



# Influences of alcoholic solvents on spray pyrolysis deposition of TiO<sub>2</sub> blocking layer films for solid-state dye-sensitized solar cells

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## ABSTRACT

Influences of alcoholic solvents for titanium diisopropoxide bis(acetylacetonate) (TPA) precursor solutions on the spray pyrolysis deposited TiO<sub>2</sub> films and the photovoltaic performance of the solid-state dye-sensitized solar cells (SDSCs) using these TiO<sub>2</sub> films as the blocking layers were investigated. Smooth TiO<sub>2</sub> films were obtained by spray pyrolysis deposition of a TPA solution in isopropanol (IPA) at a relatively low temperature of 260 °C. On the other hand, when ethanol was used as solvent, the TiO<sub>2</sub> films fabricated at the same temperature showed much rougher surfaces with many pinholes. Our results showed that ethanol reacts with TPA to form titanium diethoxide bis(acetylacetonate) (TEA), which requires a higher thermal decomposition temperature than that of TPA. SDSCs with TiO<sub>2</sub> blocking layer films fabricated using a TPA solution in IPA showed higher power conversion efficiencies with smaller variations.

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## 1. Introduction

Dye-sensitized solar cells (DSCs) have the potential to generate electricity from sunlight at low costs compared with silicon technology [1–6]. DSCs hold the highest power conversion efficiencies (PCE) up to 12.3% [7] among current organic solar cell technologies, but the shortening of their lifetimes when liquid electrolytes are used is one of the major challenges for the widespread commercialization of DSCs [8]. Studies investigating the use of quasi-solids, ionic liquids and solid-state hole transporting materials to replace liquid electrolytes have been reported. Among the various types of solid-state DSCs (SDSCs), those using solid-state hole transporting materials have drawn much attention in the past few years due to (i) elimination of the use of reactive and volatile redox components such as I<sup>-</sup>/I<sub>3</sub><sup>-</sup>, (ii) simplification of the sealing/packaging of devices and (iii) ability to fabricate SDSCs on flexible substrates and compatibility with roll-to-roll manufacturing [9–12]. To date, SDSCs using organic hole transporting materials such as 2,2', 7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spiro-bifluorene (Spiro-OMeTAD) [13 and 14] and poly(3,4-ethylenedioxythiophene) (PEDOT) [15] have shown PCEs as high as 7.2%. On the other hand, a high PCE of

10.2% for a SDSC using an inorganic hole transporting material, CsSnI<sub>3</sub>, was recently reported [16]. In a typical SDSC device with an organic hole transporting material, a hole blocking layer, usually a compact TiO<sub>2</sub> thin film, is inserted between a transparent fluorine-doped tin oxide (FTO) electrode and a mesoporous TiO<sub>2</sub> layer to avoid direct contact of FTO with the hole transporting material [12–15]. Without such a TiO<sub>2</sub> blocking layer, a loss of current through charge recombination or even current leakage would occur due to an ohmic contact of the FTO electrode with the hole transporting material [9,17]. The TiO<sub>2</sub> blocking layer films can be prepared by several methods such as chemical vapor deposition [18,19], electron beam evaporation [20], sputtering [21–24], atomic layer deposition (ALD) [25–27] and spray pyrolysis deposition [28–39]. Spray pyrolysis deposition of the TiO<sub>2</sub> blocking layer films is simple and cost-effective. The most frequently used precursor for spray pyrolysis deposition of TiO<sub>2</sub> films is a solution of titanium diisopropoxide bis(acetylacetonate) (TPA) dissolved in ethanol [34–39]. In this study, we found that the use of isopropanol (IPA) instead of ethanol (EtOH) can improve the morphology of the TiO<sub>2</sub> films and the performance of the resulting SDSCs. Our results clearly indicate that EtOH reacts with TPA to produce titanium diethoxide bis(acetylacetonate) (TEA). The resulting TEA requires a higher temperature for decomposition. At a low pyrolysis temperature in the range of 220–260 °C, the use of EtOH as a solvent yields poor TiO<sub>2</sub> films, while the use of IPA results in more complete thermal decomposition and provides smooth TiO<sub>2</sub> films. SDSCs with the TiO<sub>2</sub> blocking layer films fabricated using a TPA solution in IPA show

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improved photovoltaic performance compared to cells with TiO<sub>2</sub> blocking layer films formed using a TPA solution (or more precisely a TEA solution) in EtOH.

## 2. Experimental

Spray pyrolysis was carried out using a home-made setup comprising an airbrush with a  $\phi$  0.3-mm nozzle, a hotplate and a movement control system, as shown in Fig. 1. The spray pyrolysis deposition procedure was similar to the one reported previously [30]. FTO-coated glass substrates (Solaronix, sheet resistance: 15  $\Omega$ /square) were immersed sequentially in detergent, de-ionized water, acetone and IPA in an ultrasonic bath for 10 min at a time and then placed on a pre-heated hotplate at a specified temperature. The substrate temperature (or pyrolysis temperature) was measured and controlled with a thermocouple (k-type) in direct contact with the FTO glass substrate surface. Different substrate temperatures of 220°, 260°, 300° and 350 °C were used for the spray pyrolysis deposition. The precursor solutions were prepared by mixing a concentrated TPA solution in IPA (Sigma-Aldrich, 75 wt% or 2.06 M) with EtOH, IPA and EtOH/IPA mixtures in varying proportions, respectively, and stored at least 24 h prior to use. The concentration of all the precursor solutions was maintained at 0.2 M with respect to the TPA content. To make TiO<sub>2</sub> films, a precursor solution was sprayed on the FTO substrates on the hotplate through the airbrush using O<sub>2</sub> as the carrier gas. Each spray from the airbrush was continued for 3 s at a flow rate of 0.15 mL/s and moved at a speed of 8 cm/s. The air brush was then returned to the original position and spraying paused for 60 s before the start of the next spray cycle. The thickness of the resulting TiO<sub>2</sub> films reached 70–85 nm after 14 cycles of spray pyrolysis deposition.

A typical SDSC device was fabricated as follows. A TiO<sub>2</sub> paste (Dyesol, 18NR-T) was first spin-coated on a FTO glass substrate

having a thin TiO<sub>2</sub> film deposited by spray pyrolysis as described above. Then the substrate was sintered at 450 °C in air for 30 min to form a mesoporous nanocrystalline TiO<sub>2</sub> layer (mp-TiO<sub>2</sub>) with a thickness of  $\sim$ 1.5  $\mu$ m. Dye-loading of the mp-TiO<sub>2</sub> layer was then carried out by soaking the substrate in a 0.5 mM D102 dye solution in *tert*-butanol/acetonitrile (1/1, v/v) [33] for 15 h at room temperature. The hole transporting layer was deposited on top of the mp-TiO<sub>2</sub> layer by spin-coating a solution of 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spiro-bifluorene (Spiro-OMeTAD) (180 mg/mL in chlorobenzene) containing 15 mM Li[CF<sub>3</sub>SO<sub>2</sub>]<sub>2</sub>N and 120 mM *tert*-butylpyridine (tBP). Finally, a 200 nm Ag layer as the anode was deposited on top of the Spiro-OMeTAD layer by vacuum thermal evaporation through a shadow mask to define the active area of the cell (0.2 cm<sup>2</sup>).

The thickness of TiO<sub>2</sub> films was measured with a surface profiler (KLA-TENCOR P-10). The surface topology and nanostructure of the TiO<sub>2</sub> films were examined with an optical microscope and a field-emission scanning electron microscope (FE-SEM, JEOL JSM6700F). Molecular structures of the precursor compounds were studied using a nuclear magnetic resonance (NMR) spectroscope (Bruker, 400 MHz). To prepare the samples for the NMR analysis, the solvent in the precursor solutions was evaporated at 0 °C under reduced pressure and then dissolved in CDCl<sub>3</sub>. The chemical shifts are reported relative to an internal reference compound, tetramethylsilane (TMS, 0 ppm).

Thermogravimetric analysis (TGA) was carried out to determine the thermal decomposition properties of the precursor compounds. The photovoltaic current–voltage (*I*–*V*) characteristics of SDSCs were measured with a Keithley 2400 Source-Meter unit under 100 mW/cm<sup>2</sup> illumination (AM 1.5 G) from a 300 W solar simulator (Newport 91160). The intensity of the light source was determined by a Si reference cell (calibrated by Fraunhofer Institute for Solar Energy, ISE) and corrected according to the spectrum mismatch calculation.

## 3. Results and discussion

A commercially available 75% (v/v) TPA solution in IPA was diluted with EtOH, IPA and EtOH-IPA mixtures to form 0.2 M precursor solutions, which were then used to fabricate TiO<sub>2</sub> films by spray pyrolysis deposition on FTO glass substrates. Fig. 2 shows the microscopic images of the TiO<sub>2</sub> films fabricated at 260 °C using precursor solutions made from the following solvents: IPA/EtOH with volumetric ratios of 3/7, 5/5 and 7/3, pure EtOH (10/0) and pure IPA (0/10). As shown in Fig. 2a, the TiO<sub>2</sub> film fabricated by using pure EtOH has many dark spots with diameters of a few microns. The number of dark spots clearly decreases as the IPA/EtOH ratio increases. When pure IPA is used, a smooth film with very few dark spots is obtained (Fig. 2e). Fig. 3 shows the microscopic images of the TiO<sub>2</sub> films fabricated at different substrate temperatures (220, 260, 300 and 350 °C) using

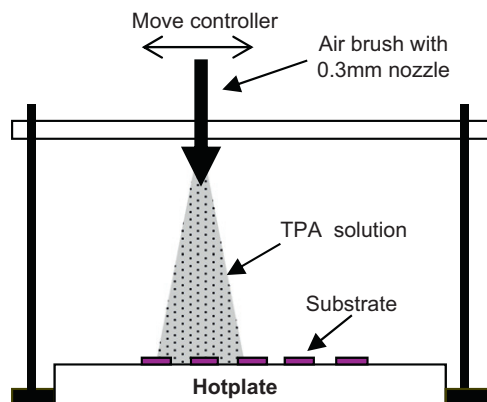


Fig. 1. The setup for spray pyrolysis deposition of TiO<sub>2</sub> films.

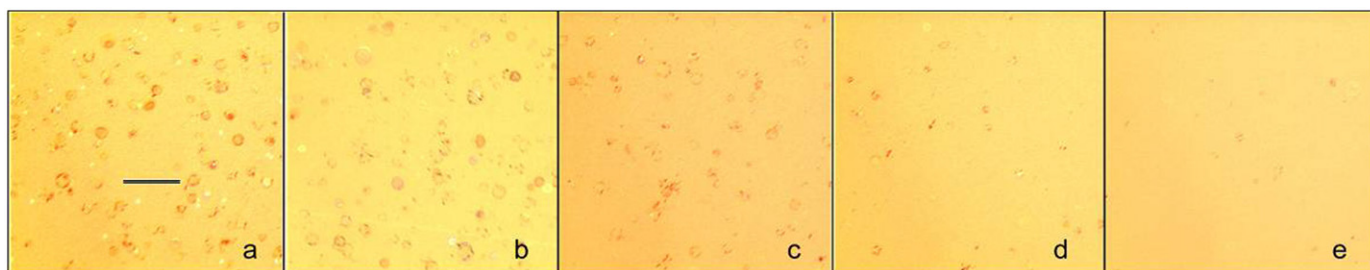


Fig. 2. Microscopic images of TiO<sub>2</sub> films fabricated using solvents at different IPA/EtOH ratios (v/v): (a) 0/10, (b) 3/7, (c) 5/5, (d) 7/3, and (e) 10/0 (substrate temperature = 260 °C). Scale bar = 50  $\mu$ m.

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