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The use of binary TiO_2–GeO_2 oxide electrodes to enhanced efficiency of dye-sensitized solar cells

Athapol Kitiyanan, Taku Kato, Yoshikazu Suzuki, Susumu Yoshikawa*

Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan

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Abstract

The preparation of titania (TiO_2), germania (GeO_2) and binary TiO_2–GeO_2 oxide with different Ti/Ge ratio gels based on sol–gel method with surfactant-assisted mechanism and their application for dye-sensitized solar cells (DSCs) were reported. The samples were calcined and characterized by nitrogen adsorption porosimetry, X-ray diffraction (XRD) and morphology was investigated by field emission scanning electron microscopy (FE-SEM). The XRD results suggested that germanium substituted for titanium in the TiO_2 lattice because of the gradual shift of 1 0 1 diffraction peak of anatase type of TiO_2. The higher surface area from binary oxides samples was due to the added oxide acting as a crystal growth inhibiter. For the application for DSCs, the electrodes fabricated from binary oxides sample gave significant higher J_{sc} when compared to cell that fabricated by sample TiO_2 electrode. The consequence effects of added germanium were analyzed and discussed.

Keywords: Dye-sensitized solar cell; Photoelectrochemical; Surfactant-assisted method; Titanium oxide; Germanium oxide

1. Introduction

Mesoporous film-based dye-sensitized solar cells (DSCs) have been developed since a light-activation mechanism similar to the plant photosynthetic process was applied to solar cells [1]. Typical DSC is composed of a few micrometer thick film consisting nanocrystalline oxide covered with monolayer of Ru-bipyridyl-based charge transfer dye, a redox electrolyte and a platinum metal electrode [2].

TiO_2 is well-known semiconductor oxide with band gap energy of 3.0–3.2 eV regardless of its tetragonal structure for both anatase and rutile. It is also well-known that band gap illumination generates electron–hole pairs in TiO_2. These electron–hole pairs can either recombine or move to the surface to react with species adsorbed on the surface, which is known to be the basis of photocatalysis [3], dye-sensitized solar cells is the well-known application of TiO_2 thin films. The DSCs which based on highly porous nanocrystalline films of TiO_2 are considerable attractive because of their rather high power conversion efficiency (10%), potential low cost and high semiconductor stability [4].

Although dye-sensitization can be achieved with porous films of non-TiO_2 semiconductors with high band gap such as SnO_2 [5], Fe_2O_3 [6], ZrO_2 [7], Al_2O_3 [8], ZnO [9], it has never been reported to be as efficient as the TiO_2 cells reported by O'Regan and Grätzel [10]. In fact, nanostructured TiO_2 is not perfect yet in that electron transport becomes more difficult with the increase of photocurrent in the absence of space charge layer [3]. The efficiency of DSCs is limited in part by back-reaction of photoinjected electrons with triiodide ions in the electrolyte [11] and the presences of electron acceptors such as oxygen and iodine will lead to loss of photogenerated electrons over the nanostructured semiconductor electrolyte interface during the transport of the charge transport of the electrons to the back contact [12]. Thus, photogenerated charge recombination should be prevented for enhanced efficiency because solely enlarging the oxide electrode surface area is not sufficient. In this study, germanium oxide was added to enhance the properties of TiO_2 nanostructured and would be an alternative approach to improve the photovoltaic efficiency.

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* Corresponding author. Tel.: +81 774 38 3502; fax: +81 774 38 3508.
E-mail address: s-yoshi@iae.kyoto-u.ac.jp (S. Yoshikawa).

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2. Experimental

2.1. Synthesis of pure TiO_2, pure GeO_2 and binary TiO_2–GeO_2 oxides

Preparation processes of binary TiO_2–GeO_2 oxide solid solution in this study are as follows. At first, the titania (tetra-isopropyl-orthotitanate, TIPT) and germania precursor (germanium ^{n}butoxide, GeBt) were mixed together by various concentration. The mixed metal precursors were firstly modified by modifying agent (acetylacetone, ACA) in order to obtain controllable sol–gel process. The ACA was slowly added to mixed metal precursor in a molar ratio [ACA] = 1:1 to get clear yellow mixture. The organic surfactant (laurylamine hydrochloride, LAHC) was used as micellar assemblies template structure to fabricate the well-defined mixed oxide nanocrystalline. The 0.1 M homogeneous LAHC solutions (pH 4–4.5) were mixed with the modified precursors in a molar ratio of [TIPT + GeBt]:[LAHC] = 4:1. After additions were completed, these mixtures were stirred at room temperature for 1 h and further in an oven at 40 °C for 24 h until a clear yellow solution was obtained. The reaction bottles were then sealed and kept in an oven preheated at 80 °C for 7 days to yield a gel. These gel samples were washed by iso-propanol to remove the surfactant template. All syntheses were performed in a similar step to obtain the sample which have 0, 5, 10, 20, 30 and 100 mol% of germania added (named hereafter TiGe*X*, where *X* is the mol% of germania added into titania (e.g. TiGr10 is 10 mol% of GeO_2 mixed with 90 mol% of TiO_2)). For the pure component, 'pure TiO_2' and 'pure GeO_2' will be used instead of TiGe0 and TiGe100, respectively.

2.2. Preparation of photoelectrodes

Conducting glass plates with fluorine doped tin oxide (FTO), sheet resistance 15 Ω/□ were cleaned with acetone, rinsed with distilled water and dried in 80 °C oven. The photoelectrode was prepared by doctor blade coating. As for the preparation of the starting coating gel, two longer rims of conduction glass plate (2 cm × 10 cm) were covered with adhesive tape (Scotch, ∼40 μm in thickness). Some drops of synthesized gel were applied to one of the bare edges of the conducting glass, and used a glass rod sliding over the tape-covered edges to spread the gel out evenly. The thickness of the film can be adjusted by repetitive coating and sintering at 450 °C 10 min for each layer until obtained the desire thickness. Finally, the coated electrodes were sintered at 450 °C for 2 h before measuring film thickness and fabricating DSCs.

2.3. Fabrication of dye-sensitized solar cells

After sintered in air at 450 °C for 2 h and left to be cooled to 80 °C, the sintered electrodes were then immersed in 50 wt.% butanol and 50 wt.% acetonitrile mixed solution of 0.3 mM [bis(tetrabutylammonium) cis di(thiocyanato) bis(2,2′-bipyridine-4,4′-carboxylic acid) ruthenium(II)] (called N719) dye at least 24 h. The dye-adsorbed electrodes were immediately assembled into thin layer, sandwich type solar cells. The counter electrodes, thin platinum layer sputtered on FTO conduction glass plates were kept in contact with these dyed electrodes. In order to prevent a direct contact between the working and the counter electrodes which result in the open-circuit voltage V_{oc} reduction to <300 mV [12], two stripes of 25 μm thick Surlyn (Dupont, Himilan 1702) were inserted as spacer between them. A drop of redox electrolyte composing of a 0.6 M dimethylpropyl-imidazolium iodide solution, a 0.1 M lithium iodide (LiI) solution, a 0.05 M iodide (I_2) solution and a 0.5 M 4-*tert*-butylpyridine in acetonitrile was introduced to the gap between the counter and working electrodes by the capillary force.

2.4. Characterization and measurement

Crystal structures of all samples were analyzed by X-ray diffraction (XRD) (RIGAKU Rint-2100) which is generating monochromated Cu Kα radiation with continuous scanning mode at the rate of 2 °/min and operating conditions of 40 kV and 40 mA. BET surface area of synthesized samples was recorded using nitrogen adsorption–desorption analysis (BELSORP 18 PLUS) with all samples degassed at 200 °C for 2 h before the actual measurements.

The film thickness of coated electrodes was determined by an Alpha-Step 200 apparatus (Tencor Instruments) and the amount of adsorbed dye concentration was measured by using the solution of 0.1 M NaOH and ethanol (1:1 in volume fraction), in which the anchored dye from dyed electrodes was desorbed. A shimadzu UV-2450 UV–vis spectrometer was exploited to record absorption spectra of the samples at room temperature. The sample morphology was observed by a field emission scanning electron microscopy (FE-SEM, JEOL JSM-6500FE).

The photovoltaic properties were measured by using a potentiostat (Bunko–Keiki Co., Ltd., Model HCSSP-25) irradiated with simulated solar light, A.M. 1.5, 100 mW/cm^2 (Bunko–Keiki Co., Ltd., Model CEP-2000).

3. Results and discussion

3.1. Characterization of binary TiO_2–GeO_2 oxide

Fig. 1 shows the results of XRD patterns of the pure TiO_2, pure GeO_2 and binary TiO_2–GeO_2 oxides at different Ti/Ge ratio after heat treatment at 500 °C. For the pure TiO_2, the peaks characteristic of the anatase phase appeared and no trace of rutile phase was detected. For pure GeO_2 sample, the XRD pattern exhibited hexagonal phase structure after heat treatment at 450 °C. For binary TiO_2–GeO_2 oxide samples, the XRD patterns from the sample TiGe5 to TiGe30 are in agreement with anatase type of TiO_2 and peaks from GeO_2