1. Introduction
Optical imaging has been an inseparable part of human life for centuries, where either reflecting surfaces were used as mirrors or transparent materials with curved surfaces were used as lenses to construct optical images. This technique improved over the time as scientist developed various kinds of microscopes and telescopes that enabled us to see an object with very small size, such as a bacteria, or an object that is too far, such as a star or a terrestrial planet. Even with the fast and remarkable progress of optical imaging techniques, observing a sample at a nanoscale resolution with optical microscope always remained a dream of scientists, because wave nature of light imposes an intrinsic limit on optical imaging. It turns out that for lenses made of glass, the resolution in optical imaging is limited to a size comparable to half of the wavelength. That means, when we talk about optical imaging with visible light, it is impossible to resolve two objects that are separated by a distance less than about 300 nm. This limit is known as the diffraction limit, and it puts a restriction on the spatial resolution in optical imaging.

If it is not possible to overcome this diffraction limit, then the alternative is to reduce the wavelength, so that the diffraction limit reduces to nanometer scale, and hence imaging at nanoscale resolution becomes possible. One of the ways to do this is by constructing images through electrons, because electrons, if considered as waves, have very small wavelengths. This idea was utilized in the development of several nano-imaging techniques such as TEM [1] or SEM [2]. Even after the development of these wonderful imaging techniques, optical imaging did not lose its charm and importance, because the visible light carries an energy that is comparable to the band gap energies of most of the naturally existing materials. This allows light to actively interact with the sample at electronic or molecular level and then carry the information related to their intrinsic properties to the image. For example, an optical image of a colored object will appear in true colors, while a TEM or SEM image of the same object will lose the information related to the color. Optical imaging turns out to be much more informative, in comparison with the images obtained from the other techniques. An ideal imaging system would be the one that can achieve high resolution and at the same time images the intrinsic properties of the object. In other words, what one needs is a probing wave that has energy (or frequency) similar to that of a visible light, but wavelength comparable to that of x-ray or electron-wave. Since the wavelength and the frequency of a wave are related through the speed of the wave, the above requirement can be achieved in visible light, if the speed of light is significantly reduced.

2. Confinement and enhancement of light
Light has two components, a propagating component and an evanescent component. The evanescent component is non-propagating, and hence it is nothing but slow light, with negligible speed in the ideal case. Optical nano-imaging should be possible if evanescent component of light is utilized in the imaging process. Since evanescent waves do not propagate, they exist only in the close proximity of a light source, which can either be a primary source, such as an oscillating dipole, or a secondary source, such as a scattering point in the form of a tiny aperture or a tiny particle. While it is practically difficult to bring a primary point...
source very close to an object that needs to be imaged, it is comparatively easy to create and control a secondary point source in the close proximity of an object.

Free charge carriers, which move collectively and freely on the surface of a metal, are known as the surface plasmons (SPs). These free changes create an electric field near the surface of the metal, which changes as the SPs move around the surface and apply force on the very charge that created it. These collectively moving SPs and the varying field near the surface make a complex combination influencing each other, known as the surface plasmon polaritons (SPPs). Since both the SPs and the associated fields are confined to the metal surface, the complex SPPs are actually evanescent fields. In other words, evanescent light naturally exists near the surface of a metal. One can think of utilizing this evanescent light for optical nano-imaging. However, this evanescent field is very weak for its practical utilization. It is necessary to drastically enhance this field before it can be used for optical imaging. One of the possible ways to enhance this field is by exciting the SPPs with propagating light. It turns out that momentum conservation prevents the excitation of SPPs by propagating light. However, if we consider a very small metallic nanoparticle with size much smaller than the wavelength of the light, then the conservation laws are relaxed due to confinement, and the localized SPPs of a metallic nanoparticle can be easily excited by propagating light. Therefore, if a metallic nanoparticle is illuminated with propagating light, it is possible to create a strongly enhanced evanescent light in the close proximity of the nanoparticle. This enhanced evanescent field would be confined close to the nanoparticle in all three dimensions, thus providing us with a nano-light-source that generates strong and confined evanescent light, an ideal probe for high-resolution optical imaging. In order to utilize this nano-light-source for optical imaging, it is required to scan the nanostructure over the sample, by means of a technique similar to AFM. Since the AFM probes are semiconductor nano-tips, we can use them as scanning metallic nano-probes after coating them with a thin metallic layer [3,4]. The left inset of Fig. 1 shows a SEM image of the tip apex of a silicon AFM cantilever coated with silver by vacuum evaporation process [5]. The size of the tip apex after silver deposition is about 30 nm. The silver grains deposited at the tip apex work as metallic nanostructure for the confinement of light. Theoretical as well as experimental results show that the confinement of light near such a metal-coated tip is as large as the size of the tip apex, and the light field enhancement for resonant excitation is as high as several orders of magnitude.

3. Tip-enhanced Raman spectroscopy
Raman spectroscopy is a powerful optical tool to study the basic physical, chemical or biological properties of a sample, because it deals with both the electronic and the vibrational energy states of the sample, extracting large amount of intrinsic information about the sample. Raman scattering is therefore frequently utilized in optical microscopy to construct Raman images of samples. However, Raman scattering is a weak optical process that requires long measurement time, particularly for nanomaterials that have small scattering volumes. The utilization of nano-light-source created at the apex of a nano-sized metallic tip as the excitation light source in Raman spectroscopy is therefore of tremendous advantage, both for the enhancement of the weak Raman signal and for
obtaining extremely high spatial resolution. This is done by the so-called tip-enhanced Raman spectroscopy (TERS), where a metallic nano-tip is added to the experimental set-up of conventional Raman spectroscopy [6–10]. Fig. 1 shows a schematic of a typical experimental set-up for TERS, which consists of an excitation laser, an inverted microscope equipped with a high-NA oil-immersion objective lens, an AFM head that controls and positions silver-coated nano-tip, a spectrometer and a CCD detector. As the tip apex comes close to the sample within the focal spot, as illustrated in the right inset of Fig. 1, a nano-light-source is created at the tip apex due to the collective oscillation of the localized SPPs. This process enhances Raman scattering by several orders of magnitude. By scanning the metallic tip over the sample, Raman image with extremely high resolution can be constructed.

Fig. 2 shows examples of TERS measurements for two different samples—nano-cluster of carbon-60 in Fig. 2 (a) and adenine nanocrystal in Fig. 2 (b) [9,10]. The lower curves for both samples correspond to the far-field measurements where the tip is far from the sample, while the upper curves correspond to the near-field measurements where the tip is in the close vicinity of the sample. The far-field Raman scattering is significantly weak due to the small volume of nano-sized samples. As soon as the tip comes close to the sample, a nano-light-source is created at the tip apex, which enhances Raman scattering from the sample right under the tip. As one can see from the upper curves in Figs. 2 (a) and (b), near-field Raman scattering is strongly enhanced for both samples [9,10].

While the far-field Raman scattering is excited from the sample volume within the diffraction-limited focal spot, the near-field Raman scattering is excited from a rather small volume of the sample that is immersed into the confined field at the tip apex, which is comparable to the size of the tip apex itself. A calculation taking the excitation volume into account reveals that the enhancement factors for both samples are of the order of several thousands. A simple visual comparison between the lower and the corresponding upper curves in Figs. 2 (a) and (b) enlightens the importance of TERS for the observation of Raman scattering from nano-sized samples.

4. Spatial resolution in TERS microscopy

Amongst many other nanomaterials, single-walled carbon nanotubes (SWNTs) provide an interesting sample for TERS measurements. Due to their ideal one-dimensional structure with remarkable chiral, mechanical, thermal and electronic properties, SWNTs have attracted great attention in both scientific and industrial communities. Since these unique structural and physical properties are reflected in their vibrational behavior, Raman spectroscopy plays an important role in studying and analyzing SWNTs. The dominant Raman features of SWNTs are the radial breathing mode (RBM), the tangential stretching mode, known as the G-mode, and a defect-induced mode, known as the D-mode [11]. The frequency position of the RBM is inversely proportional to the diameter of the nanotube [12], which provides a direct assessment of the diameters of the nanotubes present in the sample. The G-mode is sensitive to the electronic properties of the nanotube, which can be used to distinguish between the semiconducting and metallic nanotubes. Both RBM and G-mode are also related to the chirality of the nanotube. The D-mode (and also its second-order overtone, known as the G’-mode) can be used to quantify the defects in the
regular structure of the nanotubes. Thus it is interesting to explore the strength of TERS measurements on SWNTs. One of the most important features of TERS measurement is the spatial resolution, and SWNTs are one of the best samples to explore this feature. The high-resolution sensitivity of TERS has its obvious application in high-resolution imaging, for which isolated SWNTs are one of the best samples. Fig. 2 (c) shows an example of high-resolution TERS image of isolated SWNTs dispersed on a glass substrate [13]. This TERS image was constructed by scanning the sample at G’-mode (2615 cm\(^{-1}\)). The spatial resolution of this image, as estimated from the line profile across the nanotubes (indicated by white dashed line), was as high as 25 nm, which is about 25 times smaller than the wavelength of the excitation light used in the experiment. This is an example that demonstrates the possibility of achieving very high spatial resolution in TERS-based optical imaging.

5. Mechanical effects in TERS: towards molecular resolution

When the probing nano-tip comes in contact with the sample during TERS experiments, it can locally push the sample within an area that comes in contact with the tip. The sample molecules pushed by the tip apex are uniaxially deformed and hence can have a perturbed vibrational response, which can show up in TERS spectrum [10,14]. In most TERS experiments, this tip-applied pressure is unavoidable as well as uncontrollable. However, if one can have a precise control over the tip-applied pressure, it can be utilized to benefit TERS measurements, because this effect shows up in interesting Raman spectral changes such as peak-shift and intensity variation, addressing the nano-mechanical and nano-electronic properties of the deformed sample. Indeed, by precisely controlling the contact area between the sample and the tip, it is possible to make sure that a single or at most a very few molecules of sample undergo the mechanical perturbation. By sensing the modified TERS response of these sample molecules, one can potentially achieve a resolution as high as of molecular level. The effect of tip-applied pressure in TERS has been demonstrated for several samples, such as C-60 and SWNT [10,14].

Here, we will discuss SWNT and show with some experimental examples as how the addition of this mechanical effect in TERS can improve the spatial resolution significantly [15,16].

Fig. 3 (a) shows an example of TERS spectra in the G-mode spectral range at indicated tip-applied forces. As the tip-applied force in increased, a new peak starts to appear and slowly shifts towards lower frequency. This new peak corresponds to the perturbed G-mode originating from the pressurized part of the sample, while the original peak originated from the unpressurized part of the sample and remains at its initial position. (b) Topographic AFM image of an isolated SWNT, overlaid with an illustration of tip scanning across the SWNT. The tip was scanned along the dotted line at the steps of 1 nm at a constant tip-applied force of 2.4 nN. (c) Experimental data showing the line-profile for peak shift in the G-mode as a function of the lateral position of the tip. The FWHM of line-profile shows a spatial resolution of 4 nm in this one-dimensional imaging.
applied force of about 2 nN. Indeed, even at this small value of tip-applied force, owing to the small contact area, the local pressure in the sample is of the order of GPa.

A calculation of the contact area between the tip and the sample indicates that the total contact area under the maximum tip-applied pressure discussed here is less than 1 nm², confirming that only a very small part of the SWNT is under compression [15]. Indeed, the tip-sample contact region is much smaller than the region that undergoes enhancement due to the excitation of localized SPPs at the tip apex. This essentially means that the spectral changes originating from the tip-applied pressure are much more localized than the spectral changes due to the plasmonic enhancement. Therefore, a microscopy based on tip-pressurized TERS would give much better spatial resolution compared to the microscopy based on normal TERS. We performed a tip-pressurized TERS imaging by sensing the amount of peak shift under a constant tip-applied force. Figs. 3 (b) and (c) show the result of a one-dimensional imaging of an isolated SWNT under a constantly maintained tip-applied force of 2.4 nN [15]. A topographic AFM image of an isolated SWNT, overlaid with a schematic of tip scanning, is shown in Fig. 3 (b). The peak-shift of the G-mode was measured at the intervals of 1 nm, as the tip was raster scanned along the dashed line crossing over the SWNT. The corresponding G-mode peak shifts with respect to the tip position are shown in Fig. 3 (c). The full circles show the data points and the line shows the best fitting to the experimental data. As seen from Fig. 3 (c), the spatial resolution obtained from the FWHM of this scanning profile is 4 nm. This is an extremely high value of spatial resolution that could be obtained by combining the mechanical effect of tip-applied extremely localized pressure with the plasmonic effect of TERS microscopy.

6. Overview

Optical imaging gives us richest information about a sample, in comparison with many other imaging techniques. However, due to the diffraction limit of light, the spatial resolution obtained in optical imaging is not enough for true nano-imaging. In this article, we have discussed about an optical imaging technique called TERS, which is based on enhancement and confinement of light to nanometric scale. This technique allows us to overcome the diffraction limit and to obtain images with very high spatial resolution, making it possible to have optical nano-imaging. Further, by combining the mechanical effects in TERS, we have demonstrated that optical imaging can be obtained with extremely high spatial resolution of 4 nm. This is a growing technique, where we believe it would be possible to obtain molecular resolution in near future, which would be a kind of ideal optical imaging.

< References >