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Synthesis of silver nanoparticles in skim natural rubber latex at room temperature

Thanawat Suwatthanarak, Bhumin Than-ardna, Duangkamol Danwanichakul, Panu Danwanichakul *

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

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ABSTRACT

Silver nanoparticles (AgNPs) were synthesized in low cost skim natural rubber latex by adding silver nitrate as a source of silver ions. Left-over ammonia in latex was believed to form a complex with silver ions before reacting with the reducing agents which were glucose and other organic compounds in latex. Moreover, protein in latex could also control the growth of the particles by acting as a stabilizing agent. Many factors, which include ammonia content, D-glucose content and BSA protein content, were studied to clarify their effects in the synthesis. The emergence of AgNPs was checked with UV–visible spectrometer and electrical conductivity meter. Transmission electron microscope (TEM) was applied to study the particle morphology. The results showed that UV absorbance (ABS) and conductivity of the reacting suspension increased when ammonia content and D-glucose content increased, implying an increasing number or growth of particles. In contrast, ABS and conductivity decreased with increasing BSA content, showing that smaller particles were formed. The TEM images confirmed that the size of AgNPs in the none-added sample was 6–26 nm. The synthesized AgNPs could inhibit the growth of *Escherichia coli* and *Staphylococcus aureus*.

1. Introduction

Silver nanoparticles (AgNPs) have been applied to many consumer products because of their excellent properties, especially in antibacterial activity [1] and bio/chemical detection [2–4]. The applications seem to increase year after year so the production rate will be boosted soon. However, AgNPs synthesis usually involves chemical reduction reaction in which toxic chemicals are used. Therefore, more sustainable methods have been proposed which are called “green synthesis” in which the raw materials are already there in nature, particularly in plant extracts.

Previous studies have reported that many natural compounds could act as a capping agent as well as reducing agent in the green synthesis of AgNPs such as *J. curcascan* [5] and *Rhodomyrtus tomentosa* acetone extract (RAE) [6]. Hyaluronan (HA) as a reducing agent and soft template in AgNPs synthesis was investigated [7]. Moreover, Hydroxypropyl starch (HSP) was used as a reducing agent and a stabilizing agent for the formation of AgNPs [8].

Natural rubber latex from *Hevea brasiliensis* is a colloidal system of cis-1,4-polyisoprene called as rubber particles. In general, fresh latex composed of about 30 wt% dry rubber content (DRC) is commonly preserved by adding ammonia and then is centrifuged to obtain concentrated natural rubber latex with about 60 wt% DRC as a valuable raw material in rubber industry together with skim natural rubber latex (SNRL) with about 5 wt% DRC as a low cost by-product or a waste in some small factories.

Recently, Guidelli [9] synthesized AgNPs in concentrated latex at 100 °C and reported that rubber particles acted as a dispersing and/or capping agent. In addition to rubber particles, some non-rubber components in latex including protein, sugar and left-over ammonia played an important role in the synthesis. Protein could act as a natural surfactant and ammonia coupled with sugar involved in the reduction reaction by acting as the reducing agents [9,10].

As a result of centrifugation, SNRL contains the larger amount of non-rubber components, which play an important role in the synthesis, than concentrated one. On the basis of 5 wt% DRC, skim latex contains mostly water and approximately 3.25 wt% proteins, 0.425 wt% lipid, 3.125 wt% carbohydrates/sugars (L-quebrachitol, sucrose, glucose, galacose, fructose, raffinose and two pentoses) [11,12].

Previously, our group found that AgNPs could be synthesized in skim latex at 80 °C with a much higher rate, i.e. the rapid change of suspension color, than in concentrated latex and the particle sizes ranged from 70–490 nm in skim latex, which was too large [13]. Later, we lowered the reaction rate in skim latex by lowering the

* Corresponding author.
E-mail address: dpanu@engr.tu.ac.th (P. Danwanichakul).

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temperature. From SEM micrographs, the average size of particles obtained immediately after mixing latex and silver precursor at the temperature of 26, 29 and 32 °C was 26, 231 and 305 nm, respectively [14]. It showed that synthesis temperature had a considerable effect on the particle size as reported by Sun et al. [15]. Thus, this work focuses on the green synthesis of AgNPs using skim latex at room temperature.

2. Materials and experimental

2.1. Materials

SNRL with 4.345 wt% DRC (with about 0.362 wt% left-over ammonia) was obtained from Thai eastern group, Chonburi, Thailand. Silver nitrate, as a precursor for silver ions, was supplied by Merck Ltd., Germany. Bovine serum albumin (BSA) was purchased from Sigma Aldrich CO., USA. Ammonium hydroxide (NH_4OH) was supplied by J.T. Baker. D-glucose anhydrous was purchased from Ajax Finechem Pty. Ltd. Dialysis tube with molecular weight cut-off (MWCO) of 12,000–14,000 Da, was purchased from Spectrum Laboratories, Inc., USA. All chemicals were used without further purification.

2.2. Experimental

2.2.1. Silver nanoparticle synthesis and characterization

8 mM-silver nitrate solution was mixed with diluted SNRL with 0.05%wt DRC to obtain the suspension with 1.2 mM Ag^+. It was stirred at 100 rpm for 45 min at room temperature (26 °C). Next, it was immediately transferred into a dialysis tube which was kept in a beaker containing pure water with the volume ratio of suspension to water of 1 to 30. It was constantly stirred at a low speed for 24 h in order to retard or possibly stop the reaction.

Many factors were studied to confirm our hypothesis and to clarify the effect in the synthesis. Those are concentrations of ammonia, D-glucose and BSA protein in the system. Ammonia concentration in SNRL was increased from 0.362% to 0.377% by adding 5 µl-NH_4OH into 10 ml-SNRL. D-glucose concentration and BSA protein concentration were increased by adding 100 ppm-D-glucose and 100 ppm- BSA protein into the system.

The suspension was characterized both before and after dialysis for 24 h with conductivity meter (HM, COM-100), pH meter (Eutech, pH 510) and UV–vis spectrophotometer (METASH, V-5100) at the wavelength of 340–580 nm. Transmission electron microscope (TEM) (JEOL JEM-2010) was applied to study the morphology of synthesized AgNPs.

2.2.2. Antimicrobial activity test

The antimicrobial activity of the particles against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) was performed according to NCCLS M2-A9 by using performance standards for antimicrobial disk susceptibility test. Vancomycin and Gentamicin were used as a gram-positive control and a gram-negative control, respectively.

3. Results and discussion

Immediately after mixing, the color of every suspension changed from white to light brown implying the emergence of AgNPs as reported in Ref. [9]. The absorbance (ABS) band of all AgNPs suspensions in Fig. 1 showed the peak around 375–390 nm which were in the range of 350–460 nm corresponding to the absorbance peak of AgNPs [4,15,16]. On synthesis day, when the concentration of ammonia or D-glucose was increased, the ABS band of suspension increased and the peak shifted to a higher wavelength implying the formation of more and larger AgNPs. Ag^+ ions were reduced to Ag^0 nuclei or AgNP by sugar as a reducing agent because it had a free aldehyde group according to Eq. (2) [17] and/or by the transfer of electrons from amine group of ammonia to the metal ion as shown in Eq. (3) [10]. With a higher reaction rate, more AgNPs were generated yielding the darker color of suspension. However, the increase in BSA concentration caused lower ABS band indicating that smaller AgNPs were formed. Proteins could often be denatured even by unintentional foaming, thereby possessing surfactant properties [18]. In this study, proteins in skim latex probably formed a micelle around Ag^0 nuclei so it could

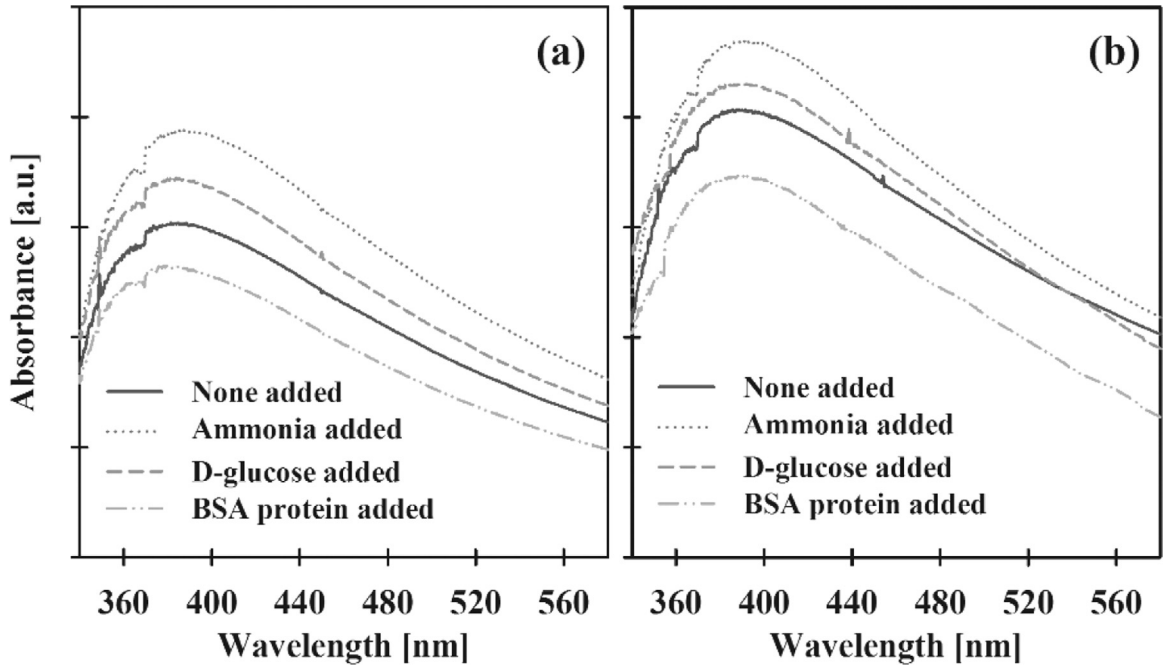

Fig. 1. The ABS of suspension. (a) On the synthesis day. (b) After 24-h dialysis.