

THE EFFECT OF pH AND MOLECULAR WEIGHT OF CHITOSAN ON SILVER NANOPARTICLES SYNTHESIZED BY γ -IRRADIATION

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1. INTRODUCTION

During the last decades, developments of surface microscopy, materials science, biochemistry, physical chemistry and computational engineering have converged to provide remarkable capabilities for understanding, fabricating and manipulating structures at the atomic level. The rapid evolution of this new science and the opportunities for application promise that nanotechnology will become one of the dominant technologies of the 21st century [1]. The study on synthesis of metal nanoparticles is of interest in both research and technology. Among metal nanoparticles, silver nanoparticles (Ag-NPs) have attracted considerable interest because of their novel properties and their potential application [2, 3].

Different methods have been used for the synthesis of Ag-NPs from Ag^+ solution such as chemical [4], electrochemical [5], photochemical reduction [6], ultrasonic spray pyrolysis [7], gamma and electron beam irradiation [3, 8],... Method for preparing Ag-NPs by exposure to ionizing rays provides several advantages such as the manufacturing process carries out at room temperature, the sizes and size distribution of the particles are easily control and purely colloidal Ag-NPs can be obtained. In addition, mass production at reasonable cost is possible [2, 3, 9]. It is well known that Ag^+ in solution could be reduced by γ -rays to Ag atoms while they would agglomerate if there is no protective substance. Hence an effective stabilizer is the key factor to fabricate densely dispersed Ag-NPs by irradiation method [10]. Several polymers having functional groups such as $-\text{NH}_2$, $-\text{COOH}$ and $-\text{OH}$ with high affinity for Ag atoms [2] to stabilize Ag-NPs such as PVA [11], PVP [3, 5], alginate [9], CM-Chitosan [12], chitosan and oligochitosan [10, 13, 14] and so on have been used for synthesis of Ag-NPs.

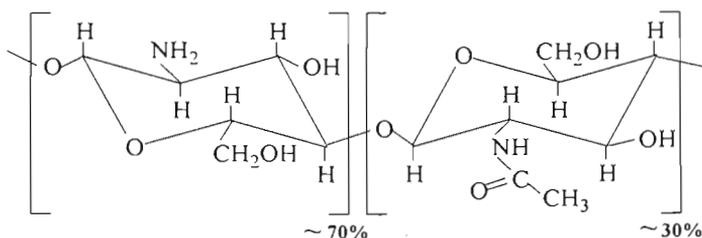


Figure 1. The molecular structure of CTS with deacetylation degree of about 70%

Chitosan (CTS), a natural polysaccharide with excellent biodegradable, biocompatible, nontoxicity and adsorption characteristics is a renewable polymer [15]. Owing to the interaction with $-\text{NH}_2$ groups of CTS chain (Figure 1), the Ag-NPs are enveloped by CTS fragments and so

the nanoparticles could be kept from agglomeration during irradiation reduction process [10, 15]. Using CTS as free radical scavenger and stabilizer for colloidal Ag-NPs prepared by γ -irradiation is appropriate to green method which should be evaluated from three aspects: the solvent, the reducing and the stabilizing agent [10, 14, 15]. In addition, Ag-NPs stabilized by CTS are positive charge enrichment in surface so that antimicrobial property is significantly improved [16]. Therefore, preparation of Ag-NPs/CTS by γ -irradiation was carried out in this work. The effect of pH and molecular weight of CTS on characteristics of Ag-NPs/CTS was thoroughly investigated.

2. EXPERIMENTAL

2.1. Materials

Analytical grade AgNO_3 , lactic acid and NaOH were purchased from Shanghai Chemical Reagent Co., China. Deionized water was pure products of Merck, Germany. CTS with deacetylation degree of about 70% and mass average molecular weight (M_w) from 3.5 to 460 kDa was prepared at VINAGAMMA Center, Ho Chi Minh City.

2.2. Methods

A stock solution of 1.5% (w/v) CTS was prepared by dissolving CTS in 1% (v/v) lactic acid solution and stored overnight. Then the pH of CTS solution (pH 3) was adjusted to about 6 by NaOH 2 M. CTS solution after mixing with AgNO_3 to final concentration of 5 mM Ag^+ and 1% CTS. The Ag^+ /CTS solution was poured in glass tubes and deaerated by bubbling with N_2 for 15 min. The γ -irradiation was carried out on a Co^{60} irradiator with dose rate of 1.3 kGy/h under ambient conditions at VINAGAMMA Center, Ho Chi Minh City. Uv-vis spectra of Ag-NPs solution which was diluted by water to 0.1 mM calculated as Ag^+ concentration were recorded on an UV-2401PC, Shimadzu, Japan. The size of Ag-NPs thus prepared was characterized by TEM images on a JEM 1010, JEOL, Japan, operating at 80 kV and statistically calculated using Photoshop software [3].

3. RESULTS

CTS has been used as an effective reducing/stabilizing agent for preparation of Ag-NPs or Au-NPs by chemical method [4, 15] and as a stabilizing/scavenging agent by ionizing irradiation method [10, 13, 14]. So in all these experiments, the external agent to scavenge $\cdot\text{OH}$ free radical which arising from radiolysis of water is not employed. According to Chen et al. [10], stabilization of CTS for Ag-NPs is due to their interaction with $-\text{NH}_2$ groups of CTS chain and the Ag-NPs are enveloped by CTS fragments. Concurrently, in aqueous solution the $-\text{NH}_2$ groups of CTS are protonated to $-\text{NH}_3^+$ and so the Ag-NPs could be kept from agglomerating through static repulsions. However, the radical $\cdot\text{OH}$ can oxidize nascent metallic Ag to Ag^+ ion that impacting on the formation of Ag-NPs. Fortunately, CTS can be scavenging for $\cdot\text{OH}$ via hydrogen abstraction and the newly formed CTS radical that itself can also reduce Ag^+ to Ag^0 as described by Long et al. [14].

3.1. Effect of pH

The λ_{\max} value of colloidal Ag-NPs depends on the size of Ag-NPs. As the size of Ag-NPs increases the λ_{\max} will shift toward longer wavelengths [2, 3, 4]. The results in Table 1 showed that the λ_{\max} of Ag-NPs was of 419.5 nm for pH~3 and 403.5 nm for pH~6 corresponding to the particle size of 15.0 nm and 7.3 nm. In addition, the size distribution of Ag-NPs prepared in pH~6 was narrower than that in pH 3 (Figure 2). The reason for that may be explained as follows, the reduction reaction of Ag^+ into Ag^0 could be unfavorable for the formation of small Ag-NPs in acidic medium with higher H^+ concentration. Moreover, Sun et al. [15] also concluded that CTS chains were broken in acidic aqueous solution that might partially reduce stabilizing activity of CTS for metallic particles. Recently, several studies on preparation of Ag-NPs by γ -irradiation in CTS solution were performed [10, 14, 17], but the effect of pH has not been investigated yet. However, the effect of pH for other stabilizers have been carried out. For instance, Huang et al. reported that pH 12.4 was an ideal condition for preparation Ag-NPs in carboxyl methyl CTS solution [12]. The results of Ramnani et al. [2] indicated that neutral and acid media (pH 2-4) were desired for synthesis of Ag clusters on SiO_2 . Thus, the effect of pH plays an important role in the formation of small size of Ag-NPs and optimal pH values may be varied upon stabilizer agents. Based on our results, it inferred that the nearly neutral medium (pH~6) of CTS solution is suitable for preparation of Ag-NPs with small size.

Table 1. Optical density (OD), maximum absorption wavelength (λ_{\max}) and diameter (d) of colloidal Ag-NPs/CTS (120 kDa) at dose 16 kGy

Samples	OD	λ_{\max} (nm)	d (nm)
pH 3	0.97	419.5	15.0 ± 5.4
pH 6	1.06	403.5	7.3 ± 1.4

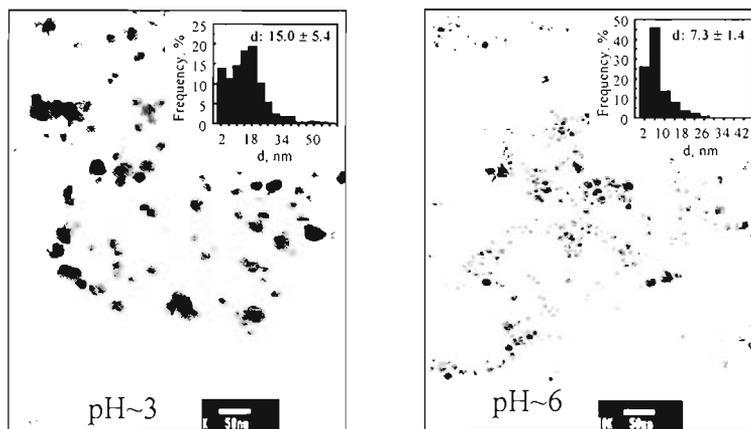


Figure 2. TEM images and histograms of size distribution of Ag-NPs/CTS with different pH

3.2. Effect of CTS molecular weight

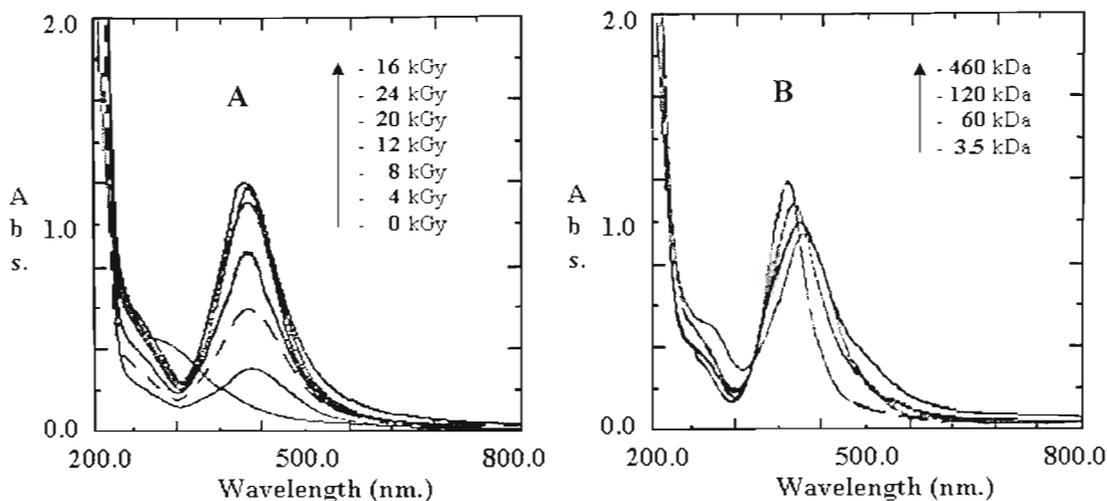


Figure 3. Typical UV-vis spectra irradiated of Ag⁺/CTS (120kDa) solution with doses (A) and UV-vis spectra of Ag-NPs/CTS solution with different M_w at conversion dose (B)

As known from Mie theory for the optical absorption bands of small metal particles, the size and amount of nanoparticles affect both the absorption wavelength and the intensity of the plasmon absorption band [11, 12]. Generally, colloidal metal nanoparticles solution with small sizes and high content of particles will have high intensity at maximum absorption band and λ_{\max} shifts to shorter wavelength. The results in Figure 3A showed that OD values of irradiated Ag⁺ solutions were increased up to a maximum at dose of 16kGy for solution of Ag⁺5mM/CTS1%. This dose is defined as conversion doses to reduce Ag⁺ into metallic silver completely [3, 8].

Table 2. The characteristics of colloidal Ag-NPs stabilized by CTS with different M_w

Samples	OD	λ_{\max} (nm)	d (nm)
CTS 3.5kDa	0.82	410.5	15.5 ± 1.6
CTS 60kDa	1.03	409.5	8.4 ± 1.3
CTS 120kDa	1.06	403.5	7.3 ± 1.4
CTS 460kDa	1.20	399.5	5.0 ± 1.7

The influence of molecular weight of CTS on characteristics of colloidal Ag-NPs was manifested in Table 2. All the λ_{\max} values of colloidal Ag-NPs appeared in the range of 399 nm – 410 nm, that is the specific surface plasmon resonance band of Ag-NPs [9, 12, 17]. It was also obvious in Table 2 that the higher the M_w of CTS, the shorter the λ_{\max} (Figure 3B) and the smaller the particles size of Ag-NPs. The exact mechanism of this process is still not clear. However, we might suggest that the cumbersomeness of CTS with high M_w could enhance the anti-agglomeration among Ag clusters that contributes to the formation of small Ag-NPs. Similar results were reported by Du et al. [3] for PVPK90 (1,100 kDa) and PVPK30 (50 kDa) in

the synthesis of Ag-NPs by γ -irradiation. Yin et al. [5] also concluded that PVP with a short polyvinyl chain was unfavorable for the electrochemical synthesis of Ag-NPs. Temgire and Joshi [11] prepared Ag-NPs by γ -irradiation using PVA as stabilizer, the particles size obtained was of 18.6, 19.4 and 21.4 nm for PVA125 kDa, PVA30 kDa and PVA14 kDa, respectively. In addition, results of Huang et al. [12] confirmed that the diameter of Ag-NPs prepared by UV irradiation in carboxyl methyl CTS (0.8 kDa) was larger than that in carboxyl methyl CTS (31 kDa).

4. CONCLUSIONS

Colloidal Ag-NPs were synthesized by γ -irradiation using CTS a stabilizer and free radical scavenger. Results revealed that pH~6 was suitable for preparation of Ag-NPs with small size (~7 nm). The particles size obtained was in the range of 16 - 5 nm for M_w of CTS from 3.5 to 460 kDa. The γ -irradiation might be useful tool for mass production of Ag-NPs/CTS for application in different fields, especially in biomedicine.

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TÓM TẮT

ẢNH HƯỞNG pH VÀ KHỐI LƯỢNG PHÂN TỬ CHITOSAN ĐẾN KEO BẠC NANO CHẾ TẠO BẰNG PHƯƠNG PHÁP CHIẾU XẠ γ Co-60

Áp dụng bức xạ γ Co-60 chế tạo keo bạc nano dùng chitosan làm chất ổn định vừa là chất bắt gốc tự do là phương pháp có tính khả thi, phù hợp với nhu cầu sản xuất sạch. Liều xạ chuyển hóa ($Ag^+ \rightarrow Ag^0$) xác định bằng phổ Uv-vis và kích thước hạt bạc nano được xác định bằng chụp ảnh TEM. Ảnh hưởng của pH dung dịch và khối lượng phân tử (M_w) chitosan đến kích thước hạt bạc nano đã được khảo sát. Kết quả cho thấy dung dịch Ag^+ /chitosan được điều chỉnh pH~6 trước chiếu xạ, nhận được keo bạc nano có kích thước hạt ~7 nm nhỏ hơn so với ~15 nm từ dung dịch không điều chỉnh pH ~ 3. Chitosan M_w cao ổn định keo bạc nano tốt hơn chitosan M_w thấp. Keo bạc nano/chitosan chế tạo được có kích thước hạt 5 nm (M_w 460 kDa) đến 16nm (M_w 3,5 kDa).

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