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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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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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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

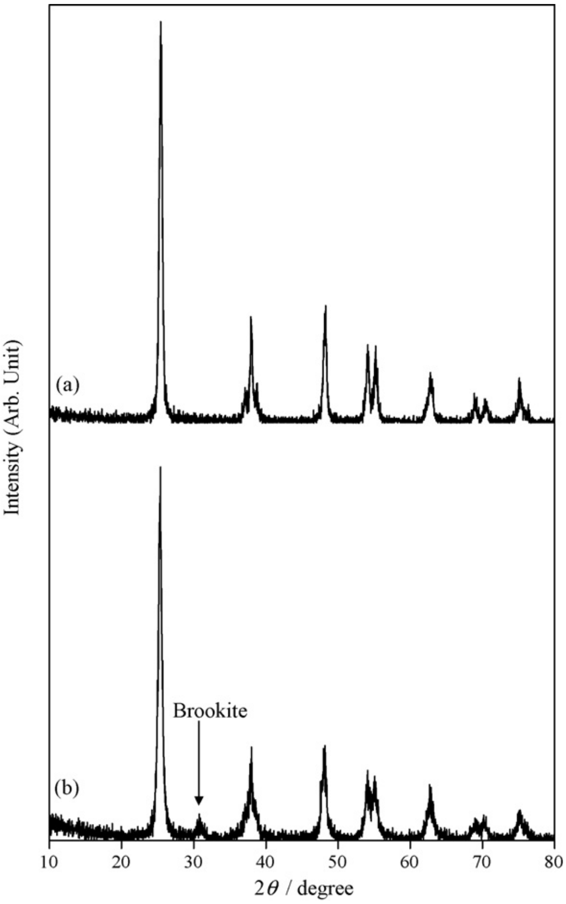

Fig. 1. X-ray diffraction patterns of nanocrystalline TiO_2 prepared from (a) $TiCl_4$ and (b) $Ti(OCH(CH_3)_2)_4$ precursors.