JURNAL SAINS MATERI INDONESIA (JUSAMI)
ISSN: 1411-1098 (print), 2614-087X (online)
VOL. 24, ISSUE 2, 2023
DOI: 10.55981/jsmi.2023.762

ORIGINAL ARTICLE

Electrochemically Synthesized Gold Nanoparticles Using Gold and Copper Electrodes

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ABSTRACT – Gold nanoparticle is one of the interesting metallic nanoparticles which can be applied to various applications due to promising plasmon effect. Gold nanoparticles are usually synthesized from gold salts using chemical procedure to precisely control of their sizes and shapes. Nevertheless, gold salt is expensive and the synthesis requirement as well as the procedure are complicated. It is a challenge to produce gold nanoparticles using affordable, rapid, simple, and massive method. Electrochemical is one of the simple procedures to synthesize gold nanoparticles. However, the utilization of platinum electrode, which is expensive, become disadvantage. In this work, copper plate is utilized to replace platinum electrode in order to synthesize gold nanoparticles. Electrolyte, stabilizer, ambient temperature, and injection current are also varied to study their effects on absorbance spectra of synthesized gold nanoparticles. It is found that ambient temperature and injection current significantly affect shape of gold nanoparticles. Combination of salt-glucose or stabilizer-glucose was unexpectedly enough to synthesize gold nanoparticles. This work brings a simple and low-cost technique for massive production of gold nanoparticles for various applications.

ARTICLE HISTORY
Received: 7 Nov 2022
Revised: 25 Des 2022
Accepted: 6 Feb 2023

KEYWORDS
Gold nanoparticles
Electrochemical
Absorbance
Simulation
Copper

INTRODUCTION

Gold nanoparticles are the interesting type of nanoparticle due to their stability and optical properties, particularly surface plasmon [1], [2]. At certain wavelength of light, the plasmon is generated and strongly absorb or scatter incident light [1]. The coupling of metal nanostructures with light is the basic for the plasmonic applications. Gold nanoparticles are small particles which made of gold with a diameter of 1 to 100 nm. Gold nanoparticles (colloidal gold) are usually well dissolved in water and have wide range of applications. It can be applied on biomedical labels [3], [4], sensors [5], optoelectronics [6], cosmetics [7], and cancer therapy [8]. Furthermore, the plasmon of gold nanoparticles plays a major role in enhanced spectroscopy techniques, such as surface enhanced raman spectroscopy and surface enhanced fluorescence spectroscopy [9].

There are two main procedures to synthesize gold nanoparticles, top-down and bottom-up procedures. In bottomup procedure, gold nanoparticle is usually made of tetrachloroaurate ($HAuCl_4$) using chemical procedure [10], [11]. By modifying synthesis protocol, several research can controlled the size, shape, solubility, and surface functionality of gold nanoparticles. For example, one may added cetyltrimethyl ammonium bromide (CTAB) for making gold nanoparticles monodispersed [12], [13]. Shape of gold nanoparticles can be tuned into triangle, cube, or nanorod [14], [15]. Even though chemical process gives precise control of gold nanoparticles, the chemical purity significantly affects the final products. High purity $HAuCl_4$ is high-priced. In top-down process, gold nanoparticles are usually made of gold bulk or gold thin film using physical process such as nanolithography [16], annealing [17], laser ablation [13], [18], and electrochemical [19]–[21]. Each of this synthesis process has limitation. Nanolithography can produce specific size and shape of gold nanoparticles. However, this process requires complicated and expensive devices [20]. Laser ablation gives simple synthesis process of gold nanoparticles, since it only requires a focused laser beam, gold bulk, and water. Nevertheless, this procedure is difficult to synthesize other shapes of gold nanoparticles, except spherical gold nanoparticles [13]. In addition, both nanolithography and laser ablation are not able to produce fast and massive production of gold nanoparticles. For large production of gold nanoparticles, electrochemical process can be the option.

The research on synthesis of gold nanoparticles using electrochemical is not frequently reported. Few research reported the synthesis of gold nanoparticles using electrochemical process [15], [20], [21]. Gold and platinum electrodes are used to make spherical gold nanoparticles. The process is simple, but the utilization of platinum electrode disturbs its simplicity. Platinum is chosen since it is less reactive than gold in electrochemical process yet its electrode is more expensive. In order that, it is a challenge to make the synthesize process simpler and affordable for mass production. The utilization of copper electrode, instead of platinum electrode, would possibly work. The purposes of this work are (1) to synthesize gold nanoparticles using electrochemical process with copper and gold electrodes and (2) to study the effect of chemicals, injection current, and ambient temperature on the synthesized gold nanoparticles. For chemicals, the research is limited on cheap and simple chemicals, i.e., trisodium citrate as stabilizer, sodium chloride as

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electrolyte, and glucose. UV-Vis Spectrometer and transmission electron microscope (TEM) is utilized to characterization and investigation.

EXPERIMENTAL METHOD

Materials and Instruments

Synthesis of gold nanoparticles was done using simple electrochemical method as shown in Figure 1. The electrochemical process used a gold plate (5 gram with purity 99.99%) from Indonesian national mining industry (ANTAM), pure copper electrode with size 1 cm width, 5 cm length, and 2 mm thickness from Rofa Laboratorium Centre, Bandung, Indonesia, a commercial DC power supply up to 2 ampere and 30 watts, glass beaker, distilled water, technical grade natrium chloride, technical grade trisodium citrate, commercial corn syrup, digital thermometer, magnetic stirrer hot plate, cables, and cable clips.

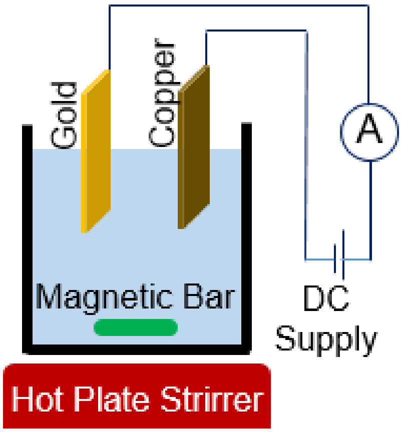

Figure 1. Schematic of electrochemical process with gold and copper electrodes

The synthesized gold nanoparticles were characterized using UV-Vis spectrometer to get absorbance spectra and transmission electron microscope (TEM) to check morphology of gold nanoparticles. In addition, simulation of gold nanoparticles was done using metallic nanoparticles by a boundary element method (MNPBEM) Toolbox in Matlab [22]. By the toolbox, absorbance cross section of gold nanoparticles for different shapes was calculated. The simulation of absorbance cross section in the MNPBEM Toolbox was done by solving full Maxwell equation using defined Green function. The boundary element methods (BEM) was used to numerically obtain the final solution [22].

Method and Procedure

The electrodes used for this process are a gold plate as anode and pure copper electrode as cathode. A DC power supply with adjustable current was used in this experiment. The electrochemical process was done in 500 ml glass beaker with magnetic bar stirrer on a hot plate stirrer. The temperature of water was observed using digital infra-red thermometer. Technical grade trisodium citrate (400 mg), technical grade sodium chloride (200 mg), and 75 micro liter glucose from commercial corn sugar were added into 500 ml DI water. The mixture was mixed and heated until certain temperature before the electrodes were inserted and started the electrochemical process. The electrochemical process was limited for 5 minutes for every sample. The experiment was done for several samples (Table 1) by varying injection current, temperature, and chemicals.

Table 1. Samples with parameters information

Sample Code	DC current (mA)	Temperature (°C)	Trisodium citrate (mg)	Sodium chloride (mg)	Glucose (µL)
G01	500	30	400	200	75
G02	500	50	400	200	75
G03	500	90	400	200	75
G04	200	50	400	200	75
G05	1000	50	400	200	75
G06	500	50	400	0	0
G07	500	50	0	200	0
G08	500	50	0	0	75
G09	500	50	400	200	0
G10	500	50	400	0	75
G11	500	50	0	200	75

RESULTS AND DISCUSSION

In general, electrochemical process is able to produce gold nanoparticles in a short time. Prior to current injection, all chemicals were mixed until well-dissolved in water using magnetic stirrer and heated to certain temperature. For every sample, electrolysis process is limited only for 5 minutes. In order to ensure quality of gold nanoparticles, different copper electrode is used for every process. The appearance of synthesized gold nanoparticles for all samples (G01–G11) are shown in Figure 2.

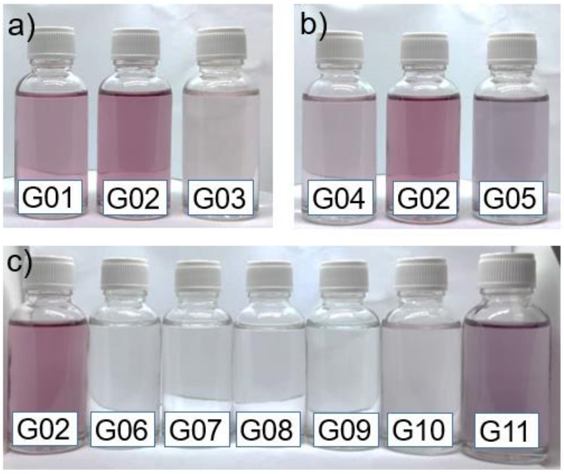

Figure 2. Appearance of synthesized gold nanoparticles under ambient illumination

G01, G02 and G03 (Figure 2(a)) are samples with different ambient temperature of water 30ºC, 50ºC, and 90ºC, respectively. Ambient temperature is selected only until 90ºC to avoid boiling temperature of water. Under ambient illumination, it is observed that all samples show color changing. The water color appearance become pink or light purple. G02 (ambient temperature 50ºC) has the most concentrated gold nanoparticles, meanwhile G03 has the least concentrated gold nanoparticles. These appearances were confirmed by absorbance spectra shown in Figure 3. Basically, absorbance spectra of G01, G02, and G03 are similar. The absorbance values of G01, G02, and G03 are 0.19 (at 525 nm wavelength), 0.39 (at 527 nm wavelength), and 0.08 (at 518 nm wavelength), respectively. It is noticed that absorbance values are proportional to absorbance peak wavelengths. Higher absorbance value makes the absorbance peak wavelength shifts to longer wavelength. The absorbance peak wavelength indicates plasmon peak as well as average size of gold nanoparticles [23]. Longer wavelength indicates larger size of gold nanoparticles. The absorbance value indicates number of gold nanoparticles in the solution. Higher absorbance value means higher concentration of gold nanoparticles. It is observed that ambient temperature of water 50ºC resulted the highest production of gold nanoparticles. From G01, G02, and G03, it is concluded that strong pink color of sample G02 indicates high number of gold nanoparticles. Low temperature (30 ºC) and high temperature (90 ºC) does not give maximum production of gold nanoparticles.

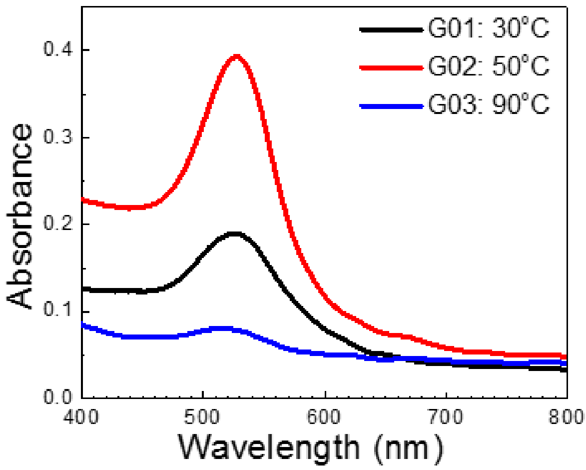

Figure 3. Absorbance spectra of synthesized gold nanoparticles at different temperatures

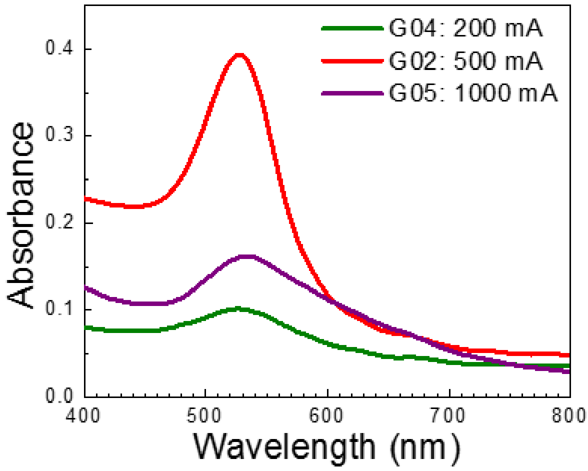

Figure 4. Absorbance spectra of synthesized gold nanoparticles at different injection currents

Experiment on different injection current during the electrochemical process was also conducted. Injection current value variation of 200 mA (G04), 500 mA (G02), and 1000 mA (G05) were set. The color appearance of G04, G02, and G05 are shown in Figure 2(b). Sample G02 with 500 mA injection current still results the most concentrated gold nanoparticles. The color of G04 (200 mA injection current) and G05 (1000 mA injection current) only result pale pink color. This pale color indicates that the concentration of synthesized gold nanoparticles is low. The absorbance spectra of G04, G02, and G05 are shown in Figure 4. It can be seen that absorbance intensity values of G04, G02, and G05 are 0.11 (at 525 nm wavelength), 0.39 (at 527 nm wavelength), and 0.16 (at 534 nm wavelength), respectively. Injection current value is proportional to the absorbance peak wavelength. Higher injection current makes the absorbance peak wavelength shifts to longer wavelength. However, higher injection current does not generate higher concentration of gold nanoparticles. The shift of absorbance wavelength peak, which indicates plasmon peak, and broadening of absorbance curve serve information that the shape and size of synthesized gold nanoparticles are varied [24], [25]. It is also noticed that for absorbance spectrum G05, the peak is broaden to longer wavelength (up to 700 nm wavelength). This indicates that there are several shapes of gold nanoparticles in the sample. This broadening may also infer that various size of gold nanoparticles existing in the sample.

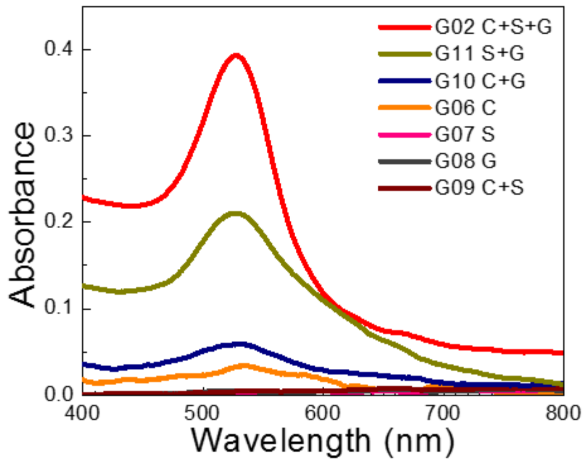

Figure 5. Absorbance spectra of synthesized gold nanoparticles for varying chemicals (C=trisodium citrate, S=sodium chloride, G=glucose)

The last parameter in this experiment is the chemicals used in the synthesis process (Table 1: G02, G06–G11). Trisodium citrate, sodium chloride, and glucose are used to synthesize gold nanoparticles. Basically, salt (ionic electrolyte) is required for electrochemical process [26]. Glucose is required to fasten the reduction of gold atoms [20]. Trisodium citrate is used for stabilizing the growth of gold ions to form gold nanoparticles [27], [28]. In this part, the role of each chemical in electrochemical process using copper electrode is studied. The appearance of synthesized gold nanoparticles is given in Figure 2(c). Noticeable color change in G02 and G11 is observed. This indicates that gold nanoparticles were successfully synthesized in high number of particles. Pale color (very light color) of pink in G06 and G10 is observed. It is assumed that there are gold nanoparticles in those samples. There is no color change in sample G07, G08, and G09. Clear appearance of G07, G08, and G09 indicates that there is no gold nanoparticles in the samples after electrochemical process. Furthermore, absorbance spectra of G02 and G06–G011 are shown in Figure 5. Absorbance spectra of G07, G08, and G09 are flat. Therefore, it can concluded that adding only sodium chloride (in

G07), glucose (in G08), or trisodium citrate with sodium chloride (in G09) is not able to generate gold nanoparticles using this electrochemical process. Pale color in G06 and G10 are noticed. Based on absorbance spectra, there are small absorbance intensity values of 0.05 in G10 (at wavelength 530 nm) and 0.03 in G06 (at wavelength 533 nm). The absorbance values are smaller than that of G02. It is unexpected to obtain gold nanoparticles in G11 (sample with sodium chloride and glucose) which has absorbance peak value of 0.21 (at wavelength 526 nm). Both color appearance and absorbance spectrum of G11 indicates that adding sodium chloride and glucose (without trisodium citrate) is possible to generate gold nanoparticles using this electrochemical process. It is also noticed that absorbance spectrum of G11 is broaden to longer wavelength, similar to G05. This denotes there is a possibility that not only spherical gold nanoparticle exists, but also other shapes of gold nanoparticles. In order to verify absorbance spectra, further investigation is required.

Transmission electron microscope (TEM) is used to observe morphology of gold nanoparticles. Only 8 samples (G01–G06, G10, and G11) are observed. The TEM images of each sample is shown in Figure 6. Due to low concentration of gold nanoparticles, many TEM images for each sample could not be captured. Nevertheless, clear morphological images for every samples can be obtained.

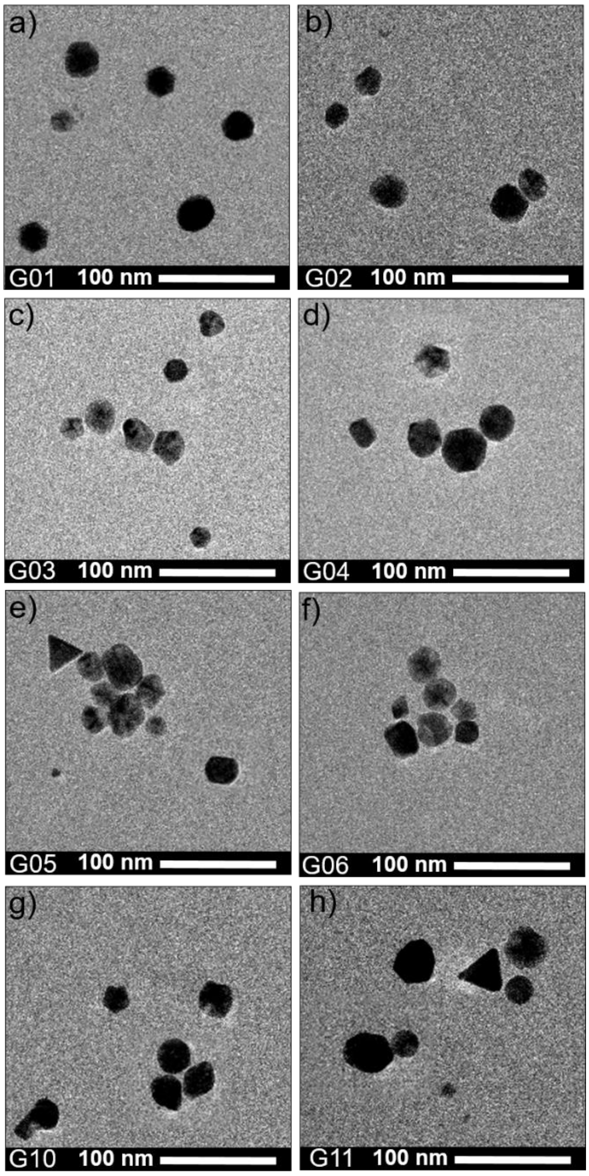

Figure 6. TEM images of synthesized gold nanoparticles for G01–G06, G10, and G11

For sample G01, G02, and G03 (samples with different temperature process), it is observed that shape of synthesized gold nanoparticles are similar. Most of gold nanoparticles are spherical. There are few gold nanoparticles with hexagonal shape or irregular shape. It is found that the sizes of gold nanoparticles in G03 are a bit smaller than that of G01 and G02. The sizes of gold nanoparticles are 30–50 nm in diameter. Smaller size of gold nanoparticles implies absorbance of peak wavelength shifts to shorter wavelength [23]. Peak shift of absorbance spectra in Figure 3 confirms this phenomenon. For gold nanoparticles samples with different injection currents (G04, G02, and G05), it is found that sample G04 has a bit larger size of spherical gold nanoparticles than that of G02. Moreover, there are other shape of gold nanoparticles found in G05, rectangular and triangle gold nanoparticles. This is interesting since different shape of gold nanoparticles will generate plasmon peak at different energy or different absorbance wavelength [23]. The size of gold nanoparticles are 30–50 nm in diameter. Furthermore, G02, G06, G10 and G11 were measured to investigate chemicals effect on synthesis process of gold nanoparticles. It is found that all samples are similar in shape and size, except for G11. In G11, rectangular and triangular shape of gold nanoparticles is noticed, similar to G05. In summary, from TEM images, morphology of synthesized gold nanoparticles at different process can be studied. Basically spherical and hexagonal shape of gold nanoparticles are generated. However, for several samples, rectangular and triangle shapes of gold nanoparticles were also observed.

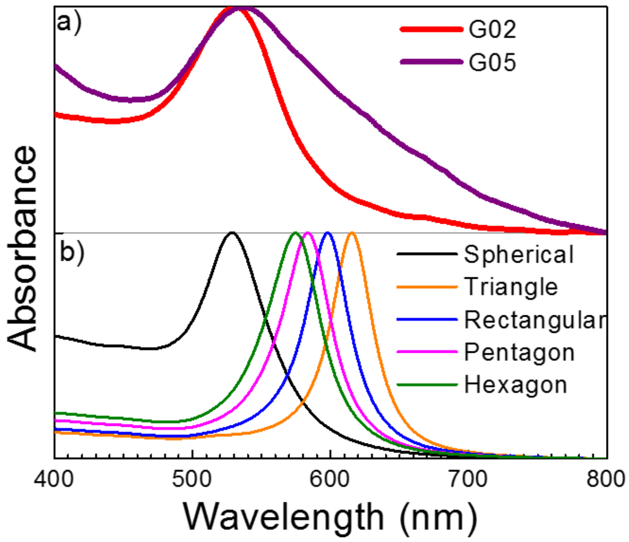

Figure 7. Absorbance spectra of (a) synthesized gold nanoparticles and (b) simulation of absorbance gold nanoparticle for several shapes.

Furthermore, in order to investigate the effect of different shapes on absorbance spectrum of gold nanoparticles, simulation tool mentioned in experimental method section is utilized. The absorbance of gold nanoparticles for different shapes, i.e., spherical, rectangular, triangle, pentagon, and hexagon, is simulated. The dimension of gold nanoparticles which is 50 nm in diameter (for spherical) or the longest dimension (for other shapes) are selected. For rectangular, triangle, pentagon, and hexagon, the thickness of gold nanoparticles was set 20 nm. The normalized of simulated absorbance spectra are shown in Figure 7(b). In Figure 7(a), absorbance spectra of G02 and G05 are normalized. From the experiment, it is shown that absorbance of G05 is broaden to longer wavelength. From TEM image, it is observed that different shapes of gold nanoparticles (rectangular and triangle) exist. From the simulation (Figure 7(b)), it is found that absorbance peak wavelength of triangle, rectangular, pentagon, and hexagon are at 580–650 nm wavelength. Meanwhile, absorbance peak of spherical gold nanoparticles is at around 530 nm. This implies that different shapes of gold nanoparticles are responsible to the broadening of absorbance spectra of G05 and G11. The simulation result proves that different shapes of gold nanoparticles can alter absorbance spectra.

In order to understand these findings, it is required to study the mechanism of gold nanoparticle growth in electrochemical process. In the experiment, two different electrodes (gold and copper) were used. In the solution, trisodium citrate, sodium chloride, and glucose are added. Injection DC current and temperature were varied. Briefly, gold bulk, as the anode, is electrolyzed by radicals (R^+) of hydrocarbon (from glucose) to produce gold ions (Au^+). These gold ions, at cathode side, are reduced to atoms controlled by stabilizer (trisodium citrate) to make gold nanoparticles, which follows these equations [20], [29].

In anode:

$$R^+ + Au \rightarrow Au^+ \tag{1}$$

$$H^+ + Au \rightarrow Au^+ \tag{2}$$

In cathode

$$Au^+ + stabilizer \rightarrow Au_{colloid} \tag{3}$$

Sodium chloride is used to make electrochemical liquid becomes more ionic. Basically, other type of salts as ion sources are possible to use. However, sodium chloride is one of the affordable and fast chemicals to make ionic water, due to sodium and chloride ions [26]. Without ionic electrolyte, it is hard for electrochemical process to occur. Therefore, G06 and G10 (samples without sodium chloride) produce small amounts of gold nanoparticles. Meanwhile, in presence of glucose, radicals (R^+) are able to oxide Au to make Au^+ ions [20]. In the absence of glucose, hydrogen ions (H^+) is able to produce oxide Au (G06, G07, and G09). Therefore, the gold nanoparticles production was in little amount or none. Trisodium citrate has the important role as stabilizer to make Au atoms (gold nanoparticles). Without trisodium citrate, gold nanoparticles are difficult to growth (G07 and G08). Unexpectedly, it is found that without trisodium citrate (G11), gold nanoparticles can be formed with only nantrium chloride and glucose. This is assumed due strong oxidation of Au in anode by radicals and strong ionic electrolyte, thus gold ions can easily migrate to cathode side to make gold nanoparticles. However, it is predicted that in the absence of trisodium citrate, the growth of gold atoms is uncontrolled. Therefore, various shapes of gold nanoparticles and bigger size of gold nanoparticles may be obtained. It was predicted that without stabilizer, aggregation of gold nanoparticles can possibly occurs [27], [28]. Furthermore, in high temperature ambient (G03) and high injection current (G05), the formation of gold nanoparticles failed to form due to uncontrolled and forced ambient. The Au ions may not form gold atoms (gold nanoparticles). Instead, gold ions were reversible into gold bulk or gold oxide [27]. In addition, it also noticed that copper electrode is more reactive that gold electrode. Accordingly, there is possibility of copper electrode being oxidized and coated by copper oxide. However, this coating is temporary and can be removed and cleaned by sand paper and alcohol after the process. Further investigation of gold nanoparticles growth and formation in electrochemical process using copper electrode are necessities.

CONCLUSION

Gold nanoparticles were successfully synthesized using electrochemical method with gold and copper electrodes. The shape and size of synthesized gold nanoparticles were investigated using absorbance spectra, transmission electron microscope (TEM) images, and simulation of absorbance spectra. Chemicals used in the synthesis process (trisodium citrate, sodium chloride, and glucose), ambient temperature, and injection current are varied to study absorbance spectra of synthesized gold nanoparticles. It is found that ambient temperature and injection current significantly affect the shape of gold nanoparticles. Strong injection current and high ambient temperature produced less gold nanoparticles. In addition, various shapes of gold nanoparticles, i.e., spherical, triangle, rectangular, pentagon, and hexagonal, are produced. The broadening of absorbance spectra is confirmed using simulation result. This broadening is due to various shape of gold nanoparticles. Unexpectedly, combination of sodium chloride-glucose and trisodium citrate-glucose are sufficient to synthesize gold nanoparticles.

ACKNOWLEDGEMENT

This project was partly supported by Program Pengembangan Teknologi Industri (PPTI) Project from Ministry of Research and Technology/National Research and Innovation Agency, Republic of Indonesia under contract number 62/G1/PPK/E4/2020, financial year 2020. All measurements were done using instrument at National Research and Innovation Agency via ELSA integrated system. The last author was the corresponding author for this manuscript. The first and the last author were the main contributors for this work.

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