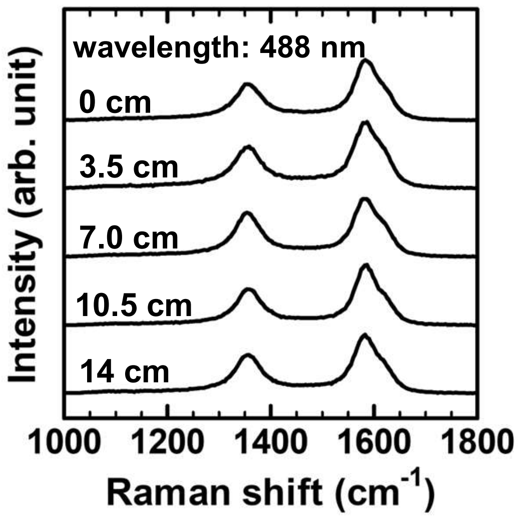
Growth lifetime: 26 h

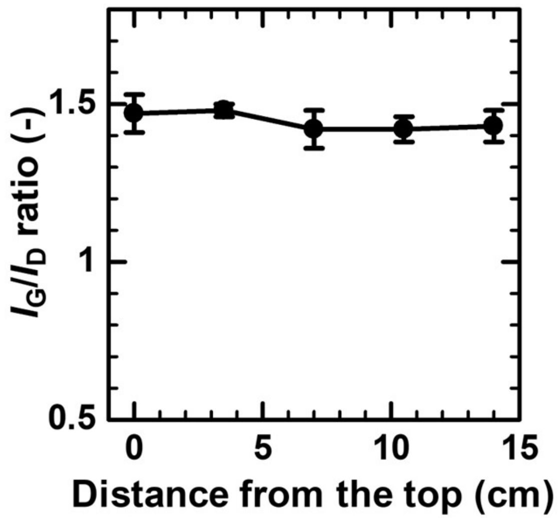
# Results

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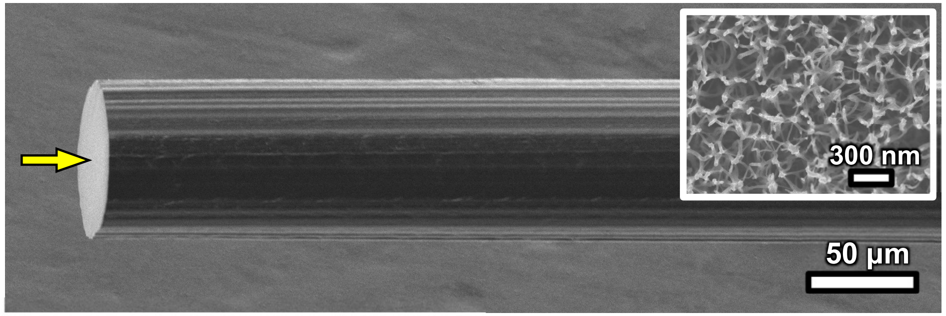
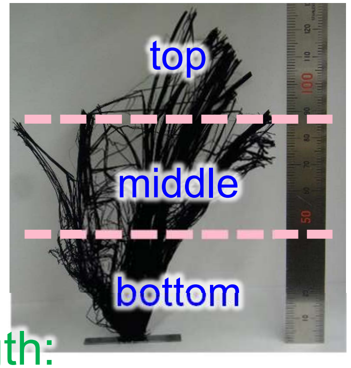
# Results

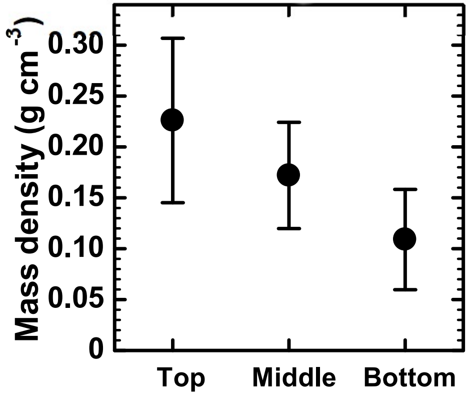


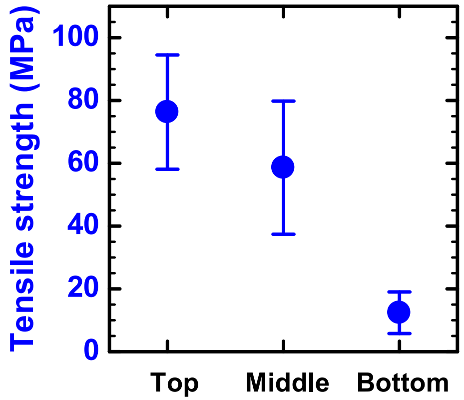

CNT wires without twisting
(Length: ~1 cm, Diameter: 30-80 μm)

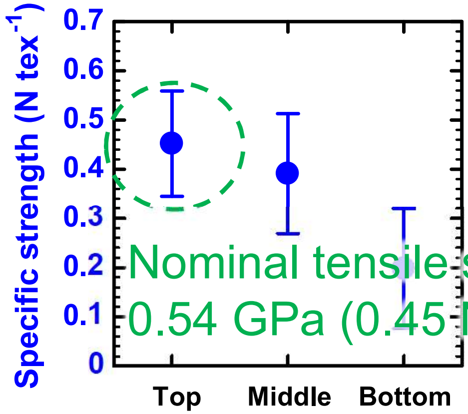
Density of individual CNT = 1.2 g $cm^{-3}$
(calculated form TEM observation)



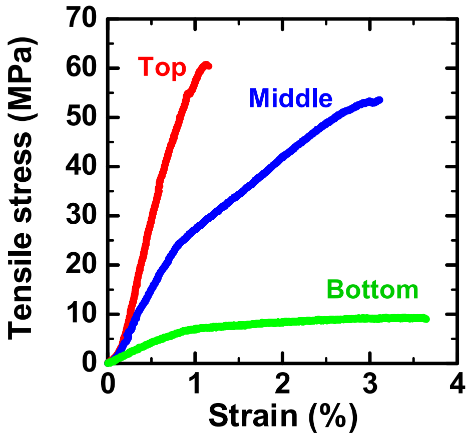

Specimen length = 1 cm

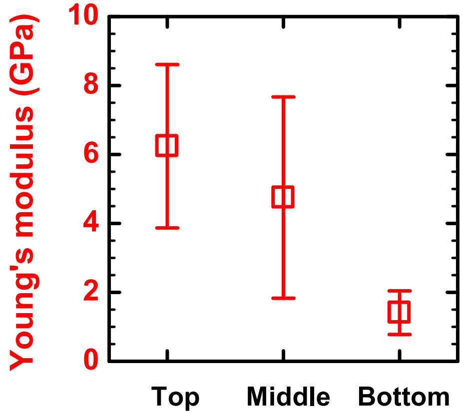


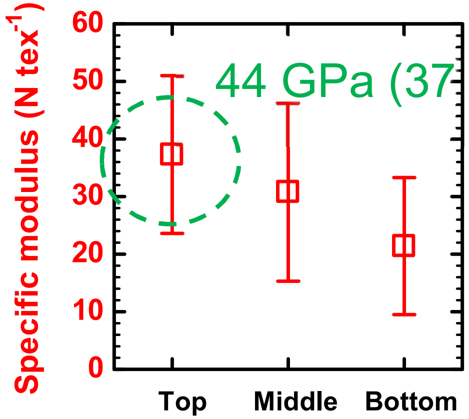




Nominal tensile strength:
0.54 GPa (0.45 N $tex^{-1}$ × 1.2 g $cm^{-3}$)




44 GPa (37 N $tex^{-1}$ × 1.2 g $cm^{-3}$)

Comparable values with millimeter-long MWCNTs (0.85 GPa and 35 GPa)

H.-I. Kim et al., Sci. Rep. 7, 9512 (2017).

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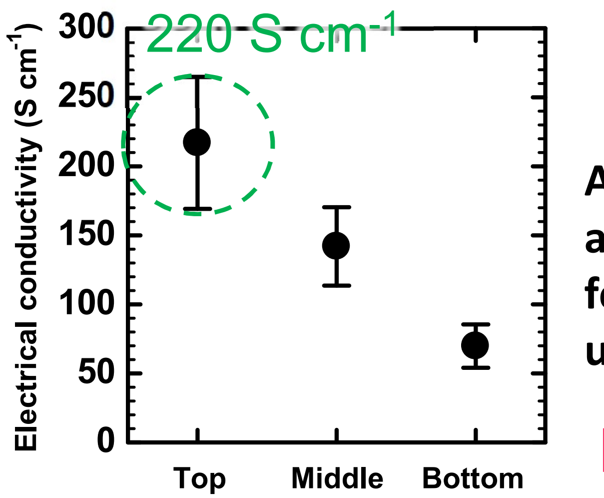
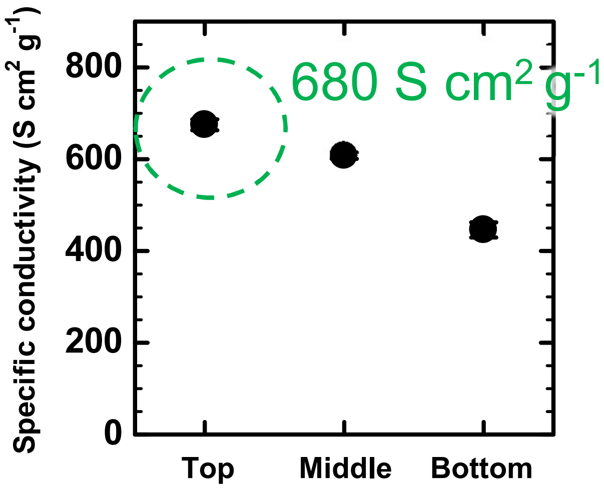
# Results

## Before annealing

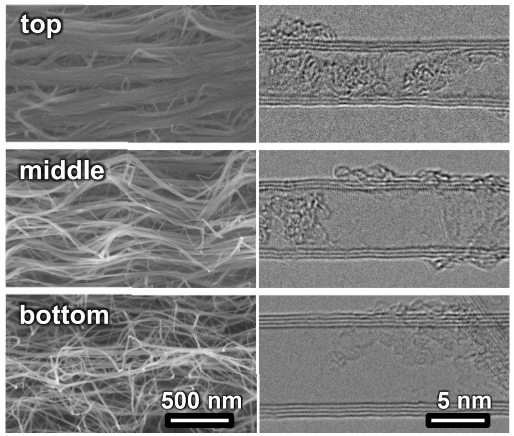


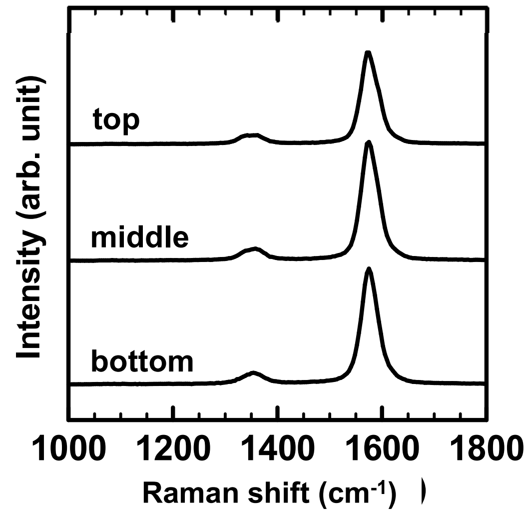

Comparable values with millimeter-long MWCNTs

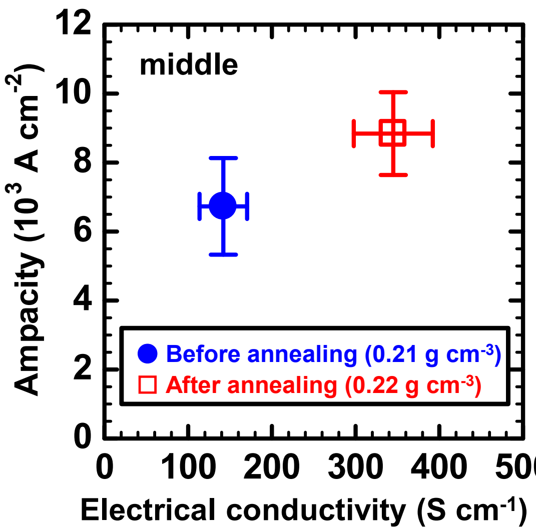
Annealing at 2800 °C for 1 h under Ar

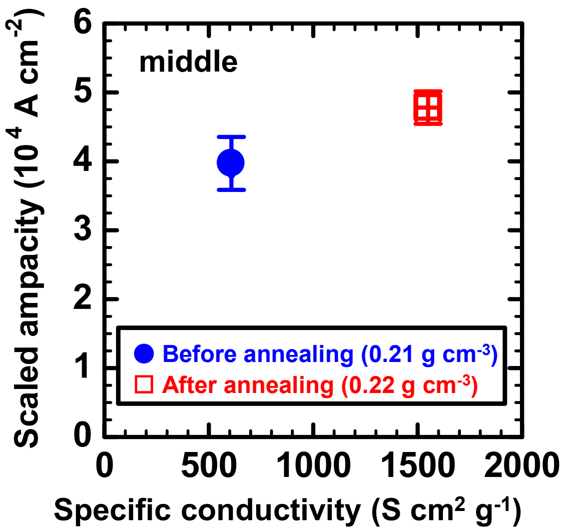
## After annealing




$I_G/I_D$ = 10 (~6 times higher)




The electrical conductivity enhanced more significantly compared with the ampacity by annealing

# Summary

- A breakthrough method for growing a 14-cm-long CNT forest with an average growth rate of 1.5 μm $s^{-1}$ and a growth lifetime of 26 h was developed.

- It was found that the combination of the catalyst system of $Fe/Gd/Al_2O_x$ and the in situ supplements of Fe and Al vapor sources at very low concentrations was crucially important for the long growth.

- The cold-gas CVD apparatus was also shown to play an important role in suppressing unnecessary reactions and depositions on the CNT forests.

- The long CNT forests enabled a detailed investigation of the tensile and electrical properties of the CNTs at different growth periods through macroscopic measurements.

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