Tuning the Band Offset Between PbSe Quantum Dots and Vertically Aligned TiO_2 Nanorods in PEDOT/PbSe/TiO_2 Nanocomposite Solar Cells

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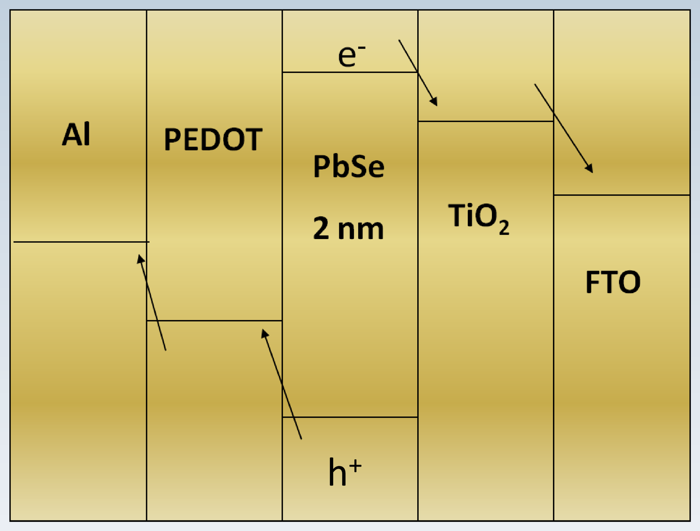
Abstract

The absorption of UV photons by PbSe quantum dots (E_g = 1.7 eV corresponds to UV absorption at 131 nm) in the size range of 2 nm can generate multiple excitons. When embedded in a second medium such as a TiO_2, the dissociation of these excitons to produce free charge carriers is affected by the band offset at the interface. When TiO_2 nanorods are used as the electron transport medium, efficient transfer of electrons from the PbSe QD to TiO_2 takes place for QD sizes below 2.5 nm. In this study TiO_2 nanopillar-PbSe QD structures were fabricated by a two-step process. The vertically aligned TiO_2 nanorods were grown by a hydrothermal process on glass substrates that were coated with a conducting fluorine-doped tin oxide film. Nanorods have an average diameter of about 200-250 nm and a length of about 1 mm. Nanoparticles of PbSe with average diameters of 1-3 nm were grown by a solvothermal method. The nanoparticles were dispersed in hexane and deposited on the TiO_2 nanorods by a Laser Assisted Spray (LAS) process. This method allowed the deposition of surfactant-free nanoparticles on the TiO_2 nanorods, providing a direct contact between the two structures. Subsequently, a layer of the polymer PEDOT followed by Al electrodes were deposited to form a cell structure. We have investigated the photocurrent generated in these cells with different PbSe QD sizes.

Introduction

From our band gap model and from experimental data it was found that PbSe with an average diameter of 2 nm are required for sufficient band gap expansion, hence permitting electron injection into TiO_2.

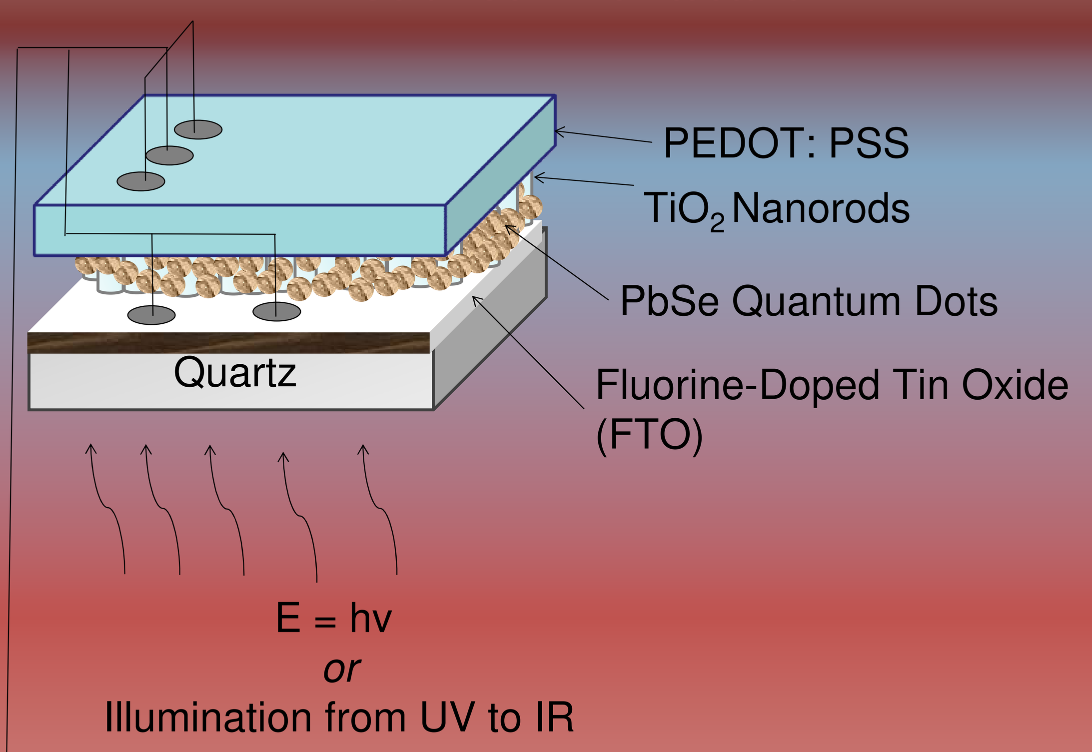


The following process will occur upon exciton generation by a photon with energy $E = h\nu$:

$$PbSe + h\nu \rightarrow PbSe\,(e + h) \rightarrow PbSe + h\nu'$$
$$PbSe\,(e) + TiO_2 \rightarrow PbSe + TiO_2\,(e)$$
$$PbSe\,(h) + Red \rightarrow PbSe + Ox$$

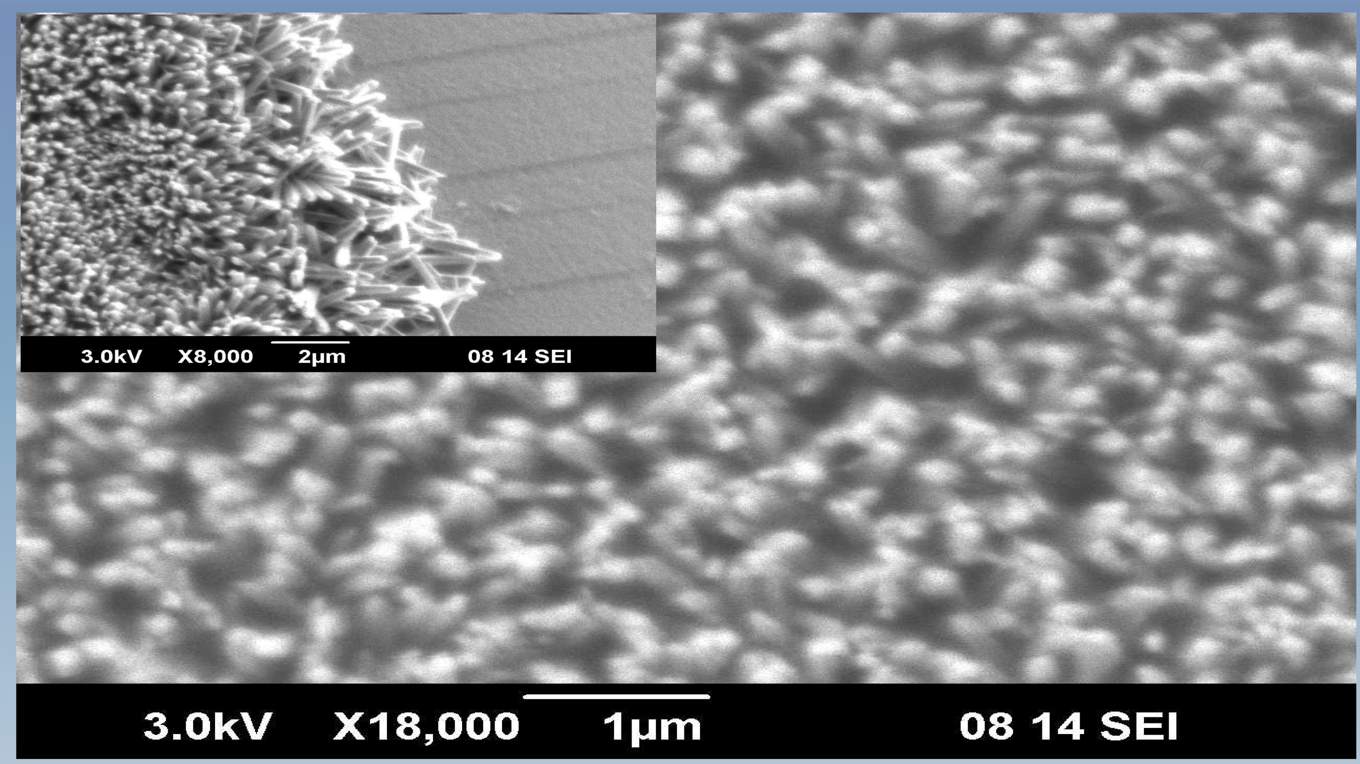
There are several components which compete with the recombination rate of the exciton pairs; namely dissociation via band bending, the electron affinity of the TiO_2, and the high hole mobility provided by the polymeric complex PEDOT: PSS.

Solar Cell Architecture

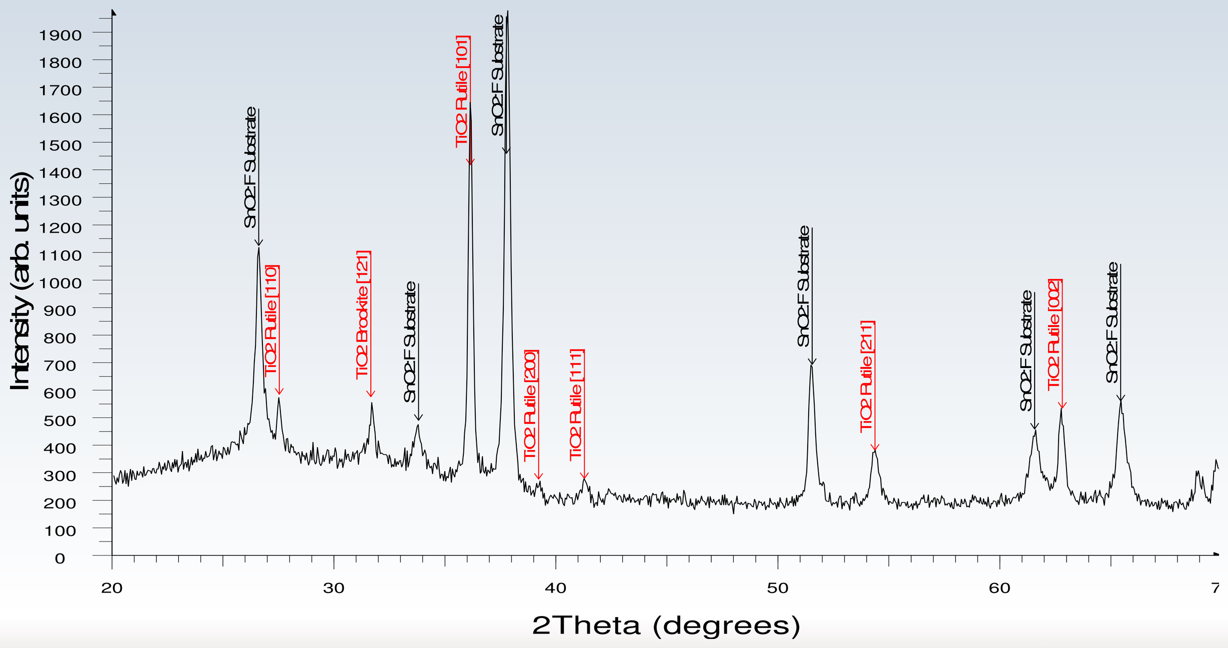


Collected light allows free carriers to be collected to calculate the external quantum efficiency; *I-V* characteristics are studied.

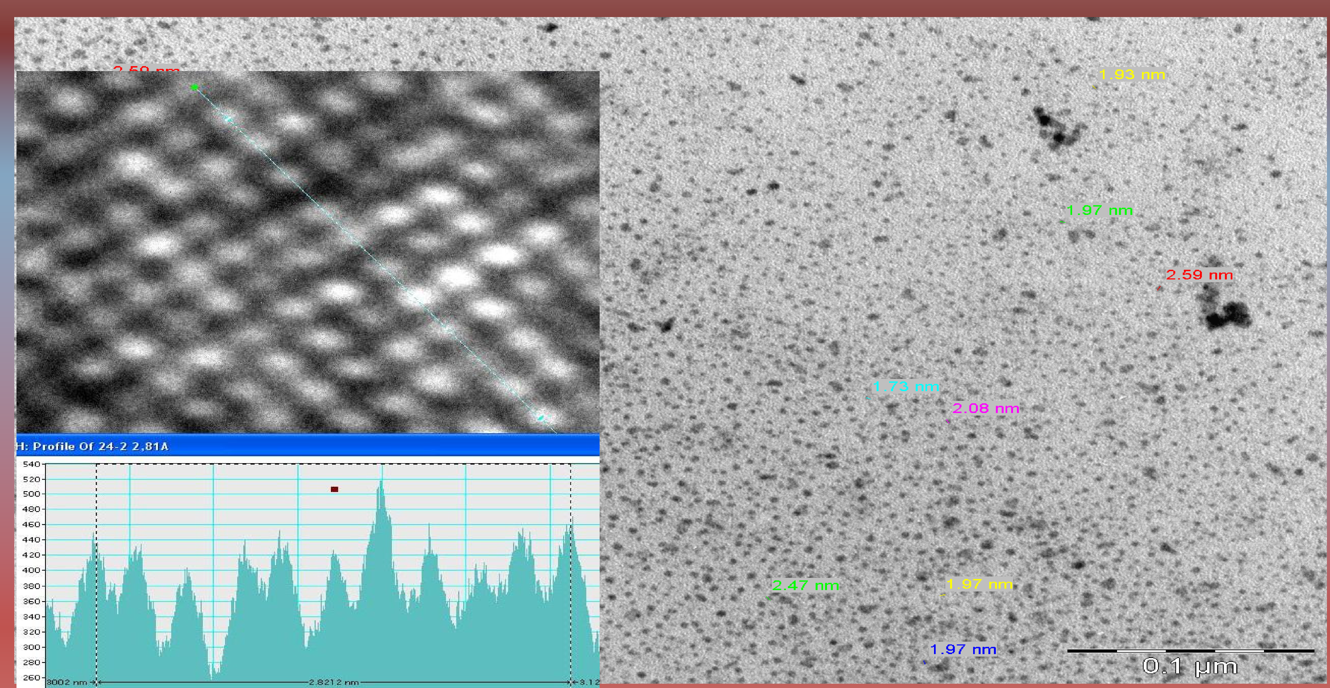
Depiction of the PbSe quantum dot/PEDOT:PSS solar cell. The capabilities of the device rely on the architecture of the PbSe QD/TiO_2 structure and the efficient hole transport of the PEDOT:PSS. The PbSe is deposited via a Laser Assisted Spray process through a novel dual nozzle design.



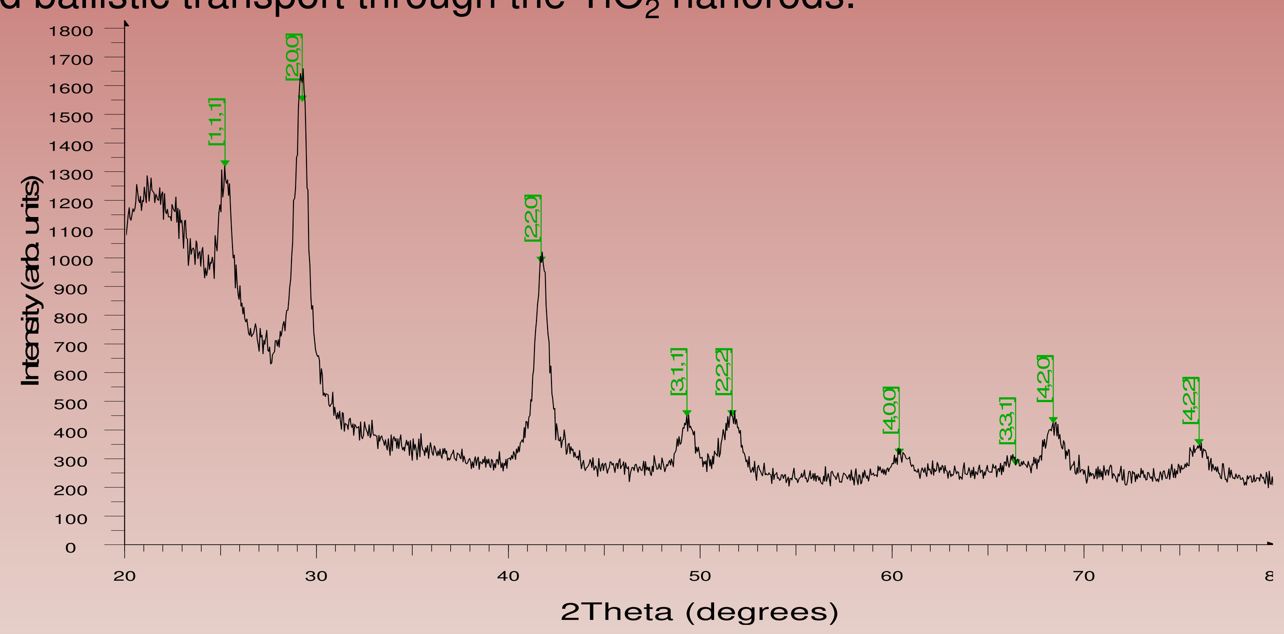
Titanium Dioxide nanorod (TiO_2) image taken with a scanning electron microscope. The TiO_2 nanorods are a good choice for the construction of solar cells due to the very large surface area they present relative to typical *pn* junction cells. Inset elucidates the average TiO_2 nanorod length of 2 μm, with 180 nm diameters. The density of the nanorods is controlled in order to yield the maximum monolayer coverage with the PbSe quantum dots.



X-Ray Diffraction Pattern for the hydothermally grown TiO_2 nanorods with average length 2 μm and a well controlled density. The site density is dependant upon the lattice mismatch between the fluorine-doped tin oxide (FTO) substrate and the TiO_2.



Scanning Electron Microscope Image of the PbSe quantum dots grown to an average diameter of 2 nm, which corresponds to a conduction band off-set of 0.35 eV, a value which will facilitate the electron injection into and ballistic transport through the TiO_2 nanorods.



X-Ray Diffraction Pattern for the PbSe quantum dots showing the crystalline result of the novel growth process.

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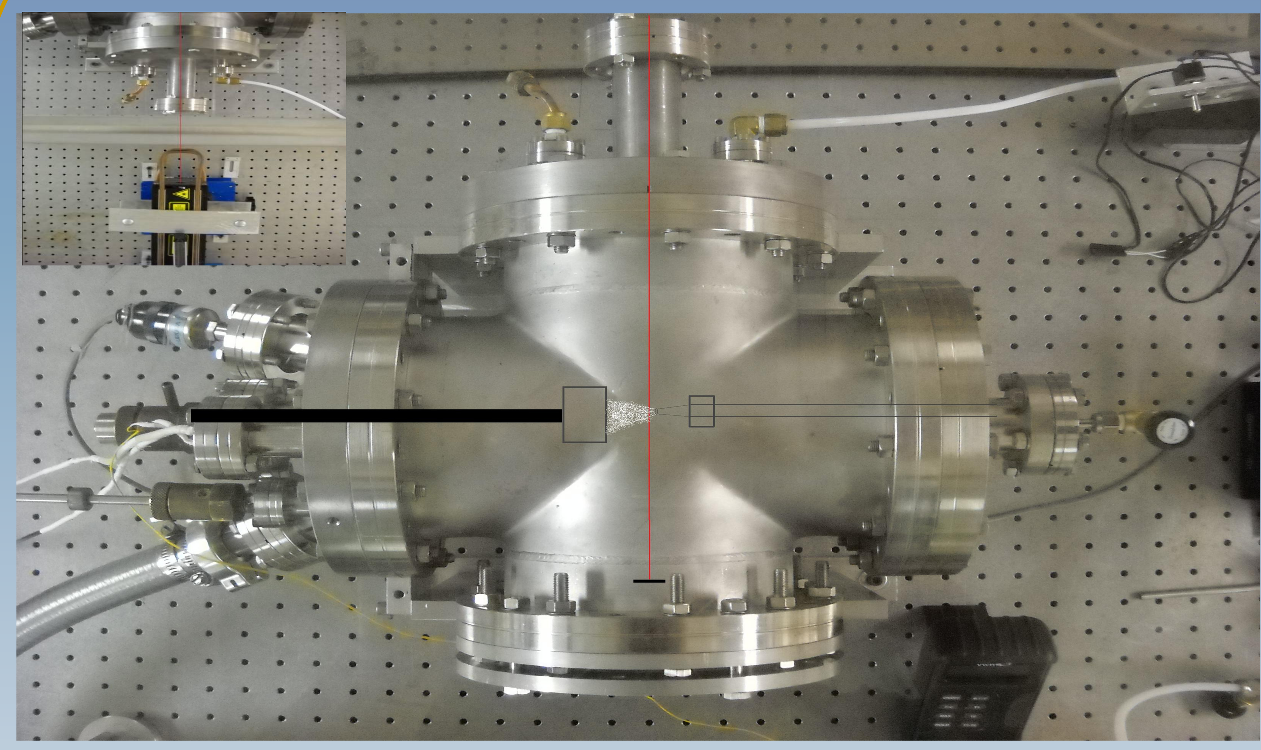
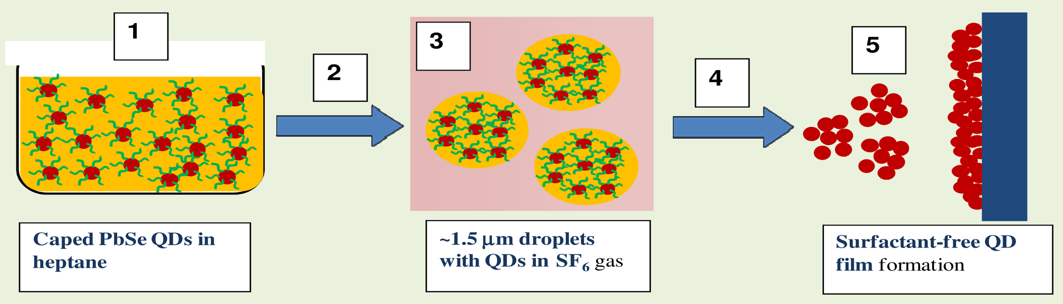


Laser Assisted Spray process top-view with diagram depicting the internal action of the process. The beam entering from the top of the picture, intercepts the aerosol in order to remove the surfactant coating of the PbSe.



(1) Suspend caped PbSe QDs in a volatile solvent
(2) form an aerosol ~1.5 μm diameter by a nebulizer
(3) Inject the aerosol through a nozzle into a growth chamber with SF_6 carrier gas
(4) Heat SF_6 gas with a CW CO2 laser causing the solvent and the surfactants to evaporate,
(5) Deposit surfactant-free PbSe QDs on a substrate.

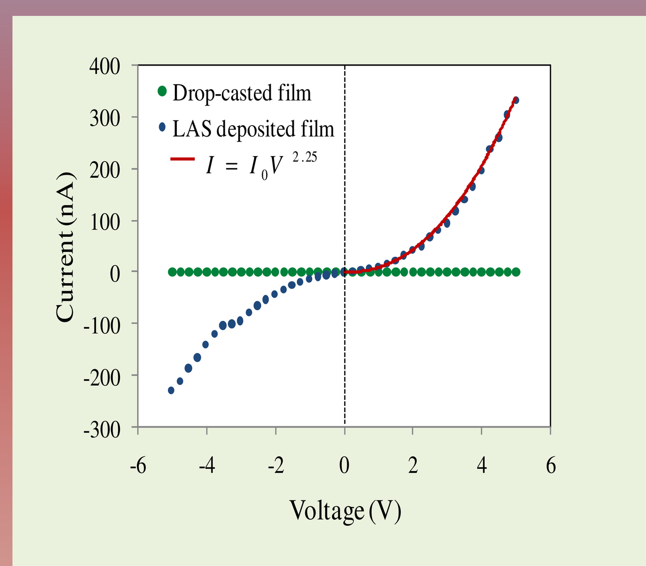
Solar Cell Characteristics

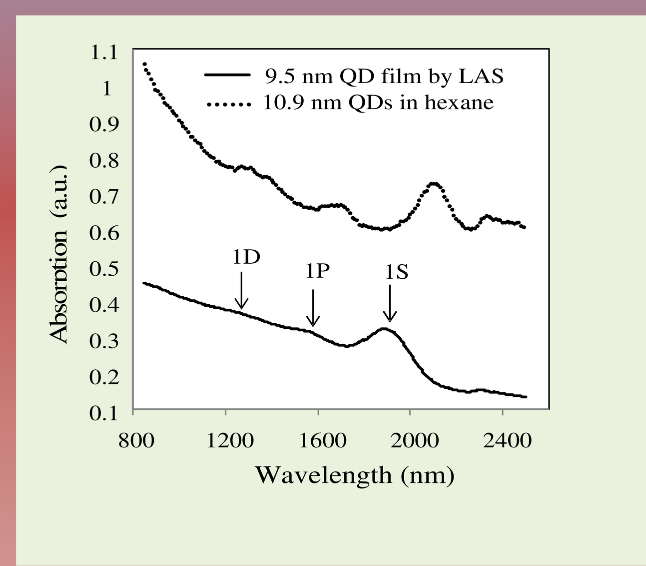
The solar cell output current I_{out} as a function of an external voltage source was characterized in order to establish two important features of the device:

(1)After thermal heating the PbSe QDs form a surfactant free layer while retaining their intrinsic quantum nature.

(2) Engineering the band gap offset between the PbSe QDs and the rutile TiO_2 allows for efficient electron transfer into and quasi-ballistic transport through the nanorods.

(3) Judicious choice of hole mobilizing polymer PEDOT:PSS which has a band gap (1.6 eV) close to that of PbSe at 2 nm (1.7 eV).





CONCLUSIONS:

We have demonstrated the production of 2 nm average diameter PbSe quantum dots with the proper band alignment. Also, hydrothermally grown TiO_2 nanorods designed have been optimized. A Laser Assisted Spray process is used to deposit a monolayer of PbSe quantum dots, as well as the polymer PEDOT: PSS which promotes hole mobility.

References:

[1] Y. Hamakawa, *Thin-Film Solar Cells*, Springer, Ch's1,2, pages 2-21

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