

Synthesis of Gold Nanoparticles Using *p*-Aminobenzoic Acid and *p*-Aminosalicylic Acid as Reducing Agent

Abdul Aji, Eko Sri Kunarti*, and Sri Juari Santosa

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia

* Corresponding author:

email: eko_kunarti@ugm.ac.id

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Abstract: Synthesis of gold nanoparticles (AuNPs) by reduction of HAuCl_4 with *p*-aminobenzoic acid and *p*-aminosalicylic acid as a reducing agent was investigated. This work was conducted in order to determine the optimum condition of AuNPs synthesis and examine the effect of the hydroxyl group in *p*-aminosalicylic acid towards the size, shape, and stability of the synthesized gold nanoparticles (AuNPs). The optimum condition of the gold nanoparticles synthesis was determined by UV/Vis spectrophotometer, the shape and size of gold nanoparticles were measured by Transmission Electron Microscope (TEM). The synthesis process was started by reacting HAuCl_4 and the reducing agents in an aqueous solution at 86 °C. The initial gold concentration, reducing agents concentration and pH were varied in order to obtain the optimum condition. In the optimum condition, the results showed that *p*-aminosalicylic acid containing both hydroxyl and amino groups performed higher reduction ability compared to *p*-aminobenzoic acid that only containing an amino group. Reducing agents which have a hydroxyl group (*p*-aminosalicylic acid) could produce AuNPs with a smaller concentration of HAuCl_4 than *p*-aminobenzoic acid. Gold nanoparticles that were synthesized with *p*-aminosalicylic acid were more stable and had a smaller particle size compared to its counterpart that is synthesized with *p*-aminobenzoic acid.

Keywords: gold nanoparticles; *p*-aminosalicylic acid; *p*-aminobenzoic acid

■ INTRODUCTION

Gold has the lowest electrochemical potential among metals. This means that gold in any cationic form will accept electrons from any reducing agent to form metallic gold. Pure gold has electrical properties and high thermal conductivity compared to other metals [1]. Generally, gold has been used in various fields such as jewelry [2]. It also used in water purifier system because of its antimicrobial activity [3].

Gold with the bulk size has a small surface area and it reduces its reactivity. To solve this problem, gold can be synthesized in nanoparticle size. The size of gold nanoparticles can increase the effectiveness of its optic performance, due to the larger surface area [4]. Gold nanoparticles are widely studied because of its extraordinary properties that might have a strong impact on different science and technology fields. The interest in

these fascinating nanostructures covers a wide range of specific areas, as heterogeneous catalysis, optics, sensitive analysis and medicine [5].

The gold nanoparticle can be formed by physical or chemical methods. Some chemical methods which used to form gold nanoparticle are a chemical reduction [6-8], electrochemical [9], photochemical and sonochemical [10], microwave-assisted synthesis [11] and recently, using of green chemistry [12]. Chemical reduction technique is also known as self-assembly process, which is done by mixing the desired precursor particles with a reducing agent and stabilizer in the form of inorganic chemicals to form nanoparticles. Chemical reduction is a popular method due to its easiness, relatively low-cost, and production possibility on a large scale [13].

In the synthesis of gold nanoparticles (AuNPs), using coordination agents that stabilize and control the

morphological evolution of the gold nanostructures in solution or suspension are useful tools [14]. Stabilizer used to protect the particles from aggregation and reduce the collision possibility between particles of gold, in order to make AuNPs become stable [15]. The formation of stable AuNPs are indicated by the colloid formation with red or purple color and has a strong adsorption of visible light at the wavelengths between 520–550 nm [16]. Previous studies have been conducted by using different chemicals as reducing agent and stabilizer, such as chitosan, thiocholine, and glucose [17] but it becomes less efficient. Therefore, alternative chemicals which can act as good reducing agent and also as stabilizer are needed. Aziz et al. [18] have carried out the synthesis of AuNPs using pamoic acid as a reducing agent as well as a stabilizer. The reduction process occurs by the presence of hydroxyl group (OH) that can reduce Au^{3+} to Au^0 and the presence of the carboxylic group (-COOH) facilitate electrostatic interactions with Au^{3+} ions in solution. This interaction prevents the aggregation of Au^{3+} ions, and as a result, precipitation could be avoided.

In this study, we use *p*-aminobenzoic acid and *p*-aminosalicylic acid as reducing and stabilizing agent, because of amino group and amino with hydroxyl group contained in *p*-aminobenzoic acid and *p*-aminosalicylic acid, respectively. Therefore, those reactants are expected to reduce Au^{3+} into Au^0 and stabilize the synthesized gold nanoparticles during the synthesis. Previous studies confirmed that *p*-aminobenzoic acid could be used as a reducing agent in reaction with 2,6-dichloroquinone-4-imide [19]. Therefore, this study critically optimized the synthesis condition of gold nanoparticles and verified the effect of hydroxyl group contained on *p*-aminosalicylic acid. The examined parameters were the size, shape, and stability of the particles.

■ EXPERIMENTAL SECTION

Materials

The materials that used in this research were gold(III) chloride acid solution (HAuCl_4 1000 ppm), *p*-aminobenzoic acid ($\text{C}_7\text{H}_7\text{NO}_2$, Merck), *p*-aminosalicylic acid ($\text{C}_7\text{H}_7\text{NO}_3$, Merck), sodium hydroxide (NaOH, Merck), and hydrochloric acid (HCl, Merck).

Instrumentation

The instruments used were laboratory glassware, hot plate with stirrer, thermometer, pH-meter (HI 98103 by Hanna Instrument), water-bath, analytical balance, UV-Vis spectra of the synthesized materials were measured with a Shimadzu UV-1700 PharmaSpec instrument, Transmission Electron Microscope imaging were recorded with a TEM JEOL JEM 1400 with a 120 kV acceleration voltage, X-ray diffraction pattern is obtained on Rigaku Miniflex600 using Cu $\text{K}\alpha$ radiation.

Procedure

Synthesis of gold nanoparticles

AuNPs were synthesized by reducing HAuCl_4 solution with the *p*-aminobenzoic acid and *p*-aminosalicylic acid as reducing agents at 1–14 pH range by adding a solution of HCl or NaOH. Three mL of 0.02 mM reducing agent which has a pH range from 1 to 14 were put into a test tube and 3 mL of 100 ppm HAuCl_4 solution was added. The mixture was heated in the water-bath at temperature 86 °C for 60 min. The color of the mixture was changing from colorless (a little bit yellowish) to pink, indicating the gold nanoparticles formation. The UV-Vis spectra of the mixture solution were analyzed using UV/Vis Spectrophotometer at a wavelength of 200–800 nm. The presence of maximum absorption at the wavelength range of 520–550 nm showed that AuNPs were formed. The optimum pH was determined by the highest absorbance on UV-Vis spectra.

Optimization of HAuCl_4 solution concentration, reducing agent concentration and study of reducing agent sensitivity

Three milliliter of reducing agent solution with optimum pH condition was added into 3 mL of HAuCl_4 solution with the varied concentration (20, 40, 60, 80, 90, 100, 110, 120, 130, 140 and 170 ppm) and also added into 5 tubes without the addition of HAuCl_4 precursor. All solutions were heated at the temperature of 86 °C on the water-bath for 60 min. The resulting solutions then were analyzed with UV/Vis spectrophotometer at a wavelength of 200–800 nm. The optimum concentration of HAuCl_4 was determined by the maximum absorbance

of the concentration series.

To determine the optimum reducing agent concentration, 3 mL of reducing agent solution with varied concentration (10, 15, 20, 25, 30, 35, 40 mM) and optimum pH condition was added into 3 mL of HAuCl₄ solution with optimum concentration. All solutions are heated at the temperature of 86 °C in a water bath for 60 min. The resulting solutions then were analyzed using UV/Vis spectrophotometer at a wavelength of 200–800 nm. The optimum concentration of reducing agent was determined by the maximum absorbance of the concentration series.

The absorbance of the solution was measured without the addition of HAuCl₄ solution as much as 5 repetitions in order to determine the sensitivity of the reducing agent. The averaged absorbance of the blank solution was calculated in order to plot on the graph of HAuCl₄ concentration and the maximum absorbance of the non-blank solution. The linear regression equation was calculated and the sensitivity of the reducing agent was determined from its slope. Higher sensitivity was defined by a sharper angle of the slope.

Study of the gold nanoparticles stability

Three milliliters of reducing agent solution with the optimum condition was added into 3 mL of HAuCl₄ solution with optimum concentration. The solution was heated at temperature of 86 °C in the water-bath for 60 min and then analyzed with UV/Vis spectrophotometer at a wavelength of 200–800 nm, at the interval of 0–4 h, 1–4 days, 1–5 weeks after the synthesis process. The absorbance change or maximum absorbance wavelength shift was observed during the storage.

Characterization of gold nanoparticles

Three milliliters of reducing agent solution with the optimum condition was added into 3 mL of HAuCl₄ solution with optimum concentration. The solution was heated at a temperature of 86 °C in the water bath for 60 min. Furthermore, the colloidal gold nanoparticles that formed were characterized using TEM to determine the shape and size of the nanoparticles.

■ RESULTS AND DISCUSSION

Synthesis of Gold Nanoparticles

The pH value is one of the important factors in the synthesis of gold nanoparticles. In this research, pH was varied from 1 to 14 by adding NaOH or HCl. For *p*-aminosalicylic acid changed its color from colorless to red in a pH condition more than 11. On the other hand, *p*-aminobenzoic acid changed its color from colorless to pink at 13 value of pH scale. Pink or red color of the solution was caused by the nanoparticle structure with a specific surface plasmon resonance (SPR). At the basic condition, the proton of hydroxyl and carboxylate group on the *p*-aminobenzoic acid and *p*-aminosalicylic acid will be deprotonated and form a negative charge that increases its metal binding activity, creating the gold nanoparticles. A higher pH resulted in a high-density solution because more reduction occurred which means more gold nanoparticles contained there. The same conclusion also reported by previous studies [20].

Furthermore, the solutions were analyzed by UV-Vis spectrophotometer at the wavelength range of 300–800 nm. The formation of gold nanoparticle was indicated by the maximum absorbance which happened in the wavelength range of 520–550 nm [21]. The result (see Fig. 1) showed that the gold nanoparticles were formed in the basic condition for both *p*-aminobenzoic acid and *p*-aminosalicylic acid reducing agent. The optimum pH for *p*-aminobenzoic acid and *p*-aminosalicylic acid reducing agent are 13 and 12, respectively. This difference happened because each reducing agent has specific deprotonated form.

One of the factors that influence the synthesis of gold nanoparticle is the concentration of HAuCl₄ precursor. The higher concentration of HAuCl₄ produced more gold nanoparticle, which could be indicated by the higher absorbance value [22]. The UV/Vis spectrophotometer measurement result (Fig. 2) showed that the higher salt precursor concentration gave higher absorbance for a *p*-aminosalicylic acid reducing agent. However, for a *p*-aminobenzoic acid reducing

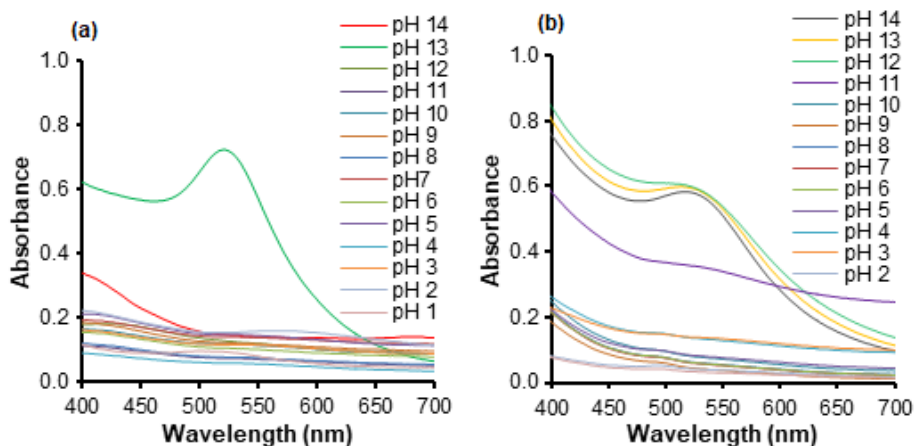


Fig 1. UV/Vis spectra of gold nanoparticle with the precursor of HAuCl_4 100 ppm and (a) *p*-aminobenzoic acid 20 mM (b) *p*-aminosalicylic acid reducing agent 20 mM at the pH range 1–14

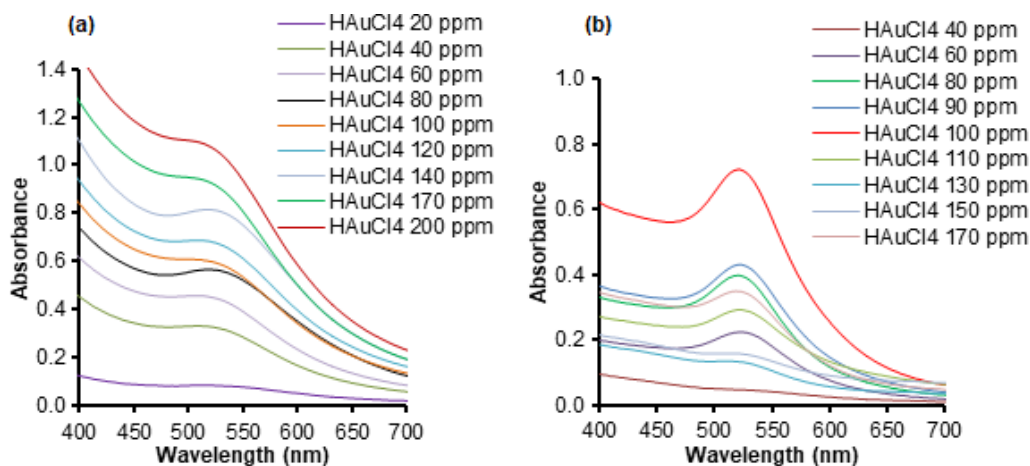


Fig 2. UV/Vis spectra of gold nanoparticle with varied concentration precursor of HAuCl_4 with (a) *p*-aminosalicylic acid 20 mM at pH 12 and (b) *p*-aminobenzoic acid 20 mM at pH 13

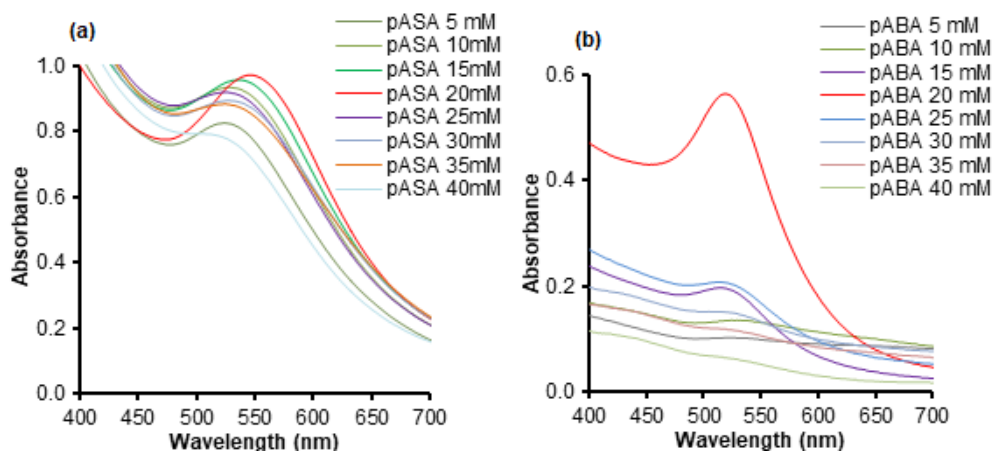


Fig 3. UV/Vis spectra of gold nanoparticle with varied concentration of reducing agent (a) *p*-aminosalicylic acid at pH 12 and (b) *p*-aminobenzoic acid at pH 13

agent, the highest absorbance showed at a concentration of HAuCl_4 100 ppm. The higher concentration of HAuCl_4 decreased the absorbance of a gold nanoparticle. Therefore, the optimum concentration of HAuCl_4 for the *p*-aminobenzoic acid reducing agent was obtained at 100 ppm.

Another factor that influences the synthesis of gold nanoparticle is the concentration of the reducing agent. The UV/Vis spectra (Fig. 3) showed that the highest reducing agent concentration for both *p*-aminobenzoic acid and the *p*-aminosalicylic acid reducing agent was 20 mM. Both spectra showed an equal tendency, where the higher reducing agent concentration gave higher absorbance until the maximum concentration at 20 mM.

A reducing agent with the concentration more than 20 mM had a lower UV-Vis absorbance. The graph in Fig. 4 obtained from the maximum absorbance of every precursor concentration and the average of the absorbance from non-precursor solution. This graph used to calculate the linear regression equation which can determine the reducing agent sensitivity. The higher slope value defines a higher sensitivity of the reducing agent.

From the slope data, the AuNPs that synthesized by *p*-aminosalicylic acid had higher slope value (0.0069) than the same material synthesized by *p*-aminobenzoic acid (0.0062). As a result, *p*-aminosalicylic acid had better sensitivity than a *p*-aminobenzoic acid reducing agent. It happened because *p*-aminosalicylic acid contained both hydroxyl group and amino group, while

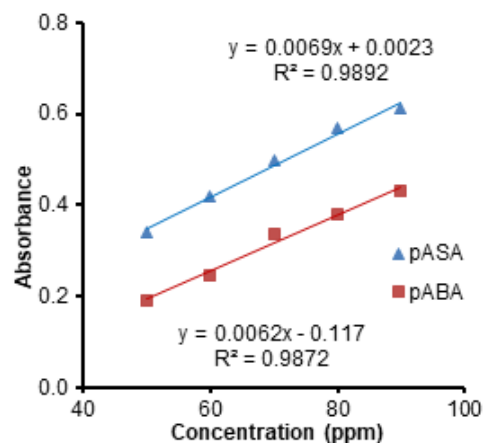


Fig 4. Relation graph of HAuCl_4 concentration with gold nanoparticles absorbance which formed by *p*-aminosalicylic acid and *p*-aminobenzoic acid

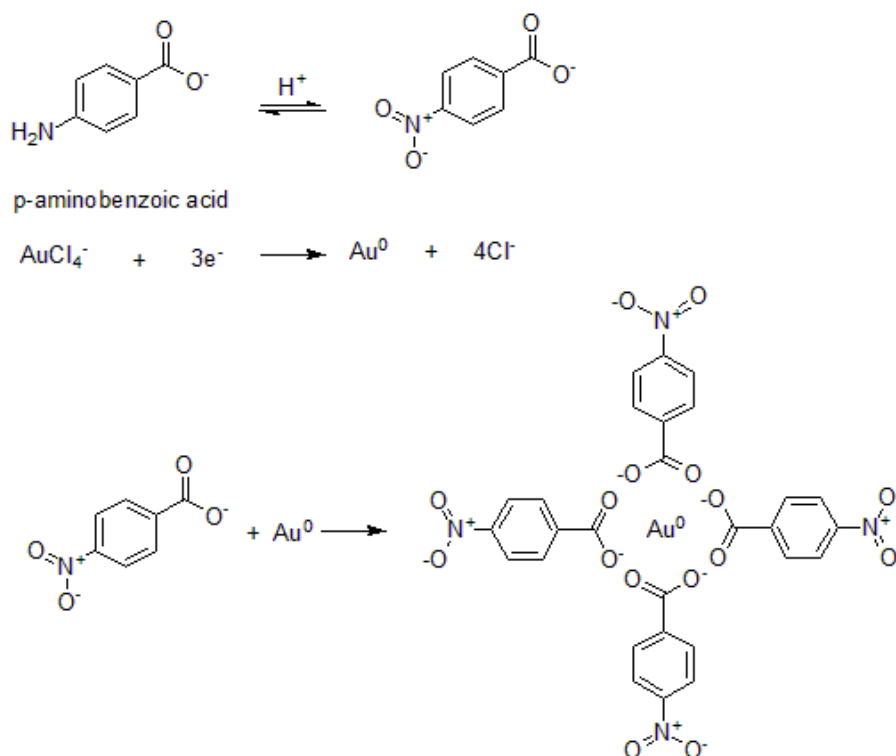


Fig 5. Possible mechanism of gold nanoparticles formation by *p*-aminobenzoic acid

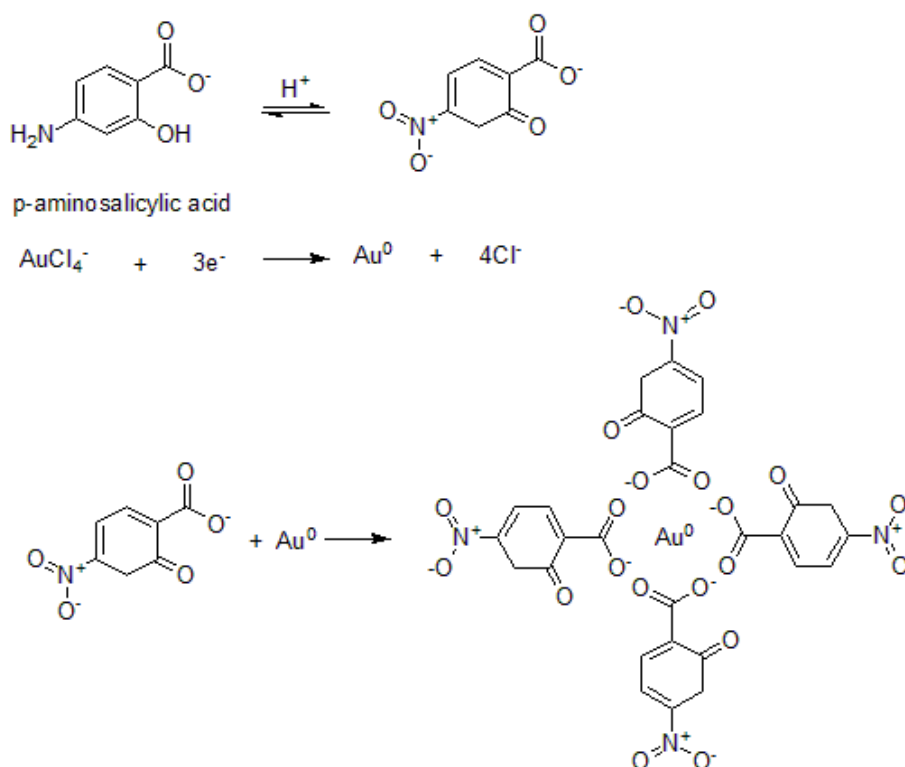


Fig 6. Possible mechanism of gold nanoparticles formation by *p*-aminosalicylic acid (pASA)

its counterpart only had an amino group. Hydroxyl group and an amino group in reducing agent acted as the lone pair electron donor for gold ion, especially Au^{3+} . The presence of hydroxyl group in reducing agent can give more lone pair electron to the gold ion, so it can react more easily with gold ion [23]. Therefore, apart from the amino group, hydroxyl group in *p*-aminosalicylic acid could also enhance the reduction ability of this reducing agent. As a result, *p*-aminosalicylic acid could reduce Au^{3+} faster than *p*-aminobenzoic acid. The mechanism of gold nanoparticles formation from the reduction of Au^{3+} with *p*-aminobenzoic acid and *p*-aminosalicylic acid is introduced in Fig. 5 and 6.

Study of the Gold Nanoparticles Stability

The stability of gold nanoparticles can be described by observing the intensity change of absorbance peak. The shift of maximum absorbance wavelength and the change of absorbance value indicated that the resulted gold nanoparticles are not stable. After the observation for several weeks, all synthesized gold nanoparticles did not give a significant decrease of absorbance value (Fig. 7),

only 0.031 for a *p*-aminosalicylic acid reducing agent and 0.098 for a *p*-aminobenzoic acid reducing agent after 5 weeks of storage. This data indicated that all gold nanoparticles were stable until the 5th week.

Apart from the absorbance decrease, the stability of gold nanoparticles can also be examined from the maximum wavelength shift. The maximum wavelength shift happened after 5 weeks as far as 2 nm for *p*-aminosalicylic acid and 6 nm for *p*-aminobenzoic acid. The longer storage could decrease the gold nanoparticle stability because of the suspension formation by agglomeration. This phenomenon indicated by the increase of the maximum wavelength and the decrease of the absorbance. However, after the peak shift, the maximum wavelength was still located around 525 nm. It proved that the gold nanoparticle had good stability.

The best stability showed by gold nanoparticles with the $HAuCl_4$ precursor concentration of 140 ppm for a *p*-aminosalicylic acid reducing agent and 100 ppm for a *p*-aminobenzoic acid-reducing agent with the concentration of both *p*-aminobenzoic acid and the *p*-aminosalicylic acid reducing agent was 20 mM. The gold

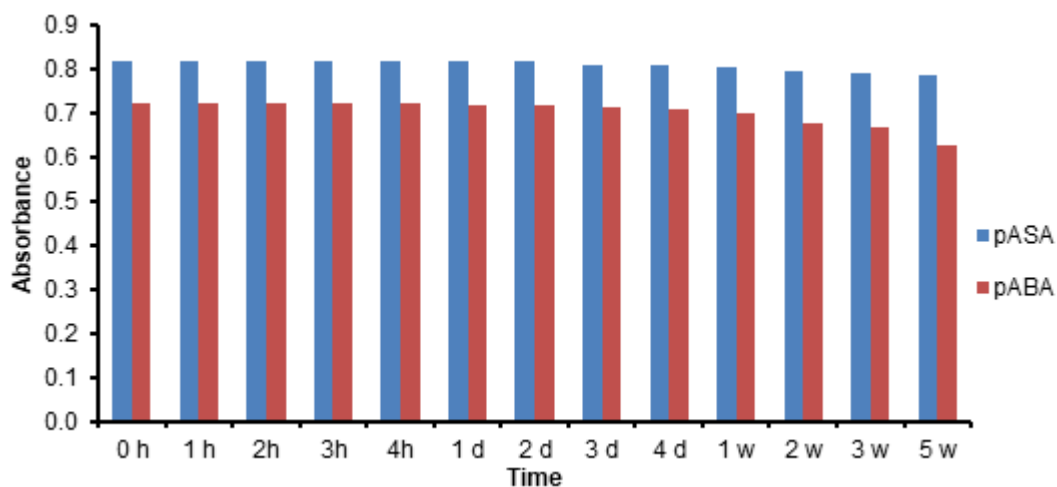


Fig 7. Stability of gold nanoparticles synthesized by *p*-aminosalicylic acid (pASA) at pH 12 and *p*-aminobenzoic acid (pABA) at pH 13 as reducing agent

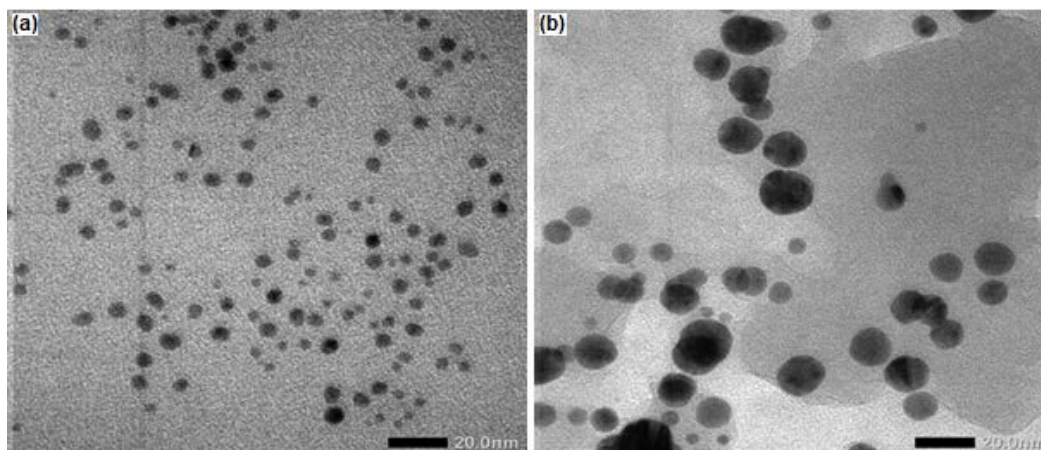


Fig 8. The TEM image of gold nanoparticle synthesized by a reducing agent (a) *p*-aminosalicylic acid at pH 12, the concentration of HAuCl_4 140 ppm and concentration of reducing agent 20 mM (b) *p*-aminobenzoic acid at pH 13, the concentration of HAuCl_4 100 ppm and concentration of reducing agent 20 mM

nanoparticles that synthesized with *p*-aminosalicylic acid were more stable compared to the gold nanoparticles synthesized with *p*-aminobenzoic acid. It happened because the *p*-aminosalicylic acid has the highest pKa value than another reducing agent so it can form a more stable organic molecule anion in the complex form of gold-reducing agent and the aggregation can be inhibited.

Characterization of the Gold Nanoparticles

The shape and size of gold nanoparticles were measured using TEM. Based on the optimum absorbance condition and their good stability, gold nanoparticles synthesized from HAuCl_4 140 ppm precursor for *p*-

aminosalicylic acid reducing agent 20 mM at pH 12 and second specimen synthesized from HAuCl_4 100 ppm precursor for *p*-aminobenzoic acid reducing agent 20 mM at pH 13 were chosen to be measured.

The TEM results showed that both of reducing agent gave same particle shape but different size of gold nanoparticles. The *p*-aminosalicylic acid reducing agent gave round shape and smaller particle size (7.45 ± 1.5 nm) than gold nanoparticles synthesized with *p*-aminobenzoic acid (see Fig. 8(a)). For *p*-aminobenzoic acid reducing agent gave round shape and less uniform size (16.05 ± 7.57 nm) of gold nanoparticles (see Fig. 8(b)). The aggregation did not happen with both *p*-aminobenzoic

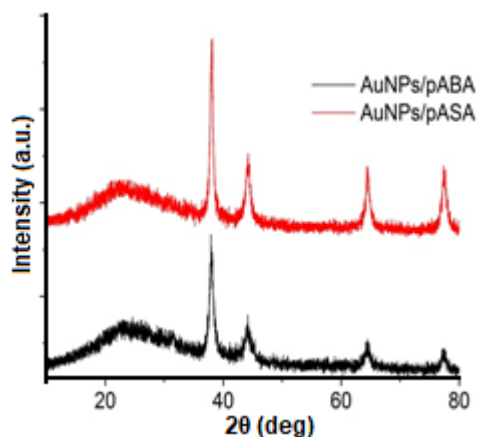


Fig 9. XRD Pattern of gold nanoparticles synthesized by *p*-aminobenzoic acid and *p*-aminosalicylic acid

acid and *p*-aminosalicylic acid reducing agent, which showed that the reducing agents could also act as a stabilizer.

The powder XRD pattern of the gold nanoparticles is shown in Fig. 9. The major diffraction peaks can be indexed as the face-centered cubic (fcc) phase based on the data from the JCPDS file (JCPDS no. 04-0784).

The diffraction peaks of gold nanoparticles that synthesized by *p*-aminobenzoic acid appeared at 38.3, 44.3, 64.4, and 77.6°, which could be assigned to (111), (200), (220), and (311) crystalline plane diffraction peaks of gold, respectively. For gold nanoparticle that synthesized by *p*-aminosalicylic acid the diffraction peaks appeared at 38.4, 44.3, 64.5, and 77.5°, which could be assigned to (111), (200), (220), and (311) crystalline plane diffraction peaks of gold, respectively. The results show that the gold nanoparticles were completely formed using *p*-aminobenzoic acid and *p*-aminosalicylic acid as the reducing agent.

Overall, gold nanoparticles which synthesized with the reducing agent have a high stability. Each reducing agent used in this study has 2 or 3 active group; they are a carboxylic group, an amino group, and a hydroxyl group. These active groups would be deprotonated in basic pH system and formed a negative charge which enables the interaction between the reducing agents and the gold ion. The stability of nanoparticles was depended on the pK_{a1} value of the reducing agent. The higher pK_{a1} value could increase the stability of gold-reducing agent complex and

prevent the aggregation, therefore it could enhance the stability of gold nanoparticles. Besides the stability, the size of nanoparticles was depended on the reducing agent properties. A reducing agent with higher reduction ability would give smaller nanoparticle size because it could reduce more gold ions.

■ CONCLUSION

Gold nanoparticles have been successfully synthesized from HAuCl_4 by using *p*-aminobenzoic acid and *p*-aminosalicylic acid as a reducing agent and also stabilizer. The reaction took place on the basic pH condition, with optimum pH for *p*-aminobenzoic acid at pH 13 and *p*-aminosalicylic acid at pH 11. The maximum concentration of HAuCl_4 was 140 ppm and 100 ppm for *p*-aminosalicylic acid and *p*-aminobenzoic acid, with maximum concentration for both the reducing agent, are 20 mM. The *p*-aminosalicylic acid reducing agent gave the smaller size gold nanoparticles (7.45 ± 1.5 nm) and more stable gold nanoparticles than the *p*-aminobenzoic acid reducing agent (16.05 ± 7.57 nm). The extraordinary properties of synthesized gold nanoparticles have a strong impact in different science and technology fields. The range of applications for gold nanoparticles is growing rapidly and includes sensors, catalysis, therapeutic agent delivery, electronics, and photodynamic therapy.

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