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In Search of the Hot-Spot.

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Molecules at surfaces and interfaces often define the macroscopic properties of materials, as well as the kinetics of surface-specific reactions. The angular orientation, spatial distribution and interactions of these molecular layers are key to a variety of fundamental interfacial processes such as protein-protein interactions at cell surfaces, electrochemical elemental events and catalytic reactions. The knowledge of these molecular properties at the single molecule level is therefore critical to further exploit their properties, individually or embedded in hybrid assemblies. Writing in *Nature Nanotechnology*, Brolo *et al.* collect ultrafast fluctuations of surface-enhanced Raman scattering signals in the vicinity of silver shells, making inferences about the origin of the dynamic nature of the metal-adsorbate interface.¹

Tip-enhanced spectroscopy and its Raman variant provide single molecule sensitivity when combined with ultra-high vacuum technology, but suffer from poor time resolution due to the long acquisition times necessary to map the atoms involved in molecular vibrations.^{2,3} On the other hand, surface-enhanced Raman spectroscopy, discovered over 40 years ago, is a more common technique, and is used for many imaging and bioanalytical applications, yet with single molecule sensitivity.⁴ In SERS, the roughness of metallic surfaces (in general Al, Ag, Au) as well as the shape and arrangement of these surfaces are exploited to enable high spatial confinement of an impinging electromagnetic field. Since the surface-enhanced Raman signal scales with both the enhanced excitation and emission fields, even a small increase of the local field in these so-called “hot-spots” yields large Raman enhancements. Yet, for low concentrations of analytes deposited onto these surfaces, the collected SERS fluctuates with time, and the cause of such signal variation is presumably assigned to the stability of the metal-adsorbate system, the chemical and physical dynamics of the molecules located in extremely confined fields, and the transient nature of the hot-spots.

Brolo *et al.* propose to further push the temporal and spatial resolution of SERS using Airyscan detection, thus jumping from the kHz range of conventional detection to a MHz detection rate. This substantial technical improvement of temporal resolution provides a much better access to the fundamental parameters associated with single-molecule SERS events through the analysis of signal fluctuations. An Airyscan detector is composed of an array of 32 photomultiplier elements organized in a hexagonal tiling arrangement. Each element has a diameter of 50 nm, which translates into a value of 0.2 Airy units. Altogether, they cover the equivalent of 1.25 Airy units, which corresponds to the central portion of the point-spread function associated with a focussed beam. The 32 detector elements are read in 1 microsecond and provide a raw spatial resolution limited by the size of the individual pixels of the detector, i.e. 50 nm. Once further fitted with Gaussian curves, the centroid position that corresponds to the highest SERS signal can be extracted with a resolution better than 7 nm.

This ultra-high speed, high spatial resolution approach was applied by Brolo *et al.* to the study of surface-deposited silica nanospheres coated with a 15 nm shell of silver that was in turn homogeneously coated with dithionitrobenzoic acid. The recorded intensity fluctuations from the particles exclude

molecular adsorption-desorption interfacial kinetics due to the absence of solvent. Rather, dynamic processes of the metal adatoms and clusters at the surface appear prominently. The transient nature of small pico-cavities with extreme localization of the EM field may be responsible for a very large, but spatially sparse, enhancement. The concept of pico-cavities was also highlighted in TERS microscopy by Deckert *et al.*, who assigned the origin of the TERS signal to a small cluster of metal atoms located at the extremity of a coated AFM tip, providing sub-nanometer spatial resolution.^{5,6}

The SERS intensity fluctuations are further analyzed over a full particle by dynamic evaluation of the average SERS activity. The characteristic “ON” time, where the SERS signal is intense, has a typical duration of 70 microseconds, but occurs for only 2% of the total recorded time; a hot-spot with average intensity has a short phase of activity followed by long dark periods. Interestingly, fluctuations recorded at different wavelengths within the plasmon resonance do not always show temporal correlation but have similar “on” and “off” statistics. This highlights the inhomogeneous response of the hot-spots, which are not driven by a specific plasmon resonance but rather by the corrugated surface of the particles. Moreover, the rate of fluctuations is increased under higher irradiances, indicating a thermally driven mechanism of constant rearrangement of the atomic-level surface structure. Altogether, the plastic nature of the hot-spots, combined with a low molecular coverage, favors a mechanism where SERS activity is high when the hot-spots have found the analyte.

Brolo *et al.* have introduced new directions to the very active SERS field. A temporal gain of three orders of magnitude is a major step towards revealing intimate mechanisms that could not be visualized before. Limitations in terms of spectral resolution could be improved in the future using high resolution spectrographs, rather than bandpass filter-based spectral selection, which would enable better discrimination of the background fluctuations from the Raman signal. Application of the proposed approach to plasmon-mediated chemistry and surface reactivity could certainly be interesting for the understanding of the intimate chemical steps in hot-electron driven chemical reactions and nanoscale photopolymerization reactions of hybrid systems.^{7,8} It will also help to better understand and possibly exploit these temperature-dependent fluctuations for critical measurements, such as in ambient tip-enhanced Raman spectroscopy.

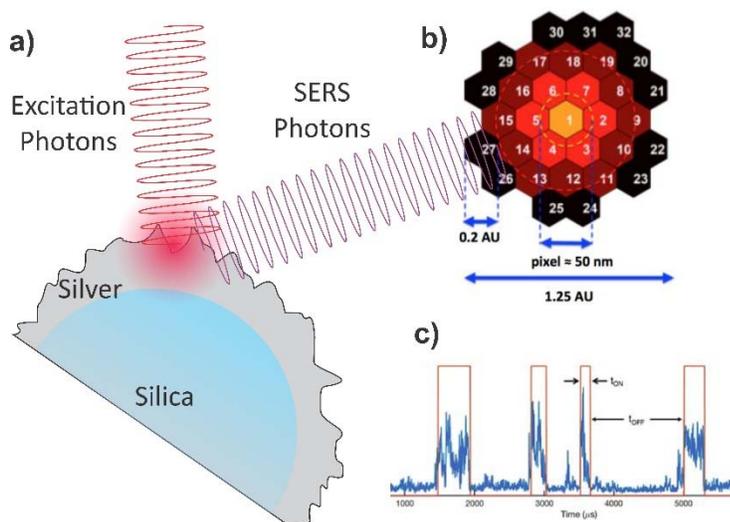


Fig. 1 Ultrafast detection of surface-enhanced Raman fluctuation. a) Laser light is focussed onto 100 nm silver-shell nanoparticles functionalized with dithionitrobenzoic acid and deposited onto a substrate. b) Airyscan detector is composed of 32 independent photomultiplier elements covering the central part of the point spread function of the focussed beam. The whole array can be read in 1.23 microseconds, yielding dynamics in the MHz range. c) Each detector element can be read independently, yielding temporal fluctuations of the SERS activity.

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