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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*.

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).

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.

TECHNICAL SPECIFICATION **ISO/TS 10798:2011(E)**

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

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

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.

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

[ISO 23833:2006, definition 4.7.1.2]

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.

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

[ISO 23833:2006, definition 3.4.10]

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.

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.

3.3.6
sub-sample
portion of a sample

NOTE Adapted from CEN/TS 15443:2006.

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 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:

$$D_{\mathrm{o}} \approx D_{\mathrm{i}} + 2(n - 1)x$$

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.

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 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)

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.

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.

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

3) With the flat side of the micro spatula, press the CNT material firmly into the indium foil to form an adhered mat of pressed powder. Repeat the process in different areas of the foil until three or more test portions are formed (see Figure A.2).

4) Remove any excess material by gently tapping the stub against a hard surface, or by gently blowing with an air gun, nitrogen jet, or aerosol duster in a vented fume hood.

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

Adequate pressure should be applied by the spatula to the mass of CNT powder to cause the powder to press into and stick to the indium foil. At the same time, a coherent mat of CNT powder should form, which strongly adheres to the foil. After any excess material is removed, there should be enough carbon nanotube material left on the foil to minimize EDX signals from the indium substrate.

NOTE This method is preferred if the sample size is limited, or if the analysis for carbon is critical.

5.3.3 Solvent dispersion on suitable substrates (wet method)

The following procedure should be used for wet CNT powder, or where nanotube powder is dispersed in a liquid. A small piece of a polished silicon wafer is recommended for the substrate. Other polished substrates may be used, such as clean copper or aluminium SEM stubs.

1) If the SWCNT material has not already been dispersed in the liquid, add a small amount (about 0,5 mg) of dry powder to 10 ml of isopropyl alcohol in a small vial.

2) Place the vial in a sonication bath for 5 min to 30 min or until a uniform appearance is achieved. An ice water bath may be used to minimize thermal damage to the SWCNTs.

3) Using a micro-pipette, place a very small drop (about 0,5 ml) of the carbon nanotube dispersion on a clean silicon wafer or SEM stub. Additional drops may be applied if a thicker coating is required.

4) Allow the sample to air dry. Place the dried sample in a clean vacuum oven set at about 75 °C for 15 min to remove all residual liquid.

5) Remove any excess material by gently tapping the substrate against a hard surface, or by gently blowing with an air gun, nitrogen jet, or aerosol duster in a vented fume hood.

6) Attach the silicon wafer to the SEM stub with double-sided conducting carbon tape.

If EDX analysis is to be performed, the composition of the cleaned substrate should be determined in advance in order to ensure that it does not contain possible catalyst or contaminant elements in the SWCNT material. Also, more than one type of substrate or sampling method might be required to prevent elemental interference during the EDX analysis.

The final thickness of the test portion of carbon nanotube material present on the sample stub should be greater than 10 µm to avoid picking up signals from the substrate (see Annex B for additional information).

6 Measurement procedures

6.1 SEM analysis

A minimum of three test area locations shall be analyzed (e.g. test areas A1, A4 and A7 in Figure A.2), with additional locations added as necessary (e.g. test areas A2, A5, A8, and if needed, A3, A6, A9 and A9; see

Figure A.2). If possible, the analysis should be performed in an HRSEM using low accelerating voltages (1 kV to 2 kV), low working distances (about 3 mm or less) and low beam currents (about 4 pA).

A minimum of six magnifications for the SEM analysis shall be acquired as shown in Table 1. Additional images at other magnifications may be obtained as necessary to give the clearest indication of the CNT structure. For each magnification, images shall be acquired in secondary electron image (SEI) and backscattered electron image (BEI) acquisition modes (a total of 36 SEM images). The obtained images from the three test areas shall be compared at the same magnification setting to address any potential uniformity issues. If there is variation in the images, then additional test areas shall be recorded. The original magnification, the accelerating voltage, and a calibrated scale marker shall be present on the recorded images.

If the SWCNTs are partially or completely obscured by impurities such as a solid shell that encases the carbon nanotubes, then cracks in the surface should be used to confirm the presence of SWCNTs.

The SEM image magnification should be calibrated using a certified reference material (CRM), in accordance with ISO 16700.

Table 1 — Recommended magnification settings for SEM and EDX analysis

Recommended magnifications for SEM analysis	Recommended magnification ranges for EDX analysis
× 1 000	× 200 to × 500
× 5 000	× 1 000 to × 5 000
× 10 000	× 30 000 to × 50 000
× 25 000	
× 50 000	
× 100 000	

NOTE 1 Very high resolutions and magnifications (> ×500 000) are required for imaging very pure, dilute SWCNT or MWCNT samples, SWCNT devices, or individual SWCNTs.

NOTE 2 The presence of impurities, charging or drifting of the sample will reduce the usual magnifications.

NOTE 3 When comparing images between different samples, it is good practice to select a series of magnification settings that demonstrate the features being identified. As the magnification is increased, the field of view becomes smaller, which provides a more detailed examination of the SWCNT fine structure.

6.2 EDX analysis

For qualitative EDX analysis, the recommended accelerating voltage is either 15 kV or 20 kV (20 kV preferred). The minimum sample thickness should be in the order of 10 µm. If possible, larger sample volumes should be used. Adjust beam currents and counting times to achieve EDX spectra with good signal-to-noise ratios (see Annex B for additional information on EDX analysis).

The EDX analysis shall be performed over a suitable scanned area so that average compositions are obtained. Point analysis may be used in order to determine if catalyst particles or elemental impurities are present. A scan control unit with drift correction software is recommended to correct for sample drift during spectrum acquisition.

One EDX scan shall be recorded for each of the three different magnification ranges specified in Table 1. The exact magnification depends upon the dimensions of the test portions (length, width and thickness). The number of EDX recordings will depend on the results of the initial three analyses (test areas A1, A4 and A7 in Figure A.2).

If the preliminary EDX analysis shows significant differences in the relative intensities of the peaks in different regions of the sample, each region should be examined in more detail, as described in 6.1.

For semi-quantitative analysis, the results from the first three areas should be averaged. Calculate the average (avg) and standard deviation (stdev). Report the data if the relative standard deviation (stdev/avg in%) is less than 20%. If the variation is larger, analyze three more areas (A2, A5, A8); and if needed, three additional areas (A3, A6, A9) to achieve the desired statistics. If the precision is still not sufficient, then the magnifications, beam currents, and counting times should be adjusted until uniform values are achieved. If uniform values still cannot be achieved, then only report qualitative results (elements detected).

EDX systems should be calibrated routinely using CRMs, with an uncertainty that is sufficiently small for calibrating purposes.

NOTE 1 Guides to calibration include ISO 14595, ISO Guide 35 and ASTM E1508-98.

NOTE 2 Because of the experimental parameters required for the SEM/EDX analysis, the spatial resolution is generally insufficient to identify individual catalyst particles in CNT materials. Dedicated TEM/STEM instrumentation with EDX capability should be used for that purpose.

NOTE 3 The precise settings for the EDX analysis depends on the specific SEM/EDX microscope system used, the elements to be analyzed and the expected accuracy of the elemental determination (see Annex B for details on recommended instrumental parameters).

7 Data analysis and results interpretation

7.1 SEM results

For each of the six SEM magnifications acquired, insert into the report three secondary electron images, and three backscattered electron images using landscape orientation. Include any additional images acquired as indicated in 6.1. Examination of the SEM images should allow the direct observation of features that are consistent with the presence of high-aspect ratio carbon nanotube materials (within the resolution limits of the particular SEM being employed). Brighter contrasting particles in the backscattered images identify the presence of catalyst particles or other impurities in the CNT material.

7.2 EDX results

Report representative EDX scans from 0 keV to 10 keV from the three areas examined (see 6.2). List all the elements detected in addition to carbon. Identify any signals present that might originate from the substrate. If required, include a summary table of the semi-quantitative EDX analysis data identifying the mass fractions and atom percentage of the elements detected, along with the average, standard deviation, and relative standard deviation.

NOTE A case study on the use of SEM/EDX analysis in the characterization of SWCNTs is given in Annex C on as-synthesized and purified SWCNT materials. Additional SEM images of SWCNT materials are given in Annex D.

8 Measurement uncertainty

8.1 SEM analysis

HRSEM images are used mainly to make qualitative comparisons of the morphology between different CNT samples. This method cannot evaluate diameters of SWCNTs that are less than the minimum probe size of the SEM being used for the analysis. Other characterization methods are required in order to study the precise carbon nanotube wall structure. Also, HRSEM imaging cannot easily differentiate between carbon nanofibres (i.e. filled tubes), SWCNTs, MWCNTs, or very thin layers of amorphous carbon that may coat individual tubes or bundles.

“Live” on-screen measurements should not be used to determine feature sizes in CNT samples. A scale marker should be used to determine the dimension of features in the sample on recorded images. When available, image processing software that has been calibrated with features of similar dimensions should be used. Uncertainties in magnification measurements are addressed in ISO 16700:2004.

8.2 EDX analysis

There are a number of factors that influence the uncertainty in EDX analysis. More detailed information on EDX test conditions, counting statistics and statistical evaluation of data can be found elsewhere (see Reference [16]. The following parameters are especially important for obtaining accurate and reproducible EDX results:

- **Counting statistics**. This is a major uncertainty in EDX analysis. While all modern software measures total counts per spectrum, the counts per peak in the region of interest is also critical (see Annex B).

- **Accelerating voltage.** The accelerating voltage used for the analysis affects the analysis volume (depth of X-ray generation), the over voltage ratio (accelerating voltage/X-ray line voltage), and the specific X-ray line being used (see Annex B).

- **Quantification issues**. All modern EDX software manufacturers have advanced routines to quantify the composition from acquired spectra. Critical issues that affect the quantification results are sample geometry, uniformity of composition within the sampling depth, and the avoidance of substrate signals (see Annex B).

- **Peak resolution**. The peak resolutions (FWHM) provided by most EDS detectors are not sufficient to resolve certain overlapping of peaks that can contribute to ambiguities in the results.

NOTE 1 Common peak overlaps that might be observed in EDX analysis of CNT materials are: Na Kα /Zn Lα ; Al Kα / Br Lα ; Si Kα /Ta Mα ; P Kα /Zr Lα /Pt Mα ; S Kα /Mo Lα /Pb Mα ; K Kα /In Lα . Additional factors affecting peak resolution are addressed in ISO 22309:2006.

- **Contamination**. There will be carbon contamination build-up on the sample under the electron beam. This can significantly affect the carbon results if carbon is included in the analysis.

- **Limit of detection (LOD).** The LOD for EDX analysis depends upon the atomic number of the detected element, but is generally in the order of a mass fraction of 1 mg/g[7][16]. Other more sensitive analytical techniques (e.g. ICP-AES) might be necessary to provide greater accuracy and full quantification of elemental compositions (mass fractions of 1 µg/g).

- **Peak artefacts**. These include background effects (Bremstrahlung radiation), escape, sum and satellite peaks which might obscure detection and quantification of other elements in the sample.

NOTE 2 The above parameters provide guidelines to the factors that affect measurement uncertainties for EDX analysis of carbon nanomaterials. The software routines usually provide compositions and standard deviations. The exact contribution of each factor discussed above, including sample geometry, operating conditions, and system dependent factors, should be evaluated, assessed and verified by each user reporting semi-quantitative EDX results.

NOTE 3 If accurate quantification of the impurity elements is required, then the EDX results should be verified by quantitative inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis, or a similar technique.

Annex A
(normative)

SEM sampling methods

SEM sampling shall be carried out as shown in Figures A.1 and A.2.

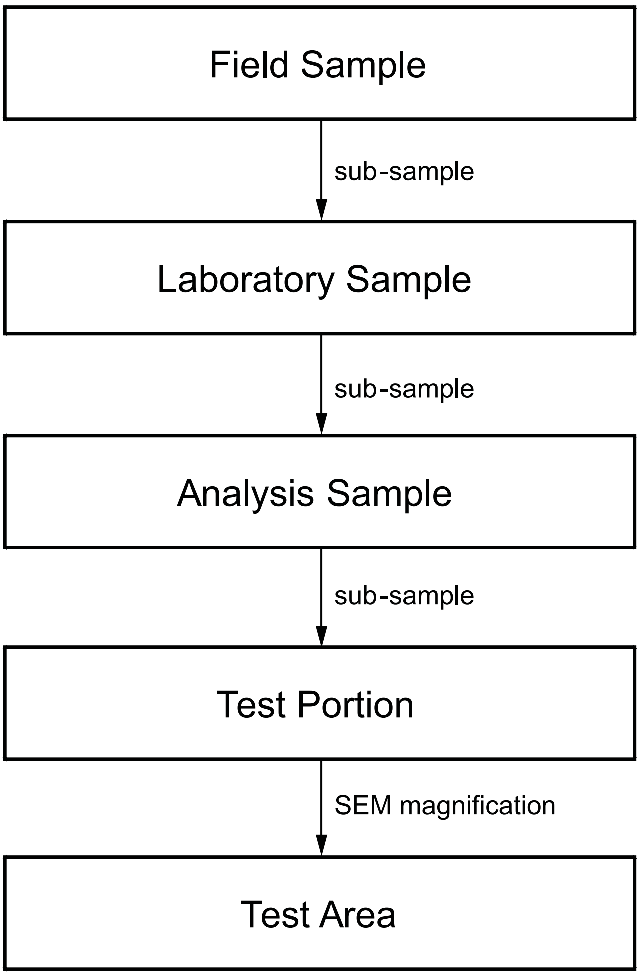

Figure A.1 — SEM/EDX sampling flow diagram

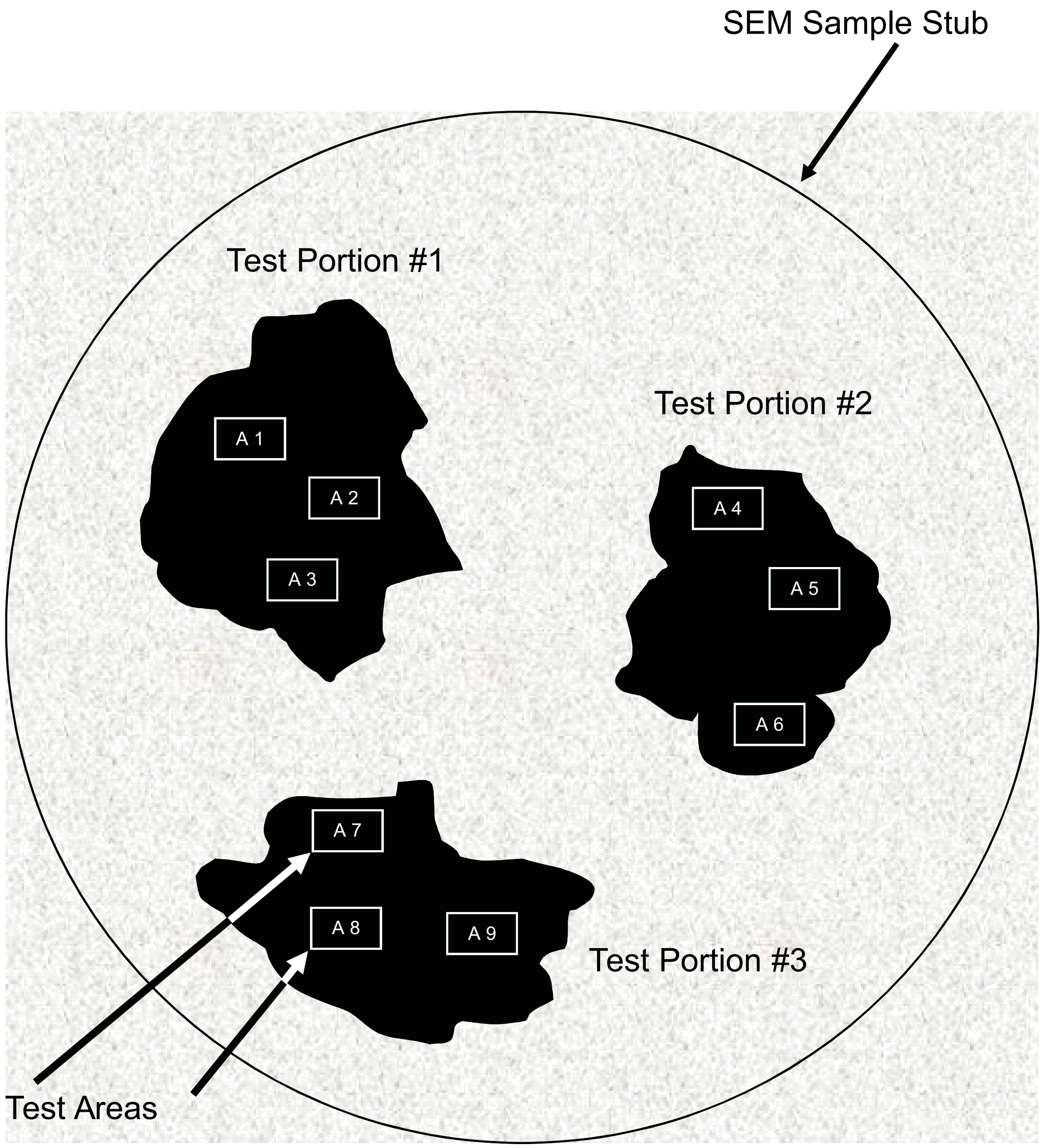

Figure A.2 — Schematic diagram showing SEM sampling method

Annex B
(informative)

Supportive information on EDX characterization of CNT materials

SWCNTs present a unique challenge as to the carbon nature (light element) of the CNTs, and the dispersion of much smaller metal/metal-like particles (heavier elements) in this light element matrix, both contained in a sample with dimensions often smaller than the typical analysis volume associated with EDX analysis. The ideal accelerating voltage used for EDX analysis is selected such that the energy is sufficient to excite the X-rays of the elements under investigation. Software packages are available that perform Monte Carlo simulations to help predict the electron range and depth of X-ray generation to assist the user in determining optimum operating conditions. For example, at 20 kV, the electrons in bulk carbon have a penetration depth of about 3 µm. Operating at 25 kV increases the depth to about 4 µm. However, at 1 kV energy the analysis depth is reduced to about 0,025 µm. At these very low accelerating voltages few X-ray lines are generated. Operating at 5 kV will reduce the beam penetration to less than 1 µm and still provide X-ray lines for analysis; however, overlaps in the low energy lines of the spectrum make element identification more difficult than when higher accelerating voltages are used.

The SEM/EDX technique draws its signal from an approximately “tear drop” shaped region below the surface of the sample. This analysis volume depends on two primary factors, assuming zero tilt of the sample:

1) the energy of the electron beam (accelerating voltage);

2) the stopping power of the specimen, which is related to the average atomic number and density of the material.

Since carbon has a low atomic number, the analysis depth of X-ray generation is large (compared to heavier elements). The combination of high voltage and low atomic number material results in maximum electron penetration into the sample. As a result, if the sample is very thin, the substrate material will probably be detected in addition to the SWCNT material. Furthermore, if the CNT samples are well dispersed on the surface of the substrate, the substrate signal might overwhelm the sample signal. Therefore, care should be taken both in preparing the sample for analysis, and in selecting locations for the analysis. This is important in order to maximize the signal from the SWCNT sample, and minimize the contribution from the substrate.

Quantification of EDX spectra obtained from CNT powder samples might be difficult or impossible due to a number of critical issues. Normally, it is required that the specimens are polished flat, and homogeneous within the sampling volume. CNT powder samples generally lack a precise geometry and might be too thin to avoid picking up substrate signals. Variation of composition with depth and X-rays generated in the substrate is not usually incorporated in EDX software corrections. Therefore, any quantitative results should be interpreted as a convenient numerical indication of concentration rather than an absolute concentration estimate.

If no standards are used, and results have been normalized to 100 %, then absolute concentrations should be compared with caution from specimen to specimen. If any one element concentration is missed or incorrect, then all element estimates will be incorrect. Concentration ratios for elements within each specimen may be compared, provided that the possible effects of specimen thickness, substrate geometry and sample uniformity are taken into consideration. If quantification is required, then the EDX results should be verified by quantitative inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis, or a similar technique.

EDX analysis is basically the same for all types of SEMs, although there may be limitations in electron beam currents in HRSEMs, and X-ray counts in some conventional EDX analysis systems. Lower beam currents require longer X-ray acquisition times in order to achieve high quality spectra with similar peak-to-background ratios.

The two primary factors that control counting statistics in an SEM/EDX system are electron beam current and collection time. The EDS count rate is a function of beam current. At very low beam currents (< 1 nA), the count rates are low in the order of a few hundred counts per second (cps). At high beam currents (10 nA), count rates could be > 30 000 cps. If the collection time is 100 s, then the total counts for the low beam current condition is 30 000 counts, compared to 3 000 000 counts using higher currents. Therefore, if 3 000 000 counts are required for good signal to noise statistics, then longer counting times are required. It should be noted that increasing the current and/or acquisition time can result in damage to the material, especially at high magnifications.

For each element analyzed by EDX analysis there is a recommended overvoltage for optimum X-ray excitation[5]. Often there will be a compromise between overvoltage for the different elements present. For example, if only Na and S were present as impurities (X-ray peaks at about 1,0 keV and 2,3 keV, respectively) then 15 kV should be used. On the other hand, if Fe and Ni are present (6,4 keV, and 7,5 keV, respectively) then 20 kV would be more appropriate. For this specification on EDX analysis of CNT materials, the recommended SEM accelerating voltages are 15 kV or 20 kV, which limits the maximum X-ray peak energy to about 6 keV to 8 keV.

The choice of X-ray line being used for the analysis is also important. Kα are the strongest lines for each element. When used in quantification, they will have the smallest contribution to the total uncertainty (typically less than ~ 1% g/g). As it is not always possible to use the Kα lines, Lα and Mα lines are often used. The uncertainty contribution then increases. For example, for M lines, the measurement uncertainty is typically 5% when optimized experimental conditions are used.

Annex C
(informative)

Case study for the analysis of as-synthesized and purified SWCNT samples

C.1 SEM/EDX analysis of graphite

Depending upon the method of synthesis and/or manufacturing of SWCNTs, there can be varying levels of residual catalyst and other trace impurities in the material. For high purity carbon materials such as graphite, diamond, or carbon nanotubes, the only element that is normally observed by EDX analysis is carbon.

Figure C.1 shows an EDX spectrum acquired at 15 kV at ×500 magnification on a pure graphite reference sample. The main spectrum is normalized to the height of the C signal. The insert in the upper right hand corner is a ×4 expansion of the main spectrum showing the absence of any additional trace signals. As expected, the only signal present is from carbon.

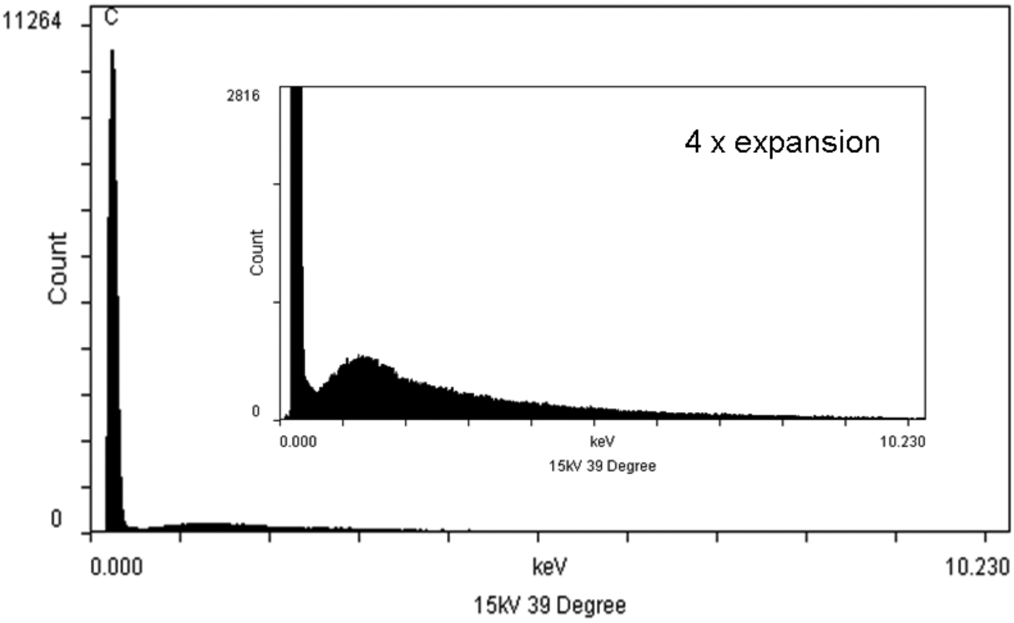

Figure C.1 — EDX spectrum of pure graphite

C.2 SEM/EDX identification of SWCNT catalyst

SWCNT materials will generally have residual catalyst present in the sample at mass fractions that are greater than the EDX limit of detection (LOD) which is generally a mass fraction of 1 mg/g. When the catalyst concentration is greater than the LOD, signals will be observed in the EDX spectrum identifying the elemental make up of the catalyst or other impurities in the sample. One objective of this study was to determine the effectiveness of the purification method used to remove the catalyst. Also included in the case study are supplemental analytical testing results which support the SEM/EDX analysis.

A test portion of as-manufactured SWCNT sample was carefully pressed into a small piece of indium foil attached to a SEM sample stub. Figure C.2 shows a BE image taken at ×2 000 and 15 kV. The bright pixels in Figure C.2 are associated with a high atomic number material, believed to be catalyst particles. They are easily distinguished from the lower atomic number carbon matrix.

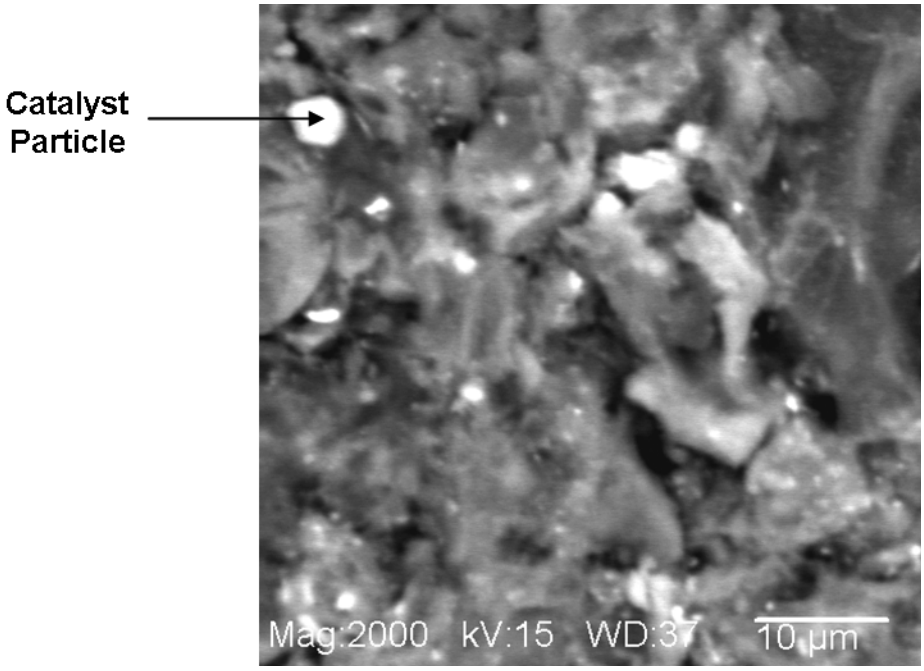

Figure C.2 — BE image of an as-manufactured SWCNT sample

An EDX scan taken at 15 kV, ×4 000 magnification, and at TV scan rates in another area of the as-manufactured SWCNT sample is shown in Figure C.3. Aside from the carbon signal, the only other elements detected are Mo and Co [along with a small signal from the indium (In) mounting foil.] The EDX spectrum of one of the larger catalyst particles shown by the arrow in Figure C.2 is displayed in Figure C.4. The Mo and Co signals are relatively larger than the C signal, since the beam is placed directly on the particle for analysis (spot mode). The carbon signal is assumed to come from the CNT walls. Confirmation for the presence of Mo can be achieved by repeating the analysis of the particle at 35 kV and recording the higher energy Mo Kα line at about 17,4 keV (spectrum not shown).

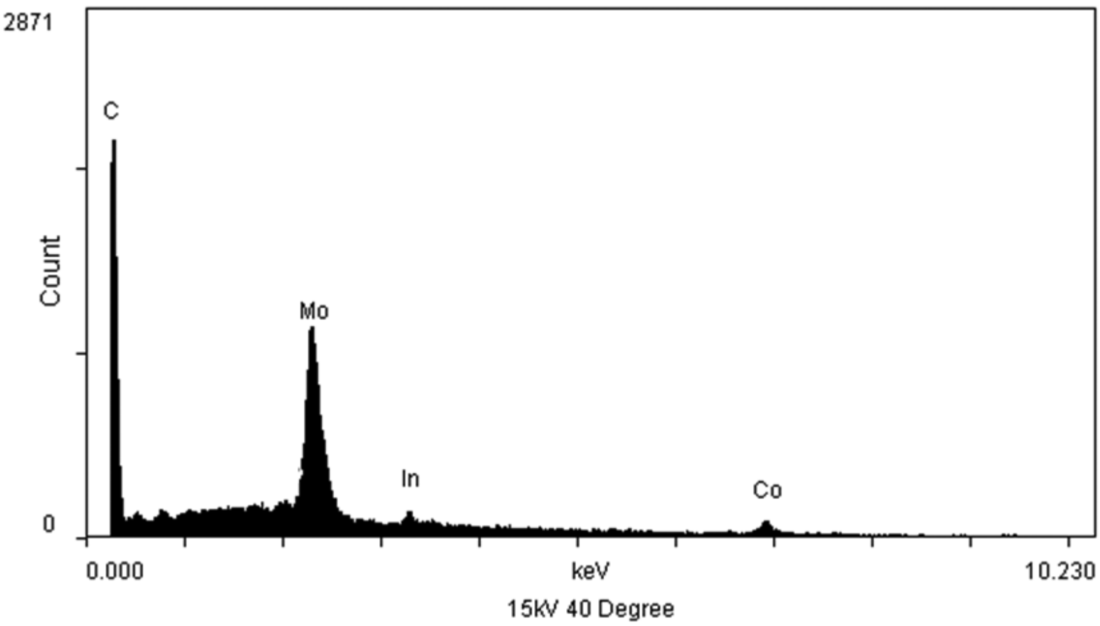

Figure C.3 — EDX spectrum of an as-manufactured SWCNT sample

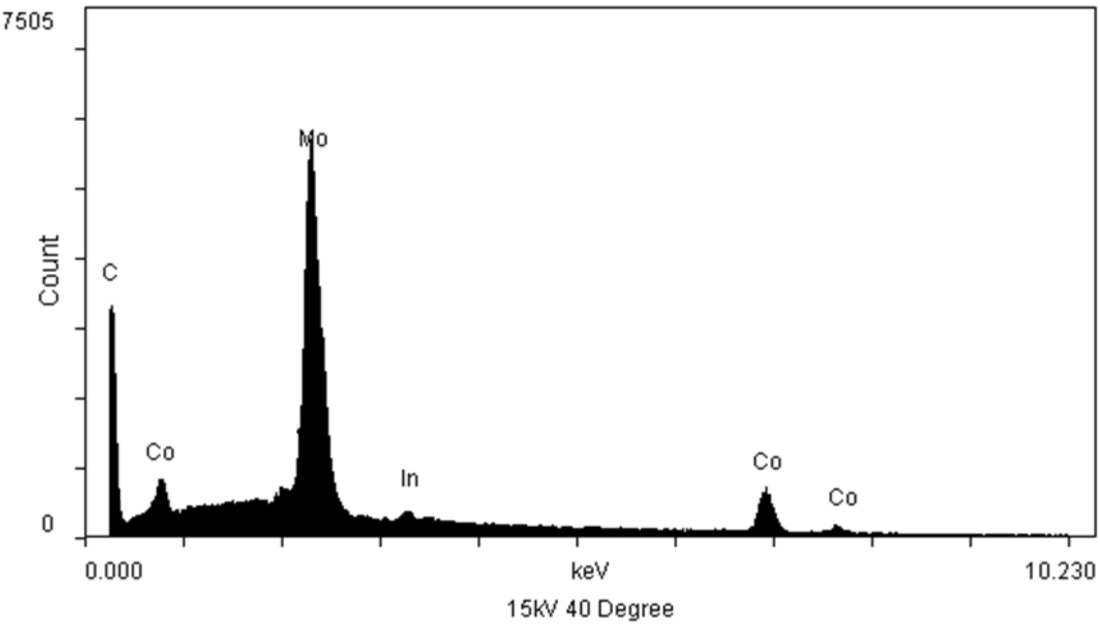

Figure C.4 — EDX spectrum of catalyst particle identified in Figure C.2.

The Mo and Co concentrations can be estimated if necessary by semi-quantitative analysis of the EDX spectrum. If obtained, these results should be verified by quantitative inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis, which is a metrologically superior technique. The ICP-AES results for these samples are presented in C.3 below.

An EDX scan of the purified SWCNT material is shown in Figure C.5. Bright catalyst particles are still observed in the BE image (not shown). However, the EDX scan taken at 15 kV and ×1 000 magnification shows that the Mo and Co signals are considerably smaller (relative to C) compared to a similar scan of the as-manufactured material (compare to Figure C.3). The EDX semi-quantitative analysis reflected a possible change in the Mo/Co ratio compared to that observed in the as-manufactured sample. This was verified by ICP-AES analysis (see Table C.1 below). The purification treatment apparently preferentially removes Co from the material.

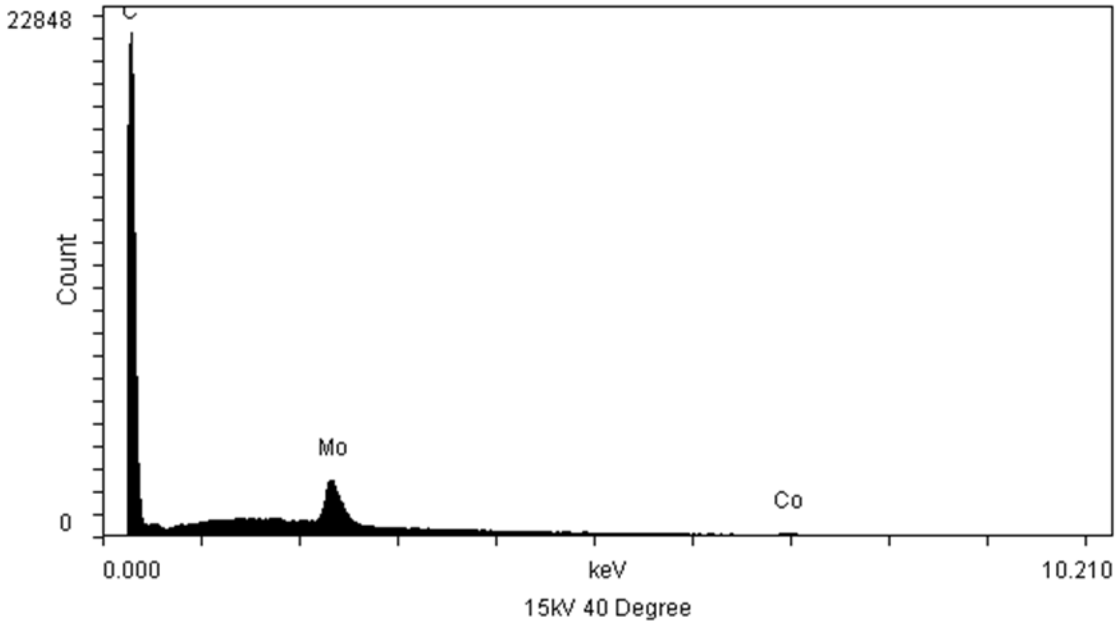

Figure C.5 — EDX spectrum of purified SWCNT sample

C.3 Other supportive characterization

In order to confirm and enhance the SEM/EDX analysis, the SWCNT samples were also analyzed by thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and high resolution transmission electron microscope (HRTEM) analysis. These results are briefly discussed here.

XPS survey scans of the purified SWCNT material detected small O, Mo and trace N signals. The N 1s binding energy at about 403 eV is typical of oxidized nitrogen (NO_X) species, which is probably a residue of the purification treatment. Two Mo peaks were observed; one at about 232,3 eV and the second at about 228,5 eV. The lower binding energy peak is consistent with a reduced Mo oxidation state associated with the catalyst alloy, and/ or molybdenum carbide. The second peak is characteristic of oxidized Mo (MoO_3).

Thermogravimetric analysis from room temperature to 850 °C in air was performed on both samples. The primary oxidative weight loss peak from the SWCNT material is around 420 °C to 425 °C. The final ash residues from the TGA are 8,9 %, and 3,1 %, from the as-manufactured and purified samples, respectively.

NOTE 1 Additional information on thermogravimetric analysis of SWCNTs is given in ISO/TS 11308.

ICP-AES analysis provides quantification of the elements detected. A “normal” scan consists of the analysis of 22 common elements of interest. A list of the major elements detected in the analysis is provided in Table C.1.

To support the EDX results, additional TGA and ICP-AES characterization of the CNT sample is highly advisable.

Table C.1 — ICP-AES quantitative analysis of SWCNT samples (mass fraction in µg/g)

Element	**As-manufactured**	**Purified**
Mo	56 900	28 160
Co	14 310	4 700
Na	1 300	300
Fe	530	570
Ca	220	460
Mn	5	10
Total (%)	7,4	3,5
Mo/Co mass ratio	4,0	6,0

A high resolution TEM micrograph of the purified SWCNT sample is shown in Figure C.6. HRTEM methods are beneficial to use as supportive evidence to the SEM/EDX analysis of SWCNTs. As shown in Figure C.6, HRTEM analysis can directly observe and measure individual SWCNTs, having diameters as small as 0,64 nm.

NOTE 2 Additional information on HRTEM analysis of SWCNTs is given in ISO/TS 10797.

Figure C.7 shows an HRSEM image originally taken at ×325 000 magnification of the purified SWCNT material which has been dispersed with surfactants, and applied onto an insulating substrate. HRSEM analysis clearly shows the presence of carbon nanotube bundles. However, on a non-ideal substrate, HRSEM analysis cannot easily measure diameters or wall thickness, differentiate SWCNTs from MWCNTs, amorphous, and other filamentous forms of nanocarbon materials. In the micrograph, there are hints of individual CNTs, but it is difficult or impossible to accurately measure their diameter and wall structure. The bright spots in the micrograph are insulating, and therefore charging under the electron beam (the sample was not metal coated). The charging areas are possibly due to incomplete coverage, residual catalyst, and/or dispersants in the coating.

This case study shows that the primary value of SEM/EDX analysis is to rapidly analyze a sample of CNT material, in order to:

1) assess the relative purity levels (catalyst content) with EDX analysis;

2) with high resolution SEM imaging, be able to directly observe features that are consistent with the presence of high-aspect ratio carbon nanotube materials (within the resolution limits of the particular SEM method being employed).

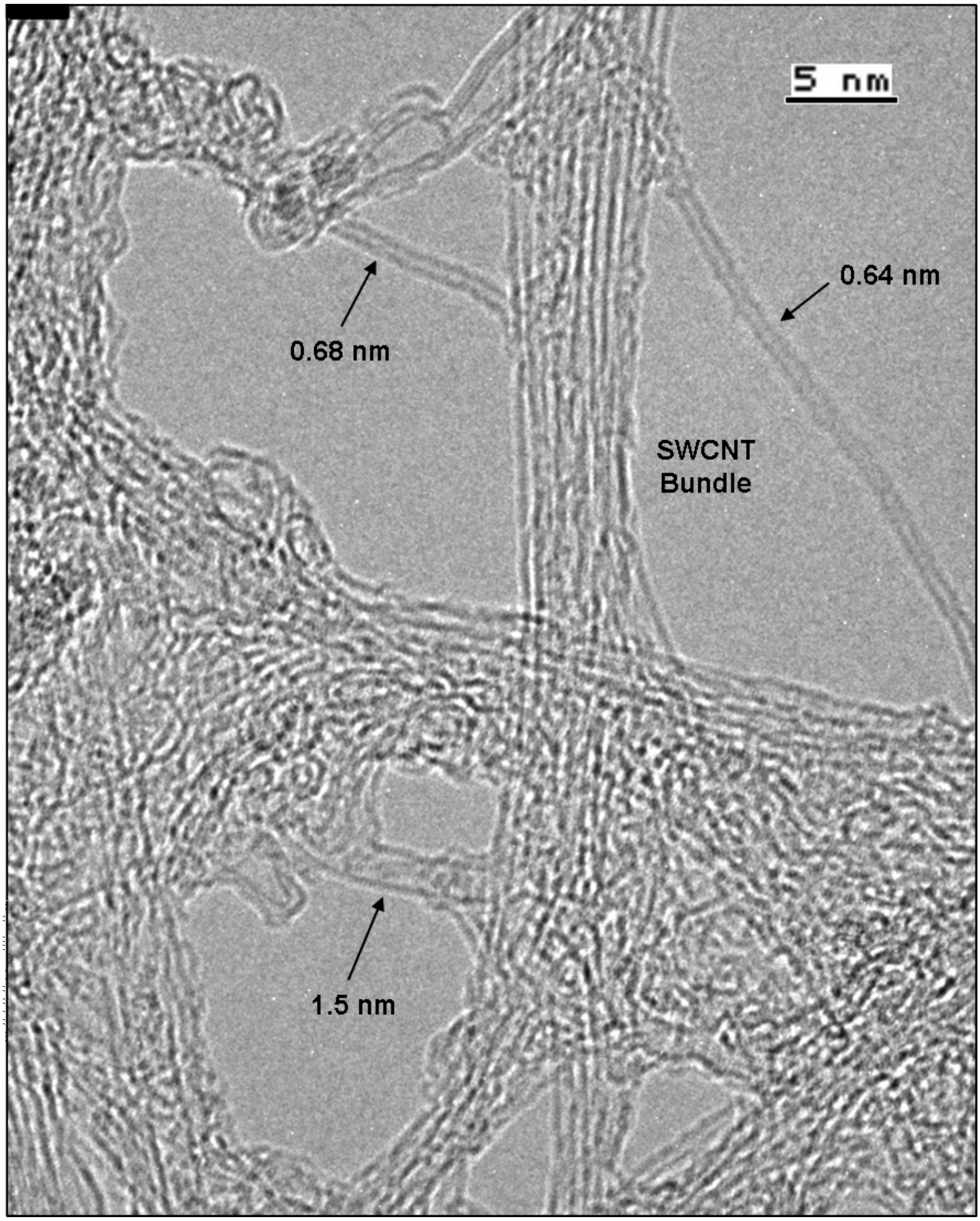

Figure C.6 — HRTEM analysis of purified SWCNT sample

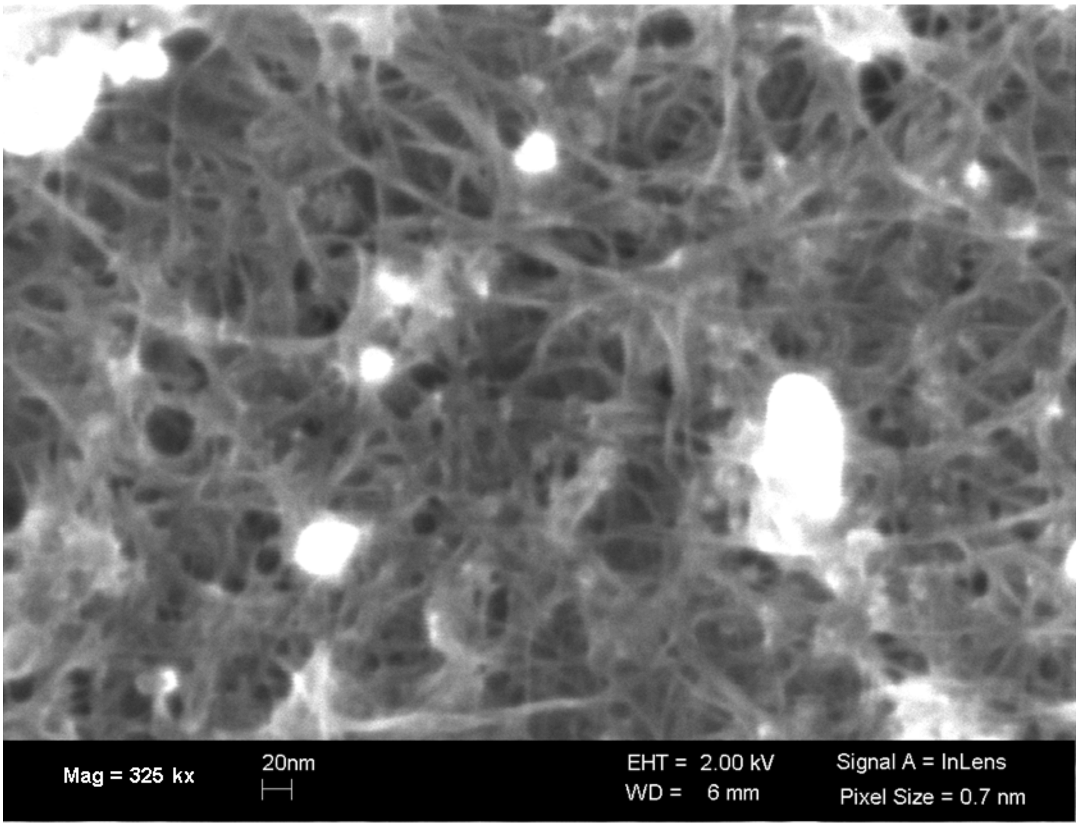

Figure C.7 — HRSEM analysis of dispersed SWCNT on an insulating substrate

Annex D
(informative)

Examples of SEM/EDX analysis of SWCNTs

D.1 HRSEM images of SWCNTs

A small amount of the SWCNT powder was placed in isopropyl alcohol, dispersed in an ultrasonic bath for 5 min. A few small drops were placed on a silicon wafer, air dried, and examined by SEM. A high resolution image is shown in Figure D.1. Extensive bundling of the SWCNTs is evident. Large bundles branch off into smaller ones, occasionally forming a single nanotube offshoot.

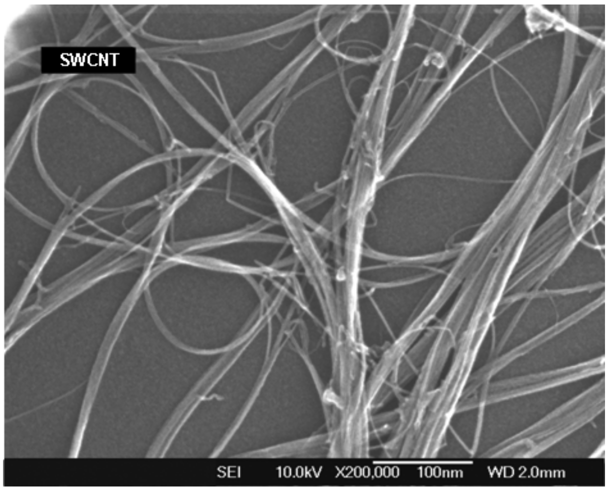

Figure D.1 — HRSEM image of SWCNT sample on a silicon wafer

Figure D.2 shows an STEM image of SWCNTs taken in a conventional HRSEM using an STEM attachment option. With this mode it is possible to resolve individual SWCNTs. Bundling of the nanotubes is also easily observed.

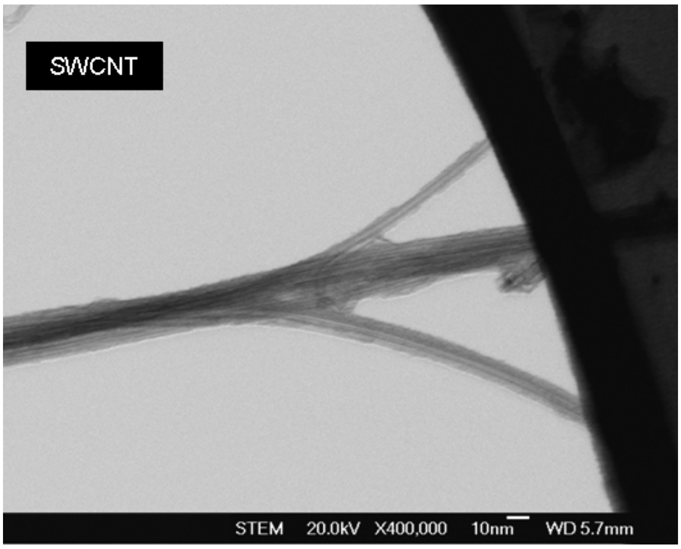

Figure D.2 — STEM/SEM image of SWCNTs

D.2 HRSEM images and EDX analysis of SWCNTs

Figure D.3 displays an HRSEM secondary electron (SE) image of SWCNT material showing the area of interest.

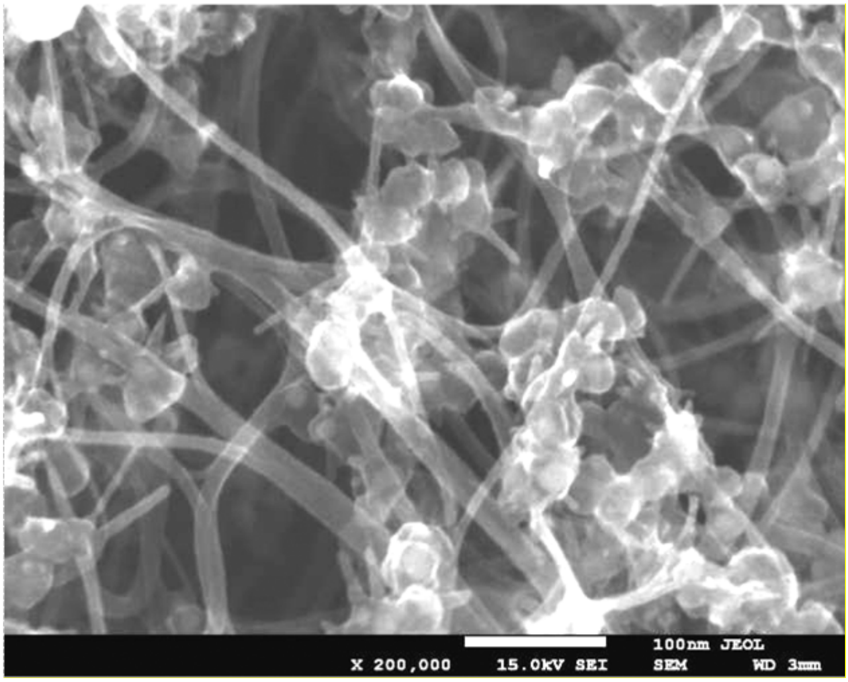

Figure D.3 — HRSEM SE image of SWCNT material

Figure D.4 shows the HRSEM backscattered electron (BE) image taken in the same area as displayed in Figure D.3. The bright pixels in the BE image arise from catalyst particles in the sample. The backscattered features are generally smaller than the larger features observed in the SE image.

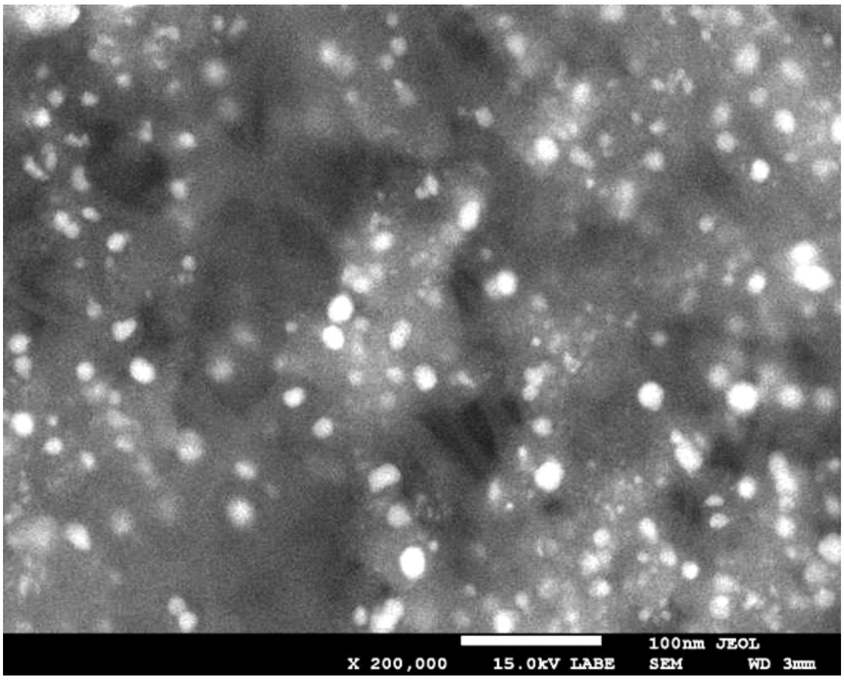

Figure D.4 — HRSEM BE image of SWCNT material

Figure D.5 shows a qualitative EDX scan of an SWCNT sample identifying the composition of the catalyst elements Ni and Y.

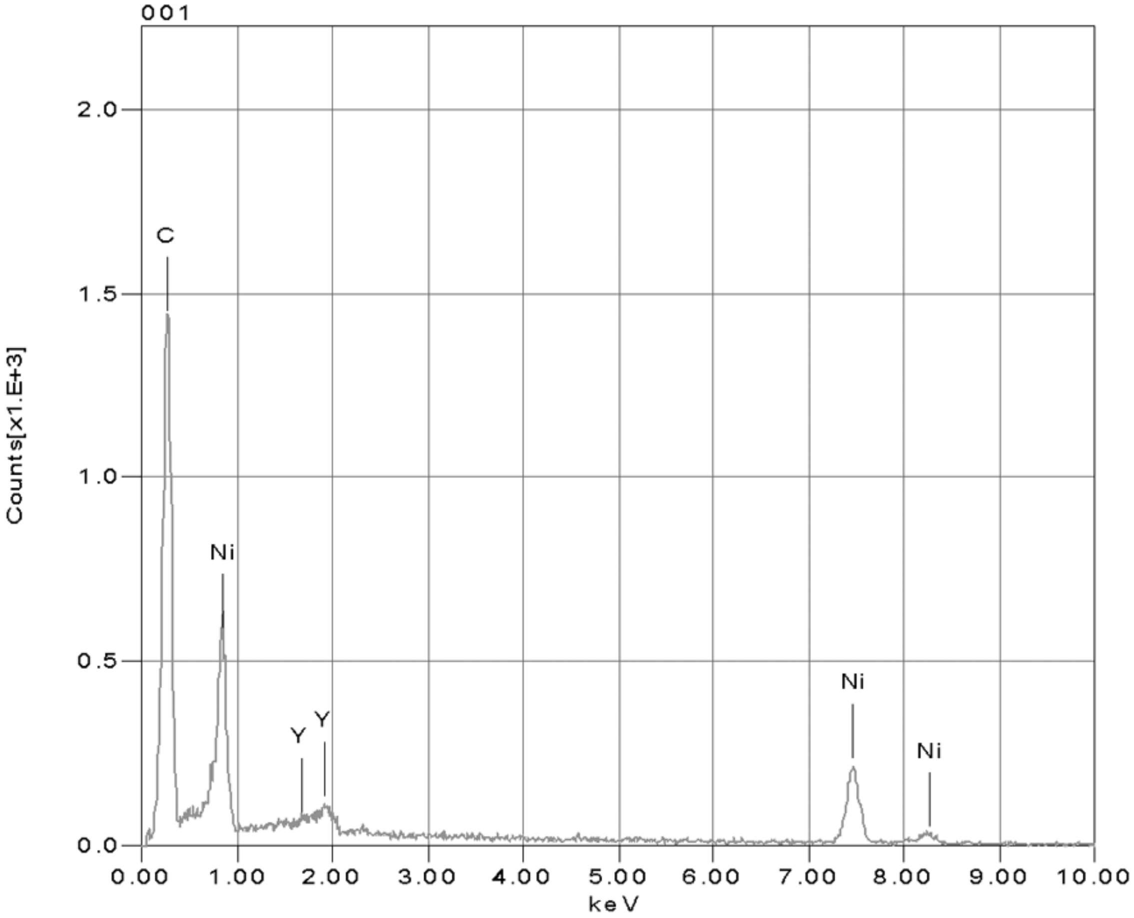

Figure D.5 — EDX analysis of SWCNT material

D.3 Au/Pd coating artefact in HRSEM images of SWCNTs

Figure D.6 shows an HRSEM image of an SWCNT sample on an insulating substrate without the application of a conductive coating. The bright spots in the micrograph are insulating, and therefore, charging under the electron beam. These are possibly due to residual catalyst and/or dispersants in the coating.

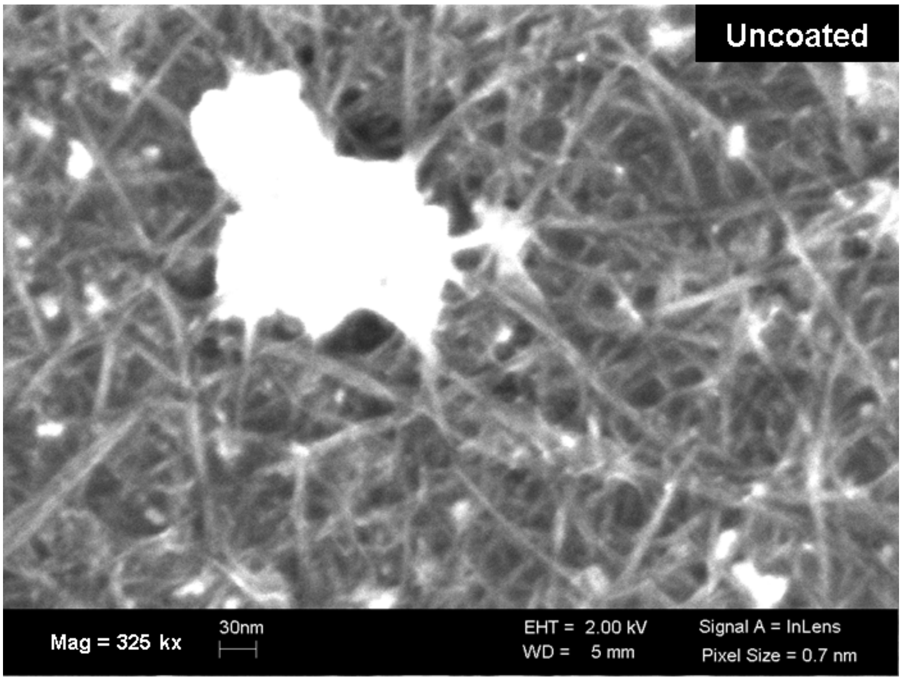

Figure D.6 — HRSEM SE image of uncoated SWCNT material on an insulating substrate

Figure D.7 shows an HRSEM image of the same SWCNT sample displayed in Figure D.6 demonstrating the coarsening effect of nanotube features resulting from sputter coating with Au/Pd. HRSEM images show that the Au/Pd particle size is about 3 nm to 5 nm.

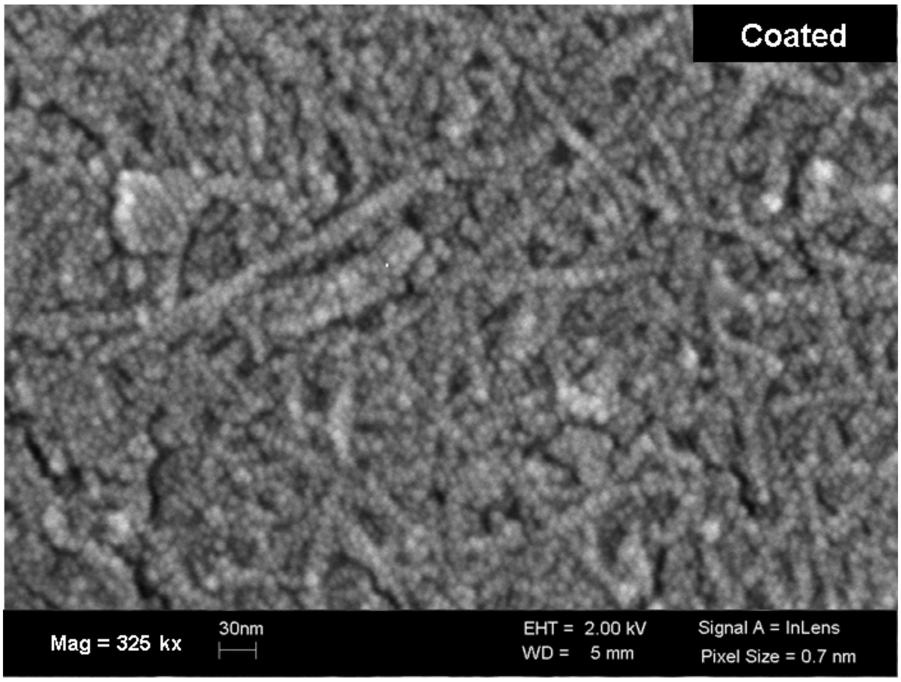

Figure D.7 — HRSEM SE image of Au/Pd sputter coated SWCNT material

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1) Under preparation.

2) Under preparation.

3) Under preparation.

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