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Effect of TiO_2 Nanoparticles on Structural and Optical Properties of Poly pyrrole, Poly vinyl alcohol Polymer Blend Thin Films

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ABSTRACT

Thin films of (Poly Pyrrole-Poly Vinyl Alcohol) PPY-PVA polymer blend doped with different concentration of TiO_2 nano particles were prepared via oxidative chemical polymerization technique (in-situ). The properties (Structural & Optical) of these thin films were studied by XRD, FTIR, SEM and UV-spectroscopic techniques. The optical band gap values of TiO_2 doped polymer blend were calculated by UV-spectroscopic studies, and also noticed that obtained band gap values were decreased with increase in the concentration of TiO_2 nano particles. XRD and FTIR results support the polymer blend formation, and dispersion of TiO_2 nano particles in the polymer blend. The modification in surface morphology of polymer blend is due to presence of TiO_2 nano particles which was confirmed by SEM results.

Keywords: Thin films, Poly Pyrrole, Poly Vinyl Alcohol, Poly Pyrrole-Poly Vinyl Alcohol blend, TiO_2 nano particles.

INTRODUCTION

Conducting polymers, Polymer blends, and their nano composites have become very popular in the recent past due to their exceptional properties which are not exhibited by individual constituents present in them[1–11]. Review of research literature shows that they find numerous applications in electronics, photonics, biotechnology, bio-medical sciences, aerospace, food industry[12–16]. PPY has extended conjugation of delocalized π-electrons, highly mobile charge carriers, across the polymer chains. PPY has wide range of applications in rechargeable batteries, sensors, anticorrosive coatings, actuators, light emitting diodes, supercapacitors, etc.,[17-25] due to its several noted chemical, and electrochemical properties. Poly (vinyl alcohol) (PVA) is an ecological synthetic polymer, grabbed distinct attention because of its high transparency, flexibility, anti-electrostatic, luster, chemical resistance, and wide commercial availability. Polymer blends of conducting PPY, PVA have drawn the attention of researchers, and motivated them to take up the research study on effect of dopants on physical, mechanical, and conducting characteristics due to their various applications in electric nanodevices[26-31]. The properties of PPY, and its composites can be easily modified suitably to requirement of desired applications by varying size, shape, and distribution of dopant particles. TiO_2 nano particles show large surface area to volume ratio, that can significantly enhance the sensors sensing property and response time[32]. Motivated by the remarkable features of PPY-PVA polymer blends as multifunctional composite thin film with suitable conductivities and superior physical properties, the authors taken up this work to study the pure PVA-PPY blend, and effect of TiO_2 nano powder as a dopant on PVA-PPY blend composites.

EXPERIMENTAL

Materials

Poly Vinyl Alcohol (Degree of polymerization 1700-1800), $FeCl_3$ & Acetone were purchased from Research lab Fine Chem Industries, Mumbai. 99.9% of pure Pyrrole monomer and TiO_2 nano powder were purchased from Sigma Aldrich Laboratory. In this study, the authors have adopted in-situ chemical oxidative polymerization method[33-34] to synthesize composite thin films of poly pyrrole (PPY)–poly viny alcohol (PVA), and PPY–PVA blends doped with TiO_2 nano powder.

Preparation of thin films

Pyrrole solution (aqueous) was obtained by dissolving 0.85 mL in 25 mL of distilled water taken a in a beaker under constant stirring for about two hours at room temperature. The obtained aqueous solution of Pyrrole and 20 mL of already prepared 4% PVA solution were mixed thoroughly under constant stirring for 4 hours. The drop wise addition of freshly prepared aqueous solution of $FeCl_3$ (about 2 g/25 mL of distilled water) to the above reaction mixture by thorough mixing for 4 h yielded a black colored solution of PPY-PVA, and a thin film was obtained upon drying the yielded solution. About 10 mg of TiO_2 nano powder is mixed with Pyrrole aqueous solution prepared as shown in the above step, and stirred it for about two hours followed by the addition of 20 mL of PVA solution under constant stirring for about two hours. Freshly $FeCl_3$ solution was added drop wise to the above reaction mixture by thorough mixing. Thin film of PPY-PVA-TiO_2 black in color was obtained after evaporating excess water. Set of different films were prepared by the same procedure by varying concentration (like 20 mg, 30 mg, and 40 mg) of TiO_2. All the films prepared were analyzed by UV, XRD, SEM, and FTIR techniques.

RESULTS AND DISCUSSION

Structural studies

XRD is a promising technique which reveals the information of materials to understand their structural properties such as size, nature, etc. The films of PPY-PVA, and PPY-PVA-TiO_2 were characterized by XRD in the range of 10°-60°. XRD spectra (Fig.1(a)) of PPY-PVA thin film shows that the increase in the broadness and decrease in the strength of peaks might be attributed to its amorphous nature of thin films.

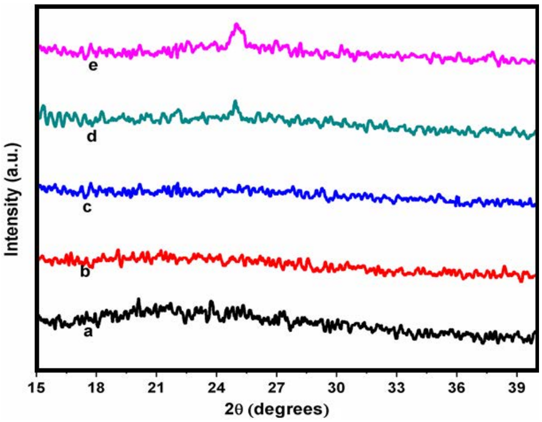

Fig.1. XRD spectra of (a) PPY-PVA, (b) PPY-PVA-10 mg TiO2, (c) PPY-PVA-20 mg TiO_2, (d) PPY-PVA-30 mg TiO_2, (e) PPY-PVA-40 mg TiO_2

XRD results (Fig.1(b), (c)) of PPY-PVA films doped with TiO_2 showed significant change in structure of composite thin films which could be due to the TiO_2 nano particle dispersion in PPY-PVA polymer blend matrix. It was also observed that, as % TiO_2 dopant increased in the polymer matrix the peak intensity was also increased which might be due to lack of lattice disorder and stress of high amount of TiO_2 dopant. The sharp peaks (Fig.1 (d), (e)) appeared in the XRD spectra of PPY-PVA-TiO_2 at higher concentration of dopant could be due to crystalline nature of the composite thin films. It also was observed that peaks have been shifted slightly towards higher angle of diffraction.

Morphological studies

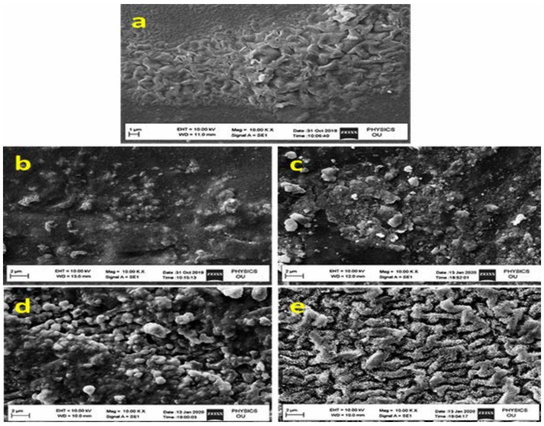

Fig. 2. SEM images of (a) PPY-PVA, (b) PPY-PVA-10 mg TiO_2, (c) PPY-PVA-20 mg TiO_2, (d) PPY-PVA-30 mg TiO_2, (e) PPY-PVA-40 mg TiO_2

SEM is an effective technique that provides high-resolution images which revels morphology of surface of the materials. SEM image (Fig. 2(a)) of PPY-PVA revealed that the surface of film was very smooth and good miscibility of polymers PPY and PVA. The Pyrrole monomer was dispersed uniformly in PVA polymer matrix, and PVA is purely responsible for improved order and reduction in agglomeration of PPY which strongly affects morphology of PPY-PVA thin film. Due to large surface of TiO_2 doped nano composite films may promote adsorption of gasses.

FITR

One of the best techniques to identify the functional groups present in a sample is FTIR spectroscopy. The thin films of PPY-PVA and nano TiO_2 doped PPY-PVA were characterized by FTIR technique.

IR spectra (Fig.3(a)) of PPY-PVA and the broad peaks appeared in the range of 3350–3240 cm^{-1}, around 1050 cm^{-1} are attributed to O-H and N-H stretching, and C-H and N-H in-plane deformation in PVA and PPY respectively. The peaks between 1626-1628 cm^{-1} may be attributed to functional groups to C=O stretching frequency of PVA in PPY-PVA polymer thin film. The slight shift in wavenumber higher side has been observed at around 1640 cm^{-1} which may be due to the addition TiO_2 nano powder to PPY-PVA thin films. The peaks (Fig.3(a-c)) which were observed between 1000-800 cm^{-1} in PPY-PVA thin films almost disappeared in case of PPY-PVA-TiO_2 (Fig. 3(c-d)) which might be due to interactions of TiO_2 at moderate to high concentration with PPY-PVA thin films.

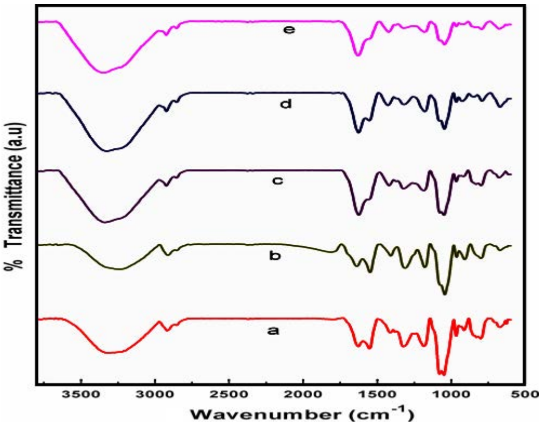

Fig. 3. FTIR spectra of (a) PPY-PVA, (b) PPY-PVA10 mg TiO_2, (c) PPY-PVA-20 mg TiO_2, (d) PPY-PVA-30 mg TiO_2, (e) PPY-PVA-40 mg TiO_2

UV studies

Electronic spectroscopy is one of the significant spectroscopic techniques used to determine optical constants i.e., transmittance, absorbance, and reflectance of polymer films. Table 1 shows direct optical energy band gap values of PPY-PVA and nano TiO_2 embedded composite thin films which were calculated by plotting $(\alpha h\nu)^2$ verses $(h\nu)$. The decrease in the direct optical energy band gap obtained may indicate role of the dopant in PPY-PVA blend polymer matrix. The increase in concentration of TiO_2 dopant causes formation of crystal imperfections which involves modification of electronic energy states and overlap of electronic energy bands in composite thin films. Concentration TiO_2 nano particles found to proportional the population density of localized energy states[35]. The decreasing order of optical energy band gap values as the concentration of TiO_2 nano particles in PPY-PVA thin films suggest increase in conductivity levels.

Table 1: Energy band gap values of PPY-PVA and PPY-PVA-TiO_2 thin films

Sample name	Concertation of TiO_2	Direct optical band gap in eV
PPY-PVA	0	2.92
PPY-PVA-TiO_2	10 mg	2.01
PPY-PVA-TiO_2	20 mg	1.72
PPY-PVA-TiO_2	30 mg	1.65
PPY-PVA-TiO_2	40 mg	1.61

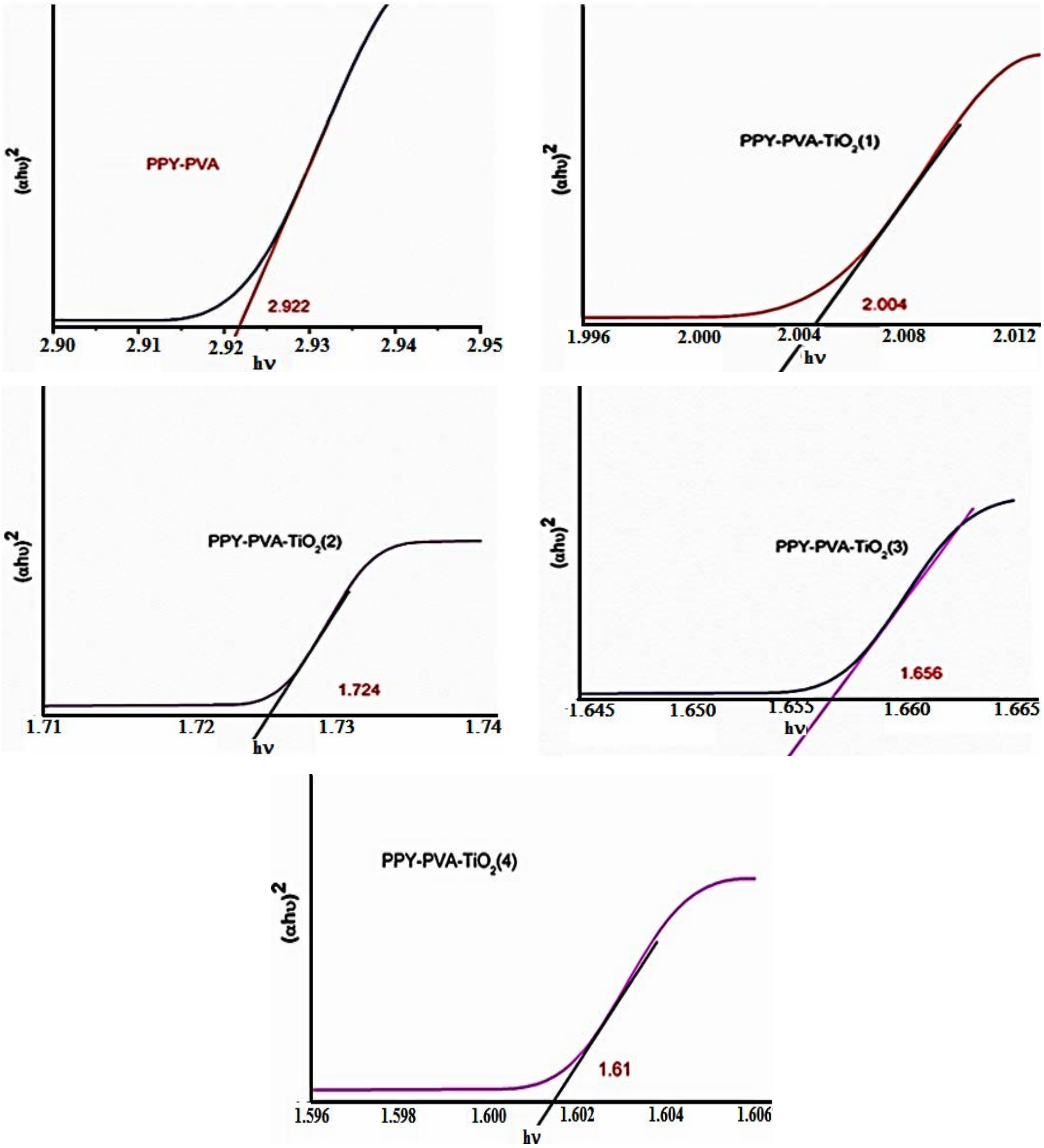

Fig. 4. UV plots of PPY-PVA and nano TiO_2 embedded PPY-PVA composite films

CONCLUSION

The authors adopted oxidative chemical polymerization (in-situ) technique to synthesize Poly Pyrrole-Poly Vinyl Alcohol and Poly Pyrrole-Poly Vinyl Alcohol-TiO_2 thin films, and the obtained samples (thin films) were analyzed by UV, SEM, XRD, and FTIR techniques. XRD studies suggest that increase in crystalline nature of PPY-PVA-TiO_2, as the concentration of TiO_2 nano particle increases. FTIR spectra of thin films shows that slight shift in wave number towards higher side, and almost disappearance of some peaks which supports the interactions between PPY-PVA with TiO_2 at moderate to high concentration. SEM results are evident that morphology of composite thin films have been modified significantly by the addition of TiO_2 dopant besides that it has also been observed the presence of pores in surface of composite thin films which may be suitable for detection leakage of certain gasses. The decrease in direct optical energy band gaps with increase in concentration of TiO_2 nano particles might suggest overlapping of electronic energy states in composite thin films and which indirectly hint the increase in conductivity levels of Poly Pyrrole-Poly Vinyl Alcohol-TiO_2 thin films. The Poly Pyrrole-Poly Vinyl Alcohol doped thin films have wide applications as electronic nano devices besides they may also be used as gas Sensors.

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Conflicts of Interest

The authors declare that no conflict of interest.

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