Annexure-IX

PROJECT COMPLETION REPORT

Notes: 1. 10 copies of the Project Completion Report (PCR) should be sent within one month of the completion or termination of the project.

2. The PCR should be in bound form.
3. Cover page should include the title of the project, file number, names and addresses of the investigation.

1. Title of the project: **"Design consideration of SERS substrate for getting extremely enhanced Raman signal"**
2. Principal Investigator(s) and Co-Investigator(s): **Dr. Pabitra Nath**
3. Implementing Institution(s) and other collaborating Institution(s): **Tezpur University**
4. Date of commencement: **3rd March, 2014**
5. Planned date of completion: **2nd March, 2017**
6. Actual date of completion: **2nd July, 2017**
7. Objectives as stated in the project proposal:
    - To simulate the structure of nanoparticle array for Ag and or Au which would provide the strongest LSPR field magnitude.
    - To obtain a template for the simulated structures by electron beam lithographic technique.
    - Using replica molding technique the pattern from the template would be transferred to a PET sheet which is inexpensive process.
    - By coating Ag/Au nanoparticle on the substrates obtained from above step
    - SERS signal of various chemicals namely malachite green, bezoic acid, rhodamine6G, ethanol would be initially studied and later would be investigated for least concentration of sample for which the designed SERS substrate can detect and record fingerprint of molecules.

8. Deviation made from original objectives if any, while implementing the project and reasons thereof:

During submission of proposal the PI planned to simulate different metal nano-structures and generate inverse template of the optimized structure (that support maximum LSPR field) using electron beam lithography technique. Then the PI planned to transfer the nano-structure in to low cost PET sheet using replica molding technique. But fabrication of SERS substrate using replica molding technique could not carried out during the project period due to non-availability of replica molding unit (**which was not able to procure during the project period due to not releasing of sufficient fund**). However, keeping the main objective in mind PI research group looked for alternative to fabricate low cost SERS substrate and finally the PI research group has come up with two alternative approaches. In the first approach the group tried to fabricate SERS substrate by incorporating gold nano-particles (AuNPs) on the diatom frustule. The substrate was then used to sense Raman signal of malachite green (MG) and fluoride level in drinking water. Cleaned diatoms were pipetted on cleaned cover slips. Taking the advantage of photonic crystal like structure of diatom frustule and utilizing the self-assembling property of diatom the AuNPs were attached on the diatom frustules. Finally the AuNPs attached diatom assembly has been used for SERS based sensing applications. With this substrate malachite green (MG) concentration as low as 1nM and Fluoride concentration upto 100nM can be detected with relative standard deviation (RSD) of 5.75% and 17.26% respectively. In the next approach the PI research group tried to developed SERS substrate using printed grade paper as base. Silver nano-particles (AgNPs) were pipetted on different GSM papers and study the Raman effect of test samples. Among all considered papers 100 GSM grade paper SERS substrate scattered intense Raman signal. This substrate was used for detection of MG and rhodamine6G (R6G). With this substrate MG concentration of 0.1nM with maximum RSD value of RSD value of 12.89% and R6G concentration as low as 1nM with maximum RSD value of 13.15% could be detected reliably. PI believe that the proposed techniques could emerge as cost efficient alternative fabrication method of SERS substrates which can be used for SERS based sensing investigations.

9. Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs:

The main objective of this research work is to developed low-cost SERS substrate. In order to do so initially we carried out rigorous simulation study by designing different metal nano structure. When incident electromagnetic field interacts with metal nanoparticle, the conduction electrons of the metal surface oscillate collectively and coherently with the incident light frequency. The oscillations occur due to Coulombic attraction between electrons and metallic nuclei. These collective oscillations of electrons in resonance with the incident light frequency is called localized surface plasmon resonance (LSPR) condition. The enhancement in LSPR field condition due to coupling of electromagnetic wave depends on how metal nanostructures have been patterned. One of the important fields of research related to LSPR field condition study in metal nanostructures is SERS. The excitation of LSPR in metal nanostructures is the key to the enhancement of Raman signal for SERS. The nano-cluster or metal nanoparticles upon interacting with the incident laser light generate strongly localized plasmonic wave in a region between two closely spaced (10–30 nm) nanoparticles also termed as hotspot. When a target molecule comes under this hotspot region, it strongly interacts with the surface plasmon wave and scatter strong Raman signal whose magnitude could be several order higher than the planer sample. Keeping it in mind, at the very beginning we simulate different metal nano-structure using COMSOL multiphysics (wave optic module) software. Initially we design two different structure namely a periodically varying height metal nano-pillar and diagonally aligned squared metal nano-pillar.

In the periodically varying height metal nano-pillar we consider a metal nano-pillar between two relatively high metal nano-pillar on silica substrate. Plane polarized electromagnetic wave is allowed to incident on the pillars and studied the generated LSPR field for different parameters of the pillars. The schematic of the design structure is shown in figure 1.

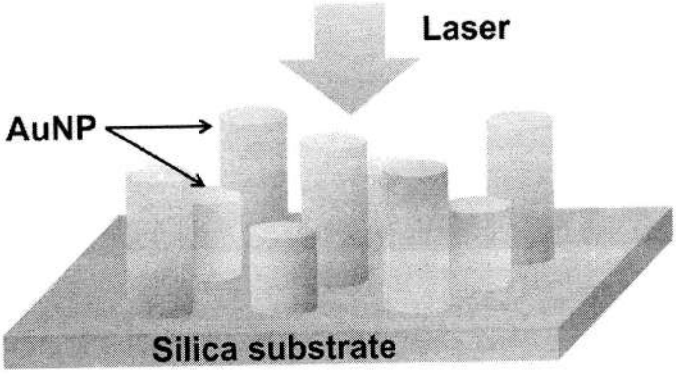


Figure 1: Schematic of the considered periodically varying height metal nano-pillar.

In order to study LSPR field enhancement in our proposed periodic gold nano-pillar (AuNP) structure, we consider AuNP on a silica substrate (n =1.453 for incident laser wavelength of 785 nm). We consider frequency-dependent complex dielectric function for AuNP. We first consider uniformly structured AuNP with pillar height of 150 nm, diameter of 50 nm, and separated by a spacing of 10 nm. Simulation study of LSPR field condition for this structure is performed for incident laser source of wavelength 785 nm along its perpendicular direction, i.e. z-axis, and the incident field is assumed to be polarized along y-axis. Maximum LSPR field condition for this structure is observed to be 2.92×10^8 V/m for the incident electric field of 4.42×10^7 V/m. For the same AuNP, we then vary the height of the pillars periodically and simulate its LSPR field conditions. Figure 2a, b shows two of the simulation results, one for uniformly patterned AuNP structure and the other for periodic varying height AuNP structures with pillar height difference of 55 nm. Figure 2c shows the characteristic curve showing the variation of LSPR field condition with change in height difference for all the considered patterned structures in the present simulation study. We maintain here same spacing of 10 nm and pillar diameter of 50 nm for all the considered patterned structures. Our simulation results show that among the considered patterned, AuNP with pillar height difference of 55 nm yields maximum LSPR field condition with the value of 3.69×10^8 V/m and compared to uniformly structured AuNP and the enhancement factor was measured to be 1.26. For AuNP structures with pillar height difference less than 35 nm, the LSPR field condition is observed to be less than that of the uniform height AuNP while for pillar height difference of 40 nm and more, the generated LSPR field condition is observed to be more than that of uniformly structured AuNP. This enhancement of LSPR field condition is attributed to the increase in effective cross section condition for incident electromagnetic wave with the patterned structure.

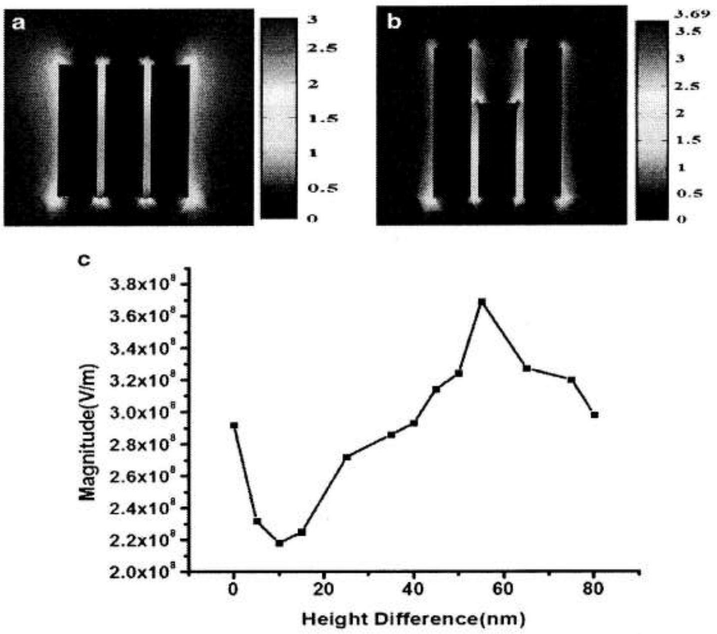


Figure 2: Simulation result of AuNP for (a) pillars with no height difference and (b) pillars with height difference of 55nm. We maintain fixed pillar diameter of 50 nm and separation of 10 nm for both the situations. (c) Characteristic curve that represents generated LSPR field conditions for AuNP structures at different pillar height differences.

After getting optimum condition of pillar height difference for which our proposed AuNP structure generates maximum LSPR field condition, we perform the LSPR field condition simulation study by varying the diameter of the pillars. We study the LSPR field condition at different pillar diameters ranging from 50 to 160 nm with increment of 10 nm while maintaining a fixed pillar height difference of 55 nm and spacing of 10 nm. Figure 3a–c shows three of the simulation results for pillar diameters of 50, 100 and 120 nm of the designed structures, respectively. Among the considered structures, the optimum LSPR field condition is observed to be 1.34×10^9 V/m which corresponds to pillar diameter of 100 nm, while a uniformly patterned AuNP and with same parameter gives LSPR field magnitude of 1.12×10^9 V/m indicating that the field enhancement in this case occurred at 1.19. Figure 3d illustrates the characteristic curve of LSPR field condition for different pillar diameter variations while maintaining a fixed pillar height difference and spacing. Among the considered periodic AuNP structures, the optimum LSPR field condition has been observed for pillar diameter of 100 nm which again can be attributed to optimum electromagnetic field coupling condition for this structure. Beyond 100 nm pillar diameter, the LSPR field condition is observed to be gradually decreasing.

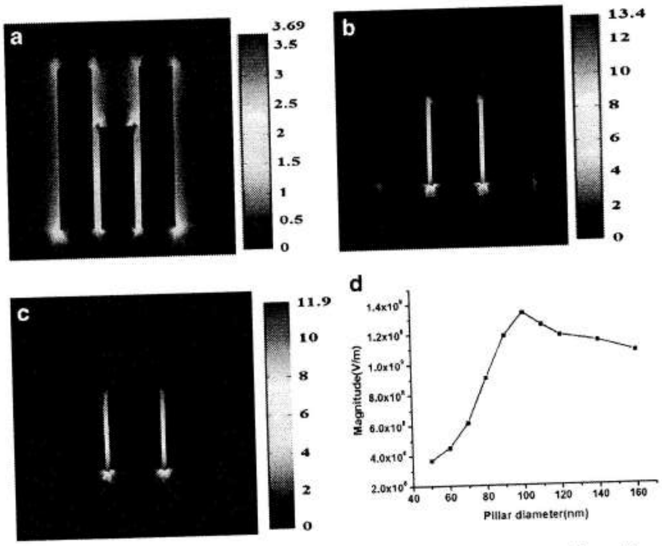


Figure 3: Simulation results of the generated LSPR field conditions for different pillar diameters of the proposed periodic AuNP structures. (a) 50 nm, (b) 100 nm and (c) 120 nm pillar diameter. In all the considered cases, we maintain a constant pillar height difference of 55 nm and spacing of 10 nm (d) representing the characteristic curve of LSPR field conditions for different pillar diameter periodically varying height AuNP structures.

The effect of LSPR field condition on pillar spacing is also investigated in our present study. We simulate the LSPR field generation for seven sets of periodic structures at different pillar spacing ranging from 10 to 50 nm while maintaining same pillar height difference of 55 nm for all sets of investigations. Figure 4 shows the characteristic of LSPR field condition for all the considered sets of structures for different pillar diameters. This characteristic curve clearly indicates that with the increase of pillar spacing, the resonant coupling condition for incident electromagnetic wave falls off rapidly, thus generates low magnitude of LSPR field. The optimum LSPR field condition is observed for AuNP with diameter 100 nm at pillar spacing of 10 nm. This is again attributed to the optimum cross section of the designed structure with the incident electromagnetic wave coupling among all the considered sets of structures.

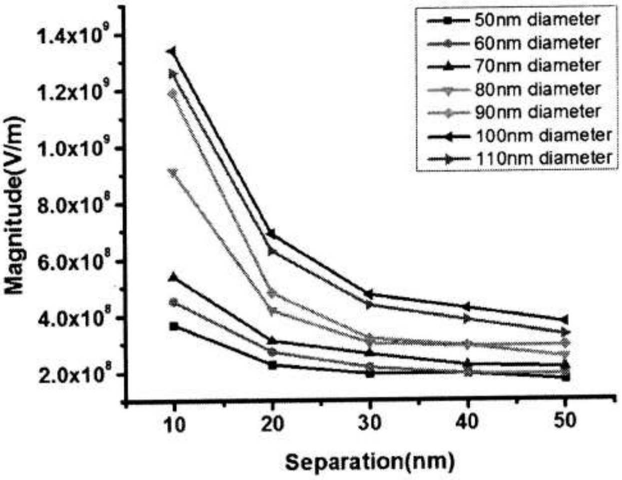


Figure 4: Characteristic curve of separation vs maximum field intensity for pillar diameter periodically verying height AuNP structures ranging from 50 to 110 nm at a height difference of 55 nm

One of the commonly used laser wavelength for SERS study is 785-nm laser. It is because of this reason that we report the present simulation study on LSPR field condition for 785-nm laser beam only. It will be more effective if the excitation frequency is equal to the localized surface plasmon (LSP) frequency. The LSP wavelength for Au is found to be around 520 nm for spherical shape nanostructures, and this value is shifted to near 785 nm for rod-like structure. Further, LSP for rod-like nanostructure also changes with its aspect ratio. Among the considered AuNP structures, we perform the simulation study of LSPR field condition for other different incident laser wavelength such as 532, 614 and 633 nm. For all the situations, we consider here the nanostructure of pillar diameter 100 nm, pillar height difference of 55 nm, and maintain a separation of 10 nm. The observed maximum LSPR condition at various incident wavelengths is shown in Fig. 5. The characteristic curve illustrates that the maximum LSPR field condition is observed for 614 nm wavelength which again can be attributed to the efficient coupling of the incident electromagnetic wave with this specific structure. As compared to uniformly patterned AuNP, we calculate the enhancement factor in LSPR field conditions of our proposed period structures. Here, we calculate enhancement factor by considering the ratio of the LSPR field condition generated in periodically varying height AuNP to the LSPR field condition observed in uniformly structured AuNP. Thus,

$$\text{Enhancement Factor}=\frac{\textit{Maximum LSPR field condition for periodic patterned AuNP}}{\textit{Maximum LSPR field condition for uniform patterned AuNP}}$$

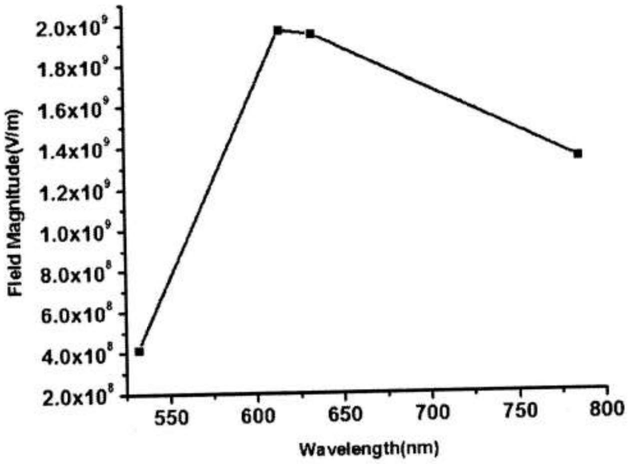


Figure 5: Characteristic curve representing the LSPR field magnitudes for different incident laser source wavelength for a same periodically varying height AuNP structure.

Figure 6 represents histograms of the field enhancement of our proposed patterned AuNP in comparison to uniformly patterned AuNP for different pillar diameters and at different pillar spacing. We observe that for all the considered situations, there has been an enhancement in the LSPR field conditions in our proposed periodic AuNP structures. We observe maximum enhancement factor of 1.32 corresponding to the pillar diameter of 80 nm at spacing of 10 nm for pillar height difference of 55 nm. Table 1 summarizes the results of the whole work done on the periodically varying height AuNP structures. It also includes the data for LSPR field conditions for analogous uniformly patterned AuNP structures.

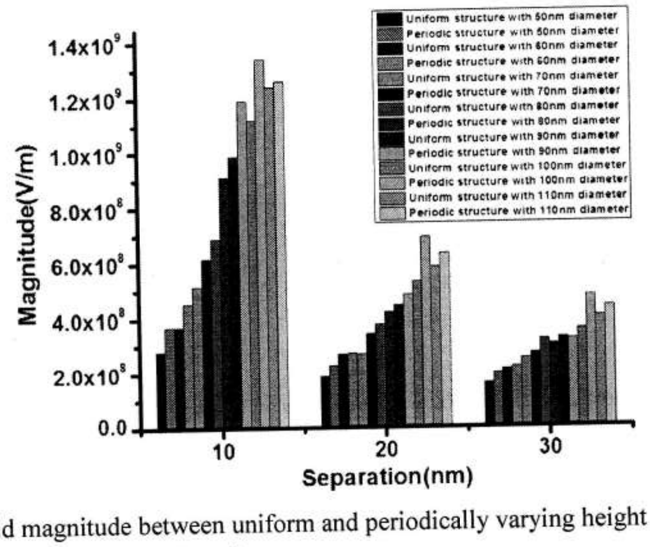


Figure. 6 Comparison of field magnitude between uniform and periodically varying height AuNP for different diameters (50–110 nm) and separations (10–30 nm)

Table 1: Maximum field magnitude for uniforml and periodically varying height AuNP structures

	Uniform AuNP structure (x10^{8} V/m)			Periodic AuNP structure (x10^{8} V/m)		
Diameter(nm)	10nm separation	20nm separation	30nm separation	10nm separation	20nm separation	30nm separation
50	2.92	1.89	1.59	3.69	2.27	1.94
60	3.69	2.69	2.1	4.53	2.72	2.17
70	5.13	2.68	2.5	6.18	3.4	2.69
80	6.89	3.76	3.17	9.12	4.19	3.02
90	9.87	4.44	3.23	11.9	4.82	3.19
100	11.2	2.29	3.56	13.4	6.9	4.74
110	12.4	5.81	4.02	12.6	6.31	4.37

To fabricate this structure we need to go through rigorous optimization of recipes in every steps fabrication process (starting from oxidation to metal deposition and liftoff) which requires a large number of slots in very sophisticated laboratory and instruments such as electron beam lithography. These facilities are very limited across the country and we try to fabricate our structure at IIT Bombay under INUP program. But due to limited availability of slot for fabrication of this specific structure was not possible during last visit of the JRF working in this project. Though PI has submitted another proposal to INUP in order to fabricate this structure till the date of writing this proposal PI not getting any confirmation from their side.

In the diagonally aligned squared metal nano-structure (SMNP) we consider squared metal nano-pillars aligned diagonally on the surface of silica substrate. The schematic of the considered structure is shown in figure 7.

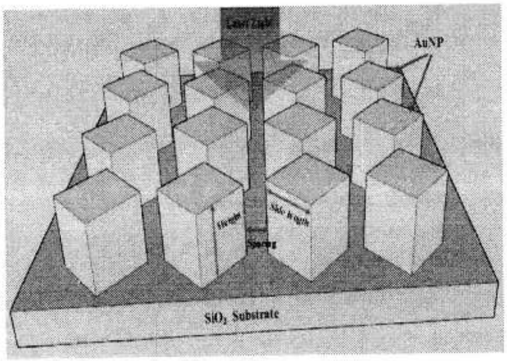


Figure 7: Schematic of diagonally aligned squared metal nano-pillar

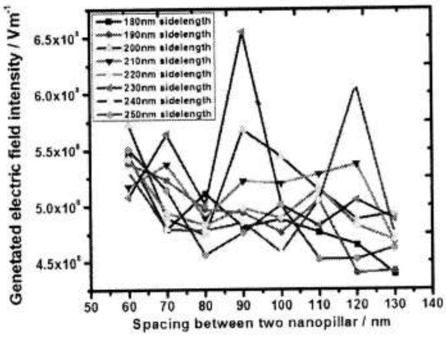


Figure 8: Characteristics curve of generated LSPR field magnitude for different sidelenght at different spacing

In order to study the LSPR field magnitude in the structure using this simulation software, the side length of the pillars have been varied from 200 to 230 nm in a step of 10 nm and vary the spacing from 60 to 120 nm in a step of 10 nm. Figure 8 shows the characteristic curves of the coupled LSPR field magnitudes as obtained from the simulation results for different side length and spacing of the SMNPs. The generated LSPR field magnitude is observed to be random with respect to the spacing and side length of the structure. This is attributed to optimum field coupling condition for different SMNP structures would be different for the same incident laser light signal. The coupled LSPR field magnitude is different at different positions of the structure, and in the present study; we consider maximum generated field intensity which is observed at the gap between the sharp edges of two squared metal nano-pillars.

In order to fabricate diagonally aligned SMNP substrate, we take a RCA cleaned silicon wafer and put it into a wet oxidation furnace to oxidize. The oxidized wafer is then cut into small pieces and then is treated in acetone and isopropyl alcohol (IPA) bath before it goes for resist coating. We coat a bilayer Polymethyl methacrylate (PMMA) (PMMA 495 A4 at 3000 rpm and PMMA 950 A4 at 3000 rpm) on the cleaned Si substrate. The pattern has been written on the PMMA coated sample using electron beam lithographic tool (Raith 150 two). The electron beam lithographic (EBL) patterned sample is then developed by dipping the substrate in 1:3 MIBK/IPA for 60 s, followed by IPA treatment for 20 s. Prior to Au deposition on the patterned substrate, chromium (Cr) has been deposited on the substrate for better adhesion between Au and the SiO. Both Cr and Au have been deposited using thermal evaporator (Hind HiVac 12A40) at a rate of 0.3 and 0.8 Å/s, respectively. The Au deposited sample is then liftoff, and the pattern has been observed under scanning electron microscope (Zeiss Ultra 55 FESEM). Figure 9a shows process flow of the important fabrication steps that have been followed to obtain the patterned SMNP structure, and Figure 9b shows the FESEM image of one such fabricated pattern obtained from above steps. The inset image shows the zoom-in and tilted view of the patterned structure. The side and top view of LSPR field distribution around the nano-pillar obtained from the simulation for the same patterned structure is shown in Figure 9c, d, respectively.

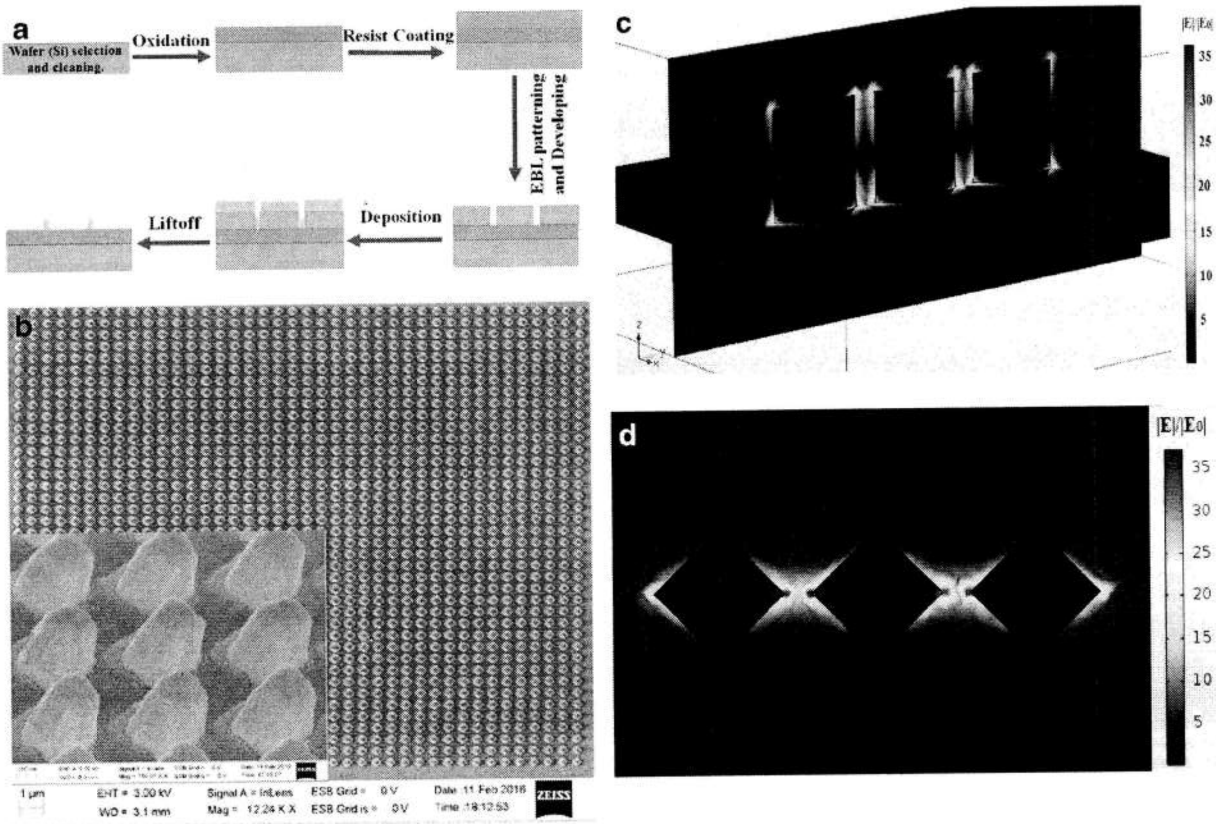


Figure 9: (a) Steps involved in fabrication of SMNP. (b) Top view of fabricated diagonally aligned squared gold nano-pillar, and the inset image shows the enlarge and tilted view of the nano-pillars. (c), (d) Side and top view of FEMsimulation result of LSPR field distribution obtained by considering dimensions taken from SEM images

To estimate the enhancement for the proposed pattern, Raman signal from a plane silicon substrate has been initially recorded for 1 mM RhB sample. Figure 10 illustrates the characteristics of Raman signals recorded by spectrometer for these two different situations. Clearly, as compared to plane substrate, the Raman signal intensity of RhB is found to be enhanced by several orders when detected with the designed SERS substrate. The Raman peak at 1282/cm is found to be consistent for RhB. In the present work, the enhancement in the Raman signal and to demonstrate the reproducibility characteristic of the proposed substrate, the enhancement of this specific peak will be studied for all different concentration samples. Figure 11 describes the characteristic Raman signals for four different concentrations of RhB samples when placed on the SERS active substrate and recorded by the Raman spectrometer. For comparison, the same figure includes the Raman signal intensity measured from a plane silicon substrate for 1 mM RhB. For all sets of investigations, the same volume (10 µL) of the sample solutions has been used for dispensing over the SERS substrate. This figure clearly indicates that with increasing molar concentration of the sample, the Raman peaks are also found to be enhanced proportionately. The enhancement factor is calculated to be 3.27×10^8 for 1282/cm Raman peak signal. In the final step, the reproducibility characteristic of the designed substrate has been investigated. Ten microliters of 1 μMRhB solution has been dispensed again on our designed SERS substrate, and the back-scattered Raman signals of the sample solution have been recorded from different positions of the SERS substrate. Seven different locations have been chosen on the SERS sensing region from where scattered Raman signal were recorded. Figure 12 shows the characteristic Raman signals recorded by the spectrometer for these seven different locations of the substrate. The Raman shift at 1282/ cm is observed to be nearly same intensity with relative standard deviation (RSD) value, which is calculated to be 13 %.

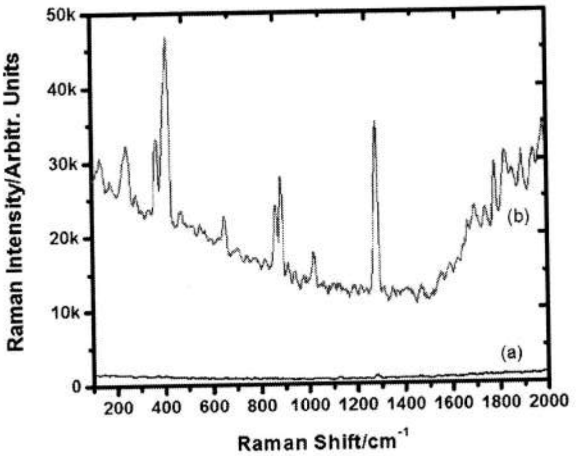


Figure 10: Comparison of Raman spectra of RhB between plane silica substrate and SMNP substrate. (a) For 1 mM RhB solution on plane silica substrate, the signal was magnified by 20 times. (b) For 1 μMRhB solution on SMNP substrate.

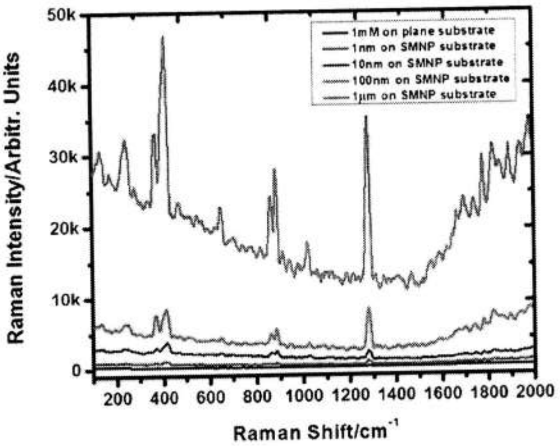


Figure 11: SERS spectra of RhB at different concentrations. For all concentrations, the excited laser of wavelength 785 nm and output power has been kept constant.

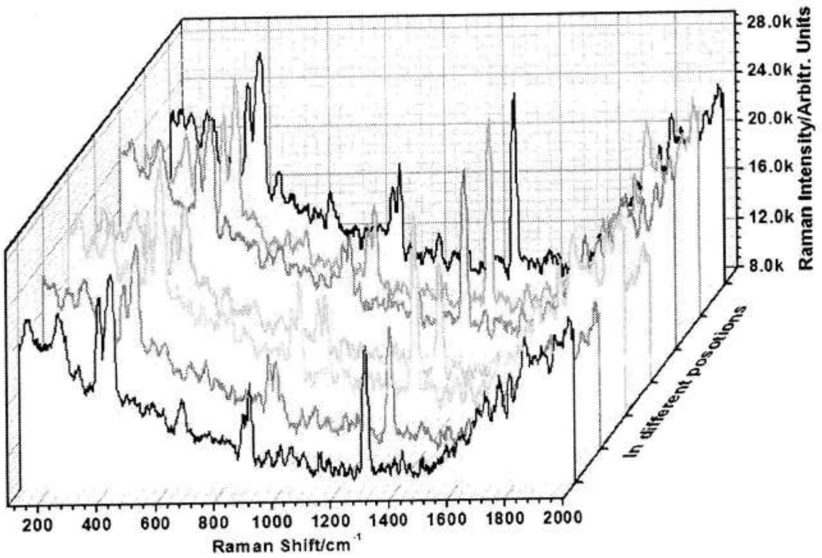
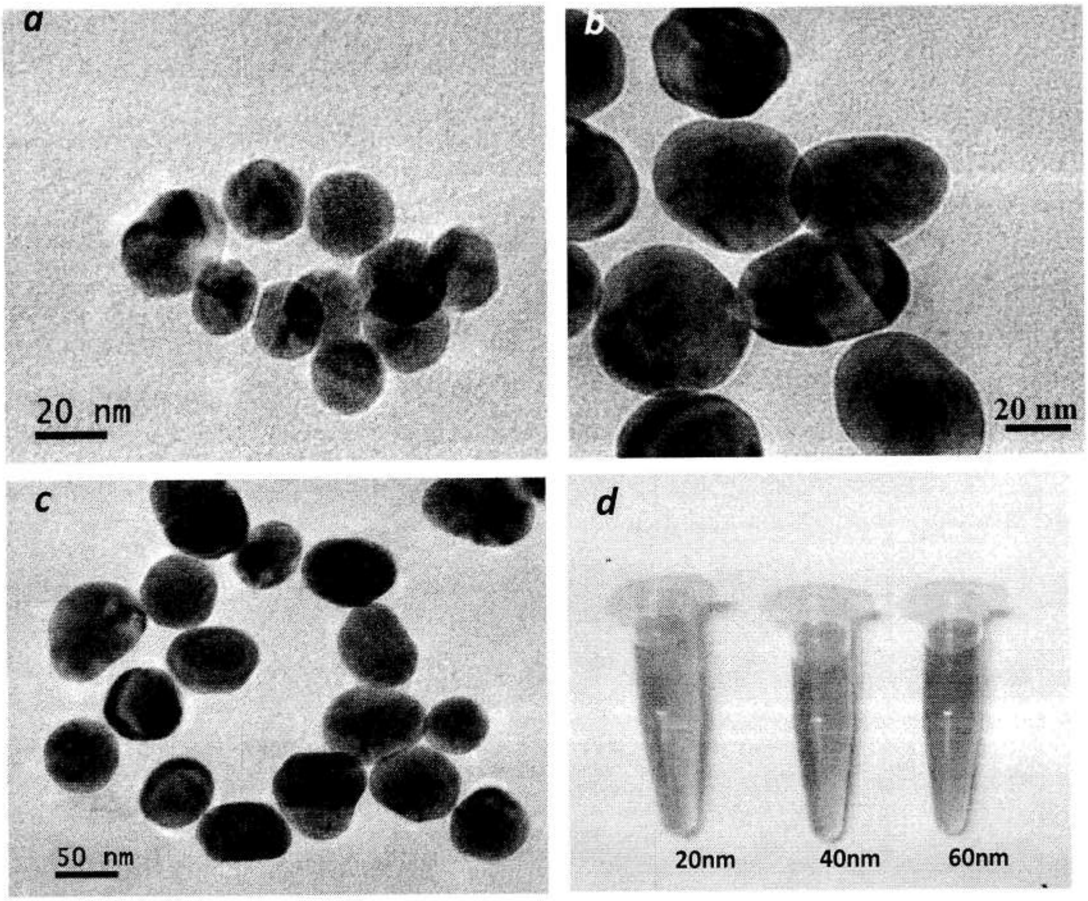


Figure 12: Raman spectra of 1 μM RhB solution at seven different locations on the SMNP substrate

Fabrication of SERS substrate using different lithographic technique such as electron beam lithography, focused ion beam lithography, nano imprint lithography etc. are in general, expensive and time consuming and requires sophisticated laboratory setup for fabrication of the SERS substrates. Keeping these issues in mind we were looking for alternative approaches by which SERS substrate can be obtained and we developed two low-cost SERS substrates namely gold nano-particles (AuNPs) assembled diatom frustule and silver nano-particles (AgNPs) diffused printed paper based SERS substrate.

In the AuNPs assembles diatom frustule, we utilize the self-assembling property of diatoms for attachment of AuNPs in the pores and on the surface of cleaned diatom frustules and subsequently has been used for SERS sensing studies. Two Raman active samples namely MG and fluoride in drinking water have been considered as the test samples to evaluate the performance of the proposed substrate.

Living diatoms were collected from the Tezpur University lake water and cultured in **biochemical oxygen demand** (BOD) incubator in the culture laboratory of Physics department, Tezpur University under controlled conditions. Finally the cultured diatoms were cleaned using chemical treatment and dispersed in ethanol. AuNPs of 20 nm, 40 nm and 60 nm diameter were synthesized using popular turkevich method, where sodium citrate was used for reducing auric chloride. Figure 13. *(a)-(c)* shows the TEM images of the synthesized AuNPs. Figure 13. (d) shows the photograph of synthesized AuNP colloidal solution. The monodispersity of the synthesized AuNPs has been studied by taking UV-visible absorption spectra of three samples. Figure 13 *(e)* shows the characteristic UV-visible absorption spectra of the synthesized nanoparticle. The absorption peaks are found to be sharp which confirm the monodispersity nature of the AuNP colloidal solution. The frustule suspension of 20 μL was pipetted on a clean cover slip and allowed to dry in room temperature environment for two hours which is followed by annealing at 400^{0}c for another 1 hour. To coat AuNPs on the surface and in the pores of diatom frustule, the substrate was placed vertically into the solution of AuNPs colloidal suspension for 12 hours at room temperature. The self-assembled AuNPs on the substrate was allowed to dry for two hour. The attachment of AuNPs on the diatom frustules has been confirmed by taking FESEM images and the elemental data from EDX of the samples. Corresponding results are shown in figure 13. *(h)* and *(i)*. The average dimension of the pores were observed to be 100 nm while maintaining a periodicity of ~ 300nm in the lateral direction and ~150nm along the transverse direction.



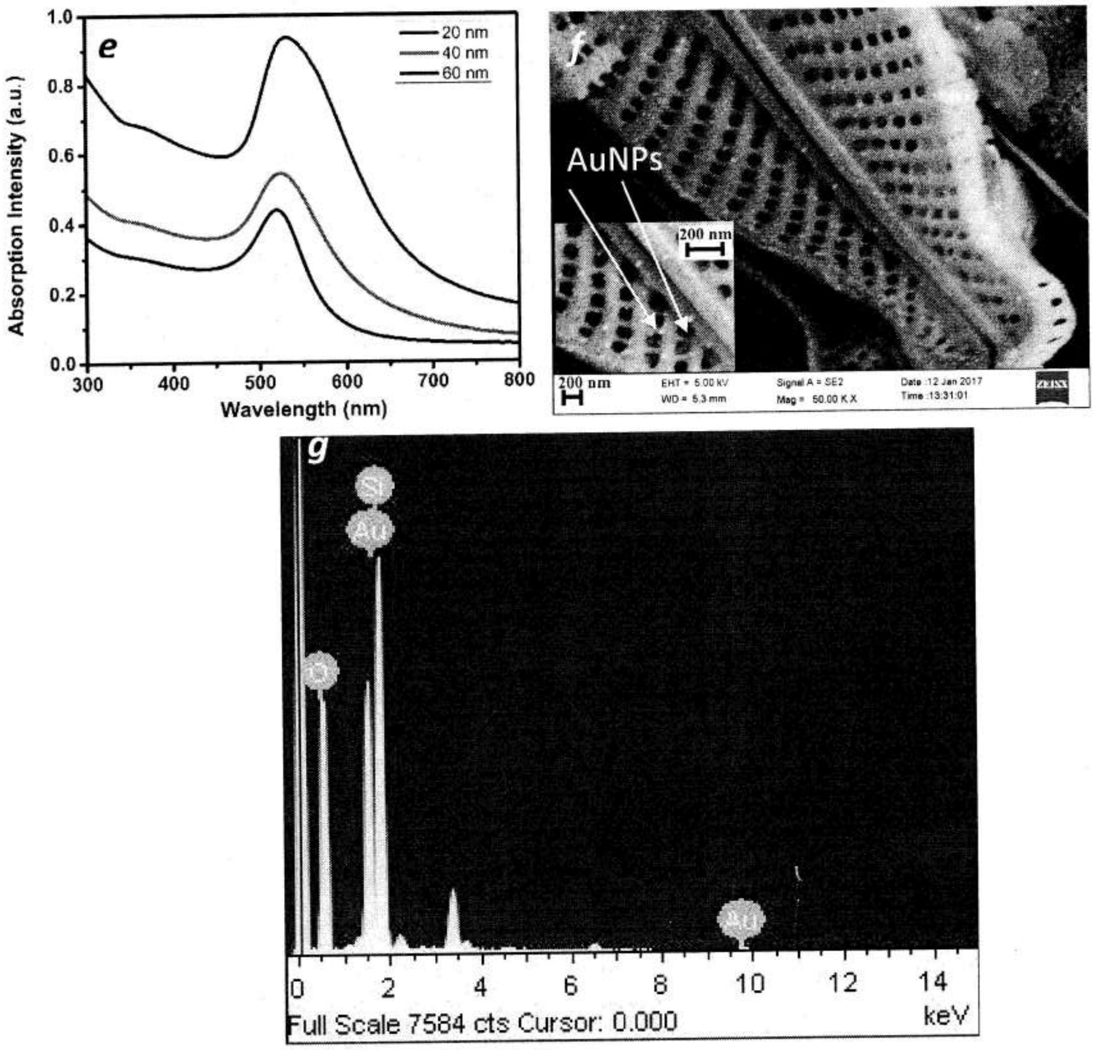


Figure 13: TEM images of chemically synthesized AuNPs (*a)* 20nm, *(b)* 40nm, *(c)* 60 nm, *(d)* shows the photograph of synthesized AuNP samples *(e)* UV-vis absorption spectra of AuNPs of the synthesized samples *(f)* FESEM images showing distribution of AuNPs on diatom and *(g)* EDX data showing the elemental composition of the self-assembled AuNPs on the diatom frustule.

Prior to start of the experimental investigation, we study the LSPR field enhancement for different dimensional self-assembled AuNPs in the pores and on the surface of diatom frustule using simulation tool. Figure 14 *(a)*-*(c)* illustrate different situations of coupled LSPR field magnitude at different locations of the diatom frustule where AuNPs can be self-assembled. Figure 14*(a)* shows the situation where AuNPs are assembled on the surface of the diatom and in the vicinity of the pores. For this case, we observe an average field enhancement of the order of 10^7 upon coupling of the 785 nm p-polarized laser beam. Figure 14*(b)* and *(c)* narrate the situations where AuNPs are found to be assembled just above and inside the pores of the frustule. For these two situations, an average LSPR field enhancement of the order of 10^8 has been observed from our simulation study. Due to guided mode resonance phenomenon (GMR) the field enhancement for assembled AuNPs on top and inside the pores of the diatom is found to be greater than that of the surface assembled AuNPs. The dependence of LSPR field magnitudes on the dimension of the assembled AuNPs has also been studied. Figure 14*(d)* shows the characteristics average LSPR field magnitude within the pores of the frustule for 20nm, 40nm, 60nm, 80nm and 100nm AuNPs and at 785nm incident laser beam. The maximum field coupling condition was found to be for 40nm AuNPs assembled in the pores of diatom in the present study.

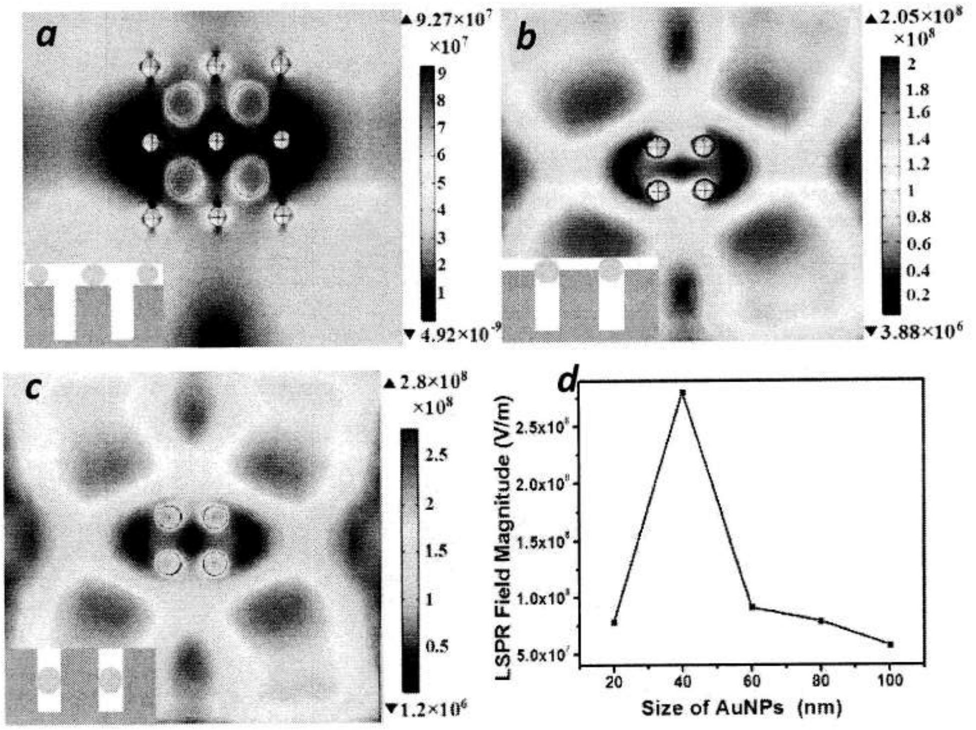


Figure 14: Simulation results showing the LSPR field enhancement in the proposed SERS substrate upon coupling of 785 nm p-polarized laser beam. Three different situation have been considered AuNPs assembled: *(a)* on the surface of the diatom frustule, *(b)* just above the pores of the diatom and *(c)* inside the pores. *(d)* shows the variation in LSPR field magnitude with respect to size of the assembled AuNPs.

In the next step, we perform the SERS investigation of the fabricated substrate for a commonly used Raman active dye sample- MG. The fabricated substrate was treated with 1 μM MG solution for 6 hours and then was allowed to dry for 1 hour in room temperature environment. Figure 15*(a)* shows the characteristic Raman signal of MG treated SERS substrate as recorded by the Raman spectrometer. The same figure also includes the characteristic Raman signal for bare diatom and AuNPs assembled diatom without the MG. To investigate the role of diatom frustule towards enhancement of Raman signal we perform another set of study. 10 μl of 1 μM MG solution was dispensed on the fabricated SERS substrate and an equal amount of the same sample was dispensed on AuNP coated plane glass substrate. Figure 15*(b)* shows the characteristic Raman signals measured by the spectrometer for these two situations. Clearly as compared to the plane, substrate Raman signal from the fabricated SERS substrate is enhanced by ~111 fold for the considered sample. This enhancement is mainly attributed to the periodical structure of the diatom frustule which contributes to the GMR of the incident laser beam and thus, strong LSPR field coupling results in the structure.

In the next step of the present work, we performed the SERS study with the fabricated substrate for different concentration Raman active samples. Four different samples of concentration 1 μM, 100 nM, 10 nM and 1 nM, of MG were treated with proposed SERS substrates. Upon attachment of these sample with the substrates, intensities of the scattered Raman signals were recorded by the spectrometer. Figure 16*(a)* depicts the strength of the Raman signals for different concentration MG samples as scattered from the SERS substrates. Three distinct Raman peaks at 808, 1186 and 1618 cm^{-1} which are the signature Raman shift of MG have been considered in the present study and the strength of these peaks are observed to be decreased with the decrement in concentration of MG in the solution. Using the fabricated SERS substrate, MG concentration upto 1 nM could be detected with the Raman spectrometer.

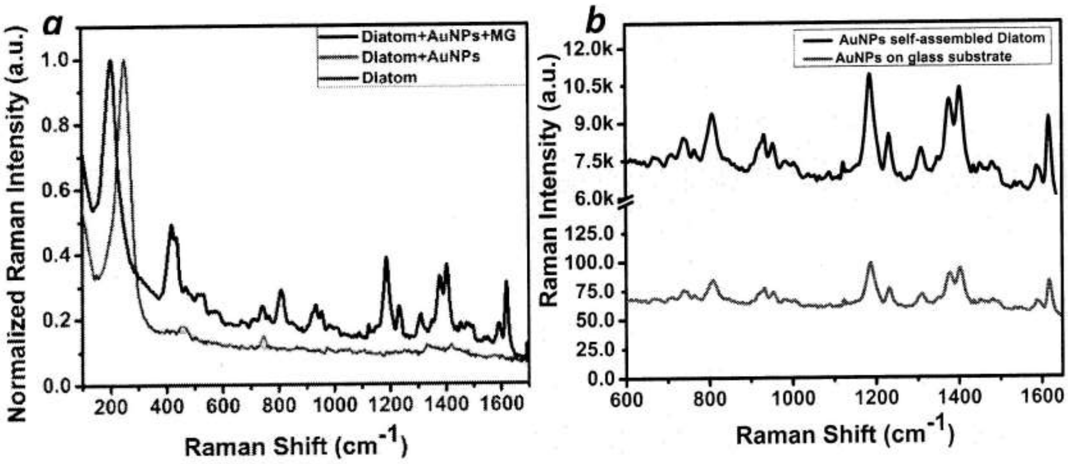


Figure 15: *(a)* Scattered Raman spectra for clean diatom frustule, AuNPs assembled diatom and MG treated SERS substrate, *(b)* comparison of Raman signal intensities of scattered from MG treated plane glass substrate and from the proposed SERS substrate.

To evaluate the performance of the proposed SERS substrate for different dimension AuNPs, the synthesized AuNPs of dimensions 20 nm, 40 nm and 60 nm were allowed to assemble on three substrate which was followed by treatment with 10 μL of 2 μM MG solution. Figure 16 (b) illustrates the characteristic Raman signal intensity scattered from the SERS substrates coated with different dimension AuNP in the present study. Clearly, among the three different sizes AuNPs, the Raman signal intensity is found to be the highest for 40nm

AuNPs. This is attributed to the enhanced coupling condition of the incident electromagnetic field from the laser source with the 40nm AuNPs which eventually scatters strong Raman signal from the Raman active samples. This has also been observed during simulation study for the proposed SERS substrate.

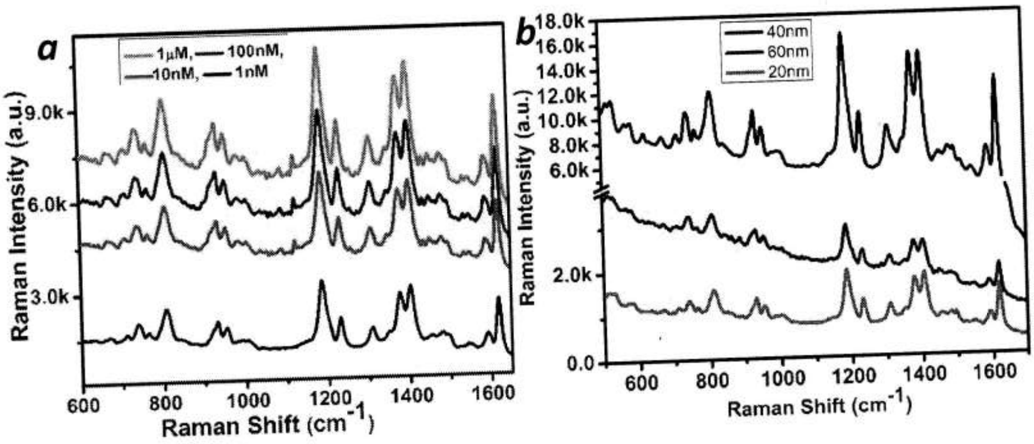


Figure 16: *(a)* Raman signal intensities measured by the spectrometer for different concentrations of MG from the designed SERS substrate, *(b)* Comparison of Raman signal intensities of 2 μM MG scattered from three different substrates treated with 20 nm, 40 nm and 60 nm AuNPs.

In the next step of the present study, we investigate the variation in back-scattered Raman signal intensity of MG for different concentration of AuNPs attached to the proposed SERS substrate. Two more different concentrations AuNPs solutions have been prepared by diluting the 40 nm synthesized AuNPs solution with distilled water in the ratio 1:1 and 1:4 and then treated with the substrates for attachment. Figure 17 shows the characteristic Raman signal intensity for 1 μM MG attached to these substrate as recorded by the spectrometer. Clearly, with the decrease in AuNPs concentration, the Raman signal intensity is observed to be decreased, which was attributed to the decrease in hot spot density in the active area of the proposed substrate.

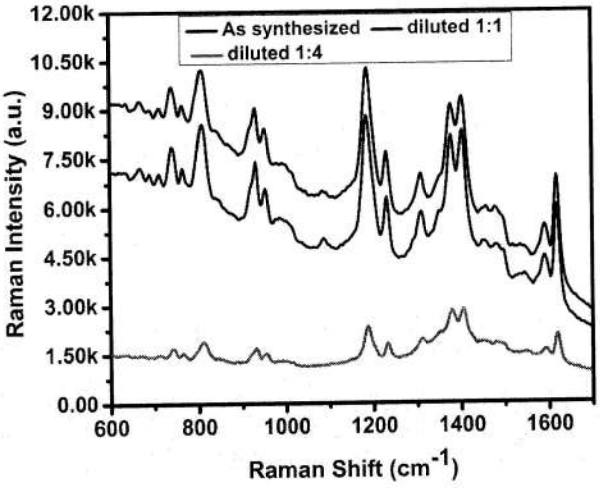


Figure 17: Characteristic Raman signal intensities of 1 μM MG scattered from three different substrates treated with AuNPs of different concentration. Clearly intensity of the scattered Raman signal reduces with decrease in concentration of the AuNPs assembled on the substrate.

We evaluate the reproducibility of the fabricated SERS substrate in the following manner. First, we estimate the size of the laser beam spot which was calculated to be 3μm. This ensures that the size of the beam is smaller than the average size of the diatom frustule. This implies average enhancement of Raman signal at different locations of the same diatom frustule by scanning of the laser beam over the substrate. The SERS substrate was mounted on a micron resolution (5 μm) x-y-z translation stage and an average Raman signal intensities of MG from different locations of the substrate were recorded. Figure 18 illustrates the scattered Raman signals measured from 10 different locations on the substrate. The RSD value for the Raman peaks 808, 1186 and 1618 cm^{-1} were calculated to be 6.81%, 7.57% and 4.74% respectively. This infers that the proposed SERS substrate could emerge as an inexpensive alternative for development of SERS substrate. This investigation has been carried out for three weeks and we observed similar results in each trail.

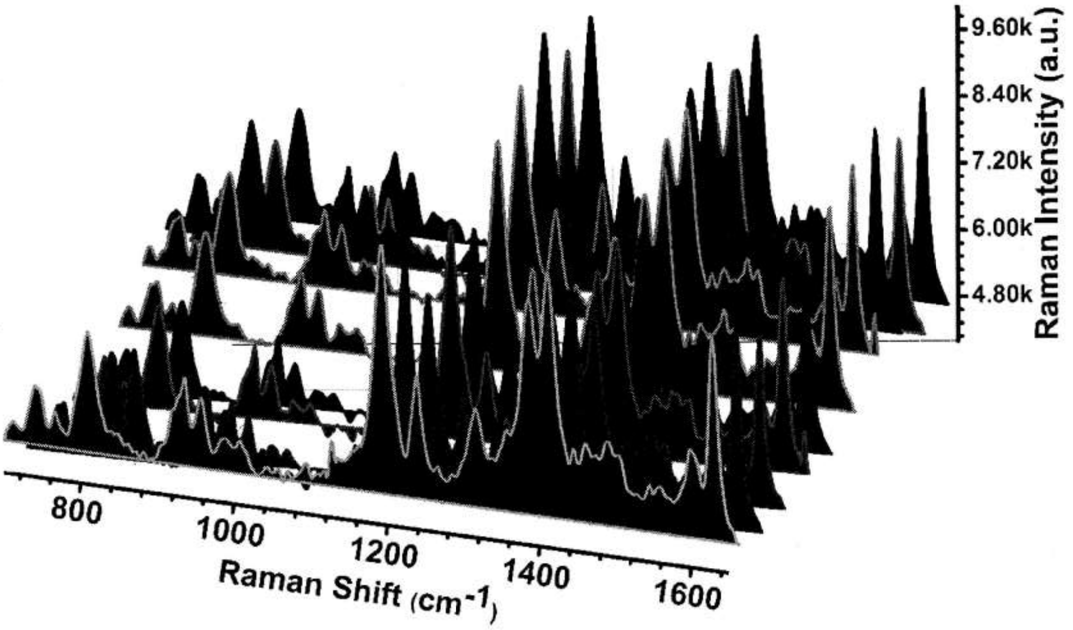


Figure 18: Back scattered Raman signal intensities of 1 μM MG recorded from 10 different locations of the proposed substrate.

In the final step, we demonstrate the practical applications of the proposed SERS substrate. Here we estimate fluoride level concentration in water using the designed substrate. The Raman peaks for fluoride are found to be prominent at 1084 and 1288 cm^{-1}. The fabricated substrates were treated with four different concentrations fluoride contained water samples for 6 hours. Upon attachment of the fluoride with the SERS substrate, we studied the intensity of back-scattered Raman signal from the substrate at 785nm laser excitation wavelength. Figure 19 shows the characteristic Raman spectrum from different concentration fluoride samples. For this specific chemical, fluoride concentration level as low as 100nM could be measured reliably by the spectrometer. Below 100nM, the measured Raman signal yields poor signal to noise ratio. Finally the reproducibility of the designed SERS substrate for fluoride sample has been tested. Raman signal intensities of back-scattered signals from 10 different locations of the fluoride treated SERS substrate have been recorded by the spectrometer. Figure 20 illustrates the reproducibility of the Raman signal recorded from 10 different locations of the substrate. We considered two prominent Raman shift at 1084 and 1288 cm^{-1} and the RSD values of the designed SERS substrate at these peaks were found to be 17.26% and 18.49% respectively. Any designed substrate that yields RSD values as low as 20% or less can be considered to be reproducible SERS substrate.

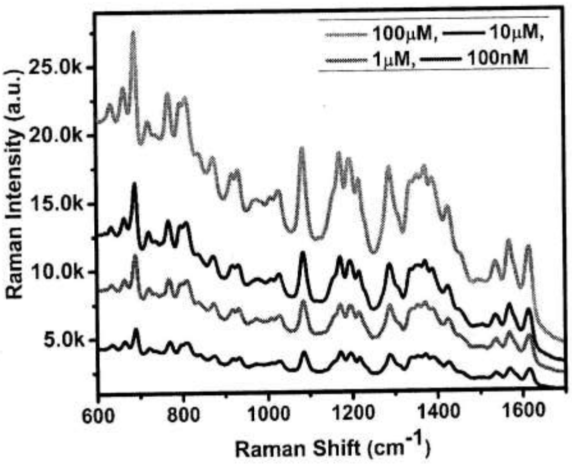


Figure 19: Raman signal intensities scattered from the SERS substrates when treated with different fluoride level concentrations in water.

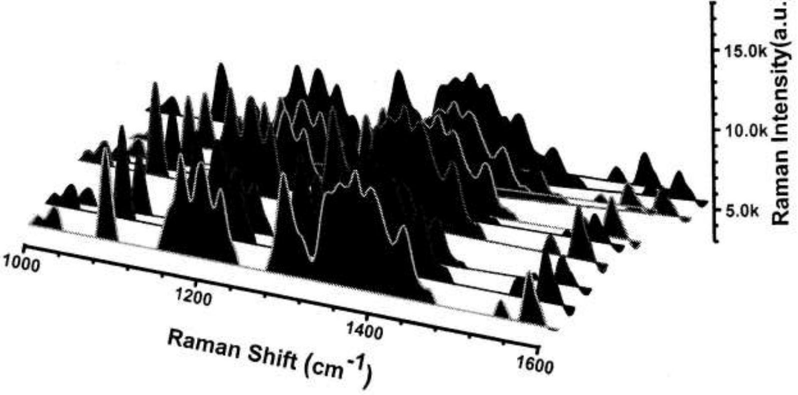


Figure 20: Back scattered Raman signal intensities of 10 μM fluoride recorded from 10 different locations of the proposed substrate.

Owing to the involvement of simple and relatively low cost approach of obtaining SERS substrate with naturally available diatom frustule we envision that the proposed technique of SERS based study could emerge as an alternative to other existing SERS substrates which could be obtained using sophisticated lithographic techniques. With RSD 20% or less from the fabricated substrate it is further believed that the designed substrate would be suitable for studying of Raman signals from an unknown sample. In order to check the stability of the substrate we record the Raman signals of the MG treated SERS substrate every day for one week and observed almost stable results under similar operating conditions of the spectrometer. This indicates the good life span and stability of the substrate. Figure 21 illustrates the histogram representation of the peak Raman signal intensities at 808 cm^{-1}, 1186 cm^{-1} and 1618 cm^{-1} of 1 μM MG scattered from the designed SERS substrate which has been observed for one week. The error bars in the histogram represent the fluctuations of the captured Raman peak signal during the period of study. For the considered peak Raman signal, the maximum fluctuations that has been observed was ~4% of its average value corresponding to 1186 cm^{-1}.

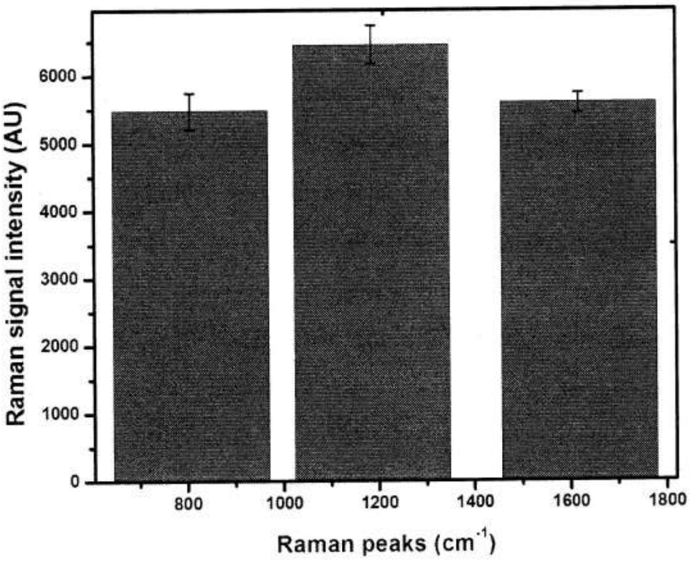
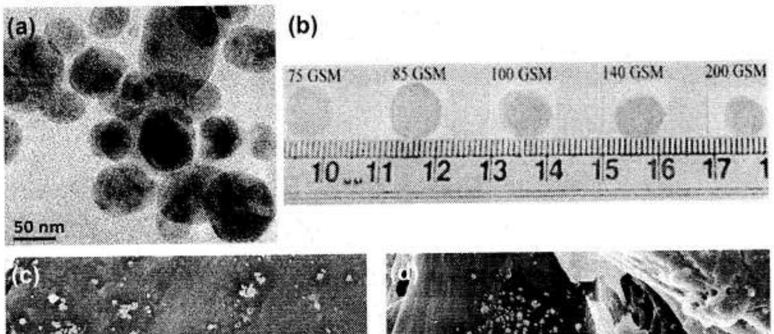


Figure 21: Stability characteristic of the proposed SERS substrate through study of Raman peaks fluctuations at 808 cm^{-1}, 1186 cm^{-1} and 1618 cm^{-1} for 1 μM MG treated on it for one week.

The proposed substrate can satisfactorily detect fluoride concentration level in water far below the danger limits (which is equivalent to 1.5 mg/L i.e. 78.954 μM) with good reproducibility. The designed SERS substrate can therefore be used for other SERS based sensing studies, which would be a cost effective technique as compared to its commercially available counterparts.

In the AgNPs diffused paper based SERS substrate we diffused synthesized AgNPs on the printed grade paper substrate and used this substrate for sensing applications. In order to synthesize AgNPs, 0.0274g of $AgNO_3$, 0.0135g of glucose, 0.05g of PVP and 0.00011g of sodium carbonate were added to 50ml of distilled water and stir for 10 minutes. The mixture was then heated to boil under vigorous stirring condition. The color of the solution gradually turned into light blackish color. 15 μL of triethylamine was then added to the mixture which turns the color of the solution into brown. Finally, the solution was centrifuged at 2500rpm for 20 min for four times by adding ethanol it. From the above steps, 17 wt% of AgNPs disperse in ethanol medium has been obtained. The formation of AgNPs in the solution was confirmed from TEM image. Figure 22 (a) shows the TEM image of the synthesized AgNPs. The average size of the sAgNPs was found to be 60 nm. In the present study 5 different grade GSM papers namely 75, 85,100, 140 and 200 GSM have been considered to evaluate the performance of the proposed paper based SERS substrate. Using a micropipette, 10µL of the synthesized AgNPs solution was pipetted on a clean paper substrate. Depending on the grade of the paper, the effective diffusion area of the paper substrate was varied between 50.26 mm^2 to 73.62 mm^2. Figure 22 (b) shows the photograph of the developed SERS substrates on different GSM papers while figure 22 (c), (d), (e), (f) and (g) show the FESEM images of AgNPs distribution on different paper substrates. Figure 22 (h) shows the EDX data that represents the composition of different elements present on the sensing region of the designed SERS substrate. From the FESEM images, it reveal that the distribution of AgNPs is primarily driven by pore size and surface morphology of the paper substrate. There could be two possible modes of diffusion namely in plane and lateral diffusion upon pipetting of the AgNPs colloidal solution on paper substrate. For lower grade GSM paper the lateral diffusion is found to be prominent while for higher grade GSM paper substrates the in plane diffusion process dominants over the later. Among the different grade paper substrate considered in the present study we notice a relatively uniform distribution of AgNPs on 100 GSM paper. This is attributed to the surface morphology and the porosity of this specific paper which causes optimized condition for lateral diffusion of AgNPs on the paper substrate. As compared to in plane diffused AgNPs, the surface deposited AgNPs will be primarily responsible for generating of the LSPR field upon coupling of the incident laser beam.



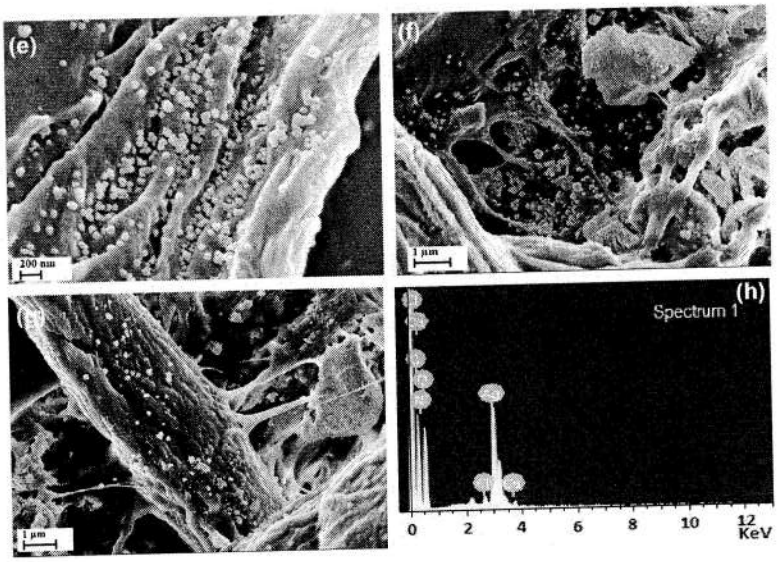


Figure 22. (a) TEM image of synthesized AgNPs, (b) Photo images of SERS substrates fabricated on different GSM papers. The dispersed area of AgNPs varies from 50.26 mm^2 to 73.62 mm^2. FESEM images of AgNPs distribution on (c) 75 GSM, (d) 85 GSM, (e) 100 GSM, (f) 140 GSM and (g) 200 GSM paper substrates. 10 µL of the synthesized AgNPs colloidal solution was pipetted on each paper substrate. (h) EDX data represent the elements composition on the sensing region of 100 GSM SERS substrate

Two commonly used Raman active chemicals namely MG and R6G in solvent form have been treated separately with the fabricated SERS substrates. Using a micropipette, 10 µL of each of the chemicals with 1µM concentration was dispensed on the sensing region of the substrate. Upon drying of the samples on the sensing region, scattered Raman signals were recorded by a Raman spectrometer. The corresponding results are shown in figure 23 (a) and (b) for MG and R6G respectively. It has been observed that with100GSM SERS substrate, the average Raman signal enhancement is found to be the highest amongst all the considered substrate for both the samples. This is attributed to the uniform distribution of AgNPs on 100GSM paper substrate that subsequently produces the highest average LSPR field magnitude upon coupling of the incident laser signal. Thus the intensity of the scattered Raman signals from Raman active samples would then be the highest for this SERS substrate.

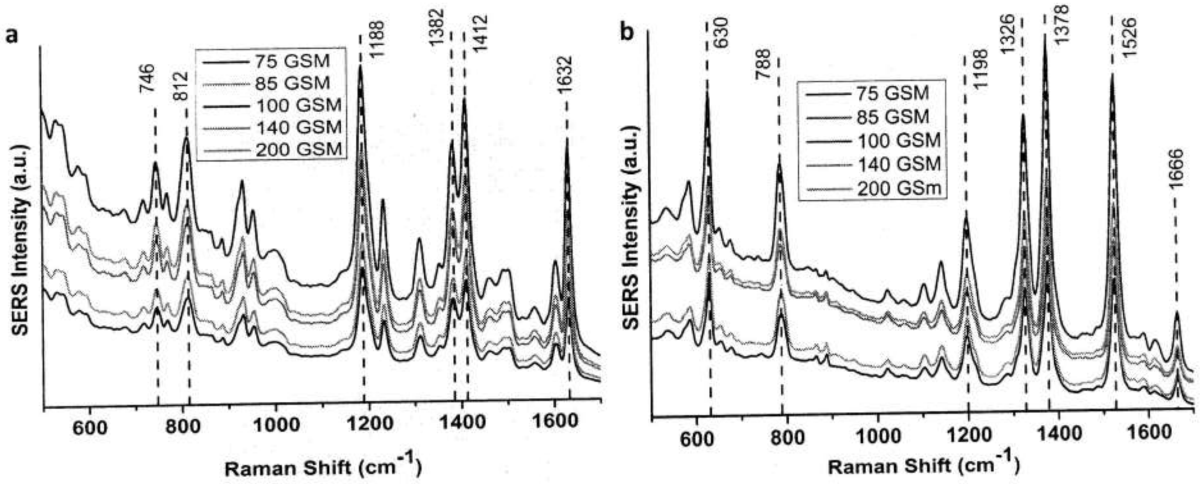


Figure 23. Raman signal intensities of (a) MG and (b) R6G on different types of papers namely 75 GSM, 85 GSM, 100 GSM, 140 GSM and 200 GSM paper substrate. 10 μL AgNPs of both the samples of concentration of 1 μM each has been dispensed on different GSM paper substrate.

In the next step, different concentrations of the considered samples have been treated on the sensing region of the substrates and scattered Raman signals from the substrates were recorded by the spectrometer. Figure 24 (a) and (b) describe the relative Raman signal intensities for different concentration of MG and R6G respectively scattered from 100 GSM SERS substrate. Here, we have considered the SERS substrate on 100 GSM paper as it yields the highest average field enhancement among all the considered paper substrates. The minimum concentration that could be recorded reliably by the spectrometer was 0.1nM for MG and 1nM for R6G. Below this concentration, we noticed poor signal to noise ratio in the scattered Raman signals. For references, we include Raman signal intensities of 1mM of both these chemicals taken on bare paper substrate.

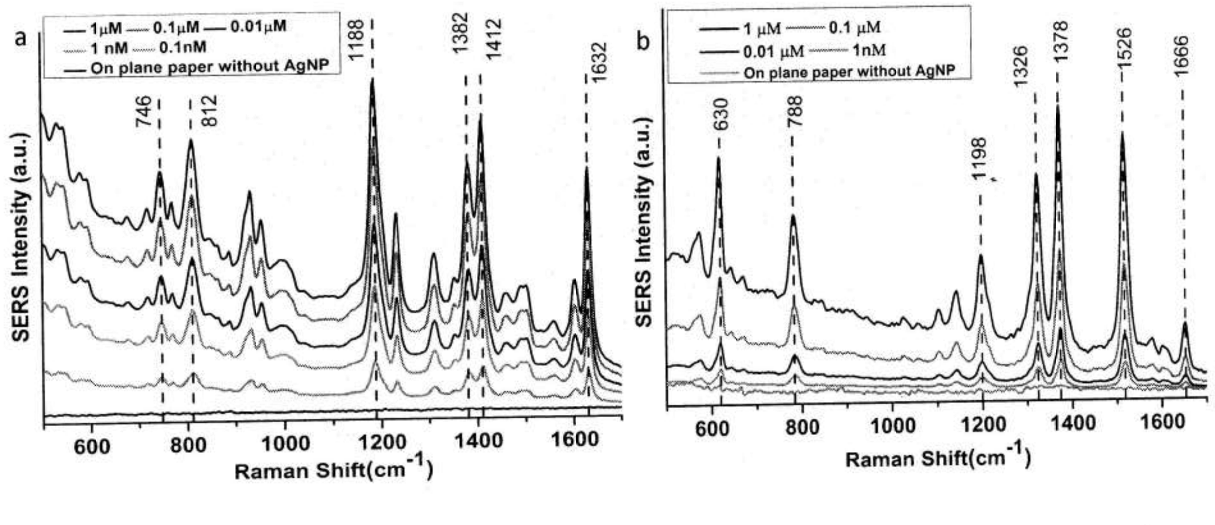


Figure 24: Recorded Raman spectra scattered from the substrate for different concentrations of (a) MG and (b) R6G along with a comparison of the design substrate with plane paper.

In order to investigate the reproducibility characteristic of the proposed SERS substrate 1μM of both the samples of MG and R6G were treated separately on 10 different 100 GSM SERS substrates. The back scattered Raman signal of these samples were recorded from 5 different locations of each SERS substrate. Figure 25 (a) and (b) shows the reproducibility characteristic of the designed substrate for MG and R6G respectively. For the signature Raman peaks of MG at 812 cm^{-1}, 1188 cm^{-1} and 1632 cm^{-1}, we notice maximum relative standard deviation (RSD) of 12.51%, 11.94% and 12.89% respectively while for R6G the maximum RSDs at 788 cm^{-1}, 1526 cm^{-1} and 1666 cm^{-1} were observed to be 8.70%, 13.15% and 10.35% respectively. The low RSD values of the Raman peaks for both the samples reveal that the proposed SERS substrate is highly reproducible. The error bars shown in these figures represent the fluctuations of the reading from its average value.

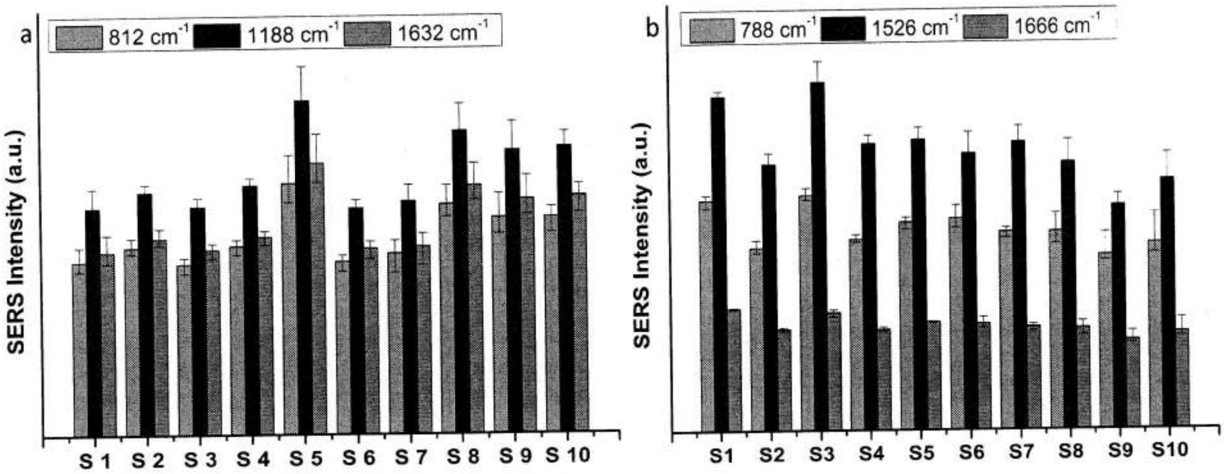


Fig 25. Reproducibility characteristics of the developed SERS substrate through a study of Raman peak intensity fluctuations of (a) MG at 812 cm^{-1}, 1188 cm^{-1} and 1632 cm^{-1} and (b) R6G at 788 cm^{-1}, 1526 cm^{-1} and 1666 cm^{-1} on 10 substrates for each sample.

Owing to the fact that PVP capped AgNPs are relatively inert towards oxidation process, we evaluate the performance of PVP capped AgNPs SERS substrate over a period of time and compare the results with respect to a bare AgNPs treated paper substrate. Following the work reported by Wei et al 2010, we synthesized 0.0033M bare AgNPs colloidal solution in deionized (DI) water medium. 10μL of the synthesized AgNPs was pipetted on 100 GSM SERS substrate and subsequently treated with MG and R6G separately. Raman signal intensities of these chemicals for both PVP capped AgNPs and bare AgNPs SERS substrates have been studied for 7 days. Figure 26 (a) and (b) illustrate the time evaluation performance of these substrates for MG, while figure 26 (c) and (d) represent the performance of the substrates for R6G. Clearly, as compared to bare AgNPs SERS substrates the PVP capped AgNPs SERS substrates yield stable Raman signals for a considered period of time. The gradual degradation of Raman peaks signal in bare AgNPs SERS substrate is attributed to the oxidation of metal nanoparticles which subsequently affects the LSPR field strength and thus, the strength of the scattered Raman signals from such substrate degrade with time.

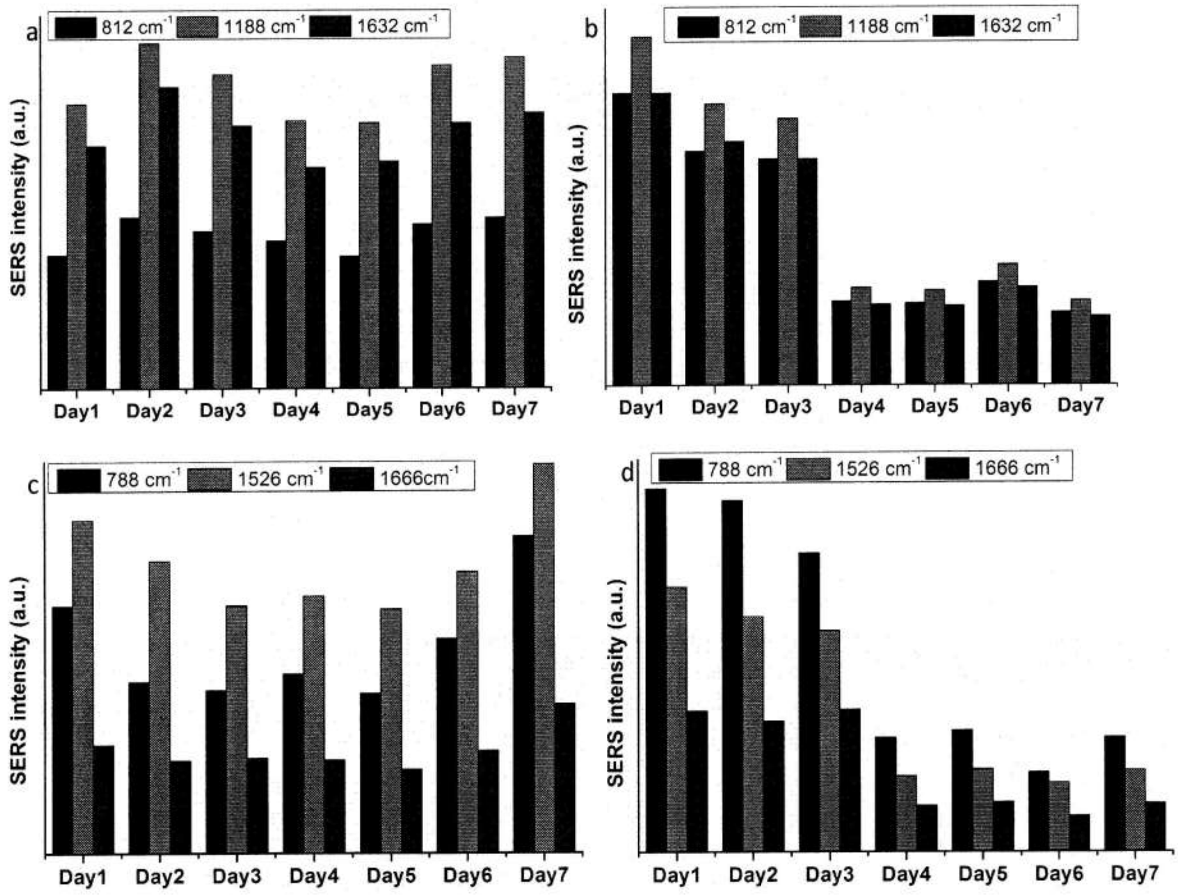


Figure 26. A comparison of performance of stability between PVPcapped AgNPs and bare AgNPs diffused SERS substrate for two considered samples MG and R6G. (a) and (b) represent Raman signal intensities variations with time corresponding to the peaks 812 cm^{-1}, 1188 cm^{-1} and 1632 cm^{-1} of MG for PVPcapped AgNPs and bare AgNPs SERS substrate respectively and, (c) and (d) represent Raman signal intensities variations with time corresponding to the peaks 788 cm^{-1}, 1526 cm^{-1} and 1666 cm^{-1} of R6G for PVP capped AgNPs and bare AgNPs SERS substrate respectively

As far as the fabrication process of the proposed SERS substrate is concerned, the technique is simple and can be easily obtained within 30 minutes upon treatment of the paper with AgNP colloidal solution followed by air-drying of the paper. To develop approximately 1cm^2 SERS active area on paper substrate the net cost involved was less than rupees 5.00 (< $0.08) which is significantly lesser than the price of a commercially available SERS substrate. For large scale production, the cost would be reduced further. Although, AgNPs colloidal solution has been synthesized in the laboratory during study of the proposed SERS substrate, the sizes of AgNPs were varied between 40 nm to 80 nm. This size variation of metal nanoparticles deposited at the pores of the paper substrate could lead to fluctuations of Raman signal intensities when measured from different locations on the substrate.

10. Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject:

The main purpose of this research work is to develop low-cost disposable SERS substrate and keeping this purpose in mind the PI research group initially tried with electron beam lithography (EBL) and then planned to transfer the pattern on to PET sheet by using replica molding technique. But non availability of replica molding unit at the host institute this approach was limited to EBL fabrication approach only. However with the help of this substrate rhodamineB concentration as low as 1nM with reasonably good reproducibility (RSD value of 13%) can be detected. Even though this substrate produces Raman signal with good reproducibility the fabrication cost and requirement of sophisticated laboratory and instruments don't serve our purpose. Therefore we were looking for alternative to the requirement of sophisticated instruments and laboratory facilities. And we developed SERS substrate by attaching gold nano-particles (AuNPs) on diatom frustules. With this substrate the malachite green concentration as low as 1nM with maximum RSD value of 7.57% and fluoride concentration of 100 nM with maximum RDS value of 18.49% could be detected. Lastly we have developed SERS substrate by diffusing silver nano-particles on printed grade paper substrate. With our developed substrate malachite green concentration of 0.01nM and rhodamine6G concentration as low as 1nM can be detected. The substrate yields a very good reproducibility with maximum RSD value of 12.89% for malachite green and 13.56% for rhodamine6G. This substrate also have good repeatability and life span. Owing to the simple and cost efficient approach in generation of these two substrates, PI believe that these two substrates can be used as disposable substrate in the SERS based investigations.

11. Conclusions summarizing the achievements and indication of scope for future work:

In summary throughout this project work the PI research group has done rigorous simulation study on different structure and finally developed low-cost disposable SERS substrate where very few simple steps are involve in generation.

In the first steps i.e. in the simulation study we studied the enhanced LSPR field conditions for different periodic AuNP structures. And our simulation results reveal that as compared to uniformly structured AuNP, periodically varying height AuNP provides relatively enhanced LSPR field conditions over the patterned region. By controlling pillar height difference, pillar diameter and spacing in the structure, a highly enhanced LSPR field condition can be achieved with enhancement factor of 1.32. We envision that the proposed periodic AuNP structure can be developed as a sensing region for different LSPR-based sensing investigations especially for SERS-based sensing investigations.

In the next step of our project work we design a highly reproducible SERS substrate with increased hot spot density. The patterned structure has been fabricated using EBL. Experimentally, the EF of the fabricated SERS substrate is measured to be 3.27×10^8 and the pattern was found to be highly reproducible. It is envisioned that the designed pattern can be produced in mass scale on low-cost plastic sheet and can be used as flexible and disposable SERS substrate. Possible real field applications of the plastic SERS substrate will be explored.

We also present a cost-effective approach to fabricate a SERS substrate with a good degree of reproducibility using a diatom frustule as a template. Owing to its cost-effectiveness and simplicity, the proposed technique is a promising alternative compared to other, more sophisticated, fabrication methods. It is envisioned that the designed substrate could be used for sensing chemicals, biomolecules and drugs at an affordable cost.

In the final step we propose a very simple and extremely cost-efficient technique to develop SERS substrate on paper. The developed SERS substrate yields a good reproducibility characteristic with maximum RSD of 12.89% and 13.56% for MG and R6G respectively. Further, it has been observed that due to the presence of capping agent the developed SERS substrate has a good life span. We envisioned that the proposed SERS substrate can be used as an ultra-low-cost disposable SERS substrate for detection and analysis of Raman signals of chemicals, biological samples in the near future.

12. S&T benefits accrued:

i. List of Research publications

S No	Authors	Title of paper	Name of the Journal	Volume	Pages	Year
1	Nabadweep Chamuah and P.Nath	Periodically varying height in metal nanopillar for enhanced generation of localized surface	Plasmonics	10	1367-72	2015

		Plasmon field				
2	Nabadweep Chamuah, G.P.Vaidya, A.M.Joseph and P. Nath	Diagonally Aligned Squared Metal Nano-Pillar with increased hotspot density as a highly reproducible SERS substrate	Plasmonics		1-6	2016
3	Nabadweep Chmauah, L.Chetia, N.Zahan, S.Dutta, G.A Ahamad and P. Nath	Naturally occurring diatom frustules as SERS substrate for detection and analysis of chemicals	Journal of Physics D: applied Physics	50		2017

ii. Manpower trained on the project

a) Research Scientists or Research Associates

b) No. of Ph.D. produced: 1

c) Other Technical Personnel trained iii.

Patents taken, if any

13. Financial Position:

No	Financial Position/ Budget Head	Funds Sanctioned	Expenditure	% of Total cost
I	Salaries/ Manpower costs		1,74,968.00	
II	Equipment		14,00,000.00	
III	Supplies & Materials		2,12,649.00	
IV	Contingencies		29,103,00	
V	Travel		32,120.00	
VI	Overhead Expenses		3,08,039.00	
VII	Others, if any			
	Total		21,56,879.00	**100%**

14. Procurement/ Usage of Equipment

a)

S No	Name of Equipment	Make/Model	Cost (FE/ Rs)	Date of Installation	Utilisation Rate (%)	Remarks regarding maintenance/ breakdown
1	Raman Spectrometer	EZRaman	USD 18,590.00	Sep 2, 2014	100%	
2	Optical bread boear	Optochem Internationals	Rs 56,678.00	Aug 1, 2014	100%	
3	COMSOL multiphysics software	COMSOL	Rs 2,43,713.00	July 1, 2014	100%	

b) Plans for utilizing the equipment facilities in future

The equipment facilities will be used in the future course of research work. Which will help the researcher in this region of country. It is also mentioned that during this project period many students of this university were got the access to the Raman spectrometer which has been procured from the equipment head of this research grant.

Name and Signature with Date

a.___________________________

(Principal Investigator)

b.___________________________

(Co-Investigator)

Consolidated Statement of Expenditure

Project title: **"Design consideration of SERS substrate for getting extremely enhanced Raman signal"** for the period **1st April 2016 to 31st March 2017**

Sr No (I)	Sanctioned Heads (II)	Total Funds Allocated (sanctioned (III)	Expenditure Incurred				Total Expenditure till 31st March 2017 (VIII = IV + V + VI+VII)	Balance as on 31st March 2017 (IX = III – VIII)	Requirement of Funds upto 31st March 2018	Remarks (if any)
			1st Year (3rd March 2014 to 31st March 2014) (IV)	2nd Year (1st April 2014 to 31st March 2015) (V)	3rd Year (1st April 2015 to 31st March 2016) (VI)	4th Year (1st April 2016 to 31st March 2017) (VII)				
1.	Manpower costs	8,40,000/- (Recurring)		1,74,968/-			1,74,968/-	1,29,276/-	2,16,000/-	
2.	Consumables		19,999/-	50,000/-	12,700/-	1,29,950/-	2,12,649/-		50,000/-	
3.	Travel			15,000/-		17,120/-	32,120/-		15,000/-	
4.	Contingencies		12,528/-		4,975/-	11,600/-	29,103/-		50,000/-	
5.	Others, if any									
6.	Overhead expenses		93,750/-	5,6024/-	93,750/-	18,360/-	2,61,884/-		1,53,000/-	
7.	Equipment	14,00,000/- (Non-recurring)		14,46,155/-			14,46,155/-	-46,155/-*		
8.	Total	22,40,000/-	1,26,277/-	17,42,147/-	1,11,425/-	1,77,030/-	21,56,879/-	83,121/-	4,84,000/-	

* Due to escalation of dollar price, an excess amount of Rs. 46,155/- has been utilized from overhead towards purchase of **Raman spectrometer.**

Name and Signature of Principal Investigator: (PABITRA NATH)

Date: June 5, 2017

Signature of Competent Financial authority: 20/8/17

(with seal) Date:

Finance
Tezpur Univers

UTILISATION CERTIFICATE (2 COPIES)

[FOR THE FINANCIAL YEAR 2016-17 (ENDING 31st MARCH 2017)]

1. Title of the Project/ Scheme: "**Design Consideration of SERS substrate for getting extremely enhanced Raman signal**"

2. Name of the Institution: **Tezpur University**

3. Name of the Principal Investigator: **Dr. Pabitra Nath**

4. Science & Engineering Research Board (SERB)
Sanction order No & date sanctioning the project: **SERB/F/5522/2013-14**
(First financial sanction order) **dated 27.11.2013**

5. Head of account as given in the original sanction order: **Recurring**

6. Amount brought forward from the previous Financial year 2016-17 quoting SERB letter no and date the said in which the authority to carry forward amount was given	i. Amount **₹. 3,06,306/-** ii. Letter No: **SERB/F/6024/2015-16 dated 5.12.2015** iii. Date: **17.12.2015**
7. Amount received during the financial year (2016-17)	i. Amount : **NIL** ii. Order No : **NA** iii. Date : **NA**
8. Total amount that was available for expenditure (excluding commitments) during the financial year 2016-2017 (Sr. No. 6+7)	**₹ 3,06,306/-**
9. Actual Expenditure (excluding commitments) Incurred during the financial year 2016-17	**₹. 1,77,030/-**

10. Balance amount available at the end of the financial year: **₹. 1,29,276/-**
(2016-17)

11. Unspent balance refunded, if any (please give details of cheque no etc.): **NA**

12. Amount to be carried forward to the next financial year (if applicable): **₹. 1,29,276/-**
(2017-18)

Finance Officer
Tezpur University

UTILISATION CERTIFICATE

Certified that out of **NIL** of grants-in-aid sanctioned during the year **2016-17** in favor of **NA** vide SERB order No. **NA** And **₹. 3,06,306/-** remain unspent during the year 2015-16. A sum of **₹. 1,77,030/-** has been utilized and **₹. 1,29,276/-** remain unspent during the year 2016-17. A sum of **₹. 1,77,030/-** has been utilized for the purpose of **1. Consumable exp. 2. Contingency exp. and 3. Overhead exp.** for which it was sanctioned and that the balance of **₹. 1,29,276/-** remaining unutilized at the end of the year 2016-17 will be adjusted towards the grants-in-aid payable during the next year i.e. 2017-2018.

Signature of PI
Date: June 5, 2017

4/7/17
Signature of Registrar/
Head of the Institute
Date:
Registrar
Tezpur University

20/6/17
Accounts Officer of the
Institute
Date:
Finance Officer
Tezpur University

(Countersigned in SERB)
Signature:__________
Designation:__________
Date:__________

REQUEST FOR ANNUAL INSTALMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE

(Two copies)

1. SERB Sanction Order No and date: SERB/F/5522/2013-14 dated 27.11.13

2. Name of the PI : Dr. Pabitra Nath

3. Total Project Cost : 27,24,000/-

4. Revised Project Cost :
(if applicable)

5. Date of Commencement: 03.03.2014

6. Statement of Expenditure:
(Month wise expenditure incurred during current financial year)

Month & year	Expenditure incurred/ committed
April 2014	Fellowship
May 2014	Fellowship and Purchase of AC
June 2014	Travel and Fellowship
August 2014	Fellowship and consumables
September 2104	Fellowship and Purchase of Printer
November 2014	Fellowship
December 22014	Fellowship
January 2015	Fellowship and consumables
February 2015	Fellowship
February 2016	Contingency, consumables and overhead
September 2016	Contingency, consumables
November 2016	Contingency, consumables and overhead
January 2017	Contingency, consumables
March 2017	Contingency, consumables, Travel

I. Grant received in each year:
a. 1st Year: 4,40,000/-
b. 2nd Year: 4,00,000/-
c. 3rd Year:
d. Interest, if any:
e. Total (a+b+c+d): 8,40,000/-

Statement of Expenditure

Project title: **"Design consideration of SERS substrate for getting extremely enhanced Raman signal"** for the period **1st April 2016 to 31st March 2017**

Sr No (I)	Sanctioned Heads (II)	Total Funds Allocated (sanctioned (III)	Expenditure Incurred				Total Expenditure till 31st March 2017 (VIII = IV + V + VI+VII)	Balance as on 31st March 2017 (IX = III - VIII)	Requirement of Funds upto 31st March 2018	Remarks (if any)
			1st Year (3rd March 2014 to 31st March 2014) (IV)	2nd Year (1st April 2014 to 31st March 2015) (V)	3rd Year (1st April 2015 to 31st March 2016) (VI)	4th Year (1st April 2016 to 31st March 2017) (VII)				
1.	Manpower costs	8,40,000/-		1,74,968/-			1,74,968/-	1,29,276/-	2,16,000/-	
2.	Consumables		19,999/-	50,000/-	12,700/-	1,29,950/-	2,12,649/-		50,000/-	
3.	Travel			15,000/-		17,120/-	32,120/-		15,000/-	
4.	Contingencies		12,528/-		4,975/-	11,600/-	29,103/-		50,000/-	
5.	Others, if any									
6.	Overhead expenses		93,750/-	5,6024/-	93,750/-	18,360/-	2,61,884/-		1,53,000/-	Due to escalation of dollar price, an excess amount of Rs, 46,155/- has been utilized from this head towards purchase of **Raman spectrometer** (Enwave Optronics)
7.	Equipment									
8.	Total	8,40,000/-	1,26,277/-	2,95,992/-	1,11,425/-	1,77,030/-	7,10,724/-	1,29,276/-	4,84,000/-	

Name and Signature of Principal Investigator:

Date: June 5, 2017

Signature of Competent 20/6/17
Financial authority:

(with seal) Date:

UTILISATION CERTIFICATE (2 COPIES)
[FOR THE FINANCIAL YEAR 2016-17 (ENDING 31st MARCH 2017)]

1. Title of the Project/ Scheme : **"Design Consideration of SERS substrate for getting extremely enhanced Raman Signal"**

2. Name of the Institution : **Tezpur University**

3. Name of the Principal Investigator: **Dr. Pabitra Nath**

4. Science & Engineering Research Board (SERB)
Sanction order No & date sanctioning the project: **SERB/F/5522/2013-14**
(First financial sanction order) **dated 27.11.2013**

5. Head of account as given in the original sanction order: **Non-Recurring**

6. Amount brought forward from the previous Financial year 2015-16 quoting SERB letter no and date the said in which the authority to carry forward amount was given
i. Amount **₹ -46,155/-**
ii. Letter No: **SERB/F/5522/2013-14**
dated 27.11.2013
iii. Date : **20.02.2014**

7. Amount received during the financial year 2016-17
(Please give SERB Sanction order no and date)
i. Amount : **NIL**
ii. Order No : NA
iii. Date : **NA**

8. Total amount that was available for expenditure (excluding commitments) during the financial year 2015-16 (Sr. No. 6+7) **₹ -46,155/-**

9. Actual Expenditure (excluding commitments) Incurred during the financial year 2016-17 **₹ NIL**

10. Balance amount available at the end of the financial year 2016-17: **₹ -46,155/-**

11. Unspent balance refunded, if any (please give details of cheque no etc.): **NA**

12. Amount to be carried forward to the next financial year (if applicable): **₹ -46,155/-**
(2017-18)

Finance Officer
Tezpur University

UTILISATION CERTIFICATE

Certified that out of ₹. **NIL** of grants-in-aid sanctioned during the year **2016-17** in favor of **NA** vide SERB order No. **NA** dated **NA**. And ₹. **-46,155/-** remain unspent during the year 2015-17, a sum of ₹. **NIL** has been utilized for the purpose of **NA** during the year 2016-17 for which it was sanctioned. The excess expenditure of ₹. **46,155/-** will be adjusted towards the grants-in-aid payable during the next year i.e. 2017-2018.

Signature of PI

Date: June 5, 2017

6/7/17
Signature of Registrar/
Head of the Institute
Date:

Registrar
Tezpur University

20/6/17
Accounts Officer of the
Institute
Date:

Finance Officer
Tezpur University

(Countersigned in SERB)
Signature:__________
Designation:__________
Date:__________

REQUEST FOR ANNUAL INSTALMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE

(Two copies)

1. SERB Sanction Order No and date: SERB/F/5522/2013-14 dated 27.11.13

2. Name of the PI : Dr. Pabitra Nath

3. Total Project Cost : 27,24.000/-

4. Revised Project Cost :
(if applicable)

5. Date of Commencement :03.03.2014

6. Statement of Expenditure :
(month wise expenditure incurred during current financial year)

Month & year	Expenditure incurred/ committed
July 2014	Equipment
July 2014	Equipment
March 2015	Equipment

1. Grant received in each year:
a. 1st Year: 14,00,000/-
b. 2nd Year:
c. 3rd Year:
d. Interest, if any:
e. Total (a+b+c+d): 14,00,000/-

Statement of Expenditure

(1^{st} April 2016 to 31^{st} March 2017)

Title: Design consideration of SERS substrate for getting extremely enhanced Raman Signal

Sr No (I)	Sanctioned Heads (II)	Total Funds Allocated (indicate sanctioned or revised (III)	Expenditure Incurred				Total Expenditure till 31st March 2017 (VIII= IV + V + VI+VII)	Balance as on 31st March 2017 (IX = III – VIII)	Requirement of Funds upto 31st March 2018	Remarks (if any)
			1st Year (3rd March 2014 to 31st March 2014) (IV)	2nd Year (1st April 2014 to 31st March 2015) (V)	3rd Year (1st April 2015 to 31st March 2016) (VI)	4th Year (1st April 2016 to 31st March 2017) (VII)				
1.	Manpower costs									
2.	Consumables									
3.	Travel									
4.	Contingencies									
5.	Others, if any									
6.	Equipment	14,00,000/-		1446155/-			1446155/-	-46155/-	46155/-	
7.	Overhead expenses									
8.	Total	1400000/-		1446155/-			1446155/-	-46155/-	46155/-	

Name and Signature of Principal Investigator:

Date: June 5, 2017

Signature of Competent financial authority: 20/6/17
Date:
(with seal)

UTILISATION CERTIFICATE (2 COPIES)

[FOR THE FINANCIAL YEAR 2016-17 (ENDING 31ST MARCH 2017)]

1. Title of the Project/ Scheme : **"Design Consideration of SERS substrate for getting extremely enhanced Raman Signal"**

2. Name of the Institution : **Tezpur University**

3. Name of the Principal Investigator: **Dr. Pabitra Nath**

4. Science & Engineering Research Board (SERB)
Sanction order No & date sanctioning the project: **SERB/F/5522/2013-14**
(First financial sanction order) **dated 27.11.2013**

5. Head of account as given in the original sanction order: **Non-Recurring**

6. Amount brought forward from the previous Financial year 2015-16 quoting SERB letter no and date the said in which the authority to carry forward amount was given	i. Amount **₹ -46,155/-** ii. Letter No: **SERB/F/5522/2013-14 dated 27.11.2013** iii. Date : **20.02.2014**
7. Amount received during the financial year 2016-17 (Please give SERB Sanction order no and date)	i. Amount : **NIL** ii. Order No : **NA** iii. Date : **NA**
8. Total amount that was available for expenditure (excluding commitments) during the financial year 2015-16 (Sr. No. 6+7)	**₹ -46,155/-**
9. Actual Expenditure (excluding commitments) Incurred during the financial year 2016-17	**₹ NIL**

10. Balance amount available at the end of the financial year 2016-17: **₹ -46,155/-**

11. Unspent balance refunded, if any (please give details of cheque no etc.): **NA**

12. Amount to be carried forward to the next financial year (if applicable): **₹ -46,155/-**
(2017-18)

Finance Officer
Tezpur University

UTILISATION CERTIFICATE

Certified that out of **₹. NIL** of grants-in-aid sanctioned during the year **2016-17** in favor of **NA** vide SERB order No. **NA** dated **NA.** And **₹. -46,155/-** remain unspent during the year 2015-17, a sum of **₹. NIL** has been utilized for the purpose of **NA** during the year 2016-17 for which it was sanctioned. The excess expenditure of **₹. 46,155/-** will be adjusted towards the grants-in-aid payable during the next year i.e. 2017-2018.

Signature of PI

Date: June 5, 2017

4/7/17

Signature of Registrar/
Head of the Institute
Date:

Registrar
Tezpur University

20/6/17

Accounts Officer of the
Institute
Date:

Finance Officer
Tezpur University

(Countersigned in SERB)
Signature:__________
Designation:__________
Date:__________

REQUEST FOR ANNUAL INSTALMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE

(Two copies)

1. SERB Sanction Order No and date: SERB/F/5522/2013-14 dated 27.11.13

2. Name of the PI : Dr. Pabitra Nath

3. Total Project Cost : 27,24,000/-

4. Revised Project Cost :
(if applicable)

5. Date of Commencement :03.03.2014

6. Statement of Expenditure :
(month wise expenditure incurred during current financial year)

Month & year	Expenditure incurred/ committed
July 2014	Equipment
July 2014	Equipment
March 2015	Equipment

1. Grant received in each year:
a. 1st Year: 14,00,000/-
b. 2nd Year:
c. 3rd Year:
d. Interest, if any:
e. Total (a+b+c+d): 14,00,000/-

Statement of Expenditure

(1st April 2016 to 31st March 2017)

Title: Design consideration of SERS substrate for getting extremely enhanced Raman Signal

Sr No (I)	Sanctioned Heads (II)	Total Funds Allocated (indicate sanctioned or revised (III)	Expenditure Incurred				Total Expenditure till 31st March 2017 (VIII= IV + V + VI+VII)	Balance as on 31st March 2017 (IX = III – VIII)	Requirement of Funds upto 31st March 2018	Remarks (if any)
			1st Year (3rd March 2014 to 31st March 2014) (IV)	2nd Year (1st April 2014 to 31st March 2015) (V)	3rd Year (1st April 2015 to 31st March 2016) (VI)	4th Year (1st April 2016 to 31st March 2017) (VII)				
1.	Manpower costs									
2.	Consumables									
3.	Travel									
4.	Contingencies									
5.	Others, if any									
6.	Equipment	14,00,000/-		1446155/-			1446155/-	-46155/-	46155/-	
7.	Overhead expenses									
8.	Total	1400000/-		1446155/-			1446155/-	-46155/-	46155/-	

Name and Signature of Principal Investigator:

Date: June 5, 2017

Signature of Competent financial authority: 20/6/17

Date:

(with seal)

Finance Officer

Tezpur University