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Synthesis of Silver Nanostructures and their Application in Highly Sensitive SERS Sensors

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ABSTRACT

A comparison of Surface Enhanced Raman Scattering (SERS) activity of chemically synthesised silver nanostructures with different shapes is reported. The silver nanostructures of cubical, prism and wire like morphology were synthesised using chemical synthesis route and utilised as SERS substrates. The sensors were fabricated by spin coating these materials over a Silicon or glass substrate. The fabricated sensors were used to analyse response with two different analytes, 4-Mercaptobenzoic acid and Rhodamine 6G under different concentrations. The signal enhancement was compared with a silver coated thin film over glass substrate and it was observed that the enhancement of the order of 10^3 is achieved. The nanowire performed better than the other forms of silver and gave a higher signal enhancement for all the analytes as compared to other nanostructures. The fabricated sensors may be useful for various applications including explosive and biowarfare agent detection.

Keywords: Nanomaterial synthesis; Silver nanowires; Nanocubes; Surface Enhanced Raman Scattering; Sensors

1. INTRODUCTION

Nanomaterials have revolutionised the materials research and their applications in the recent past, owing to their plethora of unique properties arising from large surface to volume ratio and quantum confinement effect[1-3]. Nanomaterials have found their effective utilisation in sensors, catalysis, structural components, data storage, biomedical devices, electronics alongwith many other upcoming applications[4-7]. Sensors is one area where they find their suitability extremely well, since the large surface to volume ratio leads to higher sensitivity and surface reactivity[8,9]. Amongst different types of sensors, the spectroscopy based sensors are considered most specific, since they provide fingerprints of the analyte leading to exact detection and identification[10-12]. Surface Enhanced Raman Scattering (SERS) based sensors provide spectroscopic signature details related to the analyte and help in the detection of various analytes including the chemical and biowarfare agents[13,14]. It has the advantage of being extremely sensitive, highly selective, non-destructive technique, alongwith the capability of ultralow level detection of analytes[8,12,15-17]. There are various report where they have been successfully utilised in defence for application like chemical warfare and explosive detection[18,19]. The advantage of SERS sensors is that they can effectively identify even trace amount of analyte leading to its valuable importance in security threat detection systems.

The main feature of an SERS sensor is the substrate on which the molecule to be detected is immobilised. Mostly roughened metallic substrates are used of gold, silver and copper[10,20]. Usually, the SERS signal enhancement originates from the collective oscillation of the electrons or the localised surface plasmon resonance observed in the nanorange of the above mentioned elements[1,21]. Though, the quest for an active SERS substrate has led to a number of alternatives available including various nanoforms, yet the reproducibility, stability and homogeneity remains an issue. Due to these shortcomings, the SERS technique is yet to find its way as a dependable analytical tool.

Noble metal nanostructures have appropriately found their application in the SERS sensors since they demonstrate the property of localised Surface plasmon resonance or LSPR. The LSPR phenomena is observed where confinement of surface conducting electrons occurs and there is an incident electromagnetic field which interacts with them. The availability of surface free electrons with noble metals render them as suitable candidates for LSPR based sensors. The other essential requirement for LSPR is the nanosize range for which it is necessary to synthesise nanostructure of these materials. A variety of nanostructures ranging from thin films, nanoparticles, nanowires have been utilised as active SERS substrates and the list continues to grow. The synthesis techniques also have become more and more mature and it is possible to synthesise a variety of nanostructures using simple chemical route. The morphology of the nanostructure depends on the reaction conditions and can be easily tuned to obtain

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various nanostructures like nanowires, triangular nanoparticles, nanocubes etc[22-24]. There are many ways of synthesising nanostructures including sol-gel method, gas phase synthesis, electrochemical methods, but the chemical reduction synthesis route is still more popular given the control and diversity in terms of shape offered by it[25]. Polyol reduction method is a versatile chemical synthesis route explored by many researchers for the synthesis of silver nanostructures of various shapes and size[26,27]. There have been a number of parametric studies which relate the nanostructure morphology with the reaction conditions[26]. The ratio of PVP to Silver decides whether the nanocubes, nanowires or other nanostructure is formed.

The fabrication of an active SERS substrate using different shapes and size of silver nanostructures, namely nanocubes, nanoprisms and nanowires is present. The synthesis was achieved using a variation of reaction parameters in the polyol reduction synthesis scheme. Transmission and scanning electron microscopy was utilised for morphological characterisation. The SERS signal enhancement for two different analytes Rhodamine 6-G and 4-MBA is also presented for 10 ppm and 100 ppm analyte concentration for all fabricated substrates.

2. MATERIALS AND METHODS

Silver nitrate ($AgNO_3$), Ethylene glycol (EG), Acetone, Ethanol and Polyvinylpyrrolidone (PVP) (average molecular weight, $M\ w \approx 40{,}000$) were purchased from Sigma-Aldrich and used without any further purification. Deionised water was used for all cleaning and reaction purposes wherever required.

The procedure used is as reported elsewhere with slight modification[27]. Briefly, in this procedure, 10 ml solution of PVP in EG with concentration (0.45 M - 7.5 M monomer based) was prepared. Dilute HCl was added (10 per cent) to the solution. The solution was heated to 170 °C -190 °C in a reaction vessel. Another solution of Silver nitrate in EG (0.12 M - 0.8 M) was separately prepared and added into the heated PVP solution drop by drop slowly using a syringe. The solution was kept stirring at a constant rate of 500 rpm by a magnetic stirrer during the whole reaction. The colour of the solution changes indicating the evolution of the nanostructures in the solution. The synthesis was controlled by using different ratio of PVP to silver nitrate in the solution. In order to synthesize the nano/microcubes, the ratio used was 0.8 M to 0.7 M, while for nanowires the ratio was kept at 0.8 M to 0.1 M. The nano/microprism was obtained alongwith a mixture of nanowires and nanoparticles when the ratio was kept at 0.8 M to 0.45 M.

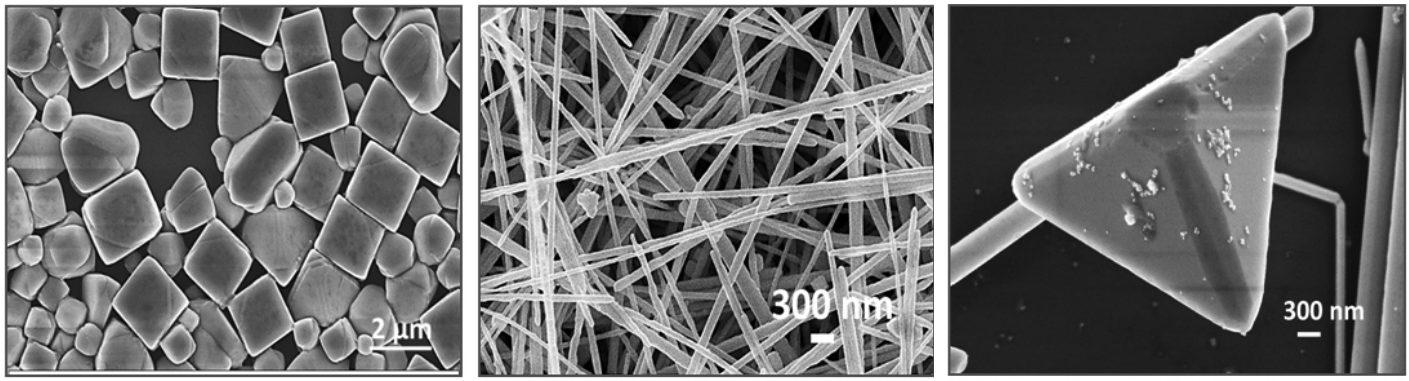
To separate the nanoparticles/nanowires, the solution was diluted with acetone in a ratio of 1:5 and centrifuged at 3500 rpm for 20 m. After that, the reaction product was dispersed in ethanol and again centrifuged at 3500 rpm for 20 m. The final product was dispersed in ethanol for further characterisation. For the size, length and diameter analysis, a diluted ethanol solution of the nanostructures was dropcast onto a silicon substrate or TEM grid. The SERS sensor was fabricated by spin coating the ethanol suspension of the nanostructures over a silicon substrate followed by drying at room temperature. The spin coating speed was kept 1000 rpm and time for spin coating was kept 60 s uniformly for all the samples prepared. The analyte solution was prepared in ethanol with 10 ppm and 100 ppm concentration and was dropcast over the fabricated sensor for SERS characterisation. For comparison purposes, a thin film of silver was deposited using magnetron sputtering process and utilised as a SERS substrate.

The synthesised nanomaterials were characterised by scanning electron microscope (SEM), high resolution transmission electron microscope (TEM) and Raman spectroscopy. Raman studies were carried out using Renishaw InVia Raman Spectrometer with 20X objective 514 nm laser source with 50 mW power. The power was kept 5 per cent of the maximum and 10 s were given for each experiment to maintain uniformity in all measurements. Standard sample was prepared by depositing thin film of silver using DC magnetron sputtering system under inert atmosphere at 350 V and 3 m deposition time resulting in around 10nm thickness of silver film.

3. RESULTS AND DISCUSSION

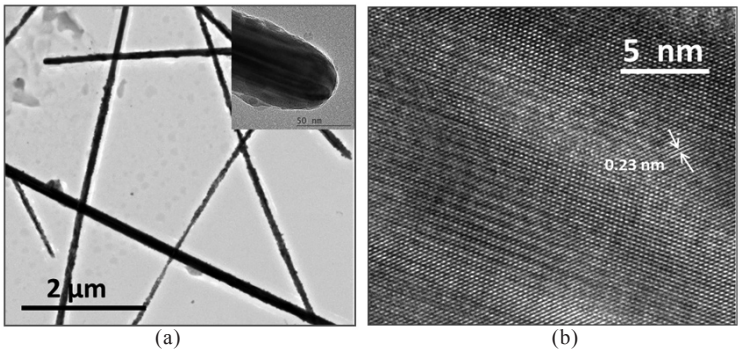
The SERS based sensors have gained a lot of attraction and excitement in the recent past. Being a spectroscopic technique, the result provided are specific in nature and hence exact detection of analyte is possible. In the present study, the nanomaterials synthesis was accomplished by using the polyol reduction method with different ratio of PVP and Silver nitrate. It was observed that on increasing the concentration of the silver nitrate as compared to the PVP, the morphology of the nanostructures obtained shifts from nanowires towards nanocubes. The results have been confirmed by microscope studies carried out to observe the morphology of the nanostructures synthesised. The SEM micrographs are shown in Fig. 1. The TEM Images of nanowires are shown in Fig. 2. It is observed from the SEM and TEM images that the nanowires diameter is in the range 40-60 nm while the cubes formed are quite polydisperse with size ranging from 100 nm to few microns. The nanocubes are formed at higher silver concentration due to the fact that lesser availability of capping agent leads to growth of all the crystal faces of nucleated particle. Also, due to lesser quantity of capping molecules, the nucleated particles grow to different sizes before getting passivated thus leading to polydisperse size ranges. The edge of the silver cubes is well defined and visible in the SEM images. The prism is formed alongwith a mixture of nanowire and nanoparticles. The diameter of the nanowires is further corroborated by the TEM images. The HRTEM image shows that the synthesised nanowires are highly crystalline in nature. The lattice fringe spacing as measured from the ImageJ® software is 0.23 nm corresponding to the {111} plane of Ag nanowire.

The morphology formed is highly dependent on the ratio of PVP and $AgNO_3$. Smaller quantity of latter favours nanowire synthesis since the capping is readily available in the form of high concentration of PVP. As we go on increasing the silver concentration, the morphology shifts from wire to prism and then cubical nanostructures. The size of the structures shifts towards micro from nano. The reason being higher concentration of PVP or the capping agent leads to faster



(a) (b) (c)

Figure 1. Scanning electron micrographs of silver nanostructures : (a) Silver nanocubes, (b) Silver nanowires, and (c) Silver nanoprisms.



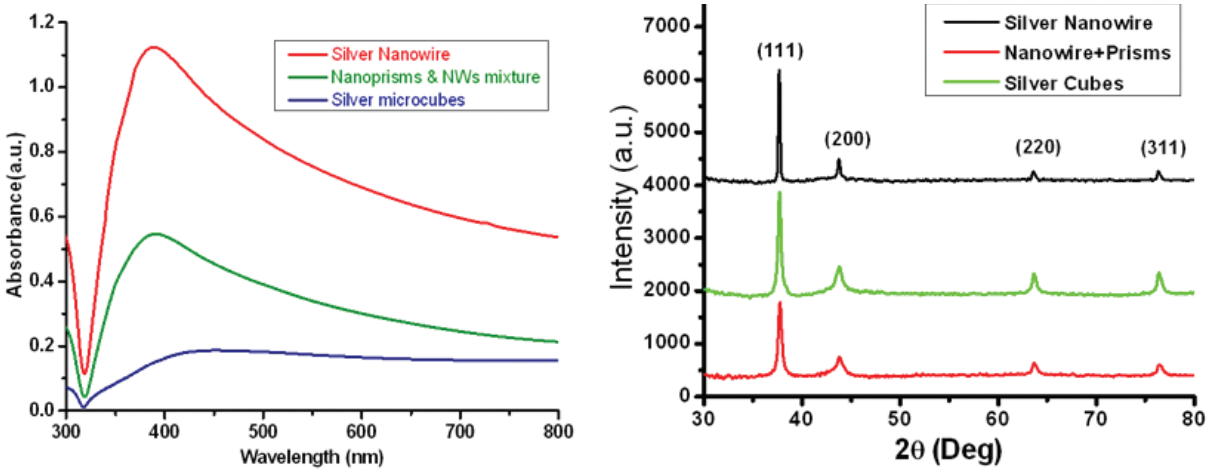
(a) (b)

Figure 2. Transmission electron microscope image of the synthesised nanostructures. (a) Silver nanowires and (b) High resolution TEM image of Ag nanowire sample depicting crystalline nature of the sample.

capping during the nucleation and growth stage. The Ethylene glycol at higher temperature, is the main reducing agent as far as the polyol synthesis scheme is concerned, while the PVP is the capping agent. After nucleation has occurred, the growth of the nanostructures begins, the morphology is determined by the face which grows at a faster rate as compared to others. PVP binds better with the {100} face as compared to {111} face leading to formation of nanowire like morphology in high concentrations of PVP[28]. When equivalent of concentration of $AgNO_3$ and PVP is used, it covers most of the faces of the nucleating particles leading to an overall growth of all crystal faces and hence cubical or prismatic particles were obtained[29].

The UV-Visible Spectroscopy data and the XRD analysis was conducted to observe the optical properties and the crystal properties of the synthesised nanomaterials. The results are presented in the Fig. 3. It is observed that as the morphology shifts towards cubical and larger nanostructures, there is a decrease in the peak height and the width increases. The plasmon response of silver nanowires is observed at 380 nm and as the diameter of the structure increases, there is a decrease in the plasmon response and hence a decrease in the peak in the UV Vis absorption spectrum is observed. Figure 3(b) shows the XRD pattern of the samples (JCPDS card No. 04-0783)[4]. The XRD graph also shows a decrease in the (111) peak as the morphology changes which is a predominant phase in the nanowire formation.

The SERS Sensors were fabricated spin coating the ethanol suspension of the nanostructures over a Silicon wafer. The sensors were dried in air under ambient atmosphere and then the analyte in known concentration was dropcast followed by further air drying. The SERS analysis results of R6G and 4-MBA at 10 ppm concentration level are as shown in Figs. 4 and 5. As observed from the figure, the characteristic



(a) (b)

Figure 3. UV -Vis absorption spectra and XRD data of the prepared samples.

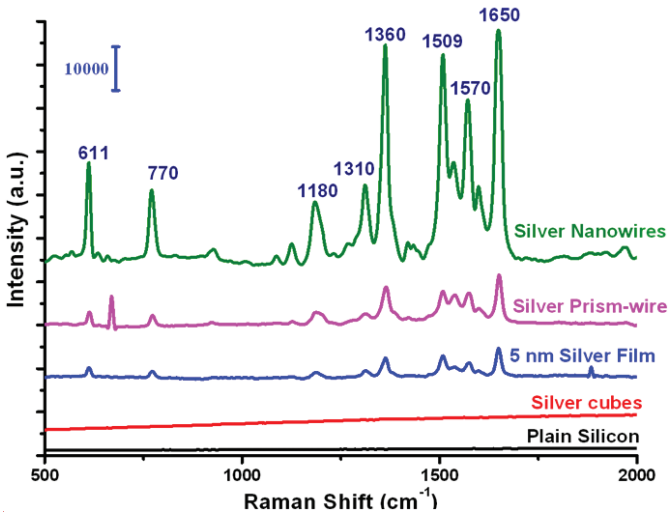


Figure 4. SERS data for different substrates for R6G analyte with 10 ppm concentration.

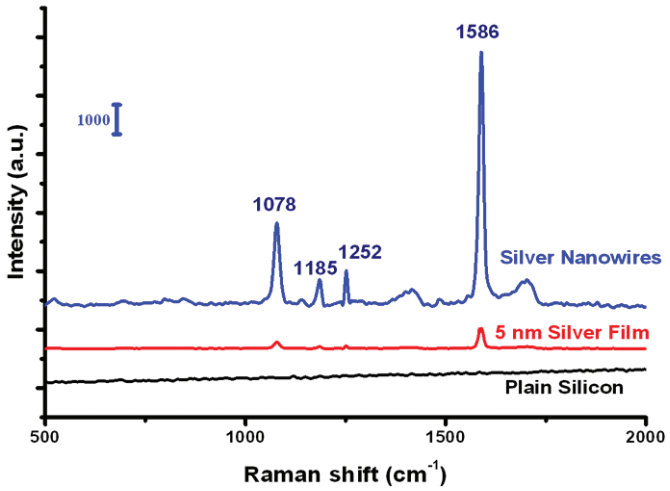


Figure 5. SERS data of 4-MBA on different substrates with analyte concentration 10 ppm.

peaks of R6G are observed at around 611 cm^{-1}, 770 cm^{-1}, 1180 cm^{-1}, 1310 cm^{-1}, 1360 cm^{-1}, 1509 cm^{-1}, 1570 cm^{-1}, and 1650 cm^{-1}. The enhancement was maximum for the nanowires followed by mixture of prism-wire. The thin film of Silver deposited on silicon substrate using magnetron sputtering demonstrated little enhancement while the cubical structures and plain silicon showed no signal enhancement. The reason may be attributed to the size which is observed in the microscopic analysis of these structures. Nanowires being in the range of 40nm in diameter demonstrate maximum enhancement due to quantum confinement effects, while cubical structures are mostly in micrometer range and hence lack the quantum confinement leading to no signal enhancement. The mixture of prisms and wire have features which are both in nano and micro range thus they demonstrate some enhancement. SERS performance is size dependent phenomena as well as it depends on the shape of the nanostructures. Particles larger than the wavelength of incident light cause multipole excitation and hence no or little signal enhancement occurs. On the other hand, a very minute particle will not show surface plasmon effect and hence the SERS phenomenon is not observed. The materials which show surface plasmon resonance and oscillations in the nanorange are Silver and gold. The nanostructures of silver are in different shapes and size and hence demonstrate different level of signal enhancements. Nanowires being in the ideal size range give maximum enhancement while nanocubes being large in size lead to lesser signal enhancement. The analyte concentration was 10 ppm which is miniscule and still there is 3 orders of magnitude enhancement in the Raman signals. The comparison was made for the 1650 cm^{-1} Raman shift for all the substrates and the results are presented in Table 1. The reference signal intensity I_o, was the intensity as observed in the case of plain silicon.

Another analyte, 4-MBA was also utilised for demonstrating the SERS signal enhancement. The substrate was prepared in a similar fashion as described above. In this case also, the signal enhancement for Silver nanowires was observed to be the maximum as compared to the other substrates. The characteristic peaks of 4-MBA are observed at 1078 cm^{-1}, 1185 cm^{-1}, 1252 cm^{-1}, and 1586 cm^{-1} on the graph. The signal enhancement is 2 orders of magnitude for 1586 cm^{-1} for silver nanowires as compared to others. The SERS results indicate that the nanowires demonstrate much better performance as compared to other nanostructures discussed above for both the analytes. The LSPR phenomena is more predominant in the case of nanowire owing to smaller diameter ranges as compared to cubical structures obtained in this study, which were much larger in size.

Table 1. Relative SERS intensity at different substrates for R6G analyte at 10 ppm concentration

Substrate	Relative intensity (I_s/I_o) @ 1650 nm
Silicon Wafer	1
Silver cubes	16
Silver thin film (5 nm)	126
Silver prism and nanowire	212
Silver nanowire	1001

4. CONCLUSIONS

Presented the synthesis of silver nanostructures with different morphologies using polyol reduction method and compared their SERS activity for different analytes. By changing the reaction conditions, it was possible to play with the morphologies of the nanostructures obtained with lower concentration of Silver nitrate giving nanowire while increasing the concentration of silver shifts the morphology towards nanocube formation. The increased silver concentration also resulted in larger size nanostructures with other parameters kept constant. The SERS activity observed both for 4-MBA and R6G, was higher in the case of nanowires as compared to other structures. The signal enhancement observed was of the order of 10^3 for R6G with nanowire based substrate. The SERS sensors fabricated by using these nanostructures may have the capability of detecting a variety of analytes with high sensitivity and are specific in nature. These sensors can also be explored for detection of chemical and biological warfare agents in defence.

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The present study was carried out under his guidance and supervision.