Effect of TiO₂ Concentration on Thermal Stability and Dielectric Properties of (PANI)_{1-x}(TiO₂)_x Nanocomposites

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The current paper deals with investigation of (PANI)_{1-x}(TiO₂)_x nanocomposites to explore possible material for optoelectronic devices. To investigate the effect of TiO₂ concentration on structural, surface morphology and chemical properties of PANI, samples were characterized by XRD, FTIR, SEM and Raman spectroscopy. The XRD pattern evidence the presence of a blend of anatase and rutile phase of TiO₂ within the PANI matrix which shows amorphous nature of the matrix. FTIR and Raman spectra confirm the formation of PANI/TiO₂ nanocomposites. SEM images show the appearance of lumps into smooth PANI samples with addition of TiO₂ nanoparticles. The thermal and dielectric properties were studied using TGA and Impedance analyzer, respectively. The results showed that the addition of TiO₂ improves the thermal stability, which clearly shows its potential application in optoelectronic devices.

Keywords: PANI/TiO₂ nanocomposite, Thermal Stability, Dielectric properties.

INTRODUCTION

In recent past, the conducting polymers have been employed widely in diverse fields such as chemical and biological sensors, optoelectronic devices (such as solar cell, LEDs, lasers), actuators microelectronic devices and lightweight batteries [1-5]. Polyaniline (PANI) is one of a versatile conducting polymers owing to its unique properties such as high environmental stability, low cost and good electrical conductivity [6-11]. The electrical properties of PANI can be altered by using protonation and/or charge transfer doping [12,13]. Such materials carry utmost importance in integrated electronic circuits such as capacitor and gate oxides. However, the bottleneck of usage of PANI lies in its thermal instability, weak dielectric properties and poor biocompatibility. To eradicate such incompatibility, the nanocomposites incorporating metal oxides could present a better solution due to the higher thermal stability and average conductivity. TiO₂ is one such wide band-gap (3.2 eV) metal oxide with acceptable utility in both optoelectronic and micro-electronic devices applications exhibiting

better mechanical flexibility, thermal and environmental stability [14-18].

Consequently, it is hoped to obtain new materials with complementary behavior between PANI and TiO₂. The composite structure of PANI and TiO₂ have received much consideration due to dissociation of exciton at the interface of TiO₂ and conjugated polymer [19]. Although there are many studies on PANI/TiO₂ composite structure but most of these reports are still focused on material preparation and morphology characterization, such as size and shape of the oxide particles, degree of dispersion, type of interaction, and interface between the organic and inorganic phase [20,21]. Thermal stability of PANI can be enhanced by introducing TiO₂. However, addition of TiO₂ decreases the conductivity of nanocomposite [22]. Therefore, the selection of appropriate concentration of TiO₂ must be selected carefully by balancing thermal stability and electrical conductivity. Keeping in mind the expected potential applications of PANI/TiO₂ nanocomposite, thermal and dielectric properties have been discussed in this article with the variation in the concentration of TiO₂ in resulting nanocomposite with PANI.

EXPERIMENTAL

Pure polyaniline (PANI) was synthesized by *in situ* chemical oxidative polymerization method at lower temperature between 0-5 °C, which has been reported earlier [23,24]. The (PANI)_{1-x}(TiO₂)_x nanocomposite ($x = 0, 0.02, 0.04, 0.08$) were prepared *in situ* by chemical oxidation polymerization of aniline using APS as an oxidant in presence of appropriate amount of colloidal TiO₂ nanoparticles at 0-5 °C in air. The phase and orientation of PANI/TiO₂ nanocomposites were characterized by X-ray diffractometry (XRD, Bruker AXS D-8 Advance Diffractometer) using CuK α ($\lambda = 1.5407$ Å) radiation. The surface morphology of the prepared samples is investigated by means of scanning electron microscopy (SEM) using quanta Fe-SEM 450 (FEI). Raman spectra of PANI/TiO₂ nanocomposites were measured using confocal Raman microscopy. FTIR spectroscopy analysis of PANI/TiO₂ nanocomposites scanned from 4000 cm⁻¹ to 500 cm⁻¹ using a perkin Elmer FTIR spectroscopy. Dielectric properties of nanocomposites were studied using impedance analyzer (Agilent 4294A precision). To measure the thermal stability, Thermogravimetric analysis (Perkin Elmer STA 6000) was done for PANI and PANI/TiO₂ nanocomposites.

RESULTS AND DISCUSSION

The pure PANI and PANI/TiO₂ (8 % w/w) nanocomposite were characterized by X-ray diffraction and the resulting diffraction pattern is plotted (Fig. 1). The diffraction pattern corresponding to pure PANI does not yield into any high intensity peaks and regarded as X-ray amorphous, however, multiple diffraction peaks are observed in spectra of nanocomposite. The diffraction pattern of nanocomposite PANI/TiO₂ (8 % w/w) is indicative of diffraction peaks originating from lattice planes (101-A), (004-A) and (200-A) at diffraction angles (2 θ) of 25.38°, 37.88° and 48.07° of anatase phase of TiO₂. Further, other high intensity diffraction peak at diffraction angle of 27.40° indicates the diffraction of X-rays from (110-R) lattice plane of rutile phase of TiO₂. The rest of spectra are identical to pure PANI which indicate no crystallization/change of phase during the preparation of PANI/TiO₂ nanocomposite.

Fig. 1. X-ray diffraction patterns of Pure PANI and PANI/TiO₂ (8%) nanocomposite

The crystallites size of PANI/TiO₂ nanocomposites was estimated from the prominent peak indexed (101-A) having a FWHM of 0.215° using Debye-Scherrer equation [3]:

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where β = FWHM (full width at half maxima of diffraction peak in radians.), t = grain size, λ = wavelength of X-ray (CuK α used in the present study) and $\cos \theta$ is the cosine of Bragg angle (θ). The estimated grain size of PANI/TiO₂ nanocomposite was 40.88 nm.

The surface morphology of pure PANI and PANI/TiO₂ (8 % w/w) nanocomposite is recorded using scanning electron microscopy (SEM). Fig. 2a displays the SEM image of pure PANI which is indicative of relatively flat and uniform structure with some coalesce grains. Fig. 2b is a indicative of formation of many uneven lumps in PANI/ TiO₂ (8 % w/w) nanocomposite which is result of incorporation of TiO₂. The polymerization

Fig. 2. SEM image of (a) pure PANI and (b) PANI/TiO₂ (8 % w/w) nanocomposite

of aniline has taken place on the surface of TiO_2 nanoparticles which has resulted into visible lumps with TiO_2 at its core. Further, the presence of similar lumps throughout the surface indicate uniform distribution of TiO_2 in nanocomposite.

To identify the change in the molecular structure of PANI and PANI/ TiO_2 nanocomposite, Fourier transform-infrared (FTIR) spectroscopy was used and obtain results are shown in Fig. 3. The characteristics peaks of PANI are evident in all the patterns corresponding to pure PANI and PANI/ TiO_2 nanocomposites. The characteristic features of pure PANI is located at 3423, 1628 and 1133 cm^{-1} . The signature of N-H stretching is observed as a peak at 3423 cm^{-1} while the band at 1628 cm^{-1} is recognized as C=N stretching mode of vibration for the quinonoid and benzenoid units of polyaniline [25,26]. The band at 1133 cm^{-1} is allocated to the C-N stretching mode of benzenoid ring which is the indicative of conducting protonated form of polyaniline. The bands in the region 1133-1000 cm^{-1} are due to in-plane bending vibration of C-H mode [27]. The low wave number region exhibits a strong vibration around 607 cm^{-1} which corresponds to antisymmetric Ti-O-Ti mode

Fig. 3. FTIR spectra for PANI and PANI/ TiO_2 nanocomposites

Fig. 4. (a) Raman spectra of PANI and (b) PANI/ TiO_2 nanocomposites

of titanium oxide [28]. The shifting of characteristics peak show a strong interaction between TiO_2 and PANI. Further, the increased shift with increasing concentration of TiO_2 indicate the possibility of formation of nanocomposite with modified absorption properties.

Raman spectra of pure PANI and PANI/ TiO_2 nanocomposites were measured to see their vibration modes as shown in Fig. 4(a, b). It is clearly noted from Fig. 4a, PANI exhibited different vibration modes near 406, 509, 575, 825, 1183, 1249, 1341, 1507 and 1603 cm^{-1} . The peak observed at 1603 and 509 cm^{-1} for pure PANI corresponds to C=C stretching vibrations of benzenoid and quinoid rings, respectively. Whereas, C-H bending vibration of benzene quinoid ring are observed at 1341 and 1183 cm^{-1} , respectively. Incorporation of TiO_2 in PANI leads to shifting these peaks towards higher wavenumber which shows more stretching in different types of bonds. It is further evidenced that scattering of visible laser light is majorly from TiO_2 nanoparticles with a very little contribution from amorphous PANI matrix.

Thermal stability and dielectric properties: The nanocomposite is synthesized with an aim to improve the thermal stability of polyaniline. Due to the excellent thermal stability of TiO_2 , the nanocomposites may found favourable to the application in the domain of sensor and optoelectronic devices [29]. The weight loss measured with temperature is indicated in Fig. 5 for pure PANI and PANI/ TiO_2 (8 % w/w) up to 900 $^{\circ}\text{C}$. The weight loss in PANI/ TiO_2 (8 % w/w) within the temperature range 150-200 $^{\circ}\text{C}$ is due to the deintercalation of water chemisorbed in TiO_2 nanoparticles. The thermal stability is evident from the relative weight loss of pure PANI and PANI/ TiO_2 (8 % w/w) among which the later show lesser weight loss at higher temperatures.

Dependence of dielectric constant and loss tangent as a function of frequency is plotted for the synthesized PANI and PANI/ TiO_2 nanocomposites [Fig. 6(a,b)], respectively at room temperature. It was observed that dielectric constant and dielectric loss are high at low frequency and decreases sharply as frequency increases before becoming constants at high frequencies indicating the usual dispersal. This behavior can be expl-

Fig. 5. TGA thermogram of PANI and PANI/TiO₂ nanocomposite Fig. 6(a). Variation of relative dielectric constant with frequency of applied field for PANI and PANI/TiO₂ nanocomposites Fig. 6(b). Variation of loss tangent with frequency of applied field for PANI and PANI/TiO₂ nanocomposites

higher value of dielectric constant but as we increase the frequency the field cannot induce the dipole moment which reduces value of dielectric constant [30–33]. As capacitance and dielectric constant are directly proportional to each other as shown by the following equation [32]:

$$\epsilon' = \frac{C \cdot d}{A \cdot \epsilon_0} \quad (2)$$

where C = capacitance, d = spacing between the electrodes, A = cross section area of the electrodes, ϵ_0 = permittivity of free space and ϵ' = dielectric constant.

The energy lost in a dielectric is measured by the angle δ between the current and charging potential. In dielectric systems relaxation effects occur if dielectric displacement $D(\omega)$ lags behind in phase with electric field $E(\omega)$. For vacuum, this angle is 90° but if dielectric material of some dielectric constant is placed, this phase angle does not remain 90° . The angle by which dielectric displacement $D(\omega)$ deviates from 90° is termed as loss angle or tangent loss. It is the ratio of dielectric loss to the dielectric constant. The higher values of $\tan \delta$ at low frequency and decrease in $\tan \delta$ at higher frequency for pure PANI and PANI/TiO₂ composites of different concentration are shown in Fig. 6(b). As frequency increases, dielectric constant and loss tangent decreases sharply and hence $\tan \delta$ decreases sharply. Decrease in dielectric constant and $\tan \delta$ with increasing frequency is a typical characteristic of conducting polymer. Our observed measurements are in good agreement with literature [33]. Further, PANI/TiO₂ nanocomposites indicate higher dielectric constant as compared to pure PANI exhibiting a uniform increase with increase in concentration of TiO₂ in PANI/TiO₂ nanocomposites. However, higher dielectric constants are coupled with higher dielectric losses in this study.

Conclusion

PANI/TiO₂ nanocomposite samples with various concentrations of TiO₂ nanoparticles were synthesized using chemical oxidation at 0–5 °C. The relative positions of peaks obtained from FTIR and XRD are attributed to the substantive interaction between PANI and TiO₂ nanoparticles. The SEM images helped to draw the conclusion that the increased concentration of TiO₂ had a strong effect on PANI morphology. The addition of TiO₂ in PANI shows higher thermal stability and higher dielectric constant as compare to pure PANI. The investigation of PANI/TiO₂ nanocomposites confirmed their stability and suitability for optoelectronics devices.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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