

Spray deposition of oxides at ambient atmosphere

Part 2: Compact TiO₂ layers as a model for the investigation of an alternative solid state concept for dye solar cells

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1 Introduction

Among the various applications of electronic processes at interfaces dye-sensitized solar cells are a fascinating example [1]. Photoinduced charge transfer interactions at the interface between TiO₂ and a dye-monolayer adsorbed to it are the basis of these cells. Generally porous TiO₂ layers with a high specific surface area between 50 -100 m²/g are applied in order to maximize light absorption.

However, for the exploration of new materials combinations it is advantageous to investigate compact planar model interfaces. Issues specific to porous interfaces such as materials interpenetration/pore filling can thus be neglected in initial studies. Compact TiO₂ layers of 100 – 300 nm were prepared by spray deposition of an ethanolic solution of titanium tetraisopropoxide stabilized by acetylacetone at 450°C similar to the description of Kavan [2]. Prepared under ambient conditions such layers typically contain pinholes. These can cause undesirable short circuits in the model interfaces in case of direct contact to metallic layers, such as Au. A post-treatment in aqueous TiCl₄x2THF solution leads to the removal of the pinholes as can be concluded by the appearance of the expected rectifying contact characteristics for the TiO₂/Au interface rather than the ohmic behavior observed before the post-treatment.

Thanks to the quality improvement of the TiO₂ layers by this post-treatment an alternative solid state concept for dye solar cells could be investigated, which is discussed briefly.

2 Experimental

The TiO₂ spray layers are deposited from an ethanolic solution containing 200 mM titanium tetraisopropoxide and 400 mM acetylacetone. This solution is sprayed onto 5x5 cm² SnO₂:F-coated conductive glass substrates (Pilkington, nominal sheet resistance 15 Ω/square) using a glass spray-head (Camag, Switzerland) producing a

conical stream of mist based on the Venturi principle. The spray head is situated at a distance of ~ 20 cm from the substrates, which are placed on a hot plate and preheated to 450 °C before starting the spray process. The spray deposition was performed in a cyclic manner, moving the spray head manually over an array of up to 24 substrates interrupted by 30s pauses between the spray cycles. For the removal of pinholes up to 3 post-treatments of the spray-layers in a closed petri dish containing an aqueous $\text{TiCl}_4 \times 2\text{THF}$ solution (50 mM). This was done at 70 °C in an oven followed by intense rinsing in distilled water, drying in air and resintering at 450 °C (15 minutes) on a hotplate in air.

For the measurements of electrical contact characteristics current-voltage measurements were recorded in the dark using a Keithley 2400 sourcemeter after applying 100 nm Au contacts (dots of 1 mm diameter) onto the TiO_2 layers by thermal evaporation in a vacuum chamber (10^{-7} mbar). For the visualization of pinholes the TiO_2 layers were exposed to an aqueous solution of 4 M citric acid containing Zn powder for the evolution of hydrogen.

Planar model dye solar cells were prepared by adsorbing a metalorganic Ru-dye ($\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$, where dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) to the TiO_2 layers by immersion of the layers in a 0.3 mM ethanolic solution overnight before the application of various contact materials to the dye. Procedures for the assembly of the cells and the application of the contact materials are described in detail in [3,4]

3 Results and discussion

3.1 Compact TiO_2 spray layers – pinholes and their removal

In contrast to expectation the current-voltage characteristics of devices composed of the compact TiO_2 spray layer and Au contacts applied to it by thermal evaporation are ohmic. Considering the work functions of Au (5.1 eV) and TiO_2 (4.2 eV) respectively the formation of a Schottky junction at the oxide/metal interface is expected and consequently rectifying rather than ohmic current-voltage characteristics. A plausible explanation for this observation is the presence of pinholes in the TiO_2 layers leading to ohmic shorts to the conductive $\text{SnO}_2:\text{F}$ -substrate. By electron microscopy the assumed pinholes could not be clearly evidenced. However we succeeded in visualizing them by exposure of the films to hydrogen evolved in aqueous solution (4M citric acid, leading to a selective reduction

of the SnO₂:F layer of the substrate in places where this layer was in direct contact to the solution (through the pinholes).

A high density of dark spots (metallic Sn) can be seen in optical micrographs after the reduction for films showing short-circuited current-voltage characteristics. For films post-treated in TiCl₄x2THF only a few Sn spots remain (figure 1).

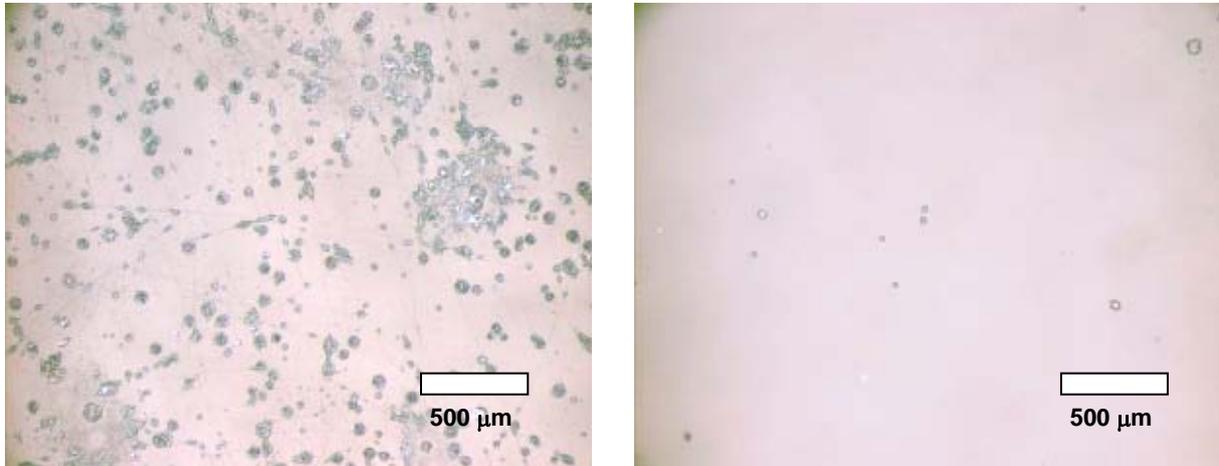


Figure 1: Visualization of pinholes in optical micrographs of TiO₂ spray layers on SnO₂:F coated glass substrates after exposure to hydrogen (left: as prepared, right: after 3 TiCl₄x2THF post-treatments - scale bar is 500 μm).

The electrical characteristics of TiO₂/Au contacts are improved substantially by the post-treatments, showing the expected rectifying behavior upon application of the treatments (see figure 2 for a sample, for which the post-treatment needed to be applied at least 2 times to remove the short-circuiting through the pinholes).

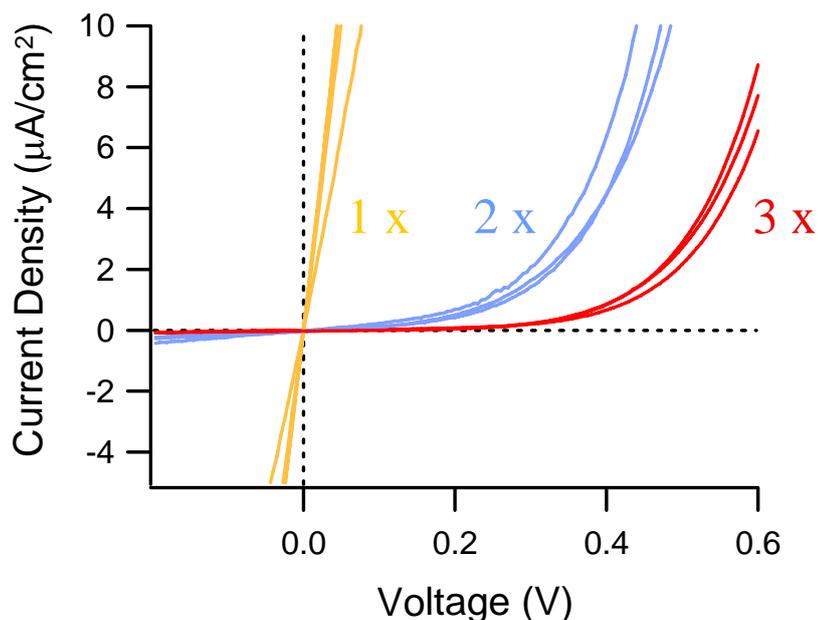


Figure 2: Change of the current-voltage characteristics of a SnO₂:F/TiO₂/Au device upon the application of up to 3 post-treatments of the TiO₂ spray layer in aqueous TiCl₄x2THF solution.

3.2 Compact TiO₂ spray layers – application for the exploration of an alternative solid state concept for dye solar cells

We explore the possibility to apply metals for one of the essential processes in dye solar cells, namely the regeneration of the charge neutral state of the dye after electron injection from the photoexcited state of the dye into the TiO₂ conduction band [5]. Typically a liquid electrolyte based on the redox couple I⁻/I₃⁻ is used for this purpose or else a transparent p-type semiconductor (like CuSCN [3]) or amorphous organic holeconductor in solid state versions of such cells. For processability and/or conversion efficiency reasons alternatives for the regeneration material are of interest.

Planar model devices using the compact TiO₂ spray layers in the general structure "glass-substrate/SnO₂:F/TiO₂/Dye-monolayer/regeneration material" are investigated, where the more typical regeneration materials (the I⁻/I₃⁻ redox couple and p-type CuSCN) are compared to a Au layer. The post-treatments of the TiO₂ spray-layers, discussed in 3.1, were a prerequisite for this investigation due to the suppression of short circuits.

We compare the devices in terms of their current-voltage characteristics under illumination (using a 480 nm cut-off filter in order to avoid bandgap excitation of the TiO₂). A very similar photocurrent response is found under these conditions for the three different systems suggesting similar overall charge separation efficiencies largely independent of the material used for dye regeneration (table 1).

	Electrolyte	CuSCN/Au	Au
I_{sc} (μA/cm²)	~ 55	~ 70	~ 65
V_{oc} (mV)	~ 655	~ 650	~ 510
FF (%)	~ 50	~ 54	~ 54

Int. = 1 sun + 490 nm cutoff-filter

From: Prog. Photovolt: Res. Appl. 2005; 13:333-340

Table 1: Characteristic photovoltaic parameters of 2D dye-sensitized model devices of the general structure glass-substrate/SnO₂:F/TiO₂/dye-monolayer/regeneration material with 3 different regeneration materials (I_{sc} = short circuit current density, V_{oc} = open circuit voltage, FF = fill factor).

For the Au this is a surprising finding considering that it offers a large density of empty electronic states into which electron injection from the excited state of the dye

could take place rather than into the TiO₂ conduction band. The observation of comparable current density suggests however, that a highly selective electron injection process into the TiO₂ is maintained even in the presence of the adjacent Au layer. We assign this to the advantageous electronic coupling between the excited state of the dye and the conduction band levels of the TiO₂ providing for the ultrafast electron injection process as described by other groups [6] and resulting in the kinetic discrimination of any other de-excitation channels.

4 Conclusion

Spray deposition of TiO₂ layers in the thickness range between 100 - 300 nm under ambient conditions leads to films which contain pinholes through which short-circuits can occur when applying Au contacts by thermal evaporation. The short-circuits can be removed by the application of a post-treatment in aqueous TiCl₄x2THF solution. Using the spray layers with improved pinhole characteristics as 2D model substrates for dye sensitized solar cells a surprising alternative concept for solid state dye cells was developed using a metallic Au layer for dye regeneration.

References

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