Electrochemical Tip-enhanced Raman Spectroscopy

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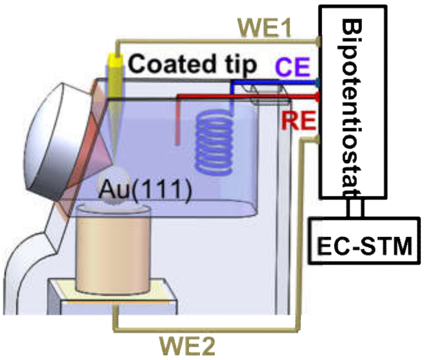
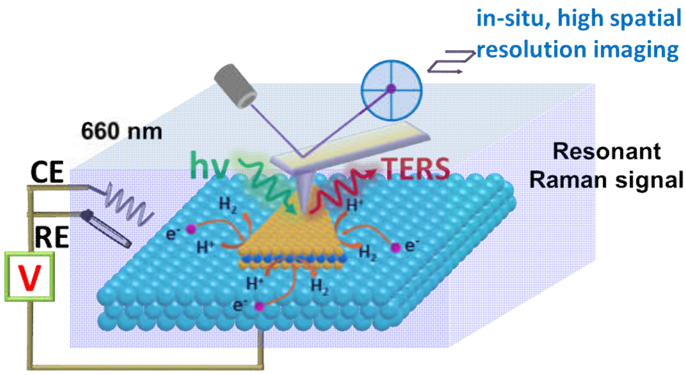
Surfaces and interfaces play a key role in heterogeneous electrochemical reactions, as the reactants need to interact with the surface. Therefore, it is extremely important to develop a method to probe the surface structure and the interaction of the reactant or product with the surface to achieve a better understanding to rationally design the electrochemical systems. In this regard, tip-enhanced Raman spectroscopy (TERS) appears to be an ideal tool for studying the complex electrochemical interfaces. TERS is an organic integration of scanning probe microscopy, Raman spectroscopy, and localized surface plasmon resonance. It can not only obtain the topological but also vibrational information of a sample at the nanometer resolution.



STM-based EC-TERS



AFM-based EC-TERS

We will first demonstrate that TERS can chemically and spatially resolve the site-specific electronic and catalytic properties of an atomically well-defined Pd(sub-monolayer)/Au(111) or Pt(nanoisland)/Au(111) bimetallic model catalyst at 3 nm resolution, with vibrational fingerprints of phenyl isocyanide (PIC) adsorbed and reacted on the surface. We then focus on our recent efforts on electrochemical TERS (EC-TERS) instrumentation, which allows us to synergistically control the reaction by both the electrode potential and laser power and characterize the reaction at the nanometer spatial resolution on STM-based EC-TERS. We then further used TERS to probe the edge-related lattice and electronic properties of atomically thin MoS2. We showed that TERS can spatially obtain distinctly different Raman features of the edge defects in mono- and bilayer MoS2 and identify the defect types (in particular the armchair and zigzag edges) in ambient. The power of TERS demonstrated in MoS2 can also be extended to other 2D materials, which may guide the defect engineering for desired properties. Finally, we will first introduce the challenge in the field and the key development in TERS.