

Mass Spectrometry & Spectroscopy

Hyphenated electrochemical-Raman spectroscopy: Another dimension for your research

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The combination of electrochemical and spectroscopic techniques yields complementary information when studying (electro)chemical reactions. Electrochemical techniques offer precise quantitation with the possibility to analyse solutions at the low part per million (ppm, mg/L) concentration range, or surface processes involving sub-monolayer coverages. The drawback of electrochemical methods is that they offer limited specificity for the target reaction. The information is rather one-dimensional as researchers can monitor the flow of electrons at a given potential, but it is difficult and often impossible to attribute the current signal to a single process. Optical spectroscopic methods like Raman spectroscopy provide molecular information and the possibility to monitor chemical processes as they occur.

This article serves as a primer on the basic principles of Raman spectroscopy and elaborates on the combination of electrochemical techniques with Raman spectroscopy as a means of better understanding electrochemical processes. Examples from the recent literature are provided to illustrate the power of hyphenated EC-Raman.

The fundamentals of Raman spectroscopy

Light can interact with matter in several ways including by absorption, transmission, and scattering. The understanding and controlled observation of these interactions make up the majority of spectroscopic analytical tools, allowing researchers to probe the structures, configurations, and properties of molecules.

Raman spectroscopy is a technique based on the phenomenon of light scattering during molecular vibration. Unlike infrared spectroscopy, it is not necessary for the frequency of the incident light to match energy levels in the sample molecule for this interaction to occur. Raman spectroscopy uses a single wavelength (frequency) of light to irradiate the sample. The incident radiation briefly distorts or polarises the electron cloud around the nuclei into a temporary virtual state. Since the virtual state is unstable, it reverts, and the photon is re-emitted. This process is called light scattering [1]. The polarisation of the electron cloud causes movement of the electrons and also the nuclei. Movement of electrons is relatively «easy» because electrons have little mass; this type of interaction results in a scattered photon that has the same energy as the incident photon. This process is known as elastic or Rayleigh scattering and it is the dominant scattering process. However, the polarisation can also result in nuclear motion when energy is transferred from the incident photon to the molecule, or vice versa, resulting in what is known as inelastic or Raman scattering. Inelastic scattering results in measurable energy shifts; the scattered photon resides at one vibrational unit of energy different from that of the incident light [1,2].

An energy level diagram (also known as a Jablonski diagram), such as the one shown in *Figure 1*, is useful for illustrating these processes. Notice that there are two types of Raman interactions shown in the diagram: Stokes and Anti-Stokes interactions. In a Stokes Raman interaction, energy is transferred to the molecule and the resulting photon has lower energy (higher wavelength) than the incident light. In Anti-Stokes interactions, the molecule transfers energy to the photon so the resulting photon is of higher energy (shorter wavelength) than the incident light. The Jablonski diagram shows how these situations can occur. The Anti-Stokes interactions start with the molecule residing in an excited vibrational state and ending up in a lower energy state, whereas the Stokes interactions start with the molecule residing in the lowest energy state. The population distribution in these vibrational states is given by a Boltzmann distribution and depends on the thermal energy (temperature) of the system. In general, at room temperature, the lowest energy states will be the most populated, so the relative contribution of Anti-Stokes interactions is low compared to Stokes interactions. In practice, Stokes interactions are the most studied in the Raman spectrum, and often Raman spectra are presented with only positive Raman shift values, corresponding to the Stokes interactions [1,2].

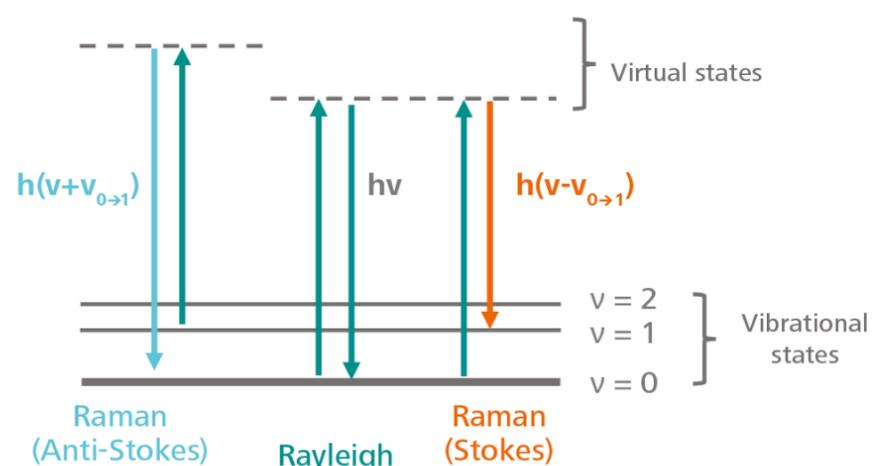


Figure 1. Raman scattering.

As previously noted, elastic scattering is the dominant process. Only one in 10^6 to 10^8 scattering events are inelastic [2]. This is why Raman scattering is said to be inherently weak. However, there are techniques available to enhance the signal and improve the probability of Raman scattering events. Several of these strategies will be discussed in a later section.

The Raman spectrum explained

A Raman spectrum is a plot of scattered light intensity (in arbitrary units) vs. a property called the Raman shift which is expressed in reciprocal centimetres (cm^{-1}) - the same units used in infrared spectra. This can lead to confusion for those who are accustomed to infrared spectroscopy but are new to Raman spectroscopy. The Raman shift is the difference between the measured frequency of the Raman scattered light (measured in wavenumbers and converted to reciprocal centimetres) and the frequency of the incident light source (i.e., the laser). The use of the Raman shift, which is a relative property as opposed to the absolute measured wavelength of the scattered light, differentiates Raman spectroscopy from infrared spectroscopy. Of course, there is a logical reason why Raman spectra are plotted this way, which can be understood by studying the interactions shown in *Figure 1*.

The Raman shift for a particular transition does not change based on the excitation wavelength, whereas the measured wavelength for the transition will be changed based on the excitation wavelength. This is because the energy of the scattered photons is a combination of the energy of the incident light and the energy transferred during the interaction. However, only the transferred energy is characteristic of the vibrational

mode that is being probed. The transferred energy is the “shift” that we refer to in this terminology. The energy of the incident light is systematically subtracted out. In other words, we set the laser excitation equal to zero cm^{-1} of Raman shift. Stokes transitions have positive Raman shifts and Anti-Stokes transitions have negative Raman shifts. Raman spectra obtained using different laser sources (e.g., 532 nm and 785 nm) can be compared directly to each other and the characteristic peaks for any given vibration are expected at the same Raman shift values [1,3].

The Raman scattering selection rule

The energy of a molecule is described by its vibrational states. Depending on the number of atoms and their geometry, the molecule can move within its degrees of freedom. Possible movements include translation, rotation, and various stretching and bending modes. The concept of molecular vibrations is well-known to chemists from the interpretation of infrared (IR) spectra. A subset of the possible molecular vibrations gives rise to strong Raman scattering and thus a peak in the Raman spectrum. The basic selection rule for Raman scattering is that it results from vibrations that change the polarisability of the molecule. The polarisability of a molecule describes how easily the electron cloud around the molecule can be distorted by an electric field [1,2].

The magnitude of this change in polarisability is also important as larger changes in polarisability result in more intense Raman scattering. The electron density distribution of a molecule will react to an external electric field with redistribution of the electron density and the formation of an induced electric dipole moment.

Lattice vibrations in crystalline materials

The topic of lattice vibrations requires some special attention because of its relevance to most electrochemical applications. Until this point, the discussion of vibrations has been in the context of molecules with covalent bonds. However, crystalline materials like salts and metal oxides also give vibrational spectra. A common example of this is crystalline quartz which gives well-defined Raman peaks, while fused quartz gives broad bands in the Raman spectrum. Raman scattering from crystalline solids occurs when the incident radiation induces vibrations throughout the lattice. The quantised vibrations of the atoms in a crystal lattice travel and propagate waves. They are called phonons. Lattice vibrations can follow the propagation direction of the incident light - these are called longitudinal modes (denoted by the letter L). Perpendicular vibrations are called transverse modes (denoted by the letter T) [4]. *Figure 2* illustrates these two types of vibrations using ordered spheres in a one-dimensional lattice. Longitudinal vibrations give rise to compression and rarefaction (increased spacing) of the distance between the spheres.

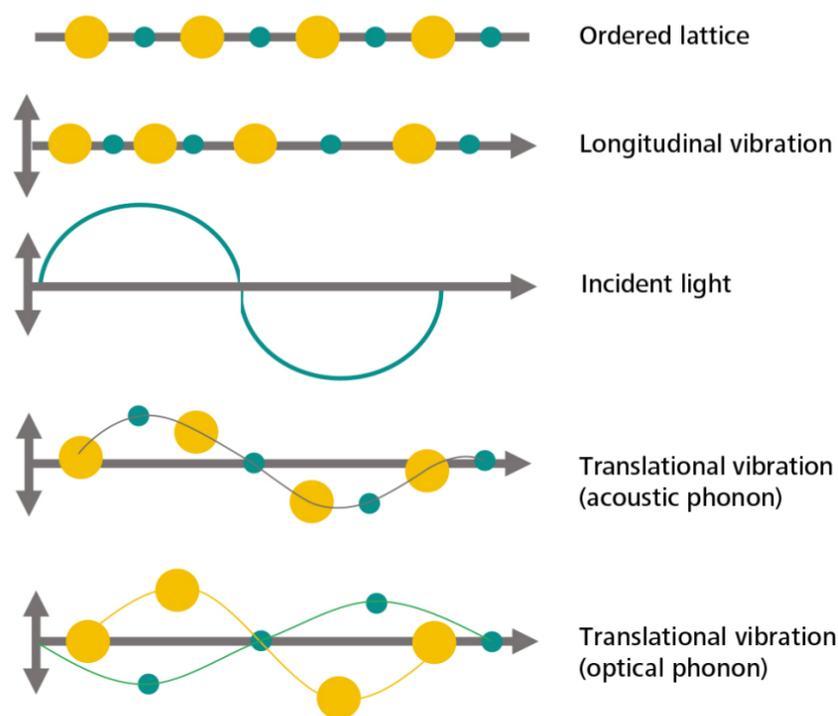


Figure 2. Lattice vibrations illustrated using ordered spheres in a one-dimensional lattice.

The appearance of Raman peaks or bands from lattice vibrations depends on the crystallinity and purity of the materials. The Raman spectrum for a perfectly ordered single crystal usually has few sharp peaks corresponding to the phonons described above. Because these materials are highly symmetrical, the number of unique vibrations is low. In the case of polycrystalline materials, the peaks are broadened. The presence of impurities in the lattice adds additional peaks. Solids with low crystallinity, like the fused quartz mentioned earlier, have broad bands in the Raman spectrum. Amorphous materials have no long range order. Waves cannot translate and propagate through such materials. Strictly speaking, there are no phonons in this case. However, there is a collection of areas of short-range order where vibrations occur, and there are also chemical bond interactions that give rise to scattering. Thus, amorphous materials like glass have peaks and bands in the Raman spectrum [2]. Raman spectroscopy can be used to study glass with different additives and dopants. In fact, Raman spectroscopy

is often used in art history and art conservation studies. For example, it was used to study the stained glass of the Sainte-Chapelle cathedral in Paris (*Figure 3*) to distinguish between glass panels from the original construction in the 15th century and panels added during later restoration projects [5].

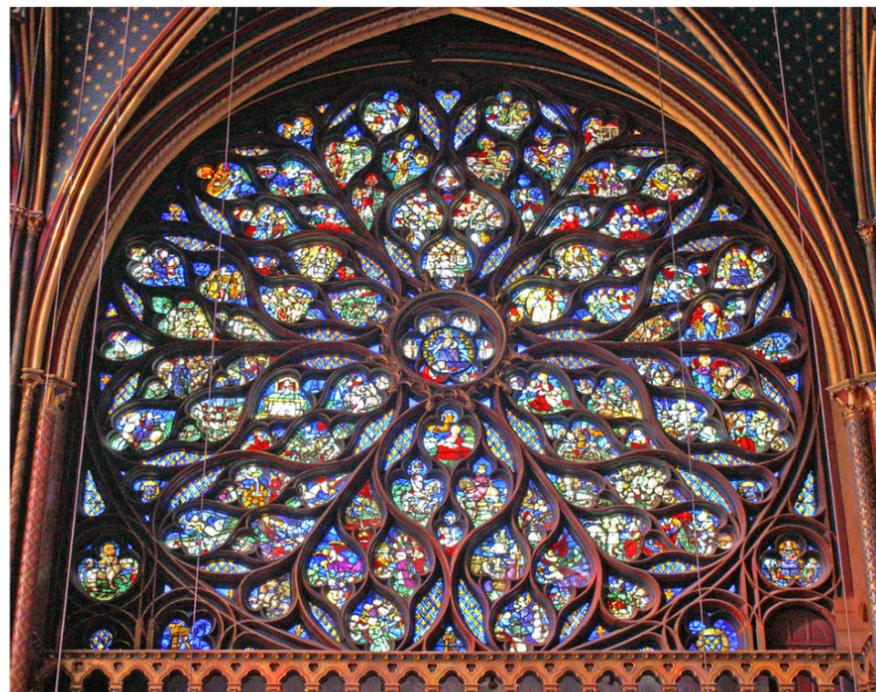


Figure 3. Stained glass artwork in the the Rose window of the Sainte-Chapelle cathedral in Paris (Credit: Didier B (2006), licensed by Creative Commons).

Signal enhancement strategies

As noted in a previous section, Raman scattering interactions are relatively infrequent compared with other vibrational processes. This makes the signal weak and introduces some challenges for the instrumentation design and the researcher. The two most obvious ways of working with an inherently weak signal are to either concentrate the sample or to increase the sampling duration. Both approaches result in a better signal-to-noise ratio in the spectrum. However, when combining Raman spectroscopy with electrochemical systems, neither of these approaches is ideal.

With electrochemical systems there is an additional consideration - many of the processes are interfacial processes, meaning that they are spatially limited to the surface of the working electrode [6]. Thus, there is a need for good spatial resolution for the sampling area for the Raman signal. Also, the fact that the target molecules are limited to the area near the electrode surface means that the sample size is generally small. This introduces a particularly strong need to enhance the Raman signal in EC-Raman applications. Thankfully, enhancement strategies are available, and they are well-suited to electrochemical applications, so these challenges are routinely overcome by researchers.

Surface-enhanced Raman scattering (SERS)

Surface-enhanced Raman scattering (SERS) refers to a phenomenon that can be exploited for Raman signal enhancement and is often used in hyphenated EC-Raman experiments. SERS makes use of the same equipment, in terms of the light source and spectrometer, as a traditional Raman measurement. However, for SERS there is an important substrate that interacts with the incident light and the target molecule. This is the “surface” part of the SERS acronym. Generally, SERS is performed on a roughened or nanostructured gold, silver, or copper substrate; the reasons for this are explained below. For hyphenated EC-Raman applications, the use of SERS is a natural progression. The gold and silver materials that make appropriate SERS substrates are already very well-characterised for use as electrodes, so it is relatively easy to design EC-Raman experiments with these materials as the working electrode. The rough surface of the SERS substrate is also beneficial for the electrochemical part of the experiment as it will enhance the EC signal through the increased surface area [6,7].

The Raman scattering signal enhancement observed during SERS is understood to originate from two processes. There is an electromagnetic enhancement process that is dominant, and a chemical process that contributes to the enhancement in a minor way [8]. In this description we will focus only on electromagnetic enhancement as it is the most important. *Figure 4a* helps to illustrate the electromagnetic part of the SERS effect. The example starts with a surface covered with spherical gold nanoparticles. Please note that the same principles could be applied to roughened surfaces or nanoparticles of various shapes. If an electric field (such as light from the laser source) is applied to the nanoparticle it will induce the formation of a dipole, shown in *Figure 4a* as the displacement of the electron cloud.

When the induced field is removed, the dipole relaxes back to the original state. The free electrons in the metal nanoparticle have an inherent oscillation frequency that depends on intrinsic properties of the material (i.e., its dielectric constant) as well as the geometry (size and shape) of the particle or the local environment (in the case of a roughened surface) [2,9]. When the frequency of the incident light matches the inherent oscillation frequency of the material, a surface plasmon will form. For certain materials like metal nanostructures, the surface plasmon can be highly localised (Localised Surface Plasmon Resonance, LSPR) [10]. In the case of silver and gold nanoparticles,

strongly localised surface plasmons are formed with incident light in the visible and near-infrared regions, making these materials ideal SERS substrates. A molecule of interest placed near the LSPR field experiences the intensified electromagnetic field leading to enhanced Raman scattering, and thus stronger signals with higher counts in the Raman spectrum [10]. The greatest SERS enhancement occurs within a few nanometres of the plasmonic particle's surface. This is ideal to study the electrode-electrolyte interface where the electron-transfer occurs at the surface of the metal: a change in the structure of a material or molecule induced by an electron transfer can be captured by SERS as it occurs. To get the most out of the enhanced electromagnetic field, the molecule of interest is sometimes anchored to the SERS substrate in creative ways. This can also be achieved by applying a potential to induce adsorption of the target molecule to the working electrode which is also the SERS substrate [7,10].

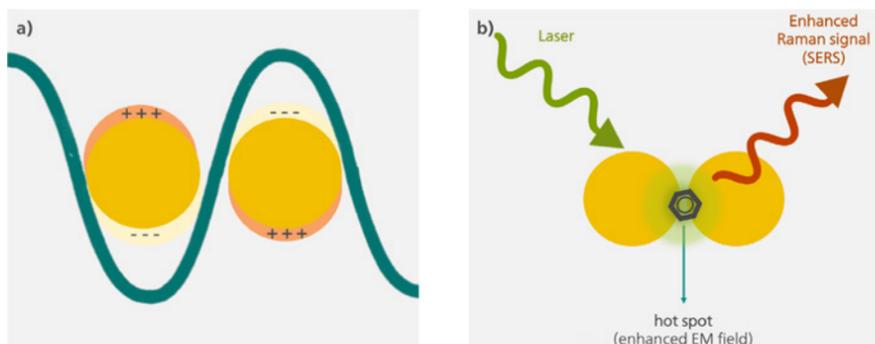


Figure 4. Electromagnetic mechanism of the SERS effect. a) Reaction of plasmonic nanoparticles to an electromagnetic field (incident laser); b) Formation of a local "hot spot" between two plasmonic nanoparticles resulting in an enhanced local electromagnetic field and enhanced Raman scattering of a molecule in its vicinity.

With real SERS substrate materials there is not a single nanoparticle or rough edge, but many of them which are in contact or close proximity to each other as shown in Figure 4b. There are positions where the electric fields from various particles or edges overlap, forming an area of intense local electric field. These enhanced locations are known as «hot spots» and they contribute significantly to the electromagnetic SERS enhancement [8]. Due to their diverse and variable properties and their importance to Raman spectroscopy applications, these hot spots have been the focus of research projects that seek to optimise the material, size, and geometry of SERS substrates [11]. Figure 4b illustrates the concept of a hot spot formed by two nanoparticles in contact with each other. In reality, nanoparticles form aggregates and intense hot spots can form in the gaps between the particles [12]. It is important to note that the hot spot is usually very small and localised near the particle surface. The SERS enhancement decreases exponentially with increasing distance from the surface and is essentially negligible at a distance of about 15 nm [8].

Although hot spots are beneficial because they greatly enhance the SERS signal, they also introduce a complication for reproducible experiments. When the concentration of the analyte is low, the interaction of a single molecule in a hot spot can have an appreciable influence on the measured spectrum because the enhancement of the signal at this position is orders of magnitude higher than a typical Raman scattering signal. If the molecule is not anchored in position at the hot spot, it can diffuse away from the ideal position leading to a change in the Raman spectrum. To minimise this issue it is desirable to have numerous hot spots on the SERS substrate. Ideally, there would be full and uniform coverage of the substrate with hot spots; researchers that are developing such materials refer to them as "hot surfaces" [8].

It is important to be aware of how surface enhancement alters the Raman spectrum of the target molecule. The SERS effect does not amplify each band in the Raman spectrum equally.

With SERS, the interaction of the molecule with the substrate is also being probed, and this may give rise to additional peaks in the SERS spectrum. In the case of large molecules, the distance between a given functional group and the LSPR will influence the appearance of the spectra as some vibrational modes will be enhanced [8]. The interpretation of Raman spectra often involves consulting spectral libraries so it is important to keep in mind that experimental SERS spectra may not match the library spectrum.

Shell-isolated nanoparticle enhanced Raman Spectroscopy (SHINERS)

Shell-isolated nanoparticle-enhanced Raman spectroscopy, known as SHINERS, is a type of SERS that was introduced in 2010 [13]. The SHINERS technique is conceptually similar to SERS. With SHINERS, the plasmonic nanoparticle is encapsulated within a thin (less than 10 nm in thickness) silica or alumina shell resulting in what is known as a «SHIN» (shell-isolated nanoparticle). The enhancement effect is the same as with SERS. A region of strong localised electromagnetic field is created as a result of the interaction of the laser light and the plasmonic nanoparticle. The oxide coating is thin and interacts very little with the incident laser light. As with SERS, the formation of hot spots is also possible with SHINERS; it is favoured when the oxide shell is thin enough that the two plasmonic particles within the shells are still sufficiently close [8,9]. Figure 5 illustrates SHINERS and the structure of a spherical gold SHIN. With SHINERS, the Raman scattering enhancement factor is dampened compared to traditional SERS because the molecule of interest is always at a distance from the plasmonic particle. The distance is dictated by the thickness of the oxide shell. Nevertheless, the shell provides several benefits that are mostly related to improved stability and inertness.

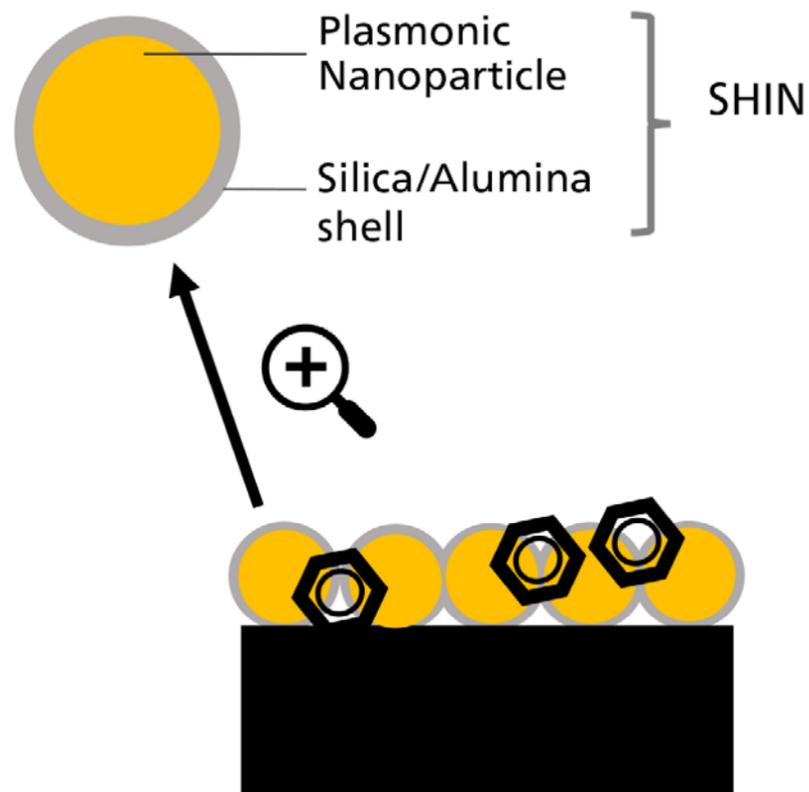


Figure 5. Illustrative example of SHINERS featuring a spherical gold nanoparticle in thin silica shell (dielectric material).

Some of these benefits are especially helpful in electrochemical environments.

1. Increased stability concerning the environment, especially in high-temperature applications. Silica and alumina coatings allow silver or gold nanoparticles to be used in SERS applications at temperatures up to 500 °C [9].
2. Elimination of plasmon-driven side reactions that may occur when the molecule of interest is anchored directly to the SERS substrate. This is often a concern for biological molecules with sensitive structures [8].
3. Possibility to functionalise the oxide coating through a variety of strategies to influence the interaction of the target molecule with the SHIN. For example, to study a chemical reaction taking place with a catalyst. The catalyst can be attached to the SHIN and SHINERS can be used to study the reaction at the catalyst, which would be within the Raman scattering enhancement zone due to its proximity to the plasmonic particle [9].
4. Specifically for EC-Raman studies, there is more flexibility for the working electrode material with SHINERS than with normal SERS. This is because the plasmonic material (i.e., Ag or Au) does not need to be in contact with the electrolyte. Thus, it is possible to use a working electrode material of choice, attach SHINs to the working electrode to create hot spots, and study electrochemical reactions taking place at the working electrode with hyphenated EC-Raman [6,7].

Hyphenated EC-Raman instrumentation and setup

For an EC-Raman experiment, the following components are recommended (see Figure 6):

- A Raman instrument, including the spectrometer and light source
- An electrochemical instrument (potentiostat/galvanostat)
- An electrochemical cell with an appropriate working electrode
- A means of controlling the position of the sample relative to the Raman optics. In EC-Raman experiments, this is usually the working electrode in the electrochemical cell. This often involves an optical microscope or a positioning stage and probe holder.

The Raman instrument contains everything needed to obtain a Raman spectrum. The excitation source is a laser that provides monochromatic light of a specific wavelength. Specialised optics bring the laser light to the sample, collect the scattered light, and guide it to the spectral analyser. The spectral analyser separates the scattered light into its constituents based on their wavelengths, and the detector converts the optical signal into an electronic signal that is then digitised and displayed as a Raman spectrum.

When designing an EC-Raman setup, consider which laser light source to work with. The most common ones are 532 nm, 785 nm, and 1064 nm. The decision is generally based on the need for strong excitation efficiency balanced with concerns related to the interference of fluorescence. Raman scattering efficiency ($P_{scattered}$) relies strongly on the wavelength (λ) of the excitation source, according to the following relationship:

$$P_{scattered} \propto \frac{I_0}{\lambda^4}$$

A 532 nm excitation source is almost five times more efficient than a 785 nm source. Having a higher excitation efficiency is relevant to EC-Raman applications because the concentrations or coverages of the molecules of interest are usually low. Fluorescence from the sample can interfere with the Raman signal. The fluorescence signal differs from Raman scattered light because it has a fixed wavelength that does not shift with the wavelength of the excitation source. Fluorescence can interfere within visible and near-infrared wavelength ranges. This is problematic for Raman spectroscopy because fluorescence is a much more efficient process compared to Raman scattering, and can obscure Raman peaks. Since there is a choice of laser wavelengths, and because the wavelength of Raman scattered light is dictated by the energy of the incident light and the resulting photon, it is possible to position the Raman spectrum (in terms of Raman shift) in a wavelength range that is less affected by fluorescence. Managing fluorescence can be a challenge for the use of Raman spectroscopy in some applications, but it is generally less problematic in EC-Raman experiments because these typically concern small molecules that are less prone to fluorescence. All things considered, the 532 nm excitation source is often the best choice for hyphenated EC-Raman applications.

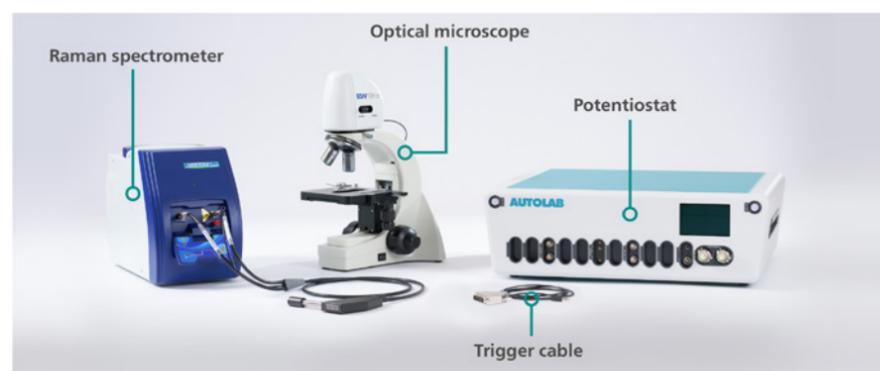


Figure 6. The main components of an EC-Raman setup.

The potentiostat drives the electrochemical measurement and provides a variety of techniques to study electrochemical reactions. A full discussion of the options and modules available in modern potentiostats is outside the scope of this article. Instrumentation needs are highly dependent on the type of research and so a flexible approach to instrumentation is often best, meaning that a system that can be upgraded with additional functionality in the future can continue to serve the researcher if their experimental needs change.

There is one aspect of the potentiostat that is crucial for hyphenated EC-Raman experiments - the ability to synchronise Raman spectra collection with the electrochemical measurement. Transient electrochemical techniques like linear sweep voltammetry (LSV) involve changing the potential over time with a fixed rate (the scan rate). A typical EC-Raman experiment could involve sweeping the potential and collecting Raman spectra at fixed potential intervals (i.e., every 20 mV). This experiment yields two types of information: the LSV plot which illustrates current as a function of potential, and a series of Raman spectra collected at various potential values.

In such an experiment, it is important to the quality of the results (and very convenient) if the electrochemical instrumentation has the possibility to communicate with the Raman spectrometer to precisely inform it when to collect each spectrum. Metrohm Autolab potentiostats are equipped with a triggering mechanism that can precisely and automatically synchronise with the Raman spectrometer. The NOVA 2 software controls the triggering mechanism and gives the researcher complete flexibility to program the collection of Raman spectra at any point in their electrochemical measurement. Figure 7 illustrates this triggering mechanism.

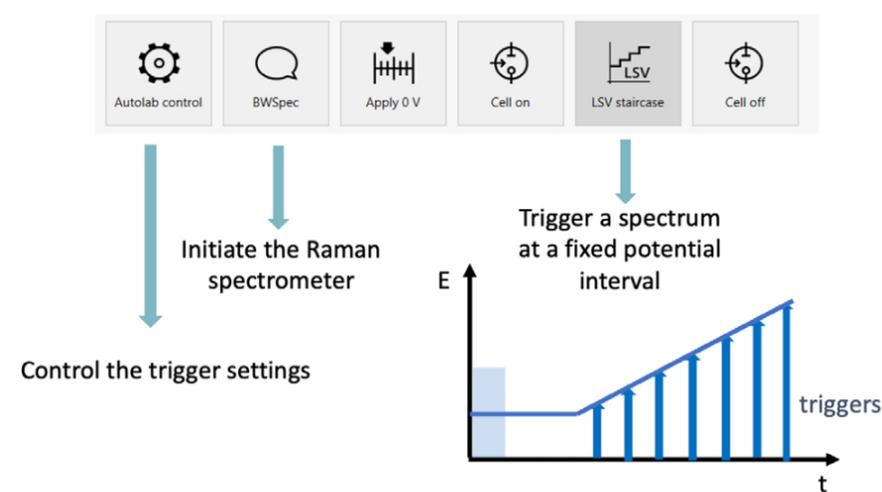


Figure 7. Triggering the collection of Raman spectra through the NOVA 2 software.

The electrochemical cell design is tailored to the experiment. There are a few things to consider when designing the electrochemical cell. The working electrode must be accessible to the incident light and the sampling optics of the Raman spectrometer. This can be accomplished by placing the working electrode slightly below a special spectroscopic window that has minimal interference with the optical signals. Single crystal sapphire (Al_2O_3) of a precise orientation that is optically polished on both sides can be used as a high-quality window material for EC-Raman applications. Some setups make use of fused quartz, optical glass, and other transparent materials for the window [14,15]. As discussed in the previous section on lattice vibrations, these materials are expected to contribute some background to the Raman spectra.

There is no truly ideal material that can be used in all EC-Raman applications. The choice of window material is usually based on the expected strength and positions of the Raman peaks from the target molecules relative to any interference from the window material, as well as the stability of the window material in the experimental conditions.

The distance between the working electrode and the spectral window requires some consideration as well. The working electrode is positioned close to the spectral window so that the laser can be focused on the surface of the electrode, however, some space is needed so that the diffusion of molecules in the electrolyte is not hindered. Researchers who have experience with combined EC and IR spectroscopy are used to working with the electrode in contact with the spectral window, leaving only a thin film of electrolyte. This configuration is needed because the water in aqueous electrolytes strongly interferes in the infrared spectrum, so the optical pathlength through the electrolyte needs to be minimised. This is one of the situations where Raman is superior in contrast to IR spectroscopy. The molecular vibrations of water are mostly Raman inactive, except for the stretching modes which give rise to a broad band at Raman shift of around 3400 cm^{-1} which is generally not problematic for EC-Raman experiments. Therefore, it is possible to leave more space between the working electrode and the spectral window, opening up the possibility of EC-Raman measurements in a flow cell as well as studying gas-forming reactions [16].

To make an elegant bridge between the electrochemical cell and the Raman instrumentation, an optical microscope can be used as a sampling aid to help position the sample and to focus the laser light on its surface. In this setup, the path of the incident light is directed through the microscope lens and to a specific area of the sample. The scattered light is collected by a probe above the sample and carried through the optics to the analyser. Any position of the working electrode that can be brought into focus with the optical microscope can be selectively sampled for Raman spectroscopy. This configuration is important in the case of inhomogeneous samples where different reactions are expected to take place at different locations on the sample (e.g., in corrosion studies). There is an inverse relationship between the laser spot size and the magnification of the microscope lens. For example, by increasing the magnification from 20 times to 50 times, the laser spot size is approximately halved. Typical laser spot sizes range from approximately 200 to $10\ \mu\text{m}$, depending on the type of laser and magnification through the microscope. This can be particularly important to reduce the contribution from the solution when Raman-active solvents and salts are used as supporting electrolytes. In other words, the use of a simple optical microscope allows for greater spatial selectivity in the XY plane and can help increase surface sensitivity when Raman-active solvents are used.

The experimental setup for hyphenated EC-Raman measurements may seem complex because it combines two independent analytical areas. Both techniques have their complexities and special quirks. Thankfully, experts from both sectors are constantly working to improve these techniques, extend their applications, and share their knowledge to make this powerful combination more accessible. Metrohm Autolab offers hyphenated EC-Raman setups that are tailored to electrocatalysis, battery, and corrosion research. Dedicated electrochemistry and Raman specialists are always available to discuss your experimental needs and help in the selection of appropriate instrumentation.

Conclusions and outlook

The combination of electrochemical and spectroscopic techniques is undoubtedly powerful. In this article, we have provided a few illustrative examples of the insights gained through the application of hyphenated EC-Raman to electrochemical systems. Hundreds of thousands of studies have been published in the past two decades as EC-Raman instrumentation and techniques have become more well-known and accessible, and also more reliable and user-friendly. Presently, the EC-Raman approach is in a growth stage where the number of applications is expanding

rapidly. Scientists from various domains are experimenting with this technique to explore cutting-edge research topics, and also to revisit and confirm (or challenge) present knowledge obtained with more primitive studies. It is reasonable to expect that this trend will continue and that we can anticipate a great deal of insight and discovery from hyphenated EC-Raman studies in the future.

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