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# Deposition of Organic Molecules on Gold Nanoantennas for Sensing

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## ABSTRACT

The deposition of organic molecules on gold nanoantennas is reported through chemisorption for sensing in the mid-infrared (mid-IR) spectral range. The specific nanostructures are gold asymmetric-split ring resonators (A-SRRs) based on circular-geometry with two different ‘arc’ lengths. The plasmonic resonant coupling technique was used to match the vibrational responses of the targeted molecules for their enhanced detection. Gold nanostructures are functionalised through chemisorption of octadecanethiol (ODT) in ethanol solution. The molecular vibrational responses were measured using a microscope coupled Fourier Transform Infrared (FTIR) spectroscopy. The experimental findings are closely supported using FDTD simulation. The modified nanoantennas surfaces are capable of supporting wide range of organic-sensing applications.

**Keywords:** Asymmetric-split ring resonators (A-SRRs), Octadecanethiol (ODT), atomic force microscope (AFM)

## 1. INTRODUCTION

The deposition of organic molecules on gold nanostructures are important for a wide range of mid-infrared (mid-IR) sensing applications such the demonstration with poly-methyl methacrylate (PMMA) [1], with proteins [2-3], and octadecanethiol (ODT) [4]. Gold is an inert material which does not readily oxidise at ambient conditions compared with those of the silver and copper [5]. The energetic bonding between sulphur and gold (S-Au) atoms are mainly responsible for the molecular self-assembly molecules when immersed in thiol solutions [6]. The deposition of octadecanethiol (ODT) molecules on the gold plasmonic nanostructures surface can be used as linker molecules and make an excellent platform for a wide range of sensing applications, such as, biomedical engineering and chemical environment applications [2-3, 7].

The methyl-terminated longer-chain octadecanethiol (SH (CH<sub>2</sub>)<sub>17</sub> CH<sub>3</sub>) molecule was chosen to form hydrophobic functionalised layer on the patterned gold asymmetric-split ring resonators (A-SRRs) surfaces. These surfaces produce much lower free surface energy, making them less vulnerable towards surface contamination for further attachment of biomolecules, such as, proteins. Also longer-chain length thiol molecules are reported to be more thermally stable compared with that of the short chain length thiols, such as, decanethiol (SH (CH<sub>2</sub>)<sub>9</sub> CH<sub>3</sub>) [6].

In this paper, different concentrations of 1 millimole (mM), 2.5 mM and 20 micromole (μM) of octadecanethiol (ODT) solution were deposited on gold asymmetric-split ring resonators (A-SRRs) surfaces through chemisorption process. The molecular vibrational responses were detected using a microscope coupled Fourier transform infrared reflection (FTIR) spectrometer. The specific deposition nature of the adsorbed ODT molecules on the patterned gold A-SRR surfaces was imaged using an ICON atom force microscope (AFM). The plasmonic resonant peaks from the gold nanoantennas were matched with those of the vibrational responses of the targeted ODT molecular deposition for their enhanced detection. The stability of the deposited 2.5 mM concentration of ODT molecules was studied after six months of their initial molecular deposition using an FTIR spectrometer. The gold A-SRRs were deposited on zinc selenide (ZnSe) substrates since ZnSe is highly transparent in both the visible and infrared regions of the wavelengths.

## 2. Methodology, Modelling and Experiment

### 2.1 Organic Materials

1-octadecanethiol ( $\text{SH}(\text{CH}_2)_{17}\text{CH}_3$ ), purum,  $\geq 95.0\%$  purity, in powder form, was purchased from Sigma-Aldrich and used as-received without further purification. First, 1 mM and 2.5 mM thiol solutions were made up to a volume of 20 mL using absolute ethanol in a closed lid volumetric flask and then the 1 mM solution was further diluted to produce a 20  $\mu\text{M}$  concentration solution using micro-pipetting techniques.

### 2.2 Modelling, Fabrication and Characterisation of Gold Nanoantennas

The asymmetric-split ring resonators (A-SRRs) are based on a basic circular geometry and consisted of two different and opposite 'arcs' lengths separated by identical gaps of  $26^\circ$ , with a strip width of 100 nm that was kept constant for all A-SRR designs. Each of the asymmetric-SRRs 'arc' exhibits an individual plasmonic resonance that is perturbed by coupling to the other arc [8]. The schematic of an A-SRR is shown in Figure 1(a). The A-SRRs were modelled using a commercial finite difference time domain (FDTD) Software Package called 'Lumerical' where the detail of the simulation technique was described elsewhere by the authors [9]. A-SRRs were fabricated on ZnSe substrates using electron-beam lithography, followed by gold-metallisation and subsequent lift-off [1-2]. The transmittance spectra were measured at normal incidence, where the incidence electric field (E-field) vector was polarised along the Y-direction, as shown in Figure 1 (a), using a microscope-coupled FTIR spectrometer. The spectra were normalised against bare ZnSe substrate to obtain the response of the A-SRRs alone. The transmittance spectral response of the 1230 nm diameter A-SRR with that of the simulated data is shown in Figure 1 (b), where both experimental and simulation results were found to match quite well. The atomic force microscope (AFM) image of an array of such A-SRRs are shown in Figure 1 (c).

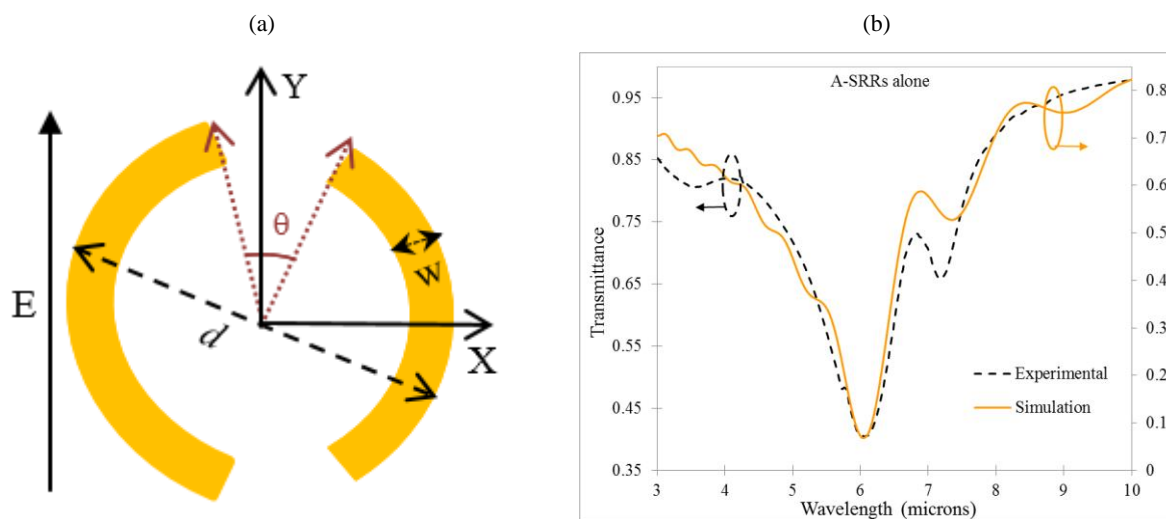




Figure 1 (a): Schematic of an A-SRR with diameter  $d$ ; gap angle,  $\theta = 26^\circ$  and strip width,  $w = 100$  nm (diagram drawn not to scale). (b) The transmittance spectral response of the 1230 nm diameter A-SRR with that of the simulated data. (c) The atomic force microscope (AFM) image of an array of A-SRRs.

### 2.3 Deposition of Organic Materials

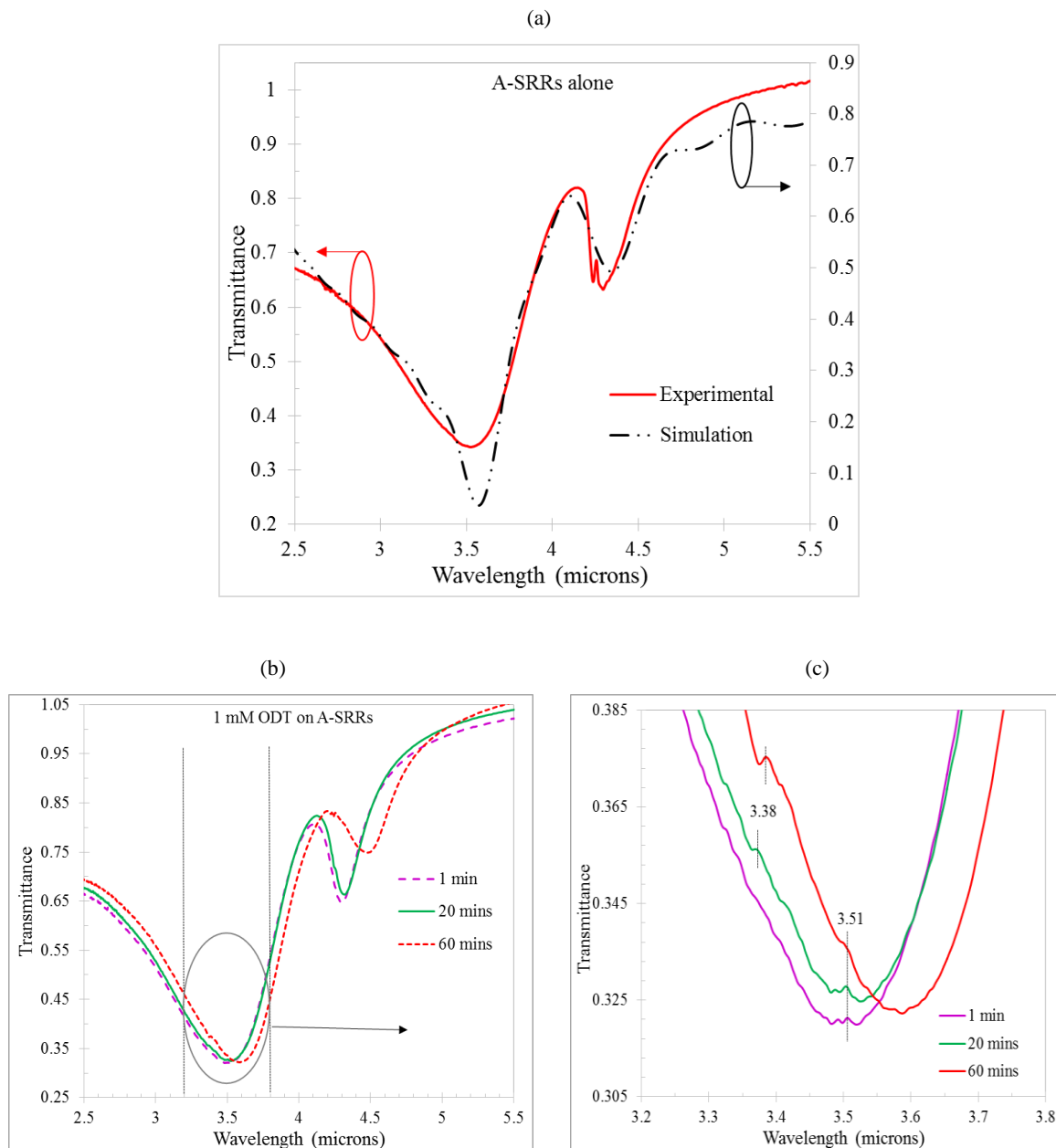
After the fabrication and characterisation of A-SRRs, both interrupted and continuous deposition of molecular self-assembly procedures were carried out by immersing the gold A-SRRs samples into different concentrations of 1 mM, 2.5 mM and 20  $\mu$ M ODT solution in ethanol. The 1 mM concentration of ODT solution was deposited for an interrupted immersion time of a minute first, followed by further 19 minutes and then finally an additional immersion period of 40 minutes, i.e. total accumulative immersion time of 1 hour. On the other hand, the 2.5 mM and 20  $\mu$ M concentrations of ODT solutions were deposited for a continuous immersion time of 3 and 24 hours, respectively. After the specific period of immersion, the samples were rinsed with pure ethanol twice and then blown dry using nitrogen. All molecular deposition process took place at room temperature.

## 3. Detection, Imaging and Stability of Organic Molecules

### 3.1 FITR Measurements

The molecular vibrational responses of the deposited 1 mM concentration of ODT molecules were measured in transmittance mode, at normal incidence, using a microscope coupled FTIR spectrometer over an area of  $\sim 280 \times 280 \mu\text{m}^2$ . The comparison between the measured transmittance spectral responses of the 730 nm diameter A-SRR array with that of the simulated data is shown in Figure 2 (a). The plasmonic resonance from the 730 nm diameter A-SRR array was found to match well with that of the vibrational responses of the ODT molecules - allowing the detection of millimolar (1 mM) concentration of ODT molecules within a minute of immersion. The 1 mM concentration of ODT solution was deposited for an interrupted period of immersion times - initially for a minute, then further 19 minutes followed by an additional 40 minutes, i.e. total accumulative immersion time of 1 hour. The transmittance spectra of the deposited ODT molecules for such an interrupted period of immersions are shown in Figure 2 (b) where the two dotted vertical lines represent the position of the ODT molecules with respect to the rest of the spectrum. Although the vibrational responses of the ODT molecules are hardly discernible over 2.5 to 5.5 microns spectral range, when the spectra were magnified over the wavelength region from 3.2 to 3.8  $\mu\text{m}$ , the peak positions became prominent, and are

shown in Figure 2 (c). For the initial 1 minute immersion, the symmetric  $\text{CH}_2$  stretching vibrational peak appeared approximately 3.51 microns, then with further subsequent immersion times, the antisymmetric peak of  $\text{CH}_3$  appear approximately 3.38 microns [10] which became prominent with evolving immersion time. For a total one hour immersion (red colour spectra in Figure 2 (c)), an average wavelength shift of approximately 115 nm red shift was obtained, compared with that the initial one minute immersion spectra (purple colour in the online version). The overall shift in the spectral responses are due to the gradual deposition of ODT molecules with mediated time of immersion on the patterned gold A-SRR surfaces.



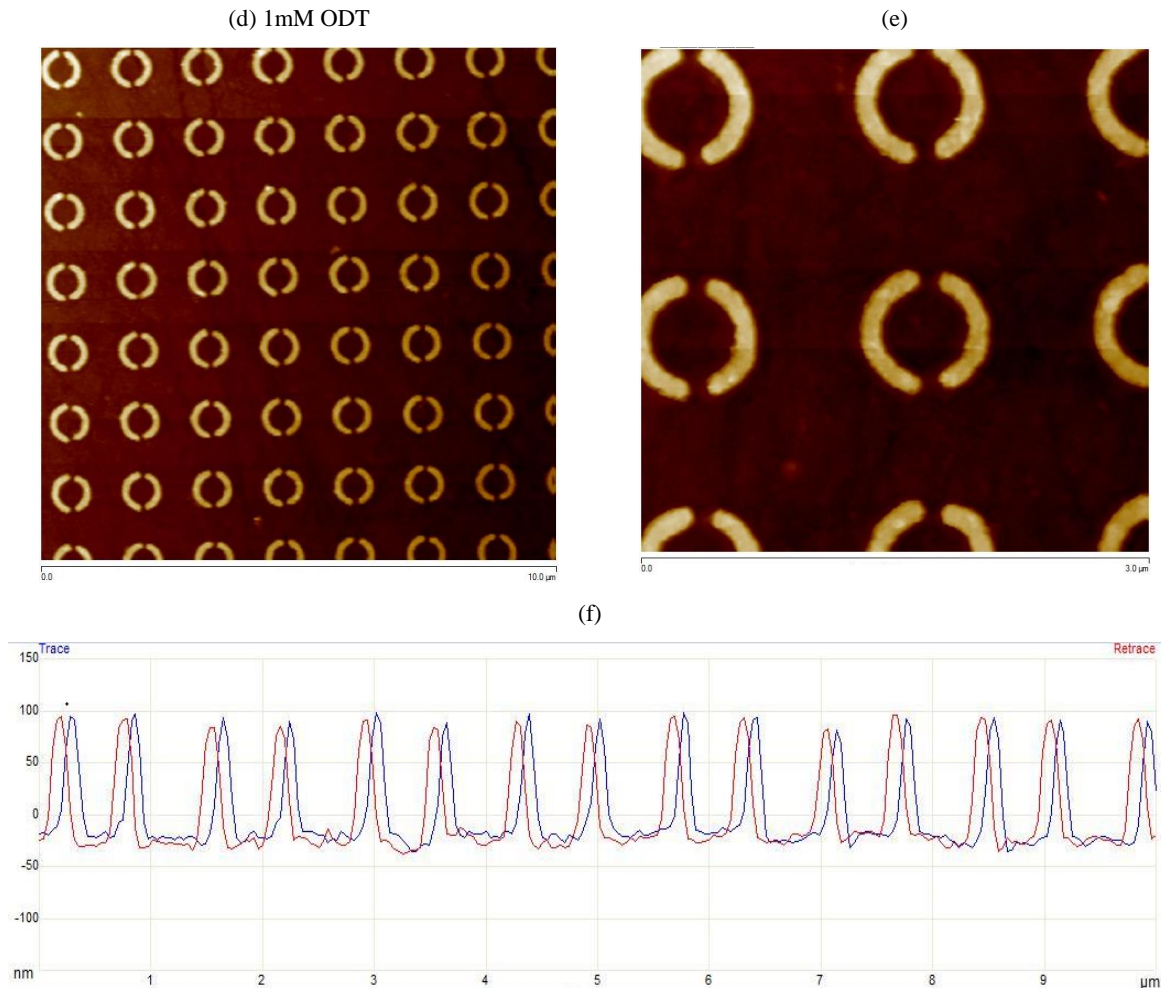


Figure 2 (a): Transmittance spectral response of the 730 nm diameter A-SRR array with that of the simulated data. (b) Transmittance spectral responses of the deposited 1 mM concentration of ODT molecules on the 730 nm diameter A-SRRs array with elapsed time of immersion - where two vertical lines show the position of the ODT molecules with respect to the rest of the spectrum. (c) the magnified spectra showing the vibrational modes of the deposited ODT molecules. (d) and (e) AFM images show with the adsorption of 1 mM ODT molecules on similar set of fabricated arrays of 710 nm diameter A-SRRs over an area of  $10 \times 10 \mu\text{m}^2$ , with the magnified view of the same image over an area of  $3 \times 3 \mu\text{m}^2$  respectively. (f) The graphic of the scan profile during the build up of the image (d).

### 3.2 AFM imaging

A Bruker ICON AFM was used to image the deposited 1 mM ODT molecules adsorbed on similar set of fabricated array of 710 nm diameter gold A-SRRs surface and are shown in Figures 2 (d) and (e) over an area of  $10 \times 10 \mu\text{m}^2$ , with the magnified view of the same image over an area of  $3 \times 3 \mu\text{m}^2$  respectively, for an interrupted immersion period of total an hour. Figure 2 (f) shows the graphic of the scan profile during the build up of the image shown in Figure 2 (d). From the images, it is clear that the adsorbed ODT molecules were deposited only on the patterned A-SRR surfaces. From the scan profile comparison data of the AFM images with and without adsorption of 1 mM ODT molecules, it was found that for an interrupted immersion time of total an hour leads to a partial monolayer adsorption of ODT molecules on the A-SRR surfaces since a complete monolayer thickness of ODT molecule is 2.4 nm [4].

Another experiments were performed for the deposition of lower concentration of 20  $\mu\text{M}$  ODT solution, for a continuous immersion time of 24 hours on the 1430 nm diameter A-SRRs array and were imaged using an AFM. The image is shown in Figure 3 (a) over an area of  $10 \times 10 \mu\text{m}^2$  where the inset shows the magnified spectra of the same image. The

image clearly shows that for a longer immersion of continuous deposition - the ODT molecules formed a non-uniform multilayers film on the surface of the A-SRRs array. The 3-dimensional (3-D) profile of the same image is shown in Figure 3 (b).

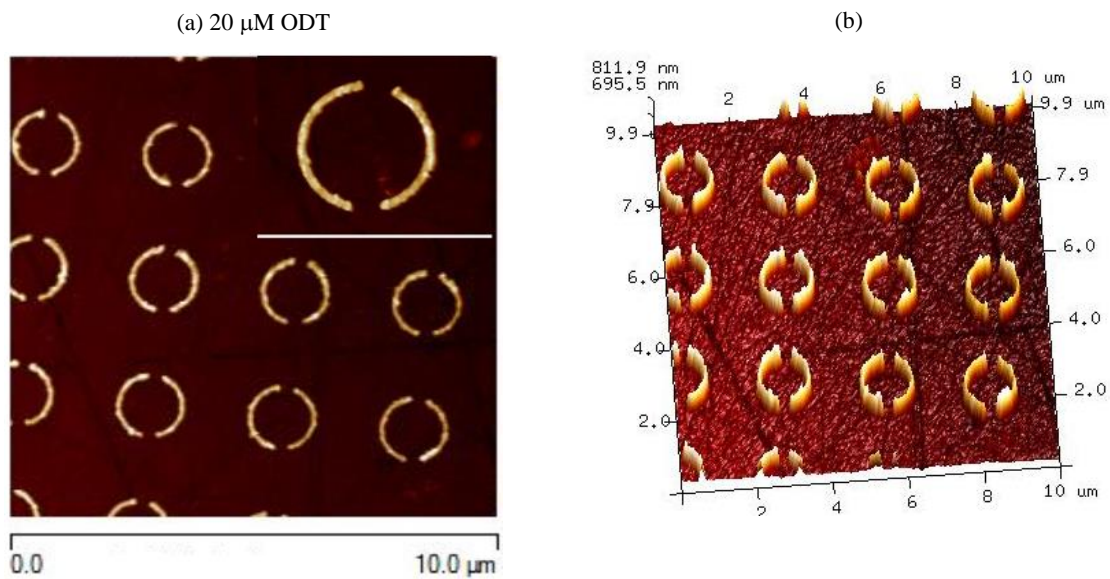


Figure 3 (a): AFM image shows the deposition of 20 μM solution concentration of ODT molecules adsorbed on the 1430 nm diameter A-SRR array surfaces where the inset shows the magnified spectra of the same image. (b) 3-D image of the same array.

### 3.3 Stability of the Deposited Molecules

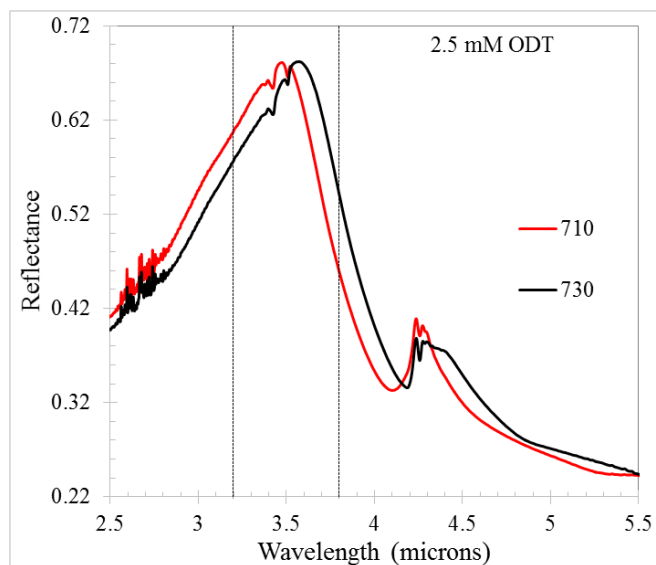


Figure 4: The reflectance spectral responses of the deposited 2.5 mM concentration of ODT molecules on 710 nm and 730 nm diameters of gold A-SRRs.

To study the stability of the deposited ODT molecules, the molecular vibrational responses of the 2.5 mM solution concentration of ODT molecules were measured after six months of their initial deposition, in reflectance mode, at normal incidence, using a microscope coupled FTIR spectrometer over an area of  $\sim 300 \times 300 \mu\text{m}^2$  and are shown in Figure 4. Both the asymmetric and symmetric  $\text{CH}_2$  stretching vibrational modes of the ODT molecules are clearly visible within the spectral region of 3.2 to 3.8 microns (highlighted by two vertical dotted lines with respect to the rest of the spectrum). The 2.5 mM concentration of the ODT solution was deposited on the 710 and 730 nm diameters of A-SRRs arrays following a continuous immersion time of 3 hours. For the stability studies, these samples were stored in vacuum storage after their initial ODT molecular deposition.

#### 4. Discussions and Conclusions

The plasmonic resonant coupling technique has enabled us to detect the millimolar (1 mM) concentration of ODT molecules within minutes of sample immersion in solution for an interrupted period of immersion. The overall red shift of approximately 115 nm was obtained after a total immersion time of 1 hour - due to the gradual deposition of ODT molecules on the patterned metallised A-SRR surfaces compared with that of the initial one minute immersion time. The AFM image reveals the formation of a partial monolayer film with the adsorption of 1 mM solution concentration of ODT molecules on the A-SRRs surface for an interrupted 1 hour total immersion time. On the other hand, for the lower concentration of 20  $\mu\text{M}$  ODT solution, with a continuous longer immersion time of 24 hours, AFM image shows a non-uniform multilayers film formation on the A-SRRs surfaces (see Figure 3 (a)). For the higher concentration of 2.5 mM ODT solution deposited on the A-SRRs surface for a continuous 3 hours immersion time clearly shows both vibrational modes of the ODT molecules even though the spectra were measured after six months of their initial deposition, which proves that the deposited ODT molecules are very stable over the long time span of the measurement.

In conclusions, the specific nanoantennas are gold asymmetric-split ring resonators (A-SRRs) deposited on ZnSe substrates using electron-beam lithography, with the particular advantage that the resonance characteristics of A-SRRs are tunable by varying the size/diameter, gap dimensions and the surrounding dielectric environments [1, 9]. The long term stability of the deposited ODT molecules onto the A-SRRs surface make this device an excellent functionalised platform for further research of biomedical engineering, such as, attachment of proteins and chemical applications. It will also be interested to study the deposition nature of the 1 mM concentration of ODT solution for a continuous immersion of 1 hour compared with that of the interrupted immersion of 1 hour in this work – which is of interest for future work.

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