Optimisation of Ruthenium Dye Sensitised Solar Cells Efficiency via Sn Diffusion into the TiO₂ Mesoporous Layer

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Abstract

Dye sensitised solar cells (DSCs) typically include a mesoporous titanium dioxide (TiO₂) scaffold, sensitised with an adsorbed dye, as the main active element responsible for the photon absorption and charge separation functionalities. The sintering process employed in the TiO₂ active layer fabrication plays a crucial role in the formation of the nanoparticle (NP) scaffold and hence in the performance of a dye sensitised solar cell, as it allows the particles to form efficient inter-crystalline electric contacts providing high electron conductivity. Furthermore, the DSC design requires a conductive transparent top electrode which is typically made of fluorinated stannic oxide. Here we report on a highly spatially resolved scanning electron microscopy study in conjunction with focussed ion beam milling and energy dispersive X-ray (EDX) mapping of the distribution of all relevant elements within a DSC subsequent to a classical sintering process in the range of 350 °C–550 °C. Additionally, the article provides quantitative results regarding the found Sn diffusion and its effect on efficiency confirmed via J-V measurements. The effective spatial resolution of the EDX studies was calculated by Monte Carlo simulations of the electron trajectories and X-ray emission region. This permits to construct a model for the migration of Sn from the transparent conductive oxide into the TiO₂ scaffold, resulting in alterations in the composition of the complex system which has a direct effect on the DSC performance. J-V measurements conclude that sintering temperature of 500 °C is close to the optimum regarding Sn diffusion enhancement of DSCs. Sintering temperatures above 500 °C were causing a drop in the DSC efficiency and are therefore not recommended. In order to optimize the DSC efficiency, the results are summarized by a model that explains how the efficiency varies with the Sn diffusion process.

Introduction

Dye sensitised solar cells have been intensively researched and improved since their invention by Michael Grätzel [1] and new efficiency records exceeding 12% have been recently set [2]. The DSC origin can be dated back to the 1960s, when it was shown by Gerischer and Tributsch [3] that photoexcited dye molecules can inject electrons into the conduction band of semiconductor substrates. Further improvements included the adsorption of dye molecules on the surface of the semiconductor [4], [5] and also the use of dispersed particles [6], [7] came as another important feature in the 1980s. Although semiconductors like ZnO sensitised with dyes like cyanine [8] have been tested, titanium dioxide has become the main semiconductor [9] employed in DSCs due to its widely known advantages. Up to 1991, the DSC efficiency was below 1% and the major step was achieved in that year when O'Regan and Grätzel reported a 7.1% efficiency record [1]. This was followed by an increasing number of inorganic dyes [10-12] that have been synthesized and multiple organic dyes [13-15] with high efficiencies having also been embedded into DSCs. The electrolyte, mostly based on the iodide/triiodide redox mediator (but also recently Co-based electrolytes), has also been continuously improved to optimally match the requirements of each DSC type [2], [16], [17]. Titanium dioxide has remained the most used semiconductor for this technology and has also been continuously researched and improved over the last decade including the TiCl₄ type [2], [16], [17].

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Funding: The authors acknowledge support from Irish Research Council RS/2010/2943, Romanian American Foundation and Science Foundation Ireland 11/RFP/MTR/3113. They also acknowledge and thank Science Foundation Ireland for their funding of the Strategic Research Cluster in Solar Energy Conversion grant no. 07/SRC/B1160. The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Competing Interests: The authors have declared that no competing interests exist.

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modifying its parameters and how can the sintering be optimised to yield maximum DSC efficiency.

Ito et al. [24] have shown how the fabrication of DSCs can be optimised and identified the major parameters that need additional research. It is well known that during the sintering process the mesoporous titania layer shrinks substantially, depending on the sintering temperature and duration of sintering. A thick layer of TiO₂ (e.g. greater than 25 μm) translates into a larger effective area for the dye adsorption (and consequently results in higher light absorption), but will also increase the path length for the electrons/excitons travelling to one of the electrodes and thus will increase the recombination losses and resistivity, resulting in a lower DSC efficiency. A viable compromise is to decrease the thickness of the TiO₂ mesoporous layer (down to 10 μm or less) in order to decrease the path length for the electrons to travel. As a result, the mean electron diffusion length in a DSC, will be in the range of 10–20 μm [25], thus light can be efficiently harvested to achieve a high incident photon-to-electric current conversion efficiency (IPCE). Although decreasing the TiO₂ thickness reduces the dark current [26], it also reduces the dye adsorption active area, resulting in a reduced light absorption and consequently a reduced photocurrent, and this latter effect can be overcome by using for example more highly absorbing dyes or plasmonic enhancement [22]. However, some underlying chemical and physical mechanisms that are at the basis of the photoanode fabrication via the TiO₂ sintering process, are not yet fully understood. One of them is the TiO₂ doping process with materials that potentially increase the overall DSC efficiency. The Sn-doping has no effect on the morphology and crystal form of the TiO₂, but it influences the $V_{oc}$ and the transfer rate of electrons. According to Duan et al. [31], the optimum Sn-doping for a TiO₂ layer is 0.5% mol. In a comprehensive study on the Sn doping effects on TiO₂, Xin et al. [32] summarize some of the previous major findings of Do et al. (1994) [30], Lin et al. (1999) [27], Cao et al. (2004) [29] and conclude that doping the anatase lattice with Sn cations enhances the separation of photogenerated pairs. This enhancement is attributed to a reduction in the recombination processes due to coupling of two semiconductors (i.e. TiO₂ and SnO₂) with non-equal Fermi levels.

We have already reported that Sn diffusion occurs automatically during the sintering process when using FTO glass electrodes [33]. It is therefore of interest to investigate the potential enhancement of the DSC efficiency using the natural Sn diffusion occurring during the formation of the active layer. An important step to control this effect is the ability to correlate the sintering parameters (e.g. temperature, time) with the induced effects in the DSC efficiency. However, to the best of our knowledge, the effect of the Sn diffusion is not thoroughly investigated over a wide range (350°C – 550°C) of sintering temperatures. Thus, this paper investigates the effects of the sintering process on the SnO₂:F substrate, TiO₂ mesoporous scaffold and more importantly on the DSC efficiency in the above-mentioned temperature range. Energy dispersive X-ray spectroscopy (EDX) analysis, together with Monte Carlo simulations of the X-ray emission region, have been used in conjunction with scanning electron microscopy (SEM) imaging to spatially resolve the Sn diffusion at various sintering temperatures, and additionally, the correlation of the sintering effects to the current density-voltage (J-V) measurements has been investigated. Therefore, the focus of this study is to investigate if the Sn diffusion during the sintering process can be used in a controlled fashion to optimise the DSC efficiency, and if so, to what extent.
Materials and Methods

The study was performed in the TiO₂ sintering temperature range of 350°C – 550°C. The lower limit of the TiO₂ sintering temperature was selected above the amorphous–to–crystalline anatase titanium oxide transition temperature (350°C [34]), while the upper limit of the sintering temperature was selected below the glass transition temperature. The DSC electrodes have been prepared on aluminoborosilicate (AlBoSi) glass slides (Schott AG, n = 1.516, 2 cm×2 cm×1.1 mm) that have been coated with a 700 nm (±2%) thick SnO₂:F layer (10 Ω sq⁻¹) by spray pyrolysis.

Figure 2. SEM and FIB imaging analysis revealed the average dimensions of the TiO₂ layer and of the TiO₂ nanoparticles. a) (top) The TiO₂ nanoparticle average diameter 24 nm; b) (bottom left) FIB milling was used to remove a cuboid with dimensions of 20 µm×30 µm×20 µm; c) (bottom right) The FTO initial (pre-sintering) thickness 710 nm (averaged cross-section).

doi:10.1371/journal.pone.0063923.g002
Prior to the TiO₂ deposition process, the glass slides were subject to a sonication treatment for 30 minutes at room temperature, have been subsequently rinsed with distilled water and ethanol (Sigma-Aldrich, 99.8%), and then allowed to dry in a clean sealed container. The photoanodes have been fabricated by depositing TiO₂ (~ 2.8 µg paste for each electrode) nanoparticle paste (11% wt. nanocrystalline anatase, with ethanol, organic binders and solvents to adjust for optimum viscosity, Ti-Nanoxide D from Solaronix SA) on each FTO glass slide (TiO₂ area 1.69 cm² for each electrode) via the tape casting technique [35]. By using this technique in conjunction with a constant thickness spacer (34.65 µm used for all of the samples), high reproducibility of TiO₂ final thickness with 2% precision are achieved herein. The final thickness of the layer, after the sintering process, shrinks by a certain factor depending on sintering time and temperature [33]. By keeping the sintering time constant and recording it as a control parameter, the sintering temperature was the varied parameter of this Sn diffusion study. The experiments were made for multiple samples with a high reproducibility, as it will be described furthermore.

Subsequent to the TiO₂ paste deposition, the photoanodes have been sintered by programming a temperature controllable oven to ramp-up from room temperature to selected maximum temperatures (in the range of 350–550°C), under normal atmospheric conditions, with a heating rate of 20°C min⁻¹. The maximum sintering temperature was kept constant for 20 minutes, followed by a slow, smooth cooling process (Figure 1). The photoanodes have been subsequently post-treated with a TiCl₄ solution (50 mM, Sigma-Aldrich, 99.0%) at 60°C for 20 minutes. Then, the electrodes were thoroughly rinsed with distilled water and re-sintered at 450°C for 20 minutes, followed by the dye adsorption process. A ruthenium N749 solution (0.2 mM) was prepared in ethanol. Subsequently, a 20 mM chenodeoxycholic acid (3α,7α-Dihydroxy-5β-cholanic acid) solution in ethanol has been added as a co-adsorbent. The TiO₂ electrodes were immersed at an initial temperature of 60°C in the ruthenium N749 dye solution for 24 hours (in a sealed environment and in darkness, and permitted to cool down to room temperature), then thoroughly rinsed with absolute alcohol (Fluka, 99.8%) and then finally assembled. The counter electrodes have been fabricated by using identical FTO coated AlBoSi glass slides as described above. A thin layer of hexachloroplatinic acid (5 mM H₂PtCl₆ in isopropanol) was deposited on the FTO, followed by a 15 minutes sintering process at 450°C with an average ramp-up rate of 20°C min⁻¹. The electrolyte was made of iodide/triiodide (50 mM) redox couple, with pyridine additive and with propionitrile as solvent.

A state of the art FEI Quanta 3D® dual beam scanning electron microscope equipped with a highly spatially resolving electron field emission gun, a highly spatially resolving Gallium ion gun and an EDAX Trident XM4 detector, was employed for imaging and depth profiling of the TiO₂ structures, providing a high spatial resolution in imaging mode of down to 1.5 nm.

**Results and Discussion**

The photoanode sintering temperature was recorded as a function of time in the chosen temperature range (350°C –550°C) as a first control parameter (Figure 1). The measurements started from room temperature, up to a maximum temperature that was
Figure 4. The TiO₂ thickness as a function of the sintering temperature for constant maximum sintering temperature times of 20 minutes.
doi:10.1371/journal.pone.0063923.g004

Figure 5. The FTO thickness as a function of the sintering temperature, showing a decrease between 350°C –550°C.
doi:10.1371/journal.pone.0063923.g005
kept constant for 20 minutes. The slow, smooth cooling process required to prevent the cracking of the electrode, was maintained over a long enough period of time (approx. 2 hours), for each sample from the maximum temperature down to 60°C before removing the photoanode from the oven.

The typical TiO2 NP size distribution with an average diameter of 24 nm for the TiO2 nanoparticles is exemplified in Figure 2a using FIB imaging. By analysing all of the samples with the FIB imaging technique, it was concluded that the TiO2 mesoporous layer surface was reasonably homogeneous and therefore the tape casting technique remained the preferred deposition technique. In order to evaluate the absolute thicknesses of the TiO2 scaffold and of the FTO layer, technique focused ion beam (Ga) was used to remove a cuboid with dimensions of 20 \( \mu \text{m} \times 30 \mu \text{m} \times 20 \mu \text{m} \) (Figure 2b). The FIB milling provides access to the buried layer structure and allows precise thickness measurements of the TiO2, FTO layers to be recorded. The FTO thickness from the images shown in Figure 3, is analysed in Figure 5 as a function of the sintering temperature. It is concluded that the FTO thickness decreases with increasing sintering temperature for the selected sintering duration and in the studied range of 350°C – 550°C.

While the decrease in the measured thickness for the mesoporous TiO2 layer can be attributed to the necking process which reduces the average spacing between the NPs, the decrease in the FTO cross-section can be attributed to the FTO diffusion. Unsurprisingly, the FTO is diffusing with higher rates when sintered at higher temperatures. To confirm and quantify the diffusion effect in the above-mentioned temperature range, EDX spatial mapping was employed for samples sintered at 350°C, 400°C, 450°C, 500°C and 550°C. The setup geometry is shown in Figure 6 with the EDX detector and the FIB gun oriented at 52° from the SEM electron gun (and normal to the sample) and consequently with the sample tilted accordingly at 52° with respect to the electron beam. In the EDX analysis, the electron beam was kept at 10 keV for all the samples to achieve an electron volume interaction depth (violet plume in Figure 6a) below the micrometer range (i.e. to gather signals from the TiO2, SnO2 down to the glass). Multiple scattering Monte Carlo simulations of the electron trajectories and the X-ray emission region have been carried out in Casino v2 [36], to determine the spatial extent of the 3-D X-ray emission region from which the EDX detector has received its spectral information. Based on these simulations, experimental EDX data as shown in Figure 7 was collected for multiple samples sintered in the studied range of 350°C – 550°C, using the 10 keV acceleration voltage. Figure 8a shows the electron trajectories, for 200,000 simulated electrons incoming with an acceleration voltage of 10 keV, an incident beam radius of 4 nm at 30° with respect to the photoanode surface. The extent of the electron plume and the X-ray emission region, simulated in Figure 8b, was measured to be within 150 nm for a minimum remaining electron energy of 3.443 keV (which corresponds to the energy of the Sn principal emission line, L\(\alpha\)).

For the spatial diffusion studies, the TiO2 active layer was not subject to any TiCl4 treatments or ruthenium dye adsorption before the shown EDX mapping. By using EDX we were able to achieve a sufficiently high spatial resolution analysis of the solar cell layers as shown in Figure 6b. It is important to note that from the Monte Carlo simulations shown in Figure 8b, it can be concluded that the spatial broadening of the EDX mapping is
approx. 150 nm, which is smaller by an order of magnitude than the experimentally identified total Sn diffusion that was measured to be at 2 μm and this offers enough resolution. Furthermore, EDX measurements performed for samples sintered at higher temperatures and thus higher TiO₂ densities due to the shrinking effect, show an increased Sn diffusion into the TiO₂, compared to lower sintering temperatures, which is an effect that cannot be explained by the spatial broadening of the EDX mapping (i.e. it is clearly not an artefact). The EDX analysis for photoanodes sintered at 350°C (Figure 7a) confirmed that the Sn (FTO - red area) diffusion into the TiO₂ starts already at comparably low temperatures. When investigating samples sintered at 400°C – 550°C (Figure 7b-e), EDX confirmed that the diffusion levels were consequentially increased proportional to the temperature. From 500°C on (Figure 7d), EDX mapping demonstrates a pronounced spatial extent of diffusion that was easily spatially resolved and quantified. Finally, when investigating samples sintered at 550°C (Figure 7c) the Sn diffusion levels were found to extend about 2 μm into the TiO₂ mesoporous scaffold. The spatially resolved EDX analysis with the superimposed FIB imaging signals (Figure 9) are confirming the Sn diffusion results presented above, and come as reinforcement to the FTO diffusion enhancement with increasing temperatures as measured in the SEM-FIB analysis. From this it can be concluded that when increasing the sintering temperature from 350°C to 550°C, the FTO thickness decreases as a result to an increase in the Sn diffusion rate. The quantified effect of the above EDX analysis on the Sn diffusion for multiple samples is plotted in Figure 10. The major finding is that with the sintering temperature increase from 350°C to 550°C, the measured Sn level (in the FIB removed cuboid) increases from 8 wt% to 13.71 wt%, while the Ti percentage decreases accordingly from 55.14 wt% to 45.8 wt%. This indicates that with the sintering temperature increasing from 350°C to 550°C, the Sn is also increasingly diffusing onto the surface of the TiO₂ layer within the removed cuboid, therefore the detected Sn signal increases, while the Ti signal decreases. The Al

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**Figure 7.** The EDX analysis on the Sn diffusion for samples sintered at: a) 350°C; b) 400°C; c) 450°C; d) 500°C; e) 550°C. doi:10.1371/journal.pone.0063923.g007

**Figure 8.** Simulations of a) electrons trajectories and b) X-Ray emission region in the EDX analysis. Incident electron plume determined to be approx. 150 nm for an accelerating voltage of 10 keV that was used experimentally. doi:10.1371/journal.pone.0063923.g008
and Si percentages (coming from the glass) remain constant at 4.1 wt% and 15 wt% respectively as shown in the EDX analysis (Figure 10), which again reinforces the fact that the Sn diffusion is not an artefact of the EDX.

The next step of the analysis was to assemble the above photoanodes sintered at temperatures of 350°C – 550°C into DSCs and to measure their efficiency. However, before assembling the DSCs, each FTO layer was tested regarding their behaviour to these sintering temperatures. The FTO conductivity was of particular importance in order to confirm that potential changes in the DSC efficiencies are not due to a change in FTO’s conductivity. The conductivity was measured for each sample, before and after sintering at temperatures up to 550°C, with a high accuracy Keithley 6514 electrometer. To determine the conductivity of the FTO, the resistance of the conductive layer was measured as the control parameter by attaching the electrometer probes to the extremities of each FTO glass slide (dimensions of 2 x 2 cm²). The high quality of the FTO slides was confirmed by measuring an initial average resistance of 23.1 Ω (±0.2%) for all the samples prior to sintering. The same measurements during the sintering also showed that the conductivity is significantly higher than the pre-sintering values, but it returns to the initial values during the cooling of the samples. Subsequent to sintering at temperatures of maximum 550°C, it was confirmed that the resistance remained constant on average at 23.1 Ω, with a difference of ±0.04–0.09% for each sample before and after the sintering. Since the resistance was constant, it was concluded that the conductivity of the FTO layer remained constant before and after sintering up to temperatures of 550°C. In order to get more results for supplemental temperatures, we have introduced in our efficiency analyses additional DSC photoanodes which have been sintered at temperatures of 425°C, 475°C and 525°C, respectively.

Photocurrent and voltage measurements under simulated 1 sun AM 1.5 irradiance conditions were quantitatively recorded with a Keithley 6514 electrometer. As can be seen from Figure 11, increasing the sintering temperature from 350°C to 500°C results in a significant increase of 273% in current density (J). Higher temperatures resulted in a decrease in current density. Regarding the voltage, increasing the sintering temperature from 350°C to 450°C improves the voltage by 129% – higher temperatures are detrimental to the DSC potential. Higher temperatures than 500°C lead to reduced current density and reduced voltage of the here prepared DSCs. The full results are shown in Table 1 that
additionally includes the changes in the fill factor and in the overall DSC efficiency.

As reported in literature, high sintering temperatures cause an excellent removal of organic binders and solvents from within the TiO₂ scaffold and improve the necking between the NPs [37]. Increasing the TiO₂ sintering temperature from 350°C to 450°C, causes shrinking of the TiO₂ thickness (Figure 4) translating into a reduced surface area but also resulting in a reduced number of charge-recombination sites, therefore the voltage increases. Furthermore, the increase in voltage can also be attributed to a negative shift (e.g. towards the dye LUMO level) in the flat band potential of the TiO₂ semiconductor. This negative shift that causes the Voc increase is attributed in our model to increasing Sn doping levels within the TiO₂ film. However, when increasing the temperature above the found optimal point of 500°C and even though the above mentioned mechanisms (Sn doping, TiO₂ layer shrinking etc.) continue to be produced as demonstrated above, the high sintering temperatures start to deteriorate the optimum interface conditions.

Regarding the Sn diffusion effects on the JSC, as the temperature is increased from 350°C to 500°C, the NP necking improves and the TiO₂ thickness decreases (Figure 4), therefore the electrons will require a shorter diffusion length to reach the electrode, which results in the measured JSC increase. However, although the temperature increase from 500°C to 525°C, and furthermore to 550°C, will cause a further shrinkage in the TiO₂ thickness (Figure 4), the FTO diffusion process recorded here (Figure 10) will cause a drop in DSC efficiency for temperatures higher than 500°C (Figure 11). Finally, Figure 12 shows an overview of the measured DSC efficiencies for each particular sintering temperature based on the data presented in Table 1. The errors bars in Figure 12 represent the accuracy for the sintering temperature (±2°C) and for the efficiency measurements (±8%).

The here presented results confirm that in order to achieve a maximum DSC efficiency, effects produced by high levels of Sn doping into the TiO₂ layer have to be taken into account and correlated with its side-effects on the Voc and JSC.

**Conclusions**

This study shows the effects of the sintering process between 350°C and 550°C on the FTO’s Sn migration into the TiO₂ active layer using spatially resolved EDX analysis and FIB imaging. The FTO diffusion was proven not to negatively alter the Voc for temperatures up to 450°C and the JSC for temperatures below 500°C. Additionally we find for the here constructed solar cells, as described in the experimental section, that DSC efficiencies reach their maximum value at approximately a maximum sintering temperature of 500°C. However, the above mentioned mechanisms (Sn doping, TiO₂ layer shrinking etc.) continue to be produced as demonstrated above, the high sintering temperatures start to deteriorate the optimum interface conditions.

**Table 1.** DSC efficiencies recorded for various FTO doping levels achieved by modifying the sintering temperature from 350°C-550°C.

| T (°C) | JSC (mA cm⁻²) | Voc (mV) | FF | η (%) |
|-------|----------------|----------|----|------|
| 350   | 4.37           | 500      | 0.62 | 1.35 |
| 400   | 5              | 510      | 0.59 | 1.51 |
| 425   | 6.79           | 517      | 0.54 | 1.89 |
| 450   | 8              | 647      | 0.63 | 3.26 |
| 475   | 9.85           | 609      | 0.65 | 3.89 |
| 500   | 11.94          | 583      | 0.62 | 4.31 |
| 525   | 8.8            | 538      | 0.56 | 2.65 |
| 550   | 7.66           | 530      | 0.57 | 2.31 |

![Figure 10. The EDX analysis (recorded for the areas in Figure 7 for each temperature) quantifying the Sn diffusion increase when increasing the sintering temperature from 350°C to 550°C.](doi:10.1371/journal.pone.0063923.g010)
temperature of 500°C. As shown by J-V measurements, it can be concluded that sintering temperatures above this value are not recommended, as the DSC efficiency was measured here to decrease and the Sn diffusion rate increases furthermore. Future studies will look into the effects of prolonged sintering times for each temperature (in the range of 350°C – 550°C) and the resulting potential DSC efficiency optimisation.
Author Contributions
Conceived and designed the experiments: CA. Analyzed the data: CA DZ. Contributed reagents/materials/analysis tools: CA DZ. Wrote the paper: CA.

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