# PREPARATION OF SILVER NANOPARTICLES ON A CHITOSAN FILM BY UV IRRADIATION METHOD

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## ABSTRACT

Silver nanoparticles can be easily prepared on the surface of chitosan film by ultraviolet (UV) irradiation method in this study. The free amine group of chitosan molecule gives it an excellent ability to chelate silver ions in the silver nitrate aqueous solution. Field-emission scanning electron microscope (FE-SEM) was employed to characterize the morphology of silver nanoparticles on the surface of chitosan film. It was found that some silver nanoparticles were in the range of 10-30 nm in diameter, individually isolated, and uniformly dispersed on the surface of chitosan film. However, it was also found that the other silver nanoparticles were aggregated together to form cubic or spherical particles and were in the range of 50-200 nm in diameter dispersed on the surface of chitosan film. The chemical structure of chitosan films with or without silver nanoparticles was examined by an attenuated total reflection–Fourier transform infrared spectrometer (ATR-FTIR).
KEYWORDS: chitosan, silver, nanoparticle, UV

## INTRODUCTION

Chitosan, a deacetylated product of chitin, is a high molecular weight heteropolysaccharide composed mainly or fully of β-(1,4)-2-deoxy-2-amino-D-glucopyranose and partially or none of β-(1,4)-2-deoxy-2-acetamido- D-glucopyranose units [1]. Thus, chitosan is the fully or partially deacetylated form of chitin. Chitin and chitosan, with excellent biodegradability, biocompatibility, and bioactivity, have been significantly interested in biomedical applications including antithromboyenic, homeostatic, immunity enhancing, and would healing [2-5]. The general degree of deacetylation (DD) of chitosan is about 70-95%. The amine group on the backbone is proportional to the degree of deacetylation (DD) for the chitosan.

Nanoparticles of noble metals are of great interest today because of their possible applications in microelectronics [6–7]. Silver (Ag) particles play an important role in the electronic industry. Since silver or silver ions have been well known to have powerful antibacterial activity, silver is widely applied in some medical fields for its high antimicrobial activity and low concentration [8].

There two major routes to reduce the silver ion to siliver. One is the chemical reduction method [9-13]. For example, Qiao et al. reported that well-dispersed silver particles with 20–80 nm size and spherical shape were prepared by reducing silver nitrate with glucose in the presence of protective agent polyvinyl pyrrolidone (PVP) [9]. Yang et al. prepared various metal–chitosan nanocomposites, including silver (Ag), gold (Au), platinum (Pt), and palladium (Pd) in aqueous solutions. Metal nanoparticles were formed by reduction of corresponding metal salts with $NaBH_4$ in the presence of chitosan [13].

The other is the irradiation reduction method [14-17]. For example, Chen et al. [14]

prepared poly(butyl acrylate-co-(glycidyl methacrylate-iminodiacetic acid)) microspheres by batch soap-free emulsion copolymerization of n-butyl acrylate with a chelating vinyl monomer. The flexible and water-insoluble films obtained from the latex were employed to adsorb Ag+ from an aqueous solution. Silver nanoparticles, appearing on the surface of the film, were prepared through the reduction of the copolymer–silver ion complexes by ultraviolet (UV) irradiation. Zhang et al. [15] prepared polyacrylonitrile/silver nanoparticle composite by a simultaneous polymerization-reduction approach. They also used UV irradiation to reduce the silver ion to silver.

The free amine group of chitosan gives it a better ability to chelate metal ions than other natural compounds; such as cellulose derivatives. In this study, a chitosan film was prepared to chelate silver ions in $AgNO_3$ aqueous solution. Then, the silver ions were reduced by ultraviolet (UV) irradiation reduction method due to this method could be operated continuously without the pollution of chemical reducing agents. In this study, the CS and CS-silver films are represented as before and after the chelating and reduction of silver ions, respectively.

## EXPERIMENTAL

### Materials

Chitosan (CS) with 95% deacetylation (prepared from $\beta$-chitin) was supplied by Ohka Enterprises Co., Ltd., Taiwan. The molecular weight of chitosan is about 200,000. Acetic Acid was purchased from Union Chemical Works Ltd., Taiwan.

Preparation of CS film

CS powder was added into a 0.1M acetic acid solution and stirred to form a 2.5wt% clear CS solution. Then, this clear solution was poured into the PP petri dish. After 48-hour settle, this CS solution was de-bubbled and moved into 60℃ oven for about 24-hour drying. Then, the CS film was vacuum dried for 24 hours at 80℃.

Reduction of Silver Ions on CS film

The CS film was cut into 3 cm X 3 cm and immersed into 0.01M silver nitrate aqueous solution for one hour. After one hour, the surface of CS film with silver ions was washed by DI water several times in order to remove the residual silver ions. After washing, the CS film with silver ions was dried at 60℃ oven for about 24 hours. The dried film was placed under a UV light (254 nm) for one hour in order to reduce silver ions to silver.

ATR-FTIR Analysis

The characteristic functional groups of CS and CS–silver films were analyzed by attenuated total reflection–Fourier transform infrared spectrometer (ATR-FTIR, Perkin Elmer, model: Spectron One, USA) in the wavelength ranged from 400 to 4000 $cm^{-1}$ with the scans frequency of 32 times per second.

FE-SEM Examination

The morphology of silver nanoparticles on the surface of CS-silver film was examined by a field-emission scanning electron microscopy (FE-SEM, Jeol Ltd., Japan, model JSM 6700F). Each sample was coated with the gold palladium film. In order to confirm the silver particles on the CS-silver film, an Energy Disperive X-ray Spectrometer (EDX) was also conducted.

## RESULTS AND DISCUSSIONS

Figure 1 shows the photograph of CS film. It looks transparency and pale yellow. Figure 2 shows the ATR-FTIR spectra of the surfaces of CS and CS-silver films. The frequency and their assignments of CS film are indicated as followed: 655 $cm^{-1}$ and 1076 $cm^{-1}$ for the characteristic peak of crystallized CS [18], 1642 $cm^{-1}$ for the bending vibration of $–NH_2$ group, 1560 $cm^{-1}$ for the bending vibration of amide group, and 3367 $cm^{-1}$ for the combination of -OH and –NH functional groups. The amine group on the backbone is proportional to the degree of deacetylation (DD) for the chitosan. The chelating ability of chitosan is also proportional to the DD of CS. After UV irradiation reduction of silver ions chelated on the surface of CS film, the ATR-FTIR spectrum of the surface of CS-silver film is significantly different from that of CS film. The characteristic peaks of 1642 $cm^{-1}$ for the bending vibration of $–NH_2$ group, 1560 $cm^{-1}$ for the bending vibration of amide group, and 3367 $cm^{-1}$ for the combination of -OH and –NH functional groups are much smaller in CS-silver film than those in CS film. This phenomeon is because that the chelating of silver ions for amine groups of CS.

Figure 3 shows the FE-SEM photograph of the surface of CS-silver film chelating silver nanoparticles. There are many silver nanoparticles on the CS-silver film. Some silver nanoparticles aggregate together to form cubic particles. The particle size of these cubic particles is in the range of 50 to 200 nm. However, other isolated silver nanoparticles, its particle size ranges from 10-30 nm. There are two possible reasons for silver nanoparticles aggregation. The first reason is that the local concentration of silver ions chelated by CS is higher than those in the other area. The second reason is that the exposure time of UV light may be too long.

Figure 4 shows the EDX analysis of the surface of CS-silver film. It shows significant signal of silver element. This result confirms that the nanoparticles on the surface of CS-silver film are silver nanoparticles.

## CONCLUSIONS

Silver nanoparticles can be easily prepared on the surface of chitosan film by ultraviolet (UV) irradiation method in this study. The free amine group of chitosan molecule gives it an excellent ability to chelate silver ions in the silver nitrate aqueous solution. Due to the chelating of silver ions by amine groups of CS, the ATR-FTIR spectrum shows the characteristic peaks of 1642 $cm^{-1}$ for the bending vibration of $–NH_2$ group, 1560 $cm^{-1}$ for the bending vibration of amide group, and 3367 $cm^{-1}$ for the combination of -OH and –NH functional groups are much smaller in CS-silver film than those in CS film. FE-SEM photograph shows many silver nanoparticles on the CS-silver film. Some silver nanoparticles aggregate together to form cubic particles. The particle size of these cubic particles ranges from 50 to 200 nm. However, the particle size of the other isolated silver nanoparticles is in the range of 10 to 30 nm. EDX analysis shows significant signal of silver element on the CS-silver film. This result confirms that the nanoparticles on the surface of CS-silver film are silver nanoparticles.

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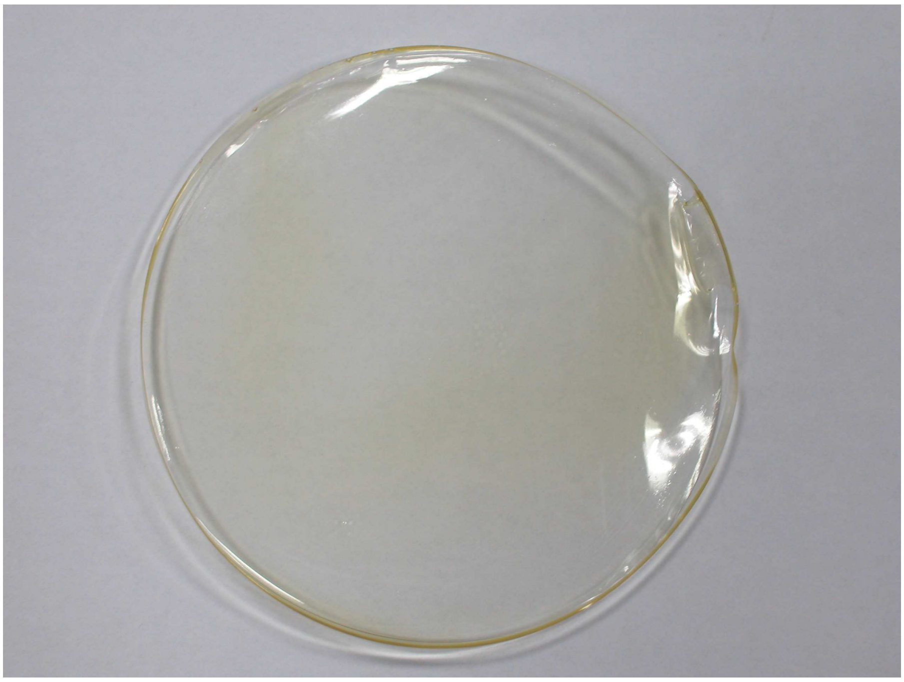


Figure 1. A photograph of CS film.

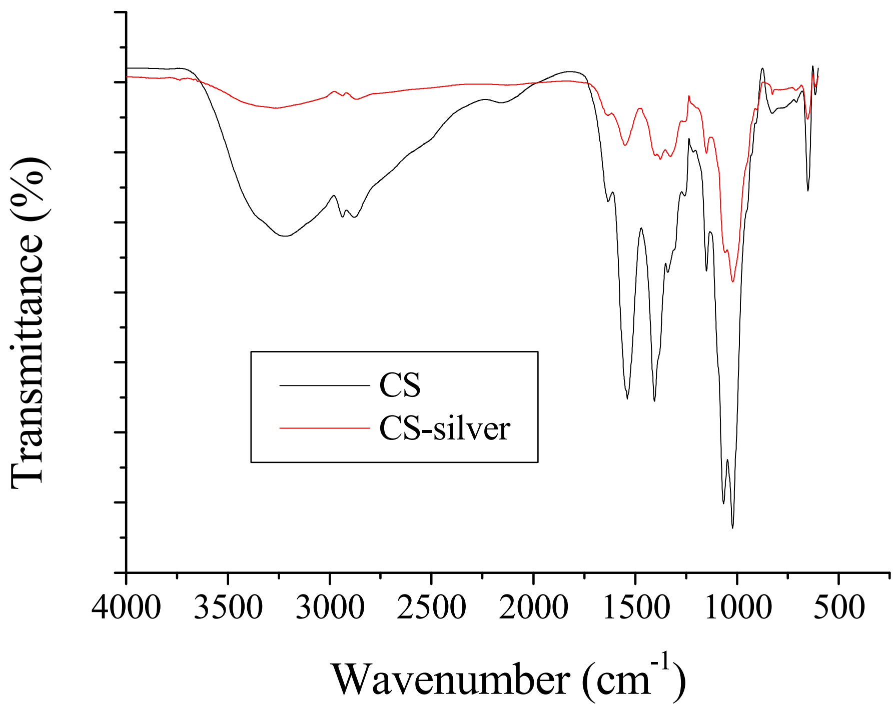



Figure 2. FTIR spectra of CS (black line) and CS-silver (red line) films .

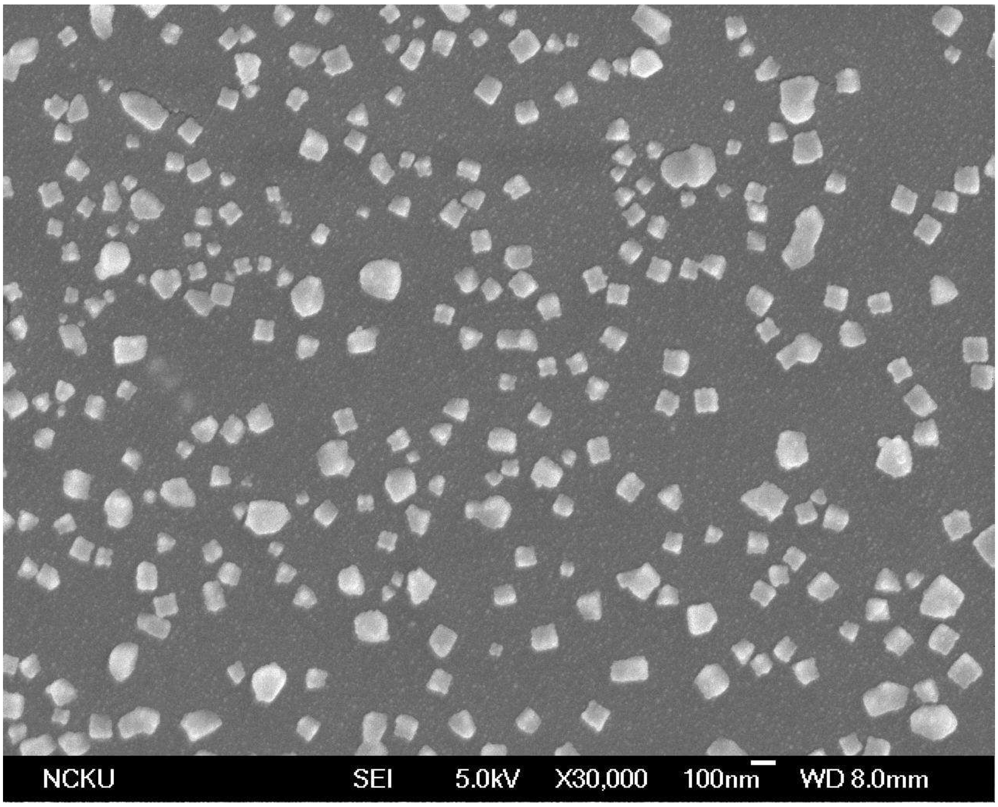
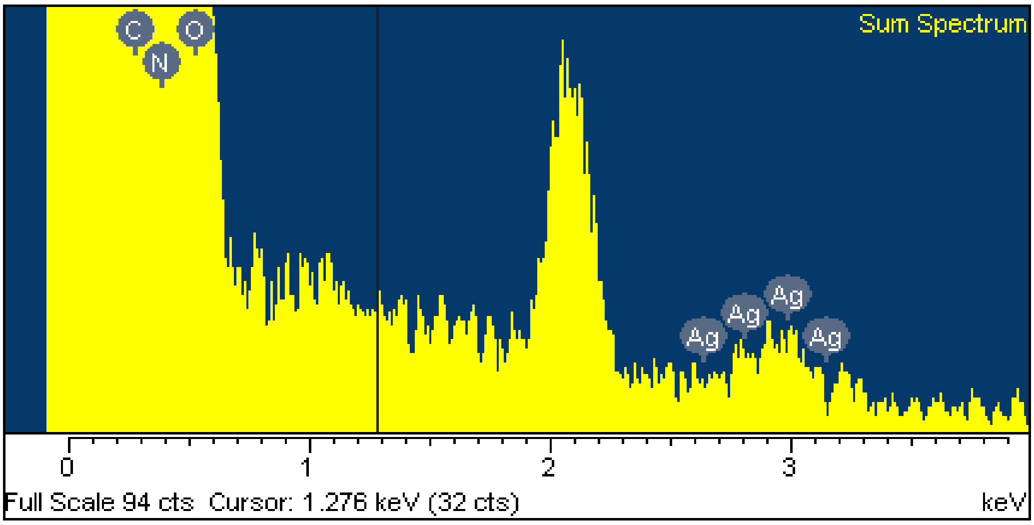



Figure 3. FE-SEM photograph of the surface of CS-silver film.


Sum Spectrum
C
N
O
Ag
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Full Scale 94 cts  Cursor: 1.276 keV (32 cts)
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