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Nanotechnologies — Characterization of single-wall carbon nanotubes using ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy

Nanotechnologies — Caractérisation des nanotubes à simple couche de carbone par utilisation de la spectroscopie d'absorption UV-Vis-NIR

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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 10868:2011), which has been technically revised.

Nanotechnologies — Characterization of single-wall carbon nanotubes using ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy

1 Scope

This document provides guidelines for the characterization of compounds containing single-wall carbon nanotubes (SWCNTs) by using optical absorption spectroscopy.

The aim of this document is to describe a measurement method to characterize the diameter, the purity, and the ratio of metallic SWCNTs to the total SWCNT content in the sample.

The analysis of the nanotube diameter is applicable for the diameter range from 1 nm to 2 nm.

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*

3 Terms, definitions and abbreviated terms

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

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

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

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

3.1 Terms and definitions

3.1.1
purity indicator
optically defined indicator of the ratio of the mass fraction of SWCNTs to the total carbonaceous content in a sample

Note 1 to entry: Purity indicator is NOT “purity” itself which is defined as the percentage of mass of SWCNTs to the total mass of the sample. This guideline cannot evaluate this general purity because absorption spectroscopy cannot detect metallic impurities that are generally contained in any SWCNT sample. In order to characterize metal impurity content, there is a different Technical Specification on thermogravimetric analysis. Metallic impurity is defined as catalytic metal particle and does not include metallic carbon nanotube. See ISO TS 11308.

3.1.2
ratio of metallic SWCNTs
optically defined compositional ratio of metallic SWCNTs to the total SWCNTs contained in the sample

3.2 Abbreviated terms

For the purposes of this document, the following abbreviated terms apply.

CMC	Sodium carboxymethylcellulose
DMF	Dimethylformamide
DOS	Density of states
NIR	Near infrared
NMP	N-Methyl-2-Pyrrolidone
SC	Sodium cholate
DOC	Sodium Deoxycholate
SDS	Sodium dodecyl sulfate
SDBS	Sodium dodecylbenzene sulfonate
SWCNT	Single-wall carbon nanotube
TEM	Transmission electron microscope
UV	Ultraviolet
VHS	van Hove singularity
Vis	Visible

4 Principle

4.1 General

All SWCNT samples contain both semiconducting and metallic SWCNTs, together with impurities consisting of carbon and other elements unless the samples have been altered after production. UV-Vis-NIR absorption spectroscopy can be used for the measurement of interband optical transitions specific to SWCNTs. The analysis of these optical transitions provides qualitative and semiquantitative information important for the characterization of SWCNT samples, such as mean diameter, purity, and the ratio of metallic SWCNTs to the total SWCNT content.

4.2 UV-Vis-NIR absorption spectroscopy

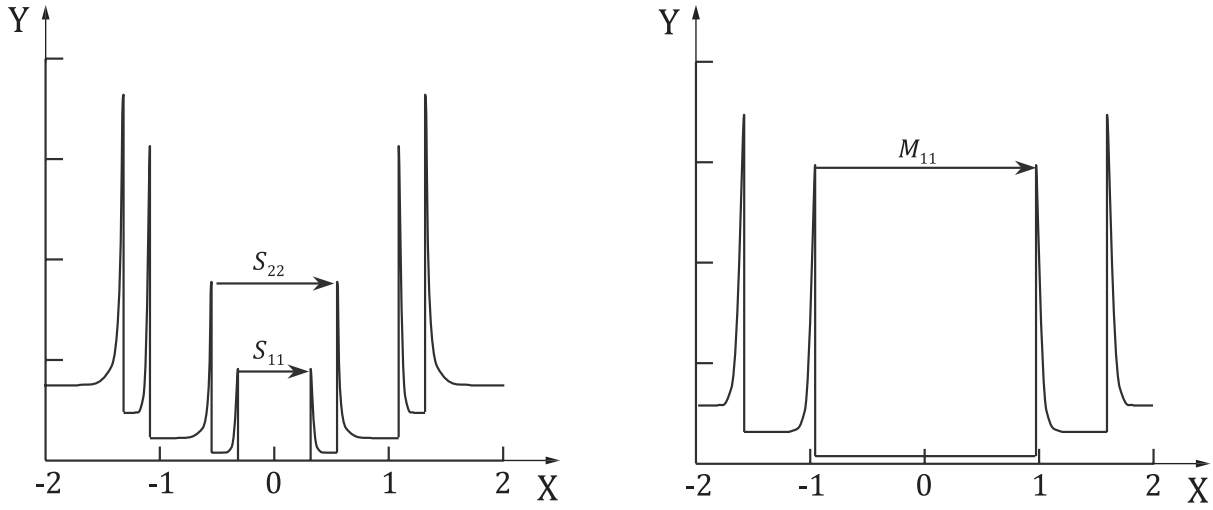
The intensity of light passing at a specified wavelength, λ, through a specimen (I) is measured and it is compared to the intensity of light before it passes through the specimen (I_0). The ratio I/I_0 is called a transmittance. The absorbance, A, is expressed as $-\log (I/I_0)$. The plot of the absorbance against wavelength for a particular compound is referred to as an absorption spectrum.

NOTE The relationship between transmittance and absorbance is only rigorously correct when reflectance is negligible and there is no scattering.

4.3 Optical absorption peaks of SWCNTs in the UV-Vis-NIR region

The shape of the electronic DOS of semiconducting and metallic SWCNTs shown in Figure 1 is a series of spikes that are referred to as VHS. The peaks observed in the optical absorption spectra of SWCNTs are attributed to the electronic transitions between these VHSs as shown by arrows in Figure 1. S_{11} and S_{22} are used as the symbols of the absorption due to the first and second interband transitions of

semiconducting SWCNTs, respectively [see Figure 1 a)]. M_{11} means the absorption arising from the first interband transition of metallic SWCNTs [see Figure 1 b)].



a) Electronic DOS of semiconducting SWCNTs **b) Electronic DOS of metallic SWCNTs**

Key

X energy (eV)

Y electronic DOS (arbitrary unit)

S_{11} first interband optical transition attributed to semiconducting SWCNTs

S_{22} second interband optical transition attributed to semiconducting SWCNTs

M_{11} first interband optical transition attributed to metallic SWCNTs

NOTE 1 Arrows represent interband transitions that result in optical absorption.

NOTE 2 See Reference [2].

Figure 1 — Electronic DOS diagram of SWCNTs near the Fermi level

To interpret the absorption spectra of SWCNTs, band structures calculated using the zone-folding method are frequently used. The electronic structure of an SWCNT is generally given by that of a two-dimensional graphite sheet expressed by the tight binding approximation as shown in Formula (1)[2]:

$$E_{2D} = \pm \gamma \left[1 \pm 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)\right]^{1/2} \quad (1)$$

where

E_{2D} is the two dimensional energy dispersion relation for a single graphene sheet;

a is the lattice parameter[3];

k_x and k_y are the components of the reciprocal unit vector;

γ is the overlap integral.

4.4 Relation between SWCNT diameter and optical absorption peaks

Within a simple tight-binding theory, in which the electronic band structure is assumed to arise from a pure p-orbital at each conjugated carbon atom, the low-energy band gap transitions take a simple analytical form. The energy gaps corresponding to the electron transitions are given by Formula (2) to Formula (4):

$$E\text{g}(S_{11}) = \frac{2a\gamma}{d} \quad (2)$$

$$E\text{g}(S_{22}) = \frac{4a\gamma}{d} \quad (3)$$

$$E\text{g}(M_{11}) = \frac{6a\gamma}{d} \quad (4)$$

where

$E_\text{g}(S_{11})$, $E_\text{g}(S_{22})$, $E_\text{g}(M_{11})$ are the energy gaps corresponding to the transitions of S_{11}, S_{22} and M_{11}, respectively;

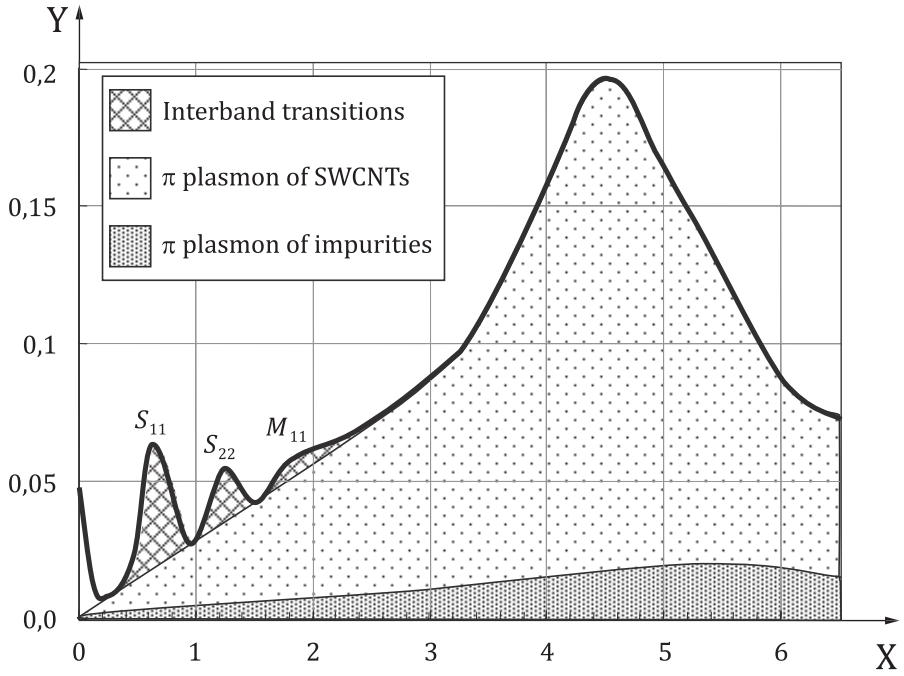
d is the diameter of SWCNTs[4].

Formula (2) to Formula (4) show a simple relationship between the diameter and the optical transition energies (and thus the peak wavelengths). This allows the estimation of the mean diameter of a SWCNT sample by the analysis of the absorption spectra originating from the optical transitions between VHSs.

Formula (2) to Formula (4) can give information related to the diameter within some limitations. One of the limitations is that the analysed peak(s) needs to be clearly resolved.

4.5 Derivation of the purity indicator from optical absorption peak areas

As mentioned in 4.3, there are the specific absorptions of SWCNTs originating from interband transition between VHSs. These absorption peaks are typically observed in the Vis-NIR region. On the other hand, in the UV region, most SWCNT samples present optical absorption with the peak at 200 nm to 300 nm[5]. This absorption is attributed to the collective excitations of π electron systems (π-plasmons) and can also be observed in most graphitic compounds[5]. Therefore, the π-plasmon absorption observed in most SWCNT samples is due to both SWCNTs and carbonaceous impurities. The π-plasmon absorption is extremely broad and is superposed on the above-mentioned specific absorption of SWCNTs as a featureless background extending to the Vis-NIR and IR region. To summarize, the absorption spectrum of SWCNT samples in the Vis-NIR region is composed of the interband transitions of semiconducting and metallic SWCNTs and π-plasmon absorbance (see Figure 2).



Key

X photon energy (eV)

Y absorbance (absorbance unit)

NOTE The relative contribution from each component is arbitrary and also has differing chiral angle distributions.

Figure 2 — Typical UV-Vis-NIR absorption spectrum of an SWCNT sample[6]

In Figure 2, the absorption from S_{nn} and M_{11} gives rise to the absorption peak areas, $AA(S_{nn})$ and $AA(M_{11})$, and that of π-plasmon as $AA(\pi)$. In addition, the total absorption [$AA(S_{nn})$+ $AA(\pi)$ or $AA(M_{11})$+$AA(\pi)$] is designated as AA_t (see Annex B). As long as samples of concern have similar mean diameters and diameter distributions, the relative magnitude of $AA(S_{nn})$ [or $AA(M_{11})$] to AA_t can be used as an indicator of purity, $P_i(S_{nn})$ or $P_i(M_{11})$[7][8], which is given by Formula 5:

$$P_i(S_{nn}) \text{ or } P_i(M_{11}) = AA(S_{nn} \text{ or } M_{11})/AA_t \quad (5)$$

Formula 5 gives information related to purity within some limitations. One of the limitations is that the analysed peak(s) needs to be clearly resolved. Another is that samples need to have almost similar mean diameters and distributions as determined by the locations of the peak positions.

NOTE Surfactants and/or dispersing agents could also add complexity to the spectra.

4.6 Derivation of ratio of metallic SWCNTs from optical absorption peak areas

On the basis of the analogy of 4.5, an analysis of the area under the peak for semiconducting and metallic SWCNTs provides an indicator of the ratio of metallic SWCNTs to the total SWCNTs, which is given by Formula (6):

$$R_{\text{Metal}} = \frac{AA(M_{11})}{AA(S_{11}) + AA(M_{11})} \tag{6}$$

Furthermore, Formula (6) can be converted into Formula (7) for R_{Metal} as the function of $AA(S_{22})$ and $AA(M_{11})$:

$$R_{\text{Metal}} = \frac{AA(M_{11})}{1{,}2AA(S_{22}) + AA(M_{11})} \tag{7}$$

Use of Formula (7) is frequently more favourable than use of Formula (6) because $AA(S_{11})$ is sensitive to the charge transfer[9].

R_{Metal} does not literally represent the ratio of metallic SWCNTs, because integrated molar extinction coefficients in the M_{11} and S_{11} regions (or their relative magnitude) are not completely clarified. In the case of the SWCNT sample with the diameter distribution of 1,1 nm to 1,3 nm, Formula (6) and Formula (7) provide the actual ratio of metallic SWCNTs because these coefficients have been determined to be equal experimentally[10].

R_{Metal}, nonetheless, can be utilized as an indicator of the ratio of metallic SWCNTs in the comparison of different samples within some limitations. One of the limitations is that all the peaks involved need to be clearly resolved. Another is that samples need to have similar mean diameters and distributions.

NOTE Most UV-Vis-NIR absorption spectra of SWCNTs show separate groups of peaks each of which can be assigned to optical transitions in the metallic or semiconducting components. At the present stage, however, determining their compositional ratio by spectral analysis is not possible, because of experimental difficulties such as the unavailability of their extinction coefficients and ambiguity in background subtraction. A qualitative comparison could still be made as to the relative abundance of each component using a certain standard sample. For example, some SWCNT samples are known to have the ratio of 0,33, as theoretically predicted under the assumption of equal synthetic probability[11], or the ratio of 1 in the sample treated by the special separation process[10], which can be used as a reference.

5 UV-Vis-NIR spectrometer

A calibrated standard spectrophotometer covering a broad, ultraviolet to NIR wavelength range shall be used. The long wavelength limit shall be 3 000 nm or longer to cover SWCNT diameter up to 2,5 nm. The spectrophotometer shall be turned on 1 h prior to the measurement to allow the baseline to stabilize.

6 Sample preparation method

6.1 General

Because all the SWCNT samples are generally produced as powder or solid aggregates, they shall be processed into a form that enables optical absorption measurements. Homogeneous, non-scattering and stable dispersion of SWCNTs in liquid or solid media is best suited for this purpose, the preparation of which requires a solvent and a dispersant. As they have their own optical absorption that can disturb a spectral measurement of SWCNT, solvents and dispersants shall be properly chosen as follows.

For measurement of the mean diameter and ratio of metallic SWCNTs, the dispersing method using water or heavy water (D_2O) and water-soluble surfactants shall be used because of high dispersing ability. Furthermore, for measurement in the wavelength region from UV-Vis to 1 800 nm, dispersion in D_2O shall be used because of its optical transparency over this region. Beyond 1 800 nm, however, because of the unavailability of such optically transparent solvents, solid films shall be used in which