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One-step green synthesis of chitosan-silver nanoparticles

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Abstract: In this work, the silver nanoparticles (AgNPs) were successfully synthesized using chitosan derived from shrimp shells through a simple and eco-friendly method called the green synthesis. The chitosan not only acted as the reducing agent for Ag^+, but also stabilized the AgNPs to protect nanoparticles from aggregation. The as-synthesized colloidal chitosan-AgNPs was yellowish-brown color with a maximum absorption wavelength at approximately 434 nm. The size and shape, and crystal structure of AgNPs were characterized by transmission electron microscopy and X-ray diffraction spectrometry, respectively. The results indicated that the AgNPs was spherical particles with a diameter of 23.5 ± 0.6 nm. The XRD pattern peaked at different diffraction angles corresponding to the (111), (200), (220), and (311) planes indicated that AgNPs had face-centered cubic (fcc) structure.

Keywords: Green synthesis, Silver nanoparticles, Chitosan, Biopolymer.

1. Introduction

In recent years, nanotechnology has been developed rapidly for widespread applications in various fields of science and technology including applied physics, materials science, chemistry, biology, electrical engineering, and mechanical engineering (Roy et al., 2013). Nanotechnology, which is multidisciplinary subject, divided into three main areas: nanobiotechnology, nanoelectronics, and nanomaterials. Nanomaterials research is a fundamental field of nanotechnology for the development of materials for supporting nanobiotechnology and nanoelectronics researches (Das and Mitra, 2014).

Nanomaterials, materials with structure in nanoscale ranging from 1-100 nm, regularly show unique properties in electronic, catalytic, optical, magnetic, physical, chemical and biological characteristics compared to their macro scale counterparts (Abou El-nour et al., 2010; Kshirsagar et al., 2011; Sharma et al., 2009). Consequently, the size-controllable synthesis of nanomaterials to obtain the specific property is an area of special scientific interest. Many researchers have attempted continually to synthesize noble metal nanoparticles for application in technological and environmental challenges in the areas of nanoelectronic devices, catalysis, medicine, consumer products and water treatment (Ahamed, 2010; Sharma et al., 2009). Among various metal nanoparticles, the silver nanoparticles (AgNPs) are the most extensively interesting metal nanoparticles because of their distinctive properties such as superior electrical conductivity, optical property, oxidative catalytic and antibacterial activity (Kassaee et al. 2008; Sharma et al., 2009). The chemical reduction is the most commonly approach for the synthesis of colloidal AgNPs dispersed in water or organic solvents. It is the reduction of silver ions (Ag^+) in aqueous solution to the formation of silver atoms (Ag^0) following with agglomeration into clusters and eventual growth into AgNPs using a reducing agent. A number of reports in the literature typically use sodium borohydride, sodium citrate, ascorbate, elemental hydrogen and ammonia as the reducing agent (Alarcon et al., 2015; Song et al., 2009; Szczepanowicz et al., 2010). Unfortunately, they

are hazardous chemicals, low material conversions, high energy requirements, difficult and wasteful purifications (Veerasamy et al., 2011).

Nowadays, the green chemistry or sustainable chemistry based on the usage of environmentally friendly materials and the development of eco-friendly processes has played an important role in many researches and developments. Three main steps based on green chemistry perspective are selection of solvent medium, selection of environmentally benign reducing agent, and selection of nontoxic substance for AgNPs stability (Abou El-nour et al., 2010; Sharma et al., 2009). Among many natural products, biopolymers, which can be acted as reducing agent and capping agent simultaneously, are the extreme interesting substances for the generation of polymer-AgNPs composites because of their potential application in numerous areas such as antibacterial packaging, drug delivery, sensor and actuator (Cheviron et al., 2014; Pandey et al., 2012; Yang et al., 2014).

Chitosan is a product of deacetylation of chitin, which is the second most abundant natural polysaccharide after cellulose. The production of chitin and chitosan is currently based on crab and shrimp shells (Kumar, 2000). Chitosan, a novel biopolymer, is nontoxic, biodegradable, biofunctional, biocompatible and antimicrobial material. Therefore, the aim of this work is to present a low cost, easy, rapid and environmentally benign method for the preparation of AgNPs using chitosan as both the reducing agent and the capping agent.

2. Materials and Methods

2.1 Preparation of chitosan solution

High molecular weight chitosan flakes with a degree of deacetylation of 90% derived from shrimp shells were provided by Seafresh Chitosan (Lab) Company Limited, Thailand. The chitosan powder was dissolved in 2%(v/v) acetic acid at room temperature for 12 h to achieve 1%(w/v) chitosan solution.

2.2 Synthesis of chitosan-silver nanoparticles

For the synthesis of the chitosan-AgNPs, the silver nitrate ($AgNO_3$) used as a source of Ag^+ was purchased from POCH. A stock solution of 52 mM $AgNO_3$ solution 15 ml of 52 mM was added into 30 ml of 1 %(w/v) chitosan solution and stirred vigorously for 1 h. Then, the homogeneous solution was heated at 121 °C and 15 psi for 15 min in an autoclave. After heat treatment, the solution color, absorption spectrum, AgNP size and morphology, and crystal structure were investigated. The characterization methods were described as follows.

2.3 Optical and physical characterization of chitosan-silver nanoparticles

The colloidal chitosan-AgNPs prepared in previous section was collected to investigate localized surface plasmon property using UV-vis spectrometer (Avantes AvaSpec-2048). In order to investigate the AgNP size and shape, the sample was dropped on a carbon-coated copper grid and monitored by transmission electron microscope (JEOL JEM-2100) operating at an accelerating voltage of 200 kV. For the examination of AgNPs crystal structure, the sample was prepared by drop casting on a silicon (100) wafer to obtain a thick film of the AgNPs colloid and subsequent drying in the air ambient conditions. The X-ray diffraction (XRD) patterns of the as-synthesized AgNPs was carried out using a D8 Advance Bruker Analytical X-ray system with a monochromatic Cu Kα radiation (λ = 1.54 Å) operating at 40 kV and 40 mA.

3. Results and Discussion

(a) (b)

Figure 1. Photographs of the colloidal chitosan-AgNPs: (a) before and (b) after heat treatments.

From experiment, the solution color was changed from light yellow (color of chitosan solution) to yellowish-brown after heating at 121 °C for 15 min as illustrated in Figure 1. This color change phenomenon indicated that Ag+ was reduced to Ag^0. Then, the silver atoms agglomerated into oligomeric clusters and eventually formed AgNPs

(Sharma et al., 2009). The formation of AgNPs was supported by appearance of a single plasmon peak at the wavelength of 434 nm as shown in Figure 2. Moreover, the plasmon band was not changed during keeping colloidal chitosan-AgNPs at the room temperature. It indicated that the highly stable AgNPs was produced.

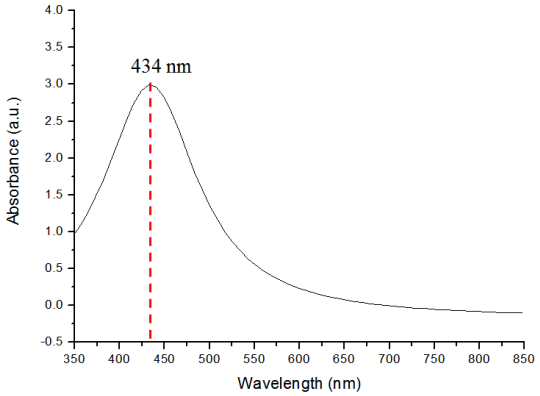

Figure 2. Surface plasmon resonance characteristic of the colloidal chitosan-AgNPs.

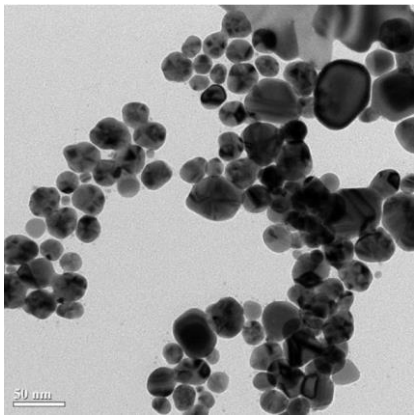

Figure 3. TEM image of the AgNPs prepared using chitosan as a reducing agent and capping agent through green method.

From TEM image as shown in Figure 3, it indicated that the as-synthesized AgNPs are mainly spherical shape. Their particle sizes were determined using the ImageJ Program. It revealed that the average particle diameter of the as-synthesized AgNPs was 23.5 ± 0.6 nm (Figure 4). Furthermore, the selected area electron diffraction (SAED) patterns in Figure 5 exhibits a set of rings suggesting that the AgNPs are polycrystalline in nature corresponding to the XRD patterns as illustrated in Figure 6.

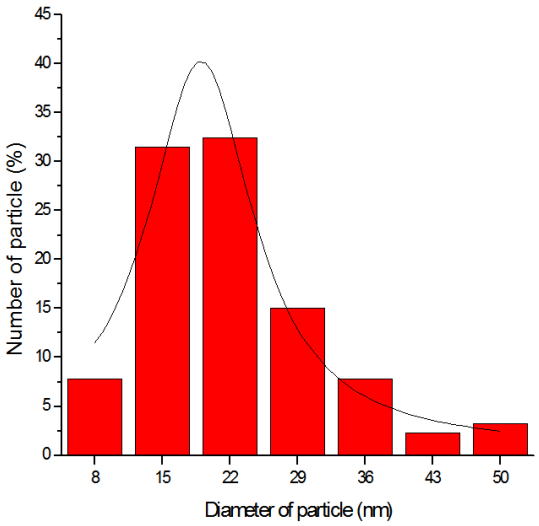

Figure 4. Particle size distribution of the AgNPs prepared using chitosan as a reducing agent and capping agent through green method.

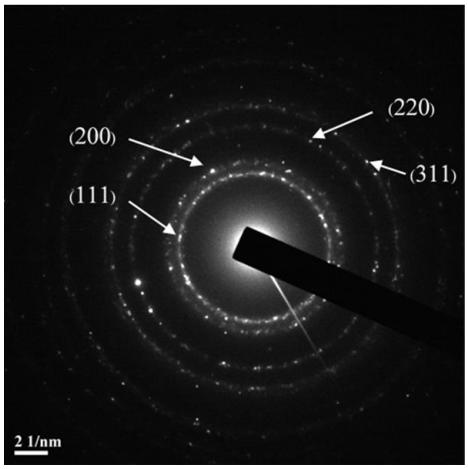

Figure 5. SAED patterns of the colloidal chitosan-AgNPs show several lattice fringes corresponding to the (111), (200), (220) and (311) planes.

From Figure 6, it showed a good agreement with the JCPDF file No. 04-0783. The sharp diffraction peaks appeared at the angles of 37º, 44º, 64º and 77º corresponding to the (111), (200), (220) and (311) facets of silver with face centered cubic (fcc) crystal structure, respectively. From all results, they confirmed that the method presented herein can be the effective approach for the synthesis of AgNPs.

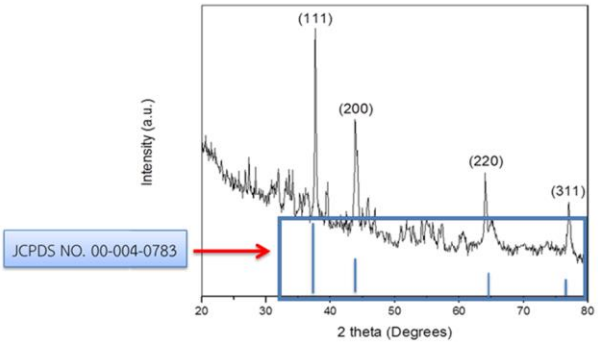

Figure 6. XRD patterns of the colloidal chitosan-AgNPs.

The obtained colloidal chitosan-AgNPs can be further used to fabricate chitosan-AgNPs composite film by casting method as shown in Figure 7.

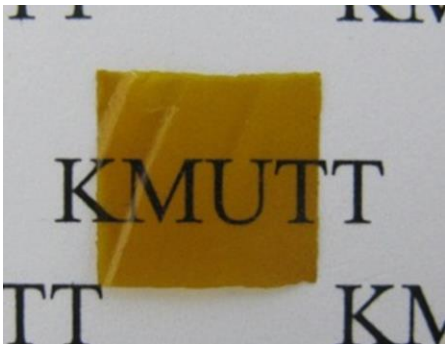

Figure 7. Example of the chitosan-AgNPs composite transparent film fabricated by casting method on the glass plate.

4. Conclusions

Chitosan from bio-waste can be used as a reducing agent and capping agent in the synthesis process of nanoscale silver particles without adding other chemical substances. Due to the characteristic of optical property of AgNPs called as surface plasmon resonance, the colloidal chitosan-AgNPs and chitosan-AgNPs composite thin film could be applied as a colorimetric sensor in many areas such as food and beverage, environment, and agriculture.

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