Structural and Optical Properties of Gold Nanosphericals in Variation of Growth Time Using Seed Mediated Growth Method

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***Abstract*—Nanogold is a type of metallic nanostructures and it is very sensitive to the dielectric environment of the materials due to strong dependency of plasmon on shapes and sizes. The unique properties of gold nanostructures can be implemented as sensing material in Localized Surface Plasmon Resonance (LSPR) sensor. This paper reports an experimental study on growth time effect towards structural and optical properties of gold nanosphericals (AuNSs). The gold nanoplates have been grown on a substrate using seed mediated growth method (SMGM). In this study, the growth time was varied from 30 minutes to seven hours. The largest size of AuNSs is ~ 82.67 nm obtained from 7 hours growth time sample. XRD analysis shows a peak of the diffraction angle occurs at the plane (111) in position ~ 38.19º. The optical absorption spectra of all samples show resonance peaks in the range of 530 nm to 560 nm, which are corresponding to the transverse surface plasmon resonance (t-SPR). Thus, in this study, it was found that the growth time affected the growth of the gold nanostructures with optimum growth time of seven hours. Longer growth time resulted in the larger size of AuNSs and therefore, it is not very suitable to be used in LSPR sensing application.**

***Index Terms*—Localized Surface Plasmon Resonance; Gold Nanoparticles; Seeding Time; Plasmonic Sensor; Seed Mediated Growth Method (SMGM).**

I. INTRODUCTION

Recently, particles with the sizes in the range of units to hundreds of nanometers or better known as nanoparticles have attracted a comprehensive attention from various research fields due to their unique electronic, magnetic, optical, physical and chemical properties as compared to their solid bulk materials [1-2]. Among nanoparticles, gold nanoparticles are one of the most useful nanoparticles especially in biotechnology and biomedical fields because of their large surface area, and high electron conductivity [2-4]. Furthermore, compare to other metal nanoparticles, gold nanoparticles have advantages due to their biocompatibility and non-cytotoxicity [2].

Gold nanoparticles have been applied in various fields namely as catalysis, optical molecular sensing, cancer therapeutics, and blocks construction in nanotechnology [3-5]. Specifically, in optical molecular sensing, the gold nanoparticle has been used in application such as LSPR sensor [5,6] as well as an optical antenna for single molecule detection [7].

So far, gold nanoparticles have been synthesized via different techniques such as oxidative etching, employment of polydiallyldimethylammonium chloride (PDDA) and seed mediated growth method (SMGM). SMGM is a wet chemical method which is carried out at room temperature and environment [5-6, 8]. The SMGM consists of two stages namely as seeding process and growth process. Seeding process is a process to deposit seeds on the substrate surface while controlling the morphology of nanoparticles [9]. Common reducing agents that usually employed in this process are ascorbic acid and hydroxylamine. Sizes of the particle can be manipulated by varying the ratios of gold (III) chloride trihydrate, $HAuCl_4$ and seeds [10]. After completing the seeding stage, the next process is the growth stage. The growth process ensures the gold nanoseeds successfully grown as gold nanoplates on the substrate surface.

In nanoscale, the size and shape of nanoparticles material are important parameters to describe its optical, electrical, and catalytic properties [11]. Therefore, preparation of this nanomaterial is very crucial to obtain required pattern and results. Gold nanoparticles exhibit various sizes ranging from 1 nm to 8 µm and they also exhibit different shapes such as spherical, sub-octahedral, octahedral, decahedral, icosahedral multiple twined, multiple twined, irregular shape, tetrahedral, nanotriangles, nanoprisms, hexagonal platelets and nanorods [2, 8]. Among all this shape, the nanosphericals has been chosen as a sensing material for LSPR application. Therefore, by adopting the SMGM as AuNSs synthesis technique, this work aims to investigate the effect of growth time has on the size of AuNSs. Several nanoparticles characterization tests such as optical, structural and morphological tests will be carried out on the resulted AuNSs in order to justify which one of the growth time can be selected as the most optimum growth time.

II. EXPERIMENTAL

The AuNSs is grown on indium tin oxide (ITO) substrate using SMGM. The chemicals used in the synthesis process were hydrogen tetrachloroaurate ($HAuCl_4.3H_2O$), trisodium citrate ($C_6H_5Na_3O_7$), sodium tetraborohydride ($NaBH_4$), Cethyltrimethy Ammonium Boromide (CTAB) and ascorbic acid. These chemicals were purchased from Sigma-Aldrich except trisodium citrate, sodium tetraborohydride and ascorbic acid which were obtained from Wako Pure Chemical Ltd. All these chemicals were used as received. The solutions of these chemicals were prepared using deionized (DI) water with resistivity around 18.2 MΩcm.

During the process of nanoparticles synthesis, two types of solutions namely as seed solution and growth solution were prepared. The first process is illustrated in Figure 1. The seed solution was prepared by mixing 0.5 ml of 0.01 M $HAuCl_4$, 0.5 ml of 0.01 M trisodium citrate and 20 ml DI water. Then, 0.5 ml of 0.1 M cold aqua $NaBH_4$ was added into the solution. Meanwhile, the growth solution was prepared by dissolves 20 ml of 0.1 M CTAB-capped seed using ultrasonic. For the final preparation step, 0.5 ml of 0.01 M $HAuCl_4$ and 0.1 ml of 0.1 M ascorbic acid was added to the solution. The step by step of growth procedures can be seen in Figure 2.

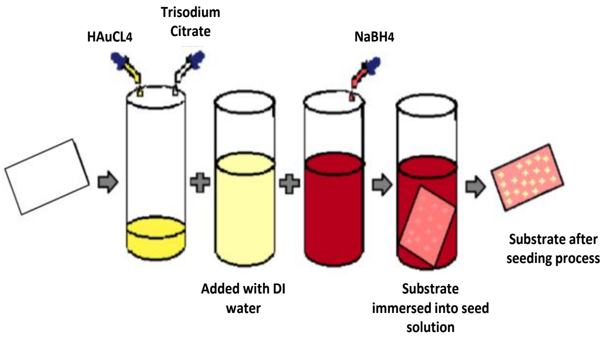


Figure 1**:** Preparation of seeding process

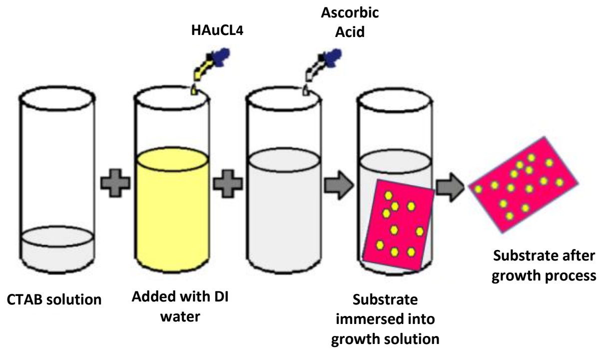
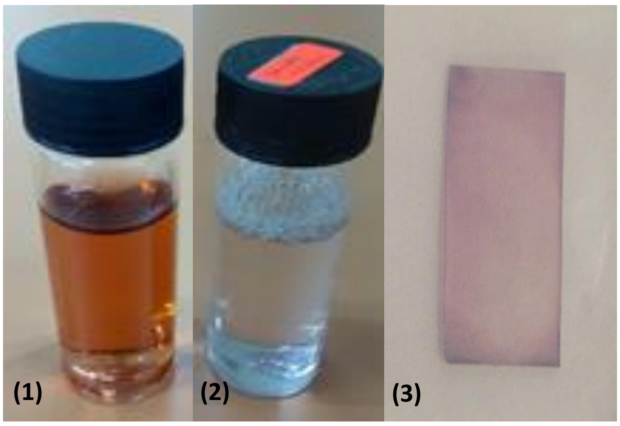


Figure 2**:** Preparation of growth process

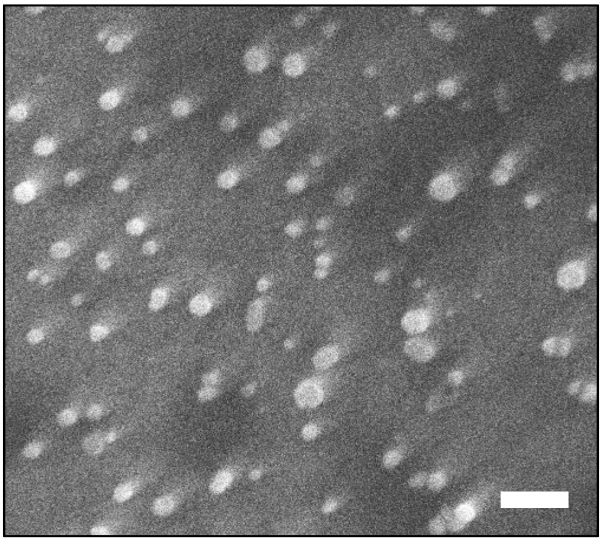
The AuNSs synthesis process was started with the cleaning of the substrate surface to remove any contaminants. Then, the substrate was immersed in the seed solution for two hours before drying them in a furnace for 1 hour at a temperature of 150 °C. In order to grow the gold nanostructure, the substrate was then immersed in the growth solution in predetermined time upon completing the dry process. Five different lengths of predetermined growth times have been selected which are 30 minutes, 1 hour, 3 hours, 5 hours and 7 hours. Once the immersing time period ended, the sample was placed into the furnace again for another 1 hour at 100 °C. Investigations of the morphological, structural and optical nanoparticles characterizations were carried out using Field Emission Scanning Electron Microscope (FESEM), X-ray Diffraction (XRD) and Ultraviolet-Visible Spectroscopy (UV-Vis), respectively.

III. Result and Analysis

The AuNSs have been successfully grown using seed mediated growth method at the room temperature based on the change of color solutions [12] as shown in Figure 3 (A). The sample color turns to pinkish after seeding and growth process completed. Then, the sample was characterized using FESEM. FESEM as a useful tool for high-resolution surface imaging has been used to observe surface morphology of the AuNSs on ITO. The ITO is a conductive material so it can be used directly using FESEM without additional coating. Meanwhile, Figure 3 (B) shows an example of FESEM images of AuNSs on the ITO glass substrate for 1 hour growth time. For investigation on growth time effect, five different growth times have been selected which are 30 minutes, 1 hour, 3 hours, 5 hours and 7 hours. The calculated average size of each sample based on these five different growth times can be seen in Table 1. The data from Table 1 obtained using this method; five different particles from each sample were randomly selected to calculate the average size.



(a)



(b)

Figure 3: (a) AuNSs formation on substrate surface (1) Seeding solution (2) Growth Solution and (3) Substrate after AuNSs synthesis process complete; (b) FESEM image of AuNSs grown on ITO substrate for 1 hour growth time. Scale: 100 nm

Table 1
Average Size for Each Sample

Time	Size (nm)
30 minutes	37.50
1 hour	40.00
3 hours	66.67
5 hours	76.18
7 hours	82.67

Exceeding 7 hours, the size of AuNSs is assumed to be larger than 100 nm based on the resulted trend shown in Table 1. Thus, since the AuNSs is proposed to be used in LSPR sensor, a size larger than 100 nm is not acceptable.

A. Structural Analysis

The XRD is used to analyze the structural properties of gold nanoparticles. Structure properties of all samples were characterized using XRD and the measurement was obtained by scanning 2θ degrees in the range of 30° to 60° with a grazing angle of 1°. The XRD results of successfully nanosphericals deposited on ITO glass at various immersion growth times can be found in Figure 4(a) – (e). From the results obtained, it shows that the gold has the highest peak on the spectra in each sample. The longer the time taken for the growth process, the bigger sizes of gold nanosphericals will be produced [12].

The obtained results are compared to the JCPDS-004-0784 file for gold standard at 38.20°. It is observed that the sharp peak of the spectrum with the highest peak indexed as (111) crystallographic planes of face centered cubic (fcc) gold nanocrystals appears from 38.18° to 38.44°. Referring to Figure 4, the results show that the (111) planes of spherical are dominantly oriented parallel to the surface of the supporting substrate [13].

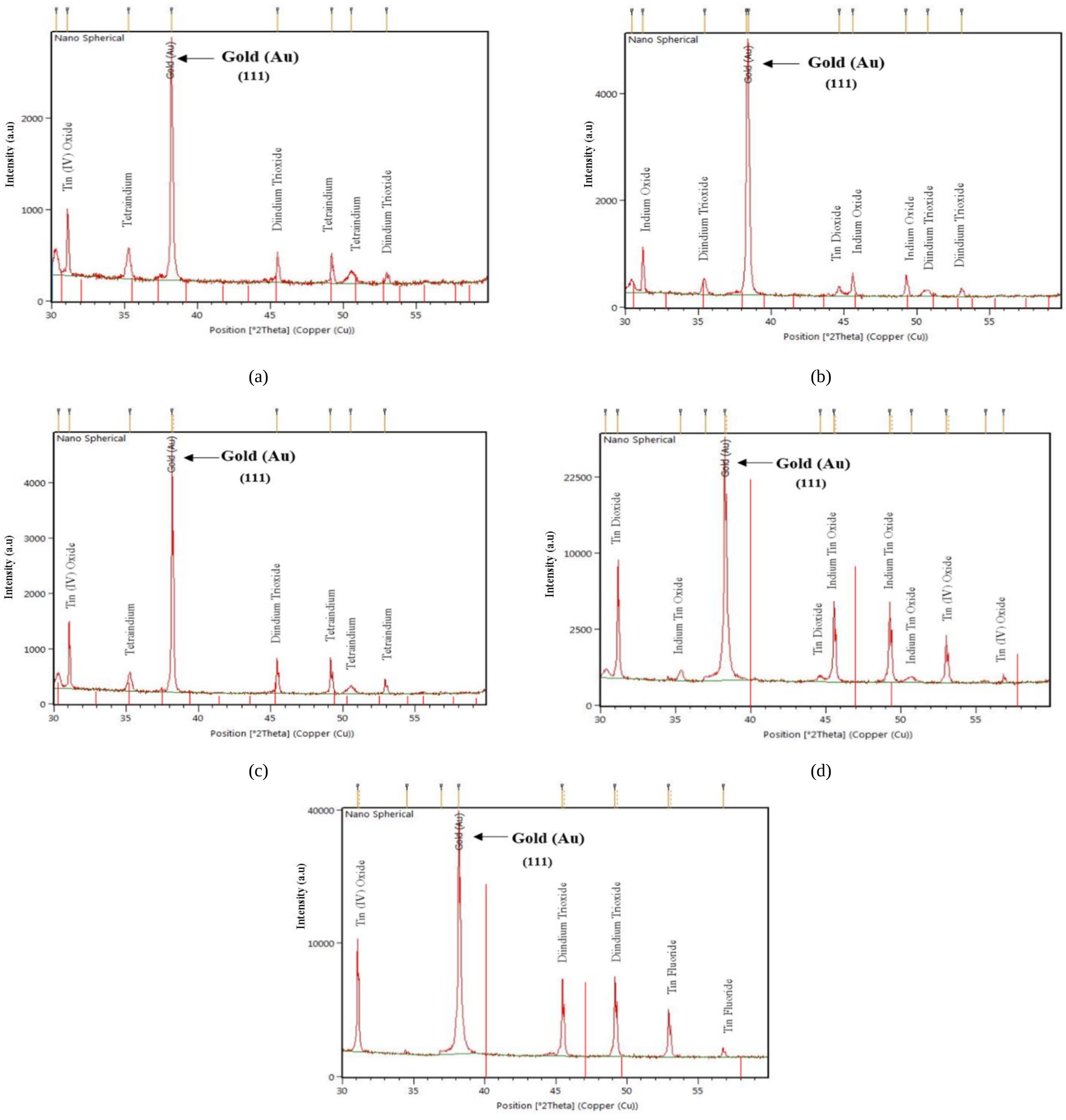


Figure 4: XRD spectra of gold nanosphericals deposited on (a) 30 minutes, (b) 1 hour, (c) 3 hours, (d) 5 hours and (e) 7 hours of growth time.

On the other hand, the lower peaks are less intense indicating there are not much of planes oriented in parallel with the ITO substrate [14]. The highest peak detected in the sample is sampled with 7 hours growth time and this sample has the best structural properties with highest possibilities in producing AuNSs. Besides that, these peak intensities do not identify the shape of the plates formatted [15].

B. Optical Analysis

The visible optical absorption spectrum of the sample can be used to confirm the formation of AuNSs on the substrate and for that reason, the Ultraviolet-Visible Spectroscopy (UV-Vis) is chosen for this task. Figure 5 shows the UV - Vis absorption spectra of AuNSs for various growth times. It was observed that the spectrum contains a single absorption peak ranging from 530 nm to 550 nm. The spectrum tends to shift right when the growth time was increased. Besides that, the intensity of the spectrum also increases with the increment of growth time. This situation occurred due to the generation of more nanoparticles on the substrate. This absorption band agrees with previous observations of the LSPR spectrum of spherical shape gold nanoparticles [12]. Meanwhile, Table 2 tabulates the result of UV-Vis according to various growth times. The results indicate that the highest absorbance occurs during the longest predetermined time that is 7 hours. The absorbance intensity shows decreasing pattern as the growth time decreases in which the lowest absorbance happened at 30 minutes growth time.

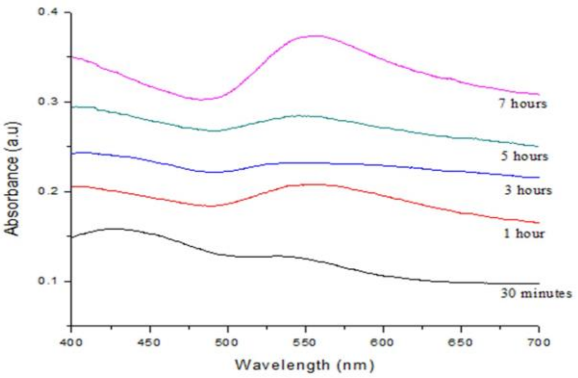


Figure 5: Optical absorption spectrum for 5 different growth time.

Table 2
UV-Vis Results for All Samples

Time	Intensity (a.u)	Wavelength (nm)
30 minutes	0.128	533.5
1 hour	0.288	555.5
3 hours	0.312	543.5
5 hours	0.484	546.5
7 hours	0.690	554.5

IV. CONCLUSION

The AuNSs was successfully grown on the substrate surface using seed mediated growth method with 7 hours as the most effective AuNSs growth time to be employed in LSPR application. Different time length of growth times will result different sizes of gold nanosphericals. It can be seen that the longer time taken for growth process, the bigger sizes of gold nanosphericals can be obtained. From the findings, the sample of 7 hours growth time has the largest size of gold nanosphericals. The trend appears in the FESEM results also suggest that by extending the growth time, larger particles size (more than 100 nm) is possible to be achieved. The larger size (>100 nm) will affect the plasmonic response in the LSPR sensor application. Therefore, 7 hours can be set as the optimum cut off time for producing AuNSs. Besides that, the structural properties of AuNSs characterized by XRD also shows that the sample of 7 hours has the highest density of gold nanosphericals at position of °2 theta at 38.19° with coincide with gold standard file. As for optical properties that characterized by UV-Vis, the result shows five absorption spectra of AuNSs for various time of growth process with each sample shows a peak of Au and another peak of ITO. The optical absorption spectrum increases with increment of the growth process. The peak of intensity is increased at wavelength 530 nm to 550 nm. The shifting of the spectrum to the right indicates the increases in growth time.

In the future, the study of gold nanostructures can be expanded to shape, inter particles spacing and density. These parameters will influence the LSPR sensing parameters in LSPR sensor application.

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