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Green Synthesis of silver nanocomposites for Electrical, Optical and Biological applications

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ABSTRACT

Silver nanoparticles were synthesized in a chitosan biopolymer by an in situ green chemical procedure by ordinary chemical reduction. Silver nano particles were doped with some transition metal oxides in Chitosan, such as ZnO, CuO. As prepared Silver–Chitosan (CS/Ag) nanocomposites were investigated using electron microscopy (TEM and SEM), UV–VIS and photoluminescence spectroscopy (PL). UV–VIS absorption spectrum of the nanocomposites exhibited a strong surface plasmon resonance (SPR) band around 406 nm. PL spectra of CS/Ag nanocomposites were enhanced by doping metal oxides. Antibacterrial activity of CS/Ag nanocomposites indicating that highest antibacterrial activity was detected with ZnO dopped film .Also, Electrical Resistivity of nanocomposites showed resistivity in the semiconducting range.

Key words: Chitosan/Silver Nanocomposites, Optical and Electrical properties, Antibacterrial activity

Introduction

Polymer nanocomposites containing metal nanoparticles have attracted a great interest due to their unique chemical and physical properties. The need of elaboration of non-toxic and cost-effective antimicrobial finishing of fabrics grows with progressive production increase of medical, healthcare and protective materials (Gao et al., 2008). The incorporation of metallic nanoparticles into easily processable polymer matrices offers a pathway for better exploitation of their characteristic optical, electronic and catalytic properties. On the other hand, the host polymers can influence the growth and spatial arrangement.

The incorporation of metallic nanoparticles into easily processable polymer matrices offers a pathway for better exploitation of their characteristic optical, electronic and catalytic properties. On the other hand, the host polymers can influence the growth and spatial arrangement of the nanoparticles during the in situ synthesis, which makes them convenient templates for the preparation of nanoparticles of different morphologies (Lu et al., 2005).

Furthermore, by selecting the polymer with certain favorable properties such as biocompatibility (Liu et al., 2008), conductivity (Balamurugan et al., 2009) or photoluminescence (Yang et al., 2009), it is possible to obtain the nanocomposite materials for various technological purposes. In the last decades the use of biopolymers in research and industry has significantly increased due to their low cost, renewability of sources, and nontoxic, environment friendly (e.g. ‘green’) processing. This has also been reflected in the metal–polymer nanocomposite research area where polysacharide biopolymers, such as starch (Raveendran et al., 2003 and Boz’anic’, 2007), alginate (Pal et al., 2005 and Brayner et al., 2007) and chitosan (Shih et al., 2009, Murugadoss and Chattopadhyay 2008, Wei et al., 2009, Sun et al., 2008 and Wei et al., 2008), proved to be good environments for controlled growth of metallic nanoparticles. Chitosan, a polysaccharide biopolymer obtained by deacetylation of the highly abundant biopolymer chitin, due to the presence of both amino and hydroxyl groups in its monomers exhibits excellent chelating and film-forming properties (Rabea et al., 2003 and Kumar, 2000).

Another, widely unnoticed, property of chitosan is its photoluminescence in the ultraviolet region of electromagnetic radiation (Mi, 2005). Recently, it was shown that biopolymers containing ultraviolet emitting chromophores can be used to induce photochemical reactions (Nowakowska et al., 2002 and Wu et al., 2005).

Along with silver is the most extensively used metal for the preparation of nanoparticles with potential biomedical functions. The motivation for these widespread investigations is its antimicrobial activity, limited toxicity and well established modes of preparation of quality silver nanoparticles (Sharma et al. 2009).

Silver nanoparticles (Ag NPs) have attracted intensive research interest for centuries because of their important biological applications especially in bactericidal effect which is the capability of killing about 650 types of diseases causing microorganisms (Raffi et al. 2008). It has a significant potential for preventing...
infections, healing wounds (Atiyeh et al. 2007) and anti-inflammatory. Hence, Ag NPs had been incorporated in textile fabrics, polymers, dental material, medical device and burn dressing to eliminate microorganisms.

Also, silver nanoparticles exhibit a surface plasmon resonance band sensitive to changes in their morphology and environment that makes them promising nanoplatforms for detection of biomolecules (Aslan et al., 2004) The ability of chitosan to complexate with silver ions originates from NH2-groups present in the b-(1–4)-glucosamine units of the polymer.

This manuscript reports studies on silver nanoparticles prepared by a ‘green’ chemical procedure using chitosan as reducing agent under mild thermal treatment. Novel CS/Ag, CS/Ag/ZnO and CS/Ag/CuO nanocomposite films with high antibacterial activities were successfully prepared. The resulting materials were investigated using electron microscopy (TEM & SEM), optical absorption (UV–VIS) and photoluminescence (PL) spectroscopy. Also, the biological activity of the as prepared materials and electrical resistivity were measured.

Experimental:

1. Materials:

Chitosan (molecular weight _400,000 g/mol), silver nitrate (AgNO3), acetic acid (CH3COOH) zinc oxide (ZnO) copper oxide (CuO ) and sodium hydroxide were purchased from Sigma–Aldrich and used as received.

2. Synthesis:

Appropriate amounts of AgNO3 and AgNO3 with ZnO or CuO powders were dissolved in 100mL of 1% (v/v) acetic acid to obtain silver and zinc cations. And 1.0 g of chitosan was added to the above solution. Then the mixture was sonicated for 30 minute after magnetic stirring and then adjusted acidity by 0.1M NaOH solution (pH 4.8) to obtain clear sol. The resulting sol was cast onto glass plates and the transparent films were obtained after solvent evaporating slowly in air. Lastly the transparent films with glass were immersed in 0.1M NaOH solution for 12 h at 333 K. After being removed from the glass plates, the blend films were obtained through sufficiently washing with deionized water and drying (Li, 2010).

3. Structural characterization and measurements:

The as-prepared samples were characterized by both transmission electron microscope (TEM, JEOL JEM-3010, 300 kv) and scanning electron microscope (SEM, JEOL JXA -840, Electronic Company, Japan).They were used to characterize the size, dispersion of Ag NPs and the morphology of CS/Ag nanocomposites. The samples for TEM were prepared by making suspension from the powder in deionized water. UV-VIS spectra of nanocomposite solutions, were measured using UV–VIS spectrometer (6100 Jusco, Japan). The photoluminescence (PL) emission spectra were recorded using a Perkin–Elmer LS55 fluorescence spectrophotometer in the wavelength range from 330 to 550 nm at room temperature using two excitation wavelengths kexc = 300 nm and kexc = 320 nm. Electrical resistivity of the surface of prepared samples thin film were measured using 6517A Electrometer/High Resistance Meter. Thin films of CS/Ag nanocomposites were tested against Gram positive bacteria (Staphyloccus aureus and Bacillus cereus) and Gram negative bacteria (Escherichia coli and Pseudomonas aeruginosa) using the disk diffusion method (Bryaskova et al., 2010).

Results and Discussion

In the present study silver nanoparticles were obtained using the ability of chitosan (CS) to form chelate compounds with metal ions. CS is characterized by the presence in its structure two polar groups (OH, NH2) donor of electrons can form a link with inorganic materials enhancing electrical, optical and biological properties qualify for various applications.

The mechanism of ZnO and silver generation:

Chitosan, zinc oxide and silver nitrate were dissolved in dilute acidic solvent. Through adjusting acidity of the solution, the sol containing Zn2+ and Ag+ ions was obtained. The –OH and –NH2 groups of CS chain reduced Ag+ ions to Ag under hot alkaline condition Murugadoss and Chattopadhyay 2008. The possible reactions of the reduction of Ag+ to Ag by the chitosan in hot alkaline solution took place as follows:

\[
\text{AgNO}_3 + \text{aq.CS} \rightarrow \text{Ag}^+ + \text{CS}^+ + \Delta \text{OH}^+ + \text{Ag}^0 / \text{CS}
\]  

(1)
In order to make Zn\(^{2+}\) ions transform into ZnO, the films were immersed in dilute alkaline solution at 333 K. The possible reactions of ZnO formation in hot alkaline solution took place according to (Perrin 1962, Spanhel and Anderson 1991 and Sepulveda-Guzman et al., 2009) as follows:

\[
\begin{align*}
\text{Zn}^{2+} + \text{OH}^- & \rightleftharpoons \text{Zn-O-H}^+ \\
\text{Zn-O-H}^+ + \text{OH}^- & \rightarrow \text{ZnO} + \text{H}_2\text{O}
\end{align*}
\]

(2)  
(3)

Since Zn\(^{2+}\) disperses homogeneously in chitosan sol, ZnO was generated homogeneously within chitosan polymer.

**UV–VIS:**

The UV–VIS spectra of chitosan CS, CS/Ag, CS/Ag/ZnO and CS/Ag/CuO films prepared at PH = 4.8 are shown in figure 1. For comparison, CS molecules exhibited an absorption band as a result of the conjugated double bonds, while the composites arises due to the excitation absorption peak of surface plasmon vibrations of Ag atoms.

![UV–VIS spectra of CS, CS/Ag, CS/Ag/ZnO and CS/Ag/CuO blend films.](image)

**Fig. 1:** UV–VIS spectra of CS, CS/Ag, CS/Ag/ZnO and CS/Ag/CuO blend films.

It can be noticed that, CS/Ag spectrum exhibited an absorption band at around (400-420) nm, which is a typical plasmon band, suggesting the formation of silver nanoparticles. composites arises due to the excitation of surface plasmon vibrations of Ag atoms.

Compared with pure CS film, CS/Ag/ZnO films showed two absorption bands. One absorption band at 343 nm was attributed to the presence of Ag nanoparticle. The other band at about 450 nm due to ZnO and CuO absorption, blue-shifted by 29 nm. This indicated that ZnO and CuO within chitosan were in the size of nanometer, which consistent with the SEM analysis. The width of the absorption band for the nanocomposites containing ZnO and CuO are broader than those containing pure chitosan and CS/Ag. Furthermore, the center of absorption band also varied and shifted to higher wave length (400-500) nm. The nanocomposites bandgap energy calculated were followed the order: CS (3.02 eV), CS/Ag (2.07eV), CS/Ag/ZnO (1.57) and CS/Ag/CuO (1.84 eV) blend films.

This observed trend was similar to that observed in particle size (table 1), where the average diameters decreased as the bandgap energy increased. The absorption edge was blue shifted to 550 nm when the particle size decreases. This shift is in agreement with earlier reports, where the absorption edge had been reported to shift with decreasing nanoparticle size for Ag particles (absorption maxima at 460 nm) by 1–60 nm range (Westphalen et al., 2000). The band can be assigned to charge transfer from oxygen to the metal center. One can expect to see the ligand field transitions in these cases. However, since these transitions are Laporte
forbidden, they have very low intensity. Hence, in the presence of intense charge transfer transitions one cannot detect them.

Photoluminescence:

![Photoluminescence emission spectra of CS/Ag, CS/Ag/ZnO and CS/Ag/CuO nanocomposite films.](image)

The photoluminescence emission spectra of CS/Ag, CS/Ag/ZnO and CS/Ag/CuO nanocomposites are shown in the Fig. 2. The emission spectrum of the chitosan film is characterized by an asymmetric band with maximum emission at 390 nm, which probably originates from the protein residues in the biopolymer (Boz’anić, 2010). This band can be resolved by deconvolution into two sub-bands that are positioned at approximately 380 and 465 nm. The corresponding photoluminescence excitation spectrum, measured at the emission wavelength $\lambda_{em} = 380$ nm, showed that a maximum luminescence of the material should be expected for excitation $\lambda_{exc} = 324$ nm. After the introduction of silver in the matrix the emission is still present, but it decreases with increasing silver for the nanocomposite.

In addition, as the silver nanoparticle doped by metal oxides, the emission bands slightly blue shifted. A possible explanation for this behavior can be drawn from an analysis of the absorption spectra of the materials. Since the silver clusters produce absorption bands in the region of chitosan emission, the observed quenching can be attributed to a non-radiative energy transfer mechanism such as charge transfer (Boz’anić, 2010). In the case of the nanocomposite, the observed decrease in the photoluminescence could be a consequence of the overlap between the absorption band of silver and the emission band of chitosan.

Since the silver clusters produce absorption bands in the region of chitosan emission, the observed quenching can be attributed to a non-radiative energy transfer mechanism such as charge transfer (Beltramini and Lerch, 1982). In the case of the nanocomposite, the observed decrease in the photoluminescence could be a consequence of the overlap between the absorption band of silver and the emission band of chitosan. PL Intensity of nanocomposites has the order:

$$\text{CS/Ag/ZnO} > \text{CS/Ag} > \text{CS/Ag/CuO}$$

It can be concluded that doping CS/Ag with CuO lowering the emission intensity, while ZnO enhance it.

TEM:

The transmission electron microscope (TEM) is currently the imaging technique of choice for the characterization of shapes and size distribution of materials. To determine the sizes of the as-prepared silver nanoparticles capped by Chitosan, TEM were performed (Fig.3) and their sizes were presented in Tables (1). Different metal oxide doped with Ag nanoparticle on CS were used to probe their effect on the size of the resulting nanoparticle CS/Ag, CS/Ag/ZnO and CS/Ag/CuO are shown. Most of Silver nanoparticles show spherical morphology.

TEM of CS/Ag nanocomposite is shown in Fig. 3(a), it can be seen that silver particle capped by chitosan has spherical particles with size range (26-55 nm). Fig. 3(b) shows TEM of CS/Ag/ZnO. It can be noticed that the particles is spherical with particle size ranging from(8-22 nm), where TEM of CS/Ag/CuO Fig. 3(c)...
nanocomposite shows that the particle size of spherical shape and particle size ranging from (24-54nm) (Murugadoss and Chattopadhyay 2008).

![TEM images of CS/Ag, CS/Ag/ZnO, and CS/Ag/CuO nanocomposites](image)

**Fig. 3:** TEM of: (a) CS/Ag (b) CS/Ag/ZnO and (c) CS/Ag/CuO

**SEM:**

![SEM images of CS/Ag, CS/Ag/ZnO, and CS/Ag/CuO nanocomposites](image)

**Fig. 4:** SEM of: (a) CS/Ag (b) CS/Ag/ZnO and (c) CS/Ag/CuO

Fig. 4 represents surface and cross-section SEM photographs of nanoparticle CS/Ag, CS/Ag/ZnO and CS/Ag/CuO nanocomposites films. CS/Ag film displayed a smooth surface. SEM images of the cross-sectional surface of CS/Ag/ZnO shows bright parts in the nanocomposite fractured films are the ends of the broken nanoparticles. SEM images CS/Ag/CuO unsymmetric morphology; that is, the nanoparticles were dispersed throughout the chitosan matrix appeared to have intercalated morphology due to complexation of the silver ions with chitosan chains, results formation in well separated nanoparticles i.e. a good dispersion of the particles within the matrix (Boz’anic’, 2010).

**Electrical Resistivity:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrical Resistivity (Ω cm)</th>
<th>Ag particle size (nm)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS/Ag</td>
<td>6.35x10^11</td>
<td>55-26</td>
<td>2.13</td>
</tr>
<tr>
<td>CS/Ag/ZnO</td>
<td>2.83x10^9</td>
<td>22-8</td>
<td>1.59</td>
</tr>
<tr>
<td>CS/Ag/CuO</td>
<td>4.20x10^8</td>
<td>54-24</td>
<td>1.79</td>
</tr>
</tbody>
</table>

The electrical properties of Ag/Chitosan thin film nanocomposites were studied under an applied external constant potential as a function of film thickness at metal loadings. The electrical properties are directly dependent on the morphology of the silver nanoparticles embedded in the chitosan matrix. Composite films with
a very low metal oxide doped (ZnO, CuO) and metallic nanoparticles well dispersed within the polymer matrix, show dielectric characteristics. Initially isolated nanoparticles in composite films with a moderate metal loading are able to coalesce into fractal nanoclusters as the films grow thicker, leading to a giant increase of conductivity before it levels off. No continuous electrical pathway has formed at this stage, and thermally activated tunneling dominates the charge transport. At metallic nanoclusters are able to initiate and accomplish the percolation process and eventually form the metallic continuum. This continuous metallic pathway leads to a second rapid increase in conductivity and the switch to ohmic electron transport. As shown in table (1), the resulting conductivity of CS/Ag is lower than that of CS/Ag/ZnO and CS/Ag/CuO films due to the presence of other metal oxide which enhance the electron mean free path.

4. Antibacterial activities of Ag-nanocomposites:

<table>
<thead>
<tr>
<th>Table 2: Inhibition zone of bacteria</th>
<th>Sample</th>
<th>Gram +ve bacteria</th>
<th>Gram -ve bacteria</th>
<th>Pseudomonas aeruginosa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Staphylococcus aureus</td>
<td>Bacillus cereus</td>
<td>Escherichia coli</td>
</tr>
<tr>
<td>CS</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CS/Ag</td>
<td>12</td>
<td>0</td>
<td>12</td>
<td>22</td>
</tr>
<tr>
<td>CS/Ag/ZnO</td>
<td>12</td>
<td>15</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>CS/Ag/CuO</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table (2) showed that all samples exhibited antibacterial activities against all types of Gram +ve and Gram –ve bacteria, except CS/Ag/CuO with Pseudomonas aeruginosa.

Antibacterial activities of the synthesized silver nanoparticles in chitosan films (CS/Ag, CS/Ag/ZnO and CS/Ag/CuO) were tested by using Disk Diffusion Method (DDM) in which the inhibition zone was monitored (Lei et al., 2008). It was found that all films exhibit antibacterial activity by appearance of inhibition zone. The test of antibacterial activities showed that CS/Ag/ZnO blend films had higher antibacterial activities than CS/Ag and CS/Ag/CuO blend films, indicating that the composite of Ag and ZnO enhanced the antibacterial activities of chitosan.

Conclusion:

Silver–chitosan nanocomposites were prepared from Silver nanoparticles by a ‘green’ chemical procedure using chitosan as the reducing agent. Novel CS/Ag/ZnO and CS/Ag/CuO blend films were prepared had uniform distribution within chitosan polymer. UV–VIS absorption spectra of CS/Ag nanocomposites films showed absorption maxima characteristic a strong plasmon resonance band, indicating the formation of the silver nanoparticles. TEM analysis showed that the nanoparticles formed within the biopolymer were spherical shape. In addition visible photoluminescence emissions are observed from the synthesized silver nanoparticles. PL emission band of CS/Ag nanocomposites films was enhanced in comparison to that of the pure biopolymer due to the overlap between the corresponding absorption and emission bands. PL behavior of CS/Ag nanocomposites were enhanced by metal oxides doping. The test of antibacterial activities showed that CS/Ag/ZnO blend films had higher antibacterial activities than CS/Ag and CS/Ag/CuO blend films, Electrical Resistivity of nanocomposites showed semiconducting range. It suggested that CS/Ag blend films had potential application in medical and food packaging fields and a precursor for the preparation of semiconductor nanoparticles containing silver doping with metal oxides as ZnO and CuO.

References