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APPLICATION OF NANOCRYSTALLINE TiO_2 PARTICLES SYNTHESIZED BY SONOCHEMICAL METHODS AS DYE SENSITIZED SOLAR CELL (DSSC)

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ABSTRACT

Nanocrystalline TiO_2 (titania) particles have been synthesized using sonochemical method. Two ultrasonic wave sources with different powers were used, 21 W 55 kHz (low power) and 130 W 20 kHz (high power), resulting in 5 different titania powders with different characteristics. This paper presents the performance of the synthesized titania powders and also of the commercially available titania powder Degusa P25, when applied as dye sensitized solar cell in the same setup as comparison. The best values of open circuit voltage (Voc) and short circuit current density (J_{SC}) for solar cell sample using synthesized powder was 442 mV and 1.40 mA/cm^2 respectively, obtained from powders sonicated for 8 hours. This V_{OC} value is near the value of solar cell prepared by comercial titania (450 mV), while the J_{SC} value is bigger compare to that prepared by commercial titania (0.89 mA/cm^2). The fill factor of all samples, including the one prepared using Degusa P25, is low which is probably due to low catalytic activity of the carbon-coated counter electrode used.

Keywords: nanocrystalline TiO_2 particle, sonochemical method, dye sensitized solar cell (DSSC)

ABSTRAK

Partikel nanokristalin TiO_2 (titania) telah disintesis menggunakan metode sonokimia. Dua sumber gelombang ultrasonik dengan daya berbeda digunakan, masing-masing 21 W 55 kHz (daya rendah) dan 130 W 20 kHz (daya tinggi), menghasilkan 5 serbuk titania yang berbeda dengan karakteristik yang berbeda. Tulisan ini menampilkan performa dari serbuk titania hasil sintesis dan juga serbuk titania komersil Degusa P25 ketika diaplikasikan sebagai sel surya tersensitisasi dye pada set-up yang sama untuk perbandingan. Tegangan open circuit *(V_{OC}) dan rapat arus* short circuit *(J_{SC}) terbaik untuk sampel sel surya menggunakan serbuk titania hasil sintesis adalah sebesar 442 mV dan 1,4 mA/cm^2 yang dihasilkan dari sampel sel surya yang menggunakan serbuk hasil sintesis pada daya ultrasonik rendah selama 8 jam. Nilai V_{OC} yang dihasilkan ini mendekati nilai yang dimiliki sel surya yang dibuat menggunakan serbuk titania komersil (sebesar 450 mV), sedangkan nilai J_{SC} justru lebih besar dari pada nilai J_{SC} menggunakan serbuk titania komersil (0,89 mA/cm^2). Nilai* fill factor *untuk semua sampel sel surya, termasuk yang menggunakan serbuk komersil, adalah rendah yang kemungkinan disebabkan rendahnya aktivitas katalitik dari* counter electrode *yang digunakan yang terbuat dari lapisan karbon.*

***Kata kunci**: partikel nanokristalin TiO_2, metode sonokimia, sel surya tersensitisasi dye (DSSC)*

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INTRODUCTION

The human need for energy is enormous. Meanwhile, the main, fossil-based, energy supply is limited. It was predicted that we will meet a major energy shortage within the next 50 years if we only depend on the main supply solely to suffice our needs. Fortunately, the energy we receive from the sun is more than sufficient, about 10,000 times more of the current need. Thus, if we can cover 0.1% of the earth's surface with solar cell having efficiency of 10%, then the human need for energy can be fulfilled [1].

Dye sensitized solar cell (DSSC) is a new type of solar cell with promising opportunity to replace the conventional solid state p-n junction type. Up till now, the efficiency of this new type of cell has reached above 11% with the wide opportunity to be increased [2]. Nanocrystalline TiO_2 particle plays important role in DSSC's performance. It must fulfill certain criteria to be able to be applied in DSSC, such as having nanometer sized particle in order to widen its effective surface area so as much as dye molecule could be anchored [2,3,4]; having certain morphology such as mesoporous[4], nanowire [5] or nanotube [6]; and also having crystalline phase of anatase [4], or mix of anatase-rutile [4,6]. To get these characteristics, several methods to synthesize TiO_2 nanoparticle have been developed. Among the methods are hydrothermal [7], sol-gel [8], anodic oxidation [9] and sonochemical method [10].

The sonochemical method has advantage in providing relatively easy and simple procedure with good results. Sonochemical means giving ultrasonic treatment to a precursor so it able to react chemically. The ultrasonic treatment causes the precursor to form oscillating gas-entrapped bubbles known as cavitations which give enormous energy and pressure when the bubbles collapse. This high energy and pressure is then used to react the precursor chemically [11]. This method has showed the ability to produce TiO_2 particle with criterias needed for application as DSSC such as nanometer-scale of crystalline size and anatase or mixture of anatase-rutile crystalline phase [12,13].

This paper present the application of the TiO_2 particles prepared by sonochemical method as the semiconductor material in DSSC, and their electrical performance under the presence of light is also discussed.

DYE SENSITIZED SOLAR CELL (DSSC)

DSSC was built in sandwich structure as shown in Figure 1. Compared to the conventional solar cell which exploit photovoltaic effect on semiconductor junction where the light absorption and electric charge separation processes occur simultaneously, the DSSC has rather different processes. Light absorption was carried out by light sensitive molecule, known as dye, which anchored to the semiconductor material (usually TiO_2 nanoparticle). When the light is absorbed by the dye, the dye's

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molecular energy will be excited, thus promoting electron injection to the TiO_2 which then facilitate the electron transfer to the conductive glass (Figure 2). Meanwhile, the hole produced from the excitation process was transfered from dye to electrolyte which then transferred to the other conductive glass as counter electrode via carbon or platinum layer as catalyst [3].

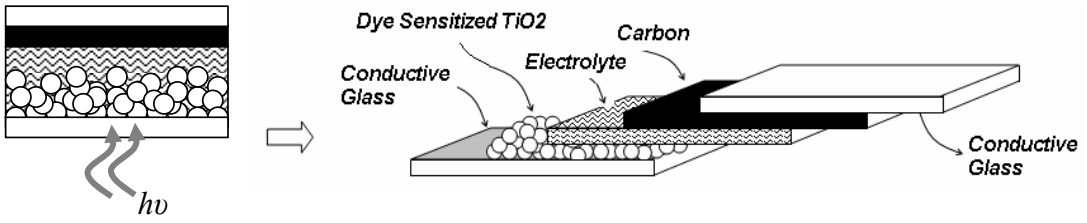

Figure 1. Schematic picture of sandwich structure of Dye Sensitized Solar Cell.

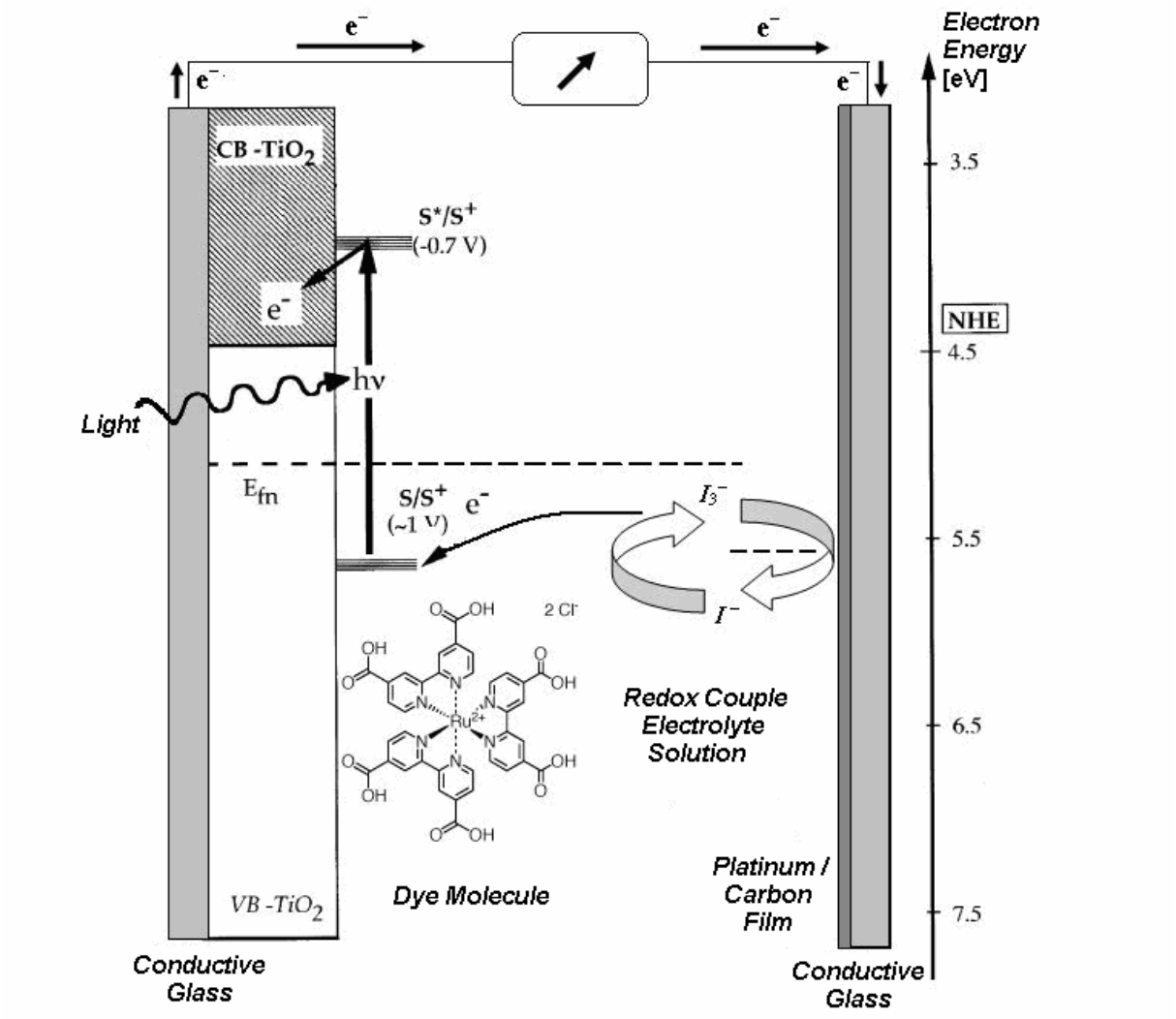

Figure 2. Schematic picture of electron transfer in Dye Sensitized Solar Cell [3,6,14].

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DSSC has relatively simpler method to assemble compared to the conventional solid state p-n junction solar cell. This new type of solar cell is also not requiring very high purity level of semiconductor material as in the conventional solar cell. Moreover, DSSC has achieved efficiency that is comparable to that of conventional solar cell. Nevertheless, this new solar cell type still has several drawbacks such as the use of heavy metal in synthetic dye molecule, lower stability when using organic dye [4], and the need for certain structure of TiO_2 nanoparticle layer with relatively easier method is not yet fulfilled.

EXPERIMENTAL METHOD

The experiment is carried out according to steps as shown in Figure 3. To prepare the nanocrystalline titania particle, procedures as reported earlier [12,13] was carried out. As much as 2 ml of $TiCl_4$ was added drop wise into 2 ml of acetyl acetone. Then, 40 ml of distilled water was added and the solution was then stirred at 300 rpm for about 5 minutes until yellow solution was formed. This solution was then half-divided and each of them was called "precursor". The procedure was repeated to obtain 5 similar precursors. Each of the precursors was then ultrasonically treated in different conditions. Three of them were sonically treated by low power ultrasonic bath (*Cole Palmer Ultrasonic Cleaner, 21 W 55 kHz*) for 4, 8 and 12 hrs, respectively. The remaining two were treated by high power ultrasonic processor (*Cole Palmer Ultrasonic Processor, 130 W 20 kHz*) for 1 and 2 hrs, respectively. All yellow-precursors were turned into white as the result of the treatments indicating the occurrence of chemical reaction. Afterwards, all precursors were dried on hot plate at 80 ^{0}C for 12 hrs and the resulting chunk was then crushed and heated in furnace at 500 ^{0}C for 2 hrs. The result of this step is the formation of white powders, which then characterized using XRD (Shimadzu XRD-7000) and SEM (Bruker 133 eV).

To form colloidal titania, add drop wise 3 drop of acetyl acetone in 1 ml of water into 0.2 g of each powders while slowly blended with mortar. These colloids were then casted on 2x2 cm^2 conductive glass substrate by doctor bladding method. Isolation tape was used as spacer to give boundary of 1 x 1 cm^2 open active area which the colloid was then casted on. About 3 drops of colloid was dropped on the edge of the active area and spreaded by wiping gently clean glass rod over all active area. Afterwards, the film was air dried for about a minute before heated in furnace at 450 ^{0}C for 30 minutes.

After cooling down to 150 ^{0}C, the film was dipped in "Ruthenium-470" dye solution for 12 hrs in order to obtain well dye-titania attachment. This dye-attached film was then used to build the solar cell with sandwich structure, placed face to face with another carbon-coated conductive glass as counter electrode. Then, the cell was paper clipped at each side. The Iodolyte solution (KI/I_2 in

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ethylene glycol) was used as the redox couple electrolyte. The performance of the cells was then measured under white lamp (Moritex100 W) using amperemeter, voltmeter and potentiometer which assembled according to circuit as described by Smestad, 1998 [3].

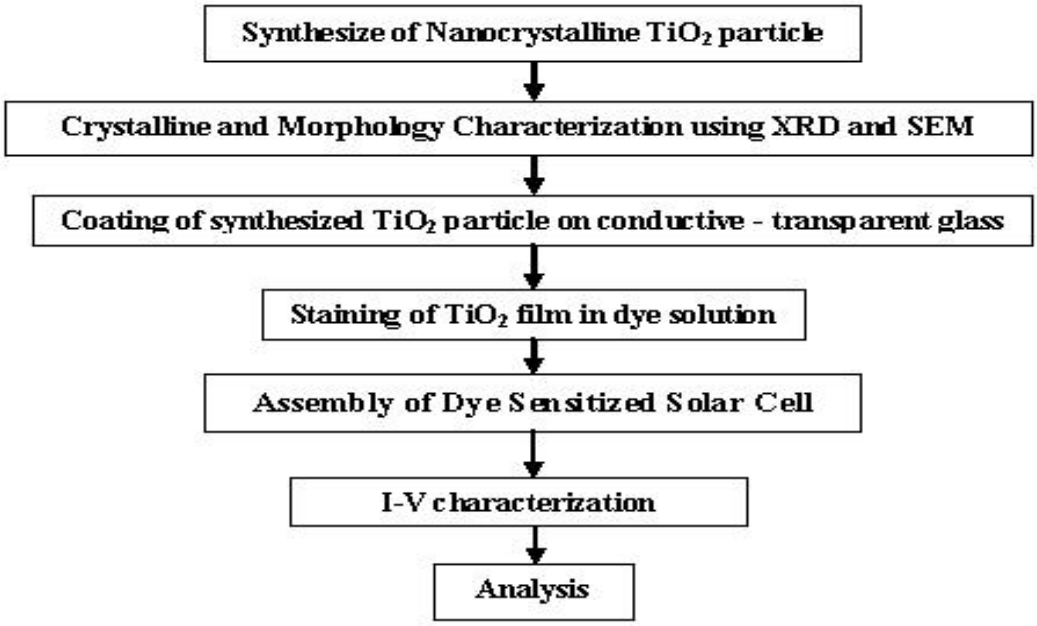

Figure 3. Schematic Diagram of Experimental Methods.

RESULTS AND DISCUSSION

Five powders were resulted from synthesize processes. These powders, along with the commercial Degusa P25 were coded according to Table 1. The code of cells built from these powders is also presented in the table.

Table 1. Code given for the titania samples.

Sources	Sonication Time (hrs)	Powder's Code	Solar Cell's Code
Ultrasonic Bath (21 W 55 kHz)	4	PUB4	CPUB4
	8	PUB8	CPUB8
	12	PUB12	CPUB12
Ultrasonic Processor (130 W 20 kHz)	1	PUP1	CPUP1
	2	PUP2	CPUP2
Degusa P25	-	P25	CP25

All powders were characterized using X-Ray Diffractometer (XRD). Analysis of the XRD patterns was detailed elsewhere [12,13], but the summary is presented in Figure 4 and Table 2.

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Powders synthesized using low power ultrasonic bath contain mixed anatase-rutile crystalline phase, similar to the Degusa P25's. Meanwhile, powders synthesized by high power ultrasonic processor contain anatase phase only only. The apparent crystal size of all synthesized powders was smaller than the Degusa P25's. The crystalline phase and size of these powders showed that they are promissing to be applied as semiconductor material for dye sensitized solar cell. As will be discussed later, these characteristics are affecting the electrical properties of the solar cell sample as can be seen from the I-V characterization. The small crystalline size is expected to cause small particle size which eventually increase the active surface area so as much as dye molecule can be attached on TiO_2 particle surface.

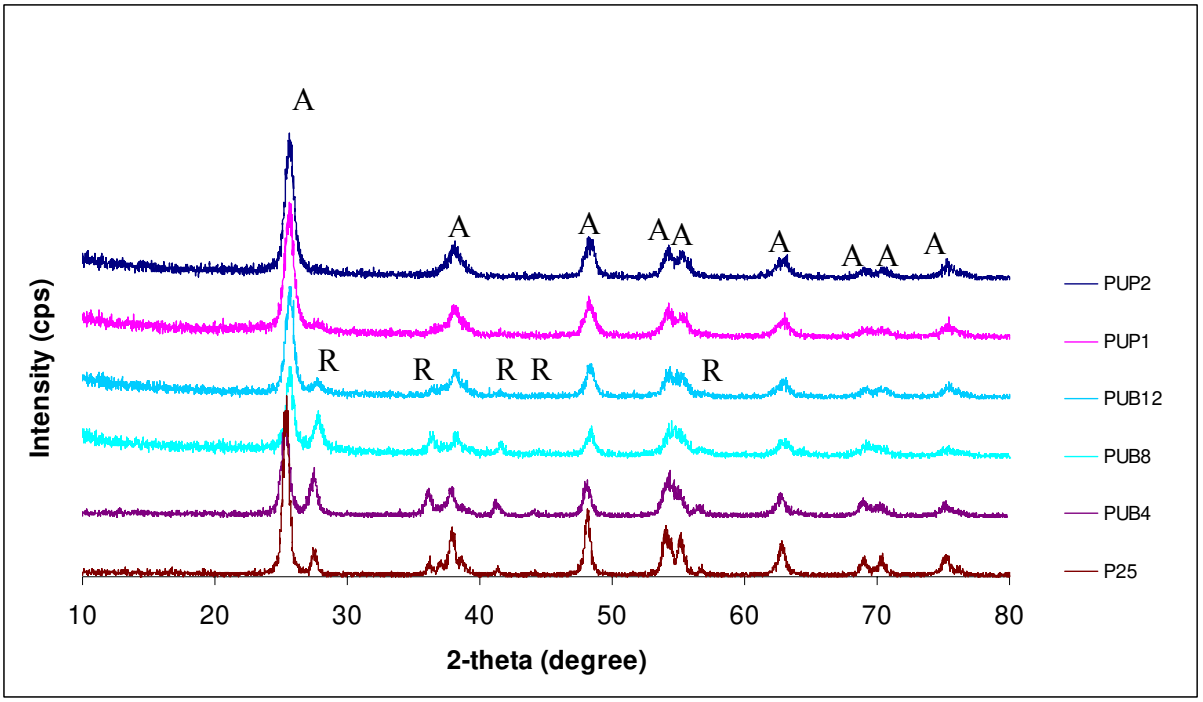

Figure 4. Summary of X-Ray Diffractogram of the TiO_2 particle. "A" refer to Anatase phase and "R" refer to Rutile phase [12,13].

Table 2. Summary of crystalline characteristics of the powders [12,13].

Sample	Crystalline Phase	Apparent Crystal Size (nm)
PUB4	Anatase - Rutile	21.70
PUB8	Anatase - Rutile	20.97
PUB12	Anatase - Rutile	18.65
PUP1	Anatase	18.65
PUP2	Anatase	16.78
P25	Anatase - Rutile	27.04

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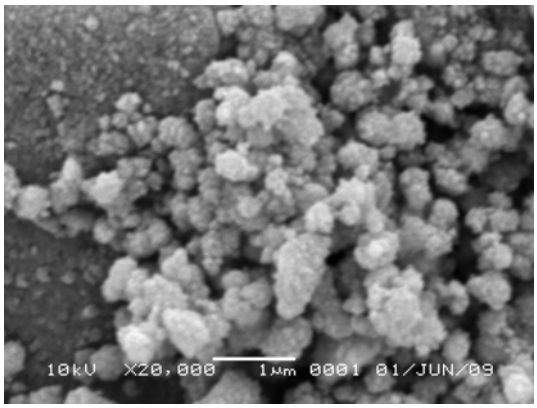
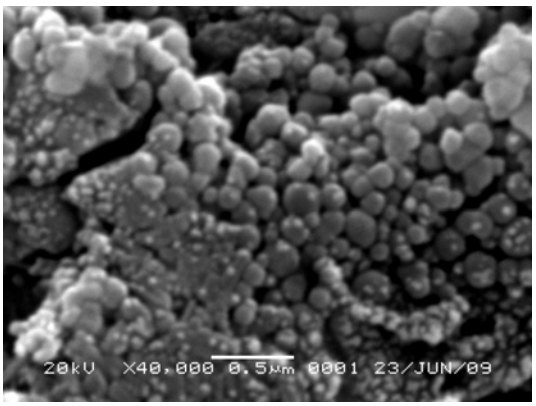
The high active surface area of TiO_2 particle can also be seen from SEM picture. Figure 5 presents the SEM picture of the powders prepared using low power ultrasonic bath, while powders prepared using high power ultrasonic processor is presented in Figure 6.

For all of this synthesized TiO_2 samples, the mesoporous morphology was likely to be the closest for all. This mesoporous morphology is desirable for it is the sign for high active surface area and allows as much as dye molecule to be attached to TiO_2 particle surface through the pore. However, agglomeration was also seen in all samples. This agglomeration can affect the solar cell's performance, because it can reduce active surface area of the powders, which eventually reduce the possibility of dye molecule which could be attached.



(a)



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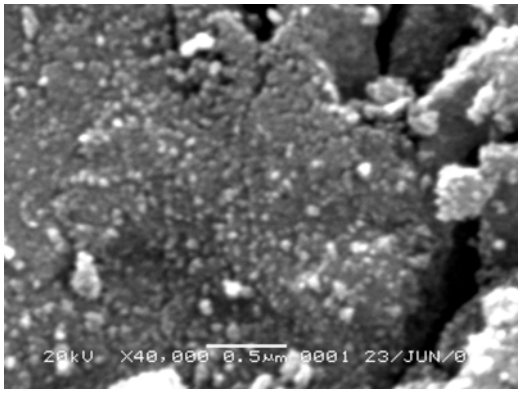

(c)

Figure 5. SEM picture of powders synthesized by low power ultrasonic bath (a) PUB4, (b) PUB8 and (c) PUB12.

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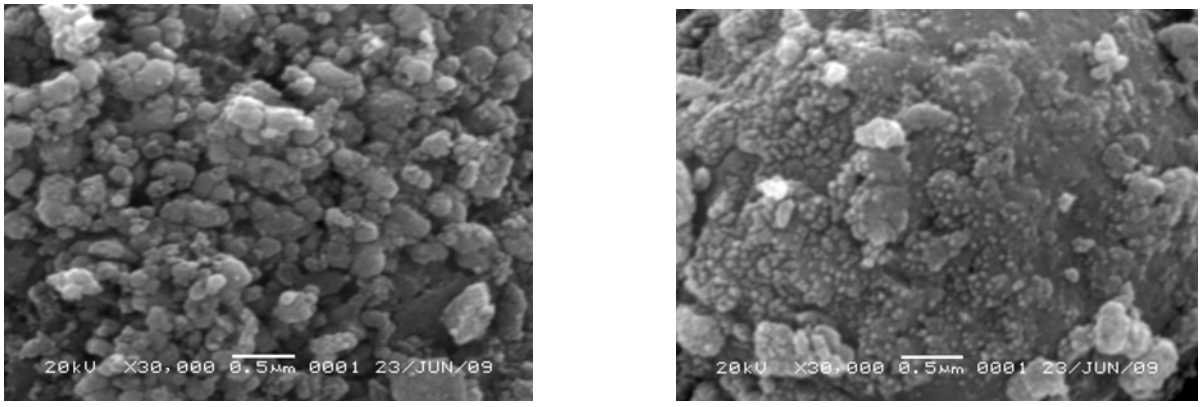

(a) (b)

Figure 6. SEM picture of powders synthesized by high power ultrasonic processor (a) PUP1 and (b) PUP2 (Reprinted from Timuda, et.al., 2010 [13]).

All powders, including Degusa P25, were used to build dye sensitized solar cell. All cells showed reactive and instant current - voltage response in the presence of light. The performance of the cells was measured, and the results were presented in Table 3. The typical J-V curve of the cells was presented in Figure 7.

Several parameters were observed to know the solar cell performance. These parameters are open circuit voltage (V_{OC}), short circuit current density (J_{SC}), and the Fill Factor (*FF*). *FF* is defined as the comparison between maximum power produced by the cell ($P_{max} = (VxI)_{max}$) with the product of open circuit voltage and short circuit current [2]:

$$FF = \frac{P_{\max}}{V_{OC} x I_{SC}} = \frac{(VxJ)_{\max}}{V_{OC} x J_{SC}} \quad (1)$$

This value represents the comparison between actual performance and the ideal performance of the cell. The ideal Fill Factor value is unity (100%).

From the J-V curve (Figure 7), it can be seen that the top three biggest short circuit current density are all achieved by cells using titania powder prepared by low power ultrasonic bath. They are 1.40, 1.20 and 1.14 mA/cm^2 for sample CPUB8, CPUB12 and CPUB4, respectively. The short circuit current density for these samples is bigger than the one prepared using comercial powder, CP25 (0.89 mA/cm^2). This result shows that the titania powders prepared by low power ultrasonic bath can be well facilitating electronic transfer between the Ruthenium 470 dye and the conductive glass, and their current production performance are even better compared to the commercially available, Degusa P25. This is probably because the crystalline size of the titania particles prepared by low power sonication are smaller compared to the commercial powder (Table 2). Furthermore, the crystalline phase of this powder is similar to the Degusa P25 (mix of Anatase and Rutile). So, the small crystalline size can

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give more effective electronic transfer from the excited state dye molecule to the conductive band of the titania nanocrystalline particle (Figure 2).

Meanwhile, the short circuit current density of CPUP1 and CPUP2 samples which were using titania powder prepared by high power ultrasonic processor is lower than the CP25's. They are 0.63 and 0.47 mA/cm^2 for CPUP1 and CPUP2, respectively. This result shows that although titania powders prepared by high power ultrasonic processor can fascilitate electronic transfer between dye and conductive glass, their current production performances are still poorer compared to commercially available titania powder, Degusa P25. This is probably because the crystalline phase of the titania prepared by high power sonication is Anatase which is different compared to the commercial titania powder (mixture of Anatase and Rutile). Although the crystalline phase of these particles are smaller than Degusa P25, the absence of Rutile phase in the titania powders is reducing the ability of transfering electron from the dye molecule to the conduction band of the titania particle.

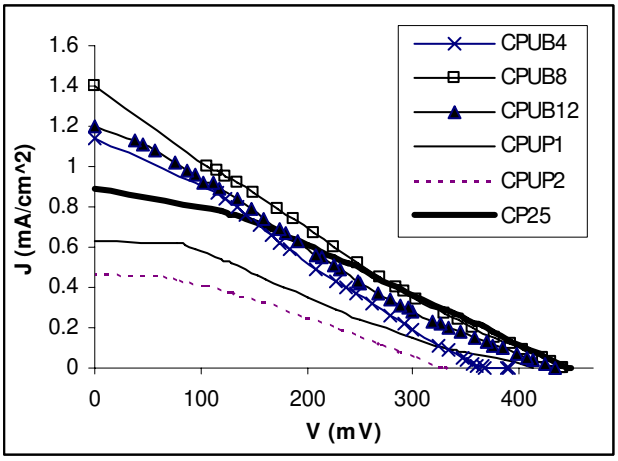

Figure 7. J-V Curve of the Dye Sensitized Solar Cells.

Table 3. Solar Cells Performance

Sample	V_{OC} (mV)	J_{SC} (mA/cm^2)	P_{max} (µW/cm^2)	FF
CPUB4	390	1.14	110.36	0.24
CPUB8	442	1.40	138.01	0.22
CPUB12	434	1.20	120.75	0.23
CPUP1	413	0.63	72.09	0.27
CPUP2	333	0.47	52.93	0.33
CP25	450	0.89	124.75	0.31

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The open circuit voltage (V_{OC}) for all samples using synthesized powders is smaller but near the V_{OC} value of CP25 (450 mV). The closest one is the CPUB8 (442 mV), while the smallest is the CPUP2 (333 mV). This is probably because the powders produced from sonochemical method were agglomerated, as can be seen from the SEM picture (Figure 5 and 6), so the active surface area of the titania nanoparticle is reduced. Thus, the amount of dye molecule which could be attached to it is relatively smaller compared to the cell prepared using Degusa P25 powder (CP25 cell).

Although the short circuit current density of the solar cell samples prepared using titania powder synthesized by low power ultrasonic bath is better than the one prepred by Degusa P25 powder, the fill factor of these samples are low. They are 0.24, 0.22 and 0.23 for samples CPUB4, CPUB8 and CPUB12, respectively, which is lower than the fill factor of CP25 (0.31). Meanwhile, the samples prepared using powder synthesized by high power ultrasonic processor has bigger fill factor than those using low power (0.27 and 0.33 for CPUP1 and CPUP2, respectively). In general, all the solar cells produced exhibit low fill factor. Probably, this is caused by the use of carbon as counter electrode's catalyst, which is known to have lower catalytic activity than the standard, platinized counter electrode.

CONCLUSION

Nanocrystalline TiO_2 particles synthesized by sonochemical methods are applicable as semiconductor material for dye sensitized solar cell which show good current-voltage respons in the presence of light, comparable with the commercially available TiO_2, Degusa P25. Short circuit current density of solar cell samples made using nanocrystalline TiO_2 particle synthesized by low power ultrasonic bath are bigger than the sample prepared using commercial TiO_2 nanoparticle, Degusa P25. In contrary, the solar cell samples made using nanocrystalline TiO_2 particle synthesized by high power ultrasonic processor show the opposite. Open circuit voltage of all solar cell samples prepared using synthesized TiO_2 particle are below but bear the open circuit voltage of the sample prepared using Degusa P25 as semiconductor material. Fill factor of all samples, including the one prepared using Degusa P25, is low which is probably due to the low catalytic activity of carbon-coated counter electrode used.

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