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Enhancement of Photocurrent and Photovoltage of Dye-Sensitized Solar Cells with TiO₂ Film Deposited on Indium Zinc Oxide Substrate

Jong-Gul Doh,[†] Jin Sup Hong,[†] R. Vittal,[‡] Man Gu Kang,[§] Nam-Gyu Park,[§] and Kang-Jin Kim*,[†]

Division of Chemistry and Molecular Engineering, Korea University, Seoul, Korea, Central Electrochemical Research Institute, Karaikudi 630 006, India, and Basic Research Laboratory, Electronics and Telecommunications Research Institute, Daejeon, Korea

The effects of using indium zinc oxide (IZO) as a conducting substrate in dye-sensitized TiO₂ solar cells (DSC) on their photocurrent–voltage characteristics are studied. We have found that both short-circuit photocurrent (J_{sc}) and open-circuit voltage (V_{oc}) of IZO-based cells are substantially improved by about 40% and 10%, respectively, when compared with those of cells based on fluoride-doped tin oxide (FTO). The J_{sc} increase is correlated to the improved contact between IZO and TiO₂ and enriched conduction band electrons in the TiO₂-on-IZO electrode, due to the blocking of surface states by the evaporated metallic components of the substrate. The combined effects of the negative shift of flat band potential and the reduction in recombination explain the V_{oc} increase. Our experimental finding suggests that IZO-coated substrate makes more efficient DSC than a FTO-coated one.

Introduction

Fluoride-doped tin oxide (FTO) glass has been widely used as a conducting substrate in Ru(II)-based dye-sensitized solar cells (DSC) employing nanocrystalline TiO₂. The DSC is based on the dye sensitization of TiO₂ to visible and near-IR light.[1] Interest in DSCs stems from their high solar conversion efficiency and their potential amenability to low cost processing techniques.

Conversely, little attention has been paid to IZO thin films as conducting substrates. Some ternary compounds such as $Zn_mIn_2O_{3+m}$ ($m = 2-7$) have been developed as n-type transparent, conductive materials for deposition on low-melting substrates like plastic film and studied for use in thin-film-transistor arrays.[2-10] The IZO film prepared at room temperature with an atomic Zn content of 24.5% has been reported to exhibit a low resistivity of 2.9×10^{-4} Ω cm, comparable to that of ITO film, and an X-ray amorphous phase.[11] As IZO is an amorphous material and as only small changes are noted in its resistivity at temperatures above 120 °C, it does not require high-temperature sputter deposition. IZO is also reported to have higher transmittance than FTO in the visible region and does not depend on the substrate temperature in this region.[12] These characteristics make it more suitable for use in flexible DSC, although its resistivity is higher than that of FTO and increases with increase in annealing temperature.

Concerning application, attempts have been made to replace TiO₂ with ZnO as the dye adsorbent in DSC, in view of the possibilities of varying particle sizes and shapes in the preparation.[13-16] To improve dye adsorption and increase the sensitized photocurrent, coating nanocrystalline TiO₂ or SnO₂ electrodes with a thin layer of ZnO was also probed.[17-23] Although In₂O₃ is not

* Corresponding author. Tel: +82-2-3290-3127. Fax: +82-2-3290-3121. E-mail: kjkim@korea.ac.kr.
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‡ Central Electrochemical Research Institute.
§ Electronics and Telecommunications Research Institute.
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employed in DSC, its photoelectrochemical properties have been reported.[24]

In this study, we substantiate for the first time that IZO conducting glass is a better substrate than FTO glass for obtaining increased solar energy conversion efficiencies of DSC. Comparisons of photocurrent−voltage ($J-V$) characteristics of solar cells based on FTO and IZO are made, and mechanisms of enhancements of J_{sc} and V_{oc} in case of IZO films are proposed.

Experimental Section

Transparent film electrodes were obtained by spin coating TiO_2 (P25) colloidal solution on conducting glass plates, using a spin coater from Laurell Technologies Corp. (WS-200-4NPP). FTO and IZO were purchased from Libbey-Owens-Ford (TEC 8, 75% transmittance in the visible) and Hynix Semiconductor Corp. (deposited by DC-magnetron sputtering), respectively. The IZO film was composed of indium oxide and zinc oxide with a $Zn/(In + Zn)$ atomic ratio of 0.16. Prior to spin coating, FTO and IZO plates were cleaned by sonication for 5 min in soap water, 10 min in distilled water, and 5 min in anhydrous ethanol. The TiO_2 film was annealed at 450 °C for 30 min in air unless otherwise specified, and its thickness was estimated to be about 2 μm as measured by a Tencor Alpha-Step 250 profiler. The TiO_2 film thus obtained was coated with 0.3 mM of N3 dye $\{[RuL_2(NCS)_2]\cdot 2H_2O$ (where L = 2,2′-bipyridine-4,4′-dicarboxylic acid)$\}$ in absolute ethanol for 12 h at room temperature. The redox electrolyte consisted of 3 mM I_2 and 60 mM LiI in acetonitrile. Pt gauge was used as counter electrode. $J-V$ curves were obtained using a Keithley M236 source measure unit. A 250-W tungsten−halogen lamp (Oriel) was used to illuminate an area of 3 mm in diameter of the working electrode, and its light intensity was adjusted with a Si solar cell.

An $Ag|Ag^+$ (0.1 M $AgNO_3$ in CH_3CN) reference electrode was used in acetonitrile containing 0.5 M $LiClO_4$ and 0.2 M tetrabutylammonium perchlorate for determining free electron concentration in the conduction band of TiO_2 with an HP 8453A diode array spectrophotometer.[25] The surface morphology was observed using a PSI Autoprobe CP atomic force microscope (AFM). XRD measurements were carried out using a MAC Science Co. MO3XHF X-ray diffractometer with Cu Kα radiation. The incident photon-to-current conversion efficiency (IPCE) was measured with an Aminco-Bowman FA-256 luminescence spectrometer. The iodine content in the TiO_2 film was estimated using a Perkin-Elmer Φ-7200 secondary ion mass spectrometer (SIMS). In and Zn in IZO and TiO_2-coated IZO were dissolved in 12 M HCl and 30% H_2O_2 and analyzed by using a Thermo Jarrell Ash Polyscan 61E inductively coupled plasma-atomic emission spectrometer (ICP-AES) and a Varian Spectr AA800 atomic absorption spectrophotometer (AAS). The depth profile of In and Zn in the TiO_2 film was determined by a PHI 680 Auger nanoprobe.

Results and Discussion

Figure 1 shows the $J-V$ characteristics of DSC at an illumination of 50 mW/cm^2. Both J_{sc} and V_{oc} of cells with TiO_2 on IZO (TiO_2/IZO) are enhanced by about 40% and about 10%, respectively, compared with those of cells with TiO_2 on FTO (TiO_2/FTO). Consequently, the con-
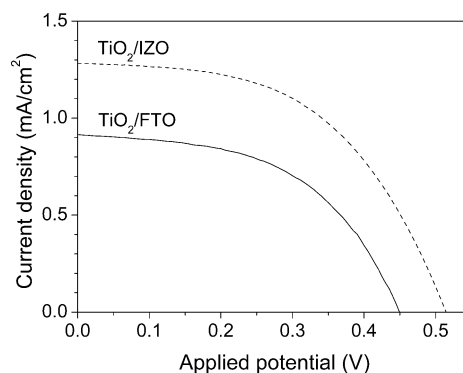
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Figure 1. $J-V$ curves of DSC prepared with TiO_2 films of 2 μm thickness on FTO and IZO substrates under 50 mW/cm^2 illumination.
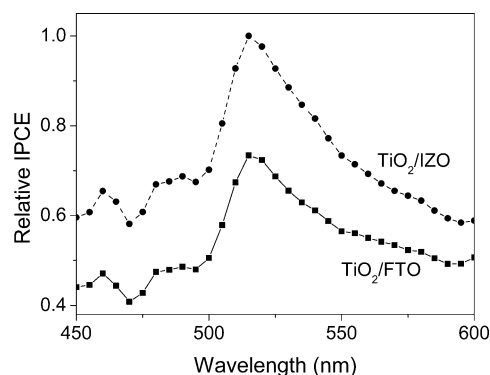

Figure 2. Comparison of IPCE spectra of DSC prepared with TiO_2/FTO and TiO_2/IZO.

version efficiency of the TiO_2/IZO cell increases by 54%, regardless of using a 400 nm cutoff filter. The conversion efficiency is, however, not optimized in absolute terms for film thickness, light scattering, electrolyte type and concentration, and cell dimension, in view of the comparative nature of this study regarding the influence of the substrate. It is mentioned that a very thin layer of about 2 μm of TiO_2 was used in this study compared to about 10 μm in usual DSC, to make the Auger depth analysis of In and Zn feasible (see below).

The J_{sc} enhancement of the TiO_2/IZO cell is the result of unfailing higher IPCE over the visible region (Figure 2). The maximum IPCE around 520 nm of an IZO-based cell, about 10%, is higher than that of an FTO-based cell by 40%, which is in good agreement with the increase of J_{sc} observed in Figure 1. The low IPCE value should be due to the thinner TiO_2 film and lower concentrations of electrolyte in an ordinary liquid electrochemical cell than those in commonly used thin cells. To obtain supporting evidence, an electrode is prepared with a 60 nm layer of chemical vapor deposited ZnO between FTO and TiO_2. The TiO_2 film deposited on FTO with a thin layer of ZnO shows an increase in V_{oc}, although its J_{sc} decreases due to the additional resistivity caused by the ZnO layer.

The J_{sc} enhancement with TiO_2/IZO may be related to the higher transmittance of IZO than of FTO in the visible region (by about 5% as measured by us), which, however, is insufficient to explain its increase by about 40%. To get further grounds for J_{sc} increase, IZO film was characterized. We have noted, on one hand that the mass of In and Zn of a bare IZO film has decreased by about 33% and 40%, respectively, when the film was

**Table 1. Amount in Micrograms of In and Zn for 4.7-cm²
IZO before and after Annealing at 450 °C for 30 min**

IZO sample		In[a]	Zn[b]
IZO	nonannealed	67.9	7.58
	annealed	45.1	4.53
TiO₂/IZO	nonannealed	82.4	9.55
	annealed	81.3	8.88

[a] Measured by ICP-AES. [b] Measured by AAS.
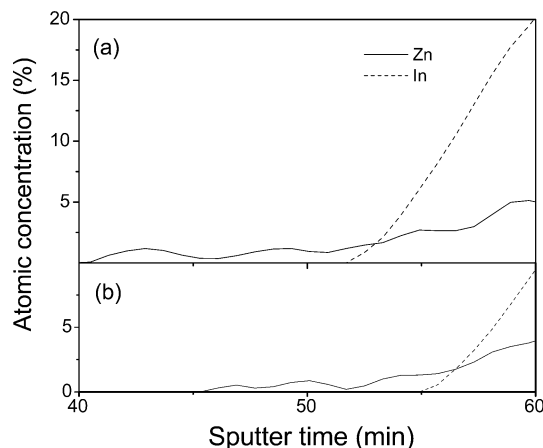
Figure 3. Auger depth profiling of TiO₂/IZO (a) after anneal-
ing and (b) before annealing at 450 °C for 30 min. Sputter rate
= 14 nm/min in SiO₂ and started from the TiO₂ side.

annealed at 450 °C for 30 min in air (Table 1). On the
other hand, the total atomic mass of In and Zn in TiO₂-
coated IZO film remained essentially the same. A
correlation of these two observations implies that In and
Zn evaporate from the IZO substrate during annealing
and subsequently adhere at the IZO–TiO₂ interface as
well as to the TiO₂ particles. This inference is also
strengthened by the Auger depth analysis (Figure 3).
Both In and Zn are detected earlier in an annealed IZO/
TiO₂ film, compared to a nonannealed one, with a
gradually higher concentration of In and Zn toward
TiO₂–IZO interface. Mention is to be made here that
the sputtering started from the TiO₂ side. It can also
be noted from the figure that, in the case of annealed
TiO₂/IZO sample, Zn is detected first after about 40 min,
which corresponds to a depth of 560 nm from the TiO₂
surface, and In appears after about 50 min, correspond-
ing to a depth of 700 nm. Due to the absence of In and
Zn on the TiO₂ surface in the case of TiO₂/IZO sample,
the SEM image of the TiO₂ surface on the IZO substrate
resembled that on FTO. In other words, morphologi-
cally, the TiO₂ layers on both FTO and IZO substrates
were found to be the same from SEM analysis.

The modification of the TiO₂ layer with the oxides of
In and Zn appears to be possible since IZO is amor-
phous, as identified by XRD. Furthermore, AFM line
profiles show surface roughness of 76.5 and 1.1 Å for
as-received FTO and IZO substrates (not shown), re-
spectively, supporting the XRD data pertaining to the
amorphousness of IZO. Such an amorphous nature of
IZO enables In and Zn to be easily released from the
matrix due to a weak chemical bond energy of amor-
phous phase in comparison with crystalline phase. To
get an idea as to the degree of the adherence, the
average surface coverage of oxides of In and Zn attached
to TiO₂ is estimated. It is found, based on the data in
Table 1, that the coverage is less than a few percent.
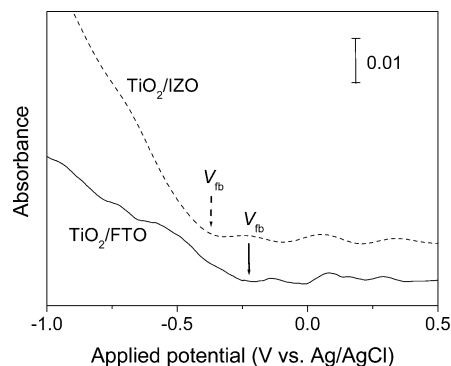
Figure 4. Comparison of absorbance at 800 nm vs applied
potential of TiO₂/FTO and TiO₂/IZO electrodes in acetonitrile,
containing 0.5 M LiClO₄ and 0.2 M TBAP at 5 mV/s. Arrows
indicate the flat band potentials of the TiO₂ films.

One explanation for the J_{sc} behavior (Figure 1)
originates from the concentration of conduction band
electrons. Figure 4 shows the absorbance measured at
800 nm as a function of applied potential, illustrating
the electrochromic behavior of TiO₂ films in Li⁺ solution.
Absorbance increases gradually as potential is applied
negatively, which is related to an increase in free
electron density.[25] Hannappel et al. have also shown
that the transient absorption signal detected in the
near-IR region for the N3 dye-covered colloidal TiO₂
electrode is due to light absorption by the injected
electrons.[26] Though Ellingson and co-workers[27] made
time-resolved IR absorption measurements with the
dye-coated TiO₂ sample exposed to air, their interpreta-
tion for the absorption spectra at lower energies (1.52,
4.63, 4.9, and 6.6 μm) is similar to ours, relating it to
the injected electrons. The higher absorbance in the
negative potential region below the flat band potential
(V_{fb}, indicated by an arrow) in the case of the TiO₂/IZO
electrode compared with that of the TiO₂/FTO electrode
indicates that surface modification of TiO₂ with In and
Zn oxides results in an increased concentration of free
electrons in the conduction band of TiO₂.[25] We assume
this to have been gained by the blocking of deep surface
trap states of TiO₂ due to its surface modification by
the oxides.[28–32] There can be an inhibition of back
electron transfer to I₃⁻ (eq 1)

$$I_3^- + 2e_{cb}^- = 3I^- \qquad (1)$$

in the presence of the barrier formed by the submono-
layers of wide band gap semiconductors such as In and
Zn oxides, which leads to the increase of conduction
band electrons, as reflected by the J_{sc} increase.

The electron transfer from the excited dye to TiO₂ is,
however, not hindered by the presence of submonolayers
of In and Zn oxides. It was recently reported that the
electron transfer from the dye, attached to In and Zn

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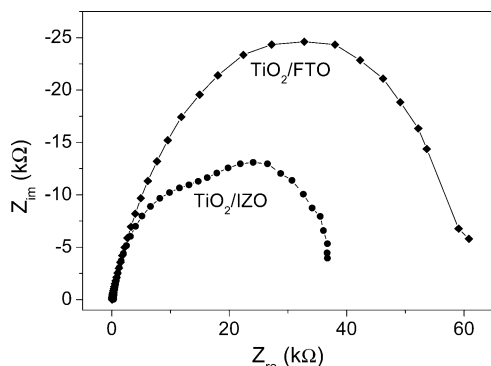1982.

Figure 5. Nyquist plots of DSC with TiO₂/FTO and TiO₂/IZO from 100 kHz to 10 mHz with an ac amplitude of 5.0 mV.

Table 2. Relative SIMS Peak Area of TiO$_2$ and Iodine

electrode	TiO$_2$	iodine
TiO$_2$/FTO	1.00	88.7
TiO$_2$/IZO	1.00	79.2

oxides, to the underlying TiO$_2$ occurs by tunneling through their layers.[17] Furthermore, the electron transfer across the TiO$_2$–IZO interface is assumed to be fast, due to improved electrical contact arising from adherence of the evaporated In and Zn at the IZO–TiO$_2$ interface. We explain this as follows: TiO$_2$ particles are assumed to be spheres. They are connected together by sintering. As they are spheres, their contacts at the substrate–TiO$_2$ interface cannot be packed and complete and some empty space is visualized at the interface. It has been earlier mentioned, based on the Auger depth analysis (Figure 3) and results in Table 1, that In and Zn evaporate from the IZO substrate during annealing and subsequently adhere at the IZO–TiO$_2$ interface as well as to the TiO$_2$ particles. These evaporated In and Zn are envisaged to occupy these empty spaces as conducting components. In such a situation, the electrical contact at the interface can be improved. As a result of the improved electrical contact at the IZO–TiO$_2$ interface and the blocking of the TiO$_2$ surface states, the overall charge-transfer resistance of TiO$_2$/IZO cell appears to be smaller compared with that of the TiO$_2$/FTO cell, as shown in Figure 5.

The J_{sc} increase when the substrate FTO is replaced by IZO is initially considered by us to be due to the difference in the adsorbed dye concentration per unit volume. The rationale for this is that a better dye adsorption on the modified TiO$_2$ surface is possible, owing to a favorable point of zero charge, pH$_{pzc}$ being 9 for In$_2$O$_3$ and ZnO, compared to pH$_{pzc}$ being 6 for TiO$_2$.[33,34] This has not been the real situation, as the amounts of the adsorbed dye molecules are found to be almost the same, regardless of substrates, as confirmed by the measurements of the desorbed dye in 10^{-3} M KOH. Obviously, the deposition of In and Zn oxides on TiO$_2$ does not affect dye adsorption. The concentration of the dye molecules being the same in both the cases, we do not expect a considerable change in TiO$_2$ surface area on the two substrates.

The V_{oc} increase in Figure 1 can be related to the V_{fb} of the TiO$_2$ film electrode. The V_{fb} of dye-sensitized TiO$_2$ electrodes is determined by an absorption spectroscopic method, utilizing Li$^+$ ion intercalation.[14] As can be seen in Figure 4, the V_{fb} of TiO$_2$/IZO is negatively shifted by about 0.15 V, relating to that of TiO$_2$/FTO. One of the reasons for the change in the V_{fb} of TiO$_2$ on the two

substrates may be due to the entry and adherence of In and Zn in the TiO$_2$ layer. The V_{fb} shift is in accordance with a recent report that the V_{fb} of a TiO$_2$–In$_2$O$_3$ composite containing a relatively small amount of In$_2$O$_3$ is more negative than that of a TiO$_2$ electrode.[16] A negative shift in V_{fb} increases V_{oc}. Furthermore, V_{oc} enhancement is a consequence of reduction in the back electron transfer in the TiO$_2$ layer of IZO/TiO$_2$,[35] as compared with the situation of FTO/TiO$_2$, according to

$$V_{oc} = (kT/e) \ln(I_{inj}/n_{cb}k_{et}[I_3^-]) \qquad (2)$$

where I_{inj} is the charge flux from sensitized injection, n_{cb} is the surface electron concentration at the TiO$_2$ surface, and k_{et} is the rate constant of the I$_3^-$ reduction. Meng et al. have very recently reported that the presence of ZnO in TiO$_2$ film suppresses the recombination between the injected electrons and dye cations or triiodide ions and therefore increases the open-circuit voltage.[36] To prove the reduction of recombination between triiodide ions and injected electrons we have estimated the iodine content in the working electrode by SIMS analysis. After the J–V measurement, the cell was dismantled and the working electrode was washed with acetonitrile and subjected to SIMS analysis. The results demonstrate that the iodine content in the TiO$_2$/IZO film of a DSC is less than that in the TiO$_2$/FTO film of an identically prepared DSC by about 11% (Table 2). The In and Zn evaporated onto the TiO$_2$ surface may reduce the pore sizes of TiO$_2$ film and thereby its void volume of the film, causing the iodine concentration to decrease in the film. The decrease in the void volume leads to a reduction in the recombination, leading to an increase in V_{oc}.

An even more pronounced advantage of an IZO substrate lies in the feasibility of deposition of TiO$_2$ film at low temperatures. The temperature-dependent photocurrent density has demonstrated that the IZO-based films gives rise to better current densities than the FTO-based films in the entire temperature range up to 450 °C. At a temperature as low as 300 °C, the J_{sc} of a IZO-based film is much higher (by about 63%) than that of a FTO-based film and even higher than that of the FTO-based film annealed at 450 °C (by about 11%), which suggests that improved characteristics can be attained with IZO substrate at lower annealing temperatures than at commonly used 450 °C. Apart from saving production costs of DSC, low-temperature annealing implies lower resistivity of IZO film with a small loss of conversion efficiency.

Conclusion

The effects of using IZO as a conducting substrate in DSC on their J–V characteristics are studied. It is

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observed that both V_{oc} and J_{sc} of such cells increase by about 40% and 10%, respectively, compared to those of cells with TiO₂ film on FTO. The J_{sc} increase is correlated to the improved contact between IZO and TiO₂ and enriched conduction band electrons in TiO₂-on-IZO electrodes, due to the blocking of surface states by the evaporated metallic components of the substrate. The accumulation of In and Zn oxides on TiO₂ is small, but their effect on the $J-V$ characteristics appears to be significant. The extent of surface coverage with In and Zn can be optimized by controlling the annealing temperature. It is advantageous to anneal and modify TiO₂ simultaneously with IZO, contrary to the FTO, which requires an additional step to modify TiO₂ with ZnO. The combined effects of the negative shift of the flat band potential and the reduction in recombination caused by the accumulation of In and Zn oxides on TiO₂ explain the V_{oc} increase. In conclusion, IZO proves itself to be a better substrate than FTO for improving the photovoltaic properties of DSC. It is worth mentioning that a better conversion efficiency may be achieved by changing the atomic composition of zinc in IZO, as the electrical conductivity of IZO depends on its atomic ratio.

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