

Tip-enhanced Raman Spectroscopy for Nanoscale Characterization of Electrochemical Systems

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Electrochemistry plays key roles in our daily life, from fuel cells, to batteries and to corrosion and electroplatings and even glucose sensing. The structure of the electrochemical interfaces determines the performance of electrochemical devices and systems, which requires a better understanding in order to rationally design the electrochemical systems. Tip-enhanced Raman spectroscopy (TERS), which is an organic integration of scanning probe microscopy (for the nanoscale control and morphology of sample), Raman spectroscopy (offering molecular fingerprint information), and localized surface plasmon resonance (LSPR, producing enhanced electromagnetic field to offer TERS with sensitivity down to single molecules), appears to be an ideal tool for studying the complex electrochemical interfaces.

In this talk, we will first introduce the challenge in the field and the key development in TERS. We then focus on our recent efforts on electrochemical TERS (EC-TERS) instrumentation. With the uniquely designed spectroelectrochemical cell, we are able 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 show that the plasmon-induced reaction can lead to a reaction region of 30 nm in radius close to the mean free path of electron in Au, indicating the hot-carrier dominated reaction as a result of LSPR excitation under TERS configuration. We further develop AFM-based EC-TERS to characterize the defects of MoS₂ with a spatial resolution better than 10 nm and identified very interesting spectral behavior of MoS₂ defects during electrocatalytic processes as a signature of electrochemical active sites. We will also demonstrate the application TERS in studying the catalytic active sites on the bimetallic catalysis surfaces with our understanding of the future of TERS.

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