

Research Article

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Poly (Vinyl Alcohol) Decorated Lithium Doped Stannous Oxide Nanocomposites as Highly Flexible UVA Shieldants

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Abstract

Herein, we report the successful fabrication of a series of mechanically flexible poly (vinyl alcohol) (PVA) nanocomposite films with varying amounts of lithium doped stannous oxide ($\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$) nanofillers (i.e., 0.0, 0.5, 1.0, 2.0 and 4.0 wt %) by mechanical shearing followed by film casting. The structural characterizations (FTIR) ascertain the success of lithium doped stannous oxide integrations with PVA matrix. While, electronic spectral studies sheds light on the changes in electronic band structure leading to a gradual decrease in optical band gaps associated electronic transition from valence band to conduction band. The UV-visible transmittance study substantiates the ability of nano fabricated polymeric films to efficiently shield UV radiations, in particular UVA radiations and thereby act as highly flexible and visible transparent UVA protective coatings.

Keywords: UVA protective coatings; Lithium doped stannous oxide; Nano composite

Introduction

High energy ultra violet (UV) photons are known to affect interesting scientific and technological applications. In contrary, UV radiations also brings about severe biological and material vandalizations including damage of genetic material (DNA), Immune suppressions and skin photo aging, in addition to significant material damages. The observed degradation effects is owed to the sufficiently high energy of UV photons that brings about significant physico-chemical changes in the material under study, leading to rapid photolytic and photo oxidative properties ensuing significant loss in material properties [1], which, in turn has led the scientific community towards the design and development of organic UV absorbers that acts as UV shieldants by transforming the absorbed high energy UV radiations into the less damaging phonons through various photo physical processes [2,3]. However, the organic UV absorbers are prone to weathering effects, thereby limiting their technological applications.

In recent years, organic-inorganic composite materials are being increasingly investigated as advanced technological materials for opto-electronic device fabrications, owing to their unique mechanical, photoelectric and thermal properties, arising from the synergistic filler (inorganic) – matrix (organic) interactions. In last few decades, the scientific community has been able to impose entirely new material properties on conventional materials by manipulation of matter at molecular levels. The molecular level engineering of matter facilitates a larger surface area which in turn accounts for the advanced material properties of nano sized materials in contrast to the bulk in accordance with earlier reports [4-9]. In the midst of the various physico-chemical properties of polymer nanocomposites, barrier protection against high energy UV radiations is of significant interest. In this context, many efforts have been addressed in the development of visibly transparent polymeric matrices with appreciable UV-shielding properties to be employed as UV protective coatings and optical filters [10-13].

Typically, metal oxide nanoparticles are integrated onto particle stabilizing polymers, allowing the preparation of hybrid nanocomposites with appreciable UV-shielding capabilities. These nanoparticles have been applied as UV-absorbing materials, owing to their low cost, and good environmental stability in addition to reduced toxicities. Thus, in the present research investigation, an attempt is

made to induce UVA shielding properties in highly flexible and visible transparent poly (vinyl alcohol) (PVA) matrix to be employed as UVA protective coatings.

Experimental Methods

Lithium doped stannous oxide ($\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$) nanoparticles have been prepared by a previously reported gel combustion technique with slight modifications. The PVA/ $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ NC films were developed by suitably dissolving varying weight fractions of $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ nano fillers. The resultant solutions were subjected to mechanical shearing followed by ultra sonication, so as to achieve uniform filler dispersions. The homogenized PVA/ $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ aqueous solutions were then casted onto clean glass molds and allowed to dry under ambient atmosphere. The fabricated visibly transparent nano composites with a thickness of 0.30-0.34 mm were subjected to spectral characterizations.

The Fourier Transform Infrared (FTIR) spectrum of the PVA and its PVA/ $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ nanocomposite (NC) films analogues were recorded in the spectral wave number range 4000-400 cm^{-1} using JASCO 4100 spectrometer, Japan, with a maximum resolution of 0.9 cm^{-1} . The electronic spectral details of fabricated films were established by Schimadzu-1800 spectrophotometer, Japan, in the spectral range of 200-800 nm.

Results and Discussion

The Fourier Transform Infrared spectroscopic (FTIR) studies of pristine PVA and its 4 wt% $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ nanofiller introduced composite film (Figure 1) reveals Infrared (IR) band around 932 cm^{-1} symbolizing the highly planar syndiotactic structure of PVA with a sequential

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distribution of -OH groups [14]. However, filler introduction leads to appreciable changes in the planarity of composite films with a blue shift towards 920 cm^{-1} , thereby inducing novel opto-electronic properties in contrast to the planar syndiotactic PVA films. The introduced nano filler also induces a considerable decline in intensities of -OH stretching vibrations, indicating a synergistic interaction between -OH groups of PVA matrix, with metallic fractals of $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ nano fillers [15]. The $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ nano fillers also affected a continuous decrease in IR band intensities in the wave number regimes $1510\text{-}1075\text{ cm}^{-1}$, owing to the decoupling of -OH and -CH vibrations. The UV-visible absorbance spectrum of PVA/ $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ nanocomposite films (Figure 2) reveals the effect of nano filler introductions on electronic band structure of composite films with a broad shouldered valley around $260\text{-}280\text{ nm}$. In contrast, the nanocomposite films display additional UVA absorption band around $320\text{-}330\text{ nm}$ due to $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ loadings [16].

The electronic spectral studies also support the UVA shielding abilities of nanocomposite films, while retaining transparencies in visible region (Figure 3). The increased UVA shielding abilities of developed films may be attributed to the incorporation of UVA absorbing $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ nanofiller (Figure 4). The excellent visible transparencies of PVA/ $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ nanocomposites may also be attributed to extremely smaller filler domains and near matching filler-matrix refractive indices that reduces the scattering losses [17,18]. The optical energy gap is the determinant factor that key establishes the portion of sunlight absorbed by a photovoltaic device leading to increased photovoltaic conversion efficiencies. The Figure 4 shows a

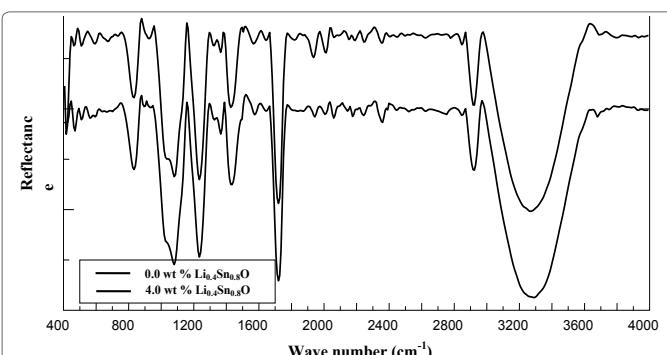


Figure 1: FTIR reflectance spectra of PVA nanocomposite films with (a) 0, (b) 0.5, (c) 1.0, (d) 2.0, and (e) 4.0 wt % of $\text{Li}_{0.2}\text{Sn}_{0.8}\text{O}$.

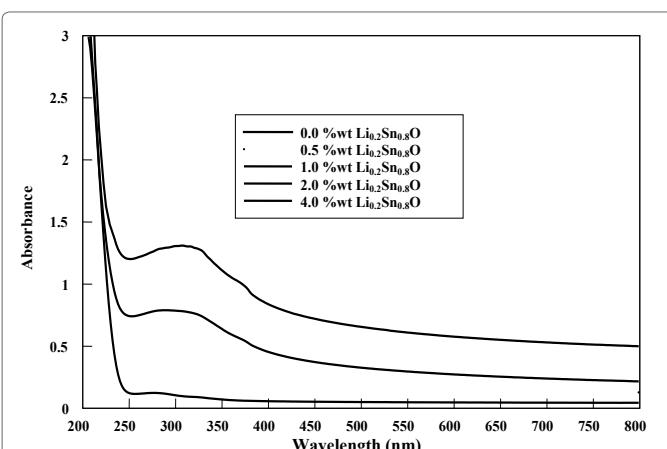


Figure 2: UV-visible absorbance spectra of PVA nanocomposites with (a) 0, (b) 0.5, (c) 1.0, (d) 2.0, and (e) 4.0 wt % of $\text{Li}_{0.2}\text{Sn}_{0.8}\text{O}$.

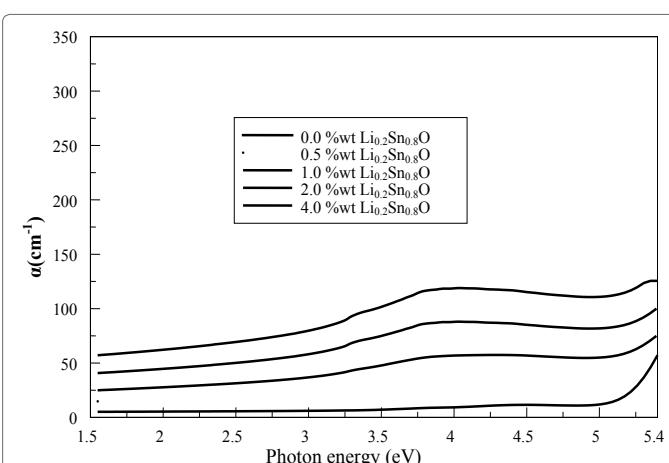


Figure 3: Absorption coefficient vs photon energy of PVA/ $\text{Li}_{0.2}\text{Sn}_{0.8}\text{O}$ nanocomposites.

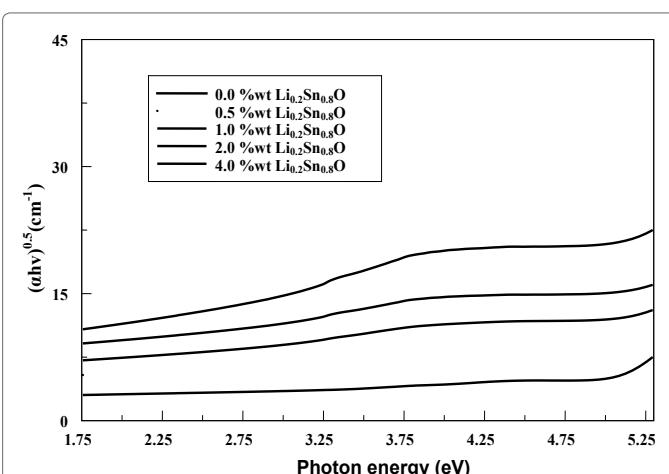


Figure 4: Tauc's plot for the determination of direct band gaps.

monotonic dependence of optical band gaps on nanofiller content, with energies allied to inter band electronic transitions showing a steady decrease nanofiller loadings. The observed variation in optical energy gap reveals a change in the optical band structure of PVA films upon nanofiller intercalations due to formation of polarons in the $\text{Li}_{0.4}\text{Sn}_{0.8}\text{O}$ introduced PVA films [19,20].

Conclusion

In summary, highly flexible and visibly transparent PVA nanocomposite films were fabricated with lithium doped stannous oxide nanofillers by aqueous solvent casting method. The introduced nano fillers were found to be well dispersed throughout the PVA matrix thereby retaining high visible transparencies (550 nm). In addition, the introduced fillers affected a continuous reduction in energies associated with inter-band electronic transitions leading to novel opto-electronic properties with enhanced UVA shielding efficacies.

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