Simple gold nanoparticles production method by ablated laser: Diameter modification

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Abstract. Recently, an improved interest in gold nanoparticles (AuNPs) with an interesting phenomenology such as plasmon resonance, has been aroused. There are many methods to synthesized AuNPs. We have successfully fabricated AuNPs base on laser ablation method. The pulsed Nd:YAG laser ablated at 1064 wavelength to a pure gold plate. The frequency was adjusted in low range to produce low energy density laser beam. Three different solution (aqueous, polyvinyl alcohol and polyethylene glycol) was applied to modify AuNPs diameter. The modified nanoparticles diameter was observed by mean UV-Vis spectroscopy exhibit different absorption peak wavelength. For comprehensive discussion, the spectrum was compared to simulation tool on MATLAB. Interestingly, AuNPs diameters have been modified by using different solution.

1. Introduction

There is a recent surge of interest in gold nanoparticles (AuNPs), mostly in field related to biomedicine and bioimaging. AuNPs are could be readily conjugated with recognition moieties such as antibodies or oligonucleotides for the detection of target biomolecules, allowing in vitro detection and diagnostics applications for diseases such as cancer [1,2]. The versatile optical and electronic properties of AuNPs also have been employed for cell imaging using various techniques [3].

The most commonly used method to synthesize gold nanoparticles is by chemical reaction. For example, Turkevich and Brust-Schifrin’s method use hydrogen tetrachloroaurate (HAuCl₄) treated by citric acid and sodium borohydride (NaBH₄) respectively to make spherical AuNPs [4,5]. There’s also seeded method that used gold salt reduced by reagent such as sodium borohydride, which widely preferred to make AuNPs in other shapes [6]. These methods could provide more controlled growth of gold nanoparticles with a little modification, but it’s sophisticated and also may be costly for some.

The chemicals methods also some major drawback, such as toxic byproduct generated in the process. In response of these concern, a method of synthetization using biological means was developed. This method uses biocomponents present in plants such as flavanoids, phytosterols, quinones etc [7]. Some
research also uses microorganism to aid AuNPs production [8], or using biomolecules as catalyst to reduce Au ions into Au atoms [7].

Another method is by using laser ablation method. A gold plate ablated inside a solvent to produce AuNPs. This method is simpler, more “cleaner” than production through chemical means, but in the other hand, it’s unable to make sophisticated shape [9,10].

In this experiment, we tried to synthesize AuNPs using laser ablation method, and measure its diameter by means of UV-Vis spectroscopy and MNPBEM simulation

2. Method

2.1. Sample preparation

First, we prepared the parameter solvent, such as aqueous, polyvinyl alcohol 0.1% (PVA), and polyethylene glycol 0.1% (PEG). These solvents will be added to modify the diameter of the AuNPs. We make sure to keep the refractive index unchanged from water’s refractive index so it won’t affect the parameters. 5ml of each solvent will be used in ablation process.

For the ablation process, we used Nd:YAG pulsed laser with 1064nm wavelength and 10Hz repletion rate for ±5 minutes. The AuNPs samples then observed by mean UV-Vis absorption spectroscopy.

![Figure 1. Illustration of ablation process.](image)

2.2. Simulation using MNPBEM

Modified nanoparticles diameter exhibit different absorption peak wavelength. For comprehensive discussion, the spectrum was compared to simulation tool on MATLAB called MNPBEM. MNPBEM is a toolbox for the simulation of metallic nanoparticles (MNP), using a boundary element method (BEM) approach developed by F. J. Garcia de Abajo and A. Howie [11]. The tool itself was developed by U. Hohenester and A. Trügler from University of Graz, Austria [12]. The simulation used boundary element method computational technique to generate extinction cross section, absorption cross section and scattering cross section.

With this tool, we could approximate the diameters of sample by matching simulation data with UV-Vis absorption data. The feature we use in this tool is simulation of plane wave excitation. The parameter
we used in the simulation are dielectric coefficient table of gold, refractive index of the solvent, and diameter of the nanoparticles sphere. Dielectric coefficient table has been provided by the developer in form of a gold.dat file. For refractive index, we use refractive index of water of 1.33. We only need to tune diameter parameter until the simulation peak approximately matched the UV-Vis data.

3. Discussions

The resulting sample are shown in figure 2. AuNPs in aqueous has a dark pink color, while AuNPs in PEG has deep purple color as do as AuNPs in PVA, albeit with a bit lighter shade.

The graph in figure 3, we saw that both data have the same wavelength for each parameter’s absorbance peak. The UV-Vis data has peak at ±520nm with absorbance peak around 1.01, 1.24, and 0.91 respectively for each parameter. They have average peak width of 130.7 nm, measured from the left most minimum point.

The simulation has ±529nm wavelength peak for each parameter, with absorbance peak around 1.02, 1.23, and 0.92 respectively. Relative difference of the peaks for the simulation compared to the UV-Vis absorbance for each sample are: 0.99% Aqueous solution, 0.81% for PEG solution, and 1.09% for PVA solution.

By comparing UV-Vis data to simulation as shown in table 1, it can be concluded that the diameter for each sample are 16.2 nm, 16.7 nm, and 15.9 nm for Aqueous, PEG, and PVA sample respectively. We can see that AuNPs solution in PEG has the biggest diameter while AuNPs solution in PVA was the
smallest of the three. If we use AuNPs in aqueous as reference, then the size difference are: 3.09% bigger for PEG and 1.85% smaller for PVA.

**Table 1.** Comparison between UV-Vis and simulation data.

| Sample         | Aqueous | PEG  | PVA  | Aqueous | PEG  | PVA  |
|----------------|---------|------|------|---------|------|------|
| Wavelength (nm)| 520.5   | 521.7| 520.5| 529     | 529  | 529  |
| Peak           | 1.01    | 1.24 | 0.91 | 1.02    | 1.23 | 0.92 |
| Peak width (nm)| 122.5   | 142.5| 127.4| 121.5   | 121.5| 121.5|
| Diameter (nm)  | 16.2    | 16.7 | 15.9 |         |      |      |

We suspect that this difference in diameter happens because the difference in polarity. PVA is more polar than PEG. This difference makes AuNPs smaller or bigger.

4. **Conclusion**

With using MNPBEM simulation, an approximation of AuNPs diameter could be calculated. These result shows that solvent for AuNPs does affect the diameter of nanoparticles. Further research needs to be done to find the rate how these solvent affect AuNP’s size.

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