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Title: **A COMPARATIVE STUDY IN SYNTHESIS OF QUANTUM DOTS FOR APPLICATION IN SOLAR CELL EFFICIENCY**

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A COMPARATIVE STUDY IN SYNTHESIS OF QUANTUM DOTS FOR APPLICATION IN SOLAR CELL EFFICIENCY

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Abstract:

The interaction of light and matter at the nanoscale can greatly enhance the absorption of light in photovoltaic devices. In this thesis we combine two components into a hybrid nanostructure to enhance the overall light absorption of an extremely thin absorber: a layer of quantum dots around a nanowire. Quantum dots can be tuned to absorb at very specific wavelengths so that the absorption is perfectly matched to the requirements in the photovoltaic device. Metal nanowires support surface plasmons and can therefore greatly enhance the local optical field, making them ideal counterparts for improved light absorption in the quantum dots. Their ability to ensure efficient carrier collection makes them appealing for solar cell applications. The past decade has already seen rapid conceptual and technological advances on various aspects of QD solar cells, and diverse opportunities, which QDs can offer, predict that there is still ample room for further development and breakthroughs. We then analyze major strategies, which have been extensively explored and have largely contributed to the most recent and significant achievements in QD solar cells. Finally, their high potential and challenges are discussed. In particular, QD solar cells are considered to hold immense potential to overcome the theoretical efficiency limit of 31% for single-junction cells.

1.0 Introduction:

Solution-processed photovoltaic devices harvest abundant solar energy for conversion into electrical power while maintaining low manufacturing costs compared to conventional crystalline semiconductor devices. Among emerging materials for third-generation photovoltaics, colloidal quantum dots (QDs) are of great interest in view of their size-dependent bandgap that allows efficient absorption across the broad solar spectrum. Advances in surface passivation and device architecture have led to consistent increases in

photovoltaic performance, beginning from <1% in 2005 to a recently certified record of 11.3%. Photovoltaic performance can be increased via charge separation using p-n junctions that interpenetrate at the nanoscale. In organic solar cells, the bulk heterojunction (BHJ) enables exciton dissociation into free carriers to avoid bimolecular recombination and thereby increase performance. The BHJ is achieved via material phase separation at the nanoscale during film preparation. The BHJ concept has been explored in QDs as well

with the goal of extending the carrier diffusion length and achieving device thicknesses comparable to optical absorption length.

Quantum Dots Based Solar Cells:

QDs are semiconductor nanocrystals with confined electrons and holes within the Bohr radius of the material. In QDs the energy levels are discrete, quantized and similar to those of an atom, rather than the continuous bands of bulk semiconductors. As a result QDs are sometimes referred to as “artificial atoms” demonstrates comparison of the band structure of bulk material and QDs of varying sizes. The energy levels and the band gap of QDs can thus be fine-tuned simply by changing the size of the QDs, not to mention the availability of materials with different chemical composition for choice to synthesize QDs. Accordingly their excitonic absorption peak position can be tuned. the absorption of PbS QDs tuned over a wide range of wavelength

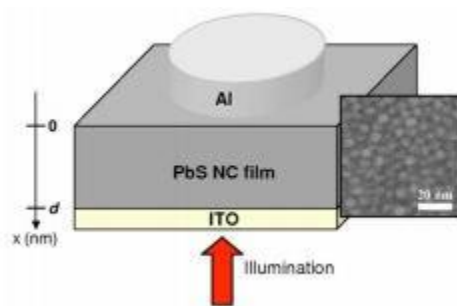


Figure: Device architecture (a) and energy band model

Characterization of QDs/TiO₂ Solar Cells:

The QDs/TiO₂ solar cell performance was measured using solar simulator device The solar simulator simulates the AM1.5

spectrum by using xenon lamp, and the light intensity could be controlled from 0.1 Sun to 1.25 Sun. The cell ambient temperature was controlled at 25°C using a control system attached to the solar simulator

Solar cell applications:

The sun is an abundant, practically unlimited source of primary energy. Within one hour it can provide enough energy to supply the whole world for a year Solar cells utilize sunlight as a clean and sustainable way to provide electricity. Yet, most of the suns energy is not being harvested due to the high costs of current solar cell technologies, which represents an economical barrier for the replacement of traditional non-renewable energy sources.

2.0 Literature review:

M. van Huis, and E. Garnett, (2011) The performance of devices that convert light to electricity (‘photovoltaic devices’) such as solar cells, is inextricably linked to their capacity for absorbing light. The more of the absorbed light is converted to electricity, the higher the efficiency. Thin-film photovoltaic technologies show promise for achieving efficiencies comparable to conventional silicon solar cells, at lower fabrication costs. Solar cell research often aims at creating high-efficiency thin-film photovoltaic devices for both enhanced efficiencies and drastically reduced material and fabrication costs

McBride, and S. J. (2005). The hybrid nanostructure was characterized using SEM imaging and spatially resolved absorption and photoluminescence. We modeled the interaction of the two systems with Mie

Theory and compared this with experimental measurements. As predicted from theory, we observe a redshift of the nanowire resonance with increasing quantum dot layer thickness - at 500nm for uncovered nanowires up to 790nm for nanowires covered with >50nm quantum dots - together with an absorption enhancement. This demonstrates an optical interaction between nanowires and quantum dots

Goldman, and H. Mattoussi, (2005) The reaction flask is heated to 150°C in air with a round bottom heating mantle. After ~30 min, the reddish-brown slurry became optically clear indicating formation of cadmium stearate. To the hot reaction vessel, HDA and TOPO were added. The reaction flask was backfilled with N₂ and heated to 320°C. At this temperature, the selenium solution was swiftly injected into the reaction flask. Upon injection, the solution temperature dropped to 280°C. The solution was maintained at 280°C for the desired amount of time to reach the desired NC size.

Wienk, R. Janssen, and A. Polman (2012) From photoluminescence measurements we found a lower emission coming from the nanowire compared to the surrounding quantum dots, even though we had seen an absorption enhancement in the shell around the quantum dots. This lower emission can be attributed to quenching of quantum dot excitation possibly due to charge transfer. Since so far we have only probed one sample successfully, more research must be done to confirm this interaction. The role of different dithiol linker molecules might as

well be interesting in researching the electronic interaction between the nanowires and quantum dots

3.0 Methodology:

In a solar cell, separating the photo generated exciton and extracting free carriers should happen with as little energy loss as possible. Since quantum dots are very small, a large percentage of their volume is surface area which is possibly creating surface defect states resolving in losses and thus poor charge transport properties. Such defect states act as trapping centers for the photo generated charges, decrease the charge mobility, enhance recombination, and thereby set a limit to the cell thickness and light-absorption efficiency. Quantum dots are most often incorporated into solar cells devices by the deposition of layers into a flexible quantum dot film, and the highest achieved quantum dot solar cell efficiency is 10.7%. One of the factors limiting the efficiency of solution-processed quantum dot solar cells is the inefficient charge extraction from the active layer of the device to the electrodes. Charges have to hop from dot to dot in order to be collected. Quantum dots are solution synthesized and are usually capped by stabilising ligands - often by long insulating carbon chains like oleic acid as is depicted to keep them in solution and avoid aggregation. By changing the chemical environment around the quantum dots after deposition the transport can be enhanced. For example by replacing the long insulating oleic acid ligands to shorter ligands that can function as a binding

agent, the electronic coupling between quantum dots is enlarged

Preparation of mixed-quantum-dot solid:

We began from a recently developed ligand substitution based on a two-phase solution exchange procedure. Concentrated QD inks were directly deposited by spin-casting to yield dense QD films. Donor- and acceptor-type QDs were prepared separately using two sets of solution-phase ligand exchange protocols. To form QDs with deeper bands, the oleic acid ligands initially capping the QDs were exchanged with lead halide anions, PbX_3^- , to passivate the surface with halogen atoms, yielding electron acceptor (henceforth called A-Type) dots. For QDs with shallower bands, various small organic molecules bearing thiol groups to anchor to the QD surface are used in a separate exchange to form electron donor (D-type) dots. The best performing devices and controls were achieved using a mixture of organohalide perovskite ligands based on methylammonium lead triiodide ($MAPbI_3$) for A-type QDs, and thioglycerol (TG) for donor (D-type) dots. Oleic acid and excess unreacted ligands were removed via purification (see Methods). Following the exchange, the hydrophilic functional groups, OH in the case of TG, and MA^+ and PbI_3^- in the case of the perovskite ligands, render each type of QD dispersible in butylamine, allowing the production of concentrated QD inks.

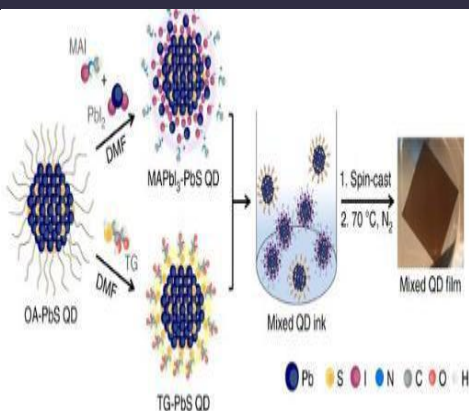


Figure: Schematic of the solution ligand exchange process

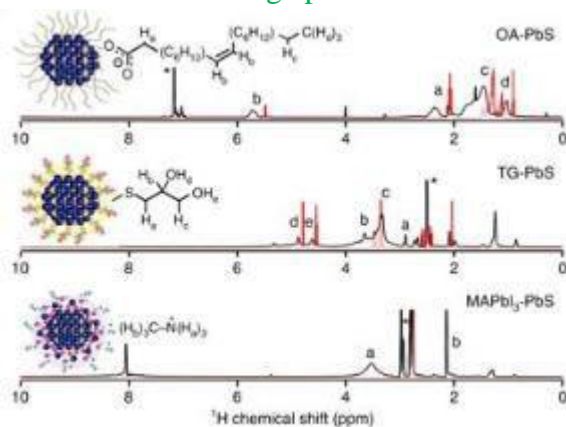


Figure: spectra of quantum dot ligands in solution (red) and bound to PbS quantum dot surface (black)

Solar cell fabrication:

The solar cells were prepared on a pre-patterned ITO substrate (2.5 cm × 2.5 cm). ZnO nanoparticles were prepared following published methods. Two layers of ZnO nanoparticles were deposited on the substrate by spin-coating at 3000 rpm for 10 s. A volume of 40 μl of concentrated and mixed QD ink was then transferred by a micropipette and deposited onto a piece of ZnO nanoparticle/ITO substrate by spin-coating at 3000 rpm for 30 s, forming a thick QD film that was further annealed at 70 °C

for 10 min under a nitrogen atmosphere. Two layers of EDT ligand-exchanged QDs were deposited on top of the QD film by spin-casting following reported method For the top electrode, 120 nm Au was thermally deposited on the PbS film to complete the device. Each ITO substrate was patterned to yield eight devices, each with an area of 7.1 mm².

Quantum dot surface characterization

Various types of QDs, including PbS and PbSe, are known to have surfaces prone to atomic rearrangement, as well labile ligand-surface bonds. Exchange among ligands for A-type and D-type QDs during mixing of the two classes would result in mixed coverage, and negate the benefit of altering the levels of the bands. We define chemical orthogonality as a property of the QD mixture wherein, in the two distinct classes of QDs, each class of QD maintains its surface ligands throughout mixing in solution and in a film To investigate whether we had indeed achieved QD chemical orthogonality, we used Fourier-transform infrared (FT-IR) spectroscopy to characterize the exchanges and the ligand exclusivity of the resultant materials The absence of a carboxylic group C=O stretch (at around 1750 cm⁻¹) from each exchanged QD sample indicates a complete ligand exchange and oleic acid removal.

Interdot carrier transfer and exciton dissociation studies

We further tested this picture of surface ligands retained on each type of dot throughout mixing and annealing by investigating the photophysical properties of

single-class QD vs. mixed-QD materials. In the mixed-QD BHJ solid, the rate of exciton dissociation is expected to be increased due to type II band alignment throughout the film, and interdot carrier transfer rates are expected to be intermediate between those of pure A-type and pure D-type films. To investigate further how the mixture of D- and A-type QDs influences excited state dynamics in the mixed-QD solid, we performed ultrafast transient absorption (TA) spectroscopy (see Supplementary Note [1](#) for detailed explanation of TA spectroscopy). Following photoexcitation, the carriers diffuse throughout the film from higher to lower energy sites due to the inhomogeneity in the QD solid.

4.0 Results and Discussion

The synthesis of PbS quantum dots was a modified version of previously reported methods by a cartoon of the setup. Two 3-neck-flasks were cleaned with ACE and IPA, equipped with a temperature probe and a teflon stirring bar, put on a hotplate and connected to a Schlenk line by the use of grease. OLA (8ml) and 3mmol PbCl₂ (0.834 grams) were degassed under vacuum by heating slowly to 80°C and maintained at this temperature for 30mins, stirring at 400rpm. While increasing the temperature to 80°C, caution must be taken not to have bubbles touching the grease and contaminating the solution. The driving force for charge separation and transport in this kind of solar cells is generated by the band alignment of the QDs and the semiconducting polymer as well as the electric field generated due to the difference

in work function between two electrodes, the transparent conducting oxide and the low work function back electrode. The light is absorbed by both the QDs and the semiconducting polymer generating the QDs have to be interconnected to efficiently transport the electrons to an electrode. To enhance the transport of electrons, QDs can be grafted onto MWCNTs and mixed with the polymer making up the photoactive layer. In this case the electrons accepted by and/or photo generated in the QDs can be transferred to the MWCNTs and transported quickly.

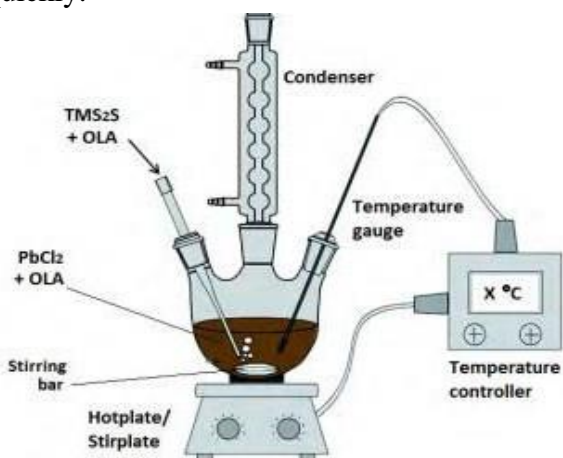


Figure: synthesis of PbS quantum dots

Then the solution was allowed to cool below 30°C and placed under nitrogen. Separately, 20ml of OLA was degassed by heating slowly to 80°C under vacuum, and then placed under nitrogen. The sulfur precursor was prepared in a glovebox by dissolving 210µl of TMS₂S in 1 ml of the degassed OLA. The degassed Pb-oleate solution was reheated slowly under stirring and when at 30°C, the sulfur precursor was rapidly injected. When at 90°C (after ± 1 min), 10ml of hexane was quickly injected

to stop the crystal growth and the solution was slowly cooled down to RT by removing the flask from the hotplate.

Morphological Analysis:

HRTEM reveals information about the particle size and shape. Figure 4 shows the HRTEM images of the S1 example for of CdSe quantum dots before purification from the excess of ligands. CdSe quantum dots are collected on the surface of large chain ligands.

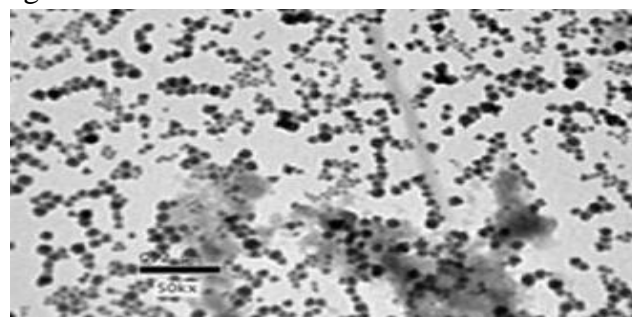


Figure: HRTEM images of CdSe QDs without purification

The concentration of the nanocrystals in samples were determined by the number of cadmium atoms contained in the samples and the size of the nearly monodisperse particles. Therefore, it was critical to remove any unreacted cadmium precursors in the sample.

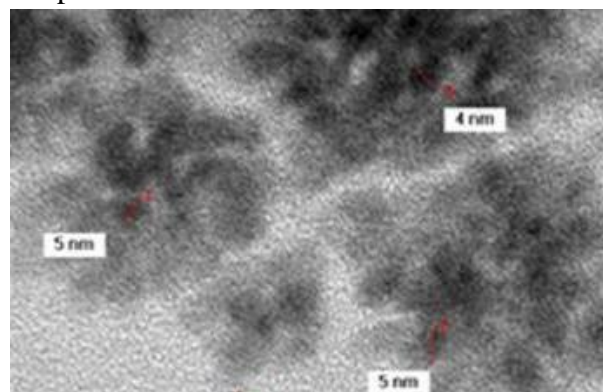


Figure: HRTEM images of Codes QDs after purification.

the concentration of colloidal Nano crystals is difficult to determine by gravimetric methods. Because the number of ligands on the surface of Nano crystals is quite difficult to identify and may also vary significantly under different conditions, measurements solely based on gravimetric methods using ligands-coated Nano crystals are accurate only when the interactions between Nano crystals and ligands are sufficiently strong to withstand necessary purification procedures CdSe QDs are soluble in toluene after purification. On the basis of the FT-IR data, the surface of the CdSe QDs is mainly coated with alkyl ligands. Flexible organic molecule such as phosphine alkyl ligands provides repulsive interactions between the QDs in toluene, thus preventing aggregation. Others show 3417 cm^{-1} at OH, 2360 cm^{-1} at PH₃, 1464 cm^{-1} at CH₂, 1155 cm^{-1} at P=O functional group

Discussion:

We report herein a mixed-QD ink that enhances charge carrier extraction in QD solar light harvesting layers. The approach relies on forming a mixture of donor and acceptor QDs that each maintains their distinct chemical character when mixed in the solution phase and when formed into a final film. The electron affinity of the QDs is controlled by the application of surface ligands in solution exchanges completed prior to the formation of the colloidal mixture. These ligands are bound tightly to the surface, allowing the intimate mixture of the two dot classes to be preserved even in the solid state, leading to electrons and holes being separated into different domains,

suppressing their subsequent recombination. Photocarriers can then migrate efficiently through their respective donor/acceptor transport media when the D:A stoichiometry is suitably optimized.

Conclusions:

The structure is both optically and electronically highly tunable because materials can be changed, ligands can be varied, and sizes of both the quantum dot and nanowire can be altered in order to perfectly match the solar spectrum. Since the metal nanowire allows for charge transport and can function as an electrode, introducing a second electrode would allow for charge collection. Research on the electronic interaction of the two nanostructures may give more insight in the actual application into photovoltaic devices CdSe nanocrystals prepared by the common pyrolysis method have an average Cd/Se stoichiometry about 1.27 and the stoichiometry is independent on the initial Cd/Se ratio in the starting material. The results also showed CdSe quantum dots with sizes ranging from 3 nm to 6 nm which enabled the control of the optical properties and consequently the solar cell performance

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