Sunlight-assisted synthesis of colloidal silver nanoparticles using chitosan as reducing agent

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Abstract. The present study we explore an environmentally friendly colloidal silver nanoparticles preparation using chitosan as reducing agent and stabilizer. It develops a new strategy on preparation of silver nanoparticles through the gel phase using sodium hydroxide (NaOH) as accelerator reagent. Sunlight irradiation was employed to assisted reducing process of silver ions to silver nanoparticles. Localized surface plasmon resonance (LSPR) phenomenon of silver nanoparticles was investigated using UV-Vis spectrophotometer. The shape and size of silver particles were analyzed using TEM. The formation of silver nanoparticles was confirmed by the appearance of LSPR absorption peak at 396.0–412.0 nm. The absorption peak of LSPR were affected by NaOH amount, time of sunlight irradiation and concentration of AgNO3. The produced silver nanoparticles were spherical with dominant size range of 5 to 8 nm as shown by TEM images. All colloidal were stable without any aggregation for 30 days after preparation.

1. Introduction

Metallic nanoparticles have possible applications in diverse areas such as electronics, cosmetics, coatings, packaging, and biotechnology [1]. Among nanostructured noble metals the most important commercialized nanoparticles are silver nanoparticles. Silver nanoparticles have attracted considerable attention for their application in antimicrobial materials [2], medical therapy [3], biomolecular detection [4] and catalysts [5]. Silver nanoparticles can be synthesized through 2 approaches with bottom up and top down approaches. The bottom up approach is more developed because it is easier to do with simple tools. Chemical reduction is one of the methods in bottom-up approach that have carried out by many previous researchers.

The silver synthesis of nanoparticles is effective when reduction using strong reducing agents eg NaBH4 but not environmentally friendly [6]. If using a weak reducing agent requires a high temperature and a long time [7, 8]. Therefore it is necessary to do alternative methods that are environmentally friendly and economical. Several eco-friendly methods that can be developed include the use of photon-assisted reduction methods of gamma ray irradiation [9], UV rays [10] and sunlight [11]. Sunlight-assisted reduction is very interesting to study because it is more efficient and does not require complicated equipment. Samples containing precursor salts are irradiated by direct sunlight in the presence of a stabilizer. Some polymers can be used as stabilizers in the synthesis of silver nanoparticles such as chitosan [12], Poly vinyl alcohol [13] and polyethylene glycol [14]. Chitosan is one biopolymer...
that is potential to be used as stabilizing agent because it has antibacterial activity and also environmentally friendly [12, 15].

In this study, silver nanoparticles were synthesized using chitosan as stabilizers and sodium hydroxide as accelerators and sunlight as a trigger for chemical reduction processes. The use of NaOH accelerators has been done by previous studies on weak reducing agents [15, 16]. Actually chitosan itself can act as a stabilizer as well as a weak reductor, but require high temperatures to be able to act as a reducer [7]. The use of sodium hydroxide accelerates the formation of silver nanoparticles at low temperatures. The combination of chitosan, sodium hydroxide and sunlight irradiation on the formation of silver nanoparticles is expected to be more efficient and effective. The formation of silver nanoparticles in the chitosan solution system is here in after referred to as colloidal silver nanoparticles. In this study also examined the effect of accelerator count, reaction time and the amount of salt perursor. In addition, stability of the colloidal silver nanoparticles produced during 4 weeks storage was observed.

2. Experimental

Chitosan with molecular degree of deacetylation (DD) of 73.44 % and weight (MW) of 1,077,919.28 Da was purchased from Biotech Surindo Cirebon Indonesia. Silver nitrate (AgNO₃), acetic acid (CH₃COOH), sodium hydroxide (NaOH) were purchased from Merck.

The preparation of colloidal silver nanoparticles was carried out by chemical reduction methods with AgNO₃ as salt precursors, and chitosan as stabilizers. A solution of chitosan (1 % w/v) in acetic acid solution (1 % v/v) was firstly prepared. Due to the poor solubility of chitosan, the mixture was stirred to achieve complete dissolution, and then kept overnight at room temperature. Aqueous solution of AgNO₃ (0.012 g/mL) of 0.5 mL was added to 12.5 mL of chitosan (1 % w/v) in a flask. These solution was stirred at room temperature for 10 min. Furthermore, various mole of aqueous solution of NaOH were added to prepare various samples i.e., 0.0 (S0); 2.0 (S1); 2.5 (S2); 3.0 (S3); 3.5 (S4) and 4.0 mL (S5). Solution is exposed to sunlight for 2 hours. In this process will form a brown gel and then dissolved in 1% chitosan of 47.5 mL and stirred until all the gel is soluble and homogeneous solution is formed. The resulting colloidal silver nanoparticles solution is stored in glass bottles at room temperature. The same method was performed using 0.5 mL AgNO₃ and 1.75 mL NaOH without sun exposure. To determine the effect of solar radiation time, the variation of exposure time was 30 (T1), 60 (T2), 120 (T3) and 180 (T4) minutes using 0.5 mL AgNO₃ and 1.75 mL NaOH. Then to know the influence of concentration of salt precursor, similar procedure was carried out at various of concentration of AgNO₃ namely 0.25 (A1); 0.50 (A2); 0.75 (A3) and 1.00 mL (A4). Furthermore, observation of nanoparticle silver stability based on LSPR on samples with variation of AgNO₃ amount.

Characterization of colloidal silver nanoparticles was performed with UV3150 Shimizu-UV3150 Ultraviolet-visible (UV-Vis) spectroscopy at 300 - 600 nm wavelengths with 2 times dilution with aquadest. Study on the size, shape and distribution of Ag nanoparticles was performed by using TEM (Transmission electron microscopy) with JEM-1400 EX microscope at 120.0 kV voltage.

3. Result and Discussion

According to Pestov et.al. chitosan may act as a reducing agent in the manufacture of gold nanoparticles under alkaline conditions through hydrolysis and degradation mechanisms to produce glucosamine molecules [17]. Furthermore, this glucosamine will reduce the metal ions as in glucose reducers under alkaline conditions [12, 15, 16]. The presence of OH ions from NaOH, chitosan will be able to act as a reducing agent that converts Ag + ions to Ag metal. The crystal growth of Ag will be confined by chitosan polymer so that Ag can be obtained by nano size (<100 nm). The formation of this nanoparticle Ag is characterized by the change of gel color to brown. The addition of 1% chitosan solution to gel containing Ag nanoparticles yields a solution hereinafter called colloidal colloidal silver nanoparticles. The silver position of these nanoparticles will be covered by hydroxyl and amino groups of chitosan.
The effect of the number of moles of NaOH used as an accelerator on the preparation of colloidal silver nanoparticles against absorbance is shown in Figure 1 with UV-Vis spectra showing localized surface plasmon resonance (LSPR) in Figure 2. In general, absorbance increases as the amount of NaOH is greater. This increased intensity of absorbance indicates that the amount of silver nanoparticles in colloidal increases [18]. Figure 5.2 (b) shows a 5 mmol NaOH addition of a considerable increase in absorbance which indicates a significant increase in the number of silver nanoparticles. The addition of NaOH amounts greater than 5 mmol did not significantly increase the amount of silver nanoparticles. Even absorbance decreased at the addition of 8 mmol NaOH. This is probably due to the formation of a more dense gel in the addition of more NaOH, thus inhibiting the process of reducing Ag\(^{+}\) ions to Ag nanoparticles.

Meanwhile, for the absorption peak there is a shift towards a longer wavelength (red-shifted) on the use of NaOH to 3.5 mmol. The red-shifted indicates that there is an increase in particle size that is likely due to the increasing number of OH\(^{-}\) ions that impose the increasing number of silver particles produced. However, further addition of NaOH of 4.0 mmol causes a shift towards a shorter wavelength (blue shift) which indicates a decrease in particle size. This may be due to an increase in the amount of NaOH until saturation leads to changes in chitosan structure so that it becomes more compressed and more effective as a stabilizer.

![Figure 1. Photograph of colloidal silver nanoparticles synthesized at different moles of NaOH](image1)

![Figure 2. The UV-Vis spectra of colloidal silver nanoparticles prepared at different mole of NaOH](image2)

| code | \(\lambda_{\text{max}}\) (nm) | Abs  |
|------|------------------|------|
| S0   | -                | -    |
| S1   | 404.00           | 0.597|
| S2   | 404.50           | 0.929|
| S3   | 405.50           | 1.055|
| S4   | 407.00           | 1.200|
| S5   | 406.00           | 1.220|

The effect of sunlight irradiation to chemical reduction on the formation of silver nanoparticles was observed by comparing with the chemical reduction process without sunlight. The result of observation on LSPR can be seen in Figure 2. In Figure 2 shows that in the absence of sunlight irradiation, the chemical reduction process can take place, but goes slowly.

From the color of the solution, it is seen that without the irradiation of colloidal sun the colloidal silver nanoparticles produced is yellow which indicates the amount of silver produced is less than if using sunlight irradiation. In the use of sunlight irradiation shows the formation of brown colloids that
indicate more silver nanoparticles produced. This is supported by the observation of LSPR phenomenon, in which the colloidal produced without sun irradiation has a much lower absorbance value than colloidal with sunlight irradiation. This proves that the irradiation of sunlight trigger the reduction process so that more silver nanoparticles produced.

Figure 3. The UV-Vis spectra of colloidal silver nanoparticles prepared with sunlight irradiation and without sunlight irradiation

| code | $\lambda_{\text{max}}$ (nm) | Abs  |
|------|-----------------|------|
| T1   | 396.00          | 0.502|
| T2   | 396.50          | 0.605|
| T3   | 407.00          | 0.940|
| T4   | 408.00          | 0.978|

Figure 4. The UV-Vis spectra of colloidal silver nanoparticles prepared at different time (h) of: 0.5 (T1); 1.0 (T2); 2.0 (T3) dan 3.0 (T4)

The sunlight-assisted reduction process is affected by irradiation time as shown in Figure 4. Figure 4 shows that in the duration of 15 minutes to 180 minutes indicate that the longer the irradiation of sunlight, the reduction process is more effective. The absorbance at 120 to 160 minutes it does not appear to be significantly different so for the reduction process by using sunlight irradiation can occur quite optimally within 120 minutes.
This study also observed the effect of AgNO₃ concentration on silver LSPR nanoparticles. Variation of AgNO₃ concentration represented by variation of AgNO₃ volume with concentration of 0.012 g/mL ie 0.25 mL (A1); 0.50 mL (A2); 0.75 mL (A3); 1.00 mL (A4). Visually colloidal and UV-Vis columns of the Ag / Kit nanocomposite spectra are presented in Figure 5. Color gradations of light brown gradually dark brown show that the amount of silver nanoparticles produced increases with the concentration of AgNO₃ used. Figure 5 shows that absorbance increases with increasing concentrations of AgNO₃ which indicates that the more AgNO₃ is added the more nanoparticle silver is formed [18]. Viewed from the position of LSPR, initially (A1-A3) occurs blue-shifted, then followed by red-shifted on A4.

| Code | $\lambda_{\text{max}}$ (nm) | Abs  |
|------|----------------|------|
| A1   | 412.50         | 0.419|
| A2   | 405.50         | 0.820|
| A3   | 403.50         | 1.465|
| A4   | 407.00         | 2.408|

Stability of colloid solutions is the result of a potential barrier due to competition between van der Waals attraction forces and Coulomb repulsive forces. The metal soles are aggregated in two ways: particle-cluster aggregation and cluster aggregation [19]. Chitosan can act as a stabilizer that controls crystal growth and prevents the aggregation of already formed particles. In this study, stability observation of colloidal silver nanoparticles during storage on glass bottles in closed condition by monitoring LSPR based on UV-Vis spectra for 4 weeks. The UV-Vis spectra of the colloidal silver nanoparticles before
and after storage for the duration of 2 weeks and 4 weeks can be seen in Figure 6, with absorbance values and peaks position ($\lambda_{\text{max}}$) shown in Table 1.

Table 1. Changes in absorbance and peak position of UV-Vis spectra of colloidal silver nanoparticles at different storage time

| Code | $\lambda_{\text{max}}$ (nm) | Absorbansi |
|------|----------------|------------|
|      | initial  | 2 weeks | 4 weeks | initial  | 2 weeks | 4 weeks |
| A1   | 412.50   | 410.50  | 409.50  | 0.419    | 0.525   | 0.493   |
| A2   | 405.50   | 407.00  | 408.00  | 0.820    | 0.820   | 0.776   |
| A3   | 403.50   | 406.00  | 405.50  | 1.465    | 1.345   | 1.229   |
| A4   | 407.00   | 414.50  | 416.00  | 2.408    | 2.696   | 2.370   |

From Table 1, the average absorbance intensity decreased and the average $\lambda_{\text{max}}$ value increased. This decrease in absorbance intensity indicates that during storage the number of particles decreases slightly with increasing time. This decrease is probably due to the aggregation of silver particles of nanoparticles during storage and will precipitate due to the instability of the stabilizer agent. This phenomenon is likely due to the chitosan that has experienced this degradation decreases its ability as a stabilizer agent. When compared between the spectra in Figures 5, 6 (a) and 6 (b), there is a baseline increase of the spectra when the colloidal sample is stored. This is probably due to the decrease in the amount of silver nanoparticles is followed by the formation of larger particles.

![Figure 7](image.png)

Figure 7. TEM image of silver nanoparticles and particles size distribution (a) S0, (b) A2 dan (c) A4

Figure 7 shows the particle size distribution based on the TEM image for S0, A2 and A4 samples. In S0 sample it is seen that nano-size silver particles are not formed. This means, without the use of NaOH accelerators, silver nanoparticles are not formed. This corresponds to the color of the solution in Figure 1 which shows the gray color of the solution. This gray color is probably related to the formation of silver oxide. When correalted with the UV-Vis spectra in Fig. 5, then based on the absorbance data, there is conformity with the TEM image in Fig. 7. The appearance of a single absorption of LSPR in this 400 nm range indicates that the particles are spherical [20]. In the same area there was an increase in the number of detected particles of 20 particles to 100 particles with an increase in absorbance from 0.820 to 2.408.

4. Conclusion

The results show that the colloidal silver nanoparticles can be prepared using a reduction method assisted sunlight irradiation with NaOH as accelerator and chitosan as stabilizer. The formation of silver nanoparticles is characterized by the appearance of LSPR phenomenon in an area of approximately 400 nm. The particles is spherical in shape with dominant size at 5-8 nm. The amount of silver nanoparticles produced is influenced by the number of accelerators, reaction time and concentration of silver...
precursors. The colloidal silver nanoparticles are quite stable at 30 days of storage. Colloidal silver nanoparticles may have many potential applications as antibacterial agents in the field of medicine.

Acknowledgements

The author would like to thank to DRPM Ristek Dikti who gave financial support through PUPT Grant 2017 of Universitas Sebelas Maret.

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