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Enhancement of Raman Scattering using Photonic Nanojet and Whispering Gallery Mode of a Dielectric Microstructure

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***Abstract*—**We report the enhancement of Raman scattering signal by one order of magnitude using photonic nanojet (PNJ) of a lollipop shaped dielectric microstructure (LSDM) fabricated by a pulsed CO_2 laser. Here, the PNJ is generated by illuminating sphere portion of the LSDM with non-resonant laser. Unlike the surface enhanced Raman scattering (SERS) technique, this technique is simple, and the obtained results are highly reproducible. In addition, an efficient technique is proposed to enhance the SERS signal with the help of high quality factor optical resonance (whispering gallery mode) of a LSDM. From the theoretical simulations, it has been found that at least an order of magnitude enhancement in the SERS signal could be achieved easily using the proposed technique. We strongly believe that this report will enable the research community for improving the Raman scattering signals.

***Keywords*—**Localized surface plasmons, photonic nanojet, SERS, whispering gallery mode.

I. INTRODUCTION

RECENTLY, the study of Raman scattering of single/few molecules has become one of the paramount interests in the field of nanophotonics [1]. However, obtaining the Raman scattering spectra of single/few molecules using conventional microscopic technique is impossible due to infinitesimally small Raman scattering cross section of molecules. Therefore, researchers have used metal nanostructures for enhancing Raman scattering, and this technique is popularly known as surface enhanced Raman scattering technique [1]. It is to be noted that the enhancement in the Raman scattering signal in this technique strongly depends upon the size, shape and electric permittivity of the nanoplasmonic structures. Therefore, researchers have been trying to obtain better enhancement using different nanostructures. So far, only a few researchers have succeeded in obtaining the Raman spectra of single molecules using this technique. However, the S/N of the observed SERS signal was visibly poor. Therefore, there is a need for enhancing the SERS signal using alternative techniques.

In contrast to the SERS technique, some of the researchers have demonstrated the enhancement of Raman scattering signal using photonic nanojet (PNJ) of single dielectric microspheres (commercial microspheres) dispersed on the substrate containing sample [2]-[6]. PNJ is a focused high intense electromagnetic beam with sub wavelength lateral sizes, generated at the shadow side surface of a non-resonant lossless microsphere of diameter greater than the illuminating wavelength [7]- [10]. So far, two orders of magnitude have been achieved using PNJ of a dielectric microsphere [4]. Interestingly, the PNJ of single commercial microspheres is also used to enhance the SERS signal [11]-[12]. However, in this technique, the microspheres dispersed on substrates containing sample are most often difficult to remove, thereby making the substrates unusable for further experimental studies. Also, the dispersed microspheres are not reusable for any other experiments. These problems could be easily overcome if we use LSDM which are easy to handle, portable, and reusable.

Therefore, herein we report (i) the enhancement of Raman scattering signal using PNJ of single lollipop shaped dielectric microstructures (LSDMs) which are useful to overcome all the problems mentioned in the above paragraph, (ii) an efficient technique to enhance the SERS signal of single molecules with the help of high quality factor optical resonance or whispering gallery mode of a LSDM obtained due to the evanescent coupling of resonant laser light, (iii) theoretical simulations based on the reactive sensing principle (RSP) for estimating the enhancement in the SERS signal due to the whispering gallery mode.

II. EXPERIMENTAL DETAILS

A. Enhancement of Raman Scattering Signal and SERS Signal Using a PNJ of a LSDM

Illustration of an experimental setup used for enhancing the Raman scattering signal is shown in Fig. 1. In contrast to the conventional microscopic technique, here an objective lens (20 X) of a Raman microscope (SekiTech, STR-750) is used to focus the excitation laser light on the sample (silicon wafer) through the sphere portion of a LSDM. In this arrangement, the intense PNJ is generated at shadow side of the microsphere that interacts with the sample. Due to this, more number of Raman photons are generated in this technique as compared with the conventional microscopic technique. The Raman scattering signal was captured using the combination of high resolution spectrograph (Princeton Instruments, SP2750i) and CCD camera (PIXIS-256E). The LSDMs were fabricated by melting the tips of tapered optical fibers using a ns CO_2 laser.

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The tapered fibers were also fabricated using same laser from commercial single mode glass fiber (core diameter: 9 µm, cladding diameter: 125 µm).

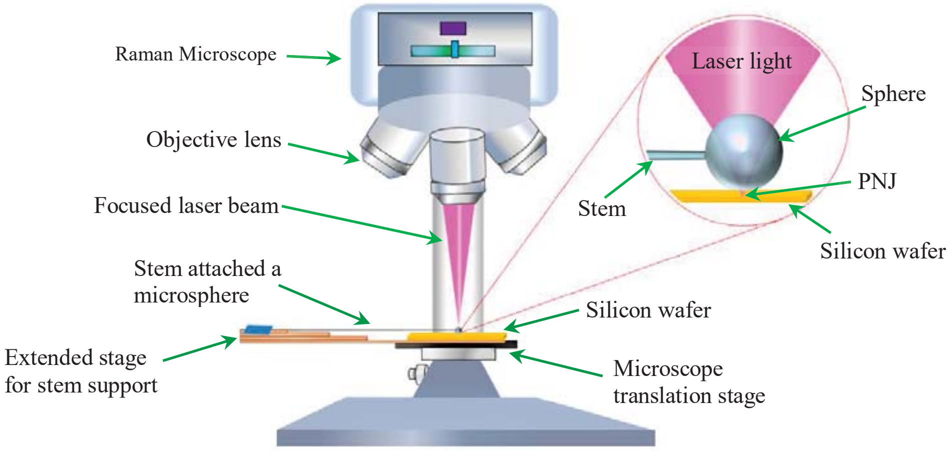

Fig. 1 Illustration of an experimental setup for enhancing the Raman scattering signal of silicon wafer using PNJ from a LSDM. Here, the extended stage is made by several glass slides for supporting the stem of the LSDM. The zoomed portion shows the interaction of PNJ with the silicon wafer.

Black curve (b) in the Panel A of Fig. 2 shows the Raman spectrum of a silicon wafer obtained from the direct excitation (in the absence of a LSDM) and pink curve (a) represents the obtained Raman spectrum when the laser light is focused on the sample through a microsphere of a diameter 35 µm. From this figure, it is clear that the Raman scattering signal is enhanced due to the PNJ, and the estimated Raman scattering enhancement factor is around 8. It is to be noted that this spectrum was obtained when the microsphere was kept away from the focal point for matching the laser beam diameter with the microsphere diameter for obtaining better enhancement. Inset of Fig. 2 shows the variation of the Raman scattering enhancement with the microsphere diameter. From this figure, it is clear that the value of enhancement increases with the microsphere diameter and this could be understood as follows.

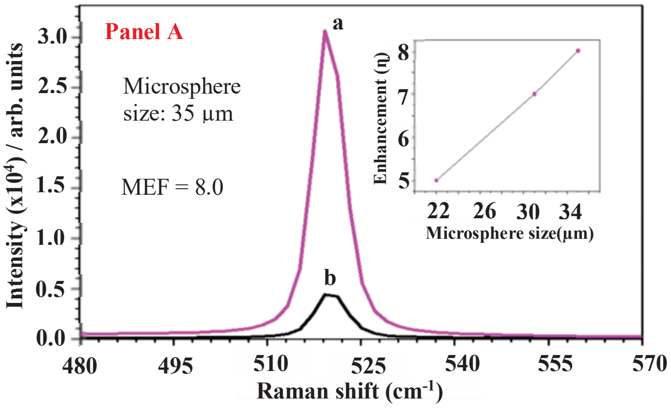

Fig. 2 Curves (a) and (b) represent the Raman scattering spectra of silicon wafer obtained with and without PNJ of a LSDM respectively. Inset shows the variation of the Raman scattering enhancement with the microsphere size.

Since the PNJ generates due to the constructive interference of incident light and strong forward Mie scattering light at the shadow side of the microsphere, the electric field of the PNJ is the sum of electric field of incident light ($\mathbf{E}_0$) and electric field of scattered light ($\mathbf{E}_{sca}$) [7]-[10]. The value of $\mathbf{E}_{sca}$ depends upon size and refractive index of the microsphere, and refractive index of the surrounding medium [13]. Its value increases with the microsphere diameter and due to this the electric field of the PNJ increases with the microsphere diameter. Therefore, the enhancement in the Raman scattering signal increases with the microsphere size. Here, it is to be noted that the fabricated LSDMs have long stems (typical length is around 10 cm). Hence, these microstructures are easy to handle, portable, and reusable. So, with the help of these microstructures, all the problems associated with commercial microspheres (which do not have the stems) mentioned in the introduction could be overcome easily.

Here, it is worthy to mention that the LSDM are very much useful even in the case of PNJ mediated SERS technique which is proved to be better than the conventional SERS technique [11], [12], [14], [15]. Illustration of an experimental

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setup for enhancing the SERS signal using PNJ of single LSDM is shown in Fig. 3.

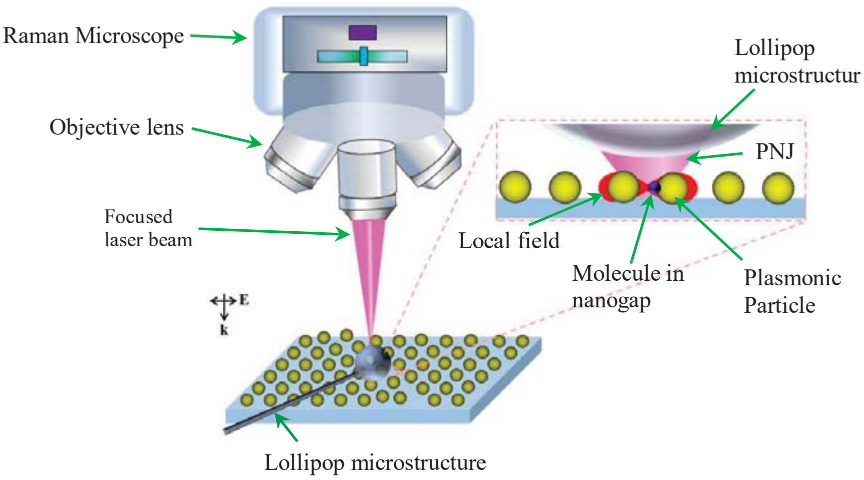

Fig. 3 Illustration of an experimental setup for PNJ mediated SERS technique for enhancing the SERS signal of single molecules. Inset shows the Raman scattered photons from a molecule with in the hotspot created by the localized surface plasmons in strongly coupled metal nanostructures illuminated with PNJ of a LSDM.

In this arrangement, the PNJ is expected to be generated at the shadow side of the microsphere when the laser light is focused through the sphere portion of the LSDM. The intense PNJ excites localized surface plasmons in the metal nanostructures in the SERS substrate and generates intense hot spots on the surface of the nanostructures as compared with the conventional SERS technique. Therefore, any molecule adsorbs at any of the hotspots generates relatively more number Raman scattered photons due to the huge local electric field. Unlike the commercial microspheres, the LSDMs allow to enhance the SERS signal without modifying the surface of the SERS substrates and this could be considered as an additional advantage of these microstructures.

B. Enhancement of SERS signal using high quality factor whispering gallery mode of a LSDM

As we know that some transparent dielectric microspheres support optical resonance or whispering gallery mode (WGM) upon illumination with resonant light [16]. High quality factor WGMs could be achieved through phase matching excitation and this is possible either with a tapered fiber or prism. The excitation of travelling transverse electric equatorial WGM with the help of a tapered fiber is shown in Fig. 4. It is to be noted that the intensity of the WGM is much larger than the coupled (or input) laser light in to the microsphere because of strong confinement at the equator due to the total internal reflection phenomenon. The radial intensity distribution curve shown in this figure shows that the intensity of the mode decays very rapidly with the radial distance away from the microsphere boundary. Therefore, the field outside the microsphere is known as evanescent field of the WGM. On the surface of the microsphere, a nanoplasmonic particle could be anchored easily with the help of light force functionalization [17]-[20]. Once the nanostructure adsorbs at the equator of the microsphere then the evanescent field of the WGM interacts with the nanostructure and excites localised surface plasmons inside and generates hotspots on its surface. The intensity at the hot spot of the nanostructure in the present case is given by

$$I_{hs} = \left| \boldsymbol{E}_{wgm} + \eta \boldsymbol{E}_{wgm} \right|^2 \tag{1}$$

where $\boldsymbol{E}_{wgm}$ is the evanescent field of the WGM and η is the enhancement of electric field due to the dipoles inside nanoplasmonic structures. In the case of conventional SERS technique, the intensity of the hot spot is given by

$$I_{hs}^{conv} = \left| \boldsymbol{E}_0 + \eta \boldsymbol{E}_0 \right|^2 \tag{2}$$

where $\boldsymbol{E}_0$ is the electric field of the incident light focused on the nanostructure with the help of objective lens. Theoretical simulations have been carried out using RSP [17] and found that the value of evanescent field intensity of the WGM (I_{wgm}) is significantly larger (at least one order of magnitude) than the incident light intensity I_0 in the case of conventional SERS technique. Hence, the SERS signal could be enhanced at least one order of magnitude with the help of whispering gallery mode microresonator.

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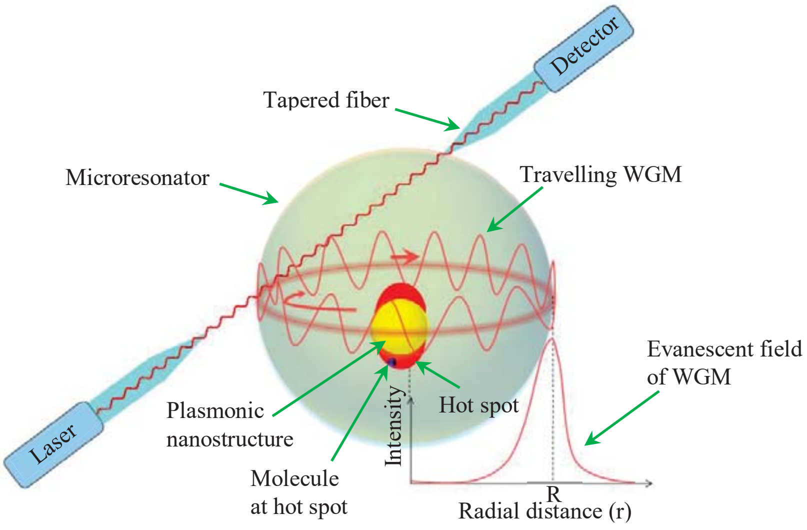

Fig. 4 Schematic of an experimental setup for enhancing the SERS signal of a molecule with the help of equatorial WGM of a LSDM using evanescent coupling of tunable laser light. The hot spots on the surface of a nanoplasmonic particle generated by WGM is also shown here.

III. CONCLUSION

We have successfully demonstrated the enhancement of Raman scattering signal using PNJ of single LSDMs fabricated using a ns CO_2 laser. In contrast to the commercial microspheres, the fabricated microstructures are easy to handle, reusable and portable. The advantage of the fabricated LSDMs in the PNJ mediated SERS technique has been explained in detail. A new approach to enhance the SERS signal using whispering gallery mode of a LSDM has been proposed and from the theoretical calculations, it has been found that the SERS signal could be enhanced in the proposed technique at least one order of magnitude.

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