



Designation: E3220 – 20

Standard Guide for Characterization of Graphene Flakes¹

This standard is issued under the fixed designation E3220; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This standard will provide guidance on the measurement approaches for assessment of lateral flake size, average flake thickness, Raman intensity ratio of the D to G bands, and carbon/oxygen ratio for graphene and related products. The techniques included here are atomic force microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. Examples will be given for each type of measurement.

1.2 This guide is intended to serve as an example for manufacturers, producers, analysts, and others with an interest in graphene and related products such as graphene oxide and reduced graphene oxide. This Standard Guide is not intended to be a comprehensive overview of all possible characterization methods.

1.3 This guide does not include all sample preparation procedures for all possible materials and applications. The user must validate the appropriateness for their particular application.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This guide is under the jurisdiction of ASTM Committee E56 on Nanotechnology and is the direct responsibility of Subcommittee E56.02 on Physical and Chemical Characterization.

Current edition approved April 1, 2020. Published May 2020. DOI: 10.1520/E3220-20.

2. Referenced Documents

2.1 ASTM Standards:²

E2530 Practice for Calibrating the Z-Magnification of an Atomic Force Microscope at Subnanometer Displacement Levels Using Si(111) Monatomic Steps (Withdrawn 2015)³

2.2 ISO Standards:⁴

ISO 13067:2011 Microbeam Analysis — Electron Backscatter Diffraction — Measurement of Average Grain Size

ISO 13322-1:2014 Particle Size Analysis — Image Analysis Methods — Part 1: Static Image Analysis Methods

ISO 18115-2:2013 Surface Chemical Analysis — Vocabulary — Part 2: Terms Used in Scanning-Probe Microscopy

ISO 18116:2005 Surface Chemical Analysis — Guidelines for Preparation and Mounting of Specimens for Analysis

ISO/TR 18196:2016 Nanotechnologies — Measurement Technique Matrix for the Characterization of Nano-Objects

ISO 18554:2016 Surface Chemical Analysis — Electron Spectroscopies — Procedures for Identifying, Estimating, and Correcting for Unintended Degradation by X-Rays in a Material Undergoing Analysis by X-Ray Photoelectron Spectroscopy

ISO 80004-1:2015 Nanotechnologies — Vocabulary — Part 1: Core Terms

ISO 80004-13:2017 Nanotechnologies — Vocabulary — Part 13: Graphene and Related Two-Dimensional (2D) Materials

ISO/IEC Guide 9:2010 International Vocabulary of Metrology — Basic and General Concepts and Associated Terms (VIM)

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <http://www.iso.org>.

3. Terminology

3.1 Definitions:

3.1.1 *Feret diameter*, *n*—perpendicular distance between two parallel lines drawn in a given direction tangential to the perimeter of an object on opposite sides of the object.

ISO 13067:2011

3.1.2 *few layer graphene*, *n*—two-dimensional material consisting of three to ten well-defined stacked graphene layers.

ISO 80004-13:2017

3.1.3 *graphene*, *n*—single layer of carbon atoms with each atom bound to three neighbours in a honeycomb structure.

ISO 80004-13:2017

3.1.3.1 *Discussion*—Note the three Notes in the ISO document.

3.1.4 *graphene oxide*, *n*—chemically modified graphene prepared by oxidation and exfoliation of graphite, causing extensive oxidative modification of the basal plane.

ISO 80004-13:2017

3.1.5 *measurand*, *n*—quantity intended to be measured or a quantity that is being determined by measurement.

ISO/IEC Guide 99

3.1.6 *nanoscale*, *n*—range from approximately 1 to 100 nm.

ISO 80004-1:2015

3.1.7 *reduced graphene oxide*, *n*—reduced oxygen content form of graphene oxide.

ISO 80004-13:2017

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *average flake thickness*, *n*—average height of the flake, which is determined by measuring the average cross section profile of the flake (measuring the position on the substrate next to the flake and the step in topography due to the flake).

3.2.2 *exfoliated graphene and related material*, *n*—products produced by exfoliation that may be present in either a powder or liquid dispersion form.

3.2.3 *flake*, *n*—graphene or layers of graphene related materials.

3.2.4 *lateral flake size*, *n*—dimension determined as the Feret diameter.

3.2.4.1 *Discussion*—Note, it is sometimes referred to as Feret's statistical diameter (**1**)⁵ or caliper diameter.

3.2.5 *peak intensity*, *n*—the maximum value of the intensity for a Raman peak or X-ray photoelectron spectroscopy peak after the baseline has been subtracted and peak fitting has been performed.

3.3 Acronyms:

3.3.1 *CVD*—chemical vapor deposition

3.3.2 *FLG*—few layer graphene

3.3.3 *FWHM*—full width at half maximum

3.3.4 *GO*—graphene oxide

3.3.5 *r-GO*—reduced graphene oxide

4. Significance and Use

4.1 The remarkable structural, physical and chemical properties of graphene — particularly its mechanical strength, high electronic mobility, lightness, and transparency (single layer or a few layers) — have generated worldwide research and industrial production efforts aimed at developing practical applications. Various industrially scalable production methods have been developed, including bottom-up approaches that grow graphene from small molecules (with or without a substrate), and top-down methods that start with graphite and exfoliate it by mechanical, chemical or electrochemical methods to produce nanoscale product such as graphene flakes. Two common exfoliation methods are: (1) oxidation of graphite to graphene oxide (GO) followed by additional processing to form reduced graphene oxide (r-GO) (**2**) and, (2) liquid phase exfoliation of graphite (**3**). The exfoliation methods, as well as substrate-less bottom-up approaches, produce materials in the form of flakes that can be dispersed in various solvents, making them suitable for applications requiring solution processing. Although there are many commercial “graphene” materials available on the market, the quality of these products is highly variable (**4**). There are many challenges in assessing the physical properties of the materials. In this guide we discuss how Raman spectroscopy (Raman) and X-ray photoelectron spectroscopy (XPS), as well as atomic force microscopy (AFM) can be used to characterize materials consisting of flakes of graphene and related materials (that is, few layer graphene (FLG), GO, r-GO). Illustrative examples are provided showing how these methods can be used to identify the type of material present and to extract important parameters including lateral flake size, average flake thickness, ratio of intensities of the D and G modes (I_D/I_G) in the Raman spectrum and carbon to oxygen ratio. Specifically, when encountering an “unknown” material or product purporting to be “graphene,” it is essential to quantify the thickness and lateral flake size distributions by AFM, to assess the level of defects in the flakes using the ratio of intensities of the D and G bands in the Raman spectrum, and to determine the level of oxidation of the material (C/O ratio) using XPS. These measurands are important for qualitative assessment of the type of material present, as well as quantitative measures of the quality of the flakes which can be correlated with properties relevant to applications based on conductivity, optical transparency, and chemical reactivity.

4.2 It should be noted that these materials and products may exist in either a powder or dispersion (in liquid) form. Other techniques and measurements (ISO/TR 18196:2016) such as X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and surface area measurement, can also be used for characterization of graphene and related products but discussion of these methods is beyond the scope of this guide.

5. Techniques

5.1 Raman Spectroscopy:

5.1.1 General Considerations:

5.1.1.1 Raman spectroscopy is a powerful technique used to characterize graphene related materials in the form of powders

⁵ The boldface numbers in parentheses refer to a list of references at the end of this standard.

or dispersions. Powders can be pressed into pellets or attached to a substrate using an adhesive film, whereas dispersions can be used to produce a film on a substrate. Raman spectra of graphene consist of three main features, two in-plane modes (D and G) and the second-order overtone of the D mode (2D). The frequency, intensity and line-shape of these modes all provide information on flake structure and can be used to distinguish monolayer graphene from FLG, GO or graphite (5-8). The G-band for graphene is typically observed at $\approx 1580\text{ cm}^{-1}$, independent of excitation energy, whereas the D and 2D peaks exhibit dispersion, so that their position will vary depending on the excitation laser used. The D peak is not visible in pristine graphene due to selection rules but is allowed in the presence of defects, leading to its use as an indicator of structural quality. The 2D mode is always allowed and is particularly prominent in high quality monolayer samples where its intensity is typically larger than that of the G mode.

5.1.1.2 Raman spectra for several types of graphene related materials are shown in Fig. X1.1 with the main peaks identified. A spectrum from a continuous monolayer film grown by CVD is shown as an example of the ideal case of graphene. Similar spectra have been reported from isolated monolayer flakes produced by micromechanical cleavage (9). In the CVD graphene spectra the D peak is barely visible and the 2D mode is seen to consist of a single Lorentzian line shape at 2640 cm^{-1} (with FWHM of $\approx 40\text{ cm}^{-1}$) and exhibiting more than twice the intensity of the G peak.

5.1.1.3 It is noted that 2D FWHMs of $20\text{--}40\text{ cm}^{-1}$ have been reported in the literature with narrower line widths indicating higher quality samples (10). The spectra for the FLG powder and FLG ink are rather similar. The D band is clearly visible, indicative of defects in the flakes or small flake size as edge sites, or both, can also contribute to the D peak. An additional defect related peak (D') is also observed at $\approx 1620\text{ cm}^{-1}$. The 2D peak is broadened and peak intensity is similar to that of the G band. The position of the 2D band is shifted to higher wavenumbers but is still lower than the 2685 cm^{-1} band observed for graphite. This suggests that the flakes in these materials are less than ≈ 6 layers, and the Raman spectra of thicker flakes are indistinguishable from graphite. For the r-GO film, all features in the spectrum are broadened, the D band is further increased in intensity and is larger than the G peak, and the 2D peak is weakened. The G peak is also seen to be shifted to higher frequency as a result of increasing D' intensity coupled with the broadening which makes these peaks difficult to separate.

5.1.2 Calculation and Significance of I_D/I_G :

5.1.2.1 The ratio of the D and G peak intensities (I_D/I_G) is a useful parameter for quantifying the structural quality of graphene. Experiments using ion bombardment to create defects in graphene have shown that at low defect densities, I_D/I_G increases with defect density before reaching a maximum and then decreases with defect density in the high density regime (11, 12). The value of I_D/I_G at the maximum, defining the cross-over between the two regimes, depends on the size of the defects (and varies depending on the type of ion used in the bombardment). An equation relating the measured I_D/I_G to the distance between defects (L_d) and the size of the defects is

given in Ref. (11). The high defect density regime (typically $L_d < 5\text{ nm}$) can be identified by an increase in the FWHM of the D band, which remains constant in the low defect density regime. In calculating the I_D/I_G ratio it is important to note that peak intensities (after background subtraction) are typically used, rather than integrated peak areas. This is due to proximity of the D' band to the G band which can make it difficult to separate the contributions of these two modes. I_D/I_G values calculated from the spectra shown in Fig. X1.1 are indicated in the figure. Edges have also been shown to contribute to the D-band intensity (13), so small flake sizes can give rise to a large D band intensity even if the interior of the flakes do not have many defects.

5.2 X-Ray Photoelectron Spectroscopy:

5.2.1 General Considerations:

5.2.1.1 XPS provides information on the chemical composition of a sample by measuring the intensity of photoelectrons ejected from the sample as a function of kinetic energy (E_k). Many of the observed peaks can be assigned to emission from particular core levels of elements present in the sample, allowing these elements, if present in sufficient quantity to be identified and quantified. For materials produced by exfoliating graphite the ratio of carbon to oxygen is a key parameter in determining the suitability of the product for various applications. Furthermore, XPS can be used to monitor the presence of contaminants that may be introduced in the processing of the material (4).

5.2.1.2 XPS is typically performed in a high vacuum environment at pressures below 5×10^{-8} mbar. Samples can be in the form of powders or thin films prepared from dispersions. For thin film samples, the film should be thick enough ($>10\text{ nm}$) to avoid contributions from the substrate. It is important to avoid contamination during sample preparation and transfer into the measurement chamber (see ISO 18116:2005). Care should also be taken to minimize sample damage during measurement due to irradiation by the X-ray beam (see ISO 18554:2016).

5.2.2 Survey Scans:

5.2.2.1 Survey scans are spectra acquired over a wide range of energies, including those representative of carbon and oxygen photoelectron peaks and often employ a large pass energy yielding favorable signal:noise. Representative survey scans for three samples (a film consisting of GO flakes as well as powders of FLG and r-GO) are shown in Fig. X2.1. The most notable difference between the spectra is the oxygen signal, which is barely visible for the FLG sample but is the largest peak for the GO sample, reflecting the different oxygen content in these samples. Small peaks associated with impurities can also be identified in the GO and r-GO samples when evaluating survey scans. These contaminants may arise from reagents commonly used in the production of graphene oxide. The intensities of the labeled peaks in Fig. X2.1, after appropriate background subtraction, can be used for quantitative analysis of the atomic composition of the sample. This requires application of relative sensitivity factors for the various core levels, which are typically dependent on the particular spectrometer used for the measurements. The atomic composition of the three different samples (presented in

percentages) is summarized in the table inset of Fig. X2.1. Each entry represents the average of three different locations on the sample, with the uncertainties corresponding to the standard deviation.

5.2.3 High Resolution Scans and Calculation of C/O Ratio:

5.2.3.1 While the survey scans allow for rapid identification and quantification of elements present in the sample, additional information on the chemical state of the elements can also be determined by examining the detailed structure of the peaks obtained from high-resolution spectra. Such spectra typically are acquired over a smaller, element specific energy window using a lower pass energy. The decreased pass energy improves the energy resolution at the cost of reducing signal intensity. Fig. X2.1 shows a high-resolution scan of the C1s region for three different types of powder samples: GO, r-GO and FLG. Apparent in Fig. X2.1 are the different shapes exhibited by the C1s peak for the different samples. For FLG, a single peak centered at ≈ 284 eV is observed, with an asymmetric tail extending to higher binding energies. This type of line shape (Doniach-Sunjić) is also observed for graphite samples. For r-GO a shoulder is observed at higher binding energy. For GO a clear second peak at ≈ 286 eV is observed with a weak shoulder at still higher binding energy. The second C1s peak and shoulder for GO are assigned to carbon atoms coordinated to oxygen (2).

5.2.3.2 The C/O ratio is calculated by integrating the areas under the C1s and O1s (not shown) peaks after background subtraction. As expected, the C/O ratios are significantly different for these different materials ranging from 2.4 for GO to 85 for the FLG sample. While theoretically perfect FLG will only contain carbon, in reality FLG powders may exhibit some oxygen related defects. However, at the small O1s signals on these samples (≤ 1 % atomic composition), adventitious contamination of oxygen containing species may also contribute. One difficulty in determining the C/O ratio can arise if the sample exhibits oxygen containing impurities such as oxides, carbonates and hydroxides. High-resolution spectra of both the impurity (that is, sulfur, manganese, sodium, calcium) and the O1s regions will usually reveal whether this is an issue. These types of impurities usually result in a substantial shift of the oxygen core level compared with oxygen bound to carbon.

5.3 Atomic Force Microscopy:

5.3.1 General Considerations:

5.3.1.1 AFM in imaging modes such as contact and intermittent contact (for example, tapping, soft tapping, or other dynamic force microscopy modes, as defined in ISO 18115-2:2013) can be used to determine graphene flake size and thickness.

5.3.1.2 It is recommended that AFM instruments be calibrated regularly (approximately every six months for open loop scanners) using a range of traceable calibration grids.

5.3.1.3 It is noted that optical microscopy, Raman spectroscopy and XRD measurements can also be used to determine the number of layers (14-16, 7), whereas SEM and TEM imaging techniques can be used to quantify the lateral dimensions of the flakes. As AFM imaging presents the capability to physically visualize individual flakes, allowing for the direct measure-

ment of both the lateral dimension and the layer heights (thickness), AFM imaging is recommended to measure the lateral flake size and height (average flake thickness) distributions of graphene and related material (for example, GO and r-GO). Additionally, all size measurements could be automated using processing software (for example, open source software ImageJ (17) or Gwyddion (18)) to reduce the influence of the bias from different analysts.

5.3.1.4 For preparation of samples used in AFM imaging to determine the dimensions of graphene and related materials, a dispersion is required. If the material was originally provided as a powder, it requires dispersing in a suitable solvent such as water, isopropanol or N-methylpyrrolidone (NMP) (19, 10). More importantly, a statistically meaningful number of individual flakes (that is, flakes are isolated from each other on a substrate) should be measured, in order to ensure the quantification analysis to be performed is representative. Typically, the number of to be counted for the evaluation of a statistically representative sample depends on the width of the size distribution. For narrow size distribution (that is, the geometric standard deviation $\sigma_g < 1.5$, see ISO 13322-1:2014), 300 flakes are sufficient, whereas for samples with a wide size distribution (for example, bimodal distributions or $\sigma_g > 1.5$), at least 700 flakes have to be measured.

5.3.1.5 Usually, mica and silicon (or silicon oxide) can be selected as substrates and spin-coating or drop casting approaches can be used to produce samples for AFM measurements. It should be noted that ultrasonication steps (for example, bath sonication or probe sonication) are usually used to disperse the graphene and related material, in order to obtain a more stable dispersion. However, a sonication step with different sonication energies may introduce lateral flake size changes and therefore affect the characterization results of the intrinsic properties of the products. For example, in the 0–20 MJ/g range of sonication energies, the average hydrodynamic diameter of commercial GO flakes varied from ≈ 2000 down to ≈ 170 nm (20).

5.3.2 Quantification of Lateral Flake Size:

5.3.2.1 AFM scanning measurement should be performed under ambient conditions, with the instrument operating in a selected AFM imaging mode allowing both the lateral size and thickness of individual flakes to be determined.

5.3.2.2 Depending on the size distribution of the flakes, a larger scan size (for example, $30 \mu\text{m} \times 30 \mu\text{m}$, with pixels of 512×512) is suggested to allow the identification of several individual flakes. Typical scan sizes of 10, 5, 2 and 1 μm with 256×256 and 512×512 pixels should be carried out to allow for graphene samples with smaller flake size (on the order of tens to hundreds of nm). Flakes or features that appear to be smaller than 10 nm (that is, Feret diameter < 10 nm) should be ignored as they cannot be distinguished from measurement artifacts. Fig. X3.1 shows an example that was used to calculate the average flake size (that is, Feret diameter) through the use of AFM.

5.3.2.3 For some commercial products, there are mixtures of different sizes of features; one example of measurement on such a product is presented in Fig. X3.2.

5.3.3 Thickness Measurement by AFM:

5.3.3.1 Qualification of Step Heights with Different Forces:

(1) Before measuring the thickness of the materials, a qualification measurement on steps between terraces on highly oriented pyrolytic graphite (HOPG) is suggested to confirm height measurements (HOPG steps between terraces separated by a height of one atom have a known height of ≈ 0.34 nm at a force range of 10 pN to 5 nN, with higher steps being an integer multiple of this height value). More details on HOPG step height measurements can be found in Section X3.2, Fig. X3.3. Alternatively, a Practice for calibration of AFM Z-magnification using Si(111) steps can be found in Practice E2530.

5.3.3.2 Height Distributions of Graphene Flakes:

(1) When the flakes are smooth and homogeneous (such as graphene oxide flakes in Fig. X3.4), one should apply multiple height profiles or histograms of height signals of the entire image with single flakes (or cropped images with individual flakes) to determine the average flake thickness. Some detailed examples can be found in Section X3.2.

(2) Practically, the surface of some graphene related products can be found rough (for example, roughness average values larger than 1 nm), so the height measurements can only be considered as an indicator for thickness estimation of the graphene product. An example of this kind of flake is shown in Fig. X3.5, where the cross section analysis shows a rough surface morphology. It should be noted that smaller scan sizes with increased pixels (for example, 500 nm or 1 μ m scan sizes with 512×512 or 1024×1024 pixels) should be carried out during data analysis.

(3) In addition, when using contact mode with applied forces larger than a few nN, some force dependent height response is likely noticeable. An example of this is shown in Fig. X3.6. In this figure three AFM images of the same area of the graphene oxide sample acquired using three different applied force values, specifically 200 pN, 1 nN, and 2 nN, are compared. Averaged cross sections (in this example each cross section is an average of 30 adjacent 1-pixel wide cross-sections) are drawn across 12 flakes (the same 12 flakes in all three images), after which thicknesses are extracted.

5.3.4 Imaging Parameters and Variation of Thickness:

5.3.4.1 Different thickness values for graphene (with thicknesses ranging from 0.35 nm to 1 nm) and graphene oxide layers (from about 0.6 nm to 1.4 nm), relative to the substrate, have been reported in the literature (21, 5, 15, 7, 19, 22, 23). This variation may be attributed to inhomogeneous samples (for example, quality or purity of materials), different controls and modes of imaging parameters (for example, free amplitude of cantilever) and changes in tip-sample interactions (for example, material properties) in AFM measurements. Therefore qualification and verification with different forces (5.3.3) or other imaging parameters (such as free amplitude of the cantilever and amplitude setpoint in tapping mode AFM) should be carefully taken into account.

6. Reporting

6.1 For the analysis of graphene and related materials as addressed in this guide, it is recommended to report the following:

6.1.1 Description of graphene material and storage conditions (manufacturer, production method, powder or dispersion, temperature, humidity, and light/dark protection).

6.1.2 Preparation methods or handling procedures by which representative samples and test specimens were acquired or produced.

6.1.3 Date(s) of measurements.

6.1.4 Description of instrument(s) — make and model.

6.1.5 Date of last calibration of an instrument (using a reference material or other means) and the result (for quantitative measurements).

6.1.6 Number of replicate measurements, appropriate expression of summary statistics (where applicable), and accompanying measurement units (where applicable) for results.

6.1.7 Description, results, and discussion of analytical findings.

7. Keywords

7.1 atomic force microscopy; graphene; graphene oxide; Raman spectroscopy; X-ray photoelectron spectroscopy

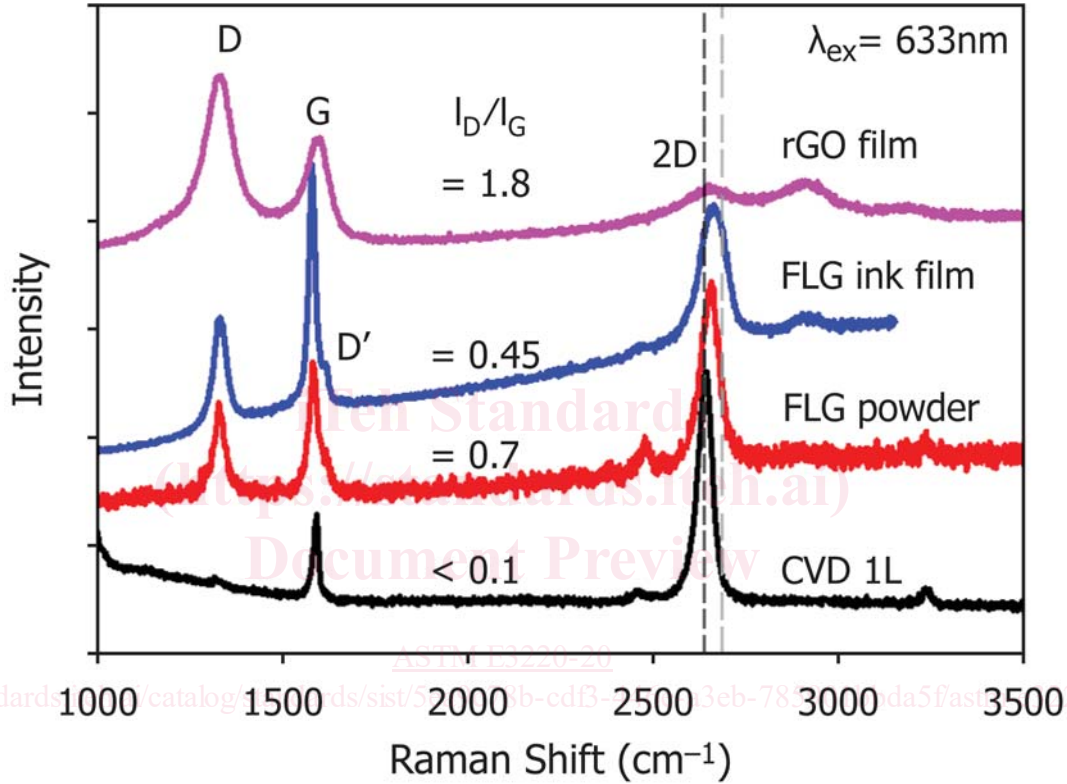
APPENDIXES

(Nonmandatory Information)

X1. CASE STUDY: RAMAN MEASUREMENTS

X1.1 Raman spectra were acquired on several different commercially available graphene related samples in the form of powders and films. Powders were attached to silicon

substrates with the aid of an adhesive film. Spectra were acquired with a commercial Raman microscope using a 50× objective and 633 nm laser excitation.



NOTE 1—The dashed lines indicate the peak positions for the CVD graphene sample (2640 cm⁻¹) and for graphite (2685 cm⁻¹). Calculated values of I_D/I_G for these spectra are also shown.

FIG. X1.1 Raman Spectra of CVD Single Layer Graphene, FLG Powder, FLG Film Deposited from a Graphene Ink, and an r-GO Film