Bull. Mater. Sci., Vol. 28, No. 6, October 2005, pp. 635–641. © Indian Academy of Sciences.

Versatile preparation method for mesoporous TiO_2 electrodes suitable for solid-state dye sensitized photocells

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MS received 25 April 2005; revised 10 June 2005

Abstract. **Nano-structured TiO_2 electrodes, suitable for dye sensitized solid-state solar cells were prepared by a new simple spraying technique (SPT). Physical properties of these electrodes were compared with the electrodes prepared by the 'doctor blade' technique (typical sliding method, DB). Dye sensitized solid-state solar cells, comprising of CuI as the hole conductor, were fabricated with these electrodes and enhanced photo responses were obtained with SPT electrodes. The effects of additives, either to the spray solution or to the hole conductor on the photoresponses of the above devices were also studied. The cells fabricated with SPT electrodes containing $Al(Bu^iO)_3$ showed ~ 2·4% efficiency and addition of 1-ethyl-3-methyl imidazolium thiocyanate into CuI layer further enhanced the efficiency up to 2·75% under the irradiance of 100 mW cm^{-2} (AM 1·5).**

Keywords. **Nano-oxides; dye sensitization; solid-state cells; spray pyrolysis; titanium dioxide.**

1. Introduction

In the past decade there has been a considerable progress achieved in the dye sensitized nanoporous TiO_2 photoelectrochemical solar cells (DSCs) employing liquid electrolyte (LEDSC) as one of the potential low cost alternatives to conventional inorganic semiconductor solar cells (Regan and Grätzel 1991; Grätzel 2001). However, due to some limitations, such as problems in encapsulation, practical applications of these cells have not yet been fully realized. This has instigated the search for alternative systems for these liquid phase electrolytes. In this context, solidification of the electrolyte or the replacement of the electrolyte with suitable materials such as CuI, CuSCN, PPy, pentacene, OMeTAD (Tennakone *et al* 1995, 2000; Bach *et al* 1998; Murakoshi *et al* 1998; Kumara *et al* 2001, 2002; Regan *et al* 2002; Senadeera *et al* 2002; Perera *et al* 2003; Smestad *et al* 2003) are the most attractive systems and they are called solid-state dye sensitized solar cells (SSDSCs). One of the major differences between these LEDSCs and SSDSCs is the nature of the charge transport. While the ionic transport controlled by diffusion prevails in the LEDSCs, the electronic transport influenced by conductivity and charge transport mobility plays the deciding role in SSDSCs. In this context, spray pyrolysis (Kavan and Grätzel 1995), "doctor blading" i.e. sliding a paste of semiconductor with a glass rod on the substrate (Barbé *et al* 1997) and screen printing techniques (Zhang *et al* 2001) have been used widely in the preparation of nano-structured electrodes suitable for LEDSCs. However, the nano-structured electrodes used in the LEDSCs will meet some difficulty on using in SSDSCs specially due to the penetration of hole conducting materials through nano-size voids to the bottom of the porous photo-electrode which creates unnecessary new electrical contacts between the hole conductor and the substrates, which eventually results in short circuiting the cell with zero efficiency. Therefore, it is important to fabricate photoelectrodes to be used in SSDSCs, having desired properties such as high porosity with good necking of the crystallite and also avoiding the direct contacts between the hole conductor and the substrate. Due to these difficulties very few techniques are currently available to prepare suitable TiO_2 electrodes for these SSDSCs having the aforementioned hole conductors. Since some of the reported methods are not suitable for mass production (Tennakone *et al* 1995, 2000; Kumara *et al* 2001a,b; Senadeera *et al* 2002), recently researchers have introduced a "double layer" technique having a spin-coated dense and less porous layer (compact) of TiO_2 (CL) between FTO glass substrate and the porous layer of TiO_2 (Murakoshi *et al* 1998; Grant *et al* 2002). In the fabrication of these cells, typical DB technique is used to fabricate the porous films on the CL coated FTO. However, due to the low viscosity of the semiconductor paste used in DB method, it is difficult to get thick enough crack free films, specially, suitable for

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*Author for correspondence (rsena@ifs.ac.lk) the solid-state devices. On the other hand, the attachment between the CL and the porous layer seems to be not rigid. Therefore, the possibility of relaxing the attachment during the application of the hole conductors at elevated temperatures cannot be ruled out. Especially in the case of CuI, an acetonitrile solution containing CuI has to be applied by keeping the substrates at elevated temperature, so that the contacts between CL/FTO and the porous layers and the contacts between the crystallites within the porous layer could be relaxed. Therefore, in many cases post surface treatments to either the *n*-type semiconductor or the hole conductor are essentially required to enhance the efficiencies of these cells (Kumara *et al* 2002).

Therefore, in this paper we propose a novel economical and simple methodology leading to deposition of well-adhered, thick TiO_2 electrodes suitable for SSDSCs especially with CuI as the hole conducting material. The compositions and the method used in this technique are completely different and simple than the usual compositions used in the conventional spray pyrolysis techniques to obtain TiO_2 electrodes which can be used only for the LEDS (Okuya *et al* 2002, 2004). Further, despite its simplicity than the usual spray pyrolysis techniques, this method has a number of advantages such as (i) it offers an extremely easy way to dope films with virtually any element in any proportion by merely adding it in some form to the spray solution and (ii) the deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical methods such as sol-gel which produces films of limited thickness.

2. Experimental

2.1 *Preparation of TiO_2 layers*

An ethanolic solution of titanium tetra-1-methylethoxide ($Ti[O^iPr)_4$) containing a few drops of HNO_3 (pH = 2) was spin-coated on pre-cleaned glass substrates having F-doped SnO_2 conducting layer (FTO, 16 Ω/sq) at 1000 rpm for 1 min. The films were then sintered at 500°C for 1 h and cooled to room temperature. The above procedure was then repeated to obtain ~ 100 nm thick dense less porous TiO_2 layer. The resulting pinhole free compact layer of TiO_2 (CL) confirmed by the cyclic voltammetry as in the literature (Smestad *et al* 2003) prevents the short-circuiting of the cell.

SPT mesoporous films of TiO_2 were deposited on the above substrates by the following method. Completely different and simple composition than the reported pyrolysis methods were prepared as follows. TiO_2 (Nippon Aerosil P-25, 0·5 g) was added to a mortar containing 2 ml of acetic acid and ground well for 1 min. Then, 0·5 ml of $Ti(O^iPr)_4$ was added. While mixing, 0·1 ml of deionized water was added to the above mixture. Three drops (~ 0·1 ml) of Triton X-100 (Aldrich) were then added and ground thoroughly. The mixture was diluted to 100 ml adding ethanol and sonicated for 10 min. The diluted spray solution (1 : 4 v/v) by ethanol was sprayed onto a preheated FTO coated glass with the CL placed on a digital hot plate at 300 ± 5°C. The temperature of the hot plate was varied from 150–300°C and it was found that better adhesion and uniform films could be obtained when the temperature was 300°C. The distance between the substrate and the nozzle of the spray gun was kept at ~ 25 cm. The compressed air was used as the carrier gas. The spraying was carried out at a rate of 20 ml min^{-1} and spray nozzle was moved back and forth over the substrate slowly.

The electrodes were then sintered at 500°C for 1 h. The film thickness of the TiO_2 electrodes were measured using a profilometer (Veeco, Dektack 3) and average thickness was ~ 12·5 μm. In order to compare the physical properties, photoelectrodes were also prepared with TiO_2 (P25) on the same compact layers by well known DB technique. TiO_2 paste was prepared following a commonly used method described in the literature (Barbé *et al* 1997).

2.2 *Characterization of TiO_2 films*

The crystallinity and crystal phase of the SPT electrodes were determined by a powder X-ray diffractometry (XRD, Rigaku, RINT 2000/PC) using CuK*a* radiation and the crystallite size of TiO_2 was calculated from a full width of half-value of the XRD peak at $2q = 25{\cdot}4°$ using Scherrer's equation. The surface morphologies of the electrodes were studied by a field emission scanning electron microscopy (FE-SEM, JEOL, JSM6700F). The BET surface area was determined using a nitrogen adsorption–desorption apparatus (Quantachrome, Autosorb-1) and the pore size distribution and pore volume were analysed by Barrett–Joyner–Halenda (BJH) method.

2.3 *$Al(Bu^iO)_3$ treatments*

In order to see the effect of aluminium tri-1-methylpropoxide ($Al(O^sBu^i)_3$) on the properties of the solar cells, TiO_2 electrodes were sprayed with desired amount of $Al(O^sBu^i)_3$ as follows. A solution of $Al(O^sBu^i)_3$ in isopropanol (1×10^{-3} mol dm^{-3}) was prepared in a glove box. The solution (1 ml) was then added to the spray solution (100 ml) and sprayed on to the surface of CL covered FTO kept at 300°C. The resulting electrodes were then dried at 110°C for 10 min to remove any solvents.

2.4 *Fabrication and characterization of solar cells*

TiO_2 electrodes treated with and without $Al(O^sBu^i)_3$ were immersed separately in ethanolic dye solutions containing $RuL_2(SCN)_2$, where L = 4,4′-dicarboxy-2,2′-bipyridine (2×10^{-4} mol dm^{-3}), for 18 h. The dyed electrodes were then rinsed with ethanol and dried. CuI deposition on the dyed electrodes was carried out as follows. A solution of CuI was prepared by dissolving 0·3 g of CuI in 10 ml of moisture free acetonitrile. The dye-coated electrodes were placed on a hot surface (80–100°C) and filtered CuI solution was lightly spread over the dyed film using a dropper. This process was repeated until all the pores were filled and the thickness of CuI extended up to ~ 6 mm. The electrical contact of the counter electrode to the CuI was made by pressing either a gold-coated FTO glass or Cr doped Pt plate onto the CuI surface. To improve the electron diffusion in TiO_2 and at the same time to see the effect of ionic liquid on CuI, 1-ethyl-3-methylimidazolium thiocyanate (3 g in 100 ml) was added to CuI solution and spread on the Al treated TiO_2 electrodes as in the previous case. A schematic diagram illustrating the construction of the cell is shown in figure 1(a). Photoenergy conversion efficiency was evaluated using the standard solar irradiation of 100 mW cm^{-2} (AM1·5) with a solar simulator (Yamashita Denso, YSS-50A) and a computer controlled voltage current sourcemeter (Advantest, R6246) at 25°C. The power conversion efficiency (*h*) was calculated according to the following equation

$$h = \mathrm{FF} \times J_{sc} \times V_{oc}/I,$$

where J_{sc} is the short circuit photocurrent density in A cm^{-2}, V_{oc} the open circuit voltage in *V*, *I* the intensity of the incident light in W cm^{-2} and FF the fill factor defined as $\mathrm{FF} = J_m V_m/J_{sc}V_{oc}$, where J_m and V_m are values of optimum photocurrent and voltage that can be extracted from the maximum power point of the *I*–*V* characteristics (Grätzel 2001).

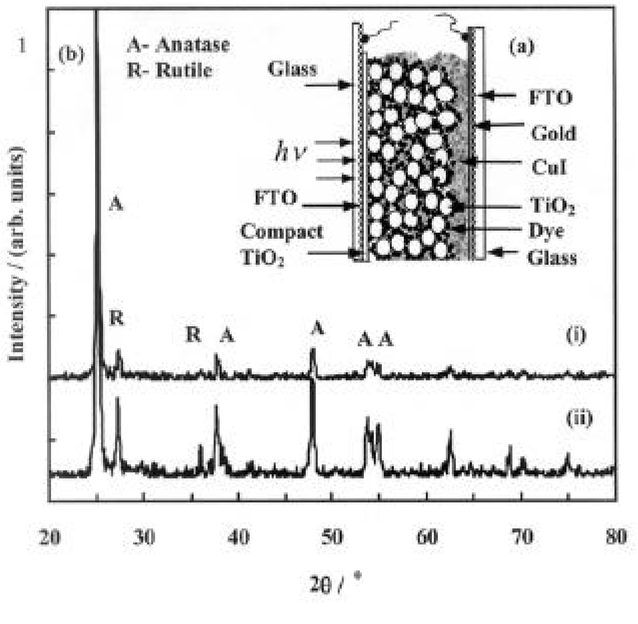

Figure 1. (a) Schematic diagram representing the fabrication of cell TiO_2/dye/CuI and (b) XRD patterns of spray type TiO_2 films (i) before sintering and (ii) after sintering.

3. Results and discussion

Figure 1(b) shows the diffraction pattern of the SP electrode, before (i) and after (ii) sintering at 500°C for 1 h. This analysis showed that TiO_2 electrodes were polycrystalline in nature. Three broad peaks identified at 25·3°, 48·0° and 55·1° corresponded to (101), (020) and (121) reflections of the anatase form of TiO_2. Therefore, as expected, the TiO_2 electrodes were mainly of anatase form. The average crystalline size calculated by the Scherrer's method was ca. 13–20 nm. It was also observed that after the sintering the relative amorphous halo area decreased by 40% and the signal to noise ratio of the XRD pattern was increased indicating enhancement of the crystallinity. The sintered mesoporous films had good adherence to the CL coated FTO and between P25 TiO_2 particles. The TiO_2 never peeled off by a stream of water and air or even with light rubbing. The film thickness measurements at different positions across the TiO_2 surfaces of the SPT electrodes showed that homogeneous thick films could be obtained by this spray method.

Table 1 shows the physical properties of TiO_2 electrodes prepared under different conditions. As it is evident from the table, the SPT electrodes possessed higher pore volume and porosity than the DB electrodes. Therefore, the hole conductors used in the SSDSCs could be penetrated more deeply into the SPT electrodes than in the DB electrodes. Nevertheless, a higher effective area was observed in the SPT electrodes than that of the DB electrodes providing larger space for dye adsorption.

Table 1. Variation of the surface properties of DB and SPT type films obtained from the BET surface area measurements.

	P-25 DB type TiO_2	Sprayed with titanium isopropoxide (SPT type TiO_2)	Sprayed with ($Al(O^sBu^i)_3$)
Surface area (m^2g^{-1})	55·23	58·44	59·67
Pore volume ($cc \cdot g^{-1}$)	0·3177	0·4862	0·3897
Pore diameter (Å)	26·58	25·59	26·94
Porosity (%)	55·70	65·85	61·27

Figure 2 shows the SEM photographs of the surface morphologies of DB and SPT electrodes. Figures 2a and b show the surfaces of the sintered DB electrodes under different magnifications. Figures 2c and e show the surface of SPT electrode just before and after sintering. Magnified SEM pictures of the SPT electrode are shown in figures 2d and f, respectively. As observed in figure 2a, very fine cracks were observed in the DB electrodes. The SPT electrodes showed an interpenetrating network ("crater") type morphology (figures 2c and e) without cracks. Enhancement in the porosity and the interconnection between the TiO_2 crystallites were observed in the SPT electrodes (figures 2d and f). Therefore, the sintering process should induce the effective necking of the TiO_2 crystallites in SPT workup without forming cracks. One of the reasons for this enhanced necking might be related to the formation of TiO_2 layer from $Ti(O^iPr)_4$ during sintering.

Figure 3 shows the average current–voltage (*I*–*V*) curves of the TiO_2/dye/CuI cells fabricated either with DB electrodes or SPT electrodes with different additives, under dark and illuminated conditions (AM 1·5, 100 mW cm^{-2}).

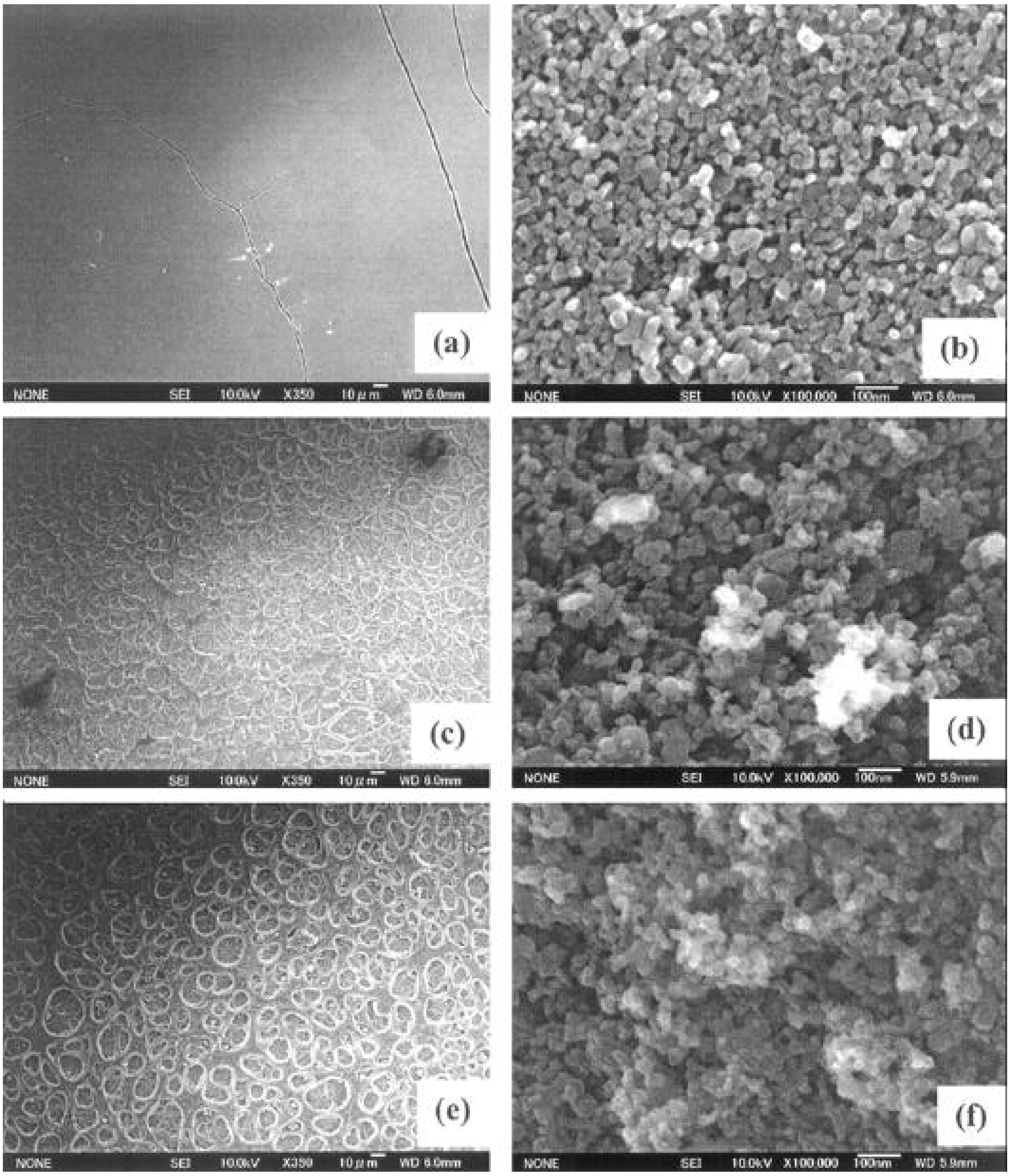

Figure 2. SEM micrographs of DB and SPT type electrodes. Sintered DB type TiO_2 electrode at (**a**) 350 and (**b**) 100000 magnification. As prepared SPT type TiO_2 electrode at (**c**) 350 and (**d**) 100000 magnification. Sintered SPT type electrode at (**e**) 350 and (**f**) 100000 magnification.

While the curves (a) and (b) represent the dark *I–V* behaviour of the cells prepared with DB electrodes and SPT electrodes, curves (c) and (d) represent their photo responses, respectively. Improved dark current properties were observed in the cells fabricated with SPT electrodes. The curve (e) shows photoresponses of the cells fabricated with $Al(O^sBu^i)_3$. The curve (f) represents the photo-responses of the above cells with addition of an ionic liquid, 1-ethyl-3-methyl imidazolium thiocyanate (EMImSCN) to the CuI solution. The corresponding values (average of five samples) for the short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and overall solar to electrical energy conversion efficiency (*h*) are tabulated in table 2. As evident from the table, the cells with SPT electrodes give higher photocurrents and voltages than the DB electrodes. Again this enhancement might be attributed to the reduction of recombination rate due to the enhanced necking of the TiO_2 crystallites itself in the porous layer and the necking between the CL on FTO and the porous layer. On the other hand, this enhanced necking and the crack free SPT electrodes should provide a good path for the electrons to transfer more efficiently than that in the DB electrodes.

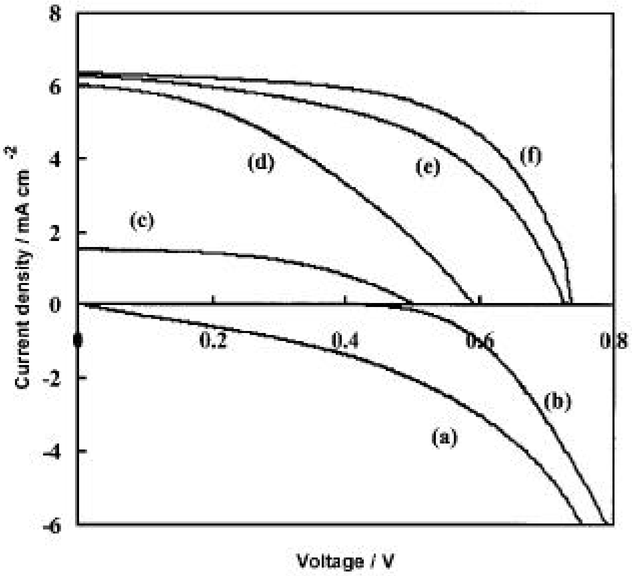

Figure 3. Dark *I–V* responses of the TiO_2/dye/CuI cells with (a) DB type, (b) SPT type electrodes and photo *I–V* responses, (c) bare DB type, (d) bare SPT type, (e) SPT type with Al composites and (f) SPT type $Al(O^sBu^i)_3$ modified TiO_2 electrodes with EMISCN in CuI.

As it is evident from the table, SPT electrodes prepared with $Al(O^sBu^i)_3$ give much higher voltage than the reported values for the dye sensitized solid-state solar cells with CuI (Tennakone *et al* 1995; Kumara *et al* 2002; Meng *et al* 2003; Zhang *et al* 2004). In this context many researchers have tried to cover the TiO_2 crystallites with a thin insulating layer of Al_2O_3 by using dip-coating methods (Palomares *et al* 2002; Zhang *et al* 2004). However, in the present work higher photo-voltages were obtained only by spraying the TiO_2 solution with $Al(O^sBu^i)_3$. Therefore, time consuming dipping processes could be eliminated. The addition of EMImSCN further improved the cell performances, specially an enhancement in fill factor because of the enhanced electron diffusion in TiO_2 phase (Kubo *et al* 2003) and thereby enhanced the overall efficiency of the cell up to 2·75%. From the preliminary tests on the stability under continued illumination with a 100 mW cm^{-2} for a week, it is observed that the cells fabricated with SPT showed improved stability with almost no change in the efficiency. However, in order to see the stability for a long time, perfect sealing should be done to avoid contacts with the moisture and further investigations should be carried out to see the real effect.

Figure 4 shows the SEM photographs of CuI crystallites deposited on DB electrodes (a) and SPT electrodes (b and c) using a saturated solution of CuI in acetonitrile. As seen in figure 5(a), larger size crystals growth occurred in the DB type electrodes as reported by the others due to the unavailability of the inhibitant to control the crystal growth of CuI (Kumara *et al* 2002). However, “crater” type nature in SPT electrodes controls the CuI growth which cannot be seen in the DB electrodes. Especially the growth of crystals inside the craters has limitations and smaller crystals than in DB electrodes were formed. In other words, nano size roughness on DB films does not affect the crystal shape but sub-micron sized roughness in the SPT electrodes prevent the formation of micron-sized crystallites. As observed by others (Kumara *et al* 2002), the addition of ionic liquid further acts as a crystallites growth inhibitor even on the outside of these crates and enhances the fillings and the interfaces, resulting in higher efficiencies in these solid state cells.

Table 2. Photovoltaic performances of the cell, TiO_2/dye/CuI, fabricated under different conditions.

Type of the electrode	J_{sc} (mAcm^{-2})	V_{oc} (mV)	FF	*h*% ~	Area (cm^2)
c (DB electrode)	1·54 ± 0·64	504 ± 7	0·40	0·31	0·16
d (SPT electrode)	6·15 ± 0·27	592 ± 4	0·41	1·50	0·23
e (SPT electrode with ($Al(O^sBu^1)_3$)	6·28 ± 0·32	730 ± 6	0·52	2·38	0·26
f (SPT electrode with ($Al(O^sBu^1)_3$) and EMISCN	6·33 ± 0·11	737 ± 2	0·59	2·75	0·24

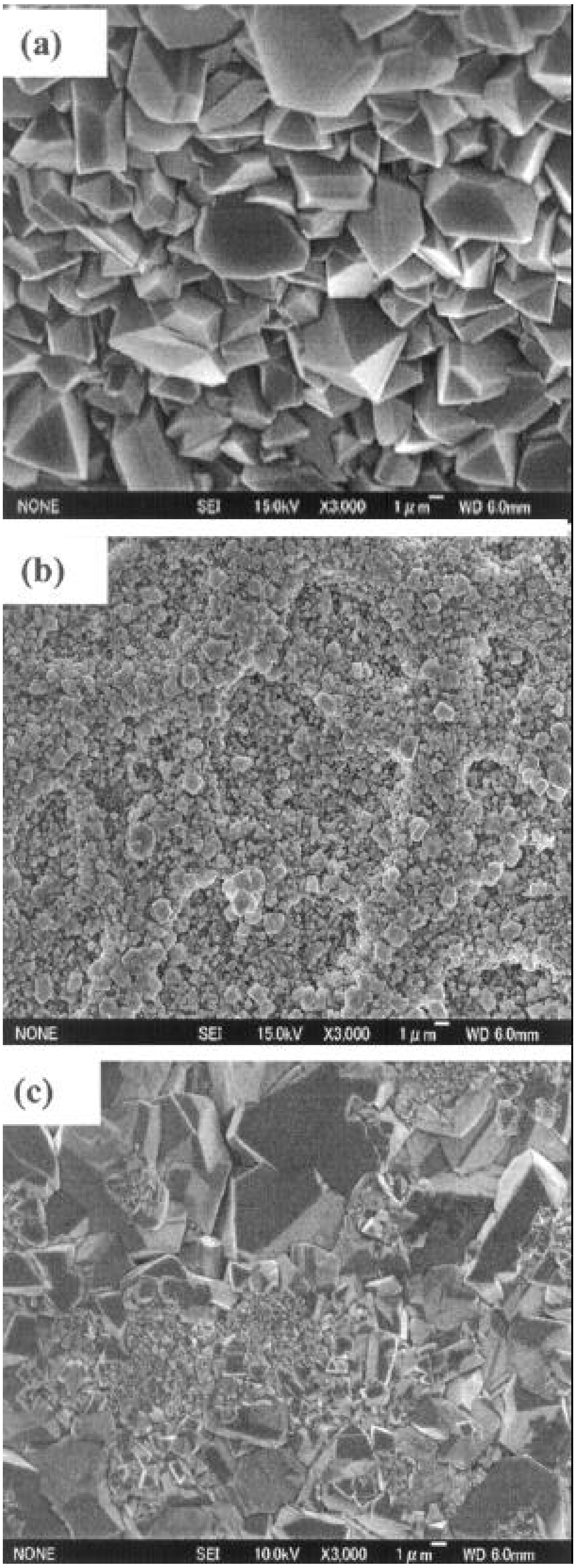

Figure 4. SEM micrographs of CuI crystallites on (**a**) DB with sufficient amount of CuI ($d \sim 6$–7 μm), (**b**) SPT electrode with small amount of CuI and (**c**) SPT type film with sufficient amount of CuI ($d \sim 6$–7 μm).

4. Conclusions

In summary, here we demonstrate a novel but a simple, rapid and versatile spray method for deposition of crack free, anatase TiO_2 thick films with enhanced necking, suitable for CuI based SSDSCs. One of the advantages of this method is, when the droplets of the sprayed solution reach the hot substrate, owing to pyrolytic decomposition of the solute, a well adherent film of TiO_2 is formed on CL. Enhancement in the efficiency of the cell fabricated with SPT electrodes, must be related with their higher porosity and good necking of the semiconducting crystallites. Preliminary studies revealed that the electrodes prepared by SPT method could be used efficiently, not only with the inorganic hole conductors but also with the highly conducting organic hole conducting polymers like poly (3,4-ethylenedioxythiophene). Owing to its simplicity and low cost, we believe that our spraying technique could be used in the mass production of the semiconducting electrodes suitable for the SSDSCs.

Acknowledgements

The authors would like to thank the Ministry of Education, Culture, Sports, Science and Technology of Japan, and the New Energy and Industrial Technology Development Organization (NEDO) under Ministry of Economy, Trade and Industry of Japan. (GKRS) acknowledges the Post-doctoral Research Fellowship from Japan Society for the Promotion of Science (JSPS).

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