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TIP-ENHANCED RAMAN SPECTROSCOPY FOR NANOSCALE CHARACTERIZATION OF MATERIALS

ABSTRACT

Tip Enhanced Raman Spectroscopy (TERS) is a super-resolution analytical imaging technique that combines Raman spectroscopy and scanning probe microscopy. TERS has been used as a chemical characterization tool in a wide range of applications including materials science, chemical engineering and biology. This review explains TERS, while focusing on its various applications.

1. INTRODUCTION- CONCEPT AND PRINCIPLES

Tip Enhanced Raman Spectroscopy (TERS) has been a powerful microscopy technique for nanoscale characterization with growing applications ever since its inception in 2000 (1). The single nanoparticle at the probe or the tip generates a highly intense, evanescent field at the apex that interacts with the sample, as shown in Figure 1. The conventional Raman spectroscopy faces two major obstacles- low sensitivity and limited spatial resolution. The low sensitivity can be overcome by using surface-enhanced Raman scattering (SERS), where a strong electromagnetic field is generated on irradiating noble metal nanoparticles with a wavelength of light matching the plasmon resonance of the TERS tip. The limited resolution can be overcome by TERS that integrates the specificity of Raman spectroscopy with the nanoscale resolution of an atomic force microscope (AFM) by increasing the incident electromagnetic field by several orders of magnitude using the plasmonic nanostructures. A single plasmonic probe tip serves as both a Raman signal enhancing unit and a topography scanner (2).

TERS gives detailed information on the chemical composition including the molecular structure or conformation, defects, purity, etc. in a sample. A TERS system uses a metallic tip (gold or silver) that greatly enhances the Raman sensitivity (by a factor of 10^3-10^7) and reduces the probed volume of the test specimen to the nanoregion right below the tip (3).

2. INSTRUMENTATION

The AFM/Raman platform combines AFM with a confocal Raman spectrometer through an opto-mechanical coupling, which brings the excitation laser to the tip, while the spectrometer analyzes the Raman signal, thus producing an image with nanometer scale chemical contrast. There are two different configurations for this coupling- in transmission and reflection modes, with their own advantages and drawbacks. The configurations mainly differ by the irradiation patterns of the TERS tip (4,5). In bottom-illumination configuration, the laser beam is focused from the bottom through a transparent substrate (glass or mica) with a high numerical aperture (NA) objective (NA≥1.4), giving a high signal-to-noise ratio. In side illumination, the laser is incident on the sample at an angle of 45–70°, from the TERS tip. Top illumination enables asymmetric focusing that is tighter than that of side illumination with the help of a microscope objective (NA=0.7) or a parabolic mirror (NA=1).

The integrated platform can provide physical sample information at the nanometer scale, including topography, hardness, adhesion, friction, surface potential, electrical and thermal conductivity, temperature and piezo response, electrochemistry, along with the chemical information obtained from Raman spectroscopy and photoluminescence (6).

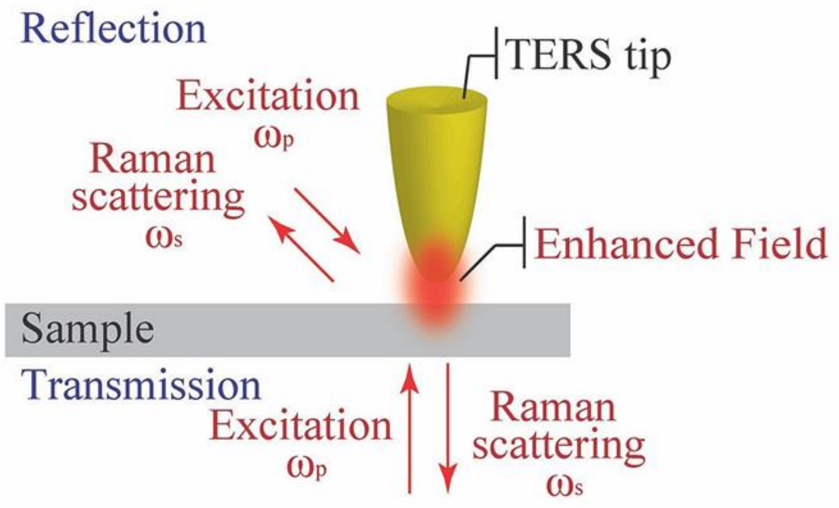

Figure 1

TERS configurations in reflection and transmission modes (Source: Horiba)

Figure 2

AFM/Raman platform (Source: Horiba)

3. APPLICATIONS

TERS has been explored for a plethora of diverse applications ranging from material science to complex molecular biology (7,8). The following are some of the most interesting and recent applications of TERS (7,9,10):

a. **Microbes:** The structural composition of disease causing pathogens such as bacteria and viruses can be probed with TERS, which can facilitate the investigation of host-pathogen interactions, formation of biofilms and bacterial pathogenesis.

b. **Biomolecules:** Complex biological systems such as those with lipid membranes can be analyzed with TERS to provide a label-free measurement of molecular distribution on the cell membrane at the nanoscale and to gain insights into the molecular dynamics. Similarly, nucleic acids can be tested to identify or confirm their structure.

c. **Proteins:** The high sensitivity and spatial resolution of TERS can be used to investigate protein structures. It can assign marker bands for proteins and track their distribution in complex biological specimens.

d. **Catalysis:** TERS can be used for monitoring chemical reactions as well as molecular dynamics occurring at catalytic sites with nanoscale resolution. Recent studies have paved the way for the use of TERS for investigating heterogeneous catalytic reactions on solid-liquid and solid-gas interfaces.

e. **Polymer blends**: The surface of the polymer blends can be studied using TERS to reveal sub-surface information and information on the interfaces between the polymer blend components with a nanoscale resolution.

f. **Semiconductors:** TERS can play a crucial role in the chemical characterization of semiconductors such as silicon. The TERS tip induces a depolarization in the near-field, thus allowing separation of the distant-field signal contribution (polarized) from the near-field signal (depolarized).

g. **Other materials:** One-dimensional materials such as carbon nanotubes have been extensively investigated using TERS mapping to study the structural details including the fraction of crystalline and amorphous regions. TERS has also been employed to study other 1-D materials like CdSe and GaN nanowires. Similarly, 2-D materials have also been tested using TERS, a prominent example among them being graphene. The presence of defects, edges, and contaminated areas within graphene can be identified with sub-diffraction-limited resolution of TERS, which otherwise cannot be resolved using confocal Raman spectroscopy.

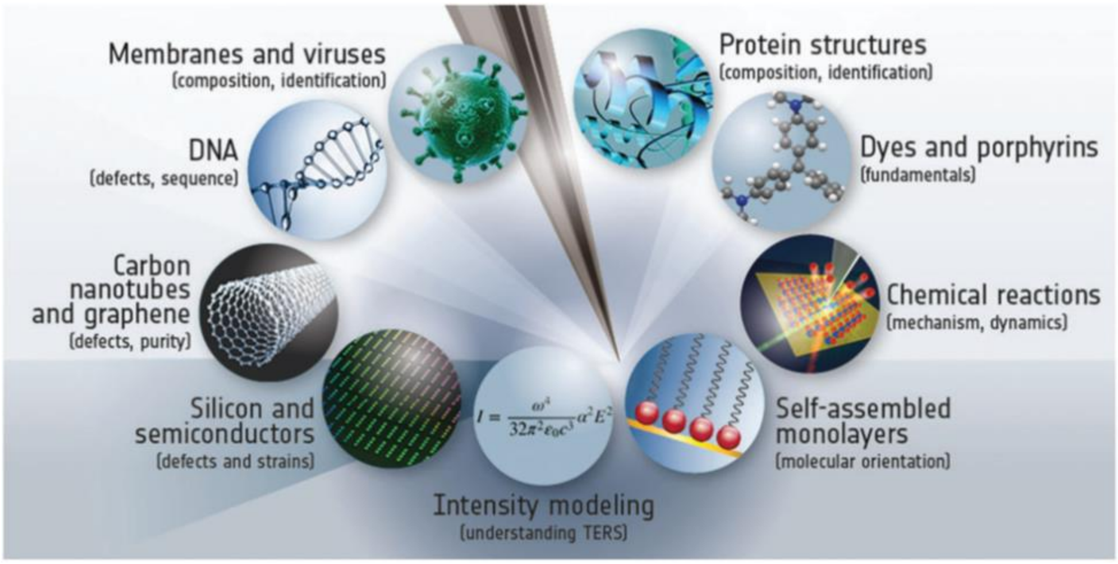

Figure 3

Various applications of TERS [Reproduced with permission from ref. (2) © 2017 RSC publisher]

SUMMARY

In the past two decades, TERS has emerged as an effective label-free nondestructive tool for nanoscale chemical and structural characterization of material surfaces. It brings together the conventional Raman spectrometer with a scanning probe microscope, such as AFM on a single platform. TERS is an ambient technique and does not require high vacuum or cryogenic conditions for its operation and can be been applied in air and liquid environments. The high sensitivity and nanoscale spatial resolution have made TERS an immensely sought-after technique for a myriad of applications. TERS has been extensively employed for the investigation of carbon nanotubes, graphene, semiconductors as well as various biological species such as proteins, lipids, nucleic acids, etc. Recent developments focus on the in situ use of TERS to monitor the chemical reactions, and derive information on the mechanisms and dynamics of the reactions.

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REFERENCES

1. Zhang Z, Sheng S, Wang R, Sun M. Tip-enhanced Raman spectroscopy. Anal Chem. 2016;88(19):9328–46. Available from: http://dx.doi.org/10.1021/acs.analchem.6b02093
2. Deckert-Gaudig T, Taguchi A, Kawata S, Deckert V. Tip-enhanced Raman spectroscopy-from early developments to recent advances. Chem Soc Rev. 2017;46(13):4077–110. Available from: http://dx.doi.org/10.1039/C7CS00209B
3. Richard-Lacroix M, Zhang Y, Dong Z, Deckert V. Mastering high resolution tip-enhanced Raman spectroscopy: towards a shift of perception. Chem Soc Rev. 2017;46(13):3922–44. Available from: http://dx.doi.org/10.1039/c7cs00203c

4. Bonhommeau S, Lecomte S. Tip-enhanced Raman spectroscopy: a tool for nanoscale chemical and structural characterization of biomolecules. ChemPhysChem. 2018;19(1):8–18. Available from: http://dx.doi.org/ 10.1002/cphc.201701067
5. Yeo BS, Stadler J, Schmid T, Zenobi R, Zhang W. Tip-enhanced Raman spectroscopy - its status, challenges and future directions. Chem Phys Lett. 2009;472(1–3):1–13. Available from: http://dx.doi.org/10.1016/j.cplett.2009.02.023
6. Wang X, Huang SC, Huang TX, Su HS, Zhong JH, Zeng ZC, et al. Tip-enhanced Raman spectroscopy for surfaces and interfaces. Chem Soc Rev. 2017;46(13):4020–41. Available from: http://dx.doi.org/10.1039/C7CS00206H
7. Kumar N, Mignuzzi S, Su W, Roy D. Tip-enhanced Raman spectroscopy: principles and applications. EPJ Tech Instrum. 2015;2(1). Available from: http://dx.doi.org/10.1140/epjti/s40485-015-0019-5
8. Shao F, Zenobi R. Tip-enhanced Raman spectroscopy: principles, practice, and applications to nanospectroscopic imaging of 2D materials. Anal Bioanal Chem. 2019;411(1):37–61. Available from: http://dx.doi.org/10.1007/s00216-018-1392-0
9. Verma P. Tip-enhanced Raman spectroscopy: technique and recent advances. Chem Rev. 2017;117(9):6447–66. Available from: http://dx.doi.org/10.1021/acs.chemrev.6b00821
10. Voylov DN, Bocharova V, Lavrik N V., Vlassiouk I, Polizos G, Volodin A, et al. Noncontact tip-enhanced Raman spectroscopy for nanomaterials and biomedical applications. Nanoscale Adv. 2019;1(9):3392–9. Available from: http://dx.doi.org/ 10.1039/c9na00322c