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## **Spray-painted nano structured TiO<sub>2</sub> electrodes for solid-state dye sensitized photocells**

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### **Abstract**

Novel spray-pyrolysis (SPY), nano-structured TiO<sub>2</sub> electrodes were prepared in the aim of developing cost-effective alternative route to the photoelectrodes for solid-state dye sensitized solar cells (SSDSC). Physical properties and photoresponses of these SPY electrodes were compared with the TiO<sub>2</sub> electrodes prepared by the typical "doctor blade" (DB) technique. Enhanced necking of the TiO<sub>2</sub> crystallites with higher porosity and larger surface area were observed in the SPY electrodes than in DB electrodes. Two sets of RuL(SCN)<sub>2</sub> (L = 4,4'-dicarboxy-2,2'-bipyridyl) dye sensitized solid-state solar cells were constructed. One with DB and the other with SPY electrodes comprising CuI as hole transporting material. Preliminary studies showed that the photocells comprised with SPY electrodes have three fold higher overall efficiencies than that of the cells made up of DB electrodes under the same conditions. Improved necking between the TiO<sub>2</sub> crystallites might be the reasons for this enhancement.

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### **1. INTRODUCTION**

Dye sensitized solar cells (DSSC) based on nanocrystalline TiO<sub>2</sub> have attracted considerable scientific and technological interest. On a laboratory scale a power conversion efficiency of more than 10 % was achieved with these devices<sup>1, 2</sup>. This promising performance is possible by the extremely large surface area of the nanocrystalline sponge-type TiO<sub>2</sub> structure, which enhances light absorption in the monolayer of dye molecules adsorbed at the TiO<sub>2</sub> surface. Light induced charge separation occurs by ultra fast electron injection from the excited state of the dye into the conduction band of the semiconductor<sup>3,4</sup> and the subsequent diffusion of these electrons through the TiO<sub>2</sub> network. The remaining

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hole is reduced by the iodide (I<sup>-</sup>) species of the redox electrolyte which itself is re-reduced at the platinum back electrode. When compared to other solar cell technologies, the DSSC has the advantage of using low cost materials as well as a simple cell technology. The main disadvantage of these devices lies in the use of the liquid I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolyte<sup>5</sup>. Encapsulation of the DSSC seems to be rather problematic because of the chemically aggressive I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple. In order to avoid that problem, several attempts of replacing the liquid electrolyte by a solid-state hole conductors such as CuI, CuSCN, Pentacene, OMETAD have been made<sup>6-8</sup>. One of the major differences between these liquid electrolyte (PEC) and the solid-state devices (SSDSSCs) is the nature of the charge transport. While the ionic transport controlled by diffusion prevails in the PECs, the electronic transport influenced by conductivity and charge transport mobility plays the deciding role in the SSDSSCs. Nano-structured electrodes used in the PECs will meet some difficulty on using in SSDSSCs specially due to the penetration of hole conducting materials through nano-size voids to the bottom of the porous photo-electrode. One of the difficulties is these processes create unnecessary new electrical contacts between the hole conductor and the F doped SnO<sub>2</sub> conducting glass (FTO) substrates, which eventually result in short circuiting the cell with zero efficiency. Therefore, it is important to fabricate photoelectrodes to be used in SSDSSCs, 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 FTO surface.

In this context, very few techniques are currently available to prepare suitable TiO<sub>2</sub> electrodes for these SSDSSCs having the aforementioned hole conductors<sup>2-13</sup>. Since some of the reported methods are not suitable for mass production<sup>2,3,8-10</sup>, recently researchers have introduced a "double layer" technique; having a spin-coated dense and less porous layer (compact) of TiO<sub>2</sub> (CL) between FTO glass and the porous layer of TiO<sub>2</sub><sup>7,14,15</sup>. In the fabrication of cells, typical "doctor blade (DB) technique"<sup>16</sup>, i.e., sliding a paste of semiconductor with a glass rod on the substrate, 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 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 can not 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 CLFTO 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<sup>12</sup>.

Therefore, in this paper we propose a novel economical and versatile methodology leading to deposition of well-adhered, thick TiO<sub>2</sub> electrodes suitable for SSDSSCs especially with CuI as the hole conducting material. Despite its simplicity, this method has

a number of advantages such as (1) 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. (2) 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<sub>2</sub> layers

An ethanolic solution of titanium tetra-1-methylethoxide (Ti(O<sup>i</sup>Pr)<sub>4</sub>) containing a few drops of HNO<sub>3</sub> (pH = 2) was spin-coated on pre-cleaned glass substrates having F-doped SnO<sub>2</sub> conducting layer (FTO, 16 Ω /sq) at 1000 rpm for 1 min. The films were then sintered at 500 °C for 1 hour and cooled down to the room temperature. The above procedure was then repeated to obtain ~ 100 nm thick dense less porous TiO<sub>2</sub> layer. The resulting pinhole free compact layer of TiO<sub>2</sub>, (CL) confirmed by the cyclic voltammetry as in the literature <sup>6</sup> prevents the short-circuiting of the cell.

SPY mesoporous films of TiO<sub>2</sub> were deposited on the above substrates by the following method. TiO<sub>2</sub> (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<sup>i</sup>Pr)<sub>4</sub> 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 minutes. 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 to 300 °C and it was found that uniform films of better adhesion 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<sup>-1</sup> 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 were measured by 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<sub>2</sub> (P25) on the same compact layers by well known DB technique but without Ti(O<sup>i</sup>Pr)<sub>4</sub> as described in the literature <sup>16</sup>.

### 2.2. Characterization of TiO<sub>2</sub> films

The surface morphology of the electrodes was 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), the pore

size distribution and the pore volume were analyzed by Barrett-Johner-Halenda (BJH) method.

### 2.3 Fabrication and characterization of solar cells

TiO<sub>2</sub> electrodes were immersed separately in ethanolic dye solutions containing RuL<sub>2</sub>(SCN)<sub>2</sub> where L = 4,4'-dicarboxy-2,2'-bipyridine ( $2 \times 10^{-4}$  mol dm<sup>-3</sup>) for 18 hours. 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 μm. 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. A schematic diagram illustrating the construction of the cell is shown in Figure 1. Photo-energy conversion efficiency was evaluated using the standard solar irradiation of 100 mW cm<sup>-2</sup> (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 ( $\eta$ ) was calculated according to the following equation;  $\eta = FF \times J_{sc} \times V_{oc} / I$ , where  $J_{sc}$  is the short circuit photocurrent density in A cm<sup>-2</sup>,  $V_{oc}$  is the open circuit voltage in V,  $I$  is the intensity of the incident light in W cm<sup>-2</sup> and FF is the fill factor defined as  $FF = J_m V_m / J_{sc} V_{oc}$ , where the  $J_m$  and  $V_m$  are values of optimum photocurrent and voltage that can be extracted from the maximum power point of the I-V characteristics<sup>18</sup>.

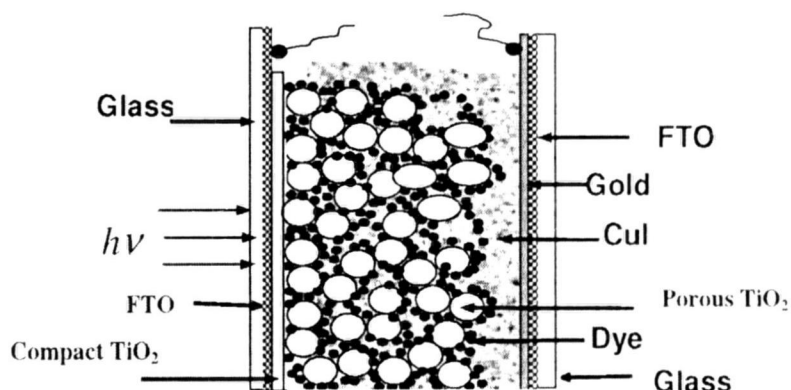


Figure 1. Schematic diagram representing the fabrication of cell TiO<sub>2</sub>/dye/CuI.

### 3. RESULTS AND DISCUSSION

The sintered mesoporous films had good adherence to the CL coated FTO and between TiO<sub>2</sub> crystallites. The TiO<sub>2</sub> 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<sub>2</sub>

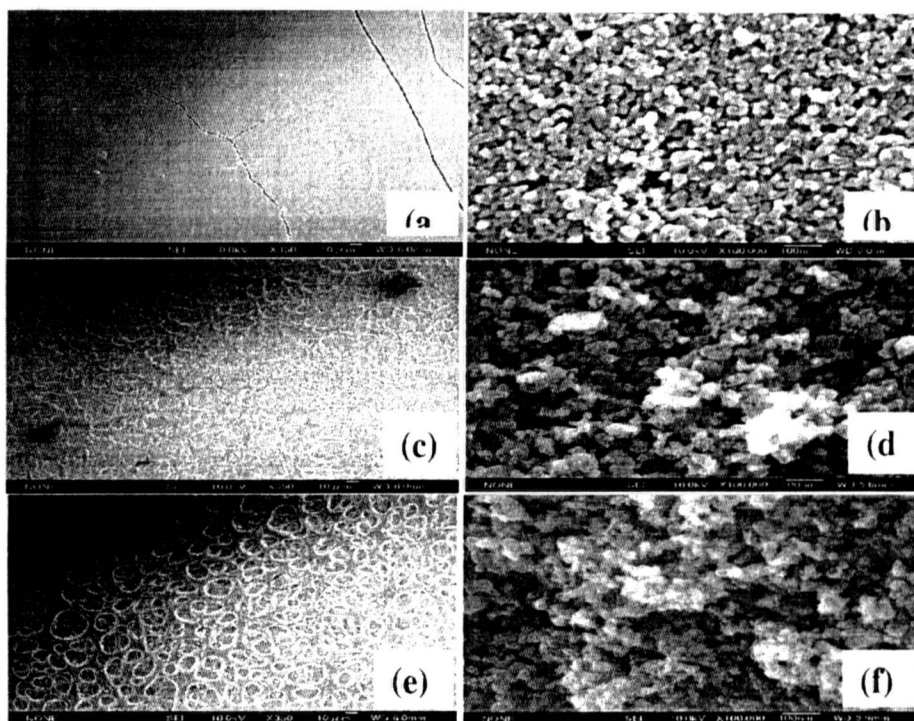
surfaces of the SPY electrodes showed that homogenous thick films could be obtained by this spray method.

Table 1 shows the physical properties of TiO<sub>2</sub> electrodes prepared under different conditions. As it is evident from the table, the SP 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 SPY electrodes than in the DB electrodes. Nevertheless, a higher effective area was observed in the SPY electrodes than that of the DB electrodes providing the larger space for dye adsorption.

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

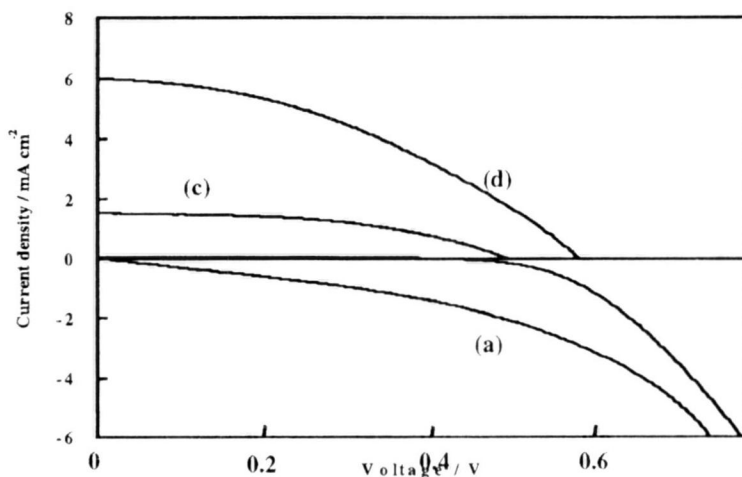
Property	Electrodes prepared with DB method	Electrodes prepared with SPY method
Surface area/ m <sup>2</sup> g <sup>-1</sup>	55.23	58.44
Pore volume /cc.g <sup>-1</sup>	0.3177	0.4862
Pore diameter/ Å	26.58	25.59
Porosity %	55.70	65.85

Figure 2 shows the SEM photographs of the surface morphologies of DB and SPY electrodes. Figure 2a and 2b show the surfaces of the sintered DB electrodes under different magnification. Figure 2c and 2e show the surface of SP electrode just before and after the sintering. Magnified SEM pictures of the SPY electrode are shown in Figure 2d and 2f respectively. As observed in the figure 2a very fine cracks were observed in the DB electrodes. The SPY electrodes showed an interpenetrating network ("crater") type morphology (figure c and e) without cracks. Enhancement in the porosity and the interconnection between the TiO<sub>2</sub> crystallites were observed in the SPY electrodes (figure d and f). Therefore, the sintering process should induce the effective necking of the TiO<sub>2</sub> crystallites in SPY workup without forming cracks. One of the reasons for this enhanced necking might be related to the formation of TiO<sub>2</sub> layer from Ti(O<sup>i</sup>Pr)<sub>4</sub> during the sintering.



**Figure 2.** SEM micrographs of (a) DB type TiO<sub>2</sub> film after sintering (b) enlargement of (a), (c) SP type TiO<sub>2</sub> before sintering and (d) enlargement of (c), (e) SP type TiO<sub>2</sub> after sintering and (f) enlargement of (e).

Figure 3 shows the average current–voltage (I-V) curves of the TiO<sub>2</sub>/dye/CuI cells fabricated either with DB electrodes or SPY electrodes with different additives, under the dark condition and illuminated conditions (AM 1.5, 100 mW cm<sup>-2</sup>). While the curves (a) and (b) represent the dark I-V behaviour of the cells prepared with DB electrodes and SPY electrodes, curve (c) and (d) represent their photo responses respectively. Improved dark current properties were observed in the cells fabricated with SPY electrodes.



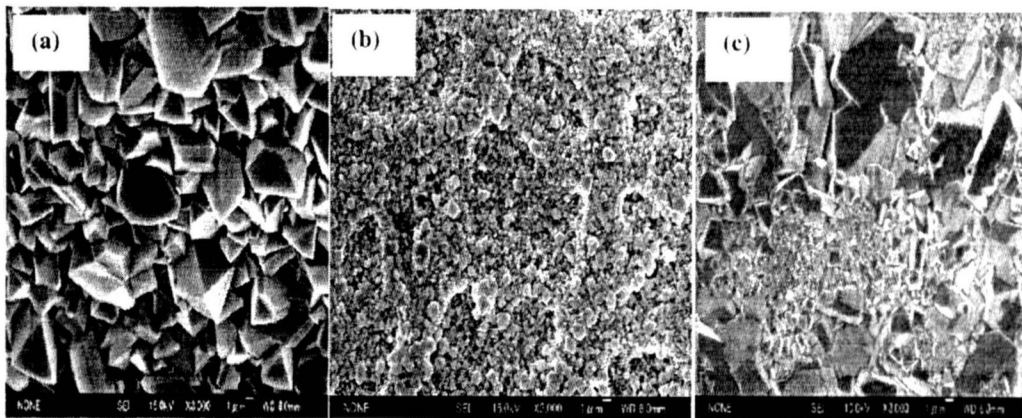
**Figure 3.** Dark I-V responses of the TiO<sub>2</sub>/Dye/CuI cells with (a) DB type and (b) SP type electrodes and Photo I-V responses (c) bare DB type, (d) bare SP type.

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 ( $\eta$ ) are tabulated in the Table 2. As evident from the table, the cells with SP 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 electrodes should provide a good path for the electrons to transfer more efficiently than in the DB electrodes.

**Table 2.** Photovoltaic performances of the cell  $TiO_2$ /dye/CuI fabricated under different condition.

Type of the electrode	$J_{sc}$ ( $mA\ cm^{-2}$ )	$V_{oc}$ (mV)	FF	$\eta\%$ ~	Area ( $cm^2$ )
c (DB electrode)	$1.54 \pm 0.64$	$504 \pm 7$	0.40	0.31	0.16
d (SP electrode)	$6.15 \pm 0.27$	$592 \pm 4$	0.41	1.50	0.23

As it is evident from the table, SPY electrodes give higher voltage than the reported values for the dye sensitized solid-state solar cells with CuI<sup>2,12,21, 22</sup>. Figure 4 shows the SEM photographs of CuI crystallites deposited on DB electrodes (a) and SPY electrodes (b and c) using a saturated solution of CuI in acetonitrile. As seen in the Figure 4 (a) larger size crystals growth occurred in the DB type electrodes as reported by the others due to the unavailability of the inhibitor to control the crystal growth of CuI<sup>12</sup>. However, "crater" type nature in SP electrodes control the CuI growth than in the DB electrodes. Especially the growth of the crystals inside of the craters has limitations and smaller crystals than in DB electrodes were formed. In the other words nano size roughness on DB films does not affect the crystal shape but sub-micron sized roughness in the SP electrodes prevent the formation of micron-sized crystallites.



**Figure 4.** SEM micrographs of CuI crystallites on (a) DB with sufficient amount of CuI ( $d \sim 6-7\ \mu m$ ), (b) SP electrode with small amount of CuI, (c) SP type film with sufficient amount of CuI ( $d \sim 6-7\ \mu m$ ).

#### 4. CONCLUSIONS

In summary, here we demonstrated a novel but a simple, rapid and versatile spray method (SPY) for deposition of crack free, anatase  $\text{TiO}_2$  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  $\text{TiO}_2$  is formed on CL. Enhancement in the efficiency of the cell fabricated with SPY electrodes, must be related with their higher porosity and the good necking of the semiconducting crystallites. Preliminary studies revealed that the electrodes prepared by SPY 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 the low cost, we believe that our spraying technique could be used in the mass production of the semiconducting electrodes suitable for the SSDSCs.

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