

How can we obtain structurally well-defined carbon nanotubes?

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Carbon nanotubes (CNTs) is famous and unique material in science. They are constructed by hexagonal sp^2 carbon networks with a tubular structure and attracted much attention particularly in material science. They have unique properties such as lightweight, high physical strength in known material, high electrical conductivity and high thermal conductivity. CNTs have structural variety, and it causes the diversity of physical properties of each CNTs. However, general synthetic methods of CNTs give mixture of many types of structure, and it is difficult to separate each of them.

CNTs were discovered in 1991 by Iijima, who reported multi-layered CNTs.¹ A year later, a geometric description of monolayered or single-walled CNTs (SWNTs) was developed that showed three structural arrangement such as armchair, helical and zigzag,² and in 1993 the experimental synthesis of SWNTs was achieved.³ Electric properties of SWNTs with different geometries were studied theoretically and experimentally⁴ to revealed that SWNT can be either metallic or semiconducting depending on its structural arrangement

and diameter; Armchair SWNTs show metallic property and most helical and zigzag SWNTs show semiconducting property. Moreover, in 2004, some atomic defects were observed on SWNTs which will cause some change in their physical and electrical properties.⁵ Due to unique properties of CNTs, many potential applications have been proposed such as nano test-tubes, H₂ storage media, batteries, field-emission materials, tips for scanning probe microscopy, chromatographic stationary phases, transistors, diodes, and sensors.⁶ Therefore, understanding of relationship between the structures and the properties is in great interest.

However, popular synthetic methods provide SWNTs as a mixture of different length, diameter, structural arrangement and chirality, right-handedness or left-handedness; The diameter of SWNTs can range from 0.4 to 2 nm, and most methods give a mixture of two-thirds semiconducting and one-third metallic tubes.⁶ This causes the difficulty of understanding the structural effect to properties of SWNTs. Many chemists tried to solve this problem, and now there are roughly two approaches; One is developing separation methods of each SWNT, and another is bottom-up methods.

Some separation methods have already been developed to purify SWNTs to some extent.⁷

Length separation can be achieved by chromatographic techniques, capillary electrophoresis or field-flow fractionation which are ordinary separation method used in chemistry. Separation according to their metallic and semiconducting property was also developed, which was achieved by the different chemical affinities of each SWNT. However, further purification is still challenging because structural variety is large and structural separation can be realized by using some interactions between the target and equipment which is still under investigation. Moreover, chirality separation is more difficult because almost all physical properties are the same in right-handed and left-handed molecules.

Bottom-up method was proposed by inorganic and organic chemists. For inorganic strategy, structure-specific growth of SWNTs using inorganic catalysts have been developed which is called catalytic chemical vapor deposition (CCVD) method.⁸ In CCVD method, inorganic catalysts act as a template and SWNTs with specific structure can grow on the catalysts. For example, Li and co-workers synthesized SWNTs of a single structural arrangement with an abundance higher than 92 per cent. This method is gathering attention for obtaining large amount of SWNTs with specific structure.

However, there should be length diversity, and chirality specific synthesis has not been achieved. Also, precise investigation of relationship between the structure and physical properties is difficult because defects can be appeared in CCVD method.

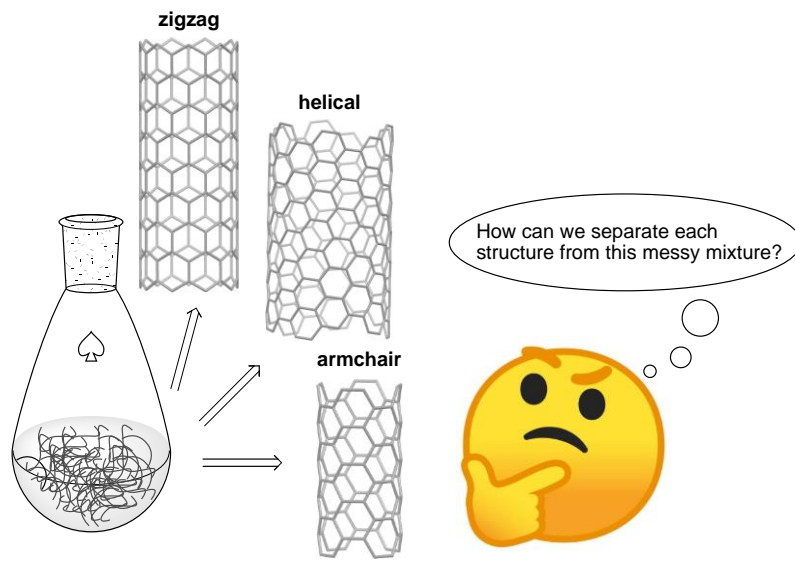
Scott and others proposed bottom-up synthesis of SWNTs without using metal catalyst,⁹ and many organic chemists are trying to synthesize small units of SWNT, which will be templates for growing structurally well-defined SWNTs, from simple organic molecules.

As a first finite model of SWNT, cycloparaphenylene (CPP), which benzenes are connected by single bond to make a ring, was synthesized in 2008 by Jasti,¹⁰ and today several finite SWNTs which has different length, diameter and structural arrangement were synthesized.¹¹ Organic synthetic strategy can give structurally well-defined SWNTs but it requires many reactions and purifications. Furthermore, the lengthening of SWNTs has not been achieved.

To obtain structurally well-defined SWNTs, I think it is needed to develop both separation and bottom-up methods. Thinking of industrial usage of SWNTs, it is necessary to obtain large amount of targets. So, bottom-up synthesis using inorganic catalysts seems to be the most efficient method. However, as I already mentioned, there must be structural

variations to some extent which requires further purification. And, for developing purification methods, understanding of fundamental relationship between the structure and the physical properties is needed. Organic synthetic strategy has an advantage to this because it can control the structure of SWNTs by using appropriate reactions. Moreover, for chiral control synthesis, this strategy will be powerful method to develop templates for lengthening.

When huge amount of structurally well-defined SWNTs can be synthesized, it will give wide impact to science and society. In science, as I mentioned above, structural effects of SWNTs to their physical properties are under investigation. So precise analysis can be conducted which will give the information of their unique curved hexagonal sp^2 carbon networks. Moreover, CNTs have many potential applications which will open new field of science. Also, if SWNTs will be used in industry, due to its metallic or semiconducting properties and light weight, very light electronic devices can be developed. So our smartphones might become much lighter in the future.



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