Effect of Seeding Time on the Formation of Gold Nanoplates

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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...
were hydrogen tetrachloroaurate (HAuCl₄·3H₂O), poly-L-lysine (PLL), trisodium citrate (C₆H₅Na₃O₇), sodium tetraborohydride (NaBH₄) ascorbic acid, cetyltrimethyl 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 NaBH₄ 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 °C 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 °C 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 nanoparticles 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 nanoparticles [15]. While pink color refers to gold nanospherical shape [5, 16]. This indicates that gold nanoparticles 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 20° to 60°. The first peak appeared in the plane (111) in position 38.175°, 38.200° and 38.225° while the second peak is seen in the plane (200) at 44.275°, 44.250° and 44.400°. The results obtained were matched with data for bulk material gold standard of JCPDS 004 - 0784, which is in the angular position 38.185° and 44.393°. 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 nanoparticles. 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 nanoparticles 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 nanoparticles (i.e corresponding to 111 plane) increases with an increment of seeding time.

![XRD Peaks](image)

**Fig. 1 The XRD for all samples**

<table>
<thead>
<tr>
<th>N o.</th>
<th>Samp le</th>
<th>Plane (111)</th>
<th>Plane (200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle (°)</td>
<td>Intensity</td>
<td>Angle (°)</td>
<td>Intensity</td>
</tr>
<tr>
<td>1</td>
<td>MP1</td>
<td>38.175°</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>MP2</td>
<td>38.200°</td>
<td>189</td>
</tr>
<tr>
<td>3</td>
<td>MP3</td>
<td>38.225°</td>
<td>302</td>
</tr>
</tbody>
</table>

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 nanoparticles - 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).
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.

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References


