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Synthesis and Characterization of Chitosan-Nanosilver Microsphere by Ultrasonic Irradiation†

HONGYAN ZHANG*, BAOHUI YAO and MENGNAN ZAI

School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, P.R. China

*Corresponding author: E-mail: zhyymq@163.com

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Chitosan-nanosilver microspheres were synthesized by emulsion cross-linking method by ultrasonic irradiation. The microspheres were characterized by means of FTIR, XRD, SEM and DSC-TGA, respectively. FTIR showed that nanocomposites were embedded in microspheres. X-ray diffraction showed that chitosan was amorphous crystal and silver nanoparticles were face-centered cubic silver. Scanning electron microscopic evidenced that the morphology of samples all spherical with mean diameters 90 μ. TGA-DSC showed that chitosan molecules were changed, crystallization of chitosan was decreased, so the heat was low when the microspheres were decomposed.

Keywords: Chitosan, Nanosilver, Synthesize, Ultrasonic irradiation.

INTRODUCTION

Chitosan (CS) is a biopolymer which is biocompatible and could be degraded by enzymes in human body[1]. Chitosan is a polymer which exhibited a broad spectrum of antimicrobial activity by bingding to the negatively charged bacterial cell wall followed by attachment to the DNA, inhibiting its replications[2]. Silver nanoparticles have been widely used in the field of antibacterial and exhibited high performance even at a very low concentration[3]. Chitosan-nanosilver nanocomposite was seen to possess a capability of being used as a biosensor as well as in the treatment of cancer as the chitosan present in the nanocomposite was specific to the cancer cells[4].

With the wide application of a variety of chitosan and its composites, to explore simple,effective and keep good biological properties of chitosan microspheres' preparation methods has been the focus in the study of people. According to the different reaction media and system characteristics, preparation methods of chitosan microspheres can be devided into chemical crosslinking method, ionic crosslinking method, condensation method and emulsion method[5]. In this work, chitosan-nanosilver nanocomposite was synthesized by the emulsion crosslinking method under ultrasonic irradiation. The nanoparticles were characterized with FTIR, XRD, SEM and TGA-DSC.

EXPERIMENTAL

A certain amount of chitosan was dissolved in 3 wt % acetic acid, a certain amount of silver nitrate solution was added to the above solution. The flask was immersed in a water bath heated at 35 ºC, while stirring followed by sonication for 0.5 h. $NaBH_4$ solution (0.045 g) was added drop wise to the above solution and sonicated for 1 h, then the chitosan-nanosilver sol was been preparated.

The composite emulsifier (6 mL) was dissolved in 50 mL of liquid paraffin in a 100 mL beaker, followed by the addition of crosslinking agent glutaraldehyde and chitosan-nanosilver sol (3 mL). The reacting system became dusk under ultrasonic irradiation for 40 min. The mixture was used to demulsify in the acetone, while leaving to the upper oil phase and centrifuging at 4000 rpm to collect the chitosan-nanosilver nanoparticle. Finally, the product was placed in a vacuum drying cabinet 40 ºC.

RESULTS AND DISCUSSION

FTIR analysis: The infrared spectra of chitosan (a) and chitosan-nanosilver (b) composites were shown in Fig. 1. It was given some characteristic peaks of the polymer, such as the 3433 cm^{-1} stretching vibration peak, the 2878 cm^{-1} stretching vibration peak responding to C-H, the 1379 cm^{-1} stretching vibration peak responding to C-N group and the 1156 cm^{-1} stretching vibration peak responding to C-O group. Absorption peak at 1558 cm^{-1} confirmed that silver particles were in the composites. Absorption peak at 2928 cm^{-1} change showed that the amino group of chitosan was modified, this was due to the

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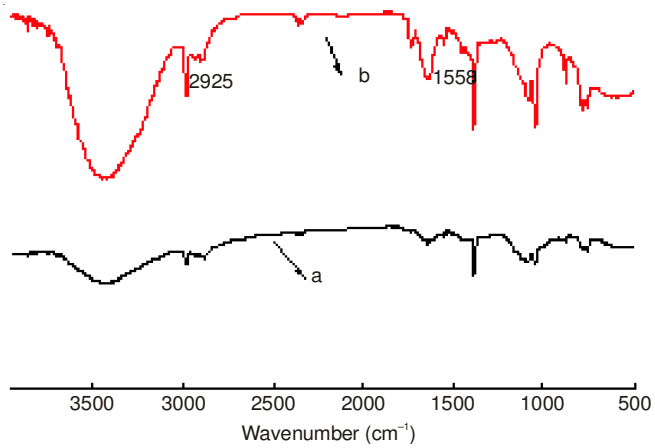

Fig. 1. FT-IR spectra of chitosan (a) and chitosan-nanosilver (b)

amino group of chitosan with aldehyde group of glutaraldehyde Schiff's base reaction happened.

XRD analysis: The XRD pattern of chitosan-nanosilver composites illuminated that there were three peaks appeared at 2θ = 37.36º, 43.64º and 63.86º, respectively, which indicated that there were nanosilver crystal particulates within the nanocomposites. The crystal plane spacing (d) was 0.2367, 0.2046 and 0.1442 nm calculated by 2d sin θ = nλ, corresponding to [111], [200], [220] crystal faces of silver, respectively, compared to PDFWIN#87-0597. Therefore, the nanosilver particles possessed face-centered cubic structure within nanocomposites. X-ray diffraction showed that the aggregation of silver nanoparticles had not occurred during the emulsion crosslinked microsphere.

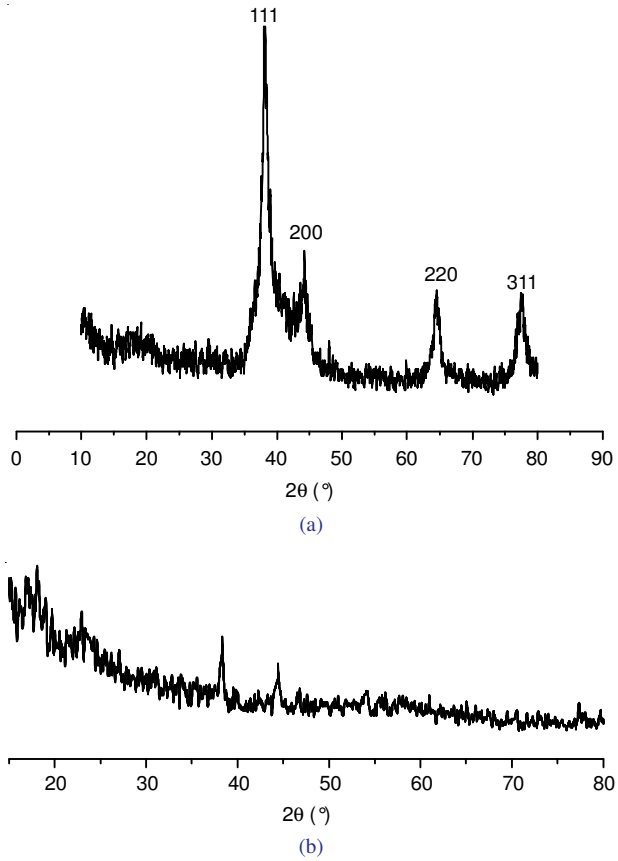

Fig. 2. XRD pattern of the nano silver (a) and chitosan-nanosilver (b)

SEM analysis: SEM (Fig. 3) showed that the surface of the chitosan-nanosilver microspheres fully cured, sleeked and sphered. Each of the microspheres particle size on average was 90 μ. This may be due to Schiff's base reaction of aldehyde groups in glutaraldehyde with amino groups in chitosan was more complete under ultrasonic irradiation.

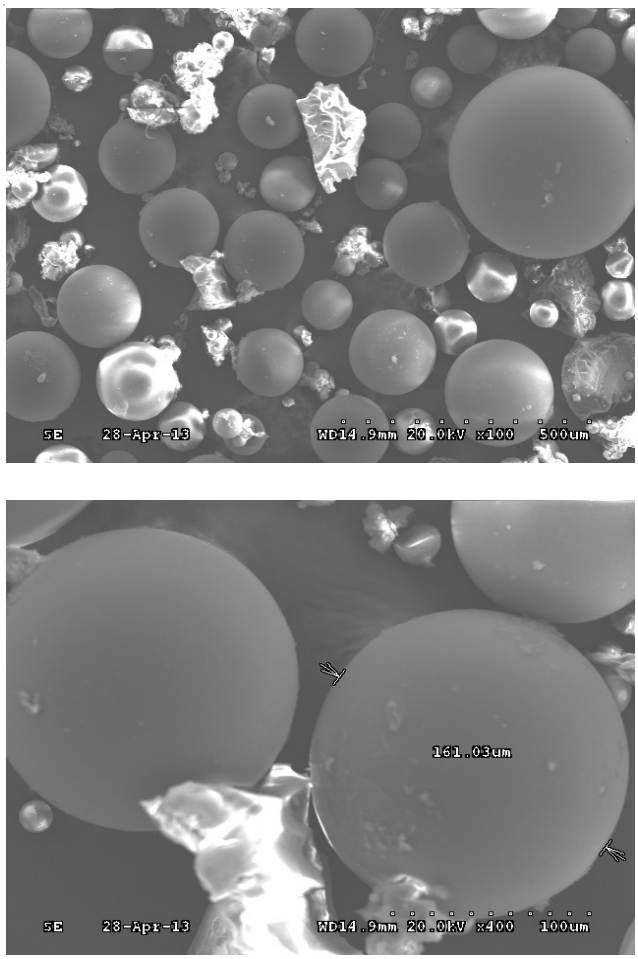

Fig. 3. SEM of chitosan-nanosilver composite

Thermal analysis: Thermal degradation of the chitosan and chitosan-nanosilver nanocomposite were shown in Fig. 4(a). Two weight losses were observed in the TGA curve of chitosan. The weight lost at (50-160 ºC) was due to the moisture vaporization .The other weight lost at (180-280 ºC) was due to the degradation of chitosan molecule. Chitosan-nanosilver microspheres of the DSC curve was stable with the change of temperature. The first endothermic peak at (20-80 ºC) was due to the moisture vaporization. The other endothermic peak at (180-280 ºC) was no obvious endothermic phenomenon. Chitosan-nanosilver microspheres decomposition temperature was 510 ºC. This kind of phenomenon was mainly due to the crosslinked chitosan molecular conformation after some changes had taken place, the molecules formed space net structure, chitosan with glutaraldehyde crosslinking reaction of chitosan properties was more stable.

Conclusion

The results showed that chitosan-nanosilver nanocomposites were prepared *in situ* by ultrasonic irradiation. Silver

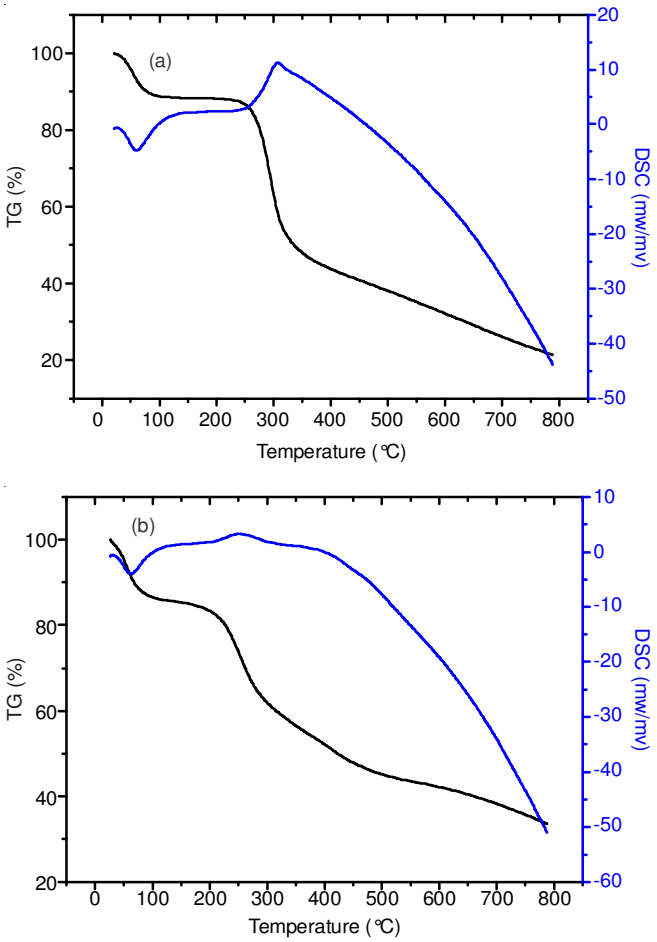

Fig. 4. TGA-DSC of chitosan and chitosan-nanosilver composite

Silver nanoparticles were dispersed into chitosan microsphere and did not happen reunion. SEM showed the preparation of microsphere surface was smooth, not touching each other, the particle size was small and uniform. XRD indicated that the nano-silver particles possessed face-centered cubic structure within nanocomposites. FTIR indicated that nanocomposite was embedded in microspheres. TGA-DSC showed that cross-linked reaction of chitosan cause the decomposition temperature increase and thermal performance was more stable.

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