International Journal of Integrated Engineering, Vol. 9 No. 2 (2017) p. 27-30

Effect of Seeding Time on the Formation of Gold Nanoplates

Marlia Morsin*[1,2], Muhamad Mat Salleh[3], Mohd Zainizan Sahdan[1,2], Farhanahani Mahmud[1,2]

[1] Microelectronics & Nanotechnology - Shamsuddin Research Centre (MiNT-SRC), Institute of Integrated Engineering (I2E), Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat Johor, Malaysia
[2] Faculty of Electronic and Electrical Engineering (FKEE), Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat Johor, Malaysia
[3] Institute of Micro Engineering and Nano Electronics (IMEN), Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

Received 2 March 2017; accepted 11 April 2017, available online 11 April 2017

Abstract: Metallic nanostructures, such as gold, is very sensitive to the dielectric environment of the materials due to strong dependency of plasmon on shapes and sizes. Thus, its unique properties are very good and can be used as sensing material in plasmonic sensor. This paper reports a study on the surface density on the formation of gold nanoplates with variation of seeding time. The gold nanoplates have been grown on a quartz substrate using seed mediated growth method. In this study, the seeding time was varied from one to three hours and labelled as MP1, MP2 and MP3. The XRD analysis shows two peaks of the diffraction angle occurs at the plane (111) in position ~ 38.2º and plane (200) at ~ 44.20º. Through variation of the seeding time, the optimum surface density is 61.8 % with a total of 43.7 % of the nanoplates shape from sample MP2. The optical absorption spectrum of the sample shows two resonance peaks, ~ 550 nm and 660 nm, which are corresponding to the transverse surface plasmon resonance (t-SPR) and the longitudinal surface plasmon resonance (l-SPR) respectively. Thus, in this study, it is found that the seeding time affected the growth of the gold nanostructures with optimum seeding time of two hours. Longer seeding time caused the growth of stacking nanogold and it is not suitable to be used in sensing application because of its broad and wider optical spectrum

Keywords: Localized Surface Plasmon Resonance, Gold Nanoparticles, Seeding Time, Plasmonic Sensor, Seed Mediated Growth Method (SMGM).

1. Introduction

Gold nanostructures have attracted researchers because of its unique physical properties and its potential applications in thermal, catalysis, photoelectronic devices, biomedical diagnostics and other related field. Thus far, many researches have been done in synthesizing gold nanostructures into various shapes such as spherical, rods, cubes, hexapods, ribbons and hollow nanocages [1-4]. As the shape and size of nanogold greatly affects the optical and electronic properties and it is also very suitable and good to be used in plasmonic sensors. Some of researches have been carried out using plasmonic sensor including the detection of formalin using gold nanospherical [5], the detection of biomarkers for Alzheimer's disease [6, 7] and cancer [8]. In addition plasmonic sensor is also used in detecting harmful gaseous such as benzene, methanol and toluene [9].

The gold nanostructures can be fabricated using two methods; physical and chemical methods. Physical method implements top-down approach using lithography technique [10]. This approach limits the size of substrate and requires high cost and establish equipment. Meanwhile, chemical method applies bottom – up approach. This bottom – up approach can also be classified into gas phase, liquid phase and solid phase methods based on the state of the reaction system [11]. These methods normally used surfactant or polymer as an agent to control the growth of particles. Each of these methods has their own advantage and disadvantage. Among those methods, one particular wet chemical synthesis method, namely Seed Mediated Growth Method (SMGM), which is able to produce anisotropic nanoparticles in high yield and structural purity with varying size, shape, structure, composition, and surface chemistry [12-13]. This method can be carried out in room temperature with simple procedures and low cost compared to physical method.

In this study, the gold with nanoplates shape fabricated on the substrate surface using SMGM. In this process, seeding time of gold nanoplates (AuNPs) was varied from one to three hours to investigate the effects on the growth of AuNPs. The AuNPs are aimed to be used as sensing materials in plasmonic sensor to detect toxic material in food preparation. Hence, the high density and homogeneity of AuNPs was sought to obtain sharp, intense and narrow absorbance peak of the optical spectrum.

2. Experimental Method

Gold nanoplates were grown on quartz substrate using the Seed-Mediated Growth Method (SMGM) [14] with some modification. The chemicals used for the synthesis

*Corresponding author: marlia@uthm.edu.my

penerbit.uthm.edu.my/ojs/index.php/ijie

were hydrogen tetrachloroaurate ($HAuCl_4$.3H2O), poly-l-lysine (PLL), trisodium citrate (C6H5Na3O7), sodium tetraborohydride (NaBH4) ascorbic acid, cethyltrimethy ammonium bromide (CTAB) and poly (vinyl pyrrolidone) (PVP). These chemicals were obtained from Sigma-Aldrich (US) except trisodium citrate, sodium tetraborohydride and ascorbic acid which were purchased from Wako Pure Chemical Ltd (Japan). All the solutions of these chemicals were prepared using deionized (DI) water with resistivity around 18.2 MΩcm from pure lab UHQ ELGA.

Prior to seeding process, the quartz substrate was dipped into 5% seed enhancer namely poly-l-lysine (PLL) for 30 minutes to impose a positive charge on the substrate surface. Meanwhile, two types of solutions were prepared which are seed solution and growth solution. The seed solution was prepared by mixing 0.5 ml of 0.01 M HAuCl4 with 2.0 ml of 0.01 M trisodium citrate and 18 ml DI water. After that, 0.5 ml of 0.1 M cold aqua $NaBH_4$ was added into the solution. The substrate was immersed into seed solution for 1 hour to 3 hours at room temperature. Then, the substrate was annealed at 150 ºC for 1 hour using a vacuum oven to strengthen the gold nanoseeds on the surface. After this treatment, the substrate was immersed in the growth solution for 5 hours. The growth solution was prepared by mixing 0.5 ml of 0.01 M HAuCl4, 10 ml of 1 mM PVP, 8 ml of 0.1M CTAB and 2 ml DI water with the addition of 0.1 ml of 0.1 M ascorbic acid. Finally, the substrate was annealed at 100 ºC for 1 hour to remove the surfactant residue.

All of the samples were characterized using X-ray diffraction (XRD)-D8 Advance, Field Emission Scanning Electron Microscopy (FESEM) – Zeiss Supra 55VP and Perkin Elmer Lambda 900/UV/VIS/NIR Spectrometer

3. Results and Discussion

The SMGM consists of two stages which are seeding process and growth process. The seeding process is very important because it determines the quality of the grown gold nanoplates on the substrate. In this study, three variations of seeding time were studied which are 1 hour, 2 hours and 3 hours. The seeding time refers to the period during the immersion process of substrate in the seeding solution. To facilitate discussion, the samples are labelled as MP1, MP2 and MP3.

There are three main characterizations done which are XRD, FESEM and UV-Vis onto the samples. During the experiments, the physical observation was done on the substrate and it shows changes of colour after each process. After the seeding process, the colorless substrate turned to pinkish color while the substrate turned to violet after the growth process is completed. **.** The presence of a purple color on the surface of the substrate corresponds to the standard color for gold nanoplates [15]. While pink color refers to gold nanospherical shape [5, 16]. This indicates that gold nanoplates has been successfully grown on the substrate surface.

3.1 XRD characterization

All the samples were characterized using X-ray diffraction (XRD) to examine the structure of the film. Figure 1 shows the X-ray diffraction pattern of each sample. From the graph, it can be seen that each sample exhibits two peaks of the diffraction angle from the angle 20º to 60º. The first peak appeared in the plane (111) in position 38.175º, 38.200º and 38.225º while the second peak is seen in the plane (200) at 44.275º, 44.250º and 44.400º. The results obtained were matched with data for bulk material gold standard of JCPDS 004 - 0784, which is in the angular position 38.185º and 44.393º. The peaks at plane (111) and plane (200) are crystal planes that coincide with the face-centered cubic structure or face - centered cubic (fcc) of gold nanoplates. Based on the height and sharpness of the peak of the plane, it can be concluded that the (111) plane is dominant. This means that the majority gold nanostructures growth on the substrate was parallel to the substrate surface, which corresponds to the formation of gold nanoplates and nanospherical. In the diffraction pattern obtained, the appearance of other peaks are not noticeable. Therefore, it can be concluded that a pure crystalline has been formed on the substrate surface. The reading of all peaks are listed in Table 1. From Table 1, it can be seen that the formation of gold nanoplates (i.e corresponding to 111 plane) increases with an increment of seeding time.

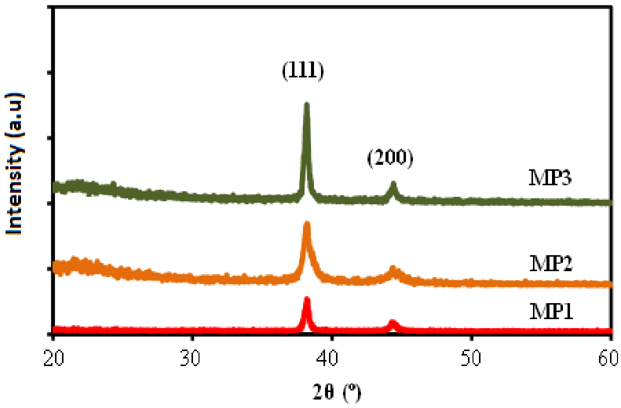

Fig. 1 The XRD for all samples

Table 1 XRD results for all samples.

No.	Sample	Plane (111)		Plane (200)	
		Angle (Θ°)	Intensity (a.u)	Angle (Θ°)	Intensity (a.u)
1	MP1	38.175º	99	44.275º	27
2	MP2	38.200º	189	44.250º	41
3	MP3	38.225 º	302	44.400º	61

3.2 FESEM characterization

FESEM was used to observe morphology for all samples and the results are shown in Fig. 2. From Fig. 2 (A) - (C), it can be seen that the growth of gold nanoplates - AuNPs (represent by white grain) increase with the increment of seeding time from one hour to three hours. However, the growth of AuNPs for two and three hours seeding time are almost the same. When the nanoparticles are zoomed as shown in Fig.2 (D) – (F), the samples with three hours seeding time shows the growth of stacking gold nanoplates. Stacked growth of AuNPs are expected to affect the optical absorption properties and it will be discussed later in the next section.

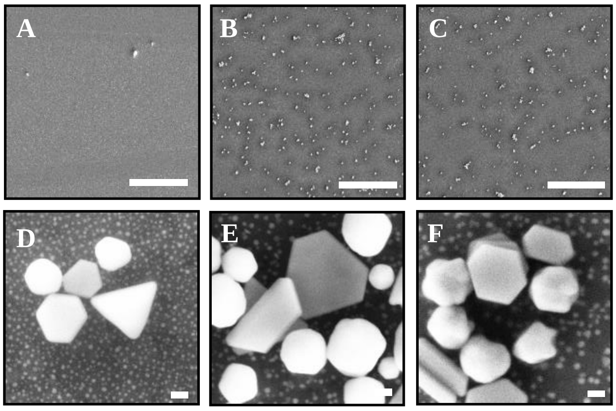

Fig. 2 FESEM image with variation of seeding time from 1,2 and 3 hours. (A), (D)- MP1, (B), (E) - MP2 dan (C), (F) -MP3. Scale: (A) - (C) : 10 µm and (D) - (F) : 100 nm

Then, the FESEM results are further analyzed and there are three (3) types of gold nanostructure observed which are nanoplates, nanorod dan nanosphericals. Nanoplates consist of hexagonal, semi-hexagonal and triangular. The growth of nanoplates can be explained as follows; the growth of gold nanoplates started with the formation of triangular shapes. The edges of triangular expanded until the shapes became hexagonal. The imperfect growth of hexagonal formed semi-hexagonal shapes. Besides, it can be seen that there are two groups of sizes of the AuNPs; (1) AuNPs with edge length more than 150 nm and (2) AuNPs with smaller edge length (less than 50 nm). For the gold nanorods, the aspect ratio (L/W) is ~ 5. The cross section is not be performed due to thinnest layer of gold.

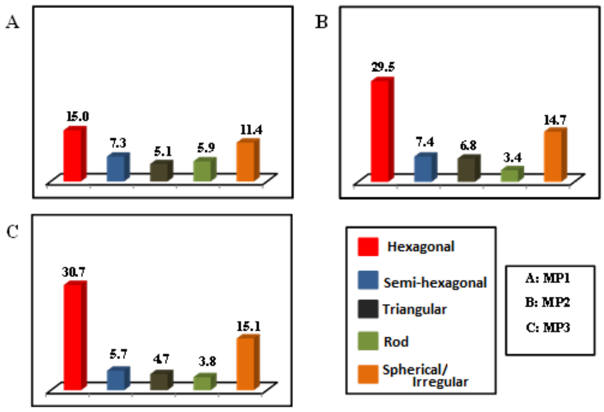

Fig. 3 Surface density (in percentage for each structure after the growth of Au for all variations of seeding time).

Fig. 3 shows the detailed analysis in percentage of each structure. The optimum surface density of AuNPS obtained from samples MP2 which is 61.8 % with 43.7 % of the growth are nanoplates. The analysis was done by measuring the area covered by nanogold. Three different areas were mesaured and analyzed and the average of surface density was calculated. The hexagonal shapes are dominant shapes for each seeding time. However, the increasing of seeding time also stimulated the growth for other irregular shapes that affected the absorbance spectrum of gold nanoplates. Instead of optimizing the process parameter, i.e seeding time, in order to increase the density and homogenity of gold nanoplates, the surfactant used in the growth process needs to be controlled [16].

3.3 UV- Vis characterization

All samples exhibit two absorption peaks with different intensities and peak positions as shown in Figure 4. MP1 sample has wide spectrum peaks at 559 nm and 658 nm. MP2 sample produces peaks at 547 nm and 662 nm, which are sharper than the other two samples. While MP3 sample has two peaks that are sharper than MP1 with the peak positions at 557 nm and 665 nm. The absorption peak is associated with gold nanostructures surface plasmon resonance. According to Umar et. All (2009) [15], gold nanoplates has two resonance peaks. The first peak is assigned as transverse SPR (t-SPR) and the second peak is assigned as longitudinal SPR (l-SPR) [15]. The t-SPR is free charges vibration in vertical direction, while l-SPR is vibration of free charges in the horizontal direction, which is parallel to the substrate surface. The t-SPR band agrees with previous observations of the spectrum of spherical shape Au nanoparticles [11] and the l-SPR band with the Au nanoplates spectrum [14, 16]. The spectrum was quite related to the percentage of gold nanostructures growth on the surface.

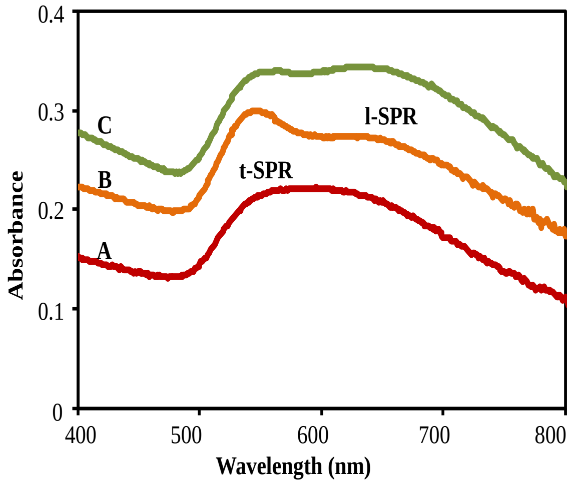

Fig. 4. Optical spectrum after the growth of Au for variations of seeding time (A) MP1, (B) MP2 and (C) MP3.

4. Conclusions

In this study, it is found that the seeding time affected the growth of the gold nanostructures. The optimum seeding time is two hours because longer seeding time could lead the growth of stacking nanogold is not very appropriate to be used as sensing material because of its broad and wider optical spectrum. Hence, the control of homogeneity must also be considered in the fabrication of sensing material

Acknowledgements

This work was supported by Universiti Tun Hussien Onn Malaysia under UTHM Contract Research Grant (U565-UTHM) and IMEN, Universiti Kebangsaan Malaysia for the laboratory facilities.

References

[1] Petryayeva, E., and Krull, J.K. Localized surface plasmon resonance: Nanostructures, bioassays and biosensing—A review. *Chimica Acta*, Vol 706(1), (2011), pp. 8-24

[2] Yi, Z., Zhang, J.-B., He, H., Xu, X.-B., Luo, B.-C., Li, X.-B., Li, K., Niu, G., Tan, X.-L., Luo, J.-S. Tang, Y.-J., Wu,W.-D., and Yi, Y.-G. Convenient Synthesis of Silver Nanoplates with Adjustable Size through Seed Mediated Growth Approach. *Transactions of Nonferrous Metals Society of China, Vol* 22(4), (2012), pp. 865-872.

[3] Cao, J., Sun, T., and Grattan, K.T.V.Gold nanorod-based localized surface plasmon resonance biosensors: A review. *Sensors and Actuators B: Chemical* , Vol 195(0), (2014), pp. 332-351.

[4] Kajita, T., and Oyama, M. Tuning of nanostructures of gold nanoparticles on indium tin oxide surfaces using a seed-mediated growth method. *Journal of Electroanalytical Chemistry, Vol 5*56(1–2), (2011), pp. 264-268.

[5] Hong, Y., Huh, Y.-M., Yoon, D.S., and Yang, J. Detection of Biomarkers Using LSPR Substrate with Gold Nanoparticle Array**.** *Journal of Nanomaterials, Vol* (111), (2012).

[6] Sajanlal, P.R., Sreeprasad, T.S., Samal, A.K., and Pradeep, T. Anisotropic nanomaterials: structure, growth, assembly, and functions. *Nano Reviews*, 2 (5883), (2011).

[7] Chen, F., Fei, W., Sun, L., Li, Q., Di, J., and Wu, Y. Surface Modification on Silver Nanoparticles for Enhancing Vapor Selectivity of Localized Surface Plasmon Resonance Sensors. *Sensors and Actuators B: Chemical*, Vol 191(0), (2014), pp. 337-343.

[8] Morsin, M., Salleh, M.M., Umar, A.A., and Yahaya, M. Localized surface plasmon resonance sensor of gold nanoplates for detection of boric acid. *Key Engineering Materials,*Vol 605, (2014), pp. 356-359

[9] Monkawa, A., Nakagawa, T., Sugimori, H., Kazawa, E., Sibamoto, K., Takei, T., and Haruta, M. With High Sensitivity and with Wide-Dynamic-Range Localized Surface-Plasmon Resonance Sensor for Volatile Organic Compounds. *Sensors and Actuators B: Chemical*, Vol 196(0), (2014), 1-9.

[10] Miranda, A., Malheiro, E., Skiba, E., Quaresma, P., Carvalho, P.A., Eaton, P., De Castro, B., Shelnutt, J.A., and Pereira, E. One-Pot Synthesis of Triangular Gold Nanoplates Allowing Broad and Fine Tuning of Edge Length. .*Nanoscale,* Vol 2(10), (2010), pp. 2209-2216.

[11] Nengsih, S., Umar, A.A., Salleh, M.M., and Oyama, M. Detection of Formaldehyde in Water: A Shape-Effect on the Plasmonic Sensing Properties of the Gold Nanoparticles. *Sensors*, Vol 12(8), (2012), pp. 10309-10325.

[12] Salleh, M.M., Umar, A.A., and Morsin, P2.2.5 Detection of Boric Acid using Localized Surface Plasmon Resonance Sensor of Gold Nanoparticles, *M. P2. 2.5. Tagungsband*, (2012), pp. 1418-1421.

[13] Marlia, M., Umar, A.A., Oyama, M., Salleh, M.M., and Majlis, B.Y. High Sensitivity Localized Surface Plasmon Resonance Sensor of Gold Nanoparticles : Surface Density Effect for Detection of Boric Acid *10th IEEE Inter. Conf. on Semiconductor Elec. (ICSE)*, (2012), 352 – 356.

[14] Umar, A. A., Oyama, M., Salleh, M. M. and Majlis, B. Y. Formation of High-Yield Gold Nanoplates on The Surface: Effective Two-Dimensional Crystal Growth of Nanoseed in the Presence of Poly (Vinylpyrrolidone) and Cetyltrimethylammonium Bromide. *Crystal Growth and Design*, Vol 9(6), (2009), 2835-2840.

[15] Veres, Á., Rica, T., Janovák, L., Dömök, M., Buzás, N., Zöllmer, V., Seemann, T., Richardt, A., and Dékány, I. Silver and gold modified plasmonic TiO2 hybrid films for photocatalytic decomposition of ethanol under visible light, *Catal. Today*, Vol 181(1), (2012), pp. 156–162 (2012),

[16] Umar, A.A., Oyama, M., Salleh, M.M., and Majlis, B.Y. Formation of Highly Thin, Electron-Transparent Gold Nanoplates from Nanoseeds in Ternary Mixtures of Cetyltrimethylammonium Bromide, Poly(vinyl pyrrolidone), and Poly(ethylene glycol), *Cryst. Growth Design*, Vol 10(8), (2010), pp. 3694-3698