Dye-sensitized TiO_2 solar cells based on TiO_2 nanotube layers

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1. Introduction

The aim of the project has been to investigate more in detail the potential application of TiO_2 nanotubes in the dye-sensitized solar cells.

The fabrication of the unconventional solar cell has gained a lot of attention since the first report of the dye-sensitized TiO_2 nanoparticles[1]. Later these unconventional solar cells have been named Grätzel type of cells[2-4]. To the best of our knowledge an efficiency of 11% has been achieved on these kind of cells[5]. Many attempts to understand in detail how the cells work and to find the right parameters for improving their efficiency have been done[6]. Methods involving Intensity Modulated Photocurrent Spectroscopy (IMPS) or Intensity Modulated Photo-Voltage Spectroscopy (IMVS) proved to give a detailed view on the kinetics and dynamics taking place in a Photo-Electrochemical cell[7]. Further, these methods where applied to the dye-sensitized solar cells[8-12]. More than this, successful attempts for modeling the dye-sensitized solar cell that makes possible the prediction of the efficiency depending on their fabrication parameters have been carried out[13].

One of the key factors that make the TiO_2 dye-sensitized solar cells so efficient is the extremely high surface of the nanoparticulate film. An alternative method to provide a structure made of titanium dioxide with a high surface area has been proposed by Zwilling et al. when an organized nanotubular structure was obtained by a simple electrochemical method (i.e. anodization of metallic Ti in F-containing electrolyte)[14]. Recently, our group has been carried out a lot of work on the investigation of the nanotubes growth. Changing the electrochemical parameters such as applied potential, pH of the electrolyte, anodization time or viscosity of the electrolyte made possible tuning of the nanotubes' diameter, wall thickness and their length[15-19]. The aspect ratio of so produced nanotubes reached an

aspect ratio of over 1000. It was successful proofed that the TiO_2 nanotubes are a very interesting nanostructure in application such as electrochromic[20], catalytic[21], biomedical[22] and photocatalytic[23,24] devices. Further, we think that a structure with a remarkably increased surface area combined with a high organization order of the nanotubes would make possible a successful application also into TiO_2 dye sensitized solar cells. A good understanding of the dye-sensitized solar cells based on nanotubes will involve a detailed study of the kinetics and dynamics, which will make possible finding of the optimum parameters (tube diameter, length and thickness of the wall) for a high efficiency. It will be also interesting to find out whether the one dimensional structure, i.e. nanotubes, has any difference in the kinetics and dynamics to the well known case of nanoparticles.

2. The aim of the visit

TiO_2 nanotubes with different thicknesses will be prepared at the Erlangen lab and after a dye-sensitization process solar cells will be constructed. Afterwards, in Prof. Peter's laboratory the characterization of the cells will be carried out using time-resolved photo-current and photo-voltage measurements.

3. Experimental and Results

I. Work carried out at University of Erlangen, Department of Corrosion and Surface Analysis:

For the realization of the above described goals, 8 samples - TiO_2 nanotubes, were fabricated on Ti metal substrate by anodization in Ethylene Glycol electrolyte containing 0.2M HF at 120 V. The experimental procedure is described elsewhere[19]. It was the aim of this work to investigate the effect of the nanotubes length on the efficiency of the dye-sensitized solar cells, therefore 4 different thicknesses of the nanotubular layer, which are: 1µm, 3µm, 10µm and 20µm where produced. The adjustment of the length was possible by variation of the anodization time. The Scanning Electron Microscopy (SEM) micrographs are presented in Fig. 1. On the left side the top view of the nanotubes is shown. On the right side the corresponding cross-section. In the high magnification SEM image a typical morphology of the tubes is shown for a closer view on their aspect and order of organization.

The "as formed" nanotubes are usually amorphous, well seen from the X-Ray Diffraction Spectroscopy (XRD) investigation. Annealing at 450^0 C for 1h, in air, transforms them to a polycrystalline anatase structure with (101) preferential crystallographic orientation. The results are presented in Fig. 2 (left).

Taking in account that many chemical processes are involved in the functioning of the dye-sensitized solar cells it will be very useful to know the chemistry of the nanotubes before using them as the active material. X-Ray Photoelectron spectroscopy (XPS) characterization has been carried out in order to make clear the chemistry of the nanotubes before annealing ("as prepared") and after

annealing at 450^0 C. The result is presented in Fig. 2(right). Before annealing, beside the TiO_2 identified structure, big amounts of fluorides as well as carbon contamination were identified. After annealing the TiO_2 material got read of fluorides. More, the carbon contamination was decreased significantly.

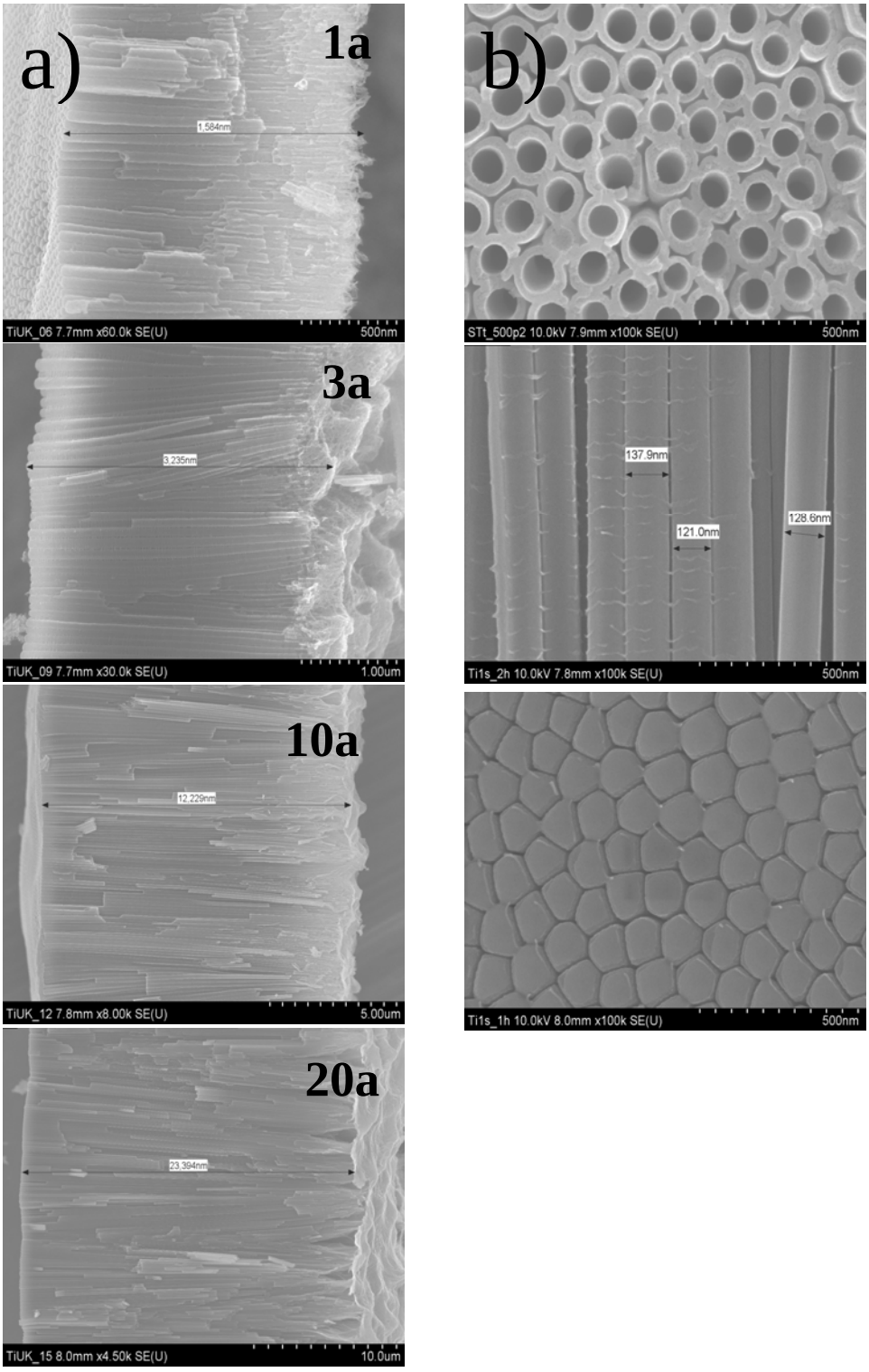


Figure 1. The cross-section SEM micrographs used in solar cell preparation a). The numbers on the picture correspond to the thickness used after in the other measurements. The high resolution of typical nanotubes micrographs of the tubes presented on left side, for showing a closer view on their top, middle and bottom

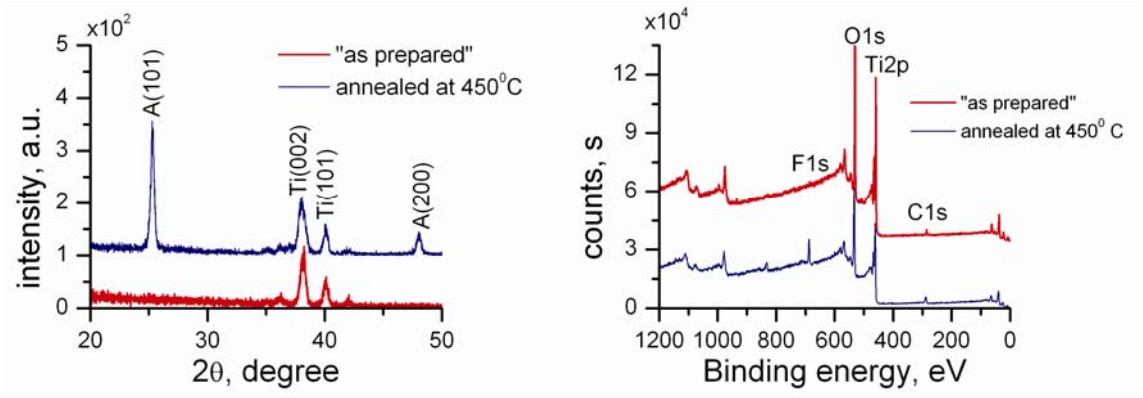


Figure 2. The XRD (left) and the XPS (right) spectra from „as prepared" TiO_2 nanotubes and after their annealing at 450^0 C for 1h in air.

II. Work carried out at University of Bath, Department of Chemistry:

4 solar cells have been fabricated, with the only difference in the thickness of the TiO_2 nanotubes, in the following way:

a) Anode preparation
   1. Annealing of the TiO_2 nanotubes samples at 450^0 for 1 h
   2. Dye-sensitization for 15 h.

b) Cathode preparation
   1. Pt deposition on glass

c) Assembling the cells together.

The schematic representation together with the photographs of the above described cells is presented in Fig. 3. The cells have been always illuminated from the back-side (through the Pt-coated glass and electrolyte). Corrections have been done accordingly for accurate data interpretation.

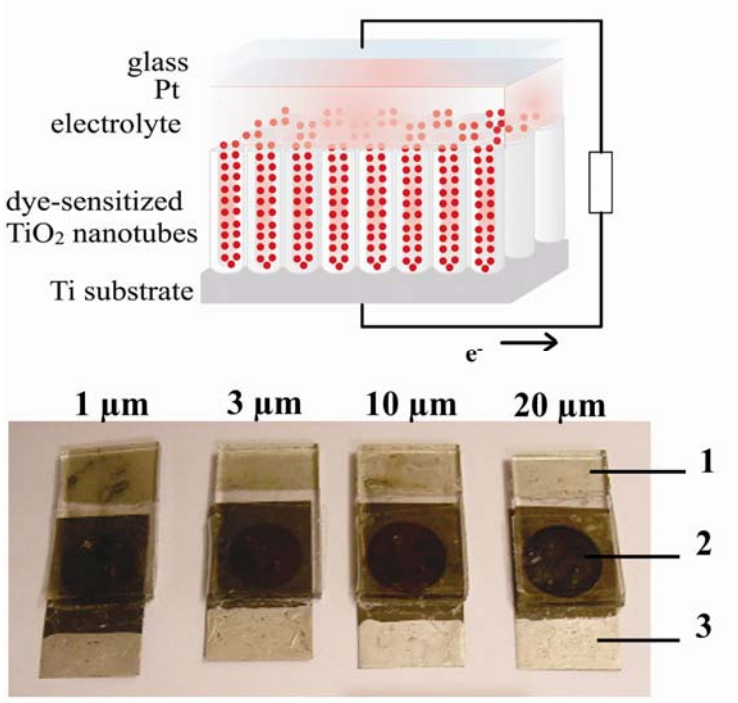


Figure 3. Schematic representation (up) and the photographs of the 4 constructed cells (down) - where the number on the top indicates the thickness of the nanotubular layer and the one on the right indicates the following: 1- the cathode, 2- the surface covered with nanotubes (the active area) and 3- the anode.

Note that the results that are to continue in this report will be given in more details in a joint publication that is to come up soon.

Two kind of measurements were done:

a) First, when the cell is in a steady state: Incident Photon to Current Efficiency (IPCE) values and the power conversion efficiency (η).

b) Second, by small perturbation of the steady state (techniques including IMPS, IMVS, Charge extraction, Photo-Voltage decay/rise and Photo-Current decay), the dynamics and kinetics of the dye-sensitized solar cells have been evaluated.

a) Regarding the steady state measurements: In Fig. 4 the IPCE values of the cells where evaluated. An increase with the nanotubes length is clearly seen. This must be connected to the different dye-loading of the samples – increasing with the thickness of the nanotubes (results not presented here). As there is still a small increase in the magnitude when comparing the 10 μm long nanotubes and the 20μm it will be worth to try even longer nanotubes (work planed to be done very soon). Nevertheless, an IPCE value close to 90 % has been measured that proofs the high potential of nanotubes to be applied in the dye-sensitized solar cells. The 1 μm long nanotubes showed a very poor IPCE value, and therefore further measurements on this sample have not been considered.

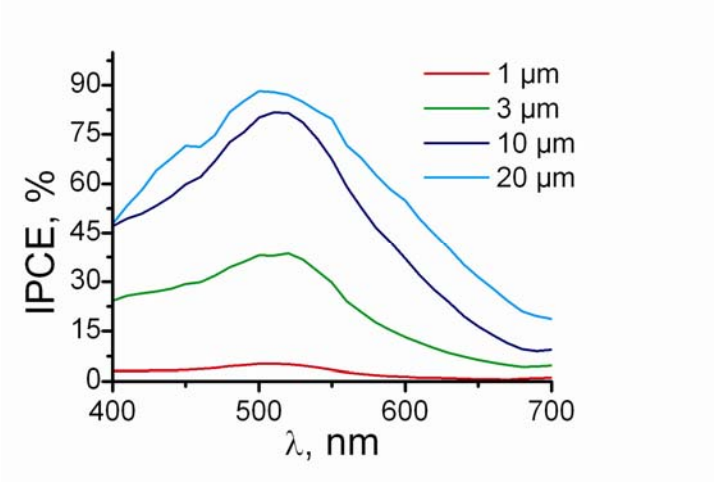


Figure 4. IPCE values calculated for the cells: 1a, 3a, 10a and 20a.

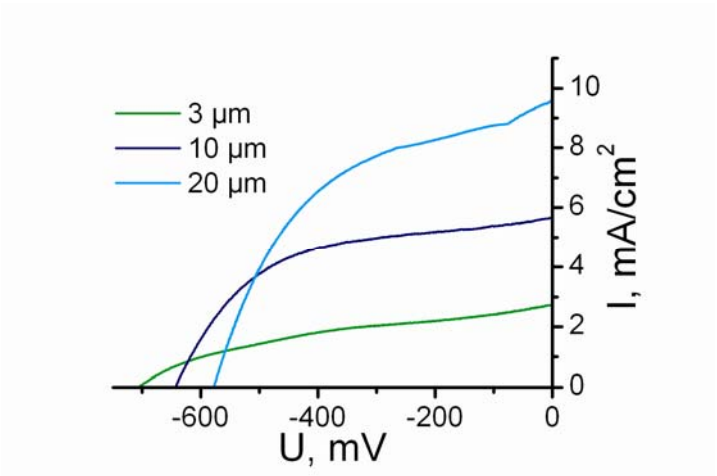


Figure 5. The I-V graphs plotted for the cells: 3a, 10a and 20a.

The I-V curves where measured under solar light simulator (AM 1.5) and the power conversion efficiency, fill factor as well as the open circuit potential/short circuit current were calculated. The

results are shown in Fig. 5.The same tendency has been observed for the power conversion efficiency as from the IPCE measurements – the increase in the nanotubes length from 3 to 10 to 20 μm leads to increase in efficiency from 0.7 to 2.6%. The results are summarized in Table 1.

Sample's name	I_{sc}, mA/cm^2	U_{oc}, mV	FF	η, %
3a	2.7	705	0.38	0.7
10a	5.6	642	0.53	1.9
20a	9.6	577	0.47	2.6

b) The information about the diffusion coefficient and life time of the charge carriers where obtained from IMPS/IMVS measurements. The results were compared to the Impedance spectroscopy and the Charge extraction results on the same samples.

In Fig. 6 the life time calculations depending on the Photo-Voltage from IMVS measurements and from Photo-Voltage decay are presented. One can clearly see that the results from both techniques used, are in accordance with each other. Data representation and formula used to clarify the mechanisms involved in the process where based on early work of Prof. Peter's group

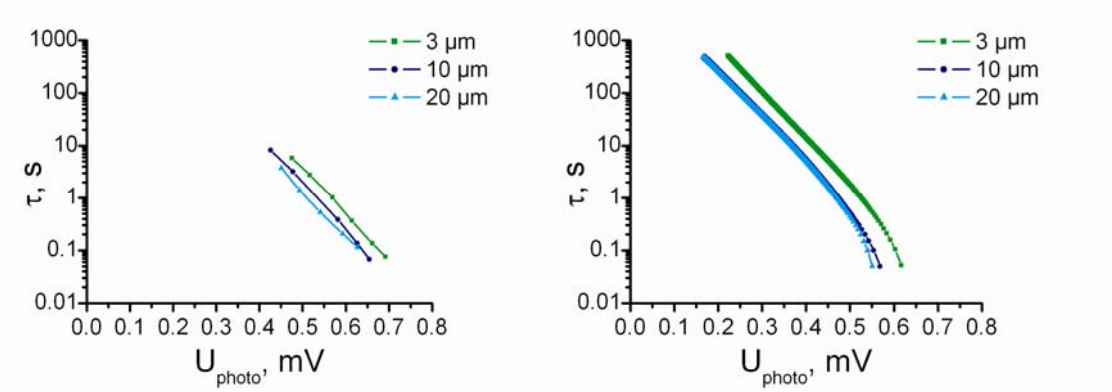
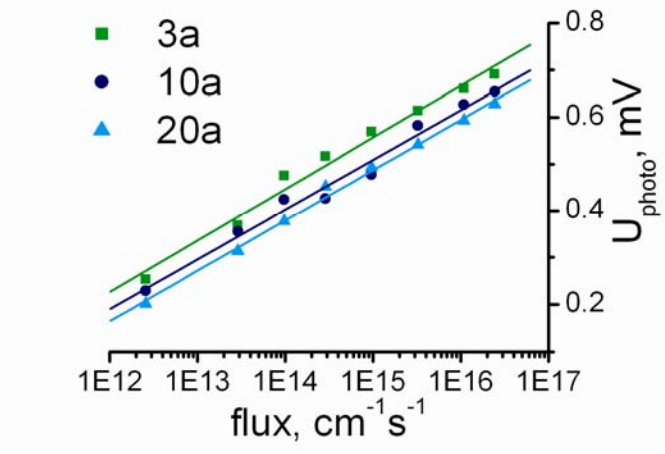


Figure 6. The life time of the electrons calculated from IMVS (left) measurements and from Photo-Voltage decay (right).

The back reaction taking place in the solar cells give a tremendous effect when the light intensity is decreased, that is, at low light intensity the shunting via conductive glass substrate become very important factor[8]. This drawback can be eliminated by using a thin TiO_2 layer between the conductive glass and nanoparticles. In the case of TiO_2 nanotubes the thin blocking layer is formed during annealing. As a result the dependence of the photo-potential with light intensity should be linear (see fro example ref. [13]). The high quality of the blocking layer is clearly seen in Fig. 7, where the Photo-Voltage is decreasing almost linear on 4 magnitude change of the light intensity.

Figure 7. The decrease of the Photo-Voltage with the decrease of the light intensity.



Further, the Diffusion coefficient and the life time of the charge depending on the light intensity has been evaluated from IMVS and IMPS measurements (Fig. 8). The effective electron diffusion coefficient (D_n) and the effective electron lifetime (τ_n) were calculated by fitting the small amplitude frequency response to intensity-modulated illumination. The intensity dependence of both D_n and τ_n for all samples (with the exception of D_n values for sample 20a) were found to obey power laws of the form $D_n \propto I_0^{-\alpha}$ or $\tau_n \propto I_0^{\alpha}$, where $\alpha \approx 0.7$ and I_0 is the incident photon flux. D_n values obtained for sample 20a seem to be affected by some kind of RC attenuation which complicates analysis of the data.

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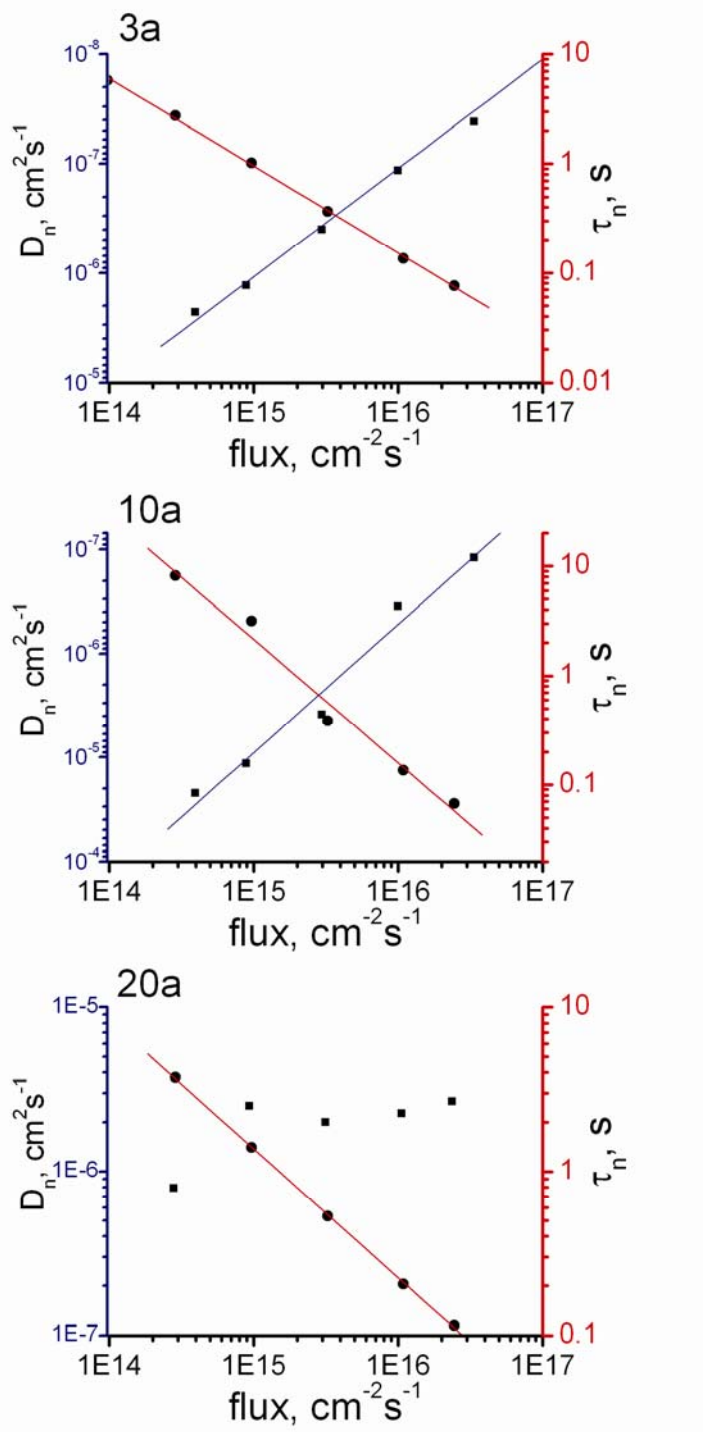

Figure 8. Calculated D_n and τ_n depending on the light intensity

The power law dependence of D_n and τ_n on I_0 is commonly attributed to the effect inter-band-gap electron trap states which follow an exponential energetic distribution[13]. Trapping of electrons in the band-gap is thought to retard both electron transport and recombination, as the probability of trapping depends on the trap occupation which in turn depends upon I_0 both D_n and τ_n are expected to vary with I_0. In this respect the cells seem to behave in exactly the same way as nanoparticle based cells. In particular, electron transport seems to be dominated by trapping phenomena and is not significantly enhanced by the morphology of the nanotubular film as has been postulated.

An important quantity regarding the overall conversion efficiency of a solar cell is the electron diffusion length L which is given by the expression $L = \sqrt{\tau_0 D_0}$ where D_0 and τ_0 are the true diffusion coefficient and lifetime in the absence of trapping effects. It has been shown by Bisquert and Vikhrenko that the vaules of D_n and τ_n can be related to their true values by taking into account the degree of trap occupancy and also that the effect of trapping is such that – at constant trap occupancy – the product $D_n \tau_n$ is equal to the product $D_0 \tau_0$[25]. This suggests that it should be possible to obtain a reliable estimate of L provided that D_n and τ_n can be measured under conditions of constant trap occupation. This is experimentally achieved by using charge extraction techniques to measure the trapped charge in the cell under different conditions which can be related to the conditions during the IMPS and IMVS experiments (i.e. short-circuit and open-circuit). Measurements to this effect are still being carried out in the laboratories at the University of Bath.

The density of trapped electrons was evaluated from Impedance spectroscopy and Charge extraction. Is very clear that the two techniques used are giving the same results which allow us to confirm the model used for the calculations.[10]

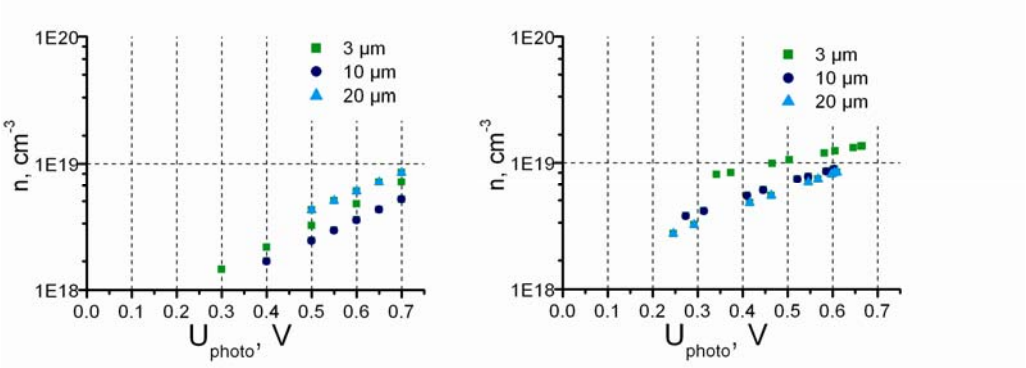

Figure 9. The density of states in TiO_2 structure depending on the Photo-Voltage calculated from two different techniques, i.e. Impedance spectroscopy and Charge extraction

The capacity value of the TiO_2 nanotubes at different Photo-Voltages was calculated from Impedance spectroscopy. Fitting the data with an exponential grow function the non-ideality factor of the cell can be calculated (see Fig. 10).

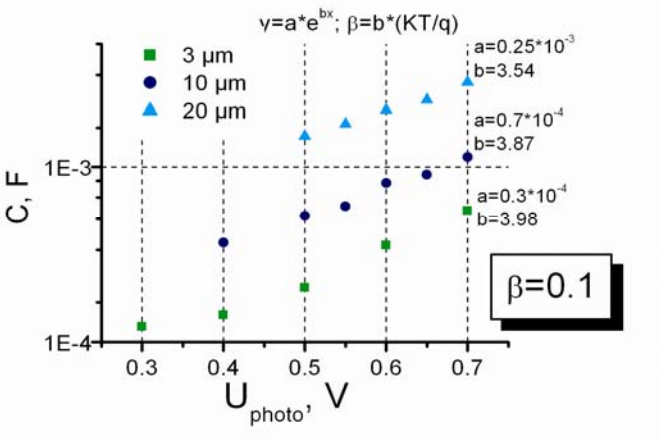

Figure 10. Calculation of the non-ideality factor from Capacitance values vs. Photo-Voltage

4. Summary

In summary, the proposed to do work at Department of Chemistry, University of Bath has been carried out successfully. Dye-sensitized solar cells based on TiO_2 nanotubes have been fabricated. Their Incident Photon to Current Efficiency (IPCE) as well as their power conversion has been evaluated. A value as high as 86% IPCE and 2.6% power efficiency has been obtained for the 20μm long nanotubes (maximum length available at that moment). Therefore it would be worth to still try to increase the length of the nanotubes to find the optimum parameters for a higher light to electricity conversion efficiency.

The dynamics and kinetics of the above described dye-sensitized solar cells have been investigated.

More details, with comparison to the nanoparticles dye-sensitized solar cells will be published soon.

5. Planned future work

TiO_2 nanotubes layer will be transferred on glass which would make possible fabrication of a dye-sensitized solar cell and its illumination from front-side (which was proved to play an important role on efficiency).

TiO_2 nanotubes can be grown on different thickness Ti foil. Construction of flexible solar cells is planned on the base of TiO_2 nanotubes fabricated on 10 μm thin Ti foil, as well as, substitution of the glass with a conductive polymer. This would significantly decrease the volume and weight making it more practical attractive.

The crystalline structure of the TiO_2 nanotubes and the size of the crystallites can be easily tuned (according to our previous and more recent results). Therefore the influence of the crystallite size, inside the nanotubes walls, will be another interesting parameter to investigate in TiO_2 nanotubes based dye-sensitized solar cells.

6. Acknowledgements:

I would like to acknowledge James Jennings, my supervisor at University of Bath, Department of Chemistry, for his high-qualified work and extremely useful discussions.

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