Tip-Enhanced Raman Spectroscopy

Takayuki Umakoshi and Prabhat Verma

Abstract Visible light can interact efficiently with the vibronic and electronic systems of a sample and fetch rich information about the intrinsic features, such as the chemical, physical and biological properties of the sample. Optical techniques have therefore been convenient tools for a long time to analyze and image various materials. However, the spatial resolution in optical microscopy is restricted by the diffraction limit of light, making it impossible to study samples much smaller than the wavelength of the probing light. This restriction can be overcome if a conventional optical microscopy, such as Raman microscopy, is combined with near-field techniques. Tip-enhanced Raman spectroscopy (TERS) is such a technique. It utilizes a sharp metallic nano-tip to intensely enhance and strongly confine light within a tiny volume near the tip-apex and enables characterization of samples at the nanoscale. In this Chapter, we discuss the details of this technique and explain how light can be tightly confined into a nanometric volume for true nanoscale exploration of samples. TERS is still a young technique and has been going through a rapid development in the past two decades, which has not only made it more reliable and sturdier over the period, but has also brought this apparently complicated technique out from the laboratories of the veterans to the market for researchers who are experts in different fields. This has obviously happened with improved adaptability, flexibility and robustness with possibilities of a wide range of applications. We will discuss some interesting applications and related instrumentations for TERS.

Keywords Tip-enhanced raman scattering · Plasmonics · Near-field optics · Near-field scanning optical microscopy · Raman spectroscopy

T. Umakoshi · P. Verma (✉)
Department of Applied Physics, Osaka University, 2-1 Yamadaoka, Suita 565-0871, Osaka, Japan
e-mail: verma@ap.eng.osaka-u.ac.jp

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1 Introduction

Tip-enhanced Raman spectroscopy (TERS) is an interesting combination of Raman spectroscopy and plasmonic near-field optical technique that takes Raman spectroscopy and microscopy to the next level beyond its conventional limits to establish it as an inevitable optical tool to investigate various materials at the nanoscale [1–3]. Raman spectroscopy has already been well-recognized as a powerful tool to investigate molecular vibrations by spectroscopically analyzing Raman scattering from molecules. Due to the inherent spectral and chemical specificities, it tells us which chemical bonds the molecules have and how the bonds vibrate [4]. As it is also an invasive and non-contact method, it has been widely used in a variety of research fields from material science to biological science as a versatile tool [5–7]. It has contributed in analyzing the physical properties of novel materials and in revealing molecular activities of biological systems.

However, just like most of the classical optical techniques, Raman spectroscopy also suffers from the issue of limited spatial resolution due to the wave nature of light. This is because an incident light cannot be focused into a size smaller than approximately half of its wavelength due to the diffraction limit of light. For the visible light that is often used in Raman spectroscopy, the spatial resolution is limited to a few hundred nanometers. Improvement of the spatial resolution in Raman spectroscopy has been in high demand, especially since nanotechnology and nanoscience have become of great importance and interests in various scientific fields.

TERS is one of the distinctive solutions to meet this demand. It is the only technique that measures scattered light from a nanometric volume of the sample and thus enables one to obtain Raman image of samples with a true nanoscale spatial resolution (typically 10–20 nm). Although there are several super-resolution optical microscopy techniques such as STED, PALM or STORM [8, 9], these techniques do not include a direct optical observation at nanoscale. TERS is the only technique where light is spatially confined to a true nanometric volume, which is done through a plasmonic approach known as the near-field scanning optical microscopy (NSOM). In NSOM, an aperture probe was initially used to generate near-field light at the tiny aperture, which is so-called aperture-type NSOM [10]. Later in 1994, Kawata et al. reported a new type of NSOM that uses an apertureless metallic tip instead of an aperture tip, which is known as scattering-type (or apertureless-type) NSOM [11]. In the scattering-type NSOM, a metallic tip that works as a plasmonic antenna is used to generate near-field light that is highly localized at the end of the tip apex [12]. Because the spatial extent of the near-field light is almost comparable to the size of nanometrically small tip apex, the tip apex practically behaves as a nano-light-source that invokes Raman scattering from a tiny volume of the sample directly beneath the tip apex. One can therefore detect Raman scattering signal from a nanoscale area of the sample with the near-field light. Therefore, by detecting Raman signal with the near-field light at the tip apex, nano-Raman spectroscopic analysis is possible. Actually, this is the basic idea of TERS. It was reported for the first time in 2000 by three different groups at almost the same time [13–15]. Since then, TERS has