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High performance dye-sensitized solar cells (DSSCs) achieved via electrophoretic technique by optimizing of photoelectrode properties

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ABSTRACT

This paper describes a simple method utilizing electrophoretic deposition (EPD) of commercial P25 nanoparticles (NPs) films on fluoride-doped tin oxide (FTO) substrate. In this process, voltage and the number of deposition cycles are well controlled to achieve TiO_2 film thickness of around 1.5–26 μm, without any mechanical compression processing. The experimental results indicate that the TiO_2 film thickness plays an important role as the photoelectrode in DSSCs because it adsorbs a large number of dye molecules which are responsible for electrons supply. Furthermore, it was found that effects of the bulk traps and surface states within the TiO_2 films on the recombination of the photo-injected electrons (electron–hole pairs) strongly depend on the TiO_2 electrode annealing temperature. Finally, a DSSC with a 24 μm thick TiO_2 film and annealed at 500 °C produced the highest conversion efficiency (η=6.56%, I_{SC}=16.4, V_{OC}=0.72, FF=0.55) with an incident solar energy of 100 mW/cm^2.

1. Introduction

Nanocrystalline TiO_2, a well-known metal oxide semiconductor, has been widely studied for numerous applications. For example, it is used as a photocatalyst, in fabrication of photo-electrodes, and for dye-sensitized solar cells (DSSCs) with high performance due to its unique physical, chemical and optical properties [1].

A typical DSSC consists of sensitizing dye, nanoporous metal oxide semiconductor film, electrolyte and counter electrode [2]. In order to optimize energy conversion efficiency of DSSCs, charge transfer and charge transport rates should be enhanced so that a significant fraction of electrons are extracted for external loads with minimal electron–hole pair recombination. In particular, as transport and transfer rates are interdependent, simultaneous optimization of the electron transfer rates is important to achieve higher-efficiency DSSCs [3,4].

Several techniques, including mechanical compression [5–9], electrophoretic deposition [10], chemical sintering [11–14], hydrothermal necking [15,16], electron beam curing [17], spin-coating [18], microwave sintering [19,20], and so on, have been reported for the fabrication of TiO_2 film on the conductive substrate. On the other hand, EPD is a simple method for the preparation of nanostructured films onto conductive substrates. Compared to other coating techniques, EPD takes a much shorter time. Further, EPD is very useful because of its low cost, requirement of simple equipment, and its ability to form uniform layers of controlled thickness with a homogeneous microstructure [21–24]. EPD is a high efficient technique for large scale production in commercial applications. In addition, EPD operates at moderate

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temperatures that result in reducing the possibility of deterioration of the raw materials and final products. In EPD, the structural, metallurgical, chemical, and physical properties of materials are extremely dependent on a huge number of film deposition parameters, especially thickness dependent [25]. By making proper TiO_2 film thickness and crystallinity, DSSCs are capable to absorb more photons to convert to electricity.

Miyasaka and Kijitori prepared TiO_2 thin films using EPD followed by sintering process under a low-temperature of 150 °C [26]. Finally, the prepared thin films were used in making DSSC, and a high energy conversion efficiency of 4.1% was achieved and Yum et al. used EPD technique to prepare a porous TiO_2 film, which was then used in cold pressure activation [27]. Without addition of the surfactant and heat treatment, an energy conversion efficiency of 1.66% was yielded.

Fujimura and Yoshikado used deionized water, as a solvent for EPD (without a binder), which possesses advantages of low cost, environmental protection, industrial safety, and minimization of pollution in produced films [28]. On the other hand, the main problem in application of water-based solution in EPD method is related to gas formation by hydrolysis of water above a DC voltage of about 1.4 V, which result ng films suffering from enormous pinholes in deposited layer, lack of film uniformity, and poor layer adherence.

Miyasaka et al. [29] and Murakami et al. [30] reported deposition of nanoporous films using EPD technique of commercially available TiO_2 nanoparticle powders, P-25 and F-5, by a dry mixed solvent of acetonitrile and *tert*-butanol. With applying 0.3 mm distance between electrodes and applied voltage of 200 V, TiO_2 nanoporous films with a thickness of 7–13 μm were obtained. The resulting DSSCs exhibited an energy conversion efficiency of 2.0%.

Kim et al. [31] reported anodic EPD of TiO_2 nanotubes for DSSC fabrication. As a result, 10 μm thick films of TiO_2 nanotubes sintered at 500 °C, and a high efficiency of 6.72% was achieved. The DSSC prepared from the same TiO_2 nanotubes by doctor-blade technique annealed at 450 °C for 30 min only demonstrated energy conversion efficiency of 0.65%.

Regarding the novelty of the current study, we found charging system of P25-iodine–acetone-acetyl acetone–water with optimum amounts, with an applied voltage of 10 V and 15 cycles electrophoresis, is promising for P25 NPs deposition via EPD technique. Totally, these efficient applied voltage and cycles of electrophoresis accompanied with productive ratio of P25-iodine–acetone-acetyl acetone–water resulted in achieving a high current density of ~18 mA that is unique among the previous EPD related literatures [25–31].

The major goal of the current study was investigating the relationship between the thickness and annealing temperature of P25 films on the performance of the DSSC related parameters including V_{OC}, J_{SC}, FF. The thickness of P25 film was controlled by varying the deposition cycle. Also, elevating annealing temperature from 150 to 500 °C is found to alter the crystal phase, crystallinity, and structural integrity of P25 NPs. As a result, it was found that P25 film thickness and annealing temperature have a considerable influence on photovoltaic properties of DSSCs. Finally, a high energy conversion efficiency of 6.56% was achieved by DSSC made by P25 film with thickness 24 μm annealed at 500 °C.

2. Experimental

2.1. Materials and chemicals

Commercially-available P25 powder (av. 30 nm by Brunauer–Emmett–Teller (BET), 80% anatase (d=21 nm) and 20% rutile (d=50 nm), via $TiCl_4$-fumed gas synthesis, Degussa, Germany), 4-tert-butylpyridine (4-tBP) (Aldrich), acetonitrile (Fluka), valeronitrile (Fluka), Chloroplatinic Acid (H_2PtCl_6) (Fluka), Iodine (I_2) (99.99%, Superpur1, Merck), lithium iodide (LiI) (Merck), acetyl acetone (acac) (Merck), acetone (Merck), Fluorine doped tin oxide (FTO) conductive transparent glass (TEC-15, Dyesol) and cis-bis(isothiocyanato)bis(2,20-bipyridyl-4,40-dicar-boxylato)-ruthenium(II)bis-tetrabutyl ammonium (N719), Dyesol] were used as received. H_2O was purified by distillation and filtration (Milli-Q).

2.2. Electrodes and cell preparation

EPD was utilized to preparation of P25 NPs-based films used in DSSCs. During the EPD process, the FTO glass had a positive potential (anode) while a steel mesh was used as the counter electrode (cathode). A distance of 2 cm was applied between the two electrodes. The applied voltage was 10 V. Power was supplied by a Motech Programmable Dc source meter. The deposition cycle was varied from 1 to 20 cycles with each cycle of 15 s and the temperature of the electrolyte solution was kept at 25 °C. The coated substrates were dried at air. The apparent area of the film was 1.5×1.5 cm^2. The resulting layer was annealed at 150–500 °C in air atmosphere for 30 min.

We observed, as it also was reported by others studies [32], that to achieve better quality of deposited layers, the amount of the additives should be minimized, since only a small fraction of the ions is adsorbed on particle surface. The ions that do not absorb on the particle surfaces raise ionic strength of a suspension which causes in reduced thickness of electrical double layer on particle surface and in particle agglomeration and a deterioration of quality of deposited layer. Furthermore, the mobility of free protons is much higher than the charged TiO_2 nanoparticles. Additionally, the increase in free proton concentration decreases amount of deposited TiO_2 particles. We found that the optimal concentrations of additives are as follows: iodine 120 mg/l, acetone 48 ml/l, and water 20 ml/l. The optimal amount of P25 NPs was adjusted in 8 gr/lit.

After cooling down to 80 °C, the sintered TiO_2 electrodes were soaked into a 0.3 mM of N719 dye in ethanol solution for up to 24 h. Transparent Pt counter electrodes were prepared by following method: a few drops of 3 mM hydrogen H_2PtCl_6 ethanol solution were spread over the FTO conducting glass, followed by heating at 400 °C for 15 min. The N719-sensitized TiO_2 electrode and Pt counter electrode were assembled into a sandwich type cell. The electrolyte, which was composed of 0.5 M LiI, 0.05 M