Dye-Sensitized Solar Cells Based on SnO₂ Nanorod and Surface Treatment with Mg(II) Film

Jingyi Bai, Kenji Murakami

Abstract:

Homocentrically grown SnO_2 nanorods were synthesized by a hydrothermal method, whose diameter and length are around 20 nm and 100-200 nm, respectively. The photovoltaic properties of dye-sensitized SnO_2 and MgO-treated SnO_2 films were investigated. A light-to-electricity conversion yield of 0.8% was achieved by applying the nanorods as a thin film layer for the dye-sensitized solar cells. Treatment with MgO on SnO_2 surface improves the photovoltage, fill factor and cell efficiency owing to preventing a recombination of the electrons injected into SnO_2 with acceptors in the electrolyte.

Keywords: dye-sensitized solar cell, tin dioxide film, nanorod, spray pyrolysis deposition, surface treatment, magnesium oxide.

1. Introduction

Dye-sensitized solar cells (DSCs) are based on a sensitization of mesoporous, nanocrystalline metal oxide films to visible light by an adsorption of the molecular dyes. Most of DSCs utilize nanoporous electrodes made from TiO₂ [1]-[6]. However, some applications require more positive conduction band potential than that of TiO₂. Tin oxide (SnO₂) is an attractive alternative to TiO₂ due to its higher electronic conductivity and electron mobility [7]. Such faster electron transport dynamics could minimize the interfacial charge recombination losses in DSCs and improve the cell performances.

Hydrothermal method, one of the solvothermal methods, enables syntheses of new materials with different morphologies. In particular, the method is useful to produce the finely dispersed, nanocrystalline materials.

In this paper, the synthesis of single crystalline SnO_2 nanorods is described through the hydrothermal route with $SnCl_4$ as a precursor. The spray pyrolysis deposition technique was applied to form the metal oxide films for DSCs. The films were analyzed by using the x-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM). Photovoltaic performances of the assembled DSCs were also investigated. Furthermore, an effect of surface treatment of SnO_2 with a MgO coating is discussed on the cell performances.

2. Experimental

2.1. Preparation of dye-sensitized solar cells

NaOH (10 mol/L) was slowly added into $SnCl_4$ (1 mol/L) solution drop by drop followed by stirring in an alcohol-water (1:1) mixture. Then, the mixing solution

was transferred into the teflon-lined autoclave. The autoclave was heated to 200°C for 24 h. The product including SnO_2 nanorods was centrifuged and washed with the distilled water and alcohol, and then dried at 60°C in an oven.

The product was mixed with acetylacetone, non-ionic surfactant and acetic acid followed by agitation ultrasonically for 60 m. The suspension was sprayed pneumatically onto a fluorine doped SnO_2 -coated glass (FTO glass) substrate heated at 130°C and it was sintered in air at 500°C for 1 h. The MgO- treated SnO_2 was prepared similarly to the procedure for SnO_2 nanorods except that a magnesium acetate aqueous was added into the SnO_2 nanorod precipitate and kept at room temperature for 12 h.

After the FTO glass plate with SnO_2 film was soaked into the solution of the N719 (n-Bu₄N) 2 [Ru(Hdcbpy)₂ (NCS)₂] dye in acetonitrile and tert-butanol (1:1) for 12 h, it was assembled into a sandwich-type cell, where the counter electrode was a platinumsputtered FTO glass. A drop of electrolyte solution (0.M LiI, 0.05 M I₂, 0.5M tert-butyl pyridine, 0.6M dimethylpropylimidazolium iodide in methoxyacetonitrile) was inserted into the assembled cell.

2.2. Characterization

The morphology of the nanoporous SnO_2 films and nanorod materials were observed by using the FE-SEM (JOEL, JSM-6320F). The XRD (Rigaku, RINT-2200) profiles enabled a characterization for crystalline phases of nanoporous SnO_2 powder. Energy-dispersive X-ray spectroscopy (EDS equipped with FE-SEM) measurements were carried out to determine a component of the nanomaterials. I–V characteristics of the cells at AM 1.5 (1000 W/m^2) were measured by using the calibrated solar cell evaluation system (Jasco, CEP-25BX).

3. Results and discussion

3.1. Sn0, film

It is found from the XRD profiles that only the diffraction peaks of tetragonal rutile SnO_2 are detected for all the sprayed films. Figure 1 shows the FE-SEM images of sprayed films. As shown in the figure, the surface is very rough and such morphology is originated from the homocentrically grown nanorods, whose diameter and length are around 20 nm and 100-200 nm, respectively. As a result, the film is mainly composed of disordered networks of the SnO_2 nanorods.

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Fig. 1. (A) FE-SEM photographs of the sprayed SnO_2 film (B) Magnified image of (A).

3.2. Mg-modified SnO₂ film

It is concluded from the XRD profiles that the surface treatment of SnO_2 with MgO has no significant influence on a grain size of nanoparticles. Surface morphology of the Mg-modified SnO_2 film is also similar to that of the non-treatment surface as shown in Fig. 2. The EDS measurements cannot reveal an existence of Mg due to a very small amount of magnesium composition.



Fig. 2. FE-SEM photograph of the sprayed Mg-modified ${\rm SnO}_2$ film.

3.3. Photovoltaic performances

Typical I–V characteristics of the fabricated solar cells are illustrated in Fig. 3. An open circuit voltage and a fill factor of the cell are improved greatly by the surface treatment of SnO_2 with MgO. Table 1 summarizes the photovoltaic performances of the DSCs made of the sprayed SnO_2 films, where J_{sc} is a short circuit current, V_{oc} a open circuit voltage, FF a fill factor and η energy conversion efficiency. In order to consider an effect of the surface treatment of SnO₂ with MgO, the performances of DSCs made of MgO-treated SnO₂ films with different Mg/Sn ratios are also listed in the table. Although the performances of DSC with SnO₂ nanorods-based film are very poor, the surface treatment of MgO improves the efficiency greatly from 0.8 to 1.63%. Very low $\rm J_{SC}$ for the $\rm SnO_2$ nanorods-based film may be attributed to the smaller surface area available for dye anchoring. Increasing the amount of Mg tends to increase V_{0c} and FF, while both J_{sc} and η decrease. The surface treatment with MgO seems to form a barrier on the SnO₂ surface preventing a recombination between the SnO_2 and the acceptors in electrolyte. The trace amount of MgO, therefore, is very effective to improve the performances as shown in the table.



Fig. 3. I-V characteristics of the dye-sensitized SnO₂ nanorod and Mg-modified SnO₂ nanorod solar cells.

Table 1. Photovoltaic performances of the SnO_2 -based DSCs with and without Mg-modification.

Sample	J _{sc} (mA·cm ⁻²)	V _{oc} (V)	FF	η (%)
SnO ₂	8.50	0.24	0.40	0.81
Mg/Sn=0.01	7.23	0.37	0.61	1.63
Mg/Sn=0.04	3.38	0.49	0.67	1.12
Mg/Sn=0.08	2.75	0.56	0.70	1.07

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