Supporting information

Influence of stearic acid coating of NaCl surface on the reactivity with NO₂ under humidity

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XY scanning Raman mapping. The XY scanning Raman mapping generates a three dimensional data set $(m \times n \times \lambda)$, that is, $m \times n$ spectra, each containing $\lambda = 1024$ spectral elements. So, each ijth pixel spectrum corresponds to a micro zone of sample for which a complete characteristic Raman spectrum can be recorded. The conventional data processing of Raman imaging consist in selecting a narrow spectral region which corresponds to a characteristic Raman band of a compound of interest (NaCl, SA, H₂O, or NaNO₃). Then, the integrated intensity of the Raman band of interest over all the m ×n spectra gives an estimation of the distribution of the compound of interest in each ij pixel.

Crystalline structures and Raman active vibration modes. NaCl crystal belongs to O_h^5 (Fm3m) space group. According to the group-theoretical selection rules of Raman scattering no crystalline vibrations of NaCl are expected in the first order Raman spectra. In contrast, the selection rules for second-order Raman scattering provide characteristic broad Raman bands in the low frequency range which can be used to characterize NaCl surface by recording Raman mapping ⁴² (see Figure S1a in supporting information).

The Raman spectra of bulk solid SA with crystalline arrangement of chain molecules CH₃-(CH₂)₁₆-CO₂H was recorded with our experimental conditions and is shown in Figure S2 of supporting information (SI) with assignment of main Raman bands. SA can crystallize in several phases including the space group $P_{2_1/a}$ (C_{2h}) with 4 SA molecules per monoclinic cell. 660 internal vibrations and 12 external vibrations are expected taking into account the effect the site and factor groups.⁴³ The Raman spectrum of solid SA exhibited many Raman bands assigned to the different internal vibrational modes of the SA chain molecule as reported in previous works⁴⁴⁻⁴⁶. The effects of site and factor groups were not resolved even at low temperature but broaden significantly the Raman bands. In the 2500-3000 cm⁻¹ region, the prominent Raman bands observed around 2846 and 2880 cm⁻¹ were assigned to the symmetric (v_s) and antisymmetric (v_{as}) stretching vibrations of the methylene (-CH₂-) groups of the alkyl chain, respectively, while the broad and weak Raman band centered at 2940 cm⁻¹ was assigned to the combination of stretching and deformation vibration modes ($v_s + 2\delta$) of -CH₂groups. The two weak bands observed at 2917 and 2953 $cm^{\text{-1}}$ were attributed to the ν_s and ν_{as} of the terminal methyl (-CH₃) motif. In the 600-1600 cm⁻¹ region, many bands with much lower Raman signal intensities (Fig. S2) were observed and assigned. The deformation, twisting and scissoring modes of -CH₂- groups were observed together with C-C stretching and C-O vibrations. The stretching modes (vC=O and vC-O) of the -CO₂H group expected at 1640 and 1440 cm⁻¹, respectively, have very low Raman band intensities due to weak Raman cross section. SA is known to form many monolayer coating and multilayer vesicles with different conformations of the alkyl chain. Solid SA is also known to exhibit several phase transitions implying chain conformation and chain order changes as a function of temperature. The prominent Raman bands in the 2500-3000 cm⁻¹ range showed characteristic Raman intensity changes as well as band broadening. In contrast, the wavenumbers of the Raman active stretching modes of -CH₂- groups are reported to change hardly. The -CH₂- stretch range contains three main components centered at 2848, 2880 and 2940 cm⁻¹, because of extensive Fermi resonance interactions with overtones of the bending modes these high frequency bands are affected by intra- and inter molecular interactions.^{47,48} The intensity ratios I₂₈₈₀/I₂₈₄₆, I₂₉₄₀/I₂₈₄₆ and I₂₉₄₀/I₂₈₈₀ can be associated to conformational and structural ordering of the alkyl chains ^{47, 48}. The intensity ratios I₂₈₈₀/I₂₈₄₆, I₂₉₄₀/I₂₈₄₆ and I₂₉₄₀/I₂₈₈₀ of every pixel spectra in the Raman images may be used to probe the conformational and structural order of SA aggregates within every 1 μ m² area of the image. The I₂₈₈₀/I₂₈₄₆ ratio close to 2.2 is attributed to a well-ordered all-trans alkyl chains of 3D crystalline SA while the I₂₈₈₀/I₂₈₄₆ ratio close to 0.7 is typical of a completely disordered "spaghetti-like" structures. Low I_{2940}/I_{2880} ratio values close to 0.4 ± 0.1 are indicative of well-ordered structures while gel-like structure or liquid-crystal phase exhibit higher I_{2940}/I_{2880} ratio values close to 1. The

 I_{2880}/I_{2846} and I_{2940}/I_{2880} ratios were calculated for every pixel of the images by using the intensity of the peaks at 2846, 2880 and 2940 cm⁻¹ after a peak fitting procedure.

Group theory shows that isolated NO₃⁻ anion (D_{3h} symmetry), in NaNO₃ aqueous solution, has 4 internal vibrations. The v₁ (A'₁) vibration is Raman active with prominent intensity and it is observed at 1050 cm⁻¹, the v₂ (A''₂) is Raman inactive, the v₃ (E') and v₄ (E') modes are Raman active with low intensities. NaNO₃ crystalline structure belongs to R₃⁻c (D_{3d}^{-6}) space group. The reduced representation of the Raman fundamentals is expected to be A_{1g} + 4 E_g. The A_{1g} mode derived from the v₁ vibration of isolated NO₃⁻ is observed as prominent peak at 1068 cm⁻¹ in the solid state while the E_g Raman bands derived from v₃ and v₄ vibrations of isolated NO₃⁻ are observed at 1385 and 724 cm⁻¹, respectively. Fig. S1. Optical image (a), Typical second-order Raman spectrum (b) AFM image (c) and AFM profil (d) of fresh cleaved NaCl (100) surface



Fig. S2. Typical ToF-SIMS mass spectrum and peak assignment of fresh cleaved NaCl (100) surface recorded in positive (a) and negative (b) modes



Fig. S3. Typical Raman spectrum of pure stearic acid and Raman band assignment in the (a) $600 - 1600 \text{ cm}^{-1}$ and (b) 2500-3200 cm⁻¹ spectral range



Fig. S4. Typical ToF-SIMS mass spectrum recorded in negative mode of Region of interest (in green) of NaCl coated with stearic acid. (a) Optical image (b) mass spectrum from 50 to 10 u.m.a. and (c) mass spectrum from 250 to 300 u.m.a



Fig. S5. Typical ToF-SIMS mass spectrum and peak assignment of pure stearic acid in positive (a) and negative (b) modes



Fig. S6. ToF-SIMS depth profiles of NaCl(100) coated with stearic acid and exposed for 1 hour to humid air (RH ~50%). The profile is reconstructed from NaCl₂⁻ (green), OH⁻ (blue) and $C_{18}H_{35}O_2^{-}$ (red) mass peak intensities of a selected region of interest (ROI).



Fig. S7. ToF-SIMS imaging of NaCl(100) coated with stearic acid and exposed to NO₂ (RH~40 %) – (a) ToF-SIMS image of $C_{18}H_{35}O_2^-$ mass peak (Blue square corresponds to the selected Region of Interest(ROI), (b) ToF-SIMS image reconstructed from ROI, (c) mean ToF-SIMS spectrum reconstructed from ROI.



Fig. S8. ToF-SIMS depth profiles of NaCl(100) coated with stearic acid and exposed to NO₂ (RH ~0%). The profile is reconstructed from NaCl₂⁻ (green), OH⁻ (blue), $C_{18}H_{35}O_2^{-}$ (red) and NaNO₃⁻ (purple) mass peak intensities of a selected region of interest (ROI).



Fig. S9. Intensity mass peak ratio of OH-/NaCl₂⁻ as function of sputtering time for all experiments i.e. NaCl coated with SA; NaCl coated with SA and exposed for 1h to RH~50%; NaCl coated with SA and exposed for 30 min to NO₂ (1000ppm) in dry conditions and NaCl coated with SA exposed first to NO₂ (1000ppm) in dry conditions and secondly for 1h to RH ~50%.

