



OPTICAL AND THERMAL PROPERTIES OF PTh-co-PANI-Ti RANDOM COPOLYMER COMPOSITE FOR PHOTOVOLTAIC APPLICATION

In the present work, a polythiophene (PTh)-co-polyaniline (PANI)-titanium (Ti) copolymer has been synthesized as a novel copolymeric composite material for photovoltaic (PV) application. The focus of the study was to evaluate optical and thermal properties of the PTh-co-PANI-Ti copolymer containing different types of monomers. The optical conductivity was determined from the UV-VIS spectra that were used to calculate the extinction coefficients. The structure and morphology of composite was analyzed through field emission-electron microscopy (FESEM). The PTh-co-PANI-Ti copolymer composite exhibited significant photovoltaic (PV) response to light intensity. $J-V$ analysis showed an increase in conversion efficiency from 0.21 to 1.50 of PTh-co-PANI-Ti with illumination light intensity. PV properties demonstrated that the PTh-co-PANI-Ti exhibited the highest power conversion efficiency $\eta = 1.5$, with a short circuit current $I_{sc} = 0.72$ mA, an open circuit voltage $V_{oc} = 0.9$ V and a fill factor $FF = 0.51$. Thermo-gravimetric (TG) and differential thermal (DTA) analyses were carried out for the thermal stability of the PTh-co-PANI-Ti copolymer composite. The results obtained from the characterization of PTh-co-PANI-Ti showed that many properties of PV action are present in as-synthesized material.

POLYMER, OPTICAL PROPERTY, OPTICAL PARAMETER, THERMAL PROPERTY, COMPOSITE.

1. Introduction

Over the last decade, the literature on photovoltaic (PV)-cell technology has developed significantly in the context of design, synthesis, and characterization of the copolymer base of PV systems, but the challenge still remained to achieve efficient charge photogeneration in PV device architectures [1]. Conjugated polymers and their composites exhibit high optoelectronic properties, universally used in low-cost electronic and optical devices [2]. Most of the organic PV cells have been based on the conjugated polymers such as polyaniline (PANI) and polythiophene (PTh) due to their excellent electrical characteristics, thermal and environmental stability and solubility [3, 4]. By using the novel effective fabrication technique of PV cells, i.e., roll-to-roll, ink-jet and doctor-blading, processing have achieved the maximum power conversion efficiency of organic PV, leading to current certified efficiencies up to 10 % [5]. PV properties are directly related

to the material's structure and its band gap [6]. Conjugated polymers generally exhibit a low band gap in the range of 1.5 – 3.0 eV. The amount of absorbed photons from the incident light has been governed by I_{sc} current of PV cell, because of the low excitation of the donor level [7]. Some attempts to increase the charge separation efficiency by increasing the TiO_2 /polymer interfacial area have been reported. PTh and PANI have been synthesized via oxidative polymerization by using FeCl_3 with the high stability in polymer/titanium dioxide (TiO_2) composites [8]. PTh and PANI have nonlinear optical responses because of high sensitive to the oxidation state and doping level [9]. The optical properties can easily be tuned by a simple organic pathway [10]. PV application has been required for fast nonlinear refractive index with response time [11]. More recently, the efficiency of polymeric PV cell has been increased up to about 6.0–7.4% by using low band-gap conjugated polymers as

an electron donors [12], although individual donor or acceptor materials can show good PV and optical properties as single-layer PV cells [13]. Most PV cells based on P₃HT (Poly (3-hexylthiophene-2,5-diyl)) have a limited absorption range in the UV region which absorbs photons only in the visible region [14].

The present work is an attempt to report the optical and PV properties of PTh-co-PANI-Ti composite. An indium-tin-oxide (ITO)-coated glass plate was used as a light transparent conducting electrode for fabrication of the PV cells. The prepared samples were characterized through field emission-electron microscopy (FESEM), ultraviolet (UV)–visible (VIS) optical spectroscopy and the thermogravimetric (TG) and the differential thermal analyses (DTA).

2. Experimental

Thiophene, aniline and titanium chloride (TiCl₄) were purchased from SD fine, India. AR grade were used as starting chemicals, without further purification. The TiCl₄ was used as an oxidizing agent to initiate the chemical polymerization. The random copolymer of PTh-co-PANI-Ti was synthesized by taking a 1:1:1 molar ratio of aniline, thiophene and TiCl₄. In a typical synthesis process, both monomer solutions were added in a beaker under rigorous magnetic stirring. As soon as TiCl₄ was added in that solution, it started the polymerization reaction with the change in the colour of PTh and PANI solution instantaneously and therefore the solution became dark brown.

In the fabrication of a PV cell, ITO-coated glass substrate was cleaned ultrasonically in a mixture of detergent, deionized water, acetone and ethanol for 90 min. The doctor blade technique was used for the deposition of the active layer of PTh-co-PANI-Ti composite on ITO substrates. During the fabrication of PV cell, aluminum foil with a thickness of 0.22 μm was used for the metallic contact. This foil was placed onto the active layer of the composite. In this way, the PV cell in the ITO/ PTh-co-PANI-Ti/Al architecture was fabricated to obtain PV response at room temperature under an incandescent light bulb with the light intensity of 100, 200, 300 mW/cm². The photovoltaic response was taken for three times

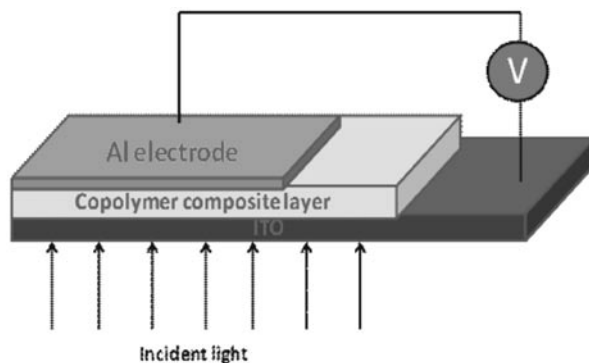


Fig. 1. Side view of PV cell in the ITO/ PTh-co-PANI-Ti/Al architecture

for reproducibility of our PV cell. A side view of the as-fabricated PV cell is shown in Fig. 1.

Material characterization. The physical and chemical and also thermal properties of as-synthesized samples were characterized through FESEM, UV-VIS and TG-DTA. The UV-VIS analysis was performed using a Perkin Elmer UV spectrophotometer in the range between 190 and 1000 nm. The structure, the morphology and the grain size of the samples were obtained by FESEM (JEOL JSM-6360).

Fig. 2 depicts a FESEM micrograph and the result of the energy-dispersive X-ray (EDX) analysis of the PTh-co-PANI/Ti composite. Fig. 2, *a* demonstrates that the SEM image of the synthesized PTh-co-PANI-Ti belongs to composites. The PTh-co-PANI-Ti composite exhibits very rough, micro-fibrillar porous structure and all particles on the surface are inhomogeneous in nature. FESEM images clearly indicate the agglomeration of particles in the as-synthesized PTh-co-PANI/Ti composite. The micrograph clearly shows that the as-synthesized copolymer system acquires fibril nature, which can be observed in the most of the micrograph picture. Similarly, some petals were observed in that micrograph which were attributed to a higher degree of polymerization. It is probable that, due to a high degree of polymerization, the fibril nature of polymeric system was lapped or reduced to a petal shape. The average size of fibril structure ranges between 0.1 and 0.3 μm. Fig. 2, *b* shows the EDX spectrum of PTh-co-PANI-Ti. There is a sharp peak of Ti, so it is confirmed that Ti was doped during the polymerization. The

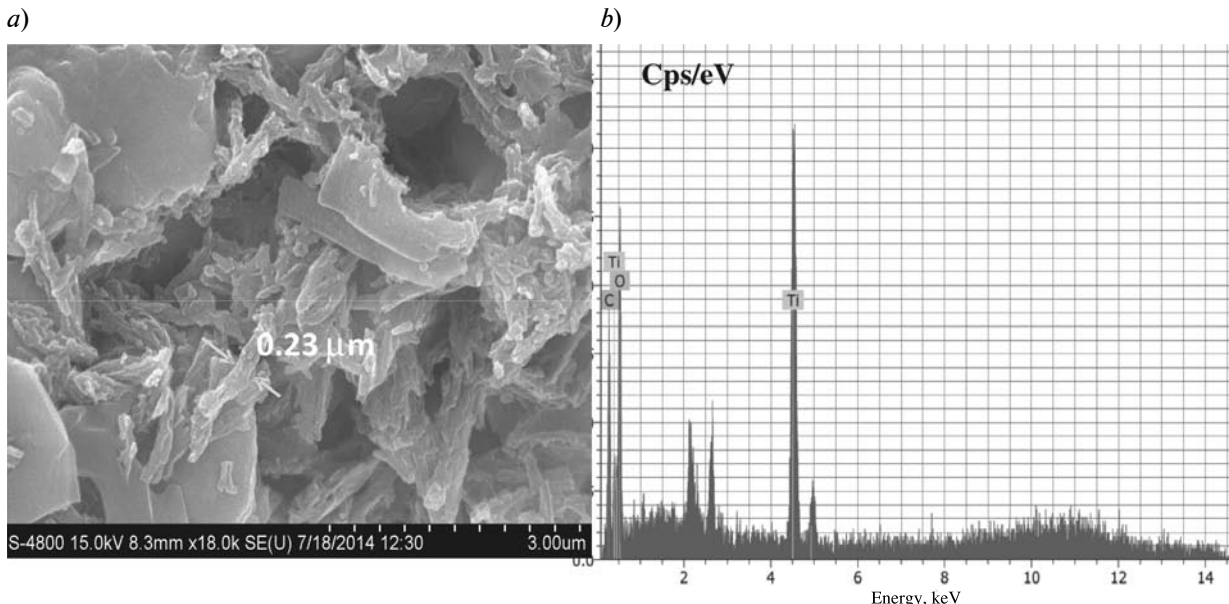


Fig. 2. FESEM image (a) and EDX spectrum (b) of the PTh-co-PANI / Ti composite

rough and inhomogeneous surface morphology of the as-synthesized PTh-co-PANI-Ti enhancing the optical and PV action in the as-fabricated PV cell may be due to the presence of Ti [15]. The micrograph clearly shows that the as-synthesized copolymer system acquires a fibril nature, which can be observed in the most of the micrograph picture.

The analysis of the UV-VIS spectra of the PTh-co-PANI / Ti composite system shown in Fig. 3 was carried out with a view to explore their optical properties. Fig. 3 shows the strongest optical absorption in the low-wavelength region appearing at ~255 nm. This may be due to $\pi \rightarrow \pi^*$ transition of the polymer backbone, the absorption tail being observed towards the higher wavelength values. As to the low wavelength edge in the absorption spectrum, the as-synthesized PTh-co-PANI/Ti composite shows the photoinduced charge-carrier confinement effects in the UV region. The PV action of the material was depending upon its optical conductivity, absorption coefficient and direct (or indirect) band gap [16].

The relation between the absorption coefficient α and the incident photon energy $h\nu$ can be expressed as

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}, \quad (1)$$

where A is the constant and E_g is the band gap of the material. The exponent n depends on the type of the transition.

The optical conductivity can be calculated from the following formula:

$$\sigma = \frac{\alpha n c}{4\pi}, \quad (2)$$

where c is the speed of light, α is the absorption coefficient, n is the refractive index.

The extinction coefficient can be determined using the formula

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

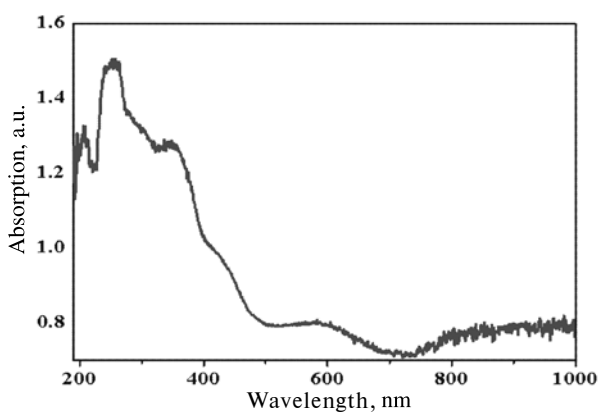


Fig. 3. UV-VIS spectrum of the PTh-co-PANI / Ti composite

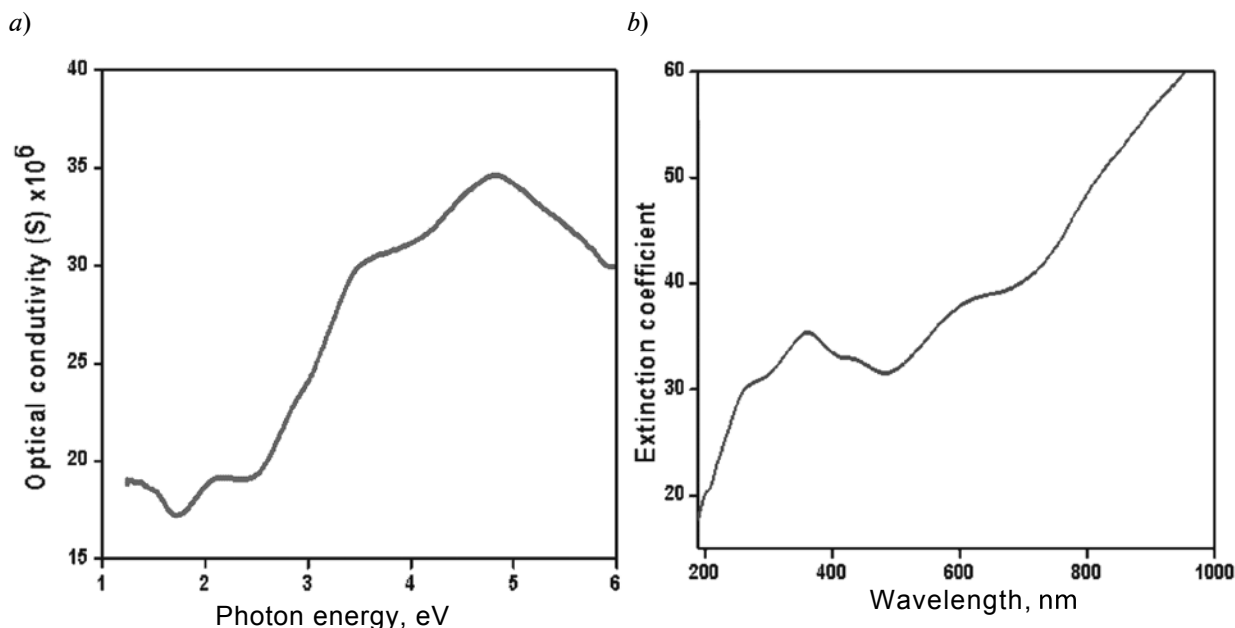


Fig. 4. The plots of photoconductivity versus energy (a) and extinction coefficients versus wavelengths (b)

where λ is the wavelength of light [17].

Fig. 4, a shows the variation of optical conductivity calculated from Eq. (2) with the incident photon energy of the as-synthesized PTh-co-PANI/Ti composite. Fig. 4, a clearly indicates that increased optical conductivity at high photon energies is due to optical conduction. Up to 2.5 eV, the optical conductivity is constant but beyond that it suddenly grows with photon energy. This may be assigned to the maximum optical absorption taking place in the UV region and lower absorption in the visible region (as displayed in UV spectrum) [18].

Fig. 4, b shows the plots of the extinction coefficient values versus photon wavelengths. The extinction coefficient continually increases with incident photon wavelength, but in the region from 350 to 500 nm the presence of a valley may be due to reflection of light from the surface of the as-synthesized of PTh-co-PANI/Ti composite.

Fig. 5 shows the J - V characteristics of PV cell fabricated from the as-synthesized PTh-co-PANI / Ti composite. These characteristics were measured under three illumination intensities (mW/cm^2): of 100, 200 and 300 using the incandescent light bulb. The various PV parameters such as I_{sc} , V_{oc} , J_{max} , V_{max} were

estimated from the J - V characteristics curve. The power conversion efficiency η calculated from Eq. 4 and the fill factor (FF) calculated from Eq. 5 are listed in Table. These are the following:

$$\eta = \frac{(J_{sc} \cdot V_{oc}) \cdot FF}{P_{in}}, \quad (4)$$

where P_{in} is the input power;

$$FF = \frac{Im(ax) \cdot V_{max}}{I_{sc} \cdot V_{oc}}. \quad (5)$$

At a low light intensity ($100 \text{ mW}/\text{cm}^2$) of incident light, the cell efficiency was 0.21% but for a high-intensity light bulb ($300 \text{ mW}/\text{cm}^2$) the cell efficiency grew up to 1.5 %. Both the open-circuit voltage and the fill factor are in the ranges from 0.75 to 0.90 V and from 0.51 to 0.57, respectively. However, at the light intensity of $200 \text{ mW}/\text{cm}^2$, the efficiency was found to be 0.70 %. On the other hand, photocurrent density increased up to the value of $0.72 \text{ mA}/\text{cm}^2$. The higher performance at lower intensity shows that the PV cell system is able to convert light energy efficiently as less photons are left unutilized. The increase in J_{sc} and PCE implies that a high intensity of incident light may be due to a higher carrier mobility [19].



Table

Parameters of the PV cell

Light intensity, mW/cm ²	V_{oc} , V	I_{sc} , mA	FF	η , %
100	0.75	0.11	0.54	0.21
200	0.84	0.32	0.57	0.70
300	0.90	0.72	0.51	1.50

Notations: V_{oc} is the open circuit voltage, I_{sc} is the short circuit current, FF is the fill factor, η is the power conversion efficiency.

The thermal decomposition of the PTh-*co*-PANI-Ti composite shows a three-step weight loss for the as-synthesized sample (see curve 1 in Fig. 6). The first weight loss of 10.09 % from 40 to 210 °C may be due to the loss of water molecules which are present in the composite. A second weight loss of 51.32 % ranging from 240 to 435 °C may be associated with the loss of small fragments of molecular weight which are present in the composite. A third weight loss is observed in the range from 450 °C to 700 °C, which may correspond to thermal degradation of the polymer.

Thermogravimetric analysis indicates the increase in thermal stability of the polymer composite compared to pure polymer [20]. The DTA curve of PTh-*co*-PANI-Ti shown in Fig. 6

(see curve 2) exhibits an endothermic peak around 172 °C due to the loss of surrounding water molecules. An exothermic peak at 347.08 °C is due to the decomposition of polymer composite.

Conclusions

In the present work, we have successfully synthesized a random copolymer between PTh and PANI. The as-synthesized copolymer was successfully employed for PV application. The power performance of the as-fabricated PV cells was enhanced by using light intensity. The short-circuit current increased from $J_{sc} = 0.11$ mA/cm² for the reference cell to 0.72 mA/cm² for the best PTh-*co*-PANI-Ti PV cell. The current gain gives a rise of the

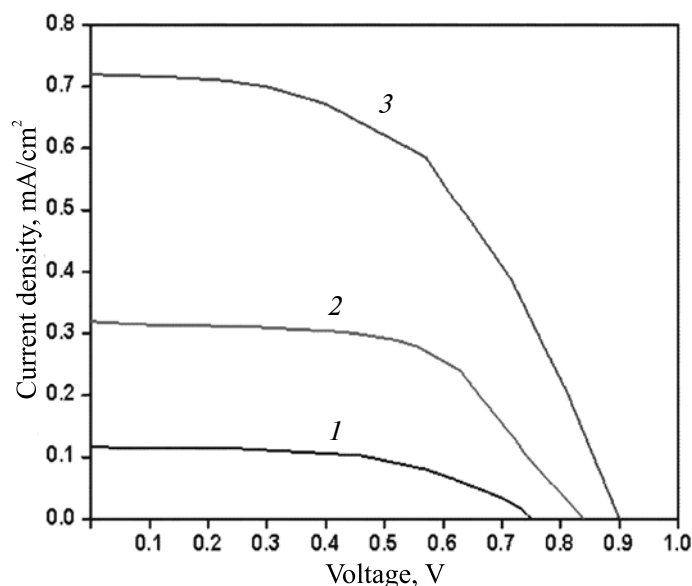


Fig. 5. J - V characteristics of the as-fabricated ITO/PTh-*co*-PANI-Ti / Al system at different values of light intensity, mW/cm²: 100 (1), 200 (2), 300 (3)

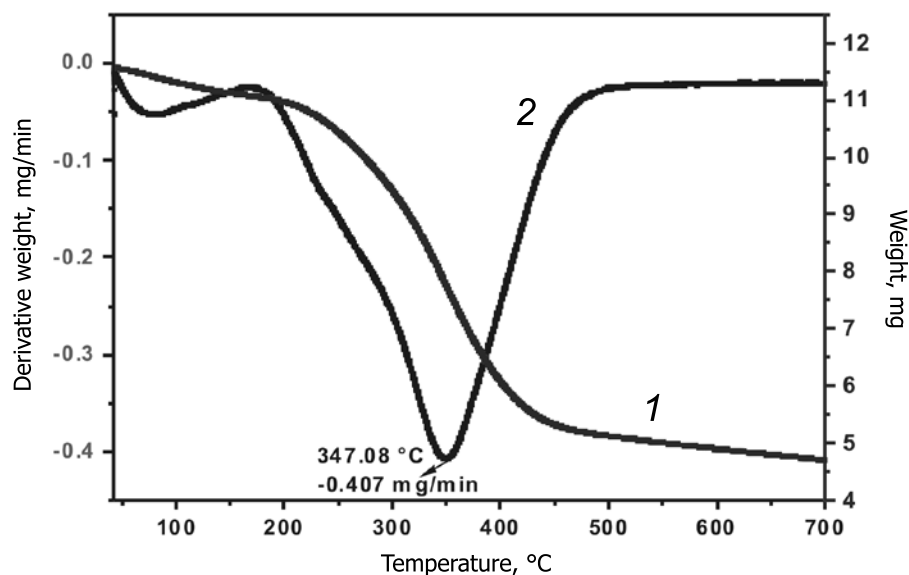


Fig. 6. TG (1) and DTA (2) curves of PTh-co-PANI-Ti. An exothermic peak with the corresponding DW value is shown

conversion efficiency from $\eta = 0.21\%$ to 1.50% . This enhancement is explained by light scattering from the surface of the PTh-co-PANI-Ti composite active layer. The copolymer composite absorbed light in a spectral range from the UV region to near 300 nm. In view of the characterization we carried out, we can conclude that material design strategies provide

us with efficient pathways for obtaining polymer composites with altered optical and thermal properties.

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Такпире С.Р., Уагхули С.А. ОПТИЧЕСКИЕ И ТЕПЛОВЫЕ СВОЙСТВА СТАТИСТИЧЕСКОГО СОПОЛИМЕРНОГО КОМПОЗИТА ПТ-СО-ПАНИ-Ti, ПЕРСПЕКТИВНОГО ДЛЯ ПРИМЕНЕНИЯ В ФОТОЭЛЕКТРИЧЕСКИХ УСТРОЙСТВАХ.

Впервые синтезирован новый сополимер политиофен(ПТ)-со-полианилин(ПАНИ)-титан (Ti) – композитный материал, предназначенный для применения в фотоэлектрических устройствах. Главная цель исследования состояла в оценке оптических и тепловых свойств сополимера в зависимости от вида содержащегося в нем мономера. Фотопроводимость измерялась по оптическим спектрам видимой и УФ-области, чтобы рассчитать соответствующие коэффициенты экстинкции. Структура и морфология композита изучалась методом сканирующей автоэмиссионной электронной микроскопии (FESEM). Объект продемонстрировал существенную чувствительность к интенсивности светового излучения. Из анализа вольтамперных характеристик сополимера установлено, что эффективность фотообразования энергии падающего на объект света в электрический ток составляет от 0,21 до 1,50. Изучение фотоэлектрических свойств материала показало, что изучаемый сополимер проявляет наивысшую эффективность преобразования энергии $\eta = 1,5$, при этом ток короткого замыкания составлял 0,72 мА, холостое напряжение – 0,9 В, а фактор заполнения – 0,51. Для определения термостабильности сополимерного композита были также проведены термogrавиметрический анализ и дифференциальный термоанализ. Результаты, полученные при исследовании вновь синтезированного материала, показали, что он обладает свойствами, характерными для фотоэлектрика.

ПОЛИМЕР, ОПТИЧЕСКИЕ СВОЙСТВА, ОПТИЧЕСКИЕ ПАРАМЕТРЫ, ТЕПЛОВЫЕ СВОЙСТВА. КОМПОЗИТ.

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