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GOLD NANOPOWDERS FOR JEWELRY AND DECORATIVE APPLICATIONS

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for the Degree of Master of Science Program in Chemistry

Department of Chemistry

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ผงอนุภาคระดับนาโนเมตรของทองคำสามารถผลิตได้สำเร็จด้วยกระบวนการที่เป็นมิตรกับสิ่งแวดล้อม โดยสารละลายทองคำที่ใช้มีความเข้มข้นสูง (10,000 ส่วนในล้านส่วน) ถูกรีดิวซ์ด้วยน้ำตาลทรายและแป้งในสถานะที่เป็นต่าง ซึ่งตัวรีดิวซ์จะถูกสร้างขึ้นจากปฏิกิริยาการสลายตัวของน้ำตาลและแป้งในต่าง อนุภาคระดับนาโนเมตรของทองคำที่สังเคราะห์ได้นั้นมีขนาดอยู่ในช่วงระดับนาโนเมตรถึงไมโครเมตร (150 – 4,000 นาโนเมตร) ซึ่งสามารถวิเคราะห์ได้จากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด และความสมบูรณ์ของปฏิกิริยาสามารถติดตามได้จากเครื่องยูวี/วิซิเบิลสเปกโตสโคปี่ ขนาดของอนุภาคนั้นสามารถควบคุมได้ด้วยการเปลี่ยนความเข้มข้นของไอออนของทองคำ ความเข้มข้นของน้ำตาลทราย และความเข้มข้นของต่าง การใช้น้ำตาลทราย และแป้งซึ่งเป็นผลผลิตจากธรรมชาตินั้นมีประโยชน์มากมาย เช่น เพิ่มมูลค่าให้กับผลผลิตทางการเกษตร ลดต้นทุนในการผลิตผงอนุภาคระดับนาโนเมตรของทองคำ ลดของเสียในปฏิกิริยารีดักชันและเป็นปฏิกิริยาที่สามารถควบคุมได้ นวัตกรรมการผลิตอนุภาคระดับนาโนเมตรของทองคำนี้สามารถผลิตได้ปริมาณมากและพร้อมถ่ายทอดสู่ภาคอุตสาหกรรม

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Gold nanopowders were successfully prepared via a novel green chemistry route. The solution of high concentration of Au³⁺ ion (10,000 ppm) was reduced by sucrose or starch solution in alkaline condition; reducing species were occurred *via* alkaline degradation of sucrose or starch. The synthesized gold nanopowders had particles size in the range of nanometer to sub-micrometer (150 – 4,000 nm) as indicated by scanning electron microscope and the complete reduction was investigated by UV-visible spectroscopy. The particle size could be selectively controlled by adjusting concentration of gold ion, concentration of sucrose, and concentration of alkaline. The use of environmentally benign substance like sucrose and starch offer number of benefits such as low production cost, toxic waste reduction, and controllable reaction. This novel route can be easily scaled-up for large-scale production of gold nanopowders.

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LIST OF ABBREVIATIONS

g/cm^3	: gram per cubic centimeter
nm	: nanometer
SPR	: surface plasmon resonance
SEM	: scanning electron microscope
w/v	: weight per volume
ppm	: part per million
eV	: electron volt

LIST OF SYMBOLS

Au	: gold
HNO ₃	: nitric acid
HCl	: hydrochloric acid
NaBH ₄	: sodium borohydride
HAuCl ₄	: tetrachloroauric acid
NaOH	: sodium hydroxide
NO ₂	: nitrogen dioxide
e ⁻	: electron
E ⁰	: standard electrode potential
RCHO	: aldehyde species
°C	: degree Celsius
C _s	: concentration of sucrose solution
C _g	: concentration of gold ions

CHAPTER I

INTRODUCTION

Gems and jewelry industry are important industries involving and inter-connecting with various industries such as tourist industry, health and recreation industry, local handicraft and etc. Gold is the main precious metal employed by jewelry and local handicraft industry. Having a novel precious-metal-based raw materials would enabled competitive advantages for Thai jewelry industry. However, in jewelry manufacturing must consume high temperature for gold metal melting, so high energy was consumed for jewelry industry. Gold nanoparticles or gold nanopowders have a much lower melting temperature compared to that of bulk gold metal. The small size has extremely high surface area also benefit the development of novel gold alloy with easy and simple fabrication technique. The major aim of this project is to develop of novel environmental friendly technique of gold nanopowders for the application in jewelry industry. The development processes also concern the cost of making the nanoparticles.

In recent years, metal nanoparticles have been actively investigated because their exclusive properties related with the quantum size effect and their applications in many areas such as optics, optoelectronics, catalysis, and chemical/biochemical sensings. Gold nanoparticles are one of the most useful nanoparticles in many applications. Although gold nanoparticles are successfully synthesized by chemical and physical methods, these processes are usually expensive and using toxic chemicals. In addition, synthesis of gold nanoparticles used chemical method such as organic solvents and toxic reducing agents. Conventionally synthetic method based on the reduction of gold ions to gold atoms with sodium borohydride [1-2] and then surface of the produced particles are modified by capping agents and organic solvents raised environmental concerns, because of the toxic compound using in process. Nowadays, many researches are attractive on eco-friendly and non-toxic in the

production of gold nanoparticles. Several synthetic approaches using biological entities like bacteria [3], yeast [4], fungi [5], and plants are nontoxic and environmental friendly. Huang, H., and Yang X. [6] proposed the green method for synthesis of gold and silver nanoparticles by using polysaccharide as reducing agent and stabilizer. The positive charge of chitosan can stabilize gold nanoparticles and the negative charge of heparin can stabilize silver nanoparticles. The morphology and size distribution of gold and silver were synthesized with varying both the metal salts and polysaccharide concentrations. Engelbrekt et al. [7] proposed the method for synthesis of gold nanoparticles by using glucose and starch as reducing agent and stabilizer, respectively. The concentration of starch, temperature and chemical nature of the buffers are key factors in the gold nanoparticles formation. This method has been extended to use of starch-rich such as potato, carrot and onion to synthesize gold nanoparticles. Song, J. Y. et al. [8] proposed the synthesis method of gold nanoparticles by using the plant leaf extracts as reducing agents. *Magnolia kobus* and *Diopyros kaki* were used for leaf extracts. Gold nanoparticles were synthesized at 95°C only a few minutes. The particles size can control with temperatures and leaf concentration. At lower temperature and leaf broth concentration, gold nanoparticles showed the combinations of plate (triangles, pentagons, and hexagons) and spherical structures (size, 5–300 nm), while smaller spherical shapes were obtained at higher temperatures and leaf broth concentrations.

This study involves the synthesis of gold nanopowders by green chemistry. Thailand agricultural products in alkaline condition were used as green reducing agent and stabilizer. The concentration of alkaline, ratios of sucrose/ gold ions, stabilizer, incubation time between gold ion and stabilizer before the reduction, and the evolution formation of gold nanopowders were investigated. The complete of the reduction and time evolution were observed by UV-vis spectroscopy. Particles size, shape, morphology were investigated by mean of scanning electron microscope.

1.1 The objectives of research

The objectives of this research are to develop green synthesis methods which can control particles size and size distribution of gold nanopowders. The synthesis route should be environmental friendly.

1.2 Scopes of research

1. Developing a novel green method for synthesizing gold nanopowders.
2. Investigating the effects of concentration of gold ion, agricultural reducing agents, and concentration of stabilizer on the size of the synthesized gold nanopowders.
3. Characterization of size, size distribution and morphology of the synthesized gold nanopowders by mean of UV-visible spectroscopy and scanning electron microscopy

1.3 Benefit of this research

A novel process for preparation of gold nanopowders *via* green nanotechnology by using Thailand agricultural reducing agents was established. The raw materials cost of gold nanopowders are substantially low comparable to the commercial products which means that our gold nanopowders are highly competitiveness advantages in Thai industrial jewelries and their applications.

CHAPTER II

THEORETICAL BACKGROUND

2.1 Nanotechnology and nanoparticles

Nanotechnology [9-10] is the design, fabrication, characterization, production and application of structures, system and device, which its shape and size can be controlled at the nanoscale.

A nanoparticle (or nanopowder)—a small particle whose size, at least in one dimension must range from 1-100 nm, or the size must be so sufficiently small that its properties can differ from those of the bulk materials [11]. Moreover, the size, shape, and properties of nanoparticles can be reproducibly synthesized.

2.2 Gold

Gold is a transition metal with the symbol Au. The Latin word of gold is aurum, which means shining dawn. It is a bright shiny yellow metal. Density of gold is 19.32 g/cm^3 , good resistance to corrosion and oxidation. The melting point and boiling point of gold are $1064 \text{ }^\circ\text{C}$ and $2856 \text{ }^\circ\text{C}$, respectively [12]. Gold is positioned on 79th in the Periodic Table. Its electronic configuration is $[\text{Xe}] 4f^{14} 5d^{10} 6s^1$. Normally, gold is chemically inert. It is insoluble in ordinary solvent, however, it can dissolve in aqua regia (HNO_3+HCl).

2.3 Gold nanoparticles

Gold nanoparticles are of great interest because of their unique physical and chemical properties. Gold nanoparticles have been widely employed for many

potential applications such as electronics [13], sensor [14], surface-enhanced Raman scattering, and medicine [15].

Gold nanoparticles are popular synthesized because they have three major reasons. The first, they are stable under atmospheric condition. The second, they have interesting optical properties. And the last one, they were easy fabricated by many methods.

2.4 Size-dependent properties of nanomaterials

The changing of size to nanoscale shows a new phenomenon such as physical, chemical, and optical properties. The materials have new properties, which enable new potential applications.

2.4.1 Physical properties

The size and shape of metal nanoparticles were changed which influence in physical properties. The physical properties of metallic nanoparticles can be obvious different from those of bulk metal. For example, the crystal structures of metallic nanoparticles different from those of the bulk solid, the splitting of the continuum conduction band into discontinuous levels, the electromagnetic field enhancement on the surface, the magnetic properties change from diamagnetic into paramagnetic, and from ferromagnetic into super paramagnetic [16].

2.4.2 Chemical properties

The changing of particle structures affected the changing in electronic properties. The ionization potential of metallic bulk is generally lower than that of the nanoparticles. These properties have effects on chemical reactivity. Metal nanoparticles have very large surface area to volume ratio and the crystallographic

structures are differing from their bulk properties of metal. Actually, the crystallographic structure is related to a radical alteration in chemical reactivity. The catalysis, which the one of all application of nanomaterials, was increased the rate, selectivity and efficiency of chemical reaction [10].

2.4.3 Optical properties

The optical properties of nanoparticles depend on the particles size, shape and local environment. The metal nanoparticles show clearly changes in optical properties. Metal nanoparticles (especially gold, silver, and copper) show UV-visible absorption band but this property does not show in their bulk. Gold nanoparticles solution have a deep red color which different from bulk metal [10].

Gold nanoparticles are well known for their surface plasmon resonance (SPR) properties. The SPR is the collective oscillation of their conduction electrons in the optical excitation. The wavelength of light is larger than the size of metal nanoparticles, it will cause the resonance as shown in Figure 2.1. The light is resonated with the surface plasmon oscillation causing the free electrons in the metal to oscillate [17]. As the wave front to the light passes, the electron density in the particles is polarized to one surface and oscillates in resonance with the light frequency causing a standing oscillation. The SPR frequency of metal nanoparticles depends on their size, shape, aggregate morphology, and surface modification. For example, the SPR peak of thin film of gold is represented at about 480 nm, while the SPR peak of 13 nm spherical gold colloids showed at about 520 nm, when gold colloids as rod shapes, they represent two SPR resonance peaks. The combination of absorption and scattering intensity are called “Extinction”. Different SPR peaks are shown in Figure 2.2.

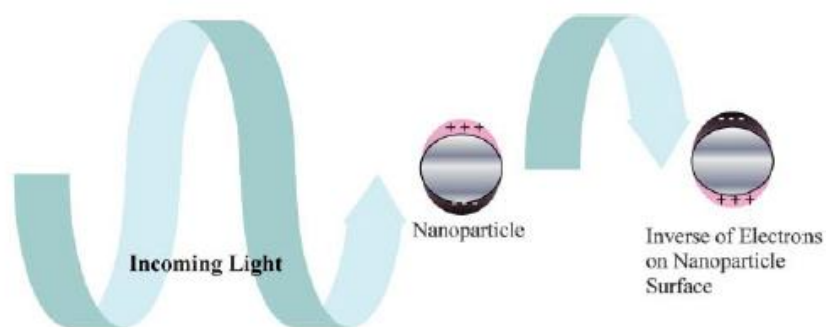


Figure 2.1 The surface plasmon resonance due to coherent interaction of the electrons in the conductive band with light [17].

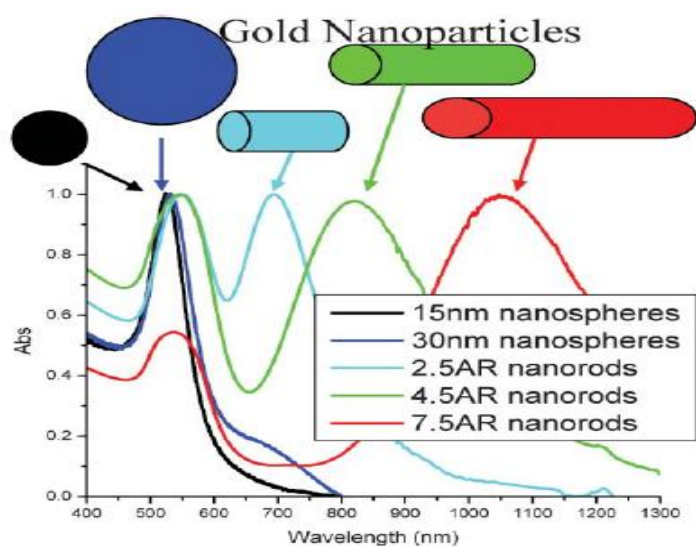


Figure 2.2 The extinction of different size and shapes of gold nanoparticles [17].

2.5 Fabrication of nanoparticles

Nanoparticles can be fabricated in numerous ways; however the fabrication techniques can be categorized into two main approaches. The first approach is “top down” in which nanoparticles are fabricated from large materials by mechanical techniques. The second approach is “bottom up” in which nanoparticles are fabricated by assembling atoms or molecules. The top down approach is largely defined as physical method, while the bottom up approach is chemical method. Normally, the bottom up approach is much effective on cost than the top down approach. The two approaches are represented in Figure 2.3.

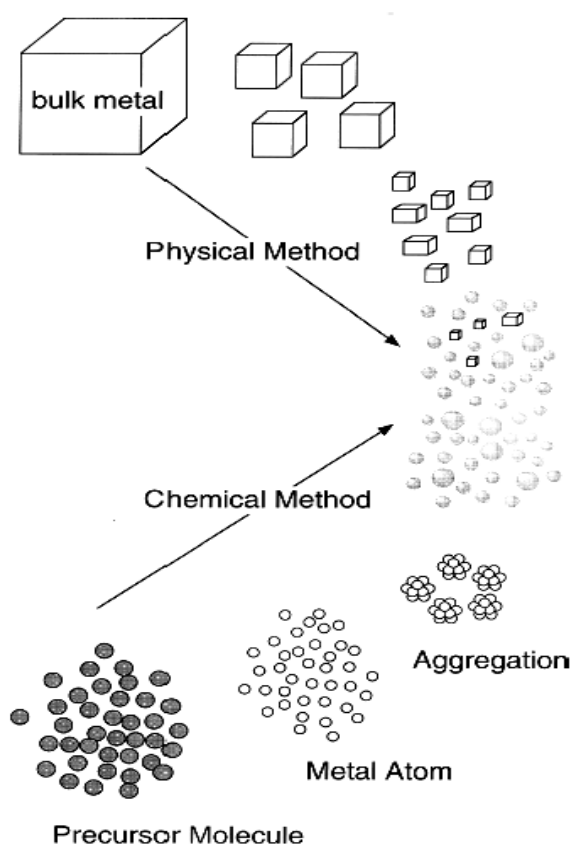
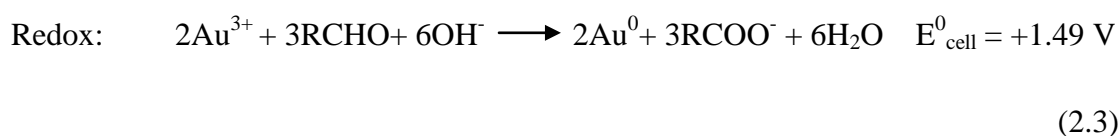


Figure 2.3 Two approaches for fabricating nanoparticles (or nanopowders): top down and bottom up [18].

2.5.1. Chemical reduction

Chemical reduction is one of the bottom up approaches, which widely used liquid phase method for synthesizing nanoparticles. This method normally requires three important chemicals: metal ions, reducing agent, and stabilizer. This method involves the reduction of metal salt by various reducing agents (e.g. borohydrides, citrate, and aldehyde) *via* the reduction and oxidation reaction. The standard electrode potential (E^0) of metal ions and reducing agents was determined. In general, metal ions must higher E^0 than reducing agent. In this work, gold ion was used as metal ions source and aldehyde species (RCHO) in alkaline conditions were used as reducing agent, both E^0 as follows [19]:



Moreover, the chemical reduction depends on multifactor process. It depends on the difference between the redox potentials of the metal salt and the reducing agent, concentration of its components, temperature, and the pH of a medium. The chemical interactions in the reduction metal ion system involve the transfer of electron from the reducing agent to metal ions. Metal ions are reduced and formed metal atoms, and then aggregated into metal nanoparticles [10].

Turkevich [20-21] established the first standard protocol for synthesizing metal colloid by chemical reduction method. He proposed a mechanism for the formation of nanoparticles *via* nucleation, growth and agglomeration mechanism.

2.5.2 Formation of nanoparticles

The formation of nanoclusters is interesting research. LaMer and co-workers [22-26] proposed the formation of nanoparticles known as the classic LaMer mechanism. LaMer mechanism is widely applied in various preparations of near-monodisperse particles in homogeneous solution. This mechanism was developed from the formation of sulfur sols.

In the case of nanoparticles were prepared by chemical reduction. Metal atom received electron from reducing agents, metal atoms were formed. So the concentration of metal atom continuously increased. Figure 2.4 shows the concentration of nucleating species vs. time. The concentration of metal atom, C , steadily increases. Once the concentration of metal atom reaches a point of supersaturation, metal atom aggregated into small cluster, this stage is nucleation. After that, the concentration of the metal atom continues to decrease while, below the critical level for nucleation, it is the ending of this stage. The growth stage will start. The remains of metal ions were consumed to growth at small cluster surface, that resulted in growing into nanoparticles. The particles size was controlled in nanometer by stabilizer.

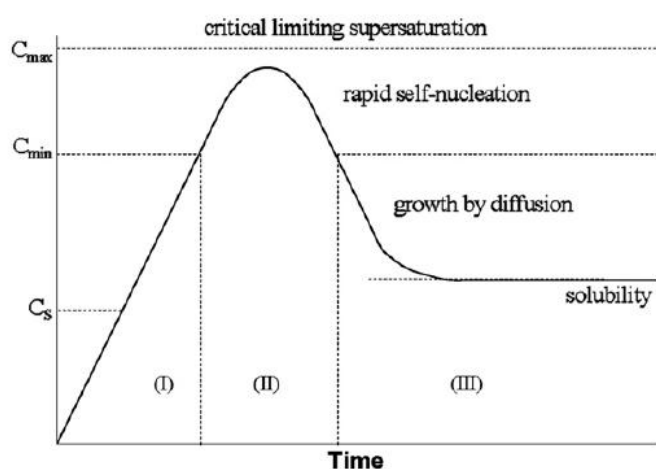


Figure 2.4 LaMer diagram elucidates the formation process of monodisperse particles. The regions I, II, and III represent the prenucleation, nucleation, and growth stages, respectively [26].

2.6 Green Chemistry

Green chemistry is the design of the chemical products and processes that reduce or eliminate the use and generation of hazardous substances [27]. Green chemistry can be applied to nanomaterial synthesis and nanomanufacturing processes in order to avoid toxic nanoparticles or by-products. The aim of green chemistry is to enhance the performance of novel nanomaterials as well as simultaneously minimize the adverse biological and environmental effects. The 12 Principles of green chemistry [28] are as follows:

1. Preventing the generation of waste

Preventing waste is better than treating or cleaning up waste.

2. Atom economy

The method of synthesis should be designed to maximize the integration of all materials used in the process into the final product.

3. Less hazardous chemical synthesis

The synthesis method should be designed to use and generate substances, which release little or no toxicity to human health and the environment.

4. Designing safer materials

Chemical products should be designed to preserve the efficiency of function while reduce toxicity.

5. Safer solvents and auxiliaries

The use of auxiliary substances (e.g., solvents, separate agents, etc.) should be avoided whenever possible.

6. Design for energy efficiency

The synthesis method should be recognized for their environmental and economic impacts. The energy used should be minimized. The synthesis should be conducted at ambient temperature and pressure.

7. Use of renewable feedstocks

A raw material or feedstocks should be renewable and economically executable.

8. Reduce the use of derivatives

The unnecessary derivative product should be avoided whenever possible.

9. Catalysis

Catalytic reagents are selectively product, less consumed energy and time and decrease separations due to increased selectivity.

10. Design for degradation

The product and raw material should be designed and determined at the end of their function. They should not remain in the environment and generate harmful degradation products.

11. Real-time analysis for pollution prevention

Analytical methodologies need to be developed to allow for real-time in process monitoring and prevent the formation of hazardous substances.

12. Inherently safer chemistry

The chemical reagents used in a chemical process, should be carefully selected so as to minimize the probability of chemical accident, including releases, explosions, and fires.

For classical synthesis of gold nanoparticles, citrate was used as reducing agent and stabilizer. This is an excellent example of an efficient, design green nanomaterial for synthesis. This reaction initiated with choosing raw materials, gold salt and trisodium citrate, with low toxicity and low hazard. The reaction does not generate by-products with significant toxicity [29].

2.7 Sucrose

Sucrose is a disaccharide. Its monomer consists of one glucose unit and one fructose unit joins by a direct glycosidic linkage between the first carbon atom of the glucose unit and the second carbon atom of the fructose unit. The molecular formula of sucrose is $C_{12}H_{22}O_{11}$. Sucrose is the nonreducing sugar because the glycosidic bond is a bond between the reducing ends of both glucose and fructose. The structural formula of sucrose is shown in Figure 2.5.

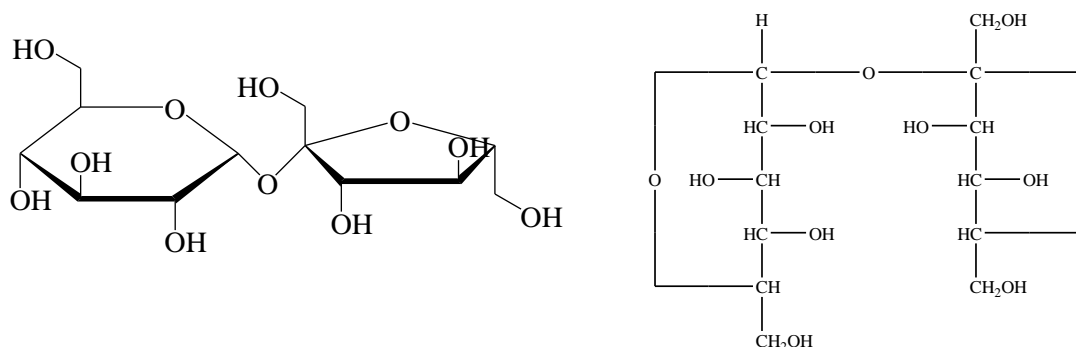


Figure 2.5 Structural formula of sucrose [30].

2.7.1 Alkaline degradation of sucrose

Sucrose is the nonreducing sugar but can generate reducing species *via* alkaline degradation reaction. The first step of the alkaline degradation of sucrose [30] is the cleavage of the glycosidic linkage. In alkaline solution, sucrose can be opened its ring turning into more stable form which represented in Figure 2.6. In glycosides, a *trans* relationship between the aglycon and 2-hydroxyl group of an aldose allows a much more facile alkaline degradation than the case for the *cis* analog. Accordingly, fructose degrades faster than glucose in sucrose molecule. Sucrose does not initially proceed *via* hydrolysis of the glycosidic linkage. Sucrose can degrade to D-glucose and D-fructose (as shown in Figure 2.6) in alkaline solution.

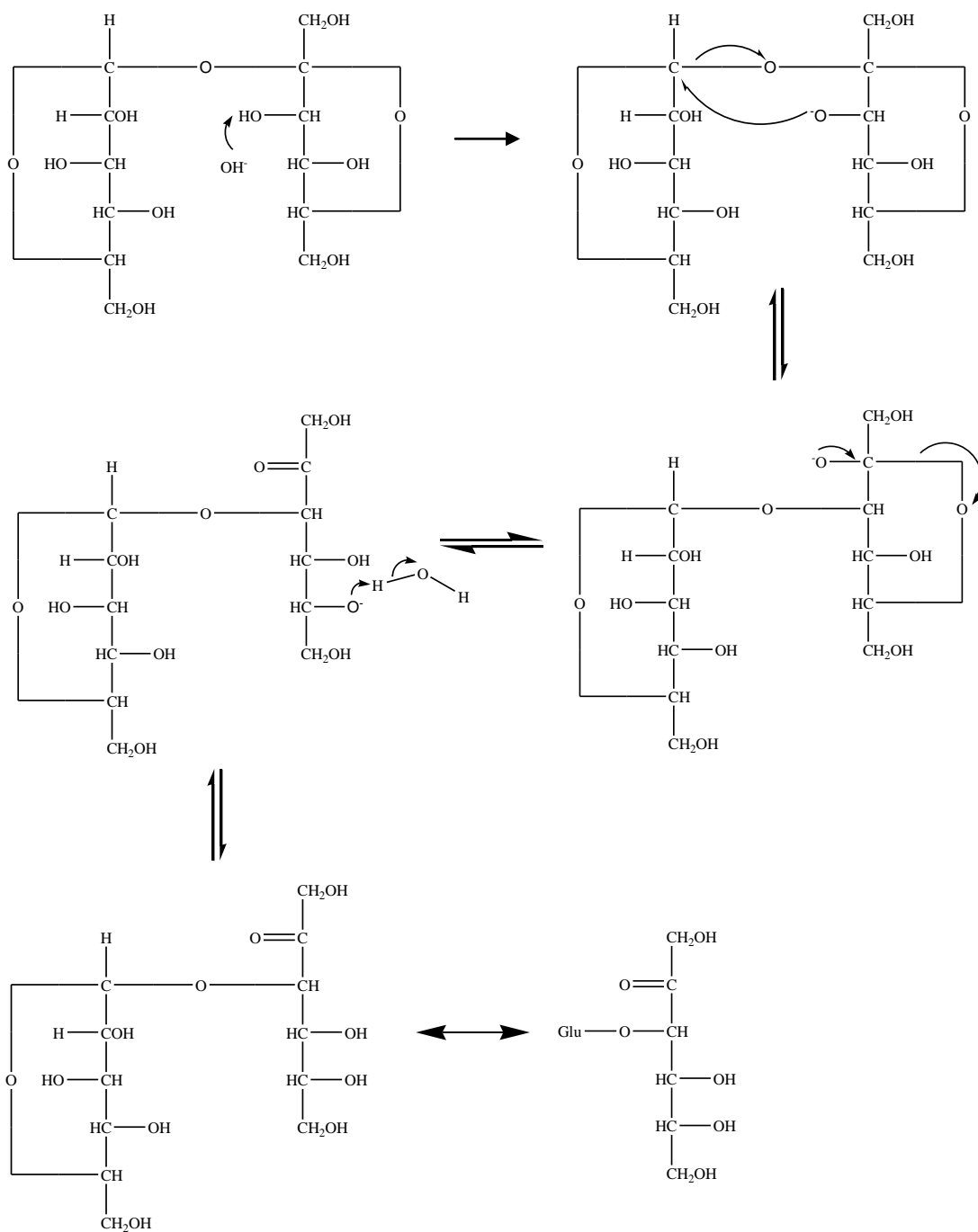


Figure 2.6 The open ring of sucrose was formed in alkaline solution [30].

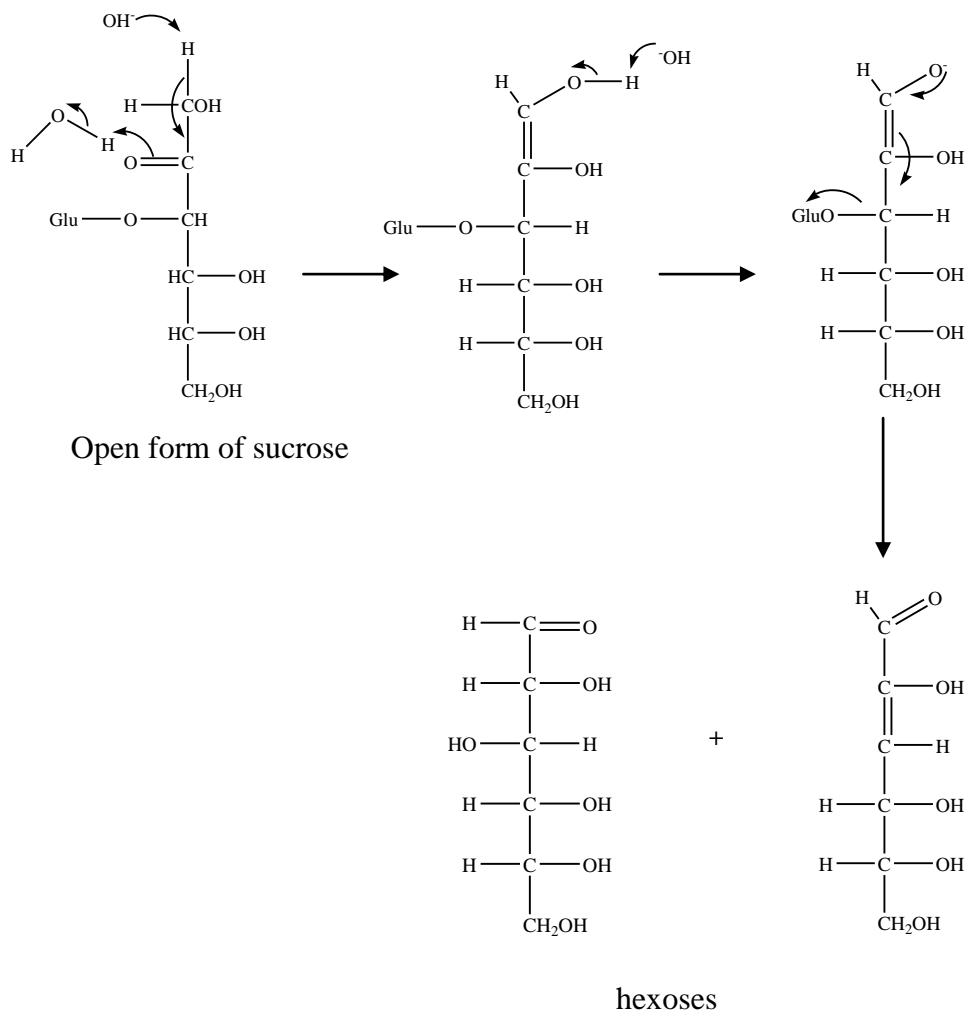


Figure 2.7 Sucrose in alkaline solution was degraded to monosaccharide [30].

After the alkaline degradation occurs, sucrose is cleaved into hexoses. Glucose and fructose is a hexose, which are reducing species.

2.7.2 Alkaline degradation of glucose and fructose

In alkaline solution, sugars undergo isomerization, internal oxidation-reduction reaction, and rearrangements of the carbon skeleton [31]. This transformation is the isomerization of glucose to fructose, which is commonly considered to proceed with the initial formation of an enediol.

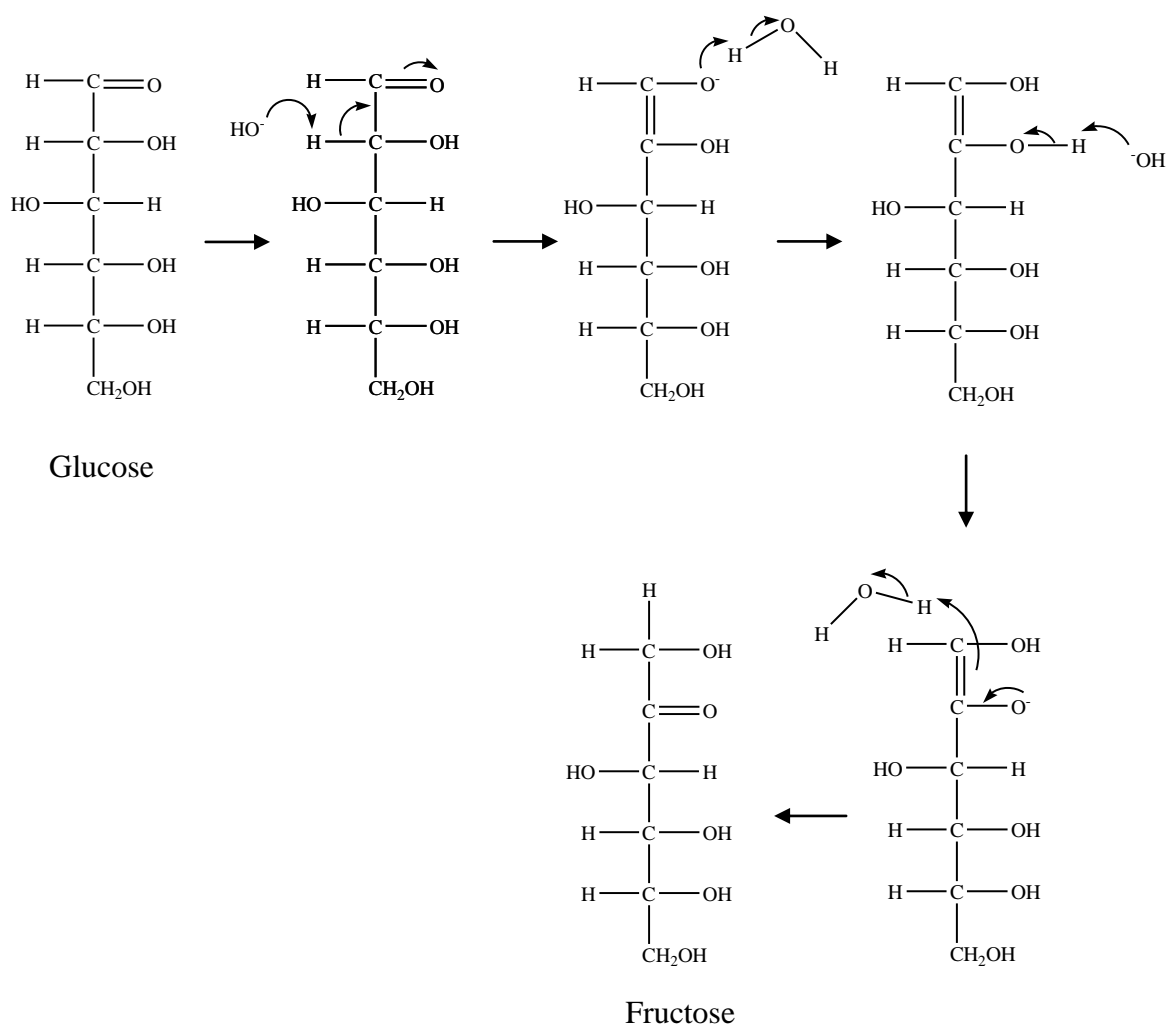


Figure 2.8 The transformation of glucose to fructose in alkaline solution

The alkaline degradation of monosaccharide [32] has been *via* initial thorough 1,2-, 2,3-, 3,4-enediol intermediates to give numerous products. Some of the intermediate products of the reaction are aldehydes that may undergo aldol condensation to give new products. The alkaline degradation reductions are similar and involved (Figure 2.9) the following reactions:

- reaction I : enediol formation
- reaction II : β -elimination of hydroxyl or glycosyloxy group from the enediol to form a deoxy diketo derivative
- reaction III : benzylic acid-type rearrangements of the deoxy-diketo derivative
- reaction IV : α -diketo cleavage to give potentially two pairs of products, each pair including an acid and an aldehyde
- reaction V : reverse aldolization of the enediol to give two reducing fragments
- reaction VI : aldol condensation of two aldehydes to give new reducing sugars.

The formation of low carbon atom in carboxylic and aldehydes is presented. Carboxylic and aldehydes are important products formed during the degradation of monosaccharide. Temperature, pH Value, and type of sugar determine the product of the reaction. Formaldehyde and acetaldehyde are found in all reaction mixture.

Formaldehyde is the smallest fragment of sugars. Its product from 1-enediol yields lower aldose. Formaldehyde is also suggested as a product of cleavage of C₁-C₂ bond of the acyclic adduct of hydroperoxide anion to ketoses [33]. Acetaldehyde could assume arising by retro-aldol cleavage of the intermediates is structure motives of 1-deoxy-2, 3-dihydroxy-4-oxo or 2-deoxy-3-hydroxy-1-oxo. However, both aldehydes are known to be products of some lower carbonyls. In alkaline solution (OH⁻), the aldehyde function group (RCHO) can be oxidised to carboxylic group (RCOO⁻) and generated two electrons, according to equation 2.4. So it can be used as a reducing agent.



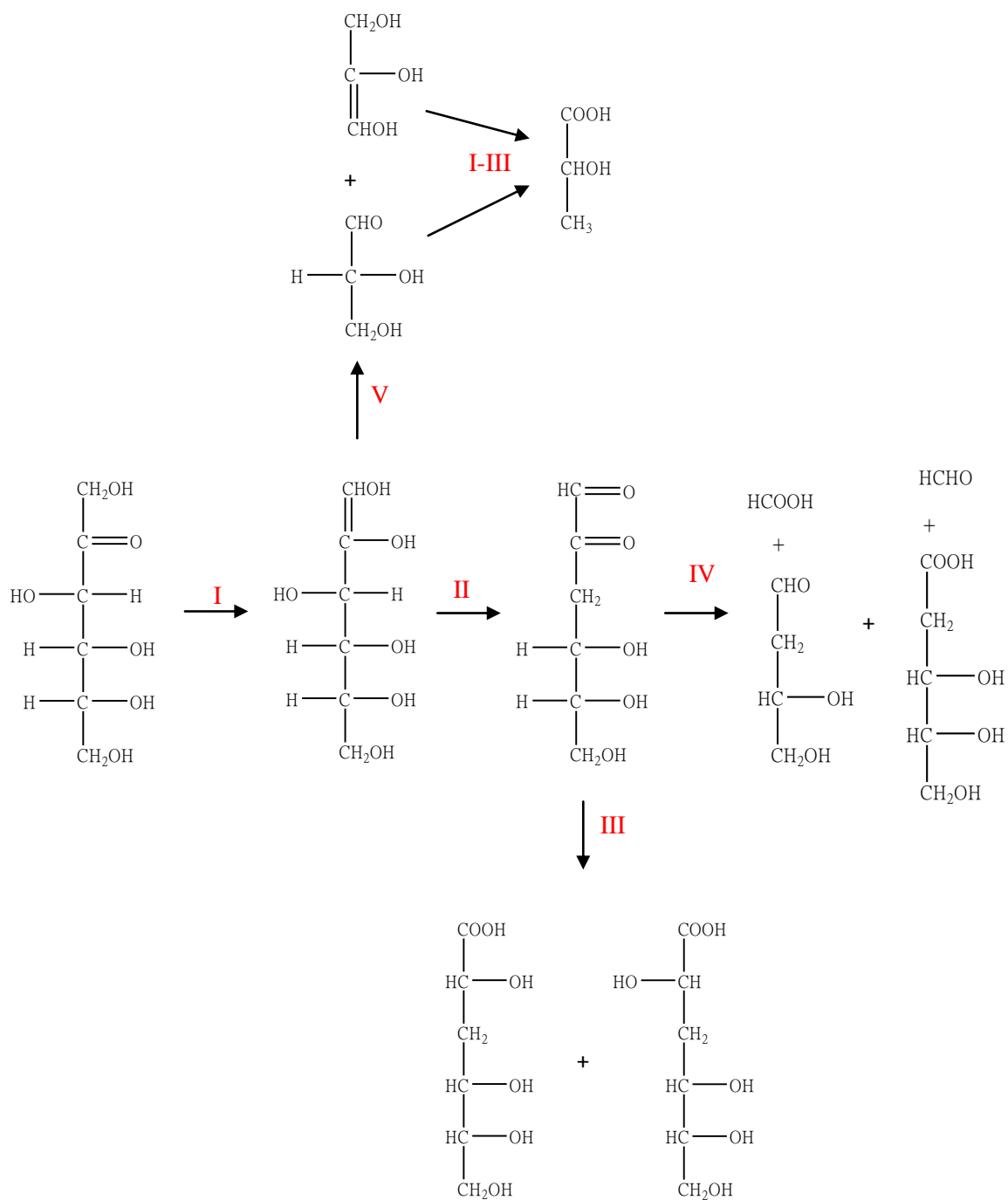


Figure 2.9 The alkaline degradation of fructose can generate aldehyde functional group having reduction capability [32].

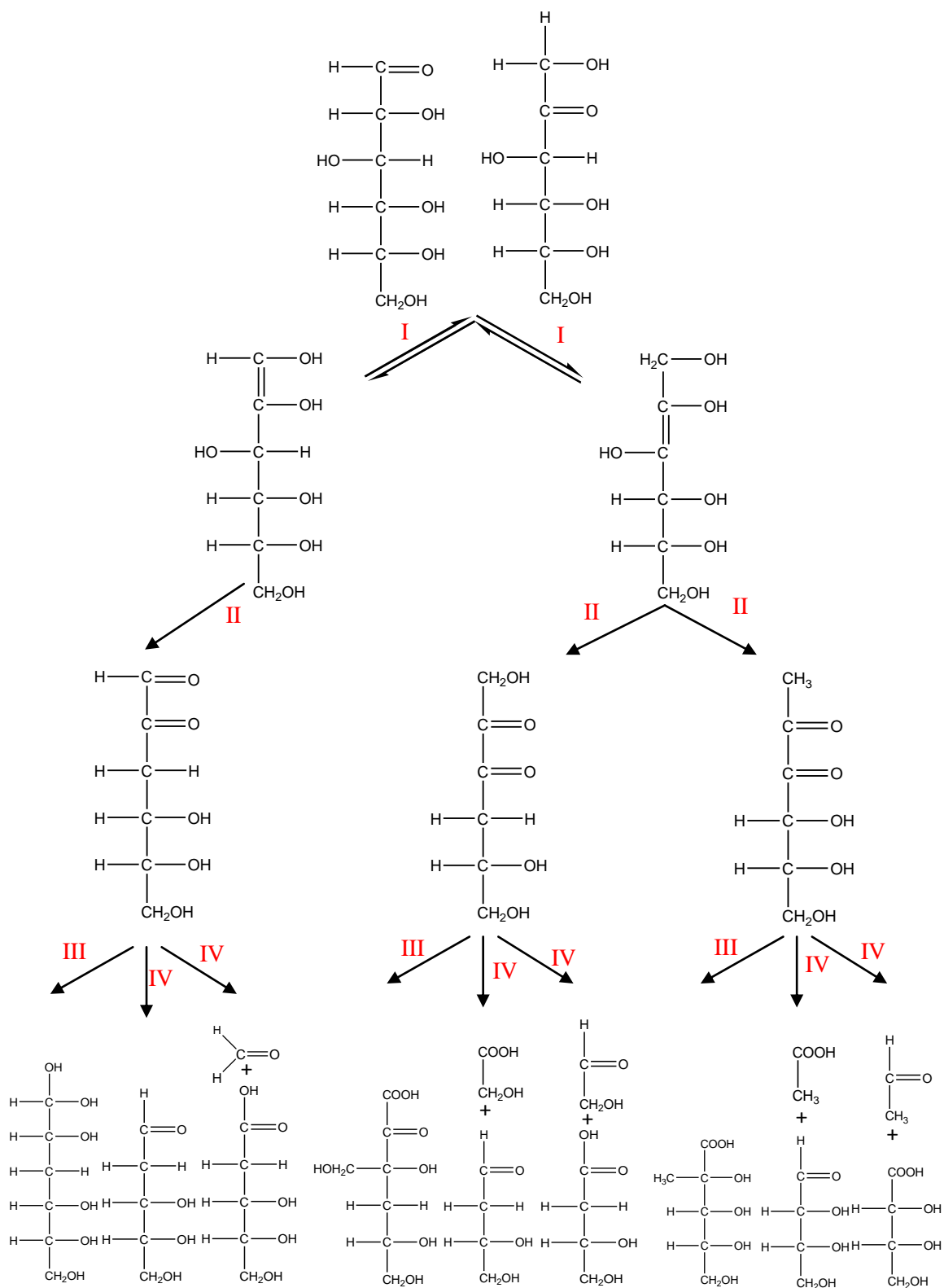


Figure 2.10 Alkaline degradation of monosaccharide [30]

2.8 Starch

Starch is a polysaccharide consisting of glucose units joined together by glycosidic bonds. Starch composes of two major components: amylose and amylopectin. The different components of starch can be separated by mixing them with hot water. The water-soluble part is amylose (about 20% of total starch) whereas the water insoluble part is amylopectin (about 80% of total starch)

2.8.1 Amylose

Amylose [34] is a linear polymer of glucose with 1, 4' glycosidic linkages. A systematic name of amylose is poly (1, 4'-O- α -D-glucopyranoside). Amylose has α -1, 4' links. The α linkage in amylose kinks the polymer chain into a helical structure. The kinking increases hydrogen bonding with water and thus provides additional solubility. The α -1, 4' glycosidic linkage is easily hydrolyzed by α -glucosidase enzyme, present in all animal.

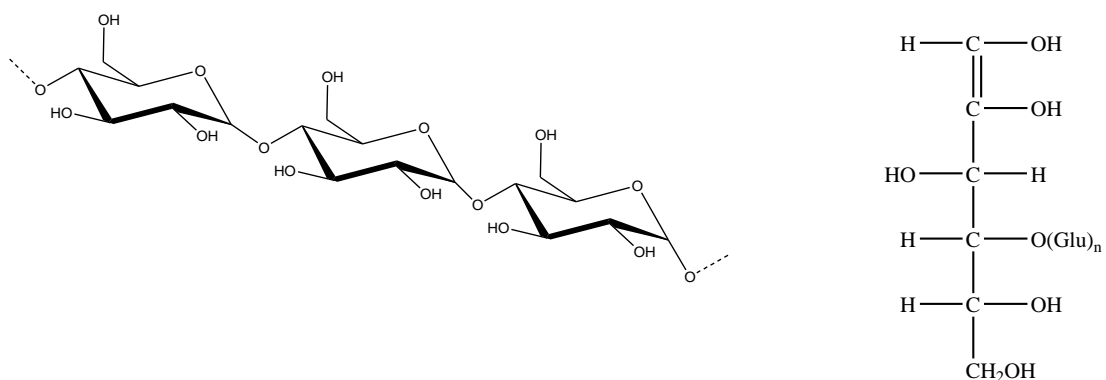


Figure 2.11 The structure of amylose, which has a branched α -1, 4' polymer of glucose [34].

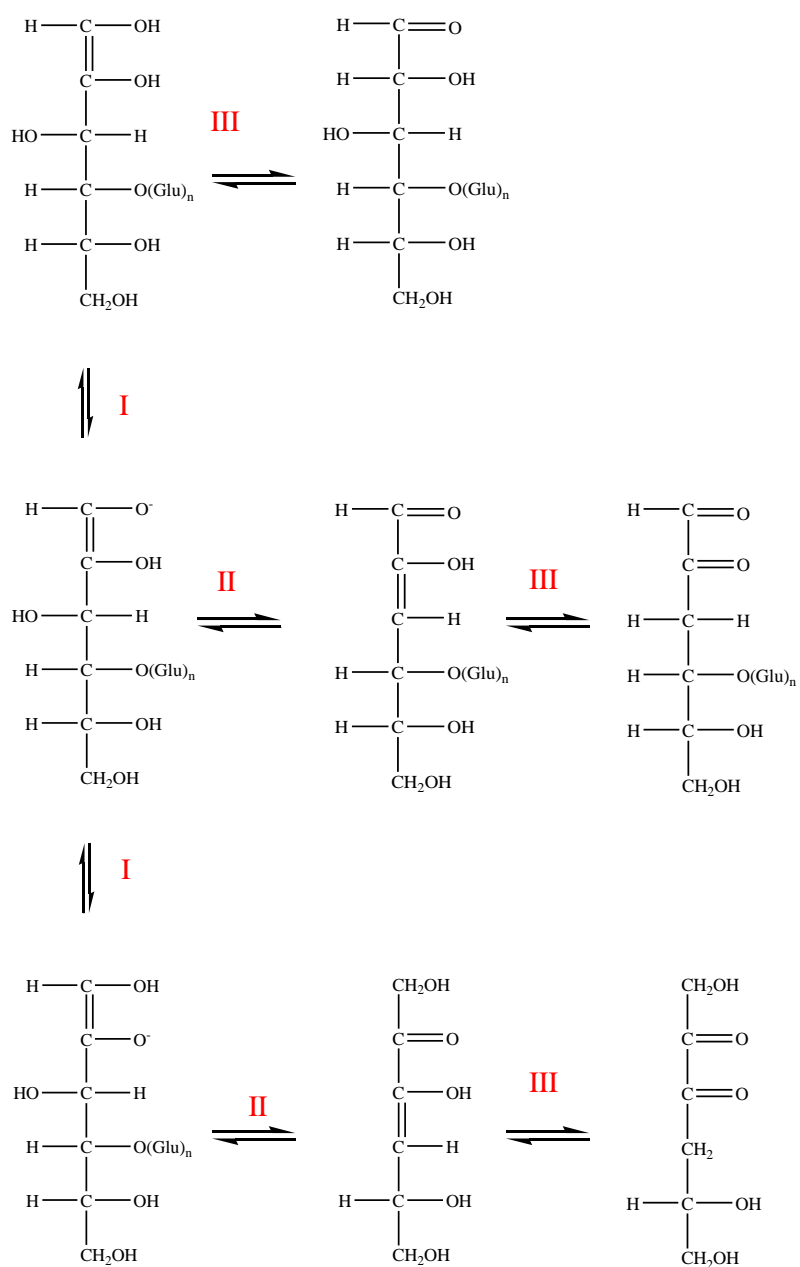


Figure 2.12 Alkaline degradation of 4-O-substituted D-glucose (amylose) in alkaline solution is shown. This reaction can generate hexoses, which each hexose is monosaccharide. The hexoses can continuously degrade to reducing species [35].

The alkaline degradation of amylose, which is a major component of starch, was reported by Knill, C.J. and Kennedy, J.F. [35] in 2003. As in the case for degradation of amylose, 4-O-substituted glucose, the first stage is the formation of enediols *via* keto-enol tautomerism and then enediol deprotonation by hydroxide ions to produce the corresponding enediols anions, which can undergo isomerisation of anion to follow by reprotonation. Anion contain the methoxyl group in the β -position relative to the negative charge of the anion and thus β -alkoxycarbonyl elimination of the enediol anion takes place. Therefore β -alkoxycarbonyl elimination produces a diketodeoxyglycitol product that is also present in the alkaline degradation of monosaccharide.

The mechanism of degradation of amylose is shown in Figure 2.12. In this mechanism glucose unit, can be generated. Glucose unit, which is a monosaccharide, can be continuously degraded in alkaline solution. Some products of alkaline degradation of amylose is an aldehyde function group, because an aldehyde group can generate two electrons in alkaline condition, starch can be used as a reducing agent. The alkaline degradation of amylose involves the reaction as follows:

reaction I : enediol formation

reaction II : β -elimination of hydroxyl or glycosyloxy group from the enediol to form a deoxy diketo derivative

reaction III : keto-enol tautomerism

2.8.2 Amylopectin

Amylopectin is a major component of starch. It is a water- insoluble fraction (the water- soluble fraction is amylose). The primary structure of amylopectin is α -1, 4' polymer of glucose. The difference between amylose and amylopectin is the branch nature of amylopectin with a branch point about every 20 to 30 glucose units. Another

chain starts at each branch point, connected to the main chain by α -1, 6' glycosidic linkage. A structure of amylopectin is shown in Figure 2.13

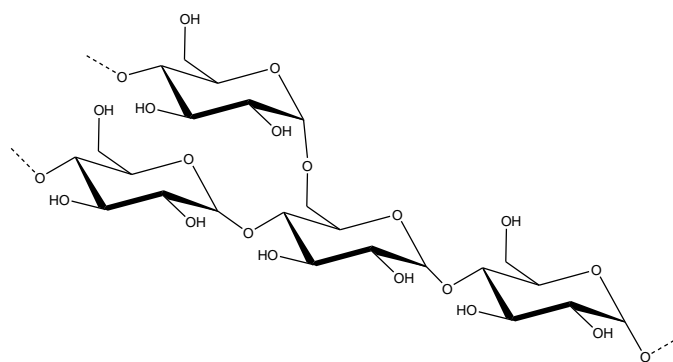


Figure 2.13 Structure of amylopectin. Amylopectin is a branched α -1, 4' polymer of glucose. At the branch points, there is a single α -1, 6' linkage that provides the attachment point for another chain [34].

CHAPTER III

EXPERIMENT

3.1 Chemicals and materials

1. Gold metal 99.99%
2. Nitric acid 65% (Merck)
3. Hydrochloric acid 37% (Merck)
4. Sodium hydroxide (Merck)
5. Sucrose (Mitrphol)
6. Tapioca starch (Pla Mungkon)
7. Corn starch (Jade leaf Brand)
8. Rough starch (Pla Mungkon)
9. Soluble starch (Merck)
10. NaBH_4 (Merck)

3.2 Preparation of tetrachloroauric acid as gold ion sources

3.2.1 Preparation of aqua regia

Aqua regia was prepared by freshly mixing nitric acid 65% with hydrochloric acid 37% in the volumetric ratio of 1:3 respectively. The color of aqua regia solution changes from colorless to orange solution which is suitable for preparation of the tetrachloroauric acid.

3.2.2 Preparation of tetrachloroauric acid

The tetrachloroauric acid (HAuCl_4) stock solution of 100,000 ppm was prepared by dissolving 10 g of gold metal 99.99% in 60 mL aqua regia. Gold metal

was rinsed with de-ionized water for 3 times in order to remove the impurities. Aqua regia was boiled by heater at 300-350°C. Gold metal was added into boiling aqua regia and then stirred with magnetic bar. The solution was continuous stirred until all gold metal completely dissolved and then continue stirred for 30 min in order to remove excess NO₂. The volume of stock solution was adjusted to 100 mL with de-ionized water.

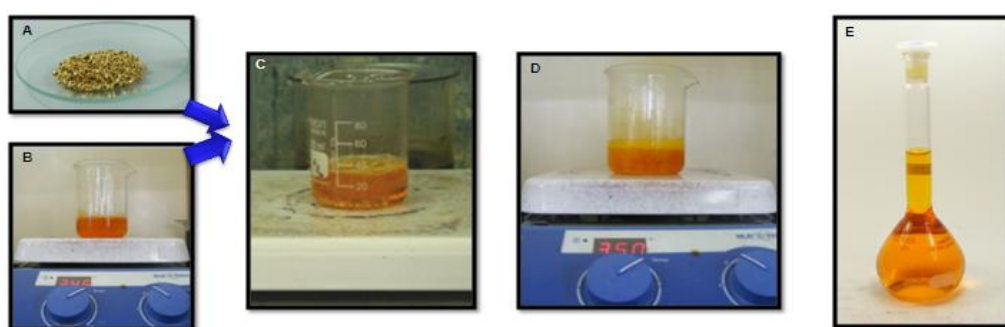


Figure 3.1 Preparation of gold stock solution 100,000 ppm A) gold metal 99.99%, B) aqua regia, C, D) gold metal was dissolved with aqua regia, E) gold stock solution 100,000 ppm

3.3 Investigation of the various factors affecting the synthesis of gold nanopowders by chemical reduction

All glasswares were cleaned with freshly aqua regia and rinsed with de-ionized water prior to use. Sucrose, tapioca, corn starch, soluble starch, and rough starch were used as green reducing agents. Sodium borohydride (NaBH₄) was used as conventional reducing agent. These materials were used without further purification. De-ionized water was used throughout the synthesis.

3.3.1 The synthesis of gold nanopowders using agricultural products as green reducing agents

The solution of green reducing agent 2% (w/v) was prepared by dissolving 2 g of each green reducing agent in 100 mL boiling de-ionized water for 30 min. The volume of solution was adjusted to 100 mL with de-ionized water. Each green reducing agent was incubated with 2 M of sodium hydroxide (NaOH) for 15 min. In this experiment, the green reducing agent was compared the efficiency to that from conventional reducing agent (NaBH_4). The solution of NaBH_4 was prepared by dissolving 2 g of NaBH_4 in soluble starch solution (0.5% w/v).

Gold nanopowders were prepared by diluting the concentration of stock gold solution from 100,000 ppm to 20,000 ppm and used as metal ion sources. The pH of gold solution was adjusted to pH 3 using NaOH 0.5 M. The solution of reducing agents, green reducing agents were already incubated with NaOH, and were added into the gold solution as well as stirred for 15 min. After addition, the color of solution changes from yellow to dark blue that indicating the formation of gold nanoparticles.

After 3 hours of the reduction, gold nanopowders were precipitated. The supernatant was separated from gold nanopowders. Gold nanopowders were washed five times with de-ionized water to remove residual molecules. Particles size, particles shape, and morphology of gold nanopowders were observed by mean of scanning electron microscope (SEM). The supernatant was diluted 125 times with de-ionized water. The supernatant was investigated with UV-visible spectroscopy. The result from this characterization technique confirmed that there were the gold ions left in the system. This experiment indicated the most suitable reducing agent for synthesis gold nanopowders.

3.3.2 The effect of NaOH concentration on the size of gold nanopowders

Size, shape, and morphology of gold nanopowders were depended on the various reaction conditions. The sucrose solution of 1% (w/v) was used for generated reducing species. Gold ions solution of 20,000 ppm (pH 3) was used as gold ions source. The soluble starch solution (1% w/v) was used as stabilizer. In this experiment, we plan to study the effect of NaOH concentrations on sizes and shapes of the gold nanopowders. The concentration of NaOH was varied from 0.25 M, 0.5 M, 1 M, 2 M, 3 M to 4 M.

Gold nanopowders were prepared by adding 5 mL of soluble starch solution into 5 mL of gold ions source solution in order to incubate for 45 min (part I). For part II, reducing agent was prepared by adding the 5 mL of sucrose solution into the 5 mL of NaOH so as to incubating for 15 min). After that, part I and part II are mixed together. After addition the color of solution changes from yellow to dark blue indicating the formation of gold nanoparticles. The mixing solution was stirred for 15 min with magnetic bar.

After 3 hours of reduction, gold nanopowders were precipitated. The supernatant was separated from gold nanopowders. Gold nanopowders were washed five times with de-ionized water to remove residue molecule. Particles size, particles shape, and morphology of gold nanopowders were observed by mean of scanning electron microscope (SEM). The supernatant was diluted 125 times with de-ionized water. The supernatant was investigated with UV-visible spectroscopy. The result suggested the residual of gold ions.

It is noticeable that after part I and part II are mixed together, the concentration of all precursors (gold ions, reducing agent, NaOH, and soluble starch) were diluted 4 times (because the final volume was increased for 4 times) as the final concentration. So, in Chapter IV the final concentration was represented.

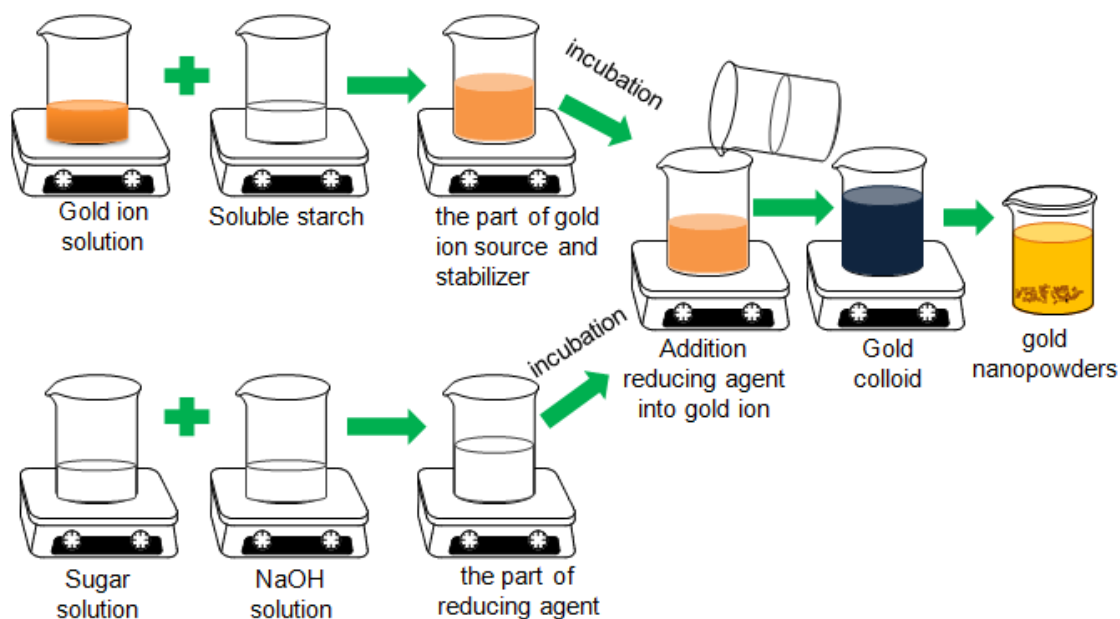


Figure 3.2 Schematic representation of method to synthesize gold nanopowders.

3.3.3 The effect of the concentration ratio of sucrose/gold ions on the size of gold nanopowders

The various concentrations of gold ion from 400 ppm, 2,000 ppm, 4,000 ppm, 10,000 ppm, 20,000 ppm to 40,000 ppm were used as gold ions source. The sucrose solution 1% (w/v) was used for generated reducing species. 2 M NaOH was used for incubation with sucrose solution. The soluble starch 1% (w/v) was used as stabilizer. In the present work, the concentration of gold ions was investigated.

Gold nanopowders were prepared by the method as described in section 3.3.2.

3.3.4 The effect of soluble starch concentration on the size of gold nanopowders

In the present work, the concentration of soluble starch was investigated. The concentration of soluble starch was varied from 0, 0.5%, 1.0%, 2%, 3%, to 4% (w/v). This solution was used as stabilizer. Gold ion solution 20,000 ppm, pH 3 was used as gold ions source. The sucrose solution (1% w/v) was used for generating the reducing species. 2 M NaOH was used for incubation with sucrose solution.

Gold nanopowders were prepared by the method as described in section 3.3.2.

3.3.5 The effect of incubation time between gold ion and soluble starch before the reduction reaction on the size of gold nanopowders

In this work, the incubation time of gold ion and soluble starch are investigated. The incubation time of gold ions and soluble starch was varied from 0, 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 165, 180, to 190 min. Gold ion solution of 20,000 ppm, with pH 3 was used as gold ion source. The sucrose solution 1% (w/v) was used for generated reducing species. 2 M NaOH was used for incubation with sucrose solution. The soluble starch 1% (w/v) was used as stabilizer.

Gold nanopowders were prepared by the method as described in section 3.3.2.

3.4 The evolution from gold colloids to gold nanopowders

In this work, it is very important to study the evolution from gold colloids to gold nanopowders. Gold ion solution of 20,000 ppm with pH 3 was used as gold ions source. The sucrose solution (1% w/v) was used for generated reducing species. 2 M NaOH was used for incubation with sucrose solution. The soluble starch was used as stabilizer.

Gold nanopowders were prepared by the method as described in section 3.3.2. After the reducing agent was added into the gold ion, which incubated with soluble starch solution, the color of solution changes from yellow to dark blue which indicating the formation of gold nanoparticles colloids. This colloid was investigated every change of the solution color by micropipette in order to dilute 500 times. UV-visible spectra of the synthesized gold colloids were measured as a function of time.

3.5 Characterization of synthesized gold nanopowders

3.5.1 UV-visible spectroscopy

The quartz cuvette was rinsed by aqua regia in order to remove all the residual of gold nanoparticles and then washed with de-ionized water. The pure de-ionized water was used to collect the spectrum as reference. The deuterium lamp was used as light source of this instrument. The USB 2000 spectrophotometer was used as the detector. The instrument setup is shown in Figure 3.3



Figure 3.3 The Ocean optics Portable UV-visible spectrometer setup

3.5.2 Scanning electron microscope

Scanning electron microscope (SEM) micrographs of gold nanopowders were recorded with JEOL, JSM-6510A. Samples were prepared by dropping gold nanopowders onto aluminum stub. After the gold nanopowders dried, size, shape, and size distribution of gold nanopowders were observed. The accelerating voltages of this instrument are in range of 20-30 kV and image magnifications are in the range of 5,000 – 30,000 times.



Figure 3.4 JEOL JSM-6510A scanning electron microscope

CHAPTER IV

RESULTS AND DISCUSSION

In this work, gold nanopowders were successfully synthesized *via* chemical reduction of gold salt by agricultural products in an alkaline solution. The Thai agricultural products in this case acted as reducing agents. This chapter is divided into 6 sections, each describing results of the investigation of size, shape size distribution, and morphology of particles that acquired with different conditions.

It is noticeable that the concentration was represented in Chapter III is a preparation concentration. The final concentration of all reagents was changed because the increasing of volume while the mixing reaction so the concentration was reduced. The final concentration was represented in this chapter.

4.1 Synthesis of gold nanopowders by chemical reduction method using Thailand agricultural products as reducing agents

After gold ions (part I) were mixed with a reducing agent incubated in NaOH solution (part II), the solution immediately turned dark and opaque and after about 3 hours the precipitate formed in all cases (Figure 4.1). This indicated that all of the reducing agents used in this experiment were capable for synthesizing gold nanopowders.

After gold nanopowders were synthesized, the supernatant from each condition was separated, diluted 125 times and further reduced with NaBH₄ in order to check whether the first reduction was complete or not. According to Figure 4.2, after NaBH₄ was added to the diluted supernatant, the color changed in the cases of

tapioca, corn starch, rough starch, and soluble starch, whereas it did not when sucrose and NaBH_4 were used as reducing agents (Figure 4.2). We could preliminarily conclude that sucrose is the only Thailand agricultural product in this experiment that can effectively and efficiently reduce gold ions into gold nanopowders just as NaBH_4 (conventional reducing agents).

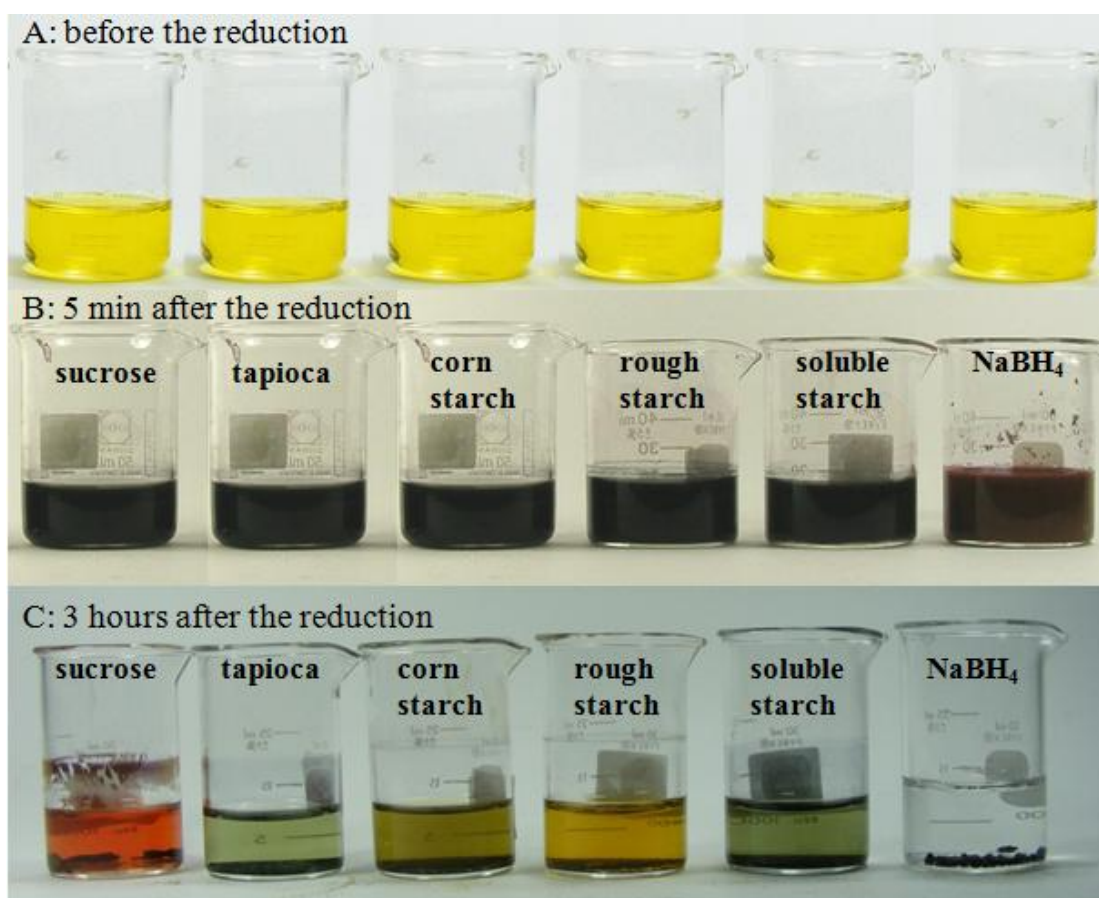


Figure 4.1 Synthesized gold nanopowders with reduction by various reducing agents: sucrose, tapioca, corn starch, rough starch, soluble starch, and NaBH_4 . A: gold ions (part I), B: 5 min after part I mixed with part II, and C: 3 hours after part I mixed with part II.

Sucrose is a suitable agricultural product for reducing gold salt which confirmed by the UV-visible results. As shown in Figure 4.3, the extinction spectra of the diluted supernatant before and after the addition of NaBH_4 are very superimposable in the case of sucrose (Figure 4.3A), whereas they are completely different in the case of tapioca, corn starch, rough starch, and soluble starch (Figure 4.3B-E) were used as reducing agents. This indicated that the complete reduction could be achieved when sucrose was used as a reducing agent.

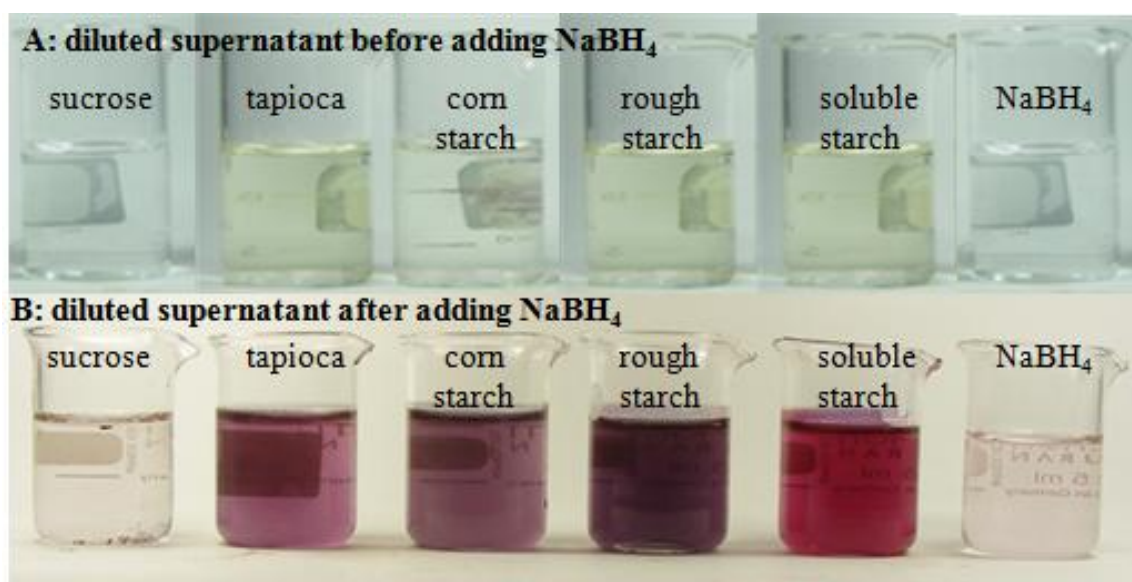


Figure 4.2 125-times diluted supernatant from gold nanopowders synthesis (A) before and (B) after adding extra NaBH_4 .

In other words, gold ions were all used up in the process of gold nanopowders synthesis. On the other hand, when tapioca, corn starch, soluble starch, and rough starch were used as reducing agents, gold ions still remained in the solution mixture after the first reduction and these ions could be further reduced when NaBH_4 was added to the solution.

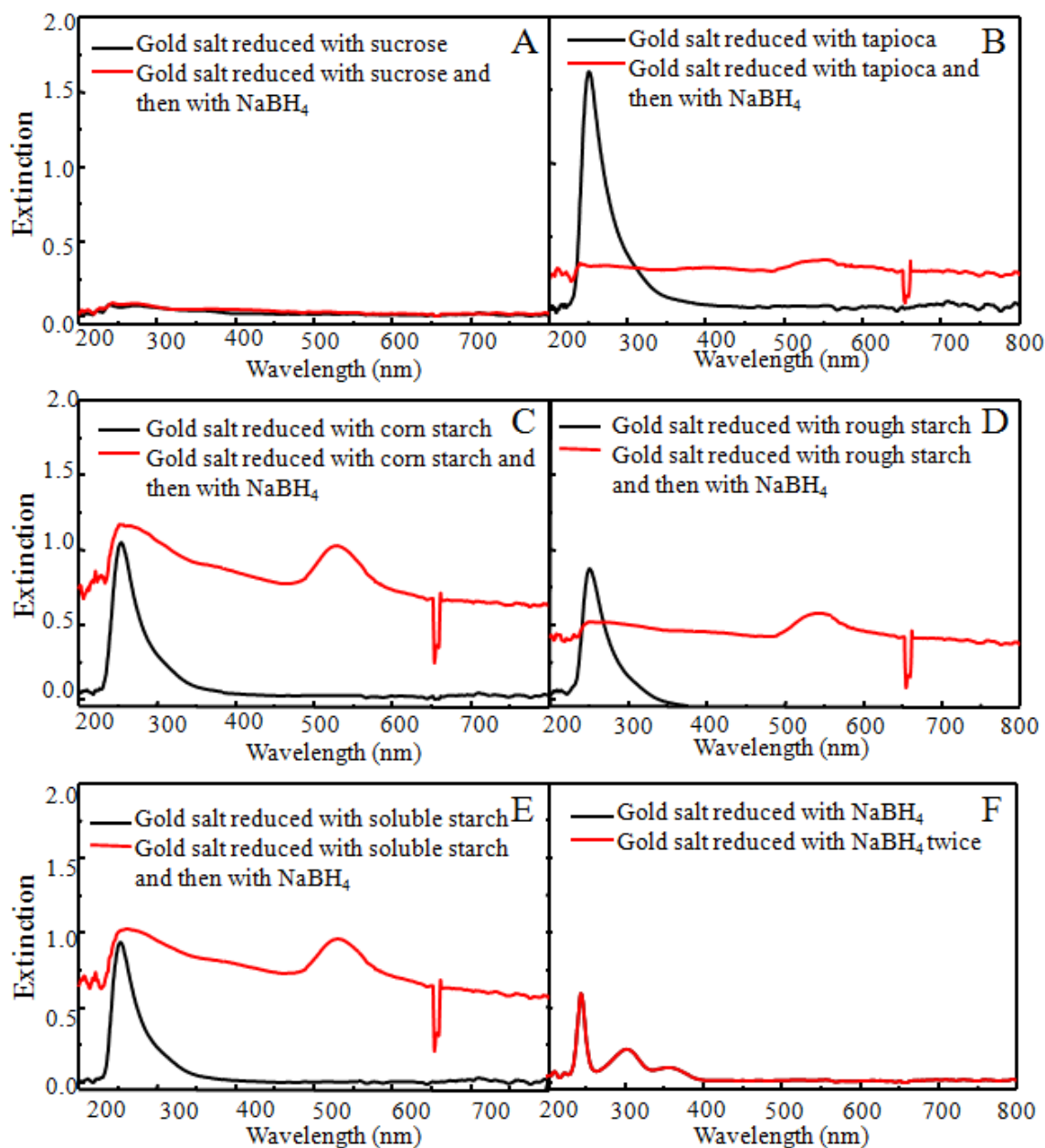


Figure 4.3 UV-visible extinction spectra of supernatant from the reduction of gold salt by various reducing agents: (A) sucrose, (B) tapioca, (C) corn starch, (D) rough starch, (E) soluble starch, and (F) NaBH_4 . Black curves represent a spectrum after the first time reduction (before adding extra NaBH_4) and red curves represent a spectrum after the second reduction (after adding extra NaBH_4).

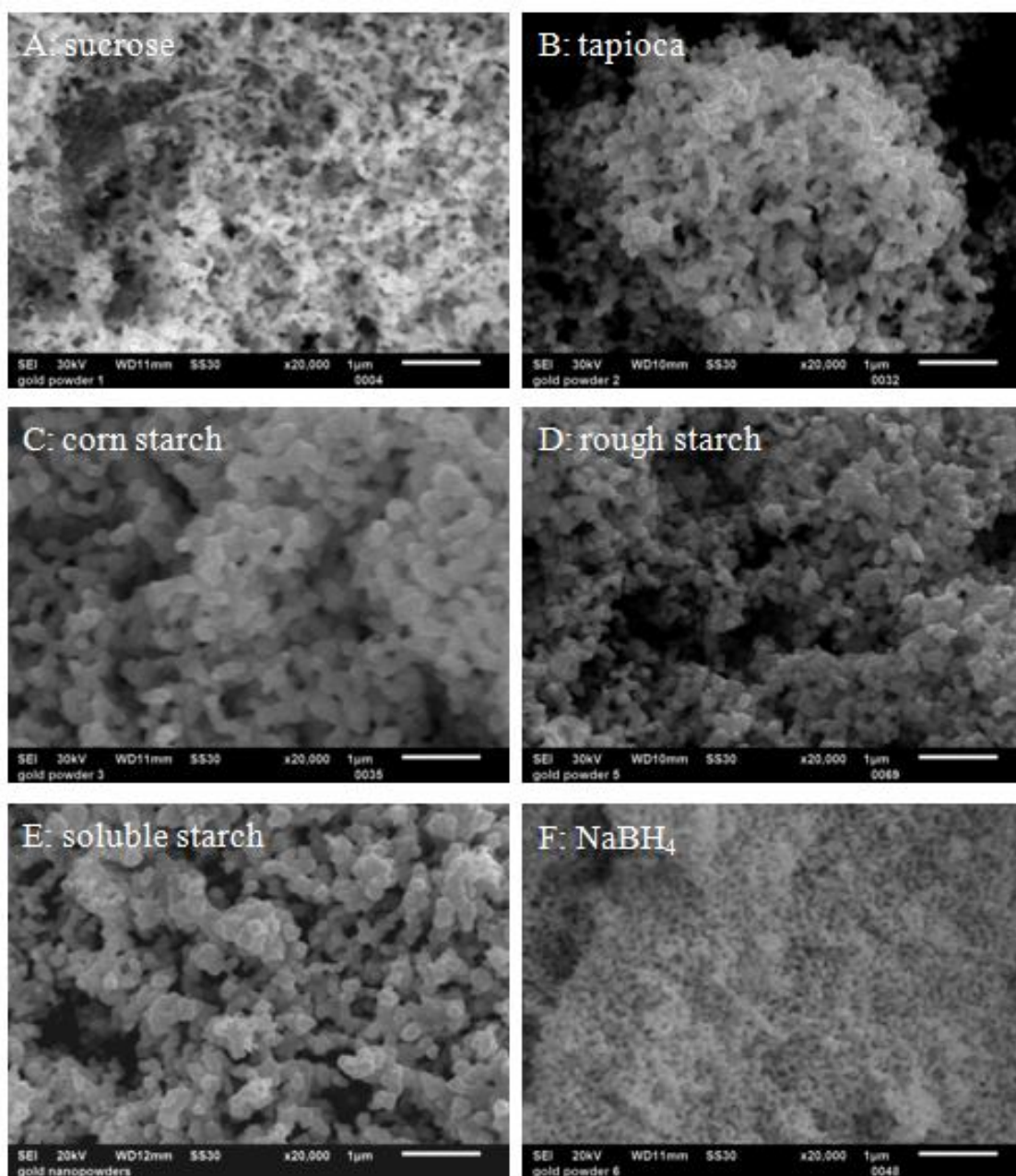


Figure 4.4 SEM micrographs of synthesized gold nanopowders by various reducing agents: (A) sucrose, (B) tapioca, (C) corn starch, (D) rough starch, (E) soluble starch, and (F) NaBH₄.

It is essential to note that the remaining gold ions show a characteristic extinction band at about 250 nm [36] which could be seen in Figure 4.3B-E. In addition, it is quite obvious (in Figure 4.3B-E) that the subsequent reduction by NaBH_4 resulted in the formation of gold nanoparticles (an emergence of a characteristic extinction at about 520 nm), that confirmed the remaining of gold ion residuals prior to subsequent reduction.

Different reducing agents also have a significant effect on the nature of the generated gold nanopowders. From SEM micrographs as shown in Figure 4.4, all of the gold nanopowders showed similar spherical shape and porous structures. However, there are noticeably seeing the difference in the size of the particles. When tapioca, corn starch, rough starch, and soluble starch were used as reducing agents, the average diameters of the generated particles were relatively large (average diameter of 100-150, 150-200, 100-150, and 150-200 nm respectively, Figure 4.4B-E). When sucrose was used, the size of particles was smaller (50-70 nm; Figure 4.4A) comparable to that of particles synthesized by NaBH_4 (Figure 4.4E). The most plausible reason is that sucrose is disaccharide and can be degraded in alkaline solution faster than tapioca, corn starch, soluble starch, and rough starch, which are polysaccharide. Thus, if an equal amount of reducing agents is being used, sucrose can generate more reducing species than tapioca, corn starch, rough starch, and soluble starch. The reduction process occurred faster and the seeds of gold nanopowders would be tremendously and rapidly formed. That mean there were less gold ion residuals left in the system in case of sucrose; so, there were fewer chances for growth mechanism to occur thereby leading to such the small average diameter of particles [37]. On the contrary, when the seeds of gold nanopowders were slowly formed, there were more chances that the generated gold nanopowders would undergo growth mechanism and resulted in larger particles.

Therefore, we conclude that sucrose is an appropriate Thailand agricultural product for using as a reducing agent for synthesizing gold nanopowders by the present method and it will be used throughout the rest of the experiment.

4.2 Synthesis of gold nanopowders by different concentration of sodium hydroxide (NaOH)

In this section, the synthesis of gold nanopowders were different from section 4.1. The soluble starch, which used as stabilizer, was added into gold ions before the reduction.

After the solution containing gold ions and soluble starch (part I) was mixed with the solution containing sucrose and NaOH (part II), the solution turned dark immediately and the precipitate formed in all cases except when 0.0625 M of NaOH was used in which the solution had no change in color and no precipitation was observed (Figure 4.5).

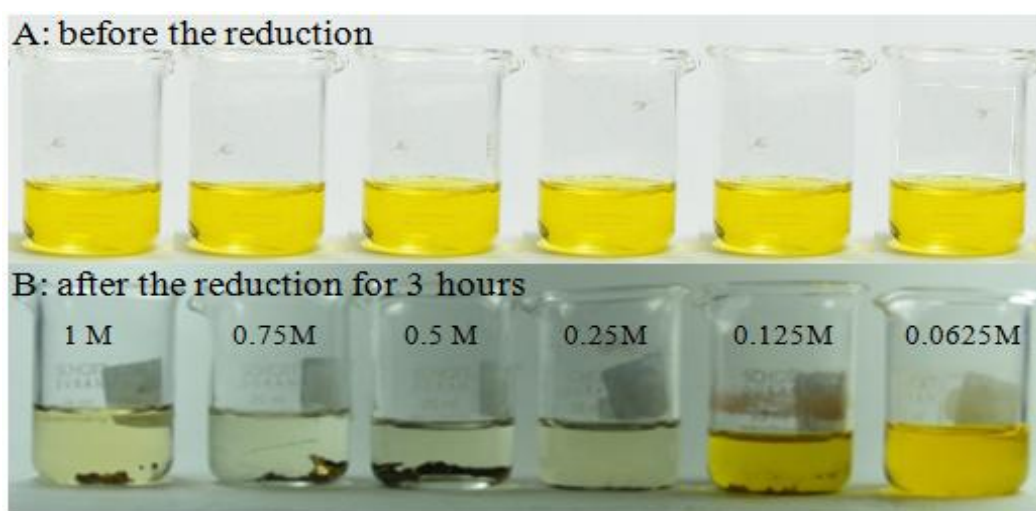


Figure 4.5 Synthesized gold nanopowders with reduction by various concentrations of NaOH solution: 1, 0.75, 0.5, 0.25, 0.125, 0.0625 M. A: gold ions in soluble starch (part I) and B: after part I was mixed with part II for 3 hours.

After gold nanopowders were synthesized, the supernatant from each condition was separated, diluted 125 times with de-ionized water and further reduced with NaBH_4 in order to check whether the first reduction was complete or not.

According to Figure 4.6, after NaBH_4 was added to diluted supernatant, the color of the solution changed only in the cases when 0.125 and 0.0625 M of NaOH were used to incubate sucrose.

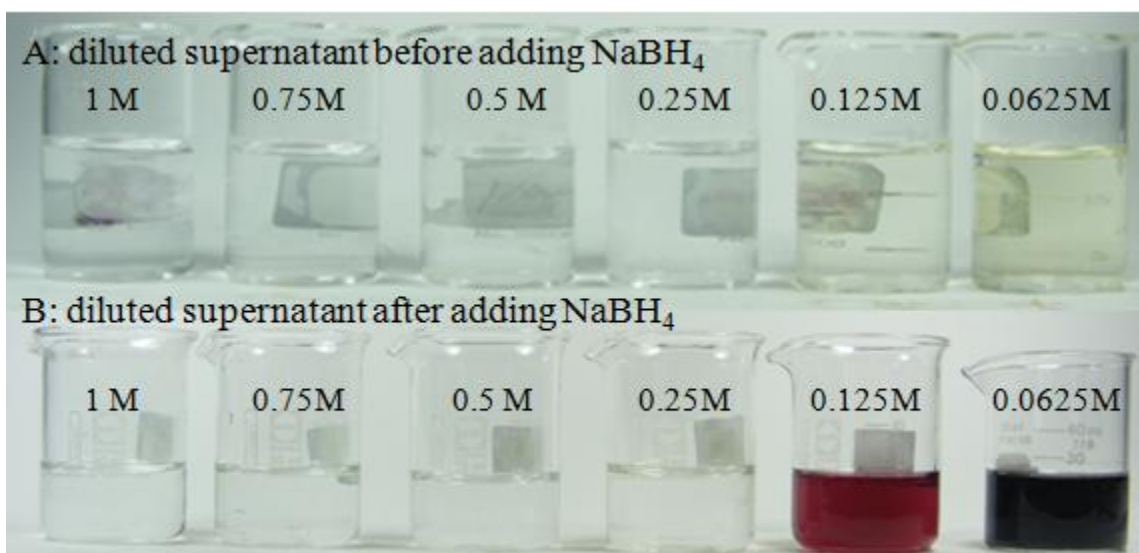


Figure 4.6 125-times diluted supernatant from gold nanopowders synthesis, (A) before and (B) after adding extra NaBH_4 .

According to the UV-visible extinction spectra as shown in Figure 4.7, in the cases of 1, 0.75, 0.5 and 0.25 M NaOH were used to incubate sucrose, the extinction spectra of diluted supernatant before and after the addition of NaBH_4 solution were very superimposable, indicating that the reduction is complete. On the other hand, when 0.125 and 0.0625 M NaOH were used, the UV-visible extinction spectra were completely different. In the cases, the extinction spectra before the addition of NaBH_4 have a characteristic of gold ions at the wavelength of about 250 nm and the extinction spectra after the addition of NaBH_4 have a characteristic of gold nanoparticles at the wavelength of about 550 nm. This result indicated that gold ions still remained after the first reduction and these ions could be further reduced to nanoparticles when NaBH_4 was added to the solution.

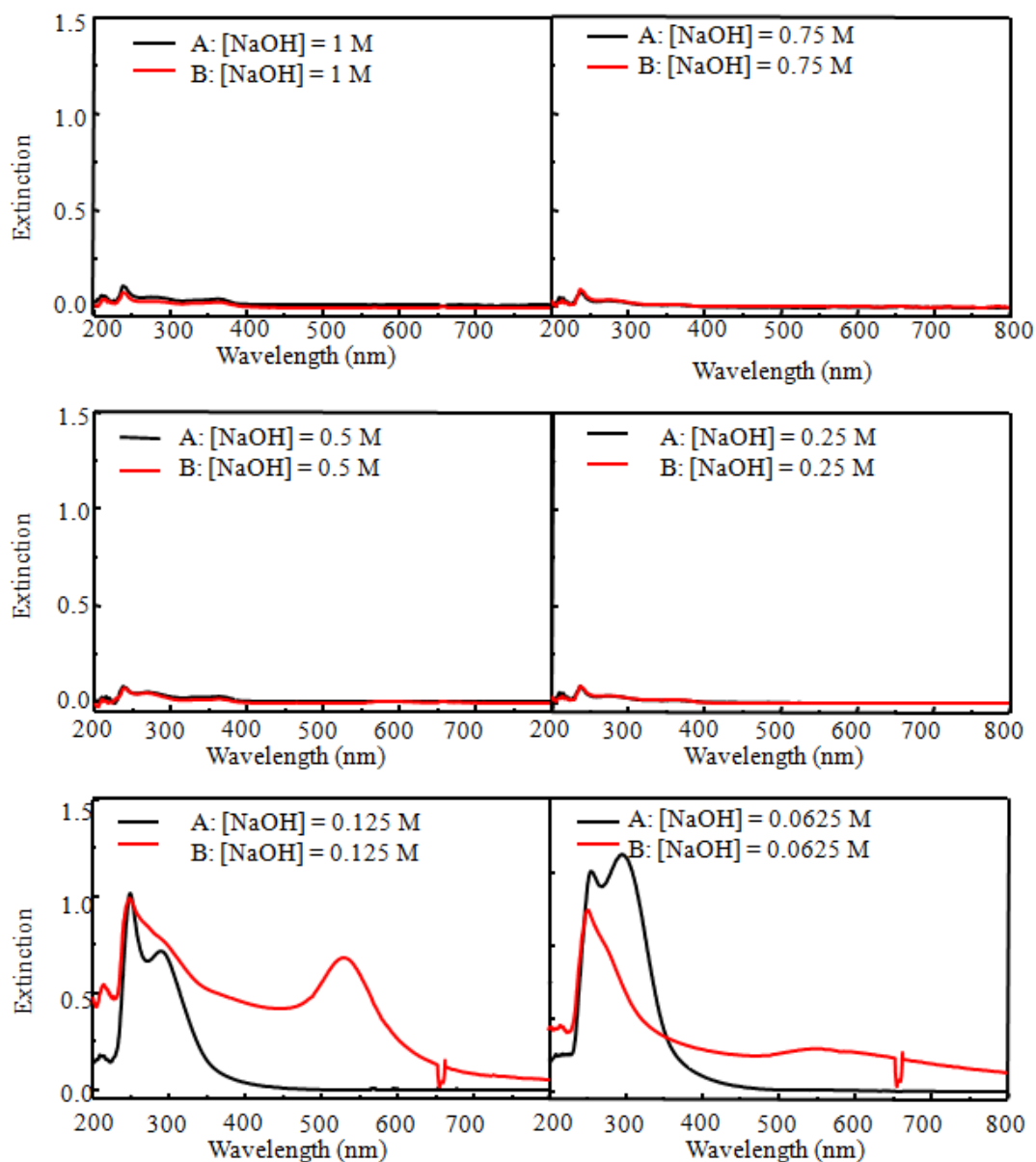


Figure 4.7 UV-visible extinction spectra of diluted supernatant from the reduction of gold salt using different concentration of NaOH: 1, 0.75, 0.50, 0.25, 0.125, and 0.0625 M. Black curves (A) represent spectra of diluted supernatant after the first time reduction (before addition NaBH_4 solution) and red curves (B) represent spectra of diluted supernatant after the second reduction (after adding NaBH_4 solution).

The relationship between the concentration of NaOH and the maxima extinction at λ_{max} 250 nm which is the characteristic of gold ions is plotted as shown in Figure 4.8. The critical NaOH concentration that determined the presence of maxima extinction at the wavelength of 250 nm is 0.25 M. Beyond this concentration, there was no peak at 250 nm which indicated that there was no gold ions in the solution after the first reduction, i.e., the reduction was complete. However, if the concentration of NaOH below 0.25 M was used to incubate sucrose, a peak at 250 nm, there were gold ion residuals in the solution after the first reduction, i.e., the reduction was incomplete.

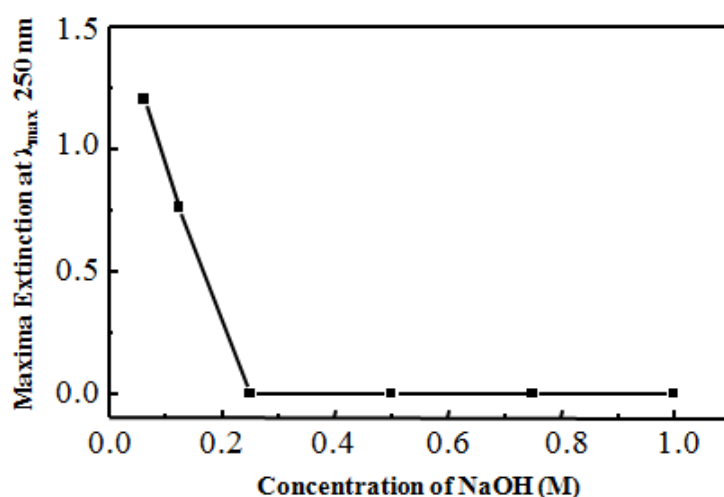


Figure 4.8 Relationship between the concentration of NaOH and the maxima extinction at λ_{max} 250 nm which represent the remaining of gold ions

The morphology and size of the synthesized nanopowders were also determined by SEM. Figure 4.9 shows the SEM micrographs of gold nanopowders synthesized by using different concentration of NaOH. Gold nanopowders showed spherical shape connecting with other particles resulting in porous nanostructures. However, the difference is in the size of the particles. When 1 M, 0.75 M, 0.5M, 0.25 M, 0.125 M, and 0.0625 M were used as incubating in sucrose, the average diameters of the generated particles were relatively large (average diameter of 150-250, 200-350, 300-400, 350-500, 500-2,000 and 1,500-4,000 nm respectively, Figure 4.9A-F).

Moreover the size of gold nanopowders was present at above, the small particles of 60-80 nm were observed in 1 M, 0.75 M, 0.5 M, and 0.25 M NaOH.

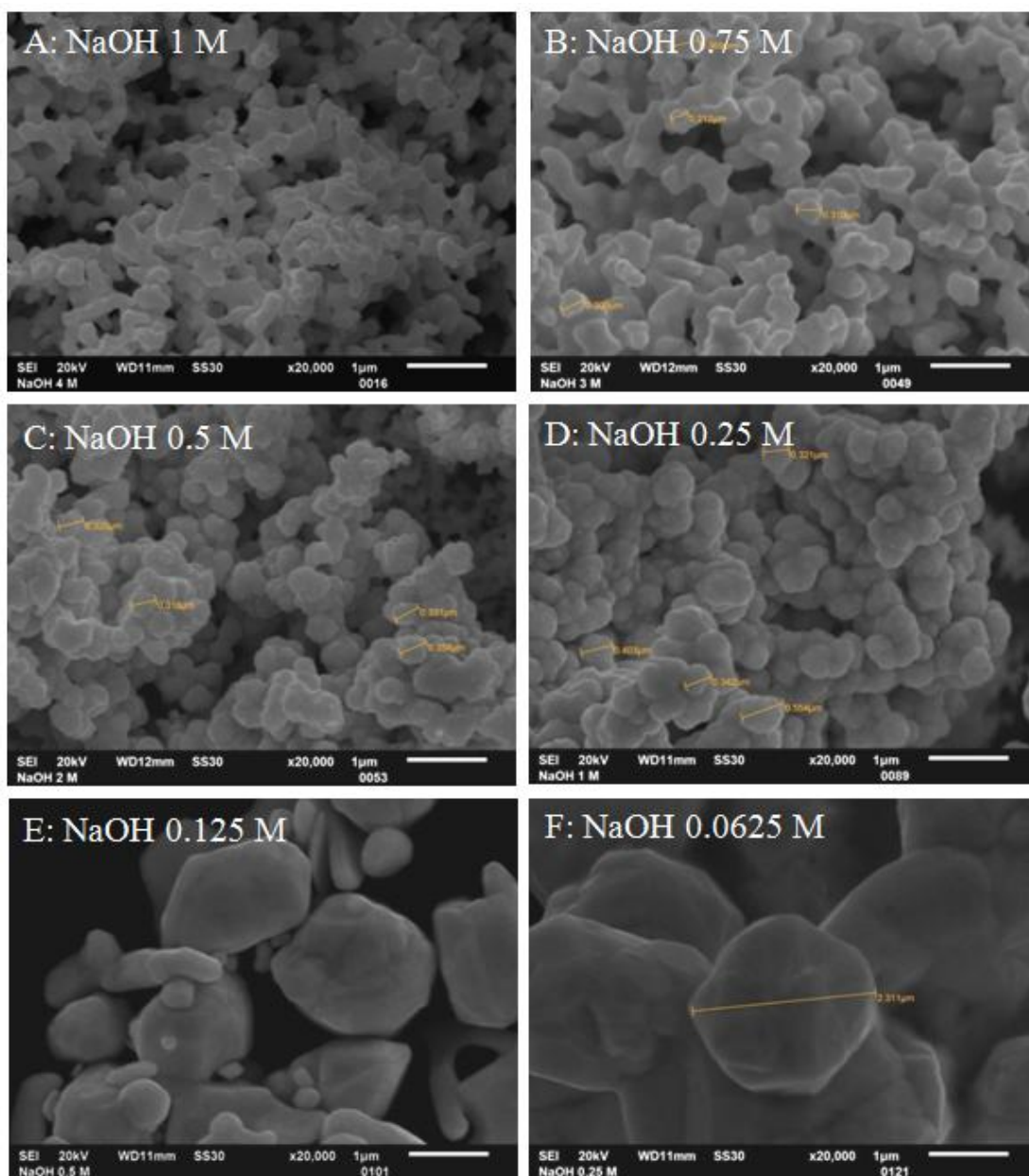


Figure 4.9 SEM micrographs of the gold nanopowders of six different sizes prepared by controlling concentration of NaOH (A) 1 M, (B) 0.75 M, (C) 0.50 M, (D) 0.25 M (E) 0.125 M, and (F) 0.0625 M.

It is of interest to note that using high NaOH concentration for incubating sucrose promoted the formation of small gold particles. On the contrary, if low concentration of NaOH was used, large gold particles were obtained.

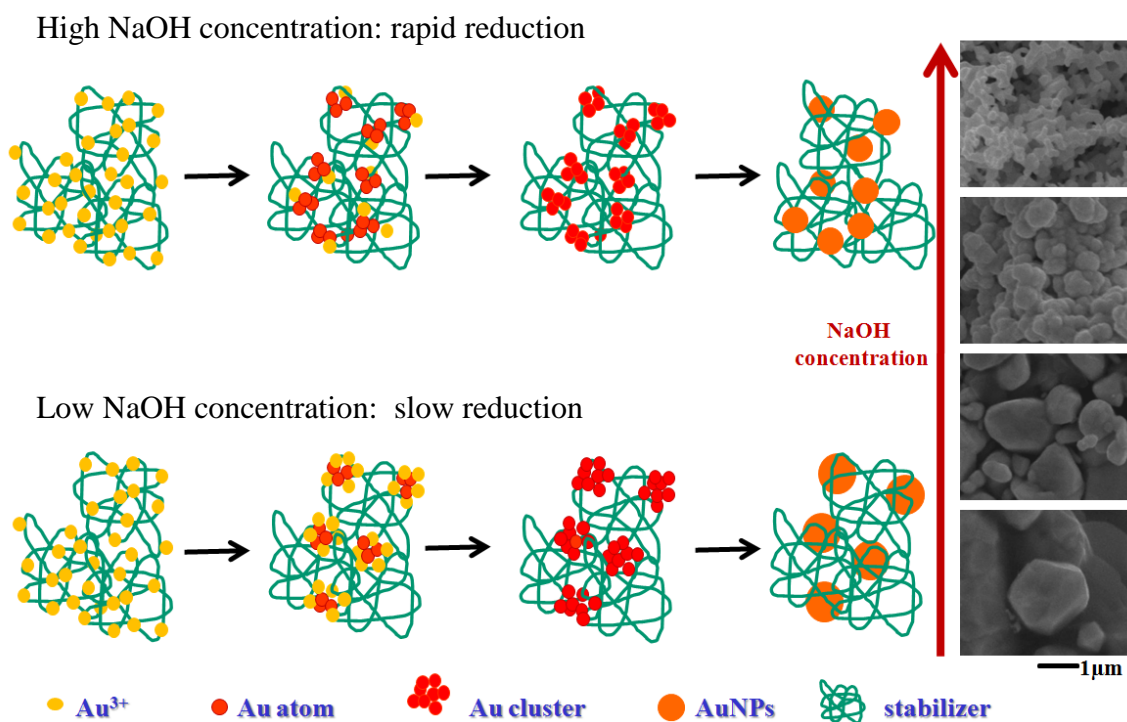


Figure 4.10 The effect of NaOH concentration on the formation of gold nanopowders

Figure 4.10 shows the illustration of the formation of gold nanoparticles prepared by chemical reduction of gold ions with sucrose in different NaOH concentration. When high NaOH concentration is used to incubate sucrose, this system generated high amount of reducing species. Small spherical particles are produced. Particles aggregated to form chain like structure. These indicated that the nucleation process was dominant and most of gold ions were consumed for gold atoms. The less remaining gold ions are consumed to growth process, particles are so small. On the contrary, if low NaOH concentration incubated in sucrose, this system

generated low amount of reducing agent. Large spherical particles are produced. This indicated that the particles growth process was dominant and most of gold ions were consumed for the growth of gold particles by the reduction reaction. Our results for gold nanopowders synthesis suggested that nucleation was a slow process at the beginning of the reaction, followed by simultaneous nucleation and growth mediated by early nucleations. Thus, rapidly increased nucleation as the reaction progresses, then slow down, and eventually stopped as growth predominates.

0.25 M NaOH concentration, the minimum concentration that makes completely reduction, is used for synthesizing gold nanopowders by the present method and it will be used throughout the rest of the experiments.

4.3 Synthesis of gold nanopowders by varying concentration ratios of sucrose / gold ions

In this experiment, gold nanopowders were synthesized by varying the concentration ratios of [sucrose solution] / [gold ion] (denoted as R) in order to investigate the suitable condition for gold nanopowders synthesis.

Table 4.1 Conditions for gold nanopowders synthesis by chemical reduction method

	Final concentration of sucrose solution % (w/v)	Final concentration of sucrose solution (C_s) (ppm)	Final concentration of gold ions (C_g) (ppm)	$R = C_s/C_g$
1	0.25	2,500	10,000	0.25
2	0.25	2,500	5,000	0.5
3	0.25	2,500	2,500	1
4	0.25	2,500	1,000	2.5
5	0.25	2,500	500	5
6	0.25	2,500	100	25

After gold ions incubated in soluble starch (part I) was mixed with the sucrose solution incubated in NaOH solution (part II), the solution turned dark and the precipitate formed in all cases (Figure 4.11).

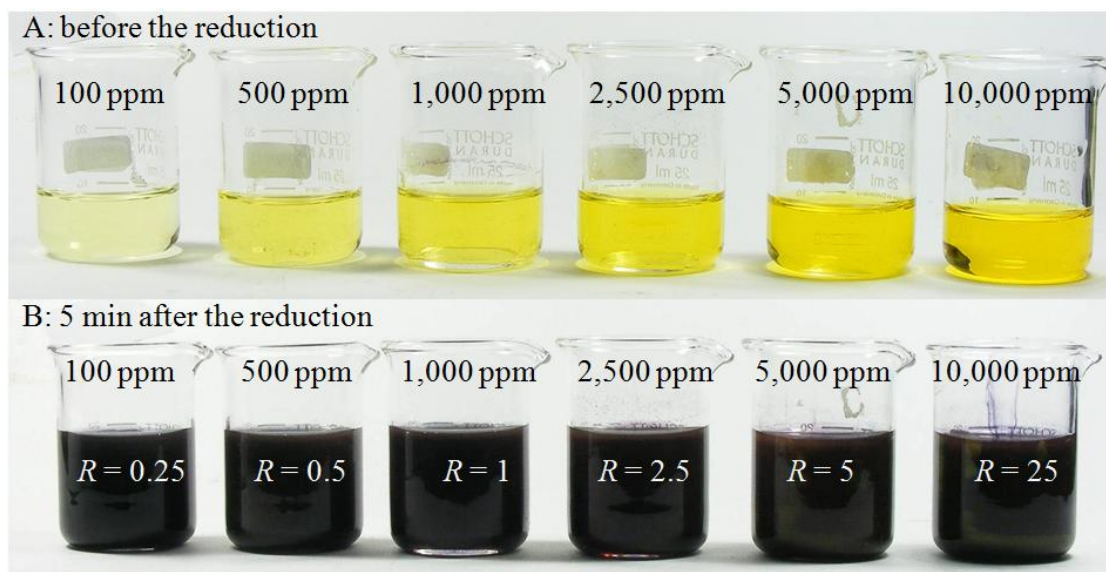


Figure 4.11 Synthesized gold nanopowders reduced by various concentration ratio (R) of $[\text{sucrose}] / [\text{HAuCl}_4]$: 0.25, 0.5, 1, 2.5, 5, and 25. A: gold ions in soluble starch (part I) by various concentrations of gold ions and B: after part I was mixed with part II for 5 min.

After gold nanopowders were synthesized, the supernatant was separated, diluted 125 times with de-ionize water and further reduced with NaBH_4 in order to check whether the first reduction was complete or not. As shown in Figure 4.12, after NaBH_4 was added to diluted supernatant, the color changed only in the case when $R = 25$.

According to Figure 4.12, the UV-visible extinction spectra of diluted supernatant before and after the addition of NaBH_4 are very superimposable in the cases when $R = 0.5, 1, 2.5, 5$ and 25 , while they are completely different in the case when $R = 25$. This result confirmed that the complete reduction could be achieved

when $R = 0.25, 0.5, 1, 2.5,$ and 5 . In other word, gold ions were all used up in the process of gold nanopowders synthesis. On the other hand, when $R = 25$, gold ions still remained after the first reduction and these ions could be further reduced when NaBH_4 was added to the solution. It is notable that the remaining gold ions show the characteristic extinction band 250 nm . In addition, it is quite obvious that reduction by NaBH_4 resulted in the formation of gold nanoparticles (an emergence of a characteristic extinction at about 550 nm) confirming the remaining of gold ion residuals before the subsequent reduction.

The morphology and size of the synthesized nanopowders were also determined by SEM. Figure 4.13 shows the SEM micrographs of gold nanopowders from different concentration ratio (R). All of the gold nanopowders formed showed similar spherical shape and porous structure. The result in different concentration ratio(R) of sucrose solution per gold ion are as follows: A: $R = 0.25\text{ M}$, the average particles size are 150 nm , B: $R = 0.5$, the average particles size are 120 nm , C: $R = 1$, the average particles size are 100 nm , D: $R = 2.5$, the average particles size are 80 nm , E: $R = 5$, the average particles size are 60 nm , and F: $R = 25$, the average particles size are $50\text{-}55\text{ nm}$. At high R , the average particle diameter is smaller.

According to the past researches [38], the amount of gold seeds nucleating in the reduction process depended on the concentration of a reducing agent. In this experiment, the concentration of reducing agent was kept constant. That is the amount of gold ions should be equally reduced to form equal amount of gold seeds in each conditions. However, we found that the amount of gold ions remaining in each condition were not the same; in the system with low R , more gold ions remained, more gold ions remained in the system. These ions adhered to the surface of the recently nucleated particles (growth mechanism) Thus, in the system with low R , more growth can be observed and the particles were larger compared to those in the system with high R (figure 4.14).

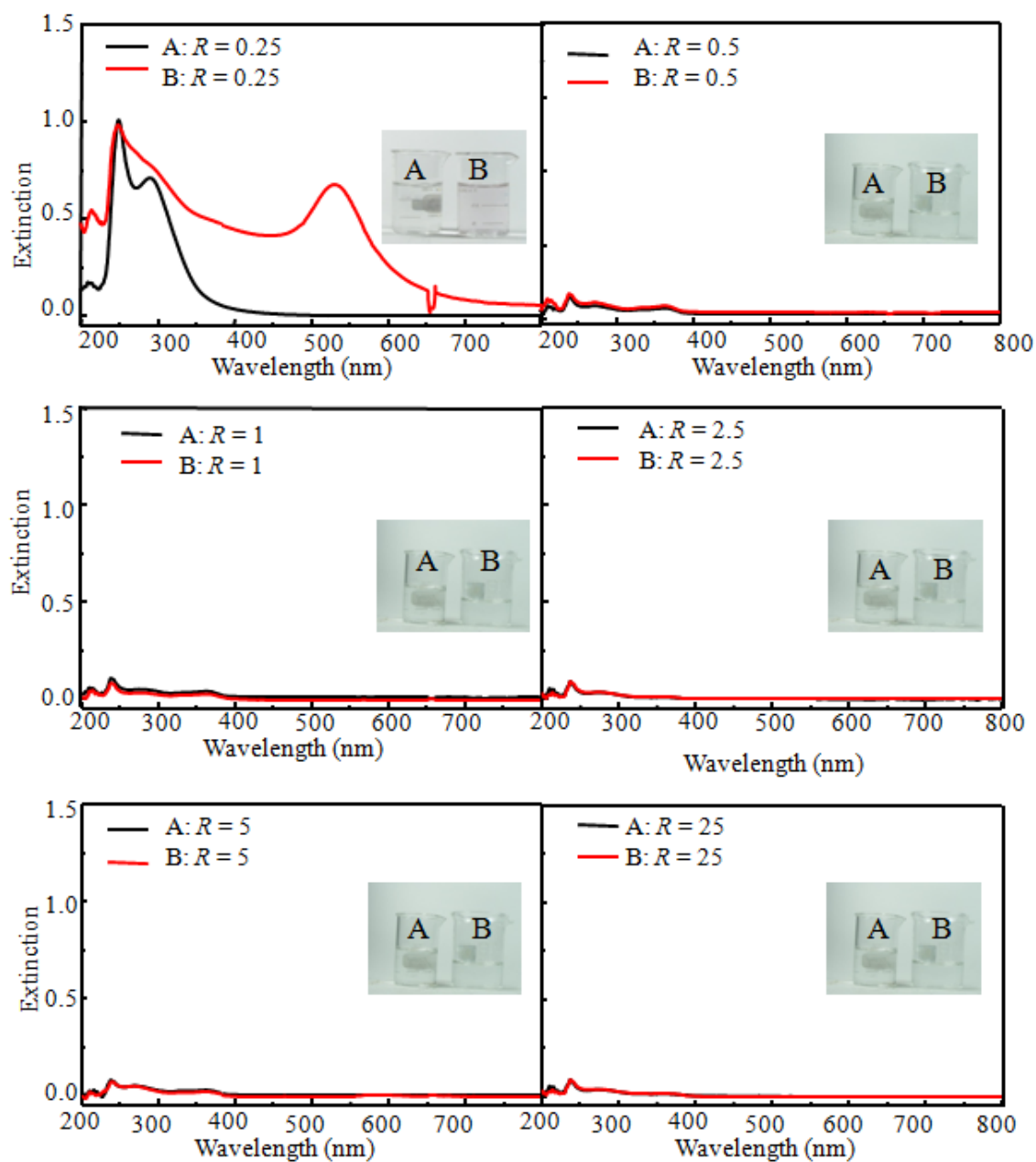


Figure 4.12 UV-visible extinction spectra of diluted supernatant from the reduction of gold ions by different concentration ratio of [sucrose] / [gold ions] (R): 0.25, 0.5, 1, 2.5, 5, and 25. Black curves; represent a spectrum after first time reduction (before addition of NaBH_4) and red curves; represent a spectrum after the second reduction (after addition of NaBH_4).

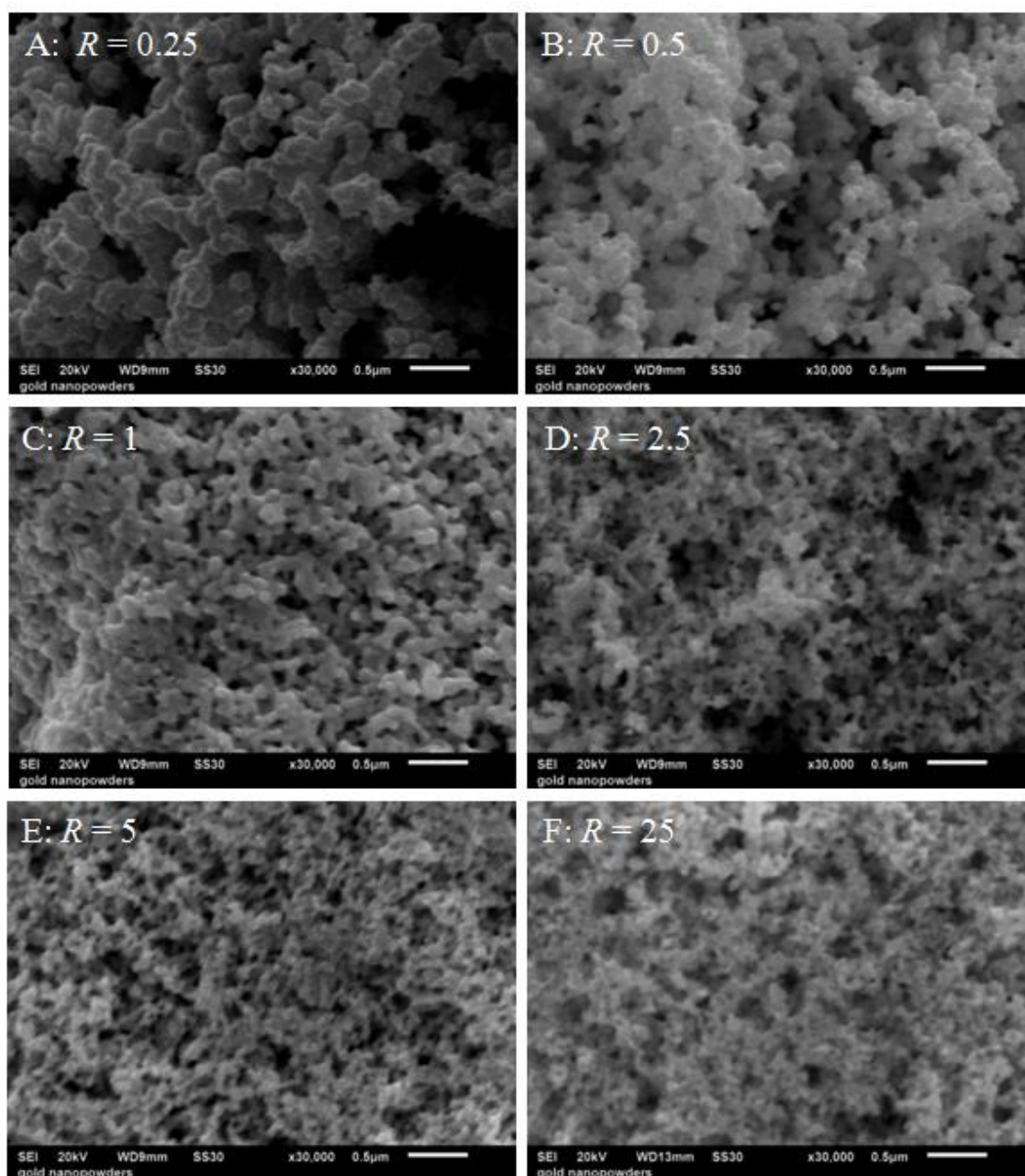


Figure 4.13 SEM micrographs of the gold nanopowders of six different concentration ratios (R) of sucrose solution per gold ions A: $R=0.25$, B: $R=0.5$, C: $R=1$, D: $R=2.5$, E: $R=5$, and F: $R=25$.

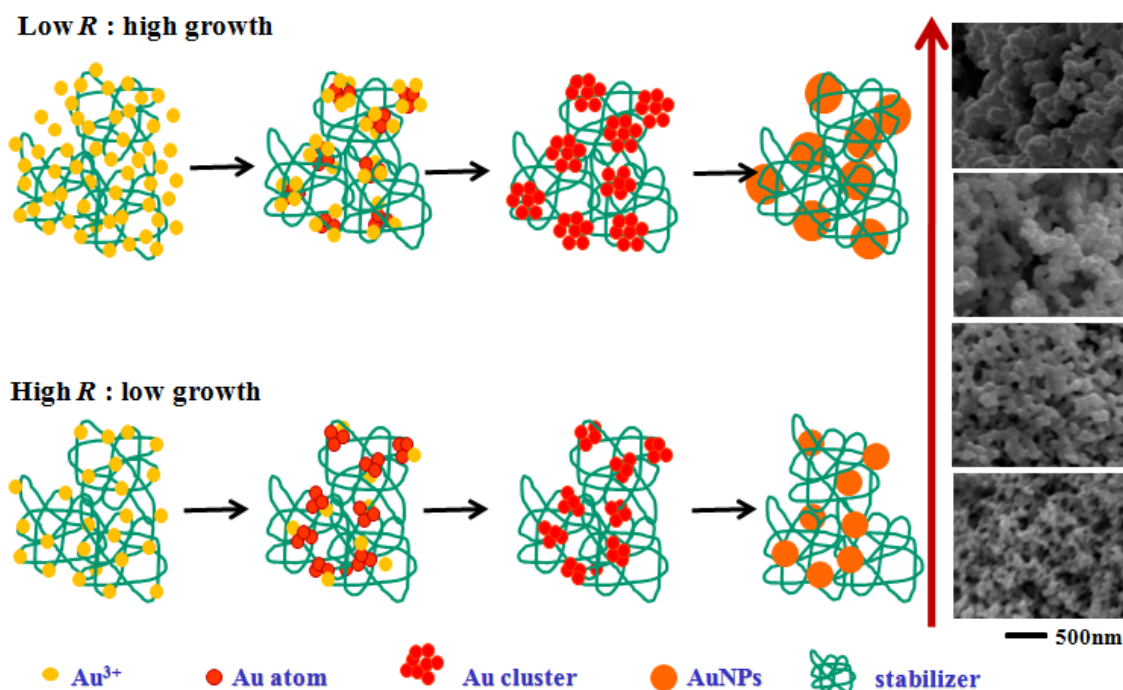


Figure 4.14 The effect of concentration ratios of [sucrose] / [gold ion] on the formation of gold nanopowders

4.4 Synthesis of gold nanopowders by different concentration of soluble starch

In this experiment, gold nanopowders were synthesized by varying the concentrations of soluble starch, which used as stabilizer.

After the solution containing gold ion and soluble starch (part I) was mixed with the solution containing sucrose and NaOH (part II), the solution immediately turned dark (Figure 4.15). This indicated that all cases in this experiment were capable of synthesizing gold nanopowders.

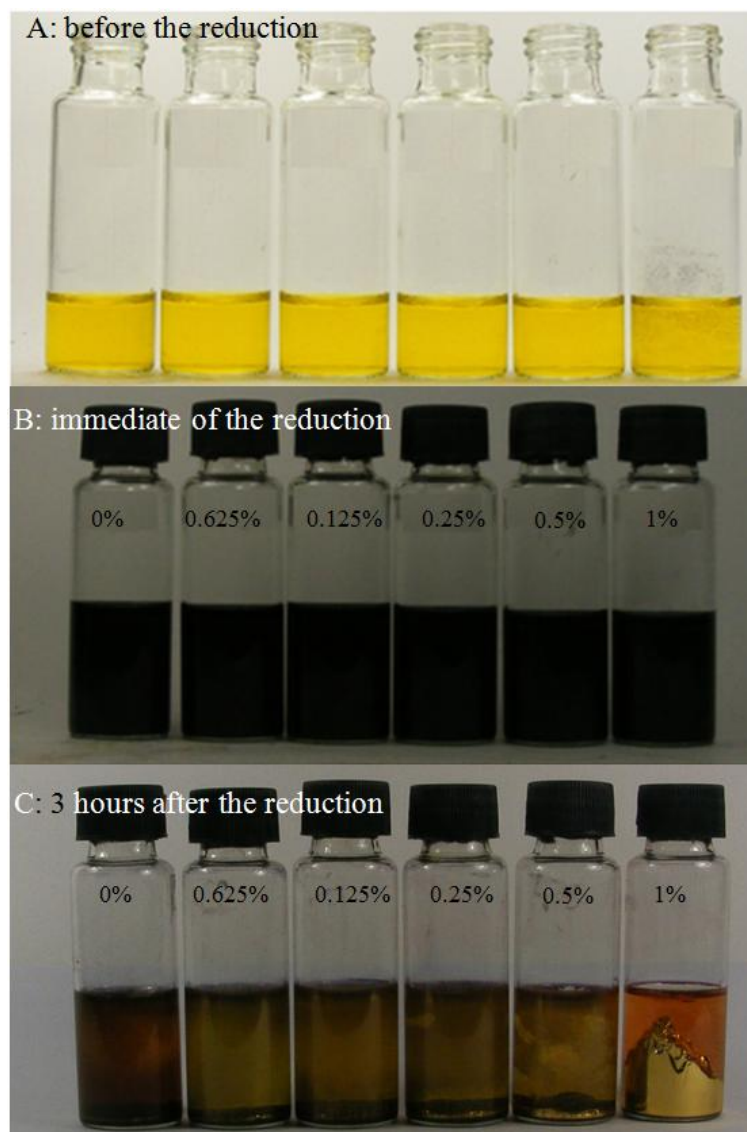


Figure 4.15 Synthesized gold nanopowders by various concentration of soluble starch: 0%, 0.0625%, 0.125%, 0.25%, 0.5% and 1% w/v. A: gold ions in soluble starch (part I), B: after part I was mixed with part II immediately, C: after part I was mixed with part II for 3 hours.

The morphology and size of the synthesized nanopowders were also determined by SEM. Figure 4.16 showed the SEM micrographs of obtained gold nanopowders from different soluble starch concentration. The size distribution and aggregation of gold nanopowders directly depends on concentration of soluble starch.

In case of A: no starch, the size distribution is in the range of 350-500 nm, B: 0.0625%w/v, the size distribution is in range 300-500 nm, C: 0.125%w/v, the size distribution is in the range of 250-350 nm, D: 0.25%w/v, the size distribution is in the range of 300-500 nm, E: 0.5%w/v, the size distribution is in the range of 300-500 nm, and F: 1%w/v, the size distribution is in the range of 200 nm. Moreover, the particle size presented on above, the small particles of 60-80 nm were observed in all conditions. Gold nanopowders stabilized in high concentration has narrow size distribution and less degree of aggregation than in low concentration of soluble starch. At 1% w/v concentration of soluble starch, relatively uniform size gold nanopowders with less degree of aggregation were generated. At without of soluble starch exhibited a broad size distribution due to aggregation of gold nanopowders.

The soluble starch contains many hydroxyl and carbonyl groups; these groups can stabilize gold nanoparticles. The core structure of starch molecules contains hydrogen-bonded amylopectin ring, which are capable around nanoparticles and thus are expected to prevent the aggregation of gold nanopowders [39]. The anionic form (COO^-) of soluble starch makes possible to stabilize gold nanopowders. The electrostatic attractive force between soluble starch (carbonyl groups) and gold ions in solution provided an effective driving force for formation and aggregation [6].

The effect of soluble starch concentrations on the degree of aggregation in gold nanopowders showed in Figure 4.17. The lower concentration of soluble starch exhibited more degree of aggregation in gold nanopowders forming an aggregated particles. The high concentration of soluble starch exhibited uniform gold nanopowders with less degree of aggregation. As the concentration of soluble starch increases, there is a significant decrease in the aggregation.

Nanoparticles are stable in solution due to electrostatic repulsion of their charge surface. Surface charge or stabilizer will cause the particles to aggregate or precipitate [41]. Stabilizers that adsorbed onto the surface of gold nanopowders are creating a steric effect that stabilizes the particles. At high concentration of stabilizer, more repulsion between neighboring gold nanopowders are due to steric that results in

less aggregation. While, at low concentration of stabilizer it is less repulsion between neighboring gold nanopowders that result more aggregation.

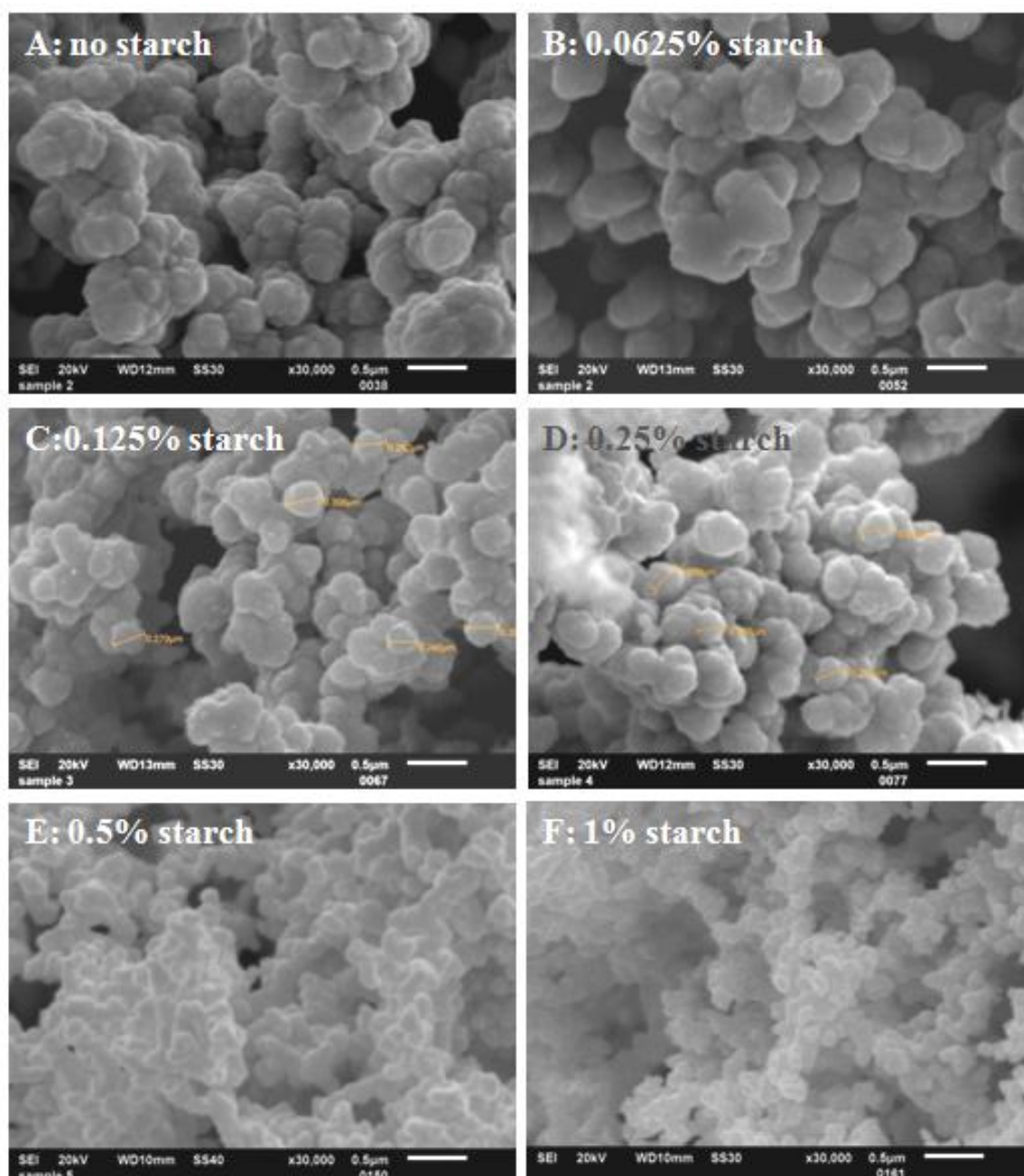


Figure 4.16 SEM micrographs of the gold nanopowders of six different concentrations of soluble starch A: no starch, B: 0.0625% w/v, C: 0.125% w/v, D: 0.25% w/v, E: 0.5% w/v, and F: 1% w/v.

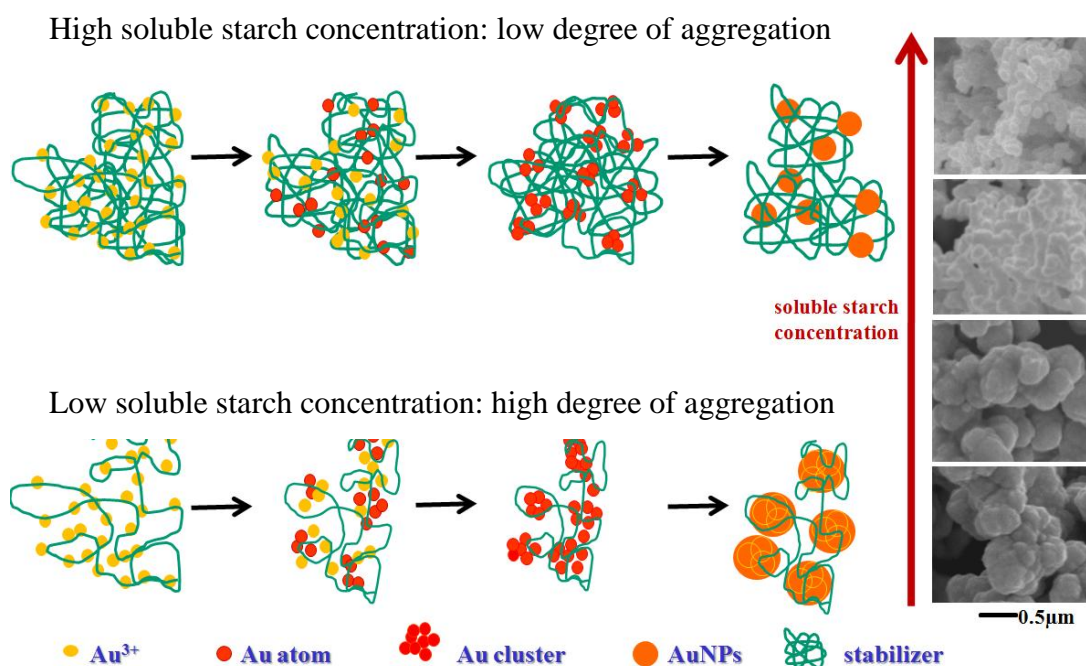


Figure 4.17 The effect of soluble starch concentrations on the formation of gold nanopowders.

4.5 Synthesis of gold nanopowders by varying incubation times between gold ions and soluble starch before the reduction reaction

In the present work, the incubation time between gold ions and soluble starch were investigated. The incubation times between gold ions and soluble starch was varied from 0, 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 165, 180, to 190 min.

After the solution containing gold ions and soluble starch (part I) were mixed with the solution containing sucrose and NaOH (part II), the solution immediately turned dark (Figure 4.18). This indicated that all cases in this experiment were capable of synthesizing gold nanopowders.



Figure 4.18 Synthesized gold nanopowders reduced by various incubation times between gold ions and soluble starch before the reduction reaction. A: gold ions in soluble starch (part I), B: after part I was mixed with part II immediately, C: after part I was mixed with part II for 3 hours.

The morphology and size of the synthesized nanopowders was also determined by SEM. Figure 4.19 showed the SEM micrographs of the obtained gold nanopowders from different incubation time between gold ions and soluble starch. Gold nanopowders were spherical shapes connected with other particles that formed to porous nanostructures. The size distribution and aggregation of gold nanopowders directly depend on incubation time. In the case A: no incubation, the size distribution is in the range of 80-100 nm, B: 15 min, the size distribution is in the range of 80-100 nm, C: 30 min, the size distribution is in the range of 80-100 nm, D: 45 min, the size distribution is in the range of 80-100 and 200-300 nm, E: 60 min, the size distribution is in the range of 80-100 and 200-300 nm, F: 75 min, the size distribution is in the

range of 80-100 and 200-300 nm , G: 90 min, the size distribution is in the range of 80-100 and 200-300 nm, H: 105 min, the size distribution is in the range of 80-100 and 200-300 nm, I: 120 min, the size distribution is in the range of 200-300 nm, J: 135 min, the size distribution is in the range of 200-300 nm, K: 150 min, the size distribution is in the range of 200-300 nm, L: 165 min, the size distribution is in the range of 200-300 nm, M: 180 min, the size distribution is in the range of 200-300 nm, and N: 190 min, the size distribution is in the range of 200-300 nm. Gold nanopowders incubated in short time has less uniform than that in long incubation time.

The morphology and size of the synthesized nanopowders were also determined by SEM. Figure 4.19 showed the SEM micrographs of the obtained gold nanopowders from different incubation time between gold ions and soluble starch. The size distribution of gold nanopowders were divided into three categories. The first category has one size distribution which is in the range 80-100 nm that synthesized by incubated gold ion and soluble starch for 0-30 min after the reduction. The second category has two size distributions that are in the range of 80-100 nm and 200-300 nm that synthesized by incubated gold ion and soluble starch for 45-105 min after the reduction. The third category has one size distributions that is in the range of 200-300 nm that synthesized by incubated gold ion and soluble starch for 120-195 min after the reduction. The uniformity particle has increased from the incubation time between gold ions and soluble starch.

Stabilizer controls both the reduction rate of metal ions and the aggregation process of atom. Preparation of polymer-stabilized nanoparticles by chemical method involves two processes: reduction of metal ions to zerovalent atoms and coordination of the stabilizing polymer to metal nanoparticles. If the reduction occurs before the interaction, the structural properties of metal nanoparticles are determined only by the reduction condition. If the interaction occurs before the reduction, the interactive forces between stabilizer and metal ions may affect the size and structure of metal nanoparticles. If the reduction occurs before the interaction, or the interaction may not occur, that the growth of metal atoms may not well-controlled by stabilizing polymer [18].

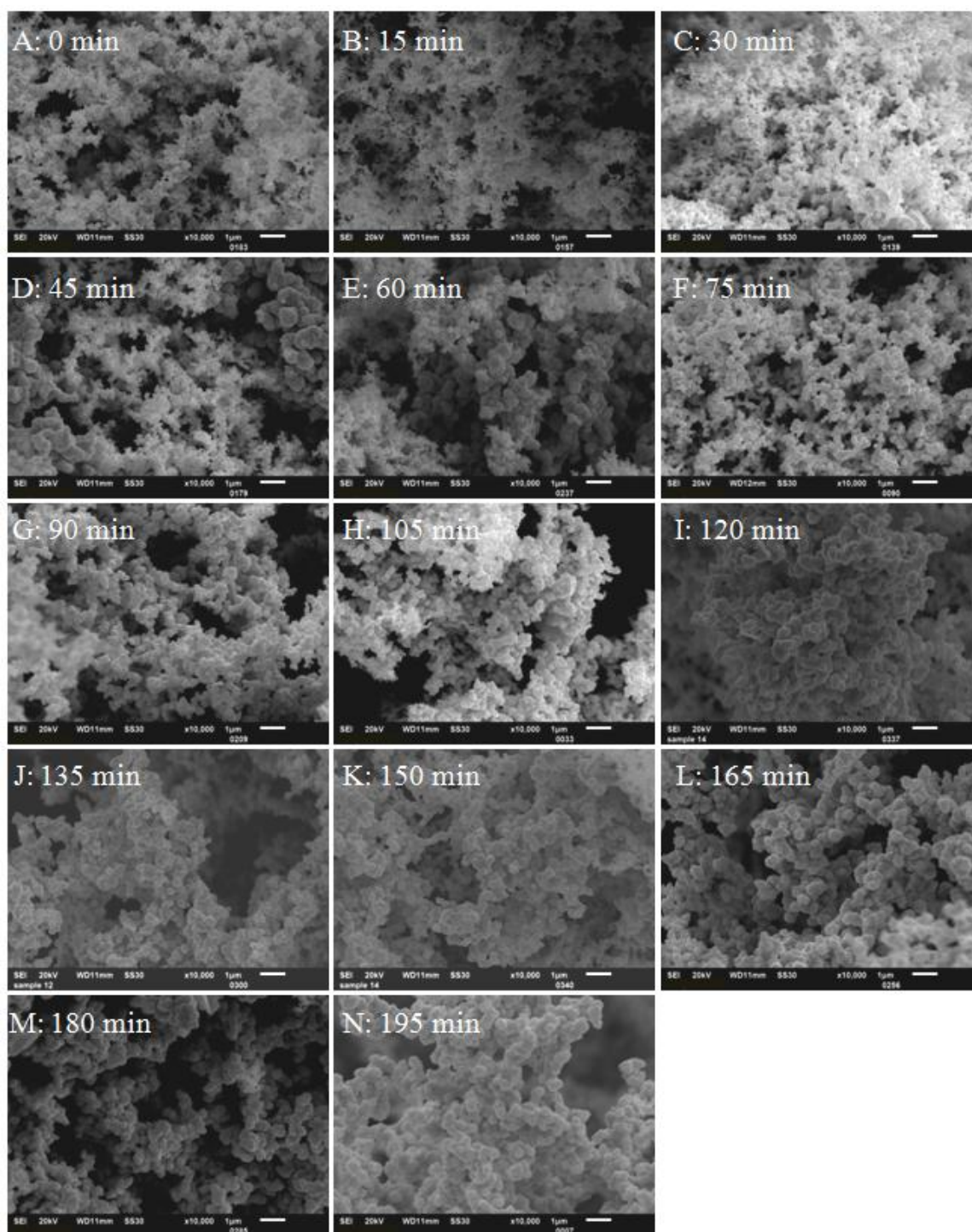


Figure 4.19 SEM micrographs of the gold nanoparticles of 15 different incubation times between gold ions and soluble starch 0-195 min (A-N), respectively.

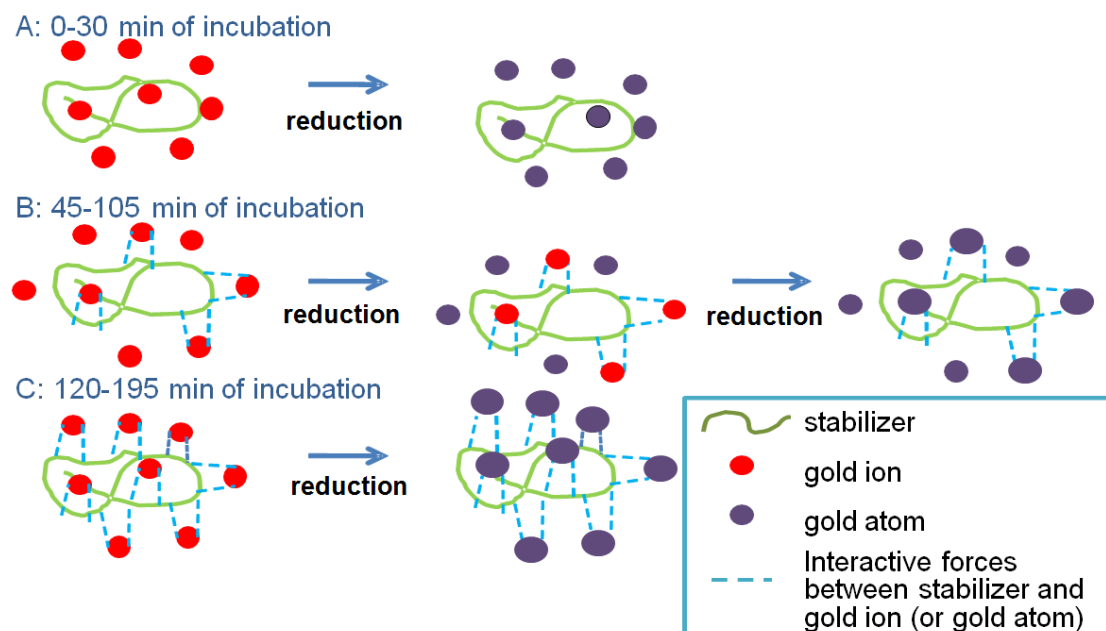


Figure 4.20 The effect of incubation time between gold ions and soluble starch on the formation of gold nanopowders

Figure 4.20 showed the interaction and the reduction process of gold ion in the presence of stabilizer. The incubation between gold ions and soluble starch for 0-30 min, the reduction occurred before the interaction so gold ions were rapidly reduced that resulted in small particles but non-uniform shape. For the incubation between gold ions and soluble starch for 45-105 min, some gold ions interacted with soluble starch and some gold ions did not interact with soluble starch. In case the interaction occurred, the reduction was slower than in the case of non-interaction that resulted in bigger particles. And particles shape can be controlled with soluble starch to result in uniform particles. In case of gold ions non-interaction with soluble starch, gold ions were free to reduce so the reduction was rapid and occurred which resulted in small particles but non-uniform. For the incubation between gold ions and soluble starch for 120-195 min, all gold ions completely interacted with soluble starch. The slow reduction occurred which resulted in large particles and uniform particles because the soluble starch can be controlled size and shape nanoparticles.

4.6 The evolution formation of gold nanopowders

In the present work, the evolution from gold colloids to gold nanopowders were investigated. Gold ions solution of 20,000 ppm, pH 3 was used as gold ions source. The sugar solution (1% w/v) was used as reducing agent. The 2 M NaOH was used for incubation with sugar solution. The soluble starch (1% w/v) was used as stabilizer.

After the solution containing gold ions and soluble starch (part I) was mixed with the solution containing sucrose and NaOH (part II), the solution immediately turned blue (Figure 4.21), that indicated the formation of gold nanoparticles. After the reduction occurred for 4 min, sampling the solution to dilute and characterization by UV-visible spectroscopy. At 35 min after the reduction, deep-blue sediment of gold powder occurred and characterized with scanning electron microscope. At 45 min after the reduction, the color of solution changed from deep-blue to green-yellow. Gold film occurred at bottom beaker. At 60 min after the reduction, the color of solution was green and more gold film occurred. At 75 min, color of the solution is violet and more gold films covered at surface boundary between solution and beaker. At 97 min, color of the solution is wine-red and more gold films covered on the surface boundary between solution and beaker (Figure 4.21).

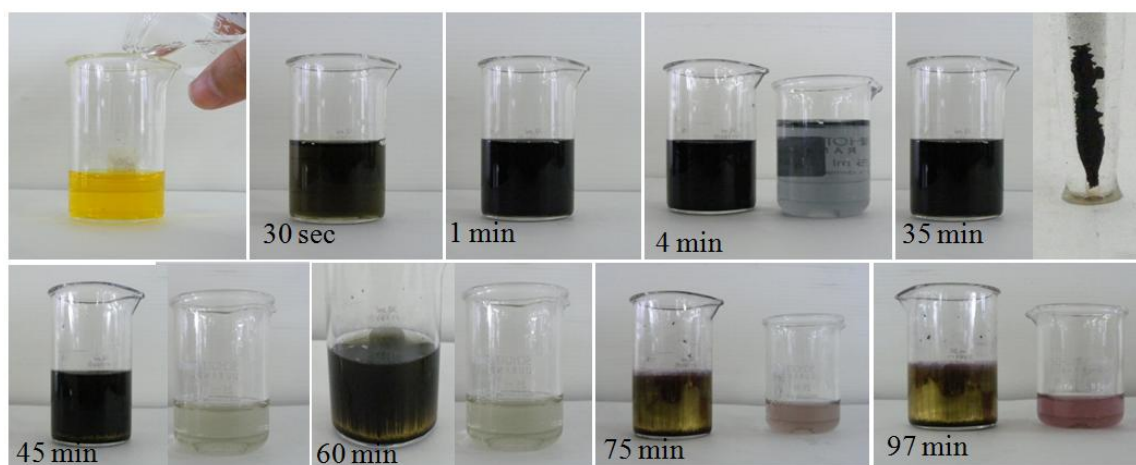


Figure 4.21 The evolution of gold nanopowders

According to Figure 4.22, the UV-visible extinction spectra of diluted supernatant in different times are shown. At 5 min of the reduction, UV-visible extinction was shown maxima extinction at wavelength 250 nm. Wavelength at about 250 nm is the character of gold ion [36]. At 25-70 min of the reduction, the maximum extinction at wavelength 250 nm reduced and the black sediment was observed. At 75-105 min of the reduction, the color of solution changed to red. The UV-visible extinction was shown maxima extinction at wavelength 530 nm and the maxima extinction at wavelength at about 250 nm disappeared at the 75 min. Wavelength at about 530 nm is the character of gold nanoparticles. At 115-150 min of the reduction, the UV-visible extinction did not show maxima extinction at any wavelength. This indicating the reduction of gold ions completed because, the UV-visible extinction did not show character of gold ions.

The morphology and size of the synthesized nanopowders were also determined by SEM. Figure 4.23 showed the time-dependent of the different size of gold nanopowders from different reduction times. Gold nanopowders were spherical shape and jointed with neighbor particles forming aggregated particles. The size distribution of gold nanopowders was different by the reduction time. At 15 and 35 min after the reduction (Figure 4.23A and B), size distribution of gold nanopowders was approximately 100 nm. At 75 min (Figure 4.23C), the size distributions has two ranges 100 nm and less than 60 nm. At 80 min (Figure 4.23D), the size distributions has two ranges 100 nm and less than 60 nm. The small size increased rapidly at the same reduction time. At 90 min (Figure 4.23E), the size distributions have two ranges 100 nm and less than 60 nm. At 120 min (Figure 4.23F), the size distributions are in range more than 200 nm, which aggregated particles, and less than 60 nm. The big particles are aggregated particles smaller coming from particles.

The results from the UV-visible spectroscopy and scanning electron microscope confirmed that in the first period (5-60 min) most gold ions were rapidly reduced. The solution color changed from yellow to blue in a short reduction time. The maximum UV-visible extinction at wavelength about 250 nm, which is the character of gold ions, reduced with long of the reduction time. Gold nanosediments

were observed at 35 min of the reduction time. This result indicated that gold ions were consumed and formed gold nanosediments which aggregated particles.

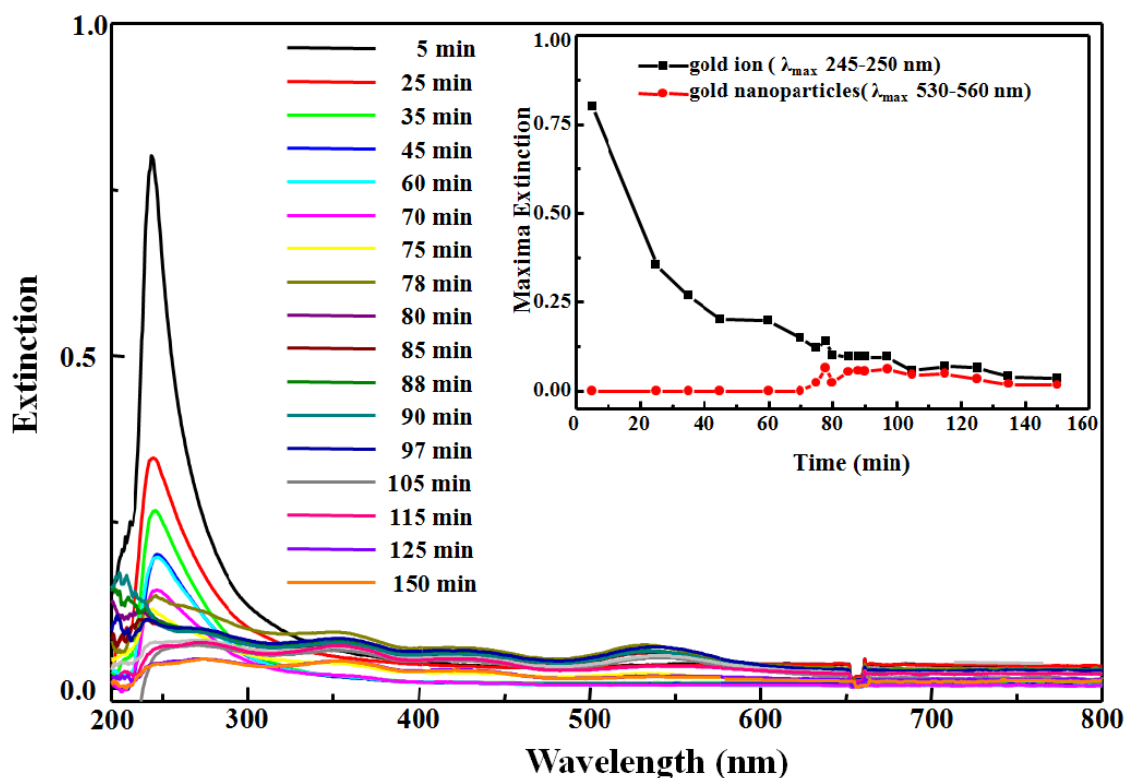


Figure 4.22 UV-visible extinction spectra of diluted supernatant synthesized gold nanopowders in different times.

Particles size of gold nanopowders is generated in the first period that is approximately 100 nm and seemed rather big particles. In the second time (60-105 min), color of solution changed from blue to red. The maximum UV-visible extinction shows at wavelength about 530 nm which is the character of gold nanoparticles that indicating the formation of small gold nanoparticles. The result was confirmed by scanning electron microscope. The small particles were observed. The small particles occurred from the reduction of low concentration gold ions, which remaining from the reduction in the first period. So in the system, we found both big and small particles.

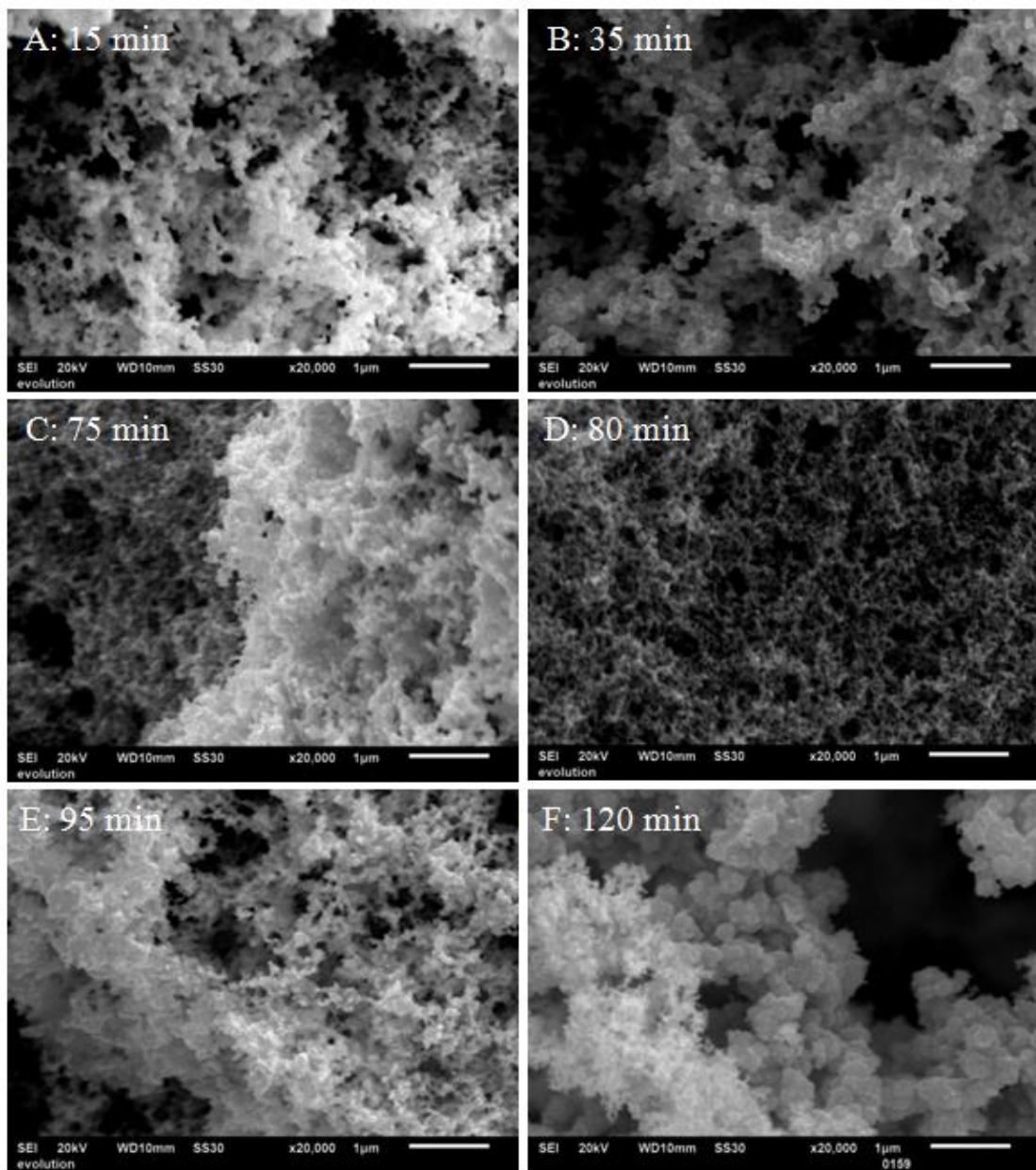


Figure 4.23 SEM micrographs evolution of gold nanopowders from different reduction times

4.7 The production of the gold nanopowders prototype

Gold nanopowders can apply for simple prototype of jewelry and decorative applications. Gold nanopowders were taken into the mold, and then they were pressed with compressor pressure. Gold nanopowders were contacted together with other particles and took the structure after the mold. This prototype was calcined at 800°C for 20 min. The residue of reducing agent and stabilizer were eliminated in this process. The prototype after calcination was 99.99% pure gold. The shrinkage of the prototype is 7.5%. The prototype consumes lower temperature to sintering that save a lot of energy.

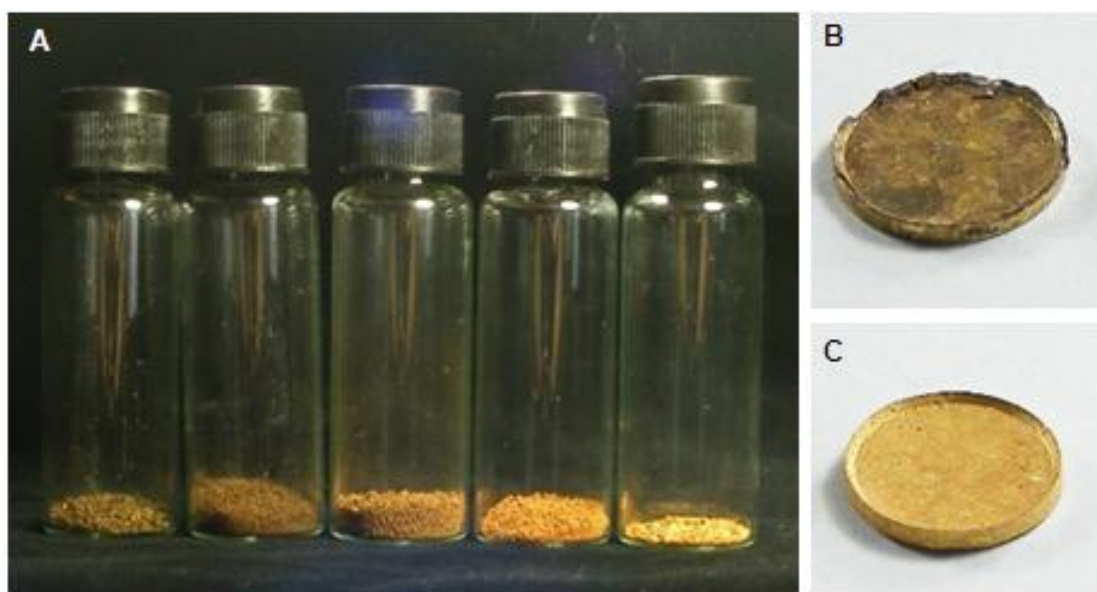


Figure 4.24 Digital images of A: gold nanopowders from different size, B: prototype before calcination, and C: after calcination.

CHAPTER V

CONCLUSIONS

Gold nanopowders were successfully synthesized by chemical reduction of tetrachloroauric acid with agricultural products in alkaline condition acting as green reducing agents as well as stabilizer. After synthesis, gold nanopowders were purified by de-ionized water. Particles size, particles shape, and morphology of gold nanopowders were observed by mean of scanning electron microscope (SEM). From SEM micrographs, it is concluded that the synthesized gold nanopowders have spherical shape which can control size from 50 nm – 4 μ m.

In this study, reducing agents was varied in order to study the effects on size and size distribution. From our experiments, it is concluded that sucrose is the efficient reducing agent for synthesis gold nanopowders. Moreover, the changing in other parameters such as concentration of sodium hydroxide, concentration ratio of sucrose / gold ions, concentration of soluble starch, and incubation time between gold ion and soluble starch before the reduction reaction affected particle size and morphology.

At lower concentration of NaOH, gold nanopowders showed large spherical particle (size, 500–4000 nm), while smaller spherical shapes (size, 150-500 nm) were obtained at higher concentrations of NaOH.

At lower concentration ratio of sucrose/gold ions showed larger size (100-150 nm), while smaller spherical shapes (size, 50-80 nm) were obtained at higher concentrations ratio.

The lower concentration of soluble starch exhibited more degree of aggregation in gold nanopowders forming aggregated particles. The high concentration of soluble starch exhibited uniform gold nanopowders with less degree of aggregation. As the concentration of soluble starch increased, there is a significant decrease in the aggregation.

The increasing of incubation time between gold ion and soluble starch has effected on the uniformity. As longer incubation time, gold nanopowders were more uniformity than that at shorter incubation times.

Gold nanopowders can apply to simple prototypes for jewelry and decoration. This prototype was calcined at 800°C for 20 min. The shrinkage of the prototype is 7.5%. The prototype consumes lower temperature to sintering that save a lot of energy.

We successfully synthesized gold nanopowders *via* green synthesis, that combination of solvent, renewable agricultural reducing agent, and synthesized at room temperature. Gold nanopowders were controlled in spherical shape and size from 50 nm – 4 μm.

REFERENCES

- [1] Samal, A. K., Sreepasad, T.S., and Pradeep, T. Investigation of the role of NaBH_4 in the chemical synthesis of gold nanorods. Journal of Nanoparticles Research 12 (2010): 1777–1786.
- [2] Sun, X.P., Zhang, Z. L., Zhang, B. L., Dong, X. D., Dong, S. J., and Wang, E. K. Preparation of gold nanoparticles protected with polyelectrolyte. Chinese Chemical Letter 14 (2003): 866 – 869.
- [3] Otaqsara, S.M.T. Biosynthesis of quasi-spherical Ag nanoparticle by *Pseudomonas aeruginosa* as a bioreducing agent. The European Physical Journal Applied Physics 56 (2011): 30402.
- [4] Sathish, K. K., Amutha, R., Palaniappan, A., and Sheela, B. Synthesis of gold nanoparticles: an ecofriendly approach using *Hansenula anomala*. ACS Applied Materials & Interfaces 3 (2011): 1418–1425.
- [5] Li, G., He, D., Qian, Y., Guan, B., Gao, S., Cui, Y., Yokoyama, K., and Wang, L. Fungus-mediated green synthesis of silver nanoparticles using *Aspergillus terreus*. International Journal of Molecular Sciences 13 (2012): 466-476.
- [6] Huang, H., and Yang X. Synthesis of polysaccharide-stabilized gold and silver nanoparticles: a green method. Carbohydrate Research 339 (2004): 2627–2631.
- [7] Engelbrekt, C., Sørensen, K.H., Zhang, J., Welinder, A.C., Jensen, P. S., and Ulstrup, J. Green synthesis of gold nanoparticles with starch–glucose and application in bioelectrochemistry. Journal of Materials Chemistry 19 (2009): 7839–7847.
- [8] Song, J. Y., Jang H. K., and Kim, B. S. Biological synthesis of gold nanoparticles using *Magnolia kobus* and *Diopyros kaki* leaf extracts. Process Biochemistry 44 (2009): 1133-1138.

- [9] Williams, D., Bridges, J., Jong, W.D., Jung, T., Rydzynski, K. The appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies. European Commission Health & Consumer Protection Directorate General (2006)
- [10] Kelsall, R.W., and Hamley, I.W. Generic methodologies for nanotechnology: classification and fabrication. Geoghegan, M. Nanoscale Science & Technology, John Wiley & Sons (2006)
- [11] Yong, K.T., Swihart, M.T., Ding, H., and Prasad, P.N. Preparation of gold nanoparticles and their applications in anisotropic nanoparticle synthesis and bioimaging. Plasmonics 4 (2009): 79-93.
- [12] Blaber, M.G., Ford, M.J., and Cortie, M.B. The physics and optical properties of gold. Corti, C., Holliday, R., Gold Science and Applications, 13-30. CRC press, Boca Raton, 2010.
- [13] Fendler, J.H. Chemical self assembly for electronic application. Chemistry of Materials 13 (2001): 3196-3210.
- [14] Krasteva, N., Besnard, I., Guse, B., Bauer, R. E., Mcullen, K., Yasuda, A., and Vossmeier, T. Self-assembled gold nanoparticle/dendrimer composite films for vapor sensing applications. Nano Letters 2 (2002): 551-555.
- [15] Bhattacharya, R., and Murkherjee, P. Biological properties of 'naked' metal nanoparticles. Advanced Drug Delivery Reviews 60 (2008): 1289-1306.
- [16] Lue, J.T. A review of characterization and property studies of metallic nanoparticles. Journal of Physics and Chemistry of Solids 62 (2001): 1599-1612.
- [17] Eusits, S., and El-Sayed, M.A. Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes. Chemical Society Reviews 35 (2006): 209-217.
- [18] Toshima, N., and Yonezawa, T. Bimetallic nanoparticles-novel materials for chemical and physical application. New Journal of Chemistry (1998): 1179-1201.

- [19] Kashiwagi, Y., Kikuchi, C., Kurashima, F., and Anzai, J. Electrocatalytic reduction of aldehydes and ketones on nickel(II) tetraazamacrocyclic complex-modified graphite felt electrode. Journal of Organometallic Chemistry 662 (2002): 9-13.
- [20] Turkevich, J. Colloidal gold part I historical and preparative aspects, morphology and structure. Gold Bulletin 18 (1985): 86-91.
- [21] Turkevich, J. Colloidal gold part II color, coagulation, adhesion, alloying and catalytic properties. Gold Bulletin 18 (1985): 125-131.
- [22] LaMer, K.V., and Dinegar, H. R. Theory, Production and Mechanism of Formation of Monodispersed Hydrosols. Journal of American Chemical Society 72 (1950): 4847-4854.
- [23] Finney, E.E., and Finke, R.G. Nanocluster nucleation and growth kinetic and mechanistic studies: A review emphasizing transition-metal nanoclusters. Journal of Colloid and Interface Science 317 (2008): 351-174.
- [24] Xia, Y. Xiong, Y., Lim, B., and Skrabalak, E. S. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? Angewandte Chemie International edition 2009, 48, 60 – 103.
- [25] Watzky, M. A., and Finke, R.G. Transition metal nanocluster formation kinetic and mechanistic studies. A new mechanism when hydrogen is the reductant: slow, continuous nucleation and fast autocatalytic surface growth. Journal of American Chemical Society 119 (1997): 10382-10400.
- [26] Sugimoto, T. Underlying mechanisms in size control of uniform nanoparticles. Journal of Colloid and Interface Science 309 (2007): 106-118.
- [27] Kirchoff, M.M. promoting green engineering through green chemistry. Environmental Science & Technology 37 (2003): 5349-5353.
- [28] Anastas, P.T., and Kirchoff, M.M. Origins, current status, and future challenges of green chemistry. Accounts of Chemical Research 35 (2002): 686-694.
- [29] Harper, S.L., Dahl, J.A., Maddux, B.L.S., Tanguay, R.L., and Hutchison, J.E. Proactively designing nanomaterials to enhance performance and minimize hazard. International Journal of Nanotechnology 5 (2008): 124-142.

- [30] Clarke, M. A., Edey, L.A., and Eggleston, G. Sucrose decomposition in aqueous, and losses in sugar manufacture and refining. Advances in Carbohydrate Chemistry and Biochemistry D. Horton, Academic press, (1997): 441 – 466.
- [31] Gleason, W. B., and Barker, R. Oxidation of Pentose in alkaline solution. Canadian Journal of Chemistry 49 (1971): 1425-1432.
- [32] Yang, B.Y., and Montgomery, R. Alkaline degradation of fructofuranosides. Carbohydrate Research 280 (1996): 47-57.
- [33] Novotny, O., Cejpek, K., and Velisek, J. Formation of carboxylic acids during degradation of monosaccharides. Czech Journal of Food Sciences 26 (2008): 117-131.
- [34] Wade, L.G. Carbohydrates and nucleic acid. Organic Chemistry 6 (2004): 1097-1147
- [35] Knill, C.J and Kennedy, J.F. Degradation of cellulose under alkaline conditions. Carbohydrate Polymers 51 (2003): 281-300.
- [36] Andreescu, D., Sau, T.K., and Goia, D.V. Stabilizer-free nanosized gold sols. Journal of Colloid and Interface Science 298 (2006): 742-751.
- [37] Finney, E.E., and Finke, R.G. Nanocluster nucleation and growth kinetic and mechanistic studies: A review emphasizing transition-metal nanoclusters. Journal of Colloid and Interface Science 317 (2008): 351–374.
- [38] Ji, X., Song, X., Li, J., Bai, Y., Yang, W., and Peng, X. Size control of gold nanocrystals in citrate reduction: the third role of citrate. Journal of American Chemical Society 129 (2007): 13939-19348.
- [39] Katti, K.K., Kattumuri, V., Bhaskaran, S., Katti, K.V., and Kannan, R., Facile and general method for synthesis of sugar-coated gold nanoparticles. International Journal of Green Nanotechnology: Biomedicine 1 (2009): B53-B59.

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