Nanoscale Visualization of Plasmon-Enhanced Hydrogen Activation on Pt(111) Surface using Tip-Enhanced Raman Spectroscopy

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Understanding and controlling molecular hydrogen activation at solid surfaces is a central challenge in heterogeneous catalysis and energy-efficient chemical transformations [1]. Despite extensive studies on plasmon-assisted catalysis, direct nanoscale visualization of light-enhanced H_2 activation on well-defined catalytic surfaces and clear discrimination between electronic and thermal mechanisms has remained elusive. Here, we address this challenge by developing a nanoanalytical strategy enabling *in situ*, spatially resolved interrogation of plasmon-enhanced H_2 activation on Pt(111) under ambient conditions.

Using tip-enhanced Raman spectroscopy (TERS) with nanometric spatial resolution and molecular specificity [2], we directly visualize H_2 activation through the reductive desorption of a self-assembled oligomeric phenylene–ethynylene (OPE) thiol monolayer serving as a molecular reporter (Figure 1). Time-resolved TERS measurements reveal accelerated desorption dynamics under visible-light illumination, while hyperspectral TERS imaging uncovers circular regions of enhanced reactivity extending 180–300 nm around the plasmonic near-field [3]. Quantitative analysis shows a ~20% increase in H_2 activation relative to the surrounding surface, providing the first real-space visualization of plasmon-enhanced H_2 dissociation at the nanoscale on a non-plasmonic catalyst.

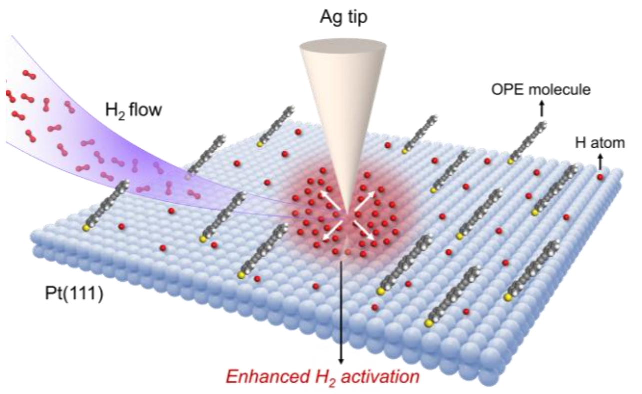

Figure 1. Scheme of the STM-TERS setup used to monitor plasmonically-enhanced H_2 activation on Pt(111) using reductive desoprtion of OPE moelcules.

To elucidate the underlying mechanism, the experimental nanoanalytical data are combined with finite element (FE) electromagnetic simulations, density functional theory (DFT), and quantum mechanical modeling. FE analysis demonstrates that plasmonic heating in the TERS junction is limited to the millikelvin range, which is orders of magnitude too small to account for the observed enhancement, thereby excluding photothermal effects. In contrast, quantum calculations reveal that localized surface plasmon resonance generates hot electrons on Pt(111) with energies sufficient to overcome H_2 dissociation barriers via an indirect hot-electron transfer mechanism. Furthermore, DFT modeling shows that the dissociated hydrogen atoms propagate far beyond the near-field through a collective surface "crowd effect," leading to long-range amplification of reactivity.

This work establishes TERS as a powerful nanoanalytical platform for disentangling electronic and thermal contributions in plasmon-enhanced catalysis and for directly mapping reactive intermediates and surface dynamics with nanometer precision. The mechanistic insights gained here open new avenues for the rational design of light-assisted catalytic systems capable of operating efficiently under mild conditions, with broad implications for hydrogenation chemistry and sustainable catalysis.

[1] Zhou *et al.*, *J. Am. Chem. Soc.*, **2006**, *128*, 1780-1781.
[2] Cai and Kumar *et al. J. Am. Chem. Soc.*, **2025**, *147*, 39838–39845.
[3] Cai and Kumar *et al.*, ChemRxiv preprint, **2025**, DOI: 10.26434/chemrxiv-2025-w41qh.