FABRICATION OF SURFACE ROUGHENED PLASMONIC NANO-ARCHITECTURES FOR HIGHLY SENSITIVE SURFACE ENHANCED RAMAN SCATTERING APPLICATIONS

A REPORT

Submitted by

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Under the guidance of

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CERTIFICATE

This is to certify that ***Sri. Abhijith.T*** *has carried out a project entitled "****Fabrication of Surface roughened Plasmonic nano-architectures for Highly sensitive Surface Enhanced Raman Scattering Applications"*** *under my supervision at Photonics and Optical Nanoscopy Laboratory, Department of Physics and Chemistry, Indian Institute of Science Education and Research, Pune. This work is carried out as a fulfillment of the award* ***National Photonics Fellowship*** *by Department of Information Technology, India.*

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ABSTRACT

Surface roughened silver nano-spheres and nano-wires were fabricated using solution based synthesize procedure. Microscopy studies reveal the well defined morphology of nanostructures with highly roughened surfaces. Surface enhanced raman scattering spectra of rhodamine 6G molecules adsorbed on roughened metal nano-architectures were collected using confocal Raman imaging microscope with 100X objective lens and 632.81 nm laser. More interestingly, the significant enhancement in raman signal of the analyte was observed at cluster of nano-spheres and surface of nano-wires.

1. INTRODUCTION

One of the key challenges of single molecule detection is finding a suitable technique with high sensitivity and chemical specificity [1]. In 1974, Fleischmann et al observed the dramatic enhancement of Raman signal from the pyridine molecule adsorbed on the roughened metal surface and the phenomena is later known as Surface Enhanced Raman Scattering (SERS) [2]. Recently, the SERS technique has been achieved great interest in various disciplines of science including molecular nano-photonics, quantum optics, biochemistry and chemical physics, and grew aggressively as a promising technique for the single molecule detection. The presence of roughened surfaces or metal nano-particles plays the key role of enhancement in Raman signal from the analyte molecule [3]. The deep understanding of the behaviour of surface plasmon polaritons (SPPs) and localized surface plasmons (LSPs) in various metal nano-architectures provides useful insight into utilization of these materials for improving the performance and efficiency of SERS and Remote Raman Scattering (RRS) technique.

Here, we developed surface roughened silver nano-spheres and nano-wires for highly efficient SERS applications. The multiple “hot-spots” (the strong optical field confined to nanoscale volumes) generated by the roughened surface of the plasmonic structures can easily handle large number

of molecules in a focal volume of incident laser. One of the possible approaches to synthesize metal nano-architectures is bottom-top method; it promotes molecular components built up into nano-assemblies. Generally, it can be achieved using chemical synthesis or self assembly technique. The section 2 and section 3 report on growth and characterization of surface roughened nano-spheres and nano-wires respectively. Section 4 of the dissertation presents conclusions of present study and scope of future work.

2. GROWTH AND CHARACTERIZATION OF SURFACE ROUGHENED SILVER NANO-SPHERES

Here, we followed the procedure of Liang et al [4] for synthesizing roughened silver nano-spheres. Initially, we prepared three solutions, A, B and C. (**solution A**= 1 ml of deionized water + .16987 gm $AgNO_3$ i.e. **1M**, **solution B** = 10 ml of water + .111 gm PVP i.e. **0.1 M**, **solution C** = 1ml of water + .176 gm ascorbic acid i.e. **1 M**). Then, **0.2** ml of A and **2** ml of B are mixed in a small vial and added in 10 ml of deionized water in a beaker with a magnetic stirrer (stirring speed = 2000-3000 rpm) at room temperature. After 10 minutes, **0.2** ml of ascorbic acid was quickly injected into the vigorously stirring mixture. The solution became dark grey immediately and then changed to grey after 20-30 minutes later, which is indicating the appearance of a large quantity of colloidal silver particles. For complete removal of excess of PVP and other possible contaminations, the sample can be washed many times with ethanol by centrifugation method. Later, the samples were kept in ethanol at room temperature for further characterization.

Field Emission Scanning Electron Microscopy (FE-SEM) and High Resolution Tunneling Electron Microscopy (HR-TEM) were used to investigate the size and shape of silver nano-particles. For SEM studies, the films were prepared by dropping the solution of silver nano-particles in ethanol, onto a clean Indium Tin Oxide (ITO) glass plate, followed by drying at room temperature. One drop of the diluted nano-particle solution was deposited on a carbon coated copper grid for TEM measurements. The Figure 3.1 (a) shows the magnified FE-SEM image of cluster of nano-particles. Figure 3.1 (b) shows the magnified TEM image of single nano-particle. Both the studies clearly reveal that particles are in spherical geometry with 300-500 nm diameters. The careful observation of SEM and TEM images shows the presence of highly roughened surface on nano-particles.

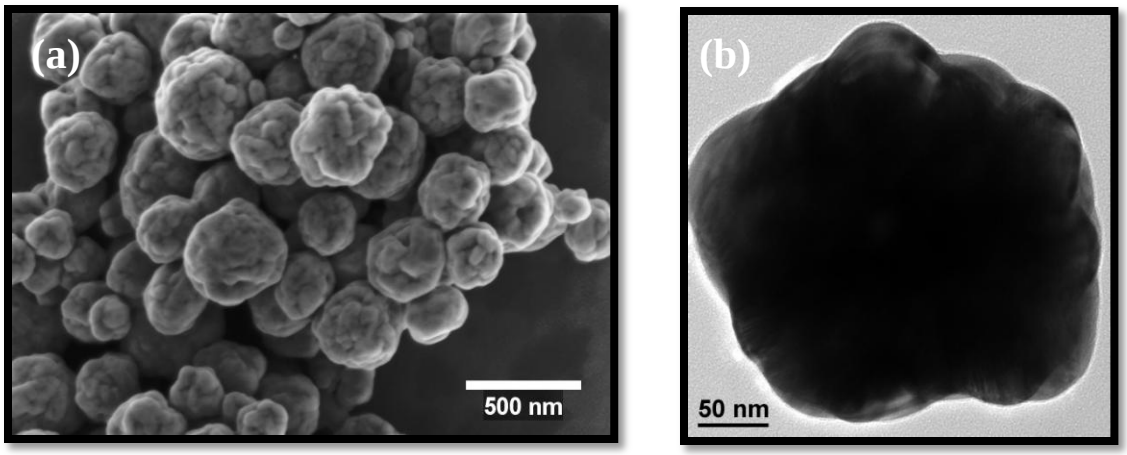

Figure 2.1. Microscopy images of surface roughened silver nano-spheres: **(a)** FE-SEM image of a cluster of nano-spheres **(b)** TEM image of single nano-sphere.

The X-ray diffractometer with CuKα radiation (λ= 0.15418 nm) was used to investigate the crystallinity of silver nano-spheres. As shown in figure 2.2(a), it exhibits multiple distinct diffraction peaks at 2θ values 38.41°, 44.65° and very weak peaks at 64.98° and 78.16° corresponding to d-spacings of .2342 nm, .2029 nm, .1435 nm and .1222 nm respectively. The (111) and (200) planes were identified from selected area HR-TEM images as show in figure 2.2 (b) and (c).

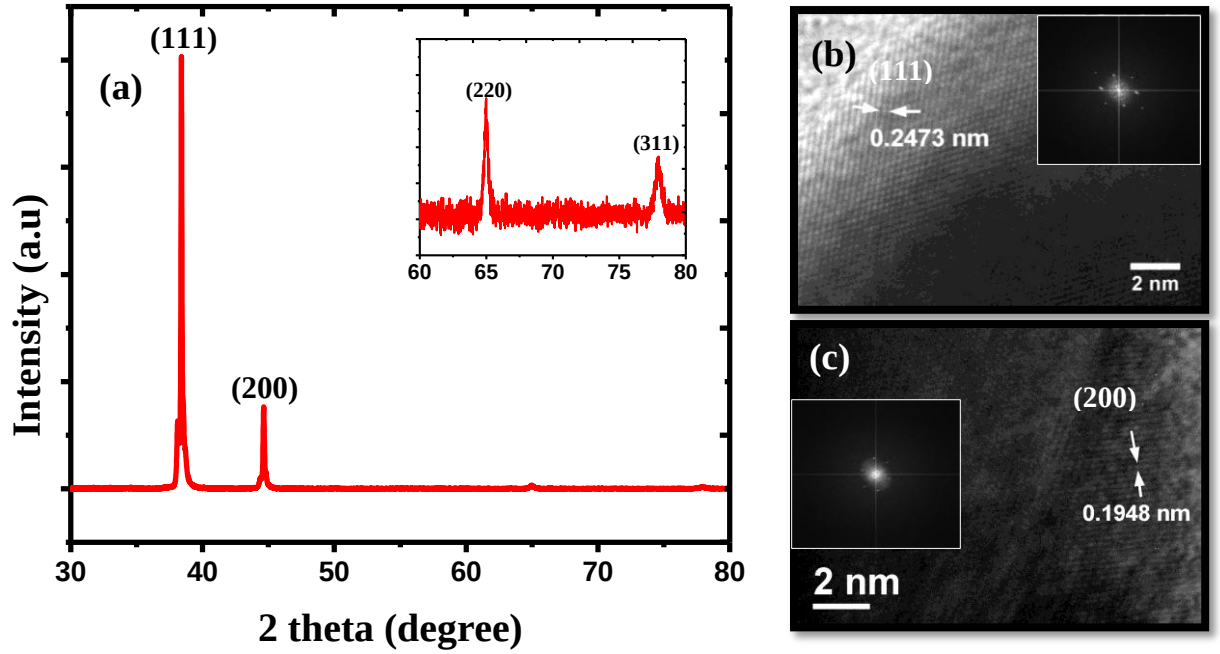

Figure 2.2. (a) XRD images of surface roughened silver nano-spheres. Inset shows the diffraction pattern of weak peaks at 64.98° and 78.16°, **(b)** and **(c)** selected area HR-TEM images and insets show electron diffraction (SAED) images.

To understand the range of plasmon band, the linear absorption spectra of surface roughened silver nano-spheres were recorded using UV – Visible – Near IR spectrophotometer. Figure 2.3 shows the absorption spectra of surface roughened silver nano-spheres in the wavelength range 300-1200 nm with plasmon band at 450-600 nm.

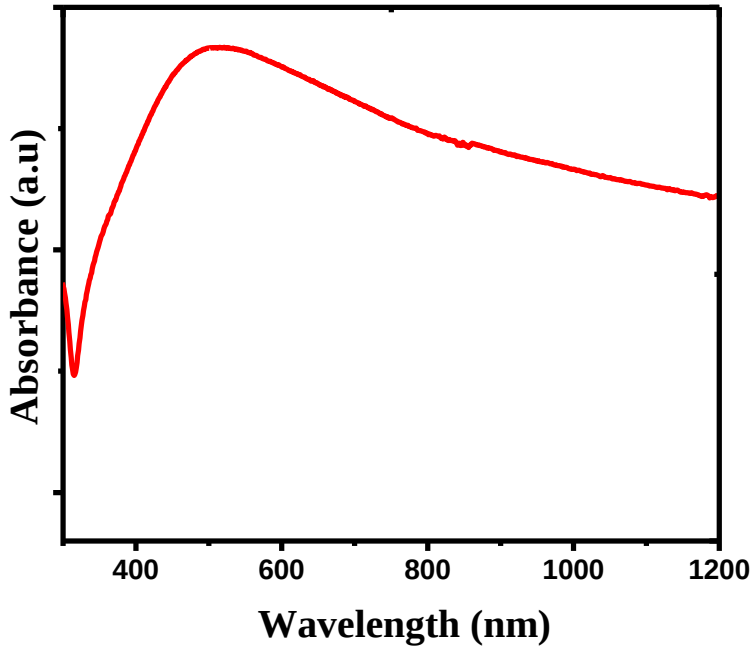

Figure 2.3. Optical absorption spectra of surface roughened silver nano-spheres

Confocal Raman imaging microscope with 632.81 nm laser was used to study the electric field localization capability of nano-spheres. For SERS sample preparation, 1 micro molar of rhodamine 6G molecules in nano-sphere solution was taken and drop casted on a well cleaned glass slide. The figure 2.4 shows the SERS spectra of rhodamine 6G molecules adsorbed at the cluster of surface roughened nano-spheres (100X objective lens at 5 second exposure time). It is really interesting to discuss that the surface roughened architecture shows huge enhancement in characteristics peaks of rhodamine 6G molecules. The tightly packed nanostructures within its clusters can provide multiple “hot-spots” between individual structures, which are capable of handling large degree of molecules at high density of optical fields. The non-uniformly distributed roughness of nano-sphere surface makes them as promising substrates for polarization independent SERS study.

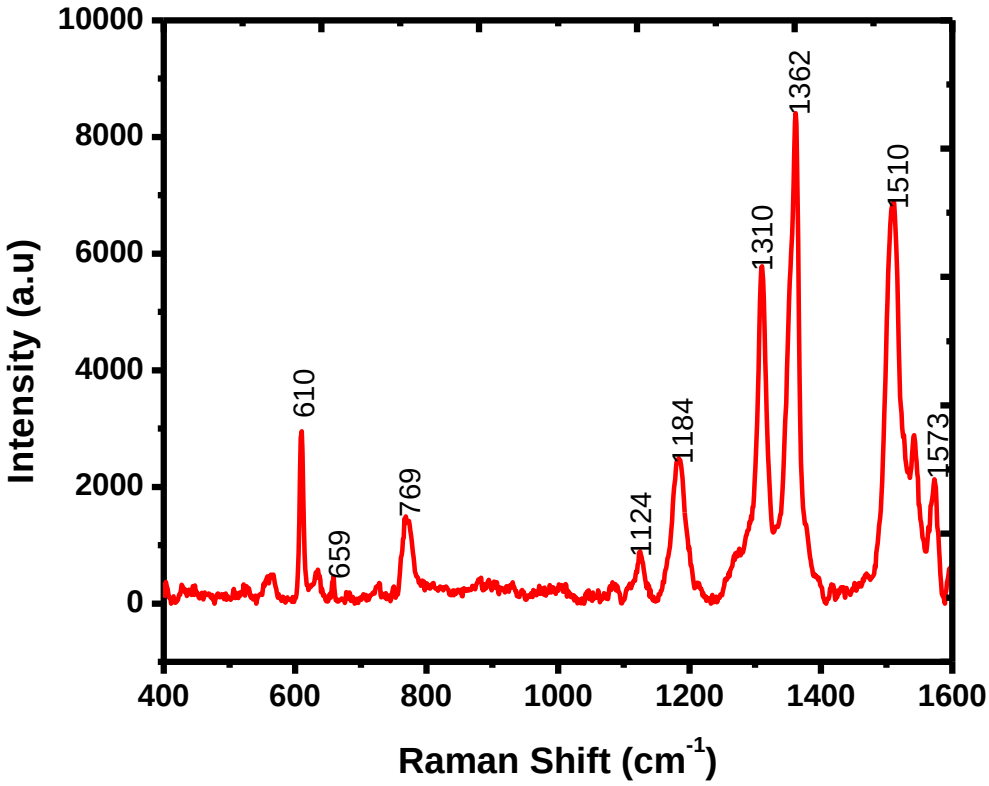

Figure 2.4. Surface enhanced Raman scattering spectra of rhodamine 6G molecules adsorbed on surface roughened silver nano-spheres.

3. GROWTH AND CHARACTERIZATION OF SURFACE ROUGHENED SILVER NANO-WIRES

There are mainly two steps for synthesizing roughened silver nano-wires. The first step is growth of conventional silver nano-wires using polyol method and second step is roughening of obtained nano-wires using the procedure mentioned in section 2.

Step1: Synthesize of Silver Nano-wires

Modified Polyol method was used to synthesize micrometer long Ag nano-wires [5]. Here, we have taken .204 g of $AgNO_3$ and .1332 g of PVP separately in 5 ml of Ethelene Glycole (EG) solvent (the molar ratio of repeating unit of PVP and $AgNO_3$ was taken 1). Then, both of the solutions were sonicated for 1 minute. The prepared solutions were injected simultaneously for 3 minutes to 20 ml of EG solvent, which was magnetically stirred in two-necked 50 ml round bottom flask, kept in 150^{o}C-155^{o}C silicon hot bath (which was already kept for 1 hour in same temperature to remove possible contamination). Immediately after the injection the reactant

mixture was changed to yellow colour and after 30 minutes, gradually it was changed to dark yellow colour. The final colloid was observed in whitish grey colour after 5 hours of reaction time (the reaction time may change from 4 hours to 6 hours). The solution was centrifuged two times at 2000 rpm for 10 minutes in ethanol and 4 times at 6000 rpm for 10 minutes in water to remove excess of PVP and EG. The figure 3.1 shows the microscopy images of obtained nano-wires.

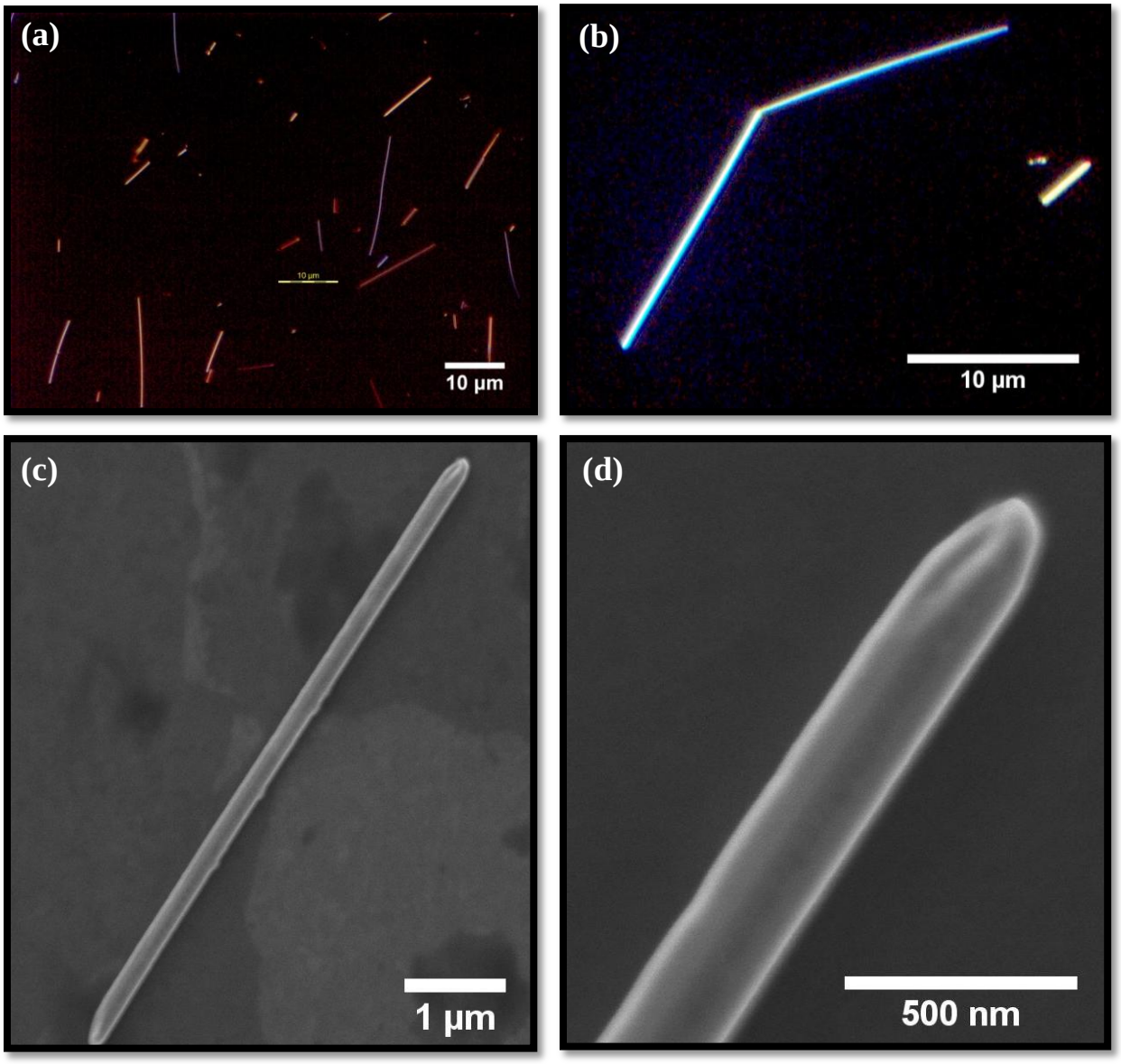

Figure 3.1. Dark field microscopy images of **(a)** dispersed silver nano-wires, **(b)** serially connected nano-wires, FE-SEM images of **(c)** single silver nano-wire **(d)** Zoomed image of (c).

Step2: Surface roughening of Silver Nano-wires

The 3 ml of washed nano-wire aqueous solution was injected in initial reactant solution of surface roughened nano-spheres to obtain roughening on nano-wires. Then the same procedure of nano-sphere growth, discussed in section 2 can be performed to obtain roughened or branched surface of silver nano-wires. The scheme of roughening procedure of nano-wire is given in figure 3.2.

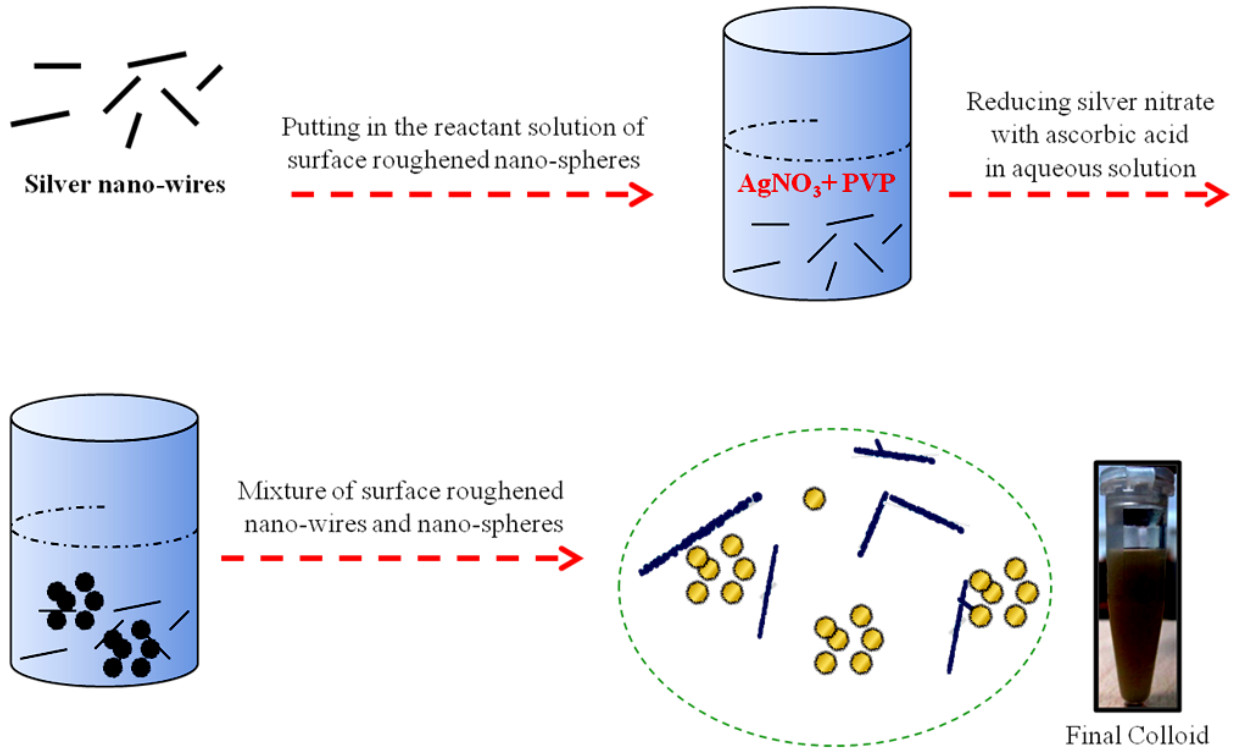

Figure 3.2. Scheme shows the roughening procedure of silver nano-wires

The figure 3.3 (a) and (b) show the SEM images of surface roughened silver nano-wires. It is interesting to point out that nano-wires were roughened uniformly throughout its surface. The tips, cavities and edges of roughness can be acted as the “hot spots” for SERS applications. Moreover, some structures are showing nano-branches and nano-spikes, grown randomly on its surface as shown in figure 3.3 (c) and (d).

Confocal raman microscope was used to study the SERS capabilities of surface roughened silver nano-wires. 100X objective lens was used for tightly focusing the laser of

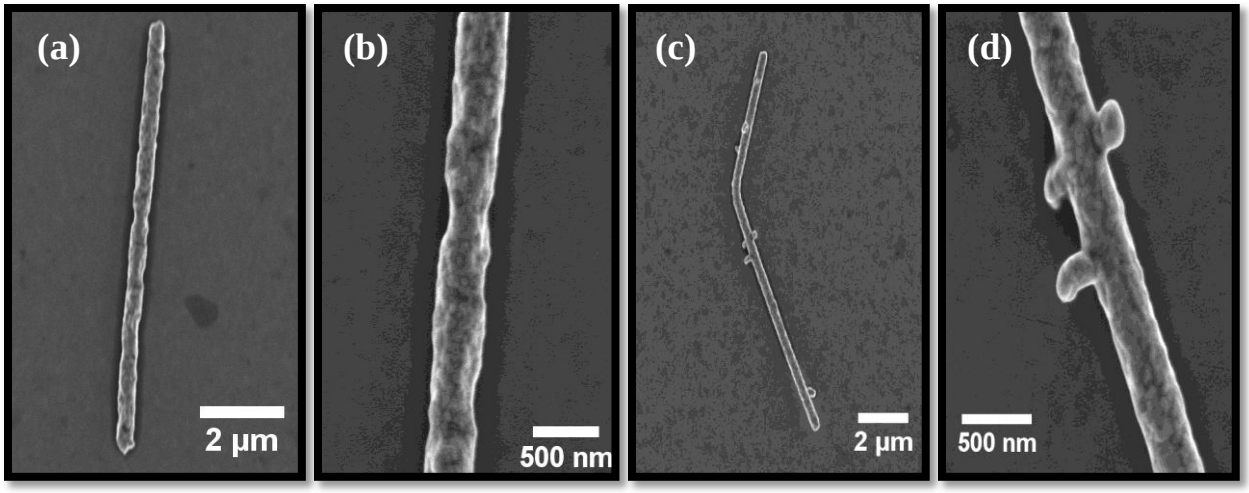

Figure 3.3. FE-SEM images of **(a)** surface roughened nano-wire, **(b)** highly roughened region of **(a), (c)** serially connected roughened nano-wires and **(d)** roughened nano-branches on roughened nano-wire.

632.81 nm wavelength at different regions of roughened nano-wire surface. Here, we have chosen serially connected nano-wires pre-coated with rhodamine 6G as analyte molecule for investigating SERS capability of nano-wires, as shown in figure 3.3 (a). Figure 3.3 (b) shows the SERS spectra of rhodamin 6G collected from region A and B of serially connected nano-wires; corresponding regions are shown in figure 3.3 (a).

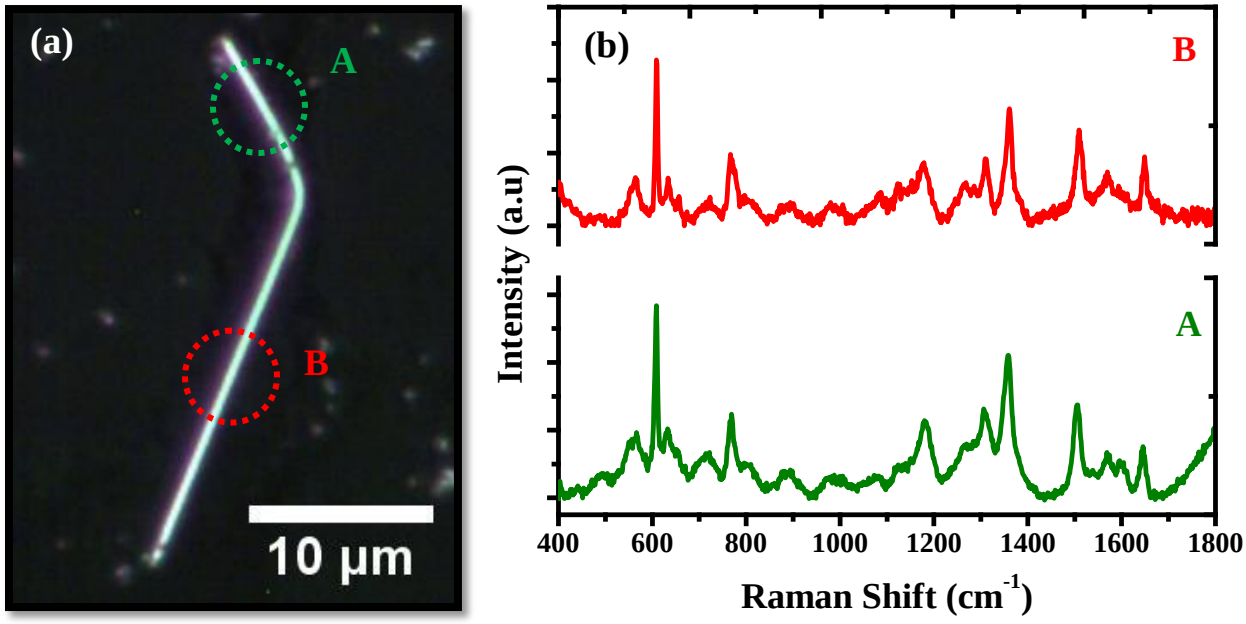

Figure 3.4. (a) Raman Microscope image of serially connected surface roughened nano-wires and **(b)** surface enhanced raman spectra of rhodamine 6G molecules adsorbed on surface of roughened silver nano-wires. One Y-axis division of spectra A represents 2000 counts and that of spectra B represents 1000 counts.

4. CONCLUSIONS AND SCOPE OF FUTURE WORK

Here, we successfully fabricated surface roughened silver nano-spheres and nano-wires. Due to their plasmonic nature, such nano-architectures are extremely promising materials for SERS applications. Microscopy images show that the surface of both architectures is highly roughened in nature, which can be utilized for single molecule SERS applications and nonlinear plasmonics applications. Highly roughened surface pushes the limit of number of "hot spots" from either ends of nano-wires or junction between the nano-wires to its whole surface. Owing to the potential key roles of these plasmonic architectures, as sources of highly intense localized field, the coupling of such structures with other plasmonic structures should be a topic of great research interest. For example, hybrid systems of roughened nano-spheres with plasmonic nano-wires can provide mainly three advantages: 1) it can provide multiple "hot spots" in the junction between wire and particle, 2) it is relatively easy to control the light propagation parameters in nano-wires as compared to nanoparticles alone and 3) it can avoid photo-damage of the analyte molecules from the direct illumination of high intensity laser. Furthermore, these architectures can be used in advanced nano-optical devices, based on non-linear optics for high speed signal propagation, confinement and detection at nanoscale.

5. REFERENCES

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