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สิ่งแวดล้อม

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SYNTHESIS OF SILVER NANOPOWDERS AT HIGH CONCENTRATIONS VIA
GREEN NANOTECHNOLOGY

Mr. Anon Dachasiripong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

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งานวิจัยนี้ได้พัฒนาวิธีการสังเคราะห์ผงอนุภาคโลหะเงินแบบใหม่โดยกระบวนการรีดักชันทางเคมีที่เป็นมิตรต่อสิ่งแวดล้อม กระบวนการนี้สามารถผลิตคอลลอยด์น้ำของอนุภาคระดับนาโนเมตรของโลหะเงินที่ความเข้มข้นสูง (50,000 – 100,000 ส่วนในล้านส่วน) และปริมาณมากได้ ผงอนุภาคโลหะเงินสามารถแยกออกมาจากสารละลายตั้งต้นได้ง่ายด้วยวิธีการตกตะกอน กระบวนการสังเคราะห์ผงอนุภาคของโลหะเงินที่พัฒนาขึ้นสามารถควบคุมขนาดและการกระจายตัวของอนุภาคได้โดยการปรับเปลี่ยนเงื่อนไขของการทดลอง ได้แก่ ความเข้มข้นของเกลือโลหะเงิน ความเข้มข้นของสารละลายน้ำตาลทราย ค่าความเป็นกรด-ด่างของสารละลาย และลำดับของการผสมสาร ผลการทดลองจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดและการวัดขนาดอนุภาคโดยเทคนิคการกระเจิงแสงพบว่าผงอนุภาคของโลหะเงินที่สังเคราะห์ได้มีขนาดอยู่ในระดับนาโนเมตรถึงไมโครเมตรขึ้นกับเงื่อนไขของการทดลอง กระบวนการสังเคราะห์ที่พัฒนาขึ้นมีความสอดคล้องกับหลักการของกระบวนการทางเคมีที่เป็นมิตรต่อสิ่งแวดล้อม ไม่ว่าจะเป็นการใช้รีดิวซ์เอเจนต์จากผลิตภัณฑ์ทางการเกษตร กระบวนการผลิตที่ไม่ก่อให้เกิดของเสียและผลิตภัณฑ์ข้างเคียง และการทำปฏิกิริยาทั้งหมดภายใต้ความดันบรรยากาศและอุณหภูมิห้อง ทำให้กระบวนการที่พัฒนาขึ้นมีต้นทุนการผลิตที่ต่ำเมื่อเทียบกับกระบวนการดั้งเดิมคือโซเดียมโบโรไฮไดรด์ ผงอนุภาคโลหะเงินที่สังเคราะห์ได้สามารถนำไปใช้เป็นวัตถุดิบสำหรับกระบวนการผลิตในอุตสาหกรรมหลายประเภท เช่น ใช้เป็นสารเติมแต่งสำหรับทำนาโนคอมพอสิต หมึกนำไฟฟ้าในอุตสาหกรรมอิเล็กทรอนิกส์ สารเคลือบผิวสำหรับป้องกันการเจริญเติบโตของเชื้อแบคทีเรีย และนาโนซิลเวอร์เคลย์สำหรับอุตสาหกรรมเครื่องประดับ

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A novel technique for a mass scale production of spherical silver particles powders was developed. A green chemical technique was employed for the preparation of high concentration silver particles colloid (50000 – 100000 ppm). The silver particles powder could be easily precipitated from the colloid. The results from scanning electron microscope (SEM) and dynamic light scattering particle size analyzer indicated a controllable size from nano-scale to micro-scale ranges associated with the employed conditions including concentration of silver salt, concentration of reducing saccharine, pH, and the mixing sequence. Since the synthetic system was designed to meet green chemistry protocols (i.e., using natural substances as the environmentally reducing agent, controlling the complete reduction of silver salt, reducing derivatives, generating no by-products, and performing all procedure under the atmospheric conditions), the production cost is very low and very economic competitive compared that using the conventional borohydride chemistry. The silver particles powders can be employed as raw materials in various industries, such as filler for nanocomposites, conductive silver ink in electronic industry, surface coating for antibacterial applications, and nanosilver clay in jewelry industry.

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LIST OF ABBREVIATIONS

nm	:	nanometer
μm	:	micrometer
SFS	:	sodium formaldehyde sulphonylate
CTAB	:	cetyl trimethyl ammonium bromine
SEM	:	scanning electron microscope
NMR	:	nuclear magnetic resonance
ppm	:	part per million
eV	:	electron volt
IGC	:	inert gas condensation
mL	:	milliliter
M	:	molar
kV	:	kilovolt
Ar	:	argon
N ₂	:	nitrogen
He	:	helium
AgNO ₃	:	silver nitrate
NaNO ₃	:	sodium nitrate
M BH ₄	:	alkaline metal borohydride
NaBH ₄	:	sodium borohydride
NaOH	:	sodium hydroxide
HNO ₃	:	nitric acid
NO ₂ ⁻	:	nitrogen dioxide
h ν	:	photo energy
^o C	:	degree Celsius
M	:	metal
M ⁺	:	metal ion
Ag ⁺	:	silver ion
E ⁰	:	standard reduction potential

CHAPTER I

INTRODUCTION

Silver nanopowders are of interest for both materials science and industries because silver nanopowders have unique properties such as optical properties, surface properties [1, 2]. They can be applied in many applications such as antibacterial [3, 4], catalyst [5], sensors [6], electrical conductive circuit [7-9], etc [10]. Additionally, silver nanopowders were also applied in the area of gems and jewelry.

The production of silver nanopowders can divide into two categories. There are physical and chemical methods [2]. For physical fabrication method, we can accurately control size and shape of the particles but this method usually use high energy and very expensive instruments as well as high cost of maintenance and the operator must have high skilled for using the machine to fabricate nanoparticles. On the other hand, chemical method fabrication consumes low energy, basic equipment in laboratory, low maintenance but the chemical method is difficult to control size and the shape of the particles. The chemical method or chemical reduction contains 3 important components that are metal ions, reducing agent, and stabilizers. The conventional chemicals method will use strong and toxic chemical as a reducing and stabilizing agent. Khanna and Subbarao, 2003 [11] used sodium formaldehyde sulphoxylate (SFS) in acid solution as a reducing agent. Nersisyan, et al. 2003 [12] used formaldehyde and hydrazine hydrate as a reducing agent and sodium dodecyl sulfate as a stabilizing agent. Wang and Gu 2004 [13] used chloroform and cyclohexane as a solvent and sodium borohydride (NaBH_4) as a reducing agent and cetyl tri-methyl ammonium bromide (CTAB) as a stabilizing agent. Guzman M. G., et al 2005 [14] used hydrazine hydrate as a reducing agent and sodium citrate and sodium dodecyl sulphate (SDS) as a stabilizing agent. The silver nanopowders form these syntheses were very uniform spherical shape and low distribute size. But the residue of the generated silver nanoparticle is toxic to environment and human health.

Recently, many groups of scientists concern about the production of chemicals that can damage the environment. So they mutually co-operated with each other by announcing 12 principles of green chemistry [15] and made the campaigns to save the environment. After that, the trend of fabrication of nanopowders also changed to use mild and safe chemicals as a reducing agent, instead of using traditionally strong and toxic reducing agent. The examples are research works of Wu and Meng, 2005 [16] used ascorbic acid (Vitamin C) as a reducing agent, Vigneshwaran et al, 2006 [17] used the soluble starch under high pressure and high temperatures as a reducing agent, Singh et al, 2009 [18] used glucose in various pH ranges as a reducing agent and used soluble starch as a stabilizing agent, as well as Bar et al, 2009 [19] used the extract from *Jatropha curcas* as a reducing agent and stabilizing agent. However, the efficiency of mild chemical were lesser than strong chemicals. Silver nanopowders from these synthesis methods have low yield and the size of the particles are uncontrollable.

Thus, this research will focus on development of innovative procedure to synthesize silver nanopowder by green chemical reduction using the agricultural products in Thailand as reducing agent, which is environmental friendly and has lower price. Moreover, we anticipate that silver nanopowders from our methods have the same quality as that of nanopowders products using sodium borohydride as reducing agent.

1.1 The objective of research

To develop the green synthesis of silver nanopowders with high concentration via green technology using agricultural products of Thailand as a reducing agent.

1.2 Scopes of this research

1. Developing the synthesis of silver nitrate as silver ions source
2. Developing a green method for synthesis silver nanopowder at high concentration.
3. Characterizing and purifying silver nanopowders.

1.3 Benefit of this research

The novel method for synthesizing silver nanopowders via green nanotechnology by using Thailand agricultural product (sucrose) as reducing agent and stabilizing agent is established.

CHAPTER II

THEORETICAL BACKGROUND

2.1 Silver metal

Silver is a precious metal which has unique properties such as shininess, conductivity, and stability. Usually, people use silver as a basic material in many fields such as architecture, medicine, food preservation, religion, jewelry and decoration, etc. Mostly jewelry applications of silver are ring, bracelets, necklaces, earrings, etc. The decoration and jewelry of silver from Thailand has been very popular because Thai people were highly skilled craftsman and were recognized around the world. The jewelry and decoration from silver are important export products of Thailand which bring in a large amount of income to the country. Moreover silver widely use in electrical industry as well as jewelry and decoration because silver has high electrical conductivity and cheaper than other precious metal.

2.2 Nanochemistry

Nano came from a Greek word. It means the size of particle in the range of 10^{-9} m. The nanochemistry, nanoscience, nanoengineering and nanotechnology, all deal with very small size of objects or systems. Officially, the United States National Science Foundation [1, 2, 10] defines nanoscience / nanotechnology as studies that deal with materials and systems having the following key properties:

1. Dimension: at least one dimension from 1 to 100 nanometers (*nm*).
2. Process: designed with methodologies, that shows fundamental control over the physical and chemical attributes of molecular-scale structures.
3. Building block property: they can be combined to form larger structures.

2.3 Synthesis of silver nanoparticles

Generally, all of the synthesis methods of nanoparticle can be separated into two main types: *top-down* and *bottom-up* approaches. In the top-down approach, the method started with standard bulk materials to generate nanomaterial. Whereas, the bottom-up approach is started from the atoms or molecules and build up to nanoparticles. However, synthesis methods of metal nanoparticles have two important types, chemical reduction method and physical method.

2.3.1 Chemical reduction method

Chemical reduction is a popularly method for synthesis nanoparticles because this method is so simple and low cost production. Metal nanoparticles are synthesized by reducing metal ion with a reducing agent (e.g. borohydrides, hydrazine, formaldehyde, alcohol, and aldehyde compound) [11-14]. Generally, the reduction of metal ions to metal nanoparticles are decided by the potential difference [20-27]:

$$\Delta E = E_{\text{silver ion}} - E_{\text{aldehyde}} \quad (2.1)$$

Where ΔE is the potential of the system. $E_{\text{silver ion}}$ is the reduction potential of silver ion and E_{aldehyde} is the reduction potential of aldehyde. When $\Delta E > 0$, the reduction of silver ion to silver atom can occur.

Generally, chemical reduction method often used sodium borohydride as reducing agent for synthesizing metal nanoparticles in aqueous media. Borohydrides reduce metal ions with high reduction potential, 1.24 V. The reactions of borohydrides were rapidly causing the immediate nucleation of metal particles. Such particles are small and have a narrow size distribution. However, sodium borohydride is harmful and toxic to human health and environment, and residue from generated silver nanopowders with borohydride can explode when spark with electricity. The metal particles form borohydride reduction was not suitable for many applications,

especially medical application because of the residues. The reduction equation of synthesis silver nanoparticles with borohydride is as follows [26-30]:



2.3.2 Physical method

Physical methods are a technique for fabricating nanoparticles. These techniques have highest purely and accurately controllable size of the nanoparticles. However, cost for this fabricating technique is very high as well as consumes high energy, high cost maintenance, and user must be highly skilled. So this technique is harder to appropriate for commercial application. The examples of physical methods are inert gas condensation [31], laser ablation [32], and spray pyrolysis [33].

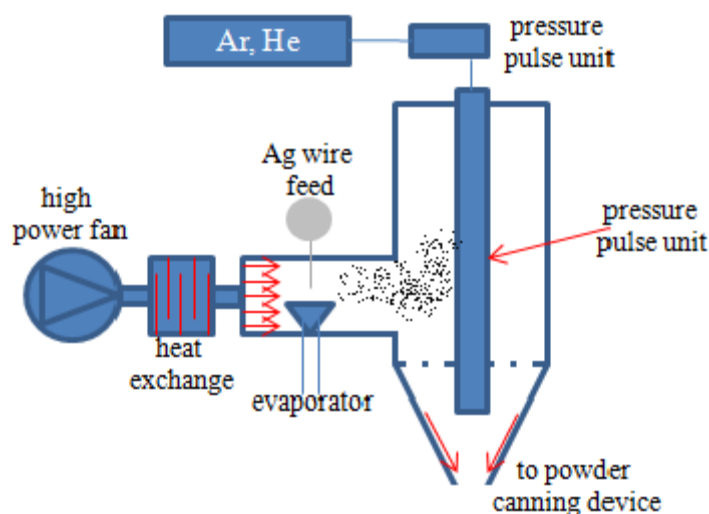


Figure 2.1. Schematic diagram for the preparation of silver nanoparticles by inert gas condensation (IGC) method. The pure inert gas (He or Ar) flows into the chamber and the source metal is vaporized into the flowing inert gas. As a result, nanoparticles are formed on suitable medium such as metal filter.

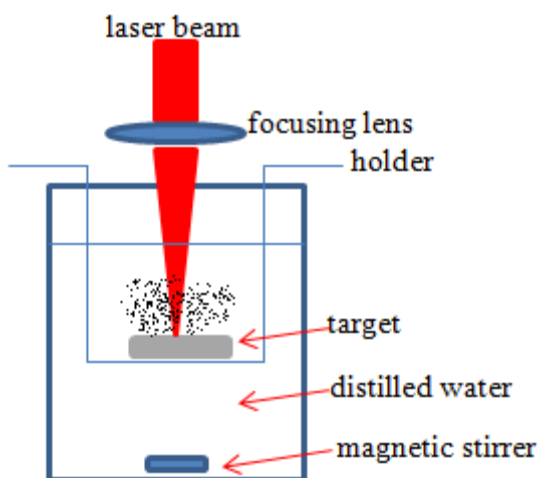


Figure 2.2. Schematic diagram for experimental set-up for colloid preparation by laser ablation in solution. Metal nanoparticles can be produced by irradiating metal sheet with intense laser in liquid solution with the presence of stabilizer. Interaction between laser and metal sheet resulted in ablation. The particles size can be controlled by changing the laser intensity and wavelength.

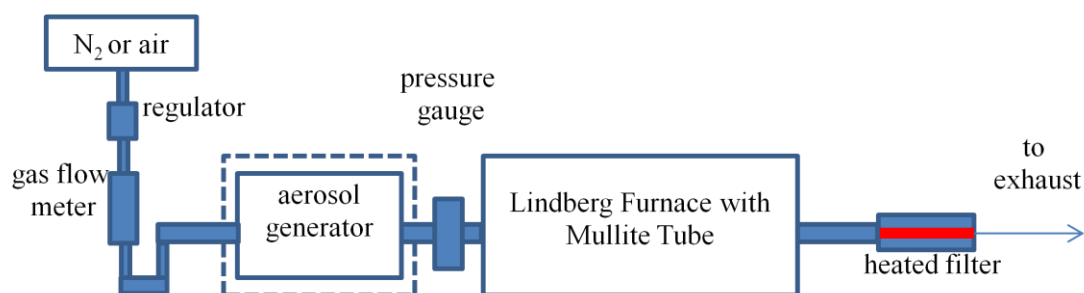


Figure 2.3. Schematic diagram for experimental setup of spray pyrolysis. The metal salt solution is atomized into droplets and sent through a hot reactor. Then, the metal salts decomposed to form the particles.

2.4 Stabilizer

Stabilizer helps the nanoparticles to be stable because the repulsion force of stabilizer on nanoparticles surface protect the collision of nanoparticles. The collision and aggregation of particles are due to of larger particles. Generally, mechanisms of surface protection can explain by electrostatic stabilization and steric hindrance stabilization.

Electrostatic stabilization mechanism involves the clouding of ions on the particles surface and the clouding of counter ions around the particles. This sufficient electrostatic repulsion can prevent particles from aggregations.

Steric hindrance mechanism can be achieved by the adsorption of the hindrance molecules as a polymers or branch polymers on the surface of metal nanoparticles. Polymer chains on metal nanoparticles surface produce steric repulsion which separated particle form each other's [34-39].

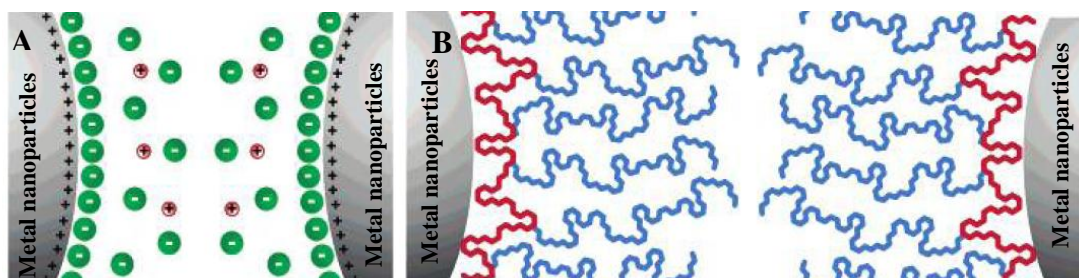


Figure 2.4. The stabilization mechanisms of silver nanoparticles; (A) electrostatic stabilization and (B) steric hindrance.

2.5 Green chemistry

2.5.1 Definition of green chemistry

Green chemistry is the design, development, and implementation of the chemical processes and chemical products to reduce or eliminate the use and generation of hazardous substances to the human health and the environment.

2.5.2 History of green chemistry

Green chemistry gained its current standing as a scientific discipline as well as practical means to pollution prevention as a result of collaboration between the US government, industry, and academic. Paul Anastas, who was the leader of the industrial chemistry, moved forward the concept of Green Chemistry. Paul Anastas and John Warner developed the 12 Principles of Green Chemistry in mid of 1990. Let us imagine about how to prevent contamination in environmental when creating new chemicals and materials. Paul Anastas and John Warner [15] work as an inventor of a new field called Green Chemistry, based on the productive collaboration of government and industry.

2.5.3 The Twelve Principles of Green Chemistry

The 12 principles of green chemistry is the rule for experimenting that harmless to human health and environment as well as the regulation of collaboration between the US government, industry, and academic. The research can be called GREEN, when experiments followed at least one item from these lists.

1. Prevent waste is rather than treat or clean up waste after it has been produced.
2. Synthetic methods should be designed to maximize the all materials used in the process.
3. Synthetic methods should be designed to use and create substances that few or no toxicity to human health and the environment.
4. Chemical products should be designed to affect their desired function while minimizing their toxicity.

5. The substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements for chemical processes should be environmental friendly, economic impacts, and minimized. If possible, synthetic methods should be processes at ambient temperature and pressure.
7. A raw material should be renewable and economically practicable.
8. Unnecessary derivative should be minimized or avoided, if possible.
9. Catalytic reagents should be selective as which are superior to stoichiometric reagents.
10. Chemical products should be designed when their function end or they break down into innocuous degradation products and do not persist in the environment.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

2.6 Green reducing agent

Green reducing agent is an environmental friendly chemical for reducing metal ion into metal nanoparticles. It must not damage or toxic to human health and environment. In this research, we use sucrose as a reducing agent as well as stabilizing agent which is one of Thailand agricultural product and environmental friendly. However, sucrose has very low reducing potential because it has no reducing groups. Thus, sucrose must be modified by acid hydrolysis and alkaline degradation before using as a reducing agent.

2.6.1 Sucrose

Sucrose is organic compound which clear color, odorless, and sweet taste. Sucrose is a disaccharide which consists of glucose and fructose and is linked via ether bond between C₁ of the glucosyl unit and C₂ of the fructosyl unit. The bond called “glycosidic linkage”. The molecular formula of sucrose is C₁₂H₂₂O₁₁ and IUPAC name is β-D-fructofuranosyl-(2→1)-α-D-glucopyranoside or β-(2S,3S,4S,5R)-fructofuranosyl-α-(1R,2R,3S,4S,5R)-glucopyranoside. Glucose exists as two isomeric "pyranoses" (α and β), but only one of these forms can link to the fructose unit. Fructose exists as a mixture of "furanoses", each of which has α or β isomer, but the only one isomer can link to the glucosyl unit. However, sucrose is unlike most disaccharides because the glycosidic bond is formed between the reducing ends of both glucose and fructose. Thus, sucrose is classified as a nonreducing group.

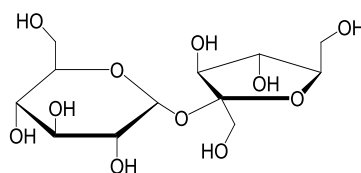


Figure 2.5. Structure of sucrose

The polarimetry is a common detection of sucrose purity by measuring the rotation of plane-polarized light of the sucrose solution. The specific rotation of pure sucrose at 20 °C using yellow "sodium-D" light (589 nm) is +66.47. Commercial samples of sucrose are assayed using this parameter. Sucrose is stable in air.



Figure 2.6. Powder and crystalline structure of sucrose

2.6.2 Acid hydrolysis of sucrose

Firstly, the introduction is involved the increasing number of a reducing group by acid hydrolysis of sucrose under acidic condition. Mega and Van Etten [40] described the acid - catalyzed hydrolysis of sucrose involved protonation of the glycosidic oxygen atom by using ^{18}O shift in ^{13}C nuclear magnetic resonance (NMR) to explain the point of bond cleavage in the acid-catalyzed hydrolysis of sucrose. Sucrose was hydrolyzed in the presence of H_2^{18}O , and the incorporation of ^{18}O into the products was determined. The results clearly indicated fructosyl-oxygen bond cleavage.

Thus, acid-catalyzed hydrolysis of sucrose product is a D-glucose and a fructose oxocarbenium ion, which can react with water to form D-fructose and regenerate the H^+ catalyst. As a consequence, further acid degradation of sucrose can be described by the action of acids on D-glucose and D-fructose [40].

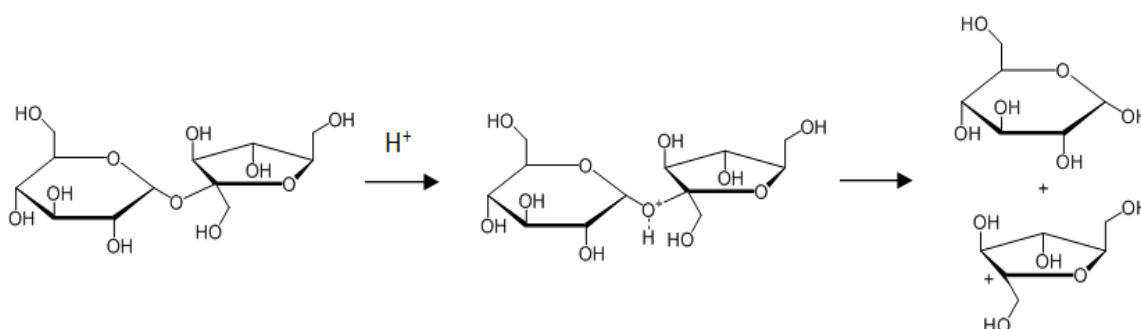


Figure 2.7. Sucrose disintegrations by protonation of the glycosidic oxygen

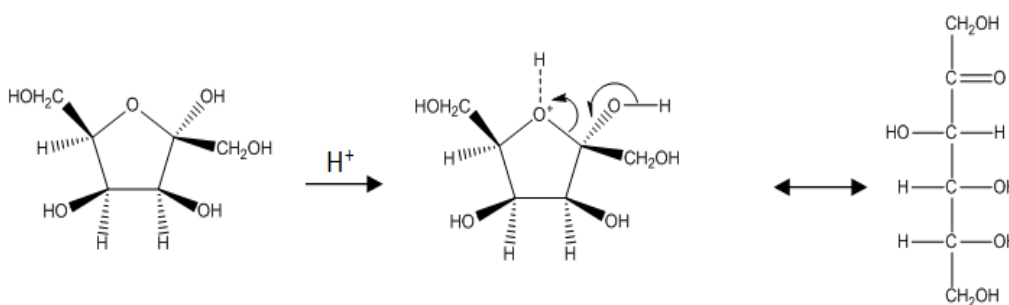


Figure 2.8. Fructose unit open chain under acidic condition

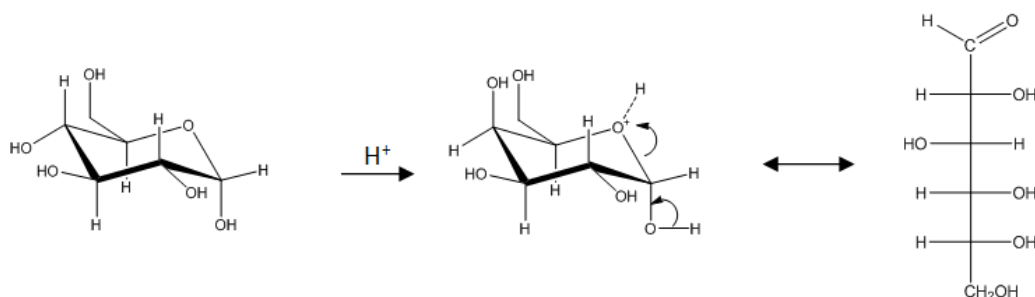


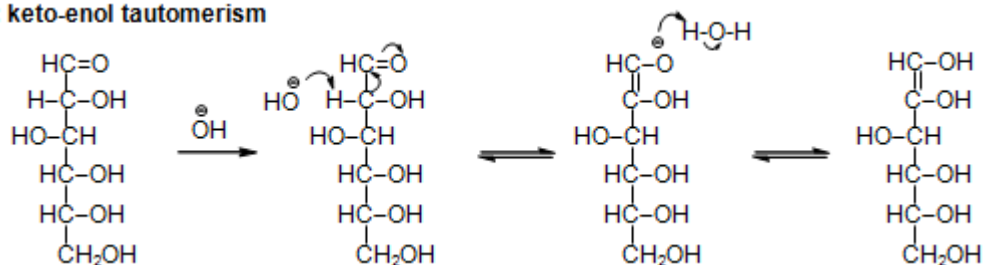
Figure 2.9. Glucose unit open chain under acidic condition

2.6.3 Alkaline degradation of monosaccharide

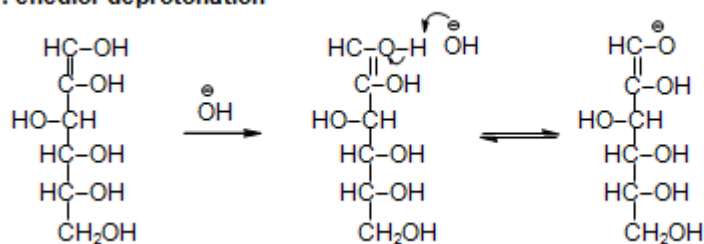
The alkaline degradation of monosaccharide is a significant step. This step can generate lower molecular weight species which have aldehyde group [40-42] and when monosaccharide reacts with hydroxide ion electrons are given for reducing silver ion into silver nanoparticles.

The nonreversible degradation reactions of monosaccharide can describe by the following five reactions, namely, *β -elimination*, *benzilic acid rearrangement*, *α -dicarbonyl cleavage*, *aldol condensation*, and *retro-aldol condensation* (Figure 2.10). All of products from nonreversible degradation reactions of monosaccharide reaction showed in Figure 2. 10. All products of acid hydrolysis and alkaline degradation of sucrose showed in Figure 2.11.

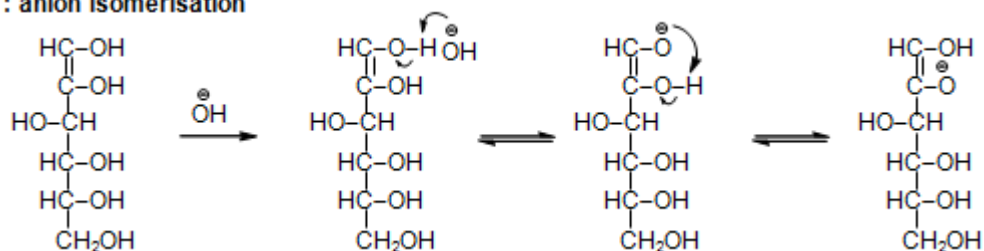
I : keto-enol tautomerism



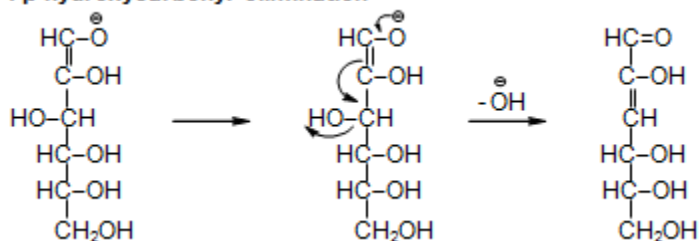
II : enediol deprotonation



III : anion isomerisation



IV : β -hydroxycarbonyl elimination



V : β -alkoxycarbonyl elimination

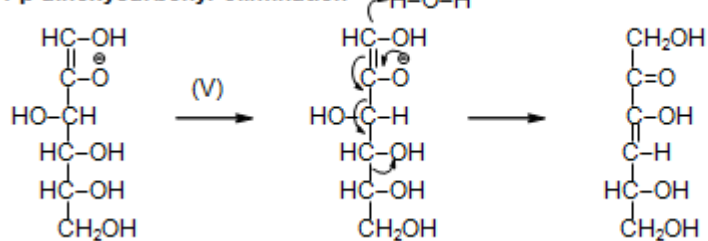
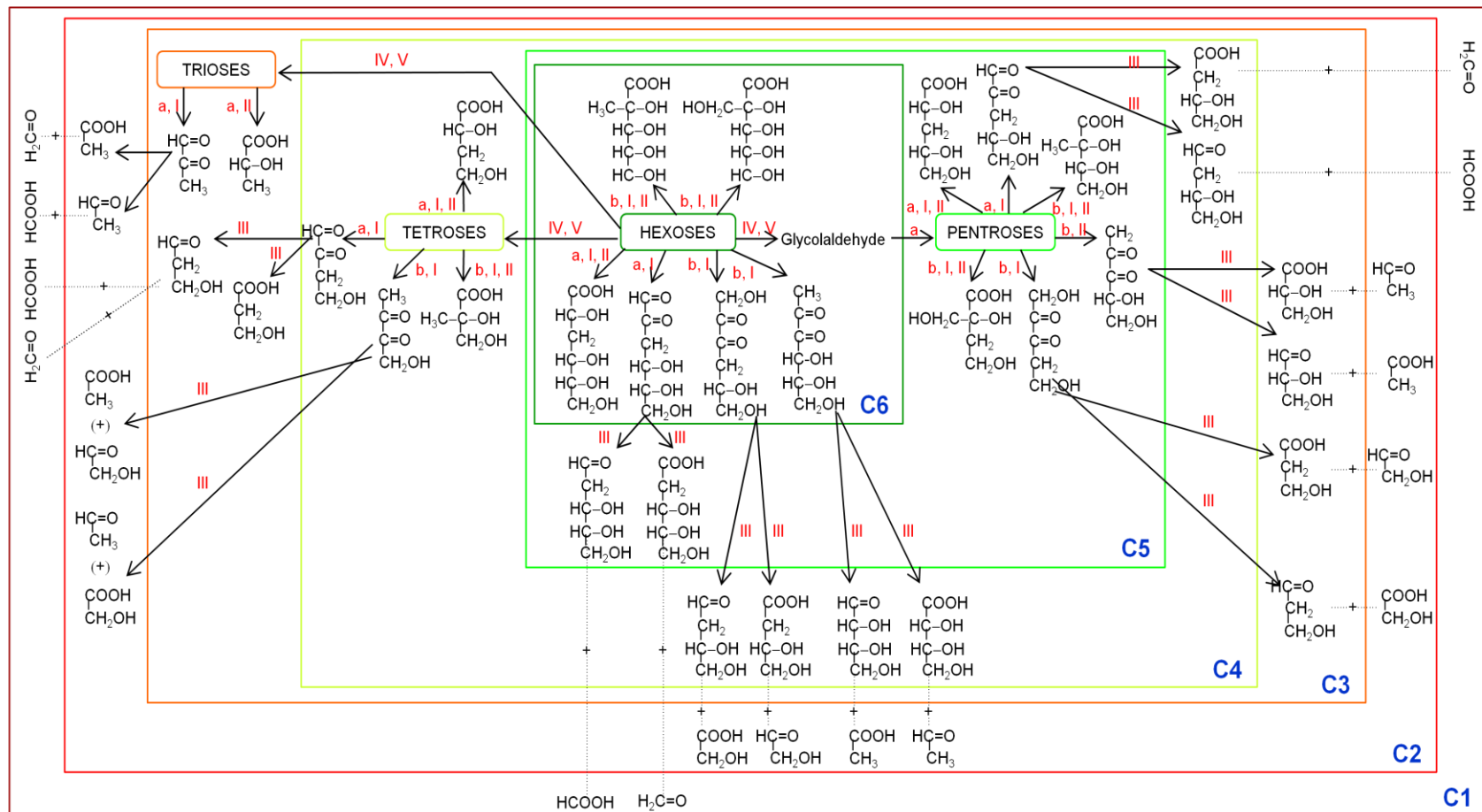


Figure 2.10. The mechanisms of alkaline degradation of monosaccharides.



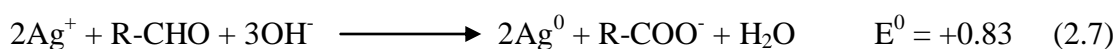
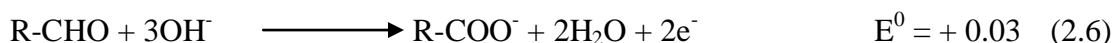
a : 1,2-enediol, b : 2,3-enediol, I : β -elimination, II : benzylic and rearrangement, III : α -dicarbonyl cleavage, IV : retro-aldolization, V : aldolization

Figure 2.11 The reaction pathways of monosaccharide under alkaline degradation.

(Duangta Tongsakul, Kanet Wongravee, Chuchaat Thammacharoen, Sanong Ekgasit, "Enhancement of the reduction efficiency of soluble starch for platinum nanoparticles synthesis", 2012, *Carbohydrate Research* (accepted)).

2.6.4 Reduction properties of aldehyde group in alkaline condition

In the solution contained with sucrose and silver ions under acidic condition, hydrolysis reaction changed sucrose into D-glucose and D-fructose, which formed complex with silver ions. After that, slightly adding sodium hydroxide into the solution, the acid condition slightly changed to alkaline condition, silver ions were compounded as oxide and alkaline degradation of monosaccharide occurred. The alkaline degradation of monosaccharide will change D-glucose and D-fructose to carboxylic and the aldehyde compound which following lower molecular weight (Figure 2.11). Finally, silver oxide reacts with aldehyde species resulting in silver metal (Ag^0) and converted aldehyde compound into carboxylic compound as follows [43, 46]:



Additionally, the lower molecular weight species can protect the nanoparticles aggregation by form protection layer on the surface of particles. The pH of the solution also plays an important role in the reaction process. At lower pH, the reaction proceeded in the acid hydrolysis, when the pH increased, the alkaline degradation became the dominant pattern. The relative ratio of silver ions and sodium hydroxide should be sufficient to reduce all silver ions in the solution. The addition of alkali is favored for higher reducing ability. However, the sodium hydroxide increased ionic strength effect and leading to aggregation of particles and became to larger particle.

2.7 Characterization techniques

2.7.1 Scanning electron spectroscopy

The scanning electron microscope (SEM) is extremely useful for imaging surface and subsurface microstructure. The basic layout of SEM instrumentation is shown in Figure 2.12. The electron gun is the electron generator. The condenser lenses made from a magnetic, the main function of condenser lenses is condensed electron beam from electron gun. While the objective lens focus the electron probe onto specimen (object). The detector will detect electron that scatter with sample then amplified output to monitor. The magnification is simply the ratio of the monitor size to the specimen size.

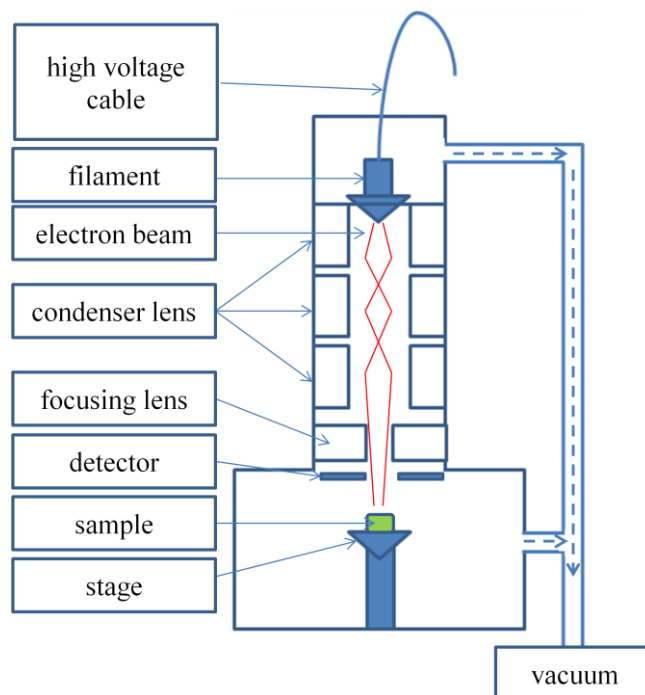


Figure 2.12. Schematic diagram of scanning electron microscope instrument

2.7.2 Particle size analyzer

Particle size analyzer is an instrument regarding to dynamic light scattering or photon correlation spectroscopy. This technique is one of the most popular methods used to determine the size of particles. The laser was used as a shining monochromatic light beam, onto spherical particles in Brownian motion in solution. The Brownian motion of particle caused the Doppler Effect shift when the laser light hits the moving particle. The wavelength of the laser light will change that is related to the size of the particle.

The basic layout of particle size analyzer instrument was shown in Figure 2.13. The instrument contains with the laser source, focusing lens, sample holder, coherence optics, photon detector, and monitor. Laser source is the light generator. Focusing lens will focus the laser beam onto sample. Coherence optics is a wavelength selector. Photon detector will detect the light after pass coherence optics and the monitor will output the data.

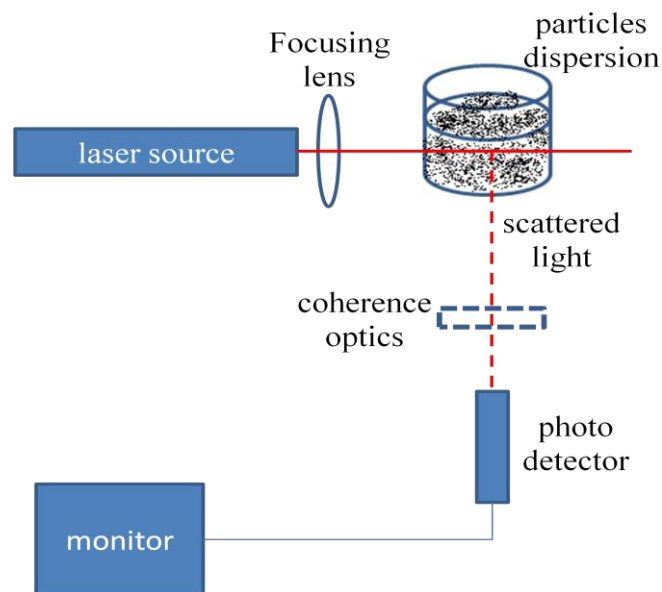


Figure 2.13. Schematic diagram of dynamic light scattering instrument

CHAPTER III

EXPERIMENT

3.1 Chemicals and materials

3.1.1 Silver metal 99.99%

3.1.2 Nitric acid (analytical grade) purchased from Merck

3.1.3 Sodium hydroxide (analytical grade) purchased from Merck

3.1.4 Sucrose purchased (food grade) from Mitr-phol sugar group

3.2 Preparation of Silver nitrate

Silver nitrate (AgNO_3) is prepared by slowly dissolving 500 g of silver metal in 700 mL of hot nitric acid mounting on hotplate until silver metal is disappeared and the total volume of dissolving silver metal solution is 300 mL. Then, adding 700 mL of de-ionized water into the mixed solution between nitric acid and the dissolved silver metal. After that, heating the mixed solution mounting on a hotplate for evaporating the residues such as water, nitric acid, and nitrous oxide until the volume of solution is less than 300 mL. Finally, when the mixed solutions cooled to room temperature, the silver nitrate formed crystal structure. After that, silver nitrate crystalline was dissolved in 1,000 mL of de-ionized water in volumetric flask. The concentration of silver nitrate stock solution is 500,000 ppm (0.93 M).

The reaction can be written as follows:





Figure 3.1 Schematic synthesis method of silver nitrate.

3.3 Synthesis of silver nanopowders

Silver nitrate 100,000 ppm was prepared by diluting the stock solution of silver nitrate (500,000 ppm) with de-ionized water, then added sucrose without purifying into silver nitrate solution with slowly stirring by mixing machine for 1 hour. Under acidic condition of silver nitrate (pH 4), acid hydrolysis of sucrose will change disaccharide to monosaccharide. After that, 3 M of sodium hydroxide (NaOH) was added into the mixed solution with vigorous stirring rate on mixing machine. When adding NaOH into the mixed solution, the condition of solution will slightly change from acidic condition to alkaline condition. The degradation of monosaccharide will change monosaccharide into lower molecular weight compounds that contained aldehyde group. The oxidation reaction of aldehyde group will convert aldehyde group to carboxylic group when reacting with hydroxide ion which released electron for reduction silver ion to silver metal. Moreover, the other function of the lower molecular weight is to protect the surface of silver metal and to stabilize the particles in nanometer range. As observed, after adding NaOH the color of solution changed from clear to black which indicated that silver nanoparticles occurred. The color of solution will change again from black to grey as well as white grey respectively because the aggregations of small particles became large particles and finally, large particles precipitated later. The precipitation was washing with de-ionized water and letting the particles dried at room temperature.

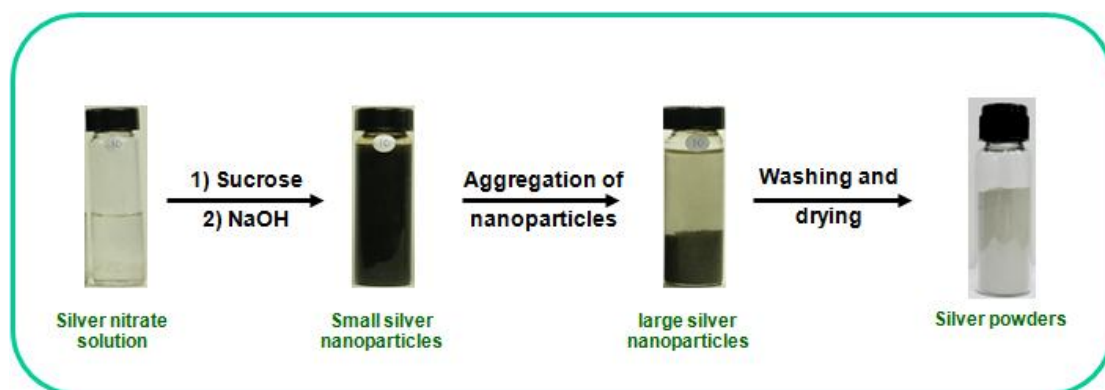


Figure 3.2. Schematic method for synthesizing silver nanopowders.

An apparatus for synthesis of silver nanoparticles was shown in Figure 3.2. There are only 3 chemicals concerning in the reaction; they are silver nitrate, sucrose and sodium hydroxide. Silver nitrate was a silver ion source; sucrose acted as a reducing as well as stabilizing agents, and sodium hydroxide was used as a catalyst for degradation of sucrose. We can say that we successfully designed our experiment for synthesis silver nanopowders by varying the amounts and the concentrations of these chemicals.

3.3.1 The effect of the amount of sucrose on silver nanoparticles

In order to observe the effect of the amount of sucrose on silver nanoparticles, the amount of sucrose in the total volume of 5 mL was varied the ratio of sucrose/silver ($\% w_{\text{sucrose}} / w_{\text{Ag}}$) as follows: 20%, 40%, 60%, 80%, and 100% and then each of the solution was incubated with 5 mL of 100,000 ppm silver nitrate for 1 hour. And then added 2.5 mL of 3 M sodium hydroxide into the mixed solution and shaken for 5 minutes. After the reaction complete; the silver nanoparticles were collected and cleaned by washing with de-ionized water and centrifuged for 5 times as well as re-dispersed the particles in de-ionized water again. Drop the solution of silver nanoparticles and dried by a vacuum pump. After the particles dried, we characterized silver nanoparticles by mean of scanning electron microscope for observing the surface structure and size of the silver nanoparticles.

3.3.2 The effect of the concentration of sucrose on silver nanoparticles

In order to investigate the effect of the concentration of sucrose on silver nanoparticles, the stock solution of sucrose was prepared by dissolving 10 g of sucrose in de-ionized water in 100 mL volumetric flask. Pipette stock solution of sucrose each of 2.5 mL and injected to 5 vials. Then, added de-ionized water 0.00, 2.50, 5.00, 7.50, and 10.00 mL into each vial with stock solution. After that, adding 5 mL of 100,000 ppm silver nitrate and incubated for 1 hour. After that adding 2.5 mL of 3 M sodium hydroxide into mixed solution and shaken on machine for 5 minutes. After the reaction complete; the silver nanoparticles were collected and cleaned by washing with de-ionized water and centrifuged for 5 times and re-dispersed the particles in de-ionized water again. Drop the solution of silver nanoparticles and dried by a vacuum pump. After the particle dried, we characterized the silver nanoparticles by mean of scanning electron microscope for observing the surface structure and size of the silver nanoparticles.

3.3.3 The effect of the amount of sodium hydroxide on silver nanoparticles

In order to investigate the effect of the amount of sodium hydroxide on silver nanoparticles, in the total volume of 2.5 mL for each vial by getting started with sodium hydroxide as follows: 0.003, 0.006, 0.009, 0.012, and 0.015 mole. Then, sodium hydroxide solution was injected to the mixed solution of 5 mL of 100,000 ppm silver nitrate and 5 mL of 50,000 ppm sucrose which incubated for 1 hour. After that, shaken the mixed solution on machine for 5 minutes. After the reaction complete; the silver nanoparticles were collected and cleaned by washing with de-ionized water and centrifuged for 5 times and re-dispersed the particles in de-ionized water again. Drop the solution of silver nanoparticles and dried by a vacuum pump. After the particle dried, we characterized silver nanoparticles by mean of scanning electron microscope as well as particle size analyzer for observing the surface structure and size of the silver nanoparticles.

3.3.4 The effect of the concentration of sodium hydroxide on silver nanoparticles

In order to investigate the effect of the concentration of sodium hydroxide on silver nanoparticles, the concentration of sodium hydroxide was varied by getting started with 3 M sodium hydroxide stock solution (weighting 12 gram of sodium hydroxide and dissolved it in 100 mL of de-ionized water in volumetric flask). Pipette each of 2.5 mL of the stock solution and injected to 5 vials. And then, added the difference volume of de-ionized water getting started with 0.00, 2.50, 5.00, 7.50, 10.00, and 12.50 mL. After that, added sodium hydroxide into 5 mL of the mixed solution 100,000 ppm silver nitrate and 5.00 mL of 50,000 ppm sucrose which incubated for 1 hour. After that, shaken the mixed solution on machine for 5 minutes. After the reaction complete; the silver nanoparticles were collected and cleaned by washing with de-ionized water and centrifuged for 5 times and re-dispersed the particles in de-ionized water again. Drop the solution of silver nanoparticles and dried by a vacuum pump. After the particle dried, then characterized silver nanoparticles by mean of scanning electron microscope as well as particle size analyzer for observing the surface structure and size of the silver nanoparticles.

3.3.5 The effect of the amount of silver nitrate on silver nanoparticles

In order to investigate the effect of the amount of silver nitrate on silver nanoparticles, getting started with each total volume of 5 mL; the amount of silver nitrate was prepared as follows: 100,000, 200,000, 300,000, 400,000 and 500,000 ppm, which each total volume of silver nitrate solution contained 5 mL of 50,000 ppm sucrose with incubating for 1 hour. Then, added 2.5 mL 3 M of sodium hydroxide into the mixed solution of silver nitrate and sucrose. After that, shaken the mixed solution on machine for 5 minutes. After the reaction complete; the silver nanoparticles were collected and cleaned by washing with de-ionized water and centrifuged for 5 times and re-dispersed the particles in de-ionized water again. Drop the solution of silver nanoparticles and dried by a vacuum pump. After the particle dried, then characterized the silver nanoparticles by mean of scanning electron microscope as

well as particle size analyzer for observing the surface, structure, and size of the silver nanoparticles.

3.4 Characterization of the synthesized silver nanopowders

3.4.1 Scanning electron microscope

The SEM micrographs of silver nanopowders were recorded with a Jeol, H-7650 analytical scanning electron microscope. Samples were prepared by placing a drop of silver nanoparticles solution onto copper stuff. After the solutions dried, size and size distribution of silver nanoparticles in silver powder were observed. The accelerating voltages of this instrument are in the range of 10 - 30 kV and the image magnifications are in the range of 1,000-30,000 times.

3.4.2 Particle size analyzer

Particle size analyzer is also known as dynamic light scattering or photon correlation spectroscopy. The average size and size distribution of silver nanoparticles were recorded with a Microtrac-Zettrac, NPA152-31-A-0000-00-20M model. Silver nanopowders were prepared by re-dispersing in de-ionized water. Then, the solution of silver nanoparticles was injected into holder of particle size analyzer instrument.

CHAPTER IV

RESULTS AND DISCUSSION

Silver nanoparticles were successfully synthesized via green chemical reduction of silver nitrate by using sucrose as a reducing agent and NaOH as an alkaline degradation catalyst.

4.1 The amount of sucrose that affects silver nanoparticles structure

According to section 3.3.1, for each total volume of 5 mL, the ratio of sucrose to silver (%w/w) was varied as follows: 20% (A), 40% (B), 60% (C), 80% (D), and 100% (E). The sucrose was injected to 5 mL of 100,000 ppm silver nitrate. The solution is clear. After 1 hour, 2.5 mL of 3 M sodium hydroxide was added into the mixed solution. When adding sodium hydroxide into the solution, the color of the solution changed from clear to brown and brown changed to black and finally precipitated. The brown is from silver oxide [44-45] and black is from silver atom [44-45]. After the reaction complete, the particle were collected, purified and characterized by mean of scanning electron microscope (Figure 4.1) as well as particle size analyzer (Figure 4.2) for observing the shape and size of the silver nanoparticles.

According to the SEM micrographs as shown in Figure 4.1, (A – E), the obtained silver nanoparticles had spherical shape with different average diameter size. As the amount of sucrose increased, the average diameter sizes reduced from 200 nm; to 150 nm; to 120 nm; to 80 nm; and to 50 nm. These results were simultaneously confirmed by the particle size analyzer (Figure 4.2).

From the literature reviews, the sucrose performs two functions on silver nanoparticles phenomena— those are reducing and stabilizing agents. The effect of the amount of sucrose are shown in Figure 4.3 (the system having greater amount of sucrose) and Figure 4.4.

Figure 4.3 shows the effect of the amount of electron (greater amount of sucrose) on the size of the generated silver nanoparticles. As the number of electron in the system increased, the size of the generated particles became smaller. On the contrary, as the number of electron in the system decreased, the size of the generated particles became larger. This is because at lower amount of electron, the nucleation of silver seed (silver atom) occurs at slow rates. This means that there are silver ions left in the system. These ions will deposit on the silver seed surface which leads to larger particles.

The amount / strength of stabilizer also influent the size of the generated silver nanoparticles as shown in Figure 4.4. The more stabilizer (greater amount of sucrose) in the system, the more stabilizing power of the nanoparticles surface. In other words, more particle prevented from agglomeration with more stabilizer. Thus the generated silver nanoparticles are smaller in the case of the greater amount of sucrose.

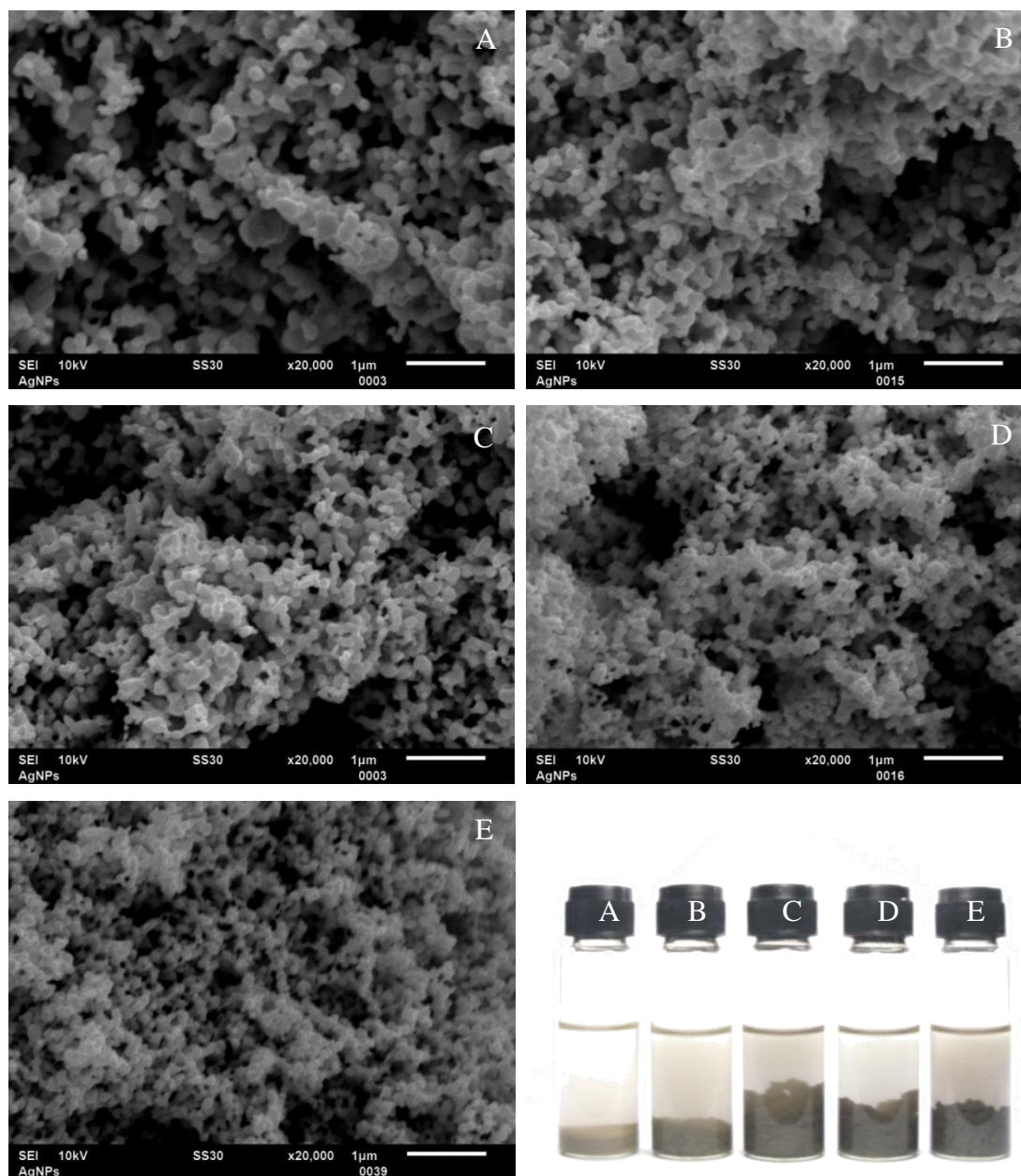


Figure 4.1 SEM micrographs of the silver nanoparticles. A - E containing 5 mL of 100,000 ppm silver nitrate, 3 M sodium hydroxide, and different amount of sucrose % ($W_{\text{sucrose}} / W_{\text{Ag}}$) as follows: 20 (A), 40 (B), 60 (C), 80 (D), and 100 (E).

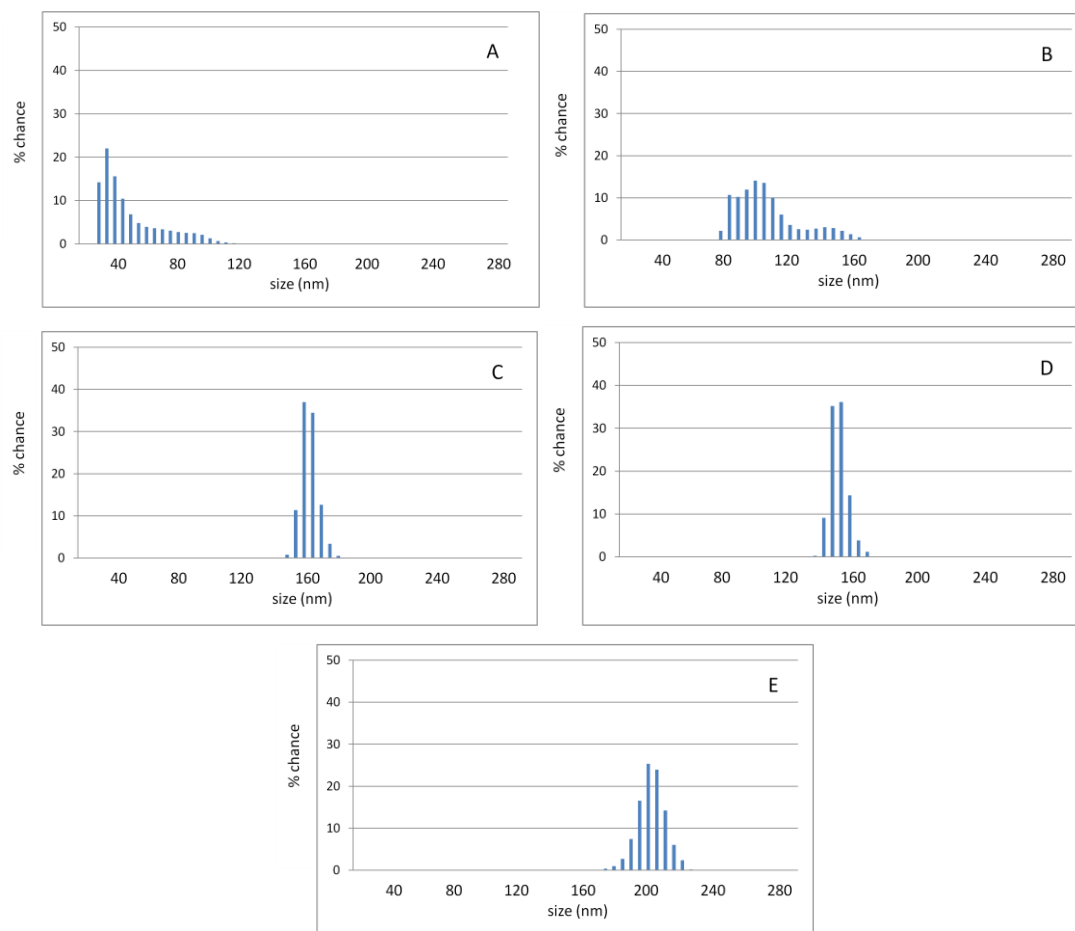


Figure 4.2 The relationship between size of particles and percent chance from particle size analyzer. A - E containing 5 mL of 100,000 ppm silver nitrate, 3 M sodium hydroxide, and different amount of sucrose form 20 (A), 40 (B), 60 (C), 80 (D), and 100 (E) % ($W_{\text{sucrose}} / W_{\text{Ag}}$).

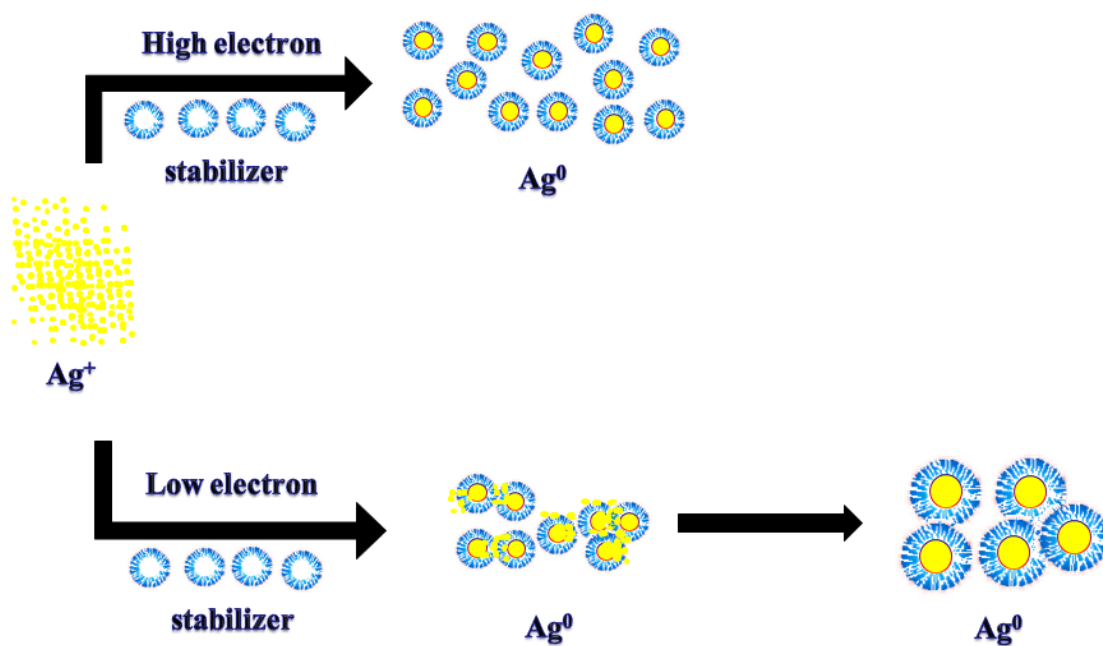


Figure 4.3 The proposed mechanism shows the effect of electron in the system

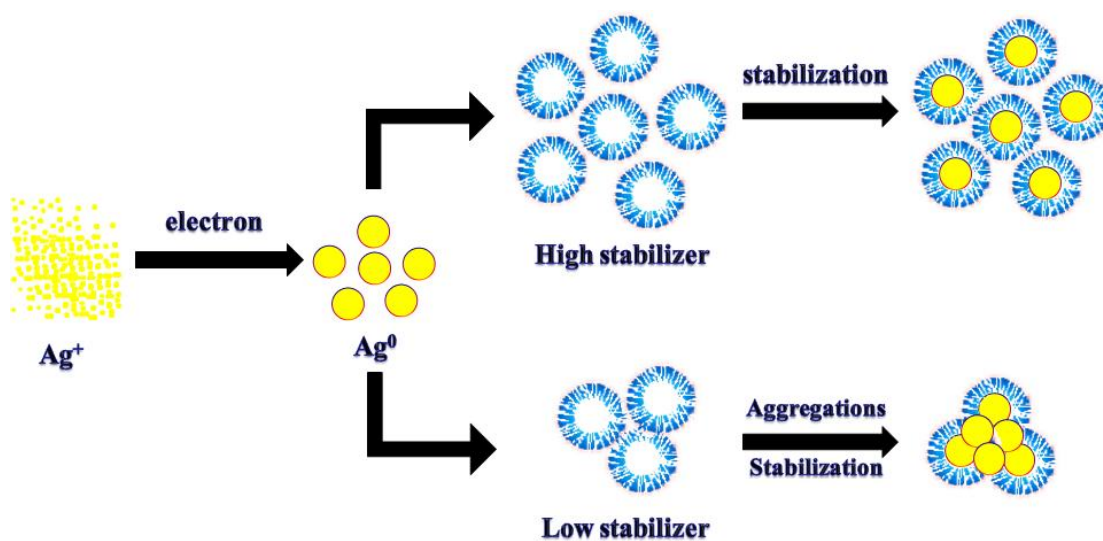


Figure 4.4 The proposed mechanism shows the effect of stabilizer on silver nanoparticles

4.2 The effect of concentrations of sucrose on silver nanoparticles

According to section 3.3.2, A – E each contains 5 mL of 100,000 ppm silver nitrate and sucrose 50 % ($W_{\text{sucrose}} / W_{\text{Ag}}$) but the volume of sucrose solution was different; the volumes was varied as follows: 2.50 (A), 5.00 (B), 7.50 (C), 10.00 (D), and 12.50 (E) mL. The color of the mixed solution is clear. After incubation for 1 hour; 2.5 mL of 3 M sodium hydroxide was added into the mixed solution. While adding the color of mixed solution are rapidly changed from clear to brown and gradually changed to black as well as grey and finally precipitated. The brown is from silver oxide [44-45] and black is from silver atom [44-45] and grey is silver atom aggregated form. After the reaction complete, the particle were collected, purified and characterized by mean of scanning electron microscope (Figure 4.5) as well as particle size analyzer (Figure 4.2.3) for observing the shape and size of the silver nanoparticles.

According to the SEM micrographs as shown in Figure 4.5, (A – E), the obtained silver nanoparticles had uniform spherical shape as well as average diameter size. The average size range of A – E is 80 – 120 nm but the aggregation of particle was reduced when the concentration of sucrose is lower. These results were simultaneously confirmed by the particle size analyzer (Figure 4.6). The peak A will show tail near the highest peak. And the tail of peak will slightly relieve in B, C, D, and E.

From the SEM and particle size analyzer data, it indicated that the concentration of sucrose had no influence on shape and size of silver nanoparticles.

Since, all of the conditions have the same amount of silver ion, reducing agent, stabilizing agent, and sodium hydroxide. However, at the situation of less concentration of sucrose, the particle is easy to separate from each other.

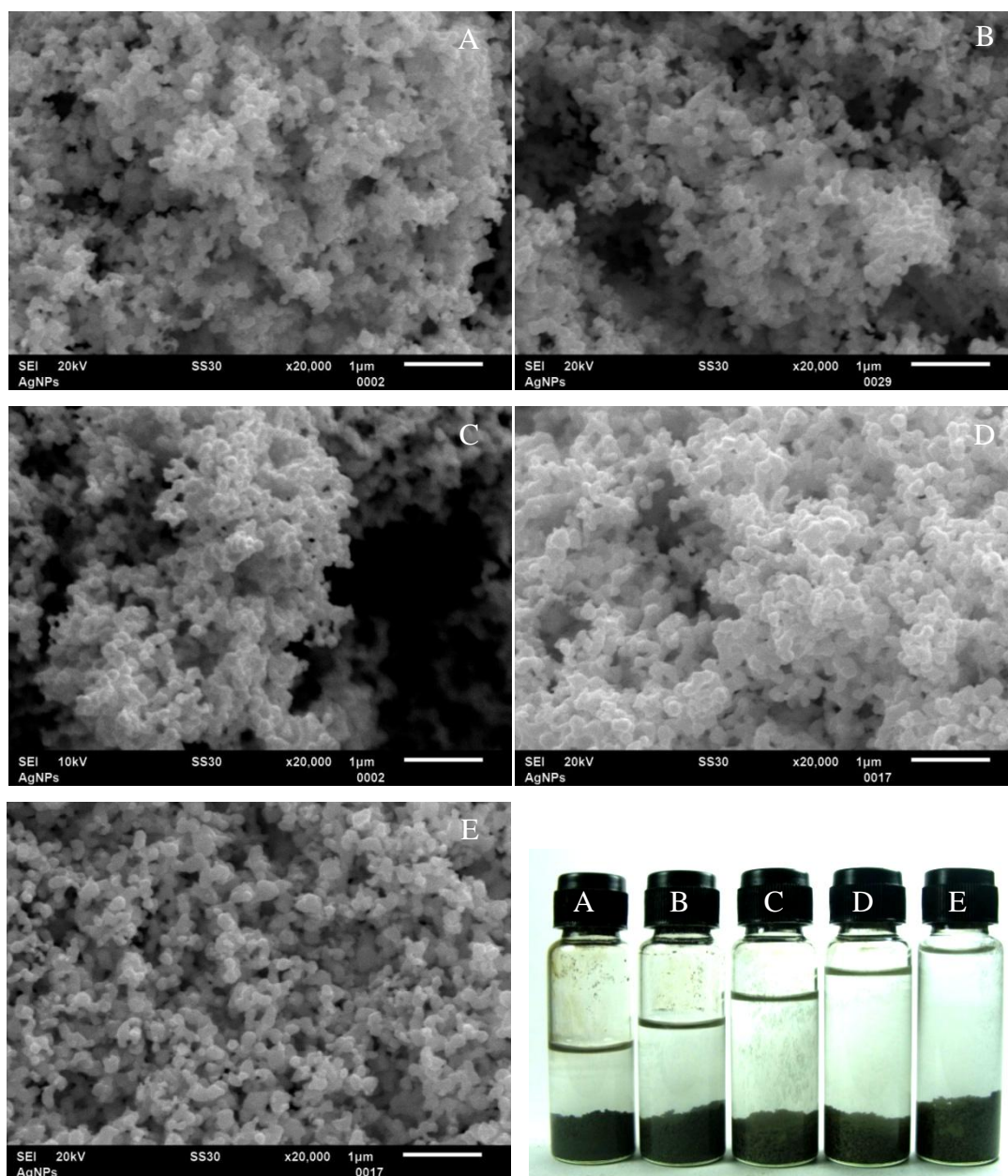


Figure 4.5 SEM micrographs of silver nanoparticles. A - E, containing 5 mL of 100,000 ppm silver ion, 2.5 mL of 3 M sodium hydroxide, and sucrose 50 % ($W_{\text{sucrose}} / W_{\text{Ag}}$) difference volume varied as follows: 2.50 (A), 5.00 (B), 7.50 (C), 10.00 (D), and 12.50 (E) mL.

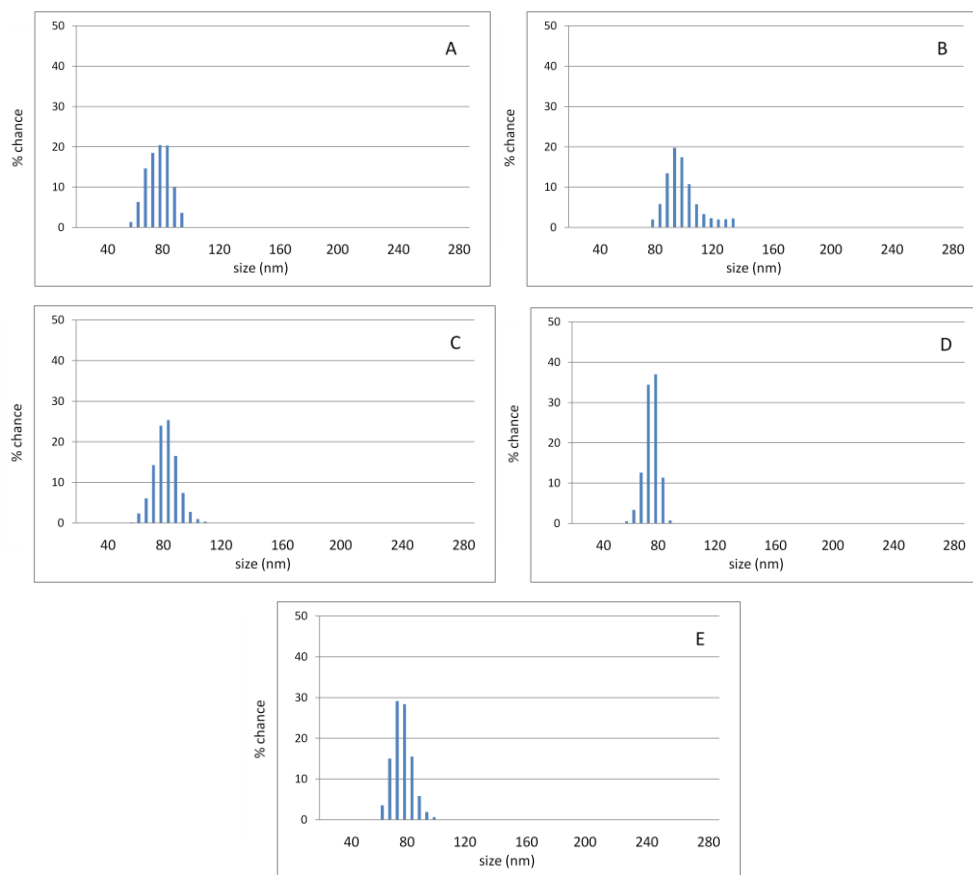


Figure 4.6 The relationship between size of silver nanoparticles and observed opportunities. A – E was containing the same of silver ion, 2.5 mL of 3 M sodium hydroxide, and sucrose 50 % ($W_{\text{sucrose}} / W_{\text{Ag}}$) with difference volume varied as follows: 2.50 (A), 5.00 (B), 7.50 (C), 10.00 (D), and 12.50 (E) mL.

4.3 The amount of sodium hydroxide affects silver nanoparticles

According to section 3.3.3, the amount of sodium hydroxide was adjusted as follows: 0.003 (A), 0.006 (B), 0.009 (C), 0.012 (D), and 0.015 (E) mole. After that 2.5 mL of each concentration of NaOH was injected to the mixed solution 5 mL of 100,000 ppm silver nitrate and 5 mL of 50,000 ppm sucrose which incubated for 1 hour. While, sodium hydroxide was adding to the mixed solution, the color of solution was rapidly changed from clear to brown and brown to black and for some conditions the color is continuous changing to grey and white. The brown is from silver oxide [44-45] and black is from silver atom [44-45] and grey is silver atom aggregated form. However, all of the conditions, the particle will be separated from the solution. After the reaction complete, the particle were collected, purified and characterized by mean of scanning electron microscope (Figure 4.7) as well as particle size analyzer (Figure 4.8) for observing the shape and size of the silver nanoparticles.

According to the SEM micrographs as shown in Figure 4.3.1, the (A – E) obtained silver nanoparticles had spherical shape with difference average diameter size. As the amount of sodium hydroxide increased, the average diameter sizes are larger from 15 – 20 nm (A), 40 – 60 nm (B), 80 – 120 nm (C), 200 – 250 nm (D), and 250 – 300 nm (E). These results were simultaneously confirmed by particle size analyzer (Figure 4.8).

From the literature reviews, the two main functions of sodium hydroxide are creating reducing species from alkaline degradation of monosaccharide and are stabilizing silver nanoparticles that formed electrostatic by forming double Debye layer [7] on the silver nanoparticles surface. The addition of alkaline was favored for higher reducing ability. The higher reducing potential will generate the silver atom rapidly, that makes a small particle. However, sodium hydroxide can destroy a chain of monosaccharide that making the shorter chain and the stabilized ability will decrease (Figure 4.9). Furthermore, sodium hydroxide is the source of ionic strength in the solution; so adding more sodium hydroxide, the ionic strength will increase. The increase of ionic strength can reduce double Debye layer because of ion repulsive

effect (Figure 4.10). The silver atom or silver nanoparticles will get closer and getting aggregated later which became the larger nanoparticles.

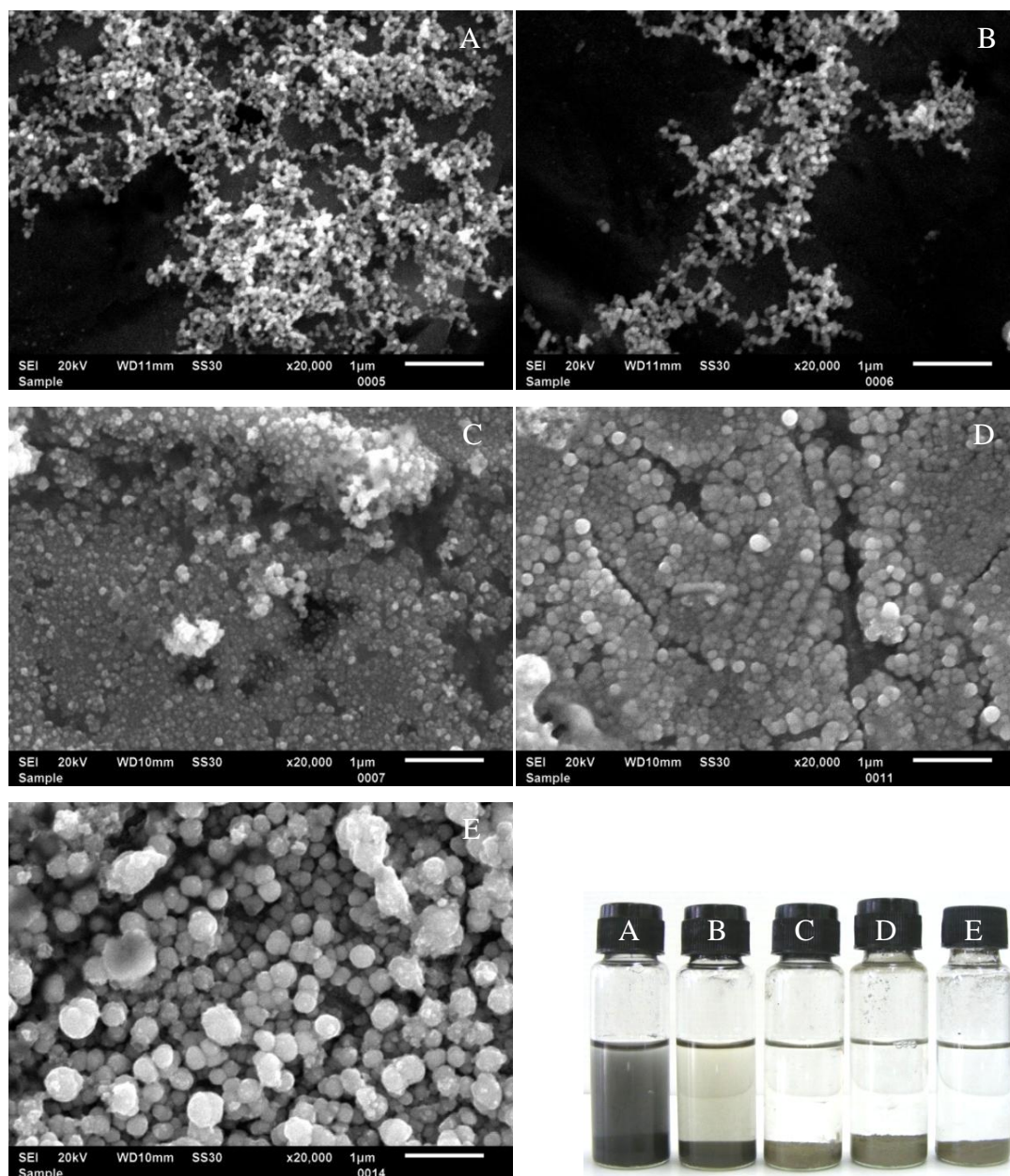


Figure 4.7 SEM micrographs of silver nanoparticles from green synthesis. A – E, each contains 5 mL of 100,000 ppm silver nitrate and 5 mL of 50,000 ppm sucrose but the difference amount of mole of 5 mL sodium hydroxide was varied as follows: 0.003(A), 0.045(B), 0.060(C), 0.075(D), and 0.090(E) mol.

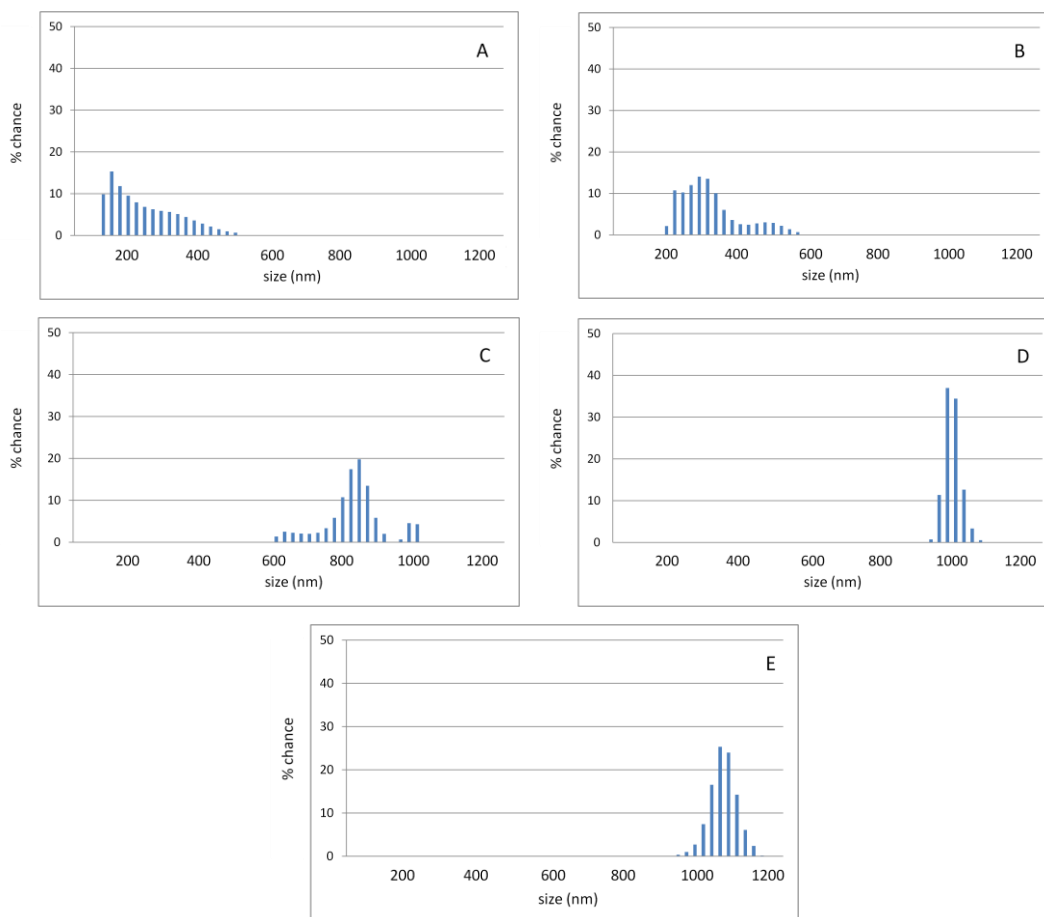


Figure 4.8 The relation shift between particles size and observed opportunities. A – E referred to the difference of mole of sodium hydroxide, which varied as follows: 0.003(A), 0.045(B), 0.060(C), 0.075(D), and 0.090(E) mole. The data was correlated to the information of SEM.

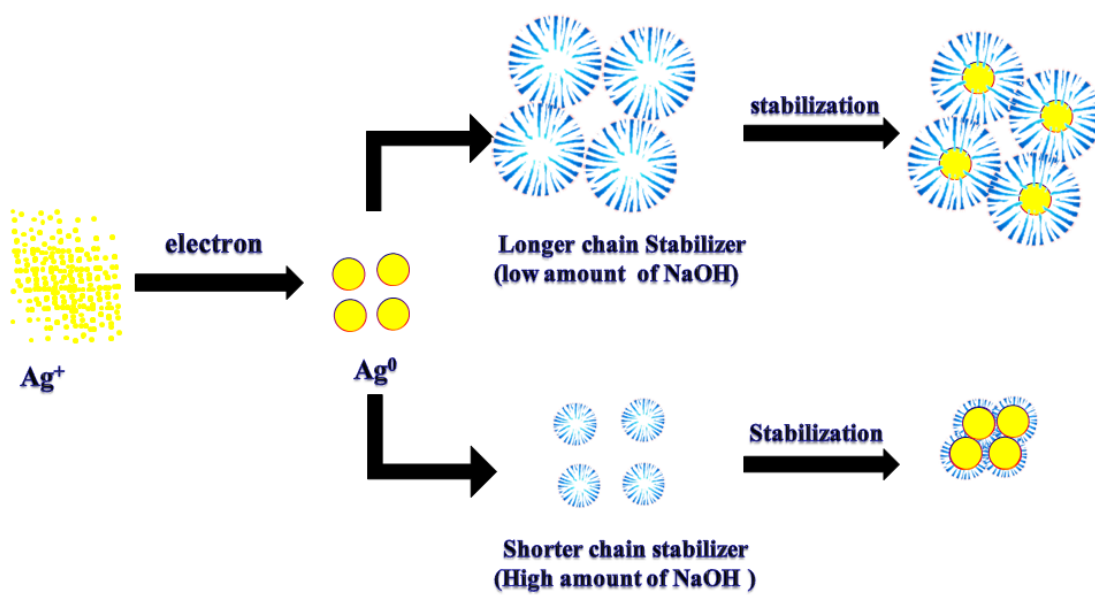


Figure 4.9 The proposed mechanism of the effect of sodium hydroxide on silver nanoparticles structure phenomena

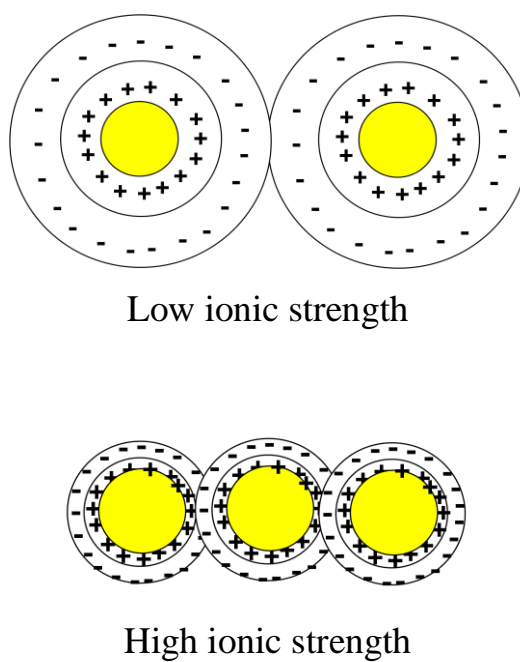


Figure 4.10 The Debye double layer that stabilizes silver nanoparticles depends on ionic strength.

4.4 The effect of concentration of sodium hydroxide on silver nanoparticles

According to section 3.3.4, all conditions were as follows: 5 mL of 100,000 ppm silver nitrate, 5 mL of 50,000 ppm sucrose and 0.09 mole of sodium hydroxide which was varied as follows: 2.50 (A), 5.00 (B), 7.50 (C), 10.00 (D), and 12.50 (E) mL. While, sodium hydroxide was adding to the mixed solution the color of solution was rapidly changed from clear to brown and brown to black and for some conditions the color is continuous changing to grey and white. The brown is from silver oxide [44-45] and black is from silver atom [44-45] and grey is silver atom aggregated form. However, all of the conditions, the particle will be separated from the solution. After, the reaction complete, the particles were collected, cleaned, and then characterized the particles by mean of scanning electron microscope (Figure 4.11.) as well as particle size analyzer (Figure 4.12) for observing the size and structure silver nanoparticles.

According to the SEM micrographs as shown in Figure 4.11, (A – E); the obtained silver nanoparticles had uniform spherical shape and average diameter size. The data from scanning electron microscope is similar to particles size analyzer (Figure 4.12). The average sizes of A - E are around 50 - 150 nm. However, the observation of the particle aggregation rarely occurred (tail near the highest peak) when concentration of sodium hydroxide increased because at high concentration, the particle is getting closer than that of low concentration. So the probability of aggregation of particle will increase too.

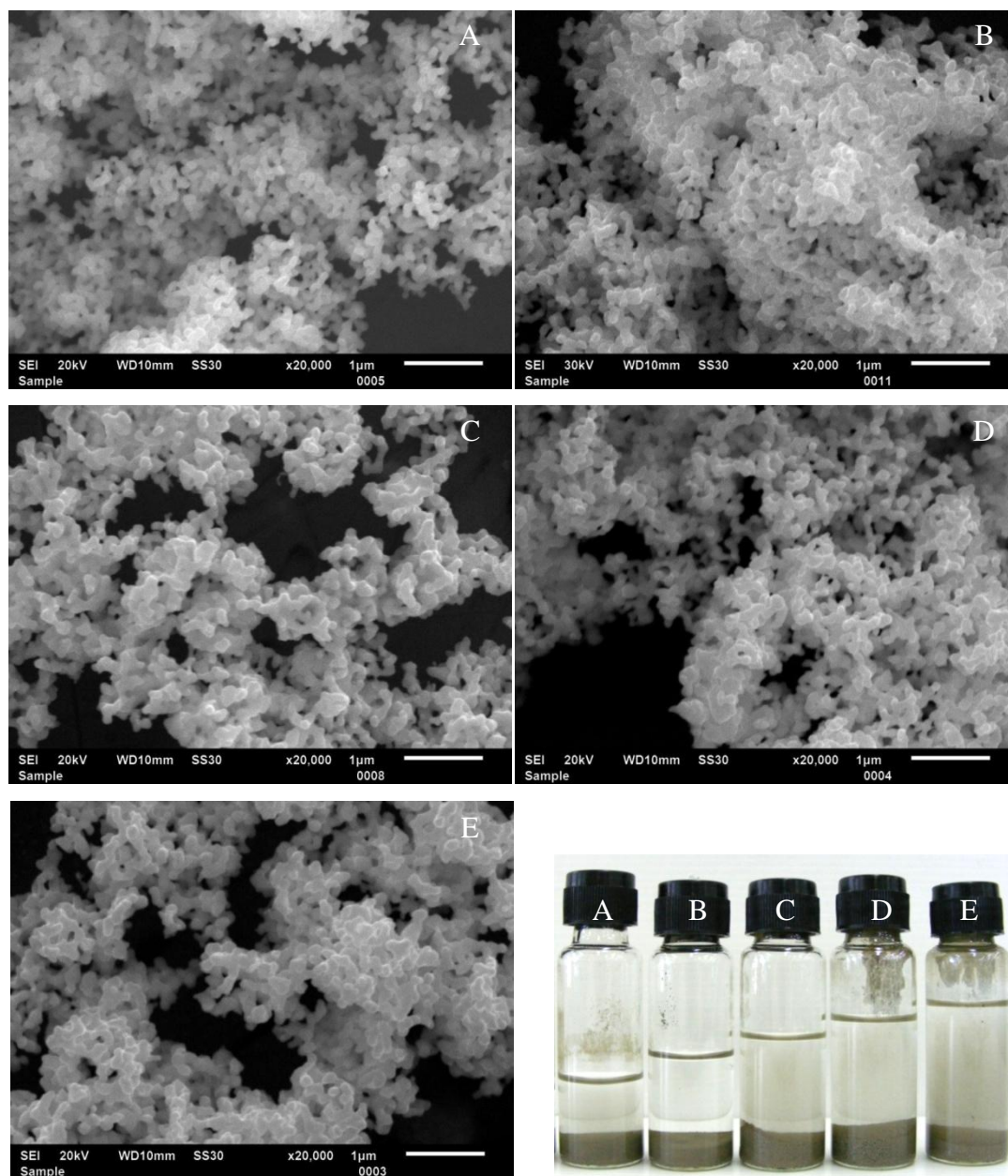


Figure 4.11 SEM micrographs of silver nanoparticles, A - E was containing with the same of silver ion and sucrose and 0.090 mole of sodium hydroxide with different volumes which varied as follows: 2.50 (A), 5.00 (B), 7.50 (C), 10.00 (D), and 12.50 (E) mL.

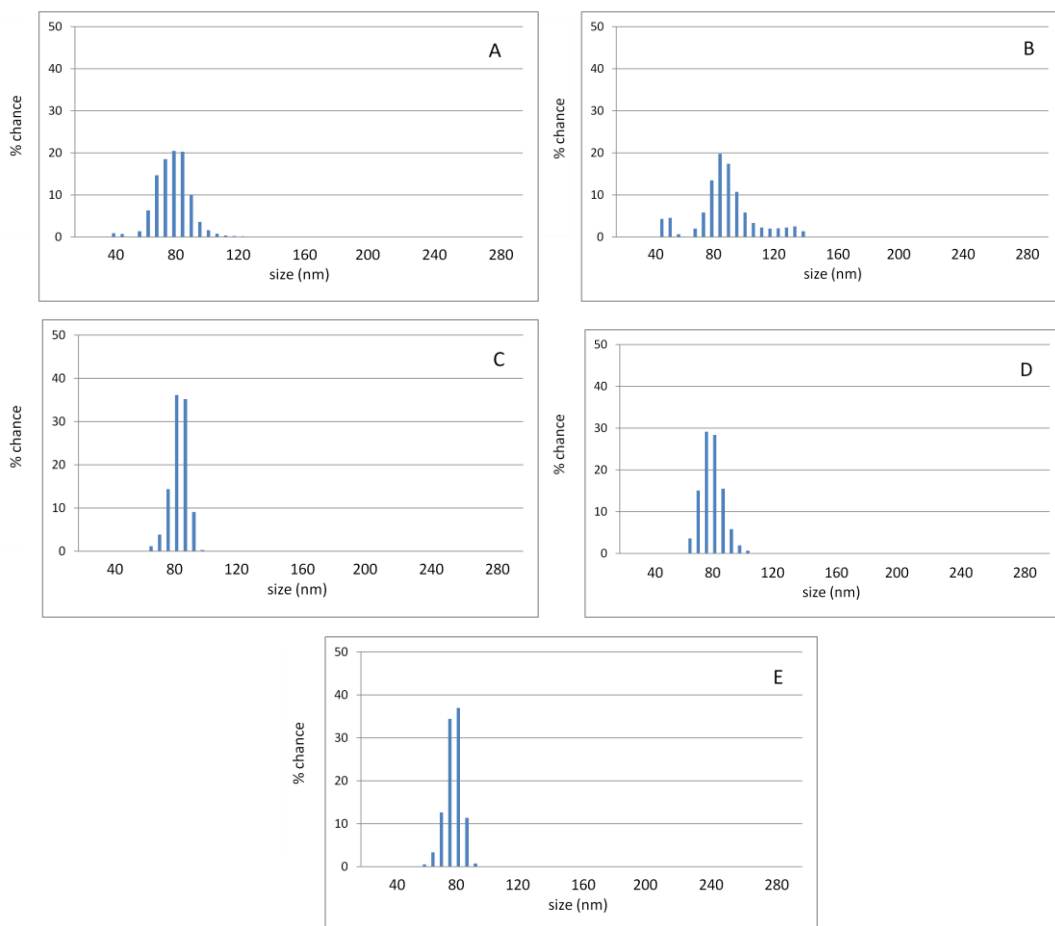


Figure 4.12 The relationship between size of silver nanoparticles and the observed opportunities. The A – E was containing the same of silver ion, sucrose, and sodium hydroxide 0.090 mole with different volumes was varied as follows: 2.50(A), 5.00(B), 7.50(C), 10.00(D), and 12.50(E) mL.

4.5 The effect of the amount of silver nitrate on silver nanoparticles

According to section 3.3.5, the amount for each of 5 mL of silver nitrate was adjusted from 100,000 (A), 200,000 (B), 300,000 (C), 400,000 (D), and 500,000 (E) ppm, which mixed with 5 mL of 50,000 ppm sucrose and 2.5 mL of 3 M sodium hydroxide. While, sodium hydroxide was injected in to the mixed solution of silver nitrate and sucrose, the color of solution was rapidly changed from clear to brown and brown to black. The brown is from silver oxide [44-45] and black is from silver atom [44-45]. However, all of the conditions, the particle will be separated from the solution. After the reaction complete. The particles were collected, cleaned and characterized with scanning electron microscope (Figure 4.13) as well as particle size analyzer (Figure 4.14) for observing shape and size of silver nanoparticles.

From SEM micrographs (Figure 4.13.); the image showed silver nanoparticles of spherical shape and two average diameter sizes in all conditions, except in A and E; the average diameter size of A is 10 - 20 nm and, of B are 40 – 60 nm and 150 – 200 nm, of C are 40 – 60 nm and 300 – 400 nm, of D are 40 – 60 nm and 400 – 700 nm, and of E is 400 – 1,000 nm. The average diameter sizes of particles agreed with those results from particle size analyzer (Figure 4.14).

In Figure 4.15, all systems have the same reducing potential all of the time. Theoretically, if the system has more amount of silver ion, the nucleation of silver atom are the same at all time. That is because of the residual silver ion in the high concentration of silver ion condition. The silver ions are the main of all factors that affect structural phenomena of silver nanoparticles. Since the silver ion has electron less than silver nanoparticles; silver ion will deposit on silver nanoparticles and is reduced to silver atom later (Figure 4.15). This phenomenon is leading to cause the aggregations of silver nanoparticles and finally become microparticles.

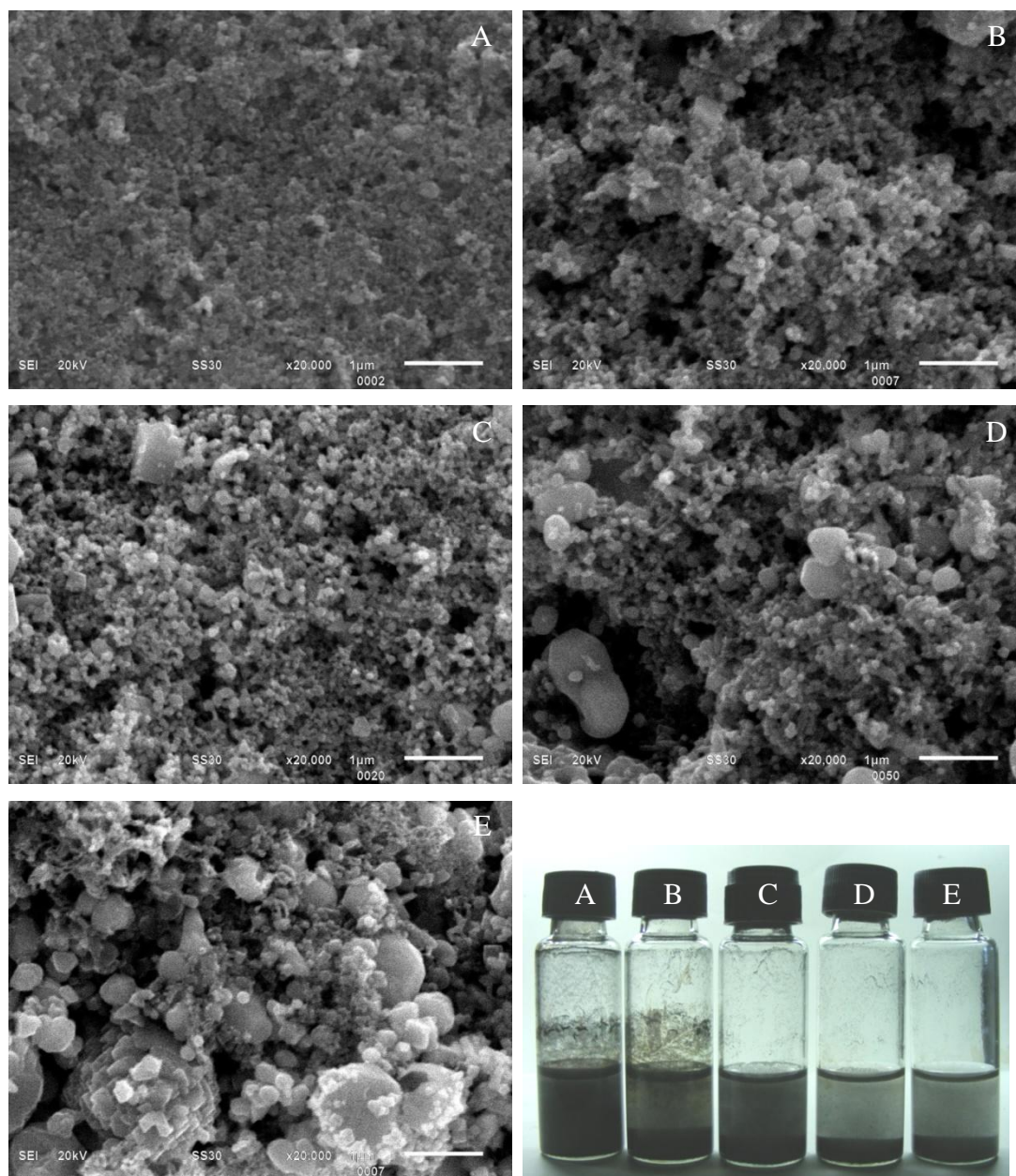


Figure 4.13. SEM micrographs of silver nanoparticles. A – E was containing with the same of sucrose, sodium hydroxide and 2.5 mL of silver nitrate was varied as follows: 100,000(A), 200,000(B), 300,000(C), 400,000(D), and 500,000(E).

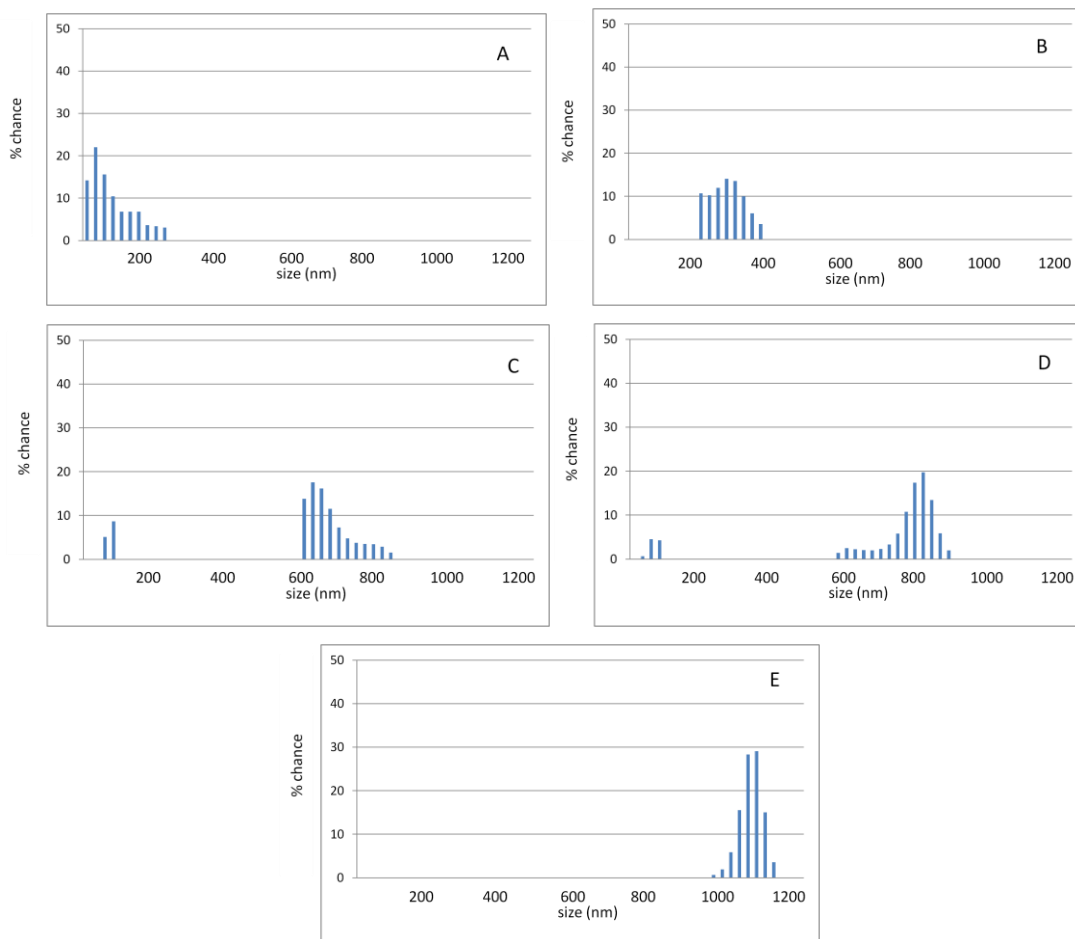


Figure 4.14. The relationship between size of silver nanoparticles and observed opportunities. A – E was obtained with the same sucrose and sodium hydroxide with 2.5 mL of silver ion was varied as follows: 100,000 (A), 200,000 (B), 300,000 (C), 400,000 (D), and 500,000 (E).

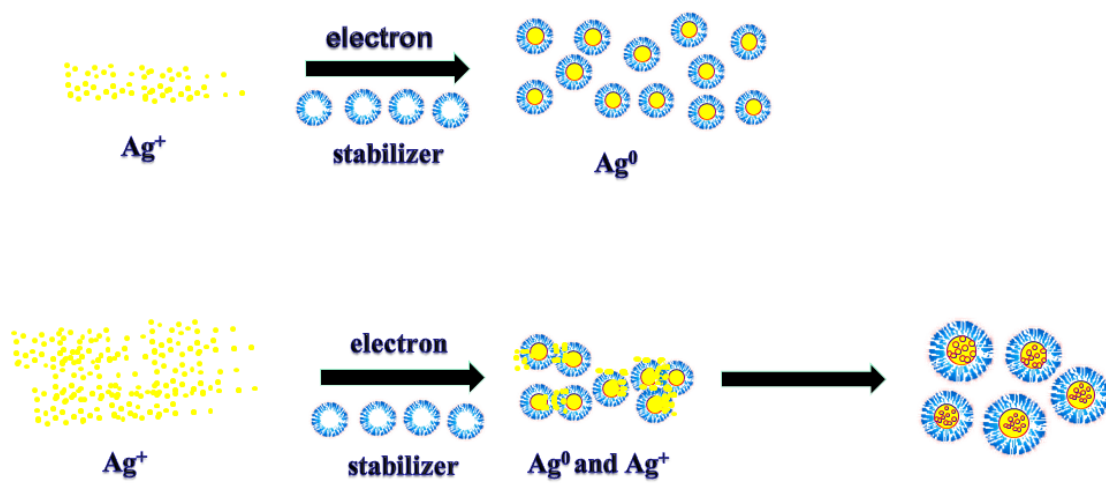


Figure 4.15. The proposed mechanism of the silver ion residue effect

CHAPTER V

CONCLUSIONS

In conclusion, silver nanopowders were successfully synthesized via green chemical reduction of silver nitrate by sucrose. Sucrose performed two functions that are reducing agent as well as stabilizing agent. Our synthesized silver nanopowders showed the same quality as that of the conventional method using sodium borohydride because silver nanopowders from this synthesis could be selectively controlled in the range of 10 nm to 1 μm and had uniform spherical shape.

In this research, the amount and concentration of silver nitrate, sucrose, and sodium hydroxide were adjusted to investigate the effect on size and shape of silver nanopowders. From the experiments, it is concluded that the amount of the chemicals (silver nitrate, sucrose, and sodium hydroxide) played stronger effects on particles shape and size distribution than their concentrations while the concentrations of chemicals have the influence on the degree of particles aggregations.

For the condition with different amounts of sucrose, the average diameter size of spherical silver nanopowders can be controlled in the range of 50 to 200 nm depending on the amount of sucrose. If the system contains more amount of sucrose, the average diameter size decreases.

For the system with different concentrations of sucrose, the average diameter size of spherical silver nanopowders are in the ranges of 80 to 120 nm. In the system with high concentration of sucrose, the degree of aggregations increases.

For the condition with different amounts of sodium hydroxide, the average diameter size of spherical silver nanopowders can be controlled in the range of 15 to 300 nm depending on the amount of sodium hydroxide. If the system contains more sodium hydroxide, the average diameter size will increase.

For the system with different concentrations of sodium hydroxide, the average diameter size of spherical silver nanopowders are in ranges of 50 to 150 nm; but in the system with high concentration of sodium hydroxide, the degree of aggregations will decrease.

For the condition of different amounts of silver nitrate, the average diameter size of spherical silver nanopowders can be controlled in the range of 40 to 1000 nm depending on the amount of silver nitrate. If the system contains more silver nitrate, the average diameter size will increase.

Lastly, we summarized all of our research results as tabulated in Table 1 and Table 2 as follows:

Table 5.1 The effect of the amount of chemicals on silver nanopowders

chemicals	amount of chemical	the average diameter (nm)
sucrose	high	large
	low	small
sodium hydroxide	high	small
	low	large
silver nitrate	high	small
	low	large

Table 5.2 The effect of the concentration of chemicals on silver nanopowders

chemicals	concentration of chemical	degree of particles aggregations
sucrose	high	increase
	low	decrease
sodium hydroxide	high	increase
	low	decrease

In this research, we successfully developed the novel method for synthesizing silver nanopowders via green nanotechnology by using sucrose, which is one of the agricultural products of Thailand as the reducing agent as well as the stabilizing agent. Furthermore, we can increase the effective reducing power of sucrose by acid hydrolysis and alkaline degradation. Lastly, the diameter of spherical silver nanopowders can be selectively controlled in the range of 15 nm to 1 μ m and their sizes are uniformed.

All in all, this objective of the research is fully fulfillment.

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