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Effect of incorporation of synthesized Fe @ Ag core-shell nanoparticles on optical parameters of polyvinyl alcohol

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Abstract. The present research work reports the fabrication of polyvinyl alcohol (PVA) based core shell nanocomposite films by assimilation of various concentrations of Fe @ Ag core shell nanoparticles in PVA matrix. Ex-situ chemical reduction approach was used for synthesis of core shell nanoparticles in which sodium borohydride (NaBH₄) and trisodium citrate were used as a reducing and capping agent respectively and subsequently Fe @ Ag-PVA nanocomposite films were fabricated via solution casting method. These nanocomposite films were further characterized to examine the effect of varying concentration of core shell nanoparticles on PVA matrix by using UV-Visible spectrophotometer so as to study the absorbance behavior and to calculate the electrical conductivity of core shell nanocomposite. Morphological studies of the Fe @ Ag-PVA nanocomposite films were carried out using Transmission electron microscopy (TEM).

INTRODUCTION

Core-shell nanoparticles have received immense attention owing to their tunable physical and chemical properties through controlling chemical composition and relative sizes of core and shell [1]. The core-shell nanoparticles are the structures having a core (inner material) and a shell (outer layer material) made up of different materials, both at nano-meter range [2]. In addition, Core shell structures with magneto-plasmonic behavior are of special interest in which the combining effects of both magnetic and plasmonic properties are observed that not only depends on the constituents but also on the core-shell volume ratio. In view point, the nanometer sized iron (Fe) nanoparticles are very promising contenders for the core material due to their controlled delivery of drugs in human beings [3] and silver (Ag) nano particles have special attention among all noble metals due to its exceptional plasmonic activity, antibacterial activities, chemical stability, good thermal and catalytic properties [4]. The pairing of plasmonic effect of silver with magnetic properties of iron has shown great promise in biomedical applications, such as integrated imaging, diagnosis, targeted delivery, and photo-thermal therapy [5]. The synthesized core shell nanoparticles can also be used for tuning different parameters of polymers.

In the present research work, Fe @ Ag nanoparticles were synthesized via chemical reduction method and their effect on the optical parameters of polyvinyl alcohol (PVA) has been studied.

EXPERIMENTAL

FeSO₄ .7H₂O (mol. wt 278.006 g/mol), AgNO₃ (mol. wt 169.87 g/mol), tri-sodium citrate dehydrate (mol. wt 294.10 g/mol) and sodium borohydride (mol. wt 37.83 g/mol) were purchased from Rankem. Polyvinyl alcohol (mol. wt 1, 25,000 g/mol) was purchased from Ranbaxy. All the chemicals were of analytical grade and were used without further purification. De-ionized water was used as solvent for synthesis

Iron (Fe) and silver (Ag) nanoparticles were prepared by the successive reduction of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and AgNO_3 using sodium borohydride as a reducing agent and tri sodium citrate were used as a capping agent. The synthesized Fe@Ag nano-sized particles were kept under the dark conditions to sustain the standardization in experiment. Subsequently, Solution casting method was approached for the fabrication of core shell nanocomposite films. 3 gm PVA was dissolved in de-ionized water at room temperature under continuous magnetic stirring. Homogeneous solution of core shell nanoparticles were mixed with 0.20 wt% and 0.40 wt % concentration in prepared aqueous solution of PVA. The resultant mixtures were used for fabrication of films that casted on the petri-dishes for approximately 10 days. After evaporation of solvent at room temperature, transparent films were obtained and were stored away from light.

HRTEM measurements were performed using “Tecnai” transmission electron microscope which was operated at an accelerating voltage of 200 kV. 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 5 nm was utilized to record the absorption spectra of virgin PVA and core shell nanocomposite.

RESULTS AND DISCUSSION

The structure of core shell nanoparticles embedded in PVA films was confirmed by using transmission electron microscopy (TEM). Figure 1 represents the TEM micrograph of nanocomposite film which confirms that the silver (Ag) nanoparticles crafted a shell layer over the iron (Fe) nanoparticles. But the shape of silver (Ag) nanoparticles is slightly deviated from spherical symmetry. This may be due to the mutual interaction of Ag nanoparticles with Fe nanoparticles. Size of the Fe @ Ag nanoparticles from TEM micrograph comes out to be 33.65 ± 4.6 nm in PVA matrix.

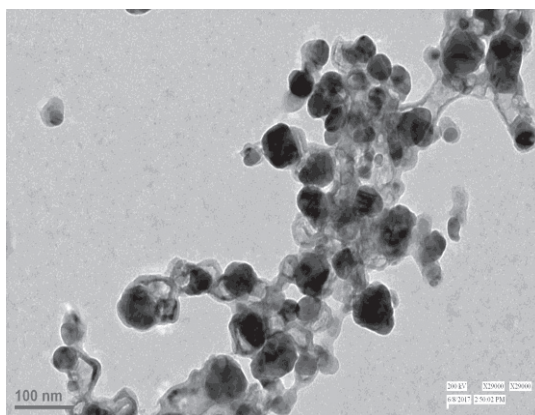


Figure 1. TEM micrograph of nanocomposite film containing 0.2 wt% of Fe @ Ag core shell nanoparticles.

Figure 2 depicts that UV-visible absorption spectra of virgin PVA and Fe @ Ag-PVA nanocomposite films with 0.2 wt% and 0.4 wt% of colloidal solution of core shell nanoparticles in PVA matrix. The absorption spectrum of virgin PVA shows that an absorption band in UV region with a peak at about 283 nm is observed. The absorption spectra for nanocomposite films show a broad surface plasmon resonance (SPR) peak at about 430 nm that confirms the formation of silver (Ag) nanoparticles [6]. The broadness in the SPR peak of nanocomposite films may be due to the incorporation of iron (Fe) nanoparticles into silver (Ag) nanoparticles. Absorption spectra of Virgin PVA and nanocomposite films represent that intensity of SPR peak increases with increase in concentration from 0.2 wt% to 0.4 wt % of core shell colloidal solution dispersed in PVA matrix.

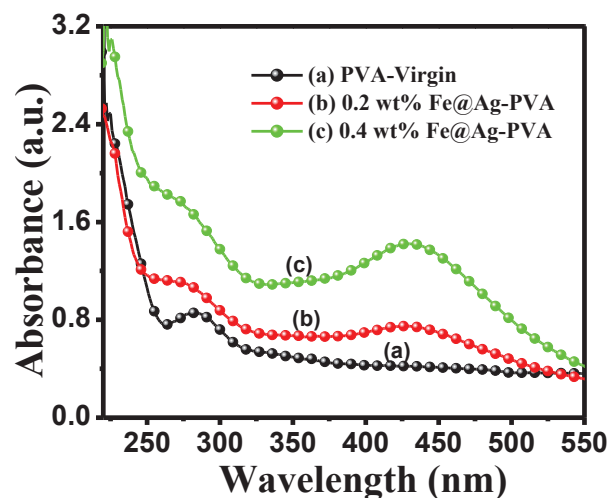


Figure 2. UV- VIS absorption spectra of Virgin PVA and Fe@Ag-PVA nanocomposite films.

Optical conductivity (σ) defines as it is the movement of charge carriers under the influence of alternating electric field of incident electromagnetic radiation and it measures of the rate at which the energy of incident electromagnetic radiation is absorbed by the medium.

Optical conductivity for virgin PVA and Fe@ Ag-PVA core shell nanocomposite films for varying concentration was calculated by using the formula:

$$\sigma = \alpha nc/4\pi$$

where α represents an absorbance coefficient, n is the refractive index and c is the speed of light.

Figure 3 depicts the optical conductivity (σ) of virgin PVA and core shell nanocomposite films. It is clear from the figure that increase in the concentration of Fe @ Ag nanoparticles in PVA matrix increases the optical conductivity which may be a consequence of the appearance of new localized states within the HOMO-LUMO gap of virgin PVA which in turn results into an increase in the rate of absorption of incident photon energy by the electrons of the medium [7].

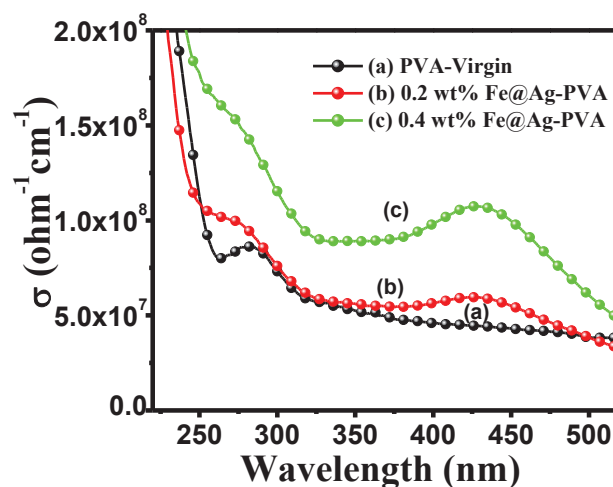


Figure 3. Variation of optical conductivity with wavelength of virgin PVA and Fe@Ag-PVA nanocomposite films.

CONCLUSIONS

In the present work Fe @ Ag core-shell nanoparticles were successfully prepared via ex-situ chemical reduction method. Consequently, the Fe @ Ag-PVA nanocomposite films were fabricated by solution casting method. The UV-Visible absorbance pattern showed an absorption band for PVA at about 283 nm and the surface plasmon resonance at about 430 nm confirms the formation of silver nanoparticles. The absorbance of nanocomposite films increases with increase in core shell nanoparticles concentration. Structural behavior was observed by Transmission electron microscopy (TEM) which confirmed the formation of core shell nanocomposite. It was also observed that the optical conductivity of the PVA showed an increase with increase in the concentration of nanoparticles.

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