Efficient dye-sensitized photoelectrochemical cells made from nanocrystalline tin oxide-zinc oxide composite films by doctor-blade method

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Dye-sensitized photoelectrochemical cells based on nanocrystalline films of TiO_2 yield energy conversion efficiencies ~ 10 %. The efficiencies of similar cells with films of other oxide materials (SnO_2, ZnO) are well below the above value. However, we have found that the cells made from SnO_2–ZnO composite films give efficiencies comparable to TiO_2 cells.[1] Originaly, these SnO_2–ZnO composite films were prepared by spraying SnO_2–ZnO mixed colloidal dispersion solution onto conductiong tin oxide (CTO) glass substrate. However, this spray method is sometimes confronted with difficulties of depositing thicker film (> 10 μm) in good reproduceability. This difficulty is usually overcome by employing doctor-blade method instead of spray method. Therefore, we have been trying to prepare SnO_2–ZnO composite films by doctor-blade method according to the report.[2] At first, it was difficult to make thicker film without crack formed during sintering process at high temperature (450 ~ 550 °C) whereas perfect film could be prepared in the case of thin film (2~3 μm). In this paper, repetitive accumulation of SnO_2–ZnO composite films by doctor-blade method and some successful results are reported.

ZnO powder (600mg) and 15% SnO_2 colloidal solution (3ml) were ground in mortar. Acetic acid (0.1ml), acetyl acetone (0.1ml) and triton-X (0.1ml) were droped into the mixture in mortar. Then, H_2O (7ml) and cellulosic thickener (0.1g) were added to the mixture and the mixture was thoroughly ground. One method of film accumuration (Method A) is as follows. Resulting dispersion paste was spread onto CTO glass substrate with glass rod and dryed under air. After repeating this process accumulated SnO_2–ZnO composite film was sinterd at 450 °C for 1 hour. In the other method (Method B), dryed film was sintered in every accumulation process. Films deposited on CTO glass plates were coated with the dye (Eosin Y) by immersing the plates in a warm (~80^0C) alcoholic solution (3 x 10^{-3} M) for 4 h. The cell was formed by clamping the dyed film surface to the counter-electrode and filling the capillary space with the electrolyte (0.5 M Pr_4NI, 0.05 M I_2 in CH_3CN, ethylene carbonate and *tert*-butyl pyridine (2.0, 7.3 and 0.7 ml, respectively).

The results are shown in figures 1 and 2 and summarized in table 1. Method B is obviously superior to Method A. From the observation by SEM, there are many cracks in accumulated SnO_2–ZnO composite film prepared by Method A. On the other hand, almost perfect film could be prepared by Method B. Two layered SnO_2–ZnO composite film afforded the best efficiency (2.2 %) which is comparable to the film prepared by conventional spray method. In the case of three layered film, Voc and fill factor decreased then efficiency decreased a little probably due to inefficient electron transport from top to bottom of thicker film. A further attempts of film accumulation such as combination of different kind of films to improve cell performance is underway.

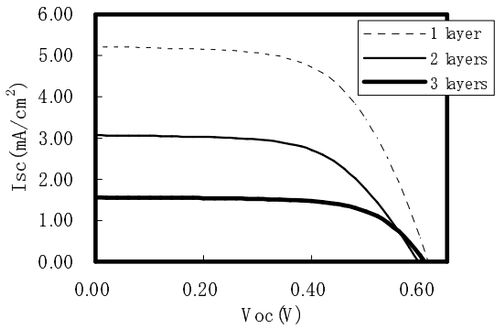

Figure 1. I-V characteristics of Eosin Y sensitized photoelectrochemical cell made from SnO_2–ZnO composite film photoelectrode by doctor-blade method (Method A).

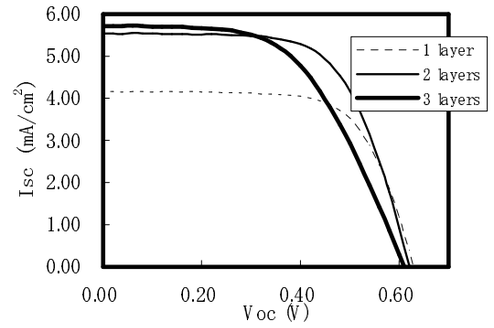

Figure 2. I-V characteristics of Eosin Y sensitized photoelectrochemical cell made from SnO_2–ZnO composite film photoelectrode by doctor-blade method (Method B).

Table 1 Cell performances of Eosin Y sensitized photoelectrochemical cell made from SnO_2–ZnO composite film photoelectrode by doctor-blade method (Method B) or by conventional spray method.

	Voc / mV	Isc / $mAcm^{-2}$	Efficiency / %
Single layer	649	4.1	1.8
2 layers	622	5.5	2.2
3 layers	610	5.7	1.9
Spray[a]	590	5.6	2.2

[a] Reference: Kumara, G.R.R.A.; Konno, A.; Tennakone, K. *Chem. Lett*., **2001**, 180-181.

References

1. Tennakone, K.; Kumara, G.R.R.A.; Kottegoda, I.R.M.; Perera, V.P.S. *Chem. Commun*. **1999**, 15-16.; Tennakone, K.; Bandaranayake, P.K.M.; Jayaweera, P.V.V.; Konno, A.; Kumara, G.R.R.A. *Phys. E*, **2002**, *14*, 190-196.; Kumara, G.R.R.A.; Tennakone, K.; Kottegoda, I.R.M.; Bandaranayake, P.K.M.; Konno, A.; Okuya, M.; Kaneko, S.; Murakami, K. *Semicond. Sci. Technol*. **2003**, *18*, 312-318.
2. Y. Makari, S. Ito, T. Kitamura, Y. Wada, and S. Yanagida, *14th International Conference on Photochemical Conversion and Storage of Solar Energy (IPS-14)*., abstract No. W1-P-59 (2002).