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TiO2-ZrO2 Mixed Metal Oxide Electrode for a Dye-sensitized Solar Cell

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Abstract: The improvement of dye-sensitized solar cell prepared by zirconia (ZrO_2) and titania (TiO_2) mixed oxides electrode is reported. The mixed oxides prepared by sol-gel methods of surfactant assisted templating mechanism possessed larger surface area than a titania pure component which prepared by the same method. As a result, the light harvesting ability of the dye, adsorbed on mixed oxide nanoporous film, is significantly increased, leading to improved a short-circuit photocurrent up to 11%. For the IPCE property, the mixed zirconia/titania electrode can absorbs UV light below 380 nm, corresponds to energy band gap (E_g) around 3.27 eV, which is higher than that of pure component of titania (E_g = 3.2 eV). Due to the conduction band energy (E_c) of ZrO_2 is approximately –1.0 eV, which is more negative than –0.3 eV of TiO_2, a larger E_g of zirconia/titania electrode could leads more negative valueof E_c than that of TiO_2 electrode. This could increase an open-circuit voltage of the cell fabricated from TiO_2-ZrO_2 electrode up to 4%. Both of these increments contributed the improvement on a solar energy conversion efficiency up to 17%.

Keywords: Dye-sensitized Solar Cell, Mixed Oxide, Surfactant-assisted Templating Mechanism, Photoelectrochemical.

Introduction

Mesoporous film based dye-sensitized solar cells (DSSCs) have recently received considerable attention as practical solar energy conversion devices [1,2]. DSSC is composed of a few micrometer-thick film consisting nonocrystalline oxide covered with monolayer of Ru-bipyridyl-based charge-transfer dye, a redox electrolyte and a platinum metal electrode. Such high efficiency of DSSCs has been achieved only when the nanoporous TiO_2 electrodes which facilitates high optical density of a dye monolayer, are applied. In general, an electrode with high surface area is of great significance since a higher amount of dye adsorbed on an electrode corresponds to a higher current density. During the past years, TiO_2 electrodes consisting of nanosized semiconductor colloids have been sintered on a transparent conduction substrate. Those resulted in a porous geometry and a very large surface area. They are one of the most commonly used electrodes for the DSSCs. However, the resulting electrode geometry introduces special characteristics, some of which reduce the performance of the DSSCs [3].

Although dye-sensitization can be achieved with porous films of non-TiO_2 semiconductors with high band gap [4,5], it has never been reported to be as efficient as the TiO_2 cells reported by Regan and Grätzel [1].To increase the open-circuit photovoltage (V_{OC}) of a cell, several research groups attempted to improve the properties of the electrode such as modifying the structure of TiO_2 [6,7] or using a bilayer technique [8-11]. This bilayer technique required another metal oxide, which has a more negative conduction band energy (E_C), coated onto base nonporous electrode to reduce the recombination rate of photo-injected electron. Since the V_{OC} is in proportion to the difference in the electron energies between redox potential level and the level of E_C of an electrode [12], another possible way to increase the V_{OC} is the increase in the conduction band energy level of the material used in electrodes.

In this study, nanostructured mesoporous mixed metal oxide was synthesized by the surfactant-assisted [13] method using laurylamine hydrochloride (LAHC) / mixed metal alkoxides modified with acetylacetone (ACA)system.A mixture of ZrO_2 and TiO_2 was used as an electrode for dye-sensitized solar cell.Many properties of this nanostructure mixed metal oxides was reported to be better than that of TiO_2 [6].These include the BET specific surface area, which can improve the amount of adsorbed dye molecules.

Experimental Details

Materials and Methods

Tetra-isopropyl-orthotitanate(TIPT) and laurylamine hydrochloride(LAHC)(Tokyo Chemical Industry Co.), acetylacetone (ACA) and 2-propanol (Nacalai Tesque Co.), and Zr-butoxide (ZrBt) (HOKKO Chemical Industry Co.,Ltd.)were used as starting chemicals.All chemicals were analytical grade and used as received.The [bis(tetrabutyl-ammonium)cis di(thiocyanato) bis(2,2'-bipyridine-4,4'-carboxylic acid) ruthenium (II)] (called N719) [9] (Solaronix SA Co.) was used as a dye. Conducting glass plates (Geomatec Co., Ltd.), with Indium doped tin oxide (ITO), sheet resistance 5 Ω/ , were cleaned with acetone, rinsed with distilled water, and dried in 80 °C oven.

The transmission electron microscopy (TEM, JEOL JEM-200CX at 200kV) was employed to investigate the morphology of synthesized material. Crystal structure of mixed metal oxide was analyzed by X-ray diffraction (XRD) with Cu Kα radiation (RIGAKU-A2).BET surface area of synthesized samples was recorded using nitrogen adsorption desorption analysis (BELSORP 18 PLUS).

The film thickness 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.The absorption spectrum was analyzed by UV-Vis spectrophotometer (SHIMADZU, model UV-2450).

Preparation of Nanostructured Mixed Metal Oxides Electrode

The mesoporous TiO_2 and ZrO_2, as a reference, were synthesized from TIPT and ACA at the same molar concentration ([TIPT]/[ACA] = 1) and [ZrBt]/[ACA] = 1, respectively.The ZrO_2-mixe mesoporous TiO_2 ($[TiO_2]:[ZrO_2]$ = 95:5) was synthesized from TIPT, ZrBt, and ACA at the molar ratio of [TIPT+ZrBt]/[ACA] = 1. After the mixing, 0.1 M LAHC aqueous solution (pH 4 - 4.5) was added to each of these solutions, so as to attain [TIPT]/[LAHC] = 4, [ZrBt]/[LAHC] = 1, and [TIPT+ZrBt]/[LAHC] = 4, and then the mixture was stirred 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 2-propanol to remove LAHC. TiO_2 or TiO_2-ZrO_2 gels were coated on ITO glass plates (0.5 cm x 0.5 cm) by glass rod, using adhesive tapes (3M) as spacers. After the films were dried in air, the coated conducting glasses were sintered at 450 °C for 90 min and left to be cooled to 80 °C Then, these two electrodes were immersed in 50 wt.% butanol and 50 wt.% acetonitrile mixed solution of 0.3 mM N719 dye at least 24 h. After the dye adsorption, these electrodes were immediately fabricated into thin-layer, sandwich-type solar cells. The counter electrodes,thin platinum layer sputtered on F-doped SnO_2 film conducting glass plates, were kept in contact with these two dyed electrodes. In order to prevent a direct contact between the working and the counter electrodes which result ni the V_{OC} reduction to less than 300 mV [9], a stripes of 25 um thick Surlyn (Dupont, Himilan 1702) was inserted as a spacer between them. The redox electrolyte composing of a 0.6 M dimethylpropyl-imidazolium iodide solution, a 0.1 M lithium iodide (LiI) solution, and a 0.05 M iodide (I_2) solution in acetonitrile was introduced to the gap between the counter and the working electrodes by the capillary force.

The photovoltaic properties of these sandwich-type cells were measured by using a potentiostat (Bunko Keiki model HCSSP-25) irradiated with simulated solar light, A.M. 1.5,100 mW/cm^2(Bunko Keiki, model CEP-2000).

Results and Discussion

Characterization of synthesized TiO_2 and TiO_2-ZrO_2 Mixed Oxide

Generally, when the sol-gel technique is used, surface area and particle size are largely affected by the sintering temperature [14]. Fig.1 (a) and (b) show TEM images and electron diffraction patterns of calcined powders at 500 °C for 4 h. of TiO_2 and 95:5 %mol TiO_2-ZrO_2 mixed oxide, respectively.

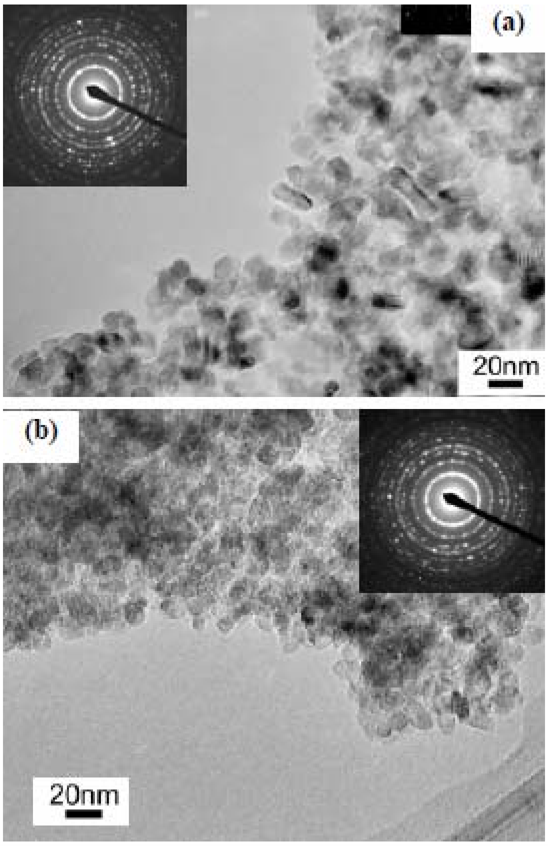

Fig. 1 TEM images and electron diffraction patterns of (a) synthesized TiO_2 and (b) 95:5 %mol TiO_2-ZrO_2 mixed oxide.

These TEM images show particle size distributions in the range of 10 to 25 nm for TiO_2-powder and 7 to 15 nm for TiO_2-ZrO_2 mixed oxide powder. The smaller particle size for the mixed oxide could be attributed to an increase in the thermal stability and the resistance to sintering caused by the doped oxide.From electron diffraction analysis, circular rings of electron diffraction patterns have been obtained as shown in insertion of Fig. 1 (a) and (b). Both of ED pattern show the Debye-Scherrer rings of anatase, which are in good agreement with the results from X-ray diffraction patterns, as shown in Fig. 2.

Fig. 2 illustrates the XRD patterns of calcined TiO_2, 95:5 %mol TiO_2-ZrO_2 mixed oxide, and ZrO_2.These results show that the prepared TiO_2-powder consists of anatase titania crystal; rutile phase could not be detected. The diffraction peaks from prepared ZrO_2 can be assigned to the tetragonal structure. In case of 95:5 % mol TiO_2-ZrO_2 mixed oxide, there are no diffraction peaks of the ZrO_2 structure. In other words, the structure of mixed oxide is an anatase-type. This means that the addition of a small amount of ZrO_2 did not change the structure of anatase-TiO_2 [15].

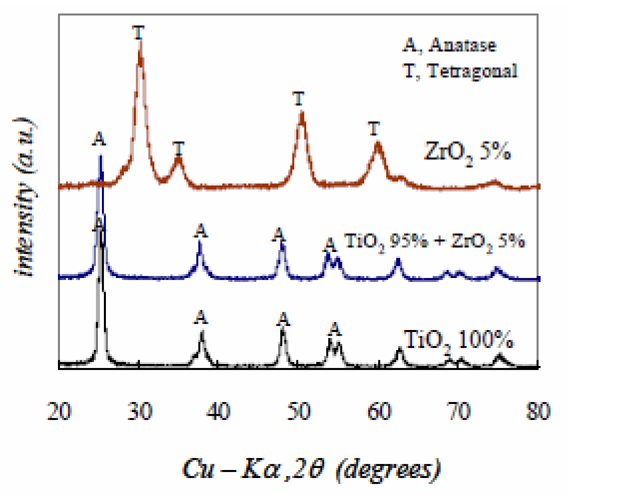

Fig. 2 XRD patterns of the sample powders of TiO_2 100%, 95:5 %mol TiO_2-ZrO_2 mixed oxide, and ZrO_2 100%.

Dye-chemisorption and I-V Characterization

The BET surface area of 95:5 %mol TiO_2-ZrO_2 mixed oxide is 109 m^2/g, that is about 35 % higher than TiO_2, which has a surface area of 80 m^2/g. As shown in Fig 3, the amount of chemisorbed dye on both type of film increases with the film thickness and of the amount of absorbed dye for TiO_2-ZrO_2 film was approximately 30% higher than TiO_2 film.Fig. 4 shows the relationship between the short-circuit current (J_{SC}) and the film thickness. This figure illustrates that, for both of TiO_2 and TiO_2-ZrO_2 film, the increasing of J_{SC} seems to get saturated with an increasing of thickness. This is probably due to the fact that, for the thicker films, electrons generated at a distance farther from the interface between the film and conducting glass are getting lost by recombination before they can reach the interface [16]. For the thickness in range of 2 – 6 microns, the average J_{SC} obtained from TiO_2-ZrO_2 electrode is approximately 11% higher than that obtained from TiO_2 electrode.

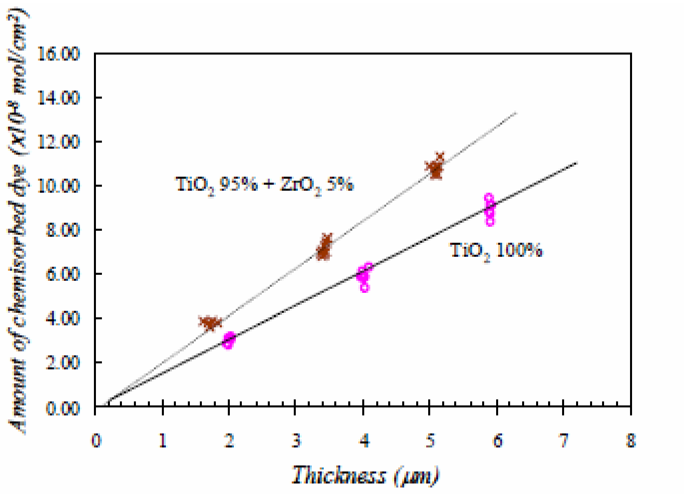

Fig. 3 Relationship between the amount of chemisorbed dye and the thickness of electrodes fabricated by TiO_2 100% and 95:5 %mol TiO_2-ZrO_2 mixed oxide.

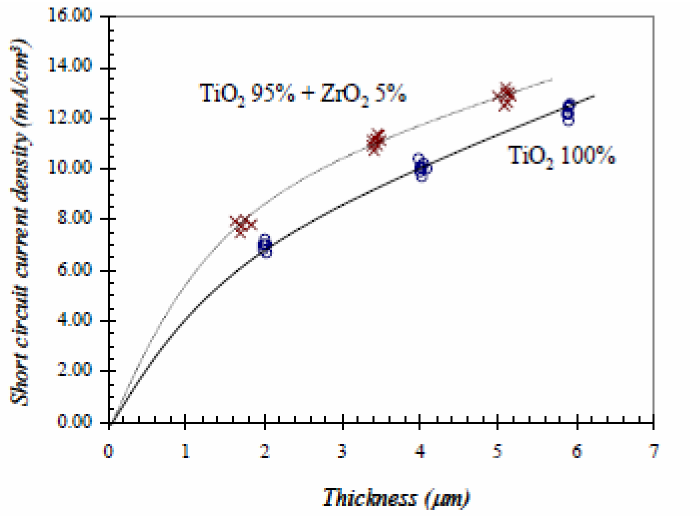

Fig. 4 Relationship between the short-circuit photocurrent density and the thickness of electrodes fabricated by TiO_2 100% and 95:5 %mol TiO_2-ZrO_2 mixed oxide.

The dependencies of open-circuit voltage (V_{OC}) and fill factor (*ff*) on the film thickness of TiO_2 and TiO_2-ZrO_2 electrode were reported in Fig 5. The results show no definite dependence of both V_{OC} and *ff* on the film thickness. The fill factor is found to be in range of 0.65–0.68 and 0.70–0.73 for TiO_2 film and TiO_2-ZrO_2 film respectively. The V_{OC} that obtained from TiO_2-ZrO_2 electrode are in the range of 565–585 mV and 585 – 605 mV for the TiO_2 electrode. These results indicated that the average V_{OC} from TiO_2-ZrO_2 electrode is about 4% higher when compare to that of TiO_2 electrode.

Fig. 6 shows the UV action spectra of un-sensitized photovoltaic cells.The energy band gap (E_g) of an electrode containing 95:5 %mol TiO_2-ZrO_2 mixed oxide adsorbs UV light below $\lambda_g \sim 380$ nm, corresponding to E_g around 3.27 eV, which is larger than that of a TiO_2 electrode (E_g ~ 3.2 eV, $\lambda_g \sim 387$ nm). The difference between the quasi-Fermi level (QFL) of electrons in the semiconductor under illumination and the potential of the redox couple (I^-/ I_3^- in al most all cases) is the driving force of the electrons in the external circuit that determine the V_{OC} of the cell [17].

As the QFL could increase up to the E_C, the maximum achievable V_{OC} is of the order of the difference between the energies of the bottom of the semiconductor conduction band and the electrolyte redox potential [18]. It could be seen that E_C of ZrO_2 is approximately –1.0 eV, which is more negative than that of TiO_2 (–0.3 eV). So, a larger E_g of TiO_2-ZrO_2 electrode could result in more negative value of E_C than that of TiO_2 electrode. This could be responsible for a higher V_{OC} of the cell fabricated from TiO_2-ZrO_2 electrode.

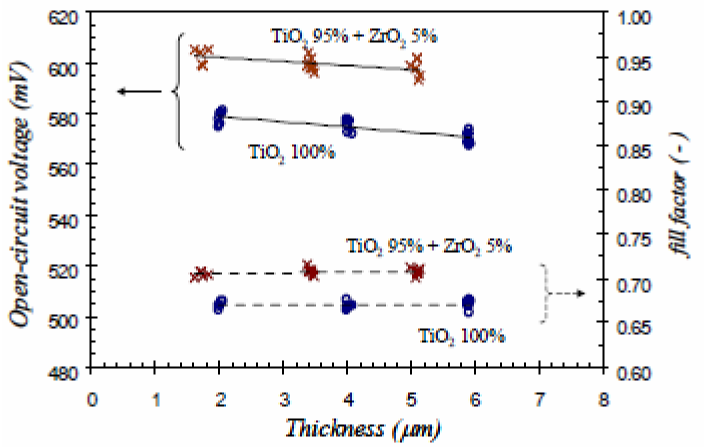

Fig. 5 Dependencies of open-circuit voltage and fill factor on the thickness of electrodes fabricated by TiO_2 100% and mixed metal oxides (ZrO_2 5% + TiO_2 95%).

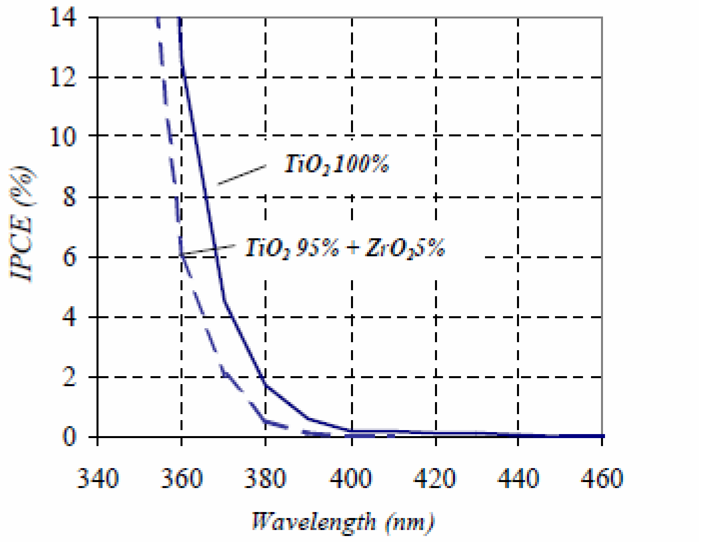

Fig. 6 UV action spectra of un-sensitized photovoltaic cells. The comparison between IPCE plotted as function of excitation wavelength of cells fabricated by synthesized TiO_2 and those of 95:5 %mol TiO_2-ZrO_2 mixed oxides.

Fig. 7 shows the relationship between the solar energy conversion efficiency (*Eff*) and the film thickness. By the increase J_{SC}, V_{OC}, and *ff,* the electrode fabricated by a 95:5 %mol TiO_2-ZrO_2 mixed oxide as describe above exhibits an efficiency of approximately 17% higher than that of TiO_2 electrode.

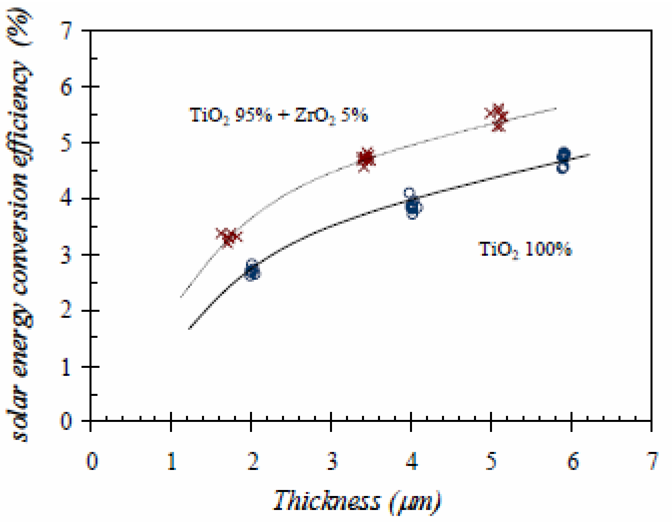

Fig. 7 Relationship between the solar energy efficiency and the thickness of electrodes fabricated by TiO_2 100% and 95:5 %mol TiO_2-ZrO_2 mixed oxide.

Conclusions

This work represents an alternative method to improve the efficiency of dye-sensitized solar cells. The TiO2-ZrO2 mixed oxide system based on sol-gel method of surfactant assisted mechanism was synthesized. By adding small amount of other metal oxides, in this case, ZrO2, into nano structured TiO2, the structure of TiO2-ZrO2 mixed oxide still maintains an anatase-type of TiO2. The addition of 5% ZrO2 can adjust both of energy band gap and BET surface area which lead to the increases of V_{OC} (Δ 4%) and J_{SC} (Δ 11%) respectively when compared to the cell that was fabricated by TiO2 electrode.These increases enhanced the solar energy conversion efficiency up to Δ 17%.

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