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Novel Approaches in Tip-Enhanced Raman Spectroscopy: Accurate Measurement of Enhancement Factors and Pesticide Detection in Tip Dimer Configuration

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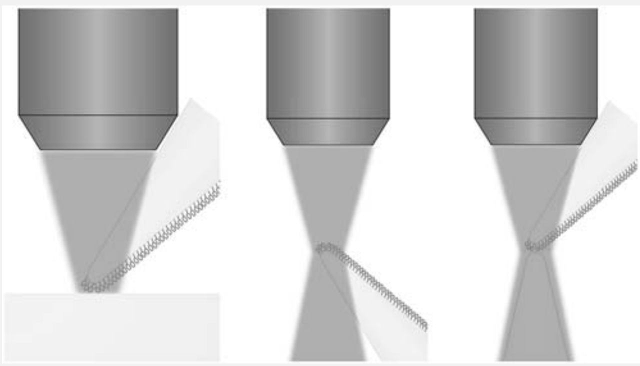
ABSTRACT: Tip-enhanced Raman spectroscopy (TERS) allows the precise manipulation of a nanometric probe for surface chemical analysis by plasmon-based amplification of Raman signals; however, acknowledged procedures and materials for assessing the enhancement factor in different configurations are still lacking. In this work, we propose a technique for the standardization of TERS intensity measurements, by chemisorption of different organic Raman-active molecules on plasmonic probes, and compare it to the conventional procedures addressed to the same goals. In addition, by ideally considering TERS as a special case of surface-enhanced Raman (SERS) involving a single nanoparticle, we experimentally realized the three most common configurations in SERS: i. isolated particle, ii. single scattering probe on a surface, and iii. nanoparticle dimers. To achieve the latter in an accessible way with plasmonic probes, we established a fabrication procedure for a substrate presenting multiple nanometric tips, intended to be easily approached and mapped for fast, reproducible assembly of tunable tip−tip dimers that further amplify Raman scattering with respect to conventional gap mode TERS; enhancement factors up to $(1.4 \pm 0.4) \times 10^{10}$ were calculated. The three configurations were successfully tested, and enhancement factors were quantified with their associated uncertainties, employing self-assembled monolayers of several probe molecules, including thiophenol, a de facto enhanced Raman standard, and thiram, a common use, law-regulated pesticide, hence opening up TERS to real world applications in agricultural and food analysis.



■ INTRODUCTION

Tip-enhanced Raman spectroscopy (TERS) is a versatile technique of surface analysis that allows topographic and chemical imaging with nanometric spatial resolution and high sensitivity, allowing surface mapping[1] and reaching single molecule detection[2,3] in diverse environments such as ambient conditions,[4] vacuum,[1,5] and liquid.[6] While TERS is quite a promising technique, with possible applications in diverse fields such as nanotechnology (e.g., nondestructive chemical characterization at the nanoscale), biology (e.g., label-free DNA sequencing and protein analysis), electronics, and fundamental studies,[7] reproducibility of probes and the results comparability among different instruments and laboratories are still open issues in the growing TERS community. In order for this technology to be adopted in commercial settings such as industry or routine research, these limits have to be overcome. In the last years, efforts have been made for the development of standard procedures and reference samples[8−11] for TERS, but the accurate evaluation of the enhancement factor (EF) remains an open issue. The accurate evaluation of the EF will enable a comparable characterization of different enhancing tips, which is the most important variable in this kind of apparatus.

■ THEORETICAL BASIS

Several different TERS system configurations exist, each having diverse efficiencies and each with specific needs and limits for probes and substrates. For instance, the cantilever shape and corresponding shadow effect of the tips or substrate transparency may be of uttermost concern for one type of apparatus, while another can be completely indifferent to it due to radically different geometries and optics. Producing effective Raman-enhancing tips has been an evolving matter of scientific investigation for the past two decades,[12] and nowadays many approaches are available, but it is usually not possible to compare measurements among setups and

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