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Facile one-pot synthesis of chitosan oligosaccharide/silver nanocomposites and their antimicrobial properties

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ABSTRACT

In this study, we demonstrate a facile approach to prepare chitosan oligosaccharide (COS)/silver nanocomposites by use of vitamin C and low molecular COS as reducing agent and capping agent. Morphology and crystalline structure of the COS/silver nanocomposites were characterized. The possible biochemical mechanism leading to the formation of the nanocomposites was investigated by FTIR. The synthesized COS/silver nanocomposites exhibited stronger antibacterial activity than the COS.

1. Introduction

Polymer nanocomposites are advanced functional materials composed of nanoparticles dispersed inside the polymeric matrix [1,2]; as a result, the produced materials combine the suitable properties of both partners [3]. In recent years, the metal nanoparticles/polymer composites have created considerable attraction due to their wide range of applications [4]. To achieve biocompatibility and biodegradability, different biopolymers such as alginate, starch and chitosan have been used as alternatives. Among the biopolymers chitosan is one of the prominent natural biomaterial for stabilizing metal nanoparticles. However, poor solubility makes them difficult to use in the applications. Unlike chitosan, its hydrolyzed products low molecular COS are readily soluble in water due to their shorter chain lengths. The low viscosity and good solubility of COS at neutral pH have attracted the interest of many researchers to utilize chitosan in its oligosaccharide form. Biological activities of COS have been extensively studied due to their high solubility, absorption, and biocompatibility [5]. Increasingly emerging evidence indicates that COS exhibit antimicrobial and antioxidation activities [6,7]. As such, COS have been recommended as healthy food supplements in Asian countries due to these properties [8]. In spite of the applications in diverse fields, an extensive literature survey revealed that there are few reports on the exploitation of COS as a protective agent for COS/silver nanocomposites formation followed by investigation on their antibacterial property in vitro.

Therefore, the present study demonstrates the use of vitamin C (Vc) and COS as reducing agent and capping agent for synthesis of COS/silver nanocomposites; meanwhile the antibacterial activities of the synthesized nanocomposites were evaluated.

2. Materials and methods

Materials: Chitosan (MW=250 kDa, 95% deacetylated) was purchased from Jinke Marine Biochemistry Co., Ltd., Zhejiang, China. Low molecular COS was obtained by enzymatic degradation method. The molecular weight (MW) of COS was controlled by reaction time of hydrolysis, which was determined by gel permeation chromatography (GPC). The low molecular weight COS of approximately 1200 Da was prepared. Silver nitrate and Vc was purchased from Sigma-Aldrich. All the other chemicals were used as received. Double distilled water was used for the experiments. Experiments were carried out in triplicates.

Preparation of COS/silver nanocomposites: The as prepared COS powder was thoroughly mixed with Vc (4:1). The mixture (1 g) was added into the silver nitrate solution (20 mL, 2 mM) and stirred with a magnetic stir bar for 5 min. All experiments were carried out in triplicates. The effect of pH on synthesis was determined by adjusting the pH to 2.34, 5.37, and 9.32. Control experiments were carried out under the same conditions.

Characterization of the synthesized COS/silver nanocomposites: The optical absorption spectra of the synthesized nanocomposites were observed by UV-2450 Shimadzu UV spectrometer. The morphology

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and size of Ag nanoparticles (dispersed inside the COS) were evaluated using a transmission electron microscope model (Jeol-JEM100SX). FTIR analysis was carried out after removal of free Vc and COS. Thereafter, the purified and dried nanocomposites were subjected to FTIR analysis (Shimadzu FTIR spectrophotometer 8400). X-ray diffraction pattern of dried nanocomposites powder was obtained using XPERT-PRO diffractometer using Cu Kα radiation (λ=0.1542 nm).

Antibacterial activity: The groups of bacteria *Escherichia coli* (gram negative bacteria) and Staphylococcus *aureus* (gram positive bacteria) were chosen to evaluate the antibacterial activities of the synthesized COS/silver nanocomposites. Nutrient agar was used as media to grow bacteria. The bacterial strains were stored in a refrigerator. The bacterial solutions were prepared in 0.86% saline. 200 μL of the samples on agar plates were inoculated with *E. coli* and *S. aureus*. These plates were then incubated at 37.0 °C for 24 h, and the inhibition zones were measured. The results represented the antibacterial activity and were expressed in mm. The antibacterial efficacy was evaluated for (1) samples treated with COS and (2) samples treated with the COS/silver nanocomposites.

3. Results and discussion

It was observed that upon addition of the mixture, the color of the silver nitrate solution was changed to yellowish brown immediately. This indicates the formation of silver nanoparticles. The initial pH of the aqueous silver nitrate solution was an important parameter in the synthesis of silver nanoparticles. The silver nanoparticles synthesized at pH of 2.34, 5.37 and 9.32 presented absorption peaks at 437.00, 426.00 and 402.00 nm (Fig. 1a A–C). The absorption peaks shifted to shorter wavelength with the elevated pH value, possibly due to the decreased size and/or anisotropy degree of the silver particles [9]. There was neither a change in color nor a characteristic peak was observed upon the addition of individual COS or Vc into the aqueous silver nitrate solution (Fig. 1a D and E). UV–visible spectroscopy is one of the important techniques to ascertain the formation and stability of metal nanoparticles in aqueous solution. The formation of silver nanoparticles was confirmed based on its surface plasmon resonance, which was captured and displayed by characteristic peaks in the UV–vis spectrum [10]. These results indicate that no silver

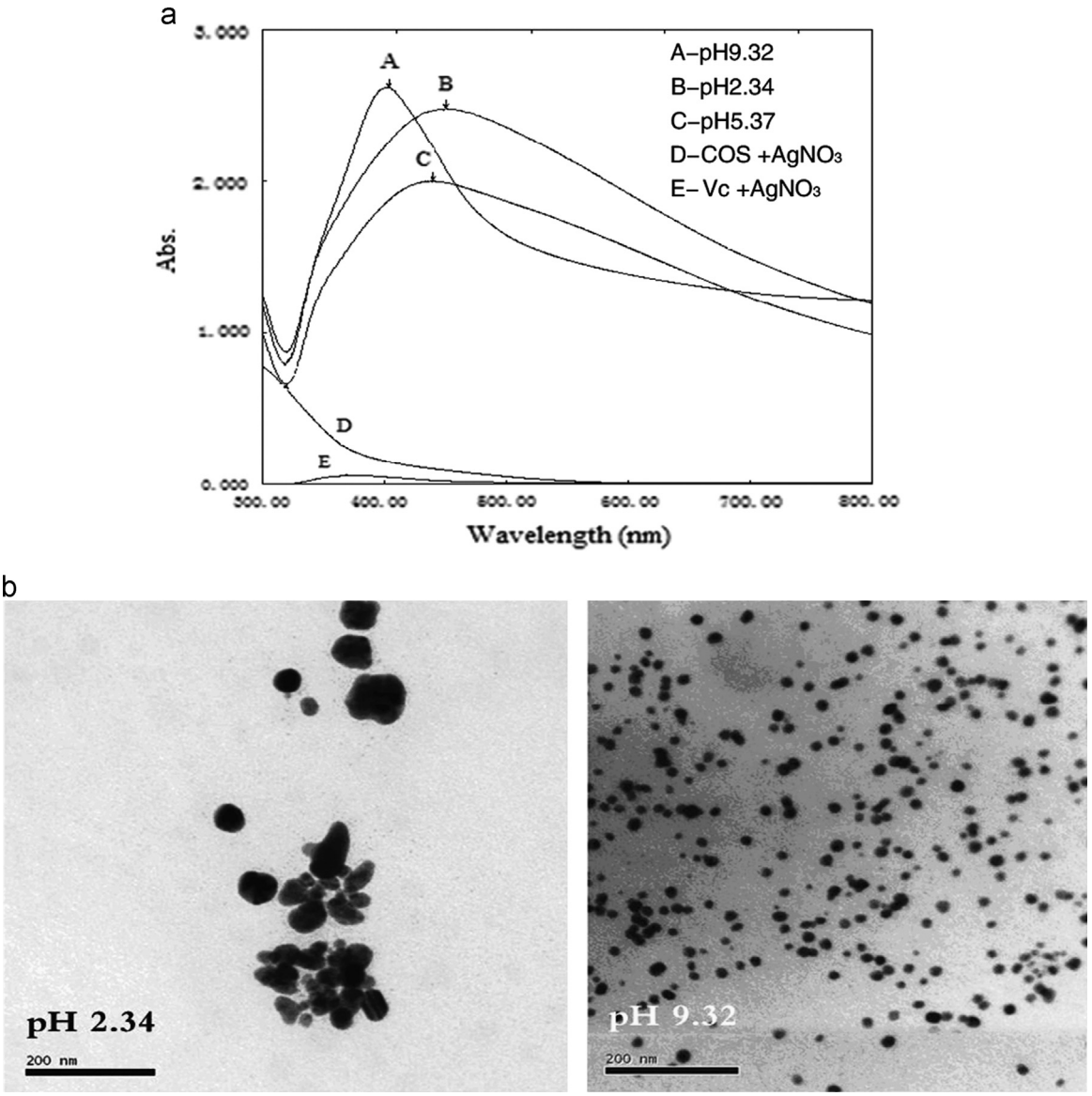

Fig. 1. (a) UV–vis spectra of silver nanoparticles synthesized at different pH values [A: 9.32, B: 2.34, C: 5.37, D: only COS, E: only Vc] and (b) TEM images of the nanoparticles prepared at pH 2.34 and 9.32.