Chirality Fingerprinting and Geometrical Determination of Single-walled Carbon Nanotubes: Analysis of Fine Structure of X-ray Diffraction Pattern

Ryo Mitsuyama^a, Shin Tadera^a, Haruka Kyakuno^a, *Ryosuke Suzuki^a, Hiroyoshi Ishii^a, Yusuke Nakai^a, Yasumitsu Miyata^{a,c}, Kazuhiro Yanagi^a, Hiromichi Kataura^b, and Yutaka Maniwa^{a,*}*

^a*Department of Physics, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji 192-0397, Japan*

^b*Nanosystem Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Central 4, Higashi-1-1, Tsukuba 305-8562, Japan*

^c*JST, PRESTO, 4-1-8 Hon-Chou, Kawaguchi, Saitama 332-0012, Japan*

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*Corresponding author. E-mail address: maniwa@phys.se.tmu.ac.jp (Y. Maniwa)

ABSTRACT

Single-walled carbon nanotubes (SWCNTs) are seamless cylindrical tubes consisting of carbon atoms with diameters ranging from less than one nanometer to a few nanometers. The arrangement of carbon atoms in a SWCNT is uniquely specified by using a pair of integers (n,m) referred to as the chiral indices. While the detailed structures, such as a carbon-carbon bond length, should be important, they have not been fully clarified yet. In this work, we examine the possibility of powder X-ray diffraction (XRD) method to characterize structures of SWCNTs. It is found that the XRD is a useful tool to “fingerprint” the chiral indices of bulk SWCNT samples. Besides, we find that information on the detailed structure within a SWCNT can be obtained from the XRD pattern. The application to a highly concentrated SWCNTs clarifies that the (6, 5) SWCNT is expanded along the radial direction compared to that of ideal rolling up structure of graphene, with a negligible change along the tube axis.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are quasi one-dimensional structures that take the form of hollow cylinders with diameters varying from less than one nanometer to a few nanometers [1,2]. Their geometry can be hypothetically obtained by rolling up a graphene sheet, and is specified by a pair of integers (n,m) referred to as the chiral indices. The chiral indices determine not only the global geometry but also the electronic properties which can range from metallic to semiconducting. The set (n,m) is unlimited in principle, and bulk samples usually contain SWCNTs with a variety of chiralities. Thus, in many experimental studies performed using macroscopic quantities of SWCNTs, the physical properties of the samples are inevitably different to those for SWCNTs with a single chirality. This hampers precise studies on bulk SWCNT samples. One example is nano-confined systems [3-13] in which atoms or molecules such as argon [9], oxygen [10] or water [3-8, 11] are confined within SWCNTs. Because the structure in such systems could be critically sensitive to the SWCNT diameter [8-9], studies using single-chirality SWCNT samples have been strongly required. Recently, the development of purification and separation techniques [14-18], as well as of chiral-selective synthetic techniques [19, 20], has allowed the preparation of bulk SWCNT samples with almost a single chirality, thus making it possible to carry out more sophisticated studies. Consequently, the development of methods for characterizing the range of chiralities present in samples has become increasingly important. For this purpose, optical absorption spectroscopy [21, 22] and photoluminescence spectroscopy [23] have been widely used, in addition to electron diffraction [24-28] and scanning probe microscopy [29]. However, these methods suffer from their own weaknesses such as limitation of quantitative estimates, insufficient

accuracy or sensitivity, or the need for complicated sample preparation processes.

In the present study, a powder X-ray diffraction (XRD) method was developed as an alternative or complementary tool for the determination of chirality. Compared to the previous methods, XRD has some advantages such as application to bulk solid samples and possible high accuracy in structural determination. We found that the XRD pattern can be used as a fingerprint for the chiral indices of SWCNTs present in a sample. We also found that information about structural details such as the C-C bond length can be obtained from the XRD analysis. The actual structure of SWCNTs is expected to differ from that of an ideal rolled-up graphene sheet, and although this is likely to lead to modification of properties such as the band gap and SWCNT diameter [27, 28, 30-33], such effects have not yet been fully clarified.

2. Simulations of X-ray diffraction (XRD) patterns

The XRD method has been successfully applied to structural characterization of SWCNT bundles [34-36], multi-walled carbon nanotubes [37, 38] and nano-confined systems [39-42]. However, in most previous analyses, SWCNTs have been approximated as uniformly charged hollow cylinders (cylinder model) [34, 35, 39, 40, 42]. In contrast, in the present study, a SWCNT is considered to be a rolled-up graphene sheet with a honeycomb structure. The graphene structure consists of a honeycomb arrangement of carbon atoms with a bond length $d_g = 1.418 \text{ \AA}$ (0.1418 nm) and a bond angle of $2\pi/3$. In this rolled-up structure (default SWCNT), it should be noted that the bond lengths and angles deviate from those in the original graphene sheet because of the curvature. In a real SWCNT, the structures are further expected to be different from those of rolled-up (default) SWCNTs [30-33], as already mentioned. In the present study,

powder XRD patterns were calculated based on the rolled-up graphene model, and the effects of expansion and compression along the axial and radial directions were investigated. The calculations were performed using the Forcite tool in Materials Studio 6.0 (Accelrys Software, Inc.), based on the Debye formula [43]:

$$I(Q) = \sum \sum f_m f_n \frac{\sin(Qr_{mn})}{Qr_{mn}}.$$

Here, Q is the amplitude of the scattering vector and is given by $Q = 4\pi \sin \theta / \lambda$ for a scattering angle 2θ and an X-ray wavelength of λ . $I(Q)$ is the diffraction intensity at Q , f_n is the scattering amplitude from the n -th atom, and r_{mn} is the distance between the n -th and m -th atoms.

FIGURE 1 Calculated XRD patterns. (a) Patterns for a default (6,6) SWCNT structure ($d_g = 1.418$ $\text{\AA}$) and a homogeneous charged hollow cylinder model with a diameter of 8.12 $\text{\AA}$. (b) pattern for graphene with $d_g = 1.418$ $\text{\AA}$. (c) Patterns for SWCNTs with a default structure, a length of 240 $\text{\AA}$, and 18 different chiralities. The patterns are shifted

vertically for clarity. (d) (10) and (11) planes based on the graphene structure for (6,6), (7,4), (8,2) and (10,0) SWCNTs.

2.1 XRD patterns of (n,m) SWCNTs

First we compare XRD patterns calculated for a default (6,6) SWCNT structure ($d_g = 1.418 \text{ \AA}$) with that of a homogeneous charged hollow cylinder model with a diameter of $8.12 \text{ \AA}$ in **Fig. 1(a)**. Here for the homogeneous charged cylinder model, the XRD intensity is given by $I(Q) \propto L(Q)[Rf_c(Q)J_0(QR)]^2$ where $2R$, $L(Q)$, $f_c(Q)$, and $J_0(QR)$ are the SWCNT diameter, the Lorentz factor, the carbon scattering factor, and the zero-order cylindrical Bessel function, respectively [4,34,41,42]. The main differences between the two patterns in **Fig. 1(a)** occur for $Q > \sim 3.0 \text{ \AA}^{-1}$, and particularly in the ranges $3.0\text{-}4.0$ and $5.0\text{-}6.0 \text{ \AA}^{-1}$. These regions correspond to the 10 and 11 Bragg peak positions for graphene, suggesting that the internal **honeycomb** structure of SWCNT determines the differences in the calculated diffraction profiles.

Figure 1(b) shows the calculated XRD pattern for graphene and **Fig. 1(c)** shows the patterns calculated for 18 default SWCNT structures with different chiralities. The diameter D and chiral angle θ are in the ranges $6.82\text{-}8.81 \text{ \AA}$ and $0\text{-}30^\circ$, where $D = d_0\sqrt{3(n^2 + m^2 + nm)} / \pi$ and $\theta = \sin^{-1}(\sqrt{3}m / 2\sqrt{n^2 + nm + m^2})$, respectively. Note that $\theta = 30^\circ$ for armchair SWCNTs with $m = n$, whereas $\theta = 0^\circ$ for zigzag SWCNTs with $m = 0$.

From **Fig. 1(c)**, it is found that the armchair and near-armchair SWCNTs ($m = n$ and $m \approx n$) exhibit distinct sharp peaks in the range $Q = 5.0\text{-}6.0 \text{ \AA}^{-1}$. On the other hand, for zigzag and near-zigzag SWCNTs ($m = 0$ and $m \approx 0$), a similar structure appears

around $Q = 3.0\text{-}4.0 \text{ \AA}^{-1}$. These features reflect the arrangement of carbon atoms in a SWCNT, as is illustrated in **Fig. 1(d)**. The (11) or (10) graphene planes, indicated by the dashed lines, are stacked infinitely along the tube axis for armchair or zigzag SWCNTs, respectively. The long tails at high Q values in **Figs. 1(c) and 1(b)** are typical for the one-dimensional and two-dimensional systems such as SWCNT and graphene [4-6]. Such a tail is not observed in three-dimensionally ordered graphite. For chiralities intermediate between armchair and zigzag, the sharp peak structures in **Fig. 1(c)** become broadened, and the oscillation period in the tail region becomes longer. The former behavior is mainly due to a reduction in the coherence length for (11) or (10) planes along the normal $\langle 11 \rangle$ or $\langle 10 \rangle$ directions, respectively. Because such fine structure in the XRD pattern depends on the chirality, it can be used as a fingerprint for the chiral indices for a given sample, particularly for $Q > \sim 3.0 \text{ \AA}^{-1}$ can be used.

Finally, it should be noted that the SWCNTs prefer to be bundle with each other. The bundle structure actually determines XRD patterns at low Q region [32, 33]. However, effect of the bundle on XRD patterns is less important in larger Q region as suggested in **Fig. 1(a)**. Besides, in the case that SWCNTs are randomly distributed with respect to rotation around the tube axis, the XRD patterns of bundles can be approximated to that of single SWCNTs at high Q region. This was actually demonstrated by XRD simulations of bundles of (6,6) and (6,5) SWCNTs (see **Figure S1** in **Supplementary Materials**).

2.2 Detailed structure of SWCNTs

Here, we investigate the effect of the detailed SWCNT structure on the fine structure of the XRD pattern. For this purpose, the default SWCNT structure was subjected to

expansion or compression along the axial or radial direction of the tube, following previous experimental and theoretical studies [27, 28, 30, 31], and the XRD patterns were calculated. Although theoretical calculations also predicted a twisting deformation of narrow SWCNTs, the associated energy gain is only about 10^{-2} meV/carbon [33], and can therefore be neglected at room temperature.

Figure 2 shows the calculated patterns for an armchair (6,6) SWCNT and a zigzag (10,0) SWCNT, in which expanded views of the 11 and 10 peak regions are presented. It can be seen that expansion along the tube axis leads to a substantial shift of the onset peak for 11 and 10 Bragg reflections for armchair and zigzag SWCNTs, respectively, reflecting changes in the d -spacings for the corresponding planes (see **Fig. 1(d)**). On the other hand, expansion along the radial direction leads to a change in the oscillatory behavior following the onset peak for 11 and 10 Bragg reflections for armchair and zigzag SWCNTs, respectively. In both cases, the oscillatory period is reduced. For SWCNTs with chiralities intermediate between zigzag and armchair, the XRD patterns are intermediate between those for armchair and zigzag SWCNTs (see **Figure S2** in **Supplementary Materials**). The pattern in the high- Q region also provides useful information on the SWCNT structure, as will be discussed later (see **Fig. 6**). Detailed structural information, such as the carbon bond length, can be obtained with an error of less than 1% by precise analysis of the XRD fine structure using a single-chirality SWCNT sample.

FIGURE 2 XRD patterns calculated for (6,6) and (10,0) SWCNTs expanded or compressed relative to the default structure with $d_g=1.418$ Å. In the left panels, the change is applied along the axial direction, whereas in the right panels, it is applied along the radial direction. The insets show the (10) peak region for a (6,6) SWCNT and the (11) peak region for a (10,0) SWCNT. The thick black line shows the case for a 2% compression. The thin line and thick gray line represent an expansion of 2 and 4%, respectively. The dashed line represents the default structure.

3. X-ray diffraction experiments

3.1 Sample preparation and XRD measurements

Powder XRD measurements were carried out to determine the effectiveness of the proposed method. A highly enriched (6,5) SWCNT sample and a metal-enriched SWCNT sample were prepared from a purchased SWCNT material (CoMoCAT 704148

SG 65, SIGMA-ALDRICH) using a combination of gel-separation [18] and density gradient ultracentrifugation purification [14,16] techniques. A purified and un-enriched SWCNT sample was also prepared [43]. The optical absorption spectra are shown in Fig. 3. They were obtained using a UV-3600 spectrometer (Shimazu Ltd.) in SDS (sodium dodecyl sulfate) solution. Assuming that the intensity of each absorption peak above a background (BG) absorption is simply proportional to the amount of SWCNTs with a particular chirality, the nominal relative concentrations were estimated. For the (6,5) SWCNT sample, they were 74.0% for (6,5), 4.0% for (6,4), 2.8% for (6,6), 2.8% for (7,4), 12.1% for (7,3), 1.0% for (8,3), 1.9% for (7,6), and 1.9% for (7,5). For the un-enriched SWCNT sample, they were 38.6% for (6,5), 5.6% for (6,4), 6.1% for (6,6), 6.1% for (7,4), 11.5% for (7,3), 6.0% for (8,3), 3.1% for (8,4), 12.0% for (7,6), 1.8 for (9,1), and 9.2% for (7,5). These were estimated from a combined analysis based on average intensity between S11 and S22 bands [1, 2, 21]. For the metal-enriched SWCNT sample, they were 9.6% for (7,3), 4.6% for (6,5), and 85.7% for a sum of (6,6) and (7,4) using M11 region. Here the (6,6) and (7,4) SWCNTs cannot be distinguished from the present absorption spectra. Similarly, note that some of them mentioned above (particularly, the values underlined) are quite uncertain because of indistinguishable peaks.

Powder XRD patterns observed for the purified sample are shown in Fig. 4. The measurements were performed using synchrotron radiation with a wavelength of 1 Å at beam lines BL8A and BL8B of the Photon Factory in Japan. The diffracted X-ray was recorded on a cylindrical type imaging plate (IP) with a pixel size of 0.1 mm and a camera length of 192.28 mm. Then, by integrating the diffracted intensity, we obtained one-dimensional XRD patterns. The SWCNT sample for XRD measurements was

sealed in vacuo inside a quartz tube after thorough evacuation at ~ 770 K to remove materials adsorbed both inside and outside the SWCNTs [35, 39]. An enriched (6,5) SWCNT sample mixed with graphite powder (99.99%, RARE METALLIC Co., Ltd.) was also measured to confirm a reliability of the present measurements. It was a superimposed of two patterns from the (6,5) enriched sample and graphite powder. The C-C bond length in graphite was determined to be 1.421 ± 0.001 Å, in agreement with previously reported values of 1.420-1.426 Å.

In Fig. 4 we find that the fine structures appear around $Q > \sim 5$ ($1/\text{\AA}$) region depending on the SWCNT samples with different chirality distributions, as expected from the XRD simulations described in the previous sections.

FIGURE 3 Optical absorption spectra of un-enriched, (6,5) enriched, and metal enriched SWCNT samples from upper to bottom panels, respectively. Thin (red) solid lines are background (BG) absorptions, (red) dashed lines are fitted curves with several

absorption peaks, which have forms of Lorentz function. (n,m) indicates possible absorption peaks due to (n,m) SWCNTs.

FIGURE 4 Observed and simulated XRD patterns for un-enriched, (6,5) enriched, and metal enriched SWCNT samples from upper to bottom panels, respectively. In each panel, the (black) noisy pattern is the observed, and the (red) solid thick line indicates the simulated. Dotted and dashed lines are contributions from graphene-BG and SWCNT-BG, respectively. Default SWCNT structures were used for the calculations. The diffraction associated with the quartz tube was subtracted. The peaks indicated by an asterisk are of spurious origin. Inset: Measured XRD pattern (solid line) for SWCNT sample sealed inside a quartz tube, that for the XRD quartz tube (dashed line), and the difference between them. The patterns are shifted vertically for clarity.

3.2 Comparison with calculated XRD patterns

The measured XRD patterns are well reproduced as the weighted sum of patterns corresponding to default SWCNTs with the different chiralities identified in the optical absorption spectra. The bundle effect was not taken into account. The comparison between the observed and simulated patterns is shown in Fig. 4. The weighting factors used in simulations were proportional to the relative concentrations obtained from the optical absorption measurements. In addition, a background (BG) component was required in order to reproduce the measured XRD pattern. The BG was tentatively assumed to be a sum of BG from small graphene sheets of square 15 Å on a side and BG from an equally weighted sum of 31 different types of SWCNTs within a diameter range of 6-10 Å. The graphene-BG was required to reproduce broad diffractions in the observed 10 and 11 peaks. The SWCNT-BG means a contribution from indistinguishable SWCNTs which would contribute to BG in the absorption spectra. Here, no zigzag SWCNTs were included in the SWCNT-BG because the 20 and 10 fine structure associated with such SWCNTs was not observed at around $Q=6.0 \text{ \AA}^{-1}$.

The contents of carbon atom of SWCNT-BG and graphene-BG used in the simulations are following: 17.5% for SWCNT-BG and 65% for graphene-BG in the un-enriched SWCNT sample, 2.5% for SWCNT-BG and 50% for graphene-BG in the (6,5) enriched sample, and 20% for SWCNT-BG and 35% for graphene-BG in the metal enriched sample. We find from the simulation results that the separation process of SWCNTs can significantly reduce the BG intensity, in addition to enrichment of specific chiral SWCNTs.

The above analysis clearly demonstrates that the XRD fine structures appear depending on the chirality of SWCNTs contained in the sample. Thus the powder XRD technique can be, in principle, used for chirality characterization of SWCNT samples. In

this point of view, more detailed discussion of the XRD patterns of the metal enriched SWCNT sample should be interesting, because this sample contains (6,6) and (7,4) SWCNTs as major SWCNTs indistinguishable in the present absorption spectrum. In **Fig. 5**, it is demonstrated how the XRD pattern changes depending on the relative content of (6,6) and (7,4) SWCNTs. We find that the XRD fine structure is sensitive to the content, and that comparable amounts of (6,6) and (7,4) SWCNTs exist in the present sample; 42% for (6,6) and 58% for (7,4).

FIGURE 5 Observed and simulated XRD patterns for metal enriched SWCNT sample. Bottom: observed. Upper three: simulated XRD patterns with (6,6) and (7,4) concentration ratios of 100:0, 42:58, and 0:100 from upper to bottom, respectively. Default SWCNT structures were used for the XRD simulations. The patterns are shifted vertically for clarity.

3.3 Structure of SWCNTs

The observed XRD patterns were analyzed within a model for SWCNT, in which

the default structure with $d_g=1.418 \text{ \AA}$ is expanded or compressed at different degrees along the radial direction and the tube (axial) direction. In the calculations of the XRD patterns, all the SWCNTs contained were expanded or compressed at the same ratio for simplicity. No expansion or compression along the axial direction was required because the onset peak in the 11 region is well reproduced in the default pattern. This implies that the tube direction is almost conservative during rolling up of graphene with $d_g=1.418 \text{ \AA}$: it is at most compressed by about 0.2% compared to that of rolled-up structure obtained using the C-C bond length of graphite for d_g . However, a radial expansion by $0.9\pm0.3\%$ was obtained for (6,5) SWCNTs from the dip structure around $Q\sim7 \text{ \AA}^{-1}$: the calculated dip position monotonically decreases with increasing radial expansion (see **Fig. 6**). The pattern around the 11 diffraction region is also well reproduced. On the other hand, a radial expansion by 0-2% was suggested in metal enriched sample without axial expansion. The reliability in the metal enriched sample would be less than in the (6,5) enriched sample, because the metal-enriched sample contains (6,6) and (7,4) SWCNTs as the major SWCNTs .

FIGURE 6 Comparison of the measured XRD patterns for (6,5)-enriched and metal-enriched SWCNT samples with calculated patterns for radial expansions of 0, 2, and 4%. The arrows indicate the experimentally observed dip positions with least square fits. The patterns are shifted vertically for clarity.

Figure 7 shows a schematic of the structure 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 for bonds aligned almost perpendicular to the tube axis is slightly larger than that in graphite. These results are in semi-quantitatively agreement with those of first-principals calculations for armchair SWCNTs [30, 31]. The results of an electron diffraction analysis of the inner tubes of multi-walled carbon nanotubes also indicated an expansion along the radial direction but no change along the axial direction [28].

However, the reported expansion was 3.8% for the innermost tube with a diameter of 17 Å, which is **much larger than** the value obtained in the present study for SWCNTs. The reason for the difference is at present not clear. Nevertheless, the results of the present study make it clear that deviations from the ideal rolled graphene structure must be taken into account when considering the detailed electronic structure of SWCNTs. For example, note that the band gap in the tight binding approximation is given by $E_g = td / D$, where t is a transfer integral between nearest neighboring carbon atoms. The band gap is therefore sensitive to changes in both the bond length and tube diameter.

FIGURE 7 Schematic structure of (6,5) SWCNT expanded by 1% along the radial direction. $\theta_{12}=119.05^\circ$, $\theta_{23}=119.58^\circ$, and $\theta_{31}=118.70^\circ$. In the default structure, $d_1=1.409$ Å, $d_2=1.418$ Å, $d_3=1.417$ Å, and $\theta_{12}=118.86^\circ$, $\theta_{23}=120.08^\circ$, $\theta_{31}=118.41^\circ$. Here, θ_{ij} is the angle between bonds i and j .

Finally, the background in **Fig. 4** that accounts for **52.5-55%** of the total intensity should be considered. This seems unexpectedly large **because the optical absorption spectra suggest an achievement of substantial purification from the starting materials.** In

the present analysis, this background was assigned to **small graphitic (graphene) impurities** and SWCNTs with chiralities other than those identified in the absorption spectrum. However, other possibilities also exist. One is the presence of extremely short SWCNTs (see **Figure S3** in **Supplementary Materials**). Another possibility is smearing of the XRD fine structure due to structural deformation of the SWCNTs. Such deformation could occur due to the presence of defects such as vacancies, or oxygen atoms attached to the SWCNTs. These possibilities will be examined in the near future.

4. Conclusion

It has been shown that powder XRD can be used as a fingerprinting method for the chirality of SWCNTs in a sample, and can also provide structural information such as the carbon-carbon bond length. **Within a model of the radial and axial expansion/compression of default SWCNTs, it was suggested** that for (6,5) SWCNTs in an enriched sample, a radial expansion of $0.9\pm0.3\%$ is present **with a negligible change along the axial direction**. Such an expansion is likely to have a substantial effect on the structure of nano-confined systems involving SWCNTs [8-10], as well as the electronic properties [30-33]. **However, further studies using higher quality SWCNT samples would be desirable. In the present analysis, the optical absorption intensity was assumed to be simply proportional to the concentration of SWCNTs. However, because the intensity also depends on the absorption probability, the concentration obtained from absorption spectrum in the present analysis should be corrected [45]. A combined study using XRD and absorption spectroscopy with high quality samples makes it possible to obtain the correction factor. Finally,** it is worth noting that the proposed technique can be widely applied to non-crystalline SWCNT samples.

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REFERENCES

- [1] Saito R, Dresselhaus G, Dresselhaus MS. Physical Properties of Carbon Nanotubes. Imperial College Press, London; 1998.
- [2] Dresselhaus MS, Dresselhaus G, Avouris P. Carbon Nanotubes Synthesis, Structure, Properties, and Applications. Springer, Berlin; 2001.
- [3] Koga K, Gao GT, Tanaka H, Zeng XC. Formation of ordered ice nanotubes inside carbon nanotubes. *Nature* 2001; 412: 802-805.
- [4] Maniwa Y, Kataura H, Abe M, Suzuki S, Achiba Y, Kira H, et al. Phase Transition in Confined Water Inside Carbon Nanotubes. *J. Phys. Soc. Jpn.* 2002; 71: 2863-1866.
- [5] Maniwa Y, Kataura H, Abe M, Uda A, Suzuki S, Achiba Y, et al. Ordered water inside carbon nanotubes: Formation of pentagonal to octagonal ice-nanotubes. *Chem. Phys. Lett.* 2005; 401: 534-538.
- [6] Maniwa Y, Matsuda K, Kyakuno H, Ogasawara S, Hibi T, Kadowaki H, et al. Water-filled single-wall carbon nanotubes as molecular nanovalves. *Nature Mater.* 2007; 6: 135-141.
- [7] Kyakuno H, Matsuda K, Yahiro H, Inami Y, Fukuoka T, Miyata Y, et al. Confined water inside single-walled carbon nanotubes: Global phase diagram and effect of finite length. *J. Chem. Phys.* 2011; 134: 244501-1- 244501-14.
- [8] Takaiwa D, Hatano I, Koga K, Tanaka H. Phase diagram of water in carbon nanotubes. *Proc. Natl. Acad. Sci. U.S.A.* 2008; 105: 39-43.
- [9] Koga K, Tanaka H. Close-packed structures and phase diagram of soft spheres in cylindrical pores. *J. Chem. Phys.* 2006; 124: 131103.
- [10] Hanami K, Umesaki T, Matsuda K, Okabe Y, Maniwa Y, Miyata Y, et al. One-Dimensional Oxygen and Helical Oxygen Nanotubes inside Carbon Nanotubes.

- J. Phys. Soc. Jpn. 2010; 79: 023601-1-023601-4.
- [11] Martí J, Gordillo MC. Temperature effects on the static and dynamic properties of liquid water inside nanotubes. Phys. Rev. E 2001; 64: 0215041-0215046.
- [12] Simon F, Kuzmany H, N'afra'adi B, Feh'er T, Forr'o L, F'ul'op F, et al. Magnetic Fullerenes inside Single-Wall Carbon Nanotubes. Phys. Rev. Lett. 2006; 97: 136801-1-136801-4.
- [13] Hodak M, Girifalco LA. Ordered phases of fullerene molecules formed inside carbon nanotubes. Phys. Rev. B 2003; 67: 075419-1-075419-4.
- [14] Arnold MS, Green AA, Hulvat JF, Stupp SI, Hersam MC. Sorting carbon nanotubes by electronic structure using density differentiation. Nature Nanotech. 2006; 1: 60-65.
- [15] Ghosh S, Bachilo SM, Weisman RB. Advanced sorting of single-walled carbon nanotubes by nonlinear density-gradient ultracentrifugation. Nature Nanotech. 2010; 5: 443-450
- [16] Yanagi K, Miyata Y, Kataura H. Optical and conductive characteristics of metallic single-wall carbon nanotubes with three basic colors; cyan, magenta, and yellow. Applied Physics Express 2008; 1: 0340031-0340033.
- [17] Zheng M, Jagota A, Semke ED, Diner BA, McLean RS, Lustig SR, et al. DNA-assisted dispersion and separation of carbon nanotubes. Nature Mater. 2003; 2: 338-342.
- [18] Liu H, Nishida D, Tanaka T, Kataura H. Large-scale single-chirality separation of single-wall carbon nanotubes by simple gel chromatography. Nature Commun. 2011, 2, 309-1-8.
- [19] Wang H, Wei L, Ren F, Wang Q, Pfefferle L, Haller G, Chen Y, Chiral-Selective

- CoSO₄/SiO₂ Catalyst for (9,8) Single Walled Carbon Nanotube. ACS Nano 2013; 7: 614–626.
- [20] He M, Jiang H, Liu B, Fedotov PV, Chernov AI, Obratsova ED, et al. Chiral-selective growth of single-walled carbon nanotubes on lattice-mismatched epitaxial cobalt nanoparticles. Scientific Reports 2013; 3 :1460.
- [21] Kataura H, Kumazawa Y, Maniwa Y, Umezū I, Suzuki S, Ohtsuka Y, et al. Optical properties of single-wall carbon nanotubes. Synthetic Metals 1999; 103 (1-3): 2555-2558
- [22] Hagen A, Hertel T. Quantitative analysis of optical spectra from individual single-wall carbon nanotubes. Nano Letters 2003; 3 (3): 383-388.
- [23] Weisman RB. Fluorimetric characterization of single-walled carbon nanotubes. Analytical and Bioanalytical Chemistry 2010; 396: 1015-1023, and references therein.
- [24] Bernaerts D, Amelinckx S, Lambin Ph, Lucas AA. The diffraction space of circular and polygonized multishell nanotubules. Applied Physics A 1998; 67: 53-64.
- [25] Lambin P, Meunier V, Henrard L, Lucas AA. Measuring the helicity of carbon nanotubes. Carbon 2000; 38 (11): 1713-1721.
- [26] Zhang XF, Zhang XB, Van Tendeloo G, Amelinckx S, Op de Beeck M, Van Landuyt J. Carbon nano-tubes; their formation process and observation by electron microscopy. J. Cryst. Growth 1993; 130: 368-382.
- [27] Hirahara K, Bando S, Kataura H, Kociak M, Iijima S. Stretching of carbon-carbon bonds in a 0.7 Å diameter carbon nanotube studied by electron diffraction. Phys. Rev. B 2004; 70: 205422-1-205422-7.
- [28] Zhang J, Zuo JM. Structure and diameter-dependent bond lengths of a multiwalled

- carbon nanotube revealed by electron diffraction. *Carbon* 2009; 47: 3515-3528.
- [29] Odom TW, Huang JL, Kim P, Lieber CM. Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature* 1998; 391: 62-64.
- [30] Kanamitsu K, Saito S. Geometries, electronic properties, and energetics of isolated single walled carbon nanotubes. *J. Phys. Soc. Jpn.* 2002; 71: 483-486.
- [31] Kato K, Saito S. Geometries, electronic structures and energetics of small-diameter single-walled carbon nanotubes. *Physica E* 2011; 43: 669–672.
- [32] Gulseren O, Yildirim T, Ciraci S. Energetics and electronic properties of twisted single-walled carbon nanotubes. *Phys. Rev. B* 2002; 65: 153405-1-153405-4.
- [33] Kato K, Koretsune T, Saito S. Energetics and electronic properties of twisted single-walled carbon nanotubes. *Phys. Rev. B* 2012; 85: 115448-1-4.
- [34] Thess A, Lee R, Nikolaev P, Dai H, Petit P, Robert J, et al. Crystalline ropes of metallic carbon nanotubes. *Science* 1996; 273: 483-487.
- [35] Maniwa Y, Fujiwara R, Kira H, Tou H, Kataura H, Suzuki S, et al. Thermal Expansion of Single-Walled Carbon Nanotube (SWNT) Bundles: X-Ray Diffraction Studies. *Phys. Rev. B* 2001; 64: 2414021-2414023.
- [36] Bandow S. Radial thermal expansion of purified multiwall carbon nanotubes measured by X-ray diffraction. *Jpn. J. Appl. Phys., Part 2* 1997; 36: L1403-L1405.
- [37] Reznik D, Olk CH, Neumann DA, Copley JRD. X-ray powder diffraction from carbon nanotubes and nanoparticles. *Phys. Rev. B* 1995; 52: 116-124.
- [38] Maniwa Y, Fujiwara R, Kira H, Tou H, Nishibori E, Takata M, et al. Multi-Walled Carbon Nanotubes (MWNTs) Grown in Hydrogen Atmosphere, An X-Ray Diffraction Study. *Phys. Rev. B* 2001; 64: 073105-1-073105-4.

- [39] Maniwa Y, Kumazawa Y, Saito Y, Tou H, Kataura H, Ishii H, et al. Anomaly of X-ray diffraction profile in single-walled carbon nanotubes. *Jpn. J. Appl. Phys.* 1996; 38: L668-L670.
- [40] Abe M, Kataura H, Kira H, Kodama T, Suzuki S, Achiba Y, et al. Structural Transformation from Single-wall to Double-wall Carbon Nanotube Bundles. *Phys. Rev. B* 2003; 68: 041405R1-4.
- [41] Kadowaki H, Nishiyama A, Matsuda K, Maniwa Y, Suzuki S, Achiba Y, et al. Rietveld analysis and maximum entropy method of powder diffraction for bundles of single-walled carbon nanotubes. *J. Phys. Soc. Jpn.* 2005; 74: 2290-2295.
- [42] Paineau E, Albouy P-A, Rouzière S, Orecchini A, Rols S, Launois P. X-ray Scattering Determination of the Structure of Water during Carbon Nanotube Filling. *Nano Lett.* 2013; 13: 1751-1756, and references therein.
- [43] Kittel, C. *Introduction to Solid State Physics*, 8th ed., John Wiley & Sons., Inc, 2005.
- [44] Miyata Y, Yanagi K, Maniwa Y, Tanaka T, Kataura H. Diameter analysis of rebundled single-wall carbon nanotubes using X-ray diffraction: Verification of chirality assignment based on optical spectra. *J. Chem. Phys.* 2008; 112: 15997-16001.
- [45] Ichida M, Mizuno S, Tani Y, Saito Y, Nakamura A: Exciton Effects of Optical Transitions in Single-Wall Carbon Nanotubes. *J. Phys. Soc. Jpn.* 1999; 68: 3131-3133.