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Review Article
Capturing of electrochemical transformations by Tip Enhanced Raman Spectroscopy

Thomas Touzalin, Suzanne Joiret, Emmanuel Maisonhaute and Ivan T. Lucas

Through the characterization of functional nanomaterials under the conditions of their operation or of molecular architecture under polarization, new insights in the comprehension of their mechanism will be accessible to propose new design orientations. This review emphasizes the powerful analytical capabilities of Tip Enhanced Raman Spectroscopy (TERS), presents the recent advances on *in situ* characterizations, and focusses on the strong potential of TERS to analyze electrochemical systems by providing chemical signatures at the nanoscale.

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Context for TERS emergence

Deciphering of intricate electrochemical mechanisms, first step toward the control of the electrochemical processes, has been achieved through the development of powerful electrochemical techniques such as cyclic voltammetry (CV) [1] and electrochemical impedance spectroscopy (EIS) [2] often coupled with complementary analytical tools run *in situ*, *i.e.* microscopy [3], spectroscopy [4] and gravimetric techniques.[5-7] However, the limited sensitivity and/or the limited spatial and temporal resolution of the associated techniques are usually the bottleneck to the disentanglement of the electrochemical mechanisms taking place at the electrodes. The detection and characterization of single/local electrochemical events, the identification of species with short lifetime (intermediates, radicals) or with extremely low surface concentration are challenging orientations currently pursued.

Since their introduction in the 80's, near-field microscopies like Scanning Tunneling Microscopy (STM) [8,9] and Atomic Force Microscopy (AFM) [10] have been successfully implemented under electrochemical conditions, allowing the characterization of surface processes at the nanoscale. Their exceptional performances allow to capture single atoms or molecules, to follow the structure evolution of a polarized interface [11,12] or to induce local surface alterations.[13] In addition to topographical features, they also give access to the conductivity of single molecules [14-17], to the local mechanical properties [18] or to the ionic transport properties in solids [19-22] among many other properties. Originating from near field microscopy, Scanning Electrochemical Microscopy (SECM) enables the control and the monitoring of the electron transfer properties at the micro/nanoscale.[23] Although really versatile and largely used today, scanning probe techniques still suffer from the lack of simultaneous composition, and structure determination at the nanoscale to complete full diagnostics of scrutinized samples.

Compositional analysis can be achieved via a myriad of spectroscopy techniques which operation conditions can however strongly limit/compromise *in situ* applications (Ultrahigh Vacuum UHV, signal screening by the solvent or by the atmosphere). Among benchtop spectroscopies, the emergence of Raman for *in situ* characterizations this last two decade is spectacular.[24] The wealth of information contained in vibrational signatures, the clear vibrational signatures, the non-invasive sampling process and the possibility to work in aqueous solutions (visible excitation and weak scattering signal of water) explain this burst of interest among the material science community. In Raman, photons are emitted through elastic and inelastic scattering processes upon illumination of a sample with a visible laser (Fig. 1b). Energy loss or gain for the emitted inelastic photons translate into small frequency shift depicted on Raman spectra. Raman bands at a given frequencies shift (υ_0 - $\upsilon_{inelast}$) therefore correspond to the energy separation between vibrational states of the excited molecules. Raman spectra as vibrational signatures of the studied samples are therefore really complementary to the IR ones [24] and are not impacted by the presence of water (no absorption and weak scattering of water).

The poor sensitivity of Raman spectroscopy (scattering efficiency: 1 Raman photon for 10^7 elastic photons) has been compensated with the introduction of Surface Enhanced Raman Spectroscopy (SERS). This latter relies on the use of substrates with surface

nanostructurations or with nanoparticles made of gold or silver, which stand as hot spots upon excitation. The free electrons of the metal oscillate at the surface of these nanostructures at the plasmon resonance (Localized Surface Plasmon Resonance: LSPR), providing a strong and localized amplification of the signal which is reported to be up to 10^{12}.[24,25] The extremely high sensitivity of SERS has brought the detection threshold of Raman spectroscopy down to the molecular level. [26,27] The discovery of signal enhancing processes and the association of Raman with confocal microscopy (µRaman) have compensated for the low efficiency of the Raman scattering and has permitted the study of functional materials with low cross section for Raman scattering (nanoparticules, thin films, nanotubes) under the condition of their operation. However, the limited lateral resolution of µRaman $\sim \lambda_{excitation}/2$ (Abbe criterion: $d = \frac{\lambda_{excitation}}{2.NA}$) limits the characterization of material to the micron scale. Thus, electron and X-ray microscopies and spectroscopies have been so far mostly used to extract information at the nanoscale, despite their potentially low contrast between compositions of interest, limited sampling capability (small volume), and likelihood of beam damages to the samples.

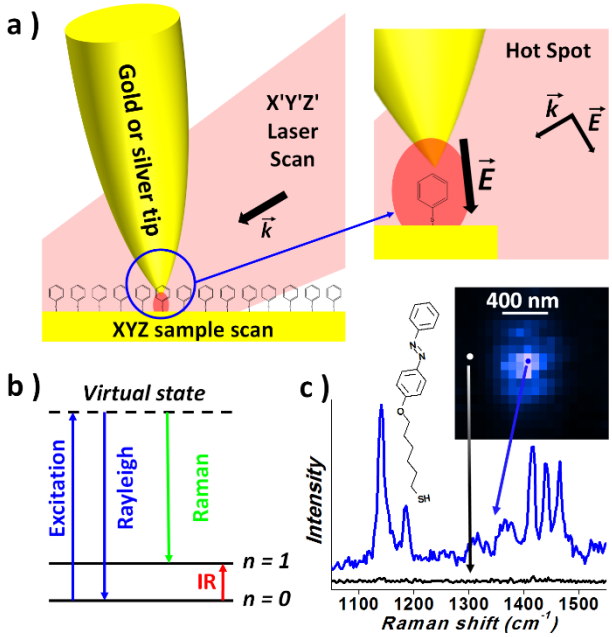
In this context, the emerging Tip Enhanced Raman Spectroscopy (TERS), which associates near-field microscopies and vibrational spectroscopy, has attracted lately a considerable attention [28] because of its extraordinary sensitivity and acute spatial resolution without the need for ultra- high vacuum (UHV) and also because of the ease to work in aqueous and non-aqueous solvent contrary to NanoInfrared spectroscopies[29-32], opening the way to *in situ*, *in vivo* and *in operando* (EC-TERS) measurements.

Principles of Tip Enhanced Raman Spectroscopy

TERS operates with a similar principle as SERS by using a gold or silver tapered tip illuminated by a visible laser source as depicted in figure 1a. This latter generates a strong localized electrical field at the tip apex, the so-called hot spot, which considerably enhances the Raman signal of the compound at the tip/sample junction and enables nanoscale compositional mapping.[33,34] Improved enhancement/sensitivity and spatial resolution can be obtained in gap-mode TERS, which refers to a configuration where the compound of interest is sandwiched in between the tip and a gold or silver surface.

While the SERS signal can originate from several hot spots simultaneously, the unique and spatially limited hot spot at the apex of the TERS probe has to be carefully localized/identified. The accurate focusing of the excitation laser on the tip and the spatial screening of the optical hot spot (Fig. 1c) are achieved using high magnification objectives mounted on piezo stages.

Figure 1



Principle of TERS: **a)** a visible excitation laser is focused at the apex of a gold/silver tip, creating a drastic enhancement of the local electromagnetic field at the tip-sample junction, and therefore of the scattered Raman signal, **b)** the energy difference between the scattered Raman photons (inelastic scattering) and the incident photons corresponds to the energy separation between the vibrational states of the excited molecules ($\upsilon_0 - \upsilon_1$), similarly to IR spectroscopy, **c)** the Raman signature of a molecular layer can only be obtained through a precise positioning of the laser on the tip apex, *i.e.* at the hot spot.

Furthermore, to trigger LSPR on TERS probes, polarized laser sources have to be used and the electric field needs to be aligned along the shaft of the tip. For opaque samples, a linearly polarized light source is focused on the tip apex through the objective positioned either to the side of the probe (for vertical tip shaft) or above the probes (angled tip shaft). For samples deposited on transparent cover slips, the tip apex can be illuminated from below through the sample using a radially polarized laser source.[35-37] If TERS ready instruments providing a robust optical coupling have emerged on the microscopy market, the main impediment to the fast emergence of TERS has been and still remains the difficult conception of

probes with controlled properties. Defined taper angle and radius of curvature, chemical stability (silver oxidation) and wear resistance are crucial parameters which determine the occurrence and the stability at the probe apex of an effective plasmon resonance at a given excitation laser wavelength, prerequisite to high and reproducible signal enhancements.[38,39] STM-TERS probes have been manufactured by electrochemical etching of metallic wires using pulsed or continuous voltage or current and acidic or alkaline bath with additives.[40,41] For AFM-TERS probes, metal layers have been evaporated onto commercial silicon probes [42]; home-made probes have also be obtained by flattening of the upper part of a wire to create a cantilever and bending of the tapered end.[43] A proposed alternative consists in gluing an etched gold or silver wire on one prong of a tuning fork (shear-force or normal force TERS).[44,45]

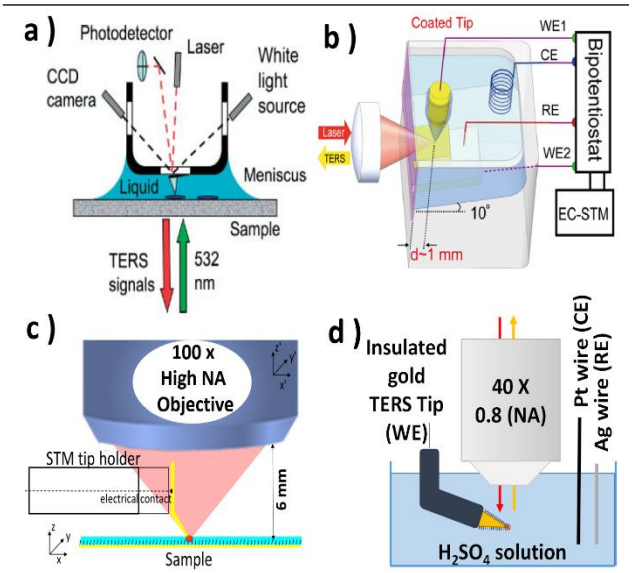
Since the introduction of TERS in the early 2000's [46-49] considerable progresses have been achieved both on the instrumentation optimization [50] and on the comprehension of the TERS enhancement processes.[38] Performances beyond expectations have been attained like subnanometer compositional mapping demonstrated in 2013 under UHV and at low temperature [51], a 2 nm spatial resolution on amyloid fibrils in the air in 2012 [52] and a 1.7 nm spatial resolution reported on carbon nanotubes in 2014.[53]

Implementation of TERS in liquid media

As mentioned earlier, a great advantage of microRaman spectroscopy is the possibility to study surfaces immerged in liquids using either long working distance air objectives or immersion objectives. Transposition to TERS is challenging because of the delicate optical alignment through a layer of liquid, compromising both the laser focusing on the tip apex and the collection efficiency of the scattered signal, but has been demonstrated as early as 2009. Improvement of the TERS signal stability has been reported and explained by the reduced photo (thermal) degradation processes (transformation, desorption) at hot spots due to greater heat dissipation and lower oxygen content as compared to measurements in the air.[54]

Different configurations summarized in Figure 2 have been proposed to implement TERS in liquids. As mentioned above, for samples deposited on transparent cover slips, the tip apex is illuminated from below through the sample and the laser source is therefore not deviated at any liquid-air interface and crosses only a very thin layer of liquid. Novotny pioneered TERS in liquid using the inverted configuration in 2008 [44,45], followed by Zenobi in 2009 [55], Fujinami in 2013 [56] and Van Duyne in 2015 [57,58] (Fig. 2a). By contrast, implementation of TERS in liquids within an upright configuration is the most challenging since the optical signal is inevitably deviated and considerably attenuated by refraction at the liquid-air interface. However Ren *et al* in 2015 [54] and Domke *et al* in 2016 [59,60] demonstrated its feasibility by proposing a configuration where the irradiation of a TERS-STM tip is carried out through a side window opened in the liquid cell wall (Fig.2b). TERS imaging within such configuration is then restricted to a very small area (about 200x200 nm^2) within which the laser focusing is not compromised. Touzalin *et al* [61] circumvented the problem by using a very thin layer of liquid (µms, see fig. 2c) and an STM-TERS tip slightly bent to reach the focal point of an air objective, so that accurate laser focusing is still possible. This approach was validated in 2016 by the first TERS imaging of a self-assembled monolayer (SAM) on gold (thioazobenzene derivative) immersed in hexadecane, a non-volatile solvent which the Raman signature overlaps with the one of the SAM. We discuss next other specific issues related to the implementation of TERS under electrochemical conditions.

Figure 2



Configurations for *in situ* TERS measurements: **a)** Inverted TERS-AFM set-up as proposed by Zenobi and Van Duyne (reprint from [55]), **b)** upright EC-STM-TERS set-up with a side illumination through the cell as proposed by Ren and Domke (reprint from [54]), **c)** upright STM-TERS configuration with a thin layer of organic solvent as proposed by Touzalin, **d)** upright EC-TERS using a functionalized TERS tapered electrode and an immersion objective.

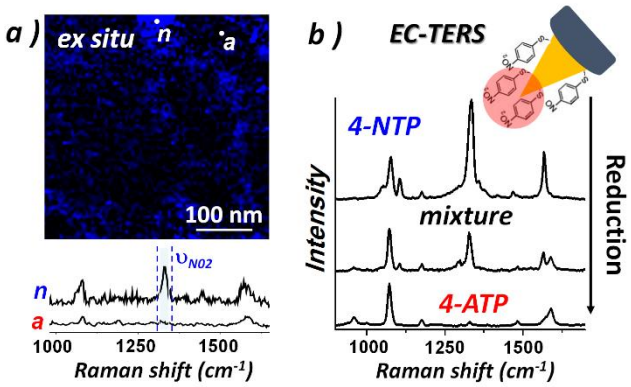
TERS of electroactive systems: facts

The characterization and the comprehension of electroactive systems using electrochemical techniques can be efficiently extended by TERS analyses run *ex situ* to assess the chemistry of the functionalized electrode at the nanoscale, *i.e.* the structure and the distribution of surface compositions. In 2016, Ren et al. evidenced by impedance spectroscopy and TERS important conformation changes during the formation of a self-assembled monolayer.[62] The aromatic C=C bond vibration was used as a marker of intermolecular pi-stacking and showed a non-monotonous evolution with the contacting time of the substrate with the precursor solution. Measurement of the charge transfer resistance by impedance spectroscopy confirmed this tendency. The transformations of SAM functionalized electrodes can be also assessed by TERS, as reported by Touzalin *et al*.[63] Their study of the electrochemical reduction of a 4-Nitrothiophenol layer assembled on large gold substrates (Fig. 3a) revealed an inhomogeneous distribution of the surface transformation products explained by the ohmic drop and the spatial dispersion of RC charging time constants across large electrodes. Finally, in supramolecular electrochemistry, detection and identification of the electroactive groups among many other functions is crucial to explain the electron transfer within such large edifice and their possible integration in electronic devices. However, for very large molecules, like giant rotaxanes bearing ten ferrocene units per molecule, the coverage of redox centers is much lower than in classical self-assembled monolayers, rendering their detection more complicated.

If the potential of *ex situ* TERS analyses to facilitate the interpretation of electrochemical processes is already established, the real-time monitoring of an electrochemical transformation by TERS (EC-TERS) represents the most interesting challenge. Presently, only three different electrochemically active systems have been studied by EC-TERS and reported so far in the literature: the potential dependent protonation of 4-PBT ((4′ - (pyridine – 4 - yl) biphenyl – 4 - yl) methanethiol) [54] the reduction of Nile Blue dye (NB) [57,58] and of 4-Nitrothiophenol (4-NTP).[63] Although the development of EC- TERS is still at its early stages, some important experimental facts have already been raised by the leaders of the fields, using the different configurations depicted in Figure 2.

The first EC-TERS characterization was carried out by Ren *et al*. in 2015 on 4-PBT layer adsorbed on Au (111) using an upright configuration and a side illumination with an insulated gold tip in the STM mode and a bipotentiostat to control the potential of the tip and of the substrate (see Fig. 2b). Distinct and stable TERS signatures associated to different protonation state of 4-PBT at pH 10 were successfully extracted when scanning the potential applied, while the protonated form could not be observed using SERS substrates made of 4-PBT functionalized Au nanoparticles. The dominant SERS signal of the double-end bonded 4-PBT molecules connecting adjacent particles (in the gap) was interpreted to mask the signal of protonated single-end-bonded, revealing the importance to control the structure of the probed interface (number of probed molecules and their organization around multiple hot spots).

Figure 3



TERS on a 4-NTP SAM: **a)** *ex situ* TERS mapping of the NO_2 vibration intensity (blue) on a polarized 4-NTP SAM revealing the non-effective reduction of 4-NTP into 4-ATP across the surface, **b)** progressive reduction of a 4-NTP SAM at a gold microelectrode monitored by EC-TERS.

Using the inverted configuration described above, a gold coated AFM probe and a conductive ITO covered coverslip, Van Duyne *et al*. have captured the electrochemical transformation of model dye NB adsorbates described in three papers released between 2015 and 2017.[57,58,64] At low NB surface coverages, individual events with different behavior (single or few molecules transformation) could be assessed at the tip-sample junction, revealing a distribution of local environments, *i.e.* of the standard potential of the molecules, an observation otherwise impossible to achieve with averaged measurements. The close proximity of the metal tip with the polarized substrate was reported to interfere locally with the electric field, potentially affecting the electrochemical response. A potential shift in the transition from oxidized and reduced forms of NB has been observed between the Raman and the current intensity, pointing out the influence of the tip on the effective potential experienced by the scrutinized NB molecules.

Touzalin *et al*. have introduced in 2017, an alternative set-up using a partially insulated TERS-active tapered gold electrode directly functionalized with the compound of interest and immersed into the electrolyte.[63] Pienpinijtham *et al*. proposed such combination using a gold tip modified by p-mercaptobenzoic acid and p-aminothiophenol to measure a local pH.[65] With the proposed design, the spatial resolution of compositional analysis is lost, but the number of molecules which contribute to the measured TERS signal is larger than in classical "gap mode" TERS, providing stable and intense Raman signatures. In addition, the electrode size is reduced to micrometric dimensions, so that the ohmic drop complications vanish and the temporal resolution is restored.[66,67] The TERS signal extraction upon exploration of reducing potentials enabled to track the progressive transformation of the nitro group of 4-NTP to amino (4-ATP) and revealed that the intermediate $4e^-$ reduction of the nitro group of 4-NTP to hydroxylamine (4-HATP) competes with the $6e^-$ reduction to amine (4-ATP) at potential where this later is not expected to occur.

Conclusion and prospects

Only a few works have been published so far on TERS combined with electrochemical measurements, because mostly of the important efforts required in instrumental development. Despite the recent progresses, TERS imaging with high spatial resolution still have to be demonstrated under electrochemical conditions. Finally, the combination of TERS measurements with ultra-microelectrodes will pave the way to time resolved EC-TERS experiments, providing new insights in the comprehension of complex redox systems.

TERS ready commercial systems are now robust and the production of efficient TERS probes continuously addressed, providing an easier access to new users. Convenient solutions for electrochemistry (EC-AFM-TERS, SECM-TERS) should arise soon and will provide an easy access to the characterization of functional nanomaterials or of molecular assemblies under the condition of their operation providing new design orientations. Immediate benefits can be expected in domains like information storage (molecular switches), conversion (electrochemical solar cell) and energy storage (Li-ion batteries, fuel cells), electrocatalysis [68,69] and bioelectrochemical systems.

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•• Paper of outstanding interest

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