
Recent developments on the EC-STM-TERS setups: characterization of Nitrobenzene-based self-assembled monolayer

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A. Fiocco¹, Alexey Belyaev¹, Alexander Yagovkin¹, Marc Chaigneau¹, Patrick Hsia¹

(1) HORIBA France SAS - 14, Boulevard Thomas Gobert - Passage Jobin Yvon - 91120 Palaiseau - France, alice.fiocco@horiba.com.



Figure 1. EC-TERS setup

In this contribution, we will illustrate the new EC-STM-TERS setup design proposed by HORIBA France for overcoming difficulties and allowing easier and more reproducible measurements. In this example, a nitrobenzene-based self-assembled monolayer was reduced while acquiring TERS spectra. Real-time following of the spectro-electrochemical transformations ongoing over such systems can indeed unravel complex reaction mechanisms, identifying areas with more or less reactivity and gathering a more accurate and complete sample characterization. In this contribution, we will illustrate an example of application of the developed EC-STM-TERS setup.

Introduction

EC-TERS setups, which combine Raman spectroscopy, scanning probe microscopy and electrochemistry, have the advantage of gathering simultaneously multiple information on the studied sample (chemical nature, morphology and electrochemical activity) [1,2] and of guaranteeing high sensitivity and nano-scale spatial resolution [3,4]. All of these aspects are particularly useful to study the behavior of active 2D materials (such as surface-immobilized sensors, catalysts, or molecular switches) under their conditions of operation. In this contribution, we will illustrate the new EC-TERS setup designs proposed by HORIBA France allowing easier and more reproducible measurements (Figure 1). In the example, it was chosen to follow *in situ* the redox behavior of a nitrobenzene-based self-assembled while simultaneously acquiring its spectral signature. Results obtained with these designs will be therefore shown, along with the perspectives of further implementation and improvements to carry out in the future.

Material and Methods

EC-STM-TERS measurements were performed on a 4-NBM SAM deposited on a gold-on-mica substrate. The sample was subjected initially to a constant potential ("initial" step), then to two successive potential ramps ("1st cycle" and "2nd cycle" steps). Parameters: 200×36 nm² map, 50×9 pixels, tunneling current $I_T = 1$ nA, bias voltage BV variable between 0.1 and 1 V, sample potential variable between -0.1 to -1 V, electrolyte =

bicarbonate buffer at pH~11. The buffer was prepared by mixing 100 mL of 0.05 M NaHCO₃ and 40.4 mL of 0.1 M NaOH. Spectra were recorded with a 633 nm laser (~10 μW power), 0.3s acquisition time per pixel.

Results and Discussion

Morphologically speaking, the 4-NBM SAM sample is expected to have a homogeneous structure due to the mechanism of self-assembling of the thiol-based molecules. These structures are not visible in STM though: in fact, because of the tunneling current mechanism, the probe tends to penetrate the molecular layers to be at close distance from the sample surface. This is why the STM map illustrated in Figure 2 does not show the molecular layer, but rather the underlying substrate made of gold terraces. Nonetheless, the 4-NBM presence can be easily unraveled by TERS, which gives a clear and recognizable signature of the monolayer (blue spectrum in Figure 2).

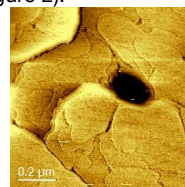


Figure 2. Example of an EC-STM map on a 4-NBM sample (1×1 μm², 256×256 pixels, $I_T = 1$ nA, BV = 0.1 V, $E_{\text{sample}} = -100$ mV, electrolyte = bicarbonate buffer at pH~11). Only the gold surface structure can be seen because the tip penetrates the molecular layer to establish the tunneling conditions.

When subjected to a reductive potential, the nitro groups of 4-NBM transform irreversibly and generate, directly or indirectly, several reduction products. These are supposed to be more stable when relatively fast cyclic potential scans are performed (from the equilibrium state towards negative potentials and back) and when working in alkaline environments [2]. This is why, in the example presented here, the bicarbonate buffer was chosen as electrolyte.

Before probing the sample reactivity, it was therefore chosen to acquire an STM-TERS map at -0.1 V (applied on the sample, $BV = 0.1$ V), which is close to the sample equilibrium potential, to avoid the initial occurrence of electrochemical reactions. Therefore, after 5 lines of the map, the potential on the sample was varied from -0.1 V to -1.0 V and back to -0.1 V, at the speed of $50 \text{ mV}\cdot\text{s}^{-1}$. Since each line of the map was composed by 50 pixels, each one acquired in ~ 0.5 s, the whole potential cycle was recorded within two scanned lines. Afterwards, a second potential scan was repeated.

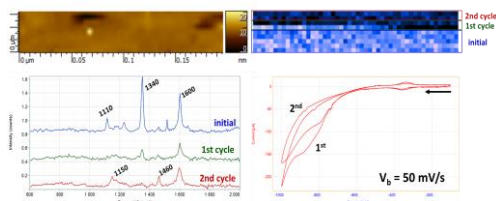


Figure 3: 4-NBM SAM deposited on gold-on-mica. (STM map on the top left, TERS on the top right)

In Figure 3, the spectra on the bottom left were averaged from the groups of pixels circled in the TERS map. On the bottom right, the graph represents the evolution of the sample current during the potential scanning (from -0.1 V to 1 V and back) for the two cycles. All spectra were subjected to background removal and normalization by the background. The spectrum averaged from the first 5 lines of the map shows the 4-NBM signature, characterized by the bands around 1340 cm^{-1} (NO_2 symmetric stretching), 1600 cm^{-1} (ring stretching) and 1110 cm^{-1} (CH bending). However, when averaging the two lines corresponding to the first potential cycle, it can be clearly noted that the NO_2 stretching and CH bending bands almost disappeared, while the ring stretching band slightly broadened. This tendency is accentuated when averaging the lines corresponding to the second cycle, where additionally new bands arose at about 1150 and 1460 cm^{-1} . This shows that NO_2 moieties have been effectively reduced and that intermediate species were formed on the sample surface. Despite the relatively fast potential scan rate, when reaching the lowest potential vertex the bias voltage had increased up to 0.9 V, thus provoking the loss of signal in a few pixels recorded during the potential scans. This issue can be avoided if the bias voltage is maintained at a “reasonable” value, i.e., if the lower potential vertex is less negative or if the probe potential is lowered at the same time as the sample’s. Nevertheless, the possibility to retrieve the signal after the temporary loss demonstrates the great stability of the sample setup for the EC-STM measurements.

Conclusions

Electrochemical tip-enhanced Raman spectroscopy (EC-TERS) is one of the most powerful analytical techniques for the study of functional nanomaterials: not only it allows performing simultaneous measurements on the chemical nature (nano Raman), morphology (scanning probe microscopy), and electrochemical behavior of the studied sample, but it also guarantees a nano-scale spatial resolution and a high sensitivity.

References

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