Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 143 (2015) 242–250

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# Synthesis and spectral characterization of silver embedded chitosan matrix nanocomposite for the selective colorimetric sensing of toxic mercury

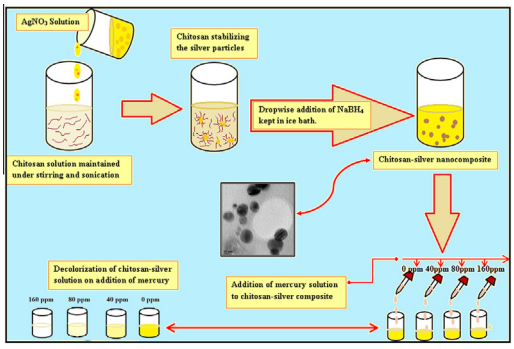
E.A.K. Nivethaa [a], V. Narayanan [b], A. Stephen [a,*]

[a] Material Science Centre, Department of Nuclear Physics, University of Madras, Guindy Campus, Chennai 600 025, India
[b] Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India

## HIGHLIGHTS

- Chitosan-silver polymer matrix composite was prepared by chemical method.
- The binding of silver to chitosan's $NH_2$ and OH groups was evident from XPS and FTIR.
- The use of the composite as a colorimetric sensor was studied.
- Shift of surface plasmon peak on addition of mercury confirms its detection.
- Color change was observed on addition of mercury but not for other elements.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 12 July 2014
Received in revised form 20 January 2015
Accepted 29 January 2015
Available online 18 February 2015

*Keywords:*
Nanocomposite
Chitosan
Silver
Photoelectron spectroscopy
Infrared spectroscopy
Colorimetric sensing

## ABSTRACT

Polymer matrix type chitosan-silver nanocomposite containing different weight percentage of silver was synthesized by the chemical method. HRTEM images confirm the embedment of silver in the chitosan matrix. The binding of silver to the $NH_2$ and OH groups of chitosan is evident from XPS and FTIR studies. An increase in the absorbance observed from UV–Vis analysis on raising the weight percentage of silver showed the increase in the amount of silver in the nanocomposite. The face centered cubic structure of silver and the semi-crystalline nature of chitosan are evident from the XRD studies. On interaction with mercury the UV–Vis spectra of the composite showed a decrease in intensity and a blue shift confirming the use of the composite as a colorimetric sensor for the detection of mercury. The limit of detection was found to be about $7.2 \times 10^{-8}$ M. High specificity and the sensitivity of the environmental friendly and non-toxic nanocomposite to detect very low concentrations of mercury make the system a perspective one.



## Introduction

Synthesis of materials having a specific morphology, leading to the enhancement of material properties and paving path to the use of the compound in new areas has gained importance in the recent past. Achievement of well dispersed and unique morphology in the case of composites containing an inorganic moiety and a polymer is a challenging task. This is because in most of the cases, prevention of agglomeration can be achieved only by the addition of surfactants which may hinder the composite's use in the biological field. Thus the choice of materials plays a major role in attaining good morphologies without masking the use of the compound in various fields. The use of various polymers like PVA, PVP in conju-

* Corresponding author. Tel.: +91 044 22202802; fax: +91 044 22351269.
*E-mail address:* stephen_arum@hotmail.com (A. Stephen).

http://dx.doi.org/10.1016/j.saa.2015.01.075
1386-1425/

gation with inorganic compounds, as a composite system has already been studied. Chitosan, a biopolymer obtained from the shell of crustaceans is a promising candidate due to the availability of $-NH_2$ and –OH groups which attribute chelating properties to it [1,2]. This property makes it suitable for use as a sensor for the sensing of glucose, catechol, etc. Apart from this chitosan possesses properties like being biocompatible, biodegradable and non-toxic which make it attractive for use in various fields including medicine [1,2].

Silver nanoparticles (AgNP's) are popular for their wide range of applications ranging from antibacterial activity [3,4], sensing of various ions [5], pH and glucose [6,7] to the inhibition of diseases like tumor [8] and HIV [9]. But disadvantages arise due to the agglomeration of silver [10], major one being the increase of particle size. As a consequence of this the target specificity of AgNP's decreases as larger particles cannot bind to the receptor [11]. The accumulation of AgNP's in kidney, spleen, and liver leading to its death ultimately have been reported [12]. These effects can be overcome by the addition of silver to chitosan because of the activity of chitosan as a surfactant and as a component attributing biocompatibility and biodegradability to the composite. Thus it helps in preventing the agglomeration of particles, making the effects of silver very specific and ensuring the easy removal of silver from the body.

Chitosan-silver nanocomposite has a combination of properties possessed by both the entities [13]. One major advantage of the composite system is that the hindrance encountered while using silver or chitosan separately are overcome. The composite is thus a promising candidate for use in a variety of medical applications including biosensors, as a drug delivery carrier and as an antibacterial agent.

In the present work the focus has been laid on the preparation and characterization of chitosan-silver polymer matrix nanocomposite containing different weight percentages of silver. Chitosan present in the composite confers qualities like target specificity, biocompatibility, biodegradability and non-toxicity to the composite, hence widening the range of applications. The prepared nanocomposite was characterized using XRD, XPS, FESEM, TEM, FTIR, and UV analysis. The use of the prepared composite for the detection of mercury has also been studied.

Detection of mercury is important since mercury is a toxic pollutant [14]. It is one of the major water contaminants which is highly carcinogenic and toxic to the cells [15]. Owing to the fact that mercury ions cause damage to the brain endocrine system and the kidneys it is important to monitor its content in water. Among the various sensors the colorimetric sensors based on the change of color on addition of mercury have attracted much attention due to the technique being simple, economic and reliable. Here, chitosan-silver nanocomposite has been successfully used to detect mercury. The colorimetric response of the composite to mercury ions has been investigated.

## Experimental

### *Materials*

Chitosan (CS) from sigma Aldrich, silver nitrate ($AgNO_3$) having 99.9% purity from s.d. fine chemicals and sodium borohydride ($NaBH_4$) extrapure from Finar reagents was used for synthesis. All experiments were carried out using double distilled water.

### *Preparation of chitosan-silver polymer matrix nanocomposite*

Chitosan-silver (CS-Ag) nanocomposite was prepared using a simple and cost effective chemical method. In this method silver nanoparticles were obtained by the in situ reduction of silver nitrate in a solution of chitosan. Composite containing 5–50 weight percentage of silver was synthesized and characterized.

Chitosan was dissolved in 2% acetic acid to obtain a polymer solution at a concentration of 0.34% (w/v). The amount of silver nitrate was chosen such that the composite would contain 5% (w/w) silver i.e. the amount of silver would be 5% of the weight of chitosan. The calculated quantity of $AgNO_3$ was dissolved in double distilled water and was added to the chitosan solution kept under simultaneous stirring and sonication in an amber flask. The pH of the solution was found to be ~2. The reduction of silver nitrate to silver was accomplished by the dropwise addition of sodium borohydride to the above solution. The pH of the final solution was found to be between 5 and 6. The solution was maintained under stirring and sonication for 2 h. The obtained product was washed several times using deionised water to remove the excessive sodium borohydride. The solution was centrifuged and the particles were collected and characterized [16].

The X-ray diffraction analysis of the prepared sample was done using GE X-ray diffraction system-XRD 3003 TT with $CuK\alpha_1$ radiation of wavelength 1.5406 Å. X-ray photoelectron spectroscopy (XPS) measurement was done using DAR400-XM 1000 (OMICRON Nanotechnologies, Germany) equipped with dual Al/Mg anodes as the X-ray source. The Al anode was used to attain the survey and elemental spectra. All spectra were calibrated using C 1s peak at 284.5 eV to exclude the charging effect on the sample. The FESEM analysis was done using a Hitachi SU-6600 instrument. HRTEM was carried out using Tecnai instrument operating at 200 kV, equipped with EDAX. The FTIR spectrum was recorded using Perkin-Elmer FTIR system and Cary 5E UV–Vis-NIR instrument was used for recording the UV spectrum at room temperature using a double beam.

### *Protocol for testing the efficiency of chitosan-silver nanocomposite as a colorimetric sensor*

The serial dilution procedure was followed for the preparation of solutions containing various concentrations of the ions (Hg, Pb and Cd). 0.1 ml of the solution containing these ions was added to a 3 ml chitosan-silver solution containing 50 weight% of silver. The UV–Vis spectra for these solutions was monitored and obtained after 5 min of interaction with the ions.

## Results and discussion

### *Structural investigation*

The XRD pattern of CS-Ag nanocomposite shows the presence of peaks of both chitosan (at ~11.9° and 20.8°) and silver (~38.2°, 44.4° and 64.6°) (Fig. 1). The peaks of chitosan have been indicated using arrows and the peaks of silver have been indexed. The silver peaks were in agreement with the JCPDS card no. 04-0783. The preponderant (1 1 1) reflection is indicative of the oriented growth of the silver nanoparticles into FCC structure. The XRD results match well with the already reported results [17–19]. The average crystallite size calculated using Scherrer's formula was ~ 8 nm. The peaks of chitosan decreased in intensity as the percentage of the silver in the composite increased. The XRD spectrum of chitosan has been given in the supporting information.

### *FTIR analysis*

Fig. 2 shows the FTIR spectrum of chitosan-silver nanocomposite containing 10, 20 and 40 weight% silver. FTIR analysis was done to characterize the chemical structure of the nanocomposite. C-N stretching at ~ 1086 $cm^{-1}$, C-O-C bridge at ~ 1155 $cm^{-1}$, C-O-C