Synthesis of gold nanoparticles by using skim natural rubber latex

Palida Pongsanon, Parichat Khonglek and Panu Danwanichakul*

*Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani 12120, Thailand

Abstract

Green synthesis is a low cost and eco-friendly method for gold nanoparticles (AuNPs). Gold (III) chloride trihydrate ($HAuCl_4 3H_2O$) was used as a precursor and skim natural rubber latex (SNRL) and only its serum was either used as a reducing agent. The initial finding showed that using the serum yielded better results regarding the size and quantity of synthesized AuNPs. The synthesis of AuNPs was done using the serum with the dilution factor of 7 and 1.2 mM $HAuCl_4$ solution at 80°C. The conductivity and pH were changed along the reaction. AuNPs were of spherical shape and their diameters were around 30 – 40 nm. The absorbance peaks were obviously seen around 520-550 nm. The reaction had not completed yet after 7 h but the rate was slower. In addition, using 2%SDS was not necessary.

Keyword: Gold, Nanoparticles, Green synthesis, Skim latex, Natural rubber

1. Introduction

Natural rubber is one of the main agricultural products of Thailand. It is usually produced in the form of rubber latex and rubber block. The latex from the field will be preserved with ammonia before entering centrifugation process to produce concentrated latex with rubber content around 60%. With this process, skim natural rubber latex (SNRL) with the rubber content around 4-6% is obtained as a by-product. Usually, it is coagulated with sulfuric acid solution at a high concentration to finally yield skim block with a large amount of acidic waste water.

Along a large production of concentrated latex, even larger volume of skim rubber latex could be expected. Considering a small fraction of rubber particles in skim latex, some research attempted to find a good application for it. SNRL was applied as raw materials for the production of glue without proteins so it did not cause allergies, which was appropriate for medical adhesive. In addition, it could also be used to produce chewing gum [1].

Taking into account a large liquid part (serum) of SNRL which contains many substances, one of them is a sugar called L-Quebrachitol which is a precursor to the synthesis of anticancer drugs. It is also a sugar sweetener for diabetics [2]. Besides sugars, there are proteins, fatty acids, resin, ammonia and other materials in the serum, which attract our attention as a source of important agents taking part in synthesis of nanoparticles.

In one of our earlier attempts, SNRL was used to synthesize silver nanoparticles at room temperature. It was found that nanoparticles could inhibit the growth of *Escherichia coli* bacteria that caused diarrhea in children and adults. They could also inhibit the growth of bacteria, *Staphylococcus aureus* that caused food poisoning, nausea, vomiting and diarrhea [3].

Such synthesis falls in the category of green synthesis, where usages of synthetic hazardous chemicals and energy consumption could be reduced. In this research, we follow the same path as to continue to apply SNRL as a source of useful substances to replace the synthetic ones. The synthesis of gold nanoparticles (AuNPs) is of interest since AuNPs have several unique properties that are different or better than other nanoparticles, such as stability and oxidation stability, sensitivity to detection, conductivity properties [4]. These properties are important for applications, such as detector, sensor, catalyst and simultaneous application of electronic equipment.

AuNPs have been synthesized before on natural rubber membranes which could inhibit the growth of Leishmania brasiliensis. So it could be applied to the bandage to enhance the ability to reduce infection on the wound [5].

This research focused on how to applied SNRL in the synthesis of AuNPs by both using the diluted SNRL or using the diluted serum from SNRL. Moreover, the aspect of adding SDS as a surfactant was also tested in this work. To one end, the AuNPs will add the value to the low cost SNRL and to the other end, this work is environmental friendly.

2. Research Methodology

2.1 Materials

Skim natural rubber latex (SNRL) with 3.7073 wt% DRC was obtained from Thai Eastern Group, Thailand. Gold (III) trihydrate, as a precursor for gold ions, was purchased from Sigma Aldrich. Polyacrylamide (PAM) (cationic type) was from Water Doctor Company, Ltd, Thailand. Sodium dodecyl sulphate (SDS) was purchased from Ajax Finechem. All chemicals were used without further purification.

2.2 Experimental

1. Synthesis of gold nanoparticles (AuNPs) by using SNRL and characterization.

AuNPs were synthesized by using 1.2 mM $HAuCl_4$ solution and using SNRL as a source of reducing agent. SNRL was diluted with pure water with the dilution factor of 7. It is called the diluted SNRL throughout this work. Once both liquids were mixed, the mixture was sonicated in an ultrasonic bath at the controlled temperature of 80°C for about 3 h. The properties of AuNPs suspension were characterized by visible spectrophotometer, electrical conductivity meter, pH meter while the structures of AuNPs was studied with transmission electron microscopy (TEM).

2. Synthesis of AuNPs by using serum from SNRL and characterization.

The serum of SNRL was obtained after coagulation of rubber particles using 0.5 mM polyacrylamide solution of 350 ml. The PAM solution was added in the 500 ml SNRL, followed by stirring the mixture well and then separating the coagulum from serum using filter paper. The experiments were done to study the effect of reaction time.

Before use, the serum was diluted with pure water with the dilution factor of 7. Throughout this work, ot is called the diluted serum. The concentration of $HAuCl_4$ solution was 1.2 mM. After the two liquids were mixed, the mixture was left for the reaction to proceed for 1, 2, 3, 4, 5, 6 and 7 h. All samples were synthesized at 80°C in the ultrasonic bath. As in Section 2.2.2, the properties of AuNPs suspension were characterized by visible spectrophotometer, electrical conductivity meter, pH meter and AuNPs pictures was obtained using transmission electron microscopy (TEM).

3. The effect of SDS in the synthesis of AuNPs in the serum from SNRL.

The experiment was done to show the effect of synthetic surfactant, which in this case is SDS, in the already presence of bio-surfactant, which is dissolvable proteins in the serum. The synthesis of AuNPs was initiated by mixing 1.2 mM $HAuCl_4$ solution with 2% SDS and the diluted serum to compare with the base condition (AuNPs synthesized by using the diluted serum and 1.2 mM $HAuCl_4$ solution), which possessed only dissolvable proteins. The mixture was then sonicated in the ultrasonic bath. All of samples were synthesized at 80°C for about 3 h.

3 Research Results and Discussion

3.1 Comparison of AuNPs syntheses in SNRL and serum

The results were compared for the case of using the diluted SNRL and the diluted serum, using the same concentration of 1.2 mM for the gold (III) chloride solution and the reaction time of 3 h. It was believed that some organic materials in the serum such as sugars and carboxylic acids could act as reducing agent and proteins could act as a stabilizing agent in the reduction reaction of gold ions. In the case of the diluted SNRL, the rubber particles could play a role of capping agent in the reaction.

The results showed that AuNPs quantity from synthesis in the diluted serum was more than that from synthesis in the diluted SNRL because rubber particles in SNRL may interfere with the reduction reaction to turn gold ions to gold nanoparticles. Figure 1(a) shows that the absorbance (ABS) peak of AuNPs synthesized by using serum is around 532 nm while there is no clear peak appearing for AuNPs synthesized in the diluted SNRL, confirming that rubber particles in the gold particles suspension absorbed more light at a wide range of wavelength from visible light source and obscured the characteristic peak of AuNPs.

As seen in Figure 1(b), the size of the AuNPs synthesized in the diluted serum was in the range of 10-60 nm and mostly found to be around 30-40 nm, whereas the size of particles in the diluted SNRL was in the range of 10-40 nm and mostly found to be around 20-30 nm. The size distributions of both systems are shown in Figures 2(a) and 2(b). One explanation for such finding would be that when gold ions were added into the diluted SNRL, the cationic ions could interact with the negatively charged surfaces of the rubber particles, leading to the loss of gold ions to undergo reduction reaction. The rate of the reaction in the diluted SNRL system might then be slower than in the diluted serum.

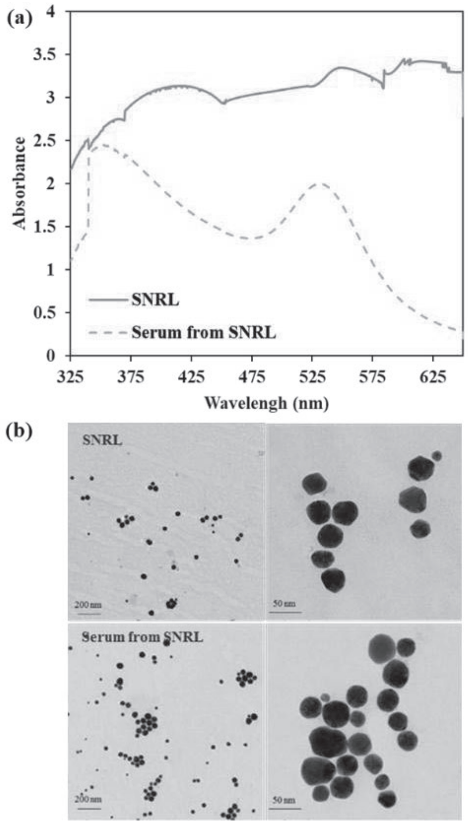

Figure 1 (a) The ABS of suspensions and (b) TEM micrographs of AuNPs synthesized by using the diluted SNRL and using the diluted serum.

When the negatively charged surfaces of rubber particles in the diluted SNRL were neutralized by some cationic gold ions, the attractive Van der Waals forces among particles could bring them closer together and form larger aggregates. Such coagulation made it more difficult to separate gold nanoparticles from rubber particles. This would not be a problem if AuNPs were directly applied for rubber products. However, for an extensive range of applications, AuNPs synthesized in the diluted serum should be studied more in detail.

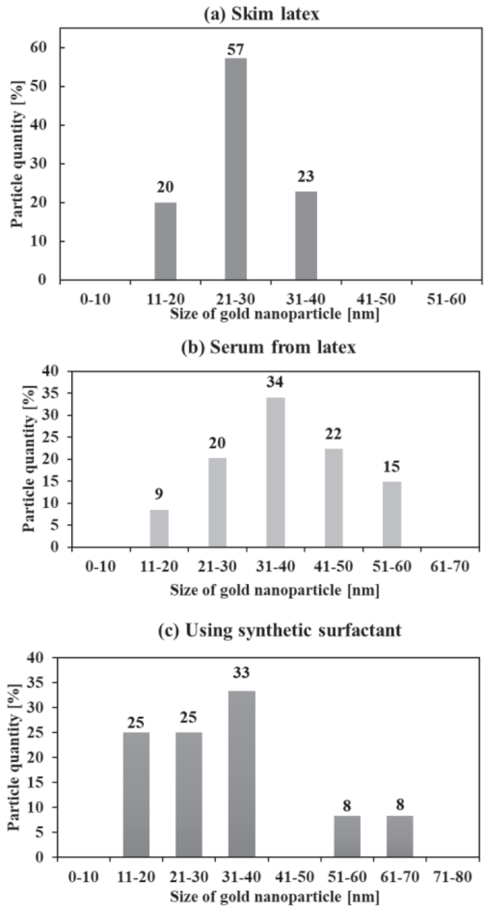

Figure 2 Size distribution of AuNPs synthesized by using (a) diluted SNRL and 1.2 mM gold (III) chloride concentration, (b) using the diluted serum and 1.2 mM gold (III) chloride concentration and (c) using the diluted serum and 1.2 mM gold (III) chloride concentration in 2% SDS solution (using synthetic surfactant)

Table 1 pH and conductivity of AuNPs suspensions using SNRL, the serum, and the serum with 2% SDS

Synthesis	At 0 h		At 3 h	
	pH	**Conductivity (μs)**	**pH**	**Conductivity (μs)**
SNRL	9.13	2050	9.22	2160
Serum from SNRL	9.05	1630	8.77	1690
Using synthetic surfactant (SDS)	9.18	1400	8.43	1480

Table 1 shows the values of pH and conductivities of synthesized AuNPs suspensions. The conductivity of all suspensions did not change much during the reaction, implying that AuNPs rarely induced the ionic motion in the suspension. It seemed that PAM used to coagulate rubber particles could remove some ions in the original SNRL, yielding lower conductivity of suspension even though PAM itself is cationic.

The pH of the diluted SNRL and the diluted serum shows that both liquids were basic since there was some content of remaining ammonia which was used as the common preservative in the production of rubber concentrate latex. Ammonia was thought to form a complex with gold ions and might be involved in their reduction reaction. In both situations, pH of the suspension would be lower when the reaction continued. The results in Table 1 imply that the reaction rate in the diluted SNRL was slower than that in the diluted serum. At this point, the effect of SDS in the synthesis should be discussed.

3.2 The effect of SDS in the synthesis using the serum

Naturally, there is some content of proteins in SNRL so after removing rubber particles using PAM, some quantity of proteins has to remain in the serum. Proteins are thought to be a natural surfactant capable of controlling the size of growing nanoparticles. Here, 2% SDS was added to the diluted serum and upon applying the same dilution factor of serum, the same concentration of gold precursor and the same reaction time, the results were obtained. Some are already shown in Figure 2 and Table 1.

Figure 3(a) shows that ABS patterns of both AuNPs suspensions are the same, showing the prominent peak at 532 nm corresponding to the presence of AuNPs. However, the peak in case of the addition of SDS was lower, implying that a smaller number of AuNPs were obtained, possibly because SDS contains anionic part that could interact with the cationic gold ions leading to fewer free gold ions to undergo the reduction reaction.

In addition, Figure 3(b) shows TEM pictures of AuNPs and the size distribution is shown in Figure 1(c). It is seen that size of particles from the synthesis using SDS ranges from 10-60 nm and most of them are 30-40 nm. However, the number of particles with small sizes is greater, showing some slight degree of particle size controlling of SDS. Because of a small number of synthesized AuNPs when using SDS, it was decided that in the next study, no SDS would be added.

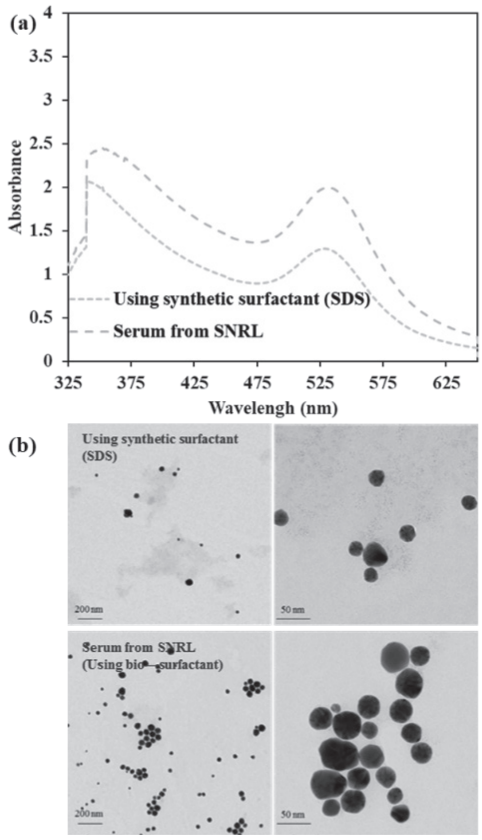

Figure 3 (a) The ABS of suspensions and (b) TEM micrographs of AuNPs synthesized by using the serum and the serum with added SDS as a synthetic surfactant

3.3 The effect of reaction time on the characteristics of gold nanoparticles synthesized by using the serum

Figure 4(a) shows the color of AuNPs nanoparticles suspensions. The color of darker red wine corresponded with a longer reaction time. It could be predicted that more AuNPs could be synthesized over time as represented by the higher ABS in Figure 4(b) when the reaction time increased. The rate of reaction time was quite rapid in the first hour as seen in the large increase in ABS of the characteristic peak around 529 nm.

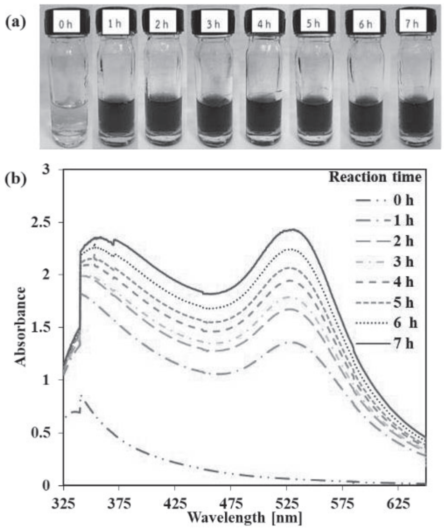

Figure 4 (a) Suspensions of AuNPs synthesized by using the diluted serum with 1.2 mM gold (III) chloride at reaction time of 0, 1, 2, 3, 4, 5, 6 and 7 h and (b) the ABS of the corresponding suspensions.

Table 2 pH and conductivity of AuNPs suspensions by the diluted serum with 1.2 gold (III) chloride concentration at various reaction times

Time (h)	pH	Conductivity (μs)
0	5.84	1020
1	6.01	1120
2	6.28	1120
3	6.21	1130
4	6.23	1200
5	6.07	1220
6	5.84	1170
7	5.74	1110

Table 2 is consistent with other tables where the fixed condition of 1.2 mM gold ion concentration and serum dilution factor of 7 was considered. It is seen that pH value increased upon increasing reaction time up to 2 hours since fewer gold ions present in the suspension and the conductivity did not change much during the prolonged time of reaction.

4. Conclusion

When fixing the dilution factor of serum and the concentration of gold (III) chloride solution, increasing the reaction time changed the color of AuNPs solution from yellow to red wine and increased the ABS peak, indicating the formation of more AuNPs (corresponding ABS peak at 520-550 nm).

In this research, AuNPs were synthesized in the diluted serum as the source of reducing agent by using the serum with dilution factor of 7 and using $HAuCl_4$ concentration of 1.2 mM at 80 °C for 2-3 hours. The conductivity and pH were not changed much along the reaction. AuNPs is of spherical shape and their average diameters were around 30-40 nm. In addition, this research showed that the serum could be applied without adding SDS as a surfactant possible because there were sufficient amount of proteins already present in the diluted serum.

5. Acknowledgments

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6. References

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