IOP Conference Series: Materials Science and Engineering

PAPER • **OPEN ACCESS**

TiO_2 Nanostructure Synthesized by Sol-Gel for Dye Sensitized Solar Cells as Renewable Energy Source

To cite this article: A H Ramelan *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **176** 012013

TiO_2 Nanostructure Synthesized by Sol-Gel for Dye Sensitized Solar Cells as Renewable Energy Source

A H Ramelan[1], S Wahyuningsih[1], S Saputro[1], E Supriyanto[2], and Q A Hanif[1]
[1]Sebelas Maret University (UNS), Jl. Ir. Sutami No. 36A Surakarta 57126, Indonesia.
[2]Jember University (UNEJ), Jember 68188 Indonesia.

E-mail: aramelan@mipa.uns.ac.id

Abstract. The use of renewable materials as a constituent of a smart alternative energy such as the use of natural dyes for light harvesting needs to be developed. Synthesis of anatase titanium dioxide (TiO_2) and fabrication Dye-Sensitized Solar Cell (DSSC) using dye-based of anthocyanin from purple sweet potato (*Ipomoea batatas* L.) as a photosensitizer had been done. Synthesis TiO_2 through sol-gel process with the addition of triblock copolymer Pluronic F127 template was controlled at pH 3 whereas calcination was carried out at a temperature of 500 °C, 550 °C and 600 °C. The obtained TiO_2 were analyzed by XRD, SAA, and SEM. The conclusion is anatase TiO_2 obtained until annealing up to 600 °C. Self-assembly Pluronic F127 triblock copolymer capable of restraining the growth of TiO_2 crystals. Retention growth of TiO_2 mesoporous produces material character that can be used as builders photoanode DSSC with natural sensitizer anthocyanin from purple sweet potatoes. Based on the analysis of X-ray diffraction patterns and surface area analyser, the higher the calcination temperature the greater the size of the anatase crystals is obtained, however, the smaller its surface area. Purple sweet potato anthocyanin's dyed on to TiO_2 was obtained a good enough performance for DSSC's and gain the optimum performance from DSSC's system built with mesoporous TiO_2 annealed 550 °C using flavylium form anthocyanin.

1. Introduction

Environmental pollution has increasingly become a worldwide concern in the past few decades. Thus, how to enhance the efficiency of natural energy use and to recycle regenerated energy has become an important research field.

Photochemical reactions have been extensively studied for water decomposition, degradation of toxic organic pollutants, organic synthesis, dye-sensitized solar cells, and energy conversion [1,2]. Titanium dioxide (TiO_2) is one of the most widely used in photocatalytic application due to strong oxidizing power of its holes, its redox selectivity, high photostability, and easy preparation. An important requirement for high TiO_2 photocatalytic efficiency is a large surface area which increases both amount of photon generated electron-hole pairs and surface adsorbates. A number of methods such as chemical precipitation [3], microemulsion [4], hydrothermal crystallization [5], and sol-gel [6] have been used to enlarge specific surface area of TiO_2, mostly, by reducing the particle size down to nanoscale. Sol-gel is one of the most successful techniques for preparing nanosized metallic oxide materials [7]. Previously, we have successfully prepared the TiO_2 nanoparticles by a sol-gel procedure [2].

A DSSC that pioneered by Grätzel and O'Regan typically consists of a monolayer of photoactive dye molecules anchored onto the nanoparticles of a wide band gap semiconductor, an electrolyte and a counter electrode [8]. Early DSSC use transition metal coordinated compounds (e.g ruthenium polypyridyl complexes) as a photoactive dye [8,9]. Although the costly synthesis and undesired environmental impact of those prototypes call for cheaper, simpler, and safer dyes as alternatives [9,10,11]. Natural pigments, including chlorophyll, carotene, and cyanin, are available in plant leaves, flowers, and fruits and fulfill these requirements. Experimentally, natural-dye sensitized TiO_2 solar cells have reached an efficiency of 7.1% while over 8.0% using synthetic organic dyes [9,12].

Purple sweet potatoes (*Ipomoea batatas L*) that widely available in Indonesia has affordable prices and purple flesh skin that contains a lot of pigment anthocyanin. Anthocyanin can bind to the surface of TiO_2 via hydroxyl groups then form cyanine-Ti2 complex [13,14]. One of the important ways to improve adsorption capacity of anthocyanin to TiO_2 surface is enhanced surface area. Triblock copolymer in the sol-gel synthesis of TiO_2 was introduced to build self-assembly arrange mesoporous TiO_2 structure.

In this paper, we examine the effect of annealing temperature on the structural and electronic properties of TiO_2 nanostructures based films from 500 to 600 °C. It is found that the higher the calcination temperature the greater the size of the anatase crystals. Self-assembly of Pluronic F127 triblock copolymers have capable to restrain the growth of TiO_2 crystals. Purple sweet potato anthocyanin's dyed on to TiO_2 was obtained a good enough performance for DSSC's. The optimum performance from DSSC system was built with TiO_2 annealed 550 ^{o}C using flavylium form anthocyanin at initial pH 3.

2. Experimental

2.1. Synthesize Titanium Dioxide

Chemicals used for the synthesis of TiO_2 is $TiCl_4$ (E.Merck) Pluronic F127 i.e. $(PEO)_{100}(PPO)_{65}(PEO)_{100}$ (Aldrich), and ethanol (E.Merck). The titania nanoparticles were synthesized by drop wise addition of titanium tetrachloride: $TiCl_4$ in ethanol and Pluronic F127. 6 g Pluronic F127 dissolved in 76 mL of ethanol, then added 3.5 mL of $TiCl_4$ in order to obtain the mole ratio of Pluronic F127: ethanol: $TiCl_4$ = 1.0: 0.41: 21.7 in order to obtain pH 3. The solution was heated at 40 ^{o}C for 7 days for the aging process to obtain a gel. The reaction was performed at room temperature while stirring under a fume hood due to the large amount of Cl_2 and HCl gases evolved in this reaction [5]. The gel subsequently was calcinated at a temperature of 500 ^{o}C (A1), 550 ^{o}C (A2) and 600 ^{o}C (A3) for 4 hours with a heating rate 5 °C/min.

2.2. Characterization of TiO_2 materials

X-ray Diffractometer (XRD) patterns were recorded using a Bruker D8 Advance diffractometer equipped with a graphite crystal monochromator, operating with a Cu anode and a sealed X-ray tube. The 2θ scans were recorded using Cu Kα radiation of wavelength 1.54 Å in the range 20-80° with 0.05° step size while the crystallite size was calculated using Scherrer equation:

$$d_c = \frac{k\lambda}{\beta\cos\theta} \qquad (1)$$

While the Surface Area Analysis (SAA) performed by the Brunauer-Emmett-Teller (BET) method from N_2 adsorption isotherms with Quantachrome NOVA 1200e series analysis at 77 K using Nova win & Nova win P. version 10.1. The BET approach was used to evaluate specific surface area from nitrogen adsorption data in the relative pressure (P/P°) range from 0.05 to 0.2. The pore size was calculated using the BJH method from the desorption branch of the isotherm.

The surface morphology of TiO_2 was determined using a FEI Quanta 250 Scanning Electron Microscope (SEM). Solar energy conversion efficiency (the photocurrent-voltage (I-V) curve) was measured by using two computerized digital Keithley multimeters under simulated sunlight (AM 1.5, 1000 mW/cm^2).

2.3. DSSCs Assembling

DSSCs were assembled following the procedure described in the literature [6], the catalyst-coated counter electrode was placed on the top so that the conductive side of the counter electrode faces the TiO_2 film. The iodide electrolyte solution was placed at the edges of the plates. The liquid was drawn into the space between the electrodes by capillary action. Two binder clips were used to hold the electrodes together.

3. Results and Discussion

3.1. Characterization of Crystalline TiO_2 XRD

Study of synthesis of TiO_2 by sol-gel process through the addition of Pluronic F127 as a template is done on the condition with several calcination temperature. The purpose of this stage is to investigate the effect of temperature on the degree of crystallinity and the crystal size of anatase TiO_2 (Figure. 1).

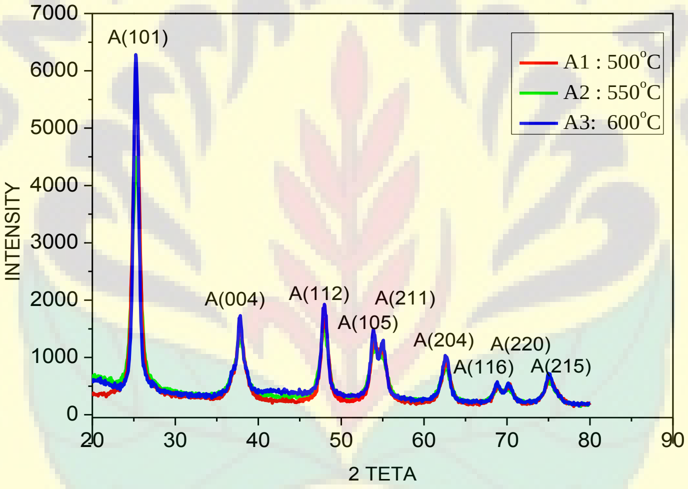


Figure 1. XRD Characterization on TiO_2 Powder Diffraction Patterns (A1, A2 and A3)

All samples synthesis of TiO_2 powder (A1, A2 and A3) have good crystallinity with high intensity and pure anatase structure shown in Figure 1. Good crystallinity helps the diffusion of electrons in the TiO_2 to be faster; thereby will improve the efficiency of solar cells performs. Synthesis of TiO_2 powder as samples A1, A2 and A3 produce pure anatase phase.

All crystalline TiO_2 obtained below 15 nm in size (Table 1). Annealing temperature affects the growth of TiO_2 crystals. The increasing calcination temperature up to 600 °C only able to grow crystals up to a size of 11-12 nm. Triblock copolymer acts as a template as well as crystal growth inhibitors. The additions Pluronic F127 can withstand rapid crystal growth so affect the crystallinity of TiO_2 obtained. Hindered the growth of crystal nucleus can prevent the formation of rutile. It also plays roles in modulating the mesostructure, surface area, pore size and wall thickness, as well as thermal stability of the resultant mesoporous TiO_2 [15].

3.2. Surface area analysis

Upon the synthesis of mesoporous TiO_2, crystallinity and surface area are directly related to the calcination temperature. Annealing temperature also affects the formation of mesoporous structure, increasing annealing temperature can increase the pore size is likely due to a more optimum pore opening and more complete combustion of the template. But increasing annealing temperature decreases the pore volumes due to collapse of mesoporous structure. In general, high crystallinity requires high calcination temperature. However, the employment of high temperature usually leads to undesirable crystal grain growth, a total collapse of mesoporous framework, and a remarkable decrease of surface area (Table 1). Thus, only semicrystalline TiO_2 with small nanocrystals embedded in an amorphous matrix can be obtained, which greatly impedes its applications. The amorphous or semicrystalline TiO_2 easily suffers from fast electron−hole recombination owing to a large number of defects. Therefore, high crystalline TiO_2 with fewer surface defects is urgently desired to improve the conversion efficiency of solar energy and optimize the fast mass and charge transport [15].

TiO_2 from calcination of 500 °C has the highest surface area, whereas TiO_2 synthesized by calcination treatment at 600 °C has the lowest surface area, but it has the highest pore radius (Table 1). It is based on the crystal structure of TiO_2; higher calcination temperature resulted in the collapse of the mesoporous structure and lead to the formation of rutile phase with a larger crystal size than anatase phase and to increase the volume of the crystal grain size.

Table 1. Crystals Size and Surface Area Analysis Results of anatase TiO_2 Sample

	FWHM	D (nm)	Surface Area (m^2/g) BET	Pore radius (nm) BJH
A1	1.15448	7.52508	112.723	6.3
A2	1.0031	8.65969	98.723	4.9
A3	0.77327	11.2228	71.354	9.0

3.3. *Surface Morphology*

Figure 2 shows the scanning electron micrograph of a typical TiO_2 (anatase) film deposited by slip-casting on a conducting glass FTO that serves as current collector. The film thickness is typically 10–15 µm and the TiO_2 mass about 1-3 mg/cm^2. Analysis of the layer morphology shows the porosity to be approximately 45%. The slip-casting TiO_2 on FTO substrate appeared to be smooth under visual inspection although the film showed some inhomogeneity at the edges. The SEM micrograph of TiO_2 film (Figure 2) shows a rough surface layer containing large TiO_2 chunks in which the individual TiO_2 particles are hardly visible. The chunk structure is likely formed through the aggregation of bar-shape TiO_2 arranged in a side-by-side configuration. Another possible reason for the appearance of irregular chunks on the TiO_2 layer is the stress-induced surface rumpling caused by the fast cooling after 550 ºC calcinations.

3.4. *The absorbance characteristics of Anthocyanin Dye Purple sweet potato (Ipomoea L.,)*

The pH values of anthocyanin dye were obtained through different preparation method. Acetic acid concentrations were 0.1% (v/v), 0.15% (v/v), and 0.2% (v/v). The result anthocyanin dye solutions have pH value of 5, 3, and 1 respectively. The lower pH condition, the more anthocyanin can be extracted. Therefore, the lower pH condition, the higher anthocyanin dye concentration reached indicating by the higher absorbance value.

The result of absorption character of anthocyanin dye at various pH (Figure 3) have the similar wavelength region of 450 nm to 600 nm. The maximum wavelength around at 530 nm was shifted by pH value. The sample pH-1 has the highest absorbance, indicate the highest anthocyanin content. At acidic pH, the dye exists mostly in the flavylium form in solution, but upon adsorption to TiO_2, the equilibrium between the adsorbed forms is thought to be shifted toward the quinonoidal form since the complexed cyanin appears purple [14]. There is an equilibrium between flavylium cation and quinonoidal form. A wide repertoire of colors in the red-blue range is available to anthocyanins as a result of their complexation with other polyphenols, pectins, and metal ions [14]. In acidic solution, the purple sweet potato anthocyanin dye appears red and has a strong absorption band at 530 nm. This visible absorption band is pH sensitive, causing the dye to appear red (flavylium form) in acidic solution and purple (quinonoidal form) as pH increases, and it is deprotonated. The visible absorption band also shifts to the red upon complexation with titanium dioxide. It is thought that the titanyl groups of titanium dioxide surface compete with the protons, displacing them and shifting the flavylium-quinonoidal equilibrium toward the quinonoidal form in a mononuclear bidentate coordination complex with metal ions.

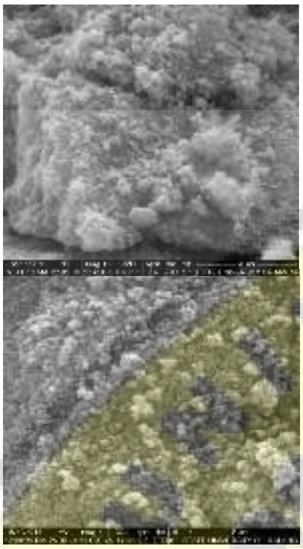


Figure 2. Morphology of TiO_2 film used in the DSSC with magnification 25,000 (top) and 50,000 (bottom).

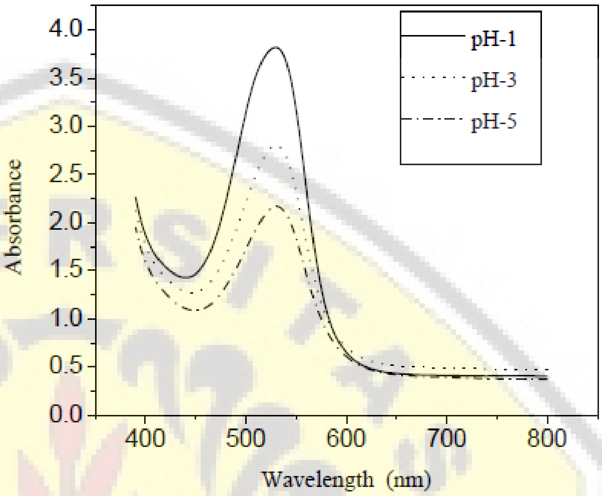
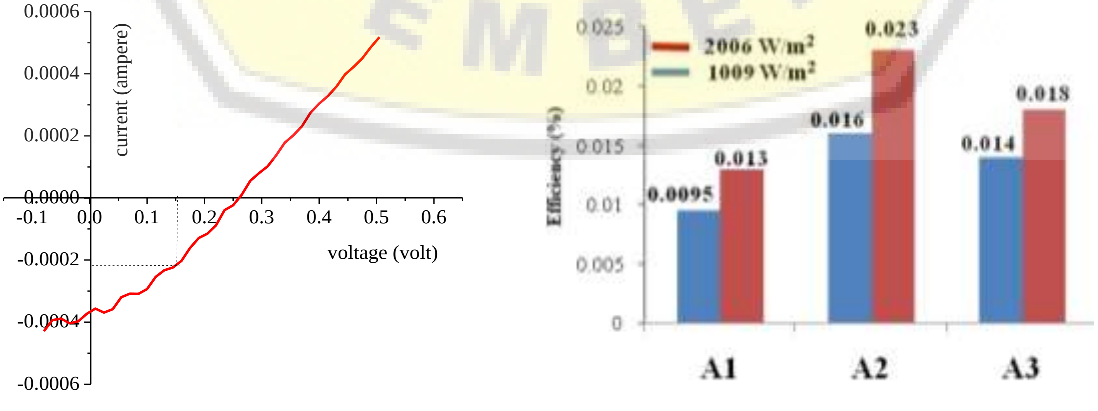


Figure 3. The visible spectrum of anthocyanin dye purple sweet potato (*Ipomoea batatas* L.,) at various pH conditions.

3.5. *The Current-Voltage Characteristics of DSSC*

The calcination temperature variations on the synthesis of anatase TiO_2 has an effect on the characteristics of TiO_2 powder and the performance of solar cells (Figure 4). Increasing the annealing temperature increases the pore size of TiO_2 material but lose surface area, thus affecting the adsorption of the dye. Immersion dye on TiO_2 surface requires a certain optimal time, and increased with time added. Irradiation of the DSSCs increased by 2006 W/m^2 from 1009 W/m^2 also increased the efficiency of the solar cell (Figure 4). The efficient of the solar cells decreased after 7 days, this is due to the evaporation of the electrolyte KI + I_2.



(a) (b)

Figure 4. (a) I-V curves of A2 and (b) Effect of intensity irradiation on all DSSC samples.

The pH 1 anthocyanin dye has a characteristic absorbance and the best conductivity value, thus also improving the performance of DSSCs. Anatase TiO_2 with high intensity character showed high crystallinity. The high crystallinity increases the electron diffusion capability and is able to reduce the recombination of electrons and holes after photo excitation process.

Finally, its performance will increase the efficiency of DSSCs. The sample A2 (550 °C calcination treatment) had gave the best performance DSSC's with the highest efficiency due to the crystal size of (8.3 nm), large surface area (87.2 m^2/g), and high absorption intensity. Performance measurement with Keithley I-V meter with 1000 W/m^2 light intensity resulting DSSC efficiency of 0.0095 % (A1), 0.016 % (A2), and 0.014 % (A3). By the controlling of the pH condition in the sol gel titania preparation at pH 3 and the anthocyanin dyed on to TiO_2, we obtained anthocyanin-sensitized anatase TiO_2 have a good enough performance for DSSC's (Figure 4).

4. Conclusion

Synthesis of TiO_2 through the sol-gel process with addition of Pluronic F127 at pH 3 produced pure anatase TiO_2. Treatment of calcination temperature affects the crystallinity, surface area and pore performance of TiO_2. The higher the calcination temperature gives the better crystallinity of TiO_2, and the larger the pore distribution but lower the surface area. The anthocyanin dye at pH 1 has the highest conductivity. The conductivity properties were influenced by the structure of the dyes. The sample A2 (550 °C calcination treatment) had gave the best performance DSSC's due to the crystal size (8.3 nm), large surface area (87.2 m^2/g), and high absorption intensity. By the controlling of the pH condition in the sol gel titania preparation at pH 3, and the anthocyanin dyed on to TiO_2 was obtained a good enough performance for DSSC.

Acknowledgment

The authors would like acknowledge the Directorate General of Higher Education (DIKTI) the Ministry of Education and Culture (KEMENDIKBUD) The Republic of Indonesia for financial support this project.

References

[1] Assmann S E, Widoniak J, and Maret G 2004 *Chem. Mat*. **16** 6-11
[2] Sivakumar S, Sibu C P, Mukundan P, Krishnapillai P, and Warrier K G K 2004 *Mat. Lett*. **58** 2664-2669
[3] Lee L H and Chen W C 2001 *Chem. Mat*. **13** 1137-1142
[4] Allen N S, Edge M, Ortega A, Liauw C M, Stratton J, and McIntyre R B 2002 *Polym. Degrad. Stab*. **78** 467-478
[5] Chang H, Kao M J, Chan T L, and Kuo H G 2011 *Am. J. Engg. & Applied Sci*. **4** (2) 214 – 222
[6] Ramelan A H, Harjana, and Sakti L S 2012 *Europe Photonics* **435** 81-86
[7] Wongcharee K, Meeyo V, Chavadej S 2006 *Sol. Mat*. **11** 005
[8] O'Regan B and Grätzel M 1991 *Nature* **353** (6346) 737–740
[9] Meng S, Ren J and Kaxiras E 2008 *Nano Letters* **8** 3266-3272
[10] Wang G, Wang L, Xing W and Zhuo S 2010 *Mat. Chem. Phys.* **123** 690-694
[11] Adachi M, Jiu J, and Isoda S, 2007 *Current Nanosci*. **3** 285-295
[12] Sirimanne P M and Perera V P S 2008 *Phys. Stat. Sol.* **245** 1828 – 1833
[13] Zhan J, Peng Sun H J, Xiaohang S 2006 *An Investigation of The Performance of Dye Sensitized Nanocrystalline Solar Cell with Anthocyanin Dye and Ruthenium Dye as The Sensitizers* [Thesis] Roskilde University
[14] Cherepy N J, Smestad G P, Gratzel M, and Zhang Z 1997 *J. Phys. Chem. B* **101** 9342-9351
[15] Li W, Wu Z, Wang J, Elzatahry A A, and Zhao D 2014 *Chem. Mater.* **26** 287−298