TECHNICAL SPECIFICATION

ISO/TS 10797

First edition
2012-06-01

Nanotechnologies — Characterization of single-wall carbon nanotubes using transmission electron microscopy

Nanotechnologies — Caractérisation des nanotubes de carbone monofeuillet par microscopie électronique à transmission

Reference number
ISO/TS 10797:2012(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

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 10797 was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

Introduction

Carbon nanotubes (CNTs) are nanomaterials composed of concentric layers of graphene sheets in the form of cylindrical tubes placed along the longitudinal fibre axis. Single-wall carbon nanotubes (SWCNTs) are seamless cylinders derived from the honeycomb lattice representing just a single atomic layer of graphene sheet. The transmission electron microscope (TEM), and especially its high-resolution version (HRTEM), were the first instruments that revealed the unique structural features of carbon nanotubes. TEM/HRTEM has played an essential role in the research and development of carbon nanotube materials. It has the advantage of being a "direct" technique that avoids the imposition of physical or mathematical assumptions. At the same time, it provides a variety of experimental results and information-rich images that make the investigation of a wide variety of samples possible. Beyond imaging, TEM, along with other techniques described in this Technical Specification, can provide qualitative purity assessment of SWCNT samples. In addition, it can also reveal detailed morphological and structural features of carbon nanotubes such as graphene wall structure, defects, diameter, length, bundle size and orientation, and the existence of materials and nanoparticles[8] besides SWCNTs. In other operational modes, it is also possible to study the chirality and thermal and mechanical characteristics of individual nanotubes. It is important to develop a systematic protocol for using TEM in order to acquire reliable and comprehensive information about a sample containing SWCNTs.

The transmission electron microscope operates on similar basic principles as the optical microscope but uses electrons instead of light. A beam of electrons is focused onto a thin, electron-transparent sample, allowing an enlarged version to appear on a fluorescent screen, a layer of photographic film, or on an array detector that is sensitive to electrons. Modern instruments are equipped with a computer-linked digital imaging system that can also record real-time images.

The HRTEM can investigate crystal structure by phase contrast imaging, where images are formed due to differences in the phase of electron waves scattered through a thin sample. Resolution of the TEM is limited by spherical and chromatic aberrations, but new generations of instruments with advanced electron-optical columns have significantly lowered these aberrations. Software correction of spherical aberration has allowed the production of meaningful images with sufficient resolution at magnifications of many millions times. The ability to determine the positions of atoms within materials has made the HRTEM an indispensable tool for nanotechnology research and development.

Nanotechnologies — Characterization of single-wall carbon nanotubes using transmission electron microscopy

1 Scope

This Technical Specification establishes methods for characterizing the morphology of single-wall carbon nanotubes (SWCNTs) and identifying the elemental composition of other materials in SWCNT samples, using transmission electron microscopy and chemical analysis by energy dispersive X-ray spectrometry.

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, *Microbeam analysis — Scanning electron microscopy — Vocabulary*

ISO 29301, *Microbeam analysis — Analytical transmission electron microscopy — Methods for calibrating image magnification by using reference materials having periodic structures*

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

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 22493, ISO/TS 80004-3 and the following apply.

3.1
aggregate of nanotubes
particle comprising strongly bonded or fused particles of individual nanotubes and/or bundles of nanotubes

NOTE 1 This is often the form of as-produced SWCNT material. The forces holding an aggregate together are strong forces, for example, covalent bonds, or those resulting from sintering or complex physical entanglement.

NOTE 2 Aggregates are termed “secondary particles” and the original source particles are termed “primary particles”.

NOTE 3 Adapted from ISO/TS 27687:2008, definition 3.3.

3.2
bundle of nanotubes
single strand of two or more nanotubes held together by van der Waals forces

3.3
bright-field TEM
TEM technique of electron illumination and imaging in which the direct electron beam passes through the sample and the image is formed only by the transmitted wave, by selecting the wave using an objective aperture on the back focal plane

NOTE 1 Generally, the portions of the sample that are thicker or that have a higher atomic number (Z) appear darker against a brighter background. In this mode the contrast, when considered classically, is formed directly by occlusion and absorption of electrons in the sample. Thicker regions of the sample, or regions with a higher atomic number will appear dark, while regions with no sample in the beam path will appear bright, hence the term “bright-field”.

NOTE 2 This will be included in a vocabulary on analytical electron microscopy, which is under preparation by ISO/TC 202/SC 1.

3.4
dark-field TEM
TEM technique of electron illumination and imaging in which the direct electron beam passes through the sample and the image is formed only by diffracted wave, by selecting the wave using an objective aperture on the back focal plane

NOTE 1 Crystalline parts of the sample disperse the electrons of the direct beam into discrete locations in the back focal plane. By the placement of apertures in the back focal plane, i.e. the objective aperture, desired portions of the reflections can be selected, thus only those parts of the sample that are causing the electrons to scatter to the selected reflections will be imaged. If the selected reflections do not include the unscattered beam, then the image will appear dark wherever no sample scattering to the selected peak is present – hence the term “dark-field”.

NOTE 2 Modern TEMs are often equipped with sample holders that allow the user to tilt the sample to obtain specific diffraction conditions. The wave that caused scattering and reflection (for example, Bragg reflection) in a crystalline sample will form a dark-field image by selecting a specific diffraction wave through objective apertures placed on the back focal plane of objective lens.

NOTE 3 High-angle annular dark-field imaging (HAADF) is highly sensitive to variations in the atomic number of atoms in the sample and produces so-called *Z*-contrast images, which yield useful information on the presence of metals on nanotubes and catalyst residues, even when these small metal particles are imbedded within amorphous carbon or catalyst support while otherwise invisible in bright-field imaging mode.

NOTE 4 This will be included in a vocabulary on analytical electron microscopy, which is under preparation by ISO/TC 202/SC 1.

3.5
electron energy loss spectrum
EELS
energy spectrum of electrons from a nominally mono-energetic source emitted after inelastic interactions with the sample, often exhibiting peaks due to specific inelastic loss processes

NOTE The electron energy loss spectrum, measured with an incident electron beam, is a function of the beam energy, the angle of incidence of the beam, the angle of emission, and the electronic properties of the sample (see Reference [3]).

3.6
energy-dispersive X-ray spectrometer
EDS
device for determining X-ray intensity as a function of the energy of the radiation

[ISO 23833:2006, definition 3.6.4]

3.7
purity of SWCNT sample
indication of the amount of material other than SWCNTs in SWCNT samples

NOTE High purity refers to a low amount of (metal) catalyst residues and other usual by-products, such as multiwall carbon nanotubes, carbon nanofibres, fullerenes, amorphous carbon and graphite onions, which can also be assessed by TEM.

3.8
transmission electron microscope
TEM
instrument that produces magnified images or diffraction patterns of the sample by an electron beam which passes through the sample and interacts with it

NOTE Adapted from ISO 29301:2010, definition 3.37.

3.9
selected area electron diffraction
SAED
technique in electron microscopy in which the crystal structure of a sample area selected by an aperture is examined

NOTE Adapted from ISO 13794:1999, definition 2.38.

3.10
scanning transmission electron microscope
STEM
instrument that produces magnified images or diffraction patterns of the sample by an electron beam, which is focused into a narrow spot, scanned over the sample in a raster and which passes through the sample and interacts with it

4 General principles

4.1 TEM imaging and analysis

TEMs are valuable in very high-resolution imaging and in the analysis of the characteristics of carbon nanotubes, other forms of carbon, and other impurities in SWCNT samples. The diameters of SWCNTs generally range from less than 1 nm to more than 5 nm. Their lengths can vary considerably and can be greater than 10 mm. Due to the attractive forces between the tubes, SWCNT samples are entangled, i.e. large numbers of individual nanotubes form so-called bundles or ropes. The diameters and the lengths of the bundles are considerably larger than those of individual tubes. TEM can be used for fine structure measurements such as tube diameter, number of walls, chirality and defects, orientation, packing morphology and detailed structure of bundles. Length measurements in the TEM are limited.

4.2 EDS analysis

Another strength of the TEM is that, in combination with EDS analysis, it can be used to determine the elemental composition of non-carbonaceous constituents of CNT samples down to the nanometre-scale. All modern TEM/EDS systems can detect carbon and other impurities with good sensitivity and are capable of identifying various constituents and performing semi-quantitative analyses that are indispensable in SWCNT sample comparisons. The characteristic beam-sample interaction volume in TEM samples is smaller and the peak-to-background ratio of the TEM/EDS is significantly better than that of the typical samples of a scanning electron microscope (SEM)/EDS case. These allow for better sample differentiation, and comprehensive semi-quantitative point, line and area elemental analysis.

4.3 Additional characterization methods

Beyond common TEM imaging and TEM/EDS analysis, there are other TEM-based imaging and analytical techniques that can help in finding and characterizing various constituents of SWCNT samples. These can provide information on elemental composition, crystal structure, chemical bonding and doping, electronic state, and the various materials within the carbon nanotubes, etc. Among them are selected area electron diffraction and electron energy loss spectroscopy. It is expected that the use of these techniques will become more widespread as the number of applications of carbon nanotubes increases in the future.

4.4 Applicability to multiwall carbon nanotube analysis

The methods described in this Technical Specification for SWCNTs may also be applied to the analysis of multiwall carbon nanotubes (MWCNTs). MWCNTs consist of two or more concentric tubes of graphite. The interlayer distance in MWCNTs is close to the distance between graphene layers in graphite, approximately 0,34 nm. MWCNTs, depending on the number of graphene layers in their walls, have considerably larger outer diameters than SWCNTs. Double-wall carbon nanotubes are especially important because their morphology and properties are similar to SWCNTs but their resistance to chemicals is significantly better, which is important when functionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. The sample preparation and dispersion methods are similar to those used

for SWCNTs and all methods described here for the imaging, characterization and analysis of SWCNTs also apply to MWCNTs.

NOTE Additional information on MWCNT characterization can be found in ISO/TR 10929.

5 Sample preparation

5.1 General principles

Carbon nanotubes might be hazardous materials, therefore it is very important to observe relevant safety procedures related to the handling, preparation, use and disposal of SWCNT materials and samples. It is recommended that only trained scientific personnel handle carbon nanotube materials. Personal protective equipment should be used, including disposable gloves, safety glasses, laboratory coats, filter respirators, etc. Sample preparations should be carried out in a vented fume hood or glove box equipped with suitable air filters to avoid inhalation of SWCNT material (see References [2] and [10]).

Appropriate sample preparation is essential for reliable and reproducible characterization and measurement of SWCNT samples and establishes a uniform basis for comparative measurements. Fabrication, treatment and sample preparation methods might significantly affect the physical properties of SWCNTs. Therefore preparation methods that produce minimal alteration of the sample material should be used wherever possible.

TEM measurements are limited to thin samples. The shallow depth of penetration of electrons into solids forces the use of very thin samples, especially in high-resolution operating mode and with low primary electron energies. Depending upon the nature of the material and the desired resolution, the optimal sample thickness varies from 10 nm to 150 nm.

Commercially available SWCNT samples are usually in the form of dry powder or liquid suspensions. SWCNTs present specific challenges in the preparation of TEM samples. The nanotubes usually form bundles, which are difficult to disperse into individual nanotubes. Ultrasonic treatment can separate them, but can also damage their structure, even shortening the tube length, and alter the macroscopic morphology. Thus, it is generally recommended that mechanical treatment be minimized or not used in the preparation of thin carbon nanotube samples. Techniques such as ion milling, electro-polishing, grinding, replication/extraction and preferential chemical etching to create thin, electron-transparent films, are generally not recommended for preparing SWCNT samples.

At least three samples shall be prepared from the SWCNT material. The number of samples to prepare depends on the quality of the SWCNT material and the success of the sample preparation, which can be established with the examination of the three samples. If those show dissimilarity, more samples shall be prepared and measured. The key is to ensure relevant and reliable results and to avoid insufficient or excessive sampling.

The sample preparation procedures, including ultrasonic treatment conditions together with time (or visual end-point), as well as any pre-treatment or pre-washing of SWCNT samples, shall be reported in detail.

NOTE Various methods of preparing carbon nanotube samples for TEM analysis have been documented in pertinent literature[11][12][13].

5.2 Choice of TEM grid

The choice of TEM grid is important in sample preparation, imaging and measurements, as the type and suitability of the grid depend on the SWCNT sample and the intended use. A regular, 3,05 mm diameter copper grid with a 200 mesh size is recommended in general and for the purpose of purity analysis of carbon nanotubes. This type of grid has many 97 µm × 97 µm openings that, with successful sample preparation, allow for a large number of measurements. Other types of grids can be also suitable but their elemental composition should not interfere with the elemental analysis of the impurities of SWCNT material.

If special treatment such as heating is required, then molybdenum grids, or grids with silicon carbide membrane windows, are suitable, as these can work at high temperatures.

NOTE 1 An index grid provides index marks along each grid line, thus allowing for observations of easily identifiable locations and quantitative measurements or multiple examinations of the same features, even by different operators.

NOTE 2 Some materials can be self-supportive on a TEM grid without additional support film. The complex macroscopic morphology of carbon nanotubes usually requires a thin section in order to achieve satisfactory contrast and resolution, and makes self-support on a bare grid rather difficult without special processing. Both carbon and holey or lacey carbon films are suitable for supporting carbon nanotubes (thinner films are preferred). See B.1.1 for additional information.

5.3 Powder and film samples

5.3.1 Dry powder sample

In this case, dry SWCNTs are used directly for sample preparation.

a) Place a TEM grid into an appropriate holder.

b) Move the grid inside the fume hood or glove box, where the sample preparation will take place.

c) Select the SWCNT sample material and transfer it to the fume hood or glove box, and open its container.

d) Attach, by lightly pressing, a very small amount (approximately 0,01 mg) of SWCNT material with a sharp needle or a pair of narrow tweezers to the top surface of the TEM grid.

e) Remove loose sample material by gently knocking the holder against a hard surface. A clean, gentle nitrogen jet, briefly applied, may also be used.

f) Alternatively, place a droplet of organic solvent such as 2-propanol (isopropyl alcohol) or 2-butanol on top of a dry sample-loaded grid and allow it to dry. This can help “pull” the dry SWCNTs down to the grid surface as the solvent evaporates.

g) Transfer the grid sample directly to the TEM or into a storage box for later work.

NOTE 1 This method has the advantage of maintaining the original macroscopic morphology, but it also sometimes creates problems by leaving the sample too thick to allow transmission of electrons.

NOTE 2 Due to its poor adhesion, a loosely applied, excessive amount of SWCNT material can easily move away from the grid surface during pump down. This loose material might adhere to the strongly magnetic parts of the instrument, which can result in detrimental effects and should thus be avoided.

5.3.2 Dry film sample

In this case, dry SWCNTs are first suspended in a solvent and turned into a thin film, or a mat, which is then deposited onto a TEM grid. Use of a dry film can improve the adhesion of the SWCNTs to the TEM grid because many of the nanotubes are “locked” in place.

a) Place a TEM grid into an appropriate holder.

b) Move the grid inside the fume hood or glove box, where the sample preparation will take place.

c) Select the SWCNT sample material and transfer it to the fume hood or glove box, and open its container.

d) With a sharp needle, or pair of narrow tweezers, insert a very small amount (approximately 0,01 mg) of SWCNT material into a 20 ml vial and add 10 ml clean water or 2-propanol.

e) Once the SWCNT material is soaked completely, filter down a droplet onto a 0,2 µm to 0,5 µm pore size, hydrophilic polypropylene or polycarbonate membrane to form a mat.

f) Peel off a small portion of the dry mat and press it onto a clean TEM grid (without a film).

g) Transfer the grid sample directly to the TEM or into a clean, particle-free storage box for later work.

NOTE 1 It is unavoidable that many sections of the mat prepared by this method will be too thick for TEM work or contain too many SWCNTs.

NOTE 2 As the suspended SWCNTs dry, differences in the spatial distribution of carbon nanotubes and impurities develop, i.e. the original distribution of the various constituents of the SWCNT material becomes altered. Additionally, an inappropriate solvent can remove some forms of impurities, resulting in an inaccurate account for the purity of the material.

5.4 Liquid suspension sample

In this case, SWCNTs in liquid suspension or small aggregates of dry SWCNTs that were first suspended in a solvent are used for sample preparation. The SWCNTs are separated by ultrasonic treatment at room temperature before being deposited onto the TEM grid.

a) Place a TEM grid into an appropriate holder.

b) Move the grid inside the fume hood or glove box, where the sample preparation will take place.

c) Select the SWCNT sample material and transfer it to the fume hood or glove box, and open its container.

d) With a sharp needle, or a pair of narrow tweezers, insert a very small amount (approximately 0,01 mg) of SWCNT material into a 20 ml vial and add 10 ml 2-propanol (or chloroform, taking appropriate safety measures).

e) Transfer the vial to an ultrasonic bath and apply ultrasonic treatment to reach adequate separation of SWCNTs. With small-size laboratory ultrasonic apparatus, 5 min to 30 min treatment is usually sufficient.

f) Deposit a droplet of the liquid containing the SWCNT material onto a bare TEM grid.

g) Allow the sample to dry completely in air.

h) Remove loose sample material by gently knocking the holder against a hard surface. A clean, gentle nitrogen jet, briefly applied, may also be used.

i) Transfer the grid sample directly to the TEM or into a clean, particle-free storage facility for later imaging.

NOTE 1 The ultrasonic treatment should last for as short a time as possible. Ultrasonic treatment that is too long or too high energy will significantly alter the properties of the sample. The right ultrasonic treatment conditions depend on the sample and on the type of ultrasonic equipment and can be found by experimentation, starting with short treatment times and energies. Ultrasonic treatment in an ice water bath minimizes possible thermal damage to the SWCNTs.

NOTE 2 As the droplet of the suspended SWCNT sample dries, differences in the spatial distribution of carbon nanotubes and impurities develop, i.e. the original distribution of the various constituents of the SWCNT material becomes altered. Dispersion by ultrasonic treatment also has a similar effect. Additionally, an inappropriate solvent can remove some forms of impurities, resulting in an inaccurate account for the purity of the material.

5.5 Composite sample

In this case, a TEM sample of SWCNTs is prepared by embedding the nanotubes in epoxy or plastic matrix and then cutting thin slices of material with an ultra-microtome. This sample preparation method damages and removes some of the SWCNTs, but certain important SWCNT characteristics can still be investigated.

a) Place a TEM grid into an appropriate holder.

b) Move the grid inside the fume hood or glove box, where the sample preparation will take place.

c) Select the SWCNT sample material and transfer it to the fume hood or glove box, and open its container.

d) With a pair of narrow tweezers, add 0,1 g of SWCNT material to 10 g of epoxy with a premixed curing agent and mix them thoroughly.

e) Let the composite cure at room temperature for as long as is needed for complete curing.

f) Shape the cured block of nanotube-epoxy into a 3 mm rod and secure it in the ultra-microtome.

g) Cut 20 nm to 90 nm thin slices of the nanotube-epoxy sample (the thickness can be judged by the light transparency of the slice). Collect the slices from the water bath.

h) Deposit a nanotube-epoxy slice directly onto a bare TEM grid by applying light pressure.

i) Transfer the grid sample directly to the TEM or into a clean, particle-free storage facility for later imaging.

NOTE The significance of this method is that it is relevant to an important, practical use of carbon nanotubes, which is the production of composite materials with desired properties. Evaluation of various properties of embedded CNTs is more limited than that of freestanding CNTs. This method can also be applied to the investigation of nanotube-polymer composite materials. See B.1.2 for additional information.

6 Measurement procedures

6.1 TEM examination of an SWCNT sample

6.1.1 Large field-of-view (more than 1 µm) examination

After setting the correct instrument parameters and attaining the optimal beam conditions for high resolution, it is important to start the SWCNT sample investigation at low magnification, i.e. at large field-of-view. The largest field-of-view (minimum magnification) depends on the TEM's capabilities and the sample.

A quick survey of the sample can determine whether the quality of sample preparation is acceptable and whether the minimum of three samples provides sufficient results. Where it is advantageous, use additional dark-field imaging to expose the presence of catalyst particles or other impurities in the SWCNT material.

Large and small impurities, such as catalyst and metal particles, large carbon fibres, MWCNTs and other carbon material are visible on various field-of-view images; therefore the best field-of-view and pixel resolution, based on the characteristics of the SWCNT sample, and the TEM, can be determined. The key is to acquire images at as high a resolution as possible at the field-of-view that provides relevant information.

Table 1 summarizes the recommended settings for large and small fields-of-view and EDS analyses.

6.1.2 Small field-of-view (less than 1 µm) examination

The finest details of SWCNT samples, including individual SWCNTs and very small, nanometre-scale impurities, elemental composition, wall structure, defects, lattice information, etc., can be examined and measured only in small field-of-view images. The very small field-of-view range is where TEM instruments provide information that is not available with other instrumentation. At smaller than 100 nm field-of-view images, fine details of SWCNTs can be revealed. Where it is advantageous, use additional dark-field imaging to expose the presence of catalyst particles or other impurities in the SWCNT material.

The TEM image scale (magnification) in both x and y directions shall be calibrated using the procedures set out in ISO 29301 and a certified reference material (CRM), if available. CRMs may have accompanying instructions to assist proper calibration. Alternatively, reference samples with known parameters (e.g. crystal lattice parameters) can be used. It is important to recognize that the magnification, and hence the scale calibration, will change depending upon the placement of the sample within the microscope column. Therefore, reproducible sample positioning is essential to minimize this problem, for example, by positioning the sample at the so-called eucentric height. This is a repeatable sample position and thus helps to maintain a consistent sample location and scale calibration.

Table 1 summarizes the recommended settings for large and small fields-of-view imaging and EDS analysis.

The quality of the TEM images, especially at small fields-of-view, can vary considerably due to sample charging, electron-beam-induced contamination and other detrimental effects. Annex B provides essential information about the key elements of TEM investigations useful for SWCNT characterization. Additional information can be found in Annexes C and D.

6.2 EDS analysis of an SWCNT sample

TEM and STEM-based EDS analysis is capable of providing information at very small fields-of-view and can identify the elemental composition of even nanometre-sized particles. An additional advantage of TEM-based EDS is that the characteristic X-ray peaks of the constituents of the sample are on a small continuous background. Therefore, better sensitivity can be realized over areas that fall into the openings of the TEM grid.