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REVIEW ARTICLE

High-vacuum tip enhanced Raman spectroscopy

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Tip-enhanced Raman spectroscopy (TERS) is high-sensitivity and high spatial-resolution optical analytical technique with nanoscale resolution beyond the diffraction limit. It is also one of the most recent advances in nanoscale chemical analysis. This review provides an overview of the state-of-art inTERS, in-depth information about the different available types of instruments including their (dis)advantages and capabilities. Finally, an overview about recent development in High-Vacuum TERS is given and some challenges are raised.

Keywords surface enhanced Raman scattering (SERS), tip enhanced Raman scattering (TERS), high vacuum

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Contents

1 Introduction

Raman scattering employs the Raman effect for materials analysis [1]. The spectrum of the Raman-scattered light depends on the molecular constituents present and their state, allowing the spectrum to be used for material identification and analysis. Raman spectroscopy is used to analyze a wide range of materials, including gases, liquids, and solids [2–6]. Highly complex materials such as biological organisms and human tissue can also be analyzed by Raman spectroscopy. However, with scattering cross-sections of 10^{-31}–10^{-26}cm^2 per molecule [7], the Raman response is weak, generally requiring probing a large molecular ensemble or bulk solids. This is the biggest disadvantage of Raman and is also the reason why Raman was not widely used for a long time, until the Surface Enhanced Raman Scattering (SERS) was discovered by Fleishman in 1974 and Van Duyne in 1977 [8].

SERS is a surface-sensitive technique that enhances Raman scattering of molecules adsorbed on rough metal surfaces. The enhancement factor can be as large as 10^{10} to 10^{15}, which means the technique may detect single molecules [9, 10].While the general sensitivity of SERS is not a problem, the main obstacle in using SERS for the investigation of interfaces is the inhomogeneity of the SERS substrate across the sample. Generally, substrates based on metals such as Ag, Au and Cu, either with roughened surfaces or in the form of nanoparticles, are required to realize a substantial SERS effect, and this has severely limited the breadth of practical applications of SERS [11, 12]. Furthermore, these physical parameters also depend critically on the substrate preparation.

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Therefore, a spatially resolved quantitative analysis of interfaces using SERS is impossible.

A number of approaches have extended this technique to non-traditional substrates, most notably Tip Enhanced Raman Spectroscopy (TERS) [13–15]. A combination of scanning probe microscopy (SPM) techniques and Ramanspectroscopy, TERS has been successfully applied to many researches in nano-sciences because of its unique possibility to provide chemical and structural information on a sample surface with high lateral resolution combined with high sensitivity. A very powerful variant of SERS, TERS operates on all molecule/substrate configurations, where the substrate may be rough or smooth, or even single crystalline, and the material of substrate can be metal, semiconductor, or an isolator and where the adsorbate may or may not be in optical resonance with the exciting laser line.

In this review, we begin with a short overview of SERS, and then we introduce TERS system in detail, including the fundamental theory, types, components and applications. The advantages and disadvantages of every kind of TERS are pointed out. Finally, we present some new HV-TERS experimental results.

2 Surface enhanced Raman scattering (SERS)

SERS from pyridine adsorbed on electrochemically roughened silver was observed by Martin Fleischman and coworkers in 1974 [16]. They justified the large signal that they saw simply as a matter of number of molecules that were scattering on the surface and did not recognize that there was a major enhancement effect. The progress was not made until 1977 when Van Duyne's group and Albrecht's group noted that the concentration of scattering species could not account for the enhanced signal and each proposed a mechanism for the observed enhancement [8, 17].

Today's consensus is that SERS involves two enhancement mechanisms, chemical and electromagnetic (EM) enhancements, often occurring at quite different strengths. The EM theory posits the excitation of localized surface plasmons (LSP) [18, 19], while the chemical theory proposes the formation of charge-transfer complexes. The chemical theory only applies for species which have formed a chemical bond with the surface [7, 20, 21], so it cannot explain the observed signal enhancement in all cases, whereas EM enhancement is thought to operate on all adsorbates equally, with the exception of some polarization and molecular orientation effects that influence the Raman intensity to some extent.

Together, chemical and EM enhancement may lead to an overall average enhancement of approximately 10^6, as already reported by Van Duyne for pyridine on Ag electrodes. Surprisingly, huge variations of surface enhancement along a rough surface or over colloidal systems were discovered in 1990s. With such structures, so-called "hot spots" occur which can provide extremely high local enhancements [22]. Theory and experiments indicate that the "hot spots" can make up most of the enhanced Raman signal, in contrast to the vast majority of sites that do not contribute significantly. Theory and experiments have shown that if a dimer of two suitable nanoparticles is illuminated, a strong enhancement of the EM field can occur in the narrow space between the two particles. With the "hot spots" of two nanoparticles, single-molecule SERS could be obtained from experiments, which could succeed only if a single molecule, located in the hot spot zone, were selectively exposed to a significant enhancement, whereas nearby molecules experienced only a minor enhancement.

Alongside the numerous benefits of SERS, some disadvantages still exist in conventional SERS [15, 23–25]. First, SERS is largely limited to substrates made of noble metals such as gold, silver, and copper. Second, it is almost impossible to achieve a spatially resolved quantitative analysis of interfaces using SERS. Finally, the most severe restriction in the application of SERS to a wide variety of problems in ultrahigh vacuum single-crystal surface science, electrochemistry, heterogeneous catalysis, micro-electronics, and tribology is the requirement that the surface must be roughened or nanostructured metal surface. These disadvantages suggest lasting challenges to develop SERS into a routine analytic spectroscopic tool.

To overcome the limitations of SERS, several groups have tried to extend the technique to non-traditional substrates. In 1985, Wessel theoretically proposed a scheme to ensure a constant field enhancement using just one single metal nanoparticle for the investigation of a surface [26]. For the first time, the potential of quantitative SERS surface analysis was introduced. In this design, the rough metal film was replaced by a sharp metal tip which would act as an exclusive active site; it also represents the limit for any SERS experiment: At least one particle is required. The metal tip should be scanned over the sample surface using scanning probe microscopy (SPM) techniques. The later experimental verification of this is now called Tip-enhanced Raman spectroscopy (TERS) and only 15 years later the experimental verification was successfully established [27]. As a slightly modified version, TERS technique can overcome almost all the limitations of conventional SERS mentioned above.

3 Tip enhanced Raman spectroscopy (TERS)

Tip-enhanced Raman spectroscopy (TERS) is high-sensitivity and high spatial-resolution optical analytical technique with nanoscale resolution beyond the diffraction limit of light. It is also one of the most recent advances in nanoscale chemical analysis. The technique has great potential for many different fields [27–36]. The main advantage is that TERS requires no special sample preparation. TERS can achieve excellent spatial resolution, which in principle is only limited by the size and shape of the scanning probe microscopy (SPM) probe tip apex. The setup of TERS also ensures that there is no variation of enhancement across the sample and automatically allows the correlation of surface topography with chemical information. In addition to the spectral information, SPM simultaneously provide topographical data, thereby this technique can be used on research and application in surface science, biology, semiconductor industry, and nanotechnology.

3.1 Theoretical background

The combination of SPM and Raman microscopy, tip enhanced Raman spectroscopy (TERS) technique is based on the same mechanism as the surface-enhanced Raman spectroscopy (SERS) effect; local electric fields are strongly enhanced in the vicinity of a metallic surface due to the coupling of its plasmon resonances with the excitation light. In TERS this metallic surface takes the form of an ultra-sharp metal tip to create a "hot site" to enhance the Raman fluorescence, or other optical signals, which simultaneously acts as a tip of a SPM device. In near-field region of tip, the optical processes are promoted with an equivalent increased excitation rate, because TERS permits the analysis of the microscopic distribution of a sample by recording the Raman intensity during the scan of the tip across the substrate surface.

Figure 1 illustrates this scheme. Since the distance between the tip apex and the sample is very short (about 1–2 nm), local surface plasmon resonance will happen and hugely enhance the electric field of this small area to be a "hot site". The tip acts as an antenna to increase the radiated intensity which similarly holds for light scattering and fluorescence. Both effects, the enhanced excitation and scattering bring about a very large total enhancement, but only for substances in the close vicinity of the tip apex. In a word, the enhanced optical signal mostly comes from the range of tip apex, thus realizes the high spatial-resolution (5–20 nm) analysis. The real sensitive and space resolution of different TERS system will be decided by the curvature of tip, size of focus spot, material, etc.

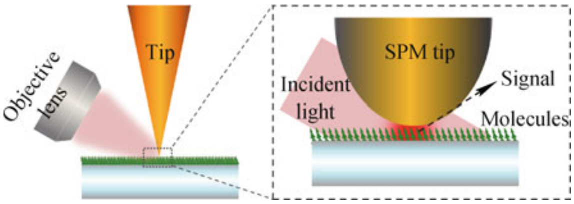

Fig. 1 The schematic of TERS.

The enhancement factor g of TERS can be given as

$$g = \frac{I_\mathrm{n}}{I_\mathrm{f}} \times \frac{V_\mathrm{f}}{V_\mathrm{n}} \tag{1}$$

where I_n and I_f are the Raman intensity from near and far fields, respectively, and V_f and V_n are the volumes probed by the far and near fields, which can be written as

$$V_\mathrm{f} = \pi R^2_\mathrm{focus} h_\mathrm{f} V_\mathrm{n} = \pi R^2_\mathrm{TERS} h_\mathrm{n} \tag{2}$$

where R_focus and R_TERS are the radius of the focus and near field, and h_f and h_n are the effective depth of the focus and near field. The R_TERS is approximately equal to a half of the radius of SPM tip. For a thin layer of molecules, thus, $h_\mathrm{f} \approx h_\mathrm{n}$. The TERS enhancement is written as

$$g = \frac{I_\mathrm{n}}{I_\mathrm{f}} \times \frac{R^2_\mathrm{focus}}{R^2_\mathrm{tip}} \cos\theta \tag{3}$$

where θ is the angle of incidence of the beam. A more detailed description of methods for calculating the enhancement factor can be found in Ref. [37].

3.2 TERS installation

The scheme of TERS is straightforward. The crucial part is the combination of a scanning probe device with a Raman spectrograph. Usually, three kinds of SPM technique can be used in TERS: Scanning Tunneling Microscope (STM), Atomic Force Microscope (AFM) and Scanning Near field Optical Microscope (SNOM). As the principle of AFM and SNOM are very similar, we only talk about the TERS system based on STM and AFM here. Both of them have their advantages and disadvantages. AFM can scan a big area of any kind of substrate very fast, but it is also more complicate and expensive. Most importantly, the material of standard AFM tip is silicon, and one needs to cover it with a thin silver layer or gold layer first upon using for TERS, which makes it somewhat inaccurate. Compared with AFM, STM works only for conductive substrate, but the tip is easier to get and it has the incomparable spatial resolution.

Another necessity to set up a TERS is focused laser light. A part of the light energy has to be localized by a TERS active SPM tip which is sufficiently close to the sample to excite the sample molecules. The emitted light is then collected and analyzed. Based on this consideration, three different major types, bottom-, side- and top-illumination depicted in Fig. 2 have been used so far.

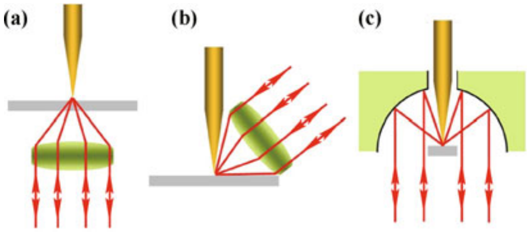

Fig. 2 Different optical concepts for the illumination of the tip, **(a)** bottom illumination, **(b)** side illumination with an objective and **(c)** top illumination with a parabolic mirror.

In the case of bottom illumination, light is focused from below through a transparent support onto the tip and the sample. The tip rests on top of the sample and interacts either directly with the laser focus or with its evanescent field. Often glass substrates are used as a sample support, which allows for the use of refractive index matching oil between the substrate and a high numerical aperture objective. The laser wavelength and NA determine the size of the focus spot. High NA allows focusing the laser more tightly around the tip, which reduces the far-field background contribution. To gather a maximum amount of Raman signal from the sample, the same objective is usually used to collect signals emitted into the glass slide with a high solid angle. The requirement of transparent substrate for bottom illumination limits the ability of TERS and also makes strong electric field impossible. Due to these reasons, bottom-illumination instruments are ideally suited in investigating biological samples.

The side illumination TERS overcome the limitation to transparent samples of the bottom illumination approach. Because of the strong coupling of metallic tip and metallic substrate surface in this kind of setup, we can observe a strong enhancement by optimizing the polarization of exciting laser. But a long working distance is necessary to reach tip and sample, thus the NA of the objectives cannot be very large. Then the collection potential of these systems is limited by the small collection angle of the low NA lenses.

These two disadvantages do not exist in the top illumination setup. As shown in Fig. 2(c), top illumination has a parabolic mirror around the tip, which makes the illumination directly perpendicular to the sample surface. It combines the advantages of side and bottom illumination, a large NA and a tighter focus can be achieved. But the disadvantage is also obvious: The sample could not be too large; it is very complex to build up and difficult to manipulate. Restricted by these considerations it cannot be widely used. Now most TERS systems based on AFM use bottom illumination, while most TERS systems based on STM use side illumination.

In addition, considering the working environment, TERS system can be divided into normal TERS and high-vacuum TERS (HV-TERS), even ultra-high vacuum TERS (UHV-TERS). As a clean dry environment for molecule, the high vacuum condition makes the signal to noise ratio greatly improved. However, it is still challenging work. Until now only three research groups have achieved the HV-TERS: Pettinger's Group, Van Duyne's Group and H. X. Xu's Group. More details will be shown later.

3.3 Tip preparation

The tip is a very important component of TERS. A pure metal or metal coated tip is necessary to confine the laser energy into the EM field at its apex, excite the molecule and transform near-field information into a propagating far-field radiation by scattering. The properties of the tip, like material, lifetime, size and shape, determine the kinds of suitable sample and the quality of the final spectrum. There are several techniques which generate TERS probes with acceptable optical quality. Nevertheless, the reproducibility and yield of good tips remain a challenge. The two techniques most frequently used for TERS probe fabrication are electrochemical etching methods of solid metal probes and the metal evaporation deposition on AFM Si tips [38–41].

In order to enhance the Raman signal, metals like gold, silver or copper are most widely used. A pure metal tip is needed with use of STM. Take gold tips for example, the electrochemical etching procedures are well established and involve mainly a voltage between a gold wire and a metal ring electrode, both dipped in concentrated hydrochloric acid solution. During the reaction, the wire becomes thinner until a sharp tip is fabricated. While for AFM feedback, we should employ a sharp standard AFM tip (Si) as a template and then make it vapor-coated with the desired metal, usually silver or gold, for a high electric field enhancement.

3.4 Samples

In principle, TERS can be used to investigate any

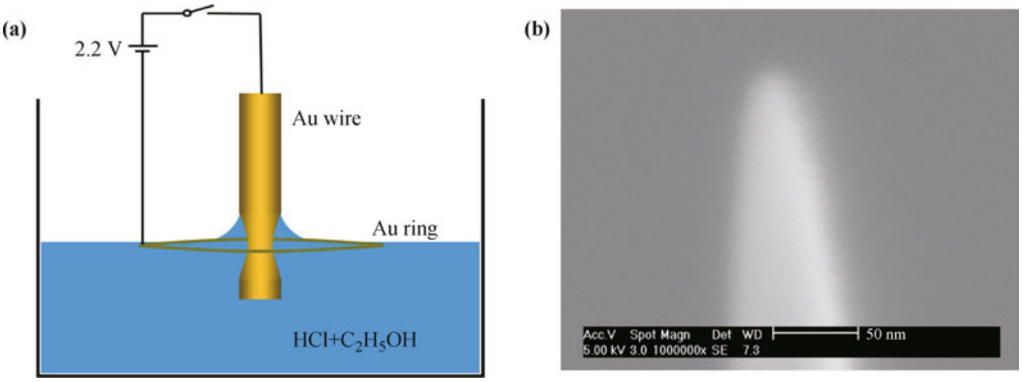

Fig. 3 **(a)** The schematic diagram of the setup for preparing the gold tip. **(b)** The SEM image of the apex of Au tip.

Raman-active materials, including organic samples and inorganic samples, such as carbon nanotubes, organic electronic polymers, phase separated polymers and biological materials. Considering the length of this paper we only list some of them here. Dye molecules have been studied from the beginning as important samples for system characterization. Molecular monolayers, thiols in air and in liquid, polymer blends, azobenzene, alginate films, biotin-streptavidin, DNA or single DNA bases, amino acids, cytochrome C, collagen, different virus strains, bacteria, supported lipid layers, cell walls, organic semiconductors and solar cell blends have been investigated by TERS. Inorganic systems that have been studied lately include silicon and strained silicon, amorphous carbon, graphite, graphene, carbon nano-tubes, GaN and GaAs species, NiO surfaces, V_2O_5 nanoribbons, TiO_2 nano-particles and Ge/Si quantum dots.

4 Progress on HV-TERS

As we know, the widely used TERS has been greatly improved in the last decade. In order to obtain better spectrum, people are trying to create a clean, dry environment for the sample, i.e., high vacuum environment. Until now, only three groups have built HV-TERS successfully. In 2007, Pettinger's Group first extended TERS to an ultrahigh vacuum system [14]. Recently, using this UHV-TERS system, they found that C_{60} molecules assume a hexagonal structure on the smooth Au(111) surface [see Fig. 4(b)].

Later, the Van Duyne's Group made the first reflective UHV-TERS system with external laser focusing and Raman collection optics [42]. It is important that the low temperature device is introduced into the UHV-TERS

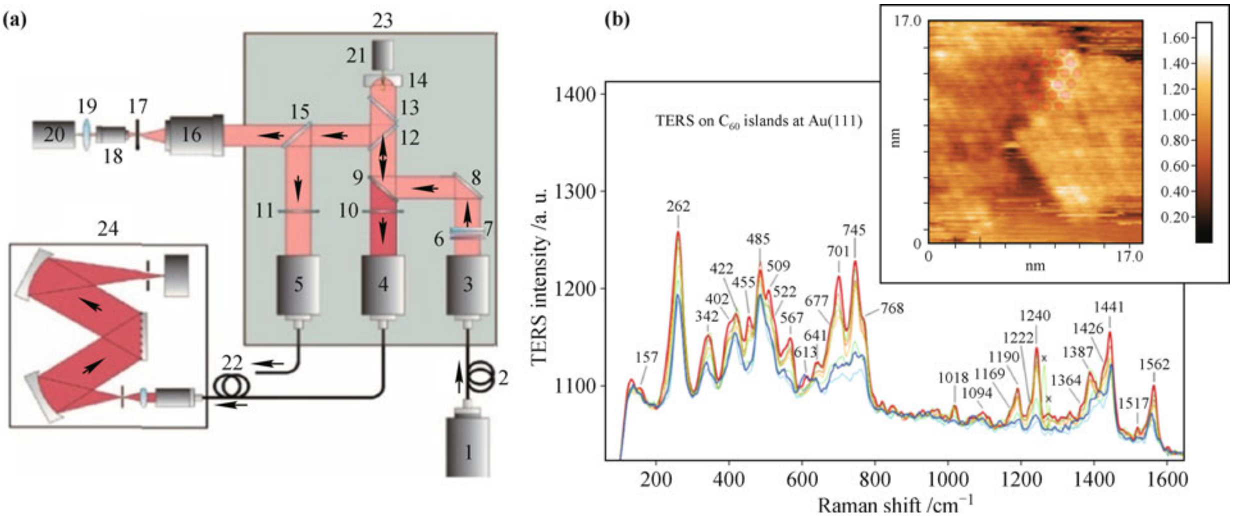

Fig. 4 **(a)** The schematic of UHV-TERS from Pettinger's Group. 1: 633 laser; 2: Single mode fiber; 3–5: Collimator objectives; 6: Filter; 7: Polarization converter; 8: Plane mirror; 9–11: Dichroic mirrors; 12, 15: Beam splitters; 13: Optical flat; 14: Parabolic mirror with tip and sample; 16: Camera objective; 17: Pinhole; 18: Microscope objective; 19: Lens; 20: CCD; 21: STM scanner; 22: Multimode fiber with vacuum feedthrough; 23: UHV chamber; 24: Raman spectrograph. **(b)** UHV-TERS spectra and STM image of a C_{60} island on a Au(111) surface [14].

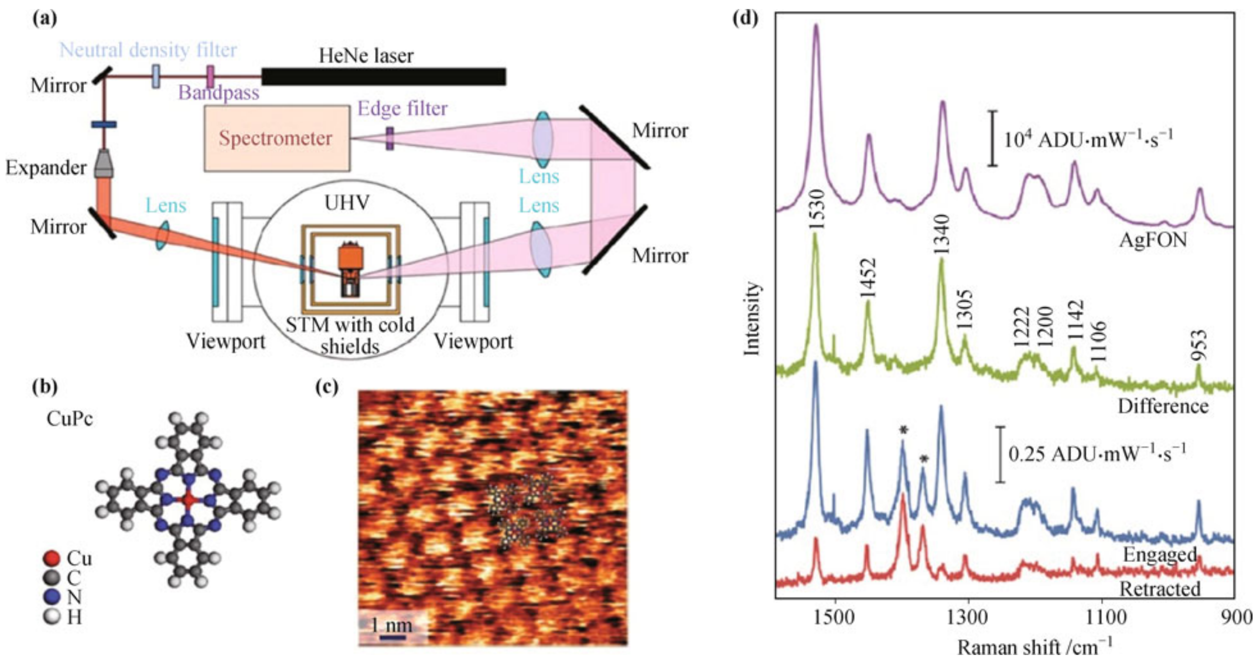

Fig. 5 (**a**) The schematic of UHV-TERS from Van Duyne's Group. (**b**) Chemical structure, (**c**) STM image and (**d**) UHV-TERS spectra of CuPc [42].

system. As shown in Fig. 5, the corresponding STM image and Raman spectra of the ordered copper phthalocyanine (CuPc) adsorbed on Ag(111) was obtained at the same time.

Third, H. X. Xu's Group, from Institute of Physics, Chinese Academy of Science, is the first to make an objective built-in side-illumination HV-TERS. Figure 6 presented some new HV-TERS experimental results in Xu's Group, including ultrasensitive Stokes and anti-Stokes Raman scattering [43], plasmon-assisted chemical reaction [44–46] and non-linear effects [47, 48] in HV-TERS. They used home-built HV-TERS to investigate the plasmon-driven in-situ chemical reaction of 4-nitrobenzenethiol dimerizing to dimercaptoazobenzene. The chemical reactions can be controlled by the plasmon intensity, which in turn can be controlled by the incident laser intensity, tunneling current and bias voltage. And the temperature of such a chemical reaction can also be obtained by the clearly observed Stokes and Anti-Stokes HV-TERS peaks. The findings offer a new way to design a highly efficient HV-TERS system and apply it to chemical catalysis and synthesis of molecules, and significantly extend the studies of chemical reactions. In addition, the strong EM field enhancements near the apex of the tip can also induce non-linear optical processes, such as second-harmonic generation (SHG), and

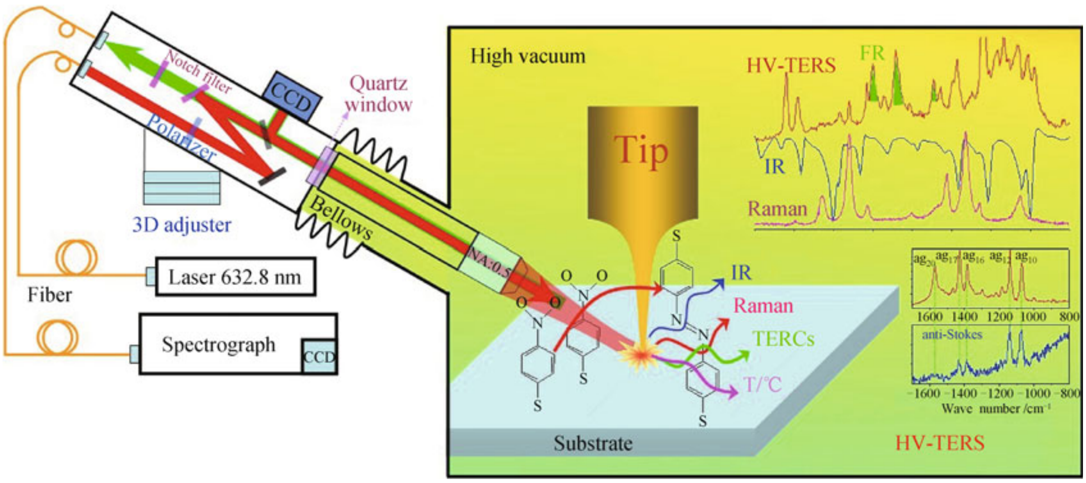

Fig. 6 The schematic of HV-TERS from Xu's Group, and the main works on ultrasensitive Stokes and anti-Stokes Raman spectra, non-linear effects and plasmon-assisted chemical reaction in HV-TERS [47].

hyper-Raman. Besides, the IR-inactive mode (usually observed in hyper-Raman) can be observed experimentally due to the electric field gradient effect in TERS.

Some challenges still remain in TERS technique. The first one is the low reproducibility of the tip. The lifetime of silver based TERS tips is in the range of several hours to a day after production. The lifetime of gold tip is longer while the enhancement is much lower. For a wide use of TERS, stable, reliable and mass producible tips are required. The second challenge comes from the temperature required in TERS. In TERS experiment, the laser beam is focused onto a very small area, thus a very confined, high intensity EM field can be created and the temperature rise can be expected. Measurements of the anti-Stokes/Stokes ratio may prove to be difficult if the enhancement is not equal in the Stokes and anti-Stokes regions, which leads to a poor estimate of the heating effect. What's more, numerical simulation for TERS including the classical EM field and the quantum process has not been realized.

5 Conclusion

TERS overcomes most of the drawbacks of SERS while keeping its advantages, such as the high sensitivity and high spatial resolution, much beyond the diffraction limit. TERS was introduced here, including the key components, classifications, applications, and also the advantages and disadvantages of every kind of TERS setup. In addition, some recent progress on HV-TERS from three groups were presented. In one word, TERS permit the correlation of topographic and chemical data, hold great promise for ultrasensitive detection and are expected to find a range of applications in fields such as surface science, material science, and biology.

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