Near-Field Raman and Luminescence Spectroscopies to Evidence Chemical Heterogeneity of Surfaces with Sub-wavelength Spatial Resolution.

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ABSTRACT

Near-field scanning optical microscopy (NSOM or SNOM) opens the fascinating opportunity to access the richness of spectroscopic information at a sub-micronic resolution. Shear-force topography coupled to localized spectral information evidence chemical heterogeneity at this challenging spatial scale, which can be crucial to understand the relationship between microscopic features and macroscopic behavior of the samples. Three examples are reported to evidence the potentiality of SNOM using aluminum-coated silica probes. Two are devoted to near-field Raman spectroscopy applied to i) a small crystal of lead sulfate covered by nano-phases of copper sulfate and ii) well-oriented single crystals of rutile TiO_2. The last example uses near-field time-resolved luminescence spectroscopy to evidence heterogeneity of the local environment of Europium(III) cations at the surface of a glass sample doped with a small amount of Eu_2O_3 oxide.

Keywords: SNOM, spectroscopy, surface, Raman, luminescence.

1 INTRODUCTION

Near-field scanning optical microscopy (NSOM or SNOM) offers the opportunity to collect optical information at a spatial scale well below the diffraction limit [1-5]. The method using aperture-less probes is well suited for imaging samples and comparing the optical images with the topographical contrast [1,2]. Another approach is valuable if one is interested by obtaining near-field Raman or luminescence spectra : the light is collected by a silica fiber coated with aluminum and having a small aperture (diameter of about 50 nm) at its apex. Using silica fiber tip authorizes to perform spectroscopy with a spatial resolution of about 80-100 nm [3-5]. This presentation is devoted to such examples of Raman and luminescence spectra of solid surfaces acquired in near-field condition.

2 EXPERIMENTAL SET-UP

Near-field Raman or time-resolved luminescence spectra were acquired using the set-up presented in Figure 1. For Raman-SNOM experiments, the excitation source was a CW argon laser emitting at 457, 488 or 514 nm, with a power of 200 mW. The detector was a CCD camera cooled by liquid N_2 placed after a Jobin-Yvon T64000 spectrograph. For measuring near-field luminescence decay kinetics, a pulsed Nd:YAG laser was selected to generate 5 ns pulses at 532 nm after frequency doubling. A photomultiplier was used as a fast detector after the T64000 spectrograph. A transient digitizer stored the signal of the photomultiplier. The excitation beam (either pulsed or CW) was focused on the sample with the help of SMA fibers and lenses.

The near-field microscope was the same as previously described [2-5]. It uses silica fiber tip coated by aluminum and having a small aperture of around 50-80 nm at its apex. Briefly, the fiber optic tip was oscillating at resonant frequency by a dither piezo coupled to an electrical oscillator. The shadow of the tip illuminated by a laser diode was imaged on a bi-cell photodiode to measure the frequency and amplitude of the tip's vibration. A lock-in amplifier locked on the amplitude of vibration was used as a feedback controller of the vertical Z piezo under the sample. After an horizontal XY scan of the sample, a shear-force topography of the surface probed by the tip was obtained. The fiber optic tip was coupled to a confocal microscope and the near-field signals were spectrally decomposed by the Jobin-Yvon T64000 spectrograph. In order to verify that the Raman or luminescence photons were properly collected in near-field, the signal intensity at a given wavelength was observed versus the voltage applied on the Z piezo (i.e. the tip-sample separation). It was found that the intensity decreased exponentially when the tip-sample separation increased, in accordance with the theory [1-3].
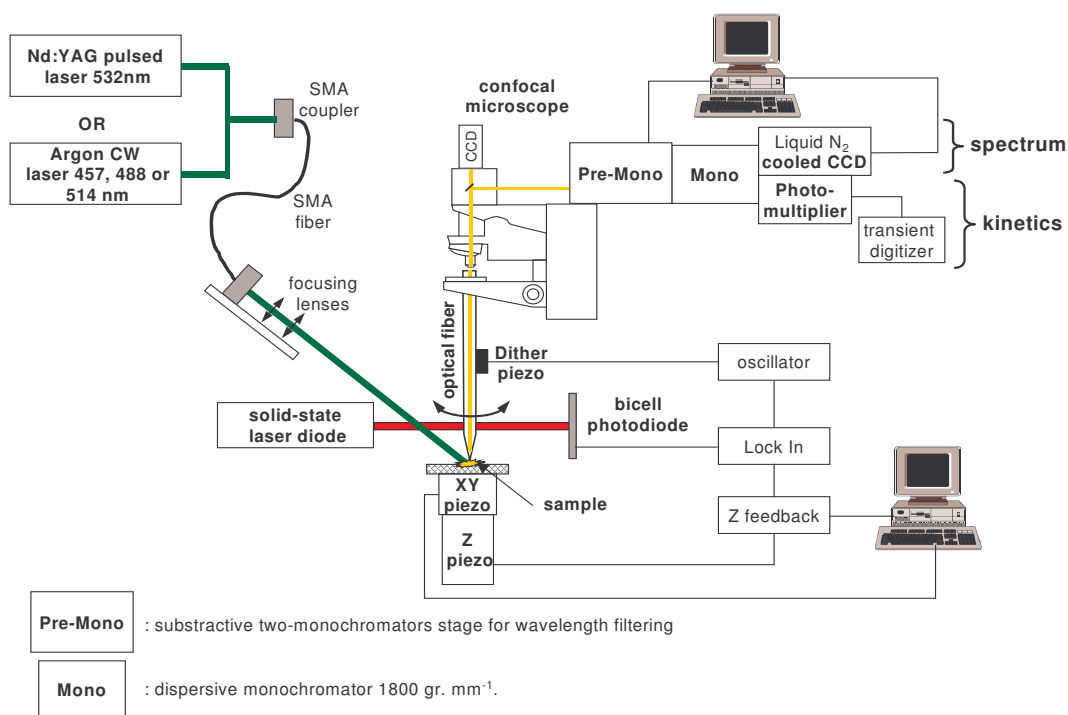
Figure 1 : Near-field Raman and time-resolved luminescence experimental set-up.

3   NEAR-FIELD RAMAN SPECTROSCOPY

3.1 Lead sulfate sample with nanophases of copper sulfate.

A first example shows the near-field Raman spectra obtained on a lead sulfate ($PbSO_4$) sample [4]. Usual back-scattered far-field Raman spectra recorded in the confocal microscopic mode did not show evidence of chemical heterogeneity of the sample. However, Figure 2 shows that the surface of the sample is heterogeneous at sub-micronic spatial scale according to shear-force topography. The isoforce image corresponds to a constant amplitude of vibration of the silica probe, i.e. to a constant tip-sample interaction. Topographical features thus come from a relief present at the surface. Figure 3 gives the corresponding Raman spectra obtained at different locations on the isoforce image of Figure 2. The peak obtained at 985 cm^{-1} was attributed to hydrated copper sulfate and not lead sulfate. Another argument was also obtained making local shear-force measurements at various tip-sample distances [4] that confirmed the presence of hydrated nano-phases of copper sulfate at the surface of $PbSO_4$.
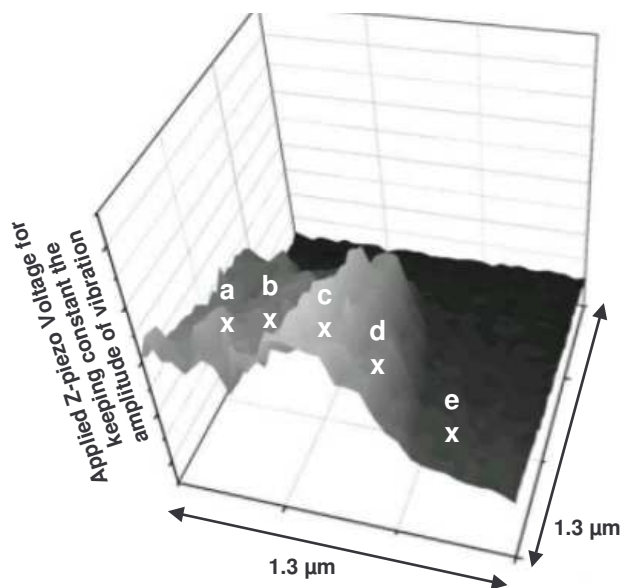

Figure 2 : Isoforce image of a small area of the $PbSO_4$ sample. Adapted from reference [4].
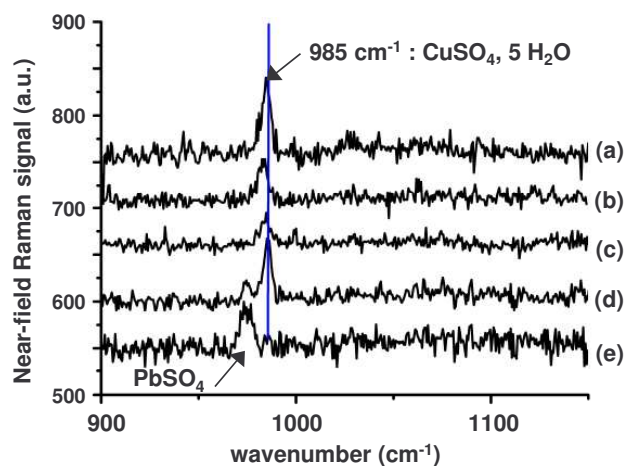
Figure 3 : Raman-SNOM spectra obtained in locations a-e in Figure 2. Adapted from reference [4].

3.2 Surfaces of well-oriented single-crystals of rutile TiO$_2$.

It is of special importance to develop a spectroscopic method that can characterize TiO$_2$ crystals at sub-micronic spatial scale in the context of the synthesis of nano-phases of TiO$_2$. Raman spectroscopy is useful to make the distinction between TiO$_2$ crystalline forms, anatase, rutile and brookite [6]. To obtain reference spectra in near-field condition, single crystals of rutile TiO$_2$ were selected and analyzed by near-field Raman spectroscopy. The polarization of the incident laser light and the angle of incidence from the normal of the sample were changed to examine the validity of the usual (far field) Raman selection rules in near-field on this material.

Figure 4 reports the Raman spectra obtained with the silica fiber tip in near-field condition for two crystallographic planes (110) and (001) of rutile single-crystals. The argon laser was used at 514 nm (laser power 200 mW) to obtain these spectra. The two major phonon modes of rutile at 405 cm^{-1} (E$_g$ symmetry) and 612 cm^{-1} (A$_{1g}$ symmetry) are rather well resolved and the signal-to-noise ratio is good (each spectrum represents an averaging of 3 spectra with an acquisition time of 45 minutes on the cooled CCD). At 235 cm^{-1}, one can observe a broad feature that is attributed to a two-phonons mode in far field experiments [6]. The change of the A$_{1g}$ band intensity with incident laser features for the (110) plane, and the lack of change for the E$_{1g}$ mode in both planes and A$_{1g}$ for the (001) plane are in agreement with the prediction one can made using the polarizability tensor of rutile [6]. These spectra thus evidence that the Raman selection rules are conserved in near-field in the case of the rutile surface. The method can therefore be applied to characterize TiO$_2$ phases in a wide variety of synthesized nano-materials.
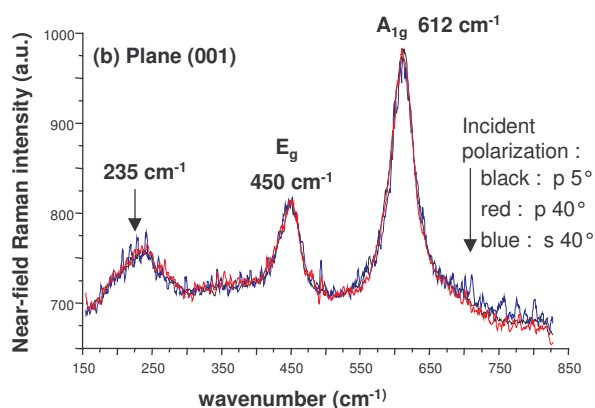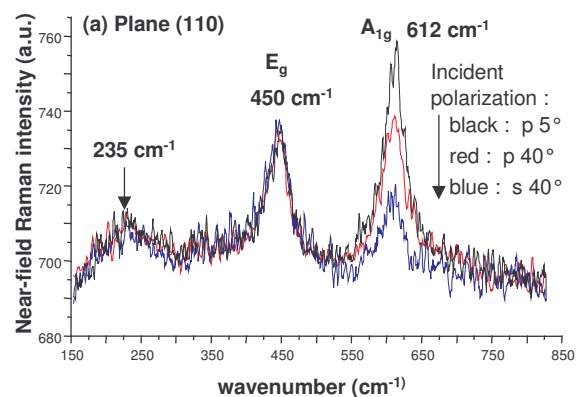

Figure 4 : Raman-SNOM spectra of oriented single-crystals of rutile TiO$_2$.

4 NEAR-FIELD LUMINESCENCE

A third example concerns the study of a glass sample doped with 1.5 % in weight of Eu$_2$O$_3$. The surface of the glass was studied using near-field time resolved fluorescence spectroscopy (SNOM-TRFS). Figure 5 reports a topographical image with two different sites A and B and the corresponding luminescence spectra of Eu^{3+} cations excited with the 532 nm light of a nanosecond pulsed Nd:YAG laser [5]. The topographical relief is associated with an important change of the $^5D_0 \rightarrow ^7F_2$ emission band of Eu^{3+} cation. As this emission band is sensitive to a local change of the symmetry around Eu^{3+} cation, it is shown that the surface of the glass sample is composed of at least two kinds of chemical sites surrounding europium(III) cations. These sites can be separated by few microns and are perfectly evidenced by near-field luminescence measurements.

Figure 6 reports the decay kinetics of the Eu^{3+} luminescence obtained in near-field condition using a photomultiplier as a transient detector. The luminescence decay was observed at 613 nm, corresponding to the maximum of the luminescence spectrum for both locations A and B in Figure 5. The signal-to-noise (S/N) ratio was rather poor for these kinetics, but they have been tentatively fitted by the following pulse equation :

$$y = y_0 + A \times \left(1 - e^{\frac{-(t-t_0)}{\tau_1}}\right) \times e^{\frac{-(t-t_0)}{\tau_2}} \qquad (1)$$

In this equation, y is the fluorescence intensity, A the amplitude of the signal, τ_1 the risetime and τ_2 the fluorescence decay time. Parameter y_0 and t_0 (fluorescence signal at time zero) are fixed to zero. The risetime τ_1 was determined by recording only the laser pulse with the monochromator set at 532 nm, and subsequently fixed to the value such obtained, i.e. 0.30 ms in near-field (mainly due to the fact that the photomultiplier signal was send to a 1 MΩ resistance to increase the signal voltage). The adjusting parameters of the fit were thus A and τ_2 and their values were retrieved by using a non-linear Marquardt-Levenberg algorithm.
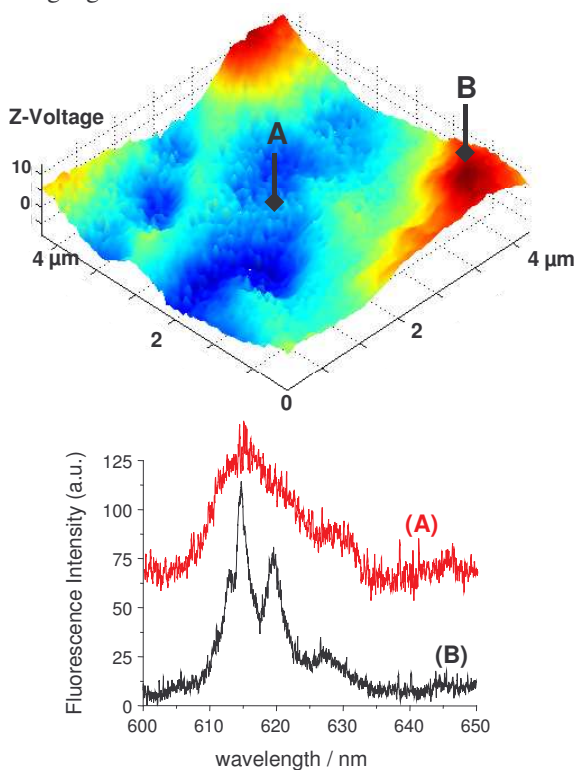

Figure 5 : Shear-force topography of a 4µm×4µm area of a glass sample doped with 1.5% wt. of Eu_2O_3. Sites A and B are examples of local areas leading to different shear-force interaction with the probe tip. The corresponding luminescence spectra of Eu^{3+} are given below. Adapted from reference 5

As shown in Figure 6, the decay time τ_2 was longer for site B than for site A, indicating a change of Eu^{3+} environment or at least a change of tip-sample interaction. Although some improvements have to be carried out on the experimental set-up to tentatively increase the S/N ratio, the SNOM-TRFS experiments performed on the glass sample confirmed that spectral and kinetic heterogeneities were associated with topographic relief at a sub-micronic spatial scale.
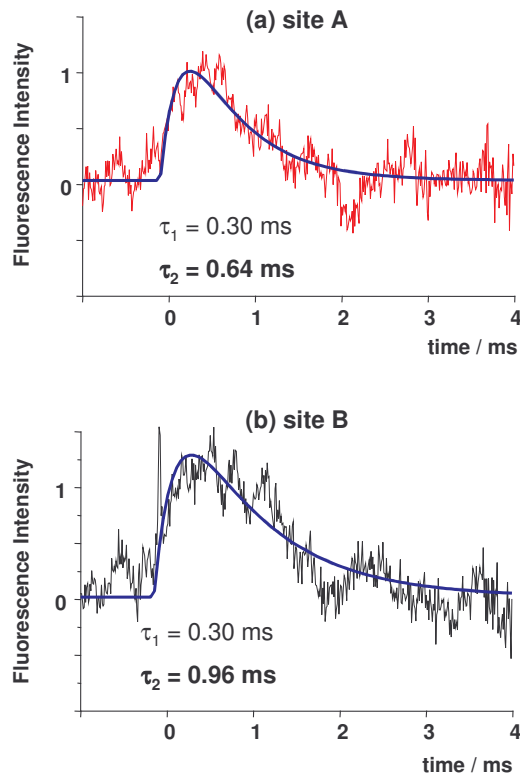

Figure 6 : near-field luminescence decay kinetics at sites A and B of Figure 5. Adapted from reference 5.

5 CONCLUSION

Aperture-less probes are nowadays commonly used with success for near-field imaging of samples, but using silica fiber tip reveals to be very useful when spectral characterization rather than imaging is needed as shown here by three different examples.

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