himac APPLICATION

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Trend in separating carbon nanotubes by ultracentrifuge

CP-WX series preparative ultracentrifuges / P40ST swinging bucket rotor / P50VT2 vertical rotor

In 1991, Dr. Sumio Iijima discovered nanometer-size tubes composed of cylindrical nano-structured carbon. This material has recently been in the limelight as a controversial material. The centrifugal technique in the carbon nanotube field has conventionally been used only to remove miscellaneous impurities such as amorphous carbon and catalytic metal from carbon nanotube suspension sample. For example, one patent application filed in February 1993 described that centrifugation was performed at speeds of 500 rpm to 50,000 rpm for 30 minutes to 96 hours," and also claimed that "amorphous carbon particles were separated as sediments by centrifugation at 500 rpm for 30 minutes, and nanometer-sized particles with a particle diameter of 20 nm or smaller and nanotubes larger than them were separated by centrifugation at 1,000 rpm for 30 minutes."

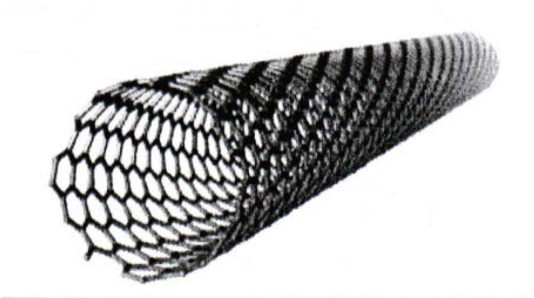

Fig. 1 Single-walled carbon nanotube model (Example)

However some centrifugal separations regarding carbon nanotubes at several hundreds of thousands xg or at speeds of several tens of thousands rpm have recently been reported. And the new centrifugal separation methods using the density gradient solutions widely used in biological field have also been reported as a new separation technique. Following report shows some examples of refining single-walled carbon nanotubes by centrifugations including density gradient centrifugation as a new technique in this field.

1. Example of centrifugation technique without using a density gradient solution

It is well known that ultracentrifuge separation without using a density gradient solution to separate and refine carbon nanotubes was reported by Dr. Michal J. O'Connell et al. in their paper in 2002. ("Band Gap Fluorescence from Individual Single-Walled Carbon Nanotubes." Dr.Michael J. O'Connel et al, 2002 [1)])

This method suspended single-walled carbon nanotubes (SWNTs) in heavy water by using sodium lauryl sulfate (SDS) and centrifuged the solution (at 122,000 xg, for 4 hours). In this centrifugation, the single-bundle SWNTs remained in supernatant without being sedimented and could be easily separated. The single-bundle SWNTs were assumed as not being settled out by centrifugation. This is because the densities of SWNTs (1.0 g/cm^3) were smaller than that of heavy water (deuterium oxide: 1.1 g/cm^3), in contrast 7-bundles SWNTs (1.2 g/cm^3), respectively. The novel technique arrow to separate impurities such as metallic catalyst and/or corrugated particles, furthermore separate the element of constitute in SWNTs by using the centrifugal technique.

2 Example of centrifugation using a density gradient solution

This example was reported in "Enrichment of Single-Walled Carbon Nanotubes by Diameter in Density Gradients" [2)] (by Dr. Michel S. Arnold et al, 2005) using iodixanol - a nonionic density gradient medium. According to the report, in this example SWNTs (in which single-stranded DNA genome is dispersed) were centrifuged at 174,000 xg for 3.5, 7, 8.75, and 10.5 hours, respectively. The band position remained constant for up to 7 hours and longer; consequently, the liquid was assumed to be in a state of sedimentation equilibrium. A colored fraction was obtained in a density band of 1.11 to 1.17 g/cm^3. Semiconductive SWNTs were also found at a density level of 1.13 +/-0.02 g/cm^3.

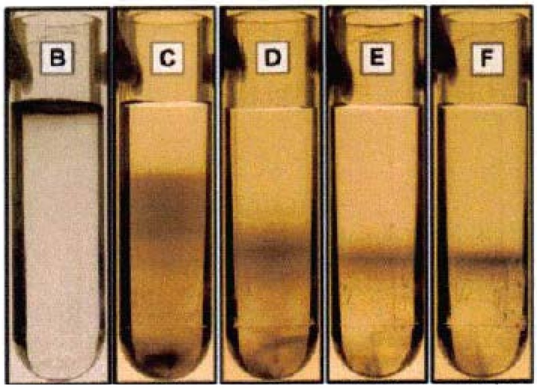

Fig.2 Example of centrifugation using density gradient solution (1) [2)]

The next year (2006), they were also reported that metallic and semiconductive SWNTs were separated by using sodium cholate (CS) derived from biliary acid, which is a dispersing agent as surface-active agent, in the density gradient centrifugation with ultracentrifuge, swinging bucket rotor and iodixanol as density gradient solution. ("Sorting carbon nanotubes by electronic structure using density differentiation" Dr. Michel S. Arnold et al, 2006.)[3)]

In this paper, it was reported that semiconductive SWNTs were located in the upper layer (low-density side) of the separation layer, on the other hand metallic SWNTs were located in the lower layer (high-density side). The density of the upper part of the layer was approximately 1.08 g/cm^3 (Fig. 3).

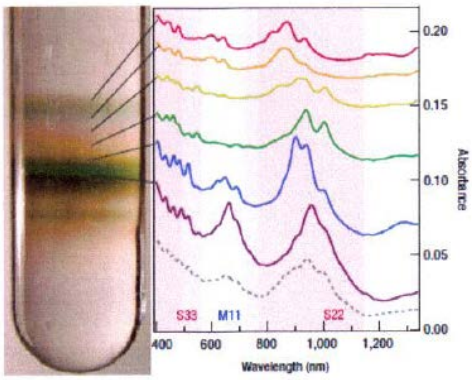

Fig.3 Example of centrifugation using density gradient solution (2) [3)]

In 2008, Dr. Yanagi (of Tokyo Metropolitan University, currently) et al. presented a report entitled "Optical and Conductive Characteristics of Metallic Single-Wall Carbon Nanotubes with Three Basic Colors: Cyan, Magenta and Yellow." [4] This report described the separation of metallic SWNTs of different colors (cyan, magenta and yellow) from three kinds of SWNTs that differ in thickness. This report contains a very noteworthy description of how the result of centrifugation depends on the different ingredients of three surface-active agents [sodium deoxycholate (DOC), SDS and CS].

The centrifugal conditions using a ultracentrifuge and its swinging bucket rotor were at 288,000 xg for about 18 hours, and iodixanol as the density gradient solution. What we find particularly interesting is where the bands of metallic SWNTs and semiconductive SWNTs are formed. In this report,[4] the band of metallic SWNTs formed above the band of semiconductive SWNTs, while the semiconductive SWNTs formed above the metallic SWNTs or on the low-density side as described in the previous report [3] (Michel S. Arnold et al, 2006). It's interesting to note that, the buoyant densities of SWNTs are reversed as these surface- active agents.

These results indicated that the buoyant densities of metallic and semiconductive SWNTs are more affected by surface-active agents than are the innate properties of SWNTs.

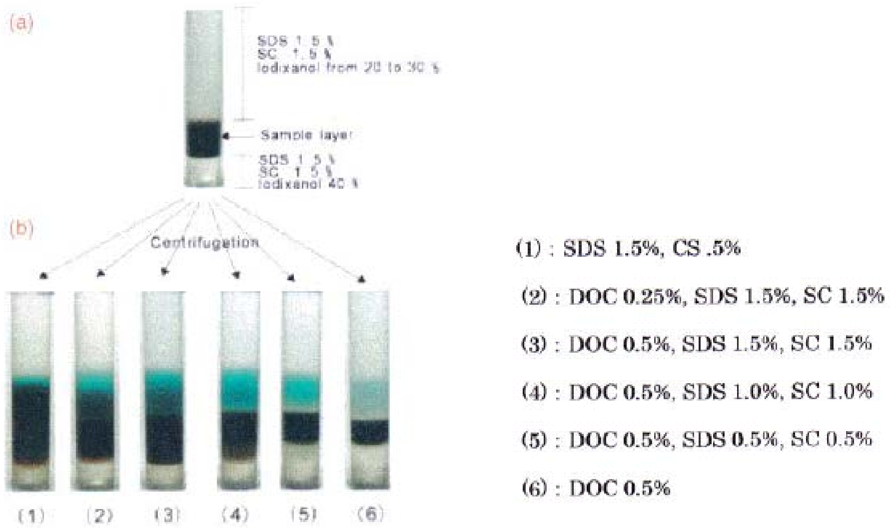

Fig. 4 Relation between ingredients of surface-active agents and centrifugation results

Dr. Yanagi et al. also reported separation method, using sucrose as a gradient medium in their paper. ("Separation of Metallic and Semiconducting Carbon Nanotubes by using Sucrose as a Gradient Medium," [5] Yanagi K. et al. 2008). Sucrose is commonly available and inexpensive as a density gradient medium for centrifugal separation. This report refer to not only optimizing the ingredients of surface-active agents in the centrifugal separation of SWNTs in sucrose density gradient solution but also to optimizing the centrifugal temperature conditions. This centrifugal separation uses vertical rotor that can simultaneously process eight tubes, each having the same capacity as that for the swinging bucket rotor. We expect that this technique could make centrifugal separation more practical together with an inexpensive gradient medium. As for the centrifugal conditions, the centrifugal time of this technique (vertical rotor, at 402,000 xg, for 20 hours) is roughly equivalent to that of the conventional technique (swinging bucket rotor, using iodixanol as density gradient medium), although this technique entails a higher rotor speed. It is assumed that this is due to the high viscosity of sucrose solution in a high-density state.

As described above, the centrifugal separation of SWNTs by using a density gradient medium is affected by combinations of various elements (such as related centrifugal force, centrifugal time, density gradient medium, types and ingredients of surface-active agents used as dispersing agents and centrifugal temperature). We also hope that more studies will be conducted on the effective separation of metallic and semiconductive SWNTs. For more information, please refer to the reference documents listed below.

References:

1) O'Connell, M. J. et al. Science 297, 593 (2002).
2) Arnold, M. S. et al. Nano Letters, 5, 713 (2005).
3) Arnold, M. S. et al. Nature Nanotechnology, 1, 60 (2006).
4) Yanagi, K. et al. Appl. Phys. Express, 1, 034003 (2008).
5) Yanagi, K. et al. J. Phys. Chem. C, 112, 18889 (2008).

Machine appearance

The isolation System for Single-walled Carbon Nanotubes

(1) CP100WX Preparative ultracentrifuge

(2) P40ST Swinging Bucket Rotor

(3) DGF-U Density Gradient Fractionator

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