Advanced Materials Research Vol 1105 (2015) pp 141-145
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doi:10.4028/www.scientific.net/AMR.1105.141
Submitted: 2015-01-23
Accepted: 2015-01-23
Online: 2015-05-20

Synthesis of Anatase and Rutile TiO2 Crystals for High-Performance Dye-Sensitized Solar Cells

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Keywords : TiO2, Nanostructures, Sol-Gel, DSSC.

Abstract. TiO_2 nanosize particles have attracted significant interest of materials scientists and physicists due to their special properties and have attained a great importance in several technological applications such as photocatalysis, sensors, solar cells and memory devices. TiO_2 nanoparticles can be produced by a variety of techniques ranging from simple chemical to mechanical to vacuum methods, including many variants of physical and chemical vapour deposition techniques. In the present research work we report the synthesis of TiO_2 nanoparticles by Sol-Gel technique. The characterization of particles was carried out by XRD and SEM techniques. The importance and applications of these nanoparticles for solar cells are also discussed in this work. Recently, the importance of tailored particles has been recognized in a number of applications such as solar cells and photonic crystals. Among the many metal oxides and their inorganic-organic hybrid materials used for the above applications, one of the most important and complex in this regard is titanium dioxide (titania). In this study, the processing parameters in an alkoxide free sol-gel synthesis of anatase titania nanoparticles were investigated. Factors affecting the sol-gel process include the reactivity of inorganic titanium salt, calcinations temperature, the influence of varying stirrer speeds on the formation of anatase particles, and the nature of hydrolytic solvent and peptisation reagent. By varying these processing parameters, materials with different microstructure and surface chemistry can be obtained.

Introduction

Photochemical reactions catalyzed by semiconductors have been extensively studied for water decomposition, degradation of toxic organic polluents, organic synthesis, dye-sensitized solar cells, and energy conversion [1, 2]. In these reactions, photogenerated electrons and holes migrate to the semiconductor surfaces where they can induce reduction and oxidation of adsorbed molecules. Titanium dioxide (TiO_2), in particular, is one of the most widely used and promising materials 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. Besides, in the larger and low surface area TiO_2, the photoexcited generated electron-hole pairs might have recombined in the bulk before reaching the surface of the crystal. 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 [7-9]. Previously, we have successfully prepared the TiO_2 nanoparticles by a sol-gel procedure [2]. The main purpose of this continuous work is to use the same approach to prepare porous TiO_2 nanoparticles yielding increased efficiencies as a result of larger surface area.

Experimental Procedure

The titania nanoparticles were synthesized by drop wise addition of titanium tetrachloride: $TiCl_4$ in ethanol and Pluronic P2243-250G. 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 resulting yellow solution was allowed to rest and cool back to room temperature as the gas evolution ceased. The suspensions obtained were dried in an oven for several hours at 80°C until amorphous and dried TiO_2 particles were obtained. The obtained powder samples were calcined for one hour in a box furnace at temperature ranging from 375 to 600 °C in an ambient atmosphere. XRD patterns were recorded on as prepared and calcined samples 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 at several resolutions using Cu K_α radiation of wavelength 1.54 Å in the range 20-80° with 0.05° step size. The surface morphology of TiO_2 was determined using a FEI Quanta Scanning Electron Microscope (ESEM). 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, 100mW/cm^2).

Results and Discussion

Characterization of Crystalline TiO_2. In Fig. 1 below is shown the X-ray diffraction pattern of the sample. Analysis is performed by comparing the peaks in the sample with the standard peaks of anatase and rutile JCPDF database. In Table 1 are shown the position of the diffraction peaks of anatase and rutile samples and of standard data JCPDF. Based on the diffractogram can be stated that a thin layer of TiO_2 generated in this study are composed of anatase phase (red line) and rutile (blue line).

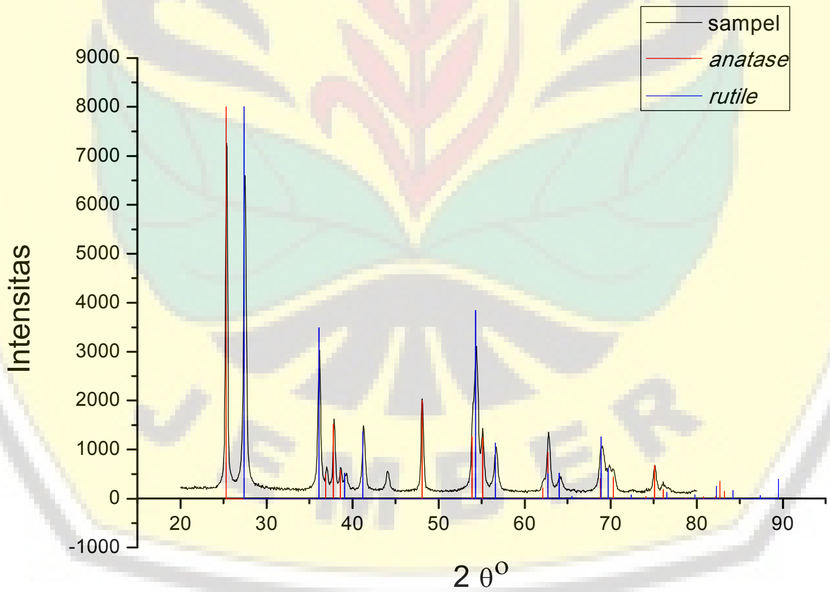


Fig. 1. TiO_2 powder XRD chart results with calcination temperature of 650° along with the standard diffraction pattern JCPDF

Table 1: Comparison of the Peak TiO_2

The peak position 2θ			
Sample	JCPDF		h k l
	Anatase	Rutile	
25.3508	25.325	-	1 0 1
27.5012	-	27.434	1 1 0
36.1525	-	36.077	1 0 1

37.8528	37.841	-	0 0 4
41.3034	-	41.237	1 1 1
48.1045	48.074	-	2 0 0
54.4055	-	54.317	4 8 0
55.1056	55.106	-	2 1 1
56.7058	-	56.622	2 0 0
62.8068	62.750	-	2 0 4
64.1070	-	64.043	3 1 0
69.0578	-	68.999	3 0 1
69.8579	70.346	-	2 2 0
75.1588	75.129	-	2 1 5

Anatase has a tetragonal crystal structure with Ti-O octahedral sharing on the 4 corners, while rutile have tetragonal crystal structure with Ti-O octahedral sharing on 4 sides. At each rutile octahedral structure surrounded by 10 octahedral other, whereas in anatase, each octahedron octahedron surrounded by eight others. The presence of a mixture of anatase and rutile are very favorable for the construction of solar cells due to the presence of rutile in the TiO_2 thin film can also reduce the possibility of recombination of electrons residing in the conduction band [7]. Therefore, a thin layer of TiO_2 produced in this study is quite good as a substrate for dye DSSC system.

Surface Morphology. Fig. 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 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 450 ºC calcinations.

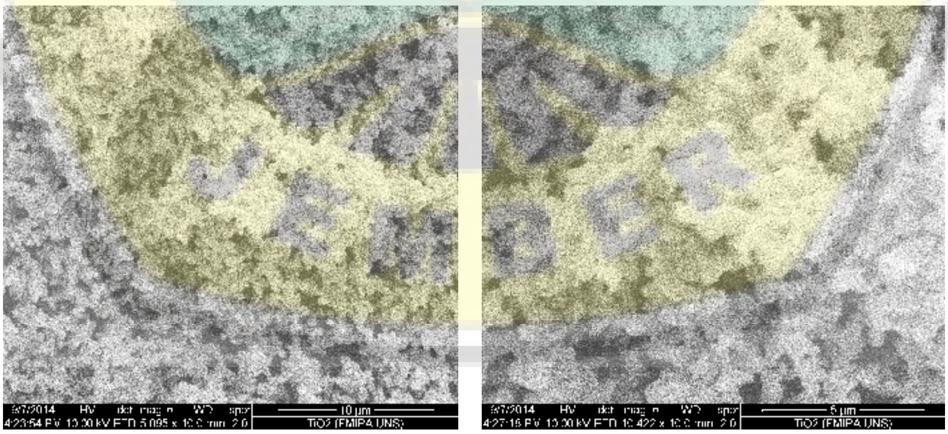


Fig. 2. Scanning electron microscope picture of a crystalline TiO_2 film with a different magnification used in the dye-sensitized solar cell (DSCC).

Characterization of Dye Absorbance. Before being used as a sensitizer, Rosella flower anthocyanin extracts tested absorbance spectrum using UV-Visible Spectrophotometer Lambda 25 with a wavelength range of 350 nm - 800 nm (Fig. 3).

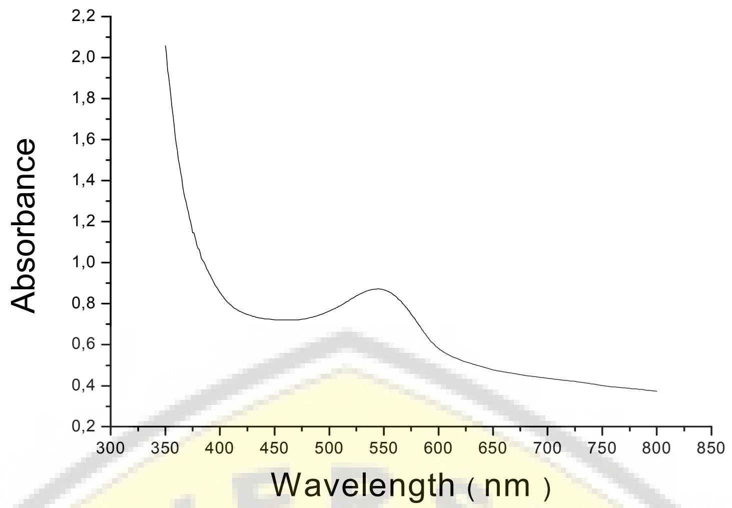
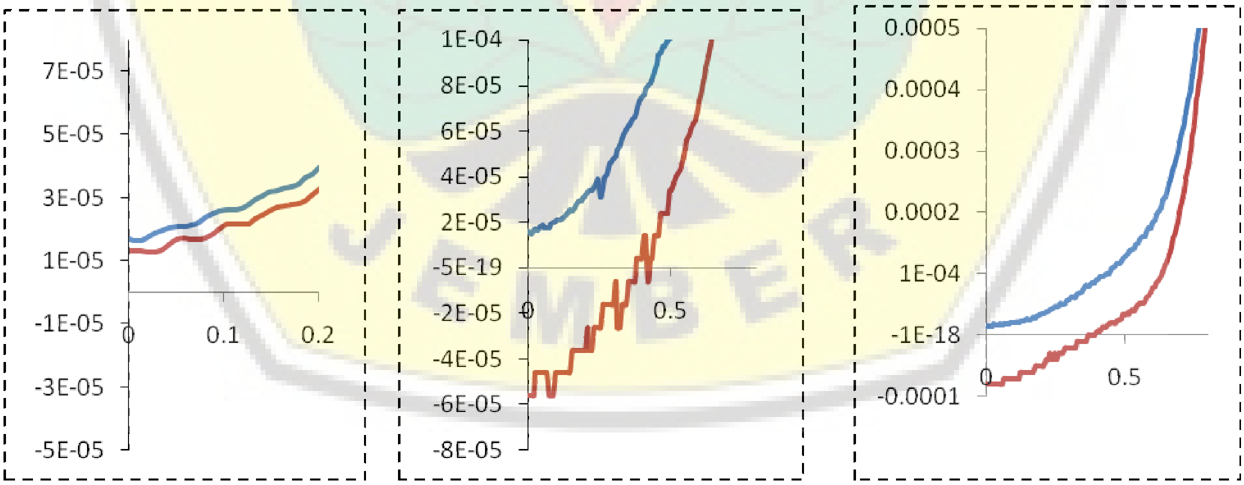


Fig. 3. Anthocyanine absorbance graphs Rosella Flowers

Absorbance spectrum characterization results showed that the absorption spectra Rosella flower extracts to be around wavelength 440 nm - 620 nm, the wavelength range of visible light.

The Current-Voltage Characteristics of DSSC. To know the current-voltage characteristics of solar cells used IV meter Keithley. DSSC in this assay system acts as a diode, which has handed nature of alternating current. Current results are legible voltage variation curve of I to V were made to determine the performance of DSSC. DSSC performance is strongly influenced by the construction of the DSSC systems, such as the working electrode (working electrode), counter electrode (counter electrode) and an electrolyte solution used. In addition, the performance measurement tool can also affect the DSSC performance measurement. IV curve of each cell DSSC with immersion time variation is shown in Fig. 4.



(blue line: dark current ; red line: light current)

(a) 5 hours immersion (b) 10 hours immersion (c) 15 hours immersion

Fig. 4. Graph I-V characteristics where y-axis : Current I (Ampere) and x-axis : Voltage V (Volt) with the immersion time (a) 5 hours, (b) 10 hours and (c) 15 hours

At 5 hours of immersion obtained an efficiency of 0.0361%. At the 10-hour immersion obtained an efficiency of 0.0592%. At the 15-hour immersion obtained an efficiency of 0.0668%. Wang et.al based research as mentioned in Qin and Peng [10] found that the efficiency of DSSC using dye Ruthenium Complex at 8.2%. Meanwhile, according to Dewi [8] using dye roses obtained an efficiency of 0.0117% for the 36-hour immersion. From the calculation results showed that the longer the soaking, the more dye is attached to the substrate so that the higher the ability to absorb light. The longer the time of immersion in the dye solar cell efficiency higher.

Conclusion

Nanoporous TiO_2 with mesostructure anatase and rutile wall have been successfully prepared using a combination of sol-gel method and block copolymer as a template. $TiCl_4$ was used as a Ti precursor and Pluronic PE6200 acted well as mesoporous template although only short-range pore ordering is observed. Calcination temperature was observed to be an important parameter for mesostructure formation as well as crystallization process. DSSCs were fabricated using a slip casting method. The I-V curve of the solar cell using antocyanine rosella (*Hibiscus sabdariffa*) adsorbed on a nanocrystalline TiO_2 electrode is characterized under light intensity of 100 $mWcm^{-2}$. It is estimated that η value was 0.067% and the FF value was 32.6%.

Acknowledgment

The authors would like to acknowledge the Directorate General of Higher Education (DIKTI) the Ministry of Education and Culture (KEMENDIKBUD) THE REPUBLIK OF INDONESIA for financial support in this project through IPTEKS 2014.

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10.4028/www.scientific.net/AMR.1105

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