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Effect of Dye on the Performance of Nitrogen Doped TiO_2 Solar Cell Prepared via Ammonia Treated Liquid Phase Deposition Technique

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Abstract: *This paper reports the utilization of nitrogen-doped TiO_2 nanoparticle in dye-sensitized solar cell (DSSC). The TiO_2 nanoparticles were synthesized on ITO substrate via a simple technique, namely, liquid phase deposition (LPD). 7.5% nitrogen from NH_3 dopant source was doped into the TiO_2 samples by spin coating technique. The nitrogen doped TiO_2 samples were then utilized as photovoltaic materials in a photoelectrochemical cell of ITO/TiO_2/electrolyte/platinum sensitized with N-719, N-3 and Z-907 dyes, respectively. It was found that the photovoltaic parameters such as short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (η) are influenced by the organic dyes. The cell sensitized with N-719 dye demonstrated the highest photovoltaic parameters. These results are supported with the UV-Vis analysis, showing that the N-719 dye possessed the broadest window absorption and the highest absorption peak in visible region of light spectrum.*

Keywords: dye-sensitized solar cell, nitrogen doping, optical absorption, TiO_2

1. INTRODUCTION

One of the disadvantages of using TiO_2 nanoparticles as photovoltaic materials is its known large band gap. The band gap of TiO_2 nanoparticles for anatase phase is 3.2 eV and for rutile phase is 3.0 eV [1]. Eventough the band gap of anatase phase is larger than rutile phase, anatase phase TiO_2 has always been chosen in solar cell as it has been reported that the light harvesting using anatase phase TiO_2 nanoparticles was 30% more than that of rutile phase [2]. The higher band gap of the anatase phase TiO_2 nanoparticles can be lowered down by modification on its electronic structure. One of the most modifications was by introducing a dopant in its crystal lattice. The dopant used might be from transition metal element or non-metal. Metal doping into TiO_2 nanoparticles has been attempted by several researchers in order to enhance the optical property and the photoelectrochemical activity of the TiO_2 nanoparticles used as photoanodes [3]. Several metals that had been chosen as doped materials into TiO_2 for PEC and DSSC such as gallium (Ga), silver (Ag), tantalum (Ta), zinc (Zn), niobium (Nb), antimony (Sb), lanthanide (La), bismuth (Bi) and lithium (Li). The main advantages of these metal doped TiO_2 nanoparticles as photovoltaic materials in dye sensitized solar cell are low production cost and simplicity in synthesizing them. Besides the possibility of the recombination of electron with metal dopants used might have lower fabricated cell performance. Recently, the association of metal doping in TiO_2 in enhancing the photoelectrochemical activity has taken a new approach. Several researchers have reported the use of metal oxide such as Er_2O_3, ZrO_2 and ZnO as dopants in TiO_2 in enhancing its photoelectrochemical performance [4-6]. The enhancement of the photoresponse of TiO_2 can also be achieved by introducing non-metal dopants in the nanomaterial such as N, F, C, B and S.

It was found that the nitrogen doped TiO_2 used in photoelectrochemical cell have found to introduce impurity energy levels and band gap narrowing with no sign of recombination reported [7]. These phenomenon has contributes towards much broader optical absorption windows. In order to enhance the performance of the nitrogen doped photovoltaic materials used modification, modified

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structure were used so that the doping process of nitrogen doped into TiO_2 crystal lattice to become more efficient. Few structures such as nanothorn [8], nanorice grain [9], nanoplate [10], nanotubes [11], nanoflower [12] and nanosheet [13], were either used or produced in studying the nitrogen doping on TiO_2 as these structures possessed large surface area in which has proved to increase the photocatalytic application. We have prepared controlled-shape synthesis of nanostructure and have been applied in solar cell and supercapacitor [14, 15].

The main objective of this work is to investigate the effect of utilizing various types of organic dye, N-719, N-3 and Z-907 dyes, on the performance of nitrogen doped TiO_2 nanoparticles solar cell. The novelty of this work was in preparing highly photosensitive nitrogen doped TiO_2 nanoparticles via a simple technique, liquid phase deposition for use in DSSC.

2. EXPERIMENTAL

2.1. Materials

ITO substrates were purchased from Vin Karola, ammonium hexaflourotitanate $(NH_4)_2TiF_6$ and boric acid H_3BO_3 were purchased from Sigma-Aldrich. Iodine, Lithium Iodide, 4-tertbutylpyridine, tetrabutyl ammonium iodide and acetonitrile for electrolyte preparation were purchased from Sigma-Aldrich. The ammonia used for TiO_2 doping was in 30% water solution purchased from Sigma-Aldrich. Platinum ring for platinum counter electrode preparation was purchased from Kurt J. Lesker. N-3, Z-907 and N-719 dye were purchased from Sigma-Aldrich. All materials were directly used without further purification.

2.2. Preparation and characterization of nitrogen-doped TiO_2 nanoparticle sensitized with dye

Thus, nitrogen-doped TiO_2 sample was prepared by spin coating technique with ammonia water as nitrogen source. Ammonia solution was first prepared by diluting the solution in deionized water. 0.06 ml of the solution with composition percentage of 7.5% was spin coated on TiO_2 sample, respectively. Fabrication of dye sensitized solar cell was performed using the nitrogen-doped TiO_2 samples with 7.5% ammonia as it was found that the TiO_2 sample treated with this composition demonstrated the best performance compared to the other samples. Three types of dye were chosen, namely, N-3, N719 and Z907 dyes. All the three dyes were firstly dissolved in ethanol solution, respectively. For the immersion of TiO_2 samples in the dyes solution, the concentration used was 0.3 mmol in a volume of 5 ml corresponding with 0.3 mM. The samples were fully immersed for 24 hours in a dark place as the dyes was easily degraded. The optical absorption of the samples was characterized by UV-Vis technique. The elemental analysis of the nitrogen doping sample was characterized by Rutherford Back Scattering technique (RBS). RBS was performed to investigate the elemental composition of NH_3 treated TiO_2 sample. In this technique, the elemental composition of the sample was studied at five different layers.

2.3. Fabrication and performance studies of dye-sensitized nitrogen-doped TiO_2 nanoparticle solar cell

A liquid electrolyte consists of an organic solvent such as acetonitrile and a redox couple I^-/I_3^- that serves as a redox medium. The electrolyte solution composes of 0.5 M LiI (Lithium Iodide) mixed with 0.05 M I_2 (Iodine) and 0.5 M TBP (4-tertiary butyl pyridine) in acetonitrile solvent. The solution was mixed with LiI and I_2. The required amount of pure I_2 solution and LiI powder was added into acetonitrile solvent. The solution was stirred uniformly until LiI was dissolved thoroughly. Finally, TBP was added to the electrolyte solution. Platinum counter electrode was prepared with an area and geometry equal to that of TiO_2 electrode. Platinum coated conductive glass acted as a counter electrode was prepared by sputtering platinum disc on ITO substrate using sputter coater Bio-Rad Microscience Division Sc500 model.

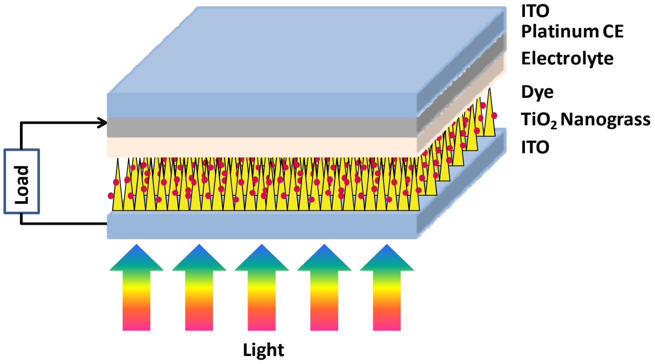

Figure 1. Structure of the dye-sensitized solar cell

The structure of DSSC utilizing nitrogen-doped TiO_2 nanoparticles is shown in Fig. 1. ITO coated glass substrate was used as a positive electrode in fabricating the photoelectrochemical cell. The TiO_2 nanostructures thin film was placed on platinum counter electrode. Both electrodes were separated by a parafilm that acts as a spacer. Several drops of the electrolyte solution were injected onto the TiO_2 nanoparticles in the sandwiched structure. The illuminated area of the cell which serves as its active area was 0.24 cm^2.

The performance of the DSSC in dark and under illumination was characterized by measuring the current-voltage curve of the cells. The cell was placed in a box in order to minimize the light that could be absorbed in measuring the performance of the cell in dark. The cell was illuminated through the solar simulator slide. Photocurrent-voltage measurements were performed using AM 1.5 Solar Simulator, Keithley high voltage and personal computer. The solar simulator was used to provide the illumination of 100 $mW \cdot cm^{-2}$. Keithley high voltage source was connected to the personal computer as a single system to provide the voltage recorded and displayed the current-voltage curves. The operating temperature was 25-27 °C in humidity of 40. The current-voltage, *I-V* curves were measured in a voltage range between -1.0 and +1.0 V, for both in dark and under illumination. From the *I-V* curves, the photovoltaic parameters such as open- circuit voltage (V_{oc}), and short-circuit current (I_{sc}), were obtained from the intersection of voltage and current axis, respectively.

3. RESULTS AND DISCUSSION

The morphology of TiO_2 nanoparticles treated with 7.5% NH_3 is shown in Fig 2. Fig. 2a represents the sample morphology taken at 10 k× magnification while Fig. 2b represents the sample taken at 50

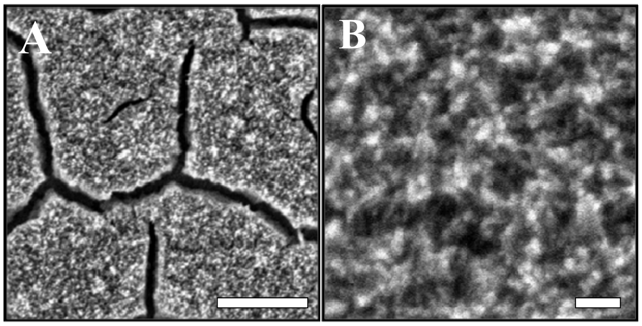

Figure 2. FESEM images of TiO_2 nanoparticle treated with 7.5% NH_3 at a) 10 k× and b) 50 k×. Scale bars are 1μm for (a) and 100 nm for (b)

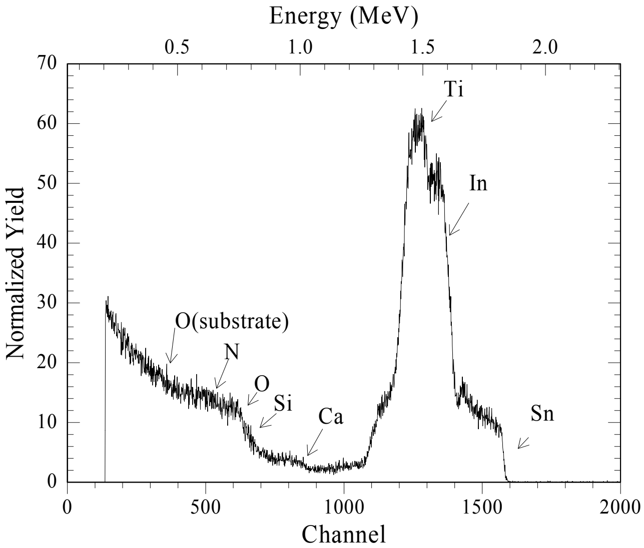

Figure 3. RBS spectrum of TiO_2 doped with 7.5% NH_3

k×. From Fig. 2a, we can see that the TiO_2 nanoparticle was well distributed even though the sample appeared to be cracking. The cracking appeared on TiO_2 nanoparticles film was due to the synthesize technique used since it is well known that LPD technique is slow reaction processed depending on the growth condition used. In preparing the TiO_2 nanoparticles, we have prepared the samples at a room temperature for 25 hours. At this time consuming growth, surface tension arise between grown nanoparticles that caused the cracking. Ammonia was known to be slightly corrosive to as deposited TiO_2 nanoparticles, but as the amount (0.6 ml) and concentration (7.5%) of the ammonia used in this work was small in quantity. It can be ensured that this visible cracking was not caused by the treatment that we have proposed. The porous structure of TiO_2 nanoparticles can be seen at higher magnification as shown in Fig. 2b. Thus, we can affirm that the treatment of ammonia on TiO_2 nanoparticles does not change the morphology.

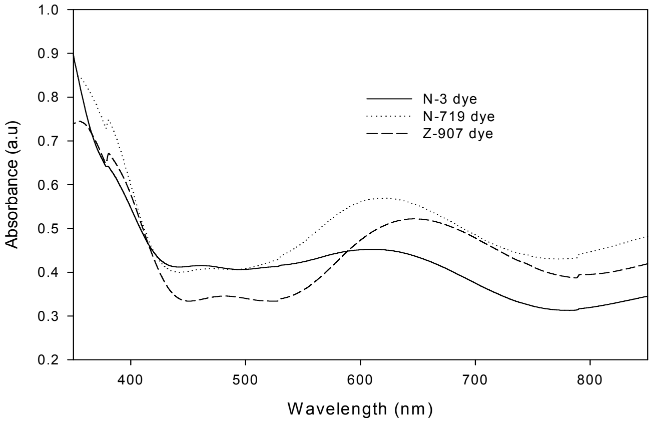

Figure 4. UV-Vis spectra of dye-sensitized N-doped TiO_2 samples

The RBS spectrum for N-doped TiO_2 treated with 7.5% NH_3 is shown in Fig. 3. Ti and O elements present in its spectrum. In and Si elements present from the substrate. The elemental composition of TiO_2 samples treated with 7.5% NH_3 is shown in Table 1 for five different thicknesses, namely, 139, 166, 204, 452 and 4000 nm. As expected, TiO_2 sample can only be detected in the first three depth thicknesses where the incorporation of the N atom can also be seen in these three layers. This result shows that the doping of N species in Ti lattice is also successful with the ion infusion treatment with amount of source dopant, 7.5% NH_3. The calculated molecular formula for N-doped TiO_2 (TiO_2N_x) for three different layers of thickness using elemental composition was found to be around ~$TiO_2N_{0.6}$.

Fig. 4 shows the UV-Vis spectra of the N-doped TiO_2 coated with three different dyes, N-719, N-3 and Z-907, respectively. The spectra show an absorbance peak at 350, 480, and 650 nm even though there is a slight shift in the peak between each sample. As expected, the absorbance peak exists at 350 nm was attributed to the TiO_2 nanoparticles absorption in visible. The broad peak that can be seem from the spectra was expected from the effect of the nitridization of the TiO_2 samples as explained earlier that the N-doped has introduced a new absorption window to the TiO_2 sensitized with the dyes. The peaks was supposed to be extended to 550 nm, which however where covered by another broad and stronger peak at 650 nm. This peak was attributed by the effect of the dye sensitization on the N-doped TiO_2. The peak of each type of dye might have slightly been shifted due to the absorption property of each dye. From these spectra, it is expected that the N-doped TiO_2 sample sensitized with N-719 dye will posses higher light to electrical energy conversion efficiency of solar cell, followed by the sample sensitized with Z-907 and N-3 dyes, respectively. This

Table 1. Elemental composition for 7.5 % NH_3 treated TiO_2

Thickness (nm)	Element					
	Ti	O	N	Sn	In	Si
139	0.825	1.690	0.520	0.204	-	-
166	0.821	1.773	0.527	0.172	-	-
204	0.860	1.743	0.535	0.157	-	-
452	-	1.327	0.475	-	0.563	-
4000	-	1.948	-	-	0.013	0.870

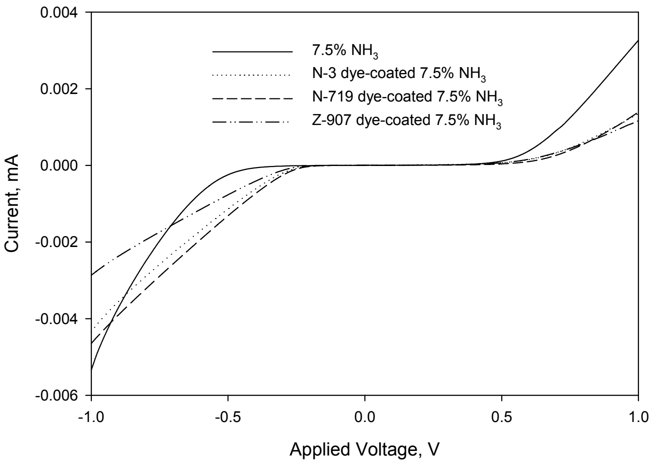

Figure 5. *I-V* curves of the solar cells with various dyes in dark

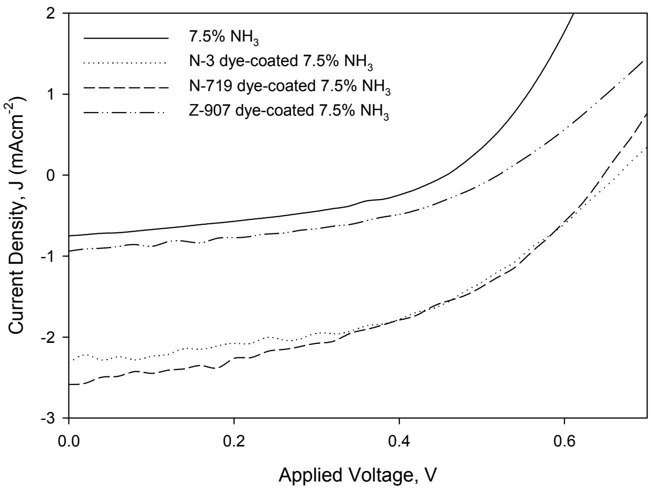

Figure 6. *J-V* curves of the solar cells with various dyes under illumination of 100 mW·cm^{-2}

prediction was made based on the optical absorbance property of each dye. From these spectra, the sample sensitized with N-719 dye shows the highest optical absorbance peak generally compared to the other two dyes, Z-907 and N-3 dye. As explained earlier in the previous chapter that one of the main factor that influences the conversion efficiency was light harvesting capability of the TiO_2 photovoltaic material. However, this prediction might have been inaccurate as the compatibility of the used dyes with the photovoltaic material needs to be also considered.

Fig. 5 shows the *I-V* curves for the solar cells in dark. It was found that the cell without dye demonstrated the highest dark current. The dark current of the solar cells was more into reverse bias. The dye affects the dark current of the DSSC since the dark currents are not the same in all devices. Thus, it can be concluded that the dye incorporation into nitrogen doped TiO_2 utilized in solar cell was found to modify the dark current of the cell.

Fig. 6 shows the *J-V* curves of the solar cells with various dyes under light illumination of 100 mW·cm^{-2}. From the figure, it was found that the cell with N-719 dye generates the highest output power, followed by the cell with N-3 and Z-907 dye, respectively. The shape of *J-V* curves for all cells follow that a typical DSSC since all cells exhibit rectification property as shown in Fig. 5. The photovoltaic parameters such as J_{sc}, V_{oc}, fill factor (*FF*) and conversion efficiency (η) are analyzed from Fig. 6 and illustrated in Table 2. The fill factor and conversion efficiency were computed by drawing maximum power rectangle of each *J-V* curve shown in Fig. 6 as reported in [16-17].

Table 2. Photovoltaic parameters for the solar cell with various dyes

Dye	J_{sc} (mA·cm^{-2})	V_{oc} (V)	ς (%)	*FF*
without dye	0.75	0.44	0.134	0.41
N-3	2.42	0.66	0.757	0.44
N-719	2.70	0.64	0.760	0.47
Z-907	0.98	0.50	0.217	0.43

From Table 2, it was found that the cells sensitized with the dyes demonstrated higher photovoltaic parameters than that without dye. This is due to the multiple effects of nitrogen doping and dye-sensitization on solar cell performance. This further enhances the light absorption in visible region. The highest J_{sc} was for TiO_2 with the N-719 dye sensitization with the value of 2.70 mA·cm^{-2}. The open circuit voltage V_{oc}, for this cell was found to be 0.64 V. The highest power conversion efficiency of this sample was 0.76 % with the fill factor of 44%. The second highest efficiency was obtained from the sample treated with N-3 dye with the efficiency of 0.757% followed by sample treated with Z-907 dye with the efficiency of 0.217%. The efficiency of the sensitized cell increased tremendously compared to the non-sensitized cell. This might due to the absorption capability of the photovoltaic materials sample that has been enhanced with the help of dye insertion. The results obtained were slightly different from what has been expected earlier. It is earlier expected that the cell with N-719 dye to demonstrate highest efficiency, followed by the cell with Z-907 and N-3 dyes based on the absorption spectra shown in Fig. 4. This is because the performance of the cell was based on the absorption capability of the dye sensitized nitrogen doped TiO_2 which has been portrayed by the absorption spectra. From the absorption spectra, the N-719 dye sensitized N-doped TiO_2 samples possesses higher absorption spectra at 650 nm followed by Z-907 and N-3 dye sensitized nitrogen doped TiO_2. However, the sample sensitized with Z-907 dye shows lower efficiency compared to N-3 dye sensitized N-doped TiO_2. There might be a possibility of the efficient absorption for dye sensitized N-doped TiO_2 might have occurred at the absorption spectra below than this region that is from near UV from 350 to 550 nm.

However, from Table 2, the best conversion efficiency was still far low compared to those reported by other research groups. Kang et al. 2010 have reported the efficiency of nitrogen doped TiO_2 DSSC prepared using sol-gel method was as high as 4.86% with its J_{sc} and V_{oc} were 10.52 mA·cm^{-2} and 0.73 V [18]. Guo et al. 2011 have reported that the nitrogen doped TiO_2 DSSC utilized two different types of photoelectrodes, i.e TTIP hydrolysis in aqueous ammonia and commercialized P25 annealed under NH_3 flow yielding the efficiencies as high as 10.2% and 8.0%, respectively [19-21]. They have concluded that the difference in efficiency might have been due to difference crystalline phase of both TiO_2 nanoparticles and the amount of nitrogen doping. The amount of the nitrogen doped incorporated in the TiO_2 lattice depends on the starting crystalline phase of photovoltaic material. Pan et al. 2011 have reported an increase in efficiency of nitrogen doped TiO_2 nanobelts DSSC might be due to the lower charge transfer resistance. The nanobelts DSSC obtained from the nanotubes TiO_2 soaked in the ammonia water for nitrogen doping demonstrated the efficiency of 2.4 % compared with 1.8% for the nontreated TiO_2 nanotubes DSSC. This shows that conductive transmission of carriers produced by photoexcited dye can be achieved by using TiO_2 in the form of nanobelt. One of possible reason why the efficiency from the work is lower compared to those reported by the other research groups might have been caused by the amount of insertion of dye into TiO_2 nanoparticles was small. The amounts of the inserted dye were determined by the molarities of the dye used and the dipping time of the TiO_2 nanoparticles into dye solution. However, the limitation of the molarities of dye depends on the thickness of the prepared TiO_2 nanoparticles. If the thickness of the TiO_2 nanoparticles was not sufficient enough, the dye might become a hindrance in the electron mobility as the charge carrier mobility might be slowing down. The suitability of the used dye also needs to be taken into account as the TiO_2 might have its own preferential. In this case, the ruthenium based dyes; N-3, N-719 and Z-907 have been studied to be suitable with TiO_2 in photovoltaic application. However, the impurity exists in the TiO_2 nanoparticles lattice for the sample from the nitridization effect might have caused a slight change in preferential of the used dyes. Thus, the cell with the Z-907 dye demonstrates the lowest photovoltaic performance as expected since it possesses the smallest absorption window as shown in Fig. 4.

4. CONCLUSIONS

The TiO_2 nanoparticles were successfully synthesized on ITO substrate via a simple technique, namely, liquid phase deposition (LPD). 7.5% NH_3 dopant source was confirmed to be successfully doped into the TiO_2 samples by RBS characterization. The cell utilizing nitrogen doped TiO_2 sample sensitized with organic dye demonstrated higher performance than the cell which is not sensitized with dye. It was found that the cell sensitized with N-719 dye demonstrated the highest J_{sc}, FF and η of 2.70 $mAcm^{-2}$, 0.47 and 0.760%, respectively. This is due to the N-719 dye possessed the broadest window absorption and the highest absorption peak in visible region.

5. ACKNOWLEDGEMENTS

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