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Nanotechnologies — Characterization of single-wall carbon nanotubes using near infrared photoluminescence spectroscopy

Nanotechnologies — Caractérisation de nanotubes de carbone monofeuillet en utilisant la spectroscopie de photoluminescence dans le proche infra-rouge

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Foreword

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Introduction

Discovery of band gap photoluminescence (PL) of single-wall carbon nanotubes (SWCNTs) has provided a new way to characterize their unique electronic properties induced by their low dimensionality. The method can provide the chiral indices of the semi-conducting SWCNTs in a sample and their relative integrated PL intensities. With the knowledge of their PL cross-sections, the relative mass concentrations of semi-conducting SWCNTs in a sample can be estimated.

Nanotechnologies — Characterization of single-wall carbon nanotubes using near infrared photoluminescence spectroscopy

1 Scope

This Technical Specification provides guidelines for the characterization of single-wall carbon nanotubes (SWCNTs) using near infrared (NIR) photoluminescence (PL) spectroscopy.

This Technical Specification provides a measurement method for the determination of the chiral indices of the semi-conducting SWCNT in a sample and their relative integrated PL intensities.

The method can be expanded to estimate relative mass concentrations of semi-conducting SWCNTs in a sample from measured integrated PL intensities and knowledge of their PL cross-sections.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 80004-3, *Nanotechnologies — Vocabulary — Part 3: Carbon nano-objects*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-3 and the following apply.

3.1
chiral vector of SWCNT
vector notation used to describe the helical structure of a single-wall carbon nanotube

[ISO/TS 80004-3:2010, definition 4.5]

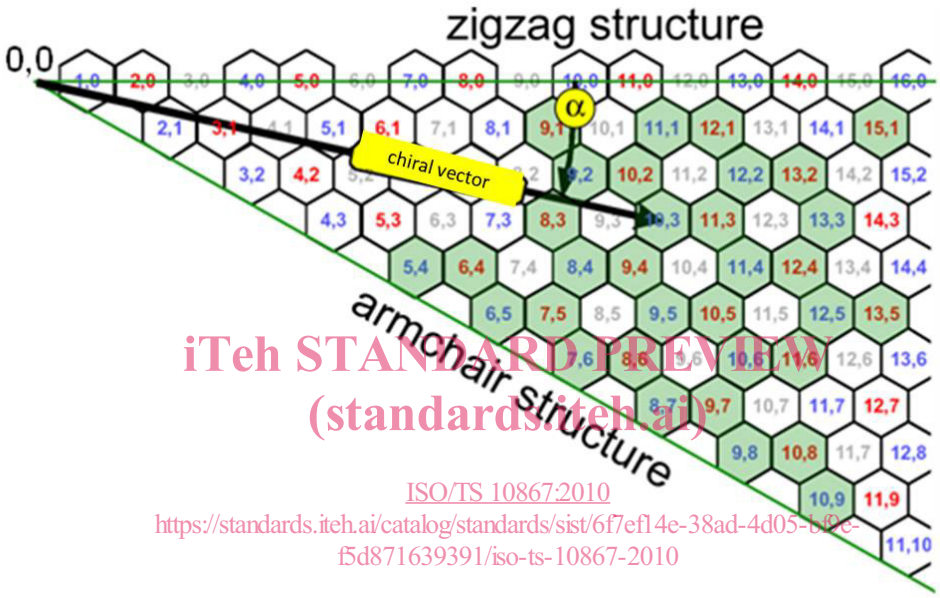
3.2
chiral indices
two integers that define the chiral vector of a single-wall carbon nanotube

3.3
relative mass concentration
mass concentration of nanotube species relative to that of the most common nanotube species

4 Principles of band gap photoluminescence of SWCNTs

4.1 Structure of SWCNTs

An SWCNT consists of a single cylindrical graphene layer. The specific geometry of SWCNTs is defined in terms of a *chiral vector* containing a length (the tube's circumference) and a *chiral angle* α (ranging from 0 to 30°). Alternatively, the structure of SWCNTs is unambiguously defined by the two integers, so-called chiral indices (n, m). Figure 1 shows the indexed graphene sheet with chiral vector for designating nanotube structure, and how the vector starting at point (0,0) to (n, m) determines the nanotube designation [1]. The chiral angle is measured between the *zigzag structure* (α = 0°) and the chiral vector. When the chiral angle is between 0 and 30°, a *chiral structure* arises. The SWCNT having the maximum chiral angle, 30°, is called the *armchair* SWCNT.



NOTE The chiral angle α and chiral vector are shown. The gray indices are for nanotubes that are not photoluminescent.

Figure 1 — Indexed graphene sheet with chiral vector for designating nanotube structure [2]

The length of the chiral vector is the circumference of the tube, or π × the tube diameter d_t. The tube diameter d_t is given in terms of (n, m) by

$$d_t = L/\pi = \frac{\sqrt{3}a_{C-C}\sqrt{m^2 + mn + n^2}}{\pi}$$

where

d_t is the diameter of the SWCNT;

L is the length of the chiral vector;

a_{C-C} is the nearest-neighbour distance (0,144 nm) between pairs of carbon atoms;

m is one of the chiral indices;

n is the other chiral index.

The chiral angle α in terms of (n, m) is defined by the equation

$$\alpha = \tan^{-1}\left[\sqrt{3}m/(2n+m)\right]$$

where

α is the chiral angle;

m is one of the chiral indices;

n is the other chiral index.

4.2 Band structure and PL peaks

Quasi-one-dimensional SWCNTs have an electronic density of states roughly as shown in Figure 2, with sharp van Hove peaks such as v_1 and v_2 (in the valence band) and c_1 and c_2 (in the conduction band).

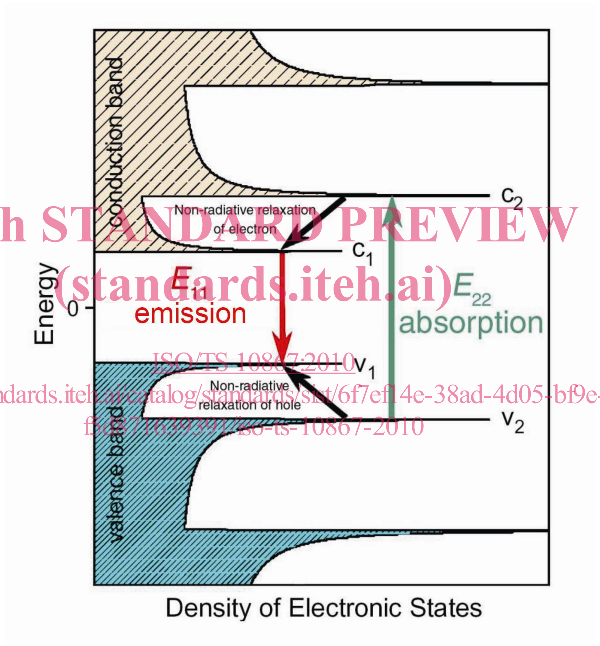


Figure 2 — Qualitative description of the electronic density of states for SWCNTs [2]

Just as the positions of the van Hove peaks depend on the structure (and chiral vector) of the particular SWCNTs, so will the absorption energy E_{22} and fluorescent emission energy E_{11}. Therefore, the positions of the spectral peaks corresponding to E_{22} and E_{11} are characteristic of the structure of each SWCNT, and can be used as a measurement method to determine the component SWCNTs of an unknown mixture. The following equation relates peak wavelength to transition energy

$$E = hc/\lambda = hc\bar{\nu}$$

where

E is energy of the transition;

c is the speed of light;

h is Planck's constant;

$\tilde{\nu}$ is the peak position, expressed in wavenumber units (cm^{-1});

λ is the wavelength of the photon absorbed or emitted.

Those structures where the difference (n – m) is divisible by three [e.g., (3,0), (4,1), or (6,3)], and those structures where n = m, do not fluoresce because SWCNTs with (n – m) = a multiple of 3 are semi-metals, with a band gap in the meV range, and those with n = m are metals (no band gap). The remaining structures are semi-conductors with a band gap of about 0,5 eV to 1 eV (1 eV = 1,602 176 53 (14) × 10^{-19} J), and can fluoresce under specific sample preparation conditions.

NOTE As-prepared SWCNTs samples contain left- and right-handed helical structures. The peak positions of the PL signals are basically the same for these enantiomers.

4.3 Exciton effects

Electron-hole pair excitations giving rise to PL are better described in terms of excitons. Excitons are the result of Coulomb interaction, which for SWCNTs is very important and significantly affects the energy spectrum, for example with phonon sidebands and excitonic manifolds of excited states, and the strength of optical transitions. The exciton binding energy was estimated to be 0,420 eV for SWCNTs with the diameter of 0,8 nm in a polymer matrix and a surfactant solution [3]. This value substantially depends on the nanotube environment.

5 NIR-PL apparatus

5.1 NIR-PL spectrometer

For SWCNTs produced by the chemical vapor deposition (CVD) method with typical diameter distribution of 0,6 nm to 1,3 nm, a NIR detector covering the spectral range from 800 nm to 1 600 nm is sufficient to detect their PL. However, to detect the PL signal of the larger diameter SWCNT produced by the laser vaporization and electric arc techniques, a spectral range of 1 200 nm – 2 000 nm is usually required.

NOTE 1 Examples of detector materials are InGaAs and InP/InGaAs.

NOTE 2 The spectral resolution, which in a scanning monochrometer is a complex function of the bandpass of the monochromators, the stepping increment and slit width, needs to be adjusted to resolve the SWCNT peaks of interest in the sample. In general, bandpass values approaching 10 nm have been shown to be sufficient for most surfactant suspensions of SWCNTs. With multi-channel NIR detection systems, a resolution of 5 nm is recommended.

5.2 Light source

Excitation sources are available such as monochromated Xenon or tungsten lamps, continuous Titan-Sapphire lasers or fixed wavelength diode lasers.

NOTE Suitable wavelengths of diode lasers can be selected to suit the diameter distribution of the SWCNT sample (see Figure A.2 and Figure A.4).

6 Sample preparation methods

6.1 Preparation of D_2O dispersion for measurement

For the preparation of a liquid dispersion of SWCNTs, the following procedure shall be used.

a) Use D_2O as the dispersing medium, which transmits light in the broad range from UV-Vis to 1 800 nm.

NOTE H_2O is unsuitable because it strongly absorbs light at 1 400nm and longer wavelengths.

b) Use water-soluble surfactants, preferably anionic ones such as sodium dodecyl sulfate (SDS) (purity > 95 %), sodium dodecylbenzene sulfonate (SDBS) (purity > 95 %) or sodium cholate (SC) (purity > 98 %) as dispersants.

NOTE Recent work suggests sodium deoxycholate over other dispersants [4].

c) Prepare a D_2O solution of a dispersant, approximately at a concentration of 1 % mass fraction.

d) Add a small amount (approximately 1 mg) of the sample containing SWCNTs into the dispersant solution, approximately 20 mL.

e) To facilitate the process and to obtain homogeneous SWCNT dispersion, sonicate the mixture using an ultrasonic homogenizer.

NOTE 1 An example of sonication conditions is given in Annex A.

NOTE 2 Even after the sonication steps, there can be a significant amount of bundled SWCNTs in the micelle solution.

f) To separate the bundled SWCNTs from the isolated SWCNTs, ultracentrifuge the dispersion and use the supernatant for the PL measurements.

NOTE 1 An example of ultracentrifugation conditions is given in Annex A.

NOTE 2 Insufficient centrifugation leaves a large amount of the bundled SWCNTs unseparated in the sample. On the other hand, excess centrifugation causes a severe reduction in the concentration of SWCNTs in the solution.

g) If the optical density (O.D.) of the probed volume is above 0,5 after sonication and centrifugation, dilute with the surfactant solution to lower the O.D. below 0,5.

h) Adjust pH of the solution to be approximately 8 by adding an appropriate amount of NaOH [5].

6.2 Preparation of solid film dispersion for measurement

When the PL signals beyond 1 800 nm are required, for example, in the case of the SWCNTs produced by electric arc technique which have a size larger than about 1,4 nm in diameter, prepare the sample by the following method.

a) Use H_2O as the dispersing medium, following the same procedures as described in 6.1, including sonication and ultracentrifugation, to obtain the supernatant.

b) Mix the supernatant with the same volume of an H_2O solution of gelatine from alkali-processed bovine bone with a concentration of 10 % mass fraction. Here gelatin is used as a film forming agent [6].

c) Cast the mixed solution on to a quartz substrate and let it dry (ten hours or longer). This results in the formation of an optically uniform film in which SWCNTs are homogenously dispersed.

7 Measurement procedures

The PL spectra of SWCNTs shall be measured as follows (see Figure A.1 and Figure A.3):

a) Turn on the light source, the spectrometer and the detector, and wait until they stabilize.

b) Calibrate the wavelength-dependent instrumental factors and excitation intensities. For the calibration of the PL system, a light source providing wavelength values traceable to the International System of Units (SI) shall be used for correcting the instrument's emission detector signal and a calibrated detector shall be used for correcting the instrument's excitation reference detector signal.