Tip Enhanced Raman Spectroscopy Imaging of Opaque Samples in Organic Liquid

T. Touzalin,^a A. L. Dauphin,^a S. Joiret,^a I. T. Lucas,^{*a}, E. Maisonhaute^{*a}

Sorbonne Universités, UPMC Univ Paris 06, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques, F-75005 Paris, France. e-mail: ivan.lucas@upmc.fr ; emmanuel.maisonhaute@upmc.fr

Materials and methods

Gold tips were made by electrochemical etching in a 50:50 (V:V) concentrated HCl/ethanol solution as described in the literature.^{1, 2} A SEM-FEG image of a representative tip is presented in Fig. 1 of the min text. It displays a radius of curvature between 10 and 20nm.

For TERS experiments, we relied on a AIST Smart SPM STM coupled with a Horiba Labram HR800 Raman spectrometer. A 632.8 nm HeNe Laser was focused from the top of the sample with a Mitutoyo 100x (NA = 0.7) long working distance (6 mm) objective. The objective was mounted on a piezo stage so that XY, XZ or YZ laser scans were performed to find the hot spot, *i.e.* the position for which the TERS signal was maximum. Polarization of the laser was along the shaft of the tip. Laser powers ranged from 14.1 to 287 μ W and exposure times during objective or sample scans were set between 100 and 500 ms.

4-(phenylazo)phenoxy]hexane-1-thiol **1** (Prochimia) and hexadecane (Aldrich) were used as received.

Gold samples were prepared by thermal evaporation of 100 nm of gold onto freshly cleaved mica heated at 400°C. They were flame annealed prior use. Monolayers of **1** were prepared by soaking the gold substrate in a 0.2 mM ethanolic solution of **1** for 1 h. After thorough rinsing, the samples were left 1 h into pure ethanol in order to remove physisorbed molecules. In comparison to literature,^{3, 4} the SAM was prepared in a more diluted solution and the sample soaked for a shorter time. This allows getting an inhomogeneous coverage of **1** on the surface and thus a contrast when performing TERS imaging (see Fig. 4 of the main text).

Far field signal

Fig. S1 presents the far field signal obtained in air when focusing the laser onto the sample but not at the tip position. The signal being much weaker a laser power of 98 μ W and an exposure time of 10 s were used. In comparison acquisition performed at the hot spot in TERS experiments necessitated only 14.1 μ W and 0.1 s exposure time.



Fig. S1: Far field signal obtained for a monolayer of 1 onto gold in air. Laser power: 98 μ W. Exposure time: 10 s.

Raman of pure hexadecane

The Raman spectrum of pure hexadecane is presented in Fig. S2.



Fig. S2: Raman response of pure hexadecane.

Hot spot position determination before TERS imaging

The hot spot position was determined as presented in Fig. 3 of the main text. Here, the hexadecane layer was thinner so that contribution from the solvent was weaker. The XY objective maps before and after the TERS imaging are presented in Fig. S3a and Fig. S3b. During TERS imaging, the laser was focused at the position of the black cross in Fig. S3a. 4 spectra at different positions are presented in Fig. S3c. Their similar intensity demonstrates that the hot spot did not move by more than 200 nm during the image acquisition.



Fig. S3: XY laser scan maps obtained before (a) and after (b) TERS imaging corresponding to Fig. 4 of the main text. c) Spectra corresponding to the crosses in FigS3a and FigS3b. Laser power 98 μ W, acquisition time 0.107s.

References

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