# ENHANCEMENT OF THE SENSITIVITY OF MEH-PPV AGAINST $NO_2$ TOXIC GAS

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***ABSTRACT**: Characterization and application of thin films composites incorporated titanium dioxide ($TiO_2$) with poly [2-methoxy-5-(2'-ethylhexoxy-p-phenylene vinylene] (MEH-PPV) deposited by spin-coating technique is reported in this work. The films were prepared by mixing 8 wt. % $TiO_2$ with MEH-PPV conducting polymer and using chloroform as solvent. These precursor solutions were firstly performed in order to deposit un-doped MEH-PPV and later, doped with $TiO_2$ films on glass and p –Si (111) substrates. The structural, optical and gas sensing properties revealed the influence of $TiO_2$ addition to MEH-PPV. X-ray diffraction results of MEH-PPV:$TiO_2$ proved the anatase phase for $TiO_2$ was predominantly observed in the composite. The morphology was demonstrated by Field Emission Scanning Electron Microscope (FESEM) images for MEH-PPV and MEH-PPV:$TiO_2$ films and prove agglomerated grains and nanorod formation respectively. The optical measurement of MEH-PPV pure film and MEH-PPV/$TiO_2$ films portrayed two peaks namely B and Q bands. The optical energy gap was calculated in the B band to be in range of 2.98 to 3.13 eV. It decreases with higher $TiO_2$ contents. While in Q band, the $E_g$ nearly constant at concentrations of 0.02, 0.04 and 0.06 for MEH-PPV:$TiO_2$. Sensing behavior was studied for these composites against toxic gas $NO_2$ in relation to different proportion of $TiO_2$ and operation temperature. The sensitivity and response time was measured at different operating temperatures such as RT, 100°C and 200°C. The maximum sensitivity of MEH-PPV pure film to $NO_2$ gas was 16% at room temperature, however the maximum value of MEH-PPV/$TiO_2$ film was 1088% at 200°C.*

**Keywords**: MEH-PPV, $TiO_2$, Composite, Conducting polymer, $NO_2$ gas sensor, Sensitivity.

## INTRODUCTION

Over the last decade, conjugated polymers have attracted great interest due to easiness of process from its solution at room temperature and their potential application in developing large scopes, flexible, light weight and low cost [1]. However, the electrical and optical properties of these polymers are not comparable to those of inorganic semiconductor materials. Thus, polymer-based devices have performed poorly in common practices. 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. The use of composites is believed to increase the electrical conduction of the polymer [2] and in addition, to improve its stability [3], which is of prime importance in organic devices. If it is used in composites, modifications of the polymer luminescence were observed in this oxide. Hence, potential development for sensory apparatus is promising.

Recently, gas sensors have fascinated researchers in various parts of the world. Nitrogen dioxide ($NO_2$) as we know is one of the many gaseous emitted into our environment overwhelmingly by automobiles. It is one of the main toxic components released from vehicular exhaust and also a main component of emissions from indoor appliances. Moreover, it transforms in the air to form gaseous nitric acid and toxic organic nitrates, hence contributing to the production of acid rain. Therefore a selective and accurate $NO_2$ sensor is of extreme importance for continuous monitoring of emission processes [4].

In order to improve the device sensitivity, it will be of great interest to work with the most appropriate sensing material in every case and to obtain its optimum detecting temperature [5]. Sensitivity can be classified into a category which represents the ability of a device to detect a variation in a physical and/or chemical property of the sensing material under gas exposure. Taking into account that sensing reactions take place mainly at the sensor's surface layer, the control of semiconductor composition, morphology and microstructure is required for enhancing the sensitivity of sensors. Working with nanostructure materials will give a higher surface owing to its exposure area.

Generally, sensitivity is defined by the resistance change when the sensor is bare to a certain concentration of gas. The sensitivity for p-type semiconductor and oxidizing gas can be calculated as given in [6]:

$$\boldsymbol{S} = \left|\frac{R_g - R_a}{R_g}\right| \mathbf{100}\% \quad \ldots\ldots (1)$$

where $\boldsymbol{S}$ is the sensitivity, $\boldsymbol{R_a}$ is the electrical resistance of the film in air and $\boldsymbol{R_g}$ is the electrical resistance of the film in the presence of gas. The response time of a gas sensor is defined as the time required for the sensor to reach 90% of maximum/minimum value of conductance upon introduction of the reducing/oxidizing gas. Similarly, the recovery time is defined as the time required recovering to within 10% of the original baseline when the flow of reducing or oxidizing gas is

removed. The response time and recovery time can be calculated as follows [7]:

$$Response\ time = \left|t_{gas(on)} - t_{gas(off)}\right| \times 0.9 \quad \text{.....(2)}$$

$$Recovery\ time = \left|t_{gas(off)} - t_{gas(on)}\right| \times 0.9 \quad \text{.....(3)}$$

where $t_{gas\ (on)}$ is the time which sensor needs to reach 90% of maximum value of conductance upon introduction of the oxidizing gas, and $t_{\ gas(off)}$ is the time required to recover to within 10% of the original base line when the flow of oxidizing gas is removed, equations (1) to (3) have been used to analyze the sensors. The sensor is mainly acquired from the fabrication of MEH-PPV/Si and, nanocomposite thin films based on (MEH-PPV) and $TiO_2$.

## EXPERIMENTAL METHOD

MEH-PPV solution was prepared by dissolving 0.05% mg/ml MEH-PPV powder (product of Aldrich, USA) in chloroform. The hybrid organic–inorganic materials based on MEH-PPV and $TiO_2$ have been obtained by dissolving $TiO_2$ powder (product of Aldrich, USA) with 8 wt. %. Thin film layer was spin-coated at a spin rate of 1000 rpm for 60 s on glass and silicon substrates at room temperature. After that, samples were put into a vacuum oven at 100□C for 1 hour drying process. In producing gas sensor film, an electrode of aluminum layer was deposited by thermal evaporation technique.

The crystal structure was inspected by using XRD-"SHIMADZU" 6000 X-ray diffractometer ($CuK_\alpha$ radiation λ=0.154 nm) and the surface morphology of samples was investigated by using "Hitachi" Field Emission Scanning Electron Microscopy (FE-SEM) S-4160. The thickness of all thin films was examined by an alpha step surface profile monitor which is 100±20 nm. The Ultraviolet–visible (UV–Vis) absorption spectra were probed by using Jasco UV-VIS-NIR V570 spectrometer. A PC-interfaced digital multimeter of type UNI-T UT81B was utilized to measure sensor resistivity when exposed to air-$NO_2$ gas mixing.

## RESULTS AND DISCUSSION:

Figure (1) shows x-ray diffraction patterns of undoped and doped MEH-PPV with 8 wt. % $TiO_2$ films. The inset of this figure illustrates a broad peak pattern in the selection of 10 to 40 of 2Θ degree. The wide-ranging peak is associated to interchain scattering of two main chain backbones separated by bulky substituents which also confirms the side chain relation with semicrystalline nature of this polymer[11]. $TiO_2$ doped MEH-PPV film has polycrystalline structure[8,9] and peaks are observed at 25.0 and 36.5 in x-ray diffractogram corresponds to (101) and (103) respectively. Further, it indicated that the $TiO_2$ doped MEH-PPV film is composed of anatase structure.

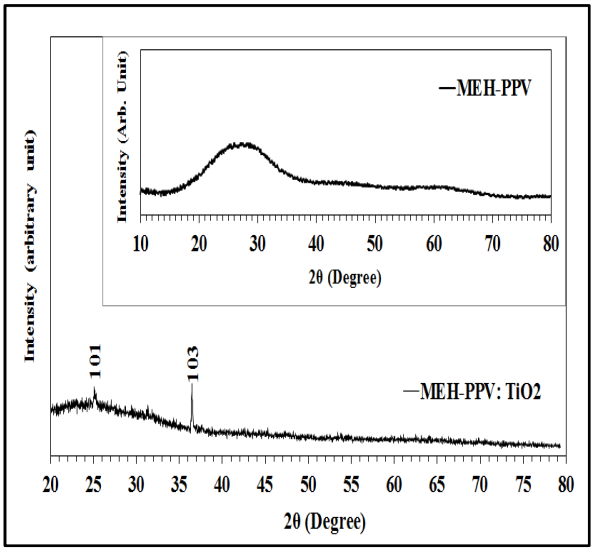


**Figure 1: XRD patterns of pure MEH-PPV and $TiO_2$ doped MEH-PPV thin films.**

Table (1) shows some structural parameters such as full width at half maximum (FWHM), crystallite size, interplaner space and (hkl) indices. The MEH-PPV:$TiO_2$ thin films indicate that the deposited atoms of these films are inclining towards nanostructure regime [10].

**Table (1): Structural parameters for undoped and doped MEH-PPV with $TiO_2$**

| $TiO_2$ content | 2θ (Deg.) | FWHM (Deg.) | $d_{hkl}$ Exp.(Å) | D (nm) | hkl | $d_{hkl}$ Std.(Å) | Phase | Card No. |
|---|---|---|---|---|---|---|---|---|
| 0 % | 26.9700 | 12.8000 | 3.3033 | 0.693 | ----- | ----- | ----- | ----- |
| 8 % | 25.1737 | 0.2874 | 3.5348 | 28.3 | (101) | 3.5169 | Anatase | 96-900-9087 |
| | 36.4551 | 0.1437 | 2.4627 | 58.2 | (103) | 2.4309 | Anatase | 96-900-9087 |

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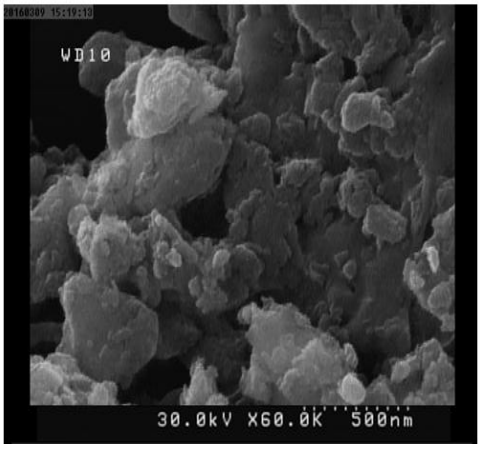
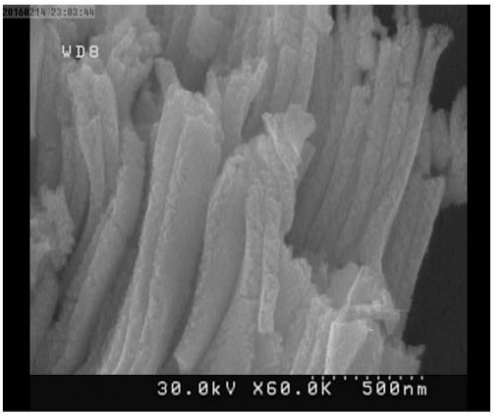
*The films morphology was recorded using Field Emission* Scanning Electron Microscopy (FESEM) for undoped and doped MEH-PPV with $TiO_2$ thin films as shown in Figure 2. The films appear generally rough which designates that the morphology of the polymers is discernible as in figure 2a. Long octyloxy chain illustrates elongated particle size [12]. Figure 2b demonstrates the FESEM image of $TiO_2$ doped MEH-PPV which form of nanorods and the rods have an orientation close to the vertical direction.




(a)




(b)

**Figure 2: FESEM images of (a) pure MEH-PPV and (b) $TiO_2$ doped MEH-PPV thin films.**

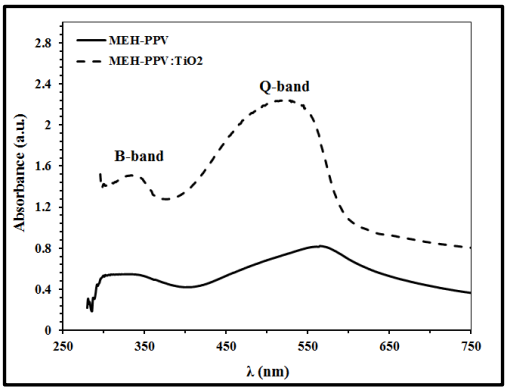



**Figure 3 : The absorbance spectra as a function of the wavelength of MEH-PPV and doped with $TiO_2$**

Figure 3 displays the absorption spectra of pristine MEH-PPV and MEH-PPV:$TiO_2$ films. There are two absorption peaks in UV -VIS region due to B and Q bands. The B band in ultra violet region is attributed to transition of π* in iLUMO, and the Q band in the visible region ascribed to the transition between π (HOMO)- π* (LUMO). Fig. (3) Illustrates absorption spectrum of pure MEH-PPV, it indicates a large number of π electron conjugated so that the electronic levels of the bonding orbital (π) and antibonding orbital (π*) are similar to an isolated molecule with the similar conjugated structure [13]. As a result, the conjugation in MEH-PPV is greatly reduced. Within the UV spectrum region, a strong absorption peak at 296 nm is attributed to partially occupied $d–\pi^*$ transitions [14]. Fig. (3) shows the absorbance increases for $TiO_2$ doped MEH-PPV and the minor changes occur in a flat area range of 400-450 nm. In addition, the spectra also depict the maximum absorption peak shifts towards the longer wavelength with the ups urge of $TiO_2$. The $TiO_2$ addition causes decrement in crystal defects and localized levels. Absorption of the composite is stronger compare to the pure MEH-PPV due to the absorption of $TiO_2$ at wavelengths lower than 400 nm. Moreover, adding $TiO_2$ results in the increasing number of interfaces between the two materials. The embedded of $TiO_2$ in polymer matrix prevents the formation of polymer aggregates in the composite films and reduces the polymer conjugation chain length of MEH-PPV, hence shifted the peak [15,16] and Table (2) illustrates these peak positions.

**Table (2): Peak positions for MEH-PPV with and without $TiO_2$ addition extracted from UV-Vis spectra**

| $TiO_2$ content | peak position (nm) | |
|---|---|---|
| | B-Band | Q-Band |
| **0 %** | 304 | 561 |
| **8 %** | 326 | 526 |

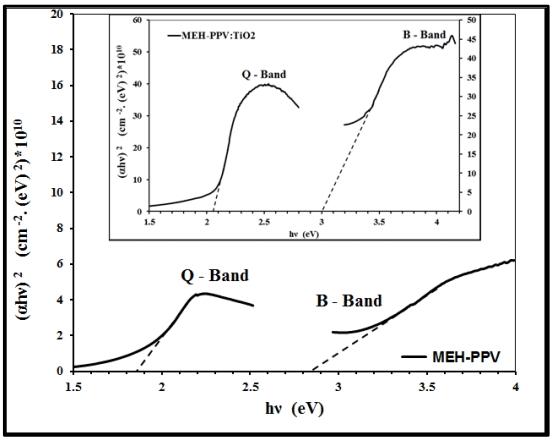



**Fig. (4) Illustrates the optical band gap $E_g^{opt}$ of MEH-**PPV films with and without $TiO_2$ calculated from Tauc relation. It is observed that the band gap decreases with $TiO_2$ addition. Table (3) depicts the energy gap of MEH-PPV for B and Q bands. Adding $TiO_2$ leads to reduction in energy gap which may affect a growth of particles size [19].

Figure 4: Tauc plot with Q band and B band for MEH-PPV and doped with $TiO_2$

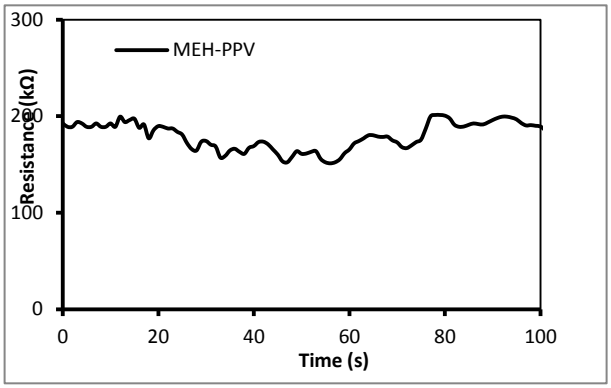



**Figure 5: No sensing response of MEH-PPV against $NO_2$ gas**

**Table (3): Optical Energy gap for MEH-PPV:$TiO_2$ composite.**

| $TiO_2$ content | $E_g$ (eV) | |
|---|---|---|
| | B-Band | Q-Band |
| **0 %** | 2.85 | 1.85 |
| **8 %** | 3.00 | 2.05 |

## GAS SENSING MEASUREMENTS:

### Sensitivity

Sensing properties of pure MEH-PPV and doped with $TiO_2$ films deposited on silicon p-type substrate are reported in this section. Toxic gas, namely $NO_2$ is used to find the $TiO_2$ addition dependency on the device sensitivity. The sensing mechanism for pure MEH-PPV was performed with concentration of 25 ppm at different operation temperatures from 30 $^oC$ up to 200$^oC$. Figure (5) demonstrates the variation of resistance with time at ON/OFF gas flow. It is proofed that there is no prominent effect for pure MEH-PPV. This could probably because of limited diffusion to polymer chains remotely located from the surface. Presumably this effect can be associated with weaker binding of molecules to polymer chains [21].

For MEH-PPV:$TiO_2$ film, there is repeatability of sensing pulses for $NO_2$ gas at different operating temperatures. It was found that the response and recovery times were almost constant for each cycle. Sensing behavior verifies lower resistance when the composite was exposed to $NO_2$ gas (valve ON), then the resistance increases with the closure of the gas (valve OFF). The reason for this observation can be attributed to the following: $NO_2$ gas undergoes an ionic reaction with the surface adsorption oxygen, where the electron on the oxygen is extracted from the composite material. Hence, the holes increase in this material and cause the resistance to decrease [11] so we can conclude that this composite stills a p-type material[17] because in the p-type semiconductor, the concentration of electrons on the p-type semiconductor surface decreases and the resistance of the p-type semiconductor decreases because the extracted electrons result in the generation of holes in the valence band [18,19]. The sensitivity factor (S%) at various operating temperatures is calculated using eq. (1). The maximum sensitivity of MEH-PPV:$TiO_2$ is more than 1000% at 200°C. Response and recovery times have been determined from equations (2) and (3). The enhancement of the sensitivity is related to the presence of $TiO_2$ inside conducting polymer matrix.

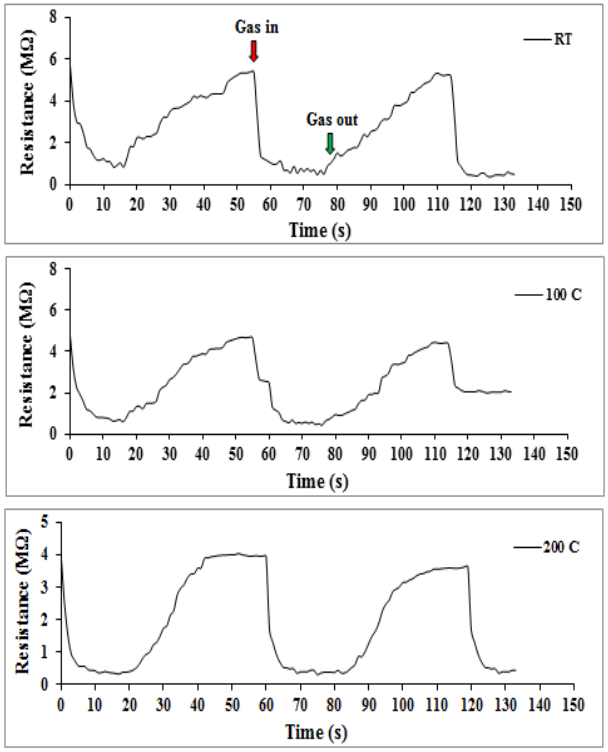



**Figure 6: The repeatability of response pulse with time for $TiO_2$ doped MEH-PPV against $NO_2$ gas at different operating temperatures.**

### Effect of operating temperature of the sensor:

The operating temperature is defined as the temperature at which the resistance of the sensor reaches a constant value. Changing of resistance is just only influenced by the presence of amount of some gases of interest [20]. The sensitivity factor (S%) is calculated at several operating temperatures. Figure 7 shows the sensitivity as a function of operating temperature for $TiO_2$ doped MEH-PPV thin film deposited on Si substrate. The gas sensitivity tests were performed at ( 30, 100, 200 )°C.

Obviously, the addition of $TiO_2$ leads to an improvement of the film sensitivity which is attributed to higher rate of surface reaction of the target gas. Also may be due to the surface that oxidizes the gas so intensively. Enhancement in morphology as illustrated in Fig. 2b earlier led to high surface to volume ratio, hence oxidation becomes huge. Maximum sensitivity value for $TiO_2$ doped polymer film is seen at 200°C which is called optimal temperature. At the optimal temperature, the activation energy may be enough to complete the chemical reaction. The increase and decrease in the sensitivity indicates the adsorption and desorption phenomenon of the gas. The higher sensitivity may return, larger rate of oxidation and the optimum surface roughness. The sensitivity as well as response time depend on operating temperature since the chemical kinetics in solid-gas reaction

is governed by the dependence of temperature. Table 4 highlights the effect of temperature on gas sensitivity.

**Response Time and Recovery Time for $TiO_2$ doped MEH-PPV Sensor:**

Figure 8 (a and b) show the relation between the response time and the recovery time for $TiO_2$ doped MEH-PPV sensor and operating temperature. The response speed is studied with operating temperature and it is found that the sensor has maximum sensitivity and fast response time at operating temperature of 200 $^0$C. Also fast return to initial state before exposure to gas has been observed at 200 $^0$C. The film $TiO_2$ doped MEH-PPV exhibits response speed ~11 s and recovery time ~25 s. This reveals that the most suited impurities in dopant to achieve good sensor with fast response. The quick response sensor for $NO_2$ gas may be due to faster oxidation of gas [20]. In addition, it can occupy energy level below conduction band and behave as an activator. Consequently, electrons easily move to conduction band, and increase the adsorption of oxygen on the surface. Thus extracts conduction electrons from the near surface region and forms an electron depleted surface layer. As a result, number of active adsorption sites increased and achieved fast response time of sensor [21].

In real situation, a fast response time is usually required also fast recovery time is greatly important in sensing measurement that means quick regressing to initial state before exposure the gas.

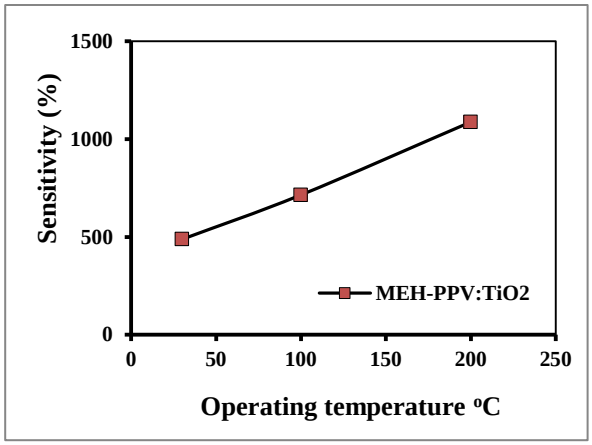



**Figure 7 : The variation of $NO_2$ sensitivity as a function of operating temperature in $TiO_2$ doped MEH-PPV thin film**

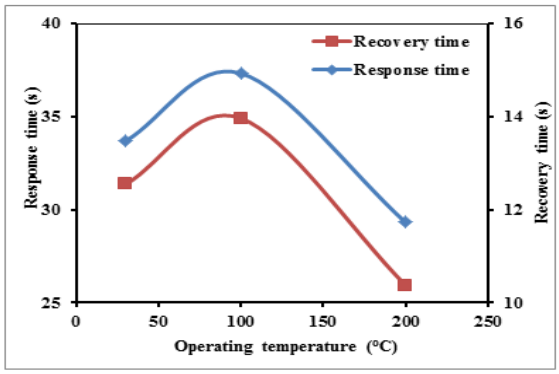



**Figure 8 : The variation of response time and recovery time for $TiO_2$ doped MEH-PPV sensor against $NO_2$ gas**

**Table (4): Response time, recovery time and sensitivity% of un-doped MEH-PPV and doped with different ratio of $TiO_2$.**

| Gas sensor parameters | Operating temperature (°C) | | |
|---|---|---|---|
| | RT | 100 | 200 |
| Response Time (s) | 13.45 | 14.93 | 11.72 |
| Recovery Time (s) | 31.36 | 34.91 | 25.94 |
| Sensitivity % | 488.25 | 715.38 | 1088.79 |

## CONCLUSIONS

In this work, un-doped and doped MEH-PPV with $TiO_2$ films on glass and Si substrates have been successfully prepared by spin coating method. The films were successfully characterized by XRD measurements that proved the composite has anatase structure belonging to $TiO_2$ embedded into polymer matrix. FESEM images of samples displayed granular structure for pure MEH-PPV and demonstrated formation of nanorods and the rods have an orientation close to the vertical direction that makes this composite suitable for working as gas sensing application where its sensitivity was 1088% against $NO_2$ gas with fast response at 200$^0$C operating temperature.

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