Characterization and Performance of PAni-TiO₂ Photovoltaic Cells Treated by RF Plasma

F. M. El-Hossary ¹, Ahmed Ghitas ², A. M. Abd El-Rahman ³¹, A. A. Ebnalwaled ⁴⁵, M. Abdelhamid Shahat ²* ¹

Physics Department, Faculty of Science, Sohag University, Sohag, Egypt.
² PV Unit, Solar and Space Research Department, National Research Institute of Astronomy and Geophysics (NRIAG), Helwan, Cairo, Egypt.
³ King AbdulAziz University, Jeddah, KSA.
⁴ Electronics & Nano Devices Lab, Physics Department, Faculty of Science, South Valley University, Qena, 83523 Egypt.
⁵ Egypt Nanotechnology Center (EGNC)/ Cairo University Sheikh Zayed Campus, 12588 Giza, Egypt.

* E-mail: m.abdelhamid999@gmail.com

Abstract. Severe research attempts are still in progress to improve the performance of polyaniline (PAni) based photoactive layers as one of the cheapest materials used for manufacturing organic solar cells. Herein, polymer solar cells were fabricated with ITO/(PAni-TiO₂)/Au system. The photoactive layers (PAni-TiO₂) were treated with a hydrogen-plasma discharge for low processing time of 0, 3 and 5 min to enhance the synthesized solar cells efficiency. The morphology, microstructure and optical properties of the prepared samples and plasma treated nanocomposite layers were investigated and discussed. The performance of bulk heterojunction (BHJ) cell samples have been systematically investigated before and after plasma treatment. The absorption and optical band gap energy is increased after the treated PAni-TiO₂ photoactive layers. It is found that, the efficiency was enhanced to 0.7% after 5 min of hydrogen plasma process compared to 0.36% for the pristine cell. The efficiency increase is ascribed to a structural change that accompanied by a rapid increase in surface roughness, which leaded to a decrease in the reflected photons and in turn an increase in the produced charge carriers.

Keywords: TiO₂ nanoparticles (NPs), Polyaniline (PAni), Nanocomposites, Hydrogen plasma, BHJ solar cells.

1. Introduction

Over the last decades, great research efforts have been exerted to synthesize more efficient conducting polymers for fabricating organic photovoltaic (OPV) solar cells. Polyaniline (PAni) is a promising type of conducting polymers used for potential semiconductor applications owing to its high conductivity, simple preparation, good environmental stability [1]-[4].

Recently, inorganic nanoparticles (NPs) were successfully introduced into polymer based-materials in order to construct an efficient photoactive nanocomposite layer for improving organic photovoltaic performance [5], [6]. Titanium dioxide (TiO₂) NPs with nanocrystalline structure have found to be efficient semiconductor material for fabricating organic solar cells for their unusual chemical and physical properties and surface nanofeatures [7]–[9]. The desired properties of TiO₂ can be easily modified to meet different application needs through optimizing the preparation.
process conditions that control NPs size, shape and their distribution [10]. Based on the extraordinary properties of both PANi and TiO₂ NPs, the PANi-TiO₂ nanocomposites have potential applications in charge storage, conductive coating, photovoltaic solar cell and electrocatalytic applications [11], [12]. In addition, semiconductor NPs or nanocomposite thin films consisting of NPs have been treated using RF plasma discharge to improve the photactive properties of these materials to accomplish special performance needs [13]. For example, several conductive metal oxide thin films have been exposed to hydrogen plasma treatment in order to increase density carrier and oxygen vacancies; leading to an increase in their corresponding carrier mobility [14], [15]. Further, low-pressure plasma discharge has been used with N₂/SO₂ gas mixture to modify the TiO₂ NPs for providing them with sulfonation and to enhance their dispersion in PANi matrix [16].

The present work focuses on using low-pressure low-temperature RF plasma processing to treat PANi-TiO₂ nanocomposite films using hydrogen gas. Preliminary attempts for the improvement of photoptical properties are carried out with applying hydrogen plasma treatment for short processing time. Structural, surface morphology, electrical and optical properties of the as prepared and treated nanocomposite PANi-TiO₂ layers are measured and discussed to evaluate the photactive layer performance. Moreover, J-V measurements of PANi-TiO₂ layers are obtained in dark and under simulated sunlight at a total light intensity of 100 mW.cm⁻² to evaluate the effect of hydrogen plasma treatment on the solar cell efficiency.

2. Materials, Preparation and Characterization Techniques

2.1. Materials

Titanium dioxide powder (titanium powder, Ranbaxy > 5μm) was used as precursor for preparation of TiO₂ NPs. Chemical materials of aniline monomer (C₆H₇N, Purity 99+ %), hydrochloric acid HCl (37%) and ammonium peroxydisulfate (APS) with a chemical formula of (NH₄)₂S₂O₈ were purchased from Sigma Aldrich, Germany.

2.2. Preparation of TiO₂ NPs

A solution of TiO₂ was prepared by adding a 10.0 g TiO₂ powder in 40 ml distilled water in a glass vial under magnetic stirring for a reaction time of 1h at room temperature as shown in Fig. 1. In order to ensure good dissolution, the mixture was allowed to sonicate for several minutes. Then, it is thermally heat treated at 75 °C for 4 hours in a Teflon lined stainless steel autoclave. Afterward, the autoclave was naturally allowed to cool down to room temperature for 24 h. The precipitation was filtered out, washed several times with ethanol and distilled water, and then calcinated at 500 °C for 3 h. The previous procedure for producing TiO₂ NPs was repeated two times (8 and 12 h) to study the reaction time effect on the photovoltaic properties of the PANi-TiO₂ nanomaterials.

![Figure 1. Synthesize of TiO₂ NPs using the hydrothermal method](image)
2.3. Synthesis of PANi and PANi-TiO2 Nanocomposite

Chemical oxidative polymerization method was used to prepare pure PANi and PANi-TiO2 nanocomposites, where aniline monomer was polymerized by acidic catalyst of HCl in the presence of ammonium persulfate (APS) as a strong oxidizing agent. APS is a colorless inorganic salt and it is a highly soluble material in water. A 0.01 mol of aniline monomer is dissolved in a 0.01 mol of HCl and mixed using an ultrasonic unit (Elmasonic S 40H) at room temperature. A 0.01 mol of APS was dissolved in a 15-mL distilled water to prepare a dilute APS solution. Finally, in order to obtain the pure PANi solution, a dilute APS solution was placed into a burette and added drop wise to the mixture of aniline and HCl with a slow drop rate, under magnetic stirring in an ice bath at a reaction time of 5.5 h. The mixing process between the reactive mixtures is obtained with a slow drop rate and continued under stirring in order to ensure good oxidation and homogenous polymerization of PANi solution, respectively. To prepare PANi-TiO2 nanocomposites, TiO2 powder was added to the pure PANi solution. Then, the obtained composites were deposited by a spin coating on ITO coated conducting glass substrates by using an 800 rpm for 30s. Finally, the obtained films were dried at 50°C.

A 0.01 mol aniline monomer is mixed in a 0.01 mol HCl solution using an ultrasonic unit (Elmasonic S 40H) at room temperature. Within another beaker, 0.01 mol of APS was dissolved to create a diluted solution of APS within 15 mL distilled water. TiO2 powder was spread in the beaker to cover the TiO2 NPs with conductive PANi as a shell, which produce aniline monomer and was put on a magnetic stirrer for 30 min. In order to confirm complete, the interaction between the aniline and TiO2 NPs, TiO2 has been blended into the aniline blends in the connection of 20% vs. 80% aniline solution, followed by several minutes in ultrasound. A dilute APS solution was put in a burette and was applied dropwise to the aniline–HCl–TiO2 mixture under magnetic stirring (1000 rpm) at a reaction time of 5.5 h in an ice bath. Accordingly, PANi-TiO2 nanocomposites can be produced using a typical physicochemical technique [17], that starts with a slow drop rate of about 1 drop / second and continues to be stirred to ensure good oxidation and homogeneous polymerization of PANi solution. At the end of the physicochemical reaction the color is observed changing to dark green. This means that an oxidation phase is underway that ends with the PANi-TiO2 composite solution for the formation process. The precipitate composites were filtered and washed to extract excess acid with distilled water and ethanol. A spin coating on an ITO coated conducting glass substrata with 800 rpm for 30 s was deposited for the last composite solutions, followed by a drying process with 50 °C for 30 min. The methods of deposition and drying were performed in the air atmosphere.

2.4. Plasma surface modification for PANi-TiO2 nanocomposite films

The photoactive layer consisting of the PANi-TiO2 nanocomposite was deposited with a thickness of 150 nm and directly introduced into a plasma reactor chamber. Then, the chamber was evacuated to a base pressure of 20 x 10⁻⁵ mbar and filled with a reactive gas of H₂ at a working pressure of 82 x 10⁻⁵ mbar. The hydrogen plasma discharge was generated with an inductively coupled technique using a rf power generator (model HFS 2500 D, 13.65 MHz). Different plasma processing times of 0, 3 and 5 min are applied on the as-prepared films for a fixed processing power 220 W. The treatment temperature was measured to be 423 K; using a Chromel-Alumel thermocouple locate in contact with the sample surface. At the end of the plasma process, the treated samples were allowed to cool down under evacuation for few minutes. Finally, in order to construct an entire solar cell system, the coated ITO (80-82% transmittance and 4 x 10⁻⁵ Ω.cm resistivity, sigma Aldrich) with photoactive layers has to be covered by a rectangular shaped Au thin film. The conductive material Au coat film was used as a highly effective cathode and deposited by a thermal evaporation method. A schematic of the stack device architecture is shown in Fig. 2.
2.5. Characterization

The phase and structure of the samples were examined by X-ray diffraction (XRD), using Philips diffractometer with a Cu target (λ=1.54056 Å) and a graphite monochromator at 40 kV and 30 mA. The scanning speed and step are 2.5°/min and 0.06°. The functional groups of inorganic NPs, pristine and treated nanocomposite thin films are evaluated using Fourier Transform Infrared (FT-IR) Spectroscopy (Jasco Model 4100 Japan). The FT-IR analysis is obtained from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹ at room temperature. Further, the surface morphology has been characterized by high resolution scanning electron microscope (SEM) (JOUL SEM model JSM-5500 - Japan), operated at an accelerated voltage of 10 KV. The optical properties of the as prepared and treated nanocomposite films were measured by a computerized SPECORD 200 PLUS spectrophotometer at room temperature with a 1 nm step and at a normal incidence angle in the wavelength range 190 – 1100 nm. The Profilometer (Talysurf 50-Taylor Hopson precision) is carried out as a mechanical test machine, and used to extract the topographical changes in the sample surface. In this study, the roughness parameter, Ra, represents the average roughness of the nanocomposite films. Furthermore, the J–V characteristics of the solar cell under a fixed illumination intensity of 1.0 Sun at 25°C is measured using a solar simulator system. The simulation test is carried out using a xenon lamp as an ideal light source for solar spectrum with the use of a KEITHLEY 2400 Source Meter.

3. Results and discussion

3.1. Microstructural analysis

Fig. 3 shows the typical XRD patterns of PANi-TiO₂ nanocomposite films treated by hydrogen plasma at processing time of 3 and 5 min compared to that of the pristine sample. Diffraction PANi peaks with different intensities and peak widths are detected in all samples between 10° and 80° owing to parallel and perpendicular periodicity of the polymer chain [18]. These diffraction peaks are found to be correspond to (110), (012), (003), (102) and (323) planes. After surface treatment, changes in the diffraction peaks are observed and found to be related to TiO₂ and corresponding to (002), (102), (103), (201) and (004) planes. The crystallite size (D) of TiO₂ NPs can be calculated using the Debye–Scherrer equation [19]:

\[
D = \frac{0.94 \lambda}{\beta \cos(\theta)}
\]

(1)

Where \(\lambda\) is the wavelength, \(\beta\) is the full width at half maximum of the peak, and \(\theta\) is the diffraction angle. The degree of crystallinity and crystallite size of TiO₂ NPs achieved 86.6% and 11.86 nm, respectively.

The polycrystalline diffractions match well with the standard powder diffractions of tetragonal TiO₂ phase with anatase crystal phase (a = b = 3.7335 Å, c = 9.3788 Å, α = β = γ = 90.0) (ICSD, Code no 9852) [20], and orthorhombic polyaniline [21]. The diffraction peak at 20 of 23° is due to polymer chains placed parallel and closed to each other producing crystalline zones surrounded by amorphous areas [22]. The polycrystalline diffractions of the pristine and
treated PAni-TiO$_2$ nanocomposites are identical to those caused by the standard powder diffractions of tetragonal anatase TiO$_2$ structure and orthorhombic PAni. This indicates that no phase transformation involved in the hydrogen plasma surface treatment. Generally, the crystallinity in a particular sample relies on the periodicity, which implies a long-range sequence of atoms, ions or molecules. As noted, the XRD pattern of the plasma-treated nanocomposite films showed an increase in the crystallization and peaks intensity with increasing plasma processing times. The strong effects on the surface of PAni-TiO$_2$ of hydrogen plasma leading to changes in the chemical bonds in the nanocomposite films between PAni and TiO$_2$ and the physical dependence of the polymer on the area of TiO$_2$ NPs are attributed to this fact.

![Figure 3. XRD patterns of plasma treated and pristine PAni-TiO$_2$ nanocomposite samples](image)

### 3.2. FT-IR spectroscopy

The composition of the pure PAni, pristine nanocomposite and plasma treated PAni-TiO$_2$ nanocomposite films is characterized by FT-IR spectroscopy and the obtained spectra is shown in Fig. 4. FT-IR spectra was obtained in the range 4000-400 cm$^{-1}$ in order to confirm the composition of the chemical compounds that formed before and after plasma treatment. The FT-IR spectra show that, the main peaks of the pure PAni domains continued to appear clearly in the pristine and treated PAni-TiO$_2$ nanocomposites with hydrogen plasma.

FT-IR spectra of pure PAni exhibits the main absorption peaks at the region 3121–472 cm$^{-1}$ and continued to distinctly appear in the pristine and treated nanocomposites with intensity changes and a small peak shift towards higher wavenumbers, which assigned to the presence of TiO$_2$-NPs in the nanocomposite structure. The wide absorption peak between 3690–2983 cm$^{-1}$ can be attributed to the stretching O–H and the hydrogen-bond N–H stretching of aromatic amine [23], [24]. Compared to the pristine sample, the peak at 3121 cm$^{-1}$ is detected with a wide stretching shape and a small shifting towards short wavenumber. The peak broadening and shifting effect is higher for sample treated at processing time of 5 min with that of 3 min. This might be attributed to the attraction by a group of adjacent atoms or two nearby functional groups [25]. On the other hand, this peak shifting has found to be associated with the highest crystallinity of the nanocomposite compound that found in Fig. 3, which in turn leads to an increase in the energy gap and results an increase in the light absorption. Photo-induced holes and hydroxylic radicals may be produced on surfaces of hydroxyl bonds [26]. It allows these radicals to improve the composite's photocatalytic efficiency [27]. The characteristic peaks at 1537 cm$^{-1}$ and 1412 cm$^{-1}$ are assigned to C=N and C=C ring asymmetric and symmetric stretching vibrations, due to the presence of quinonoid structures and benzenoid ring, respectively. Whereas the peaks at
1301 cm\(^{-1}\) and 1193 cm\(^{-1}\) correspond to C–N stretching of the benzenoid and quinonoid unit of doped PANi, respectively. This calculated the delocalization rates and characterized as a PANi conductivity peak [28]. In the spectrum of PANi-TiO\(_2\) nanocomposite, the appearance of PANi main peaks (i.e. C=C and C–N peaks) confirmed PANi formation on nanoTiO\(_2\) surface [29]. The good interactions between PANi and TiO\(_2\) NPs resulted in a coordination between the N atoms of PANi chains and the TiO\(_2\) NPs shielding the nanoparticles with a PANi layer coating [30], [31]. The peaks at 860 cm\(^{-1}\) is associated with C–C and C–H in the benzenoid unit [17]. Whereas, the peak at 616 and 472 cm\(^{-1}\) was relatively changed compared to pure PANi, which may be attributed to the out-of-plane bending flexural vibration of C–H aromatic rings of PANi and vibrations in the stretching Ti–O–Ti bonds of TiO\(_2\) [23]. Thus, indicates a structural change in the polymer matrix resulting from a strong H-bonding interaction exists between PANi and TiO\(_2\)-NPs.

![FT-IR spectra of pure PANi and nanocomposites films were treated by H-plasma for different processing times](image)

**Figure 4.** FT-IR spectra of pure PANi and nanocomposites films were treated by H-plasma for different processing times

3.3. **Morphology**

Fig. 5 illustrates SEM images for the pure PANi film, pristine and plasma treated PANi-TiO\(_2\) nanocomposite thin films. Based on previous literature, an increased active layer with a micro-structure results in a relatively rough surface, which increases the surface contact between the layers of the nanocomposite and the electrode surface [32]. In the microporous surface of the active layer of the composite, the increased capacitance can take place as a result of maximum absorption [33]. The morphology of the nanocomposite particles depends on the conditions of polymerization such as pH, temperature, polymerization time as well as the TiO\(_2\) structure and ratio [34]. Besides, the white area is assigned to be TiO\(_2\), while the grey and black areas refer to the polymer chain. As observed, the surface morphology of PANi-TiO\(_2\) shows a featured structure with non-agglomerated TiO\(_2\) NPs and some porous fibrous networks. These results are consistent with previous results indicated that with the presence of a PANi shell on the surface of TiO\(_2\) NPs, which causes repulsion between the nanoparticles to prevent their agglomeration [33], [35], [36]. However, after hydrogen plasma treatment, the surface morphology of the samples is drastically changed and the needle structure is appeared. Further, the structure of PANi-TiO\(_2\) nanocomposite changes from an agglomerated needle to mostly needle structure with the variation of plasma processing time from 3 min to 5 min; offering suitable plasma energy to the imbedded nanoparticles for the formation of needle structure.
Figure 5. SEM images of (a) Pure PANi film, (b) Pristine and (c, d) Treated PANi-TiO$_2$ nanocomposite samples at 3- and 5-min using hydrogen plasma surface treatment, respectively.

3.4. Roughness measurements

Fig. 6 shows the effect of hydrogen plasma treatment on the roughness factor (Ra) of PANi-TiO$_2$ nanocomposite films as a function of plasma treatment time. Ra is abruptly increased with the increase of plasma treatment time. As it is found in other works, the change in surface roughness is mostly ascribed to the structural and morphological changes [37]. The increase in surface roughness of PANi-TiO$_2$ nanocomposites that composed of elastic/plastic hybridized materials is expected to be a physical response to heat effects produced by a RF-electric field generated plasma. This is mostly acceptable in case of using a low melting point elastic material like polymer combined with plastic NPs of metal oxides. The flow of heat stress in polymer matrix is mostly a reason for a fast-mechanical response and in turn partially responsible for increased surface roughness. The high heat capacity of TiO$_2$ (0.69 kJ/kg K) [38], can be considered as another contributing factor for the high increase in $R_a$ of plasma treated PANi-TiO$_2$ nanocomposites. The interpretation of this dissimilar trend is mostly ascribed to the difference in the structural features of both nanocomposites. The agglomeration of TiO$_2$ NPs in PANi matrix and their size effect leads to an increase in surface roughness [39]. However, the fibrous network structure is mostly responsible for surface smoothness. The change in the surface roughness of the nanocomposite films affects their optical properties including transmittance, absorbance and optical constants [40], [41].
Figure 6: Roughness factor (Ra) of plasma treated and pristine PANi-TiO2 nanocomposite samples

3.5. Optical Properties

3.5.1. Optical constants

Fig. 7 demonstrates the absorbance spectra obtained for pristine and hydrogen plasma treated nanocomposite samples for different wavelengths. The pristine and treated nanocomposite films reveal similar absorbance behavior with distinct absorbance values. Accordingly, their transmittance values are expected to have different values as well. The absorption and transmittance values as a function of the wavelengths of the different plasma processing time show a change proportional to those of the pristine nanocomposite film of PANi-TiO2 as one can see in Fig. 7a, b. As shown in Fig. 7a, a broader absorption peaks are appeared with a similar spectrum in the range of 300–800 nm. The nanocomposite films exhibit wide absorption peaks at 320 nm and 595 nm with limited peak shifts towards lower wavelengths with increased hydrogen plasma surface treatment up to 5 min compared to the pristine nanocomposite film. This peak shift indicates the effect of the plasma modification on the electronic structure of TiO2 NPs in the valence band that could interact with the higher occupied molecular orbital (HOMO) of PANi [42]. Moreover, the nanocomposites show equivalent energy absorption peaks at wavelengths of 320, 595 and 740 nm which in turn leads to transitions of π→π* within the benzenoid rings, Polaron→π* of quinoid rings, and π→polaron excitonic of the quinoid rings, respectively [11]. Determination of optical energy gap and the transition type were obtained using Tauc equation [43]:

$$a\nu = B(\nu - E_g)^{1/2}$$  \hspace{1cm} (2)

Where $\nu$ is photon energy and $B$ is a transition probability dependent parameter, $a$ is the absorption coefficient, $E_g$ is the optical band gap [37].
Figure 7. (a) The absorbance and (b) transmittance behaviors obtained for plasma treated and pristine nanocomposite samples

Fig. 8 shows a variation in the optical band gap of pristine and treated PAni-TiO$_2$ films with hydrogen plasma at 3 and 5 min. The optical band gap ($E_g$) is estimated from the strong absorption region, which depends on the short-range order in the amorphous state and defect state [44]. It is found to be increased with the increase of plasma treatment time and has values of 1.99, 2 and 2.16 eV at treatment time of 0, 3 and 5 min, respectively. These results may be attributed to the reduction of the system disorder and the increase of the defect state density. As a result of a relatively wide band gap, the PAni-TiO$_2$ nanocomposites films have large visible transmittance [45].

![Figure 8: Optical band gap of pristine and treated PAni-TiO$_2$ nanocomposite by hydrogen plasma for processing time of 3 and 5 min](image)

3.5.2. Optical dispersion characteristics

The refractive index ($n$) and the extinction coefficient ($k$) are considered as the most efficient optical dispersion parameters for many applications of optoelectronics. For polymer-based materials, the $n$ has a direct effect on physical, chemical, and molecular characterization and in turn on their optical, electrical, and magnetic properties. The optical constants ($n$, $k$) are estimated from reflectance and absorption coefficient based on the famed equation which developed by Wemple and DiDomenico [46].

$$\left( n^2(h\nu) - 1 \right)^{-1} = \frac{-1}{E_0 E_d} (h\nu)^2 + \frac{E_0}{E_d}$$  \hspace{1cm} (3)

Where $h$ is the Plank's constant, and $h\nu$ is the photon energy, $E_0$ is the average excitation energy for electronic transitions or the oscillator energy, $E_d$ is the dispersion energy which measures the average strength of inter-band optical transitions or the oscillator strength, which is a measure of the intensity of the inter band optical transitions, does not depend significantly on the band gap. The dispersion curves of $n$ and $k$ versus $h\nu$ for hydrogen plasma PAni-TiO$_2$ samples for different treatment times are demonstrated in Fig. 9. As observed, $n$ and $k$ parameters of the PAni-TiO$_2$ nanocomposites are highly affected after the hydrogen plasma process compared to the untreated one. These results may be attributed to changes in the absorption coefficient as a result of the plasma process which are directly proportional to the optical dispersion parameters ($n$, $k$) of the PAni-TiO$_2$ films [47].
Figure 9. (a), (b) Dispersion curves of $n$ and $k$ versus photon energy ($h\nu$), respectively, for PAni-TiO$_2$ samples treated using hydrogen plasma for processing time of 3 and 5 min.

3.5.3. Optical conductivity

Optical conductivity $\sigma_{opt}$ is a complex optical quantity that significant for describing optical properties of materials and their applications. The complex optical conductivity is composed of real and imaginary parts ($\sigma_{opt} = \sigma_1 + i\sigma_2$); both are positive and dielectric constant dependent ($\varepsilon$) [48]. The real ($\sigma_1$) and imaginary ($\sigma_2$) parts can be expressed as in the following equations [48]:

$$\sigma_1 = \omega \varepsilon_2 \varepsilon_0, \quad \sigma_2 = \omega \varepsilon_1 \varepsilon_0$$

Where $\omega$ is the angular frequency. As seen from the previous equations, $\sigma_1$ and $\sigma_2$ are photon energy dependent parameters. Fig. 10 expresses $\sigma_1$ and $\sigma_2$ as a function of photon energy ($h\nu$). In general, one can see that both real and imaginary parts have appeared with fewer fluctuations after hydrogen plasma treatment compared to that of the pristine nanocomposite film. Further, they have a maximum value appears in a broad peak located close to the end of the applied photon energy region. Then, their values are abruptly decreased. Furthermore, the plot has a plateau region free from any fluctuations or with little fluctuations is detected for treated samples compared to that of the pristine film. With more precise description, the behavior of the pristine sample is nearly comparable to that of the treated sample at treatment time of 5 min. Further, the lowest values of $\sigma_1$ and $\sigma_2$ optical conductivity are found for the PAni-TiO$_2$ treated at treatment time of 3 min.
The optical conductivity ($\sigma_{opt}$) and electrical conductivity ($\sigma_{elec}$) can be determined according to the following equations [49], [50]:

$$\sigma_{opt} = \frac{a n c}{4 \pi}, \quad \sigma_{elec} = \frac{2 \lambda \sigma_{opt}}{\alpha}$$

Fig. 11 shows the value of the optical and electrical conductivity of the treated nanocomposite films as a function of the photon energy. As found, the behavior of optical and electrical conductivity is photon energy dependent too. The electrical conductivity increases over a low energy range of visible light (until 2.7 eV), then the $\sigma_{elec}$ starts to gradually decrease with the increase of visible light energy. This behavior continues within the relatively low energy-UV until the energy of 3.7 eV, followed by a sudden decrease with further increase of photon energy. As known, the solar light reaching the earth surface combines about 40% of visible and less than 10% from the ultraviolet radiation. Therefore, the visible light has substantial effects on optical properties of the active layer of nanocomposite metal oxides. The increase in conductivity as a function of visible photon energy has to be ascribed to the enhancement in the transition process of the charge carriers by absorbing the energy of the incident photons. Accordingly, the excess conductivity can be called optical conductivity. The optical conductivity increases with the increase in photon energy within visible region.

This behavior continues until reaching a maximum value at about 3.7 eV and then it is abruptly decreased. After hydrogen plasma treatment, the optical conductivity is only improved in the visible region for the sample treated at treatment time of 5 min. This is positively reflected on the light absorption in the active layer and certainly on the solar cell efficiency. The improvement in the optical properties of PANi nanocomposites films leads to extend their photonic applications [51], [52].

**Figure 10.** (a) Real and (b) imaginary optical conductivity of pristine and plasma treated nanocomposite films versus photon energy ($h\nu$)

**Figure 11.** (a) Optical and (b) electrical conductivity of pristine and treated PANi-TiO$_2$ nanocomposite films as a function of photon energy
3.6. Performance evaluation of PAni-TiO$_2$ nanocomposite photovoltaic cells

Current density-voltage (J-V) characterization is a common technique used to determine the performance of solar cells. J-V measurements of solar cells are obtained in dark and under simulated sunlight with a total light intensity of 100 mW/cm$^2$ and with a solar spectrum under Air Mass 1.5 global. The A M 1.5 G is the solar spectrum arriving on the Earth's surface after passing the atmosphere at a zenith angle of about 48° [53], [54]. Herein, PAni's hybrid photoactive layers were designed as a donor mixed with TiO$_2$ NPs as acceptor in the fabricated solar cells. Fig. 12 shows the current density-voltage (J-V) characteristics of the solar devices structured by pure PAni, PAni-TiO$_2$ nanocomposite layers in dark. As observed, it exhibits the same asymmetric diode-like behavior.

![Figure 12](image)

**Figure 12.** Diode-like behaviour of J-V curves obtained in the dark of designed photovoltaics based on pure PAni film, untreated nanocomposite film (pristine) and treated PAni-TiO$_2$ nanocomposite films using hydrogen RF-plasma at different processing times.

Fig. 13 shows the J-V curves obtained from photovoltaics based on pure PAni and pristine composite PAni-TiO$_2$ layers under illumination. As observed, the J-V curve is shifted towards higher values of current densities for the pristine composite device structured by ITO/(PAni-TiO$_2$) 0 min/Au compared to that one fabricated with ITO/Pure PAni /Au. These results show that the presence of TiO$_2$ NPs into the PAni matrix increases the carriers transport in PAni structure significantly through the contribution of polarons and bipolarons that move at a smaller distance in polymer chains [55]. Moreover, the J-V curves gradually shifted towards higher values of current densities of 4.19 and 4.71 mA/cm$^2$ for device structured by the photoactive layer treated with hydrogen plasma at 3 and 5 min, respectively, compared to 3.15 mA/cm$^2$ which obtained for a pristine layer designed cell. This shifts vertically under illumination due to light induced current generation. The possible reason of the higher current density may be ascribed to a reduction in the interfacial resistance between TiO$_2$ and PAni with the increase in the surface treatment time due to the increase in the number of polarons in PAni structure and the structural homogeneity of nanocomposites [2].
Figure 13. J-V characteristic curves of pure PAni film, pristine and treated PAni-TiO2 solar cell devices obtained in the standard conditions and in a simulated light.

Photovoltaic parameters of the solar cell device such as short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF) and power conversion efficiency ($\eta$) can be attained from J–V characterization curves. $V_{oc}$ depends mostly on the trade-off energy between highest occupied molecular orbital (HOMO) of the donor and lowest unoccupied molecular orbital (LUMO) of the acceptor. Table (1) illustrates a comparison of photovoltaic parameters for the fabricated solar cells.

Herein, measurements of $V_{oc}$ showed nearly constant values as the photoactive material (PAni) and have constant value (around 0.56 V) for all designed photovoltaic devices [56]. As observed, the photovoltaics efficiency of ITO/pure PAni/Au is 0.24% and improved to 0.36% by incorporating the pristine TiO2 NPs into PAni structure. This is due to an increase of photocurrent density within composites structure [2]. The solar cells designed with PAni-TiO2 nanocomposites treated for 3 min exhibited a gradual improvement in efficiency values of 0.49% and achieved the optimum value of 0.7% at a treatment time of 5 min. In contrast to other similar devices manufactured from active layers PAni-TiO2 [57]–[59], these fabricated devices show better performance based on their measured efficiency. This performance improvement might be ascribed to the following reasons:

(i) The increase in the number of polarons and bipolarons in the PAni structure, which creates an efficient charge carries transfer network in the nanocomposite material. This interprets the conduction mechanism of the PAni-TiO2 nanocomposite [60].

(ii) The rapid increase in surface roughness decreases the reflected photons and thus increases the produced charge carriers.

Table 1. Characteristic parameters for pure PAni, pristine and treated PAni-TiO2 nanocomposites solar cells

| Time (min) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | $\eta$ (%) |
|------------|-------------|----------------------|--------|------------|
| ITO/pure PAni/Au | 0.56 | 1.20 | 35.1 | 0.24 |
| ITO/(PAni-TiO$_2$) 0 min/Au | 0.56 | 3.15 | 20.1 | 0.36 |
| ITO/(PAni-TiO$_2$) 3 min/Au | 0.56 | 4.19 | 21.0 | 0.49 |
| ITO/(PAni-TiO$_2$) 5 min/Au | 0.56 | 4.71 | 26.2 | 0.70 |
4. Conclusion

The effects of RF hydrogen plasma treatment on structural and optical properties of PAni-TiO₂ nanocomposites have been investigated. The as-prepared PAni--nanocomposite thin films were achieved with a mixing ratio of 20% TiO₂ at a reaction time of 12 h. After hydrogen plasma treatment, the crystallinity is improved with the increase of plasma treatment time. Further, morphology and roughness of the obtained nanocomposites is highly affected. The absorption and optical band gap have higher values for the treated PAni-TiO₂ photoactive layers compared to that of the pristine film. Consequently, the efficiency was enhanced to 0.7% after 5 min of hydrogen plasma process compared to 0.36% for the pristine cell. The improvement in photovoltaic efficiency is mostly ascribed to structural effects beside the rapid increase in surface roughness, which decreases the reflected photons and in turn increases the produced charge carriers. As a future objective, it is essential to optimize the structural and optical properties of the unmodified PAni-metal oxide nanocomposite thin films. In addition, intensive research work should be concentrated on optimizing the plasma treatment conditions of RF hydrogen discharge for the treatment of the photoactive PAni nanocomposite thin films.

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