Elucidation of Tip-Broadening Effect in Tip-Enhanced Raman Spectroscopy (TERS): A Cause of Artifacts or Potential for 3D TERS

Dmitry Kurouski

Department of Biochemistry and Biophysics and The Institute for Quantum Science and Engineering, Texas A&M University, College Station, Texas 77843, United States

The tip-broadening effect (TBE) is an intrinsic phenomenon of atomic force microscopy (AFM), which makes the apparent dimensions of the imaged objects larger than they truly are. At the same time, TBE also provides an opportunity to achieve three-dimensional (3D) tip-enhanced Raman spectroscopy (TERS) if the plasmonically active zones located at the shaft of the used tip.

In this talk, I will demonstrate the first evidence of TBE in TERS showing that side parts of the p-nitrothiophenol (pNTP)-modified Au microplates (AuMPs) can be observed using 3D TERS. My group also used this novel spectroscopic approach to monitor reduction species of pNTP catalyzed by Au microplates (AuMPs). Our results showed that the 3D TERS was capable of distinguishing signals from both the side and top part in a single piece of AuMP, corresponding to Au{100} or Au{110} with low catalytic activity and Au{111} with higher catalytic activity, respectively (Figure 1).

Figure 1. TER imaging of catalytic activity of different crystal surfaces of AuMP using 3D TERS. This novel spectroscopic approach allows for probing sides of AuMP with Au{100} or Au{110} that have lower catalytic efficiency of pNTP reduction comparing to the top surface that has Au{111}.