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Synthesis and Complex Optical Characterization of Polythiophene/Poly (vinyl acetate) Composite Thin Films for Optoelectronic Device Applications

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In the present communication, Polythiophene/poly(vinyl acetate) (PTh/PVAc) composite thin films were synthesized by chemical oxidative polymerization method in methanol is reported. The prepared composite were characterized through X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), ultraviolet-visible (UV-Vis) spectroscopy and photoluminescence (PL) measurement. The broad peak was displayed in the PL spectra for the prepared composite at around 390 nm, proposed prodigious charge generation efficiency. The analysis of the optical parameters of the prepared composite was carried out by spectral analysis using a UV-Vis spectrophotometer. The obtained results, which were as follows: energy band gap of 4.58–5.31 eV, complex refractive index coefficient values of 1.175–1.193 and optical conductivity values in the range of 2.58×10^8–5.24×10^8 S.cm^{-1} at 270 nm. The above results shows the studied composite films are expected to offer potential applications in optoelectronic devices.

Keywords: Chemical oxidation; PTh/PVAc composite; ultraviolet-visible spectroscopy; photoluminescence

1 Introduction

In the current years, extensive usage of conjugated polymers has accelerated the studies on the synthesis and development of new efficient composite conducting polymers that can find a large number of potential applications emerging in the markets[1,2]. The composite conducting polymers have riveted a lot of attention owing to their distinct optical and electrical properties in addition to their superior environmental and thermal stability[3,4]. The composite conducting polymers have become an important class of amorphous semiconductor and find their potential applications not only due to electrical, thermal properties but also due to their optical properties such as dielectric constant, refractive index, extinction coefficient, permittivity, *etc*. These parameters provide significant information for optimizations of prepared materials in technological applications[5, 6]. The improvement in the electrical properties of the conjugated composite polymers is accomplished through chemical oxidation or reduction reaction by using a series of ionic or cationic species called dopant. In order to improve the physico-chemical properties of conducting polymers, many researchers have focused towards the easier synthesis and development of new composites polymers by using the conducting polymers such as polyaniline, polythiophene, polypyrrole, polyindole, *etc*[7-10].

Among these conjugated conducting polymers, thiophene based materials have emerged as one of the most possible auspicious materials due to the easiness of its synthesis, its relatively high electrical conductivity, superior optical properties, good environmental and thermal stability and the ability to modify it with different chemical groups[11-13]. Polythiophene (PTh) in its original state act as a non-conducting materials. However, the formation of a conducting polymer takes place through chemical as well as electrochemical process with oxidants followed by anion intercalation[14]. So PTh and its derivatives are used in different industrial areas and finds potential applications as the electricity dissipative coatings[15], components of diodes and field effect transistors[16], electrochemical supercapacitors[17], flexible electroluminescent lamps[18], photocatalytic fuel cell[19], solar cells[20], photochemical resists[21], nonlinear optic devices[22], batteries[23], organic LED[24], electrochromic display[25], and other devices. Bobade *et al*. synthesized polythiophene-poly(vinyl acetate) composite films through chemical oxidative polymerization method and studied the effect of oxidizing agent on electrical conductivity of the prepared composite[26]. Waghuley *et al*. successfully prepared PTh-PVAc composite films through

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*Corresponding author: (E-mail: nswadatkar81@gmail.com) chemical oxidative polymerization technique and studied the sensing application of films for CO_2 gas at room temperature[27].

In the scope of this work, we have reported on one pot chemical synthesis of PTh/PVAc composite thin films. The X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), ultraviolet-visible (UV-Vis) spectroscopy and photoluminescence (PL) analysis were employed to characterize the as-synthesized composite.

2 Experimental details

2.1 Synthesis of PTh/PVAc composites thin films

Analytical grade of monomer thiophene, oxidant anhydrous iron (III) chloride ($FeCl_3$), and hydrogen peroxide (H_2O_2), methanol (organic media) were procured from SD Fine Chemicals, India. Poly(vinyl acetate) was procured from Hi media Chemicals, India. All these chemicals are used in chemical polymerization process as received without any further purification. PTh/PVAc composite films were prepared by the chemical oxidative polymerization technique at room temperature by using $FeCl_3$ as an oxidizing agent. Initially, mix solution of monomer indole with anhydrous iron (III) chloride in the ratio 2:1 M and PVAc (1 g) in 5 mL methanol and then add 0.1 ml of H_2O_2 dropwise in this solution in a volumetric flask. This reaction mixture was stirred over magnetic stirrer for about 3 h and kept it for 24 hr to develop the homogenous solution. Thereafter, the samples of PTh/PVAc composite were prepared by varying different stoichiometric ratio of thiophene-PVAc with oxidizing agent $FeCl_3$ as 80:20 wt.%, 70:30 wt.%, 60:40 wt.% and 50:50 wt.% and continuously stirred for 3 h to complete reaction of polymerization. Then these reaction solutions were kept for 1 h to settle down. In this way, a system of PTh/PVAc composites materials was synthesized.

3 Results and discussion

3.1 Structural study

The X-ray Diffraction (XRD) profile of the synthesized PTh/PVAc composites were recorded on Rigaku (Miniflex II) diffractometer with CuKα radiation in the range 10°−70°. The XRD pattern for the prepared PTh/PVAc composites is as shown in Fig. 1. The pattern of PTh/PVAc composites shows a broad peak at 2θ region of $22-29^0$ which can be associated with the amorphous nature of the prepared composites materials. The relative intensity of these humps decreases with increase in concentration of an oxidizing agent. In addition to this, the 2θ position of the amorphous halos is different from each other for each sample and increases with increase in concentration of oxidant. The polymer chain separation was computed using the relation[28]:

$$R = (5\lambda)/(8\sin\theta) \qquad \dots (1)$$

Where, λ is wavelength of X-ray source used for XRD analysis and θ is diffraction position. The peak value of amorphous hollow was employed to compute the polymer chain separation for the prepared composite thin films.

3.2 Microstructural investigation

The morphological study of PTh/PVAc composite was carried-out through field emission scanning electron microscopy (FE-SEM). Fig. 2 represents the FE-SEM micrograph, depicting the surface morphology of PTh/PVAc composite having stoichiometric ratio of thiophene to $FeCl_3$ as (60:40) wt.%. The micrograph revealed similar features but slightly more agglomeration compared to PTh, which might be due to the nucleation effect of PVAc. In case of p-toluenesulfonic acid (pTSA) doped polyaniline (PANI):titanium dioxide (TiO_2) nanocomposites, a similar nucleation effect has been reported[29]. Also, some fibrous microstructures are formed which may be ensued due to the nucleation effect of PVAc. The non-visibility of PVAc can be explicated by thiophene

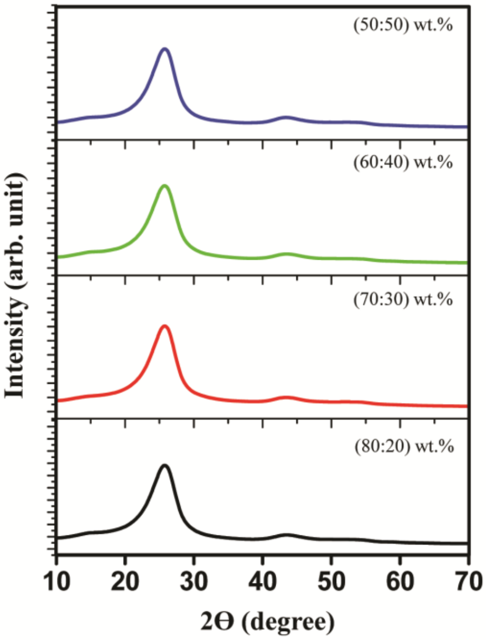

Fig. 1 — XRD profile of PTh/PVAc composite thin films.

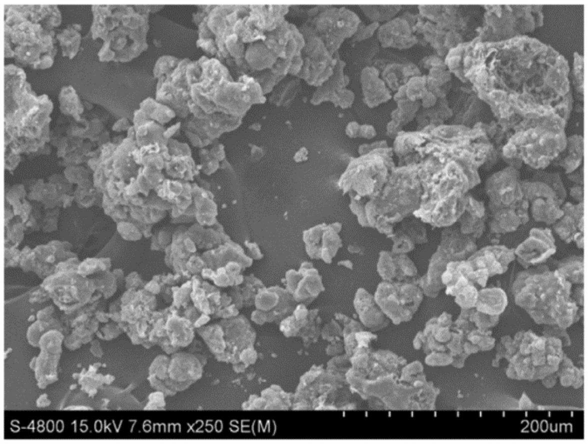

Fig. 2 — FE-SEM micrograph of PTh/PVAc composite thin films.

monomers being initially absorbed on PVAc and later on its polymerization consequences in the encapsulation of PVAc[30].

3.3 Optical study

To study the optical performance of PTh/PVAc composite thin films, absorption spectra were recorded in the wavelength range 200–320 nm as displayed in Fig. 3(a). The absorption found in ultraviolet region to visible region. The spectra exhibits peaks in the UV-region at 200 nm which is attributed the n–π^* transition and at 238 nm which corresponds to π–π^* transition[13]. Also, the plot exhibited that absorption spectra shifted towards the longer wavelength side which corresponds to red shift. This red shift is found to be more in case of PTh/PVAc composite having stoichiometric ratio of thiophene to $FeCl_3$ as (60:40) wt.% which indicates an increase in the conjugate bond length of the polymer matrix. The existence of red shift exhibited the change in optical band gap of the obtained composite films. The shift in absorbance spectra towards the longer wavelength side suggests a fall in the values of optical band gap.

The spectra of the optical transmission (T %) were recorded, for PTh/PVAc composite films, between 200 nm and 320 nm. Fig. 3(b) reveals the optical transmission spectra for PTh/PVAc composites in the ultraviolet and visible range (200 nm–320 nm). It can be observed from this figure that, the transmissions in the spectral range extended from 260 nm to 320 nm for the prepared composite are approximately unchanged but a dramatic change occurs in ultraviolet region from 200 nm to 260 nm. The transmitting value was measured for the prepared composites found to be ranges over 76 % to 54 %.

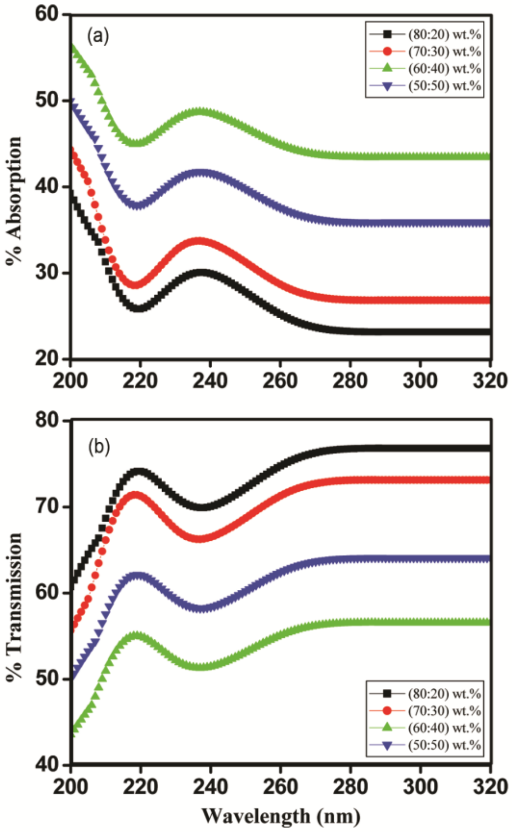

Fig. 3 — (a) UV-Visible absorption spectra and (b) Optical transmission spectra for PTh/PVAc composite thin films.

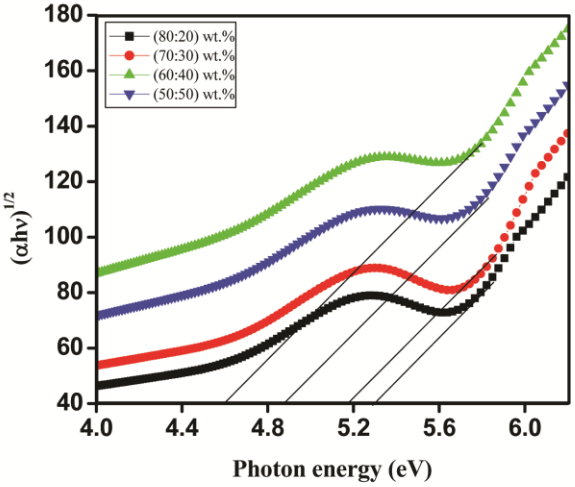

Fig. 4 — Plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for PTh/PVAc composite thin films.

The optical energy band gap values (indirect E_{in}) for the obtained samples of PTh/PVAc composite were estimated by plotting the graphs within photon energy ($h\nu$) *vs* $(\alpha h\nu)^{1/2}$ as shown in Fig. 4, in accordance with the Mott and Davis relation:[31]

$$(\alpha h\nu)^{1/2} = \beta^{1/2}(h\nu - E_{in}) \quad \dots (2)$$

Where, α is the absorption coefficient, $h\nu$ is the incident photons energy, β is a proportional constant related to the extent of the band tailing and depends on the transition probability (band tailing constant).

The optical energy band gap values were computed by extrapolating the linear portion of the curves to zero value of absorption[32]. The plots clearly depicts that the composite having stoichiometric ratio of thiophene to $FeCl_3$ as (60:40) wt.% has the minimum optical energy gap. This upshot proved that the obtained composite thin films offers potential applications in the optoelectronic devices such as supercapacitor, phototransistor, solar cell, *etc*[33-35].

The extinction coefficient is one of the crucial optical parameter which measures the absorbance of light per unit distance inside the composite materials and attenuation light due to scattering[36]. The extinction coefficient (k) was determined using the equation (3)[37].

$$k = \frac{\alpha\lambda}{4\pi} \quad \dots (3)$$

where α is the absorption coefficient.

As seen from Fig. 5, the plot shows broad absorption peak approximately around 240 nm for all the obtained samples of PTh/PVAc composite. As extinction coefficient is a measure of trapping of light, therefore we conclude that wavelength beyond 260 nm trapped in the composite materials and degree of trapping of light increases gradually with increase in wavelength. The optimized value of extinction coefficient observed for the studied composite obtained with stoichiometric ratio of monomer to oxidant as (60:40) wt.%.

The refractive index (n) is another significant parameter which helps to explored the optical nature of the materials, which is the measure of how much the speed of light is lowered inside the material medium. The refractive index was determined using the equation (4)[38]

$$n = \frac{1}{T_s} + \left(\frac{1}{T_s} - 1\right)^{1/2} \quad \dots (4)$$

where, n is refractive index and T_s is % transmission coefficient.

The variation of refractive index as a function of wavelength for the obtained composite thin films is displayed in Fig. 6. From the plot it is seen that, the refractive index of the prepared composites offers lower values on the smaller wavelength side and increases with increase in wavelength. Also, the plot shows broad humps for all the samples approximately at 218 nm. Thereafter, the refractive index values increases on longer wavelength side nearly from 240 nm. Beyond 270 nm, the values of refractive index becomes almost constant. The increase in the values of refractive index is associated with the compactness of composite thin films which results into a dense structure. The sample having (60:40) wt.% ratio of PTh/PVAc composite shows optimized value of refractive index. The values of refractive index and extinction coefficient were listed in Table 1.

The optical dielectric constant being intrinsic property of the material is one of the most significant optical parameter. The band structure of the material can be explored with the help of optical dielectric

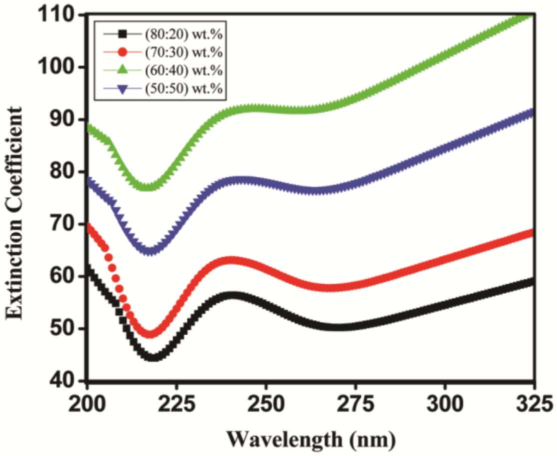

Fig. 5 — Variation of refractive index as a function of wavelength for PTh/PVAc composite thin films.

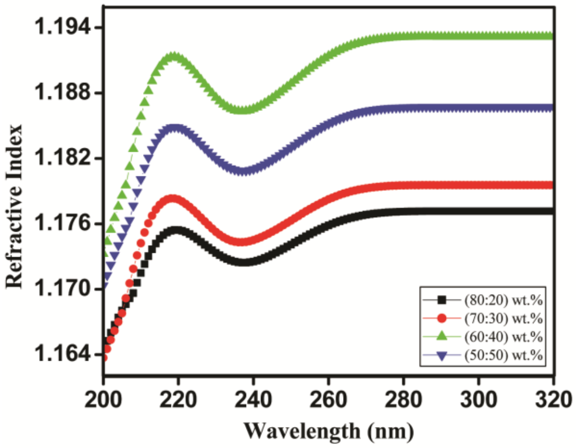

Fig. 6 — Variation of extinction coefficient as a function of wavelength for PTh/PVAc composite thin films.

Table 1 — Optical parameters for PTh/PVAc composite thin films.

PTh/PVAc composites	E_g (eV) (Indirect)	Extinction coefficient at (270 nm)	Refractive index at (270 nm)	Real dielectric constant at (270 nm)	Imaginary dielectric constant at (270 nm)	$\sigma \times 10^8$ (Scm^{-1}) at (270 nm)
(80:20) wt.%	5.31	51	1.175	2784	484	2.58
(70:30) wt.%	5.18	59	1.177	3654	562	3.38
(60:40) wt.%	4.58	92	1.193	8386	823	5.24
(50:50) wt.%	4.86	78	1.184	6112	718	4.45

constant. The complex dielectric constant depends upon refractive index and extinction coefficient values of the studied composite thin films. The complex dielectric constant can be estimated by using the following relation[39]:

$$\varepsilon_r = n^2 - k^2 \text{ and } \varepsilon_i = 2nk \qquad \dots (5)$$

Where, ε_r is real part of dielectric constant, ε_i is imaginary part of dielectric constant, n is refractive index, and k is extinction coefficient.

Figure 7(a) depicts the variation of real dielectric constant with wavelength for the prepared composite. The real dielectric constant represents how much it slow down the velocity of light in the polymer composite material. The real dielectric constant (ε_r) is strongly related with the refractive index of the materials. Fig. 7(b) shows the variation of imaginary dielectric constant with the wavelength for the prepared composite. The parameter imaginary part of dielectric constant (ε_i) which measures the dielectric loss describe how much amount of incident energy from an electric field is absorbed by the composite materials due to dipole motion[40]. The dielectric loss is closely related to the extinction coefficient as well as to electron transition. The Fig. 7(a) & (b) shows broad deep approximately around 220 nm and low intense deep at around 270 nm and thereafter the values of optical dielectric constant increases gradually as a function of wavelength which attributed to increase the absorption and incident light. The prepared composite with stoichiometric ratio of thiophene to $FeCl_3$ as (40:60) wt.% shows optimized values of the optical dielectric constant.

The term optical conductivity (σ_{op}) is used to determine the optical response of polymer composites (σ_{op}). The optical conductivity (σ_{op}) was computed using relation (6)[41];

$$\sigma_{opt} = \frac{nc\alpha}{4\pi} \qquad \dots (6)$$

where, a is absorption coefficient, n is refractive index and c is velocity of light

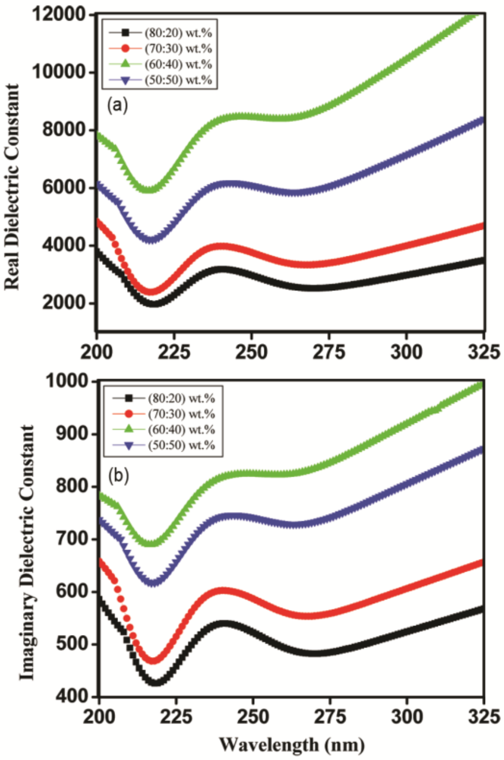

Fig. 7 — Variation of (a) real dielectric constant, (b) imaginary dielectric constant as a function of wavelength for PTh/PVAc composite thin films.

Figure 8 represent the optical conductivity plot of obtained PTh/PVAc composite thin films. As seen from the plot, values of the optical conductivity (σ_{op}) for the composite found more at shorter wavelength side which attributed to the excitation of electrons at shorter wavelength side. The optical conductivity (σ_{op}) curves for the studied composite exhibit a broad peak approximately around 240 nm. Thereafter, the conductivity values remain almost constant from 270 nm. The optical conductivity values for all studied composite are found in the range 2.58×10^8–5.24×10^8 $S.cm^{-1}$ at 270 nm. The prepared PTh/PVAc composite with stoichiometric ratio of thiophene to $FeCl_3$ as (60:40) wt.% found to have maximized value of optical conductivity. The values of optical conductivity values were listed in Table 1.

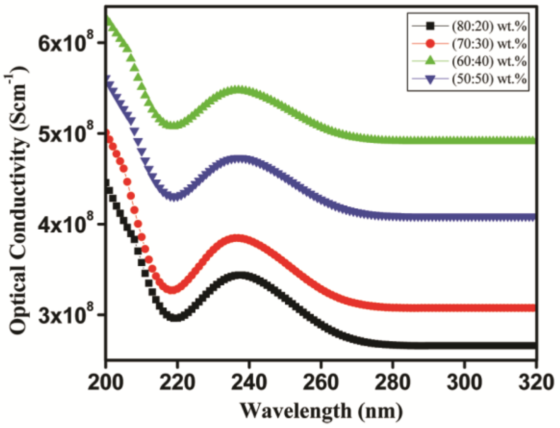

Fig. 8 — Variation of optical conductivity as a function of wavelength for PTh/PVAc composite thin films.

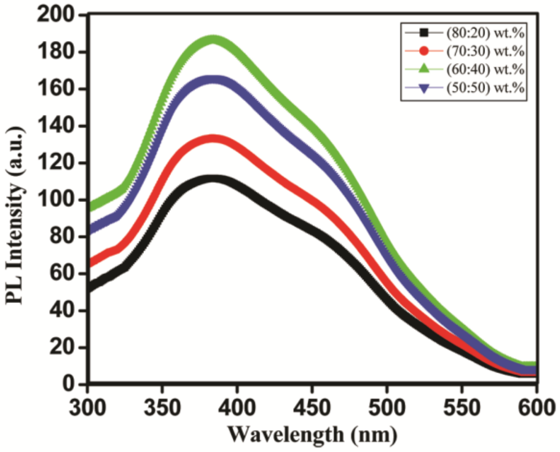

Fig. 9 — PL emission spectra for PTh/PVAc composite thin films.

Fig. 9 depicts photoluminescence spectra for PTh/PVAc composites films. The PL signal peak maximum for the prepared composite was measured at 390 nm when the composite was excited using 250 nm UV radiation. The intensity of obtained PL spectra increases without distortion in spectrum shape or alterations of peak energy position, as seen in Fig. 9. The PL intensity of the studied composite increases with increase in oxidant concentration up to (60:40) wt.% and then decreases with further increase in oxidant concentration. Thus, when the composite polymer materials are optically excited, a greater number of photons are emitted as a function of concentration oxidant[42]. The nature of PL curves for the polymer composites were almost the similar, which exhibits that there is intramolecular energy transfer of the excitons from the conjugated side chain to the main chain[43].

4 Conclusions

In summary, we have successfully synthesized composites PTh/PVAc films by one pot chemical oxidation polymerization technique. The XRD analysis clearly highlighted the amorphous nature of the obtained PTh/PVAc composite. The FE-SEM displayed the rougher morphology preferred for optoelectronic applications. The UV-Vis spectroscopy were employed to explored the complex optical parameters of as-synthesized composite. UV-Vis analysis depicted that the obtained composite influenced high absorption in UV region. The least value of indirect optical energy band gap was measured for PTh/PVAc composite having stoichiometric ratio of thiophene to $FeCl_3$ as (60:40) wt.%. Also, for the same sample the optimized value of optical conductivity was determined. The photoluminescence spectra displayed the emission peaks centered at 390 nm in UV region for the studied composite. Hence, the prepared PTh/PVAc composite thin films are expected to offer significant insight into their optoelectronic applications.

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Conflict of interest

Authors declare that they have no conflict of interest.

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