Vibrational and Optical Spectroscopies Integrated with Environmental Transmission Electron Microscopy

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Highlights

- Broadband, high-efficiency design adaptable to other electron microscopes
- Raman spectroscopy integrated with environmental transmission electron microscopy
- Raman spectra peak frequency shifts enable temperature measurement at micron scale
- Multiple types of optical spectroscopy enabled, e.g. cathodoluminescence

Abstract

Here, we present a measurement platform for collecting multiple types of spectroscopy data during high-resolution environmental transmission electron microscopy observations of dynamic processes. Such coupled measurements are made possible by a broadband, high-efficiency, free-space optical system. The critical element of the system is a parabolic mirror, inserted using an independent hollow rod and placed below the sample holder which can focus a light on the sample and/or collect the optical response. We demonstrate the versatility of this optical setup by using it to combine *in situ* atomic-scale electron microscopy observations with Raman spectroscopy. The Raman data is also used to measure the local temperature of the observed sample area. Other applications include, but are not limited to: cathodo- and photoluminescence spectroscopy, and use of the laser as a local, high-rate heating source.

Keywords

Environmental Scanning Transmission Electron Microscopy; Raman Spectroscopy; Cathodoluminescence; TEM Sample Temperature Measurement.

1. Introduction.

In recent years, the environmental scanning transmission electron microscope (ESTEM), has been successfully employed to decipher nanoscale elementary processes, [1-3] e.g. oxidation/reduction,[4] sintering and Ostwald ripening,[5] surface reconstruction,[6] catalyst dynamics.[7] But a chemical reaction or physical phenomenon might be intrinsically heterogeneous at small length scales. The limited area measured in a typical experiment may therefore not be representative of the behavior of the whole sample. Furthermore, the highenergy electron beam used for imaging can be intrusive and may affect the reaction processes.[8] These issues can be addressed by making independent in situ measurements using other techniques such as X-ray diffraction (XRD), X-ray photon spectroscopy (XPS), Raman Spectroscopy, etc. However, the direct comparison of such measurements with those from the ESTEM is problematic as the two reaction chambers may not be operating under identical conditions. Moreover, additional ex situ measurements are also limited by the possibility of sample altering during the transfer from the ESTEM reaction chamber to the external characterization system. Thus, combining *in situ* high resolution imaging with a complementary global measurement technique, such as *in situ* Raman spectroscopy, is highly desirable.[9-11]

An additional benefit of this combination is that Raman spectroscopy can be used to measure the temperature of the sample in the vicinity of the ESTEM observations.[12-14] This is essential if, for example, quantitative kinetic data is needed. But measurements of the sample temperature from the area under study are not trivial.[15] Significant discrepancies can exist between the temperature reported by the heating holder thermocouple and the actual sample temperature. Large transients can also follow the introduction of room temperature gases, i.e. high gas

pressures and or/thermal conduction/convection can lead to unacceptable measured versus actual temperature differences.

Currently, two main types of heating holders are available on the market: furnaces and microelectro-mechanical system (MEMS) devices. The furnaces heat the entire sample. They are equipped with a thermocouple, but the measuring point is some distance away from the area under transmission electron microscope (TEM) observation. Therefore, the actual temperature of the observed region will depend on the thermal conductivity of the TEM grid and support material, as well as the level of contact between the grid and the furnace. On the other hand, most MEMS heating devices have no direct measure of the temperature, and temperature measurements are inferred from calibrations made under high vacuum conditions. Recently, devices that maintain the temperature constant by power compensation have become commercially available. But in either case, the localized nature of these heating devices tends to generate substantial temperature gradients, hence it is critical to implement a reliable real-time and local temperature measurement technique. These issues can be resolved by focusing a laser to a small (few micrometer) diameter spot on the sample and measuring the Raman peak shifts with temperature.

Introduction of light inside the TEM to investigate photo-catalysis reactions, perform nanosecond pulsed *in situ* TEM measurements, or make real-time observations of laser-material interactions has been reported.[16-18] Similarly, a prototype for cathodoluminescence signal collection in a scanning transmission electron microscope (STEM), and a commercial system for TEM are also available.[19] In the past a parabolic mirror has been used either to focus the light on to the sample or to collect the CL but has not been used for both. The novelty of our design is

that same parabolic mirror is used to focus the light from external source and simultaneously collect the sample response. Moreover, most of these set-ups are integrated into a TEM holder, making them application-specific and not compatible with specialty holders, e.g. heating, cooling, and straining.

Here we present a free-space, broadband (wavelength $\lambda > 200$ nm), high-efficiency (1.5 sr) light delivery and collection system that is independent of the TEM sample holder and enables multiple types of spectroscopy under reaction conditions. As a demonstration of its capability, we show that Raman or cathodoluminescence (CL) signals with high signal to noise ratios (SNR) can be obtained during ESTEM experiments.

2. Design

The delivery of light to and collection of light from the sample is made possible by the insertion of a parabolic mirror between the sample holder and the lower objective pole piece of the ESTEM. The parabolic mirror can be used to focus light onto on the sample and/or collect scattered/emitted photons. Light reaches the parabolic mirror along a free-space beam path through a viewport on a hollow rod into the vacuum system. By eliminating any fiber optic components, this arrangement has the advantages that it decouples the spectrometer mechanically from the microscope (i.e. eliminating a possible source drift and/or vibrations), the sample holder from the optics, and permits the use of a very wide spectral bandwidth. This dramatically improves the coupling efficiency into a spectrometer. Finally, the system is capable of handling high continuous-wave and pulsed-laser powers.



Fig. 1. (a) Schematic 3-D view of the parabolic mirror. (b) Top view.

In our current system, we use a parabolic mirror to focus a 532 nm laser onto the sample and collect the resulting Raman signal. The parabola design is similar to the one used for CL measurements in a STEM by Kociak et al.[19-22] Both the space between the pole-pieces and the diameter of the port available to insert the parabola constrain the design and were taken into account to calculate the dimensions of the parabolic mirror with the maximum collection angle. The surface of the parabola has an aluminum coating that permits a high reflectivity for a large range of wavelengths (> 80 % for wavelengths longer than 200 nm and > 90 % beyond 2000 nm). A 300 µm diameter hole is drilled in the parabola to let the electron beam pass (Fig. 1). The position of the hole is aligned with the parabola focal point to make the laser light and the electron beam positions coincide on the sample. Thus, it is possible to work in two configurations: i) aligned: where the Raman probed area includes the ESTEM observation area ii) misaligned: where Raman and TEM probe two distinct areas (see supporting information section 3 for details about the alignment procedure). The laser spot on the sample surface is round with a diameter of $(11 \pm 4) \mu m$ (see Figure S1 in supporting information. Here and in the following, reported uncertainties represent one standard deviation). Thus the probed area is (100 \pm 60) μ m², which is about 5 orders of magnitude larger than the typical field of view used for atomic resolution ESTEM imaging ($\approx 1000 \text{ nm}^2$). This probed area is too large to enable TEM /

Raman correlations at the individual nano-object level, but is important as it allows simultaneous collection of micro-scale spectroscopy data and nanoscale ESTEM imaging to complement atomic scale information with large scale picture of the structure and kinetics, mitigating the need for two separate in situ measurements. The mirror is connected to a hollow rod by two tungsten wires. This rod-mirror assembly replaces the objective aperture holder (Fig.2). The rod is O-ring sealed to the pre-existing column port and has a sapphire optical window to allow the incoming excitation light and outgoing signal to travel to and from the sample with minimum intensity loss (Fig. 2). It is important to note that the objective aperture rod and this holder are easily interchangable. Also, just like the objective aperture, the parabola is kept in a retracted position and is inserted during optical measurements only.



Fig. 2. Schematic view of the integrated optical spectroscopy system. The laser goes through the optical window and then is focused on the sample membrane after hitting the parabola located below the sample. It also collects a portion (1.5 sr) of the photons emitted by the sample.

A spectrometer equipped with a N₂ cooled charge-coupled detector is used for spectra collection. Raman data is collected with a 532 nm diode-pumped, solid-state laser and a neutral-density filter wheel which allows adjustment of the laser power from 0.1 mW to 300 mW. In Raman mode, the laser light passes through a dichroic beam splitter, then through the sapphire window and is finally focused on the sample by the parabolic mirror. The backscattered light from the sample passes directly through the dichroic mirror to the spectrometer and focused on its entrance slit using a set of two mirrors and one adjustable lens.

3. Applications

3.1. Raman data acquisition

In situ calibration of the Raman spectrometer is done using the silicon peak at 521 cm⁻¹ [23] from the silicon area surrounding a MEMS heating device (Fig. 3a). Figure 3b shows a 30 s acquisition time room-temperature Raman spectrum obtained from single-wall carbon nanotubes (SWCNT) after their growth in the ESTEM at 625 °C under acetylene flow using a Co/MgO catalyst/support. It exhibits the typical Raman features of SWCNTs: radial breathing modes (RBM), D band, G bands (G- and G+) at ≈ 300 cm⁻¹, 1300 cm⁻¹ and ≈ 1600 cm⁻¹, respectively.[24] The shapes and positions of these peaks provide structural information about the nanotubes such as diameter distribution, global defect density, and chirality (e.g. semiconducting/metallic).[25] Moreover, the high efficiency of the signal collection (1.5 sr) enables us to follow the temporal evolution of the G band (the most prominent feature of SWCNT spectra) intensity during the growth, in spite of the peak broadening and weakening that occurs with increasing temperature (Fig. 3c and 3d). Spectra with 20 s acquisition times were recorded during a 60 min growth period. Continuous Raman acquisition permits us to estimate the temporal evolution of nanotubes [9] and extract the reaction kinetics while atomic resolution movies are recorded simultaneously. The observed growth period can be divided in following steps: I) an incubation period of 1500 s during which only a very weak signal from G band is observed, II) an

acceleration of the growth between 1500 s and 2000 s, and III) deceleration of the growth after 2000 s. The existence of these three growth regimes for long SWCNTs can only be evidenced with the optical spectroscopy approach, as by the time the Raman signal is measurable, the nanotubes are already longer than the typical high-resolution imaging field of view (Fig. 3e, shows an ESTEM image after 1700 s of growth). Thus, large-scale information about the nanotubes' growth kinetics cannot be retrieved from ESTEM data alone. It also enables us to better diagnose the termination of the growth processes. In fact, the Raman data clearly show a steady but slow increase of the G+ peak which implies that, even if the growth may have stopped for the observed area, it is not terminated for the entire sample. On the other hand, high resolution imaging is ideal to identify the elementary processes and phenomena explaining the existence of these different growth regimes. It is important to note that at high temperature, the spectra acquisition can be hindered by the black body emission from the incandescent specimen. For 532 nm laser used here, this effect starts to become an issue at 600 °C (see figure S3 of supporting information section 4), and it makes spectra acquisition above 1,000 °C impracticable.



Fig 3. (a) 0.5 s silicon spectrum used to calibrate the position and the intensity of the Raman peaks (laser power = 200 mW). (b) 30 s spectrum obtained at room temperature from single-walled carbon nanotubes grown in the ESTEM (laser power = 1mW). (c) Evolution of the nanotube G+ signal during growth at 625 °C and acetylene pressure of 10^{-3} Pa. (d) Corresponding temporal evolution of the G+ band intensity during the growth, showing three different growth regimes, marked as I, II and III. (e) Low magnification TEM image of the nanotubes obtained after 1700 s of growth.

3.2. Temperature measurement

The frequencies of Raman peaks typically downshift with increasing temperature because of the softening of the interatomic bonds, making the measure of peak shifts a simple and viable option for temperature measurement. SWCNTs are ideally suited for such measurement as they have

high thermal conductivity, sharp G band in Raman spectra and have large contact areas with the sample support. [24, 26] A solution of dispersed SWCNTs was deposited on a MEMS heating device and the temperature was derived from the relation between the G+ band position, v_{G+} , and the temperature: $d(v_{G+})/dT = (0.0275 \pm 0.0013) \text{ cm}^{-1}\text{K}^{-1}$, a value that has been consistently reported in the literature [27] (5 % relative error, that is +/- 38 °C at 500 °C. The presented uncertainty corresponds to the single standard deviation from the averaged $d(v_{G+})/dT$ value. See section 2 of supporting information for further details about temperature calculation and uncertainties estimation methods). Thus in the following, the reported absolute temperature value are given with a 5% uncertainty. Nonetheless, the relative temperature variations can be monitored with a better precision, which corresponds to the ability to determine the Raman peaks position shifts. This uncertainty increases with increasing temperature because of the Raman peak broadening and weakening: the measurement uncertainty is $\pm 0.07 \text{ cm}^{-1}$ at 150 °C, i.e. ± 3 °C, and $\pm 0.24 \text{ cm}^{-1}$ at 750 °C, i.e. $\pm 9 \text{ °C}...$ The spatial resolution for temperature measurements corresponds to the laser beam spot size, that is $(11 \pm 4) \mu \text{m}$.

Such measurements also allow us to evaluate sample heating by laser power. Thin membranes, used as sample support in a MEMS heating device, are susceptible to laser heating due to the lack of heat dissipation pathways in vacuum. However, Fig. 4a shows that the 532 nm laser has negligible sample heating below a threshold of 1.2 mW, where no temperature increase is observed; in other words, no Raman peak shift is observed. For this reason, all Raman measurements are performed at 800 μ W. Substantial heating was observed as the power was increased above the threshold: a maximum of 880 °C temperature can be reached at a power of 29.1 mW. Above this power, the laser heating melted the membrane and drilled holes.

Interestingly, the heating of the MEMS device was found to be reproducible from one device to other similar ones, so that the laser can be used as a controlled local heating source.

Figure 4b presents a typical calibration of a MEMS heating device. Here, the temperature is found to linearly increase with applied current in the 200 °C to 900 °C range. Figure 4c shows the existence of strong temperature gradients on the membrane heaters, obtained by measuring the nanotube Raman G+ peak position on each membrane hole. This reveals the critical aspect of doing all the experiments on the same hole of a MEMS based heating holder in order to get reproducible and reliable results.

During ESTEM experiments we are faced with another issue: the temperature drops when a room-temperature gas is introduced. Figure 4d illustrates the temperature drop after the introduction of nitrogen. At a pressure of 2 Pa of nitrogen, the temperature dropped from 630 °C to 595 °C, from 490 °C to 460 °C, and no drop was observed at 320 °C. For a pressure of 60 Pa, the temperature drop was found to be much more severe: from 630 °C to 460 °C, from 490 °C to 220 °C. It is important to note that the temperature drop is expected to be even worse for higher gas pressures than used for current measurements or when using gases with high heat conductivity, like H₂ or He.



Fig. 4 (a) Evolution of the SWCNT G+ Raman peak frequency as a function of the laser power (black squares). The red squares represent the corresponding temperature. (b) Evolution of the temperature as a function of the current applied on the TEM membrane. (c) Evidence of temperature gradients along the three dashed lines of the TEM sample heating membrane. White disks represents the membrane holes. (d) Temperature drop as a function of pressure. The reported uncertainties represent one standard deviation (see supporting information for more details about uncertainties estimation).

3.3. Cathodoluminescence data acquisition

The multifunctional nature of our design was tested with cathodoluminescence spectroscopy (CL). The parabolic mirror can also be used to collect photon emitted by a sample as a result of electron excitation. CL in an electron microscope provides optical and structural characterization with high spatial resolution [28], e.g. luminescence properties of semiconductors, [29] plasmonic modes of nanomaterials, [30] defect localization, [31] etc. Here, we show concurrent collection of CL and electron energy loss spectroscopy (EELS) along with STEM imaging from a nanometer region of a gold nanoparticle (Fig. 5). The CL spectral resolution is below 1 meV compared to the 100 meV resolution of monochromated EELS. This makes CL an interesting technique to analyze small energy shifts that can be induced by extrinsic factors *in situ*, e.g. adsorption of gases, temperature changes, chemical reactions, surface restructuring, etc. In addition, while the EELS signal results from an absorption phenomenon, CL is an emission process. Correlating both techniques at the same time and from the same area gives a broader picture of the local optical properties of the probed material. The CL obtained from nano-scale areas can also be compared with photoluminescence generated from micrometer scale areas via laser irradiation, thus providing local and global information at the same time.



Fig 5. (a) STEM image of a triangular gold nanoparticle sitting on TiO₂. The white circle at the top corner of the nanoparticle indicates the location of the electron beam for the spectroscopy measurements. (b) Corresponding electron energy loss spectroscopy (EELS) and cathodoluminescence (CL) spectra. The energy loss peak, attributed to the surface plasmon resonance of the gold nanoparticle, is found to be (2.326 ± 0.002) eV. The surface plasmon resonance emission peak is measured at (2.0077 ± 0.0007) eV.

4. Conclusion

In summary, we have presented the design and application of a broadband, highly-efficient optical system integrated into the ESTEM that is capable of delivering light to and collecting light from the sample. It enables the generation and/or collection of multiple spectroscopic signals such as Raman and cathodoluminescence during high-resolution imaging under dynamic conditions. We have demonstrated the utility of the system, combining global measurements

acquired by Raman spectroscopy with local information collected via ESTEM. This combination provides comprehensive structural and kinetic data. Moreover, high spatial resolution cathodoluminescence can be concurrently compared with electron loss spectroscopy data. These complementary measurements, obtained at the same time, from the same area, under controlled pressure and temperature, enable a complete characterization approach. This versatile platform allows the local temperature of a TEM sample to be monitored under reactive conditions by analyzing frequency shifts of Raman peaks. It can also be used for fast, precise, local laserinduced heating.

By modifying the optical parabola support rod dimensions to fit in the sample chamber of a given instrument, this broadband, free space, stand-alone optical platform can be used with any TEM/STEM/ESTEM instrument. It can be further modified for more specific applications: the use of a pulsed laser source would enable local pulsed heating; or the optics cart can be modified to incorporate a different light source and can be adapted in order to measure signals in the deep UV and far IR ranges by an appropriate choice of detector and optical components.

Associated Content

Supporting information

On the laser beam spot size and shape. On the temperature measurement method and on uncertainties estimation. This material is available free of charge via the internet at http://www.sciencedirect.com

Notes

The authors declare no competing financial interests.

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[1] R. Sharma, An environmental transmission electron microscope for in situ synthesis and characterization of nanomaterials, Journal of materials research, 20 (2005) 1695-1707.

[2] T.W. Hansen, J.B. Wagner, R.E. Dunin-Borkowski, Aberration corrected and monochromated environmental transmission electron microscopy: challenges and prospects for materials science, Materials Science and Technology, 26 (2010) 1338-1344.

[3] P.L. Gai, E.D. Boyes, Advances in atomic resolution in situ environmental transmission electron microscopy and 1Å aberration corrected in situ electron microscopy, Microscopy research and technique, 72 (2009) 153-164.

[4] S. Chenna, R. Banerjee, P.A. Crozier, Atomic-Scale Observation of the Ni Activation Process for Partial Oxidation of Methane Using In Situ Environmental TEM, ChemCatChem, 3 (2011) 1051-1059.

[5] S.B. Simonsen, I. Chorkendorff, S. Dahl, M. Skoglundh, J. Sehested, S. Helveg, Direct observations of oxygen-induced platinum nanoparticle ripening studied by in situ TEM, Journal of the American Chemical Society, 132 (2010) 7968-7975.

[6] H. Yoshida, Y. Kuwauchi, J.R. Jinschek, K. Sun, S. Tanaka, M. Kohyama, S. Shimada, M. Haruta, S. Takeda, Visualizing gas molecules interacting with supported nanoparticulate catalysts at reaction conditions, Science, 335 (2012) 317-319.

[7] S. Hofmann, R. Sharma, C. Ducati, G. Du, C. Mattevi, C. Cepek, M. Cantoro, S. Pisana, A. Parvez, F. Cervantes-Sodi, In situ observations of catalyst dynamics during surface-bound carbon nanotube nucleation, Nano letters, 7 (2007) 602-608.

[8] R. Egerton, P. Li, M. Malac, Radiation damage in the TEM and SEM, Micron, 35 (2004) 399-409.

[9] M. Picher, E. Anglaret, R. Arenal, V. Jourdain, Self-deactivation of single-walled carbon nanotube growth studied by in situ raman measurements, Nano letters, 9 (2009) 542-547.

[10] B.S. Yeo, A.T. Bell, In situ Raman study of nickel oxide and gold-supported nickel oxide catalysts for the electrochemical evolution of oxygen, The Journal of Physical Chemistry C, 116 (2012) 8394-8400.

[11] E.-S.M. Sherif, R. Erasmus, J. Comins, In situ Raman spectroscopy and electrochemical techniques for studying corrosion and corrosion inhibition of iron in sodium chloride solutions, Electrochimica Acta, 55 (2010) 3657-3663.

[12] G. Viera, S. Huet, L. Boufendi, Crystal size and temperature measurements in nanostructured silicon using Raman spectroscopy, Journal of Applied Physics, 90 (2001) 4175-4183.

[13] R. Cuscó, E. Alarcón-Lladó, J. Ibanez, L. Artús, J. Jiménez, B. Wang, M.J. Callahan, Temperature dependence of Raman scattering in ZnO, Physical Review B, 75 (2007) 165202.

[14] C. Fantini, A. Jorio, M. Souza, M. Strano, M. Dresselhaus, M. Pimenta, Optical transition energies for carbon nanotubes from resonant Raman spectroscopy: Environment and temperature effects, Physical review letters, 93 (2004) 147406.

[15] S. Vendelbo, P. Kooyman, J. Creemer, B. Morana, L. Mele, P. Dona, B. Nelissen, S. Helveg, Method for local temperature measurement in a nanoreactor for< i> in situ</i> high-resolution electron microscopy, Ultramicroscopy, 133 (2013) 72-79.

[16] B.K. Miller, P.A. Crozier, System for In Situ UV-Visible Illumination of Environmental Transmission Electron Microscopy Samples, Microscopy and Microanalysis, 19 (2013) 461-469.

[17] J.S. Kim, T. LaGrange, B.W. Reed, M.L. Taheri, M.R. Armstrong, W.E. King, N.D. Browning, G.H. Campbell, Imaging of transient structures using nanosecond in situ TEM, Science, 321 (2008) 1472-1475.

[18] B. Xiang, D.J. Hwang, J.B. In, S.-G. Ryu, J.-H. Yoo, O. Dubon, A.M. Minor, C.P. Grigoropoulos, In Situ TEM near-field optical probing of nanoscale silicon crystallization, Nano letters, 12 (2012) 2524-2529.

[19] L.F. Zagonel, S. Mazzucco, M. Tencé, K. March, R. Bernard, B. Laslier, G. Jacopin, M. Tchernycheva, L. Rigutti, F.H. Julien, Nanometer scale spectral imaging of quantum emitters in nanowires and its correlation to their atomically resolved structure, Nano letters, 11 (2010) 568-573.

[20] M. Kociak, L.F. Zagonel, M. Tence, S. Mazzucco, Flexible cathodoluminescence detection system and microscope employing such a system, in, Google Patents, 2011.

[21] M. Kociak, L.F. Zagonel, M. Tence, S. Mazzucco, Adjustable cathodoluminescence detection system and microscope employing such a system, in, Google Patents, 2011.

[22] L. Tizei, M. Kociak, Spatially resolved quantum nano-optics of single photons using an electron microscope, Physical Review Letters, 110 (2013) 153604.

[23] H. Richter, Z. Wang, L. Ley, The one phonon Raman spectrum in microcrystalline silicon, Solid State Communications, 39 (1981) 625-629.

[24] M. Dresselhaus, G. Dresselhaus, A. Jorio, A. Souza Filho, R. Saito, Raman spectroscopy on isolated single wall carbon nanotubes, Carbon, 40 (2002) 2043-2061.

[25] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Raman spectroscopy of carbon nanotubes, Physics Reports, 409 (2005) 47-99.

[26] M. Biercuk, M.C. Llaguno, M. Radosavljevic, J. Hyun, A.T. Johnson, J.E. Fischer, Carbon nanotube composites for thermal management, Applied Physics Letters, 80 (2002) 2767-2769.

[27] S. Chiashi, Y. Murakami, Y. Miyauchi, S. Maruyama, Temperature dependence of Raman scattering from single-walled carbon nanotubes: Undefined radial breathing mode peaks at high temperatures, Jpn. J. Appl. Phys., 47 (2008) 2010.

[28] Z. Mahfoud, A.T. Dijksman, C.m. Javaux, P. Bassoul, A.-L. Baudrion, J.r.m. Plain, B. Dubertret, M. Kociak, Cathodoluminescence in a Scanning Transmission Electron Microscope: A Nanometer-Scale Counterpart of Photoluminescence for the Study of II–VI Quantum Dots, The Journal of Physical Chemistry Letters, 4 (2013) 4090-4094.

[29] P.R. Edwards, R.W. Martin, Cathodoluminescence nano-characterization of semiconductors, Semiconductor Science and Technology, 26 (2011) 064005.

[30] E.J.R. Vesseur, R. de Waele, M. Kuttge, A. Polman, Direct observation of plasmonic modes in Au nanowires using high-resolution cathodoluminescence spectroscopy, Nano letters, 7 (2007) 2843-2846.

[31] P. Jaffrennou, J. Barjon, J.-S. Lauret, B. Attal-Trétout, F. Ducastelle, A. Loiseau, Origin of the excitonic recombinations in hexagonal boron nitride by spatially resolved cathodoluminescence spectroscopy, Journal of Applied Physics, 102 (2007) 116102.

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Supplementary Data

Section 1: Laser beam spot size and shape.

Section 2: Temperature measurement details.

Supplementary data references list.



Figure S1. a) Transmission electron microscope image of a hole drilled in the sample membrane by the 532 nm laser at 200 mW, showing that the laser beam has a round shape. **b)** Cartoon showing the x-axis laser scan direction to collect Raman signal from nanotubes deposited on a TEM grid. **c)** The nanotube Raman signal decay across the edge of a sample covered by nanotube is shown in black. The derivative of the Raman intensity as a function of the x position, shown in red, gives the Gaussian profile of the laser beam. The beam size is obtained by measuring the full half width maximum (FWHM) of the corresponding fitted curve (red dashed line). A (11 ± 4) µm laser beam spot size is obtained (the uncertainty is the standard deviation of the obtained FWHM).

Section 2: Temperature Measurement

Here, we estimate the temperature of the TEM sample support by measuring the G band peak position of carbon nanotubes (CNTs) deposited on it. Because of their high thermal conductivity and large contact area with the sample support, the measured intrinsic temperature of CNTs is a good estimation of the actual sample temperature.

The G+ Raman frequency downshifts with temperature due to the softening of the in-plane C-C bond,[1] whose vibrations are along the nanotube axis so their frequency is essentially independent of the nanotubes diameter.[2] The G+ peak is sharp which ensures a good position measurement precision. Thus, this kind of sample is ideal to measure the temperature of micron scale region of the heating devices. As reported by Zhang et al,[3] the temperature dependence of G+ frequency is approximately equal to the corresponding one of graphite G band, that is $d\nu/dT$ = -0.027 cm⁻¹K⁻¹.[4] The reported du/dT values for carbon nanotubes are -0.028 cm⁻¹K⁻¹.[4] - $0.026 \text{ cm}^{-1}\text{K}^{-1}$, [5] -0.027 cm $^{-1}\text{K}^{-1}$. [3] This temperature dependence, which has been shown to be unaffected by the laser wavelength [6] is in close agreement with the value that was previously obtained in a furnace equipped with a thermocouple: (0.0295 ± 0.0009) cm⁻¹K⁻¹ at 514 nm from catalytic chemical SWCNTs (Figure S2). Therefore, for further calculation, the average value of $d\upsilon/dT = (0.0275 \pm 0.0013)$ cm⁻¹K⁻¹ has been used. This fluctuation of the υ G+ temperature dependence may be explained by the variation observed from one individual SWCNTs to another, leading to a slight du/dT variation depending on the SWCNTs chirality distribution.[3] Thus, the absolute temperature value cannot be known with an accuracy better than 5%, which corresponds to the standard deviation of the averaged du/dT mentioned above. Nonetheless, the relative temperature variations can be monitored with a better accuracy, corresponding to the ability to determine the Raman peak position shifts (standard deviation of the calculated position). Hence, the error increases with increasing temperature because of the Raman peak broadening and weakening: the error is ± 0.07 cm⁻¹ at 150 °C, i.e. ± 3 °C, and ± 0.24 cm⁻¹ at 750 $^{\circ}$ C, i.e. \pm 9 $^{\circ}$ C.



Figure S2. a) Evolution of the G band of single walled carbon nanotubes with increasing temperature (25 °C in black, 100 °C in dark blue, 200 °C in blue, 300 °C in cyan, 350 °C in green, 400 °C light green, 450 °C in orange, 500 °C in red). **b)** Evolution of the G+ band Raman frequency with increasing temperature.

Section 3: Laser beam alignment

In order to make the sample height coincide with the focal plane of the parabola (Z direction), the height of the parabola and/or of the holder are adjusted to obtain maximum intensity for a Raman or a CL peak.

In order to make the laser beam and the electron beam coincide (X and Y directions), two different ways can be used:

 By using a high laser power, holes can be drilled in the TEM sample membrane. Therefore, the parabola can be moved in the X&Y directions, until the drilled hole (focal point of the parabola) is aligned with the electron beam.

2) A less destructive technic is to adjust the X-Y position of the parabola to obtain maximum cathodoluminescence (CL) signal emitted as a result of electron beam excitation of a relevant material, such as GaAs, deposited on a TEM grid. Once the CL intensity is maximized, the focal point of the parabola is aligned with the CL emission point, i.e. the electron beam.

Section 4: Raman spectra acquisition at high temperature

The black body emission of the specimen can be a significant issue for high temperature Raman spectra acquisition. In the present case of a 532 nm laser, the incandescence starts being visible at 600 °C. This effect is worst for longer wavelength lasers (red and infra-red). Therefore, this issue can be partially addressed by using a shorter wavelength laser (blue, UV light).



Figure S3. Evolution of the G band of single walled carbon nanotubes with increasing temperature, showing the appearance of the black body emission continuous background at 600 °C, at 532 nm. (25 °C in black, 300 °C dark grey, 550 °C in light grey, 600 °C in red, 650 °C in orange, 700 °C yellow).

Supplementary Data References List:

[1] N.R. Raravikar, P. Keblinski, A.M. Rao, M.S. Dresselhaus, L.S. Schadler, P.M. Ajayan, Temperature dependence of radial breathing mode Raman frequency of single-walled carbon nanotubes, Physical Review B, 66 (2002) 235424.

[2] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Raman spectroscopy of carbon nanotubes, Physics Reports, 409 (2005) 47-99.

[3] Y. Zhang, L. Xie, J. Zhang, Z. Wu, Z. Liu, Temperature coefficients of Raman frequency of individual single-walled carbon nanotubes, The Journal of Physical Chemistry C, 111 (2007) 14031-14034.

[4] F. Huang, K.T. Yue, P. Tan, S.-L. Zhang, Z. Shi, X. Zhou, Z. Gu, Temperature dependence of the Raman spectra of carbon nanotubes, Journal of applied physics, 84 (1998) 4022-4024.

[5] X. Zhang, F. Yang, D. Zhao, L. Cai, P. Luan, Q. Zhang, W. Zhou, N. Zhang, Q. Fan, Y. Wang, Temperature dependent Raman spectra of isolated suspended single-walled carbon nanotubes, Nanoscale, (2014).

[6] S. Chiashi, Y. Murakami, Y. Miyauchi, S. Maruyama, Temperature measurements of singlewalled carbon nanotubes by Raman scattering, Laser, 1590 (2005) 530.