Photovoltaic Performance of Spherical TiO₂ Nanoparticles Derived from Titanium Hydroxide Ti(OH)₄: Role of Annealing Varying Temperature

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Abstract: High-quality titanium dioxide (TiO₂ or titania) nanoparticles (TiO₂NPs) with tailored morphologies are desirable for efficient photovoltaic applications. In this view, some thin films containing spherical TiO₂NPs were prepared on indium tin oxide (ITO) and silicon (Si) substrates from titanium hydroxide Ti(OH)₄ using the unified sol-gel, spray and spin coating method followed by thermal annealing at different temperatures (in the range of 200–650 °C). Samples were characterized using various analytical tools to determine the influence of annealing temperatures on their structures, morphologies, and optical and photovoltaic characteristics. A field-emission scanning electron microscope (FESEM) and energy-filtered transmission electron microscopy (EFTEM) images of the annealed films displayed the existence of spherical TiO₂NPs of average size in the range of 3.2 to 33.94 nm. XRD analysis of the films showed their amorphous nature with anatase and rutile phase. Optical UV-Vis spectral analysis of the annealed films exhibited a decrease in the bandgap energy from 3.84 to 3.24 eV with the corresponding increase of annealing temperature from 200 to 650 °C. The optimum films obtained at 500 and 600 °C were utilized as electron transport layers to fabricate the metal-insulator-semiconductor solar cells. The cells’ power conversion efficiency assembled from 3.84 to 3.24 eV with the corresponding increase of annealing temperature from 200 to 650 °C.

Keywords: TiO₂NPs; sol-gel; spray-spin coating; solar cell; annealing temperature

1. Introduction

Among different types of metal oxides, TiO₂ is greatly beneficial for various applications, including solar cells, gas sensors, light-emitting diodes (LED), and bactericidal and anti-fungal agents. Several distinct attributes of TiO₂ such as direct and wide energy bandgap, high chemical stability, cost-effectiveness, biocompatibility, low toxicity, and simple preparation protocols make this material technologically versatile [1,2]. In addition, the surface properties of the TiO₂ can be modified using various acids (carboxylic, formic, propanoic, oleic, acetic, and oxalic acid) to achieve desired properties needed for different applications [3,4]. Long-chain carboxylic acid with other functional groups effectively modifies TiO₂ surface morphology [5]. Over the years, metal oxides have been utilized to improve the performance of the solar cell by reducing the reflection and recombination rate [6], the surface passivation through the anti-reflection layer of TiO₂ to reduce the total reflection [7], improve energy absorption, and produce a large number of photo-generated
carriers. Heterogeneous solar cells based on TiO$_2$/Si and ZnO/Si layers have been used to overcome the high recombination rate by producing small conduction band barriers ($\Delta E_C$), which enabled the extraction of photo-generated electrons and high valence band barriers ($\Delta E_V$) that prevented the extraction of the photo-generated hole. These hetero-structured films acted as electrons transport layers (ETLs) or hole blocking layers (HBLs) [8]. Schottky junction metal-semiconductor (MS) solar cells with simple structures can be produced at a low manufacturing cost.

Up till now, the performance of these solar cells remains poor because the low open-circuit voltage ($V_{OC}$) originates from the low barrier height ($\Phi_b$) at the metal-semiconductor interface [9,10]. An insulating ultra-thin film-like oxide layer [11,12] was placed at the MS interface to raise $\Phi_b$, thereby increasing the value of $V_{OC}$. Consequently, an increase in the series resistance ($R_S$) could lower the fill factor (FF), power conversion energy (PCE), and short circuit current ($J_{SC}$) [13]. However, despite many efforts, an effective ETL based on TiO$_2$NPs is far from being achieved. This research did not aim to develop high-efficiency solar cells but rather to (1) synthesize and characterize non-toxic and low-cost nanoparticles, which will be used in solar cells. In addition, (2) to understand better the mechanisms that control the performance of the solar cells based on PSi and TiO$_2$NPs. The energy level alignment between the conduction band for different layers allows or prevents the extraction of electrons. For example, the conduction band energy for bulk Si and TiO$_2$ is $-4.0$ and $-4.02$ eV, respectively. Also, the band energy for bulk Si and TiO$_2$ is $-5.1$ and $-7.25$ eV, respectively. Therefore, the conduction band and the valence band energy for nanoparticles will be expanded and split due to reducing the particle size. Consequently, the conduction band energy and valence band energy for SiQDs become larger than bulk Si. As a result, increasing the injected electrons were transferred swiftly from the interface of the layers and reducing recombination losses by increasing the relaxation time. Hence, the extraction of electrons and holes is growing, thereby enhancing solar cell performance. In addition, the relaxation time for the nanoparticle is larger than the bulk state because of the increase in the distance between the energy levels, thereby leading to a reduced recombination process and increasing the extraction probability of charge carriers [14].

2. Materials and Methods

2.1. Preparation of TiO$_2$NPs

All chemical reagents such as TiCl$_4$ (purity of 99%), NH$_4$OH (virtue in between 28.0 to 30.0%), and C$_2$H$_4$O$_2$ (purity of 99.9%) were procured from the Sigma-Aldrich and used to prepare the thin films consisting of spherical TiO$_2$NPs. Figure S1 shows a flowchart of TiO$_2$NPs preparation and characterization. To dissolve the TiCl$_4$, 3 mL of TiCl$_4$ was mixed with 20 mL DI water and vigorously stirred until the TiCl$_4$ was entirely dissolved. Then, drop by drop, NH$_4$OH was added to the resulting mixture until the pH reached 8. Finally, NH$_4$OH was incorporated into TiCl$_4$ to produce Ti(OH)$_4$ and control the pH of the mix. The chemical reaction among TiCl$_4$ and NH$_4$OH, achieving the final product can be explained using the following two pathways:

$$\text{TiCl}_4 + 4\text{NH}_4\text{OH} \rightarrow 4\text{NH}_4\text{Cl} + \text{Ti(OH)}_4$$ (1)

$$\text{Ti(OH)}_4 \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O}$$ (2)

Several studies have been conducted to determine the influence of pH on various characteristics of the synthesized TiO$_2$NPs. It was found that for pH value below 6, the Ti(OH)$_4$ gel formation is limited, inhibiting the growth of TiO$_2$NPs through the generation of Ti(OH)$_2$\textsuperscript{+4}. In contrast, for pH values above 7, some dense TiO$_2$NPs were produced due to the presence of a negative surface charge on TiO$_2$ that induced the repulsive force, forming a large number of tiny TiO$_2$NPs. Although the pH value is necessary to generate TiO$_2$NPs, the pH must be in the range of 8–10 due to the aggregation of smaller particles [15]. The resultant Ti(OH)$_4$ gel was washed many times using DI water and filtrated to remove the chloride ions that could cause the particles aggregation, suggesting that the chloride
ions percentage must be minimum (<0.005 M) [16]. Next, 3 mL of Ti(OH)$_4$ gel was added to 18 mL of DI water under agitated stirring until the complete dissolution occurred. Ti(OH)$_4$ acted as the nucleation center through hydrolysis. Next, the resultant Ti(OH)$_4$ was heated on a hotplate (60 °C) for 2 h before being deposited onto ITO and Si substrate via the combined spray and spin coating approach as displayed in Figure 1b [17]. It is essential to mention that the ITO glass and Si, the available substrate for most photovoltaic devices, were chosen in this work. First, three pieces of the ITO glass and four pieces of p-c-Si substrate were cleaned by the standard method [18,19], firmly placed on the edge of the spin coating plate, while the spray was performed 25 cm away and at an angle of 45° from the plate center. Later, Ti(OH)$_4$ was sprayed on these substrates, and the spin coater was revolved at 1500 rpm to 90 s. Finally, each obtained thin film was annealed at 200, 300, 400, 500, 550, 600, and 650 °C for 3 h in an electrical furnace (Nabertherm) at the heating rate of 2 °C per minute.

![Figure 1.](image)

(a) FESEM image deposited on ITO glass substrate and (b,c) the corresponding EDX elemental traces.

2.2. Characterization of TiO$_2$NPs

The morphology of the samples was examined using a field emission scanning electron microscope (FESEM, FEI Nova SEM 450, FEI Company, Hillsboro, OR, USA). The elemental compositions of the samples were determined using an energy dispersive X-ray
diffraction (EDX, FEI Nova SEM 450, FEI Company, Hillsboro, OR, USA) spectrometer. The morphologies of colloidal TiO$_2$ were studied using an energy-filtered transmission electron microscope (EFTEM, Libra 120, Zeiss GmbH, Oberkochen, Germany). The Agilent Carry 5000 absorption spectrophotometer was used to record the samples’ UV–Vis–NIR absorption spectra. The atomic force microscopic (AFM, Kratos Analytical Ltd., Manchester, UK) was utilized to scan the surface of a sample with a tiny physical probe or sharp tip. X-ray diffraction (XRD, Bruker D8 Advance, AXS GmbH, Karlsruhe, Germany) is a quick and easy non-destructive characterization methods technique for determining the crystalline phases of nanomaterials and information about the structure such as preferred orientation and crystallite size. The Bragg equation underpins X-ray diffractometry. The spin coating device was used to deposit the thin film of TiO$_2$NPs, while Auto HHV500 Sputter Coater or Radio Frequency (RF) and Direct Current (DC) Sputtering Magnetron Sputtering was used to deposit a thin film of conductive materials such as Ag and Al. the electrical circuit measurement system (LED simulator) was used to measure the PCE, FF, $J_{SC}$, and $V_{OC}$.

3. Results and Discussion

Morphology, Structure, and Optical Properties of Samples

Figure 1 illustrates the cross-sectional FESEM micrograph of the annealed film deposited on ITO glass substrate. The table shows the detected elemental compositions obtained from EDX spectral analyses when scanned at two regions marked as 1 and 2. The main elements in region 1 were Ti and O, which contributed to improving the TiO$_2$NPs yield in the film. The XRD patterns in Figure 2a–c illustrate the effect of various annealing temperatures (200, 300, and 400 °C each for 3 h) on the crystalline structures and phases of the thin film containing TiO$_2$NPs deposited ITO substrate. The XRD profiles consisted of several sharp crystalline peaks corresponding to the ITO in the range of 20–70°. The observed intense peaks at 2θ values of 25.7°, 30.12°, 35.17°, 50°, 57°, and 60.3° corresponded to the crystalline lattice planer directions of the ITO glass substrate. The formation of the main phase of TiO$_2$ as the elementary material was very much sensitive to the annealing temperature and deposition procedure [20]. Figure 2(a1–c1) illustrates the EFTEM micrographs together with their particles size distribution of three TiO$_2$NPs annealed at temperatures of 200, 300, and 400 °C after sonicating the thin film in ethanol to 30 min. The images consisted of spherical-shaped tiny nanocrystallites of average size approximately 3.2, 4.78, and 11.8 nm. The obtained TiO$_2$NPs synthesized at 200 and 300 °C having a size below 5 nm corresponded to the quantum dots structure [21,22]. The Imagej software program analyzed the micrographs and estimated the average particle size [23].

The XRD patterns (in the 2θ range of 20–60°) in Figure 3a–d depicts the influence of various annealing temperatures (500, 550, 600, and 650 °C each for 3 h) on the crystalline structures and phases of the thin film containing TiO$_2$NPs deposited on Si substrate. The XRD profiles of the annealed films displayed many significant Bragg diffraction peaks related to the crystalline anatase and rutile phase of TiO$_2$NPs. In addition, the intensities of these sharp XRD peaks were increased with the increase of annealing temperatures, indicating an improvement in the crystallinity of the films. The main phase of TiO$_2$NPs became anatase with the tetragonal lattice structure at annealing temperature above 400 °C. The film annealed at 650 °C showed the rutile phase formation with the tetragonal structure, due to the sufficient thermal energy-driven (at higher temperature) phase transformation (anatase to rutile) of the TiO$_2$NPs.
Figure 2. XRD patterns of the thin film deposited on ITO substrate after annealing at temperatures (a) 200, (b) 300, and (c) 400 °C. EFTEM morphology of the thin films annealed at (a1) 200, (b1) 300, and (c1) 400 °C.
Figure 3. XRD patterns of the thin film deposited on Si substrate after annealing at temperature (a) 500, (b) 550, (c) 600, and (d) 650 °C. (e) Annealing temperature-dependent variation in the crystallite size and FWHM of the studied films. (f,g) The optical absorbance of the thin films annealed at different temperatures. (h) Effect of annealing temperature on the $E_g$. 

The characteristic parameters (value of FWHM ($\beta$) and peak position at the Bragg angle ($\theta$)) extracted from the most intense (101) XRD peak of the film obtained at each
annealing temperature was utilized to determine the diameter of the TiO$_2$ crystallites ($D$) calculated by Scherrer formula. Figure 3e displays the annealing temperature-dependent variation in the TiO$_2$ crystallite size and FWHM of the intense XRD peak, wherein the crystallite sizes were ranged from 12.15 to 34.02 nm. Furthermore, the TiO$_2$ crystallite sizes were remarkably enlarged with the increase of annealing temperature, suggesting the strong sensitivity of the structure and morphology of the films on the thermal annealing process. The sharpness (high intensity) and broadness (low intensity) of the XRD peaks indicated large crystallite size (strong crystallinity or long-ranged order) and small grain size (weak crystallinity or short-ranged order), respectively. The film annealed at 650 °C showed the formation of the largest TiO$_2$ crystallite [24]. Figure 3f demonstrates the optical absorbance of films containing TiO$_2$ NPs deposited on Si substrate and annealed at different temperatures after sonication in ethanol for 30 min. The spectral absorption data of the films were used to generate the Tauc’s plot, and the annealing temperature-dependent modification of the optical bandgap energies was evaluated. Irrespective of the annealing temperature changes, the optical absorbance of the film in the wavelength region of 300 to 400 nm was appreciably increased, indicating the significant structural and morphological modifications due to annealing. In addition, the UV absorption edge of the proposed film enclosing the TiO$_2$ NPs showed some notable red-shift (towards longer wavelength) with the increase of annealing temperature, indicating a lowering in the $E_g$.

Figure 3g presents the variation in the optical absorbance of the TiO$_2$NPs as a function of annealing temperature. The optical absorbance of TiO$_2$NPs was significantly dropped with the increase of annealing temperature, indicating the strong structural modifications in the electronic energy states. Additionally, TiO$_2$NPs annealed at 500 °C exhibited the highest absorbance. Figure 3h shows the effects of various annealing temperatures on the $E_g$ values of the films deposited on Si substrate. The values of $E_g$ were remarkably decreased from 3.84 to 3.24 eV, with the increase of annealing temperature. This observation was attributed to the annealing temperature-mediated enlargement in the TiO$_2$ crystallite size, a phenomenon called the quantum de-confinement effect [25,26]. Present results are consistent with the reported values of $E_g$ for TiO$_2$ (between 3.2 to 3.8 eV) [27,28].

Figure 4 shows the FESEM micrographs (top-view and cross-section view) of the TiO$_2$NPs thin films deposited of Si substrate obtained at different annealing temperatures. Regardless of the annealing temperatures, all the films exhibited spherical-shaped nanocrystallites. In addition, all the films were smooth without any holes or splits, indicating their suitability as a HBL in the HHSCs and QDSCs. The nanocrystallite sizes were increased from 11.3 nm (at 500 °C) to 33.4 nm (at 650 °C), supported by the size estimated via EFTEM and XRD analysis. The observed significant influence of the varying annealing temperatures on the TiO$_2$NPs morphology was consistent with the other findings [29–32]. Earlier reports argued that the nanocrystallites at the film boundary are weakly attached to their neighbors. Thus, with the increase of annealing temperature, the small crystallites gain enough energy to merge with other crystallites, producing large crystallites in the film.

Figure 5a shows the diffuse reflectance spectrum of the bare c-Si substrate and a thin film containing TiO$_2$NPs annealed at 600 °C. Kubelka–Munk (K-M) function ($\alpha$) was used to calculate the $E_g$ of the film [21,22,33,34] by generating a plot of ($\alpha \times E_g$)$^m$ versus $E_g$. The value of $E_g$ obtained using K-M function (3.53 eV) was close to the one estimated from Tauc’s method (3.6 eV). The expression of $\alpha$ in terms of the molar absorption coefficient ($K$) and scattering factor ($S$) takes the form $\alpha = \frac{4K}{\pi S}$, with $K = (1 - R)^2$ and $S = 2 \times R$ (where $R$ refers to the diffuse reflectance value of film and $E_g = \frac{1240}{\lambda}$ eV). Figure 6b displays the thin film’s FESEM image (top view), which was somewhat uneven with small bumps and zigzag patterns (yellow circle). The observed rapid reduction in the diffuse reflectance of the grown films was mainly due to increased surface roughness [7].
Figure 4. FESEM images top-view together with corresponding particles size distribution and cross-section view (inset) of the films deposited on Si substrate and annealed at temperatures (a) 500, (b) 550, (c) 600, and (d) 650 °C.

Figure 5. (a) Diffuse reflectance spectrum of c-Si substrate and thin-film annealed at 600 °C and (b) FESEM image (top view) of the same film deposited on c-Si and annealed at 600 °C.
To confirm the photovoltaic potential of the deposited film containing TiO$_2$NPs, an MIS solar cell of the form Al/p-c-Si/PSi/TiO$_2$NPs/Ag was fabricated. Electrical properties, as shown in Figure 6a–c, illustrate the basic architectures of the proposed solar cells of the form Al/p-c-Si/Ag (reference cell), Al/p-c-Si/PSi/Ag (cell with extra PSi layer), and Al/p-c-Si/PSi/TiO$_2$NPs-/Ag (cell with extra thin-film TiO$_2$NPs and PSi layer), respectively. The Al and Ag layer served as back and forwarded electrodes in these designs. Figure 6d illustrates the cross-sectional FESEM image of P-Si with the corresponding K-M function (inset) used to determine the value of $E_g$. The P-Si layer revealed indirectly to direct band gap energy transition due to the quantum confinement effect, which was due to the shrinkage of Si particle size below 5 nm [35,36]. The value of $E_g$ for PSi (~2.78 eV) was comparable with the one obtained previously (2.2 eV) from the photoluminescence spectral analyses [37–39]. The solar simulator was used to determine the cell characterization, which gives the value automatically.

Figure 7a–c shows the performance of the three solar cells designed without and with TiO$_2$NPs thin film (annealed at 600 °C). The results clearly showed that the PCE, FF, and I-V characteristics of the photovoltaic cell designed with TiO$_2$NPs thin film were improved compared to those constructed without TiO$_2$NPs. The PCE of the cell with TiO$_2$NPs (0.28%) was much higher compared to the reference cell (0.001%) and the cell with an extra PSi layer (0.007%). The cell’s short circuit current ($J_{SC}$) with TiO$_2$NPs was almost 153 times and 30 times higher than the reference cell and the PSi layer, respectively. In addition, the...
open-circuit voltage ($V_{OC}$) of the cell with TiO$_2$NPs film was almost 1.7 times and 1.1 times higher than the reference cell and the cell with the PSi layer, respectively.

The current density improvement was related to the extraction of the photo-generated carriers. If the electron in the valance band absorbed enough energy, it would transfer to a conduction band, which was left behind a hole in the valance band. These e-h pairs possess two choices, (1) recombination which leads to generating electromagnetic waves (photoluminescence), (2) extraction of the electron and hole, which were improved the current density. In this experiment, the current density increased from 0.458 mA/cm$^2$ to 8.75 mA/cm$^2$, meaning the $J_{SC}$ was enhanced by 19 times. This improvement in the current density refers to increasing the electrons and holes extraction or reducing the recombination process.

Figure 7. Photovoltaic performance of the proposed cells fabricated without and with TiO$_2$NPs (a) I-V characteristics (b) PCE and FF, (c) $J_{SC}$ and $V_{OC}$.

The observed improvement in the performance of the cells fabricated with TiO$_2$NPs film can be explained. The carriers’ recombination rate played a significant role in the PCE enhancement or quenching of the solar cells. It is known that the recombination rate is minimized to improve solar cell performance. The primary sources of the charge carriers on the PSi surface was oxygen defects/vacancies that served as a trap level through the PSi bandgap region. The implementation of TiO$_2$NPs thin film in the cell (size of 27.44 nm) on the top of the PSi layer led to the surface passivation, thereby reducing the oxygen vacancy by covering the surface and infiltrating into the macro-pores (size above 50 nm) of the PSi layer [40]. The micro-pores (size below 2 nm) and mesopores (size range of 2 to 50 nm) [41] were predominant in the PSi layer. However, TiO$_2$NPs with larger dimensions than the mesopores or micro-pores of PSi could prevent their infiltration into those pores.
Crystallization and the crystallite size of samples at 600 °C is more excellent than for samples at 500 °C, and both have anatase phases. The TiO$_2$NPs annealed at 600 °C were deposited on the PSi to passivate the surface. Unfortunately, it cannot penetrate the micropores, so TiO$_2$NPs annealed at 500 °C were used to penetrate in the smallest pores. The deposit time for both was the same, and the PCE of the solar cells contained TiO$_2$NPs annealed at 500 °C more than at 600 °C. The deposit time was decreased to reduce the thickness of the film, which will be acted as a tunneling layer. Consequently, it increased the carriers’ recombination rate through the oxygen vacancies and hence the accumulation of the photo-generated carriers (e$^-$-h$^+$) was reduced. To improve the solar cell performance, the thickness of the TiO$_2$NPs film was reduced by lowering the deposition time to 0.5 min. The TiO$_2$NPs thin-film acted as a tunneling layer for the electrons at the Ag and PSi interface. Furthermore, the mean size of TiO$_2$NPs in the film annealed at 500 °C was 11.3 nm, chosen to coat the PSi layer as optimum ETL to get the highest photovoltaic performance in terms of PCE and FF.

Figure 8a shows the photovoltaic performance of the proposed cells (in terms of terms I-V characteristics, cell configuration together with PCE, FF, $J_{SC}$, and $V_{OC}$ under sunlight exposure, AM1.5G) fabricated using annealed (500 °C) TiO$_2$NPs film. The value of PCE (1.02%) and $J_{SC}$ (8.75 mA/cm$^2$) of the thermally annealed TiO$_2$NPs film incorporated solar cell was much higher compared to the film annealed at 600 °C (PCE of 0.28% and $J_{SC}$ of 0.458 mA/cm$^2$). In addition, the PCE was enhanced by 3.6 times and $J_{SC}$ by 19 times compared to the film annealed at 600 °C. Conversely, the values of $V_{OC}$ and FF were reduced due to the more isolation of the TiO$_2$NPs originated from the increased bandgap energy of the film [42,43].

Figure 8b displays the energy band diagram of the ETL-based cell, indicating the mechanism of electrons tunneling, carriers’ generation, and recombination across the energy bandgap. The carrier’s concentration in the p-c-Si and PSi layer calculated using the theory of Hall effect was $\sim 3 \times 10^{16}$ cm$^{-3}$ and $3 \times 10^{11}$ cm$^{-3}$, respectively. This indicated that PSi behaved as an intrinsic semiconductor with the Fermi level located at the centre of the bandgap [44,45]. The conduction band energy for Si and TiO$_2$ being 4.01 and 4.02 eV, respectively [46], the energy difference ($\Delta E_c$) between the conduction states of Si and TiO$_2$ were too small, enabling the extraction of the photo-generated electrons in the ETL. In contrast, the valance band energy for Si and TiO$_2$ was 5.1 and 7.25 eV. The energy difference ($\Delta E_v \sim 2.15$ eV) between the valence states of Si and TiO$_2$ were too large, preventing the holes extraction at Si-TiO$_2$ interface and thus acted as HBL [47]. In addition, work functions ($\Phi$) of Ag (4.28 eV) and Al (4.26 eV) facilitated the rapid acceptance of the carriers towards the electrodes [6,48,49]. On top, the values of $E_C$, $E_V$, and $\Phi$ of the materials in the proposed solar cell were fluctuated, slightly depending on the method of thin films deposition [50]. Table 1 compares the performance of the proposed cell with the other state-of-the-art works reported in the literature. In short, the proposed solar cell was fabricated using the thermally annealed TiO$_2$NPs film outperformed the existing cells reported in the literature.

The current density improvement was related to the extraction of the photo-generated carriers. If the electron in the valance band absorbed enough energy, it would transfer to a conduction band, which was left behind a hole in the valance band. These e-h pairs possess two choices, (1) recombination and which leads to generating electromagnetic waves (photoluminescence), (2) extraction of the electron and hole, which were improved the current density. In this experiment, the current density increased from 0.458 mA/cm$^2$ to 8.75 mA/cm$^2$, meaning the $J_{SC}$ was enhanced by 19 times. This improvement in the current density refers to increasing the electrons and holes extraction or reducing the recombination process.
Figure 8. Photovoltaic performance of the proposed cells (under sunlight exposure) fabricated with annealed (500 °C) TiO$_2$NPs film (a) I-V characteristics, cell configuration together with PCE, FF, $J_{SC}$, and $V_{OC}$, and (b) energy band diagram showing the mechanism of electrons tunneling, carriers' generation across the energy bandgap.
Table 1. Comparative evaluation of the performance of the proposed cell with other state-of-the-art works reported in the literature.

| Solar Cell Structure                  | Improvement by       | Enhancement $\eta$ (%) | Ref. |
|--------------------------------------|----------------------|-------------------------|------|
| Glass/Cu/n-Si/Si NW + G/SiO$_2$/Ag   | Si NW + G            | 100                     | [51] |
| FLG/2GBD/n-Si                        | 2GBD                 | 56.2                    | [52] |
| DSSC                                 | 719dye + TiO$_2$ nanotube | 87.5                  | [53] |
| Al/p-c-Si/SiO$_2$/Cr/Au/Ag           | Ag nanoparticle + SiO$_2$ | 80.4                  | [54] |
| Al/p-c-Si/P-Si + Ag/TiO$_2$/Au       | P-Si + Ag            | 111.2                   | [43] |
| Au:TiO$_2$ based DSSC                | Au/TiO$_2$           | 65.1                    | [55] |
| TiO$_2$ nanotube based DSSC          | TiO$_2$ nanotube     | 53.6                    | [56] |
| GO-TiO$_2$ based DSSC                | GO-TiO$_2$           | 126.4                   | [57] |
| Nd-TiO$_2$ based DSSC                | Nd-TiO$_2$           | 34.3                    | [58] |
| DSSC                                 | TiO$_2$              | 50.5                    | [59] |
| FTO/Li-TiO$_2$/perovskite/Spiro-OMeTAD/Au | Li-TiO$_2$       | 1.97                    | [60] |
| FTO/TiO$_2$:Yb$^{3+}$,Er$^{3+}$/perovskite/Spiro-OMeTAD/Ag | TiO$_2$: Yb$^{3+}$,Er$^{3+}$ | 16.5                  | [61] |
| FTO/cTiO$_2$/mpTiO$_2$/perovskite/Spiro-OMeTAD/Ag | mpTiO$_2$          | 9.2                     | [62] |
| Al/p-c-Si/PSi/TiO$_2$NPs/Au          | P-Si                 | 264.3                   | Present |

4. Conclusions
Thin films TiO$_2$NPs were prepared via the pyrolysis process on ITO glass and Si substrate. The obtained thin films were annealed at various temperatures (200 to 650 °C) to achieve the optimum ETL for the solar cell fabrication. The variation of annealing temperature was shown to play a significant role in the film’s structures and absorbance properties beneficial for the ETL design in the solar cells. The MIS-SC was constructed with the thermally annealed TiO$_2$NPs film as ETL excellent photovoltaic performance with the corresponding PCE and $J_{SC}$ values of 1.02 and 8.75 mA/cm$^2$. The sizes of TiO$_2$NPs and the thickness of the film strongly influenced the cell’s performance.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en15051648/s1, Figure S1: (a) Flowchart of the TiO$_2$NPs procedure, (b) TiO$_2$ thin films deposition procedure.

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