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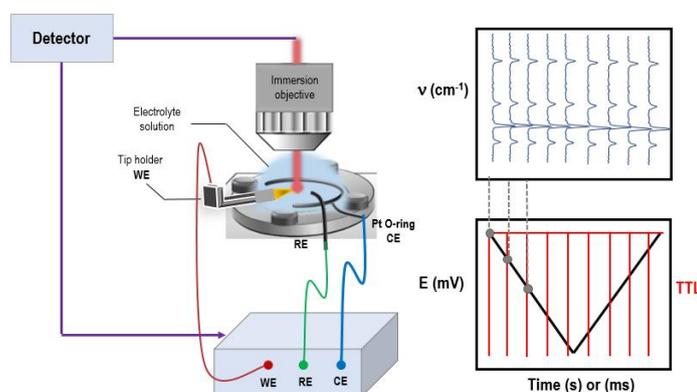
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## Transient Electrochemical Tip Surface-Enhanced Raman Spectroscopy (EC-Tip-SERS): Concept and Applications in Electrocatalysis and Material Science

The development of electrochemical techniques combined to Raman spectroscopy such as electrochemical Tip- or Surface- Enhanced Raman spectroscopy (EC-TERS or EC-SERS) have attracted considerable attention over the past years by the scientific community. This spectro-electrochemical combination provides an accurate view over electrochemical processes occurring at an electrode by acquiring simultaneously local topography, and vibrational fingerprints about the material or molecules under potential control.<sup>[1]</sup> Based on the use of an insulated TERS tip, we introduced recently a new approach that we called EC-Tip-SERS (Figure 1). Here, electroactive molecules are adsorbed directly onto the tip that acts both as working microelectrode and single hotspot for SERS.<sup>[3]</sup> Although the spatial resolution is lost in this configuration, interesting transient mechanistic information can be obtained. In this communication, we will present first the use of this technique on a redox- and Raman- active model molecule, the Nile blue, in which a temporal resolution in the order of millisecond can be easily attained. Then, we will consider the use of Tip-SERS in probing molecular motion within rotaxane-based giant assemblies containing porphyrins derivatives. Finally, we will demonstrate the use of transient EC-Tip-SERS in scrutinizing electrocatalytic transient mechanisms, such as those associated to the oxygen reduction reaction towards hydrogen peroxide in water using viologen SAMs as electrocatalysts.

### References

- [1] Ding, S. Y., Yi, J., Li, J. F., Ren, B., Wu, D. Y., Panneerselvam, R., & Tian, Z. Q. *Nature Reviews Materials*, 1, (2016) 1-16.
- [2] Touzalin, T., Joiret, S., Maisonhaute, E., & Lucas, I. T. *Analytical chemistry*, 89 (2017) 8974-8980.



**Figure 1.** Transient EC-Tip-SERS setup and operando acquisitions.