Single Chirality Separation of SWCNTs using Gel Column Chromatography
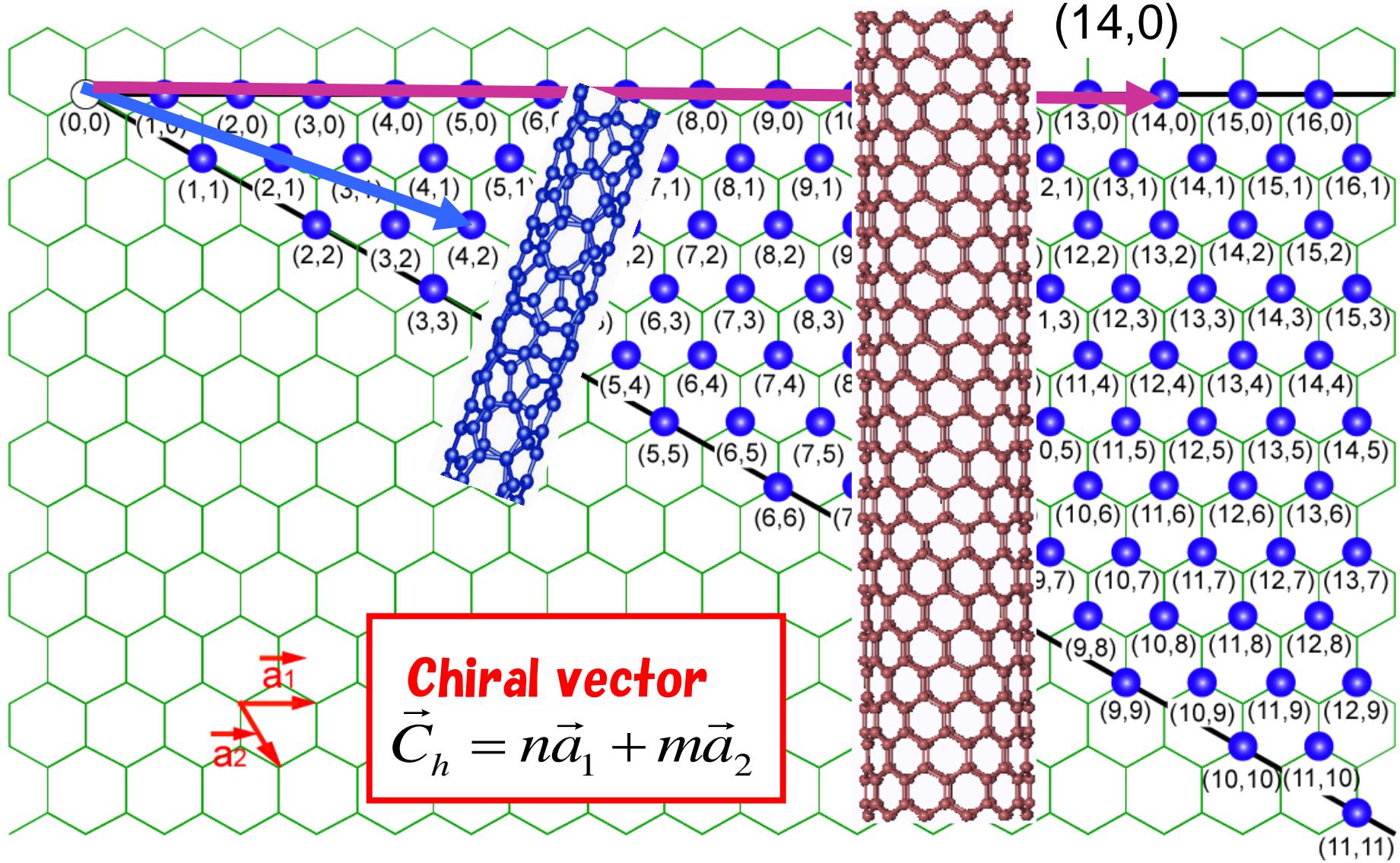
Hiromichi Kataura

[1]*Nanosystem Research Institute, AIST, Japan*
[2]*CREST, JST, Japan*
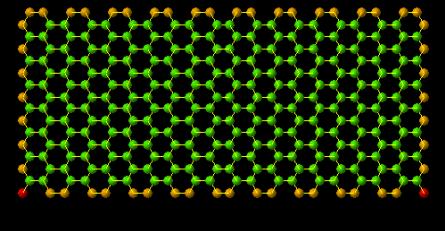
Chiral map

$(14,0)$

(0,0) (1,0) (2,0) (3,0) (4,0) (5,0) (6,0) (8,0) (9,0) (1) (13,0) (14,0) (15,0) (16,0)

(1,1) (2,1) (3,) (4,1) (5,1) (7,1) (8,1) (9,1) 2,1) (13,1) (14,1) (15,1) (16,1)

(2,2) (3,2) (4,2) ,2) (7,2) (8,2) (9) (12,2) (13,2) (14,2) (15,2)

(3,3)) (6,3) (7,3) (8,3) 1,3) (12,3) (13,3) (14,3) (15,3)

(5,4) (6,4) (7,4) (8 (11,4) (12,4) (13,4) (14,4)

(5,5) (6,5) (7,5) 0,5) (11,5) (12,5) (13,5) (14,5)

(6,6) (7 (10,6) (11,6) (12,6) (13,6)

9,7) (10,7) (11,7) (12,7) (13,7)

(9,8) (10,8) (11,8) (12,8)

(9,9) (10,9) (11,9) (12,9)

(10,10) (11,10)

(11,11)

$\vec{a}_1$

$\vec{a}_2$

**Chiral vector**
$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$
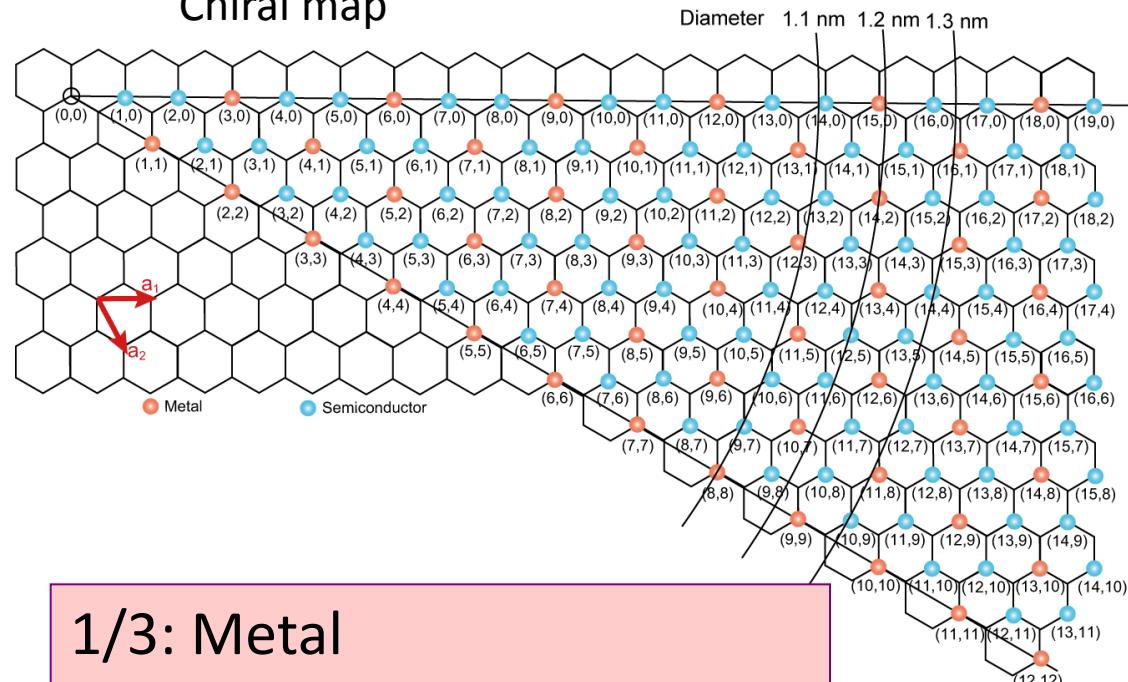
Two types of SWCNT, metal and semiconductor

There are two (three) types of Single-Wall Carbon NanoTubes

Chiral map

Diameter 1.1 nm 1.2 nm 1.3 nm

Metal   Semiconductor

● Metal   ● Semiconductor

(5,5): Metallic SWCNT

M_{11}

E (eV)

Γ X   Density of State

k

(7,0): Semiconducting SWCNT

S_{11} S_{22}

E (eV)

Γ X   Density of State

k

30°
Armchair
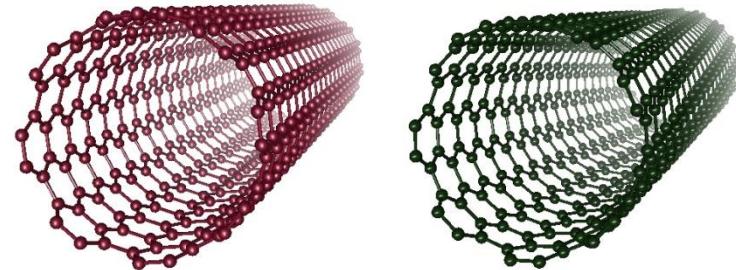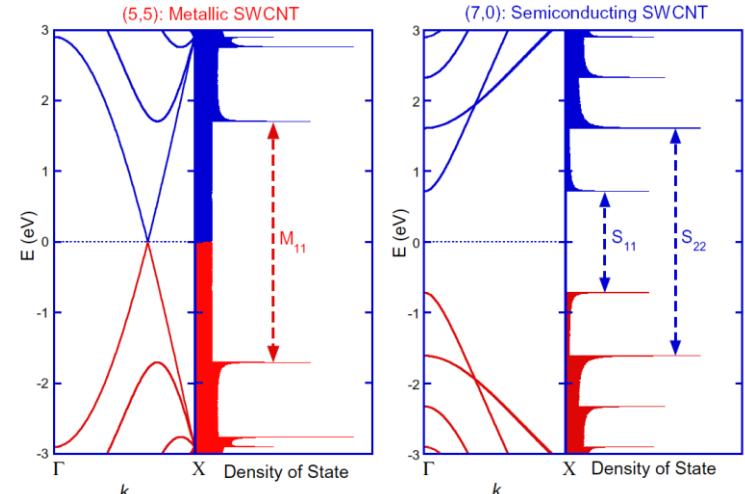
1/3: Metal
2/3: Semiconductor
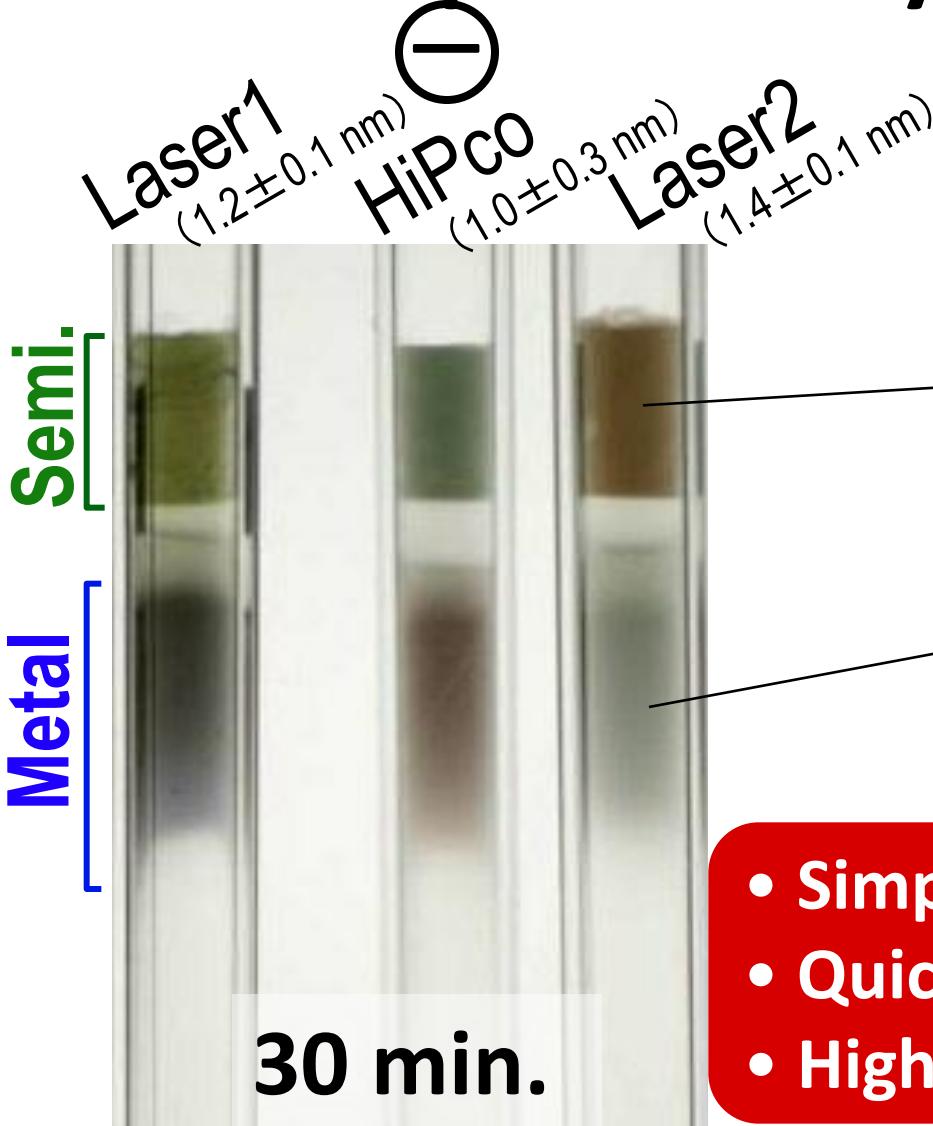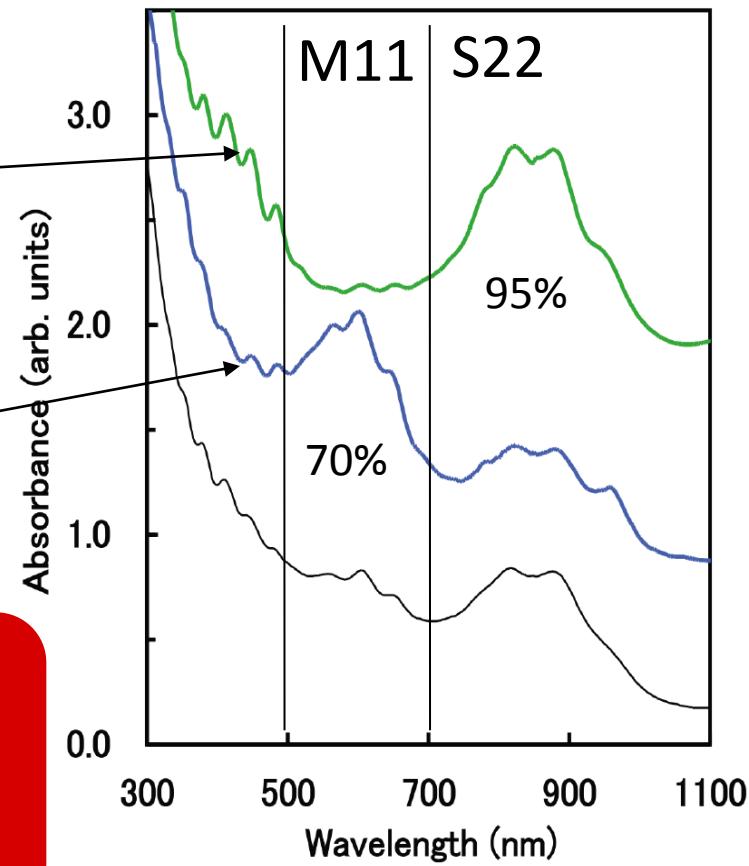
MS separation by AGE

⊖
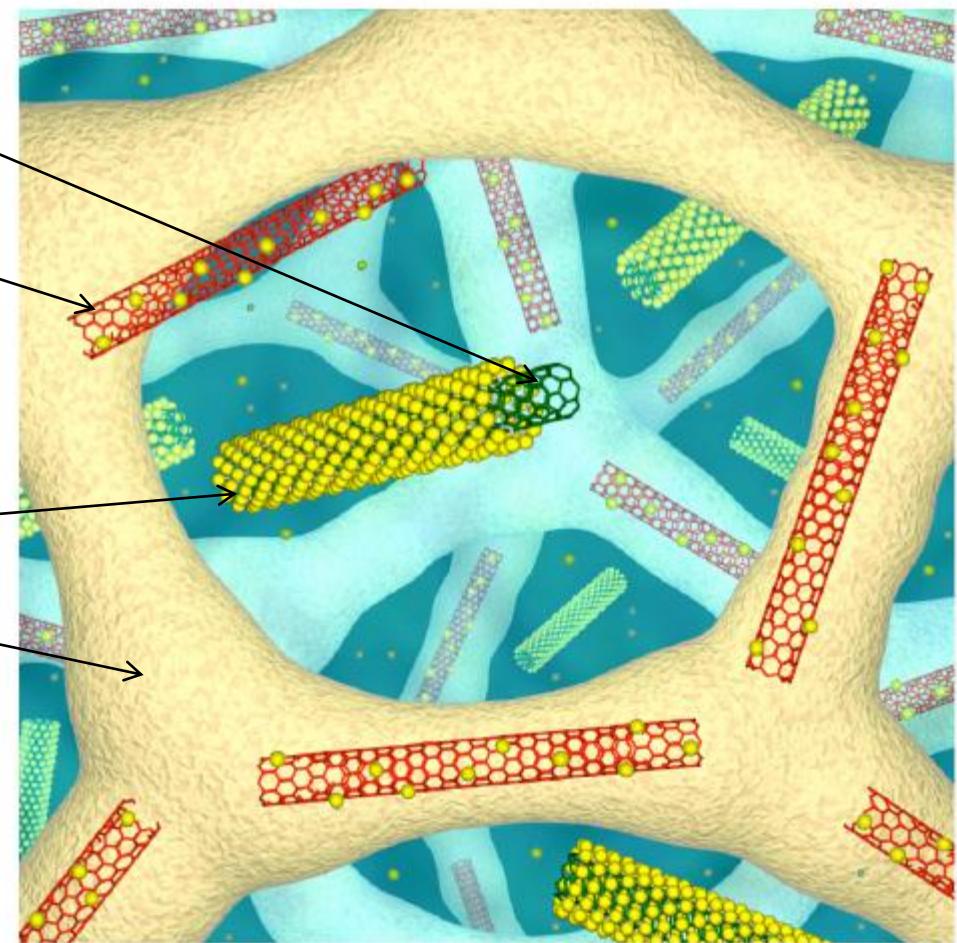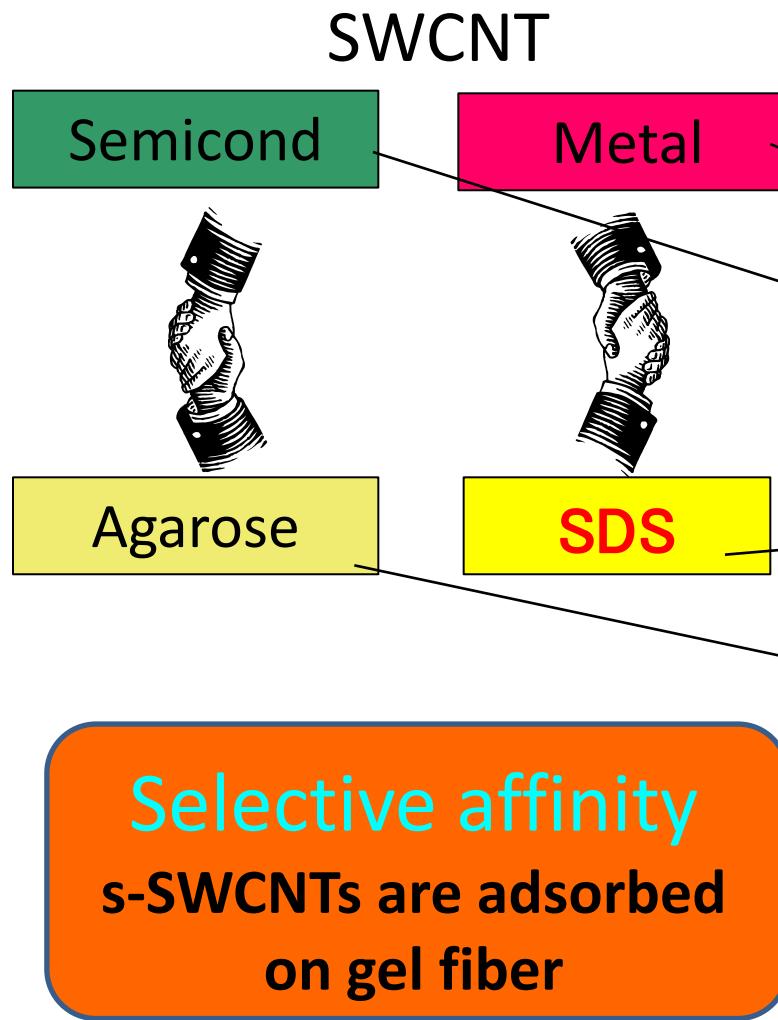
Agarose
Gel
Electrophoresis

Laser1 (1.2±0.1 nm)
HiPco (1.0±0.3 nm)
Laser2 (1.4±0.1 nm)

Semi.

Metal

30 min.

- **Simple**
- **Quick**
- **High-yield**

M11 | S22

95%

70%

⊕

T. Tanaka *et al*. Appl. Phys. Express **1** (2008) 114001.
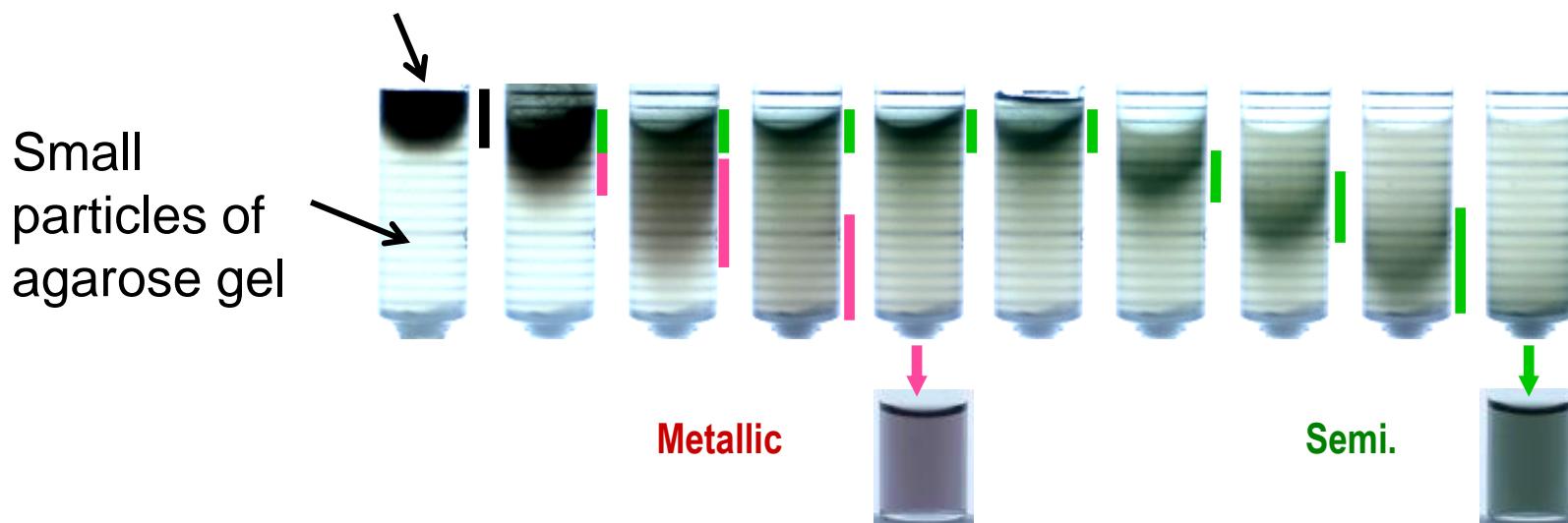
Mechanism of gel separation

SWCNT

Semicond | Metal

Agarose | SDS

Selective affinity
s-SWCNTs are adsorbed on gel fiber

Fundamental technology of M/S separation of SWCNTs

SWCNTs in **SDS** aqueous solution

SDS: Sodium Dodecyl Sulfate

Small particles of agarose gel

Metallic

Semi.

APEX (2009) 125002

M-SWCNT: no interaction with gel
S-SWCNT: adsorbed in gel column

Large-scale M/S separation

Pilot Plant

8.5 litter column

ÄKTA Pilot

コントロールユニット

分離溶媒

8.5L
カラム

2 g/day
4,000 €/g

Commercial products
800,000 €/g
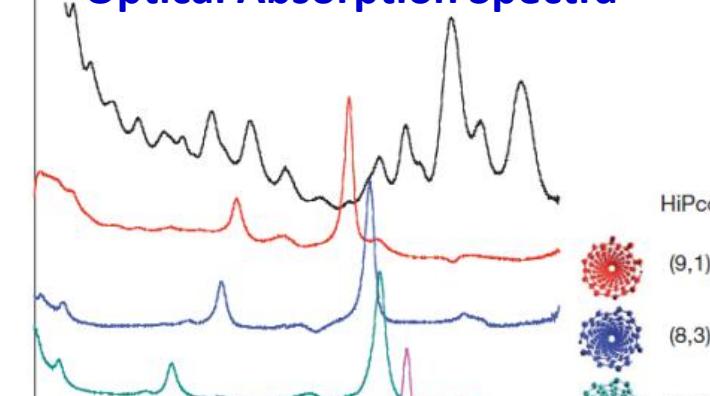
Appl. Phys. Express **2** (2009) 125002

Today's topics

- Single chirality separation using temperature controlled multicolumn method

- Filtration of ultra-long SWCNTs using glass beads column

Separation of SWCNTs by DNA wrapping
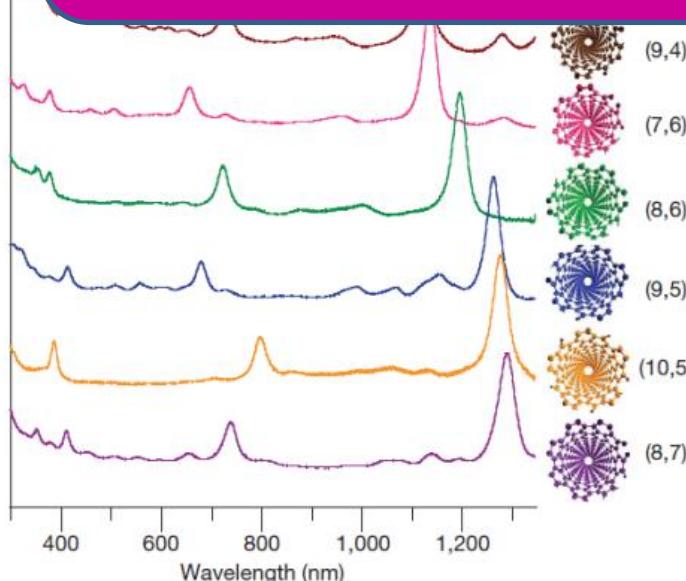
Optical Absorption Spectra

Table 1 | DNA sequence versus SWNT chirality

Chirality (n,m)	Sequences
(9,1)	$(TCC)_{10}$, $(TGA)_{10}$, $(CCA)_{10}$
(8,3)	$(TTA)_4TT$, $(TTA)_3TTGTT$, $(TTA)_5TT$
(6,5)	$(TAT)_{...}$, $(CGT)_{...}C$
(9,3)	$(TGTT)_2TGT$
(10,5)	$(TTTA)_3T$
(8,7)	$(CCG)_2CC$
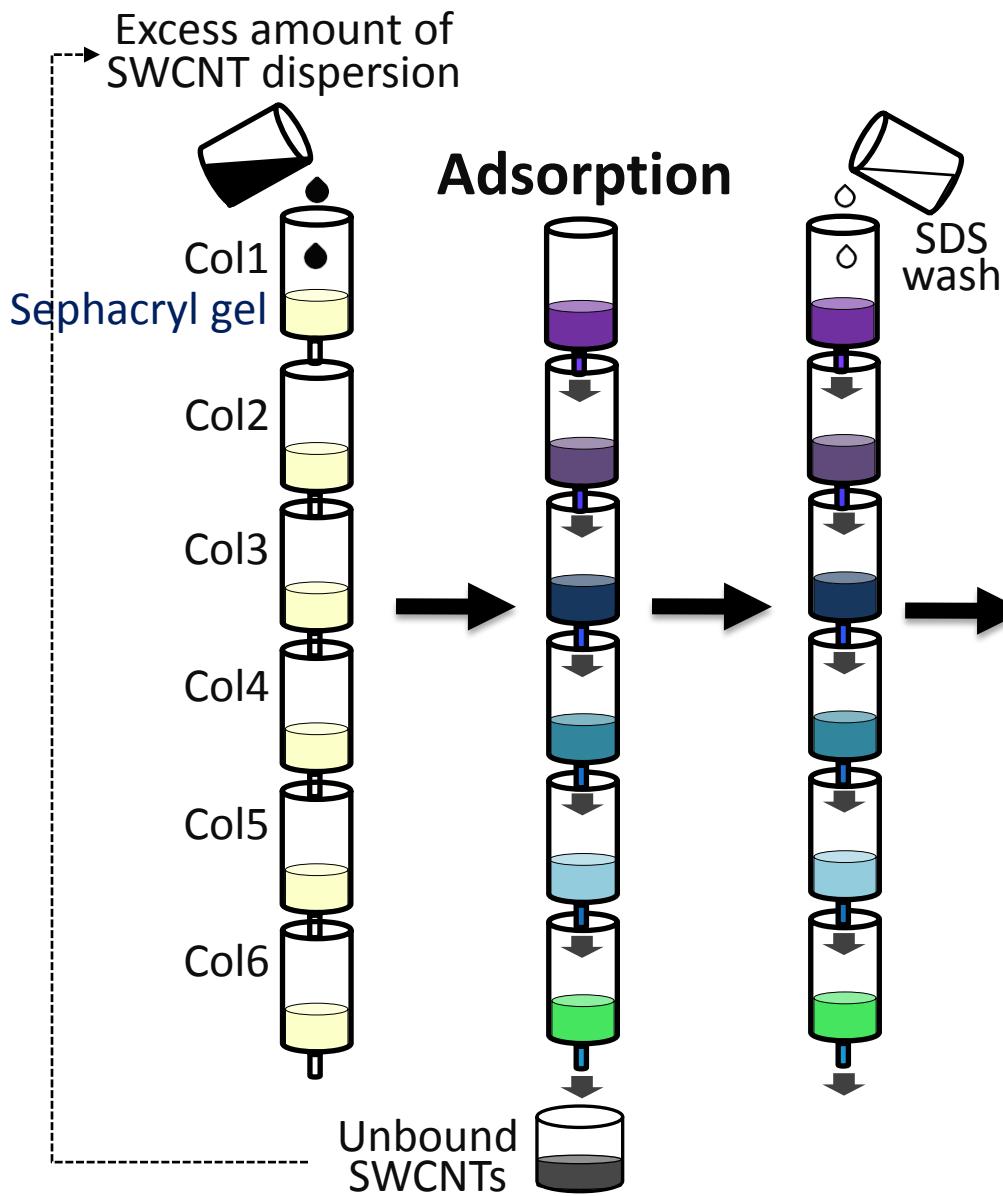
DNA sequences enabling chromatographic purification of single chirality semiconducting SWNTs.

High cost
Limited scalability

Different chirality,
Different DNA sequence
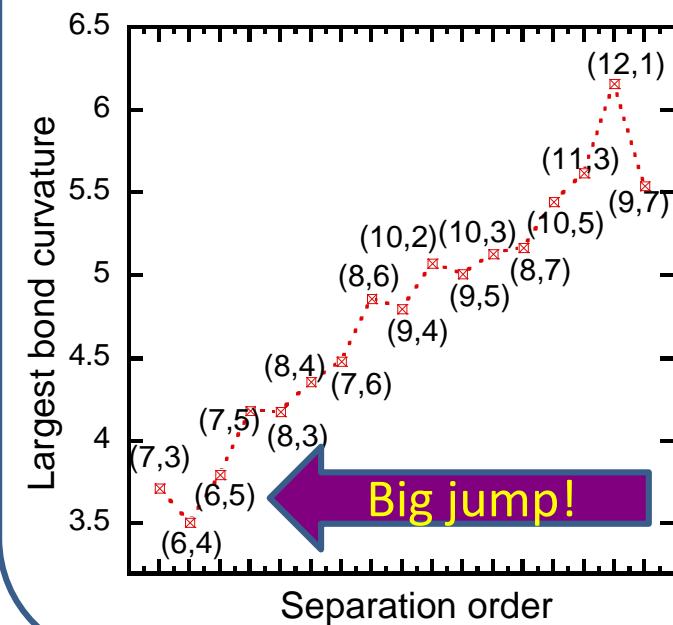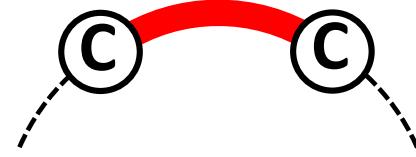
Tu, et al., Nature, 460(2009)250

Multicolumn gel chromatography

Excess amount of SWCNT dispersion

Adsorption

Col1
Sephacryl gel
Col2
Col3
Col4
Col5
Col6

SDS wash

Unbound SWCNTs
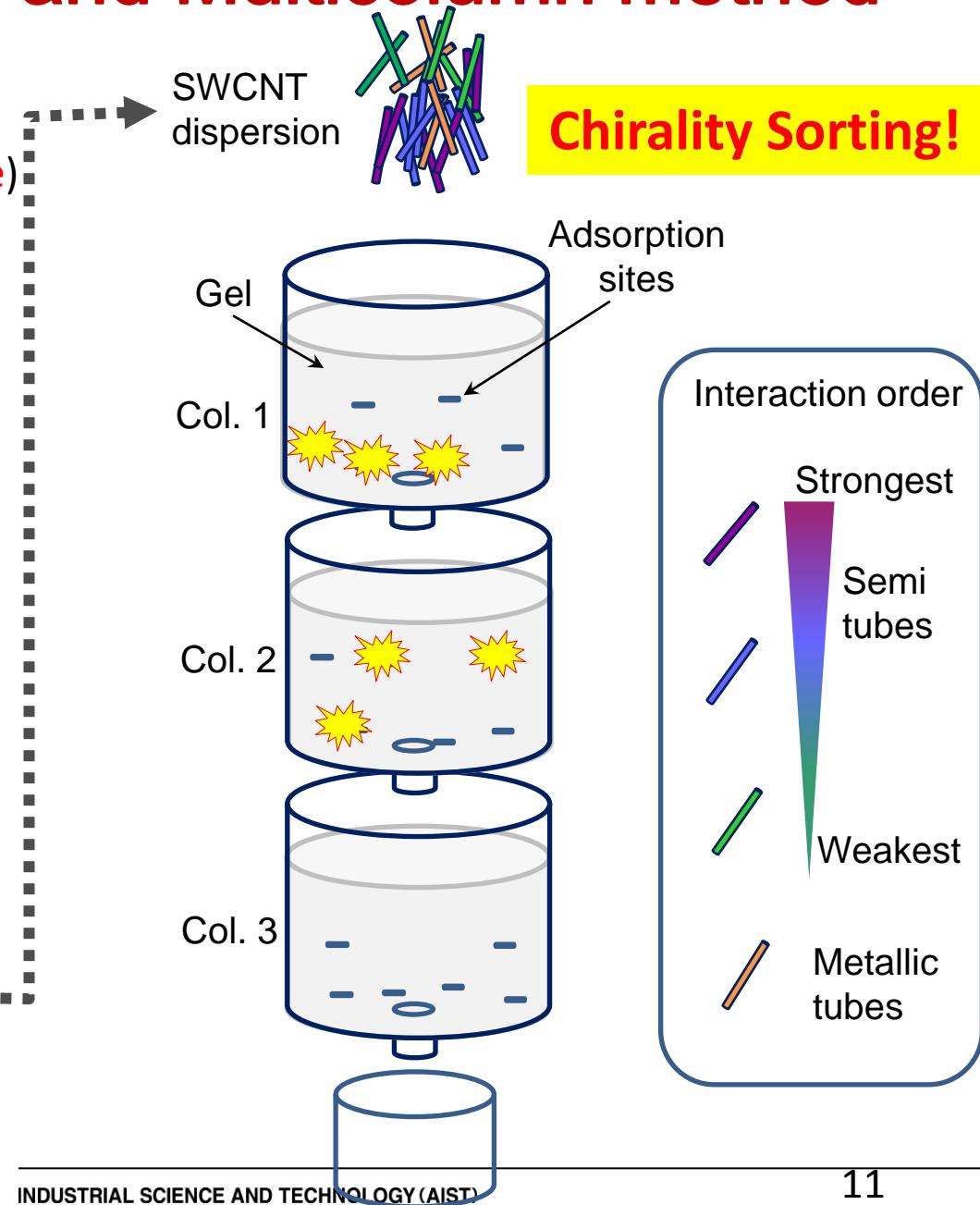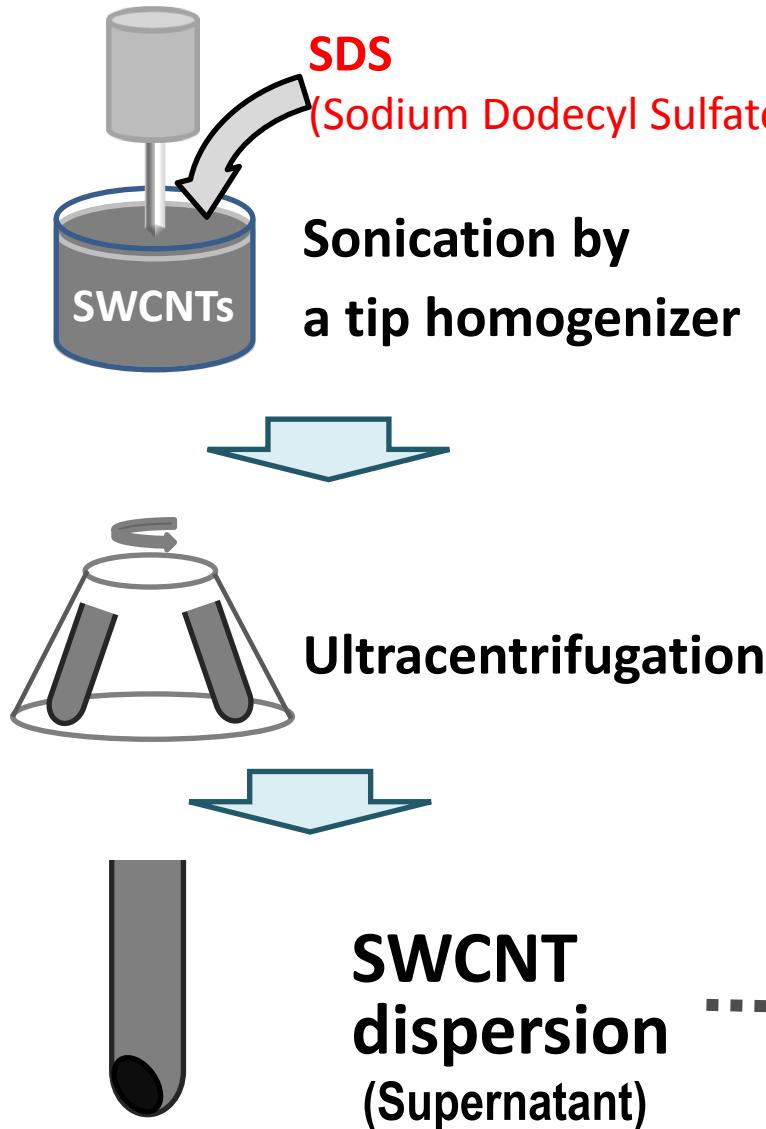
C-C bond curvature

The degree of C-C bond bending in SWCNT

Largest bond curvature vs Separation order

(12,1) (11,3) (9,7) (10,2) (10,3) (10,5) (8,6) (8,7) (9,5) (9,4) (8,4) (7,6) (7,5) (8,3) (7,3) (6,5) (6,4)

Big jump!
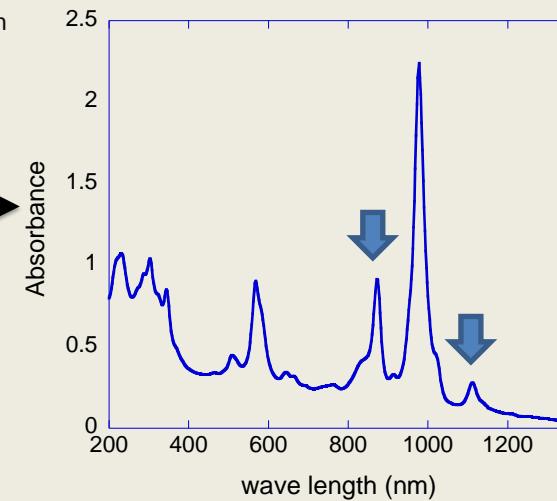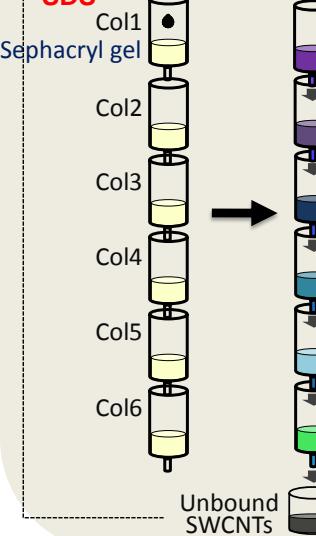
Overloading Effect and Multicolumn method

SDS
(Sodium Dodecyl Sulfate)

Sonication by a tip homogenizer

SWCNTs

Ultracentrifugation

SWCNT dispersion
(Supernatant)

SWCNT dispersion

Chirality Sorting!

Gel

Adsorption sites

Col. 1

Col. 2

Col. 3

Interaction order

Strongest

Semi tubes

Weakest

Metallic tubes

Liu, H. et al., Nat. Commun. 2 (2011)309

INDUSTRIAL SCIENCE AND TECHNOLOGY (AIST)

11

Multicolumn method

1st step

Dr. H. Liu

2nd step

PL mapping of Single-chirality S-SWCNTs
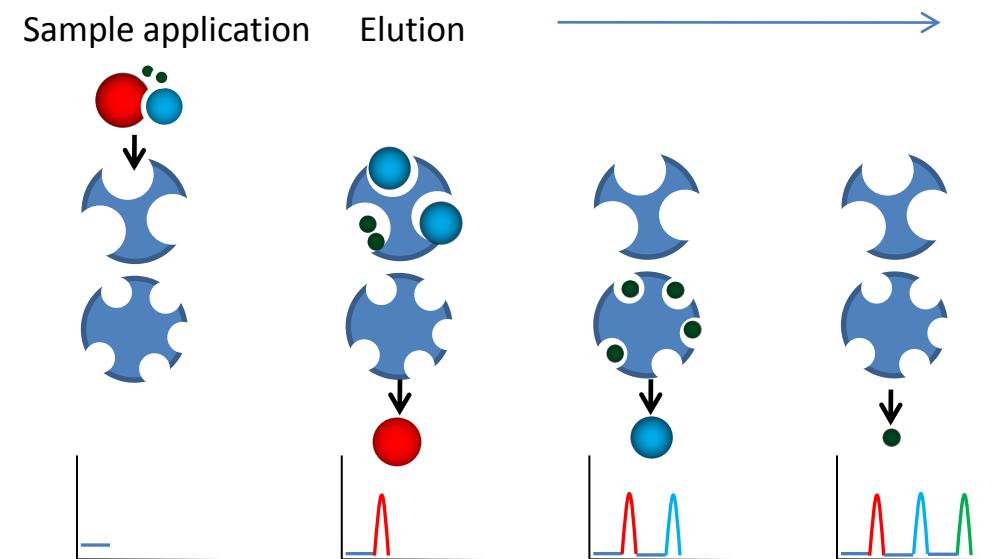
Length sorting of SWCNTs

Size-Exclusion Chromatography
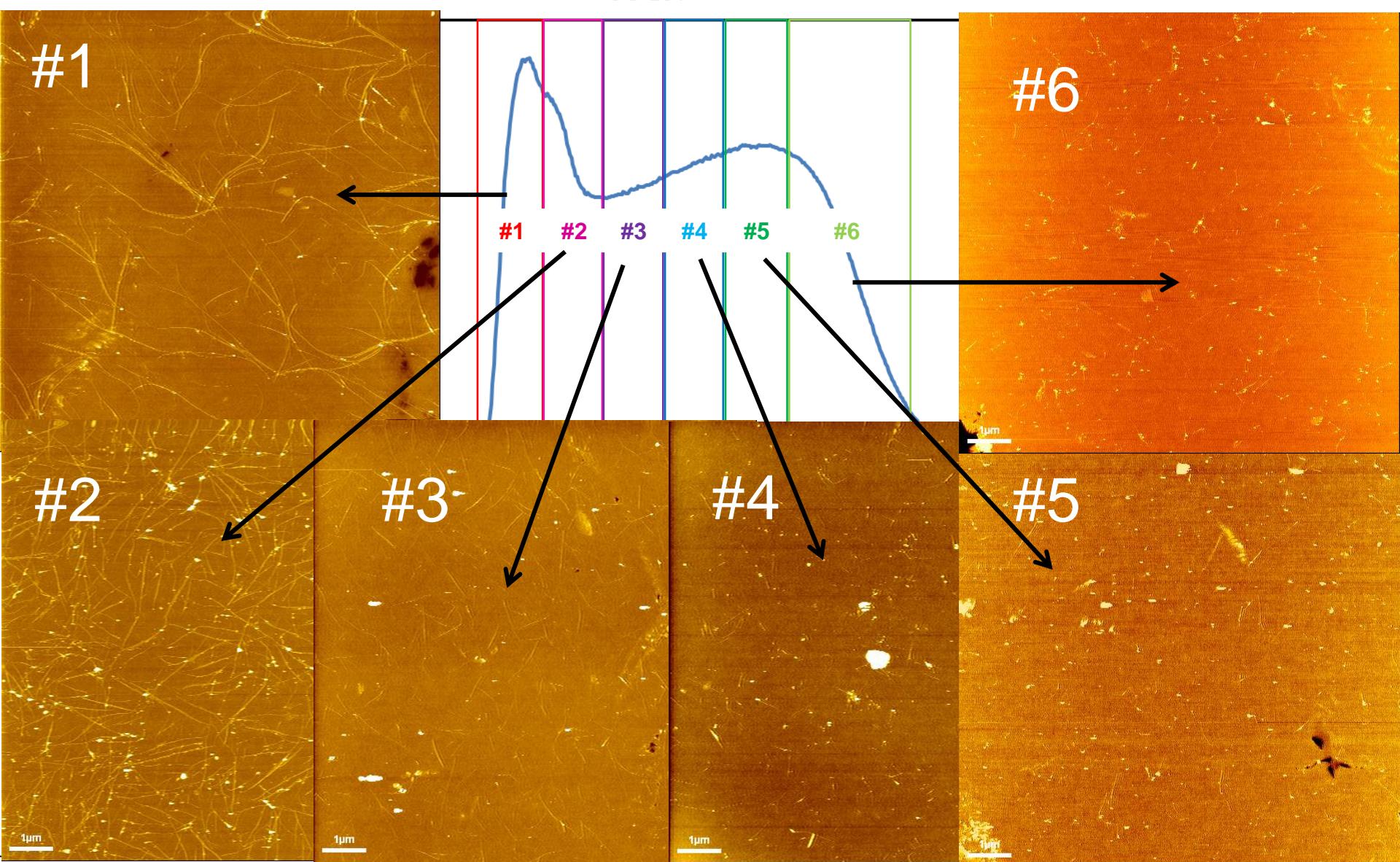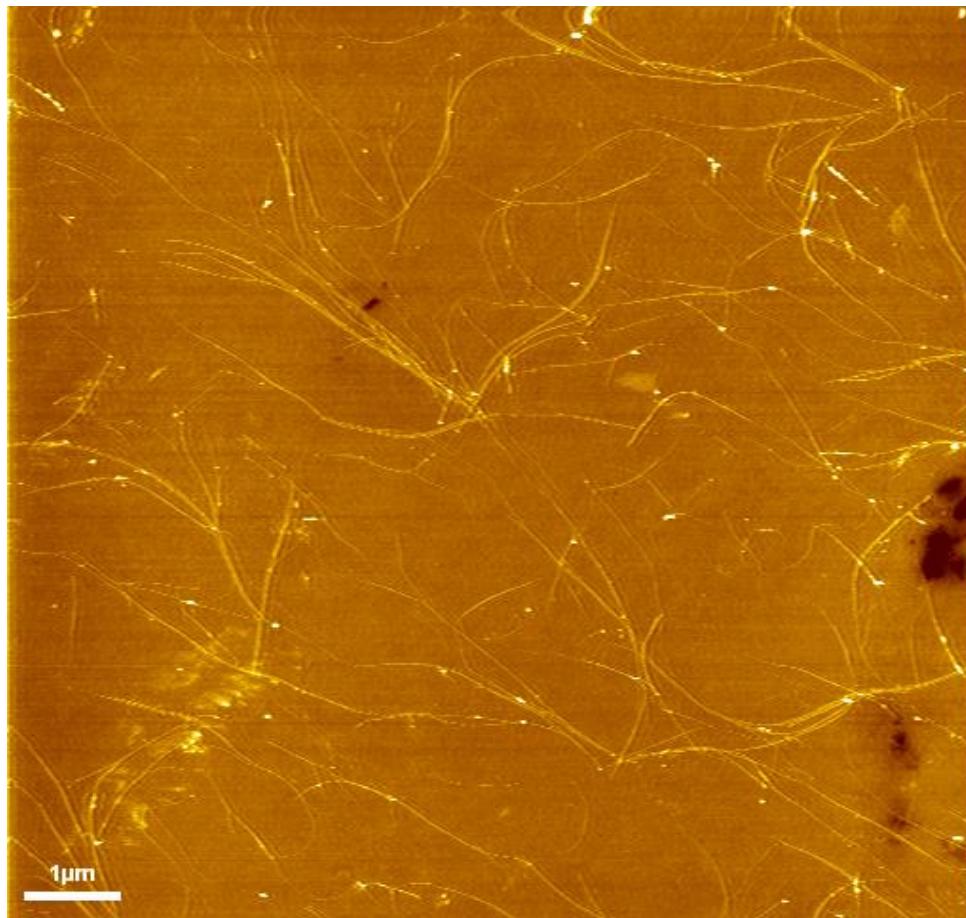
System:	AKTA Explorer 10s (GE Healthcare)
Column:	XK26/20（GE Healthcare)
Matrix:	Sephacryl S1000 (GE Healthcare)
Matrix volume:	106 ml (φ26 mm /200 mm length (26/200))
SWCNT:	HiPCO (2.0% Sodium Cholate dispersion)
Sample volume:	2.0 ml
Running Solution:	2.0% Sodium Cholate
Flow rate:	2.0 ml/min
Fraction Volume:	2.0 ml

XK26/20

Sample application   Elution

Size-Exclusion Chromatography of HiPco

Long SWCNTs from HiPco
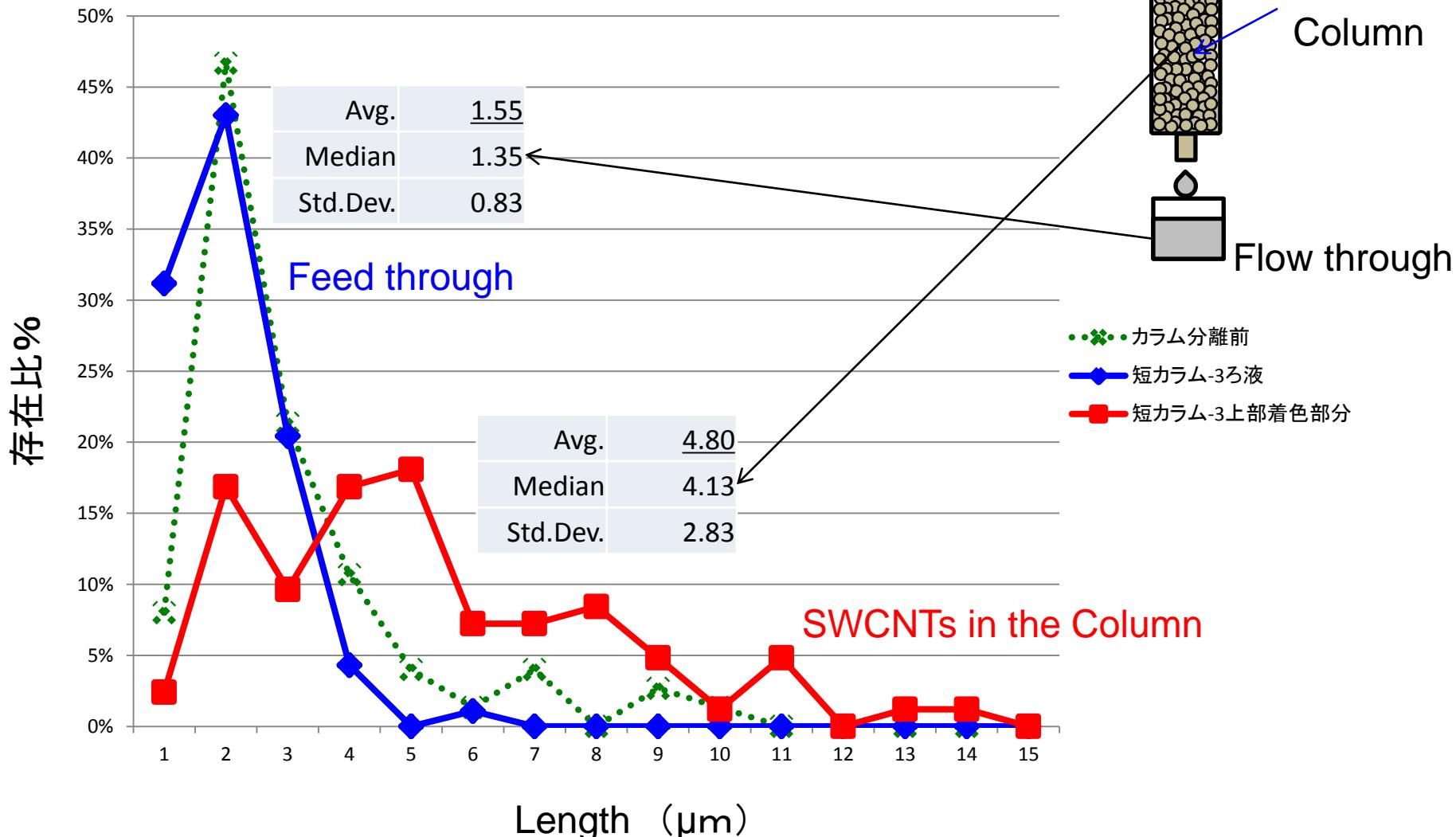
AFM image

- Length: 2~ 5μm
- Uniform
- Less impurities (purified)
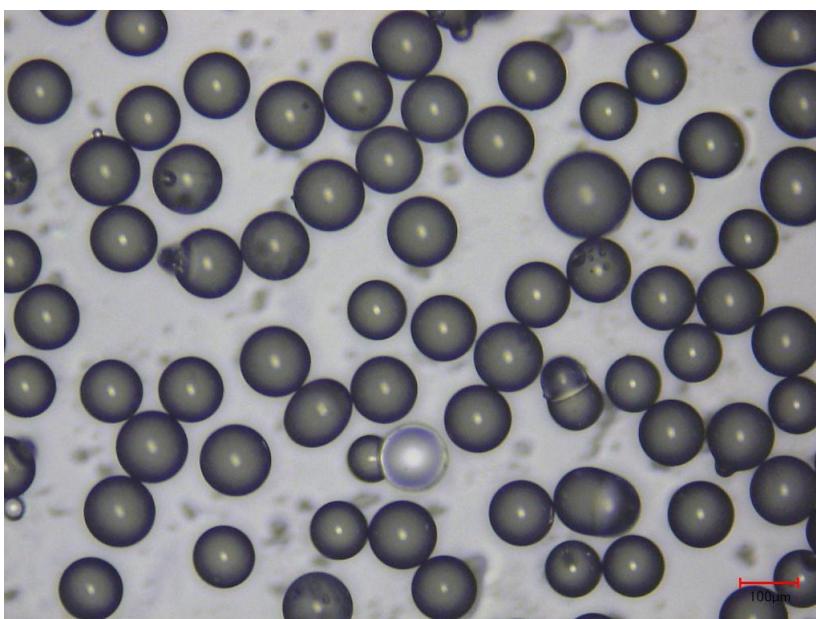
eDIPS/DNA
# What's in the column?

NATIONAL INSTITUTE OF **ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY（AIST）**
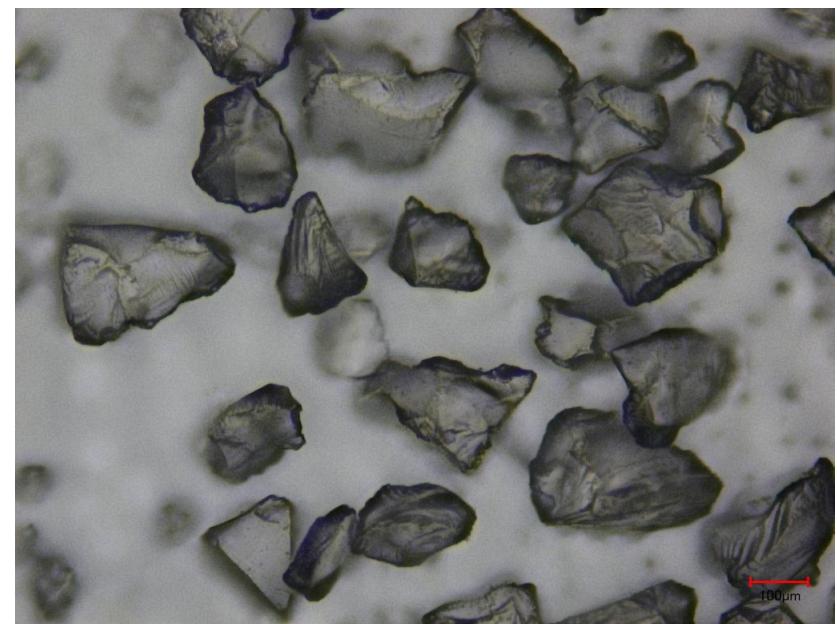
# How about the glass beads column for length sorting

Glass beads （100μm）
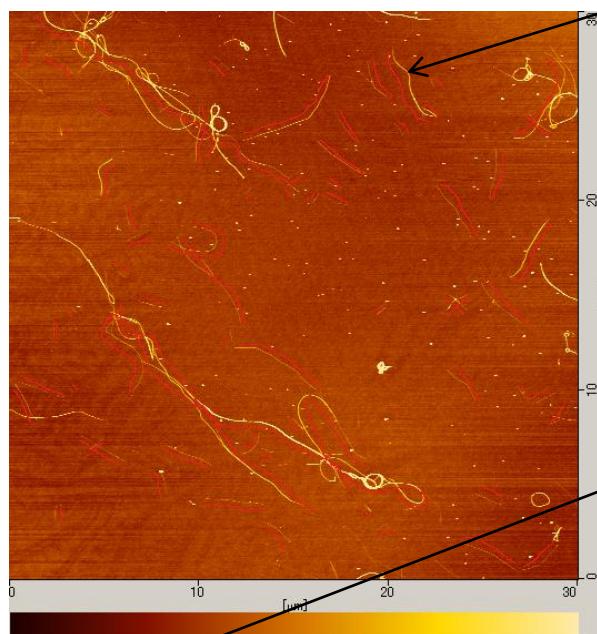
Wakogel® C-100 （150〜425μm 75%以上）

Glass beads 3D Filtration

Selective adsorption of over 10 μm CNT

Before filtration
CNT/DNA(PBS)
Scannning   30μm

Glass beads column
(100 μm)
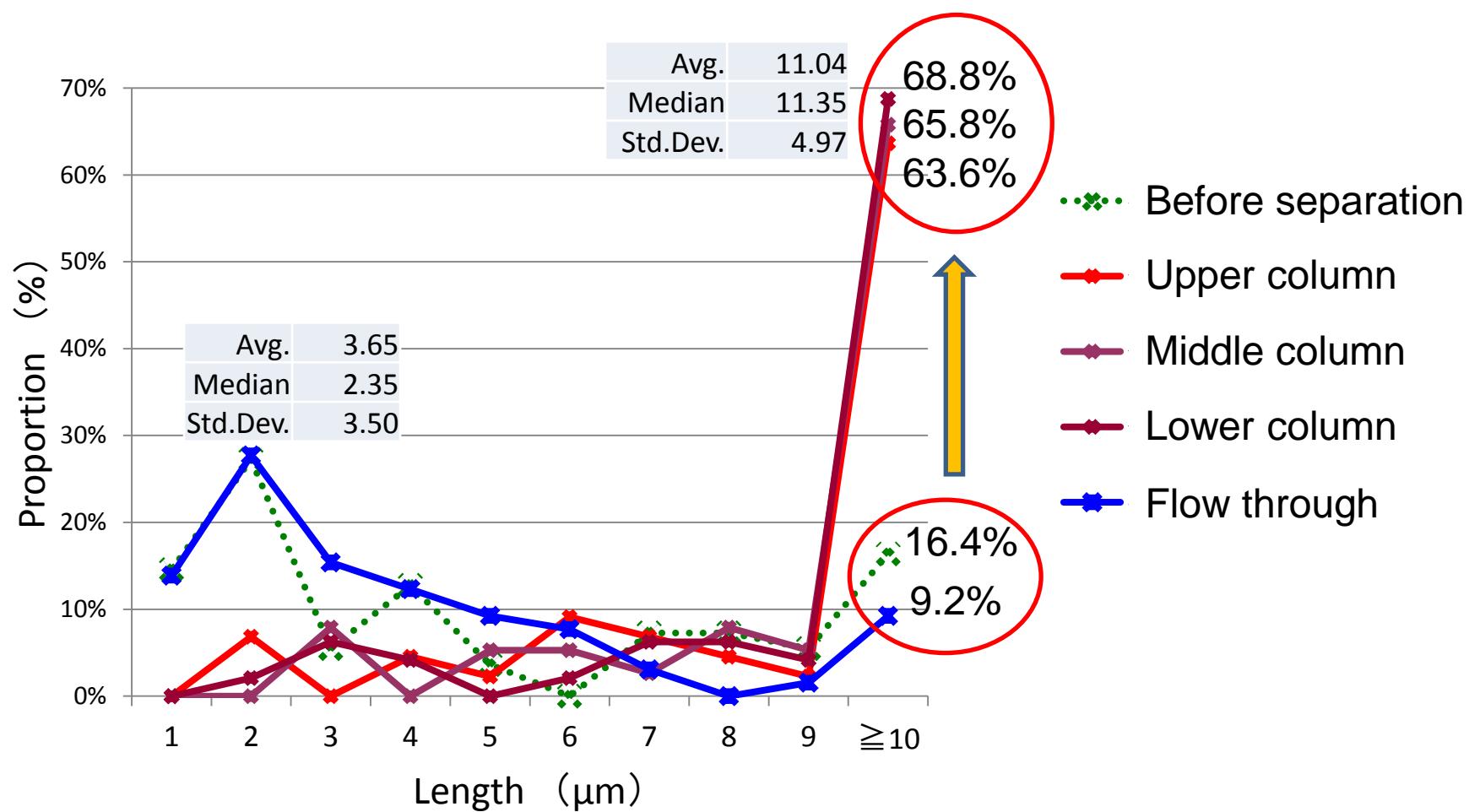
Flow through
Scanning   30μm

In the column
Scanning   30μm

20

Length distributions

Summary

- <u>13 kinds</u> of single chirality SWCNTs were separated by 2-step multicolumn method.
- Length sorting is now possible

Thank you!

$ CREST, JST