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Echinoid-like particles with high surface area for dye-sensitized solar cells

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Abstract

Echinoid-like particles were synthesized and applied to dye-sensitized solar cells (DSSCs). When echinoid-like particles were used in the DSSCs, dye-loading was increased because of its large surface area. Moreover, it was observed by diffused reflectance that scattering effect was induced by the micron size of echinoid-like particles. Although it was observed by electrochemical impedance spectroscopy (EIS) analysis that more recombination was occurred in the echinoid-like particles, the enhancement of J_{SC} resulting from the increase of dye-loading compensated the decrease of V_{OC}. As a result, the overall power conversion efficiency (PCE) was enhanced from 6.63% to 6.74%.

Keywords: Echinoid-like particles; Dye-sensitized solar cells; Large surface area; Electrochemical impedance spectroscopy

1. Introduction

Recently, development of renewable energy is being required because the demand of energy is increasing constantly and the fossil fuels are running out. Solar energy is one of the potential candidates, because it is a permanent energy source. The supply of solar energy from the sun to the earth is about 3×10^{24} J year^{-1}, which would amount to 10^4 times of mankind energy consumption. This value means that covering 0.1% of the earth's surface with solar cells of which the power conversion efficiency is 10% satisfy the energy need of mankind (Gratzel, 2005). Therefore, many researchers are studying intensively on solar cells to obtain high conversion efficiency and to commercialize. Conventionally, silicon-based solar cells were developed and the power conversion efficiency reached about 24%, and that of module reached about 15% recently. However, commercialization of them is limited because of its relatively high cost of production (Luque and Martı, 2008). DSSCs were developed as an alternative to *p–n* junction solar cells in 1991, and have received much attention during two decades because of its futuristic properties such as low cost of production, and high efficiency, (O' Regan and Gratzel, 1991). DSSCs are generally composed of dye-sensitized nanocrystalline TiO_2 electrode, Pt-coated counter electrode, and electrolyte containing redox couple (I^-/I_3^-). Among them, the property of nanocrystalline TiO_2 influences to the overall power conversion efficiency (PCE) significantly because TiO_2 nanoparticles are used as electron transfer pathway and the supporter for chemical adsorption of the dye. There have been many efforts to enhance the PCE by controlling the structure of TiO_2.

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TiO_2 nanoparticles, one of the major components of DSSCs, have been received much attention because of its unique opto-electronic properties. The physical and chemical properties of TiO_2 are influenced by the size, morphology, and crystal structure. There are three crystal phase of TiO_2 (anatase, rutile, brookite), and anatase phase shows the best performance in DSSCs because of its large surface area compared with rutile phase (Park et al., 2000). To obtain high PCE, photoanode should satisfy some requirements; good light harvesting, large surface area, less charge recombination (Dai et al., 2012). Generally, 10–20 nm-sized TiO_2 nanoparticles are applied to a semiconductor layer on the FTO glass. These small particles have very larger surface to anchor the sensitizer. However, there are many contact faces between each particle, where many trapping/detrapping events occur at (Fisher et al., 2000). Most of the trapped electrons are recombined with I^- ions, which is in the electrolyte, at the TiO_2/electrolyte interface, and the recombination phenomenon lowers the power conversion efficiency of DSSCs. Many efforts were conducted to overcome the recombination and enhance the cell performance. One-dimensional structures, such as nanorod, nanotube, nanowire, were one of the candidates reducing the recombination by providing a direct pathway of electrons (Feng et al., 2008; Huang et al., 2011; Hwang et al., 2011; Lamberti et al., 2013; Li et al., 2010; Liu and Aydil, 2009). Although these structures supply a fast electron transfer rate, DSSCs based on these structures showed low power conversion efficiencies because of their low surface area, resulting in small amount of adsorbed dye (Santulli et al., 2011). In addition, morphology control of TiO_2 particles has been researched to improve the cell performance. Ellipsoidal TiO_2 nanoparticles were synthesized by sol–gel method without using templates in the presence of excess H_2O_2, and the power conversion efficiency of the cells using these nanoparticles showed 6.90% (Baek et al., 2009). Cubic-shaped TiO_2 nanoparticles in the size of 5–10 nm were also synthesized and PCE of 9.77% was obtained (Chae and Kang, 2011). Moreover, TiO_2 nanoleaves were hydrothermally synthesized and the surface area of 93 m^2/g. 6.5% of PCE was attained when nanoleaves and nanoparticles were mixed (Dhas et al., 2011). Meanwhile, sea-urchin TiO_2 particles were prepared and found that DSSCs based on these TiO_2 particles showed low performance because of poor film morphology leading to loss of surface area (Santulli et al., 2011). Single-crystalline rutile TiO_2 microspheres with the size of 1.5–2.5 μm were synthesized. The PCE of the cells based on the rutile microspheres showed 3.57% PCE under AM 1.5 illumination, which is relatively higher than that based on P25. However, they suffered from the low current density because of low BET specific surface area (Sheng et al., 2011).

Herein, we report the applicability of echinoid-like TiO_2 particles to DSSCs for the enhancement of the power conversion efficiency. Generally, large spherical TiO_2 particles (about 400 nm) ware used as scattering layer to improve the light harvesting. However, large spherical particles have relatively small surface area which lowers the amount of dye loading. This is one of the limits that hinder the high photovoltaic efficiency of the cells. Consequently, it is necessary to overcome this limit for the enhancement of PCE by increasing the amount of dye loading. Our group reported earlier the synthesis of echinoid-like TiO_2 particles which have larger surface area (Jang et al., 2012). The size of these particles is about 1 μm, and they have large surface area. These particles can act as a dual functional material by providing sufficient site to anchor dyes because of large surface area, and inducing the light scattering effect resulting in the increase of light harvesting. We fabricated solar cells using echinoid-like TiO_2 particles, and evaluated the photovoltaic performance. Additionally, the power conversion efficiency was compared to that of spherical TiO_2 particles of which the size is about 1 μm, which are synthesized by sol–gel method because the size is similar to the echinoid-like particles.

2. Experimental

2.1. Synthesis of TiO_2 particles

Echinoid-like TiO_2 particles were synthesized as a same process reported earlier by our group (Jang et al., 2012). 0.6 g of poly(vinyl alcohol) (PVA) was dissolved in 18 mL of dimethyl sulfoxide (DMSO) at 100 °C and titanium(IV) isopropoxdie (TTIP) was added to 30 mL of 2-propanol at room temperature. The PVA/DMSO solution and TTIP/2-propanol solution were added drop by drop to 600 mL of acetic acid under stirring at 100 °C. The mixture was stirred vigorously and refluxed at 100 °C. After 4 days, the synthesized particles were centrifuged and washed with acetone several times and dried at 70 °C. The dried products were calcined at 450 °C for 2 h.

TiO_2 beads particles were synthesized by sol–gel method as reported in the literature (Chen et al., 2009). In Brief, 1.32 g of 1-hexadecylamine was dissolved in 200 mL of ethanol, and then 0.8 mL of KCl solution (0.1 M) was added. 4.4 mL of TTIP was added to the solution drop by drop under room temperature. After 18 h, the particles were washed with ethanol and dried at room temperature. The final products were calcined at 450 °C for 2 h.

2.2. Fabrication of DSSCs

TiO_2 paste was prepared using α-terpineol, dibutyl phthalate, lauric acid, and ethyl cellulose to fabricate photoanode. Four types of the TiO_2 film were manufactured; SE for a single-layer film using echinoid-like particles, SB for a single-layer film using beads particles, DE for a double-layer film using echinoid-like particles above nanocrystalline TiO_2, and DB for a double-layer film using beads particles, respectively. In the case of double-layer films, commercial TiO_2 paste (STP-50N, ENB Korea) was used as an under layer. The paste was deposited on the FTO glass by doctor blade method and the film was annealed