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Nanotechnologies — Characterization of single-wall carbon nanotubes using scanning electron microscopy and energy dispersive X-ray spectrometry analysis

Nanotechnologies — Caractérisation des nanotubes de carbone à simple paroi par microscopie électronique à balayage et spectroscopie à dispersion d'énergie

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Foreword

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Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 10798 was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

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Introduction

Single-wall carbon nanotubes (SWCNTs) are made from a unique form of carbon that has desirable mechanical, thermal and electronic properties. They are composed of carbon atoms arrayed in a hexagonal network in the shape of a hollow tube. SWCNT diameters are in the order of 0,5 nm to 3 nm, while SWCNT lengths can range from less than one μm into the millimetre range.

Possible applications for SWCNTs range from composite reinforcing materials, drug delivery systems and electronic devices, to mention a few. SWCNTs can be grown *in situ* as part of an electronic or electromechanical device, or produced in bulk through electric arc, laser or chemical vapour deposition methods. Details on the structure and manufacturing methods for SWCNTs can be found in relevant literature[12][18].

The production of SWCNTs is driven by a catalyst-based growth mechanism, with metallic nanoparticles as the catalyst material. These nanoparticles can be found in the raw, as produced SWCNT material. The raw material can also contain other impurities in the form of inorganic oxides, along with different nanocarbon structures such as fullerenes, nanocrystalline carbon and amorphous carbon. Solvents, acids and other chemical agents are used to purify the raw SWCNT materials. Impurities are reduced or removed during the purification process. Some of the purification methods include oxidation by acid reflux[17], gas phase oxidation[14], microfiltration[11], and column chromatography[15]. However, depending on the purification method, the SWCNTs can be shortened in length, functionalized with acid groups, bundled (many SWCNTs adhered together), or damaged (defects in the wall structure that can affect the properties of the material).

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High resolution scanning electron microscopy is an extremely useful technique for characterizing both raw and purified SWCNT materials. The high resolution scanning electron microscope (HRSEM) is used here to differentiate features that are consistent with high-aspect ratio carbon nanotubes from other non-filamentous carbon impurities. SEM-based energy dispersive X-ray spectrometry (EDX) analysis is also used to identify the elemental composition of catalysts and other inorganic impurities in the material.

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Nanotechnologies — Characterization of single-wall carbon nanotubes using scanning electron microscopy and energy dispersive X-ray spectrometry analysis

1 Scope

This Technical Specification establishes methods to characterize the morphology, and to identify the elemental composition of, catalysts and other inorganic impurities in raw and purified single-wall carbon nanotube (SWCNT) powders and films, using scanning electron microscopy and energy dispersive X-ray spectrometry analysis.

The methods described here for SWCNTs can also be applied to the analysis of multiwall carbon nanotubes (MWCNTs).

2 Normative references

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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.

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ISO 22493:2008, *Microbeam analysis — Scanning electron microscopy — Vocabulary*

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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 22493:2008 and ISO/TS 80004-3 and the following apply.

3.1 Terms related to scanning electron microscope

3.1.1
SEM
scanning electron microscope
instrument that produces magnified images of a specimen by scanning its surface with a well-focused electron beam

NOTE 1 See Reference [16] for details of the instrumentation, the SEM process and the different types of SEMs.

NOTE 2 A conventional SEM utilizes an electron source filament either made from W or LaB_6 materials that are heated to produce a source of electrons by thermionic emission. The electron beam probe sizes (d_p) are between 3 nm and 4 nm, which is not sufficient to resolve individual SWCNTs. The range of useful analysis is generally under ×100 000 magnification and can be considerably less in non-conducting materials. Conventional SEMs typically operate at high accelerating voltages (5 kV to 30 kV) and often require the samples to be coated. These SEMs can be used for EDX analysis.

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NOTE 3 A field emission scanning electron microscope (FESEM) has an extremely fine cathode tip that generates a smaller diameter probe size compared to a conventional SEM, even at very low accelerating voltages (0,5 kV to 5 kV). In FESEMs, electron beam probe sizes can be 1 nm or less, expanding the useful magnification range an order of magnitude higher. Non-conducting materials can be imaged without applying a conductive coating through the use of low accelerating voltages. An FESEM is sometimes referred to as a high resolution SEM (HRSEM). This can also be used for EDX analysis and offers better spatial resolution when low accelerating voltages are used.

NOTE 4 Variable pressure SEM (VPSEM) is another type of SEM where the pressure around the specimen can be controlled from a few Pa to hundreds of Pa, to eliminate surface charging and to minimize surface damage to the specimen. Although currently outside the scope of this specification, this method is included here to provide the basis for possible future VPSEM characterization of SWCNTs that might be present in biological tissue or in a fluid environment. In this case, EDX analysis is possible but electron beam scattering in the residual gas means that results from point analysis are contaminated by spurious contributions from all over the specimen stub.

3.2 Terms related to electron probe microanalysis

3.2.1
accelerating voltage
potential difference applied between the filament and the anode to accelerate the electrons emitted from the source

[ISO 23833:2006, definition 4.1]

3.2.2
analysis depth
maximum depth from which a defined fraction (e.g. 95% of the total) of the X-rays are emitted from the interaction volume after absorption

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[ISO 23833:2006, definition 4.7.1.2]

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3.2.3
analysis volume
volume from which a defined fraction (e.g. 95% of the total) of the X-rays are emitted after generation and absorption

[ISO 23833:2006, definition 4.7.1.3]

3.2.4
BE
backscattered electron
electron ejected through the entrance surface of a sample by a backscattering process

NOTE 1 By convention, an electron ejected with an energy greater than 50 eV may be considered as a backscattered electron.

NOTE 2 Adapted from ISO 23833:2006.

3.2.5
BEI
backscattered electron image
scanning electron beam image in which a signal is derived from a dedicated backscattered electron detector (e.g. passive scintillator, solid-state diode, channel plate or negatively-biased Everhart-Thornley detector)

[ISO 23833:2006, definition 3.4.2]

3.2.6
coating artefact
undesirable modification of the sample structure and/or X-ray spectrum arising from the characteristics of the coating material and which may interfere with the interpretation of the true sample details

NOTE Adapted from ISO 23833:2006.

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3.2.7
EDS
energy dispersive X-ray spectrometer
device for determining X-ray intensity as a function of the energy of the radiation

[ISO 23833:2006, definition 3.6.4]

3.2.8
EDX
energy dispersive X-ray spectrometry
form of X-ray spectrometry in which the energy of the individual photons is measured and is used to build up a digital histogram representing the distribution of X-rays with energy

[ISO 23833:2006, definition 3.6.5]

3.2.9
EPMA
electron probe microanalysis
technique of spatially-resolved elemental analysis based upon electron-excited X-ray spectrometry with a focused electron probe and an electron interaction volume with micrometer to sub-micrometer dimensions

[ISO 23833:2006, definition 2.1]

3.2.10
point analysis
analysis obtained when the electron probe is placed at a single location and held there for the duration of the spectrometric measurement

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[ISO 23833:2006, definition 3.4.10]

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3.2.11
SE
secondary electron
electron of a sample emitted as a result of inelastic scattering of the primary beam electron by loosely bound valence-level electrons of the sample

NOTE 1 Secondary electrons have conventionally energies less than 50 eV.

NOTE 2 Adapted from ISO 23833:2006.

3.2.12
SEI
secondary electron image
scanning electron beam image in which the signal is derived from a detector that selectively measures secondary electrons (electrons having less than 50 eV) and is not directly sensitive to backscattered electrons

[ISO 23833:2006, definition 3.4.11]

3.3 Terms related to sampling

3.3.1
field sample
sample taken from the production lot or from the material that needs to be characterized

NOTE Adapted from CEN/TS 15443:2006.

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3.3.2
laboratory sample
sub-sample of a field sample having undergone certain sample preparation steps (e.g. drying, etc.) in a laboratory

NOTE Adapted from CEN/TS 15443:2006.

3.3.3
analysis sample
sub-sample of a laboratory sample having a nominal size of a few millimetres, or a mass of tens of milligrams, used for a number of chemical and physical analyses

NOTE Adapted from CEN/TS 15443:2006.

3.3.4
test portion
sub-sample of an analysis sample consisting of the quantity of material required for a single execution of a test method

NOTE Adapted from CEN/TS 15443:2006.

3.3.5
test area
specific x-y area location on the test portion defined by the SEM magnification setting

NOTE Adapted from CEN/TS 15443:2006.

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3.3.6
sub-sample
portion of a sample

NOTE Adapted from CEN/TS 15443:2006.

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4 General principles

4.1 SEM analysis

SEM analysis is used to differentiate between features in SWCNT samples that are consistent with the morphology of SWCNT structures, other forms of carbon, and other impurities. SWCNTs have diameters in the range of less than 1 nm to about 3 nm. Lengths are extremely variable and sometimes can be greater than 10 μm. Diameters in the nm range result in very high attractive forces between the particles, while extremely long nanotubes can easily become entangled. As a result, carbon nanotubes are typically observed in “bundles” or “ropes”, where large numbers of individual nanotubes are clustered together. The dimensions of the bundles are considerably larger than individual tubes.

4.2 EDX analysis

EDX analysis is used here to determine the elemental composition of non-carbonaceous impurities in CNT samples. All state-of-the-art SEM/EDX systems can detect carbon and have good sensitivities to other impurities in the material, such as residual catalysts, surfactants, and acid functionalized products. Advanced software routines are available from suppliers to calculate semi-quantitative data from acquired X-ray spectra without the use of standard materials.

4.3 Applicability to MWCNT analysis

MWCNTs are composed of nested, concentric or near concentric graphene sheets with interlayer distances similar to those of graphite. They have considerably larger outer diameters due to the increased number of

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graphene layers in the wall structure. The number of walls range from two or three (double-wall and triple-wall, respectively) to n walls. These structures can easily have outer diameters in the 10 nm to 15 nm range, which is considerably larger than the minimum probe size of HRSEMs (typically about 1 nm). The dispersion and sample preparation methods are also similar to those used for SWCNTs. Therefore, all the methods described for the SEM/EDX characterization of SWCNTs also apply to the analysis of MWCNTs.

NOTE 1 The interlayer distance in MWCNTs is ≈ 0,335 nm, which is close to the distance between graphene layers in graphite. Therefore, the outer diameter (D_o, expressed in nanometres) of a MWCNT is:

$$D_o \approx D_i + 2(n - 1)x$$

where:

D_i is the inner diameter, expressed in nanometres;

n is the number of walls;

x is the interlayer distance, expressed in nanometres.

NOTE 2 Additional information on MWCNT characterization can be found in Reference [3].

4.4 Other supportive analytical methods

There are a number of other analytical techniques that are required to determine the precise wall structure, defect level, carbon type, diameter distribution, and quantity of impurity levels in carbon nanotube materials. Examples of some of these other analytical techniques that are commonly used to support the SEM/EDX analysis of SWCNTs are presented in C.3.

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5 Sample preparation methods

5.1 Precautions and safety concerns

It is recommended that only trained scientific personnel handle carbon nanotube materials. Samples should be prepared using appropriate safety procedures for the handling of carbon nanotubes and other forms of nanoparticles. Personal protective equipment (PPE) should be used, including disposable gloves, safety glasses, laboratory coats, filter respirators, etc. Sample preparations should be carried out in a vented fume hood equipped with suitable air filters to avoid inhalation of any CNT dust.

Evaporative or sputter coating of the samples should be avoided when performing high resolution imaging of SWCNTs.

NOTE Sputter coating can create artefacts which obscure details of the images at high magnifications and are likely to be confused with undesirable amorphous carbon coatings produced during the production process. An example of a HRSEM coating artefact is shown in D.3.

5.2 Preparing samples for SEM/EDX analysis

5.2.1 Sample preparation protocols

Reliability of the SEM/EDX measurements is supported by uniform sample handling and preparation methods. Details of the sample preparation protocols for the realization of reproducible characterization of SWCNTs can be found in Reference [13].

5.2.2 Sample selection

The sampling flow diagram in Figure A.1 shows a hierarchy of samples starting at the very large field sample followed by the laboratory sub-sample. The analysis sample is much smaller with just enough material to

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complete a number of chemical and physical laboratory tests. The procedures described here for sample selection are limited to the test portion size which is typical for SEM/EDX analysis.

The schematic diagram shown in Figure A.2 represents a typical SEM sample stub, the size of which could be in the order of 10 mm to 25 mm in diameter. Three separate test portions of the same sample should be mounted on the same sample stub for analysis as shown. Alternatively, three separate sample stubs may be prepared. The selection of the test portion from the analysis sample shall be done in such a way as to completely randomize the sampling. This can be done by shaking the bottle to obtain a homogeneous mixture prior to sampling, or by dispersing the sample in a solvent (see 5.3.3).

5.2.3 Types of CNT samples

The SEM sample preparation and attachment technique will depend upon the physical form of the material:

a) as-produced dry mats of carbon nanotubes sometimes referred to as “bucky paper”,

b) beads or soft agglomerated powder,

c) loose powder, or

d) wet powder, where the nanotubes are dispersed in a liquid.

5.3 SEM sample preparation/attachment techniques

5.3.1 Double-sided carbon tape method (dry method)

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The following procedure may be used for SEM analysis of bucky paper, beads, or agglomerated CNT powder.

1) Attach a piece of double-sided carbon tape to an SEM sample stub.

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2) With a clean stainless steel micro spatula, tweezers, or similar tool, carefully place a small amount (mg to μg quantity) of CNT powder sample, paper or film on the tape.

3) Excess material should be removed by gently tapping the sample holder against a hard surface, or by gently blowing with an air gun, nitrogen jet, or aerosol duster in a vented fume hood.

4) Check to see that there is visually enough material present on the stub for SEM analysis. If not, apply more.

NOTE 1 Care should be taken to obtain good adhesion of the sample to the tape in order to prevent the removal of CNTs into the SEM vacuum system during evacuation.

NOTE 2 Carbon tape has the disadvantage of potentially drifting for as long as several hours after mounting, and is especially notable at high magnifications.

NOTE 3 Double-sided tape can produce C and O signals which could interfere with the EDX analysis of the carbon nanotube sample. If that is the case, then the use of other substrates might be necessary (see 5.3.2). If only qualitative EDX data is required (for instance to identify the catalyst), then the carbon tape method might be sufficient.

NOTE 4 This method is also useful when the SWCNT sample has been grown on and is still attached to a substrate material (such as a CNT “forest”).

5.3.2 Pressing powder into indium foil (dry method)

The following procedure may be used for SEM analysis of beads, agglomerated, or dry CNT powder samples.

1) Attach a piece of indium foil to an SEM sample stub using double-sided carbon tape.

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