Optical and Structural Study of Biocompatible Silver-Chitosan Colloids

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Abstract: Nontoxic and biocompatible silver-chitosan colloids were prepared by direct chemical reduction. The Ag-chitosan colloids are drop cast on a glass slide and left to dry to obtain uniform, homogeneous films. The presence of chitosan prevented the growth of silver nanoparticles from agglomeration. The occurrence of localized surface plasmon resonance (LSPR) at ~ 400 nm in the optical absorption spectra indicated the formation of Ag nanoparticles which is the characteristic property of metal nanoparticles. The -prepared colloidal Ag nanoparticles are chemically stable and remain colloidal even after aging. The estimated average particle size is about 14nm and the face-centered cubic phase was observed in the XRD pattern. SEM images clearly showed the homogeneous distribution of silver nanoparticles.

Keywords: chitosan; silver nanoparticles; surface plasmon resonance; biocompatibility; XRD.

1. Introduction

Over the years, noble metal (Au, Ag) nanoparticles have attracted researchers due to their environmental benignity, ease in processibility via green chemistry, controlled tunability of optoelectronic properties for a wide spectral range, and so on [1-4]. The exceptional features such as localized surface plasmon resonance, plasmon-enhanced emission, surface-enhanced Raman spectroscopy make them potential candidates in various applications such as storage, optoelectronic, chemical, biosensing, catalysis, and other devices [5-9]. Various synthetic protocols have been developed to obtain noble metal nanoparticles. Metal nanoparticles synthesized using biomimetics has several advantages over other physicochemical preparation protocols [10-13].

Silver (Ag) nanoparticles are well-known candidates in various biological applications due to their distinctive features: high electrical conductivity, thermal conductivity, catalytic activity, non-linear optical properties, and good antimicrobial activity [14-20]. It releases silver ions due to unstable silver nanoparticles, leading to antimicrobial properties [21]. Chitosan is a well-known synthetic linear polysaccharide derived from natural chitin and is also found in abundance next to cellulose. It is mainly found in the fungi cell walls and crustaceans’ shells, shrimps, crabs. Chitosan is a biodegradable, biocompatible, nontoxic natural biopolymer with high permeability. It forms chelate compounds with metal ions and thus acts as a mild reducing agent [22]. Also, the amino and hydroxyl functional groups present in chitosan show various biological activities for infection resistance in numerous human cell types. Chitosan composite
has a large number of applications such as biomaterials, drug delivery, wastewater treatment, nanofibers, food coating [23-27].

The present work reports the synthesis of chitosan chitosan-mediated silver nanoparticles under ambient conditions. Chitosan acts as a stabilizer, and sodium borohydride (NaBH₄) is used as a reducing agent. As-synthesized silver nanoparticles are in colloidal form, stable for several months. Ag-chitosan colloidal films are prepared and used for further characterization by the solution casting method.

2. Materials and Methods

2.1. Experimental details.

All chemicals reagents used were of analytical grade. Silver nitrate (AgNO₃), sodium borohydride(NaBH₄), and chitosan were obtained from sd-Fine chemicals, India. A wet chemical route is used to synthesize Ag-chitosan colloids in the present work. Silver nitrate (AgNO₃) is used as a silver source, readily soluble in water. 0.025M of AgNO₃ is prepared by dissolving silver salt in 30ml of distilled water. 0.0025M of chitosan solution is prepared by dissolving chitosan in 40ml of distilled water to which acetic acid is added to maintain pH~6. Both these solutions are mixed by stirring for 15 mins to which 1.2 ml of 0.01M freshly prepared sodium borohydride solution is added dropwise. The solution turns from colorless to pale yellow, which is in colloidal form, as shown in figure 1. The colloidal silver nanoparticles are stable for more than 6 months. The solution turns darker day by day, indicating the growth of nanoparticles.

2.2. Sample characterization.

Optical absorption of as-synthesized silver-chitosan nanocomposite is measured by using UV-Visible-NIR Spectrometer, model JASCO V-670, and Photoluminescence (PL) spectrum is recorded using Horibha fluoromax-4 fluorospectrometer. The Fourier Transform Infrared(FTIR) spectroscopic patterns are taken by Nicolet iN10 FTIR spectrometer in transmission mode. These measurements were carried out in the spectral range of 500-4000 cm⁻¹ with a linear scan velocity of 0.632 cm/s, and each spectrum is an average of 100 scans. To know the crystal structure and size, a scan carried out powder X-ray diffraction (XRD) measurements using a Philip X’Pert powder diffractometer with Cu Kα1 radiation (λ = 1.54056 Å) with a scan step of 0.016 deg/s. The surface morphology of composite films is studied by EVO LSscanning electron microscope (SEM) (Carl Zeiss, Germany).
3. Results and Discussion

Ag-chitosan colloids are significant due to their biocompatibility, and nontoxic behavior and hence can be implemented in various biological applications. The hydrophilic nature of chitosan arises due to the presence of primary amino acids, which facilitate the interaction with metal nanoparticles [28]. It is well reported that chitosan acts as a stabilizing and mild reducing agent [29]. As prepared, Ag-chitosan colloids are cast on the glass slide to dry, and yellowish-brown films are obtained.

![Image](a) Optical absorption spectrum of Ag-chitosan colloids. (b) Photoluminescence spectrum of Ag-Chitosan colloids.

Metal nanoparticles exhibit size-dependent surface plasmon resonance over a large spectral range in the nano regime. Herein, the formation of silver nanoparticles is confirmed from the optical absorption spectra, taken just after preparation. The characteristics LSPR peak is observed at 409 nm, as shown in figure 2(a). The slow change in color from udfp pale yellow to yellow-brown indicated the formation of silver nanoparticles. The colloid remained stable for months without coagulating. Photoluminescence studies are carried out for the freshly prepared colloid in the range of 200nm to 550 nm and are shown in figure 2(b). The emission at 433 nm is due to the surface plasmon resonance radiative decay, also known as plasmon scattering or plasmon emission, and is well reported in the case of metal nanoparticles [30,31]. SPR and energy of plasmon emission depend on the nanoparticle's size [32].

![Image](a) FTIR spectrum of Ag-Chitosan powder. (b) X-ray diffraction pattern of Ag-Chitosan powder.

The chemical binding of various functional groups of chitosan and metal nanoparticles could be confirmed from the FTIR spectra, as shown in figure 3(a). A band at 1035 cm\(^{-1}\) represents the CO- stretching vibration, vibrations at 1388 cm\(^{-1}\) correspond to the carboxylate group's symmetric stretching, and 1638 cm\(^{-1}\) corresponds to asymmetric stretching of the
carboxylate group. The peak at 3282 cm⁻¹ attributes bands of amide A and 2874 cm⁻¹ represents the amide B bands. The peak representing amide A is due to stretching vibrations of N-H and O-H groups. The peak of amide B is because of stretching vibrations of aliphatic C-H bands [32]. The three amide bands of chitosan shifted from 1083 cm⁻¹, 1399 cm⁻¹, and 1653 cm⁻¹ to 1022 cm⁻¹, 1335 cm⁻¹, and 1635 cm⁻¹, respectively, compared to standard chitosan FTIR peaks, which indicates the chelating of hydroxyl group and amino group in the chitosan [29]. Figure 3(b) represent the XRD pattern of Ag-chitosan colloidal films. The diffraction peak at 20 = 22° indicates the presence of semicrystalline chitosan. The peak at 38.47°, 44.97°, 64.78°, and at 77.74° confirm the formation of Ag nanoparticles, which pertain to the respective Bragg’s planes (111) (200), (220), and (311) of face-centered cubic (fcc) crystal structure (JCPDS No. 87–0717) [32]. The peak corresponding to (111) plane is more intense compared to other planes, which shows that (111) plane is predominant in the arrangement. Size of Ag nanoparticles are nanoparticles is calculated using Bragg’s equation;

\[
D = \frac{(0.89 \lambda)}{\beta \cos \theta}
\]

\( \lambda \) represents the wavelength of X-ray radiation, \( \theta \) is half of the angle between the incident ray and diffracted ray, \( \beta \) is the full-width at half maximum (FWHW) of the peak. The estimated average size is about 14 nm. SEM images show the homogeneous distribution of Ag nanoparticles as chitosan prevents the formation of agglomeration, as shown in figure 4. Thus, chitosan plays a crucial role in controlling particle size, morphology, and homogeneity.

![SEM images of Ag-Chitosan colloidal films with different resolutions.](https://nanobioletters.com/)

4. Conclusions

This work reports the synthesis of nontoxic, biocompatible Ag-chitosan colloidal. XRD studies confirm the formation of silver nanoparticles’ face-centered cubic (fcc) crystal structure. Surface plasmon resonance peak is observed in the absorbance spectrum. The photoluminescent spectrum shows that prepared silver nanoparticles are fluorescent and emit blue. SEM images show proper dispersion of silver nanoparticles because chitosan acts as a mild reducing and stabilizing agent during the growth of metal nanoparticles. Because of its bio-friendly nature, Ag-chitosan colloids can be used in biomedical applications, as well as wearable electronics and food processing etc.

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Conflicts of Interest

The authors declare no conflict of interest.

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