Aggregation effect on absorbance spectrum of laser ablated gold nanoparticles

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Abstract. Plasmon of gold nanoparticles is one of the hot topics nowadays due to various possible applications. The application is determined by plasmon peak in absorbance spectrum. We have fabricated gold nanoparticles using laser ablation technique and studied the influence of CTAB (Cetyl trimethylammonium bromide) effect on the optical characterization of fabricated gold nanoparticles. We ablated a gold plate using NdYAG pulsed laser at 1064 nm wavelength, 10 Hz pulse frequency at low energy density. We found there are two distinctive plasmon peaks, i.e., primary and secondary peaks, where the secondary peak is the main interests of this work. Our simulation results have revealed that the secondary plasmon peak is affected by random aggregation of gold nanoparticles. Our research leads to good techniques on fabrication of colloidal gold nanoparticles in aqueous solution using laser ablation technique.

1. Introduction
Nanoparticles have been creating a lot of promising advanced nano-technologies. One of potential nanoparticles is gold nanoparticles [1, 2]. There are a lot of researches have been done to study the properties of gold nanoparticles. One unique property of gold nanoparticles is plasmon, which is energy of oscillating electrons inside gold nanoparticles due to external electromagnetic field [1, 2]. In the case, the plasmon is well known as localized surface plasmon, which exists in limited plasmon region surrounding gold particle [2, 3]. The plasmon region only occur few nanometers surrounding the surface of gold nanoparticles. Although the plasmon region is very restricted, the effect of plasmon is very powerful. One of potential applications of plasmon produced by gold nanoparticles is emission enhancement of fluorescent nanoparticles located nearby gold particle [3-5]. However, there are some conditions must be meet to have good enhancement by gold nanoparticles [4, 5]. First, there must be a resonant condition between emitting nanoparticles and plasmon of gold nanoparticles. Second, the distance between emitting nanoparticles and gold nanoparticles must be close enough, approximately 10 nanometers (nm). Based on those conditions, it is difficult to apply specific gold nanoparticle to many emitting nanoparticles. Thereorefore, some modification of plasmon region and plasmon frequency is required. Some studies have been conducted to modify plasmon regions and frequencies. Changing diameter of gold nanoparticles is a simple way to vary plasmon frequency. However, this...
way only changes plasmon frequency up to certain frequency [6]. Fabricating multishell of metallic nanoparticles is one effective way to produce two plasmon frequencies [7]. Many researchers also have proven that gold nanorods produce dual plasmon frequencies due to longitude and transverse waves [8]. Another interesting arrangement of gold nanoparticles is cluster of gold nanoparticles. Plasmon range and distribution significantly change when gold nanoparticles are close to each other. Researches on the change of optical properties due aggregation of gold nanoparticles are very few due the uninteresting application of gold nanoparticle aggregation. Nevertheless, the change of plasmon frequency and distribution is still interesting to study. The aggregation of gold nanoparticles is a well-known knowledge, however, so far only few studies have reported the plasmon effect due to aggregation. In addition, there several ways to fabricate gold nanoparticles, including chemical process and laser ablation. In this work, we will use laser ablation to fabricate gold nanoparticles. The purpose of this work is to study the change of plasmon frequency due to aggregation of gold nanoparticles fabricated using laser ablation method. In addition, we will use simulation result to explain our experimental findings.

2. Experimental
In order to clarify the effect of aggregation to plasmon frequency and distribution, we conducted experimental and simulation works. In the experimental work, we fabricated gold nanoparticles using laser ablation method as shown in figure 1(a). One gram of gold plate purchased from ANTAM (Indonesian government owned general mining company), with purity of 99% was cleaned using methanol and then placed in a glass beaker filled by purified water. Pulsed laser from NdYAG laser with wavelength 532 nm was focused onto gold plate. Detail optical setup used in this experiment is shown in figure 1(b). It took about 1 until 2 hours to ablate gold plate to obtain gold nanoparticles. UV-Vis spectrometer was utilized to analyze fabricated gold nanoparticles. The absorption spectrum was used to characterize plasmon frequency and its other properties. In order to make aggregation and monodispersed gold nanoparticles, we used CTAB (Cetyl trimethylammonium bromide) that was dissolved in purified water solvent prior ablation process. In addition, we also varied the ablation energy of pulsed laser from 12 mJ, 23 mJ, 29 mJ, and 36 mJ.

In the simulation work, we use MPBEM tool box, which was obtained online and run it in MATLAB program [9]. We modified size of gold nanoparticles, space distance in between gold nanoparticles and number of gold nanoparticles. The simulation used boundary element method computational technique to generate extinction cross section, absorption cross section and scattering cross section. We used simulation results to analyze and explain experimental results.
Figure 1. Fabrication process of laser ablation to fabricate gold nanoparticles (a) and laser ablation optical setup used in this work (b).

3. Results and discussion
Laser ablation technique used in this work, has successfully fabricated gold nanoparticles. The direct indication of successfully fabricated gold nanoparticles is the liquid color has changed from colorless into pink and red color as shown in figure 1(a). In general, the color of gold nanoparticle solution determines size, distribution and aggregation of fabricated gold nanoparticles [1, 3]. Pink color usually indicates small size or monodispersed of colloidal gold nanoparticles. On the other hand, purple or dark red color indicates large size or aggregated gold nanoparticles. We have noticed that our fabricated gold nanoparticles were stable until few weeks after fabrication. This good stability gives us enough time to characterize our fabricated gold nanoparticles. Experimentally, we investigated our gold nanoparticles using UV-Vis spectrometer to study the plasmon peak in absorbance spectrum and using TEM (transmittance electron microscope) to study size distribution of gold nanoparticles.

Figure 2. Absorption spectra of fabricated gold nanoparticles with (a) and without (b) CTAB.
We used three different energy of laser to ablate gold plate in aqueous solution. The effect of laser energy is described below. Figures 2(a) and 2(b) describe absorption spectrum of fabricated gold nanoparticles with different ablation laser energy with and without CTAB. Although there is no clear trend, but we can clearly see that higher ablation energy produced higher absorbance values. High absorbance values indicate high concentration of fabricated gold nanoparticles. Visually, we also observed (not shown in the figure) that higher ablation energy produced darker color of colloidal gold nanoparticles. The inconsistence of absorbance value as the function of ablation energy is probably due to aggregation effect. Detail of aggregation effect will be discussed later.

![Figure 3](image.png)

**Figure 3.** TEM images of gold nanoparticles with (a) and without (b) CTAB. The inset figures are visual appearances of corresponding gold nanoparticles in ambient illumination.

Further effect of aggregation was conducted by investigating fabricated gold nanoparticles without the addition of CTAB. The fabricated gold nanoparticles with CTAB have very distinctive single plasmon peak and absorption spectra as shown in figure 2(a). There is only one plasmon peak occurs for every absorption spectra at around wavelength 523 nm until 524 nm. This indicates that CTAB can protect fabricated gold nanoparticles very well against self-aggregation. The evidence of less aggregation is given by a TEM image as shown in figure 3(a). The fabricated gold nanoparticles is well separated one to another. Visual appearance (inset image in figure 3(a)) also shows that fabricated gold nanoparticles have clear pink color.

On the order hand, without addition of CTAB, the fabricated gold nanoparticles have two distinctive peaks in absorption spectra as shown in figure 2(b). The first peak is the primary plasmon peak. This peak varied from 520 nm until 533 nm. The second peak occurs at around 640 nm. This peak is assumed as secondary plasmon peak that occurs due to aggregation effect of fabricated gold nanoparticles. The evidence of aggregation is shown by TEM images in figure 3(b). The fabricated gold nanoparticles are aggregated making a group of cluster or a chain group of gold nanoparticles. Actually, the sizes of fabricated gold nanoparticles with and without CTAB are comparable. We found that the size fabricated gold nanoparticles vary from 5 nm until 80 nm. The only different between those samples is only aggregation.
In order to confirm the origin of aggregation, we conducted simulation work to produce absorption spectra using various gold nanoparticles properties. First, we study the effect of size of gold nanoparticles on absorbance spectra. We simulated absorbance spectra of single gold nanoparticles with different size from 5 nm until 100 nm. The simulated absorbance is shown in figure 4. We found that the plasmon peak slightly shifts to longer wavelength when the size of gold nanoparticles increases. The plasmon peak shifts from 508 nm (for 5 nm gold nanoparticles) to 518 (for 100 nm gold nanoparticles). We found that there is only one distinctive peak in absorbance spectrum. There is no secondary peak occurs at longer wavelength. This simulation agrees with prior researches on basic optical properties of gold nanoparticles [1-3]. Therefore, we can conclude that although fabricated gold nanoparticles have large size distribution, the plasmon peak does not strongly influence by size distribution of gold nanoparticles and there is no secondary plasmon peak that occurs.

Furthermore, we simulated aggregation effect of gold nanoparticles. We simulated absorbance using six gold nanoparticles with diameter 10 nm as shown in figure 5(a). First, we varied space distance between gold nanoparticles from 0 nm until 5 nm. We found that the space distance significantly influences absorbance spectrum of gold nanoparticles. The space distance from 0 nm until 1 nm strongly creates secondary peak of absorbance spectrum as shown in figure 6(a). In addition, main plasmon peak shift to longer wavelength by more than 80 nm, compare to plasmon peak of individual gold nanoparticles, when gold nanoparticles are separated by 1 nm. The plasmon peak shifts to shorter wavelength when the space distance between gold nanoparticles increases from 1 nm until 5 nm. It is predicted that the plasmon peak return to its original wavelength when the space distance between gold nanoparticles is more than its diameter. In order to reproduce absorbance spectrum of fabricated gold nanoparticles, we simulated six gold nanoparticles with random space distance between 0 nm until 1 nm as shown in figure 5(b). The simulated absorbance spectrum is shown in the bottom curve of figure 6(a). We compared the simulated the absorbance spectrum of gold nanoparticles having random space distance to the absorbance spectrum of fabricated gold nanoparticles without CTAB as shown in figure 6(b). We clearly see that there are two peaks in
absorbance spectrum. The first peak is the primary plasmon peak of gold nanoparticles at around 530 nm. The secondary peak is at wavelength longer than 600 nm. Based on our simulation results, we can confirm that the secondary peak is attributed to aggregation of gold nanoparticles. The wavelength of secondary peak positions of simulated gold nanoparticles is not exactly similar to that of fabricated gold nanoparticles. This is probably due to random distribution of gold nanoparticles and the unknown number of gold nanoparticles in the aggregated cluster. Nevertheless, our simulation results have shown that aggregation plays an important role in secondary plasmon peak. We assume that aggregation of gold nanoparticles constructs overlapped plasmon distribution of individual gold nanoparticle. This overlapping region may generate new plasmon frequency probably due to interference effect in the overlapping region.

**Figure 6.** Simulated absorbance spectrum of gold nanoparticles with different space distance (a) and comparison of absorbance spectrum between simulated and fabricated gold nanoparticles (b).

Further work still remains to investigate how powerful the secondary plasmon peak and the possible application of this secondary plasmon peak in the practical technologies. For some application, this secondary plasmon peak is not required. Nevertheless, we still believe that this secondary peak is still useful for certain applications, especially applications in near-infra red region.

4. Conclusions
We have successfully fabricated gold nanoparticles using laser ablation technique with and without CTAB. We have observed that the absence of CTAB strongly affects aggregation of fabricated gold nanoparticles. The aggregation of gold nanoparticles is indicated by secondary plasmon peak in peak absorbance spectrum. We have carefully studied and simulated the effect of gold nanoparticles size and aggregation of gold nanoparticles cluster. We found that size of gold nanoparticles does not generate secondary plasmon peak in absorbance spectrum. Furthermore, random aggregation clearly creates primary plasmon peak around 530 nm and secondary plasmon peak at wavelength longer than 600 nm. The secondary plasmon peak was generated at gold nanoparticles space distances of 0 - 1 nm. These results demonstrate new potential applications in utilizing surface plasmon effect.

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