Thin film deposition of N-Doped TiO_2 nanofibrous by using electrospinning method for photovoltaic applications

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***Abstract*—Titanium dioxide have a bright future on photovoltaic application with intention to provide alternative energy method. Titanium dioxide have the ability to produce high performance for photovoltaic application. The successful exploitation of titanium dioxide required development of technique to improve the physical and chemical properties. This research study aims on fabrication of fine size nitrogen doped titanium dioxide fiber under objectives to produced fine nitrogen-doped titanium dioxide nanofiber by using electrospinning method, characterized the chemical and physical properties of produced fiber and evaluate the performance of produced N-doped titanium dioxide nanofiber photovoltaic cell under visible light. Hydrolysis of titanium isopropoxide, doping with nitrogen source which was ammonium nitrate and electrospinning technique was used to produce N-doped titanium dioxide nanofiber. Doping the titanium oxide with nitrogen element improved its chemical properties by successfully lowered the band gap energy to 2.76 eV and shift its optical response to the visible light region. The presence of O-H stretching vibration, O-H bending and vibration of the N-Ti bond contributed to increase the performance of the photovoltaic cells. The produced electrospun N-doped was proved to have better power output. Since, the nitrogen doped gives higher absorbance wavelength and lower band gap energy. The improvement on the chemical and physical properties of the produced N-doped titanium oxide had overcome the drawback of titanium oxide and used for better photovoltaic performance.**

Keywords— Titanium Dioxide; Electrospinning; Nitrogen-doped titanium dioxide.

I. INTRODUCTION

The essential of nanoparticle cannot be denied nowadays with quickly grow in number of scientific research and publications. Nanoparticles are very fine particles with nanometer scale size. The word “Nano” was arised from the Greek expression which mean ‘dwarf’. Nano is a unit prefix express a factor of ten to the power of minus 9 or 0.000000001. Nanometer (nm) which was used in this topic was referred to the unit length represent fine particles 10nm to 20nm in size. The solid materials physical properties changes drastically in this scale [1].

For a past few decades, nanoparticles were studied for their size-dependent chemical and physical properties[2]. The nanomaterials are at the most advanced level at present in scientific knowledge and even in commercial application. The potential advantages of such a technology are great. The capability of nanotechnologies is that it is possible to create more efficient materials with very useful characteristics like better strength, ductility, lightness, water repellency, very small particle size, thermal and electrical conductibility. Nanoparticles established itself as a key enabling technology for a wide range of applications, it already used in hundreds of products among the industrial sector, mostly, electronic, energy, composites, chemical, cosmetics and healthcare.

Nanoparticles technology is discovery application in common energy sources and it is a significant enhancing alternative energy method to help on the world’s rising energy demands. Numerous scientists are looking forward into approaches to develop affordable, renewable and clean energy sources, and also to reduce energy consumption and reduce toxicity release to the environment.

Titanium dioxide has been widely studied for its ability to photocatalytic and application have high performance for photovoltaic application[3]. It also shows low pollutant load, low toxicity, chemically stable and available at low price.

There are methods which can improve the chemical properties of the titanium oxide to enhance its efficiency as a catalyst in photovoltaic application which is by doping the titanium oxide with metal and non-metal element. Photochemical response toward visible light can be enhanced by titanium oxide doping, this will effect on narrowing the band gap energy[4].

Beside from improving the chemical properties, titanium dioxide can be reduced in size into nanoscale to increase the surface area to improve photocatalytic efficiency. Nanofibers can be made from many polymers with various physical properties and application potentials. There are many different techniques to produce nanofiber, including electrospinning, self-assembly, drawing, template synthesis and thermal-induced phase separation. Electrospinning is a normally used technique to fabricate nanofibers because of the effortless setup and the capability to mass-produce nanofibers continuously from many types of polymers, and the capability to fabricate super thin fibers with controllable diameters, orientations, and compositions [5].

II. METHODOLOGY

A. Synthesis Un-Doped and N-Doped Titanium Oxide Suspension

There were three titanium oxide suspension were produces in this procedure, which are un-doped titanium oxide, 10wt% N-doped titanium oxide and 30wt% N-doped titanium oxide suspension. Ammonium nitrate was chosen as nitrogen source for doping in titanium dioxide. N-doped titanium oxide was fabricated by using sol-gel method. Firstly, 6 ml of nitric acid was added to 200 ml of distilled water. Next, the solution of water and nitric acid was stirred on the magnetic stirrer. After that, 40 ml of titanium (IV) isopropoxide and 3.75g (10wt%) ammonium nitrate was added to the solution and continue stirring for 1 hour at 500rpm under room temperature. The procedure was repeated with another amount of nitrogen source of 11.24g (30wt%). For the un-doped titanium oxide suspension, same procedure was used but without the ammonium nitrate dopant precursor.

B. Synthesis Un-Doped and N-Doped Titanium Oxide Nanoparticle

The un-doped, 10wt% N-doped and 30wt% N-doped titanium oxide suspension was then poured into the crucible for drying and calcining. For the drying process, oven was used and the temperature was set to 90ºC for 3 hours to dry the suspension. After that, the dried material was calcined in the furnace at 400ºC for 2 hours in air. White crystal which consist of titanium oxide was obtained and the materials were then further grind into a powder by using pestle and mortar. White un-doped, 10wt% N-doped and 30wt% N-doped titanium oxide powder was obtained.[6].

C. Synthesis of Un-Doped and N-Doped Titanium Oxide/PVA Blended Solution

2 g of polyvinyl alcohol (PVA) was dissolved into 20 ml distilled water under vigorous stirring room temperature for 5 hours. After the PVA was fully dissolved into the water, 1 g of un-doped titanium oxide was added into the solution and continue stirring for 30min. Same procedure was done to obtain 10wt% and 30wt% N-doped titanium oxide/PVA blended solution.

D. Electrospinning Deposition of Un-Doped and N-Doped Titanium Oxide/PVA Blended Solution

Electrospinning was done by using a 5 ml disposable plastic syringe equipped with a 23 G flat-end metal needle. The blended solution was transfer into the 5 ml disposable plastic syringe. The transfer was done carefully to avoid air bubble get into the syringe. The collector plate was set up by wrapping the plate with an aluminum foil. An indium tin oxide coated (ITO) glass was placed at the middle of the collator plate with the intention of depositing titanium oxide nanofiber. The ITO glass with the dimension of 2cm x 2cm was stick to the collector plate using a conductive plate. Make sure the conductive side of the ITO glass was facing the syringe pump. Conductive side of the ITO glass can be tested by using multimeter, there should be a continuity at the conductive glass surface. The distance between the collector plate and the needle tips was fixed at 15cm. The collector should be connected to the ground cable before electrospinning. Syringe pump was manipulated to feed the blended solution from the plastic syringe into the needle tips. The feed rate was fixed at 2mL/h.

After that, high voltage was applied to the tips of the needle by using high voltage power supply. Alligator clip was used to connect the needle tips to the high voltage power supply. The voltage was adjusted at 50-20kV until stable Taylor cone achieved. Lower voltage was preferable in favor to obtain fine fiber. Figure 1 shows the setup of the collector plate and ITO glass for electrospinning.

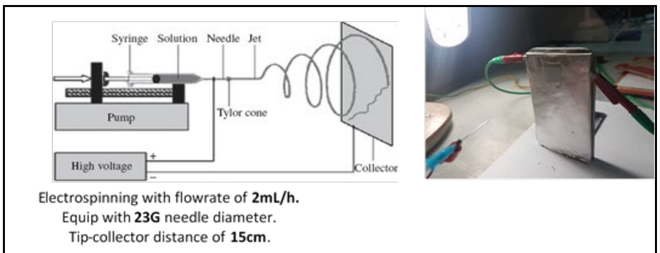

Fig. 1: Shows the setup diagram of the collector plate and ITO glass for electrospinning.

After the un-doped and N-doped titanium oxide nanofiber was deposited on the ITO glass, the titanium oxide nanofiber was put into the furnace to for calcine at the temperature of 400ºC. After the calcination process the ITO glass that deposited with titanium oxide nanofiber were to cooled to the room temperature.

E. *Doctor Blade Method Deposition of Un-Doped and N-Doped Titanium Oxide/PVA Blended Solution*

The ITO glass was tape 4mm at the top end and 2mm at the left and right side. Then, a drop of the un-doped titanium oxide/PVA blended solution was applied at the top edge of the ITO glass between the two pieces of tape. The blended solution was spread across the ITO glass with a glass rod. The gap between the strips of tape should be filled with a layer of blended solution. The operation was repeated with the 10wt% and 30wt% N-doped titanium oxide/PVA blended solution. After the un-doped and N-doped titanium oxide/PVA blended was deposited on the ITO glass, the ITO glass with was put into the furnace for calcine at the temperature of 400ºC. After the calcination process the ITO glass that deposited with titanium oxide layer were to cooled to the room temperature.

F. Photovoltaic Cell Assembly

The Un-doped and N-doped titanium dioxide nanofiber and Un-doped and N-doped titanium dioxide layer that obtained from the electrospinning and doctor-blading was then soak into the Anthocynin pigment dye for 10 minutes. The Anthocynin pigment dye was obtained from a red flesh dragon fruit. The fruit was crush and put into the beaker. The juice from the fruit containing Anthocynin pigment dye which was used for staining the titanium oxide. After the titanium oxide was soak in the dye. A carbon counter electrode was prepared by passing the ITO glass under a candle until the ITO glass was fully covered with carbon soot. Afterward, the photovoltaic cell was assembled by sandwiching together the ITO glass using paper chip and 2 drop of potassium iodide and glycol solution electrolyte for the photovoltaic cell sandwich. Figure 2 shows the diagram of the full assembly dye sensitizes solar cell. The photovoltaic was then analyzed by digital multimeter to obtain the data for photovoltaic cell performance.

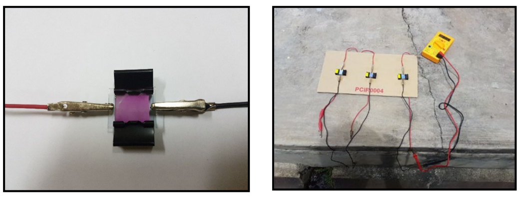

Fig. 2: The diagram of the photovoltaic cell sandwich.

G. Characterization of the N-Doped and Un-doped Titanium Oxide

UV-Visible Spectroscopy (UV-Vis) was used to study the changes in absorption wavelength for both un-doped and N-doped titanium oxide samples. After electrospun, the fibers were removed from the aluminum foils and tested. Absorbance data for all samples were recorded at wavelength in a range from 200 nm to 800 nm and presented in a graphical form of absorbance versus wavelength.

Fourier Transform Infrared Spectroscopy (FTIR) was used to study changes in functional group for the electrospun N-doped titanium oxide samples. After electrospun, the deposited fibers were removed from the aluminum foils and tested. The scan spectra were recorded in the range from 500 cm^{-1} to 4000 cm^{-1}.

The performance of the photovoltaic cells produced in this experiment were determine by measuring the open circuit voltage, V_{oc}, and short circuit current, I_{sc} by using digital multimeter at Innovation Laboratory, Faculty of Chemical Engineering, UiTM Shah Alam. The photovoltaic cell was tested under the sunlight at 3 different time which was at 1.00PM, 3.00PM and 5.00 PM.

III. RESULTS AND DISCUSSION

A. UV-Vis Absorption Spectra and Band Gap Calculation of Un-Doped and N-Doped Titanium Oxide

Un-doped and N-doped titanium oxide samples prepared from electrospun technique were expected to be used under visible light irradiation. Therefore, all prepared un-doped and N-doped titanium oxide samples were tested using Ultraviolet-Visible Spectroscopy to identify its absorption spectra and used to calculated its band gap energy. The optical response for the un-doped and N-doped titanium samples were shown in Figure 3 below. By comparing the N-doped titanium oxide samples with the un-doped titanium oxide sample absorption spectra, there are no significant changes in absorption wavelength for the two N-doped samples with dopant concentration of 10 wt.% and 30 wt.%. But the absorption wavelength slightly increased with increasing dopant concentration from 10 wt.% 30wt.%.

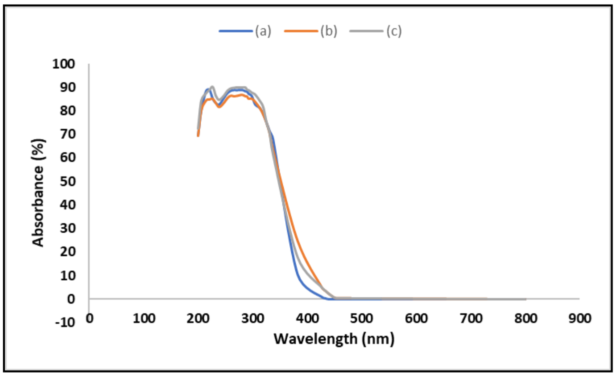

Fig. 3: UV-Vis absorption spectra of (a) un-doped TiO_2, (b) 10 wt.% N-doped TiO_2, (c) 30 wt.% N-doped TiO_2

The band gap energy of both un-doped and N-doped TiO_2 samples can be calculated based on the cut off wavelength obtained from UV-Vis absorption spectra in Figure 3. The relationship between the band gap energy and the cut off wavelength in absorption spectra was shown in equation below:

$$Band\ gap\ energy,\ E_{bg}(eV) = \frac{hc}{\lambda}$$

$$Plank\ constant, h = 6.626 \times 10^{-34} Js$$
$$Speed\ of\ Light, c = 3.0 \times 10^{8} m/s$$
$$Conversion\ factor$$
$$1eV = 1.6 \times 10^{-19} J$$

Sample	Cut Off wavelength (nm)	E_{bg} (J)	E_{bg} (e
(a) un-doped TiO_2	395	5.032 x 10^{-19}	3.14
(b) 10 wt.% N-doped TiO_2	450	4.417 x 10^{-19}	2.76
(c) 30 wt.% N-doped TiO_2	415	4.790 x 10^{-19}	2.99

Table 1: Band gap energy for un-doped and N-doped TiO2 samples

The UV-Vis absorption spectra depend on the nitrogen content in the N-doped titanium oxide samples with varying dopant concentration. Therefore, it gave an effect to the band gap energy of titanium oxide samples as shown in Table 1. Band gap energy of the un-doped titanium oxide sample was 3.14 eV and in consistence with what has been reported in literature which is in range of 3.0-3.2 eV [7]. As nitrogen dopant introduced in titanium oxide, the band gap energy of the prepared N-doped titanium oxide samples was lower than un-doped titanium oxide sample. As shown in Table 4.3, when the nitrogen dopant concentration increased, the band gap energy of titanium oxide sample was also increase. The lowest band gap energy recorded at 10wt.% N-doped titanium oxide sample which is 2.76 eV. This was consistence with the reported literature that stated the p-orbitals of the dopant element extensively overlapped to facilitate the transference of photo-generated charge carriers to the surface of titanium oxide and consequently increase its photocatalytic activity[8].

Nitrogen doping of titanium oxide was indeed enhancing the photocatalytic activity of titanium oxide. The high intensity of visible light absorption and low band gap energy in N-doped titanium oxide samples were caused by nitrogen doped. When N-doped titanium oxide photo-catalyst was irradiated, holes (h+) formed were less reactive because it's trapped at interface state localized by nitrogen doping. Lesser mobility was expected for holes (h+) but not for electrons (e-) because it's exited into conduction band. Holes (h+) that trapped at nitrogen doping site do not serve as effective charge recombination centers and nitrogen doping favors the formation of oxygen vacancies.

In conclusion, the decreasing and increasing pattern in band gap energy for N-doped titanium oxide samples depend on the varying nitrogen content of the sample. Nitrogen in titanium oxide play as impurity to form interface states that effectively shift the optical response of titanium oxide toward visible light region and lower its band gap energy.

B. Chemical Bonding and Chemical State of Un-doped and N-Doped Titanium Oxide

The bonding characteristics of functional groups in N-doped titanium oxide samples and un-doped titanium oxide sample were identified by FTIR. Figure 4 of FTIR spectra show an absorption peaks for the N-doped samples at two different concentrations and un-doped sample and after calcination. The observed peak in the range of 3324.94-3369.00 cm^{-1} is attributed to O-H stretching vibration and the peak detected at 1634.70-1635.06 cm^{-1} is assigned to O-H bending. It known that hydroxyl group plays an important role in photocatalytic mechanism. Hydroxyl group trapped by hole generated when titanium oxide irradiated under UV light. Hyd … ination of electro… tanium oxide ph… around 1433.73 a… tion of the N-Ti b… in the vicinities … A with the titaniu… e PVA absorption … osition of PVA[11

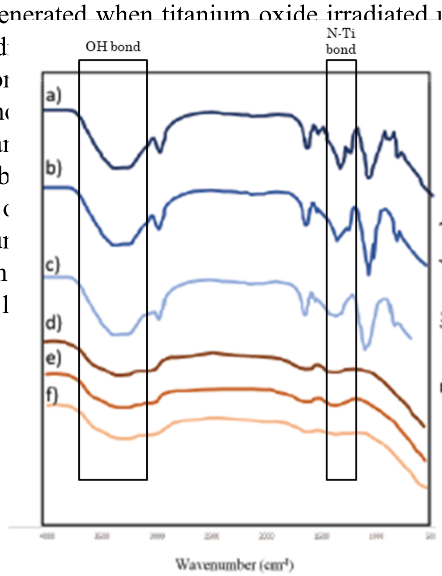

Fig. 4: FTIR spectra for un-doped and N-doped titanium oxide fiber samples at different dopant concentration. (a) 30 wt.% N-doped titanium oxide, (b) 10 wt.% N-doped titanium oxide, (c) un-doped titanium oxide, (d) 30 wt.% N-doped titanium oxide after calcination (e) 10 wt.% N-doped titanium oxide after calcination, (f) un-doped titanium oxide after calcination.

C. Particle Size of Titanium Oxide Produced by Sol-Gel Technique

Un-doped and N-doped titanium oxide was produced by using sol-gel technique. The un-doped and N-doped titanium oxide suspension produced was then analyzed by Zetasizer Nano ZS to identify the size of the titanium oxide particle. Table 2 shows the average particle size of titanium oxide produced:

Table 2: Average particle size of titanium oxide in the suspension

Suspension component	Average particle size (nm)
a) Un-doped titanium oxide	623.0
b) 10wt% N-doped titanium oxide	2943
c) 30wt% N-doped titanium oxide	590.9

From the result, the titanium dioxide particle produced from the sol-gel techniques was larger than 100nm. Particle size which larger than 100nm was considered as microparticle. Microparticles are particles between 0.1 and 100 µm in size. It can be concluded that the titanium oxide particle produced from the sol-gel technique was a microparticle.

D. Performance of Electrospun and Doctor Blade Method of Un- Doped and N-Doped Titanium Oxide on Photovoltaic Application

Total of six sample of dye sensitized titanium dioxide solar cells produced which consist of two methods, doctor blade method and electrospinning method. Three sample types of photovoltaic cell were produced from the doctor blade method and three sample types of photovoltaic cell from electrospinning method of titanium oxide deposition with different N-doped concentration. The performance of all six photovoltaic cell was determined by using a digital multimeter to measure the circuit voltage, V_{oc}, and current, I_{sc}. The photovoltaic cells were tested under the sunlight at three different time. The performance of dye sensitized titanium dioxide solar cells can be seen by comparing the reading of the circuit voltage and current for each photovoltaic cell

Table 3: Result of three samples dye sensitized titanium dioxide solar cells by using doctor blade method

Time	1.00 PM		3.00 PM		5.00 PM		Average		Power
Sample	V_{oc} (mVolt)	I_{sc} (µA)	V_{oc} (mVolt)	I_{sc} (µA)	V_{oc} (mVolt)	I_{sc} (µA)	V_{oc} (mVolt)	I_{sc} (µA)	P mW
a) Un-doped TiO_2	158	142.9	153	142.3	149	142.2	**153.3**	**142.5**	**0.022**
b) 10 wt.% N-doped TiO_2	179	152.0	169	151.4	166	151.1	**171.3**	**151.5**	**0.026**
c) 30 wt.% N-doped TiO_2	167	150.1	159	149.9	155	149.1	**160.3**	**149.7**	**0.024**

Each sample performance for doctor blade method was shown in the table 3. The 10 wt.% N-doped dye sensitized titanium dioxide solar cells have the higher performance compared to the un-doped and 30wt.% N-doped dye sensitized titanium dioxide solar cells, by the reading of circuit voltage**,** V_{oc}, and current, $I_{sc,}$ 171.3 mVolt and 151.5 µA respectively. From the result, un-doped dye sensitized titanium dioxide solar cells had performed the worst compared to the N-doped dye sensitized titanium dioxide solar cells which mean that by doping the titanium oxide have increase the performance of the dye sensitized titanium dioxide solar cells.

The result was similar with the dye sensitized titanium dioxide solar cells which produced by using electrospinning method. Table 4 shows the result of three samples dye sensitized titanium dioxide solar cells by using electrospinning method. The 10 wt.% N-doped dye sensitized titanium dioxide solar cells have the highest performance compared to the un-doped and 30wt.% N-doped dye sensitized titanium dioxide solar cells, by the reading of circuit voltage**,** V_{oc}, and current, $I_{sc,}$ 245.7 mVolt and 162.8 µA respectively.

Table 4: Result of three samples dye sensitized titanium dioxide solar cells by using electrospinning method

Time	1.00 PM		3.00 PM		5.00 PM		Average		Power
Sample	V_{oc} (mVolt)	I_{sc} (µA)	V_{oc} (mVolt)	I_{sc} (µA)	V_{oc} (mVolt)	I_{sc} (µA)	V_{oc} (mVolt)	I_{sc} (µA)	P mW
a) Un-doped TiO_2	184	140.9	177	139.1	175	138.7	**178.7**	**139.6**	**0.0249**
b) 10 wt.% N-doped TiO_2	250	165.0	248	162.4	239	161.0	**245.7**	**162.8**	**0.040**
c) 30 wt.% N-doped TiO_2	234	160.1	229	159.4	222	155.5	**228.3**	**158.3**	**0.036**

From the table 3 and 4, it is shown that dye sensitized titanium dioxide solar cells produced by using electrospinning method performed better compared to the doctor blade method. The higher value of V_{oc} and I_{sc} shows higher power output and better performance and higher efficiency of photovoltaic cell[6].

As conclusion, Electrospinning have great advantages like high in porosity and large surface area. This shows that by using electrospinning method had successfully increase the surface of the titanium oxide for more absorption of photon that will trigger the photocatalytic reaction.

IV. Conclusion

Nitrogen element was introduced to the titanium oxide by doping and electrospinning un-doped and N-doped titanium oxide should be active in visible light radiation. The properties of electrospun un-doped and N-doped titanium oxide produced were analyzed. From the UV-Vis analysis, the un-doped and N-doped samples shows an increases of absorbance wavelength toward visible light region. The band gap energy of the N-doped titanium oxide sample was reduces compared to the un-doped titanium oxide sample. From the UV-Vis results, the 10wt% N-doped was proved to have the highest absorbance wavelength and lowest band gap energy compared to other sample. It was proved that the best nitrogen dopant concentration of 10wt% N-doped titanium oxide. For the FTIR analysis, the presence of O-H stretching vibration, O-H bending, vibration of the N-Ti bond, chelating of PVA with the titanium compound. After calcination at 400°C, the PVA absorption peaks disappeared shows that the decomposition of PVA.

Based on the analysis performed, the produced electrospun N-doped was proved to have better power output since, the nitrogen doped gives higher absorbance wavelength and lower band gap energy. It can be concluded that by electrospun N-doped titanium oxide particles produced better performance and higher efficiency of photovoltaic cells under visible light radiation. Therefore, it satisfies the objective of this study the performance of electrospun titanium oxide nanofibers on photovoltaic application and to study the efficiency of un-doped titanium oxide and N-doped titanium oxide in photovoltaic application.

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