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Surface Cleaning and Modification by High Intense UV-Irradition for TiO_2 Nanoparticle Films in Dye Sensitized Solar Cells

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Abstract. The preparation of the front electrodes in high efficient dye sensitized solar cells usually need high process temperatures to remove dispersal additives and to enable sintering effects. This leads to a reduction of the serial resistance caused by potential barriers inside the nano particulate TiO_2-layer, and to a better dye adherence. Nevertheless this temperature treatment is not applicable on ITO-covered foils used for flexible devices, but this limitation can be partly compensated by an intensive UV-exposure. Furthermore it is possible to increase the efficiency of a sintered DSSC applying an additional UV-irradiation by about 26 %.

Key words

dye sensitized solar cell, surface cleaning, surface modification, UV-irradiation, flexible solar cell.

1. Introduction

Silicon is one of the best known materials for solar cell integration. Therefore and because of the good efficiencies silicon solar cells are the most common cells for private and industrial usage. Due to the high production costs of these cells researchers try to find low cost alternatives. A promising device is the dye sensitized solar cells (DSSC), first developed by O´Regan and M. Grätzel [1]. Here, with the help of high efficient synthetic dyes and a platinum catalyst efficiencies of up to 13 % are achieved under laboratory conditions [2]. Unfortunately these materials are expensive, and such high efficiencies are only achievable in very small devices. It was shown that an increase of the area from 0.25 cm² up to 2 cm² leads to a power loss of 65 % [3]. Otherwise a decrease of the active area from 0.28 cm² to 0.07 cm² leads to an increase of ~56 % [4].

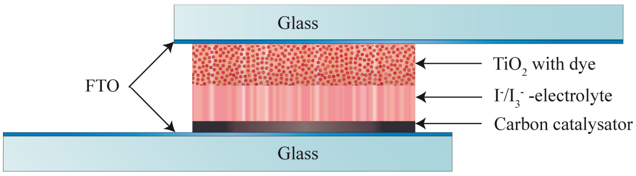

Fig. 1: Schematic of a DSSC

To enable sintering effects and to remove dispersal additives out of the nano particulate TiO_2-layer usually a temperature treatment of around 450 °C is used. After this process step nearly all organic solvents are evaporated and the bindings between the particles and onto the transparent conductive oxide (TCO)-layer are at their best giving a decreases in the serial resistance [5][6]. Nevertheless such high temperatures are not applicable for flexible substrates like foils.

For surface cleaning UV-irradiation is a well-known process [7]. This paper presents an alternative roll-to-roll capable process step for flexible low cost solar cells which facilitates an effective cleaning process of the TiO_2-layer by high intense UV-irradiation instead of high temperature treatments. Furthermore the surface modification after a sintering process is illustrated, and its capability for synthetic dyes is tested.

2. Device Integration

Typical glasses with a transparent conductive oxide

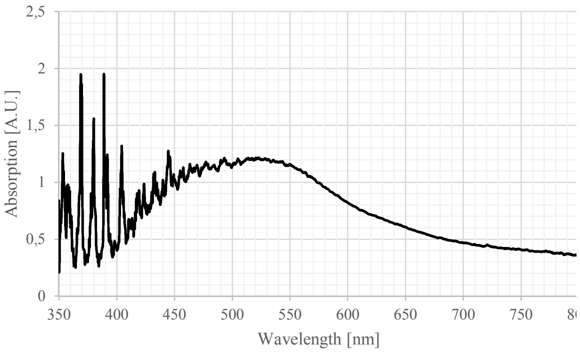

Fig. 2: Absorption spectrum of hibiscus dye on a TiO_2-layer

(TCO) layer of Indium-Tin-Oxide (ITO) or Fluor-Tin-Oxide (FTO) are used as electrodes in DSSC. These TCO layers have to possess a high transparency and conductivity because of the direct influence on the quantum efficiency and serial resistance of the device. Typical sheet resistances of about 20 Ohm/square require small devices to achieve high efficiencies.

Upon the front electrode a TiO_2 layer is deposited using a dispersion with several additives for preventing agglomeration of the nanoparticles and to decrease the surface tension for a better uniformity and adhesion on the TCO layer. Afterwards these additives have to be removed, and the bindings between the single particles have to be increased. Usually this is done by a sintering process at 450 °C at atmospheric condition.

The TiO_2–particles have to be sensitized to the visible light spectrum. Hence, synthetic dyes like N3 or N719 basing on Ruthenium-complexes with wide absorbance spectra have to be applied to achieve high performances.

Thin platinum layers on TCO coated glasses are used as a counter electrode for high efficiency DSSC. The used platinum catalyst leads to a reduction of the charge transfer resistance into the mainly used Iodide-/Triiodide electrolyte; it has a high influence on the serial resistance of the solar cell, too.

To reduce the costs of DSSCs alternatives for the synthetic dyes, TCO-coated glasses and platinum catalysts have to be used. In this paper the synthetic dye has been replaced by an organic hibiscus dye. It shows adequate absorbance in the visible spectrum, but it is still not comparable to a synthetic dye which shows a much higher quantum efficiency. The absorption spectrum of the hibiscus dye can be seen in figure 2. The peaks between 350 nm and 415 nm are interferences caused by the TiO_2 nanoparticles. A carbon layer is often used for low cost DSSCs, it replaces the platinum catalyst for further cost reduction. The TiO_2-layer was built by a dip coating process using a dispersion based on Triton X-100, acetylacetone and polyethylene glycol. After drying under atmospheric conditions and structuring a DSSC with an active area of 4 cm² and a thickness of about 7 µm is integrated. The electrolyte bases on an Iodide-/Triiodide redox couple. FTO-coated glasses are used as front and back electrodes.

The high intense UV-irradiation is performed by a 3000 W Xe Arc lamp. The substrates are placed in a distance of 20 cm for pulsed and permanent irradiation. As shown in [8] pulsed irradiation is necessary when foil substrates are used. To prevent foils from excessive heat a shutter was installed directly above the substrate and controlled by a stored program control (SPC).

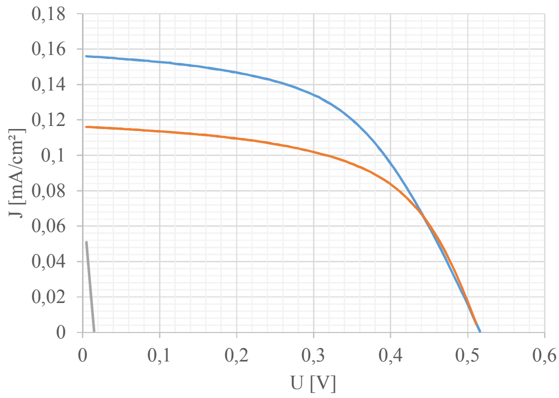

Fig. 3: J-V-characteristics of DSSC with no (grey), pulsed (orange) and permanent (blue) UV-irradiation

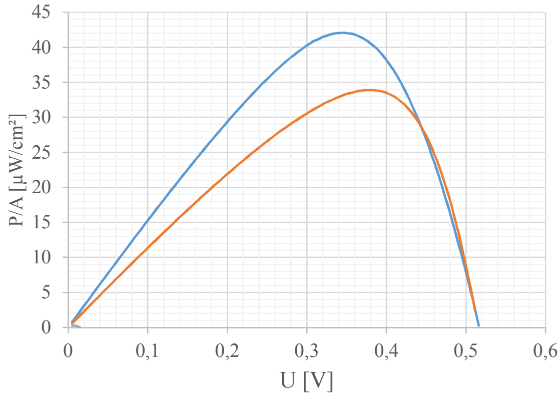

Fig. 4: Comparison of the electrical output power between no (grey), pulsed (orange) and permanent (blue)UV-irradiated DSSC

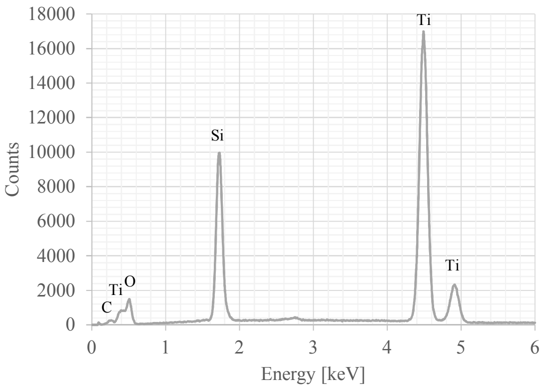

Fig. 5: EDX analyze of an TiO_2-layer on an silicon substrate before UV-irradiation

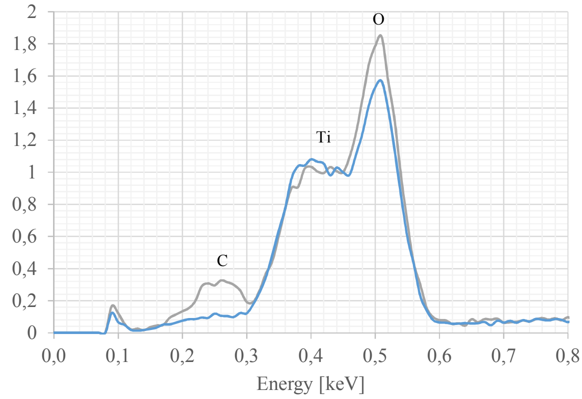

Fig. 6: Comparison of the EDX analyze of the TiO_2-layer before (grey) and after (blue) a 90 min UV-irradiation. The values are normalized on the titan peak

3. Results and Diskussion

To analyze the performance of the fabricated solar cells the I-V- and P/A-V-measurements were performed under AM1,5 conditions using the semiconductor parameter analyzer HP 4145B. Before the TiO2-layers are sensitized with the hibiscus dye the devices were irradiated with the UV-light. Figure 3 and 4 show the J-V- respectively P/A-V-characteristics when pulsed or permanent irradiation is used.

As shown in figures 3 and 4 DSSC with no treatment after the TiO_2-deposition show nearly no electrical performance. With increasing irradiation time the electrical output power rises. A maximum is reached at a permanent irradiation time of 90 min. A further increase of the irradiation time does not result in any increasing efficiency so that the effect is saturated after 90 min. The resulting power amounts to 42 µW/cm² which equals an efficiency of 0.042 % with a fill factor of 0.52.

As mentioned before such a long permanent irradiation time is not applicable for flexible devices. Thus a pulsed UV-irradiation with an irradiation time of 30 seconds followed by a cooling period of 30 seconds was executed. To enable a comparison with the 90 min permanent irradiation the number of pulses was defined to be 180 so that the same total irradiation time was achieved. The resulting J-V-characteristics illustrated in figure 3 show again that there is an effect on the TiO_2-layer although the maximum power with a value of 33.87 µW/cm² is ~20 % lower than that of the layer with permanent irradiation. So the occurring effect does not seem to be able to influence the whole layer.

A comparison between a DSSC irradiated for 240 times, which is not pictured here, with this cell shows that a raise of the pulse number just leads to a lower raise of the efficiency. So it does not seem to be reasonable to increase the number of pulses anymore.

The fact that there is nearly no electrical performance without irradiation can be explained by the remaining additives of the dispersion. The additives are still encapsulating the TiO_2-nanoparticles, and an injection of electrons from the LUMO (Lowest Unoccupied Molecular Orbital) into the conduction band of the TiO_2 is blocked as well as the charge carrier transport between the single particles themselves. The UV-irradiation removes the remaining $C_xO_yH_z$ molecules, and the electrical power rises. This effect is at its maximum after about 90 min of permanent irradiation time.

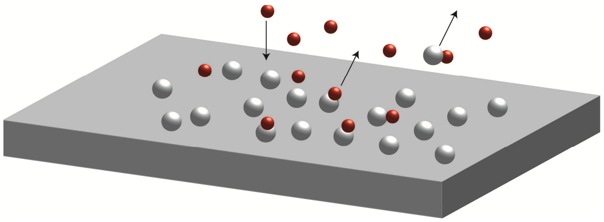

Fig. 7: Cleaning process with radicals. Oxidized molecules desorb from the surface

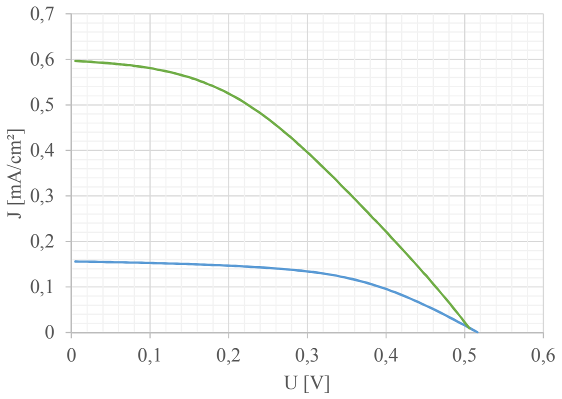

Fig. 8: After a sintering step (green) the short circuit current increases compared to 90 min UV-irradiation (blue)

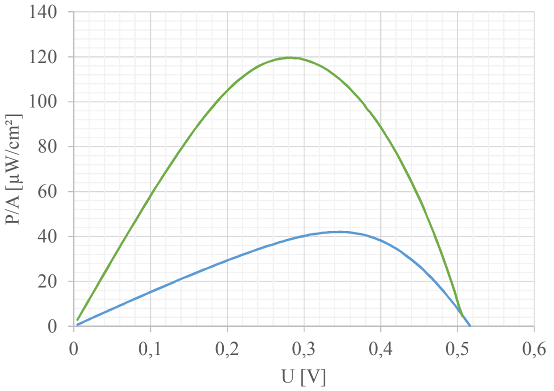

Fig. 9: Thermal treatment (green) enables the sintering effect and leads to better performances compared to 90 min UV-irradiation (blue)

Figure 5 depicts the result of an energy dispersive X-ray spectroscopy (EDX)-analysis of a TiO_2-layer prepared on a silicon substrate. In this case no temperature treatment or UV-irradiation took place before the measurement. As it can be seen in the figure, parts of the silicon substrate, titanium and oxygen are found in the TiO_2-layer as well as in the additives. Additional there is a peak in the range of 0.277 keV which is typical for carbon. It only occurs in the additives. When the additives are removed out of the TiO_2-layer this carbon peak should disappear. Figure 6 compares the results of the EDX-analyzes before and after a 90 min UV-irradiation. To present the carbon peak more in detail it focusses only on the lower energy region up to 0.8 keV. Additionally to simplify a comparison the results are normalized on the appearing titanium peak, because the value of titanium atoms should not change before and after the treatment. One can see that there is no carbon peak left after a permanent UV-irradiation of 90 min. This indicates a cleaning effect of the UV-irradiation. Furthermore the amount of appearing oxygen is decreased. This is another indicator for the potential of the cleaning process.

The occurring cleaning effects are based on two processes. First is the cleaning by the UV-irradiation itself. Here similar to a treatment with O_2-plasma the

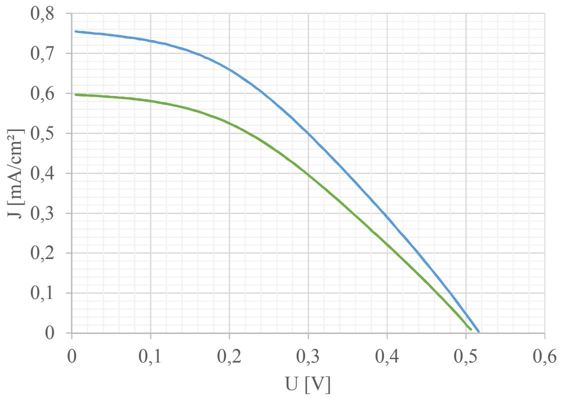

Fig. 10: The short circuit current is increased again by an additional UV-irradiation (blue) compared to only sintered DSSCs (green) while the fill factor is not influenced.

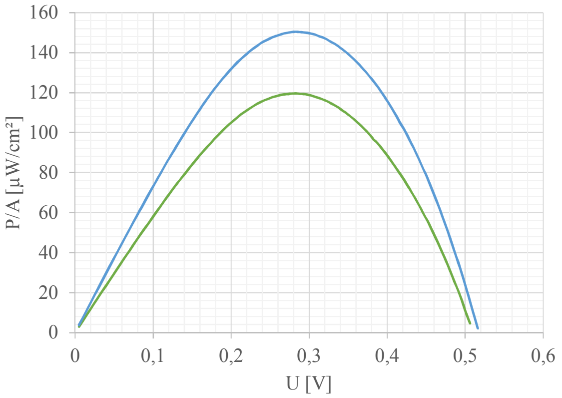

Fig. 11: Additional UV-irradiation after the sintering (blue) leads to a power gain of 25.8 %

cleaning is performed by highly reactive radicals [9]. In the case of an O_2-plasma the radicals are build when the gas is dissociated. In the case of UV-irradiation two different wavelengths are needed. First, with a wavelength of 185 nm, ozone is build. Afterwards, this ozone is dissociated with a wavelength of 245 nm into highly reactive radicals which oxidize organic materials. An optical test with a dispersion without nanoparticles placed on a FTO-coated foil showed that after 20 min permanent irradiation no dispersion is left.

The second cleaning process is performed by the TiO_2 itself. TiO_2 has a bandgap of 3.2 eV, which corresponds to a wavelength of ~387 nm. Here, UV-irradiated electrons can be lifted from the valence band into the conduction band of the TiO_2. These free electrons are able to perform a photodegredation of organic compounds, and they build for example alkane which desorb from the surface [10].

These two cleaning processes lead to the extinction of the carbon compounds out of the TiO_2-layer as seen in the EDX-analysis and enable the function of the DSSC.

As mentioned before the high temperature treatment has the additional positive effect of enabling a sintering effect between the TiO_2-particles. Because of the better binding between the single particles and the TCO-surface the charge transfer and according to that the serial resistance are improved. To compare the occurring effects a DSSC was fabricated where the TiO_2-layer was sintered for 1 hour at a temperature of 450 °C under atmospheric conditions. The resulting J-V- and P/A-V-characteristics are compared in figures 8 and 9 with the 90 min permanent UV-irradiation. Obviously the electrical efficiency is much higher when the sintering effect is enabled by the high temperature. Here, the maximum power output of PMPP=119.6 µW is 2.8 times higher compared to cells with only UV-irradiation. But also the fill factor has decreased. The influence of the charge transfer resistance of the catalyst in combination with the electrolyte and size of the cell seems to increase. This reduces the quality when higher currents are applied. It leads to a reduction of the fill factor to FF=0.396. In another experiment for example a fill factor of 0.53 was achieved simply by changing the catalyst to platinum. Nevertheless the difference between the short circuit currents shown in figure 8 is significant.

Thus the sintering effect and therefore the better interparticular bindings cannot be achieved with the high power UV-irradiation. It leads to larger losses caused by the high serial resistance of the TiO_2-layer. Nevertheless the UV-irradiation represents an alternative process step for substrates with limited thermal stability.

Additional to the cleaning effect of the UV-irradiation the surface gets modified. The activation of the surface leads

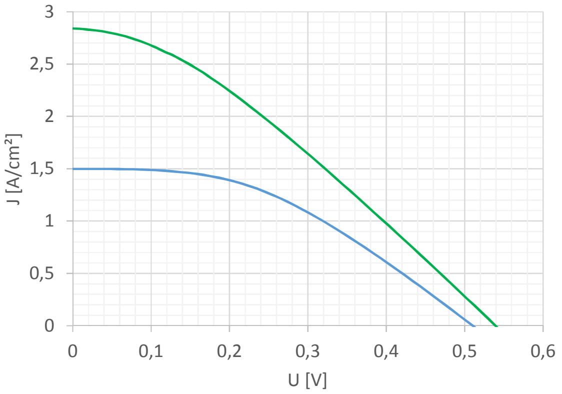

Fig. 12: An UV-irradiation (blue) in combination with N3-dye leads to a power loss of ~48 % compared to non-irradiated DSSC (green).

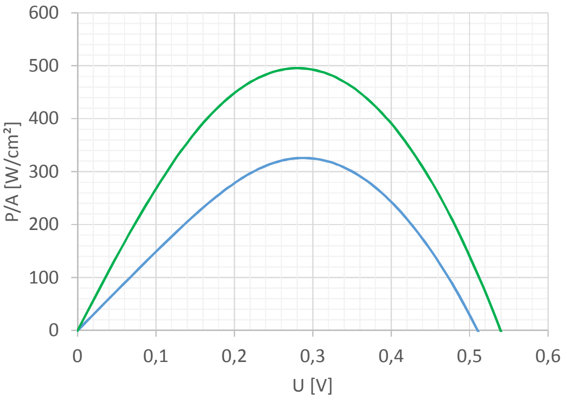

Fig. 13: Power of sintered (green) and after the sintering UV-irradiated (blue) DSSC.

to a better adhesion of the dye. To illustrate this effect a DSSC was fabricated with a sintered TiO_2-layer. Additional to the standard process the TiO_2-layer was UV-irradiated for 90 min and sensitized with the hibiscus dye afterwards.

A comparison of the J-V-characteristics demonstrated in figure 10 shows that the short circuit current is increased again. As the gradients of the curves are nearly equal the fill factor stays almost the same with FF=0,386. This indicates that the internal resistances are not influenced and the higher electrical power seems to base on an increased quantum efficiency caused by a better contact between the dye and the TiO_2. A similar effect can be seen by activating the surface with the help of an O_2-plasma treatment which is not capable for foil substrates. In this case radicals out of the plasma lead to a cleaning and activation of the surface. Such radicals can be created by an UV-irradiation as well. These radicals are able to clean the surface as mentioned before and make it hydrophilic by formed OH-groups. Organic dyes like hibiscus dye base on anthocyanin. The binding on the surface of such anthocyanins is performed by OH-groups [11]. Therefore the UV-irradiation leads to better adhesion effects and to higher quantum efficiencies. So, with the help of an additional UV-irradiation supporting the standard high temperature treatment the power could be increased up to 150.4 $\mu W/cm^2$ which equals a gain of 25.8 %.

Nevertheless, this surface activation effect is not capable for synthetic sensitizers like the N3-dye. The binding is performed about carboxylate linkage which is highly sensitive towards humidity [12], [13]. Usually the prepared TiO_2-layer has to be immersed in the dye-solution directly after sintering before it is cooled down. Additional chenodesoxycholic acid in the dye solution makes the surface more hydrophobic and increases the adherence. So, the hydrophilic surface after the UV-irradiation has a contra-productive effect, and a temperature step has to be performed before the immersing.

The effect of an UV-irradiation using N3-dye can be seen in the figures 12 and 13. For these measurements FTO-coated glases with a 200 nm palladium layer prepared by PVD was used as a counter electrode. Obviously the bad dye adherence of irradiated samples has a big influence on the short circuit current. Here we can see a loss of ~48 % compared to non-irradiated cells. In the case of the output power the effect is with a loss of ~34 % comparative low but still very high. Because of the good cleaning effects an additional step before the immersing in the N3-dye has to be performed. A heat treatment with a temperature of 150 °C for one hour should be able to remove the hydrogen from the surface and the substrates should be drowned in the dye-solution immediately.

4. Further Information

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5. Conclusion

The remaining additives in the TiO_2-layer of a DSSC can be removed without high temperature treatment. A 90 min permanent UV-irradiation is a highly effective cleaning step, and nearly no carbon compounds remain in the TiO_2. Such a long irradiation time is not applicable for flexible foil substrates. A comparison between the pulsed and permanent irradiation with the same application of energy leads to the assumption that additives remain in the deeper layers when a pulse time of 30 seconds is used. These remaining additives lead to a power loss of ~20 %. To further optimize this process step the pulse-time will be increased and the pulse-pause-ratio will be modified in further researches.

Furthermore the surface of the TiO_2 can be modified with an additional UV-irradiation step after the 450 °C sintering. This step leads to a better organic dye adhesion, and according to that to a better quantum efficiency and a higher short circuit current. The occurring effect is caused by OH-groups on the surface of the TiO_2-layer which make it more hydrophilic. Therefore, this step isn´t capable for hydrophobic synthetic dyes like the N3. Although the surface modification is not capable the cleaning of the TiO_2-layer by UV-irradiation is still a good alternative when temperature sensitive substrates are used. Thus, when synthetic dyes should be used an additional heat treatment has to be applied to remove the hydrogen from the surface.

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