

## Chirality Fingerprinting and Geometrical Determination of Single-Walled Carbon Nanotubes

The recent development of a technique for purifying single-walled carbon nanotubes (SWCNTs) makes it possible to study the physical properties of 2<sup>nd</sup> and 3<sup>rd</sup> generation SWCNT solids, which are highly-enriched metallic (or semiconducting) and single-chirality SWCNT materials, respectively. However, the methods for characterizing their purity and structures are very limited. For example, the detailed structures, such as carbon-carbon bond lengths in a SWCNT, have not been fully clarified yet. Here, we demonstrate that a powder X-ray diffraction experiment is useful to fingerprint the chiralities of SWCNTs in a solid and examine the detailed structures.

Single-walled carbon nanotubes (SWCNTs) are quasi one-dimensional hollow cylinders with diameters ranging from less than one nanometer to a few nanometers [1]. The structure of SWCNTs is often hypothetically obtained by rolling up a graphene sheet, and is specified by a pair of integers ( $n, m$ ) referred to as chiral indices. Although it has been almost 25 years since SWCNTs were discovered, their detailed structures and the intrinsic physical properties of bulk SWCNT solids remain to be fully elucidated. This is because the SWCNT materials usually contain SWCNTs with various chiralities. Very recently, however, the development of purification and separation techniques [2-4] has made it possible to study almost-pure metallic (or semiconducting) SWCNT materials as well as single-chirality SWCNT materials. These are referred to as 1<sup>st</sup>, 2<sup>nd</sup>, and

3<sup>rd</sup> generation SWCNT materials (see Fig. 1). However, existing methods for characterizing the purity of bulk samples and SWCNT structures are very limited. For example, electron diffraction [5] and optical absorption spectroscopy [6] suffer from weaknesses such as limitation of quantitative estimates, or insufficient accuracy or sensitivity.

In this work, we developed a powder X-ray diffraction (XRD) method to characterize the geometrical structures of SWCNTs and purity of bulk materials based on a simulation study of XRD patterns [7]. Here rolling-up structures of a graphene sheet, which consists of a honeycomb arrangement of carbon atoms, are used as default structures for the modeled SWCNTs. The calculations were performed using the Debye formula.

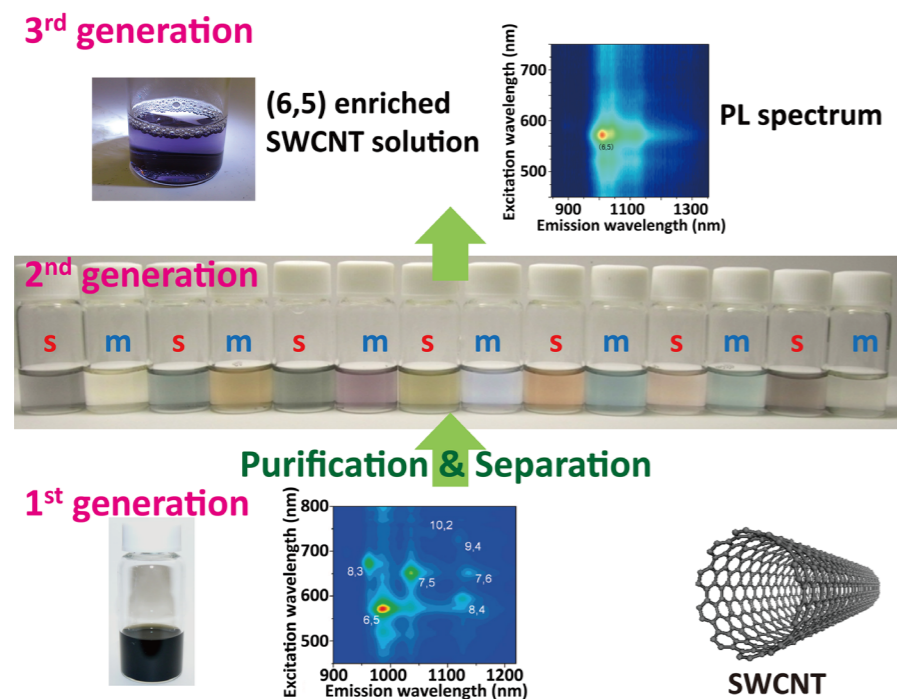


Figure 1: SWCNT solutions of the 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> generation SWCNT materials. The 1<sup>st</sup> generation material contains SWCNTs with various chiralities. In the 3<sup>rd</sup> generation material, SWCNTs with a specific chirality are enriched, while the metallic or semiconducting SWCNTs are enriched in the 2<sup>nd</sup> generation materials. For the (6,5)-enriched sample, 2D maps of the photoluminescence excitation/emission peak intensities are shown before and after the enrichment. The metallic (semiconducting) solution is shown by "m (s)".

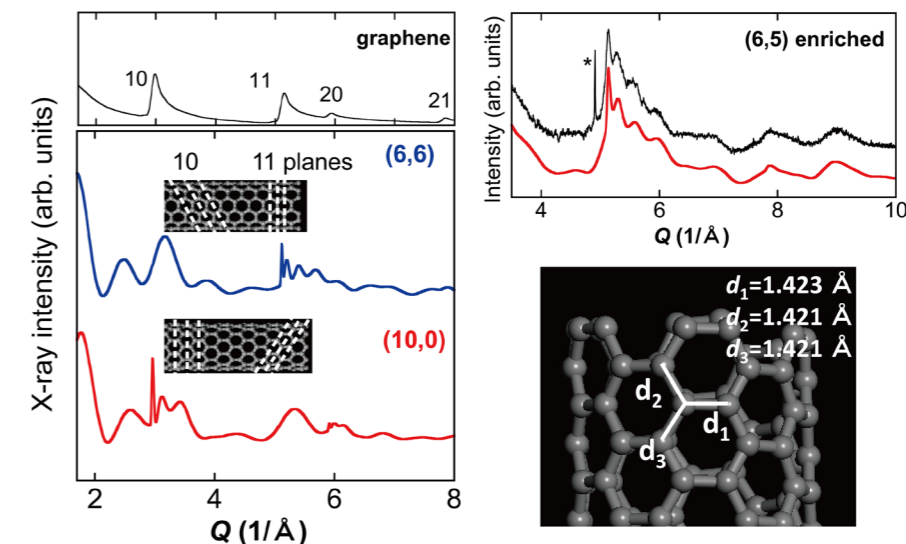


Figure 2: Left panel: calculated XRD patterns for graphene, (6,6) and (10,0) SWCNTs. Right panel: an observed XRD pattern (black solid line) of the (6,5)-enriched SWCNT sample and the simulated pattern (red solid line). Bottom: a schematic structure of a (6,5) SWCNT which is the rolled-up structure of a graphene sheet expanded by 1% along the radial direction.

We found that the XRD patterns sensitively depend on the chiralities of SWCNTs even for non-crystalline samples. An example is shown in the left panel of Fig. 2. SWCNTs with  $m = n$  and  $m \approx n$  exhibit distinct sharp peaks in the range  $Q = 5-6 \text{ \AA}^{-1}$ , or the 11 diffraction region of graphene. On the other hand, similar structures appear around  $Q = 3-4 \text{ \AA}^{-1}$ , or the 10 diffraction region of graphene, for  $m = 0$  and  $m \approx 0$  SWCNTs. These features reflect the arrangement of carbon atoms in a SWCNT. In other words, such fine structures in the XRD patterns can be used as a fingerprint for the chiral indices for a given sample. Besides, it was also shown that the XRD patterns depend sensitively on the detailed structures of SWCNTs such as the carbon-carbon bond length.

The proposed method was used to analyze observed XRD patterns of (6,5) enriched and metal-enriched SWCNT films (see the right panel in Fig. 2 for the (6,5) enriched sample). The measurements were carried out using synchrotron radiation with a wavelength of 1.00 Å at beamlines BL-8A and BL-8B of the Photon Factory in Japan. The observed pattern for the (6,5) enriched sample was well reproduced as the weighted sum of patterns for default SWCNTs with the different chiralities identified in the optical absorption spectra. It was also found that the metal-enriched sample contains (6,6) and (7,4) SWCNTs with a ratio of 42:58 as major SWCNTs. This information was first obtained from the present study; it was indistinguishable in an absorption spectrum.

To obtain more detailed structural information, the observed XRD patterns were analyzed based on a model in which a default structure is expanded or compressed by different degrees along the radial direction and the tube (axial) direction. As a result, a radial ex-

pansion of  $0.9 \pm 0.3\%$  was obtained for (6,5) SWCNTs with a negligible change along the tube axis compared to the rolled-up structure. The bottom right panel of Fig. 2 shows a schematic illustration of a (6,5) SWCNT with a radial expansion of 1%. The bond lengths  $d_2$  and  $d_3$  are nearly equal to those in graphite, while  $d_1$  aligning almost perpendicular to the tube axis is slightly larger than that in graphite. The present results are in semi-quantitative agreement with those of first-principles calculations for armchair SWCNTs [8].

In summary, the present study demonstrated that powder XRD patterns can be used to fingerprint chiralities of SWCNTs present in the samples. Furthermore, it was found that the structure of SWCNTs substantially deviates from that of the ideal rolled-up graphene structure.

### REFERENCES

- [1] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998.
- [2] M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, and M. C. Hersam, *Nature Nanotech.* **1**, 60 (2006).
- [3] K. Yanagi, Y. Miyata, and H. Kataura, *Applied Physics Express* **1**, 034001 (2008).
- [4] H. Liu, D. Nishida, T. Tanaka, and H. Kataura, *Nature Commun.* **2**, 309 (2011).
- [5] J. Zhang and J. M. Zuo, *Carbon* **47**, 3515 (2009).
- [6] A. Hagen and T. Hertel, *Nano Lett.* **3**, 383 (2003).
- [7] R. Mitsuyama, S. Tadera, H. Kyakuno, R. Suzuki, H. Ishii, Y. Nakai, Y. Miyata, K. Yanagi, H. Kataura, and Y. Maniwa, *Carbon* **75**, 299 (2014).
- [8] K. Kato and S. Saito, *Physica E* **43**, 669 (2011).

### BEAMLINES

BL-8A and BL-8B

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