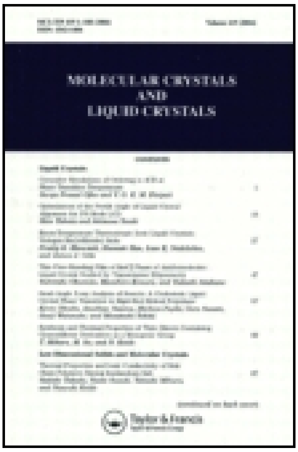

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Effect of p-Type Semiconductor Electrode on Photovoltaic Properties in n/p Tandem-Type Dye-Sensitized Solar Cell

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To improve the light-to-electric energy conversion efficiency of a dye-sensitized solar cell, a p-type semiconductor electrode was introduced to the cell so that n/p tandem-type solar cell was composed. In the tandem cell, the TiO_2 *adsorbed with N719 dye molecules and the p-type semiconductor were used an anode and a cathode, respectively, and acetonitrile solution containing iodide was done as an electrolyte. The cathode was prepared on a surface of platinum layer formed on a FTO glass plate by plasma spattering* $Cu_xBi_yO_z$ *as the p-type semiconductor. Short-circuit current density and conversion efficiency of the tandem cell were larger than those in a cathode without the p-type semiconductor layer. The p-type semiconductor layer will be able to absorb low energy photons passed through the anode. After ZnO particles were coated on a surface of the p-type semiconductor layer, open-circuit voltage was increased. Such coating of the particles will be effective to depress a back-transfer at the interface between the p-type semiconductor layer and the electrolyte and band-bending of the p-type semiconductor.*

Keywords p-type semiconductor; titanium dioxide; zinc oxide; tandem; dye; solar cell

1. Introduction

A solar cell developed by Gräzel et al. [1] has a photoactive anode and a passive cathode which only serves as a regenerator of the redox species oxidized at the dye-sensitized nanostructured photoanode. On the other hand, Lindquist et al. [2] demonstrated a tandem cell in which both anode and cathode were dye-sensitized nanostructured photoactive electrodes. It was shown using the cis-di(thiocyanato)-N,N-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)-ruthenium(II)-coated TiO_2 anode in a tandem dye-sensitized solar cell that a combination of erythrosine B as a dye and a nanostructured NiO thin film on a conducting substrate can form a dye-sensitized photocathode that can be an active part in the tandem cell [2]. The maximum open-circuit voltage will be a difference in potential between the lower edge of the conduction band of the photoanode and the upper edge of the valence band of the

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photocathode. Higher open-circuit voltage should be possible to reach without any significant drop in the photocurrent compared to the best photoanode DSC by avoiding spectral overlap between the two dyes. A tandem cell comprising TiO_2 anode and NiO cathode prepared as porous nanostructures films exhibited actually a high open-circuit voltage of 0.92 V [3].

In this work, p-type semiconductor electrode was noted in n/p tandem-type dye-sensitized solar cell, in which TiO_2 adsorbed with N719 dye molecules and $Cu_xBi_yO_z$ as a p-type semiconductor were used an anode and a cathode, respectively, and acetonitrile solution containing iodide was done as an electrolyte. The cathode was prepared on a surface of platinum layer formed on a FTO glass plate by plasma spattering $Cu_xBi_yO_z$. Effects of plasma sputtering condition and $Cu_xBi_yO_z$ composition on light-to-electric energy conversion efficiency were investigated in the tandem cells.

2. Experimental Methods

2.1 Preparation of TiO_2 electrode

To prepare TiO_2 paste, TiO_2 particles (P-25, supplied by Degussa Co., Dusseldorf, Germany) with an average diameter of ca. 28 nm and specific surface area of 50 m^2g^{-1} were dispersed in 1M acetic acid solution to obtain a TiO_2 concentration of 30 wt% and then mixed with polyethylene glycol (PEG) with a weight-average molecular weight of 20,000 under ultrasonic agitation to obtain a PEG/TiO_2 weight ratio of 2/5. A thin film of the paste was coated in air at room temperature on a conductive glass plate that had been coated with a fluorine-doped stannic oxide layer (sheet resistance of 25 Ω per square), using a spin-coating technique. The speed of the spin-coating was 4,000 rpm and the spin-coating time was 20 sec. The film was sintered in air at 723 K for 30 min and then cooled to room temperature. The process of coating and sintering was repeated one to three times to prepare TiO_2 electrode.

2.2 Fixation of dye molecules to the TiO_2 electrode

The TiO_2 electrode was immersed for two days in an ethanol solution containing 0.3 mM ruthenium dye, cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxilato) ruthenium(II)bis-tetrabutylammonium, (N719, supplied by Peccell Technologies, Inc., Kanagawa, Japan). The electrode was then rinsed with acetonitrile and dried in a vacuum at room temperature.

2.3 Preparation of p-type semiconductor electrode

To prepare p-type semiconductors as raw materials for plasma spattering, CuO particles of 2 μm average diameter were mixed with Bi_2O_3 particles of 2 μm average diameter in a mortar thoroughly at full hand force. The molar ratios of CuO/Bi_2O_3 in the mixtures were 90/10 and 50/50. The mixtures were sintered in air at 973 K for 24 h to prepare $Cu_xBi_yO_z$ materials as p-type semiconductors. UV-vis diffuse reflectance spectra of the p-type semiconductors were measured with a JASCO V-500 UV-vis spectrophotometer (JASCO International Co., Tokyo, Japan) equipped with an integral-sphere attachment to measure light absorbance behavior.

To form a cathode, the p-type semiconductor layer was formed on a conductive glass plate having a platinum layer 50 nm thick with argon plasma sputtering of $Cu_xBi_yO_z$ materials, using magnetron-type plasma reactor. The plasma was generated in an atmosphere of 15 Pa argon at 200 W discharge power. The p-type semiconductor layer was annealed in air at 723 K for 30 min after the sputtering. The surface of the p-type semiconductor layer was covered with ZnO particles with an average diameter of ca. 20 nm by spin-coating in air at room temperature, using pure water dispersed with 0.5 wt% of the ZnO particles, and then dried in air at 673 K for 2 h. The speed of the spin-coating was 6,000 rpm and the spin-coating time was 10 sec. Surface morphology of the p-type semiconductor layer covered with ZnO particles was observed with a Seiko SPI3800N scanning probe microscope (Seiko Instruments, Inc., Chiba, Japan).

2.4 Solar cell assembly

The electrolyte solution for the tandem cell was composed of 40 mM iodine, 500 mM lithium iodide, and 580 mM 4-tert-butylpyridine dissolved in acetonitrile (all the chemicals were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan). The p-type semiconductor electrode was placed directly on top of the dye-coated TiO_2 electrode. Both electrodes were clamped tightly together. A thin layer of the electrolyte solution was attracted into the interelectrode space by capillary forces. The dye-coated TiO_2 electrode was illuminated through the conductive glass plate. Photovoltaic properties of the tandem cells were characterized in air at room temperature by current-voltage characteristics under illumination with AM 1.5G simulated solar light with 100 $mWcm^{-2}$ using a Peccell solar simulator PEC-L11 (Peccell Technologies Co., Kanagawa, Japan).

3. Results and Discussion

3.1. Characterization of p-type semiconductor

According to XRD analyses on the p-type semiconductors of molar ratio $CuO/Bi_2O_3 = 50/50$ and $CuO/Bi_2O_3 = 90/10$, $Cu_xBi_yO_z$ prepared with $CuO/ Bi_2O_3 = 50/50$ was composed of $CuBi_2O_4$ crystallites and two crystalline phases composed of $CuBi_2O_4$ and CuO crystallites were formed in $Cu_xBi_yO_z$ prepared with $CuO/ Bi_2O_3 = 90/10$ [4]. Figure 1 shows diffuse reflectance UV-vis spectra of CuO, $CuO/ Bi_2O_3 = 90/10$, $CuBi_2O_4$, and Bi_2O_3. Absorbance in wavelength range above 460 nm increased with increasing CuO content in $Cu_xBi_yO_z$.

3.2. p-type semiconductor of $CuBi_2O_4$

Figure 2 shows photocurrent density-voltage curves for dye-sensitized solar cells without and with $CuBi_2O_4$ as the p-type semiconductor, respectively. The TiO_2 electrode was prepared with one spin-coating time. The p-type semiconductors were prepared with plasma spattering $CuBi_2O_4$ for 5 min and then annealed in air at 723 K for 30 min. Table 1 shows the values of short-circuit current density J_{sc}, open-circuit voltage V_{oc}, fill factor FF, and light-to-electric energy conversion η in Figure 2. J_{sc} and η were increased with the formation of the p-type semiconductor layer in the tandem cell. It can be confirmed that the p-type semiconductor layer is able to absorb low energy photons passed through the anode. The hole transport in the p-type semiconductor layer will be improved with an increase in the crystallinity of $CuBi_2O_4$ which is originated by the annealing, since the amounts of J_{sc} and

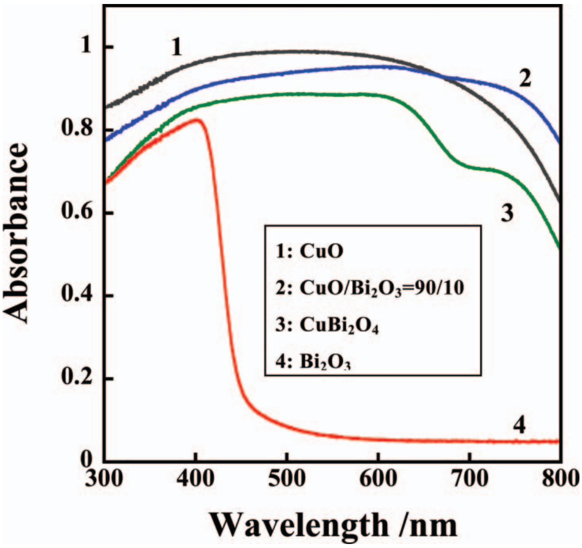


Figure 1. UV-vis diffuse reflectance spectra of CuO, $Cu_xBi_yO_z(CuO/Bi_2O_3 = 90/10)$, $CuBi_2O_4$ and Bi_2O_3.

η were decreased by introduction of the p-type semiconductor without the annealing. Since the amount of J_{sc} in the p-type semiconductor electrode was higher than that in platinum electrode, it is assumed that the reductive ability of the p-type semiconductor electrode is higher than that of platinum electrode. The redox potential of I^-/I_3^- of +0.44 V (versus

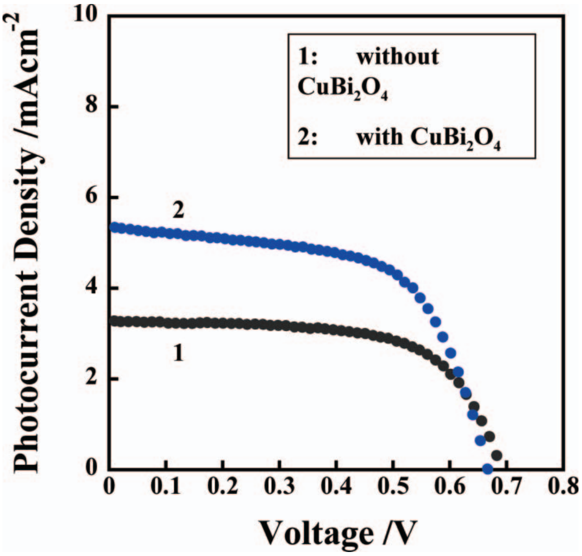


Figure 2. Photocurrent density-voltage curves for dye-sensitized solar cells without and with $CuBi_2O_4$ as the p-type semiconductor, respectively. The TiO_2 electrode was prepared with one spin-coating time. The p-type semiconductors were prepared with plasma spattering $CuBi_2O_4$ at discharge powers of 200 W for 5 min and then annealed in air at 723 K for 30 min.

Table 1. Characteristics of the solar cell in Figure 2.

$CuBi_2O_4$	J_{sc} ($mAcm^{-2}$)	V_{oc} (V)	FF	η (%)
unused	3.27	0.694	0.639	1.45
used	5.35	0.665	0.613	2.18

NHE) [1,5] will be higher than that of the Fermi potential of the p-type semiconductor and therefore the band bending of the p-type semiconductor is formed so that the Fermi level of the p-type semiconductor will coincide with the redox potential of I^-/I_3^-. Therefore an electron photo-excited to the conduction band of the p-type semiconductor can be easily reduced iodide ion in the electrolyte solution, if an electron transported from the anode to the p-type semiconductor through outer circuit is smoothly combined with a hole in the valence band of the p-type semiconductor.

The amount of J_{sc} was largely decreased by adsorbing N719 dye on the surface of the p-type semiconductor. Figure 3 shows energy diagram in the solar cell composed of $CuBi_2O_4$ electrode adsorbed with N719 dye. Since LUMO energy level of the dye is higher than the lowest level of the conduction band of the p-type semiconductor, an electron photo-excited to the conduction band of the p-type semiconductor can not reduce iodide ion in the electrolyte and therefore preferentially recombine with a hole in the valence band of the p-type semiconductor. It is supported from the adsorption of the dye to the p-type semiconductor that the photo-excited p-type semiconductor contribute to an increase in J_{sc}.

It is expected in the tandem cell that the amount of open-circuit voltage V_{oc} may be 1.5 V, since a difference in Fermi level between TiO_2 and $CuBi_2O_4$ is 1.5 V. However the measured amount of V_{oc} was less than 0.7 V. Therefore it will be considered that the Fermi level of the p-type semiconductor becomes almost equal to the redox potential of I^-/I_3^-.

Figure 4 shows photocurrent density-voltage curves for dye-sensitized solar cells without and with $CuBi_2O_4$ as the p-type semiconductor, respectively. The TiO_2 electrode was prepared with three spin-coating times. The p-type semiconductors were prepared with

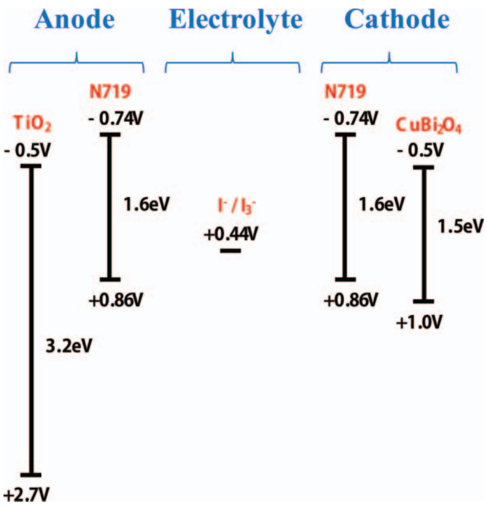


Figure 3. Energy diagram in the solar cell composed of $CuBi_2O_4$ electrode adsorbed with N719 dye.

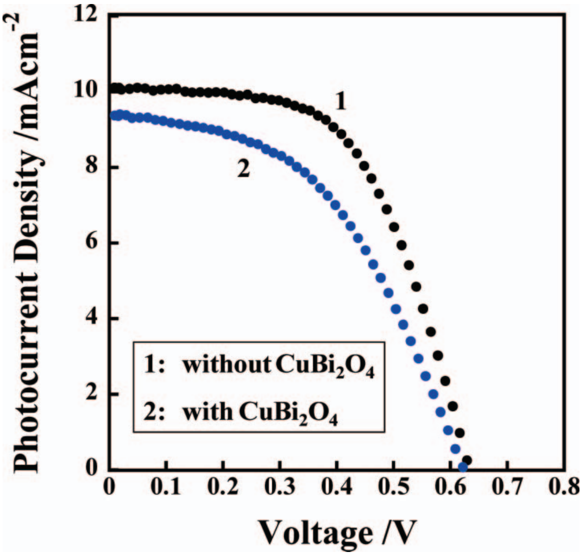


Figure 4. Photocurrent density-voltage curves for dye-sensitized solar cells without and with $CuBi_2O_4$ as the p-type semiconductor, respectively. The TiO_2 electrode was prepared with three spin-coating times. The p-type semiconductors were prepared with plasma spattering $CuBi_2O_4$ at discharge power of 200 W for 20 min and then annealed in air at 723 K for 30 min.

plasma spattering $CuBi_2O_4$ for 20 min and then annealed in air at 723 K for 30 min. Table 2 shows the values of J_{sc}, V_{oc}, FF, and η in Figure 4. It becomes apparent from Figures 2 and 4 that J_{sc} and η were increased with increasing spin-coating time of the TiO_2 electrode in the cathode without the p-type semiconductor layer. The J_{sc} and η of the tandem cell were increased with increasing discharge time and then decreased in the discharge time above 20 min. The number of photons absorbed in the anode is higher than that in the cathode prepared with the discharge time below 20 min. Such a difference in the absorbed photons between the anode and the cathode results in decreases in J_{sc} and η. It is considered in cathode prepared with the discharge time above 20 min that the number of holes reached on the platinum layer depresses with increasing the thickness of the p-type semiconductor layer.

3.3. *Surface modification of p-type semiconductor electrode*

Figure 5 shows photocurrent density-voltage curves for dye-sensitized solar cells without both $Cu_xBi_yO_z$ and ZnO, With $Cu_xBi_yO_z$, and with both $Cu_xBi_yO_z$ and ZnO, respectively. The TiO_2 electrode was prepared with one spin-coating time. The p-type semiconductors

Table 2. Characteristics of the solar cell in Figure 4.

$CuBi_2O_4$	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF	η (%)
unused	10.09	0.637	0.566	3.64
used	9.37	0.625	0.476	2.79

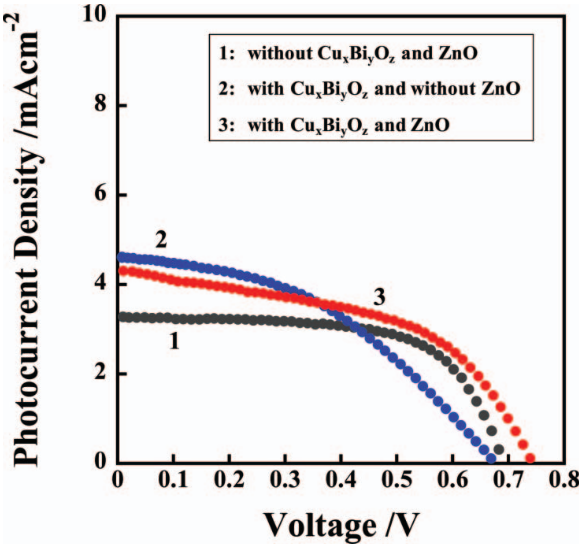


Figure 5. Photocurrent density-voltage curves for dye-sensitized solar cells without both $Cu_xBi_yO_z$ and ZnO, with $Cu_xBi_yO_z$, and with both $Cu_xBi_yO_z$ and ZnO, respectively. The TiO_2 electrode was prepared with one spin-coating time. The p-type semiconductors were prepared with plasma spattering $Cu_xBi_yO_z(CuO/Bi_2O_3 = 90/10)$ at discharge power of 200 W for 10 min and then annealed in air at 723 K for 30 min.

were prepared with plasma spattering $Cu_xBi_yO_z$ $(CuO/Bi_2O_3 = 90/10)$ for 10 min and then annealed in air at 723 K for 30 min. ZnO layer as a n-type semiconductor was formed on a surface of the $Cu_xBi_yO_z$ layer by means of spin-coating method. Table 3 shows the values of J_{sc}, V_{oc}, FF, and η in Figure 5. The J_{sc} in the tandem cell was increased by the formation of the $Cu_xBi_yO_z$ layer. It is considered that the p-type semiconductor layer is able to absorb low energy photons passed through the anode. Figure 6 shows energy diagram in the solar cell composed of $CuBi_2O_4$ electrode covered with ZnO. The highest levels of valence bands of the p-type semiconductors $CuBi_2O_4$ and CuO are +1.0 V (versus NHE) [6] and +0.98 V (versus NHE) [7], respectively, whereas the lowest levels of conduction bands of them are −0.5 V (versus NHE) [6] and −0.37 V (versus NHE) [7], respectively. The highest level of valence band and the lowest level of conduction band in ZnO are +3.0 V (versus NHE) and −0.2 V (versus NHE), respectively [8]. Since the crystalline phases composed of $CuBi_2O_4$ and CuO crystallites are formed in the p-type semiconductor $Cu_xBi_yO_z(CuO/Bi_2O_3 = 90/10)$, it is expected that an electron generated under light irradiation in the p-type semiconductor can smoothly transfer to the electrolyte through the conduction band of ZnO to avoid the recombination of electron and hole in the

Table 3. Characteristics of the solar cell in Figure 5.

$Cu_xBi_yO_z$	ZnO	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF	η (%)
unused	unused	3.29	0.693	0.636	1.45
used	unused	4.66	0.678	0.415	1.31
used	used	4.35	0.744	0.501	1.62

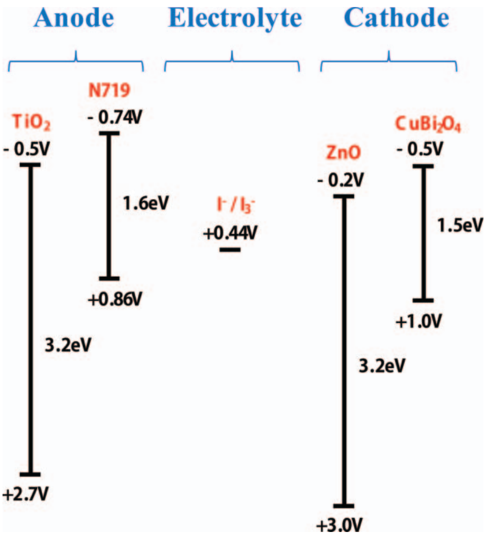
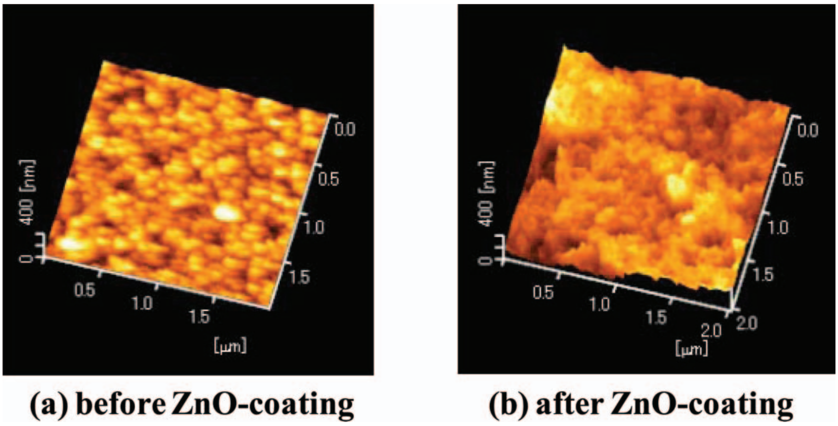


Figure 6. Energy diagram in the solar cell composed of $CuBi_2O_4$ electrode covered with ZnO.

p-type semiconductor, and a back-transfer from the electrolyte to the p-type semiconductor is depressed. Figure 7 shows AFM images of the p-type semiconductor layer before and after coating with the ZnO particles. It is confirmed that the p-type semiconductor electrode was coated with the ZnO particles. The open-circuit voltage V_{oc} was increased by the formation of the ZnO layer in the tandem cell. Since the value of V_{oc} was clearly increased by the formation of the ZnO layer, it is considered that the back-transfer is depressed by the ZnO layer and the band-bending is also depressed, since the p-type semiconductor is depressed to contact with the electrolyte solution by the ZnO layer. The Fermi level of ZnO is higher than that of the redox potential of I^-/I_3^- and therefore space charge layer will be formed in ZnO layer. If photo-excited electrons of the p-type semiconductor are transformed to the conduction band of ZnO, the space charge layer may be disappeared and then the electrons



(a) before ZnO-coating (b) after ZnO-coating

Figure 7. AFM images of the p-type semiconductor layer (a) before and (b) after coating with the ZnO particles.

may be smoothly able to reduce I_3^- ions in the electrolyte solution without a significant decrease in J_{sc}.

4. Conclusion

The p-type semiconductor of $CuBi_2O_4$ introduced into the cathode can absorb low energy photons which are not able to absorb with N719 dye adsorbed on the TiO_2 electrode and is effective on an increase in conversion efficiency. The ZnO layer formed on the p-type semiconductor of $Cu_xBi_yO_z$ will depress the back-transfer from the electrolyte to the p-type semiconductor and the band-bending of the p-type semiconductor, so that an increase in open-circuit voltage becomes effective. It is necessary to optimize the thicknesses of the ZnO and the p-type semiconductor layers to obtain higher conversion efficiency.

References

[1] O'Regan, B., & Grätzel, M. (1991). *Nature*, *353*, 737.

[2] He, J., Lindström, H., Hagfeldt, A., & Lindquist, S.-E. (2000). *Solar Energy Materials & Solar Cells*, *62*, 265.

[3] Nakasa, A., Usami, H., Sumikura, S., Hasegawa, S., Koyama, T., & Suzuki, E. (2005). *Chem. Lett.*, 34, 500.

[4] Yamada, K., Yamamoto, K., Sonoda, T., Yamane, H., Matsushima, S., & Nakamura, H., *Nanosci. Nanotechnol. Lett.*, to be submitted.

[5] Barbe, C. J., Arendse, F., Comte, P., Jirousek, M., Lenzman, F., Shklover, V., & Grätzel, M. (1997). *J. Am. Ceram. Soc.*, *80*, 3157.

[6] Arai, T., Yanagida, M., Konishi, Y., Iwasaki, Y., Sugihara, H., & Sayama, K. (2007). *J. Phys. Chem. C*, *111*, 7574.

[7] Koffyberg, F. P. & Benko, F. A. (1982). *J. Appl. Phys.*, *53*, 1173.

[8] Kalyanasundaram, K., & Grätzel, M. (1998). *Coord. Chem. Rev.*, *177*, 347.