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The road to the successful electrochemical tip-enhanced Raman spectroscopy

Electrochemical tip-enhanced Raman spectroscopy (EC-TERS), which combines electrochemical scanning probe microscopy (EC-SPM) and plasmon-enhanced Raman spectroscopy (PERS), is a powerful technique for the in-situ characterization of the electrochemical interface at the nanoscale and molecular level[1]. It is challenging to realize this technique since both a high sensitivity and a high stability are required. In the past 10 years, we have been developing EC-TERS so that it becomes possible to study the electrochemical interface[2][3][4]. We introduced water-immersion objectives to EC-TERS to avoid the optical path distortion between air and water, which allowed us to achieve a higher sensitivity. Both home-designed rigid EC-TERS cells and SPM heads were adopted to achieve a high stability. TERS tips with high TERS activity were fabricated by electrochemical method or nanofabrication (focused ion beam, FIB) method. These tips were then carefully insulated or protected for EC-TERS to give a long-time TERS enhancement. Benefited from the above improvements, we achieved EC-TERS imaging with a spatial resolution around 4 nm. With this powerful tool, we successfully probed the spatial distribution of plasmonically excited hot carries[5] and visualized the structural evolution of individual active sites of MoS_2 during hydrogen evolution reaction (HER). These discoveries offer new insights into our understanding of the electrochemical interface and may help the design of more active catalysts.

References

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Figures

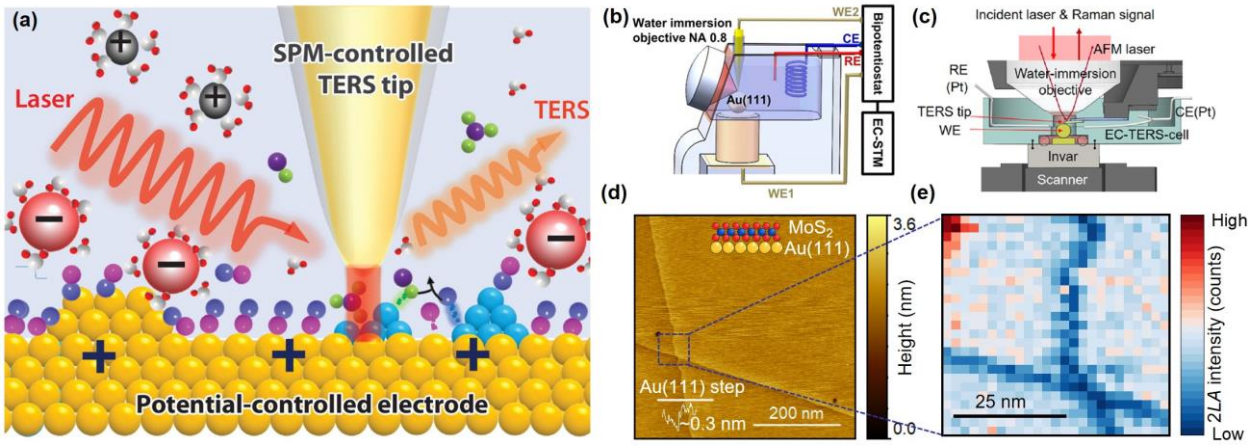

Figure 1: (a) Schematic illustrations of EC-TERS. Side-illumination EC-STM-TERS (b) and top-illumination EC-AFM-TERS (c) setups with water-immersion objectives. (d) EC-STM image of MoS_2 on Au(111). (e) EC-TERS image of the blue region in Figure 1 (d).