Journal of Photochemistry and Photobiology A: Chemistry 200 (2008) 294–300

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Influence of light scattering particles in the TiO_2 photoelectrode for solid-state dye-sensitized solar cell

Soon Hyung Kang[a], Jae-Yup Kim[a], Hyun Sik Kim[a], Haeng-Deog Koh[b], Jae-Suk Lee[b], Yung-Eun Sung[a,*]

[a] School of Chemical & Biological Engineering & Interdisciplinary Program in Nano Science and Technology, Seoul National University, Seoul 151-744, Republic of Korea
[b] Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea

ARTICLE INFO

Article history:
Received 4 January 2008
Received in revised form 19 May 2008
Accepted 15 August 2008
Available online 29 August 2008

Keywords:
Light scattering particle
Solid-state dye-sensitized solar cell
Polymer beads

ABSTRACT

A TiO_2 film was modified by adding light scattering particles and applied to an anode electrode in solid-state dye-sensitized solar cells (DSSCs). The TiO_2 films with 10 wt% (vs. TiO_2 weight) light scattering particles showed enhanced performance (28%), compared with nanocrystalline TiO_2 films, which were used as the controls. In particular, the photocurrent density (J_{sc}) reached approximately 12.6 mA/cm^2 under a one-sun condition. This was attributed to the light scattering effect and decrease in internal resistance through the macroporous structure with a minor loss of electron transport. However, in the case of a larger concentration of light scattering particles (>10 wt%), there was a decrease in the efficiency of DSSCs, which resulted from the decreased surface area and degraded electron transport and charge recombination properties, as confirmed by the measurement of stepped light-induced photocurrent and photovoltage transients. Furthermore, the diffusion properties and kinetics of the composite polymer electrolyte with the nanoporous and macroporous TiO_2 films were compared and evaluated from the electrochemical impedance spectra.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Recently, there has been considerable attention concentrated on dye-sensitized solar cells (DSSCs) composed of nanoporous TiO_2 particles [1]. As a promising alternative energy device to conventional Si solar cells, the combination of clean and unlimited solar energy as well as low production costs can allow commercialization of DSSCs, even though the conversion efficiency should be >11%. For the production of commercial DSSCs, liquid electrolyte-based DSSC should be substituted for solid- or quasi-solid type electrolyte-based DSSC due to their many practical limitations, such as dye desorption, solvent evaporation resulting from imperfect sealing of the cell, cell degradation by reactions between permeated water/oxygen and the electrolyte, and high temperature instability [2–4]. In this regard, enormous effort has moved to solid- or quasi-solid type electrolyte materials.

Recently, the Grätzel group [5] reported quasi-solid-state DSSCs with high efficiency (7.5%) employing a composite ionic liquid-based electrolyte. The high conversion efficiency was explained by the increased conductivity of I_3^- ions in the viscous solvent resulting from an increase in the range of the amorphous phases after SiO_2 or TiO_2 nanoparticles (in size of 15–20 nm) had been inserted [6]. Accordingly, the simple procedure for preparing a composite polymer electrolyte is expected to inject new momentum into new fields, such as electrochromic devices [7], polymer batteries [8,9], and fuel cells [10]. Unlike the operation of a liquid electrolyte, the mass transport of the charge carrier in the viscous polymer electrolyte is controlled by ion diffusion, which relies mainly on the diffusion coefficient of I_3^- ions and the viscosity of the solvent, and is affected slightly by the structure of the porous TiO_2 film electrode. This is because a porous and three-dimensional TiO_2 network obstructs the diffusion of electroactive species to the surroundings of a close substrate [4].

In addition, the effective internal surface area of a nanocrystalline TiO_2 film is approximately one thousand times higher than that of a flat TiO_2 film, which has a significant effect on the light harvesting yield. However, the conversion efficiency begins to degrade above limited certain point because the relationship between the specific surface area and photocurrent in a nanoporous TiO_2 film is not proportional. The commercial dye (N719) molecules used show particularly poor absorption ability of solar light, especially in the longer wavelength range λ = 600–800 nm. Therefore, many different dyes have been investigated in an attempt to extend the spectral response toward a longer wavelength range. However, many synthesized dyes have limited utility [12,13]. Hence, modification of the TiO_2 working electrode with larger TiO_2 nanoparticles (~200 nm), which behave as light scattering particles (LS), was attempted with

* Corresponding author. Tel.: +82 2 880 1889; fax: +82 2 888 1604.
E-mail address: ysung@snu.ac.kr (Y.-E. Sung).

1010-6030/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2008.08.010

the aim of extending the spectral wavelength range for light absorption by increasing the optical path length. Recently, Wan In Lee and co-workers reported that a nano-embossed hollow spherical TiO_2 particle-based photoanode with bifunctional properties improved the conversion efficiency (21% increase), compared with that of a 400 nm-diameter scattering particle-based photoanode. This was attributed to the light scattering effect of large nano-embossed hollow spheres in the longer wavelength region and the generation of photo-excited electrons because the walls of the obtained hollow spheres were composed of nanocrystalline anatase TiO_2 particles [14]. In addition, TiO_2 electrodes with microtube-network structures showed enhanced photovoltaic performance (30%) compared to that of nanocrystalline TiO_2 films using an ionic liquid type electrolyte [15]. Herein, the main contributing factors were the extension of the light path length (light scattering effect) and decrease in the transport resistance (macroporous structure). Similarly, in the situation where ion diffusion in the viscous polymer electrolyte becomes problematic, the random distribution of light scattering particles might promote the favorable penetration of a viscous polymer electrolyte into a nanoporous TiO_2 film. It should be noted that too many large particles might significantly reduce the internal surface area, resulting in lower conversion efficiency. In addition, photoinjected electrons should experience frequent trapping/detrapping events that would limit transport through the nanoporous TiO_2 layer due to the reducing electron diffusion length.

Therefore, this study investigated the effects of a suitable mixture of small particles, which would have a large effective internal surface, and larger particles, which would be effective light scattering agents, on a modified TiO_2 electrode for applications to solid-state DSSCs.

2. Experimental

An optically transparent conducting glass (FTO (fluorine doped SnO_2), Pilkington TEC Glass™, sheet resistance 8 Ω/sq, transmittance 77% in the visible range) was used as the substrate. The substrate was cleaned sequentially in acetone, ethanol and deionized (DI) water for 20 min in each step to remove the organic pollutants. The TiO_2 electrode as a control sample was fabricated as reported in a previous paper [16]. The modified sample showed more efficient performance due to the increased porosity and specific surface area, which are associated with an increase of the photocurrent of the cell. Furthermore, a somewhat uniform pore distribution was obtained. More detailed results and discussion are reported elsewhere [11].

TiO_2 powder (0.6 g), 1 wt% Vulcan spherical carbon nanopowder with a 30 nm particle size as a porosity inducing material, and light scattering particles (ST1, Ishihara Sanyo, Japan) ranging in size from a length of 200 nm and a width of 50 nm were mechanically ground together. Subsequently, acetylacetone, polyethylene oxide, and solvent (water/ethanol) were added. The quantity of light scattering particles incorporated in TiO_2 was controlled. A black colored TiO_2 film was made from the paste using a doctor blade technique, and dried for 5 min using a hot air dryer. The thermal treatment in the second-step (450 °C for 30 min → 550 °C for 30 min) was performed to completely remove the incorporated elemental carbon through a chemical reaction with oxygen.

For the formation of large pores and an increase in light scattering [17] in the nanoporous TiO_2 film, the polymer beads were synthesized using a methyl metacrylate (MMA) monomer by emulsion polymerization. The beads were spherical approximately70 to 100 nm in radius [18]. A surface functional group on the polymer beads was a substituted hydrophilic chain that was soluble in water-based solvents. The concentrated polymer bead was diluted in water to a ratio of 1:20 by volume.

After a high temperature thermal treatment for a short time, the polymer beads were burnt out leaving a reverse structure or polymer bead-sized pores in the TiO_2 films. The thickness of the TiO_2 film was controlled using transparent adhesive tape (Scotch, nominal thickness: 50 μm) as a spacer and was measured to be approximately 4.7 μm (±0.5 μm) using an Alpha-Step 200 apparatus (Tencor Instruments).

For the adsorption of the dye, the baked electrodes were immersed in an ethanol solution containing 5×10^{-4} M *cis*-bis (isothiocyanato)bis(2,2′-bipyridy-4,4′-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium (Ru 535-bisTBA, Solaronix) for approximately 12 h at room temperature. The electrode was then rinsed with ethanol and dried under an air stream. The polymer electrolyte was composed of a low molecular weight poly(ethylene oxide dimethyl ether) (PEODME, M_w = 500 g/mol, R_g = 1.4 nm), fumed silica nanoparticles (20 nm, Degussa), 1-methyl-3-propyimidazolium iodide, iodine, and acetonitrile as the volatile solvent [19]. The composite solution was stirred for 12 h and the solvent was evaporated in an oven at 60 °C. In the case of the silica nanoparticle inserted polymer electrolyte, the improved ionic conductivity and a high interfacial contact resulted in improved conversion efficiency. Pt-coated counter electrodes were prepared by spreading a drop of 10 mM H_2PtCl_6 in 2-propanol onto the FTO glass and heating it to 400 °C for 20 min under air ambient. Only one-side of the dye-adsorbed TiO_2 electrodes (active area 0.16 cm^2) was pressed using the thermal adhesive films (Serlyn, thickness: 60 μm), which controlled the thickness of the polymer electrolyte. Finally, the polymer electrolyte solution was cast on the TiO_2 electrode, which was covered by the Pt-coated counter electrode.

The absorbance spectra were investigated using a Shimadzu model 3100 UV–vis (ultraviolet–visible) spectrophotometer over the wavelength range, 500–1000 nm, at room temperature. The photocurrent–voltage (*J*–*V*) measurements were performed using an XIL model 05A50KS source measurement unit at a power of 100 mW/cm^2. A 500-W Xenon lamp was used as the light source and its light intensity was calibrated to AM 1.5 radiation (one-sun condition) using a NREL fabricated Si reference solar cell. The light was homogenous up to 5 cm × 5 cm.

The stepped light-induced measurements of the photocurrent and voltages transients (SLIM-PCV) were used to measure the electron diffusion coefficient (D), which was correlated to the electron transport in the TiO_2 film, and the electron lifetime (τ), which was related to the extent of charge recombination. The transient photocurrent and photovoltage were deduced by a stepwise change in the intensity of a 632 nm laser pulse stepped down by ND filters to 10 mW/cm^2. The D values were obtained by the time constant (τ_c), which was determined by fitting an exponential function of the photocurrent transient with exp ($-t/\tau_c$), according to the following equation, $D = \omega^2/(2.35\tau_c)$ with a TiO_2 film thickness (w). In addition, the τ values were derived by fitting an exponential function of the photovoltage transient to exp($-t/\tau$) [20,21].

The photocurrent action spectra (IPCE) were collected under short circuit conditions with a tungsten lamp source and a 20 nm bandwidth monochromator, resulting in an illumination intensity of approximately 1 mW/cm^2.

The electrochemical impedance spectra were obtained by applying a sinusoidal perturbation of ±5 mV over an open-circuit voltage at frequencies ranging from 0.01 Hz to 100 kHz in the dark or under illumination (AM 1.5, one-sun condition) using a Zahner impedance analyzer to examine the diffusion properties and ionic conductivity in the polymer electrolyte. The measurements were also used to

Download English Version:

https://daneshyari.com/en/article/29000

Download Persian Version:

https://daneshyari.com/article/29000

Daneshyari.com