RamanFest Frankfurt | GERMANY July 02-03 2025

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Tracking On-Surface Degradation Pathway of 4-Mercapto Phenyl Boronic Acid using Tip-enhanced Raman Spectroscopy

Mercaptophenylboronic acid (MPBA) compounds plays an important role in surface chemistry and functional materials. For instance, MPBA-functionalized surfaces are widely used as probes for detecting molecules such as glucose and dopamine.[1] However, despite their broad utility, the on-surface degradation mechanism of MPBA remains poorly understood. This lack of insight limits the rational design of MPBA-based stable and high-performance sensors and nanomaterials.

In this study, we investigated the on-surface degradation pathway of 4-MPBA under excitation laser illumination using tip-enhanced Raman spectroscopy (TERS). Upon irradiation with high laser power during the laser-power dependent TERS measurements, an initial formation of crosslinked structures between the phenyl rings of 4-MPBA molecules was observed, followed by progressive oxidation of the thiol groups chemisorbed on the Au(111) surface. Hyperspectral TERS measurements indicate that as sulfur oxidation proceeded, cleavage of the carbon–sulfur (C–S) bond occurred, ultimately resulting in the formation of oxidized sulfur species such as -SO_3H as final degradation products. Molecular orbital (HOMO–LUMO) energy calculations suggest that the on-surface degradation of 4-MPBA likely could proceed through a surface-mediated plasmon-driven process. This study demonstrates that hyperspectral TERS analysis can provide novel insights into the degradation of 4-MPBA, which are directly relevant for the chemical stability and functional durability of MPBA-based plasmonic sensors and functionalized nanostructures.

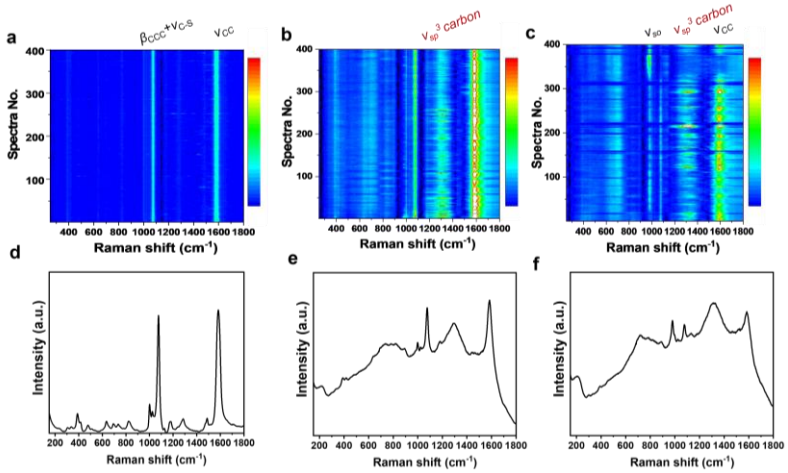

Figure 1: TERS waterfall plots (top panels) and corresponding averaged TERS spectra (bottom panels) showing the on-surface degradation of 4-MPBA on Au(111). The transformation proceeds from the intact molecular state of 4-MPBA self-assembled monolayer (a,d), through phenyl ring crosslinking (b,e), to the oxidized sulfur species (c,f). Laser power in panel a: 0.2mW panel b: 2.6mW, panel c: 2.6mW.

References

[1] Zhang, K., Liu, Y., Wang, Y., Zhang, R., Liu, J., Wei, J., Qian, H., Qian, K., Chen, R., Liu, B., ACS Applied Materials & Interfaces, 10(18) (2018) 15388–15394.