Sub-Nanoscale Chemical Analysis with Nano-Confined Localized Surface Plasmons

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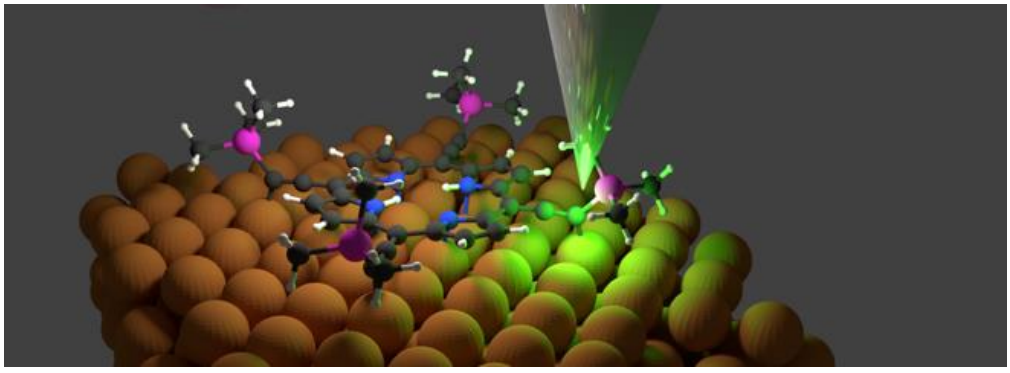
It is of significant importance but a challenging task to probe how local chemical environments affect single-molecule behaviors with angstrom scale resolution. Tip-Enhanced Raman Spectroscopy (TERS) affords the spatial resolution of traditional Scanning Tunneling Microscopy (STM) while collecting the chemical information provided by Raman spectroscopy. By using a plasmonically-active probe tip, the Raman signal at the tip-sample junction is incredibly enhanced, allowing for single-molecule probing. This method, further aided by the benefits of ultrahigh vacuum, is uniquely capable of controlling localized plasmons via an atomistic approach. We are able to obtain (1) single-molecule chemical identification;1 (2) adsorbate-substrate interactions of individual molecules on the surface;2 (3) local strain effects in 2D heterostructures;3 (4) atomic-level insights into surface oxidation reactions.4 By investigating substrate structures, molecular superstructures, 2D material lattices, and adsorption geometries obtained from vibrational modes, we extract novel surface-chemistry information at an unprecedented spatial (< 1 nm) and energy (< 10 wavenumber) resolution. Another important application of localized surface plasmons is to achieve site-selective chemical reactions at sub-molecular scale. Recently, we selectively and precisely activated multiple chemically equivalent reactive sites one by one by scanning probe microscopy tip-controlled plasmonic resonance.5 Our method can interrogate the mechanisms of forming and breaking chemical bonds at the angstrom scale in various chemical environments, which is critical in designing new atom- and energy-efficient materials and molecular assemblies with tailored chemical properties.



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