Mechanistic Insights in Oxygen Activation on Bulk Au(111) Surface Using Tip-Enhanced Raman Spectroscopy

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Over the past two decades, Tip-Enhanced Raman Spectroscopy (TERS) has emerged as a powerful tool for surface chemical analysis at the nanoscale [1]. By combining the high spatial resolution of scanning probe microscopy with the chemical sensitivity and specificity of surface-enhanced Raman spectroscopy, TERS allows visualization of surface chemical processes beyond the diffraction limit of visible light [2].

In this talk, I will first provide a brief overview of the fundamental principle of TERS, with a particular focus on the strengths and limitations of AFM- and STM-based TERS techniques for nanoanalysis of heterogenous catalytic systems. In the second part of my talk, I will demonstrate the practical application of TERS in the field of heterogeneous catalysis by sharing findings from a recent study conducted in our laboratory [3]. Specifically, we investigated oxidation of 4-aminothiophenol (4-ATP) to 4-nitrothiophenol (4-NTP) on Au(111) surface using hyperspectral TERS imaging as schematically illustrated in Figure 1. Nanoscale TERS images revealed a markedly higher oxidation efficiency in disordered 4-ATP adlayers compared to the ordered adlayers signifying that the oxidation of 4-ATP molecules proceeds via interaction with the on-surface oxidative species. These results were further validated via direct oxidation of the 4-ATP adlayers with H_2O_2 solution. Finally, TERS measurements of oxidized 4-ATP adlayers in the presence of H_2O^{18} provided the first empirical evidence for the generation of oxidative species on bulk Au(111) surface via water-mediated activation of molecular oxygen [3]. This study expands our mechanistic understanding of oxidation chemistry on Au by elucidating the oxygen activation pathway.

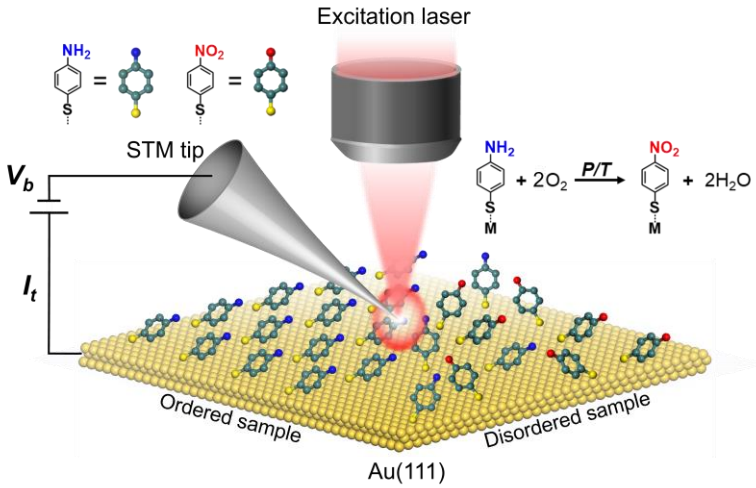

Figure 1. Schematic diagram of the scanning tunnelling microscopy (STM) based TERS setup used in this study to investigate the on-surface oxidation of ordered and disordered 4-ATP adlayers on Au(111) surface.

Overall, this talk will highlight the potential of TERS in the nanoscale investigation of surface catalytic processes. Through high sensitivity and nanoscale hyperspectral imaging, TERS can offer valuable insights to advance our mechanistic understanding of surface chemistry.

[1] Z.-F. Cai, N. Kumar, R. Zenobi, *CCS Chem.*, **2023**, *5*, 55-71
[2] N. Kumar, S. Mignuzzi, W. Su, D. Roy, *EPJ Tech. Instrum.*, **2015**, *2*, 9
[3] Z.-F. Cai, Z.-X. Tang, Y. Zhang, N. Kumar, *Angew. Chem. Int. Ed.*, **2024**, e202318682