Vibrational and optical spectroscopies integrated with environmental transmission electron microscopy

Matthieu Picher [a,b], Stefano Mazzucco [a,b,1], Steve Blankenship [a], Renu Sharma [a,*]

[a] Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899-6203, United States
[b] Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, MD 20740, United States

ARTICLE INFO

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.

Published by Elsevier B.V.

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 high-energy 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 micro-electro-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.

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 ± 4) μm (see Fig. S1 in Supporting information. Here and in the following, reported uncertainties represent one standard deviation). Thus the probed area is (100 ± 60) μm^2,
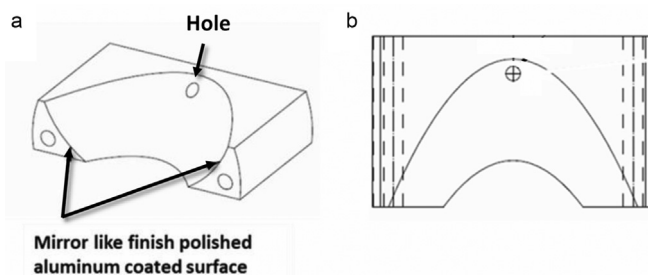

Fig. 1. (a) Schematic 3-D view of the parabolic mirror. (b) Top view.
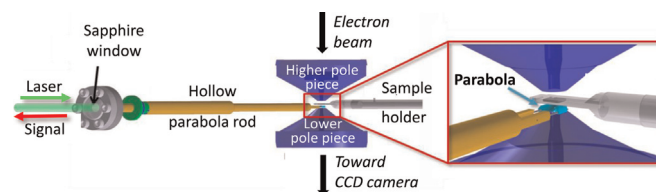

Fig. 2. Schematic view of the integrated optical spectroscopy system. The laser goes through the optical window and then is focused on the sample membrane after hitting the parabola located below the sample. It also collects a portion (1.5 sr) of the photons emitted by the sample.

which is about 5 orders of magnitude larger than the typical field of view used for atomic resolution ESTEM imaging (≈ 1000 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.

A spectrometer equipped with a N_2 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). Fig. 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},