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ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 189 (2007) 100–104
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Improved performance of Black-dye-sensitized solar cells with nanocrystalline anatase TiO_2 photoelectrodes prepared from $TiCl_4$ and ammonium carbonate

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Received 12 September 2006; received in revised form 22 November 2006; accepted 15 January 2007
Available online 20 January 2007

Abstract

To improve the performance of tris(isothiocyanato)-ruthenium(II)-2,2′:6′,2″-terpyridine-4,4′,4″-tricarboxylic acid, tris-tetrabutylammonium salt (Black-dye) sensitized TiO_2 solar cells, nanocrystalline TiO_2 particles, which were used as film photoelectrodes, were synthesized from $TiCl_4$ and ammonium carbonate. The resulting nanocrystalline TiO_2 particles, which had a pure anatase crystal structure, had smaller surfaces areas, larger size distribution and mean size compared to nanoparticles prepared by the traditional method using titanium(IV) tetraisopropoxide ($Ti(OCH(CH_3)_2)_4$) and HNO_3. The dye-adsorbed TiO_2 photoelectrode synthesized from $TiCl_4$ and ammonium carbonate had a more thorough surface coverage of the Black-dye. The short circuit photocurrent density (J_{sc}) and the incident monochromatic photon-to-electron conversion efficiency (IPCE) value of the cell using TiO_2 prepared from $TiCl_4$ were higher than that prepared from $Ti(OCH(CH_3)_2)_4$. Consequently, the solar energy conversion efficiency (η) is 16% larger under AM 1.5 (1sun, 100 mW/cm^2). The characterizations of the TiO_2 photoelectrode suggested that pure anatase crystallites, the less surface area and the more thorough surface coverage of the sensitizing dye enhance the absorbed photon to current efficiency (APCE) and the light harvesting efficiency (LHE), respectively, which improves the IPCE, J_{sc}, and the η values.

Keywords: Dye-sensitized solar cell; TiO_2; $TiCl_4$; Ammonium carbonate

1. Introduction

Dye-sensitized solar cells have been extensively investigated since O'Reganoulos and Grätzel reported a 7.1% solar energy conversion efficiency in 1991 [1]. A typical solar cell consists of a nanostructured TiO_2 film photoelectrode covered with a sensitizing dye such as a Ru(II) complex, a redox electrolyte of I^-/I_3^- in an acetonitrile solution, and a Pt counter electrode. In this type of solar cell, nanocrystalline TiO_2 plays an important role since it increases the specific surface area of the TiO_2 photoelectrode where the sensitizing dye molecules are adsorbed. Using a nanocrystalline TiO_2-based photoelectrode, the surface area can be increased 2000 times compared to a flat-layered photoelectrode [1]. In addition, the crystal structure of TiO_2 influences the cell performance. Among the three types of TiO_2 crystal structures, anatase, rutile and brookite, typically the anatase form gives a better cell performance due to its broad band gap [2].

Typically TiO_2 nanoparticles are synthesized by the hydrolysis of $Ti(OCH(CH_3)_2)_4$ in 0.1 mol/dm^3 HNO_3 (pH 1) followed by autoclaving at 503 K. However, this method does not provide pure anatase TiO_2 [2–4]. To create a uniform nanocrystalline anatase TiO_2 photoelectrode for dye-sensitized solar cells, Yanagida and co-workers used $TiCl_4$ and $TiSO_4$ precursors with ammonia and HNO_3 [5]. Although successful, a simple, more effective, and economical method for preparing pure anatase nanostructured TiO_2 from a chloride precursor is desirable. In this paper, we report a new method for preparing pure anatase TiO_2 nanoparticles from $TiCl_4$ and ammonium carbonate and its application, which remarkably improves the Black-dye [6]-sensitized solar cell performance.

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doi:10.1016/j.jphotochem.2007.01.013

2. Experimental

A $TiCl_4$ solution (Ti: 16.0–17%, Wako Pure Chemical Industries, Ltd.) was gradually added to an aqueous solution of ammonium carbonate ($(NH_4)_2CO_3$, Wako Pure Chemical Industries, Ltd.). Then the mixture was stirred at 288 K for 1 h. The resulting precipitate was filtered and washed repeatedly by deionized water. After the pH of the sol was 8, it was hydrothermally treated in a titanium autoclave at 503 K for 13 h (heating rate 70 K/h). The dispersion medium of the resultant TiO_2 colloidal suspensions was transferred from water to ethanol. The colloid was thoroughly dispersed using a high-speed homogenizer by adding ethyl cellulose (Fluka) as a binder and α-terpineol (Wako Pure Chemical Industries, Ltd.) as a solvent for the TiO_2 paste [6]. An evaporator was used to concentrate the paste. In order to compare to the traditional method, a different sol was also prepared from $Ti(OCH(CH_3)_2)_4$ (Kanto Chemical Co.) and HNO_3 (Wako Pure Chemical Industries, Ltd.) using the previously reported procedure [2,7].

The X-ray powder diffraction (XRD) pattern using Cu Kα radiation (Mac Science, MX Labo.) was used to elucidate the crystallinity and crystal phase of the resulting TiO_2. The TiO_2 surface area was determined by a BET surface area measurement (Shimadzu, Gemini2360). Scanning electron microscope (SEM) images were taken on a JEOL JSM 7401F at an accelerating voltage of 5.0 kV.

Each type of TiO_2 paste was deposited onto a separate fluorine-doped stannic oxide conducting glass (FTO, 10 Ω/cm^2, Nippon Sheet Glass Co.) using a screen printing technique. The resulting layers were calcined for 2 h at 798 K in an air-flow of 1.5 dm^3/min. The TiO_2 film measured 27 μm thick using a Tencor Alpha-Step 500 surface profiler. Then the TiO_2 electrodes were cooled to 438 K and immediately soaked in a Black-dye (Solaronix S.A.) solution. Soaking the TiO_2 photoelectrode in an ethanol solution of the Black-dye (concentration: 2×10^{-4} mol/dm^3) and deoxycholic acid (DCA, Tokyo Kasei Kogyo Co., Ltd., concentration: 2×10^{-2} mol/dm^3) [6] for 24 h at 293 K allowed the dye to adsorb onto the TiO_2 surface.

For the photocurrent measurements, a sandwich-type electrochemical cell, which was composed of a dye-adsorbed TiO_2 photoelectrode, a polyethylene spacer film (thickness: 60 μm), and a counter electrode, was used. A Pt sputtered FTO conducting glass was the counter electrode. The electrolyte solution was injected into the space between the two electrodes by a micro syringe. The electrolyte solution was composed of 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide, 0.1 mol/dm^3 LiI, 0.05 mol/dm^3 I_2, 0.5 mol/dm^3 4-*t*-butylpyridine, and acetonitrile (Tomiyama Pure Chemical Industries, Ltd.) as the solvent.

The dye-coated semiconductor film was illuminated through a conducting glass support. The simulated AM 1.5 solar light was obtained from a solar simulator (Wacom Co., Japan, WXS-80C-3 with a 300-W Xe lamp and an AM 1.5 filter). The *I*–*V* curves were measured with a direct current voltage current source/monitor (Advantest, R6243). The incident light intensity was calibrated using a standard Si solar cell equipped with a KG-3 filter, which was produced by the Japan Quality Assurance Organization (JQA). The photocurrent action spectra and the IPCE plotted as a function of excitation wavelength were recorded on a CEP-99W system (Bunkoh-Keiki Co., Ltd., Japan). The intensity of the incident monochromatic light was calibrated with a Si photodiode (Bunkoh-Keiki Co., Ltd., Japan). The apparent cell area of the TiO_2 photoelectrode was 0.25 cm^2 (0.5 cm × 0.5 cm).

The absorption spectrum of their desorbing amount in a 0.01 mol/dm^3 NaOH aqueous/ethanol solution was used to determine the surface coverage of photoelectrode adsorbed by the Black-dye [8].

3. Results and discussion

3.1. Characterization of TiO_2

Various kinds of characterizations were performed on TiO_2 samples calcined at 798 K for 2 h. Fig. 1 shows the XRD spectra. The sample prepared from the chloride precursor only exhibits peaks that correspond to the anatase phase (Fig. 1(a)), perhaps indicating that the pure TiO_2 anatase is formed. On the other hand, a small peak at $2\theta = 30.8°$, which corresponds to (1 2 1) of the brookite crystal phase (JCPDS #29-1360), is observed in the sample prepared from the tetraisopropoxide precursor (Fig. 1(b)). This finding indicates the presence of brookite, which

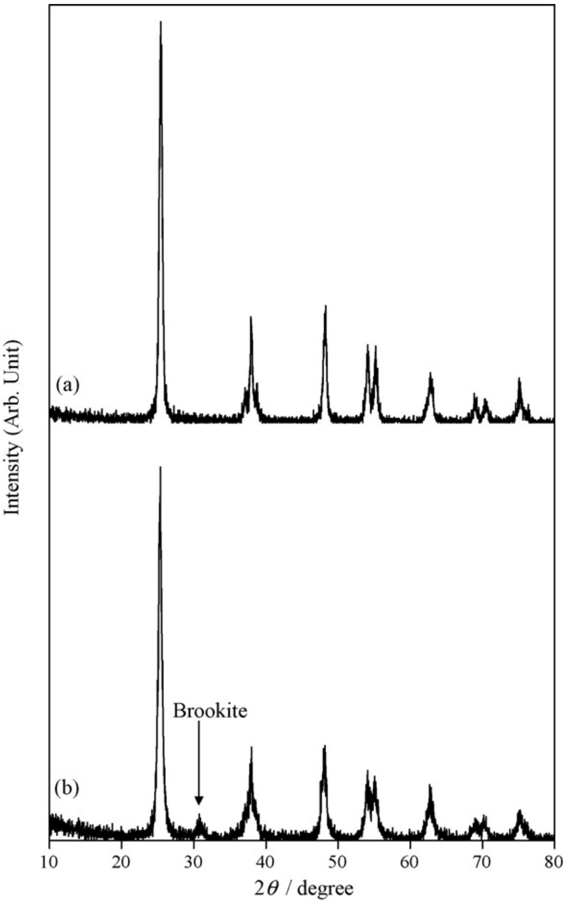

Fig. 1. X-ray diffraction patterns of nanocrystalline TiO_2 prepared from (a) $TiCl_4$ and (b) $Ti(OCH(CH_3)_2)_4$ precursors.

Table 1
BET surface area and particle size of the prepared TiO_2

TiO_2 precursor	BET surface area (m^2/g)	TiO_2 particle size (nm)		
		BET surface area[a]	Mode[b]	Mean[c]
$TiCl_4$	64	24	24	28
$Ti(OCH(CH_3)_2)_4$	101	15	16	19

[a] Average diameter back-calculated from the BET surface area assuming that the particles are spherical.

[b] Mode diameter determined by SEM in Fig. 3.

[c] Mean diameter determined by SEM in Fig. 3.

is consistent with previous results [2–4,9]. The ratio of brookite phase for TiO_2 prepared from the tetraisopropoxide precursor, which was estimated from integrated peak intensities by the method of Hashimoto and co-workers [10], was about 20%. This value also agrees with previously reported one [9].

Table 1 lists the BET surface area and the particle size back-calculated using the BET surface area. The BET surface area of TiO_2 prepared from $TiCl_4$ is smaller than TiO_2 prepared from $Ti(OCH(CH_3)_2)_4$. Consequently, TiO_2 prepared from the chloride precursor displays a larger particle size than that prepared from the tetraisopropoxide precursor.

Fig. 2 represents the SEM images and Fig. 3 illustrates the distribution of TiO_2 particle size observed by SEM. These results indicate that the size distribution of TiO_2 particle prepared from the chloride precursor was larger than tetraisopropoxide precursor's one. The mode diameters of TiO_2 particles determined by SEM, which are listed in Table 1, corresponded with the ones calculated by the BET surface area completely. The mean particle sizes of TiO_2 determined by SEM also appear to be very similar to the ones back-calculated from the BET surface area, showing that TiO_2 prepared from the chloride precursor has a larger particle size than that prepared from the tetraisopropoxide one.

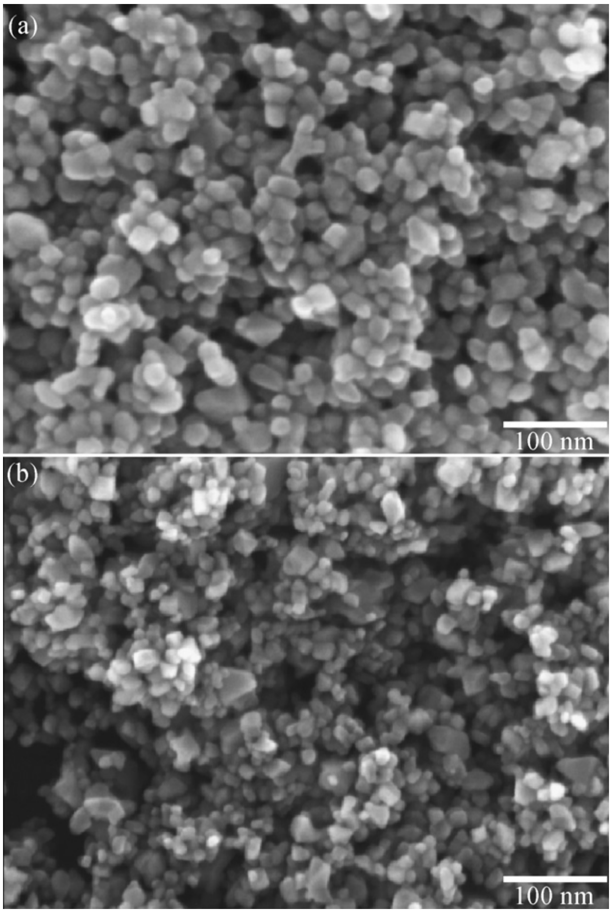

Fig. 2. SEM images of nanocrystalline TiO_2 prepared from (a) $TiCl_4$ and (b) $Ti(OCH(CH_3)_2)_4$ precursors.

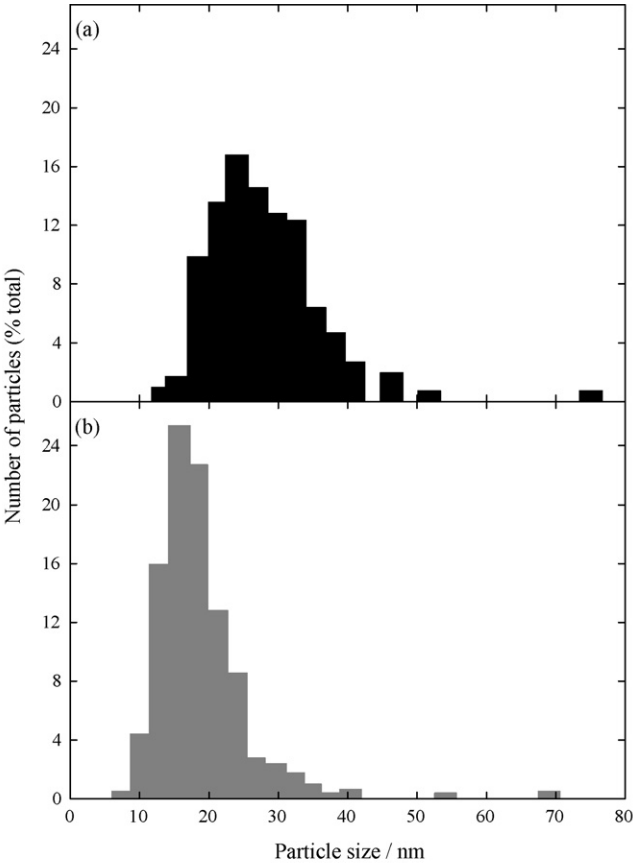

Fig. 3. Distribution of TiO_2 particle sizes observed by SEM. (a) TiO_2 prepared from $TiCl_4$ and (b) $Ti(OCH(CH_3)_2)_4$ precursors.

3.2. Solar cell performance

Fig. 4 depicts the current–voltage characteristics of the solar cell using the two types of TiO_2 photoelectrodes under 100 mW/cm^2 illumination (AM 1.5). Table 2 summarizes the photovoltaic properties. The J_{sc} value of the cell using TiO_2 prepared from $TiCl_4$ is higher than that prepared from $Ti(OCH(CH_3)_2)_4$. Although they display similar open-circuit photovoltages (V_{oc}) and fill factor (ff) values, η for the cell prepared from the chloride precursor is 16% higher than that prepared from the tetraisopropoxide precursor.

J_{sc} can be calculated from the overlap integration of the global AM 1.5 solar emission spectrum and the photocurrent action

Table 2
Dye-sensitized solar cell performance

TiO_2 precursor	J_{sc} (mA/cm^2)	V_{oc} (V)	ff	η (%)	Max IPCE[a] (%)	$10^7 \Gamma$[b] (mol/cm^2)	LHE[c] (%)	APCE[d] (%)
$TiCl_4$	16.00	0.724	0.728	8.44	60.3	1.94	96.5	62.5
$Ti(OCH(CH_3)_2)_4$	13.81	0.713	0.740	7.28	57.0	1.73	95.0	60.0

[a] Maximum incident monochromatic photon-to-electron conversion efficiency from Fig. 5.
[b] Spectroscopically determined surface coverage of the Black-dye.
[c] Light harvesting efficiency at the maximum IPCE wavelength.
[d] Absorbed monochromatic photon-to-electron conversion efficiency at the maximum IPCE wavelength.

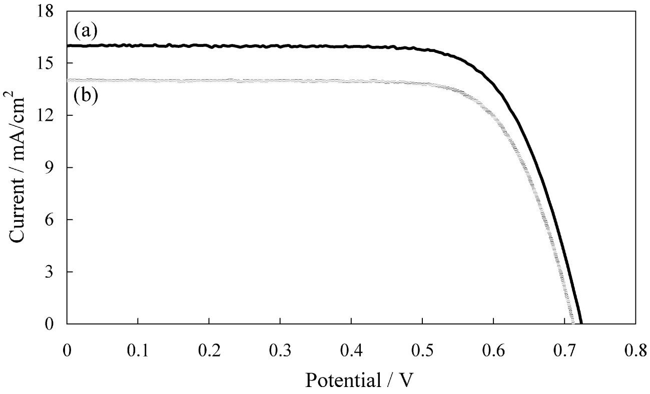

Fig. 4. Photocurrent–photovoltage characteristics of Black-dye-sensitized solar cells using TiO_2 prepared from (a) $TiCl_4$ and (b) $Ti(OCH(CH_3)_2)_4$ precursors.

spectrum over the wavelengths where the dye absorbs.

$$J_{sc} = \int qF(\lambda)[1 - r(\lambda)]\mathrm{IPCE}(\lambda)\,\mathrm{d}\lambda \quad (1)$$

where q is the electron charge, $F(\lambda)$ the incident photon flux density at wavelength λ, and $r(\lambda)$ is the incident light loss due to absorption and reflection of the conducting glass [4]. According to Eq. (1), J_{sc} is related to IPCE. Thus, the IPCE action spectra were measured (Fig. 5). The IPCE values for the TiO_2 photoelectrode prepared from chloride precursor are larger than those from the tetraisopropoxide precursor over the entire visible region. The maximum IPCE increases by 6% from 57.0 to 60.3%.

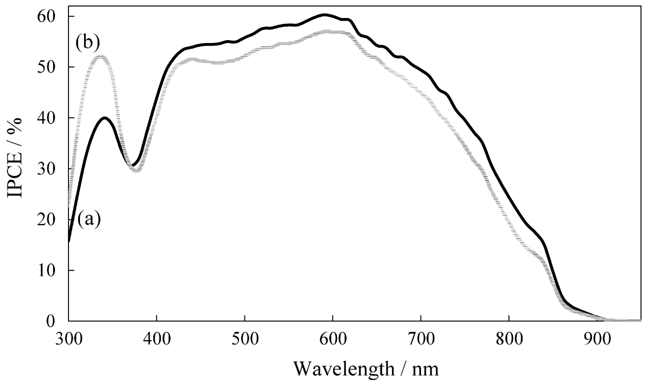

Fig. 5. IPCE action spectra for Black-dye-sensitized solar cells using TiO_2 prepared from (a) $TiCl_4$ and (b) $Ti(OCH(CH_3)_2)_4$ precursors.

To clarify the factors that contribute to the improved IPCE and J_{sc}, let us consider the following equation [7]:

$$\mathrm{IPCE} = \mathrm{LHE} \times \phi_{\mathrm{inj}} \times \phi_{\mathrm{coll}} \quad (2)$$

IPCE is expressed as the product of LHE of the photoelectrode, the quantum yield of electron injection (ϕ_{inj}), and the efficiency of the conducting glass substrate to collect the injected electron (ϕ_{coll}). LHE at wavelength λ can be estimated using the following equation:

$$\mathrm{LHE}(\lambda) = 1 - 10^{-A} \quad (3)$$

A is the absorbance of the dye on TiO_2 at the maximum wavelength and given by [6],

$$A = 1000(\mathrm{cm}^3/\mathrm{dm}^3) \times \varepsilon(\mathrm{dm}^3/\mathrm{mol \cdot cm}) \times \Gamma(\mathrm{mol/cm}^2) \quad (4)$$

where Γ is the surface coverage and ε is the dye molar absorption coefficient at wavelength λ [11]. The product of ϕ_{inj} and ϕ_{coll} is the APCE, which can be calculated from the following equation [12]:

$$\mathrm{APCE}(\lambda) = \mathrm{IPCE}(\lambda)/[1 - 10^{-A}] \quad (5)$$

Table 2 also lists the measured surface coverage and maximum IPCE (Fig. 5), and the calculated LHE and APCE at the wavelength of maximum IPCE using Eqs. (3)–(5). The surface coverage of the TiO_2 photoelectrode by the Black-dye prepared from $TiCl_4$ is larger than the value of the photoelectrode prepared from the $Ti(OCH(CH_3)_2)_4$ precursor. Therefore, the larger dye adsorption contributes to their higher LHE, which consequently contributes to the higher IPCE and J_{sc}. The LHE of the photoelectrode prepared from chloride precursor is 1.6% higher than that prepared from the tetraisopropoxide precursor. Nevertheless, the increase in IPCE is 5.8%. Thus, the higher IPCE value is caused by the higher LHE and the 4.2% higher APCE value. One possible reason for the higher APCE of the photoelectrode prepared from chloride precursor is that the less surface area, which is mentioned in Section 3.1, is less exposed to the redox species [12]. The less surface area with larger particle size also causes the increase of the neck cross-section between particles [9], which will facilitate the percolation of the electrons from one particle to other. Consequently, the recombination probability of the electron in the photoelectrode with electrolyte is lower [2], which improves ϕ_{coll} and enhances the APCE. The larger the LHE and the APCE values, the higher the IPCE value, which results in the higher J_{sc} and η values. Another possible reason is that TiO_2 particles prepared from $TiCl_4$ and $(NH_4)_2CO_3$ have a high purity and a more uniform crystal structure. Unlike carbonates or hydroxides of alkali metals such as Na_2CO_3, NaOH, K_2CO_3 and KOH, using $(NH_4)_2CO_3$ as a neutralizing agent must increase purity of the TiO_2 photoelectrode because $(NH_4)_2CO_3$ decomposes easily by calcination in airflow and disappears [13]. In addition, the XRD results in Fig. 1 indicate that TiO_2 prepared from $TiCl_4$ seems to have a more uniform crystal structure than that prepared from $Ti(OCH(CH_3)_2)_4$. Arakawa and co-workers have reported that the impurities and the disordered crystal structures in a TiO_2 photoelectrode would prevent electron transport, resulting in a lower cell performance [4]. Their results suggested that a higher purity and a more uniform crystal structure of the TiO_2 photoelectrode increases the APCE, leading to a larger J_{sc} and η in the same manner above.

Regardless, preparing a TiO_2 photoelectrode from $TiCl_4$ is a simple, effective and economical method because chloride precursor is about 1/10 the cost of the alkoxide one in terms of TiO_2 [14]. The TiO_2 photoelectrode prepared from $TiCl_4$ enhances the Black-dye-sensitized solar cell performance and improves the η of solar cell with N719 sensitizing dye [15]. These findings will be worthwhile for practical applications of dye-sensitized solar cells.

4. Conclusion

Film photoelectrodes, which consist of nanocrystalline TiO_2 particles synthesized from $TiCl_4$ and ammonium carbonate, improved the performance of Black-dye-sensitized solar cells. The maximum IPCE and J_{sc} values using TiO_2 prepared from a chloride precursor were higher than that prepared from the tetraisopropoxide precursor and resulted in a higher η value. TiO_2 photoelectrodes prepared from $TiCl_4$ also had a pure anatase crystal structure, less surface area and more thorough Black-dye surface coverage. These properties enhanced both LHE and APCE values, which enhanced IPCE and J_{sc}, and consequently led to a higher η.

Acknowledgments

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) under the Ministry of Economy Trade and Industry (METI).

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