The project “ULTRADSSC” has been developed in the University of Rome “Tor Vergata” in a period of 13 months. The work was planned to be developed in a period of 36 months but the researcher involved resigned for personal reason on 1st May 2009, consequently it was necessary to ask for an early termination of the project. The first year of the work plan has been respected and the planned goals achieved.

The first seven months the researcher has familiarized with the instruments of the host institution for the fabrication and the first phenomenological electro-optical characterization of new DSSCs.

The DSS cell has been prepared in different steps: 1) deposition of TiO_2 on ITO and particle sinterization, 2) dye adsorption, 3) making the counter electrode, 4) assemble the two electrodes (25-50 µm distance), 5) filling with electrolyte and 6) sealing the solar cell. Many experimental techniques could be performed in this first period i.e. the deposition techniques of TiO_2 have been performed using different techniques like squeegeeing, spin-coating and blade coating; the electro-optical properties have been investigated for different annealing temperature and/or different types of dyes. This fabrication steps, especially the preparation of TiO_2film, play a fundamental role in the way charge transport mechanism take place, such as for instance diffusion by percolation in the TiO_2 film. Different materials (other than platinum compounds) have been tested in order to optimize the counter electrode.

Figure 1. DSSCs realized by using different complex dyes: N719; 505 and Ru 455-PF6.

The structural and textural properties of the films were characterized via Atomic Force Microscopy (AFM) imaging of the top surface of the TiO_2 film. The films have a rough surface with average roughness in the µm range (Figure 2).

Figure 2. AFM images of the surface of TiO_2 film.

A collaboration with Physics Department of the University of Rome “Tor Vergata” has been established to perform surface potential measurements using scanning Kelvin-probe microscopy. Preliminary tests seem to be promising in order to investigate the relationship between dye characteristics and open circuit voltage (V_{oc}).

The second step has been the electro-optical characterization with a sun simulator in order to define the device electrical characteristics and the behavior under day long solar exposition. In particular, it has been studied the angular dependence of the photocurrent. We made use of a refractive element on the topside (insets of Figure 3). We quantify the strong dependence of photocurrent on the angle of incidence of light in a dye solar cell (DSC). Under laser illumination the photocurrent increases for large incidence angles. The observed enhancements up to 25% can be useful for evaluating novel designs of an efficient photon management in DSCs. Even an effective refractive index $n_{\text{eff}} \approx 2.0$ for the mesoporous titania/electrolyte phase was retrieved from the angle dependent photocurrent [1]. A collimated single line light beam, He-Ne laser source at λ = 632.8 nm, is used to illuminate the cell, either directly or through the input face of a 45° BK7 glass coupling prism mounted on the cell substrate ($ns \approx n_{\text{BK7}}$ =1.515). For each angle, the photocurrent is acquired by means of a Keithley SMU-236 sourcemeter connected to the cell electrodes. Such a basic setup allows to finely resolve the angular variations of the short circuit current I_{SC}. It represents also a simple case of photon management in DSCs.

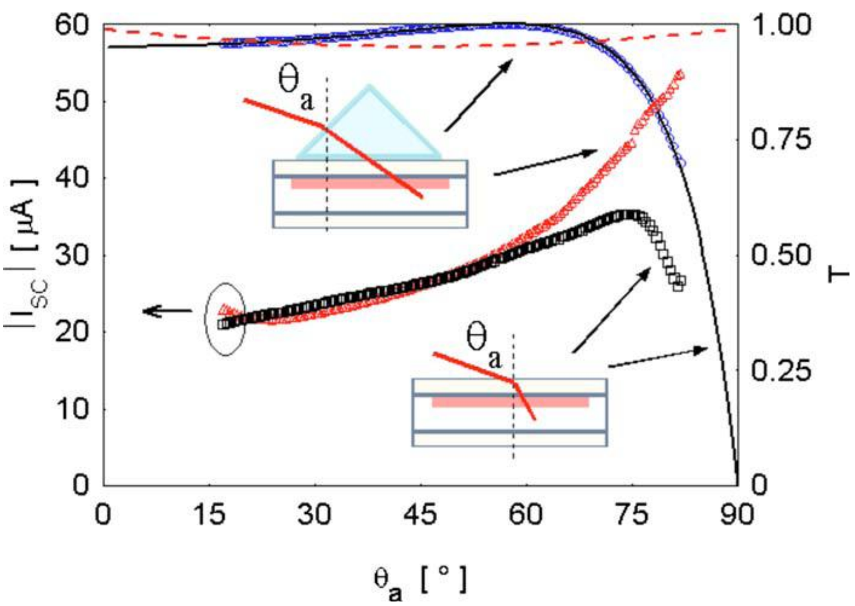


Figure 3. I_{SC} measurements on a thin DSC.

In Figure 3, we show the measurements obtained on a thin ($h_1 \approx$ 3μm titania layer) DSC. The used dye is N719 (Solaronix). The thickness is less than that typically used (10 μm) in order to enhance the angular dependence. The photocurrent I_{SC} is plotted both for a bare cell (□) and for a cell with coupling prism (Δ). A strong angular dependence is observed. We also plot the air/glass (experimental) transmittance T for TM polarized light for the bare cell (○), that follows the Fresnel law (solid line). Unexpectedly, the maximum of I_{SC} does not occur at the maximum of T and I_{SC} remains high for large angles. We explained this in terms of an interplay between transmittance from the air/cell interface and light path L lengthening inside the active titania layer [2]. Furthermore, upon using the prism the I_{SC} is boosted even if the power transmitted to the active area is almost constant. The enhancement factors with respect to the minima are 75% ($\theta_a \Rightarrow 75^\circ$) and 145% ($\theta_a \Rightarrow 82^\circ$), respectively, without and with the coupling prism. We did not observe any appreciable variation in the open circuit voltage V_{OC}.

Usually angular effects are known as *detrimental* on the output of photovoltaic devices. This is mainly due to a geometrical factor. To deeper investigate the physics of such angular factors, we prefer using the internal angles in glass, ϑ_s, and inside the titania, ϑ_{eff}. The same external ϑ_a converts by geometrical and Snell transformations into two different ϑ_s when using or not the prism. For the refraction angle in the titania we have $\theta_{eff} = \arcsin[n_s \sin(\vartheta_s)/n_{\mathrm{eff}}]$, with n_{eff} the effective refractive index of the titania/electrolyte phase. The light path L inside the titania layer depends not only on its thickness h but also on the propagation angle as $L = h/\cos(\theta_{\mathrm{eff}})$. To analyze the I_{SC} curves of Figure 3, they can be first normalized to the transmittance factor $T(\vartheta_s)$ since this is well known. The normalized curves are reported at the bottom of Figure 4. They both clearly show an increasing trend with the incidence angle and the two curves exhibit different slopes. This can be only due to the $\eta(\vartheta_s)$ dependence, since the internal behavior of the optical path $L(\vartheta_s)$ is independent on the external condition (the use or not of the prism). Substantially, when pulling out from saturation the $\eta(\vartheta_s)$ factor strongly enhances the dependence on the angle well beyond the effect of the optical path. To gain a better insight solely on the optical path, we repeated the measurements using following suitable experimental conditions:

(i) We fabricated a thicker DSC ($h_2 \approx 12$ μm titania) to test the phenomena in a more standard device [2].

(ii) The incident photon flux density was lowered increasing the beam size A_0 at constant incident photon flux ϕ_0. This allowed to move in a range for which $\eta(\varphi)$ may be considered as a constant [3].

(iii) The angular variations in the photon flux density itself $\varphi(\vartheta_s)$ are reduced when using the prism.

In Figure 4 it is reported the photocurrent of the standard cell normalized to the transmittance $I_{SC}/T(\theta_s)$ (top ▲). The refractive factor $[1- e^{-\alpha L(\vartheta s)}]$was used for the fit (solid curve). Respect to the thin cell (Figure 3), the photocurrent is higher because of both the higher thickness and the lower light intensity. On the other hand, since the higher LHE and IQE offering lower margin improvement, the observed enhancement is lower [4] but still significant as 25%. The prospected enhancement in the wider $\theta_s \,\epsilon\, [0^\circ, 75^\circ]$ range is 33%.

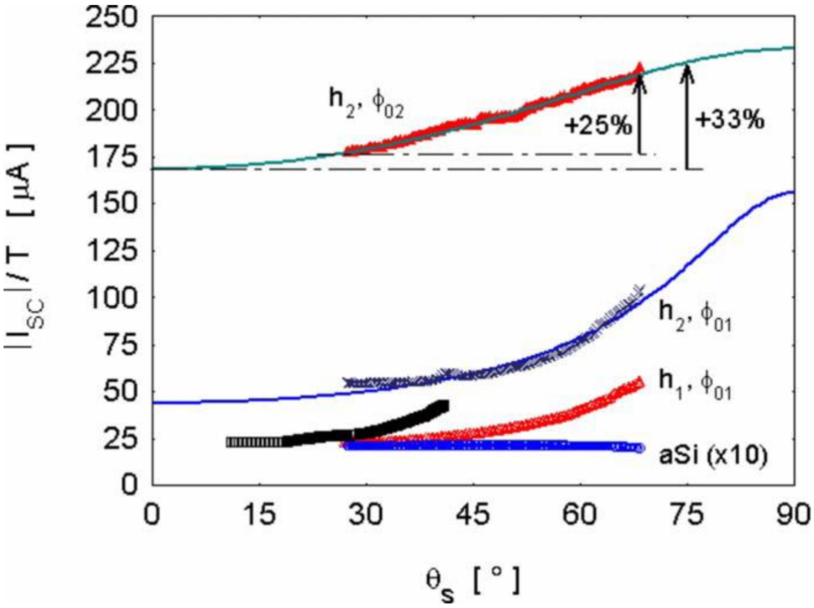
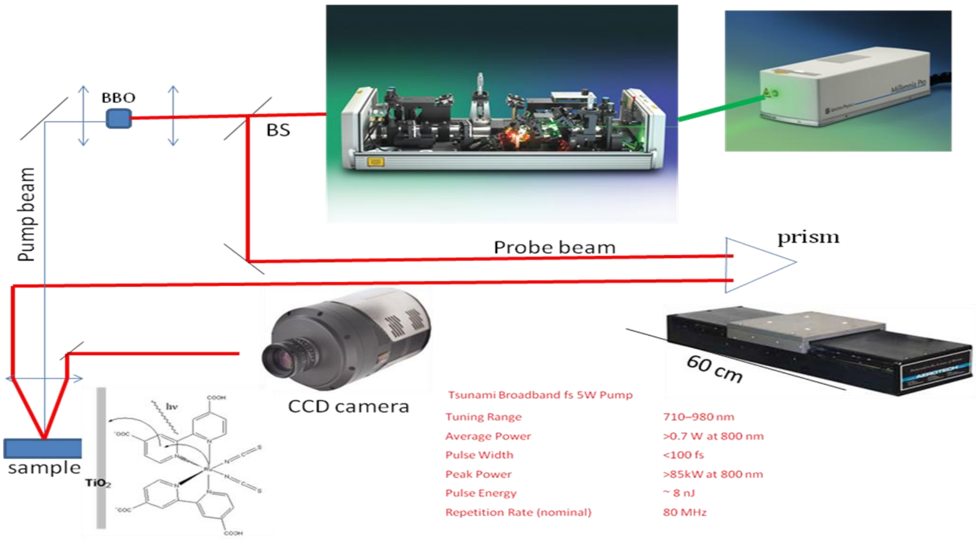


Figure 4. Normalized photocurrent measured on a standard (titania $h_2 \approx 12$ μm) DSC when using the prism (▲).

Extrapolating the I_{SC} at $\vartheta_s = 0°$ leads to reasonable values of external quantum efficiency $EQE^{633nm} \approx 43\%$. By using this value (together with an internal quantum efficiency $IQE_{N719} \approx 1$ for the sensitizing dye [5] in the low intensity range [6] and a zero absorbance at $\lambda = 632.8$ nm for the electrolyte inside the titania), makes it possible to retrieve an absorption coefficient $\alpha_{N719}{}^{633\ nm} \approx 513\ cm^{-1}$ for the dye adsorbed in the present thin film [7]. Moreover, as a collateral and original result, the fit also allowed us to extract the effective refractive index of the mesoporous titania/electrolyte phase from angular measurements of the photocurrent. Usually, n_{eff} is theoretically evaluated in the frame of the Bruggemann model [8], known the refractive indexes and volume fractions of the different constituents [9], or experimentally measured with optical techniques [10]. We obtained the value $n_{eff} \approx 2.03$ in a very good agreement with literature [9,10], thus validating the used model further.

Starting from the eight month, the ultra-fast time resolved spectroscopy laboratory has been implemented: in this period, after a first valuation of the different solutions proposed by the laser sources and analyzing devices markets, the ultra-fast time resolved spectroscopy laboratory has been improved buying the items necessary to perform the different experiments. In order to obtain the best temporal resolution a pump and probe set-up must be used with an appropriate fs laser source. The goal for this part of the project has been accomplished buying a tunable ultrafast Ti:Sapphire oscillator (Tsunami series) with a pulse duration of ~80 fs pumped by all-solid state pump laser (Millennia® series). The detection part of the set-up has been realized by means of Acton series imaging spectrometer implemented coupled to PIXIS thermoelectric cooled CCD camera platform. The time resolved set-up includes a high speed and low vibration mechanical delay line suitable for femtosecond experiments (Figure 5).



Tsunami Broadband fs 5W Pump

Tuning Range	710–980 nm
Average Power	>0.7 W at 800 nm
Pulse Width	<100 fs
Peak Power	>85kW at 800 nm
Pulse Energy	~ 8 nJ
Repetition Rate (nominal)	80 MHz

Figure 5. Time-resolved pump-probe set up for electron transfer measurements.

The goal of the whole experiment is the study of electron transfer from the excited electronic state of dye molecules adsorbed on the surface of a solid functioning as electrode. This process has considerable practical and theoretical importance for the efficiency of the DSS cells. There is considerable controversy and confusion in the literature on the time scale and the nature of the primary light-driven electron transfer process of different dyes chemisorbed on a colloidal TiO_2 electrode. The reintegrated researcher has been charged of investigating the rise time of one of the product states in this light-driven reaction, i.e. the electrons injected into TiO_2, with femtosecond time resolution. Actually, this goal couldn't be achieved due to the early termination of the project.

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