Single Chirality Separation of SWCNTs using Gel Column Chromatography

Hiromichi Kataura

1Nanosystem Research Institute, AIST, Japan
2CREST, JST, Japan
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

1/3: Metal
2/3: Semiconductor

30° Armchair
MS separation by AGE

- 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

Mechanism of gel separation

SWCNT

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

ÄKTA Pilot

8.5 litter column

2 g/day
4,000 €/g

Commercial products
800,000 €/g

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

Different chirality, Different DNA sequence


Table 1 | DNA sequence versus SWNT chirality

<table>
<thead>
<tr>
<th>Chirality (n,m)</th>
<th>Sequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9,1)</td>
<td>(TCC)<em>{10}, (TGA)</em>{10}, (CCA)_{10}</td>
</tr>
<tr>
<td>(8,3)</td>
<td>(TTA)<em>{4}TT, (TTA)</em>{3}TTGTT, (TTA)_{5}TT</td>
</tr>
<tr>
<td>(6,5)</td>
<td>(TAT), (CGT), C</td>
</tr>
</tbody>
</table>

High cost
Limited scalability

Optical Absorption Spectra

DNA sequences enabling chromatographic purification of single chirality semiconducting SWNTs.
Multicolumn gel chromatography

Excess amount of SWCNT dispersion

Sephacryl gel

Col1
Col2
Col3
Col4
Col5
Col6

Unbound SWCNTs

Adsorption

SDS wash

C-C bond curvature

The degree of C-C bond bending in SWCNT

Separation order

3.5
4
4.5
5
5.5
6
6.5

Big jump!
Overloading Effect and Multicolumn method

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

SDS (Sodium Dodecyl Sulfate)

Sonication by a tip homogenizer

Ultracentrifugation

SWCNT dispersion (Supernatant)

SWCNT dispersion

Adsorption sites

Gel

Col. 1

Col. 2

Col. 3

Interaction order

Strongest

Semi tubes

Weakest

Metallic tubes

Chirality Sorting!
Multicolumn method
H. Liu et al., Nat. Commun. 2 (2011) 309

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

Sample application

Elution
Size-Exclusion Chromatography of HiPco

$OD_{254}$

#1 #2 #3 #4 #5 #6

#1 #2 #3 #4 #5 #6

1 µm

NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY (AIST)
Long SWCNTs from HiPco

- Length: 2~ 5μm
- Uniform
- Less impurities (purified)

AFM image
eDIPS/DNA
What’s in the column?

<table>
<thead>
<tr>
<th>Length (μm)</th>
<th>Avg.</th>
<th>Median</th>
<th>Std.Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed through</td>
<td>1.55</td>
<td>1.35</td>
<td>0.83</td>
</tr>
<tr>
<td>SWCNTs in the Column</td>
<td>4.80</td>
<td>4.13</td>
<td>2.83</td>
</tr>
</tbody>
</table>
How about the glass beads column for length sorting

Glass beads (100μm)  
Wakogel® C-100 (150～425μm  75%以上)
Glass beads 3D Filtration

Before filtration
CNT/DNA(PBS)
Scanning 30μm

Flow through
Scanning 30μm

Glass beads column
(100 μm)

In the column
Scanning 30μm

Selective adsorption of over 10 μm CNT
Length distributions

Proportion (%)

<table>
<thead>
<tr>
<th>Length (μm)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>≥10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before separation</td>
<td>68.8%</td>
<td>65.8%</td>
<td>63.6%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper column</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Middle column</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lower column</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flow through</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Avg. 11.04
Median 11.35
Std.Dev. 4.97

Avg. 3.65
Median 2.35
Std.Dev. 3.50
Summary

• **13 kinds** of single chirality SWCNTs were separated by 2-step multicolumn method.
• Length sorting is now possible
Thank you!

$\text{CREST, JST}$