Synthesis Ag nanoparticle by laser fragmentation for high sensitive ammonia residue detection

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Abstract. We have been synthesis silver nanoparticles by using chemical analysis and successfully reduce silver nanoparticles with femtosecond laser fragmentation method with various silver nanoparticles size ranges from 60 - 75 nm, 10 - 35 nm and 9-17 nm. Characterization is carried out by Modular UV-Vis Spectrometer (MayaPro200, Ocean Optics) and Transmission Electron Microscope (TEM FEI Tecnai G20 S-Twin 200kV). Based on the results, silver nanoparticles (particles size are 9-17 nm) is high potential for detection of ammonia residues by ammonia PPM enhancement (10 PPM, 100 PPM, 150 PPM, 200 PPM, 250 PPM, 300 PPM, 350 PPM, 400 PPM, 450 PPM, and 500 PPM) and a maximum shift of absorbance at a wavelength of 433.39 nm, while TEM characterization have the structure is round.

1. Introduction

Study for nanotechnology is increasing, particularly on silver-based nanomaterials, encourage the researchers conduct further study to extend these nanomaterials. Study on silver nanoparticles (AgNPs) as one of the results of the progress of nanotechnology has been widely developed including; synthesis of AgNPs ingredients [1], highly sensitive detectors [2], and research for optical properties, AgNPs size and AgNPs shape [3].

AgNPs can be created by using physical, biological and chemical methods. Among the three methods of create AgNPs above, physical method have not been widely studied through femtosecond laser fragmentation although it involve chemical bonds, electron transfer, and electrostatic interactions in the manufacturing process. Making AgNPs also can be obtained chemically, by react AgNO₃ with reducing agent chemicals such as sodium borohydride, citric acid, etc. [4].

In 2017, Thanawan Ritthichai and Vimolvan Pimpan, AgNPs were synthesized by using tannic acid to detect ammonia (NH₄OH) [5]. In 2018, Alessandro Buccolieri and friends investigated the ability of AgNPs to detect ammonia (NH₄OH) with various ppm ammonia concentrations 0.01, 0.1, 1.5, 10, 100, 1000 [6], and 2000. Then in 2006, S. Besner and friends, made nanoparticles by using a femtosecond laser by fragmentation method [3].

Based on this description, this study combines 2 methods to create AgNPs, chemical and physical methods. The first AgNPS creation was carried out chemically and then physically by using femtosecond lasers with fragmentation method to reduce the particle size of AgNPs that had previously been created, then AgNPS were test to investigate the ability of these AgNPs in ammonia (NH₄OH) residues detection.

2. Experiment

2.1 Material

H₂O (Aquades), Trisodium Citrate (TSC), AgNO₃ (Sigma Aldrich, 99.9%), Ascorbid Acid, and NH₄OH (Merck, 35%)

2.2 AgNPs
AgNPs was created by mixing 100 mL of aquades with 1.75 g of TSC powder, 2.5 mL of AgNO₃ solution, and 0.5 g of ascorbic acid powder in sequence. For each mixing, they were homogenized by using stirrer. Then, the solution spectra was measured by using UV-Vis spectrometer.

2.3 Reduce the size of AgNPs by using femtosecond lasers with the fragmentation method
The previous AgNPs were carried out with TEM to determine the particle size of the solution ranges from 60-75 nm. Irradiation by using different femtosecond laser with fragmentation method was used to create a different size at a power of 800 nm and energy of 2.03 Watt for each 3 mL sample in 10 mL biker. The first particle size was 10-35 nm which it was obtained by irradiating the solution for 7.5 minutes and the second particle size was 9-17 nm which it was firstly obtained by diluting the AgNPs solution with a ratio of 1: 2, and then irradiate the solution for 5 minutes.

2.4 Characterization
2.4.1 UV-Vis Spectrometer. Characterization was carried out with UV-Vis spectra for 3 times. First, spectra of AgNPs solution which had been created by chemical methods were measured. Second, spectra of AgNPs solution which its particle size has been reduced by physical methods were measured and third, spectra of various solution which it had been doped by various concentration of PPM (Part Per Million) (10 PPM, 100 PPM, 150 PPM, 200 PPM, 250 PPM, 300 PPM, 350 PPM, 400 PPM, 450 PPM, 500 PPM) were measured to determined spectra shift which before and after NH₄OH had given and the ability of AgNPs to detected NH₄OH residues.
2.4.2 TEM. Characterization was carried out with TEM to determined morphology and particle size of AgNPs in this study.

3. Results and Discussion
3.1 AgNPs Particle Size
In theory, nanoparticles have a size of about 1 - 100 nm. AgNPs were synthesized by combined 2 methods, chemically and physically. Figures 1a, b, and c showed morphology of round silver nanoparticles with sizes range from 60 - 75 nm for parent solution (1.a), 10 - 35 nm for nanoparticles were irradiated by laser for 7.5 minutes (2b) and 9 - 17 nm for nanoparticles were irradiated for 5 minutes with parent solution had been diluted before (3c), as shown in figure 1. Based on these results, fragmentation can reduce the size of AgNPs.

The size of silver nanoparticles could be predicted by UV-Vis data and maximum wavelength of absorbance peak [4].

**Table 1.** Size of silver nanoparticles by TEM in this study and ref data [4] by David Paramelle for a comparison.

| No | Sample Name                  | $\lambda_{\text{max}}$ (Maximum Wavelength) | Nanoparticle Size       |
|----|-------------------------------|--------------------------------------------|-------------------------|
| 1. | Parent Solution               | 442.01 nm                                  | 60 – 75 nm              |
| 2. | irradiated by laser for 7.5 minutes | 410.92 nm                                  | 10 – 35 nm              |

**Figure 1.** Histogram data and TEM results (a) Parent Solution (b) irradiated by laser for 7.5 minutes (c) irradiated laser for 5 minutes after been diluted.
3. Irradiated by laser for 5 minutes diluted first

|       | 395.2 nm | 9 – 17 nm | 12 nm |
|-------|---------|-----------|-------|

Based on the comparison of the size of silver nanoparticles between TEM data and reference data [3] as a comparison were related to table 1 for samples of parent solution nanoparticles and samples were irradiated by laser for 5 minutes diluted first. The size of silver nanoparticles had been predicted by reference [3] were related to TEM results of the sample, while nanoparticle samples were irradiated by laser-fired for 7.5 minutes had difference of 3 nm than TEM data of sample.

3.2 AgNPs for detection ammonia residue

AgNPs had the smallest particle size were used. Based on the three AgNPs samples which have been created and test for particle size, the AgNPs sample which have been irradiated by laser for 5 minutes with the parent solution diluted first was used because its particle size was 12 nm. After that, sample was divided into 10 parts at a size of 1 mL and then given by 1 mL ammonia with various PPM concentrations. Sample was characterized by using UV-Vis to identified spectrum shift of samples.

![Graph of AgNPs testing for its ability to detect ammonia residues with different concentrations by UV-Vis and insert is enlarge absorbance peak of wavelength 380 – 480 nm.](image)

Figure 2. Graph of AgNPs testing for its ability to detect ammonia residues with different concentrations by UV-Vis and insert is enlarge absorbance peak of wavelength 380 – 480 nm.

Molecule reaction between ammonia and AgNPs could occur to AgNPs synthesis have pendants element. Therefore, AgNPs are stabilized by OH truss where in pendantsant. Thus, OH truss adhere on AgNPs surface. While, addition ammonia onto samples will be scavenger to OH truss which increasing ammonia concentration addition will effect OH truss affiliate to NH₄⁺. AgNPs will not have OH truss on the surface which cause it to be stable.

Figure 2 showed the ability of AgNPs in ammonia residue detection which was marked by wavelength shifting of each ammonia PPM value even though the shift in each sample is very slight and not shift significantly. According to Thanawan Rithichai and Wimolvan, one of cause wavelength shifting is increasing pH of each samples. Furthermore, shifting peak absorbance to height as long with increasing ammonia PPM is caused by increasing particle size which it is consequence of increasing pH. Sample before ammonia were given had a wavelength of 417.29 nm while the sample after ammonia with the highest PPM value were given has a wavelength of 433.39 nm. Although it only has a difference of around 16 nm than those samples, but if it was compared with reference [4], AgNPs were used in this study had a higher level of sensitivity.
4. Conclusion
Based on the study above, femtosecond laser with fragmentation method can be used to reduce the particle size of AgNPs. The particle size of AgNPs determines the sensitivity of nanoparticles. If particle size was decrease, level of sensitivity was increase. AgNPs testing in detection of ammonia residues has proven the ability of AgNPs as a detector by absorbance peak shifting.

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