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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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This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies.*

This second edition cancels and replaces the first edition (ISO/TS 10867:2010), which has been technically revised.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The discovery of the band-gap photoluminescence (PL) of single-wall carbon nanotubes (SWCNTs) has provided a useful method to characterize their unique electronic properties induced by their low-dimensionality. This method is described in this document.

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

1 Scope

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

It provides a measurement method for the determination of the chiral indices of the semi-conducting SWCNTs in a sample and their relative integrated PL intensities.

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 80004-4, *Nanotechnologies — Vocabulary — Part 4: Nanostructured materials*

ISO/TS 80004-6, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-4, ISO/TS 80004-6 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
chirality
vector notation used to describe the structure of a single-wall carbon nanotube (SWCNT)

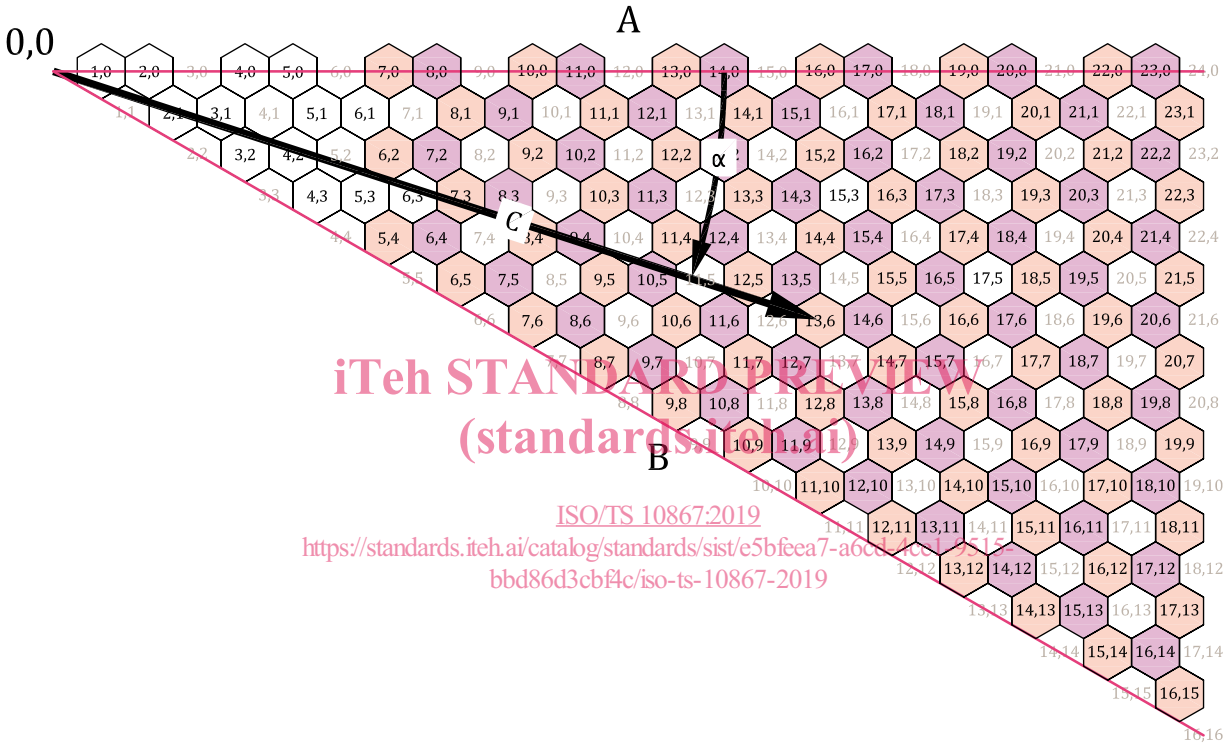
3.2
chiral indices
two integers that define the chiral vector of a single-wall carbon nanotube (SWCNT)

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

4 Principles of band gap photoluminescence of SWCNTs

4.1 Structure of SWCNTs

A 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 defined by the chiral indices (n, m). Figure 1 shows the indexed graphene sheet with chiral vector for designating the 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 that has the maximum chiral angle, 30°, is called the armchair SWCNT.



Key

A zigzag structure

B armchair structure

C chiral vector

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

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

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) as shown by Formula (1):

$$d_t = L/\pi = \frac{\sqrt{3}a_{C-C}\sqrt{m^2+mn+n^2}}{\pi} \quad (1)$$

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 as shown by Formula (2):

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

where

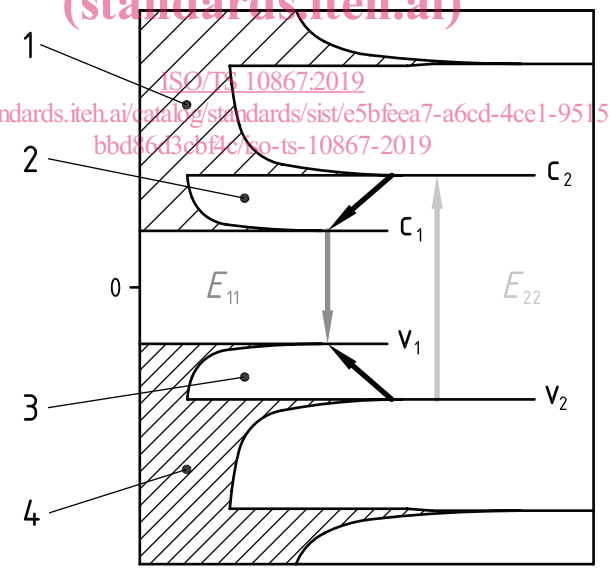
α is the chiral angle;

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).



Key

1 conduction band
2 non-radiative relaxation of electron
3 non-radiative relaxation of hole
4 valence 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. Formula (3) relates peak wavelength to transition energy:

$$E = hc/\lambda = hc\bar{\nu} \quad (3)$$

where

E is energy of the transition;

c is the speed of light;

h is Planck's constant;

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

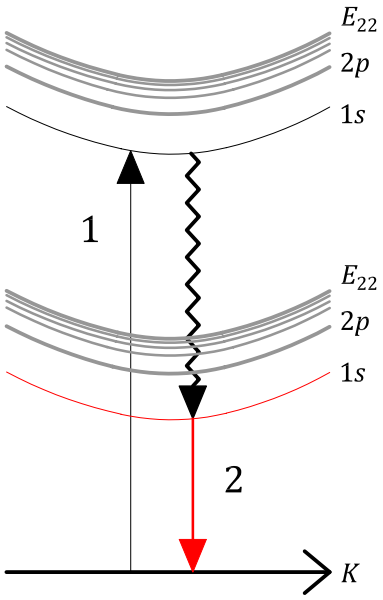
λ is the wavelength of the photon absorbed or emitted.

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 three are quasi-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 SWCNT samples contain left- and right-handed helical structures. The intrinsic peak positions of the PL signals are basically the same for these enantiomers although they can be affected differently by absorbates. Also, their cross-sections with respect to polarized light can differ.

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 (e.g. 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 a diameter of 0,8 nm in a polymer matrix and a surfactant solution[3]. This value substantially depends on the nanotube environment. An exciton band structure is shown in Figure 3.



Key

1 absorption

2 emission

Figure 3 — Qualitative description of the exciton band structure of SWCNTs

5 NIR-PL apparatus

5.1 NIR-PL spectrometer

For SWCNTs produced by the chemical vapor deposition (CVD) method with a 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 a larger diameter SWCNT produced by laser vaporization and electric arc techniques, a spectral range of 1 200 nm to 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 Titanium-Sapphire lasers, fixed wavelength diode lasers or white light lasers.

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