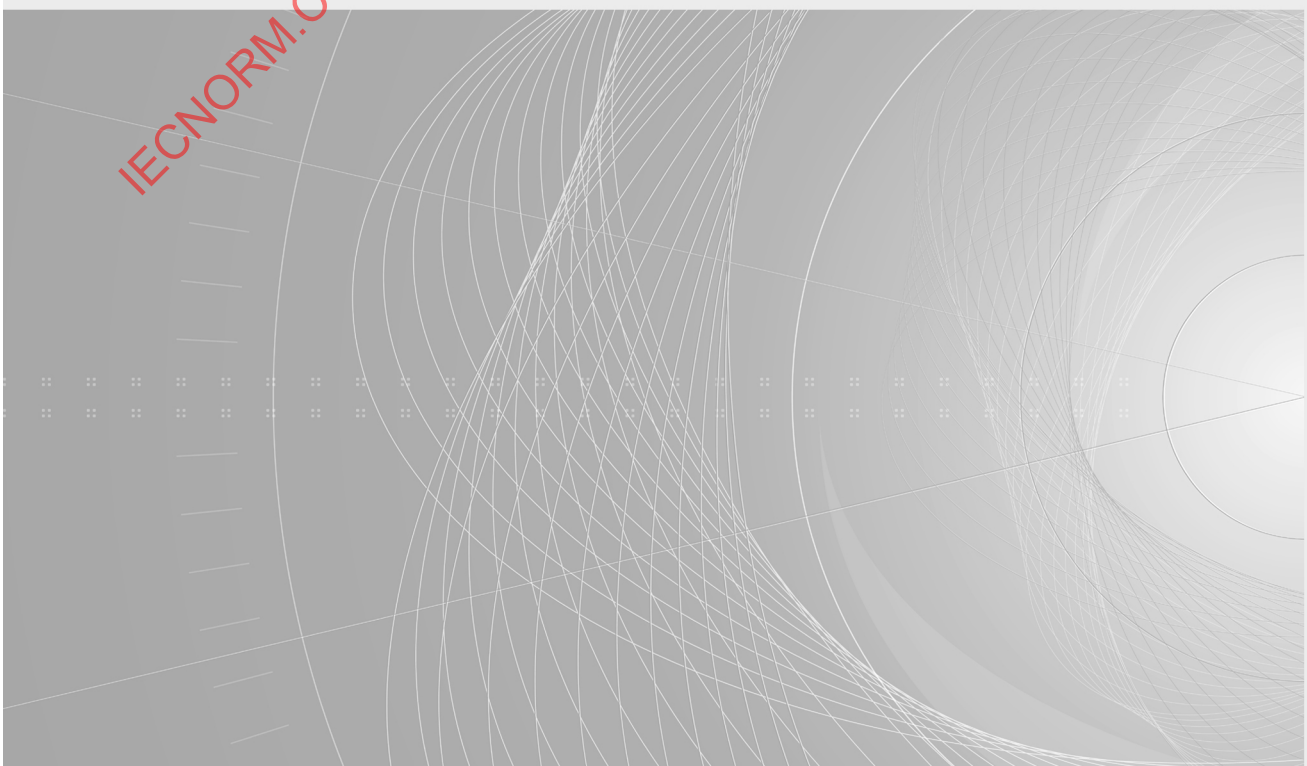
IEC TS 62607-6-14

Edition 1.0 2020-10

TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics – Part 6-14: Graphene-based material – Defect level: Raman spectroscopy



IEC TS 62607-6-14:2020-10(en)

IEC Central Office
3, rue de Varembé
CH-1211 Geneva 20
Switzerland

Tel.: +41 22 919 02 11
info@iec.ch
www.iec.ch

About the IEC
The International Electrotechnical Commission (IEC) is the leading global organization that prepares and publishes International Standards for all electrical, electronic and related technologies.

About IEC publications
The technical content of IEC publications is kept under constant review by the IEC. Please make sure that you have the latest edition, a corrigendum or an amendment might have been published.

IEC publications search - webstore.iec.ch/advsearchform
The advanced search enables to find IEC publications by a variety of criteria (reference number, text, technical committee,…). It also gives information on projects, replaced and withdrawn publications.

IEC Just Published - webstore.iec.ch/justpublished
Stay up to date on all new IEC publications. Just Published details all new publications released. Available online and once a month by email.

IEC Customer Service Centre - webstore.iec.ch/csc
If you wish to give us your feedback on this publication or need further assistance, please contact the Customer Service Centre: sales@iec.ch.

Electropedia - www.electropedia.org
The world's leading online dictionary on electrotechnology, containing more than 22 000 terminological entries in English and French, with equivalent terms in 16 additional languages. Also known as the International Electrotechnical Vocabulary (IEV) online.

IEC Glossary - std.iec.ch/glossary
67 000 electrotechnical terminology entries in English and French extracted from the Terms and Definitions clause of IEC publications issued since 2002. Some entries have been collected from earlier publications of IEC TC 37, 77, 86 and CISPR.

IEC TS 62607-6-14

Edition 1.0 2020-10

TECHNICAL SPECIFICATION

Nanomanufacturing – Key control characteristics – Part 6-14: Graphene-based material – Defect level: Raman spectroscopy

INTERNATIONAL ELECTROTECHNICAL COMMISSION

ICS 07.120

ISBN 978-2-8322-8940-2

CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

_____

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-14: Graphene-based material – Defect level: Raman spectroscopy

FOREWORD

1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as "IEC Publication(s)"). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.
2) The formal decisions or agreements of IEC on technical matters express, as nearly as possible, an international consensus of opinion on the relevant subjects since each technical committee has representation from all interested IEC National Committees.
3) IEC Publications have the form of recommendations for international use and are accepted by IEC National Committees in that sense. While all reasonable efforts are made to ensure that the technical content of IEC Publications is accurate, IEC cannot be held responsible for the way in which they are used or for any misinterpretation by any end user.
4) In order to promote international uniformity, IEC National Committees undertake to apply IEC Publications transparently to the maximum extent possible in their national and regional publications. Any divergence between any IEC Publication and the corresponding national or regional publication shall be clearly indicated in the latter.
5) IEC itself does not provide any attestation of conformity. Independent certification bodies provide conformity assessment services and, in some areas, access to IEC marks of conformity. IEC is not responsible for any services carried out by independent certification bodies.
6) All users should ensure that they have the latest edition of this publication.
7) No liability shall attach to IEC or its directors, employees, servants or agents including individual experts and members of its technical committees and IEC National Committees for any personal injury, property damage or other damage of any nature whatsoever, whether direct or indirect, or for costs (including legal fees) and expenses arising out of the publication, use of, or reliance upon, this IEC Publication or any other IEC Publications.
8) Attention is drawn to the Normative references cited in this publication. Use of the referenced publications is indispensable for the correct application of this publication.
9) Attention is drawn to the possibility that some of the elements of this IEC Publication may be the subject of patent rights. IEC shall not be held responsible for identifying any or all such patent rights.

The main task of IEC technical committees is to prepare International Standards. In exceptional circumstances, a technical committee may propose the publication of a Technical Specification when

- the required support cannot be obtained for the publication of an International Standard, despite repeated efforts, or
- the subject is still under technical development or where, for any other reason, there is the future but no immediate possibility of an agreement on an International Standard.

Technical Specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 62607-6-14, which is a Technical Specification, has been prepared by IEC technical committee 113: Nanotechnology for electrotechnical products and systems.

The text of this Technical Specification is based on the following documents:

Enquiry draft	Report on voting
113/495/DTS	113/536/RVDTS

Full information on the voting for the approval of this Technical Specification can be found in the report on voting indicated in the above table.

This document has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts of the IEC TS 62607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

IMPORTANT – The 'colour inside' logo on the cover page of this publication indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

INTRODUCTION

Graphene has been intensively studied by researchers from both academic and industrial communities due to its unique properties, which include exceptional thermal conductivity, great strength and excellent transparency. Defects in graphene influence its optical and magnetic performance, electronic structure and thermal conductivity, thus influencing its applications. Therefore, defect is a key control characteristic for the fabrication of high-quality graphene for desired applications.

One of the most useful methods to evaluate defect level in graphene is Raman spectroscopy, which is sensitive to the structure of samples. This method is efficient, non-contact and well-understood. The defect states and boundary states of realistic graphene material will induce a series of Raman scattering processes (Figure 1). Some of scattering processes are only associated with defective states, which are used in this document to analyse defect level in graphene powder.

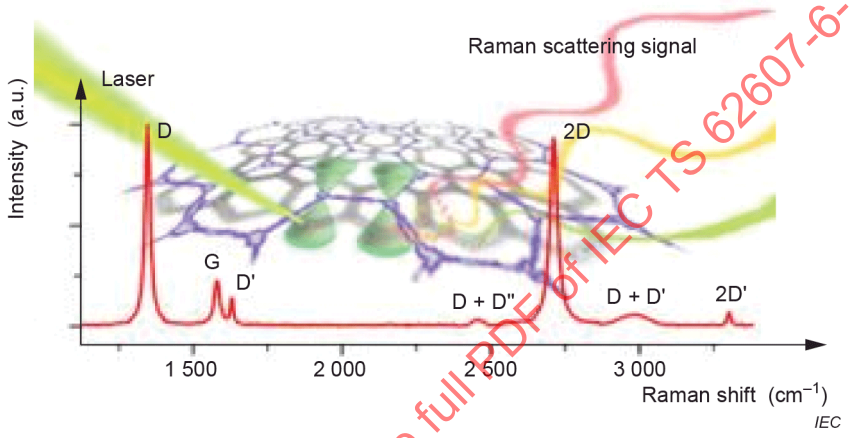


Figure 1 – Schematic diagram of Raman scattering processes in realistic graphene material

Commercialized graphene samples can be classified by their physical forms as graphene film, graphene powder and graphene solution. Figure 2 shows the schematic packing configurations of graphene flakes in graphene film (left side of Figure 2) and graphene powder (right side of Figure 2) and their corresponding SEM images.

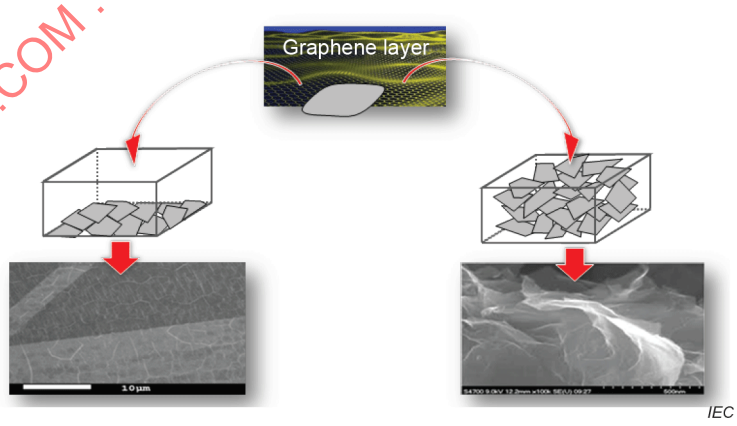


Figure 2 – Different packing configurations of graphene flakes in film (left) and powder (right)

Usually, defects in graphene films are characterized by the intensity ratio of two principle bands – D band and G band – in Raman spectra (symbolized by I_D/I_G) [1],[2]. However, in graphene powders consisting of flakes with sizes below 10 µm there are numerous edges and boundary states, which all contribute to the D-band signal and make its correlation to various defects problematic. The D-band intensity could result from the contribution of edges, boundary states or defects, so it is not appropriate to determine the defect level of graphene powder with the parameter I_D/I_G.

D+D′ band is only relevant with defects in graphene powder, but not with edges and boundary states. Therefore, in order to characterize defect level in graphene powder, the intensity ratio of D+D′ and 2D bands (symbolized by $I_{D+D'}/I_{2D}$) is proposed as a more relevant parameter in this document. Detailed information can be found in Annex D.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-14: Graphene-based material – Defect level: Raman spectroscopy

1 Scope

This part of IEC TS 62607 establishes a standardized method to determine the structural key control characteristic

- defect level

for powders consisting of graphene-based material by

- Raman spectroscopy.

The defect level is derived by the intensity ratio of the D+D′ band and 2D band in Raman spectrum, $I_{D+D'}/I_{2D}$.

- The defect level determined in accordance with this document will be listed as a key control characteristic in the blank detail specification for graphene IEC 62565-3-1 for graphene powder.
- The method is applicable for graphene powder or graphene-based material, e.g. reduced graphene oxide (rGO), bilayer graphene, trilayer graphene and few-layer graphene.
- Typical application areas are quality control and classification for graphene manufacturers, and product selection for downstream users.
- The method described in this document is appropriate if the physical form of graphene is powder.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1 General terms

3.1.1
two-dimensional material
2D material
material, consisting of one or several layers with the atoms in each layer strongly bonded to neighbouring atoms in the same layer, which has one dimension, its thickness, in the nanoscale or smaller and the other two dimensions generally at larger scales

Note 1 to entry: The number of layers when a two-dimensional material becomes a bulk material varies depending on both the material being measured and its properties. In the case of graphene layers, it is a two-dimensional material up to 10 layers thick for electrical measurements, beyond which the electrical properties of the material are not distinct from those for the bulk (also known as graphite).

Note 2 to entry: Interlayer bonding is distinct from and weaker than intralayer bonding.

Note 3 to entry: Each layer may contain more than one element.

Note 4 to entry: A two-dimensional material can be a nanoplate.

[SOURCE: ISO/TS 80004-13:2017, 3.1.1.1]

3.1.2
graphene
graphene layer
single-layer graphene
monolayer graphene
single layer of carbon atoms with each atom bound to three neighbours in a honeycomb structure

Note 1 to entry: It is an important building block of many carbon nano-objects.

Note 2 to entry: As graphene is a single layer, it is also sometimes called monolayer graphene or single-layer graphene and abbreviated as 1LG to distinguish it from bilayer graphene (2LG) and few-layered graphene (FLG).

Note 3 to entry: Graphene has edges and can have defects and grain boundaries where the bonding is disrupted.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.1]

3.1.3
graphene-based material
GBM
graphene material
grouping of carbon-based 2D materials that include one or more of graphene, bilayer graphene, few-layer graphene, graphene nanoplate, and functionalized variations thereof as well as graphene oxide and reduced graphene oxide.

Note 1 to entry: "Graphene material" is a short name for graphene-based material.

3.1.4
bilayer graphene
two-dimensional material consisting of two well-defined stacked graphene layers

Note 1 to entry: If the stacking registry is known, it can be specified separately, for example, as “Bernal stacked bilayer graphene”.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.6]

3.1.5
trilayer graphene
two-dimensional material consisting of three well-defined stacked graphene layers

Note 1 to entry: If the stacking registry is known, it can be specified separately, for example, as "twisted trilayer graphene".

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.9]

3.1.6
reduced graphene oxide
rGO
reduced oxygen content form of graphene oxide

Note 1 to entry: This can be produced by chemical, thermal, microwave, photo-chemical, photo-thermal or microbial/bacterial methods or by exfoliating reduced graphite oxide.

Note 2 to entry: If graphene oxide was fully reduced, then graphene would be the product. However, in practice, some oxygen containing functional groups will remain and not all sp^3 bonds will return back to sp^2 configuration. Different reducing agents will lead to different carbon to oxygen ratios and different chemical compositions in reduced graphene oxide.

Note 3 to entry: It can take the form of several morphological variations such as platelets and worm-like structures.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.14]

3.1.7
graphite
allotropic form of the element carbon, consisting of graphene layers stacked parallel to each other in a three dimensional, crystalline, long-range order

Note 1 to entry: Adapted from the definition in the IUPAC *Compendium of Chemical Terminology*.

Note 2 to entry: There are two primary allotropic forms with different stacking arrangements: hexagonal and rhombohedral.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.2]

3.1.8
blank detail specification
BDS
structured generic specification of the set of key control characteristics which are needed to describe a specific nano-enabled product without assigning specific values and/or attributes

Note 1 to entry: The templates defined in a blank detail specification list the key control characteristics for the nano-enabled material or product without assigning specific values to it.

Note 2 to entry: Examples of nano-enabled products are: nanomaterials, nanocomposites and nano-subassemblies.

Note 3 to entry: Blank detail specifications are intended to be used by industrial users to prepare their detail specifications used in bilateral procurement contracts. A blank detail specification facilitates the comparison and benchmarking of different materials. Furthermore, a standardized format makes procurement more efficient and more error robust.

3.1.9
sectional blank detail specification
SBDS
specification based on a blank detail specification adapted for a subgroup of the nano-enabled product

Note 1 to entry: In general, the sectional blank detail specification contains a subset of those key control characteristics listed in the blank detail specification. In addition, sectional specific key control characteristics can be added if they are not listed in the blank detail specification.

Note 2 to entry: The templates defined in the sectional blank detail specification can contain key control characteristics with and without assigned values and attributes.

Note 3 to entry: The section can be defined by application, manufacturing method or general material properties.

3.1.10
detail specification
DS
specification based on a blank detail specification with assigned values and attributes

Note 1 to entry: The properties listed in the detail specification are usually a subset of the key control characteristics listed in the relevant blank detail specification. The industrial partners define only those properties which are required for the intended application.

Note 2 to entry: Detail specifications are defined by the industrial partners. SDOs will be involved only if there is a general need for a detail specification in an industrial sector.

Note 3 to entry: The industrial partners can define additional key control characteristics if they are not listed in the blank detail specification.

3.1.11
key control characteristic
KCC
key performance indicator
material property or intermediate product characteristic which can affect safety or compliance with regulations, fit, function, performance, quality, reliability or subsequent processing of the final product

Note 1 to entry: The measurement of a key control characteristic is described in a standardized measurement procedure with known accuracy and precision.

Note 2 to entry: It is possible to define more than one measurement method for a key control characteristic if the correlation of the results is well-defined and known.

3.2 Key control characteristics measured in accordance with this document

3.2.1
defect
local deviation from regularity in the crystal lattice of a 2D material

Note 1 to entry: Many different types of defect are present in the graphene material, including Stone-Wales defect, single vacancy defect, multiple vacancy defect and interstitial defects. Broadly speaking, even doped heteroatoms or foreign atoms can be regarded as one type of defect. It is worth noting that grain boundaries are not referred to as defects here because the grain boundaries break the translational symmetry rather than the particular intrinsic symmetry.

Note 2 to entry: Stone-Wales defect is generated by a pure reconstruction of graphene lattice (switching between pentagons, hexagons, and heptagons) [3].

Note 3 to entry: Single vacancy defect or multiple vacancy defect is generated by an atomic disappearance of graphene lattice [3].

Note 4 to entry: Interstitial defect is generated by an atomic addition that formed carbonyl bridge configuration on the graphene lattice [3].

[SOURCE: ISO/TS 80004-13:2017, 3.4.1.1]

3.3 Terms related to the measurement method

3.3.1
Raman spectroscopy
spectroscopy in which the radiation emitted from a sample illuminated with monochromatic radiation is characterized by an energy loss or gain arising from rotational, vibrational or phonon excitations

[SOURCE: ISO/TS 80004-13:2017, 3.3.1.6]

3.3.2
2D band
G′ band
band generated by two inelastic intervalley scattering processes, which involves an iTO phonon around the K-point

Note 1 to entry: The 2D band is related to a two-phonon process located at approximately twice the frequency of the D band. Therefore, it is often called the 2D band or G′ band. It does not need lattice defects for activation.

Note 2 to entry: The 2D band is always present in the Raman spectrum of graphene and does not need defects to be activated.

Note 3 to entry: The position of 2D band varies as a function of the excitation energy, and appears near 2 700 cm^{-1} for the excitation wavelength of 532 nm [4].

3.3.3
D+D′ band
band generated by one intervalley phonon around K-point, one intravalley phonon around K′-point and defects

Note 1 to entry: In prior literature [5], this band is also noted as D+G band. However, this is not correct because the activation mechanism determines that this band is not the overtones of the D and G bands [6].

Note 2 to entry: This band generally occurs near 2 960 cm^{-1}, and is also labelled as S3 band [7],[8].

4 General

4.1 Measurement principle

Figure 3 schematically shows typical Raman spectra for ion-bombarded defective graphene (upper spectrum) and pristine graphene (lower spectrum). Interpretation of the Raman spectra focuses on the feature bands for defective graphene, D, G, D′, 2D and D+D′ bands, which are shown in the upper panel of Figure 3. This document specifies the evaluation of defect level in graphene powder using the intensity ratio between D+D′ band and 2D band, $I_{D+D'}/I_{2D}$.

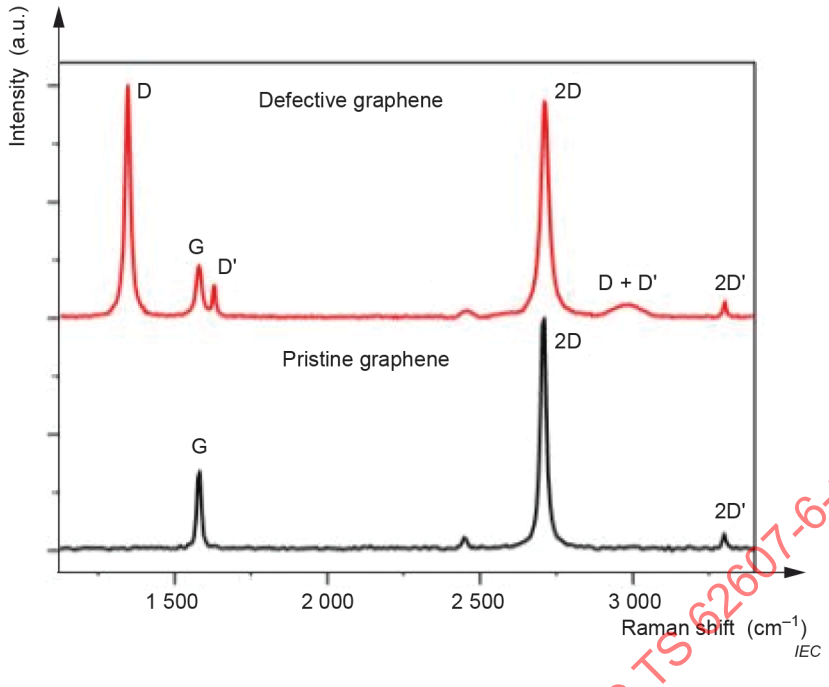


Figure 3 – Schematic drawing of Raman spectra of defective graphene (upper) and pristine graphene (bottom)

4.2 Sample preparation method

Defect level in graphene powder can be reliably evaluated by Raman spectroscopy. Firstly, put some graphene powder on a flat substrate, then gently press the sample with a glass slide to obtain graphene tablet for further measurements. The graphene tablet should be thick enough so that the Raman signals from the substrate can be neglected. A schematic drawing of the sample preparation method is shown in Figure 4.

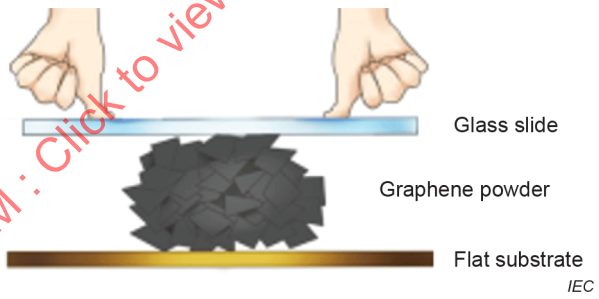


Figure 4 – Schematic drawing of sample preparation method

Note that any nonstandard treatment of the sample may change the structural quality and morphology and therefore influence the outcome of measurements. Also, it should be ensured that the feature bands of defective graphene are not masked by Raman signals originating from the metallic substrates.

4.3 Description of measurement equipment/apparatus

The measurements are carried out using a confocal Raman micro-spectrometer equipped with a high magnification objective (numerical aperture > 0,7).

4.4 Supporting materials

Metallic substrate (e.g. aluminium plate), flat glass substrate or silicon wafer, cover glass and gloves for sample preparation.

4.5 Ambient conditions during measurement

Raman measurements shall be carried out at room temperature and relative humidity below 70 %. Specific temperature and relative humidity are not required, but should be recorded.

5 Measurement procedure

5.1 Calibration of measurement equipment

Prior to use, the test equipment shall be calibrated in accordance with the requirements of the equipment manufacturer. One commonly used way to calibrate the equipment is using a monocrystalline silicon substrate with a typical band at 520,7 cm^{-1}. The difference between the measured band position and typical band position should be smaller than ±0,2 cm^{-1}. Another way to calibrate the equipment is using a polystyrene sample with a typical band at 1 004 cm^{-1}.

5.2 Detailed protocol of the measurement procedure

The Raman measurements are carried out at room temperature under ambient conditions in a dark room. Calibrate the equipment in accordance with the manufacturer's requirements. A laser with an excitation wavelength of 514 nm, 532 nm and 633 nm can be used. The spectral resolution of Raman spectroscopy not larger than 2 cm^{-1} is necessary. The incident power density of laser should be 0,4 mW/μm^2 to 1,2 mW/μm^2 in order to avoid burning samples due to heat effects.

After the sample is placed on the microscope stage, adjust the focus knob for sample focusing. The measurements shall be taken over a square scan area of 10 µm × 10 µm. At least five points of each sample should be measured. It should be noted that all the measurements are conducted with the same measurement settings (e.g. laser power, spectral range, number of accumulations and acquisition time), so that all the spectra are comparable. The spectral range should be chosen such that the relevant Raman bands (such as D, G, 2D, D+D′) appear in a single spectrum to reduce measurement time.

5.3 Measurement accuracy

To make sure that the line width of the bands can be well extracted by Gaussian fitting, the integration time for each individual spectrum shall be adjusted to exceed a signal-to-noise ratio of 10:1 for bands. The signal-to-noise ratio is defined as follows: the difference of band intensity and background intensity, divided by the root mean square of background intensity associated with noise.

5.4 Measurement uncertainty source

The measurement uncertainty source should be considered from several possibilities as listed below:

a) uncertainties associated with chemical adsorption of graphene sample due to the van der Waals force (e.g. adsorbing small molecules in air);

b) uncertainties associated with the statistical error, mechanical error and stochastic error from the instrument.

6 Sampling plan

Selecting a sampling plan with multiple measurement points at different spatial positions can be used to control the measurement accuracy and uncertainty over the measured area. The number of points measured depends on desired requirements. See Annex B for detailed sampling plans.

7 Data analysis / interpretation of results

Noise, such as cosmic rays and other interference should be firstly removed from data. Obtain the background baseline by fitting the spectrum without bands. Afterwards, the data should be processed by peak fitting techniques. Prior to analysis of the defect level, the data of any sample should be analysed by the 2D band signal to determine its layer structure. If the ratio between main band and shoulder band is approximately larger than 1,25, this set of data will not be appropriate for analysis of defect level due to the possible presence of graphite structures.

The intensity ratio of D+D′ band and 2D band $I_{D+D'}/I_{2D}$ is calculated as a parameter characterizing the defect level. After removal of signals from the cosmic rays, mean values of $I_{D+D'}/I_{2D}$ are calculated as the defect level of the sample. The lower the ratio $I_{D+D'}/I_{2D}$, the lower the defect level. Note that this band analysis method is not applicable to too defective samples in which the 2D band is hardly observable [5].

Detailed information can be found in Annex C.

8 Results to be reported

8.1 General

The results of the measurement shall be documented in a measurement report, including the date and time of the measurement as well as the name and signature of the person responsible for the accuracy of the report. Guidelines are given in Annex A.

8.2 Product/sample identification

The report shall contain all information to identify the test sample and trace back the history of the sample:

- General procurement information, in accordance with blank detail specification IEC 62565-3-1.
- General material description in accordance with blank detail specification IEC 62565-3-1, including a technical drawing:
  - top view, indicating the inspected area and location of the measurement positions;
  - cross section, showing the layer structure.

8.3 Test conditions

The laboratory ambient conditions during the test:

- Temperature range: 17 °C < T < 24 °C.
- Range of relative humidity: 40 % < RH < 70 %.

8.4 Measurement specific information

- Calibration status of equipment.
- Spectral resolution of the spectrometer.
- Wavelength, spot size and power of the laser used.
- Signal-to-noise ratio for the Raman spectra.
- A typical measured Raman spectrum.
- The intensity ratio of D+D′ band and 2D band, $I_{D+D'}/I_{2D}$.
- The measured area if the sampling plan contains several measurement spots.
- The histogram of the 2D band widths in the scan area if the sampling plan contains several measurement spots.
- The [2D-FWHM-(80 %)] value derived from the histogram or a table of the values if the sampling plan contains several measurement spots.

8.5 Test results

- Sampling plan used.
- Results of KCC defect level measured in accordance with this document.
- Table of mean values and standard deviation of the KCC measured in accordance with this document at the positions defined by the sampling plan.

Annex A
(informative)

Recommended format of the test report

The form of the test report should be oriented on the relevant material specification,[1] a related sectional blank detail specification or detail specification. Table A.1 to Table A.4 are guidelines to write the test report and can be customized to fulfil the requirements of the involved parties.

Table A.1 – Product identification (in accordance with IEC 62565-3-1)

Item No	Item		Information
1.1	Supplier		
1.2	Trade name		
1.3	ID number		
1.4	Typical batch quantity	Weight [g]	
1.5	Traceability requirements	☐ Batch number ☐ Serial number ☐ Others, specify	
		Manufacturing date	
1.6	Specification	Number	
		Revision level	
		Date of issue	
1.7	Material Safety Data Sheet (MSDS) available	☐ No	
		☐ Yes Reference	

Table A.2 – General material description (in accordance with IEC 62565-3-1)

Item No	Item		Information
2.1	Material type		
2.2	Manufacturing method		
2.3	Physical form		
2.4	Substrate	Material	
		Technical drawing (Top view)	
		Technical drawing (Cross section)	
2.5	Shelf life		
2.6	Typical batch size		

[1] A blank detail specification for graphene is under development (IEC 62565-3-1).

Table A.3 – Information related with test

Item No	Item	Information
3.1	Sampling plan	Specify……
3.2	Excitation wavelength	
3.3	Laser power	
3.4	Substrate	
3.7	Pressing pressure	
3.8	Pressing time	
3.9	Number of spectra/measurements	
3.10	Signal-to-noise ratio	
3.11	Intensity ratio $I_{D+D'}/I_{2D}$	
3.12	Mean value and standard deviation of FWHM(2D) distribution	
3.13	Environmental temperature	
3.14	Environmental relative humidity	
3.15	Raman maps	☐ attached ☐ available on request

Table A.4 – Measurement results

Measurement points in accordance with sampling plan	$I_{D+D'}/I_{2D}$ of first measurement	$I_{D+D'}/I_{2D}$ of second measurement	$I_{D+D'}/I_{2D}$ of third measurement	Average $I_{D+D'}/I_{2D}$	Standard deviation
1					
2					
3					
4					
5					
…					

Annex B
(informative)

Sampling plan

The Raman measurement of one point on graphene sample cannot represent the overall Raman spectrum. In order to evaluate the overall defect level of graphene sample, a sampling plan is required to ensure that the users can obtain enough representative spectral information by selecting a certain number of sampling points. Below, a standardized approach for sampling is given.

Figure B.1 depicts the five-point-sampling method used for Raman measurement. In the confocal Raman measurement of the pressed graphene powder, the sample area should at least cover most of the microscope vision so as to determine the test quadrats.

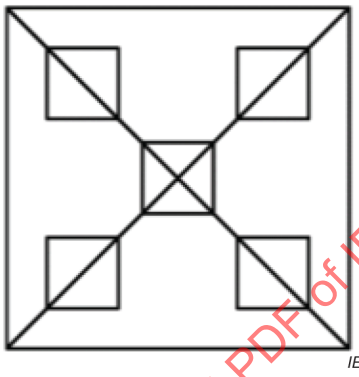


Figure B.1 – Schematic drawing of five-point-sampling method

In the five-point-sampling method, the overall rectangular sampling area should be identified first in the microscope view. Figure B.2 shows all the suitable measurement points in each sample. The midpoint (0) of the rectangular diagonals is the centre of one test quadrat. Select another four points (1,2,3,4) in the two diagonals such that the distance between each point and midpoint is equal. Based on point 1, 2, 3 or 4, another four rectangular-shaped areas can be developed as test quadrats. The length and width of each quadrat should be the same. The measurements points can be randomly sampled from the corners, the midpoint of each edge or the three equal points in the diagonals of each quadrat. The sample points should cover at least five areas. Which point is chosen and how many points are chosen depend on the required information and measurement time that relate to cost. The number of sampling points should be determined by desired requirements.

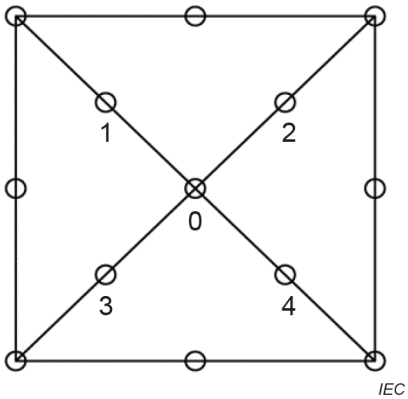


Figure B.2 – Location of measurement points

Annex C
(informative)

Case study: measurement and data analysis

C.1 Step 1: sample preparation

A blank sample of unknown graphene is deposited on a metal aluminium plate. Put a glass slide above the sample, and gently press the sample into a tablet. The schematic drawing of sample preparation is shown in Figure 4.

Caution: Take the necessary nanosafety precautions when handling the powders, e.g. wearing gloves and a mask.

C.2 Step 2: Raman test

Put the well-prepared sample beneath the microscope of a confocal Raman spectrometer, with a 10× objective lens. Figure C.1 shows the field of view in which each test point is marked with a red circle.

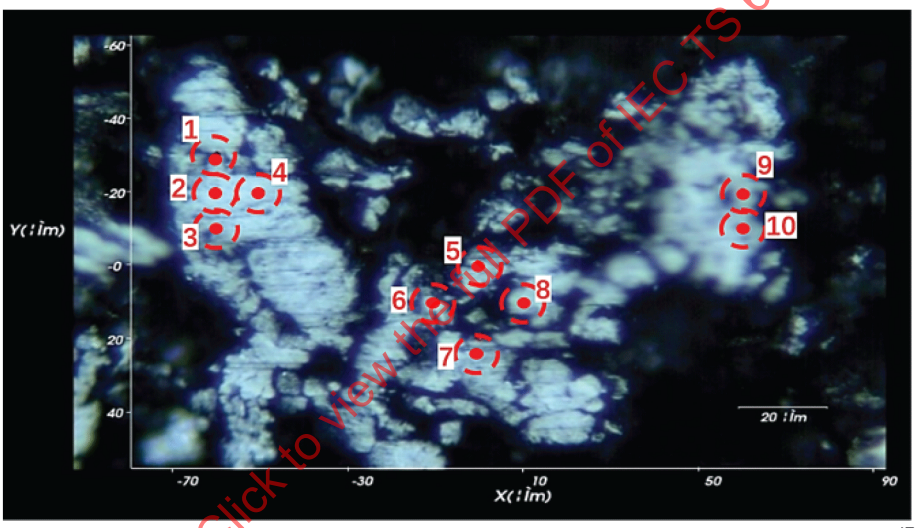


Figure C.1 – The field view of graphene sample beneath Raman microscope

The excitation wavelength of laser is 532 nm and the excitation power density is 0,8 mW/μm^2. During Raman measurement, integration number is set to be 20, and integration time is set to be 2 s. Each test point will be measured at least three times, and all the Raman spectra will be processed and analysed.

C.3 Step 3: Raman spectra processing

Use a percentile filter to remove the band from cosmic ray in the original Raman spectra. Obtain the background baseline by fitting the spectrum without bands. Smooth the data with Savitzky-Golay filter, and the ratio between the signal band and the band of background noise is 10:1. Afterwards, the bands should be fitted with Gaussian fitting technique. The procedure of Raman spectrum processing is illustrated in Figure C.2.

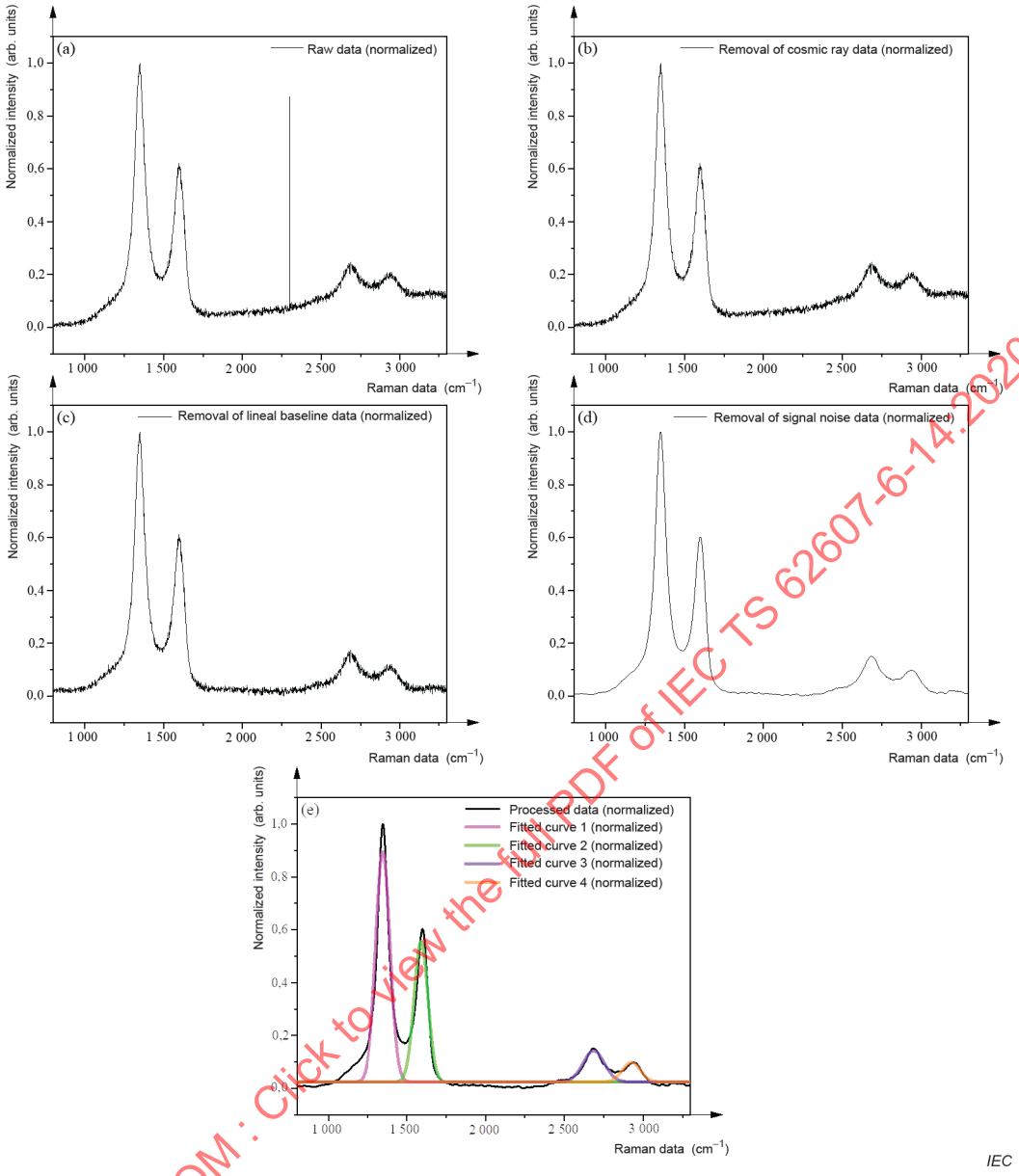


Figure C.2 – The procedure of Raman spectrum processing

C.4 Step 4: Data analysis

As for the case study in Annex C, one typical Raman spectrum after processing is shown in Figure C.3. Differentiate G, D, D+D′ and 2D bands in the processed Raman spectrum by Gaussian fitting. Based on the intensity of D+D′ and 2D bands, the ratio of $I_{D+D'}/I_{2D}$ can be calculated. The average ratio can be obtained from the three-time measurement of each test point. Table C.1 lists the average $I_{D+D'}/I_{2D}$ of each test point.

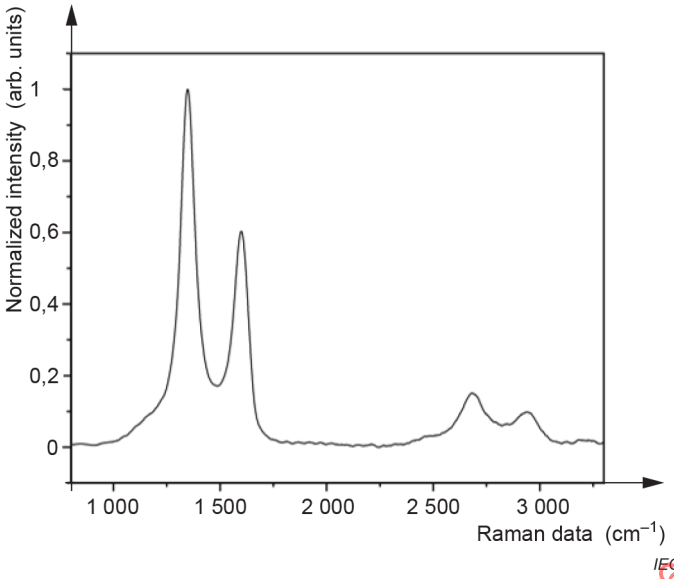


Figure C.3 – Typical Raman spectrum after processing

Table C.1 – Average $I_{D+D'}/I_{2D}$ of each test point

No.	First measurement	Second measurement	Third measurement	Average $I_{D+D'}/I_{2D}$	Standard deviation
1	0,356 344	0,374 088	0,381 942	0,370 79	0,013 11
2	0,386 94	0,386 465	0,377 616	0,383 67	0,005 25
3	0,417 931	0,420 147	0,430 844	0,422 97	0,006 91
4	0,418 421	0,416 296	0,436 014	0,423 58	0,010 82
5	0,445 258	0,431 649	0,444 346	0,440 42	0,007 61
6	0,457 526	0,453 724	0,482 906	0,464 72	0,015 86
7	0,457 828	0,484 638	0,462 047	0,468 17	0,014 42
8	0,518 609	0,523 083	0,504 005	0,515 23	0,009 98
9	0,515 553	0,564 277	0,535 396	0,538 41	0,024 50
10	0,597 056	0,590 456	0,579 813	0,589 11	0,008 70
AVG	0,457 147	0,464 482	0,463 493	0,461 71	0,011 72

By calculating the average $I_{D+D'}/I_{2D}$ of all test points, the overall defect level of one test sample can be obtained. The data is presented in Figure C.4. Such results can be recorded in the tables in Annex A.

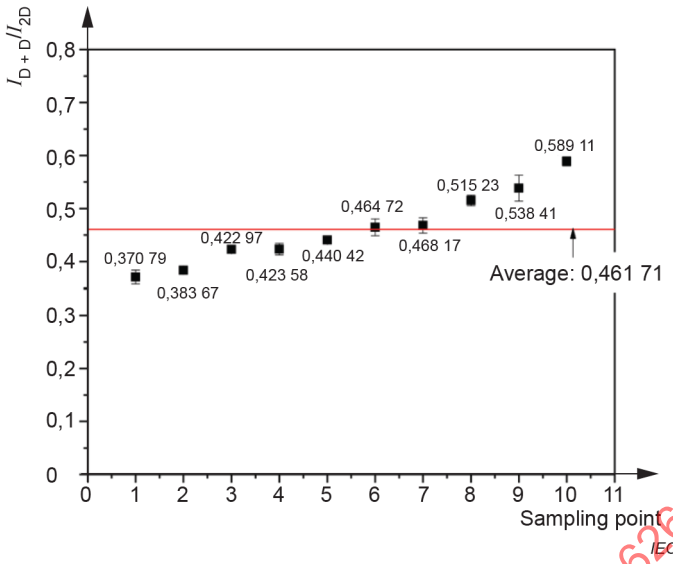


Figure C.4 – The overall defect level of one test sample

Comparative experiments were conducted by different testing organizations, including universities, institutes and instrument companies. The results plotted in Figure C.5 prove that the data has good repeatability.

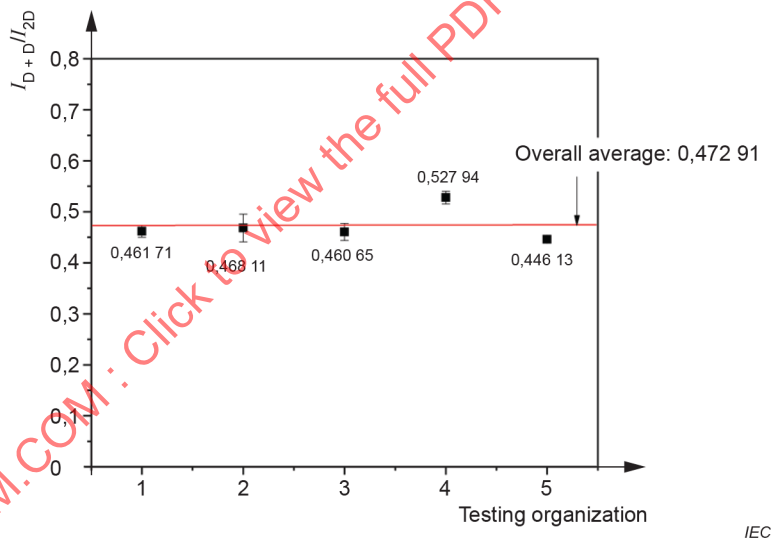


Figure C.5 – Measurement results of different testing organizations

Annex D
(informative)

Why use the intensity ratio $I_{D+D'}/I_{2D}$ for defect level characterization of graphene powder?

D.1 Interpretation of characteristic bands in the Raman spectrum of graphene and Raman scattering mechanism

Figure D.1 shows the characteristic bands in the Raman spectrum of graphene and Raman processes. The D band originates from the in-plane breathing mode of the carbon rings and requires lattice defects for its activation. It comes from transverse optical (TO) phonons around the K or K′ point in the first Brillouin zone, involves an intervalley double resonance process and is strongly dispersive with excitation energy. This momentum needed for connecting the K and K′ points is required to be perpendicular to the armchair edge. Only armchair-type boundary or defect can satisfy the requirement. A perfect zigzag edge can hardly produce the D band signal. So the D band relates to defect, armchair-type boundary and hybrid boundary. The G band corresponds to the E_{2g} phonon at the Brillouin zone centre. The 2D band is generated by two inelastic intervalley scattering processes, which involves an in-plane TO phonon around the K point. Since 2D originates from a process where momentum conservation is satisfied by two phonons with opposite wavevectors, no defects are required for its activation, and are thus always present. With defects, one intravalley phonon around the K′ point and one intervalley phonon around the K point can be emitted, producing the D+D′ band. This band is highly correlated with defect level in graphene. The D+D′ band was labelled as D+G band or S3 band in previous work [5],[7],[8]. Note that the D+G band is a wrong label because the band is not the overtone of D and G bands [6].

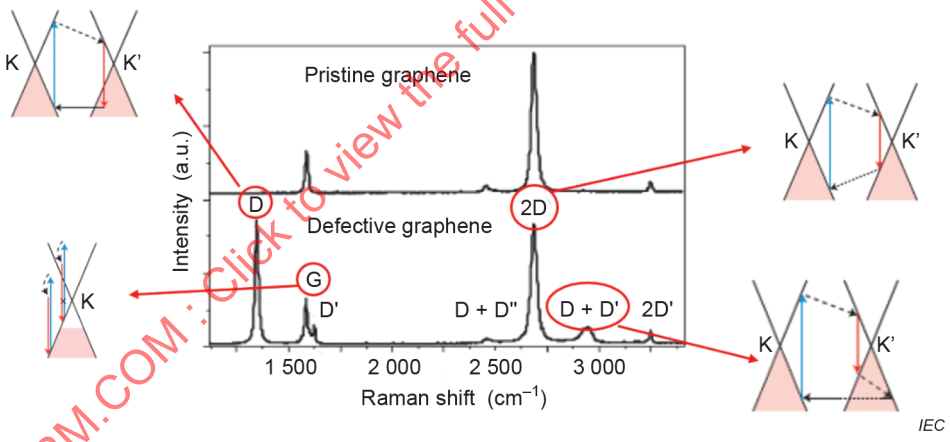


Figure D.1 – Characteristic bands in the Raman spectrum of graphene and Raman processes [6]

D.2 Example – Influence of edges in the Raman spectrum of graphene

Measurements performed on closely related armchair and zigzag graphene edges showing different intensity ratios I_D/I_G are presented in Figure D.2 [9] and Figure D.3 [10]. Figure D.2 shows the Raman spectra obtained from the edges of a monolayer graphene sample. The D band measured at the edge with preferential zigzag orientation (dashed line spectrum) is considerably less intense than the D band obtained at the edge with preferential armchair orientation (solid line spectrum).

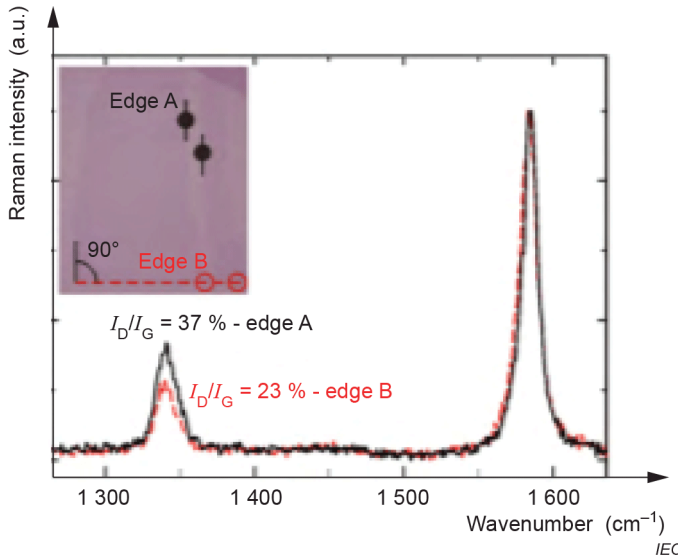


Figure D.2 – Raman spectra from the edges of a monolayer graphene sample [9]

In Ref. [10], the authors performed Raman analysis of monolayer graphene samples with hexagonal and circular holes, respectively. While the hexagonal pits were proven to be composed of zigzag edges, the circular holes are formed by edges consisting of a mixture of armchair and zigzag segments (see illustration in the bottom part of Figure D.3). Accordingly, statistical Raman analysis performed in these two types of samples showed that the ratio I_D/I_G obtained from the boundaries of the hexagonal holes (zigzag edges) is up to a factor of 30 smaller than for the edges of round holes.

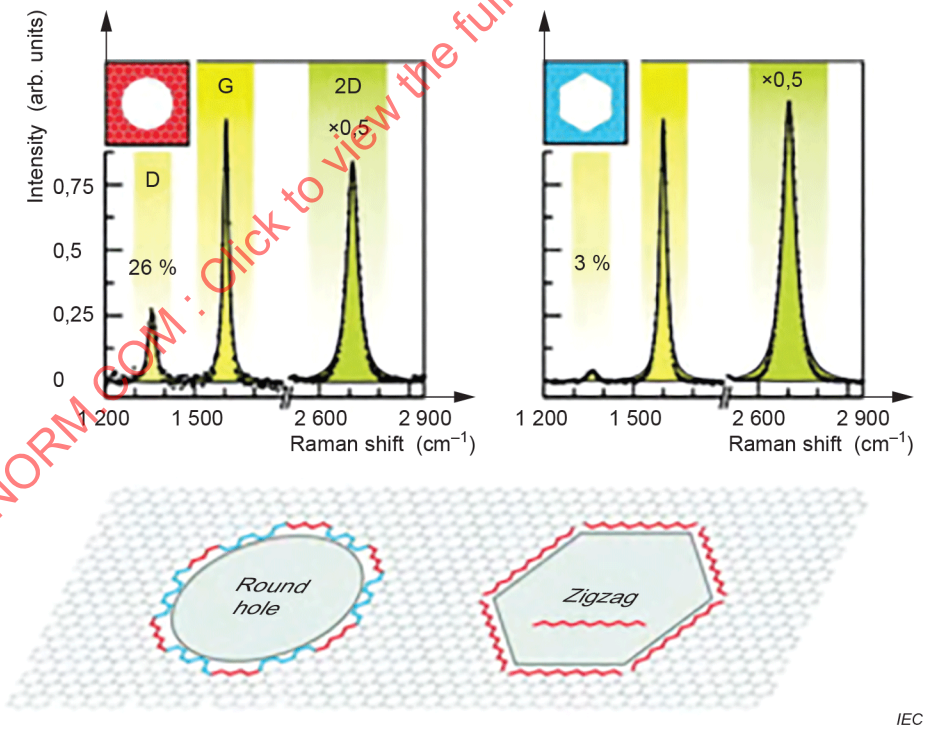


Figure D.3 – Raman spectra obtained from monolayer graphene samples with hexagonal and circular holes [10]

In conclusion, the signal of D band may result from defect and edges emission. Armchair edges influence the intensity of D band significantly, but zigzag edges influence the D band signal little.