

# Double-layered TiO<sub>2</sub> photoelectrode with particulate structure prepared by one-step soaking method

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**Abstract:** Nanostructured TiO<sub>2</sub> films with double-layered structure are prepared by a facile one-step soaking method. We have investigated the morphology of nanostructured TiO<sub>2</sub> films by the reaction time of the soaking method, which has an effect on the thickness and layered structure of the TiO<sub>2</sub> films. The TiO<sub>2</sub> films prepared by this method have a unique double-layered structure, which is composed of a dense TiO<sub>2</sub> bottom layer and TiO<sub>2</sub> particulates on the bottom layer. By manipulating the reaction time of the soaking method, control of TiO<sub>2</sub> particulate formation on the surface of the dense TiO<sub>2</sub> bottom layer is possible. The double-layered structure of nanostructured TiO<sub>2</sub> films is effective for achieving sufficient adsorption of Sb<sub>2</sub>S<sub>3</sub> sensitizer and light scattering effect of photoelectrodes for inorganic sensitized solar cells, which induces the enhancement of short circuit current of solar cell devices. Our solar cell device, using a double-layered TiO<sub>2</sub> film with particulate structure as a photoelectrode, exhibited J<sub>SC</sub>, V<sub>OC</sub>, FF, and η values of 12.94 mA/cm<sup>2</sup>, 498 mV, 57.0%, and 3.67%, respectively.

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## Introduction

TiO<sub>2</sub> is a very attractive and important material for photoelectrodes of dye-sensitized solar cells (DSSC) and is also widely applied to inorganic-sensitized solar cells (ISSC) because TiO<sub>2</sub> possesses a wide band gap and relatively high chemical stability. One of the research strategies of TiO<sub>2</sub> photoelectrodes for high efficiency solar cells focuses on searching for novel nanostructured TiO<sub>2</sub> photoelectrodes with large surface area and reduced light loss by transmittance of light. The morphology of nanostructured TiO<sub>2</sub> films is closely related to the surface area and light scattering characteristics of TiO<sub>2</sub> photoelectrodes, which determines the photovoltaic properties of sensitized solar cells. Therefore, tailoring of the TiO<sub>2</sub> nanostructure is a crucial aspect of improving the performance of sensitized solar cells. Methods for preparing the TiO<sub>2</sub> photoelectrodes with various nanostructures are widely studied, such as nanoparticles, nanotubes, nanorods, nanoflowers, porous spheres, and hollow spheres [1–5]. Among these various nanostructures, the spherical structure of TiO<sub>2</sub> films is generally used for light harvesting because of its large surface area and high surface permeability [6]. A large surface area is essential for TiO<sub>2</sub> photoelectrodes to load large amounts of organic or inorganic sensitizer molecules that will generate electrons by absorbing sunlight [7]. In addition, TiO<sub>2</sub> spheres are well known to be effective for obtaining light scattering effects for absorbed sunlight [8–10]. Therefore, most sensitized solar cell devices are normally based on nanoparticle-based TiO<sub>2</sub> photoelectrodes.

Recently, research on ISSC is being actively studied by many researchers to overcome the drawbacks of conventional DSSC. Especially, interest in all-solid-state ISSC devices has greatly increased in recent years to avoid using liquid components in solar cell devices because of leakage problems [11–13]. The use of alternative sensitizers to dyes, such as inorganic semiconductors, is also one of the attractive topics in these technologies. Typically, inorganic semiconductors such as CdSe, CdS, Cu<sub>2-x</sub>S, In<sub>2</sub>S<sub>3</sub>, or Sb<sub>2</sub>S<sub>3</sub> that are based on the II-VI or V-VI families are used as sensitizers for solar cells [14,15]. Among these materials, the

Sb<sub>2</sub>S<sub>3</sub> semiconductor is an excellent material due to its high absorption coefficient ( $\alpha = 1.8 \times 10^5 \text{ cm}^{-1}$  at 450 nm) and energy band gap of 1.7 ~1.9 eV [15,16]. However, in the case of ISSC, the recombination reaction of electrons between the hole transport material and substrate is rapid and thus the main loss of efficiency comes from the charge recombination [17]. Therefore an additional blocking layer, such as a compact TiO<sub>2</sub> thin film under 100 nm, must be placed between the mesoporous TiO<sub>2</sub> photoelectrode and the glass substrate [18].

In this study, novel double-layered nanostructured TiO<sub>2</sub> films were applied to the photoelectrode for ISSC based on the inorganic semiconductor Sb<sub>2</sub>S<sub>3</sub>. Double-layered TiO<sub>2</sub> films composed of a dense TiO<sub>2</sub> bottom layer and a particulate TiO<sub>2</sub> top layer were easily fabricated by a simple one-step soaking method. The dense TiO<sub>2</sub> bottom layer plays the role of the blocking layer and the particulate TiO<sub>2</sub> top layer takes charge of the large surface area and light scattering effect of photoelectrodes. We investigated the growth behavior of double-layered TiO<sub>2</sub> films based on the reaction time of the soaking method, which was closely related to the thickness and morphology of the TiO<sub>2</sub> films. To determine the effect of the nanostructure of double-layered TiO<sub>2</sub> films on the photovoltaic characteristics of ISSC, solar cell devices were fabricated by deposition of Sb<sub>2</sub>S<sub>3</sub> on the TiO<sub>2</sub> photoelectrode using atomic layer deposition (ALD) and device characteristics were investigated.

## 2. Experimental details

### 2.1 Preparation of double-layered TiO<sub>2</sub> films

TiO<sub>2</sub> films were deposited onto fluorine-doped SnO<sub>2</sub> (FTO, 7 ohm/square) transparent conducting glass substrates. The substrates were ultrasonically cleaned with deionized (DI) water and acetone for 10 min each, followed by rinsing with isopropyl alcohol for 10 min. The substrates were then dried with nitrogen gas before the deposition process. A precursor aqueous solution for the TiO<sub>2</sub> films was prepared by dissolving 0.3 M titanium tetrachloride (TiCl<sub>4</sub>) in DI water. For the deposition of TiO<sub>2</sub> onto the FTO substrate, the substrate was soaked in the precursor solution at 70 °C statically without stirring. To investigate the growth rate of TiO<sub>2</sub> films by the soaking method, several reaction times were used: 30, 60, 90, and 120 min. After the deposition process, the substrates were rinsed with DI water and dried with nitrogen gas. The annealing process of the TiO<sub>2</sub> films was conducted at 450 °C for 30 min in an air furnace. To maximize the surface area of TiO<sub>2</sub>, the prepared TiO<sub>2</sub> films were dipped in 0.5 M TiCl<sub>4</sub> aqueous solution with stirring at 70 °C for 60 min. The last heating treatment of the TiO<sub>2</sub> films proceeded at 500 °C for 15 min in an air furnace.

### 2.2 Fabrication of solar cells

Double-layered TiO<sub>2</sub> films were used as the photoelectrode of solar cells. These films were approximately 1 μm thickness and were deposited by the soaking method on FTO (7 ohm) glass substrates. The atomic layer deposition (ALD) of amorphous antimony sulfide (Sb<sub>2</sub>S<sub>3</sub>) to form an inorganic sensitizer was performed at 120 °C from Sb(NMe<sub>3</sub>) and H<sub>2</sub>S gas. A 15 mg / ml solution of poly-3-hexylthiophene (P3HT) was prepared in 1,2-dichlorobenzene and deposited by spin coating on TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub> at 2500 rpm for 60 s. The TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/P3HT layer was then annealed at 90 °C for 30 min in a vacuum oven. The back contact was finished by thermal evaporation of gold (Au) with a 100 nm thickness as a counter electrode. The evaporation was performed with a metal mask, yielding an active area of 0.05 cm<sup>2</sup>.

### 2.3 Characterization of TiO<sub>2</sub> films and solar cells

The surface morphology and grain growth of the prepared TiO<sub>2</sub> films were investigated by scanning electron microscopy (FE-SEM) (Hitachi, SU8200) and transmission electron microscopy (TEM) (Hitachi, HF-3300) with focused ion beam (FIB) system (Hitachi, NB5000). The crystalline phase of the TiO<sub>2</sub> films was analyzed by X-ray diffraction (XRD) (CuKα, 40kV, Panalytical MPD for thin film) with grazing angle of 2° and scan rate of 10°/min. The diffuse reflectance of TiO<sub>2</sub> films was measured by UV-vis spectrophotometry (UV-VIS-NIR, CARY5000).

The photovoltaic properties of the solar cells were characterized using a source meter (Keithley, 2400) unit and a solar simulator (Newport, 94022A) to simulate 1.5 AM solar irradiation. External quantum efficiency (EQE) measurements were conducted using an incident photon-to-current efficiency (IPCE) measurement system (McScience, K3100).

### 3. Results and discussion

SEM was used for the investigation of the surface morphology and nanostructure of TiO<sub>2</sub> films prepared from the soaking method. SEM images of the TiO<sub>2</sub> films are presented in Fig. 1. Figures 1 (a)-(d) are surface images of the TiO<sub>2</sub> films obtained by the soaking method with reaction times of 30, 60, 90, and 120 min, respectively. In the cross-sectional images of TiO<sub>2</sub> films, the thickness of TiO<sub>2</sub> films was increased with longer reaction times. TiO<sub>2</sub> films with 30 and 60 min of soaking show only flat layers, however, 90 and 120 min of soaking resulted in TiO<sub>2</sub> films with a double-layered structure, namely, a particulate layer on a flat layer (particulate-flat layer). In the case of the TiO<sub>2</sub> film soaked for 120 min, the thickness of the particulate-flat film was approximately 1.38 μm, and the thickness of the individual flat and particulate layers were approximately 500 and 700 nm, respectively.

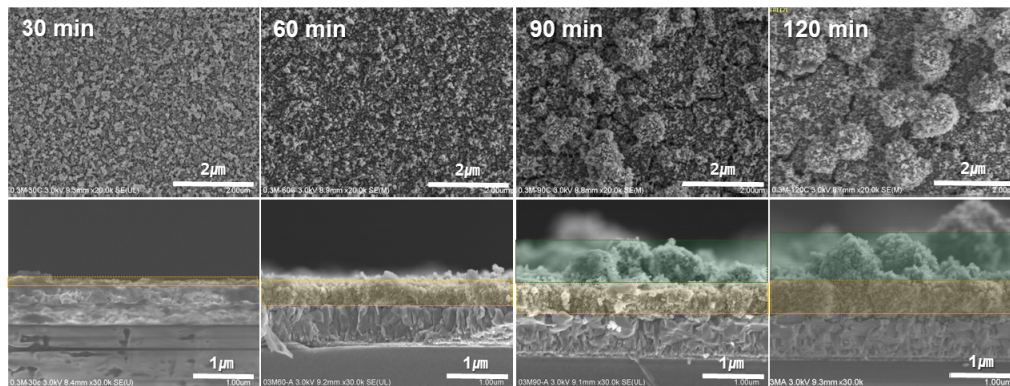


Fig. 1. Cross-sectional and surface SEM images of TiO<sub>2</sub> films deposited by the soaking method with different reaction time. Yellow and green regions in cross-sectional SEM images represent the flat and particulate layer, respectively.

The nanostructure of double-layered TiO<sub>2</sub> films deposited by the soaking method is flat at short reaction times such as 30 min and 60 min. At longer reaction times (over 60 min), the films had many particulates on the flat layers. The particulate-flat structure of double-layered TiO<sub>2</sub> films seems to be formed by the continuous growth of TiO<sub>2</sub> particulates, followed by the formation of flat TiO<sub>2</sub> layers. When the reaction time is short, only small grains of TiO<sub>2</sub> are grown by the reaction of TiO<sub>2</sub> precursors thus, a flat and dense TiO<sub>2</sub> layer is formed on the substrate. However, as the reaction time of soaking increases, a dense TiO<sub>2</sub> flat layer covers the substrate completely, and some of the TiO<sub>2</sub> grains abruptly start to grow into larger TiO<sub>2</sub> particulates on the already formed flat TiO<sub>2</sub> layer. Nanostructured TiO<sub>2</sub> films prepared by the soaking method with sufficient reaction times showed a distinctive double-layered structure with particulate and flat shapes. Unlike the paste-coating method with multiple deposition cycles, double-layered TiO<sub>2</sub> films prepared by simple one-step soaking methods can play multiple roles of blocking layer and light scattering layer due to the dense bottom TiO<sub>2</sub> layer and many TiO<sub>2</sub> particulates on the bottom layer. In addition, TiO<sub>2</sub> films with this particulate-flat structure might have larger surface areas than those with a flat structure, which would be advantageous for the improvement of power conversion efficiency.

Figure 2 shows the X-ray diffraction (XRD) pattern of the TiO<sub>2</sub> film prepared by the soaking method for 120 min on FTO substrates. As shown in Fig. 2, the peaks of the TiO<sub>2</sub> film were located at  $2\theta = 27.53^\circ, 36.17^\circ, 41.37^\circ, 56.65^\circ, 62.90^\circ, 68.86^\circ, \text{ and } 69.87^\circ$ , which correspond to the (110), (011), (111), (121), (002), (130), and (031) crystallographic planes of the TiO<sub>2</sub> structure, respectively. These diffraction peaks closely match the values of the

standard data (JCPDS No.98-005-3997), which confirms the formation of a rutile  $\text{TiO}_2$  phase without any impurities [19]. Based on this result, our soaking method is suitable for the preparation of rutile nanostructured  $\text{TiO}_2$  films.

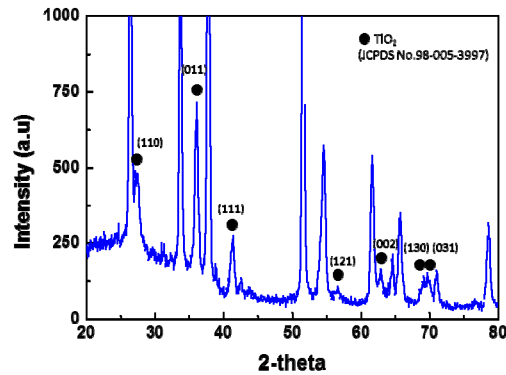


Fig. 2. XRD graph of  $\text{TiO}_2$  film deposited on FTO substrate by soaking method with reaction time of 120 min.

To investigate the effect of the nanostructure of double-layered  $\text{TiO}_2$  films on photovoltaic properties, we have fabricated solar cell devices of FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /P3HT/Au and measured I-V characteristics using a solar simulator (Table 1, Fig. 3). Because our double-layered  $\text{TiO}_2$  films have a dense  $\text{TiO}_2$  layer on the bottom side, we did not deposit a compact  $\text{TiO}_2$  blocking layer on the FTO substrate. The performance of solar cell devices was closely related to the reaction time of the soaking method. The power conversion efficiency was improved from 1.78 to 3.67% as the reaction time increased. Among the  $\text{TiO}_2$  films prepared by the soaking method, the solar cell using a  $\text{TiO}_2$  film with 120 min of soaking showed the best performance, with short-circuit photocurrent density ( $J_{\text{SC}}$ ), open-circuit voltage ( $V_{\text{OC}}$ ), fill factor (FF), and efficiency ( $\eta$ ) values of 12.94  $\text{mA} / \text{cm}^2$ , 498 mV, 56.98%, and 3.67%, respectively, under AM 1.5G full sunlight (99.8  $\text{mW} / \text{cm}^2$ ). Whereas  $V_{\text{OC}}$  had similar values regardless of soaking time,  $J_{\text{SC}}$  was considerably dependent on the reaction time. This difference of  $J_{\text{SC}}$  would be closely related with the existence of particulate structure on double-layered  $\text{TiO}_2$  films. In the case of 90 and 120 min, there are many particulates on top of the  $\text{TiO}_2$  photoelectrode, which might be advantageous for the sufficient adsorption of  $\text{Sb}_2\text{S}_3$  sensitizer and light scattering effect of  $\text{TiO}_2$  photoelectrode.

**Table 1. Device characteristics of ISSC fabricated using nanostructured  $\text{TiO}_2$  films by soaking method under AM 1.5G.**

Time (min)	$V_{\text{OC}}$ (mV)	$J_{\text{SC}}$ ( $\text{mA}/\text{cm}^2$ )	F.F. (%)	Efficiency (%)	$R_s$ ( $\Omega$ )	$R_{\text{sh}}$ ( $\Omega$ )
30	518	7.94	43.2	1.78	19.88	183.63
60	509	10.49	52.4	2.80	12.28	306.39
90	496	12.17	56.3	3.40	7.83	399.67
120	498	12.94	57.0	3.67	7.35	353.35

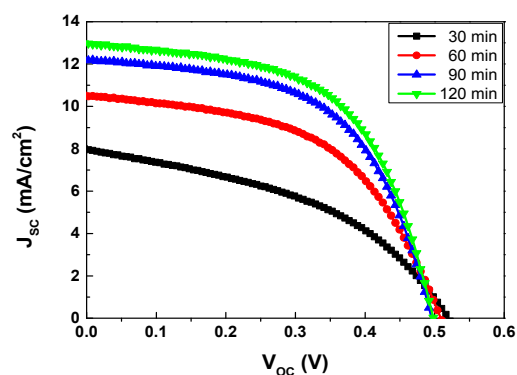


Fig. 3. Photocurrent-voltage (J-V) curve of ISSC fabricated using nanostructured TiO<sub>2</sub> films by soaking method under AM 1.5G.

In order to investigate the structure of photoelectrode and solar cell devices in detail, FE-TEM analysis of solar cell devices was performed. Figure 4 shows cross-sectional TEM images of solar cell devices with different soaking time with EDX mapping. In the case of 30 min soaking time, a very thin TiO<sub>2</sub> layer (pink color) is deposited on the FTO substrate and Sb<sub>2</sub>S<sub>3</sub> (green color) covers the top of the TiO<sub>2</sub> layer. As the soaking time increases to 60 min, thickness of the TiO<sub>2</sub> layer increases to about 300 nm. However, for both 30 and 60 min soaking times, there was no particulate on flat TiO<sub>2</sub> films. Contrary to 30 and 60 min soaking time, TiO<sub>2</sub> films with 90 and 120 min soaking times show double-layered structure of TiO<sub>2</sub>. Sb<sub>2</sub>S<sub>3</sub> sensitizers are uniformly distributed on not only the surface but also the particulates of TiO<sub>2</sub> photoelectrodes. Because Sb<sub>2</sub>S<sub>3</sub> sensitizers are deposited using an ALD process, Sb<sub>2</sub>S<sub>3</sub> sensitizers are uniformly distributed on the double-structured TiO<sub>2</sub> films. In the case of particulate-flat TiO<sub>2</sub> films with 90 and 120 min soaking time, a large amount of Sb<sub>2</sub>S<sub>3</sub> sensitizers seems to be located in the surface region of TiO<sub>2</sub> photoelectrodes compared with 30 and 60 min.

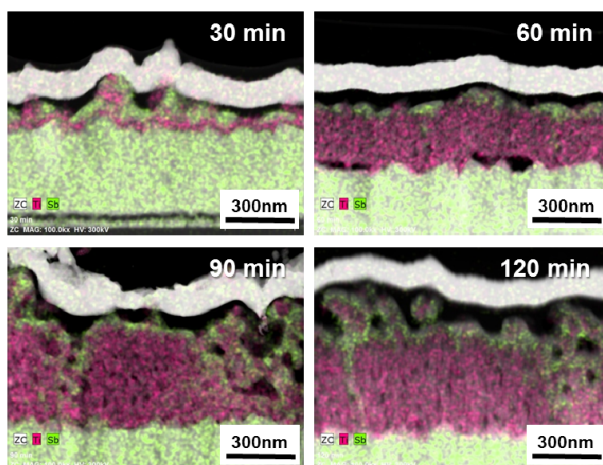


Fig. 4. TEM cross-sectional images of TiO<sub>2</sub> films deposited by soaking method with different reaction time with EDX mapping. (pink: Ti, green: Sb)

The particulate structure of double-layered TiO<sub>2</sub> films also could contribute to the light scattering effect of photoelectrodes. In order to confirm the enhanced light-scattering of nanostructured TiO<sub>2</sub> films prepared by the soaking method, diffuse reflectance spectra were measured (Fig. 5). The reflectance over the entire wavelength range increased with increased

TiO<sub>2</sub> reaction time for TiO<sub>2</sub> prepared by the soaking method. Further observation indicates that the TiO<sub>2</sub> film with 120 min soaking time exhibited the highest diffuse reflectance, approximately 30% in the range from 400 to 800 nm wavelength. The diffuse reflectance of TiO<sub>2</sub> films with 90 and 120 min of soaking is higher than that of TiO<sub>2</sub> films with 30 and 60 min of soaking, indicating that the particulate structure of the nanostructured TiO<sub>2</sub> has a higher light-scattering ability than that of flat TiO<sub>2</sub> films. In the case of conventional photoelectrodes, 10 ~20 nm-sized TiO<sub>2</sub> nanoparticles are used for transparent photoelectrodes, which has a weak light scattering effect. Therefore, large nanoparticles (100 ~400 nm) have been incorporated as light scattering centers to increase the optical length in TiO<sub>2</sub> films, and enhanced light harvesting has been demonstrated both experimentally and theoretically [8–10]. Therefore, it is reasonable to infer that TiO<sub>2</sub> films with large nanoparticles (100 nm) and those with the particulate-flat structure would have similar light scattering effect [20,21]. The nanostructure of double-layered TiO<sub>2</sub> films prepared by the soaking method was easily controlled by the reaction time, and it is expected that the double-layered TiO<sub>2</sub> films can contribute to the solar cell performance through the light scattering effect. TiO<sub>2</sub> particulates of double-layered TiO<sub>2</sub> films are beneficial for enhancing the reflectance of light, and the optical path length of light in the photoelectrode can be effectively improved [22,23].

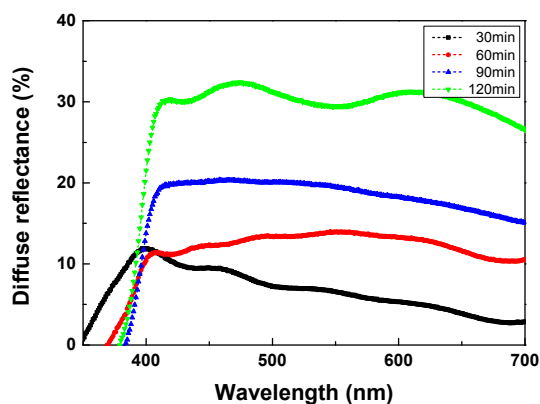


Fig. 5. Diffuse reflectance of TiO<sub>2</sub> films deposited by soaking method with various reaction time.

From the above TEM and diffuse reflectance analysis, it was found that particulate structure of double-layered TiO<sub>2</sub> films is beneficial for the sufficient adsorption of Sb<sub>2</sub>S<sub>3</sub> sensitizer and the enhancement of light harvesting of photoelectrodes by light scattering effect. These two factors are closely related with photocurrent generation of solar cell devices. For a more detailed investigation of the effect of the nanostructure of TiO<sub>2</sub> films on the photocurrent characteristic of solar cells, we have measured EQE data for the solar cell devices. Figure 6 shows the EQE spectra of solar cells using nanostructured TiO<sub>2</sub> films prepared by the soaking method. A solar cell using TiO<sub>2</sub> films with 120 min soaking time exhibited the highest EQE of all other solar cells. Overall, EQE increased as soaking time increases and the absolute EQE of 120 min soaking time is higher than the other TiO<sub>2</sub> films over the entire wavelength region, which is in good agreement with the higher J<sub>SC</sub> of 120 min soaking time in Fig. 3. By the way, contrary to EQE at wavelengths over 450 nm, a solar cell using TiO<sub>2</sub> film with 120 min soaking time exhibits a similar EQE with 60 and 90 min soaking time in the short wavelength region below 450 nm. The similar EQE at shorter wavelength might be attributed to the similar presence of the Sb<sub>2</sub>S<sub>3</sub> inorganic sensitizer (absorption coefficient =  $1.8 \times 10^5 \text{ cm}^{-1}$  at 450 nm). However, a solar cell using the TiO<sub>2</sub> film with 30 min soaking time shows incomparably lower EQE even at wavelengths below 450

nm, which might be attributed to the smaller amount of  $\text{Sb}_2\text{S}_3$  sensitizers on a  $\text{TiO}_2$  photoelectrode. The higher IPCE at long wavelength is most likely due to the superior light-scattering effect of double-layered  $\text{TiO}_2$  films. At wavelengths over 450 nm, solar cells using  $\text{TiO}_2$  films with 90 and 120 min soaking time show higher EQE than 60 min soaking time, which might be closely related with the particulate structure of double-layered  $\text{TiO}_2$  films. Light-scattering is effective in the long wavelength region because most light is transmitted through a  $\text{TiO}_2$  electrode and scattered in this wavelength region [22–24]. This result indicates that the nanostructure of double-layered  $\text{TiO}_2$  photoelectrode is essential for improving the solar cell performance through photocurrent improvement.

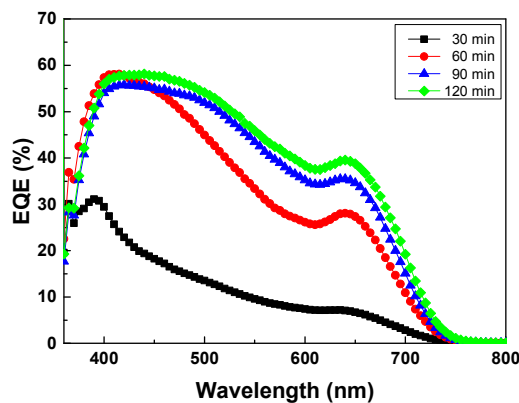


Fig. 6. IPCE of ISSC based on nanostructured ISSC fabricated using nanostructured  $\text{TiO}_2$  films by soaking method with various reaction time.

#### 4. Conclusion

We have fabricated double-layered  $\text{TiO}_2$  films using a simple one-step soaking method. Thickness and morphology of double-layered  $\text{TiO}_2$  films were closely related with the reaction time of soaking method. The nanostructured  $\text{TiO}_2$  films with sufficient soaking time (over 90 min) show unique double-layered structures, which are composed of dense  $\text{TiO}_2$  bottom layer and  $\text{TiO}_2$  particulates on the bottom layer. The dense  $\text{TiO}_2$  bottom layer could substitute for the existing blocking layer and  $\text{TiO}_2$  particulates could play an important role of inorganic sensitizer adsorption sites and light scattering effects. To determine the effect of the nanostructure of double-layered  $\text{TiO}_2$  films on the photovoltaic characteristics, ALD  $\text{Sb}_2\text{S}_3$ -based solar cell devices using double-layered  $\text{TiO}_2$  as photoelectrodes were fabricated. The  $\text{TiO}_2$  particulate was found to be advantageous for securing sufficient adsorption of  $\text{Sb}_2\text{S}_3$  sensitizer and enhancement of light harvesting through light scattering effects, which could contribute to the increase of short circuit current of solar cell devices. A solar cell device using a double-layered  $\text{TiO}_2$  film with 120 min soaking time showed the best result with  $J_{\text{SC}}$ ,  $V_{\text{OC}}$ , FF, and  $\eta$  values of 12.94 mA / cm<sup>2</sup>, 498 mV, 57.0%, and 3.67%, respectively. Double-layered  $\text{TiO}_2$  photoelectrodes prepared by a simple one-step soaking method were found to be useful for the fabrication of high performance ISSC.

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