Iraqi Journal of Science, 2019, Vol. 60, No. 4, pp: 754-761
DOI: 10.24996/ijs.2019.60.4.9

ISSN: 0067-2904

Fabrication and Characterization of Hybrid MEH-PPV / TiO_2 for Photodetector

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Abstract

In this work, the characterization and application of thin films composite incorporated titanium dioxide (TiO_2) (0.8)% volume ratio for (Rutile) nanostructure with poly [2- methoxy-5-(2'-ethylhexoxy-p-phenylene vinylene] (MEH-PPV) were deposited by a spin-coating technique. The optical properties for deposited (MEH-PPV/TiO_2) nanocomposite thin films have two peaks which are the Q-band in the visible region and B-band in ultraviolet. This study shows that the absorption spectrum of organic polymer mixing with TiO_2 increased with increasing the volume ratios TiO_2. The I-V characteristic of nanocomposite thin films shows that the current at dark and light condition varies approximately with applied voltage. We observed that the current increases with the mixed ratios of TiO_2 and the operation voltage decrease. The MEH-PPV/TiO_2 nanocomposite material has been worked as (UV-Vis.) light detector with high responsivity and high detectives in the Rutile TiO_2 at the mixed rate (0.8) mg/ml, 14.32 at 350nm and 16.73at 510nm.

Keywords: Hybrid, MEH: PPV, photodetector, MEH-PPV / TiO_2

تصنيع و دراسة المتراكب MEH–PPV/TiO_2 الهجين لتطبيقات الكاشف الضوئي

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الخلاصة

في هذا البحث تم دراسة خصائص و تطبيقات الأغشية الرقيقة النتاتجة من مزج (0.8)ملغم/مول من ثاني أوكسيد التيتانيوم TiO_2 ذا التركيب النانوي مع [2– methoxy–5–(2'–ethylhexoxy–p–phenylene vinylene] (MEH–PPV) تم ترسيبها بتقنية الطلاء الدوراني .الخصائص البصرية للأغشية الرقيقة النانوية للمتراكب الهجين (MEH–PPV / TiO_2) اظهرت ان لديها قمتان هما الاصرة Q في المنطقة المرئية والاصرة B في الأشعة فوق البنفسجية.بينت هذه الدراسة ان طيف الامتصاص للبوليمرات العضوية الممزوجة مع ثنائي اوكسيد التيتانيوم تزيد عند المزج مع ثنائي اوكسيد التيتانيوم . أوضحت فحوصات التيار – فولتية لاغشية المركب النانوي في حالة الظلام والضوء علاقة اسية مع تغير الفولتية. ولاحظنا ان التيار يزداد مع زيادة نسبة الخلط لثنائي اوكسيد التيتانيوم وفولتية التشغيل تقل. وقد تم العمل على مادة MEH– PPV / TiO_2 ككاشف ضوئي للمنطقة (.UV–Vis) مع استجابة وكشفية عاليين حيث كانت نسبتها(14.32) عند الطول موجي 350 نانومتر و (16.73) عند الطول موجي 510 نانومتر.

1. Introduction

Over the last decade, conjugated polymers have attracted great interest due to the easiness of process from its solution at room temperature and their potential application in developing large scopes, lightweight, flexible, and low cost [1]. The organic semiconductors, oligomers, polymers and

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dendrimers, all of them are based on conjugated" π- electrons". The system of conjugated is represented by an alternation between single and double bonds. The π-electrons are more mobile than σ electrons [2]. Thus, π-electrons transport from position to another one by hopping. The light absorption in organic solar cell and light emission in the organic light emitting diode, the responsible of theses process is π-electrons [3] However, the polymers have electrical and optical properties are not comparable to those of inorganic semiconductor materials. The polymers are found to have a good effect on the conductivity of the polymer host while the Nano-metal oxide can influence its photovoltaic properties. The use of composites is believed to increase the electrical conductivity of the polymer [4] and also used to improve its stability [5], which is very important in organic devices. The preparation conditions such as solvent type, spin coating speed, concentration and molecular weight effect on optical parameters and film morphology[6]

Given the high stability, low cost, photo-active properties, and wide band gap (>3 eV for all crystalline phase) of titanium dioxide (TiO_2) based semiconductors, they are receiving significant interest and are considered as some of the most promising materials for optoelectronic devices [7–8].

Several studies have been carried out on composites made with polymers and Nano-metal oxide such as titanium dioxide (TiO_2). The former is found to have a good effect on the conductivity of the polymer host while the second can influence its photovoltaic properties[9]. Recently, considerable attention was focused on polymers due to their charge generation under illumination, high absorption coefficient in the visible region and easy deposition on substrates even at room temperature. The more promising candidates for application in optoelectronic devices are Conjugated polymers. However, one of the problems observed in the past studies is the low mobility of electrons due to high internal resistivity. This high internal resistivity is often associated with its amorphous structure [10]. (MEH-PPV) has been strongly absorbing visible light and excitations at the interface of the blend inject electrons to the conduction band of TiO_2 is thermodynamically allowed [10].

In the present study, we propose a new approach which blends TiO_2 nanostructures into MEH-PPV polymer in order to form percolation network geometry. We investigate the effect of the addition of these TiO_2 nanoparticles for enhancement of photoconductive applications.

2. Experimental

The polymer (MEH-PPV) and (Rutile) TiO_2 powder were dissolved by Chloroform solvent. MEH-PPV solution was prepared at the concentration of about 1 mg/ml and (0.8) mg/ml while MEH-PPV/TiO_2 mixed solution was prepared at the volume ratio (1:0.8)% mg/ml , of Rutile TiO_2. The mixed solutions were spin coated (The spin parameter was 1500 rpm for 1 minute, the thickness obtained is about (110)nm) on glass for (UV-Visible Spectra Measurements) and on silicon P-type(111) for photodetector device. The Al finger contacts were deposited on the surface of the thin film, figure below shows the schematic diagram of the photodetector setup.

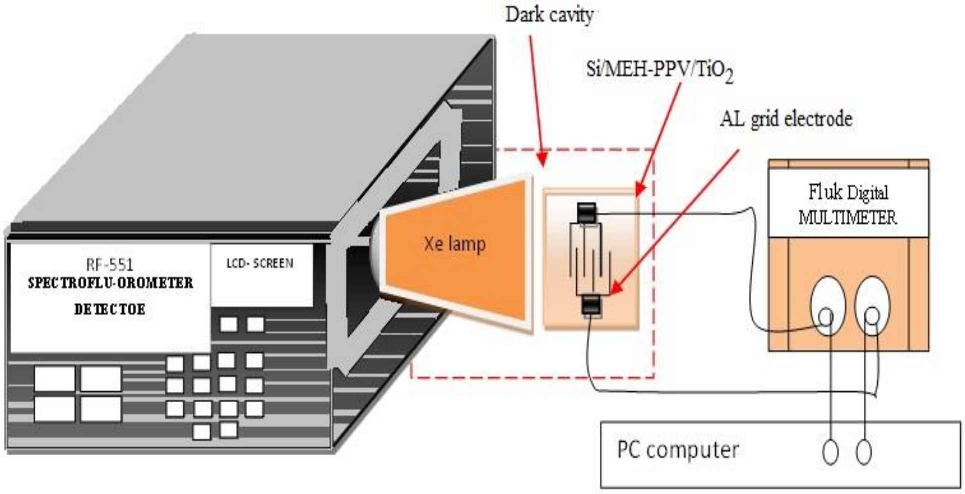


Figure 1-A schematic of the photoconductive sample

The optical absorbance spectra of the MEH-PPV and MEH-PPV mixing with (0. 8)mg/ml of TiO_2 solutions deposited on a glass substrate as thin films within the wavelength ranging (190 - 1100 nm) at room temperature were measured using UV-Visible SP – 8001 spectrophotometers over (Meterrech). The incident photon-to-current efficiency (IPCE) spectral response is done by the (SPECTROFLUOROMETER DETECTOR (RF-551) 2.3A programmable & scanning with FLUKE, 8846A -6-1/2 DIGIT precision multimeter to measure responsivity spectrum). With this setup, it was possible to shine the light of different wavelengths from (200 to 900) nm with steps of 10 nm. Spectral Responsivity $\mathbf{R}_\lambda$ or Radiant Sensitivity is a performance parameter is calculated from equation [11]:

$$R(\lambda) = \frac{J_{ph}(\lambda)}{P_{inc}(\lambda)} \qquad (1)$$

Where $J_{ph}(\lambda)$ is the photocurrent density from the tested detector and $P_{inc}(\lambda)$is the incident power density measured with the photodetectors as a function of wavelength.

The noise-equivalent power (NEP) is calculated from [11].

$$NEP = I_n/R_\lambda \qquad Watts \qquad (2)$$

Where I_n is noise current (If noise from the dark current is the dominant contribution) so noise current is given by [11]:

$$I_n = \sqrt{4k_B T \Delta f / R_d} \qquad (3)$$

Where k_B is Boltzman constant,T is room temperature Δf is bandwidth, R_d is the resistance of detector in the dark. An important figure of merit of a photodetector is detectivity calculated from equation [11]:

$$D^* = \sqrt{\Delta f . \frac{Ad}{NEP}} \qquad (4)$$

Where A_d is the detector active area.

The photocurrent gain (G) of a detector is calculated from [11]:

$$G = \frac{\tau}{t_{tran}} \qquad (5)$$

Where τ is the carrier lifetime, t_{tran} is the transit time between the electrodes.

The following relation was used to calculate the sensitivity (S) [11]:

$$S(\%) = (I_{ph} - I_d)/ I_d \times 100 \qquad (6)$$

I_{ph} is light current and I_d is dark current

3. Results and discussion

3.1 UV-Visible Spectra Measurements

Absorption spectra of organic polymer MEH-PPV and MEH-PPV mixing with (Rutile) concentration of TiO_2 (0.8) mg/ml were carried out as shown in Figure-2. The concentration ratio of inorganic TiO_2 nanoparticles greatly influence both optical and optoelectronic properties of MEH-PPV [12]. Films are characterized by two peaks in both spectra, which are B-Band (absorption which is a (S_0 to S_2) absorption (i.e ground state to second excited state)) at the wavelength region between (280-375) nm and Q-Band (that are S_0 to S_1 absorption) at the wavelength region between (375-620) nm. Figure-2 reveals that the addition of TiO_2 nanoparticles into the MEH-PPV, the optical density of absorption spectra of hybrid MEH-PPV/TiO_2 increase compared to MEH-PPV films and the absorption peak of MEH-PPV shifts to longer wavelength (red-shift).

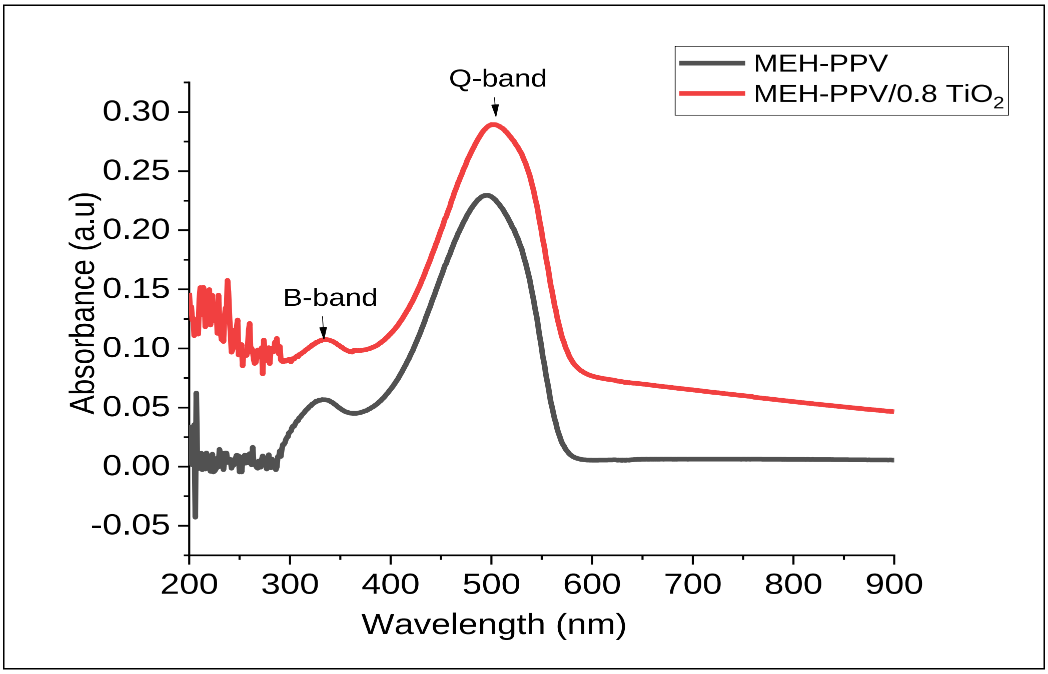


Figure 2-The absorption spectra of MEH-PPV and (MEH-PPV/0.8 Rutile TiO_2) Nanocomposite thin films.

3. 2 (I-V) characteristic of MEH-PPV/TiO_2

Figure-3, shows that the current-voltage characteristic of MEH-PPV and MEH-PPV/TiO_2 nanocomposite thin film by mixing with TiO_2 under dark and illumination condition in range (-1 to 1) v. This figure reveals that enhancement of current with the addition of TiO_2 nanoparticles. The threshold voltage under dark condition decrease (0.2 to 0.01) volt with mixed volume rate (0.8), It also could be seen that current value at respective voltage increase as the composition (0.8 %) of TiO_2 which is n-type inorganic material in MEH-PPV increased which indicate the increment of electron concentration at higher composition of TiO_2. Based on this result, it supported the results report by Le Ha Chi *et.al* which states that by introducing TiO_2 nanoparticle in MEH-PPV thin film could enhance the I-V characteristics compared to the standard polymer alone [13].

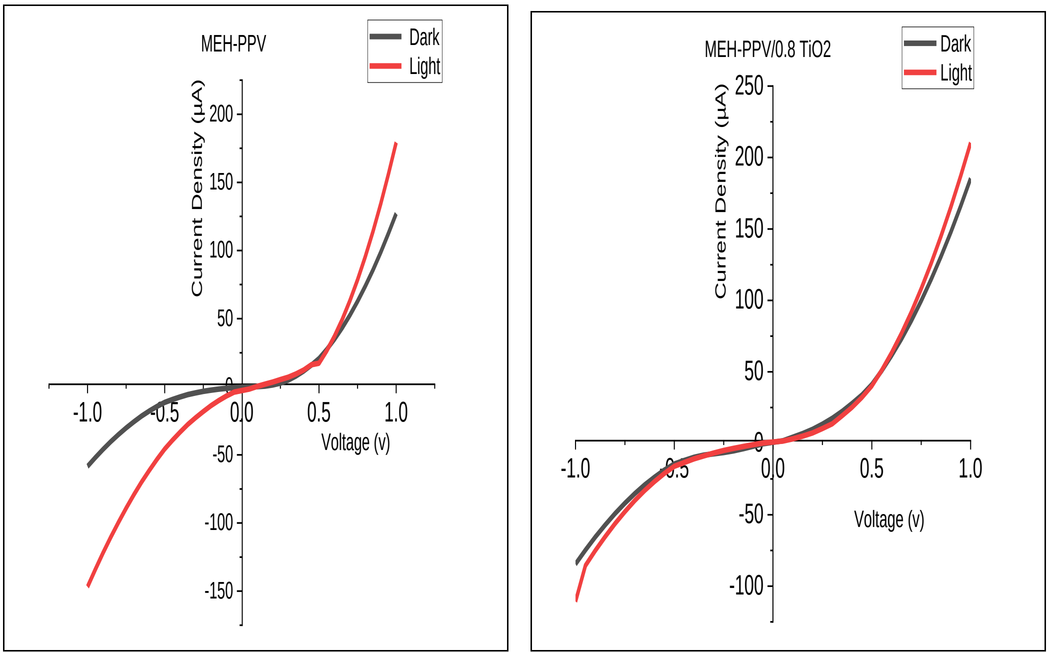


Figure 3-Current – Voltage comparison between Dark and Light (104.98 mW/cm^2) of a) MEH-PPV and b)MEH-PPV/0.8 TiO_2 thin films

To calculated the ideality factor β, potential barrier ϕ_β and tunneling factor A_t , these factors which tableted in (1) from the table the barrier potential and ideality factor increase with increase in the volume ratio of TiO_2.

Table 1-The Ideality factor, Barrier potential and tunneling factor at Dark of MEH-PPV/Rutile TiO_2 nanocomposite thin films at a different rate

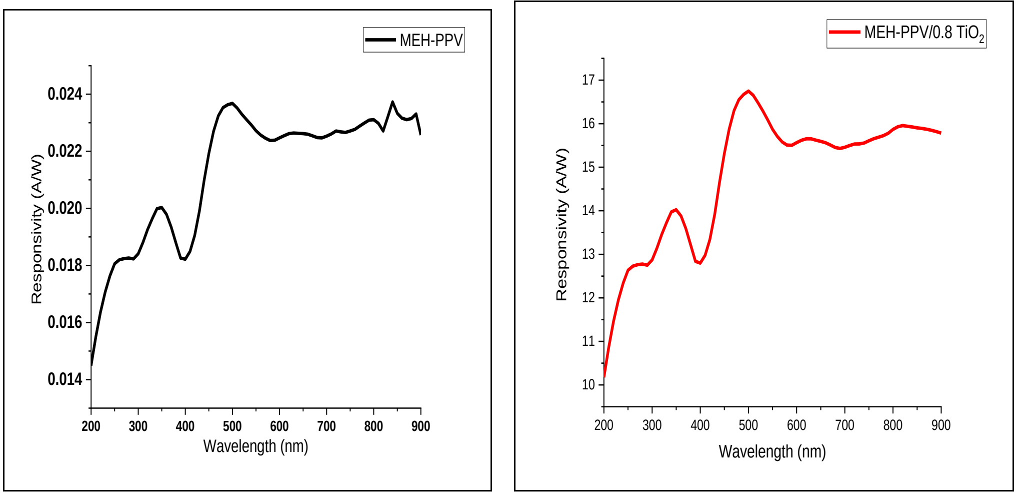
Volume ratios of (Rutile)TiO_2	β	ϕ_β	A_t
MEH-PPV	3.8531	0.7253	1.3927
0.8 TiO_2	3.9389	0.6504	3.2012

3.3 Photodetector Measurement for MEH-PPV/TiO_2 nanocomposite thin films

3.3.1 Responsibility R_λ and Figure of Merit

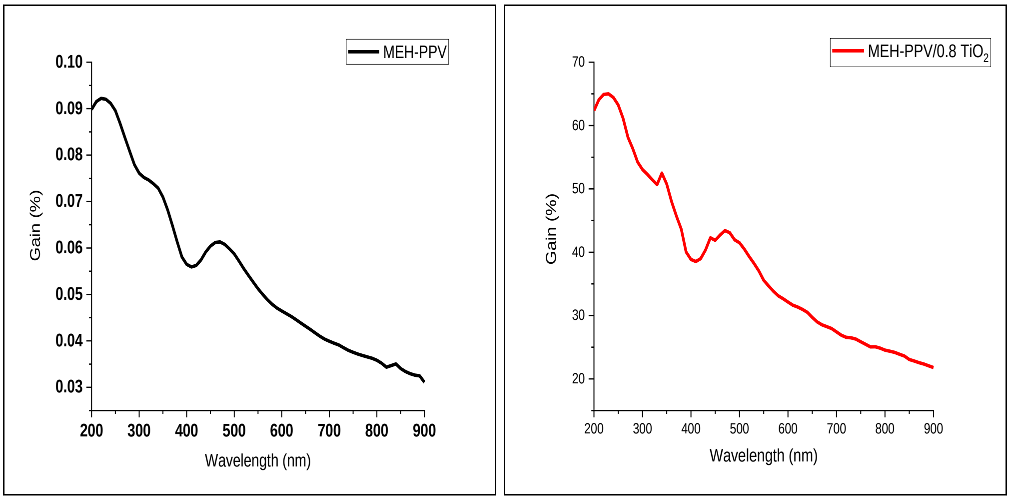
Figures-5 show the spectral response characteristics film of the MEH-PPV and MEH-PPV Mixing with Rutile TiO_2 as nanocomposite detector deposit on Si p-type (111) substrate. The responsivity parameter R_λ (applicable of all detectors) according to Eq. (1)

The Responsibility and gain of organic polymer MEH-PPV increase with an increase in the rate of TiO_2 at (0.8) mg/ml as shown in Figures-(5 and 6). Table-2 shows the Responsibility of the active common wavelengths of all spectra. Figure-7 shows the noise equivalent power (NEP) of MEH-PPV/Rutile TiO_2, NEP decrease with an increased rate of TiO_2. The detecting capability of the detector improves as the NEP decreases. Figure-8 shows the detectivitive of MEH-PPV/Rutile TiO_2, The detective increasing with an increase, the maximum Responsivity is 16.7 for MEH-PPV/TiO_2 at excitation wavelength 500 nm.



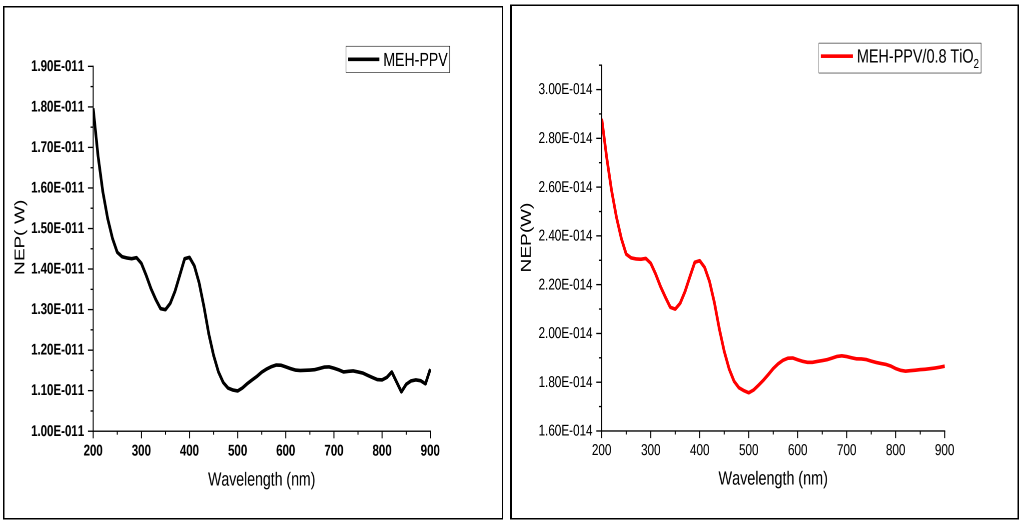
(a) (b)

Figure 5-The Responsivity of a) MEH-PPV, b) MEH-PPV/0.8 (Rutile) TiO_2 nanocomposite.



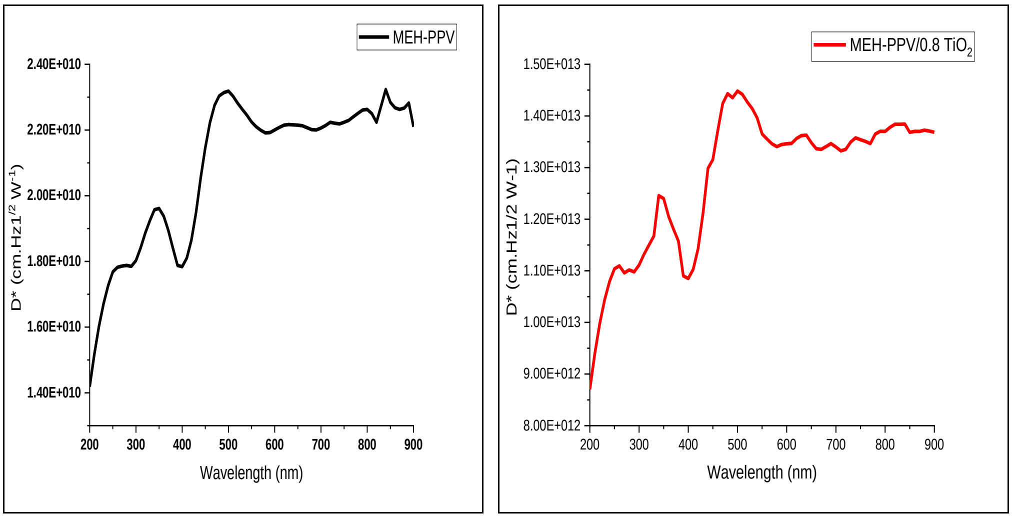
(a) (b)

Figure 6-The Gain of a) MEH-PPV, b) MEH-PPV/0.8 (Rutile) TiO_2 nanocomposite.



(a) (b)

Figure 7-The Noise equivalent power of a) MEH-PPV, b) MEH-PPV/0. 8 (Rutile) TiO_2 nanocomposite



(a) (b)

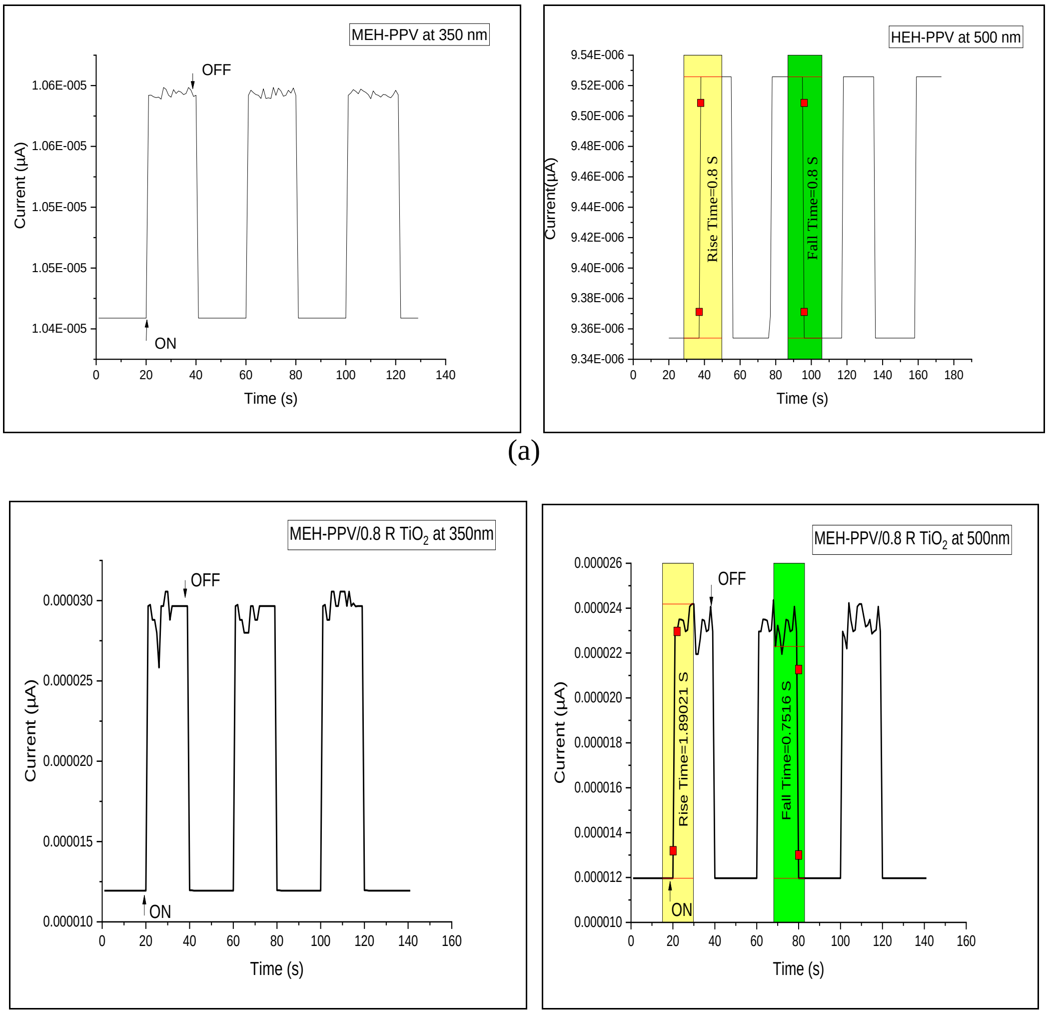
Figure 8-The Detective of a) MEH-PPV, b) MEH-PPV/0.8 (Rutile) TiO_2 nanocomposite

Table 2- The peak position and Responsivity value of MEH-PPV and MEH-PPV/ 0. 8 RutileTiO_2

Rate	Peak position		Rλ (A/W)	
MEH-PPV	340	490	0.0020	0.0023
0.8 TiO_2	350	510	14.32	16.73

3.3.2 Time-Dependent Photocurrent

Figure-9 shows, the time-dependent photocurrents of the organic polymer and that mixing with Rutail) TiO_2 at the rate (0. 8)mg/ml, the most influential properties of the photodetector are the rapid response and fall times, where the current increase with increasing the volume ratio of TiO_2. From this figure, the light was switched ON/OFF periodically every 20s. The sensitivity values of the photodetector were calculated using Eq (6) at the λ_{exc}= (350 and 500) nm which illustrate in the Table-3. Photons absorption by the MEH-PPV and MEH-PPV/TiO_2 composites occur when the photon energy is equal to or exceeds the semiconductor bandgap [14], thus generating electron-hole pairs within the TiO_2 semiconductor, the sensitivity increase with the mixed rate of TiO_2 as shown in Table-3.



(a)

(b)

Figure 9-the time-dependent photocurrent of the MEH-PPV/(Rutile)TiO_2 in the excitation wavelength (350 and 500) nm (a) MEH-PPV, (d) MEH-PPV/0.8 Rutile TiO_2

Table 3-Sensitivity of MEH-PPV mixing with Rutile TiO_2 at a rate (0.8) mg/ml

sample	λ excitation		Sensitivity	
MEH-PPV	350	500	1.6	1.9
0.8 TiO_2	350	500	148.2	91.8

Conclusions

In this work, un-mixed and mixed MEH-PPV with TiO_2 films on glass and Si substrates have been successfully prepared by a spin coating method. The absorption spectrum increases with the loading of Rutile TiO_2 nanoparticales (0.8 mg/ml). The maximum responsivity appears at the peak between (340 and 490) nm for the (rutile) TiO_2. The very fast detector is manufactured, where the rise time and recovery time is about 0.8 sec for the square pulses.

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