Experimental and theoretical studies on interaction of hybrid 'micro-flowers like' structures on graphene

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ABSTRACT

We report experimentally and theoretical studies of formation in hybrid of silver (Ag)'micro-flowers like structures' in graphene. An agglomeration silver nanoparticles were deposited on graphene surfaces using electrochemical deposition technique and thus formed the 'micro-flowers like structure'. The properties of these structures in interaction with graphene substrate will be explored in the meaning of localized surface plasmon resonance (LSPR). The deposition time was varied in order to control the sizes and shapes of deposited microstructures. The morphology of graphene surfaces these structures was observed using the Field Emission Scanning Electron Microscope (FESEM), Atomic Force Microscope (AFM) and surface profiler. Images from FESEM shows the structures increases with the deposition time. The presence of graphene and Ag composition confirmed using Raman Spectroscopy and Energy Dispersive X-ray Spectroscopy (EDX). Raman spectra shows the intensity of LSPR generated was the highest at the sample with deposition time of 1.5min. *CST Microwave Studio* has been used to simulate the absorption characteristics of the samples. Findings from simulation shows the intensity of LSPR increased with deposition time. It is also observed that the absorption peak was redshifted and broadened due to the increase of the structure size.

1. INTRODUCTION

Plasmonics has drawn a lot of attention due to the fact that light can be controlled and manipulated on the length scales far below the wavelength [1]. Particularly, plasmons in graphene hold great potential in plasmonic applications [2]. The plasmons in graphene have wavelengths in micron and submicron range but frequencies in 1-100 terahertz range [3]. Graphene plasmons can be tuned through chemical doping and external gate voltage. As compared to normal metals, the plasmon losses in graphene are considerably smaller [4]. Nowadays, graphene becomes a promising material for optoelectronic device due to its high carrier mobility, zero bandgap [5], unique broadband light absorption and electrical tunability [6]. Graphene has a great potential to replace indium tin oxide (ITO) as transparent conductive electrodes in optoelectronics

applications [7]. However, graphene based optoelectronic device such as photodetector usually has low optical absorption and thus generating low photocurrent [6]. This can be improved by incorporating the LSPR effect caused by the plasmonic nanostructures such as Ag and Au nanoparticles on the surface of graphene in order to enhance the light absorption with surface plasmonic effect [8,9]. Moreover, the surface plasmon of the graphene film can be tuned by changing the size and structure of the metallic nanoparticles. This allows detection of light with a variation of wavelength. In this research, Ag nanoparticles were chosen to be deposited on the graphene surface as Ag has strong LSPR in the range of visible light [10]. Moreover, Ag nanoparticles can be fabricated easily [11] and their surface plasmon experiences low loss at optical frequencies [3]. Nowadays, although there are several methods for the deposition of nanoparticles on substrates, most of them are expensive and technically complicated. For example, electron beam lithography is too slow and expensive to be used in large area fabrication while wet chemical reduction method usually contains stabilizers or binders which will influence the properties of nanoparticles [12]. In contrast with those methods, electrochemical deposition is a rapid, high selective and cost effective technique to synthesis nanoparticles [13,14].

In this research, the behaviour of localized surface plasmon resonance (LSPR) of graphene surfaces containing Ag micro-flowers with different structures and thickness was investigated. Electrochemical deposition technique was used to deposit Ag nanoparticles on the graphene surfaces. In order to vary the structure and thickness of Ag nanoparticles, 4 samples were fabricated by using different deposition times, which are 1 min, 1.5 min, 2.5 min and 5 min respectively. The structures have been observed using Field Effect Scanning Electron Microscope (FESEM) while the thickness and separation distance, d of each structure measured using surface profiler and Atomic Force Microscope (AFM) respectively. The presence of graphene and Ag structures was confirmed by Raman Spectroscopy and Energy Dispersive X-ray Spectroscopy (EDX). Moreover, LSPR on graphene surfaces can be confirmed by interpreting the Raman spectra produced. Lastly, the absorption characteristics of the sample were simulated by using *CST Microwave*

Studio based on FEM technique to support the experimental result.

2. EXPERIMENTAL SETUP AND CHARACTERIZATION

In this project, the electrodeposition of Ag nanoparticles was conducted in a three-electrode electrochemical cell with silver-ammonia [Ag $(NH_3)_2OH$] solution and phosphate buffer solution (PBS) as the electrolyte solution. Silver-ammonia solution was obtained by adding ammonia (1 wt%) to silver nitrate solution (50 mM) until the precipitates disappeared. The concentration of prepared Ag $(NH_3)_2OH$ was approximately 40 mM [21]. Both Cyclic voltammetry (CV) and Chronoamperometry (CA) electrodeposition were carried out in solutions on a potentiostat/galvanostat (Versastat 3 Applied Research Princeton, USA) using a three-electrode system: graphene on silicon wafers with SiO_2 coating as the working electrode, a platinum coil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. This can be represented in the schematic diagram below:

The current passes between the working and auxiliary electrodes.
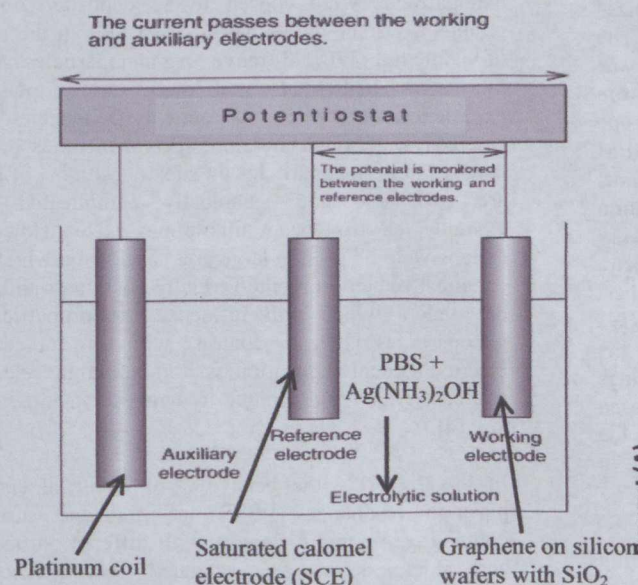

Figure 1: Schematic diagram potentiostat (Versastat 3 Applied Research Princeton, USA) using a three-electrode system

First of all, CV was conducted by using silver ammonia solution in order to find the optimal potential for the electrodeposition of Ag on graphene surfaces. Four potential cycles were performed between -1.8 and 0 V at a scan rate of 25 mV s^{-1} to electrodeposit silver on the working electrode. Without changing the settings, CV was carried out again to deposit Ag nanoparticles on graphene surfaces using solutions which contained different ratio of phosphate buffer solution (PBS) to silver ammonia solution (3:1, 6:1 and 12:1) in order to find the optimum ratio for Ag electrodeposition. By using the optimum condition determined, Ag nanoparticles were deposited on

graphene surfaces by using CA method. 4 deposition times were set: 1 min, 1.5 min, 2.5 min and 5 min.

For samples characterization, Quanta 400F Scanning Electron Microscopy (FESEM) used to obtain high resolution images of the fabricated structures up to nanoscale while Energy Dispersive X-ray Spectroscopy (EDX) which was attached to SEM, has been used to obtain elemental composition of the samples. KLA-TENCOR P6 Surface Profiler and Agilent 5500 Atomic Force Microscope (AFM) were used to measure the thickness of the Ag nanoparticles and the separation distance between the Ag nanoparticles respectively. Moreover, Renishaw InVia Raman Spectroscopy was used to measure the Raman Spectra of the samples. For simulation, *CST Microwave Studio* was used to simulate the absorption characteristics of the models drawn.

3. RESULTS & DISCUSSIONS

3.1 Optimizing Ag Electrodeposition

In Cyclic Voltammetry (CV), different potentials were applied to the system and the change of the current resulting from the applied potential was measured. The graph of current versus the applied potential was plotted in order to determine the optimum potential for the electrodeposition of Ag nanoparticles on the graphene surfaces.
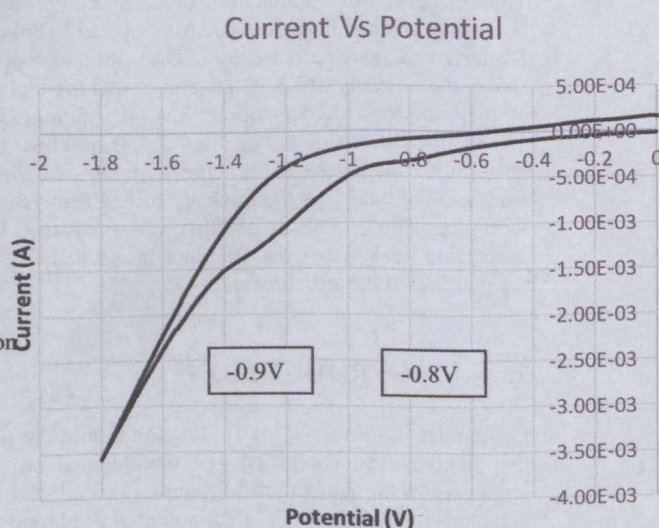

Figure 2: Data of Current vs Potential, performed between -1.8V and 0V.

As shown in Figure 2, it was observed that there was a small sudden increase of current at -0.8V which created a small peak on the graph. This is the peak where the applied potential was high enough to reduce the Ag ions into stable Ag nanoparticles and deposited on the surface of graphene. This implied the applied potential of -0.8V is the optimum potential for the

electrodeposition of Ag nanoparticles on graphene surfaces. Another cathodic peak was observed, which started at -0.9V, was attributed to the irreversible electrochemical reduction of graphite oxide. Without changing the setting, silver nanoparticles were deposited on graphene surfaces using 3 different ratios (3:1, 6:1 and 12:1) of phosphate buffer solution (PBS) to silver ammonia solution as the electrolyte solution in order to determine the optimum ratio of PBS to silver ammonia solution for Ag electrodeposition. PBS was used because the phosphate ions in PBS help in assisting and channelling the Ag cations towards graphene surfaces. Moreover, PBS maintained the pH value of the electrolyte solution at pH 6.5.
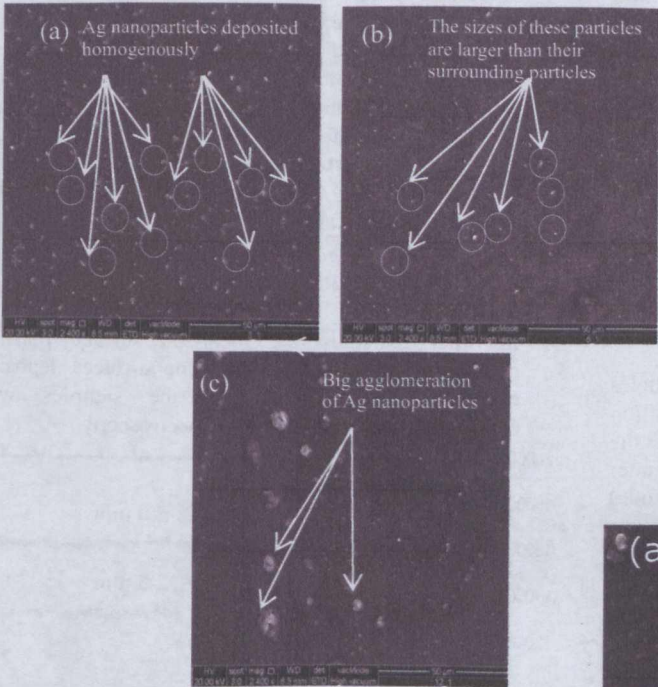

Figure 3: SEM images of graphene surfaces after the CV electrodeposition of silver nanoparticles using different ratio of phosphate buffer solution to silver ammonia solution (a) 3:1, (b) 6:1 and (c) 12:1. All the samples are viewed under the same magnification, which is 2400x for the ease of comparison.

Table 1: EDX analysis of graphene surfaces after the CV electrodeposition of silver nanoparticles using different ratio of phosphate buffer solution to silver ammonia solution.

Samples	Weight %			
	Si (Silicon)	O (Oxygen)	C (Carbon)	Ag (Silver)
bare graphene (control)	85.61	9.53	4.85	-
3:1	40.81	29.00	8.51	12.86
6:1	50.21	19.94	11.82	14.72
12:1	58.31	13.61	9.44	18.63

Figure 3 shows the SEM images of the Ag nanoparticles deposited on graphene surfaces with 3 different ratio of phosphate buffer solution to silver ammonia solution, which were (a) 3:1, (b) 6:1 and (c) 12:1, respectively. From Figure 3(a), it was observed that the Ag nanoparticles were deposited homogenously on the graphene surface with all the nanoparticles were about the same size. In Figure 3(b), the sizes of Ag nanoparticles were not uniform. It was also observed that those nanoparticles are generally smaller as compared to the nanoparticles in Figure 3(a). In Figure 3(c), big agglomeration of Ag nanoparticles can be seen on the surface of graphene, which was not desirable. The sizes of the nanoparticles differ a lot with one another. With this, it can be concluded that ratio of 3:1 is the optimum ratio for the electrodeposition of Ag nanoparticles on the surface of graphene. Based on the EDX analysis as shown in Table 1, the presence of carbon (C), silicon (Si) and Oxygen (O) atoms represents the substrate used, which is graphene with silicon dioxide wafer. Moreover, the presence of Silver (Ag) atoms proved that Ag nanoparticles had been successfully deposited on graphene surfaces.

3.2 Ag Electrodeposition with Different Deposition Time

After the optimum conditions for Ag electrodeposition were known, Ag nanoparticles were deposited on graphene surfaces using CA method. 4 deposition times were set, which were 1 min, 1.5 min, 2.5 min and 5 min.
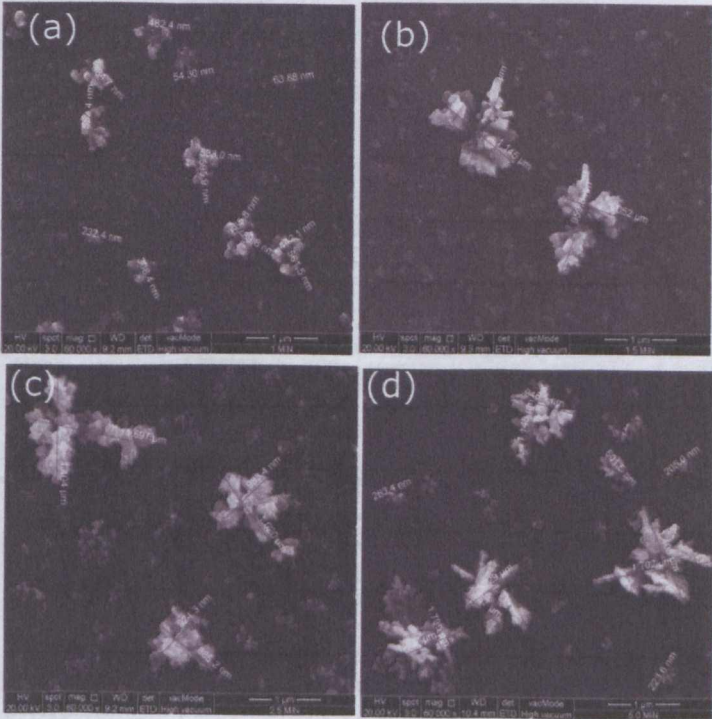

Figure 4: SEM images of graphene surfaces after the deposition of silver nanoparticles with the deposition time of (a) 1min, (b) 1.5min, (c) 2.5min and (d) 5min using

Chronoamperometry (CA) method. All samples are viewed under the same magnification, which is 60 000x for the ease of comparison.

Table 2: EDX analysis of the samples with different deposition time

Samples	Weight %			
	Si (Silicon)	O (Oxygen)	C (Carbon)	Ag (Silver)
bare graphene (control)	85.61	9.53	4.85	-
1.0 min	62.29	13.70	13.65	**10.35**
1.5 min	60.62	12.04	16.02	**11.32**
2.5 min	57.60	10.33	16.21	**15.85**
5.0 min	49.38	14.23	15.61	**20.79**

Table 3: Measurement of the height of the Ag nanoparticles from graphene surfaces using surface profiler

Deposition time (min)	Samples			
	1.0 min	1.5 min	2.5 min	5.0 min
Average height of Ag microstructure	57.11	122.74	187.52	232.68

Figure 4 shows the SEM images of Ag nanoparticles deposited on graphene surfaces at different deposition time. When the CA electrodeposition started, the electrons moved from the platinum coil (counter electrode) to the graphene surfaces (working electrode) as shown in Figure 1. The freely moving Ag cations inside the electrolyte received the electrons on the graphene surfaces and reduced to become stable Ag atoms, which can be shown by the simple chemical equation below:

$$Ag^+ + e^- = Ag \qquad (1)$$
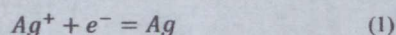
The Ag atoms deposited randomly on graphene surfaces. When the deposition time went longer, more Ag cations were reduced to become Ag nanoparticles and deposited on graphene surfaces randomly. In Figure 4(a), some parts of graphene surfaces had separate Ag islands due to the agglomeration of Ag nanoparticles on those particular areas. The Ag islands increased the conductivity of their surrounding areas, resulting in the agglomeration of electrons on those areas. Since then, the freely moving Ag cations chose to move towards the rich electrons areas and deposited on those areas. They were no longer deposited randomly on graphene surfaces. When the amount of Ag nanoparticles deposited on the surrounding of Ag islands were big enough, flower-like microstructures were formed, as shown in Figure 4(b). It was also observed that the tips and valleys of the micro-flowers formed at 1.5 min were clearly visible and their overall sizes were a lot bigger than the Ag islands observed in Figure 4(a). From Figure 4(c), it was observed that more flower-like Ag microstructures were formed at

2.5min and their sizes were generally larger than those micro-flowers formed at 1.5 min. Figure 4(d) has the largest number of Ag micro-flower and their sizes were slightly bigger than the flowers formed in 2.5 min. This proved that with longer deposition time, more nanoparticles were deposited at the surrounding area of the Ag islands or micro-flowers which resulting in the increase in size of the Ag structure. In Table 3, the average thicknesses of the Ag micro-structures (Ag island or Ag micro-flower) on graphene surfaces were measured using the surface profiler. 5 readings had been recorded at different areas on graphene surfaces and the average values of those readings were calculated. It was observed that by increasing the deposition time, the average thicknesses of the Ag micro-structures became larger. This is because when the deposition time went longer, more Ag nanoparticles were reduced and deposited on the surface of the previously deposited Ag islands or micro-flowers, creating the stacking of Ag nanoparticles with several layers. The presence of the graphene, silicon dioxide and Ag nanoparticles were confirmed with the emergence of Si, O, C and Ag atoms at the EDX analysis (refer to Table 2).

3.2.1 Raman Spectroscopy

In order to study the localized surface plasmon resonance (LSPR) of the graphene surfaces deposited with Ag nanoparticles, all the samples were characterized by using Raman Spectroscopy.
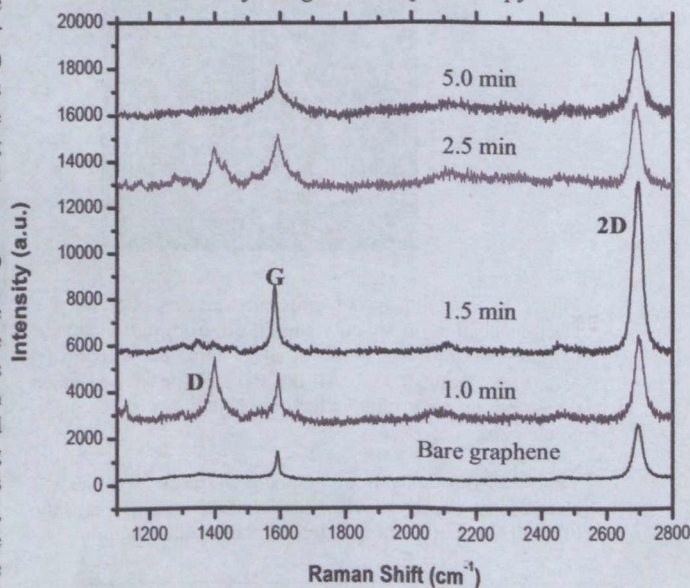

Figure 5: Raman Spectra of the samples with different deposition time

Table 4: Raman shift and intensity of the G and 2D peak of the samples

Sample	G		2D	
	Raman shift (cm^{-1})	Intensity (with reference to corresponding base line)	Raman shift (cm^{-1})	Intensity (with reference to corresponding base line)
Bare	1591.45	1146.31	2695.31	2381.61
1.0 min	1596.39	1811.07	2700.26	3349.95
1.5 min	1586.50	2732.31	2695.31	7139.58
2.5 min	1596.39	2208.87	2690.37	3575.03
5.0 min	1591.45	1894.81	2692.99	3130.11

Figure 5 shows the Raman spectra of all the samples. The Raman shift shown above represents the energy difference between the incident light and scattered light. Through investigating the Raman spectrum, the lattice vibration, electron state and the composition of the material can be identified [15]. With reference to Figure 5 and Table 4, all Raman spectra have 2 prominent peaks, which were located at around 1600 cm^{-1} and 2700 cm^{-1}, corresponding to the typical G- and 2D-bands of graphene. It was also observed that the 2D peak was much more intense than the G peak and this is a useful tool to differentiate graphene from graphite [16]. Moreover, another prominent peak was observed at around 1400cm^{-1} which corresponds to the D-peak of carbon. D-peak originated from the defects and bindings of carbon atoms with other materials [15]. In this case, it could be attributed by the presence of Ag nanoparticles on graphene surfaces which created the strain effect on the atomic position of the carbon atoms [17]. In Table 4, it was also observed that for all the samples with Ag nanoparticles, the intensity of the typical G and 2D peaks had been enhanced with reference to the bare graphene, which is located at the lowest position on the graph. The peak enhancement was attributed to the LSPR that occurred on the surfaces of Ag nanoparticles or micro-flowers. Inside the Raman Spectroscopy, when the laser shined on the graphene surfaces which contained Ag nanoparticles, the interaction between the incident laser with the electrons on the surfaces of the nanoparticles induced a strong LSPR effect around the surfaces of the nanoparticles. LSPR enhanced the inelastic light scattering (Raman scattering) of graphene and hence increasing the intensity of Raman peaks. The characteristic of LSPR is affected by the type of material used, size, shape, dielectric environment and the distance between the nanoparticles [18]. In this project, the LSPR of the graphene was tuned by changing the shape, thickness and the separation distances of Ag micro-structures. During the electrodeposition, some of the Ag nanoparticles agglomerated to form separate islands. These separate island-like structures created localized "hot spot" at the gap between them which greatly enhanced the local electric field intensity [19]. This led to the increase of LSPR effect of Ag nanoparticles. When the gaps between the Ag nanoparticles or micro-structures

decreased due to the increase of the deposited Ag nanoparticles, the number and intensity of the hot spots increased due to the enhancement of the coupling between plasmons across the gap [19]. These were the reasons behind the enhancement of Raman peaks for all samples. Moreover, the formation of Ag flower-like microstructures also contributed to the enhancement of Raman intensity. The tips and valleys of the flower-like microstructures act as antennae producing electromagnetic enhancement, resulting in the further enhancement of the LSPR as well as the Raman spectrum [20, 21]. In Table 4, it was observed that the Raman intensity was further enhanced from 1min to 1.5min. This is because at 1.5min, the tips and valleys of the micro-flowers were more obvious and their sizes were a lot bigger. Moreover, the gaps between the micro-flowers as well as the Ag nanoparticles were smaller at 1.5min. These all contributed to the enhancement of the Raman intensity. After 1.5 min, it was observed that the enhancement of Raman intensity was decreasing, from 2.5min to 5min. This is because although the number of micro-flowers increased after 1.5min, more and more Ag nanoparticles were deposited at the gaps where the hot spots of LSPR located, resulting in the decrease of the number of hot spots available on the graphene surfaces. Moreover, when the Ag nanoparticles filled up the gap between the Ag particles, the effective surface areas of the Ag micro-flowers for the emergence of LSPR effect decreased. This reduced the LSPR interaction in between the Ag nanoparticles. With this, it can be concluded that the LSPR effect of the sample with 1.5min of deposition time is the strongest among all the samples.

3.2.2   Simulation

In the following section, *CST Microwave Studio* was used to simulate the absorption characteristics of the samples. All the simulations were conducted using Finite Element Method (FEM). In the simulation, the structures and dimensions of Ag micro-flowers deposited at each deposition time were drawn based on the data obtained from SEM, EDX and surface profiler.
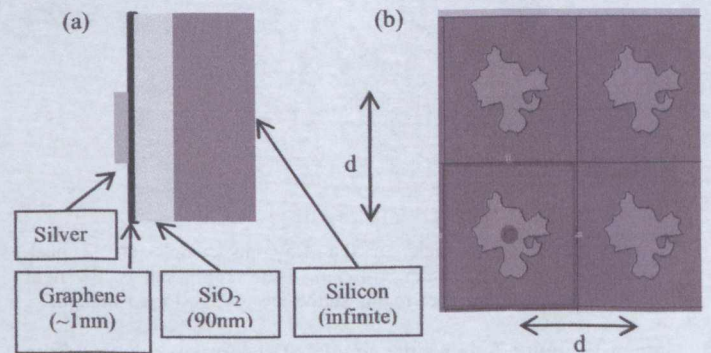

Figure 6: (a) Side view of the model, (b) Arrangement of structure

In order to mimic the real sample, all the Ag micro-flowers were put on the graphene surfaces with silicon dioxide and silicon as the substrate, as shown in Figure 6(a). For each sample, all the Ag structures were arranged in order with constant distance, d in between each other, as shown in Figure 6(b). By using Atomic Force Microscope (AFM), the values of d were estimated and summarized in Table 5.

Table 5: Distance, d in between Ag particles

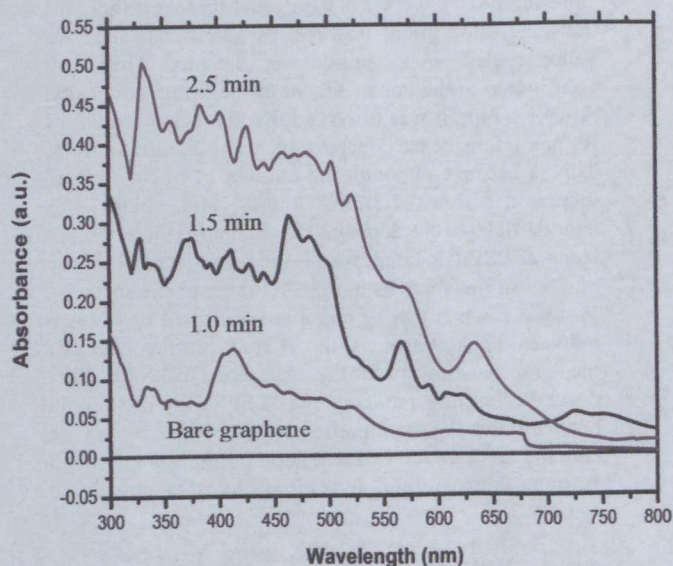| Sample	1.0 min	1.5 min	2.5 min
d (nm)	387	220	157

Figure 7: Simulated absorption spectrum of the samples with different deposition time
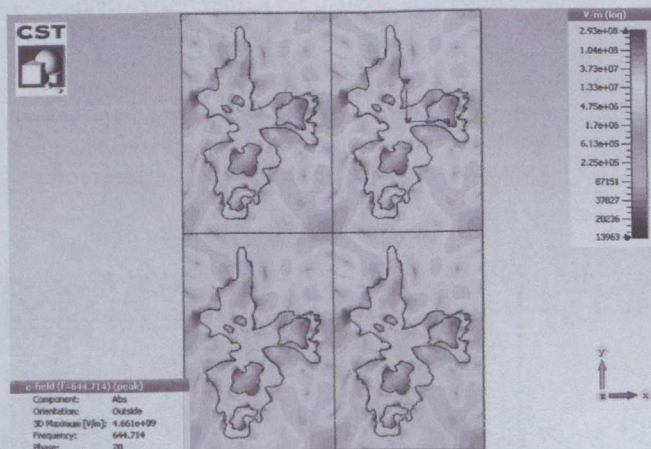

Figure 8: E-field of the 1.5 min sample at its peak wavelength, which is 465nm. Blue region shows low field strength while red region shows the strongest field strength.

Figure 7 shows the simulated absorption spectra of the samples with different deposition times while Figure 8 shows the electric field of the micro-flower. The strength of the electric field was indicated with different colors with blue color showed low field strength while red color showed high field strength. The enhancement of the electric field was due to the emergence of LSPR. Stronger LSPR will lead to higher electric field enhancement. In Figure 7, it was observed that the absorbance of the graphene was enhanced after depositing Ag on it. At 1 min, the absorption peak is located at 414nm with the intensity of 0.13. At 1.5 min, it was observed that the absorption peak was wider and it was redshifted to 465nm. The broadening and redshift was usually caused by the increase of the particle size [22]. Moreover, it was observed that besides the main peak, there were several small peaks emerged along the absorption spectrum of 1.5 min. Basically, these small peaks represent the emergence of strong LSPR at the tips of the micro-flower structures [20], which was shown in Figure 8. The red regions at the tips of the micro-flowers indicated the emergence of strong LSPR. The absorption spectrum of 2.5 min shows a very wide peak with several peaks and troughs in between the range from 325 nm to 525 nm. This was caused by the further increment of particle size as well as the number of tips of the micro-flower structures for the emergence of strong LSPR. From Figure 7, it was also observed that the intensity of the absorption spectrum enhanced with deposition time. The enhancement was caused by the increase of the thickness [23] of Ag micro-flowers and also the decrease of distance, d in between the particles when the deposition time increased. Thicker Ag micro-flowers provided more effective surface area for LSPR. In Figure 8, it was observed that there was a strong enhancement of electric field, represented by the orange region at the gap in between the micro-flower. As shown in Table 5, the separation distance, d in between the micro-flowers decreased when deposition time increased. Closer separation distance, d increased the strength of plasmons coupling effect in between the gaps of the Ag micro-flowers. Moreover, from Figure 8, it was observed that most of the red regions appeared around the tips of micro-flowers and the number of tips increased with deposition time. This implies that the tips of the micro-flowers played a very important role in enhancing LSPR.

As discussed earlier, the experimental results indicated that the intensity of LSPR was enhanced from 1 min to 1.5 min and the intensity dropped at 2.5 min and 5min. This differed from the simulation result which showed that the intensity of LSPR increased with deposition time. In the experiment, when the deposition time became longer, more Ag particles were deposited at the gap in between the Ag micro-flowers, resulting in the decrease of the number of hotspot available for LSPR in 2.5min and 5min. However, in simulation, the number of hotspot available was the same for all samples because all Ag structures were arranged orderly on graphene surfaces with constant separation distance, d for each sample, as shown in Figure 6(b). This implied that for simulation, the intensity of LSPR was only dependent on the structure, thickness and separation distance, d of the Ag micro-structures

without considering the number of hotspot available for LSPR.

4. CONCLUSION

In this project, the optimum potential and electrolytic solution ratio (PBS to silver ammonia solution) for the Ag electrodeposition were found to be -0.8V and 3:1 respectively. Ag micro-flowers had been successfully deposited on graphene surfaces by using electrochemical deposition technique. With longer deposition time, the size and thickness of Ag micro-flower became larger. It was also observed that the number of large Ag micro-flower increased and the separation distance, d in between Ag particles decreased when deposition time increased. The result from Raman spectroscopy showed the presence of Ag on graphene surfaces enhanced the Raman peak of graphene by the emergence of LSPR effect. At 1.5 min, the intensity of LSPR was the highest. Based on the simulation result, the redshift and broadening of absorption peak can be observed due to the increase of the particle size. Moreover, it was observed that the absorption spectrum increased with deposition time due to the increase of thickness of the Ag micro-flowers and decrease of separation distance, d in between Ag micro-flowers. Moreover, the increase of the number of tips of the Ag micro-flower also contributed to the enhancement of LSPR. There was a difference in between experimental and simulation result because in simulation, all the Ag particles were arrange orderly in between each other. This was not the case in the experiment where the particles were deposited without an order. With this, the number of hot spot available for LSPR was neglected in simulation.

5. FURTHER WORK

Different plasmonic materials such as gold, copper, aluminium and magnesium can be electrodeposited on graphene surfaces in order to study the LSPR of those materials on graphene surfaces.

6. ACKNOWLEDGMENTS

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