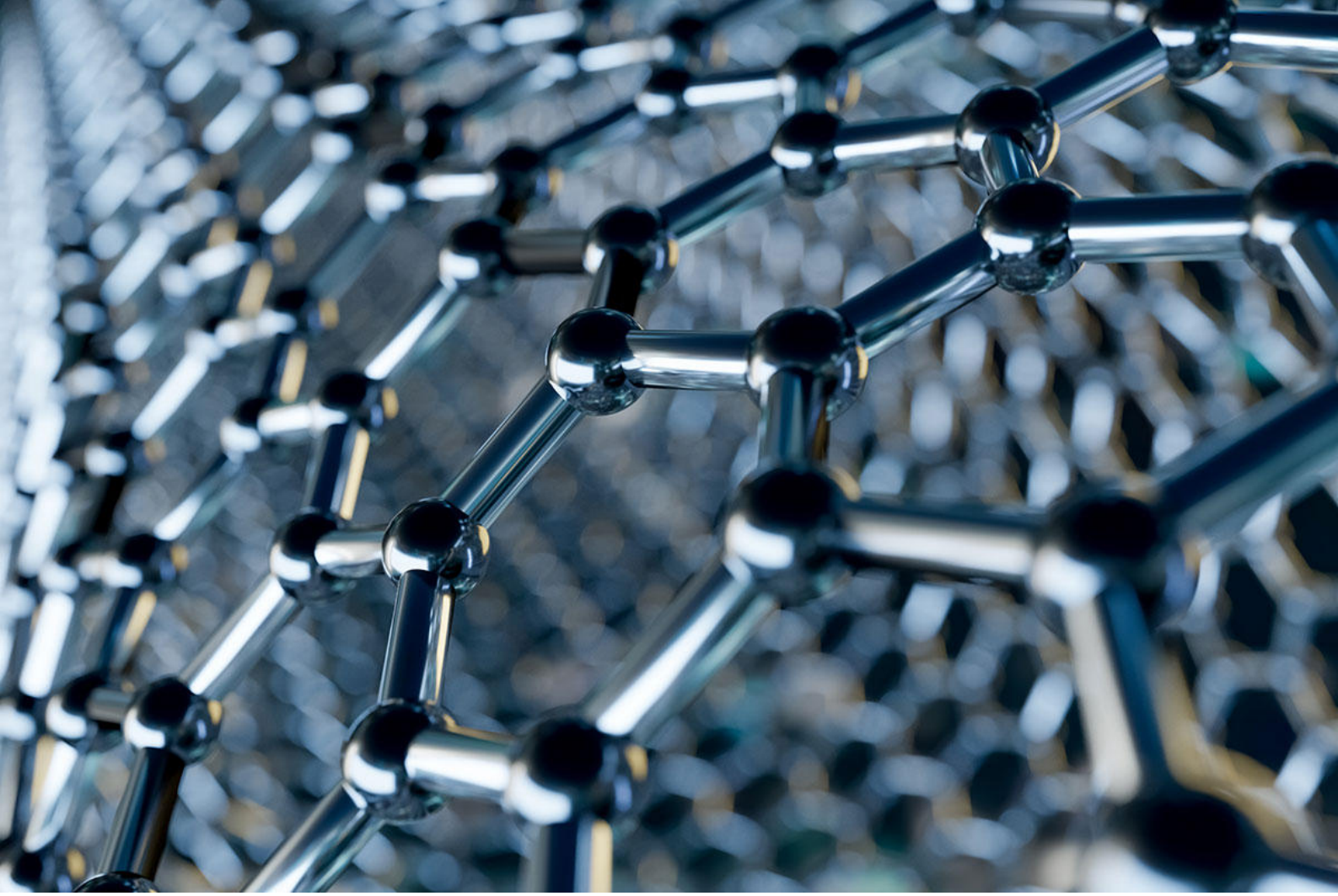


Application Note AN-RA-009

Comparison of SPELEC RAMAN and standard Raman microscopes

Larger laser spot size can provide representative results with a single measurement

Standard Raman microscopes are traditionally used to perform Raman measurements or Raman spectroelectrochemical experiments when they are coupled with electrochemical equipment. Raman spectra collected with confocal microscopes allows the characterization of very small areas. However, these instruments can exhibit several limitations.

SPELEC RAMAN, a new generation of spectroscopic and spectroelectrochemical instruments, offers powerful and interesting features to overcome these issues.

In this Application Note, a detailed comparison is made between the main features of a standard Raman instrument and the SPELEC RAMAN by analyzing the results obtained with both instruments.

INSTRUMENTATION AND SOFTWARE

Measurements were performed using a SPELEC RAMAN instrument (785 nm laser), a Raman probe corresponding to the laser wavelength, and a Raman spectroelectrochemical cell for screen-printed electrodes. This cell (Figure 1) has a small aluminum crucible holder to facilitate the precise optical characterization of solid and liquid samples.

A sample of single-walled carbon nanotubes (SWCNT) was placed in the aluminum crucible to obtain the characteristic Raman spectrum.

The SPELEC RAMAN instrument was controlled with DropView SPELEC, a dedicated software for electrochemical, spectroscopic, and spectroelectrochemical measurements. All hardware and software used for this study is compiled in Table 1.



Figure 1. Raman spectroelectrochemical cell.

Table 1. Hardware and software equipment overview.

Equipment	Article number
Instrument	SPELECRAMAN
Raman probe	RAMANPROBE
Raman cell	RAMANCELL
Software	DropView SPELEC

CHARACTERIZATION OF SINGLE-WALLED CARBON NANOTUBES

Different aspects must be considered to compare the measurements performed with SPELEC RAMAN and a standard Raman microscope.

Although standard Raman microscopes are traditionally limited to spot sizes on the order of 0.5–10 µm, the laser spot diameter depends on the laser wavelength and the objective used. Raman spectra collected with confocal microscopes allow the characterization of very small areas due to the miniature spot diameter, but they provide limited information in bulk and microscopic analysis. For instance, the small spot size can cause misinterpretations in non-homogeneous samples when the Raman response of a specific area is considered representative of the whole sample.

Figure 2a shows the Raman spectra recorded with a standard Raman microscope at four different positions of a sample of single-walled carbon nanotubes (SWCNT). Not only the intensity, but also the ratio of D and G bands (I_D/I_G), located at 1350 cm^{-1} and 1598 cm^{-1}, respectively, differ depending on the position: 0.679, 0.843, 0.837, and 0.448 (average I_D/I_G = 0.702, RSD = 26.44%).

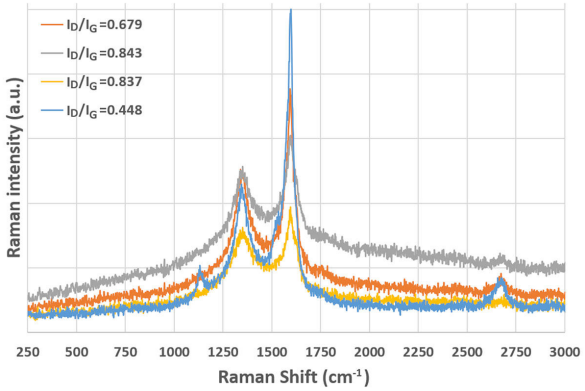


Figure 2a. Raman spectra recorded with a standard Raman microscope.

SPELEC RAMAN's larger spot size (190 µm practical diameter of the Raman probe) allows characterization of a broader area in a single experiment. With SPELEC RAMAN, one Raman spectrum is representative of the analyzed system. This avoids the need to perform additional measurements, saving time and costs. Here, the same SWCNT sample that was previously analyzed in Figure 2a was characterized with SPELEC RAMAN (Figure 2b). The ratio obtained with SPELEC RAMAN in a single spectrum, I_D/I_G = 0.701, exactly matches the average of the four spectra taken with the Raman microscope.

In order to assess the reproducibility of SPELEC RAMAN, three additional spectra were recorded in the same sample, and the following ratios were obtained: 0.733, 0.726, and 0.713. The average of the four measurements results in the following values: I_D/I_G = 0.718 and RSD = 1.97%. Then, the good reproducibility of measurements performed with 190 µm spot laser of SPELEC RAMAN is demonstrated.

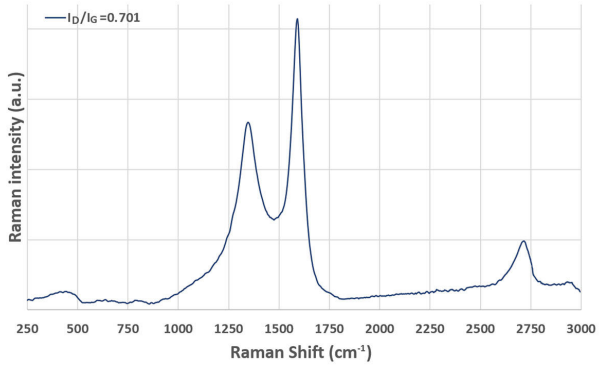


Figure 2b. Raman spectra recorded with SPELECRAMAN.

Furthermore, higher laser power can be applied to the sample with SPELEC RAMAN. This is because the large focal area (0.028 mm^2) on the sample allows the energy to be distributed.

The Raman probe can be easily adapted to a wide variety of different configurations, demonstrating the versatility of SPELEC RAMAN. The optimal focal distance of the Raman probe (8 mm) facilitates its combination with different cells—it is not limited to Metrohm DropSens cells (Figure 3) and allows the study of different electrochemical processes and the characterization of myriad samples. The Raman probe can be customized and adapted to specific laboratory and industrial applications. However, the universal connectors of SPELEC RAMAN instrument (FC/PC and SMA905 for excitation and collection fibers, respectively) allow coupling with a Raman microscope in case it is needed for further study.



Figure 3a. Combination of RAMANPROBE and SPELECRAMAN with RAMANCELL for screen-printed electrodes

Traditional Raman microscopes have a specific compartment for samples, and therefore cells must be designed according to the specifications of each instrument (sample compartment, objectives, focal distance, etc.).

Apart from the excitation laser source and the spectrometer, Raman microscopes require more components (e.g., the microscope module) which increase the price. SPELEC RAMAN is a fully integrated instrument with laser, spectrometer, and potentiostat/galvanostat combined in a single housing.

The small size (25 × 24 × 11 cm) of SPELEC RAMAN makes it an easily portable instrument; it does not require a fixed location nor specific furnishings to operate. Furthermore, the small dimensions of this Metrohm DropSens instrument allows its use in a glovebox without issues.



Figure 3b. Combination of RAMANPROBE and SPELECRAMAN with RAMANCELL-C for conventional electrodes.

Raman microscopes are designed for spectroscopic measurement, and the coupling with external equipment to obtain an additional response (e.g., electrochemistry) is a very complicated task. SPELEC RAMAN is an integrated instrument not only for spectroscopic measurements but also for electrochemical and Raman spectroelectrochemical experiments. Synchronization between electrochemical and Raman measurements is completely ensured.

DropView SPELEC is a dedicated software that allows for integrated data acquisition of electrochemical, spectroscopic and spectroelectrochemical signals as well as the data analysis. Additional software is not required. Experiment film, smoothing, automeasurement, baseline correction, derivative representation, and monitoring of spectra vs. potential (or time), are some of the tools included in DropView SPELEC software.

SPELEC RAMAN and DropView SPELEC software are both very intuitive and user-friendly. As they are simple and straightforward, everyone can use them – not just specifically trained staff as with traditional Raman microscopes.

CONCLUSION

SPELEC RAMAN exhibits a number of competitive advantages over standard Raman microscopes. For instance, the spot size of SPELEC RAMAN allows the characterization of a large area in a single experiment, obtaining representative results with only one measurement. The versatility of the Raman probe is demonstrated since it can be used with different cells. The portability as well as the simplicity of SPELEC RAMAN facilitate the performance of optical experiments. It also ensures the synchronization of electrochemical and optical signals in case Raman spectroelectrochemical measurements are carried out.

In addition, DropView SPELEC software allows real-time acquisition of the data and the performance of operando measurements. The easy data treatment and analysis of the results is done using one-click tools.

RELATED APPLICATION NOTES

AN-RA-002 The carbon battle characterization of screen-printed carbon electrodes with SPELEC RAMAN

AN-RA-003 In situ, fast and sensitive: Electrochemical SERS with screen-printed electrodes

AN-RA-005 Characterization of single-walled carbon nanotubes by Raman spectroelectrochemistry

AN-RA-006 New strategies for obtaining the SERS effect in organic solvents

AN-RA-007 Enhancement of Raman intensity for the detection of fentanyl

AN-RA-008 Easy detection of enzymes with the electrochemical-SERS effect

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CONFIGURATION



Raman Probe

Reflection probe designed to be used with a single excitation 785 nm wavelength (up to 500 mW). Suitable to work with DropSens Raman Cell for Screen-Printed Electrodes or with any conventional Raman set-up.



Raman Cell for Screen-Printed Electrodes

Black teflon reflection cell for performing Raman Spectroelectrochemistry with screen-printed electrodes in combination with ref. RAMANPROBE.



Single-Walled Carbon Nanotubes modified Screen-Printed Carbon Electrode

Single-Walled Carbon Nanotubes modified Screen-Printed Carbon Electrode designed for the development of (bio) sensors with an enhanced electrochemical active area.



Spectroelectrochemical Raman instrument (785 nm laser)

SPELECRAMAN is an instrument for performing spectroelectrochemical Raman measurements. It combines in only one box a laser class 3B (785 nm ± 0.5), a bipotentiostat/galvanostat and a spectrometer (wavelength range 787 – 1027 nm and Raman shift 35 - 3000 cm^{-1}) and includes a dedicated spectroelectrochemical software that allows optical and electrochemical experiments synchronization.