

Synthesis and Characterization of Nanostructured Titania Films for Dye-Sensitized Solar Cells

Kyung-Jun Hwang, Seung-Joon Yoo,[†] Sung-Hoon Jung, Dong-Won Park,[‡] Sun-Il Kim, and Jae-Wook Lee*

Department of Chemical and Biochemical Engineering, Chosun University, Gwangju 501-759, Korea

E-mail: jwlee@chosun.ac.kr

[†]Department of Environmental and Chemical Engineering, Seonam University, Namwon 590-711, Korea

[‡]Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongseup, Jeonbuk 580-185, Korea

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The nature and morphology of titanium dioxide films play a significant role in determining the overall efficiency of dye-sensitized solar cell (DSSCs). In this work, the preparation of nanostructured titania particles by sol-gel method (SG-TiO₂) and its characterization were investigated for the application of DSSCs. The samples were characterized by XRD, XPS, FE-SEM, BET and FT-IR analysis. The energy conversion efficiency of SG-TiO₂ was approximately 8.3 % under illumination with AM 1.5 (100 mW/cm²) simulated sunlight. DSSCs made of SG-TiO₂ nanocrystalline films as photoanodes achieved better energy conversion efficiency compared to those prepared using commercially available Degussa P25.

Key Words: Nanostructured titania films, N719 dye, Dye-sensitized solar cell, Adsorption

Introduction

Silicon-type solar cells have been extensively studied because of their high performance and good stability.¹⁻² Compared to the conventional silicon-type cells, dye sensitized solar cells (DSSCs) have been widely investigated because they offer attractive advantages including low cost, less toxic manufacturing, easy scale-up, light weight, and use of flexible panels compared to conventional p-n junction devices.³⁻⁵ Among many metal oxides, nanocrystalline titania materials have been extensively studied because of their interesting physical and chemical properties.

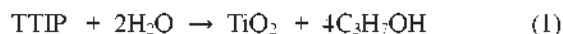
DSSC consists of sensitizing dye, TiO₂ porous film (anode electrode), electrolyte, and opposite electrode (cathode electrode). A light is absorbed by a dye molecule leading to the excitation of the dye to an electronically excited state (S_{adsorbed}^*). The excited dye molecule injects an electron into the conduction band of the TiO₂ electrode and is oxidized (S_{adsorbed}^+). The original state of the dye (S_{adsorbed}) is subsequently restored by electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide couple. The regeneration of the dye by iodide intercepts the recapture of the conduction band electrons by the oxidized dye. The iodide is in turn regenerated by the reduction of triiodide at the cathode electrode. The circuit is completed by electron migration through an external load.^{6,7} It has been known that the nature and morphology of TiO₂ films highly affect the overall conversion efficiency of DSSCs.

This study focused on the synthesis and characterization of nanostructured TiO₂ films for DSSCs. A colloidal SG-TiO₂ suspension was prepared by the sol-gel method based on the hydrolysis of titanium-tetraisoopropoxide. The samples were characterized by XRD, XPS, FE-SEM, BET and FT-IR analysis. The solar cell performances of the TiO₂/dye sensitized nanocrystalline solar cells were evaluated from the over-

all conversion efficiency (η_{eff}), fill factor (FF), open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}).

Experimental

A colloidal TiO₂ suspension was prepared by the hydrolysis of titanium-tetraisoopropoxide (TTIP, Junsei Chemical Co., > 98%) represented by the following reaction:



TTIP was used as a main starting material without further purification. An appreciated amount (20 ml) of TTIP was slowly dropped in ethanol (200 ml) at room temperature for 5 min. Consequently, a drop-wise addition of hydrochloric acid solution (0.05 M) into the TTIP solution was conducted for 24 h under vigorous stirring condition. The suspension was then ultrasonicated at room temperature for 1 h and centrifuged at +4°C and 8,000 rpm for 20 min. The white precipitate formed was filtered and dried at room temperature for 1 h. Finally, the dried TiO₂ particles were calcined at 450°C for 30 min in air gas flow (5 ml/min). For the preparation of TiO₂ thin-film, TiO₂ slurry was prepared by the addition of 2 g TiO₂ particles, 0.68 ml 10% acetyl acetone, 1 g hydroxypropyl cellulose (Mw. 80,000, Aldrich), and 10.68 ml water for 12 h at 300 rpm using a Zr ball mill (Planetary Mono Mill, FRITSCH). Thus, a TiO₂ film was fabricated by coating a precursor paste onto the fluorine-doped SnO₂ conducting glass plates (FTO, 10 Ω/cm², Asahi glass Co., Japan) by using a squeeze printing technique (adhesive tape was used as spacer of ca. 43 μm thickness). The TiO₂ film was treated by heating at 500°C for 2 h because hydroxypropyl cellulose is perfectly removed at over 500°C based on the TG analysis. To fabricate the DSSCs, the prepared thin film electrode was immersed in the N719 dye (Solaronix) solution of 5 × 10⁻⁴ M at 80°C for 24 h, rinsed with

anhydrous ethanol and dried. Pt coated glass-SnO₂:F electrode was prepared as a counter electrode. The Pt electrode was placed over the dye-adsorbed TiO₂ electrode, and the edges of the cell were sealed with sealing sheet (SX 1170-60, Solaronix). Sealing was accomplished by hot-pressing the two electrodes together at 80°C. The redox electrolyte was into the cell through the small holes and sealed with a small square of sealing sheet. The redox electrolyte consists of 0.3 M 1,2-dimethyl-3-propyl-imidazolium iodide (Solaronix), 0.5 M LiI (Aldrich), 0.05 M I₂ (Aldrich), and 0.5 M 4-*tert*-butylpyridine (4-TBP, Aldrich) and 3-methoxypropionitrile as a solvent.

The crystallinity and surface state of the synthesized TiO₂ was characterized by X-ray diffractometer (XRD: D/MAX-1200, Rigaku) using a CuK α X-ray and Ni filter at 35 kV and 15 mA. XPS analysis was conducted using a photoelectron spectrometer VG Scientific MultiLab 2000 system equipped with a non-monochromatic MgK α radiation of 1253.6 eV. The C 1s peak (285.0 eV) was used to calibrate the binding energy values. The film thickness and surface morphology were measured by field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi). The morphology of the TiO₂ electrode was also examined on an atomic force microscope (AFM; CP-2, VEECO) in the non-contact model. Nitrogen adsorption and desorption isotherms were measured for the BET surface areas, pore size and pore volume at 77 K using a Micromeritics ASAP 2010 automatic analyzer. Before the measurements, the samples were outgassed for 2 h in the degas port of the adsorption apparatus. In addition, the pore size distributions were also calculated from the adsorption branches of the isotherms by using the Barrett, Joyner, and Halenda (BJH) method.⁸ Moreover, the Fourier transform infrared spectrophotometer (FT-IR: DA-8, BOMEM) was used for the analysis of the bonding structure between dye molecules and TiO₂ surface. The adsorption amount of TiO₂ film was measured by completely desorbing the adsorbed dye molecules from TiO₂ film using 0.1 M NaOH solution /ethanol (50/50, v/v). The photocurrent-voltage (*I*-*V*) curves were measured using a source measure unit under irradiation of white light from a 1,000 W Xenon lamp (Thermo Oriol Instruments, USA). The incident light intensity and the active cell area were 100 mW/cm² and 0.25 cm², respectively. The *I*-*V* curves were used to calculate the short-circuit current (*I*_{sc}), open-circuit voltage (*V*_{oc}), fill factor (*FF*), and overall conversion efficiency (η_{eff}) of DSSCs.

Results and Discussion

The results of the characterization of the SG-TiO₂ nanoparticles are depicted in Figure 1 and Figure 2. Figure 1 shows XRD patterns of SG-TiO₂ synthesized in this work and commercial TiO₂ (Degussa P25) with heat treatment at 450 °C for 30 min. SG-TiO₂ showed single-phase anatase nanocrystallites almost without rutile, while P25-TiO₂ has the mixture of anatase and rutile phases (8:2). From the line width of XRD peak of the samples, we have also roughly estimated the particle sizes of TiO₂ using the Scherrer's equation:⁹ 22 nm for P25-TiO₂ and 14 nm for SG-TiO₂. XPS analysis provides important information about physicochemical changes of porous materials.

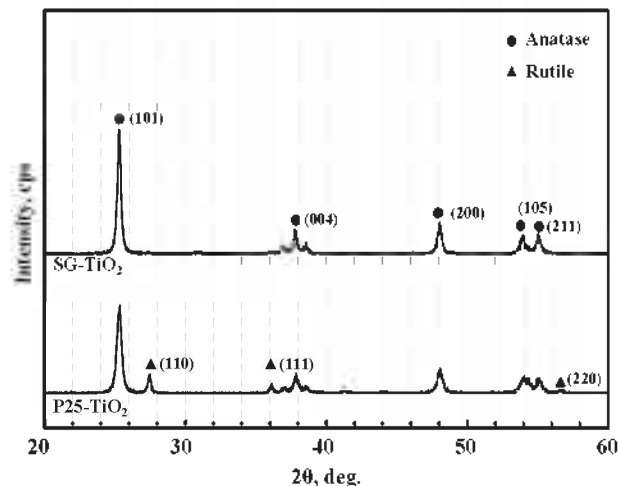


Figure 1. X-ray diffraction spectra of SG-TiO₂ and P25-TiO₂.

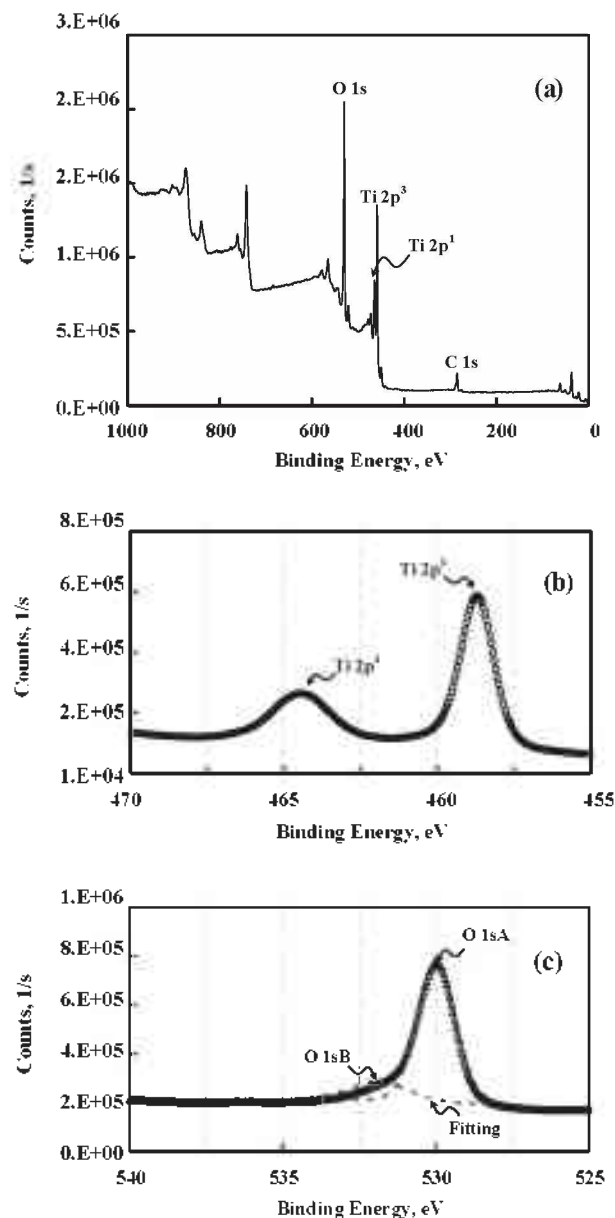


Figure 2. XPS survey spectra of (a) SG-TiO₂ film, (b) Ti 2p core level, and (c) O 1s core level.

Figure 2 is the quantitative XPS analysis of SG-TiO₂. The survey spectrum of the SG-TiO₂ contains the Ti 2p and O 1s peaks of the titanium dioxide. The Ti 2p¹ and Ti 2p³ spin-orbital splitting photoelectrons are located at binding energies of 464.4 eV and 458.7 eV, respectively (Figure 2(b)). The O 1sA peak of SG-TiO₂ is shown at 530.64 eV and a shoulder located toward the side of higher binding energies (Figure 2(c)). The contents of Ti and O of SG-TiO₂ are 27.01% and 52.23% corresponding to closely Ti⁴⁺ state. Generally, similar results are observed in TiO₂ porous materials.^{10,11}

To characterize the nanocrystalline TiO₂ film properties, FE-SEM, XPS, and BET measurements were performed. Figure 3(a, b) exhibits the FE-SEM images of surface morphology and the cross-section of TiO₂ thin films coated on FTO glass. TiO₂ film has a porous structure in which the TiO₂ spherical nanoparticles are all bonded together through a sintering process. The spherical nanoparticles of P25-TiO₂ (Figure 3(a)) and SG-TiO₂ (Figure 3(b)) are well distributed and maintain their original size and shape. The pattern reveals the TiO₂ particles to be composed of a three-dimensional network of interconnected particles. We also found that the particle size of SG-TiO₂ was smaller than that of P25-TiO₂. The film thickness was ca. 3–4 μm. These results are consistent with those estimated from XRD data. According to the AFM images of P25-TiO₂ (Figure 3(c)) and SG-TiO₂ (Figure 3(d)), the films have heterogeneous surface with a few separated islands. The surface roughness is summarized in Table 1. Thus, it was found from these results that nanoparticle TiO₂ with a well ordered structure and high surface area can be successfully synthesized.

The N₂ adsorption-desorption isotherm and pore size distribution of the samples are depicted in figure 4(a). It was also observed from N₂ adsorption-desorption isotherm measurement. The physico-chemical properties of commercial P25-TiO₂ and synthesized SG-TiO₂ are listed in Table 2. It has been known that the anatase TiO₂-based solar cells exhibit better photovoltaic characteristics compared to the rutile TiO₂-based solar

cells because of higher surface area (i.e., higher amount of dye adsorbed).¹² The surface area determined by nitrogen adsorption/desorption isotherm data of SG-TiO₂ was found to be 69

Table 1. Physico-chemical properties of TiO₂ films

Characteristic	Unit	Degussa P25	SG-TiO ₂
Rms Roughness of AFM	Nm	25.14	28.86
Average Roughness of AFM	Nm	20.31	22.96
Adsorption amount of N719	mM/cm ²	7.612 × 10 ⁻⁵	12.693 · 10 ⁻⁵

Table 2. Physical properties of TiO₂ particles

Property	Unit	Degussa P25	SG-TiO ₂
Surface area (BET)	m ² /g	50 ^a (40.19 ^b)	69.54
Pore volume	cm ³ /g	0.19 ^b	0.14
Average pore size (BJH)	Å	69 ^b	62
Average particle size	nm	approx. 21 ^{a,*}	approx. 15
Density	g/l	approx. 130 ^d	128
Purity	%	> 99.5 ^e	-

^afrom the manufacturer's report, ^bmeasured in this work, ^{*}the size of the primary particles

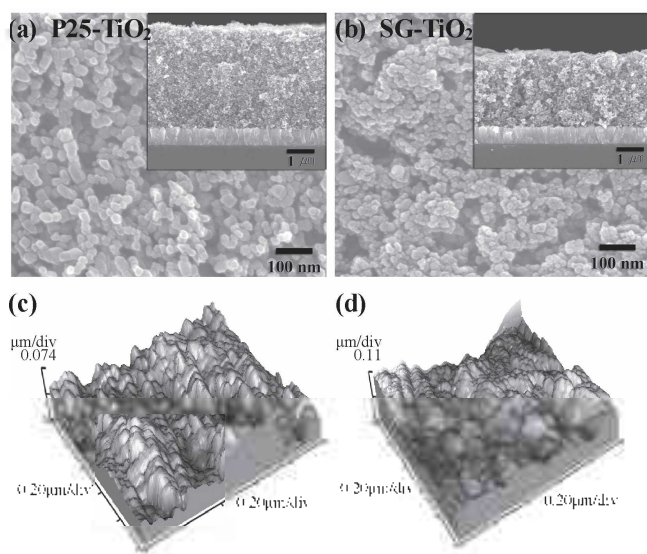


Figure 3. FE-SEM images of (a) P25-TiO₂ film, (b) SG-TiO₂ film and AFM image of (c) P25-TiO₂ film, (d) SG-TiO₂ film.

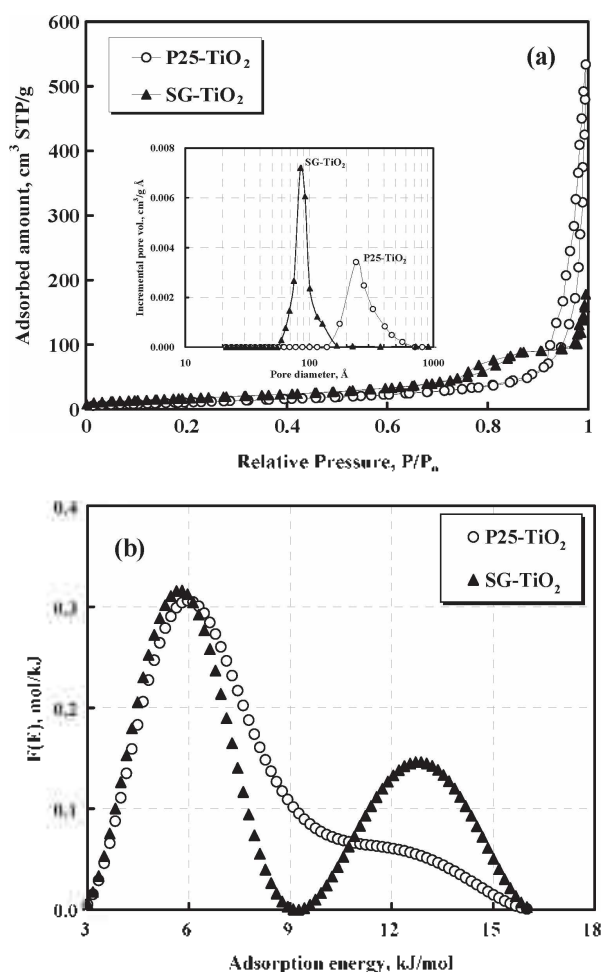


Figure 4. (a) N₂ gas adsorption and desorption isotherms and pore size distribution of TiO₂ films. (b) Adsorption energy distributions of SG-TiO₂ and P25-TiO₂ films.

m^2/g and the average pore size calculated by BJH method was 62 Å.

Adsorption energy distributions have been extensively applied for characterizing the numerous adsorption systems and understanding the surface energy heterogeneities. In general, geometrical heterogeneity comes from the differences in size and shape of pores while chemical heterogeneity is associated with different functional groups and various surface defects on a surface. The fundamental adsorption integral equation for energetically heterogeneous solid surfaces is given as follows:¹³

$$\theta(p) = \int_{E_{\text{min}}}^{E_{\text{max}}} \theta(p, E) \cdot F(E) \cdot dE \quad (2)$$

where p is the equilibrium concentration. E is the adsorption energy. $F(E)$ is the adsorption energy distribution function, $\theta(p, E)$ is a local adsorption isotherm with an adsorption energy. $\theta(p)$ is the experimental adsorption isotherm data. The adsorption integral equation is the well-known linear Fredholm integral equation of the first kind, and the calculation of adsorption energy distribution is an ill posed problem.¹⁴ The generalized nonlinear regularization method can avoid the difficulties resulting from the ill-posed nature of an adsorption integral equation.¹⁵ In this work, therefore, we employed the generalized nonlinear regularization method based on smoothness constraint (i.e., Tikhonov regularization) and edge preserving regularization methods.¹⁶

Figure 4(b) shows the adsorption energy distribution functions of TiO_2 films formed on the FTO glass. The adsorption energy distribution curves of SG- TiO_2 synthesized in this work exhibited two peaks indicating the existence of energetically two different adsorption sites. The first and second adsorption energy curves were distributed mainly in the range of 3–9 and 9–16 kJ mol^{-1} , respectively. The energy intensity of the first peak is about 2 times higher than that of the second one. However, the second peak of P25- TiO_2 was not evident compared to the synthesized SG- TiO_2 samples. The energy distribution peaks proceeded to higher energy with the increase of surface area (Table 2). The increase of surface area (i.e., increase in adsorption capacity of dye molecules) will served for the enhanced energy conversion efficiency of DSSCs. It was also found that the shape and the intensity of the adsorption energy distribution curve were highly related with the physical property (i.e., geometrical heterogeneity) and chemical characteristics (i.e., energetic heterogeneity) of nanocrystalline TiO_2 for DSSCs. The results can be successfully applied for the design, synthesis and optimization of nanocrystalline TiO_2 for DSSCs because the adsorption energy distribution functions obtained in this work will offer the fundamental and informative data to fully understand the surface heterogeneity of the nanostructured TiO_2 materials.

Interfacial binding between the dye molecules (N719) and the surface of TiO_2 was investigated by FT-IR spectra of the dye-anchored TiO_2 films. In general, the efficiency of the charge injection process is highly dependent on bonding structure of the dye molecules adsorbed on the TiO_2 film. In addition, the electron transfer in DSSC is strongly influenced by

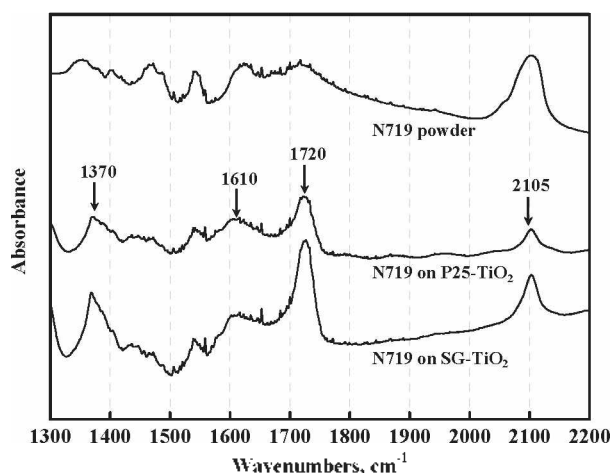


Figure 5. FT-IR spectra of N719 dye adsorbed on TiO_2 films compared to the signals of the N719 dye powder.

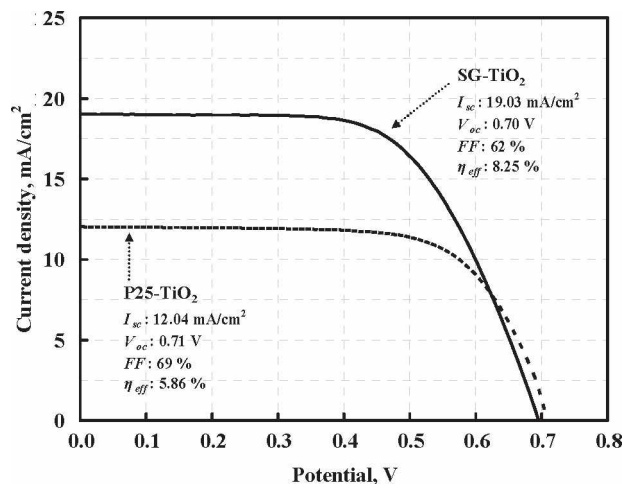


Figure 6. Photocurrent-voltage (I - V) curves of SG- TiO_2 and P25- TiO_2 films.

electrostatic and chemical interactions between TiO_2 surface and the adsorbed dye molecules.¹⁷ Figure 5 shows the FT-IR spectra of N719 dye adsorbed on TiO_2 films (P25- TiO_2 , SG- TiO_2) compared to the signals of the dye powder. Absorption at 2105 cm^{-1} of N719 dye is attributed to the SCN stretch model of N-bonded SCN ligand.^{18,19} The IR spectra were observed at 1370 cm^{-1} , 1610 cm^{-1} , and 1720 cm^{-1} when the dye molecules were adsorbed on P25- TiO_2 and SG- TiO_2 films. The IR spectra located at 1370 cm^{-1} and 1610 cm^{-1} is consistent with the bidentate coordination. Compared to the dye-anchored P25- TiO_2 films, the dye-anchored SG- TiO_2 films have strong absorptions at 1720 cm^{-1} , indicating the C=O stretch mode of the protonated carboxylic acid (i.e., ester-like linkage). Similar results were reported that the coordination of N719 dye on TiO_2 films occurs mainly by the contribution of unidentate (i.e., ester-like linkage) and partially by bidentate linkage.¹⁷⁻¹⁹

Figure 6 shows the photocurrent-voltage curves of P25- TiO_2 and synthesized SG- TiO_2 . The fill factor (FF) and overall energy efficiency (η_{eff}) were determined by the equations which was described in detail elsewhere.^{1,20} A dye-sensitized

solar cell assembled with SG-TiO₂ gave an open-circuit voltage of 0.70 V and short-circuits current density of 19.03 mA/cm² for an incident light intensity of 100 mW/cm². The power conversion efficiency of over 8.3 % was achieved using the single-phase anatase crystallites synthesized (SG-TiO₂) in this work. It was found that DSSCs made of nanostructured SG-TiO₂ films showed better photoelectrochemical properties compared to those prepared using Degussa P25-TiO₂ films.

Conclusions

The colloidal TiO₂ suspension was prepared by sol-gel method based on the hydrolysis of titanium-tetraisopropoxide. The TiO₂ films of single-phase anatase crystallites were formed on the FTO glass for a working electrode of DSSCs. The films were characterized by XRD, XPS, FE-SEM, AFM, and BET analysis. The contents of Ti and O of SG-TiO₂ are 27.01 % and 52.23 % corresponding to closely Ti⁴⁺ state. The nanoparticle size of SG-TiO₂ is about 14 nm and the film thickness was ca. 3~4 μm. According to the AFM image, the films have heterogeneous surface with a few separated islands. A dye-sensitized solar cell of SG-TiO₂ gave an open-circuit voltage of 0.70 V and short-circuits current density of 19.03 mA/cm² for an incident light intensity of 100 mW/cm². It was found that DSSCs made of SG-TiO₂ nanocrystalline films as photo-anodes achieved better photo-energy conversion efficiency compared to those prepared using commercially available Degussa P25 films. The power conversion efficiency of over 8.3% was achieved using the single-phase anatase SG-TiO₂ crystallites synthesized in this work.

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