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Temperature dependence of surface enhanced Raman from nanocavity arrays

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Abstract

Surface enhanced Raman scattering (SERS) from molecules absorbed onto plasmon active substrates is known to possess continuum emission profiles upon which Stokes Raman peaks are super-imposed. We study here the effect of temperature upon the continuum emission and Stokes Raman peak ratios from a monolayer of probe molecules prepared on a plamon active nanocavity array from an active spherical cap architecture nanomaterial substrate. Our results show that there is partial recover of SERS spectral profile following heating. This change is interpreted in terms of a molecular rearrangement of molecules on the substrates surface.

1. Introduction

Considerable amount of research has been undertaken to advance the understanding of the properties of nanomaterials such as quantum dots, nanodisks, fullerenes and metallic nanostructures to apply them to nanophotonics [1-5]. There is significant interest in characterising and applying metallic nanostructured materials as optical imaging and sensing platforms [6,7]. Raman spectroscopy is a well-established analytical method widely applied across chemical and biological substrates [8,9]. Surface enhanced Raman (SERS) enables significant increases in both the Raman signal strength to be obtained[10]. Raman scattering is a weak process and significant enhancement is required to make it more broadly applicable in analytical science. One approach to overcome this limitation is to use plasmonic substrates, these substrates enable an enhancement in Raman scattering of many orders of magnitude a technique referred to as surface enhanced Raman scattering (SERS)). The development of plasmon active substrates with regular and periodic features is attractive as it offers the possibility of a substrate that supports SERS with reproducible features.

The plamon active nanocavity arrays studied here are in an spherical cap architecture (SSA) [11-17]. Silver is commonly used for plasmonic platforms as it produces chemically and structurally stable high quality arrays with visible plasmonic absorbance. SSA substrates were reported to support localised (Mie) or delocalised (Bragg) plasmons depending on the dimensions of the nanovoids themselves [12-17]. Bragg plasmons were shown to be present for thin films while localised Mie plasmons were seen at larger thicknesses. To date, while a number of studies have been performed investigating the SERS properties of silver SSA substrates, few studies on temperature dependence of the SERS spectra from such substrates have been carried out. We outline here studies of the effect of temperature on the SERS signals originating from an absorbed monolayer on a plasmon active SSA array. In order to investigate the SERS activity as a function of temperature a monolayer of 4-Aminobenzenethiol (4-ABT) was prepared on a SSA substrate. SERS spectrum from 4-ABT possess a combination of totally symmetric (a_1) vibrations and non-totally symmetric (b_2) vibrations [18]. Studies have shown that the b_2 vibration arise from intensity borrowing from an intense $\pi-\pi^*$ molecular transition ($^1A_1$ - $^1B_2$) at 300 nm as a consequence 4-ABT has is used as a model adsorbate for probing the chemical enhancement mechanism in SERS.

2. Experimental

The nanocavity arrays studied are made of silver formed onto glass. Polystyrene spheres (430, 600 and 820 nm) were obtained from Bangs Laboratories Inc. Polydimethylsiloxane (Sylgard 184-Dow Corning) was obtained from Farnell. Silver nitrate (99%), glucose (analytical standard), ammonia (25%), sodium hydroxide (98%), ethanol (99%) and benzenethiol (98%) were obtained from Sigma Aldrich. Epoxy glue (Araldite) was obtained from Farnell. All solutions were prepared using Milli-Q water. Tollens reagent was prepared by adding a few drops of 0.5 M NaOH to 20 mL of a 5 % w/w solution of $AgNO_3$ until a brown precipitate was formed. Ammonia (3 M) was then added until the precipitate dispersed and 5 g of glucose was added to the solution. At this point the samples to be silver coated were immersed and the solution heated to 60 ^oC for 1 hour. After silver deposition the samples were rinsed copiously using milli-pore water. The polystyrene sphere template was assembled on a cleaned glass slide by placing the slide upright into a 1% sphere solution (w/w) and allowing evaporation in ambient conditions. PDMS is poured onto the array template and is cured at 1000 ^oC for one hour. After curing the PDMS is cut and peeled off the glass slide. The nano-void arrays are created by sputtering an 80 nm silver layer onto these polymer templates. The resulting silver nanocavities were investigated using AFM (Atomic Force Microscopy). The silver nanocavity array was sonicated in a 1 mM water solution of 4-aminobenzenethiol (4-ABT) for 30 minutes. Excess physisorbed material was then removed from the electrode by sonicating in water and rinsing prior to the measurements. The sample was excited at 532 nm with the laser focused using a 10 cm focal length lens. The Raman and luminescence signals were collected at a backscattered angle and directed onto an EMCCD (Electron Multiplying Charge Coupled Device) via a monochromator. Spectra were accumulated for 30 seconds. Heating of the sample was performed using a heating plate (accuracy 0.1 ^{o}C).

3. Results and discussion

The silver nanocavity samples studied here were characterized using AFM. Topography images of the nanocavity are shown in Fig 1a. The AFM image shows the presence of arrays of nanocavities, the size of these cavities was measured (see Fig 1b) to be 120 nm in height and 480 nm in width. A Raman spectrum recorded using a 532 nm excitation wavelength is shown in Fig 1c. The Raman spectrum shows several peaks which are characteristic of modes observed previously from surface enhanced Raman spectra of 4-ABT [18]. A transmission spectrum of the substrate is shown in Fig 1d. The transmission spectrum of the nanocavity substrate (see Fig 1d) shows that the optimum plasmonic enhancement induced by the cavity is likely to occur between c.a. 600-700 nm i.e. the plasmon resonance is strongest over this wavelength range. The SERS window of observation reported here was c.a. 570 nm which occurs in a region where partial absorption of light by the cavity occurs supports SERS. The Raman spectrum of 4-ABT shown in Fig 1 adsorbed on the Ag nanocavity arrays exhibits five very intense bands. These intense Raman peaks are assigned to a combination of a and b type vibrational symmetries and are in agreement in both their frequency position and relative intensities with literature Raman studies for 4-ABT on silver [16]. The Raman spectra is assigned to arise from surface enhanced Raman scattering ie SERS [16-18].

The effect of changing the temperature on the observed SER spectra was studied. Fig 2a shows the SER spectra from 4-ABT recorded on the silver nanocavity at temperatures between 22 and 60 ^{o}C. The SERS show a steady change in spectral features with increasing temperature. In order to see more clearly the spectral changes the SERS spectra recorded at 22 and 60 ^{o}C are shown in Fig 2b. The effect of reversing the temperature change by cooling the sample from 60 to 22 ^{o}C was investigated shown in Fig 2c. The SERS spectra for cooling (Fig 2c) when compared to the SERS spectra for heating (Fig 2a) show that cooling the sample recovers the spectral features originally present at room temperature, noting that a larger continuum emission background (on which the SERS peaks sit) is present in the SERS spectrum recorded at 22 ^{o}C following heating then cooling, than was present initially. In order to assess changes in the SERS with temperature a plot of the observed SERS band at 1437 cm^{-1} as a function of temperature was made, shown in Fig 2d. This plot shows that the SERS intensity steadily increases with heating and reduces with cooling. SERS intensity as a function of laser exposure is also plotted to show the effect of laser irradiation on the sample, thereby accounting for laser induced heating or degradation of the sample over the time of the experiment. Inspection of the graph shows that laser induced effects such as localised heating has a relatively minor effect on the SERS intensity relative to the applied heating.

Curve fitting was applied to enable the continuum emission background and the SERS peaks to be independently assessed. Fig 3a shows a SERS spectrum (recorded at 22 ^{o}C) with fits made to the SERS spectrum. The fits show six bands overlying a broad band assigned to the continuum emission. Plots of peak area intensity derived from these fits for SERS spectra for peaks at 1076, 1146 1393, 1437 and 1580 cm^{-1} over a 22 to 60 ^{o}C range are shown in Fig 3b and c. Fig 3d shows a plot of the fits assigned to the continuum emission background as a function of temperature. Inspection of Fig 3b and c shows that for the peaks at 1076, 1147 and 1580 cm^{-1} the peak area intensity increases. The background continuum emission band (shown in Fig 3d) also increases in intensity. In contrast bands at 1393 and 1437 cm^{-1} show a decrease in peak area intensity. The degree of change for peaks at 1393 and 1437 cm^{-1} is a decrease in peak area intensity of -34 and -14 % respectively while the peak area intensity at 1076, 1147 and 1580 cm^{-1} increases by +14, +8 and +52 % respectively. The continuum emission background band area intensity increases by +54 %. Fig 4 shows the continuum emission for three temperatures, with increasing temperature there is a shift in the continuum emission maximum toward higher energy from 1396 cm^{-1} at 22 ^{o}C to 1412 cm^{-1} at 60 ^{o}C accompanying the increase in band area intensity.

Studies into the experimental contribution of chemical enhancement mechanism effects in SERS of 4-ABT has been reported [18]. This study centred on SERS of 4-ABT on silver with a thin PVP layer placed between the Au layer and 4-ATP molecules thereby eliminating any possibility of chemical bonding between Au atoms and 4-ATP molecules. In 4-ABT modes enhanced through the electromagnetic enhancement (EM) effect are the so-called a_1-type vibrational modes, whereas the modes enhanced through the chemical enhancement mechanism (CM) effect are the b_2-type vibrational modes. Plots in Fig 3 show that for the peaks at 1076 (a_1 type-mode), 1146 (b_2) and 1580 (a_1) cm^{-1} all increase in peak area intensity. The bands at 1393 (b_2) and 1437 (b_2) cm^{-1} decrease in peak area intensity. The degree of change for the SERS peaks at 1393 and 1437 cm^{-1} is a decrease in peak area intensity of -34 and -14 % respectively while the peak area intensity at 1076, 1147 and 1580 cm^{-1} increases by +14, +8 and +52 % respectively. The bands that decrease are b_2 modes and the bands that increase in intensity are a_1 modes, with exception of the b_2 1147 cm^{-1} band, however this band increases by a relatively small amount of 8%. In addition is noted that analysis of the curve fitting for peak height intensity showed that the 1147 cm^{-1} band charged by <1% while the other bands changed in relative magnitudes that mirrored changes outlined above for peak area intensity. One interpretation for these changes is associated with temperature induced molecular rearrangement of the 4-ABT molecules. As temperature is increased reorientation of the 4-ABT molecules on the surface potentially occurs in such a way to reduced molecule-substrate interactions key to CM SERS enhancement.

4. Conclusion

In conclusion surface enhanced Raman scattering (SERS) from molecules absorbed onto plasmon active substrates is known to possess continuum emission profiles upon which Stokes Raman peaks are super-imposed. We study here the effect of temperature upon the continuum emission and Stokes Raman peak ratios in order to advance the understanding of the origin of SERS spectral properties. Our results show that there is a change in both the SERS peaks and continuum background emission ratios. Specific Raman modes are affected differently relative to each other and to the continuum emission background. This change is interpreted in terms of a molecular rearrangement of molecules on the substrates surface.

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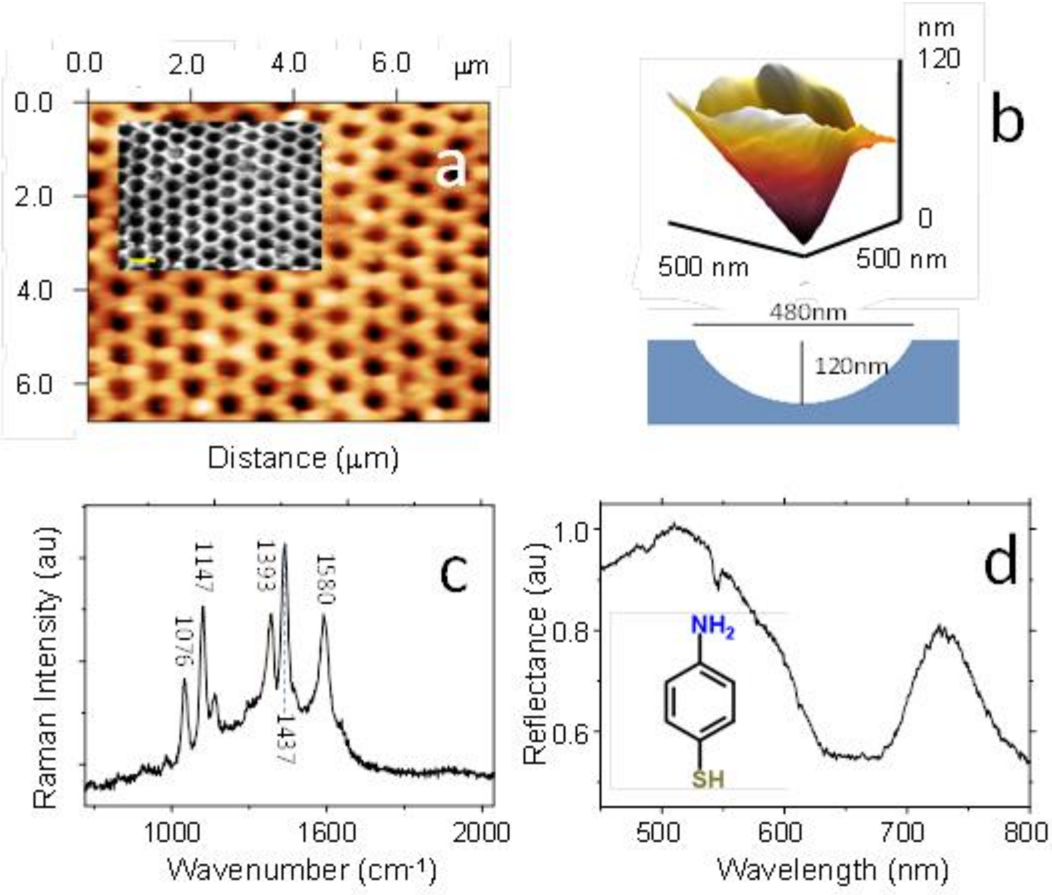

Fig 1. a) AFM image of the cavity showing the presence of a regular array of cavities across the sample, inset shows the cavity following heating. b) bottom, schematic diagram of the cavity dimensions, top, shows a AFM 3D image of a single cavity. c) SERS spectrum from the sample under 532 nm excitation, laser power 10 mW, accumulation time 40 sec. (d) reflection spectrum from the nanocavity substrate, insert is a schematic drawing a of 4-ABT molecule.

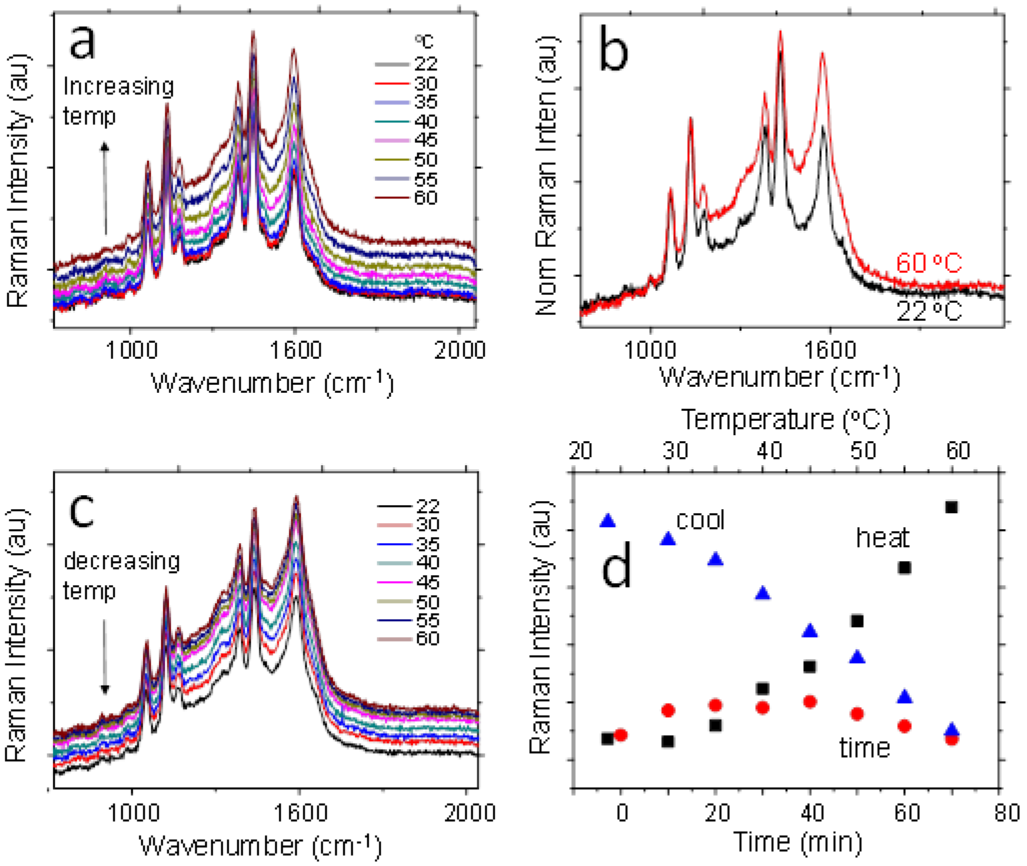

Fig 2. a) SERS spectra as a function of increasing temperature. b) Two SERS spectra taken from a). c) SERS spectra as a function of decreasing temperature following heating (as shown in a). d) Plot of SERS Raman intensity (at 1437 cm-1) as a function of time.

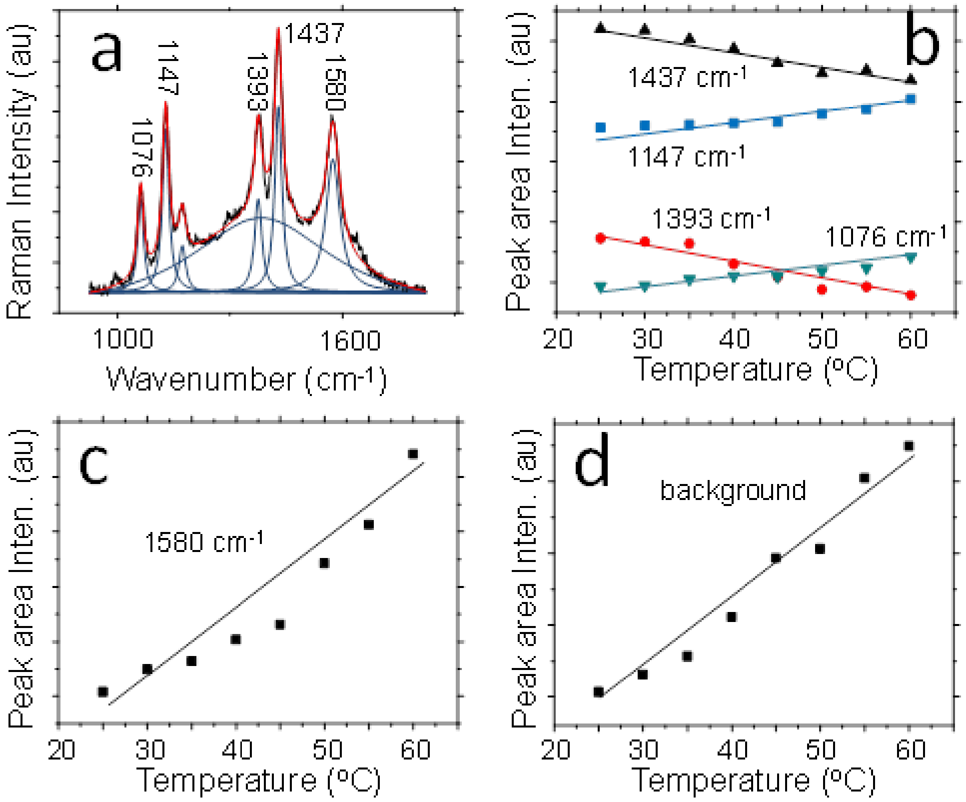

Fig 3. a) SERS spectrum recorded at room temperature (22oC) following peak fitting using Lorentzian fits. In blue are six peaks, with a large and broad band assigned to the continuum emission. b) Plot of SERS Raman peak intensity as a function of time for four peaks. c) plot of the band at 1580 cm-1 as a function of temperature. d) SERS of the continuum emission peak intensity as a function of time.

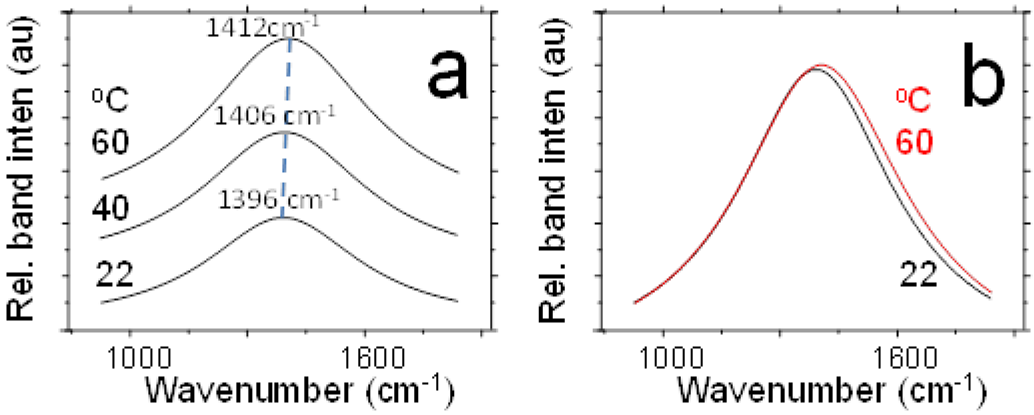

Fig 4. SERS spectra for the continuum emission as extracted from curve fits a) curve fits for three temperatures. b) Overlap of curve fits for two temperatures, the bands are normalized.