

Modifications induced in the optical properties of starch by embedded Ag nanoparticles

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Abstract

Bio-degradable polymers such as starch, chitosan, cellulose etc which are extracted from renewable resources are attracting increasing interest in the recent years due to their environmentally friendly nature, low cost and high availability. In the present work, synthesis of colloidal silver nanoparticles and subsequently Ag-starch nanocomposite films were carried out via a green process. For synthesis of Ag nanoparticles water, soluble starch and fructose have been used as solvent, reducing agent and stabilizing agent respectively. The effect of varying concentration of colloidal Ag nanoparticles on the optical and structural properties of starch was investigated. The structural analysis of the nanocomposites was carried out using Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Size of the Ag nanoparticles from TEM micrograph comes out to be 10.75 ± 0.8 nm in the starch matrix. UV-visible absorption was further utilized to ascertain various optical constants like optical energy gap, Urbach's energy, optical conductivity etc. The optical energy gap of starch decreases from 4.08 eV to 2.21 eV for Ag-starch nanocomposite film containing 0.50 wt% of Ag nanoparticles and the Urbach's energy increases from 0.77 eV to 1.37 eV. Copyright © 2017 VBRI Press.

Keywords: Nanoparticle, nanocomposite, starch, optical energy gap, Urbach's energy.

Introduction

Nano dimensional materials are of immense scientific interest as their size, shape and number of surface atoms governs the physical properties exhibited by them [1]. In the case of metal nanoparticles as the diameter of nanoparticles becomes comparable with, or smaller than the wavelength of incident light they show, interesting optical behavior known as surface plasmon resonance (SPR). SPR is the light induced collective oscillations of the free electrons in metal nanoparticles, which becomes localized due to the reduced dimensions of the particles [2]. SPR depends upon the size, shape as well as dielectric environment of the metal nanoparticles. Owing to their unique optical properties metallic nanoparticles have potential applications in solar cells, wave guides, optical fibers etc [3, 4]. Among various metal nanoparticles, Ag nanoparticles have received significant attention in recent years due to its exceptional plasmonic activity, antibacterial activities, chemical stability, good thermal, electrical conductivity and catalytic properties [5, 6].

In the recent years biopolymers (e.g., starch, cellulose, chitin, protein) are attracting increasing interest as a host matrix for embedding metal nanoparticles as they act as both, capping as well as stabilizing agent [7, 8]. Among them starch has been considered as one of the most promising candidates because besides being

nontoxic it is an excellent reducing agent for the metallic salts and one of the best stabilizing agent for metal nanoparticles.

Also starch has good film forming ability [9-11]. Thus tuning of optical, dielectric, electrical, mechanical properties of starch by incorporation of Ag nanoparticles is important from both fundamental as well as application point of view. Numerous reports are available on the synthesis and characterization of Ag-starch nanocomposites. Cheng et. al. has reported the synthesis of Ag-starch nanocomposites using ascorbic acid as reducing agent and have depicted the enhancement of antibacterial activity of starch with the incorporation of Ag nanoparticles [12]. Bashir et. al. synthesized Cu-starch nanocomposites by using hydrazine hydrate as the reducing agent and have reported that the thermal stability of starch has been improved by Cu nanoparticles [13]. Hebeish et. al. synthesized starch stabilized Ag nanoparticles in the powder form using a uniquely prepared alkali treated starch for reduction of Ag⁺ to Ag nanoparticles and have reported the high stability of prepared nanoparticles on the basis of zeta potential [14]. Optical properties of Ag-starch nanocomposites have seldom been studied.

Hence in the present research work an attempt has been made to synthesize Ag-starch nanocomposites via

chemical reduction route and to study the effect of increasing concentration of Ag nanoparticles on optical properties of starch. Study of optical properties of Ag-starch nanocomposites is useful in exploring their potential application in optoelectronic devices etc [15].

Experimental

Materials

All chemicals used were of analytical grade and were used as received without any further processing. AgNO_3 (molecular weight = $169.87 \text{ g mol}^{-1}$), glycerol (molecular weight = 92.10 g mol^{-1}) and sodium citrate dihydrate (molecular weight = $294.10 \text{ g mol}^{-1}$) were purchased from Rankem; soluble starch (molecular weight = $342.30 \text{ g mol}^{-1}$) was purchased from HIMEDIA. Fructose (molecular weight = $180.16 \text{ g mol}^{-1}$) was purchased from S.D fine chemicals limited Mumbai. Sago starch was procured from local market. All solutions were made with millipore water.

Material synthesis

Synthesis of Ag nanoparticles

Ag nanoparticles were prepared by reduction of silver nitrate (AgNO_3) by using starch. 0.1g of soluble starch was dissolved in 25 ml distilled water at 85°C for 1hr 30 min. 10 ml of 0.04M silver nitrate prepared separately in a flask was added into 25 ml of hot aqueous solution of soluble starch under vigorous stirring in the absence of light. Later on 15 ml of 0.12M fructose solution was added. Resultant solution was held at 85°C under vigorous stirring [16]. Magnetic stirrer was used to maintain constant stirring throughout the reaction process. After half an hour of the reaction the color of the solution turned light yellow which darkened with increasing time, indicating the formation of Ag nanoparticles.

Preparation of Ag-starch nanocomposites

Sago starch was dissolved in distilled water at the gelatinization temperature (85°C) of starch under continuous magnetic stirring for 2 hr. Varying concentrations of the prepared colloidal solution of Ag nanoparticles along with 1 ml of 1 wt% sodium citrate dihydrate were dispersed in the prepared aqueous solution of sago starch by magnetic stirring for 20 minutes. To draw nanocomposite films the prepared solutions were casted in the petri-dishes. After the evaporation of the solvent at room temperature, yellow Ag-starch nanocomposite films were peeled off from the petri-dishes. Pure starch film was also prepared in the same manner. The samples were stored away from light.

Characterization techniques

Shimadzu Double Beam Double Monochromator Spectrophotometer (UV-2550) equipped with an Integrating Sphere Assembly ISR-240A in the wavelength range of 190-900 nm with a resolution of 0.5 nm was

utilized to record the absorption and reflection spectra of Ag nanoparticles and Ag-starch nanocomposite films. The absorption spectra of colloidal solution of Ag nanoparticles was recorded by taking distilled water as reference and for recording reflection spectra BaSO_4 was taken as the reference. From these spectra various optical constants such as optical energy gap, Urbach's energy and optical conductivity were determined.

The size, shape and distribution of the Ag nanoparticles in colloidal solution and in Ag-starch nanocomposite films were determined using transmission electron microscopy (TEM). TEM measurements were performed using a Hitachi H-7500 transmission electron microscope operated at an accelerating voltage of 80 kV and samples for microscope analysis were prepared by placing a drop of colloidal solution of Ag nanoparticles on carbon coated copper grid and for Ag-Starch nanocomposite film a small piece of the film was dissolved in the distilled water under ultrasonication, after that a drop of the solution was put on the carbon coated copper grid. The grid was allowed to dry before the measurements.

The surface morphology of Ag-starch nanocomposite film was studied using a JEOL (JSM-6390) scanning electron microscope operated at an accelerating voltage of 20 kV. With the help of sputtering technique a very thin layer of gold was coated on the prepared Ag-starch nanocomposite film and the coated sample was subjected to SEM analysis.

Results and discussion

The formation of Ag nanoparticles in colloidal solution and Ag-starch nanocomposite films was confirmed using transmission electron microscopy (TEM). **Fig. 1(A)** and **(B)** shows the TEM micrograph of colloidal solution of Ag nanoparticles and Ag-starch nanocomposite respectively. TEM micrograph of colloidal solution of Ag nanoparticles (**Fig. 1(A)**) reveals that the Ag nanoparticles are almost spherical in shape. **Fig. 1(B)** displays Ag nanoparticles present in starch matrix. It reveals that the shape of Ag nanoparticles is slightly deviated from spherical symmetry. This may be due to the interaction of Ag nanoparticles with starch matrix. Size of the Ag nanoparticles from TEM micrograph comes out to be $10.75 \pm 0.8 \text{ nm}$ in the starch matrix.

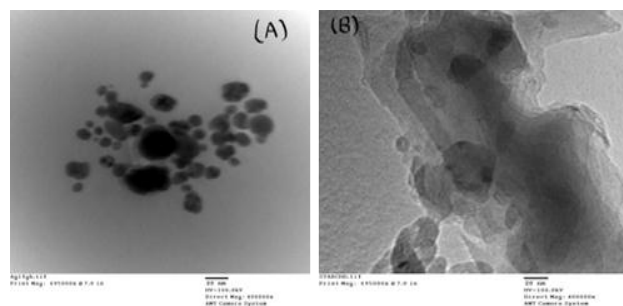


Fig. 1. TEM image of (A) colloidal Ag nanoparticles and (B) TEM image of Ag-starch nanocomposite films containing 0.47 wt% Ag nanoparticles in starch matrix.

SEM image of Ag-starch nanocomposite film is shown in **Fig. 2**. SEM image illustrates that Ag nanoparticles are deviated from the spherical symmetry. These results are consistent with TEM.

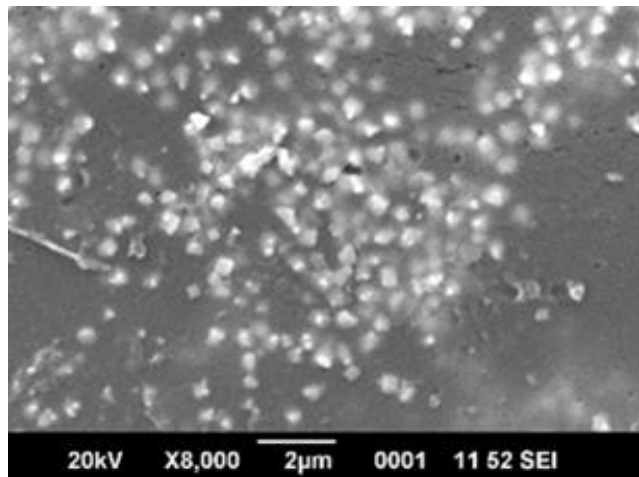


Fig. 2. SEM image of Ag-starch nanocomposite film containing 0.47 wt% of Ag nanoparticles in starch matrix.

Optical energy gap

Optical properties of nanocomposites are of unsurpassed importance due to their potential applications as waveguides, optical fibres, sensors etc [17, 18]. Optical energy gap of a material is defined as the energy difference between valence band and the conduction band of the material. Metals have smaller band gap energy and the polymers (insulators) have higher band gap energy. When the metal nanoparticles are introduced into the polymer matrix then the optical energy gap of polymers gets changed. To determine the optical energy gap of the films, the absorption coefficient, α , was determined using the following formula:

$$\alpha = 2.303 \times A \quad (1)$$

where A is the absorbance and d is the film thickness. Optical energy gap of starch and Ag-starch nanocomposite films has been calculated using Tauc relation [19]:

$$ah = B(hv - E_g)^n \quad (2)$$

where $h\nu$ is the photon energy, E_g is the optical energy gap, B is the constant known as band tailing parameter and n may have different values such as 1/2, 2, 3/2 or 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. E_g has been calculated by plotting $(ah\nu)^{1/n}$ vs $h\nu$ and then extrapolating the linear portion of the plot to $(ah\nu)^{1/n} = 0$. **Fig. 3(A)** shows such a plot for starch and Ag-starch nanocomposite film with $n = 2$. Graph for $n = 1/2$ (not shown here) was also plotted, but best linear fit was obtained for $n = 2$, pointing towards existence of allowed

indirect transition in starch and Ag-starch nanocomposite films. It is clear from the **Fig. 3(A)** that indirect energy gap decreases from a value of 4.08 eV for starch to 2.21 eV for Ag-starch nanocomposite film containing 0.5 wt % Ag nanoparticle. The decrease in the optical energy gap may be attributed to the increase in the degree of disorder in the films. After the addition of Ag nanoparticles, levels are introduced in the Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital (HOMO-LUMO) gap of starch due to which the lower energy transitions become possible and the optical band gap reduces. The results are in good agreement with Krstic et al. [20] and other authors [21, 22]. Mahmoud et al. found that optical energy gap of PVA decreased after the incorporation of Ag nanoparticles. They interpreted these result by saying that the decrease in optical band is due to the formation of trap levels in between the HOMO-LUMO gap which makes the lower energy transitions feasible [23].

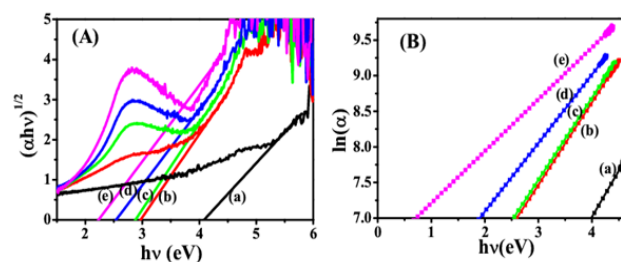


Fig. 3. Plot of (A) $(ah\nu)^{1/2}$ vs $h\nu$ and (B) $\ln(\alpha)$ vs $h\nu$ for (a) virgin starch and Ag-starch nanocomposite films containing (b) 0.34 wt% (c) 0.40 wt% (d) 0.47 wt% (e) 0.50 wt% of Ag nanoparticles in starch matrix.

Urbach's energy

The optical absorption spectra of the materials can be divided into three main regions; these are weak absorption region, which arise from defects and impurities, absorption edge region, which arise due to perturbation of structural and disorder of the system and the region of strong absorption that determine the optical energy gap. There is an exponential part near the optical band edge which is called as Urbach tail. This exponential tail appears in poor crystalline, disordered and amorphous materials because these materials have localized states which extended in the band gap [15]. Hence Urbach's energy E_u , is the measure of disorder content which was calculated by the analysis of absorption data using the following equation [24]:

$$\alpha = \alpha_0 \exp \frac{h\nu}{E_u} \quad (3)$$

Urbach's energy was calculated as the reciprocal of the slope of linear fit data of a plot of $\ln(\alpha)$ vs $h\nu$ as shown in **Fig. 3(B)**. It is clear from **Fig. 3(B)** that the value of Urbach's energy increases from a value of 0.77 eV for starch to 1.37 eV for Ag-starch nanocomposite film containing 0.50 wt% Ag nanoparticles. Since Urbach's energy is a measure of

disorder content, therefore from **Fig. 3(B)** it can be inferred that degree of disorder increases with the incorporation of increasing concentration of Ag nanoparticles in starch matrix.

Optical conductivity

The term optical conductivity is related with the movement of the charge carriers due to alternating electric field of the incident electromagnetic waves. The optical conductivity σ was determined by using the following equation [25]:

$$\sigma = \frac{\alpha n c}{4\pi} \quad (4)$$

where n is the refractive index and c is the speed of light.

Fig. 4 shows variation of the optical conductivity with wavelength for starch and Ag-starch nanocomposite films. From the **Fig. 4** it can be inferred that the optical conductivity increases with increasing concentration of Ag nanoparticles. This increase may be attributed to the creation of new levels in the energy gap which leads electrons to move from the valence band to the conduction band through these new levels, as a result the energy gap decreases and the optical conductivity increase. The increase of the optical conductivity indicates that the rate to absorb the incident photons by the electrons at a given energy increases [26, 27]. Optical conductivity is maximum at the surface plasmon resonance (SPR) wavelength of Ag nanoparticles.

Thus, the addition of Ag nanoparticles in starch matrix leads to the formation trap states in the HOMO-LUMO gap. These states are responsible for the observed changes in optical energy gap, Urbach's energy and optical conductivity. These results may enable these material properties to be adjusted for potential use of Ag-starch nanocomposite films in various practical applications.

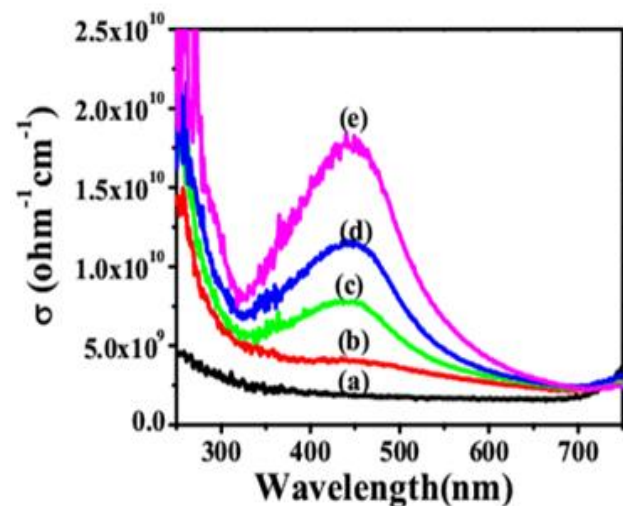


Fig. 4. Variation of optical conductivity (σ) with wavelength for (a) virgin starch and Ag-starch nanocomposite films containing (b) 0.34 wt% (c) 0.40 wt% (d) 0.47 wt% (e) 0.50 wt% of Ag nanoparticles in starch matrix.

Table 1. Value of optical parameters corresponding to Ag concentration in starch matrix.

Sample	Optical energy gap (eV)	Urbach's energy (eV)	Optical conductivity ($\text{ohm}^{-1}\text{cm}^{-1}$)
Virgin starch	4.08	0.77	1.94×10^9
0.34wt% Ag-starch	2.97	0.86	4.06×10^9
0.40wt% Ag-starch	2.89	0.87	7.79×10^9
0.47wt% Ag-starch	2.52	1.04	1.15×10^{10}
0.50wt% Ag-starch	2.21	1.37	1.79×10^{10}

Conclusion

Ag-starch nanocomposites were prepared by ex-situ chemical reduction method. Formation of Ag nanoparticles was confirmed by using Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Size of the Ag nanoparticles from TEM micrograph comes out to be 10.75 ± 0.8 nm in the starch matrix. TEM and SEM investigations reveal that Ag nanoparticles are well dispersed in the starch matrix and slightly deviated from the spherical symmetry. The variations in the values of optical energy gap, Urbach's energy and optical conductivity of starch after the addition of Ag nanoparticles may be due to the formation of trap levels within the energy gap of nanocomposite.

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