

PROJECT FINAL REPORT

MARIE CURIE ACTIONS

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Publishable Summary

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Project acronym: XSC

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The report below will summarize the work carried out to achieve the project objectives.

PbS QDs/TiO₂ heterojunction solar cells (Objective i)

PbS QDs were used as light harvesters in conjunction with films composed of 18nm-sized TiO₂ nanocrystals containing both meso-and macropores. Also, at the same time the PbS acts as a hole conductor, rendering superfluous the use of an additional p-type material for transporting positive charge carriers.

The best photovoltaic performance of the PbS QDs solar cells was achieved using anatase TiO₂ nanosheets. The TiO₂ nanosheets has an exposed (001) facet, which is different than the normal anatase TiO₂ nanoparticles (NPs) which have (101) dominant exposed facet. Researches have shown that the (001) facet has a higher surface energy than the (101) facet therefore their surface is more reactive. Thin films of those nanosheets were deposit by spin coating on the FTO glass.

Figure 1 shows HR-SEM of the cross section of the device using the TiO₂ nanosheets.

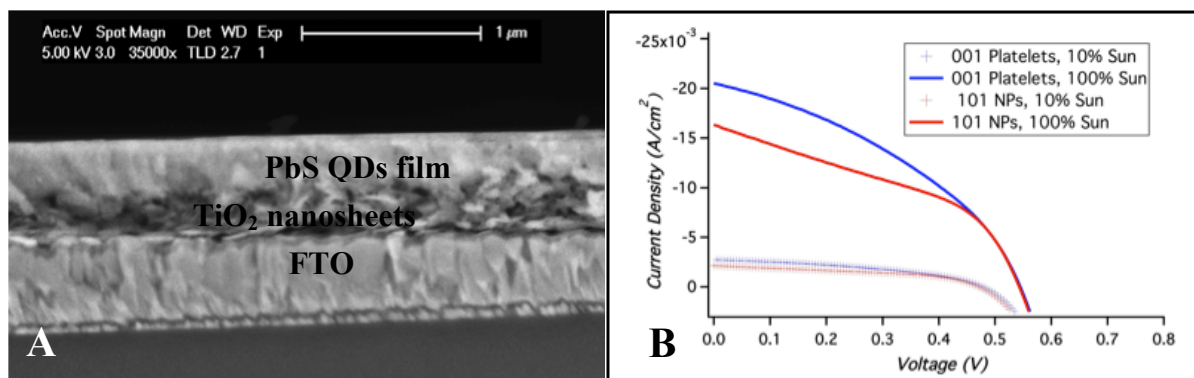


Figure 1: (A) Cross section of the heterojunction solar cell using the nanosheets TiO₂ (shown in the middle), (B) J-V curves of the comparison between cell made of 101 TiO₂ NPs and 001 TiO₂ nanosheets.

Two sizes of PbS QDs were tried, Energy gap (E_g) of 1.38eV and E_g of 1.24eV, in addition two sizes of TiO₂ nanosheets, 30nm and 80nm were tried as well.

The best results were achieved with 30nm size of nanosheets and PbS QDs with E_g of 1.38eV. The power conversion efficiency in this case was 4.73%, which is one of the highest reported in literature. Figure 1B shows the J-V curve of the best cell in comparison with cell made of (101) TiO₂ NPs. The incident photon to current conversion efficiency (IPCE) of the solid state QDs (figure 2B) cell shows a good response from the visible through the near infra-red (NIR), the IPCE spectrum using the TiO₂ nanosheets is reaching its maximum of 100% at 420nm (rectangles) while the IPCE spectrum using the TiO₂ NPs is reaching its maximum of 90% at 400nm. Photons of these wavelengths are converted most efficiently as they are absorbed by PbS particles located close to the TiO₂ interface.

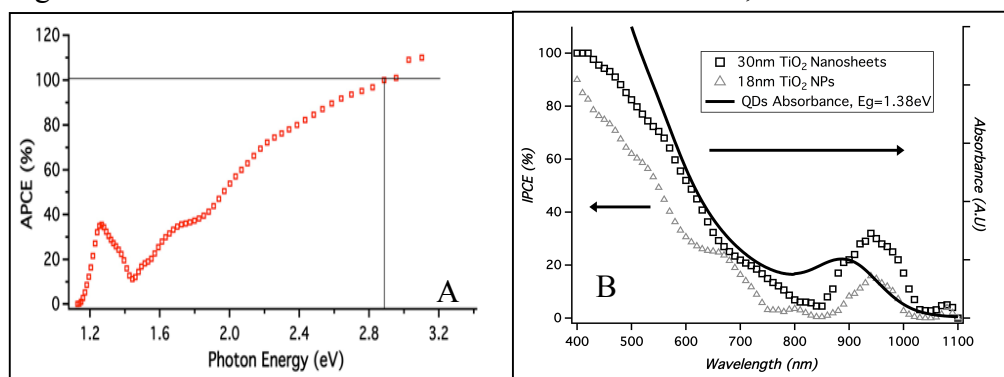


Figure 2: (A) Absorbed photon-to-current efficiency (APCE) as a function of the photon energy; (B) IPCE spectra of the PbS QDs / TiO₂ heterojunction solar cell. The rectangles show the heterojunction solar cell using (001) 30 nm nanosheets which produced the highest power conversion efficiency; The triangles show the heterojunction solar cell using TiO₂ NPs; and the solid curve shows the absorbance spectrum of the PbS QDs with E_g of 1.38 eV.

Multiple - Exciton Generation

According to eq. 1 it is possible to calculate the Light Harvesting Efficiency (LHE) of the QDs film from the absorbance spectra.

$$(1) LHE(\%) = 1 - 10^{-\text{Absorbance}}$$

The absorbed photons-to-current efficiency (APCE) values taking into account the light-harvesting efficiency (LHE), or light actually absorbed by the monolayers of QDs. The APCE can be calculated according to eq.2.

$$(2) APCE(\%) = IPCE(\%) / LHE(\%)$$

The APCE spectra against the photon energy can be seen in figure 2A. The APCE values are over 100% for photon energies of 2.8 eV - 3.1 eV, which are around 2 times the QDs E_g. Those APCE values, which exceed 100%, can suggest the possibility of multiple exciton generation (MEG) effect in our PbS QDs solar cells.

Molecular relays-Energy transfer between Squaraine dyes and CdSe QDs (Objective ii)

This work presents a simple structure of Förster resonance energy transfer (FRET) system inside a dye-sensitized solar cell. The donors are CdSe QDs, which have broad absorption spectrum in the visible regions. The acceptor is a molecularly engineered squaraine sensitizer labelled as VG1-C10, this dye has an additional carboxylic acid group and two long carbon chains compared to the standard squaraine dye. The presence of two carboxylic acid anchoring groups, and the hydrophobic long chains provides better dye stability and allows efficient energy transfer from the high energy QD's to squaraine sensitizer. The use of cobalt complex (Co⁺²/Co⁺³) as electrolyte in these cells permits direct contact between the QDs and the electrolyte. Moreover there is no need to change the original ligands of the QDs prior to deposition; the two C₁₀ chains of the dye molecules and the oleic acid ligands coated the QDs provide the optimum distance for FRET, hence the preparation and the structure of the cell are simple. As a result of the energy transfer the cell power conversion efficiency (table1) was increased and its solar response was expanded from the visible to the near infra-red.

Figure 3 shows a schematic presentation of the cell structure, the energy level of the component using in the cell and the possible orientation between the Squarine dye and the CdSe QDs giving the most efficient distance for energy transfer.

Cell type	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	η @ 1 sun
VG1-C10 dye	2.73	542	0.536	0.79
VG1-C10 dye+CdSe QDs (FRET cell)	3.25	653.4	0.69	1.48
Δ	+19%	+20%	+29%	+87%

Table 1 : The photovoltaic performance (PV) of the acceptor cell composed of the VG1-C10 dye only and the donor-acceptor cell (composed of the dye and the QDs).

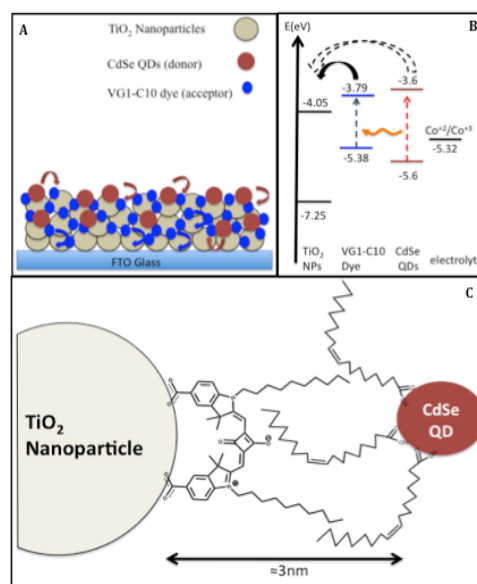


Figure 3: (A) Schematic presentation of the cell structure; (B) Energy level diagram of the components involved in the cell; (C) Schematic representation showing orientation of the QDs and the VG1-C10 inside the cell.

To summarize, this work presents the enhancement of light harvesting in dye sensitized solar cell due to Förster resonance energy transfer using unique design of the acceptor and the donor in order to achieve the optimum distance for FRET.

ZnO NWs New type of Photo-anode electrodes (Objective iii)

In this task ZnO nanowires (NWs), various core-shell based ZnO NWs core and doped ZnO nanowires were examined as photo-anode electrodes in a complete DSC. The work in this task includes the assembly of the cells and their photovoltaic characterization more than 200 cells were made in this task.

Four organic dyes C101, B11, C205 and C220 were selected because of their high molar extinction coefficient and spectral response in the visible region and tested using liquid electrolyte. C220 dye gave the best PV results. The Z960 electrolyte was used for all cells, because this electrolyte already has been tested, which gave the best efficiencies in DSCs and good stability using C220 sensitizer.

Therefore, the rest of the experiments were made using with the C220 dye and the Z960 electrolyte.

The cell structure of Nanowire based DSC is shown in figure 4A and the dye used for those cells presented in figure 4B:

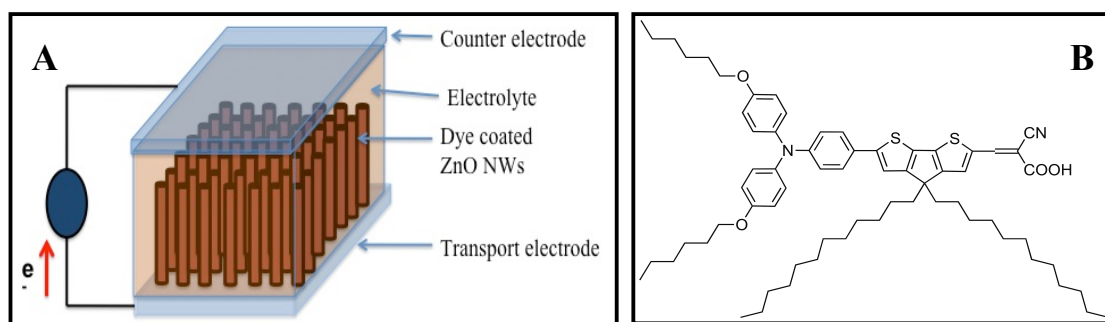


Figure 4: (A) The structure of the Nanowires based DSC; (B) C220 dye used for the experiments.

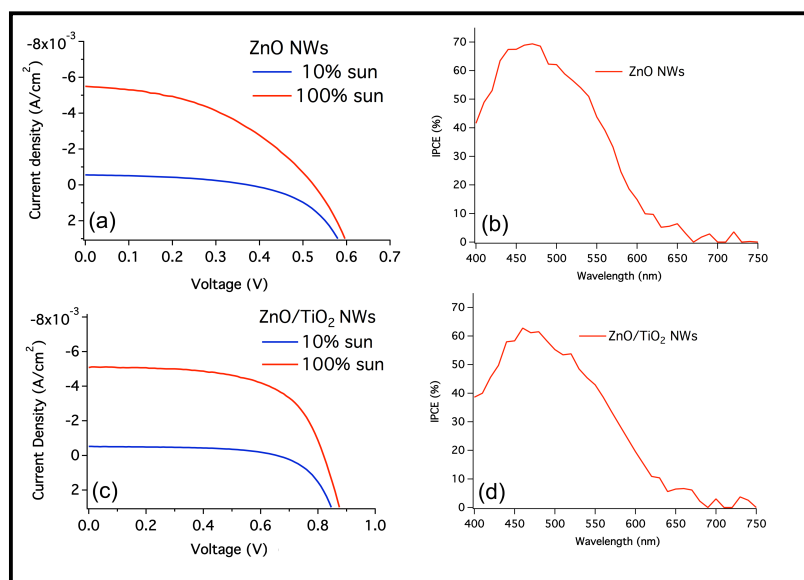
The best performance was achieved using long NWs. The longer ZnO NWs reached 10 μm length. Using those long ZnO NWs we were able to achieve an efficiency of 1.25% at 1.5AM (full sun conditions). This is one of the highest efficiency in the literature for bare ZnO NWs cell. Figure 5A and 5B show the J-V curve and the IPCE of the ZnO NWs based DSC.

Improvements in device performance for ZnO NW-based photovoltaic devices have been observed when the NWs have been coated with thin layers of semiconducting or insulating materials. The purpose of these shells is to provide a more stable binding site for dye absorption and suppress carrier recombination. Core-shell structures of ZnO-TiO₂ have been synthesized using ALD methods, allowing precise control of the shell thickness coating the NW surface.

By trying different TiO₂ shell thickness such as 10nm, 20nm and 40nm we observed that the TiO₂ shell thickness of 20 nm gave the best photovoltaic performance using 1 μm thickness of ZnO/ TiO₂ core shell film. Using this finding we made 10 μm long core ZnO NWs covered with 20nm TiO₂ shell creating $\sim 10 \mu\text{m}$ thickness ZnO/TiO₂ film.

The photocurrent-voltage characteristic of the ZnO/ TiO₂ core shell structure is shown in figure 5C. The cell shows an open-circuit voltage (V_{oc}) of 819.6 mV, a short circuit current density (J_{sc}) of 5.08mA cm⁻² and a fill factor of 60.6% with power conversion efficiency of 2.53% under 1.5AM. The fill factor and the V_{oc} improve significantly with the 20nm TiO₂ shell compare to the bare ZnO NWs.

Figure 5: (a) Photocurrent-voltage characteristics and (b) IPCE spectrum of as-made 10 μm length ZnO NW C220 DSSC. (c) photocurrent-voltage characteristics and (d) IPCE spectrum of core-shell ZnO-TiO₂ C220 NW-based DSSCs. The length of the ZnO NWs is 10 μm , the thickness of the shell is 20 nm.



Summary and Conclusions

To summarize, during the project period all the objectives were fulfilled. (i) In the QDs based solar cell an innovative cell structure was presented which enhances the photovoltaic performance dramatically achieving state of the art results. (ii) Forster resonance energy transfer between new designed squarine dye and CdSe QDs was observed due to careful engineering of the cell component and structure. (iii) A new type of photoanode using ZnO NWs with modifications such as: shell and doping was developed achieving high PCE and good stability. Total of 8 papers and one book chapter were published in scientific journals during the two years of the project.