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Durian Peeling Extract Mediated Green Synthesis of Silver Nanoparticles

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Abstract. In this work, silver nanoparticles (AgNPs) were successfully synthesized from $AgNO_3$ through a simple and eco-friendly method, also called the green synthesis, using Mon Thong durian (*Durio zibethinus* L.) peeling extract. The main role in synthesis mechanism of AgNPs is using polysaccharides in durian rind as a reducing agent as well as stabilizer. The appearance of a yellowish-brown color in mixture of $AgNO_3$ solution and durian rind extract is the indication of formation of AgNPs. The synthesized AgNPs were characterized by UV-visible spectroscopy, transmission electron microscopy (TEM) and X-ray diffraction (XRD) spectrometry. The AgNPs were found to be polycrystalline in nature and spherical particles with diameter of 11.7 ± 3.2 nm. The crystallinity with fcc phase is evidenced by clear lattice fringes in SAED pattern and diffraction peaks in the XRD pattern corresponding to the (111), (200), (220), and (311) planes.

Introduction

In the recent phase of rapid developments in nanotechnology, nanoparticles of noble metals such as silver, gold, and copper, have been created widely due to their exceptional electronic, catalytic, optical, magnetic and other physical and chemical properties that exhibit completely new or improved properties as compare to the bulk one [1-2]. Among various metal nanoparticles, AgNPs are the most extensively studied material because of their distinctive properties, such as good conductivity, chemical stability, catalytic and antibacterial activity [3]. A number of techniques including chemical and physical method were developed to synthesize AgNPs such as chemical reduction, electrochemical reduction, photochemical reduction, and heat evaporation [4]. Chemical reduction is the most frequently applied method for preparation of AgNPs as stable, colloidal dispersions in water or organic solvents [3]. Unfortunately, many reducing agents are hazardous chemicals, low material conversions, high energy requirements, difficult and wasteful purifications [5]. To eliminate these problems, green synthesis have emerged recently. The key issues of green synthesis are cost effective, an eco-friendly benign as reducing agent, and a nontoxic material as a stabilizer.

The concept of green AgNPs preparation was first developed by Raveendran *et al*. [6]. They used β-D-glucose as the reducing agent and starch as a capping agent to synthesize AgNPs. Subsequently, many researchers have attempted to use plants/plant parts and natural products, such as lemongrass plant extract [7], basil plant extract [8], honey [9] and edible mushroom [10], in the green synthesis of AgNPs. They are the potential foodstuff or food ingredient in our daily life, therefore, they should be preserved for mankind consumption instead of theirs application for preparing nanoparticles. Here, it is a report on a simple, cost effective, and environmentally benign synthesis of AgNPs using biowaste or agricultural waste as a resource of valuable reducing and capping agent.

Durian (*Durio zibethinus* L.) - the king of fruit - is cultivated in Thailand about 200 varieties for consumption and exportation [11]. Between May and August, massive amounts of durian peeling are disposed of as waste which could lead to environmental problems [12]. Therefore, research and development to derive benefit from plant waste is an interesting subject for Thailand and other countries which export agricultural foods. Due to the durian peeling composed mainly of carbohydrate [12-13], it is naturally-occurring polysaccharides that can be both the reducing and stabilizing agent for synthesis of AgNPs without needing other chemical reducing agents. The

reaction is carried out in an aqueous solution in a process that is benign to the environment. For that reason, an efficient synthesis of AgNPs using durian peeling extract has been demonstrated in this work.

Experimental

Preparation of Durian Peeling Extract. The Mon Thong durian peeling, white peel part, was used throughout this work. The fresh durian peelings collected during the durian season from fruit market were cleaned, dried, powdered and kept in a freezer at -20 ºC until use.

About 100 g of powdered durian peelings were boiled in distilled water for 30 min. The resultant extract was filtered through Whatman filter paper No.5. This solution was treated as source extract and used for further experiments.

Synthesis and Characterization of AgNPs. For AgNPs preparation, $AgNO_3$ was purchased from Poch chemical. 20 ml of source extract prepared in previous section was added to 20 ml of 1 mM $AgNO_3$ solution. Then, pH of the solution was adjusted to 8.5 using NaOH solution. The mixture solution was stirred properly with magnetic stirrer under ambient conditions until the solution color changed from light yellow to yellowish-brown. The bioreduction of Ag^+ ion in solution at different reaction time was monitored using UV-visible spectrometer (Avantes AvaSpec-2048). In order to investigate the particle size and shape of AgNPs, the AgNPs were imaged by Transmission electron Microscopy (JEOL JEM-2100) operating at an accelerating voltage of 200 kV. The TEM sample was prepared by drop-casting the AgNPs colloids on a carbon-coated copper grid followed by air-drying. X-ray diffraction (XRD) measurements were carried out using a D8 Advance Bruker Analytical X-ray system with a Cu Kα (λ = 1.54 Å). The sample for XRD measurement was prepared by casting the AgNPs colloid on silicon (100) wafer and subsequently air-drying under ambient conditions.

Results and Discussion

The solution color was changed from light yellow (source extract) to yellowish-brown due to reduction of Ag^+ ion to AgNPs, see Fig. 1(a). The color changes are due to the surface plasmon resonance of AgNPs in the visible region [14]. Formation of AgNPs in solution was confirmed using UV-vis spectra. Fig. 1(b) shows the absorption spectra of the reaction mixture at a pH of 8.5. The appearance of a single plasmon band has wavelength of maximum absorbance λ_{max} at 426 nm and broadening of peak indicates poly-dispersed nanoparticles [5, 9]. The reaction was completed within 3 h which can examine by no alteration of absorbance intensity.

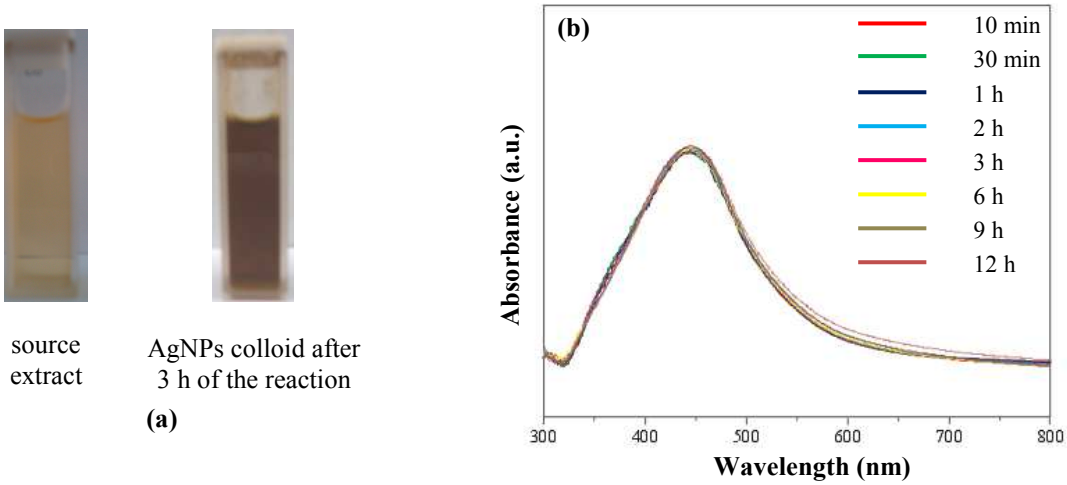

Fig. 1 (a) The figure shows two cuvettes containing powdered durian peeling extract solution and AgNPs colloid after 3 h of the reaction. (b) UV-visible absorption spectra of AgNPs colloid at different reaction times: 10 min to 12 h.

Durian peeling extract can reduced Ag^+ ion to AgNPs (Ag^0) because source extract composes of water-soluble polysaccharides that consists of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units and low protein content [12]. Glucose is normally used to be reducing agent in environmentally AgNPs preparation process. Determining glucose structure, a numerous amounts of hydroxyl group perform as a reducing agent as following mechanism [15]:

$$>R\text{-}OH + Ag^+ \rightarrow >R\text{-}O\text{-}Ag + H+$$
$$>R\text{-}O\text{-}Ag \rightarrow -R{=}O + Ag^0.$$

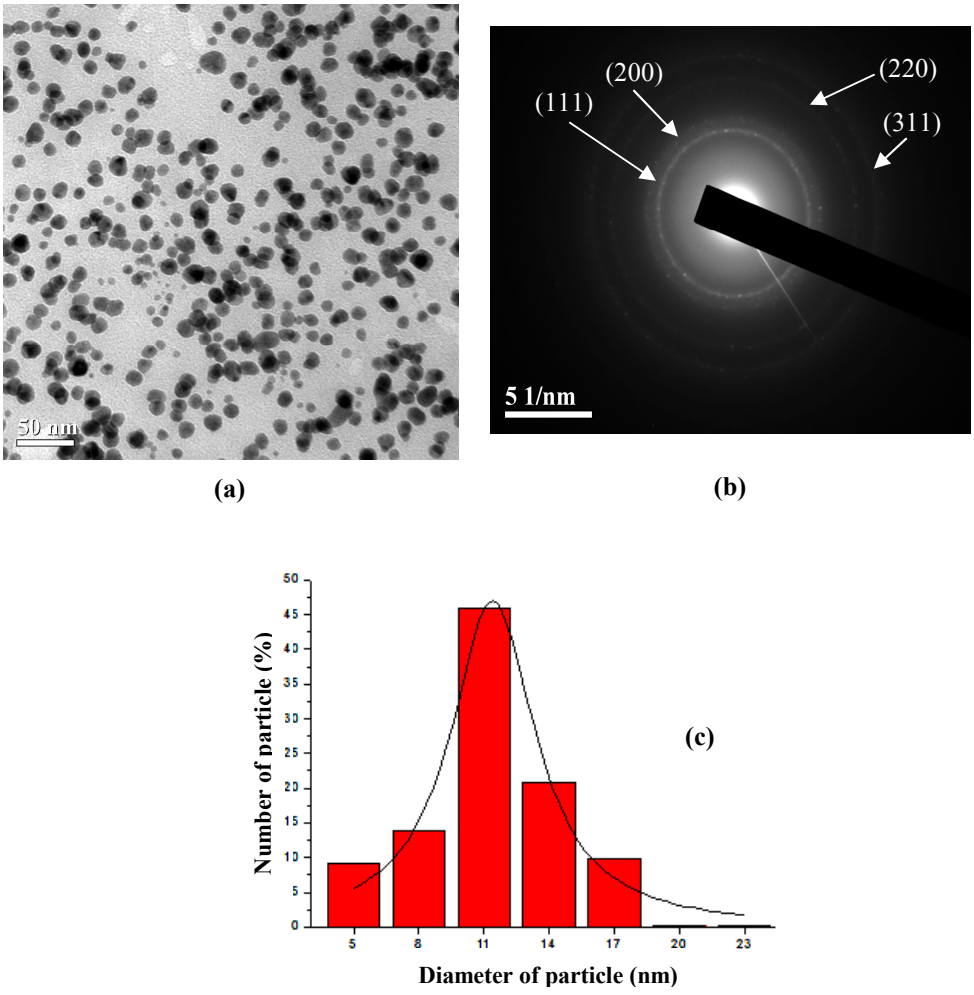

Fig. 2 TEM analysis results. (a) TEM image of AgNPs synthesized from 1 mM $AgNO_3$ solution and durian peeling extract at ambient conditions (solution pH = 8.5). (b) The SAED pattern of polycrystalline AgNPs. (b) Corresponding particle size distribution histogram of AgNPs.

Fig. 2 shows the TEM image of the synthesized AgNPs. Fig. 2(a) and (c) indicate that the synthesized AgNPs are mainly spherical and exhibit a relatively narrow size distribution with a mean particle diameter of 11.7 ± 3.2 nm. Futhermore, SAED pattern, as shown in Fig. 2(b), exhibits a set of rings suggesting that AgNPs are polycrystalline in nature. This corresponds to the XRD pattern as illustrated in Fig. 3. Fig. 3 shows the XRD patterns of AgNPs synthesized using durian peeling extract. The XRD pattern shows the clear peaks of face centered cubic (fcc) crystal structure (JCPDS file no. 04-0783) with diffraction peaks at 37º, 44º, 64º and 77º in the 2θ range of 20º to 80º which correspond to the (111), (200), (220) and (311) facets of silver, respectively. Therefore, the UV-visible spetra, TEM images and XRD pattern are a strong evidence to confirm that the method described here can be the effective approch to synthesis AgNPs.

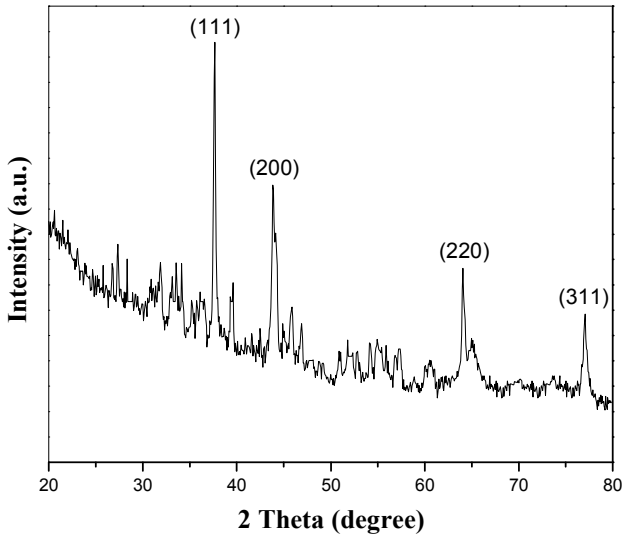

Fig. 3 XRD patterns of synthesized AgNPs.

Conclusions

In this work, we have proved that use of biowaste, fruit-hulls *Durio Zibethinus* L., as a low cost biological reducing agent is a reliable and eco-friendly process, and challenging alternative for synthesis of AgNPs. Furthermore, this method is possible to utilize agricultural waste more efficiently and it is a way to dispose of waste which could lead to environmental problem. The successful use of fruit-hulls *Durio Zibethinus* L. to single-pot biosynthesis of AgNPs may be involve with hydroxyl group of glucose as a reducing agent and starch or protein as a stabilizer. Only spherical particle with average diameter of 11.7 ± 3.2 nm was found.

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